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# Reduction of Dinitrogen with an Yttrium Metallocene Hydride Precursor, $[(C_5Me_5)_2YH]_2$

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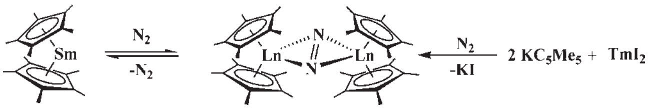
Treatment of $[(C_5Me_5)_2YH]_2$, **1**, with $KC_8$ under $N_2$ in methylcyclohexane generates the unsolvated reduced dinitrogen complex, $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **2**, and extends the range of yttrium and lanthanide $LnZ_2Z'/M$ (Z = monoanion; M = alkali metal) dinitrogen reduction reactions to $(Z')^- = (H)^-$. The hydride complex, **1**, is unique in this reactivity compared to other alkane-soluble yttrium metallocenes, $[(C_5Me_5)_2YX]_x$ $\{X = [N(SiMe_3)_2]^-, (Me)^-, (C_3H_5)^-$, and $(C_5Me_5)^-\}$ which did not generate **2** when treated with $KC_8$. $[(C_5Me_5)_2LnH]_x/KC_8/N_2$ reactions with Ln = La and Lu did not give isolable dinitrogen complexes. Complex **2** and the unsolvated lutetium analogue, $[(C_5Me_5)_2Lu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **3**, were obtained using benzene as a solvent and $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ as precursors with excess $KC_8$. Complex **2** functions as a reducing agent with PhSSPh to form $[(C_5Me_5)_2Y(\mu\text{-}SPh)]_2$, **4**, in high yield.

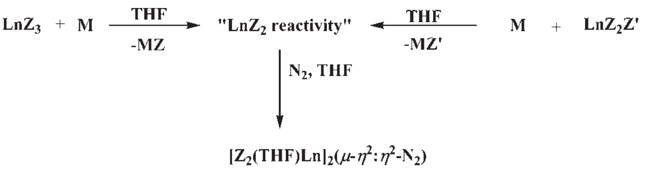
## Introduction

Reduction of dinitrogen with lanthanide complexes was originally accomplished via the reactive divalent metal ions, $Sm^{2+}$,[1] $Tm^{2+}$,[2] $Dy^{2+}$,[3] and $Nd^{2+}$,[4] as exemplified in Scheme 1 for samarium and thulium. Recent studies have shown that reductive lanthanide chemistry is not limited to these divalent ions, since "$Ln^{2+}$" reactivity can be accessed by combinations of homo- and heteroleptic trivalent yttrium and lanthanide complexes in the presence of an alkali metal, Scheme 2. These $LnZ_3/M$ and $LnZ_2Z'/M$ reactions (Z, Z′ = monoanions that allow this reaction to occur, M = alkali metal) provide $Ln^{2+}$-like reactivity even if the divalent ion has never been isolated.[5] Exploration of this "$Ln^{2+}$" reduction chemistry has generated a growing family of tetrahydrofuran (THF) solvated reduced dinitrogen complexes of general formula, $[Z_2(THF)Ln]_2(N_2)$ where $Z = [N(SiMe_3)_2]^-$,[5a] $(C_5Me_5)^-$,[5f] $(C_5Me_4H)^-$,[5f] $(C_5H_2{}^tBu_3)^-$,[5h] and $Z' = [BPh_4]^-$.[5a] These reduced dinitrogen complexes have independently interesting reductive chemistry.[5e,6]

**Scheme 1.** Initial Syntheses of Lanthanide Dinitrogen Complexes, $[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$[1,2]



**Scheme 2.** Formation of Lanthanide Dinitrogen Complexes from Trivalent $Ln^{3+}$ Precursors



$Z = [N(SiMe_3)_2]^{1-}, (C_5Me_5)^{1-}, (C_5Me_4H)^{1-}, (C_5H_2{}^tBu_3)^{1-}$ $Z' = (BPh_4)^{1-}, I^{1-}$

Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu, Y M = Na, K, $KC_8$, NaK

We report here that the scope of $LnZ_2Z'/M$ reactions can be broadened to $(Z') = H$ using the precursor $[(C_5Me_5)_2YH]_2$, **1**,[7] providing a new route to unsolvated $(Z_2Ln)_2N_2$ complexes. This contrasts with the syntheses of $[Z_2Ln(THF)]_2N_2$ complexes shown in Scheme 2, which are performed in THF and invariably result in isolation of complexes as THF adducts. Unsolvated lanthanide complexes are typically more reactive than THF solvates. However, only a few unsolvated $(Z_2Ln)_2N_2$

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complexes are known, and all involve paramagnetic metals: $[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$ (Ln = Sm,[1] Tm[2]), $\{[C_5H_3(SiMe_3)_2]_2Tm\}_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$,[2] $\{[C_5H_3(SiMe_3)_2]_2Dy\}_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$,[3] and $[(C_5H_2{}^tBu_3)_2Nd]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$.[5h]

The dinitrogen reduction chemistry of **1** reported here was unexpected since metallocene hydrides of this type usually react via insertion[8] and $\sigma$ bond metathesis[8e,9] and $LnZ_2Z'/M/N_2$ reactions generally work best with weakly bound $(Z')^-$ ligands like $(BPh_4)$[1−5f] and $I^-$.[5h] The efficacy of **1** in the $LnZ_2Z'/M/N_2$ reaction is compared with that of other yttrium metallocenes, $[(C_5Me_5)_2YX]_n$ where X = $[N(SiMe_3)_2]^-$, $(C_3H_5)^-$, $Cl^-$, $Me^-$, and $(C_5Me_5)^-$, with other yttrium hydrides $[(C_5Me_4H)_2YH]_2$[10] and $[(C_5H_4Me)_2Y(THF)H]_2$,[11] and with analogous $[(C_5Me_5)_2LnH]_x$ hydrides of Ln = La,[8a] Sm,[9a] and Lu.[12] Although past studies suggested that $[(C_5Me_5)_2Ln][(\mu\text{-}Ph_2)BPh_2]/KC_8$ reactions would not succeed in solvents less polar than THF, the tetraphenylborate complexes[13] were found to be viable precursors in benzene when longer reaction times and excess $KC_8$ was used.

## Experimental Section

The manipulations described below were performed under nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were dried over Q-5 molecular sieves, and saturated with UHP argon using GlassContour columns.[14] Benzene-$d_6$ and cyclohexane-$d_{12}$ were dried over NaK alloy, degassed by three freeze−pump−thaw cycles, and vacuum transferred before use. $[(C_5Me_5)_2LnH]_x$ (Ln = La, Sm, Y, and Lu) were prepared as previously reported for Nd.[13] $[(C_5H_4Me)_2YH(THF)]_2$,[11] $[(C_5Me_4H)_2YH]_2$,[10] $(C_5Me_5)_2Y(C_3H_5)$,[15] and $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ (Ln = La, Y, Lu)[13,16] were prepared according to the literature. $(C_5Me_5)_2YCl(THF)$ was made from $Me_3SiCl$ and $[(C_5Me_5)_2YH]_2$ in methylcyclohexane followed by addition of THF; its $^1H$ NMR spectrum matched that reported in the literature.[17] $[(C_5Me_5)_2YMe]_x$ was made as previously reported for Lu.[18] PhSSPh was purchased from Aldrich and sublimed before use. $^{15}N_2$ (98%) was purchased from Cambridge Isotope Laboratory and used as received. $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker DRX 500 MHz spectrometer. $^{15}N$ NMR spectra were recorded with a JEOL 600 MHz spectrometer and calibrated using an external reference, $^{15}N$-formamide in DMSO (−269 ppm with respect to nitromethane at 0 ppm). Infrared spectra were recorded as KBr pellets on a PerkinElmer Spectrum One FT-IR spectrometer. Elemental analyses were performed on a PerkinElmer Series II 2400 C/H/N/S elemental analyzer. Except where noted, the following reactions were conducted in a nitrogen-filled glovebox free of coordinating solvents.

**$[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$, 2.** A solution of $[(C_5Me_5)_2YH]_2$, **1**, (102 mg, 0.142 mmol) in methylcyclohexane (5 mL) was added to a suspension of $KC_8$ (43 mg, 0.32 mmol) in methylcyclohexane (5 mL). The mixture was stirred for 2 h and then centrifuged and filtered to leave a red-orange solution. Ruby red crystals of **2** were obtained from a saturated methylcyclohexane solution by slow evaporation (38 mg, 36%). $^1H$ NMR (benzene-$d_6$) $\delta$ 1.98 ppm (s, $C_5Me_5$). $^{13}C$ NMR (benzene-$d_6$) $\delta$ 11.9 ($C_5Me_5$), 117.6 ($C_5Me_5$). IR: 2969s, 2904s, 2857s, 2724w, 1496w, 1437s, 1379s, 1021m, 801w, 656s, 625m cm$^{-1}$. Anal. Calcd for $C_{40}H_{60}N_2Y_2$: C, 64.34; H, 8.10; N, 3.75. Found: C, 63.64; H, 8.34; N, 3.23.

**2 from 1 and NaK/$N_2$/$H_2$.** In an argon-filled glovebox free of coordinating solvents, a solution of **1**, (90 mg, 0.12 mmol) in methylcyclohexane (10 mL) was transferred to a sealable Schlenk flask containing excess sodium potassium alloy. After degassing the solution, 1 atm of $N_2/H_2$ (90:10) was introduced to the flask and stirred for 24 h. Brought back into the glovebox, the red-orange solution was centrifuged, filtered, and solvent removed under vacuum leaving a red-orange powder. Crystallization from a saturated benzene solution over 3 d gave pure **2** (24 mg, 26%). The $^1H$ NMR spectrum of the crude product showed that no $(C_5Me_5)_2Y(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)Y(C_5Me_5)$[19] was present. In contrast, when this reaction is done with NaK without $H_2$, $(C_5Me_5)_2Y(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)Y(C_5Me_5)$ is a significant byproduct.

**$[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2:\eta^2\text{-}{}^{15}N_2)$, 2-$^{15}$N.** In an argon-filled glovebox free of coordinating solvents, a light pink solution of **1** (100 mg, 0.139 mmol) in methylcyclohexane (8 mL) was added to a suspension of $KC_8$ (41 mg, 0.30 mmol) in methylcyclohexane (3 mL) in a sealable Schlenk flask. After degassing the solution, 1 atm of $^{15}N_2$ was introduced to the flask, and the solution was stirred for 3 h. The red-orange solution was brought into the glovebox, centrifuged, filtered, and the solvent was removed under vacuum. The resulting solid was redissolved in benzene and solvent removed under vacuum to yield a red-orange powder. $^{15}N$ NMR (60.87 MHz, benzene-$d_6$): $\delta$ 496 (t, $J_{YN}$ = 7 Hz).

**2 from $[(C_5Me_5)_2Y][(\mu\text{-}Ph)_2BPh_2]$.** $KC_8$ (20 mg, 0.15 mmol) was added to a solution of $[(C_5Me_5)_2Y][(\mu\text{-}Ph)_2BPh_2]$ (50 mg, 0.074 mmol) in benzene (2 mL). After stirring for 20 h, the suspension was centrifuged and filtered leaving a red-orange solution. Solvent was removed under vacuum leaving a red-orange powder. Cooling of a saturated solution of methylcyclohexane to −35 °C yielded crystalline **2** (28 mg, 66%).

**$[(C_5Me_5)_2Lu]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$, 3.** $KC_8$ (18 mg, 0.13 mmol) was added to a solution of $[(C_5Me_5)_2Lu][(\mu\text{-}Ph)_2BPh_2]$ (50 mg, 0.065 mmol) in benzene (2 mL). After stirring for 20 h, the suspension was centrifuged and filtered leaving a red-orange solution. Solvent was removed under vacuum leaving a red-orange powder, which was extracted with methylcyclohexane to separate any unreacted $[(C_5Me_5)_2Lu][(\mu\text{-}Ph)_2BPh_2]$, leaving red-orange **3** (35 mg, 59%). X-ray quality crystals were grown from a saturated solution of **3** in methylcyclohexane at −35 °C. $^1H$ NMR (benzene-$d_6$) $\delta$ 2.00 ppm (s, $C_5Me_5$). $^{13}C$ NMR (benzene-$d_6$) $\delta$ 12.2 ($C_5Me_5$), 117.4 ($C_5Me_5$). IR: 2971s, 2907s, 2858s, 2724m, 1438s, 1379s, 1022m, 802w, 737w, 702m, 676s, 495s cm$^{-1}$. Anal. Calcd for $C_{40}H_{60}N_2Lu_2$: C, 52.29; H, 6.58; N, 3.05. Found: C, 51.68; H, 6.55; N, 1.46 (Repeated attempts to get elemental analysis on crystalline samples consistently gave acceptable CH values but low values

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**Table 1.** X-ray Data Collection Parameters for $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$, **2**

| | **2** |
|---|---|
| Empirical formula | $C_{40}H_{60}N_2Y_2\cdot 1/2(C_6H_{12})$ |
| Fw | 788.80 |
| temperature (K) | 103(2) |
| crystal system | tetragonal |
| space group | $P\bar{4}2_1c$ |
| $a$ (Å) | 14.2815(3) |
| $b$ (Å) | 14.2815(3) |
| $c$ (Å) | 19.7300(8) |
| α (deg) | 90 |
| $\beta$ (deg) | 90 |
| $\gamma$ (deg) | 90 |
| volume (Å$^3$) | 4024.2(2) |
| $Z$ | 4 |
| $\rho_{calcd}$ (Mg/m$^3$) | 1.302 |
| $\mu$ (mm$^{-1}$) | 2.900 |
| $R1$ [$I > 2.0\sigma(I)$] | 0.0340 |
| w$R2$ (all data) | 0.0877 |

for nitrogen. This is possibly due to the limited thermal stability of **3**: samples of **3** are stable at −35 °C but degrade at room temperature.

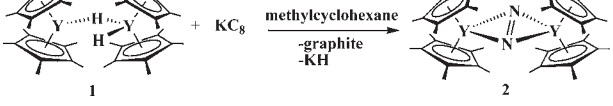
**$[(C_5Me_5)_2Lu]_2(\mu\text{-}\eta^2:\eta^2\text{-}^{15}N_2)$, 3-$^{15}$N.** This was done in a similar manner to that reported for **2-$^{15}$N**, except where noted. $KC_8$ (53 mg, 0.40 mmol) was added to a stirred solution of $[(C_5Me_5)_2Lu][(\mu\text{-Ph})_2BPh_2]$ (150 mg, 0.20 mmol). After addition of $^{15}N_2$ the reaction was stirred 20 h and following the workup reported for **3** resulted in the isolation of **3-$^{15}$N**. $^{15}$N NMR (60.87 MHz, benzene-$d_6$): $\delta$ 527.

**$[(C_5Me_5)_2Y(\mu\text{-SPh})]_2$, 4.** A solution of PhSSPh (11 mg, 0.050 mmol) in benzene (2 mL) was added to a solution of **2** (38 mg, 0.050 mmol) in benzene (3 mL). The solution quickly turned yellow with visible evolution of gas. After stirring for 30 min, the solvent was evaporated under vacuum leaving **4** as a pale yellow powder (49 mg, 99%). The $^1$H NMR spectrum of this material showed only the resonances of the previously reported $[(C_5Me_5)_2Y(\mu\text{-SPh})]_2$,[20] consistent with a quantitative yield.

**X-ray Data Collection, Structure Determination, and Refinement.** Crystallographic information on complexes **2** and **3**, are presented in Table 1 or in the Supporting Information.

## Results and Discussion

**Synthesis of $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$, 2.** The reaction of $[(C_5Me_5)_2YH]_2$, **1**, with $KC_8$ was originally examined in efforts to combine the high reactivity of yttrium and lanthanide metallocene hydrides, $[(C_5Me_5)_2LnH]_x$,[20] with $Ln^{2+}$ reactivity accessible via $LnZ_2Z'/M$ reactions, Scheme 2. Since divalent lanthanide hydrides are rare,[21] this could provide an option to access a combination of $Ln^{2+}$ and $H^-$ reactivity in a single system. As part of this investigation, the blank reaction of $[(C_5Me_5)_2YH]_2$ with $KC_8$ in the absence of substrate was examined. Surprisingly, these two species in methylcyclohexane under $N_2$ generate a soluble red-orange product in 2 h along with white and black precipitates. The major product isolated in this reaction is the unsolvated reduced dinitrogen complex, $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$, **2**, eq 1.



(1)

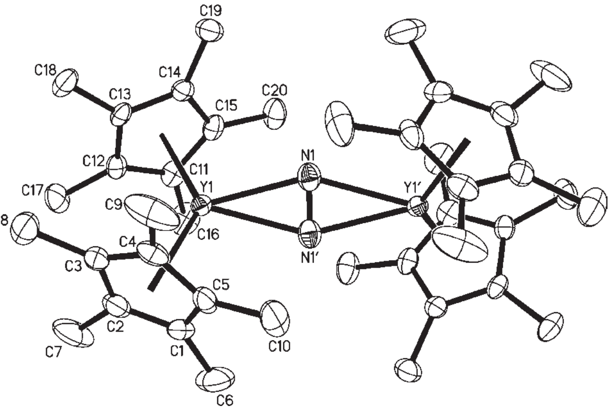


**Figure 1.** Thermal ellipsoid plot of $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$, **2**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been removed for clarity.

Complex **2** was characterized by $^1$H, $^{13}$C, and $^{15}$N NMR and IR spectroscopy, elemental analysis, and structurally identified by X-ray crystallography, Figure 1. This is the first example in our laboratory that the reactions of the type shown in Scheme 2 could be accomplished in a solvent other than THF or diethyl ether. The only other example in the literature is $\{[C_5H_2(CMe_3)_3]_2Nd\}_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$, also made in methylcyclohexane from $[C_5H_2(CMe_3)_3]_2NdI$ and $KC_8$.[5h] Since $[(C_5Me_5)_2YH]_2$ reacts with THF,[7] it was not a viable solvent for eq 1. As described below, arene solvents were also problematic with $[(C_5Me_5)_2LnH]_x$ because of C−H bond activation reactions that occur in these solvents.[9a,22]

An analogous synthesis of **2** from **1** was also examined with NaK as the reductant instead of $KC_8$, to probe the presence of KH as the insoluble byproduct without the complicating presence of potassium graphite residuals. The NaK reaction was slower than the reaction in eq 1, and took 24 h to complete. During this time, C−H bond activation occurred and some **1** was converted to the tuck-over complex, $(C_5Me_5)_2Y(\mu\text{-H})(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)Y(C_5Me_5)_2$,[19] which readily forms from $[(C_5Me_5)_2YH]_2$ when it remains in methylcyclohexane for several hours. Separation of the tuck-over complex and **2** from the reaction mixture left a gray insoluble material that reacted with $D_2O$ to form HD (identified by $^1$H NMR spectroscopy)[23] with no evidence of $C_5Me_5D$. This is consistent with the formation of an MH byproduct in eq 1, that is, the MZ′ byproduct of this $LnZ_2Z'/M$ reaction exemplified in Scheme 2 is MH.

To avoid the depletion of $[(C_5Me_5)_2YH]_2$ via decomposition to the tuck-over complex, the $[(C_5Me_5)_2YH]_2/NaK/N_2$ reaction was conducted with a 90:10 mixture of $N_2/H_2$ since the formation of tuck-over is reversible[22] in the presence of $H_2$. Complex **2** could be synthesized under these conditions without the tuck-over compound in the product mixture, but the yield was still not as high as observed in the $KC_8$ reaction. The $[(C_5Me_5)_2YH]_2/KC_8/N_2/H_2$ reaction was also examined with benzene as the solvent. While **2** is observed, $(C_5Me_5)_2Y(C_6H_5)$ is also

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**Table 2.** Selected Bond Distance (Å) and Angles (deg) for $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **2**, and for $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$

| | **2** | | **Sm** |
|---|---|---|---|
| Y(1)−Cnt1 | 2.400 | Sm(1)−Cnt(1) | 2.451 |
| Y(1)−Cnt2 | 2.375 | Sm(1)−Cnt(2) | 2.449 |
| Y(1)−N(1) | 2.279(3) | Sm(1)−N(1) | 2.348(6) |
| Y(1)−N(1′) | 2.292(3) | Sm(1)−N(1′) | 2.367(6) |
| N(1)−N(1′) | 1.172(6) | N(1)−N(1′) | 1.088(12) |
| Cnt1−Y(1)−Cnt2 | 134.3 | Cnt1−Sm(1)−Cnt2 | 140.1 |

present as a byproduct as observed by $^1$H NMR spectroscopy. This arene metalation has previously been described by Teuben and co-workers.[22] Thus from $[(C_5Me_5)_2YH]_2$, the preferred synthesis of **2** is via eq 1.

**Structure of 2.** Although **2** is an analogue of the $[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ complexes in Scheme 1 (Ln = Sm, Tm), it crystallizes in a different space group, $P\bar{4}2_1c$, rather than in $C_2/c$ for Sm[1] and $P\bar{1}$ for Tm.[2] Direct comparisons of the structure of **2** with the thulium analogue cannot be made since the crystals of the thulium complex were not of sufficient quality to provide good metrical data.[2] The 1.172(6) Å N−N distance in **2** is intermediate between the short 1.088(12) Å N−N distance of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, and the 1.236(8)−1.305(6) Å range for other $[Z_2(THF)Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ complexes.[1,2,5f] The differences in the N−N distances in the unsolvated yttrium and samarium complexes from the other, mostly THF-solvated, complexes cannot be due solely to the lack of solvation since unsolvated $[(C_5H_2{}^tBu_3)_2Nd]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ and $\{[C_5H_3(SiMe_3)_2]Tm\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ have N−N bond distances within the normal range for $Ln_2N_2$ complexes, 1.23 and 1.259(4) Å, respectively.[2,5h]

Comparisons with $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ are of interest since the samarium complex differs from all the other $Ln_2N_2$ complexes subsequently isolated.[24] The samarium complex is unusual in that the 1.088(12) Å N−N distance shows no reduction of dinitrogen, despite the fact that NMR and X-ray crystallography indicate the metals are both $Sm^{3+}$, that is, a two electron reduction has occurred.[1] The short N−N distance is consistent with the fact that $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ readily reverts back to $(C_5Me_5)_2Sm$ and $N_2$, a situation not seen with other $Ln_2N_2$ complexes. Facile loss of dinitrogen has also been observed with $[(C_5Me_5)_2Zr]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, $[U(NN'_3)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ $[NN'_3 = N(CH_2CH_2NSiBu^tMe_2)_3]$, and $[U(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_4\{Si^iPr_3\text{-}1,4\}_2)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ which have N−N distances of 1.182(5), 1.109(7), and 1.232(10) Å, respectively.[25] Complex **2** is stable with respect to loss of dinitrogen.

Complex **2** is similar to $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ in that both have a coplanar arrangement of the two metals and the two nitrogen atoms. As shown in Table 2, the Ln-($C_5Me_5$ ring centroid) and Ln-N($\mu\text{-}\eta^2{:}\eta^2\text{-}N_2$) distances in **2** are 0.05-0.08 Å smaller than those in $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ which matches the 0.06 Å difference in Shannon ionic radii for eight coordinate $Y^{3+}$ and $Sm^{3+}$.[26] The orientation of the metallocene units around the dinitrogen ligand is also similar. This can be evaluated by the dihedral angle between the planes defined by the two $C_5Me_5$ ring centroids and yttrium for each metallocene. The dihedral angle is 79.2° in **2** and 87.9° in the Sm complex. These values are close to the 90° value expected for a space efficient, tetrahedral arrangement of $(C_5Me_5)^-$ rings about the metal centers.

With $[(C_5Me_4H)_2M]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (M = Zr, Hf),[27] Chirik and co-workers have shown the importance of the geometry of the metallocene units for hydrogenation of $N_2$. Complexes with dihedral angles of ~60° can hydrogenate $N_2$.[28] This geometry allows $\pi$-bonding between Zr and $N_2$ in the highest occupied molecular orbital (HOMO) and significant Zr=N character, whereas a more square planar arrangement of four $(C_5Me_4H)^-$ ligands does not allow sufficient back bonding to activate $N_2$.[29] The 2.279(3) Å and 2.292(3) Å Y−N distances in **2** are typical of Y−N single bonds and do not show any significant Y=N character. For **2**, while the dihedral angle of 79.2° is even greater than those observed by Chirik, no evidence of hydrogenation of $N_2$ has been observed. This is consistent with the fact that the two yttrium metals in the dimer in **2** bring two less electrons to dinitrogen than can be provided by the two group 4 metals in the Zr and Hf complexes. This results in an N−N bond distance in **2** that is typical of an N=N double bond rather than the N−N single bond found with Zr and Hf.

**$(C_5Me_5)_2$YX Reactions.** Attempts were made to generate **2** from other yttrium metallocene precursors under analogous conditions. Treatment of the alkane soluble complexes $[(C_5Me_5)_2YMe]_x$,[18] $(C_5Me_5)_2Y(C_3H_5)$,[15] $(C_5Me_5)_2YCl(THF)$,[17] $(C_5Me_5)_3Y$,[16] and $(C_5Me_5)_2Y[N(SiMe_3)_2]$[30] with $KC_8$ under $N_2$ in methylcyclohexane for 24 h gave only starting materials by $^1$H NMR spectroscopy. The fact that eq 1 is not readily extended to other $(C_5Me_5)_2$YX complexes suggests that the hydride ligand is special in this reduction system.

**Reactions with Other Yttrium Hydrides.** To examine the breadth of the hydride reduction chemistry, reactions analogous to eq 1 were examined with mono- and tetramethylcyclopentadienyl metallocene hydride precursors, $[(C_5MeH_4)_2YH(THF)]_2$[11] and $[(C_5Me_4H)_2YH]_2$, respectively.[10] In neither case was a reduced dinitrogen complex isolated even though $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ is known and $[(C_5Me_4H)_2YH]_2$ is soluble in methylcyclohexane.[10]

**$[(C_5Me_5)_2LnH]_x$ Reactions.** Reactions with $[(C_5Me_5)_2LaH]_x$,[8a] $[(C_5Me_5)_2SmH]_2$,[12] and $[(C_5Me_5)_2LuH]_x$[9a] were also examined. $[(C_5Me_5)_2SmH]_2$ does react with $KC_8$ and $N_2$ to make the $(C_5Me_5)_2Sm/[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ equilibrium in Scheme 1. However, since $[(C_5Me_5)_2SmH]_2$ reacts with $KC_8$ under argon to make $(C_5Me_5)_2Sm$, which reacts with dinitrogen according to Scheme 1, this reaction may proceed in two steps through a well-defined $Sm^{2+}$ intermediate.

$[(C_5Me_5)_2LaH]_x$ does not react with $KC_8$ or NaK in methylcyclohexane when under a $N_2/H_2$ atmosphere,

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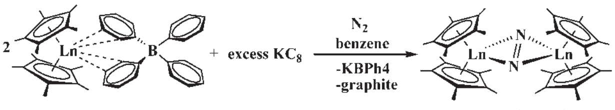
even though the related THF adduct, $[(C_5Me_5)_2La(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, is known and is highly reactive on its own.[5a] When the reaction is done only under nitrogen, $(C_5Me_5)_2La(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4)La(C_5Me_5)$ forms,[31] but not $[(C_5Me_5)_2La]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$. $[(C_5Me_5)_2LuH]_x$ reacts in methylcyclohexane to make a complicated mixture of products from which no analogue of **2** was isolable. The Lu reaction under a $N_2/H_2$ atmosphere did not clarify the complicated product mixture. It is possible that for the hydrides to react in this type of reaction, a terminal hydride must be available. Both $[(C_5Me_5)_2LnH]_x$ Ln = Y,[22] Lu[8a] exist as asymmetric dimers in solution, while other hydrides that were unreactive are more symmetric, that is, $[(C_5Me_5)_2LaH]_x$[8a] and $[(C_5Me_4H)_2YH]_2$.[10] Alternatively, the $KC_8$ reduction chemistry of yttrium may differ from that of lanthanum and lutetium.

**$[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ Complexes as Precursors in Non-Polar Solvents.** $[(C_5Me_5)_2Y][(\mu\text{-}Ph)_2BPh_2]$,[16] a member of a class of precursors commonly used for $LnZ_2Z'/M$ reactions,[5a,6,10] was also treated with $KC_8$ in methylcyclohexane to determine if it would form **2**, but no reaction was observed. This was expected since the tetraphenylborate complex is insoluble in this solvent. However, when the $[(C_5Me_5)_2Y][(\mu\text{-}Ph)_2BPh_2]$ reaction was examined in benzene, a second synthesis of unsolvated **2** was identified with improved yield over the hydride route, eq 2. This was surprising since earlier studies of the reduction of $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ in arenes did not give reduced dinitrogen products. The lanthanum and lutetium complexes, $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$, also react as shown in eq 2.



(2)

Ln = Y, **2**; Lu, **3**

The amount of $KC_8$ used in eq 2 proved to be crucial for the success of the reaction. When a slight excess of $KC_8$ (1.2−1.5 equiv) was used, in each case the La, Y, and Lu reactions were incomplete. NMR spectroscopy showed the presence of only small amounts of reduced dinitrogen products, along with large amounts of the lanthanide oxides, $[(C_5Me_5)_2Ln]_2(\mu\text{-}O)$,[32] and the starting lanthanide cations. Even when the concentration of the reactants was increased 3-fold, reactions with a slight excess of $KC_8$ were incomplete.

However, when 2 or more equiv of $KC_8$ were used, unsolvated reduced dinitrogen complexes could be obtained. For each metal, a red-orange solid resulted from these reactions. In the yttrium reaction, this was primarily **2**, which could be isolated in 66% yield. With lutetium, the unsolvated complex $[(C_5Me_5)_2Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **3**, was isolated for the first time in 60% yield. **3** was fully characterized by $^1H$, $^{13}C$ NMR, and $^{15}N$ NMR and IR spectroscopy, elemental analysis, and X-ray crystallography. X-ray data established connectivity, but were not of high enough quality to permit a discussion of bond distances and angles. The analogous reaction with lanthanum gave multiple products by $^1H$ NMR spectroscopy. Addition of THF to an NMR sample of the lanthanum product mixture in benzene-$d_6$ resulted in a set of resonances that matched those for the previously reported $[(C_5Me_5)_2La(THF)_2]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$,[5f] but this was only a minor component of the product mixture.

**Table 3.** $^{15}N$ NMR Chemical Shifts of $[Z_2Ln]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ Complexes

| $[Z_2Ln]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ | $^{15}N$ NMR shift $(\delta)^a$ | Reference |
|---|---|---|
| a $[(C_5Me_5)_2La(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ | 569 | 5f |
| b $\{[(Me_3Si)_2N]_2Lu(THF)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ | 557 | 5b |
| c $[(C_5Me_5)_2Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **3** | 527 | this work |
| d $[(C_5Me_4H)_2Lu(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ | 521 | 5c |
| e $\{[(Me_3Si)_2N]_2La(THF)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ | 516 | 33 |
| f $\{[(Me_3Si)_2N]_2Y(THF)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ | 513 | 5a |
| g $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **2** | 497 | this work |
| h $[(C_5Me_4H)_2La(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ | 495 | 5f |
| i $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ | 468 | 10 |

[a] Calibrated against nitromethane at 0 ppm.

Both **2** and **3** readily decomposed in the presence of small amounts (less than 1 equiv) of THF over 18 h at room temperature. The red-orange benzene solutions immediately turned to dark maroon solutions upon addition of THF, but over 18 h, the solutions faded to colorless. Neither NMR nor EPR spectroscopies were informative on these species. Earlier attempts to isolate $[(C_5Me_5)_2Ln(THF)_x]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes for yttrium and lutetium in the presence of THF likely failed as the coordination of THF may have sterically oversaturated the smaller metal centers leading to their instability.

**2-$^{15}$N and 3-$^{15}$N.** Complexes **2** and **3** were also synthesized under $^{15}N_2$, and their $^{15}N$ NMR spectra obtained. For **2**, the resonance for the reduced dinitrogen ligand was observed at 496 ppm as a triplet because of splitting from the two $I = 1/2$ $^{89}Y$ nuclei. The chemical shift and 7 Hz $^1J_{YN}$ values are similar to those reported for other yttrium dinitrogen complexes that range from 468 to 513 ppm, Table 3.

For **3**, the observed 527 ppm resonance is in the 521−557 ppm range of previously reported lutetium dinitrogen complexes. For a given metal, the THF solvated complexes in Table 3 generate a trend that the highest field $^{15}N$ resonances are found for $(C_5Me_5)^-$ complexes followed by $[(Me_3Si)_2N]^-$ complexes followed by $(C_5Me_4H)^-$ compounds (entries a, e, and h; b and d; f and i). The only unsolvated compounds in Table 3, **2** and **3**, both exhibit slightly lower field resonances than would be expected of the THF-solvated analogues. Since the resonances of **2** and **3** now fall in between those of the $[(Me_3Si)_2N]^-$ and $(C_5Me_4H)^-$ compounds (entries f and i; b and d), this trend is apparently affected by the presence or absence of a coordinating ligand.

**Reactivity of 2 and 3.** The reductive reactivity of **2** and **3** was probed by treatment with PhSSPh, a substrate that recently has proven to be a good standard to evaluate f element reductive chemistry.[20,34] As shown in eq 3, reduction

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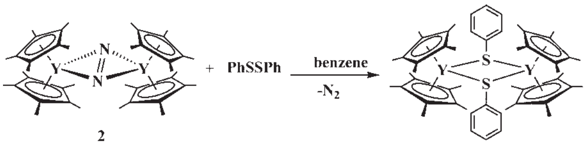
rapidly occurs to form $[(C_5Me_5)_2Y(SPh)]_2$, **4**,[20] in quantitative yield with concomitant release of gas, presumed to be $N_2$. NMR evidence indicates that **3** reacts analogously.



2

4

(3)

## Conclusion

The formation of $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **2**, from $[(C_5Me_5)_2YH]_2$ and $KC_8$ expands the scope of the $LnZ_2Z'/M$ reduction system for the production of reduced dinitrogen complexes to $(Z')^- = (H)^-$ and to methylcyclohexane, beyond the commonly used ether solvents. Complexes **2** and **3** can also be made from $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ precursors in benzene when excess $KC_8$ is used. These two routes provide access to unsolvated pentamethylcyclopentadienyl metallocene dinitrogen complexes, $[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, a class previously accessible only from the divalent lanthanides, $Sm^{2+}$ and $Tm^{2+}$. These routes have also provided access to dinitrogen complexes, $[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ Ln = Y and Lu, not previously available for the smaller lanthanides. The fact that these $[(C_5R_5)_2LnX]_x/KC_8$ reductions in nonpolar solvents are limited to $(X)^- = (H)^-$ and $(BPh_4)^-$ is another example that the $LnZ_3/M$ and $LnZ_2Z'/M$ reductions are not general for all combinations of Ln and Z.[35] Understanding these variations will require a better understanding of the mechanism(s) of these reductions.

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**Supporting Information Available:** X-ray data collection, structure solution and refinement (PDF) and X-ray diffraction details of compound **2** (CIF, CCDC No. 787015). X-ray data collection and unit cell of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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