Supporting Information for

$(C_5Me_4H)^{1-}$-Based Reduction of Dinitrogen by the Mixed Ligand Tris(polyalkylcyclopentadienyl) Lutetium and Yttrium Complexes, $(C_5Me_5)_{3-x}(C_5Me_4H)_xLn$

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Experimental

The syntheses and manipulations described below were conducted under argon or nitrogen with rigorous exclusion of air and water using glovebox, vacuum line and Schlenk techniques. Solvents were dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotope Laboratories) were dried over sodium potassium alloy, degassed, and vacuum transferred prior to use. KC_5Me_5,[1] KC_5Me_4H,[2] $(C_5Me_5)_2La(\mu\text{-}Ph)_2BPh_2$,[3] $(C_5Me_4H)_2Ln(\mu\text{-}Ph)_2BPh_2$ (Ln = Lu,[4] Y[5]), $(C_5Me_5)_2(C_5Me_4H)Ln$ (Ln = Lu, **1**;[6] Y, **2**[6]), and $(C_5Me_4H)_3Sc$, **9**,[7] were prepared according to the literature. ^1H NMR spectra were obtained on a Bruker DRX500 MHz spectrometer with a BBO probe at 25 °C. ^{13}C NMR spectra were obtained on a Bruker DRX500 MHz spectrometer operating at 126 MHz with a TCI cryoprobe at 25 °C. IR samples were prepared as KBr pellets and the spectra were obtained on a Varian 1000 FT-IR system. Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS analyzer.

$(C_5Me_5)(C_5Me_4H)_2Lu$, 3. In an argon-filled glovebox, KC_5Me_5 (358 mg, 2.05 mmol) was added to a stirred white slurry of $(C_5Me_4H)_2Lu(\mu\text{-}Ph)_2BPh_2$ (538 mg, 0.730 mmol) in benzene (15 mL). After stirring for 18 h, the yellow slurry was centrifuged, filtered, and the solvent was removed under reduced pressure to yield a pale yellow solid. The pale yellow solid was stirred in hexane (15 mL) for 30 min, centrifuged, filtered, and the hexane was removed under reduced pressure to yield a bright yellow solid (336 mg, 83%). ^1H NMR (C_6D_6): δ 5.55 (s, 2H, $C_5Me_4\mathit{H}$), 2.02 (s, 12H, $C_5\mathit{Me}_4H$), 1.87 (s, 15H, $C_5\mathit{Me}_5$), 1.74 (s, 12H, $C_5\mathit{Me}_4H$). Variable temperature spectra are shown in Figure S1 below. ^{13}C NMR (126 MHz, C_6D_6): δ 125.2 (C_5Me_4H), 119.2 (C_5Me_5), 116.4

(C_5Me$_4$H), 102.6 (C_5Me$_4$H), 13.6 (C$_5$$Me_4$H), 12.1 (C$_5$$Me_4$H), 11.9 (C$_5$$Me_5$). IR 3056w, 2956s, 2906s, 2857s, 2726w, 2600m, 2462w, 2369w, 1439s, 1382s, 1326m, 1277m, 1137m, 1107w, 1068w, 1022m, 973w, 812m, 794m, 736m, 705m, 635m, 612s, 593m, 564m cm^{-1}. Anal. Calcd for $C_{28}H_{41}Lu$: C, 60.86; H, 7.48. Found: C, 60.64; H, 7.98.

$(C_5Me_5)(C_5Me_4H)_2Y$, 4. Following the procedure for **3**, in a nitrogen-filled glovebox, KC_5Me_5 (490 mg, 2.81 mmol) was added to a stirred white slurry of $(C_5Me_4H)_2Y(\mu\text{-Ph})_2BPh_2$ (627 mg, 0.964 mmol) in benzene (15 mL) to yield a bright yellow solid (374 mg, 83%). ^{1}H NMR (C_6D_6): δ 6.20 (s, 2H, C$_5$Me$_4$$H$), 2.06 (s, 12H, C$_5$$Me_4$H), 1.94 (s, 15H, C$_5$$Me_5$), 1.84 (s, 12H, C$_5$$Me_4$H). Variable temperature spectra are shown in Figure S2 below. ^{13}C NMR (126 MHz, C_6D_6): δ 124.9 (d, $^1J_{YC}$ = 1 Hz, C_5Me$_4$H), 120.5 (d, $^1J_{YC}$ = 1 Hz, C_5Me$_5$), 115.4 (br, C_5Me$_4$H), 113.5 (d, $^1J_{YC}$ = 1 Hz, C_5Me$_4$H), 13.5 (C$_5$$Me_4$H), 12.7 (C$_5$$Me_5$), 12.3 (C$_5$$Me_4$H). IR 3124w, 2966s, 2905s, 2859s, 2725m, 1904m, 1439s, 1384m, 1372m, 1331w, 1020m, 972w, 937w, 785s, 700w, 608w, 595w cm^{-1}. Anal. Calcd for $C_{28}H_{41}Y$: C, 72.09; H, 8.86. Found: C, 71.60; H, 9.28.

$[(C_5Me_5)_2Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, 5. In a nitrogen-filled glovebox, $(C_5Me_5)_2(C_5Me_4H)Lu$, **1**, (86 mg, 0.15 mmol) was dissolved in toluene (10 mL) and added to a vial containing KC_8 (24 mg, 0.18 mmol). After stirring for 30 min, black and white solids, presumably graphite and KC_5Me_4H, were removed by centrifugation and filtration resulting in a red-orange solution. The solvent was removed under reduced pressure to produce a red-orange tacky solid which was washed with a minimal amount (2 mL) of cold hexane (–35 °C) to yield a red microcrystalline solid (34 mg, 49%) whose ^{1}H NMR spectrum matched that of the previously characterized $[(C_5Me_5)_2Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}$

N_2), **5**.[12] No evidence was observed for the mixed ligand complex $[(C_5Me_5)(C_5Me_4H)Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **7**, described below.

Isolation of KC_5Me_4H Byproduct. In a nitrogen-filled glovebox, the black and white solids removed by centrifugation from the reaction of **1** with KC_8 were slurried with C_6D_6 and added to an NMR tube. The NMR tube was capped with a rubber septum, removed from the glovebox, and sealed with Parafilm M. Degassed D_2O was transferred *via* syringe into the sealed NMR tube. The solution was filtered into a new NMR tube in air and the ^{1}H NMR spectrum displayed multiple peaks, none of which matched that of C_5Me_5D.

$[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, 6. Following the procedure for **5**, the previously characterized $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **6**,[12] (14 mg, 37%), confirmed by ^{1}H NMR spectroscopy, was isolated from the reaction of $(C_5Me_5)_2(C_5Me_4H)Y$, **2**, (49 mg, 0.10 mmol) with KC_8 (15 mg, 0.11 mmol) under a dinitrogen atmosphere.

Alternative Synthesis of 6. In a nitrogen-filled glovebox, $(C_5Me_5)_2(C_5Me_4H)Y$, **2**, (10 mg, 0.021 mmol) was dissolved in C_6D_6 (1 mL), placed in an NMR tube which was capped with a rubber septum and sealed with Parafilm M. The NMR tube was stored in a glovebox containing a dinitrogen atmosphere and taken out briefly to obtain spectroscopic measurements on the sample. The slow decomposition of **2** was monitored by ^{1}H NMR spectroscopy. Over the course of 3 weeks, red X-ray quality crystals formed. These red crystals were washed with hexane to yield **6**[12] (4 mg, 51%) and their identity was confirmed by X-ray crystallography. The ^{1}H NMR spectrum of the remaining solution showed multiple products including resonances consistent with $(C_5Me_4H)_2$.[13] No evidence for $(C_5Me_5)_2$ was observed.

In a nitrogen-filled glovebox, $(C_5Me_5)_2(C_5Me_4H)Y$, **2**, (74 mg, 0.15 mmol) was dissolved in C_6H_6 (4 mL) and transferred to a sealed 50 mL sidearm Schlenk flask equipped with a greaseless stopcock. Over the course of 4 weeks, the yellow solution became a deep red solution containing no insoluble material. The solvent was removed under reduced pressure to produce a red-orange tacky solid which was washed with pentane to yield **6** (38 mg, 67%), confirmed by ^1H NMR spectroscopy.[12]

$[(C_5Me_5)(C_5Me_4H)Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, 7. Following the procedure for **5**, $[(C_5Me_5)(C_5Me_4H)Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **7**, (14 mg, 23%) was isolated from the reaction of $(C_5Me_5)(C_5Me_4H)_2Lu$, **3**, (77 mg, 0.14 mmol) and KC_8 (23 mg, 0.17 mmol) in toluene (20 mL). X-ray quality crystals of **7** were grown from a concentrated toluene solution at –35 °C. ^1H NMR (C_6D_6): δ 5.69 (s, 1H, $C_5Me_4\mathit{H}$), 2.05 (s, 6H, $C_5\mathit{Me}_4H$), 2.04 (s, 6H, $C_5\mathit{Me}_4H$), 1.97 (s, 15H, $C_5\mathit{Me}_5$). Due to the low solubility of this complex (~1 mg/mL at 25 °C in C_6D_6), ^{13}C NMR data was not obtained. IR: 2966s, 2908s, 2860s, 2725m, 1736m, 1484m, 1444s, 1382s, 1331m, 1251w, 1183w, 1143w, 1110w, 1059w, 1023m, 973w, 937w, 920w, 784s, 709w, 626m, 595w, 5571w, 554w, 475vs cm^{-1}. Anal. Calcd for $C_{38}H_{56}Lu_2N_2$: C, 51.24; H, 6.34; N, 3.14. Found: C, 51.10; H, 6.24; N, 2.97.

Alternative Synthesis of 7. In a nitrogen-filled glovebox, $(C_5Me_5)(C_5Me_4H)_2Lu$, **3**, (10 mg, 0.018 mmol) was dissolved in C_6D_6 (1 mL), placed in an NMR tube which was capped with a rubber septum and sealed with Parafilm M. The NMR tube was stored in a glovebox containing a dinitrogen atmosphere and taken out briefly to obtain spectroscopic measurements on the sample. The slow decomposition of **3** was monitored by ^1H NMR spectroscopy. Over the course of 3 weeks, orange X-ray quality crystals formed. These orange crystals were washed with hexane to yield **7** (6 mg, 75%) and their identity was confirmed by X-ray crystallography. The ^{1}H NMR spectrum of the remaining solution showed multiple products including resonances consistent with $(C_5Me_4H)_2$.[13] No evidence for $(C_5Me_5)_2$ was observed.

In a nitrogen-filled glovebox, $(C_5Me_5)(C_5Me_4H)_2Lu$, **3**, (55 mg, 0.10 mmol) was dissolved in C_6H_6 (3 mL) and transferred to a sealed 50 mL sidearm Schlenk flask equipped with a greaseless stopcock. Over the course of 3 weeks, dark orange crystals formed. These orange crystals were washed with pentane to yield **7**, (22 mg, 50%) confirmed by ^{1}H NMR spectroscopy.

Reactivity of $(C_5Me_5)_{3-x}(C_5Me_4H)_xLn$ Complexes in the Presence of KC_5Me_4R (R = H, Me). At the suggestion of a referee, in a nitrogen-filled glovebox, samples of 0.049–0.058 mmol of $(C_5Me_5)_{3-x}(C_5Me_4H)_xLn$ complexes were dissolved in C_6H_6 (3 mL), mixed with 0.03 mmol of KC_5Me_4R and transferred to a sealed 50 mL sidearm Schlenk flask equipped with a greaseless stopcock. Over the course of 4 weeks, the following results were obtained with the combinations indicated.

$(C_5Me_5)_2(C_5Me_4H)Lu$, **1**, (33 mg, 0.058 mmol) / KC_5Me_4H (5 mg, 0.03 mmol): The solution was pale orange indicating formation of small amounts of a reduced dinitrogen complex and the ^{1}H NMR spectrum showed compounds **1**:**7** in a 1:11 ratio as well as multiple other resonances that do not correspond to **1** or **7**. .

$(C_5Me_5)_2(C_5Me_4H)Y$, **2**, (27 mg, 0.056 mmol) / KC_5Me_4H (5 mg, 0.03 mmol): The solution did not turn the red color observed in the absence of KC_5Me_4H; the solution was orange and the ^{1}H NMR spectrum showed compounds **2**:**6** in a 3.25:1 ratio.

$(C_5Me_5)(C_5Me_4H)_2Lu$, **3**, (27 mg, 0.049 mmol) / KC_5Me_5 (5 mg, 0.03 mmol): No red crystals formed as observed in the absence of KC_5Me_4H; the solution remained yellow and the ^1H NMR spectrum showed no evidence for **7**.

$(C_5Me_5)(C_5Me_4H)_2Y$, **4**, (27 mg, 0.058 mmol) / KC_5Me_5: The solution was pale orange indicating formation of small amounts of a reduced dinitrogen complex. The ^1H NMR spectrum showed several sets of $(C_5Me_4H)^{1-}$ resonances including resonances for $Y(C_5Me_4H)_3$ and **6**, but no remaining **4**.

$[(C_5Me_5)(C_5Me_4H)Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}^{15}N_2)$, 7–^{15}N. In an argon-filled glovebox, **3** (10 mg, 0.018 mmol) was dissolved in C_6H_6 (1 mL) and transferred to a J-Young NMR tube equipped with a Teflon stopcock. The J-Young tube was connected to a high vacuum line (10^{-5} torr) and degassed by three freeze–pump–thaw cycles. $^{15}N_2$ (1 atm) was introduced to the sample at room temperature and the J-Young tube was sealed. Over the course of 3 weeks, orange crystals formed. The J-Young tube was brought into an argon-filled glovebox and the orange crystals were washed with hexane to yield **7–^{15}N** (6 mg, 75%). The IR spectrum of **7–^{15}N** was identical to that of **7**, except the 1736 cm^{-1} absorption in **7** was shifted to 1678 cm^{-1} in **7–^{15}N**.

$[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, 8. Following the procedure for **5**, $(C_5Me_5)(C_5Me_4H)_2Y$, **4**, (89 mg, 0.19 mmol) in toluene (5 mL) was added to a vial containing KC_8 (10 mg, 0.21 mmol) to yield an orange solid (24 mg). ^1H NMR spectroscopy of the orange solid showed the major product to be the ligand redistribution product $(C_5Me_4H)_3Y$[5] along with multiple additional products. Upon addition of THF to the NMR sample, resonances consistent with $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$[5] were observed. However, this was a minor product in the reaction. IR (mixture of products): 2963s, 2907s, 2859s, 2726m, 1442m, 1382m, 1329w, 1111w, 1023w, 973w, 781m, 673w, 623w, 487s cm^{-1}.

$[(C_5Me_4H)_2Sc]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, 10. In a nitrogen-filled glovebox, $(C_5Me_4H)_3Sc$, **9**, (10 mg, 0.024 mmol) was dissolved in C_6D_6 (1 mL), placed in an NMR tube which was capped with a rubber septum and sealed with Parafilm M. The NMR tube was stored in a glovebox containing a dinitrogen atmosphere and taken out briefly to obtain spectroscopic measurements on the sample. The slow decomposition of **9** was monitored by ^{1}H NMR spectroscopy. Over the course of 3 weeks, red X-ray quality crystals formed. These red crystals were washed with hexane to yield **10** (4 mg, 54%) and their identity was confirmed by X-ray crystallography. The ^{1}H NMR spectrum of the remaining solution showed resonances for unreacted $(C_5Me_4H)_3Sc$, **9**,[7] and resonances consistent with $(C_5Me_4H)_2$.[13]

X-ray Data Collection, Structure Solution and Refinement for $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, 6. Although $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **6**, has previously been characterized, X-ray data, collection, structure solution and refinement (CCDC 814919) are included here as **6** was found to crystallize in a different space group than previously reported, Table S.1.[12]

A red crystal of approximate dimensions 0.19 x 0.21 x 0.33 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[14] program package and the CELL_NOW[15] were used to determine the unit-cell parameters. Data was collected using a 25 sec/frame scan time for a sphere of diffraction data. The raw frame data was processed using SAINT[16] and TWINABS[17] to yield the reflection data file (HKLF5 format)[17]. Subsequent calculations were carried out using the SHELXTL[18] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[19] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.1189 and Goof = 1.052 for 417 variables refined against 8205 data (0.78Å), R1 = 0.0459 for those 6529 with $I > 2.0\sigma(I)$. The structure was refined as a non-merohedral twin.

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)(C_5Me_4H)Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, 7. A yellow crystal of approximate dimensions 0.15 x 0.22 x 0.31 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[20] program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[21] and SADABS[22] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[18] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space groups *Pnma* and $Pna2_1$. It was later determined that space group $Pna2_1$ was correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[19] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0407 and Goof = 1.025 for 398 variables refined against 8209 data (0.74Å), R1 = 0.0167 for those 7987 data with $I > 2.0\sigma(I)$. The absolute structure could not be unambiguously assigned by refinement of the Flack parameter.[23] Inversion of the model led to better convergence in terms of esd's, wR2 and GooF values. The structure was refined as a twin yielding BASF = 0.313(6). Attempts to solve the structure using the centrosymmetric space group were not successful. Details are given in Table S.1.

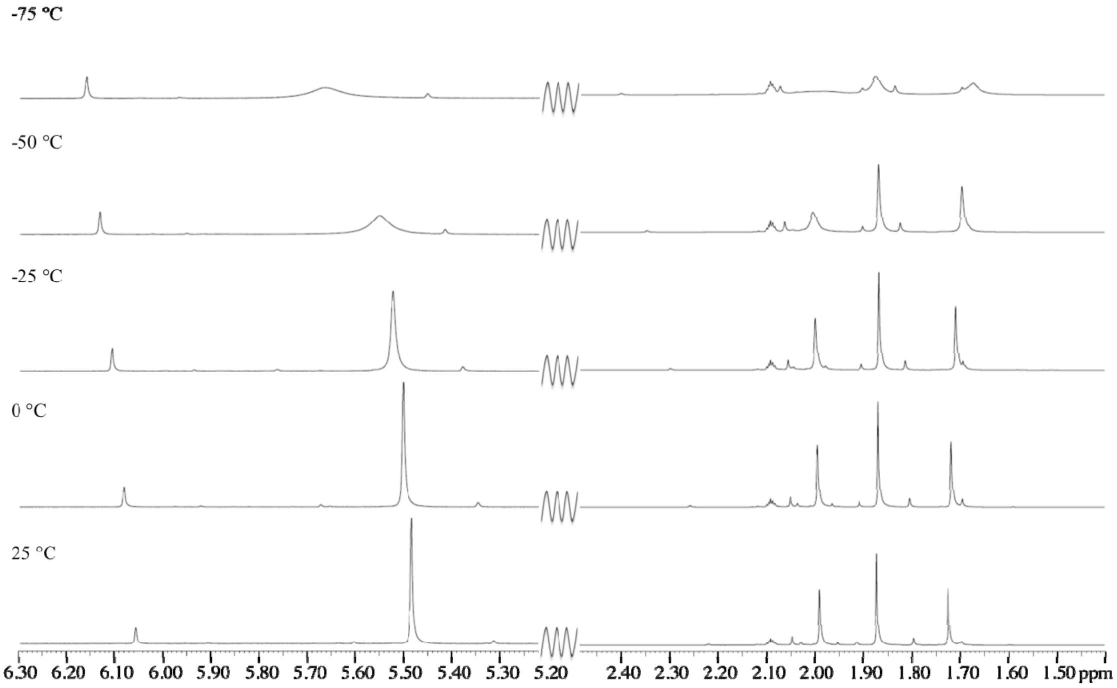

Figure S.1. Variable temperature ^{1}H NMR spectra (25 to –75 °C) of $(C_5Me_5)(C_5Me_4H)_2Lu$, **3**. For clarity purposes, the left and right sides of the spectra are not drawn at the same intensity scale.

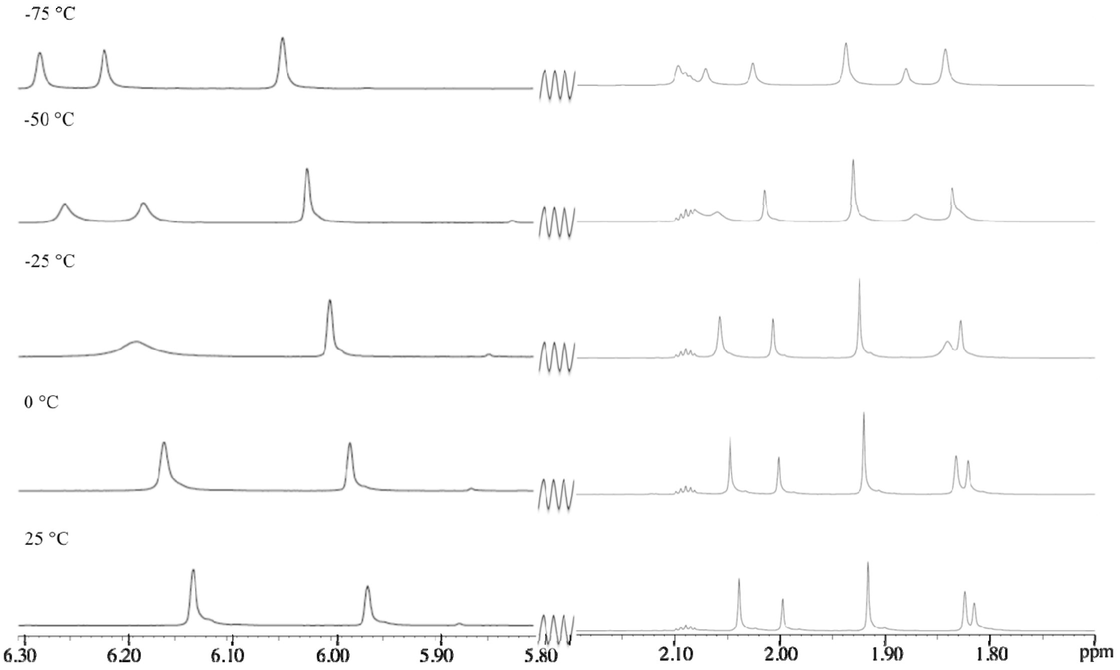

Figure S.2. Variable temperature ^{1}H NMR spectra (25 to -75 °C) of (C_5Me_5)(C_5Me_4H)$_2$Y, **4**. For clarity purposes, the left and right sides of the spectra are not drawn at the same intensity scale.

Table S.1. X-ray Data Collection Parameters for $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$, **6**, and $[(C_5Me_5)(C_5Me_4H)Lu]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$, **7**.

	6	**7**
formula	$C_{40}H_{60}N_2Y_2$	$C_{38}H_{56}Lu_2N_2$
fw	746.72	890.79
space group	$P\bar{1}$	$Pna2_1$
crystal system	triclinic	orthorhombic
a (Å)	10.6716(11)	21.9504(13)
b (Å)	10.9978(11)	8.4448(5)
c (Å)	16.7386(17)	18.7468(11)
V (Å^3)	1873.4(3)	3475.0(4)
α (deg)	77.9317(13)	90
β (deg)	77.8776(13)	90
γ (deg)	83.5536(13)	90
Z	2	4
ρ_{calcd} (mg/m^3)	1.324	1.703
μ (mm^{-1})	3.110	5.676
temp (K)	93(2)	143(2)
R1 $[I > 2\sigma(I)]^a$	0.0459	0.0167
wR2 (all data)^a	0.1189	0.0407

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

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