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Synthesis and Reactivity of Bis(tetramethylcyclopentadienyl) Yttrium Metallocenes Including the Reduction of Me_3SiN_3 to $[(Me_3Si)_2N]^-$ with $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$

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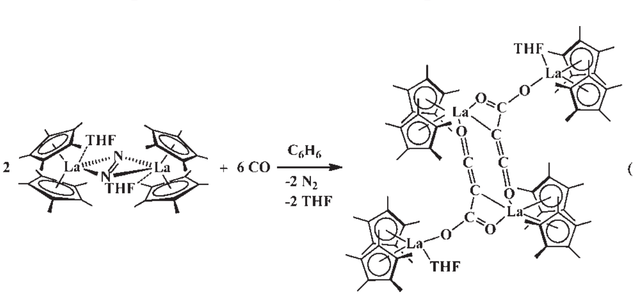
The metallocene precursors needed to provide the tetramethylcyclopentadienyl yttrium complexes $(C_5Me_4H)_3Y$, $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, and $[(C_5Me_4H)_2Y(\mu\text{-}H)]_2$ for reactivity studies have been synthesized and fully characterized, and their reaction chemistry has led to an unexpected conversion of an azide to an amide. $(C_5Me_4H)_2Y(\mu\text{-}Cl)_2K(THF)_x$, **1**, synthesized from YCl_3 and KC_5Me_4H reacts with allylmagnesium chloride to make $(C_5Me_4H)_2Y(\eta^3\text{-}C_3H_5)$, **2**, which is converted to $[(C_5Me_4H)_2Y][(\mu\text{-}Ph)_2BPh_2]$, **3**, with $[Et_3NH][BPh_4]$. Complex **3** reacts with KC_5Me_4H to form $(C_5Me_4H)_3Y$, **4**. The reduced dinitrogen complex, $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **5**, can be synthesized from either $[(C_5Me_4H)_2Y]_2[(\mu\text{-}Ph)_2BPh_2]$, **3**, or $(C_5Me_4H)_3Y$, **4**, with potassium graphite under a dinitrogen atmosphere. The ^{15}N labeled analogue, $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}^{15}N_2)$, **5-^{15}N**, has also been prepared, and the ^{15}N NMR data have been compared to previously characterized reduced dinitrogen complexes. Complex **2** reacts with H_2 to form the corresponding hydride, $[(C_5Me_4H)_2Y(\mu\text{-}H)]_2$, **6**. Complex **5** displays similar reactivity to that of the analogous $[(C_5Me_4H)_2Ln(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ complexes (Ln = La, Lu), with substrates such as phenazine, anthracene, and CO_2. In addition, **5** reduces Me_3SiN_3 to form $(C_5Me_4H)_2Y[N(SiMe_3)_2]$, **7**.

Introduction

Recent advances in reductive lanthanide chemistry have revealed that dinitrogen complexes of general formula, $[(C_5Me_4R)_2Ln(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (R = Me, H), can be effective reductants for accomplishing unusual transformations. The reductive trimerization of CO to form a ketenecarboxylate dianion shown in eq 1 is one example.[1] The pentamethylcyclopentadienyl dinitrogen complex in eq 1,



(1)

$[(C_5Me_5)_2La(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, can be synthesized by the reaction of $[(C_5Me_5)La][(\mu\text{-}Ph)_2BPh_2)]$ with KC_8 in tetrahydrofuran (THF) under a nitrogen atmosphere,[2] but analogous reduced dinitrogen complexes of the late lanthanide metals with $(C_5Me_5)^-$ ancillary ligands have not been reported in the literature. These would be expected to be more sterically crowded and consequently more reactive and difficult to isolate.[3]

To expand the available chemistry of the $Ln_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ system, analogues with the smaller tetramethylcyclopentadienyl ligand, $[(C_5Me_4H)_2Ln(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, were explored to determine if $Ln_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ complexes for both large and small lanthanide metals were isolable. $[(C_5Me_4H)_2Ln(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ complexes can be isolated for both La[2] and Lu,[4] but different synthetic routes are preferable in each case. $[(C_5Me_4H)_2La(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ can be prepared by the reaction of $(C_5Me_4H)_3La$ with excess KC_8 under nitrogen[2] in a preparation that is facile since $(C_5Me_4H)_3La$ is obtainable directly from anhydrous $LaCl_3$ and 3 equiv of KC_5Me_4H.[5] This route is not as viable for lutetium since $(C_5Me_4H)_3Lu$ requires a four step synthesis.[4,6]

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A desirable member of the $[(C_5Me_4H)_2Ln(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ family of complexes is Ln = Y, since Y^{3+} is a diamagnetic ion with $I = 1/2$ (100% natural abundance) and can therefore provide more detailed structural information by NMR than other lanthanide ions. The 9-coordinate Y^{3+} (1.075 Å)[7] is similar in size to the 9-coordinate trivalent lanthanide ion, Ho^{3+} (1.072 Å),[7] and typically displays reactivity analogous to the late lanthanides. Therefore, $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ would be expected to be reactive like $[(C_5Me_4H)_2Lu(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$[8] and have the capacity to provide additional information via NMR spectroscopy.

However, none of the tetramethylcyclopentadienyl metallocene precursors needed to make $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ were known. The closest complex in the literature was $(C_5Me_4H)Y(\mu\text{-}Cl_2)Na(Et_2O)_2$.[9] Here we report the synthesis of the series of precursors, $(C_5Me_4H)_2Y(\mu\text{-}Cl)_2K(THF)_x$, **1**, $(C_5Me_4H)_2Y(\eta^3\text{-}C_3H_5)$, **2**, and $[(C_5Me_4H)_2Y][(\mu\text{-}Ph)_2BPh_2]$, **3**, as well as a high yield synthesis of $(C_5Me_4H)_3Y$, **4**, another precursor to $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **5**. Synthesis of the hydride member of this yttrium $(C_5Me_4H)^-$ family $[(C_5Me_4H)_2Y(\mu\text{-}H)]_2$, **6**, is also reported for comparison to the $[(C_5Me_5)_2Y(\mu\text{-}H)]_x$ analogue.[10] The reductive capacity of **5** has been explored and includes a new type of $Ln_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ reaction involving conversion of Me_3SiN_3 to an amide complex, $(C_5Me_4H)_2Y[N(SiMe_3)_2]$, **7**.

Experimental Section

The manipulations described below were performed under nitrogen or argon with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were saturated with UHP grade argon (Airgas) and dried by passage through Glasscontour drying columns before use.[11] NMR solvents were dried over NaK alloy and vacuum transferred before use. ^1H and ^{13}C NMR spectra were recorded with a Bruker DRX 500 MHz spectrometer. ^{15}N NMR spectra were recorded with an Avance 600 MHz spectrometer and calibrated using an external reference, ^{15}N-formamide in dimethyl sulfoxide (DMSO, −269 ppm with respect to nitromethane at 0 ppm).[12] ^{11}B NMR was calibrated using $BF_3 \cdot$etherate as an external reference (0 ppm). Infrared spectra were recorded as thin films obtained from benzene-d_6 on the silicon window of the probe of an ASI ReactIR 1000 spectrometer[13] or as KBr pellets on a PerkinElmer Spectrum One FT-IR spectrometer. H_2 and CO_2 were purchased from Airgas and used as received. Allylmagnesium chloride (2.0 M in THF) and 1,4 dioxane (anhydrous) were purchased from Aldrich and used as received. 1,2,3,4-tetramethylcyclopentadiene, $C_5Me_4H_2$, was purchased from Aldrich, distilled onto 4A molecular sieves, and degassed by three freeze−pump−thaw cycles prior to use. $K[N(SiMe_3)_2]$ was purchased from Aldrich, dissolved in toluene, centrifuged to remove insoluble impurities, and recrystallized before use. KC_5Me_4H was prepared similarly to the reported synthesis of KC_5Me_5.[14] $^{15}N_2$, 98% was purchased from Cambridge Isotope Laboratory and was used as received. Elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany) or on a PerkinElmer Series II 2400 CHN elemental analyzer.

$(C_5Me_4H)_2Y(\mu\text{-}Cl)_2K(THF)_x$, 1. $(C_5Me_4H)_2Y(\mu\text{-}Cl)_2K(THF)_x$ was prepared in a reaction analogous to the synthesis of $(C_5Me_4H)_2Lu(\mu\text{-}Cl)_2K(THF)_2$.[4] In a nitrogen-filled glovebox, KC_5Me_4H (3.09 g, 19.3 mmol) was slowly added to a stirred white slurry of YCl_3 (1.88 g, 9.63 mmol) in 300 mL of THF. After the mixture was stirred for 48 h, the solution was centrifuged to remove insoluble material, presumably KCl, and the solution was evaporated to dryness. The resulting off-white powder was washed with toluene and the solid was dried to yield a bright white powder, **1** (3.87 g, 91% for $x = 0$ as determined by elemental analysis). ^1H NMR (500 MHz, THF-d_8): δ 5.51 (s, 2H, $C_5Me_4\mathit{H}$), 1.90 (s, 12H, $C_5\mathit{Me}_4H$), 1.83 (s, 12H, $C_5\mathit{Me}_4H$). ^{13}C NMR (126 MHz, THF-d_8): δ 119.78 (C_5Me_4H), 115.73 (C_5Me_4H), 109.56 (C_5Me_4H), 13.84 ($C_5\mathit{Me}_4H$), 12.22 ($C_5\mathit{Me}_4H$). IR: 3069w, 2959s, 2908s, 2859s, 2726w, 1479w, 1443m, 1435m, 1381m, 1324w, 1147w, 1023m, 975w, 785s, 619w cm^{-1}. Anal. Calcd for the THF free complex, $C_{18}H_{24}Cl_2KY$: C, 49.21; H, 5.51. Found: C, 48.45; H, 5.51.

$(C_5Me_4H)_2Y(\eta^3\text{-}C_3H_5)$, 2. In a nitrogen-filled glovebox, allylmagnesium chloride (2.2 mL of a 2.0 M solution in THF, 4.4 mmol) was added to a stirred white slurry of $(C_5Me_4H)_2Y(\mu\text{-}Cl)_2K$, **1**, (1.93 g, 4.39 mmol) in 75 mL of toluene. A yellow solution immediately formed. After the mixture was stirred for 24 h, the solution was evaporated to dryness to yield a pale yellow powder. This material was triturated with 2% 1,4 dioxane in hexanes (75 mL), and a white precipitate was removed via centrifugation to yield a yellow solution. Evaporation of the solvent left a yellow powder that was placed in a glass tube fitted with a greaseless Teflon stopcock and heated to 55 °C at 10^{-6} Torr for 48 h. The yellow solids were transferred to an argon-filled glovebox free of coordinating solvent and extracted with hexanes. Slow removal of the solvent left yellow crystals of $(C_5Me_4H)_2Y(\eta^3\text{-}C_3H_5)$, **2**, (1.39 g, 85%). Crystals suitable for X-ray analysis were grown from a concentrated toluene solution of **2** at −35 °C over the course of 24 h. ^1H NMR (500 MHz, benzene-d_6): δ 6.99 (m, 1H, $CH_2C\mathit{H}CH_2$), 5.85 (s, 1H, $C_5Me_4\mathit{H}$), 5.76 (s, 1H, $C_5Me_4\mathit{H}$), 3.50 (dd, J_{HH} = 15 Hz, J_{HH} = 2 Hz, 2H, allyl *anti* CH_2), 2.28 (d, J_{HH} = 9.5 Hz, 2H, allyl *syn* CH_2), 1.97 (s, 6H, $C_5\mathit{Me}_4H$), 1.95 (s, 6H, $C_5\mathit{Me}_4H$), 1.90 (s, 6H, $C_5\mathit{Me}_4H$), 1.68 (s, 6H, $C_5\mathit{Me}_4H$). ^{13}C NMR (126 MHz, benzene-d_6): δ 158.0 ($CH_2\mathit{C}HCH_2$), 120.0 (C_5Me_4H), 117.0 (C_5Me_4H), 110.7 (C_5Me_4H), 69.0 ($\mathit{C}H_2CH\mathit{C}H_2$), 13.0 ($C_5\mathit{Me}_4H$), 11.9 ($C_5\mathit{Me}_4H$). IR: 3067m, 2902s, 2858s, 2726m, 1657w, 1832w, 1599w, 1543s, 1438br, 1382s, 1324m, 1235m, 1022s, 832s, 779s, 672s, 651w, 620m cm^{-1}. Anal. Calcd for $C_{21}H_{31}Y$: C, 67.73; H, 8.39; Y, 23.88. Found: C, 67.23; H, 8.36; Y, 23.68.

$[(C_5Me_4H)_2Y][(\mu\text{-}Ph)_2BPh_2]$, 3. In an argon-filled glovebox free of coordinating solvents, $[HNEt_3][BPh_4]$ (0.89 g, 2.1 mmol) was added to a stirred yellow solution of $(C_5Me_4H)_2Y(\eta^3\text{-}C_3H_5)$, **2**, (0.80 g, 2.1 mmol) in 50 mL of toluene. Within 45 min the mixture had turned into a colorless solution. After the mixture was stirred for 24 h, the solution was evaporated to dryness to yield an off-white powder. This material was washed with a minimal amount of toluene and dried to yield a white powder, **3**, (0.81 g, 67%). Crystals suitable for X-ray analysis were grown from a concentrated toluene solution of **3** at −35 °C over the course of 48 h. ^1H NMR (500 MHz, benzene-d_6): δ 7.79 (br d, 8H, *o*-C_6H_5), 5.02 (s, 2H, $C_5Me_4\mathit{H}$), 1.60 (s, 12H, $C_5\mathit{Me}_4H$), 1.53 (s, 12H, $C_5\mathit{Me}_4H$) (the other two phenyl resonances overlap in the 7.10 to 7.16 ppm region and cannot be distinguished from the solvent). ^{13}C NMR (126 MHz, benzene-d_6): δ 129.7 (C_6H_5), 128.9 (C_6H_5), 126.0 (C_5Me_4H), 124.3 (C_5Me_4H), 121.6 (C_5Me_4H), 13.6 ($C_5\mathit{Me}_4H$), 11.8 ($C_5\mathit{Me}_4H$). One of the C_6H_5 resonances could not be unambiguously distinguished from the benzene-d_6

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signal. ^{11}B NMR (160 MHz, benzene-d_6): δ −6.63 (s, BPh_4). IR: 3130w, 3060s, 3007w, 2989w, 2971m, 2940m, 2907s, 2863m, 2733w, 1945w, 1871w, 1812w, 1605m, 1578m, 1477s, 1427s, 1260m, 1182m, 1146m, 1058m, 968m, 929w, 879m, 849m, 801s, 742s, 733s, 704s, 613s cm^{-1}. Anal. Calcd for $C_{42}H_{46}B_1Y_1$: C, 77.54; H, 7.13. Found: C, 77.14; H, 7.59.

$(C_5Me_4H)_3Y$, 4. In an argon-filled glovebox free of coordinating solvents, KC_5Me_4H (0.050 g, 0.33 mmol) was added to a stirred colorless solution of $[(C_5Me_4H)_2Y][(\mu\text{-}Ph)_2BPh_2]$, **3**, (0.22 g, 0.33 mmol) in 20 mL of benzene. Within 2 h the solution had turned bright yellow. After the mixture was stirred for 24 h, white solids were removed by centrifugation, and the solution was evaporated to dryness to yield a yellow powder. This material was extracted with toluene, and the solution was evaporated to dryness to yield yellow microcrystalline, **4**, (0.13 g, 87%). Crystals suitable for X-ray analysis were grown from a concentrated toluene solution of **4** at −35 °C over the course of 1 week. ^1H NMR (500 MHz, benzene-d_6): δ 6.03 (s, 3H, $C_5Me_4H_5$), 2.03 (s, 18H, C_5Me_4H), 1.83 (s, 18H, C_5Me_4H). ^{13}C NMR (126 MHz, benzene-d_6): δ 124.5 (C_5Me_4H), 114.8 (C_5Me_4H), 114.2 (C_5Me_4H), 13.2 (C_5Me_4H), 12.1 (C_5Me_4H). IR: 2967m, 2906s, 2859s, 2724m, 1484w, 1438s, 1383m, 1370m, 1329m, 1174w, 1136w, 1020m, 971m, 782s cm^{-1}. Anal. Calcd for $C_{27}H_{39}Y$: C, 71.67; H, 8.69. Found: C, 71.88; H, 8.31.

$[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, 5. In a nitrogen-filled glovebox, $[(C_5Me_4H)Y][(\mu\text{-}Ph)_2BPh_2]$, **3**, (0.90 g, 1.4 mmol) in 10 mL of THF was quickly added to a stirred slurry of KC_8 (0.23 g, 1.7 mmol) in 2 mL of THF. After the mixture was stirred for 2 h, black and white solids (presumably graphite and $KBPh_4$) were removed by centrifugation, and the solution was evaporated to dryness to yield a tacky yellow-green material. This material was washed with hexanes to yield a yellow-green powder which after two recrystallizations from toluene yielded microcrystalline, **5**, (0.56 g, 51%). Crystals suitable for X-ray analysis were grown from a concentrated toluene solution of **5** at −35 °C. ^1H NMR (500 MHz, benzene-d_6): δ 5.54 (s, 4H, C_5Me_4H), 3.94 (br s, 8H, THF), 2.18 (s, 24H, C_5Me_4H), 1.93 (s, 24H, C_5Me_4H), 1.48 (br s, 8H, THF). ^{13}C NMR (126 MHz, benzene-d_6): δ 116.83 (C_5Me_4H), 114.91 (C_5Me_4H), 110.70 (C_5Me_4H), 72.45 (C_4H_8O), 26.13 (C_4H_8O), 13.39 (C_5Me_4H), 12.49 (C_5Me_4H). IR: 2966s, 2907s, 2858s, 2719w, 1559w, 1438m, 1381m, 1329m, 1174w, 1143w, 1109w, 1031s, 918w, 876m, 783s, 764w, 742w, 613m cm^{-1}. Anal. Calcd for $C_{44}H_{68}N_2O_2Y_2$: C, 63.30; H, 8.21; N, 3.36. Found: C, 63.10; H, 8.58; N, 2.94.

$[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}^{15}N_2)$, 5-^{15}N. A sealable Schlenk flask outfitted with a Teflon stopcock was charged with $[(C_5Me_4H)Y][(\eta^2\text{-}Ph)_2BPh_2]$, **3** (0.45 g, 0.69 mmol), KC_8 (0.11 g, 0.83 mmol), and a stir bar. A separate sealable Schlenk flask outfitted with a Teflon stopcock was charged with THF (10 mL) and a stirbar. Both flasks were sealed and attached to a transfer tube that was connected to a high vacuum line (10^{-6} Torr). Each flask was degassed independently, and the THF was vacuum transferred to the flask containing **3** and KC_8, which was kept in a bath of liquid nitrogen to ensure its contents remained frozen. After the THF transfer was completed, $^{15}N_2$ (1 atm) was introduced into the reaction vessel. The solution was allowed to slowly thaw and was stirred at room temperature for 2 h. The solution was degassed by three freeze−pump−thaw cycles, and the flask was transferred into a glovebox. Black and white solids (presumably graphite and $KBPh_4$) were separated by centrifugation, and the solution was evaporated to dryness to yield a tacky yellow-green material. This material was washed with hexanes to yield a yellow-green powder, **5-^{15}N**, (0.09 g, 31%). ^{15}N NMR (50.67 MHz, benzene-d_6): δ 467.51 (t, J_{YN} = 5 Hz). The ^1H and ^{13}C resonances matched those of **5**.

$[(C_5Me_4H)_2Y(\mu\text{-}H)]_2$, 6. In an argon-filled glovebox free of coordinating solvents, a sealable Schlenk flask was charged with $(C_5Me_4H)_2Y(\eta^3\text{-}C_3H_5)$, **2**, (0.71 g, 1.7 mmol), 20 mL of pentane, and a stirbar. The flask was attached to a high vacuum line (10^{-6} Torr), and the bright yellow solution was degassed by three freeze−pump−thaw cycles. To the stirred solution, H_2 (1 atm) was added, and the solution was allowed to stir for 2 h resulting in the formation of a white precipitate. The precipitate was isolated by filtration yielding $[(C_5Me_4H)_2Y(\mu\text{-}H)]_2$, **6**, (0.545 g, 98%). ^1H NMR (500 MHz, cyclohexane-d_{12}): δ 6.66 (s, 4H, C_5Me_4H), 3.82 (t, 2H, H, J_{YH} = 33 Hz), 2.13 (s, 24H, C_5Me_4H), 1.91 (s, 24H, C_5Me_4H). ^{13}C NMR (126 MHz, cyclohexane-d_{12}): δ 129.40 (C_5Me_4H), 128.70 (C_5Me_4H), 128.63 (C_5Me_4H), 12.85 (C_5Me_4H), 11.95 (C_5Me_4H). IR: 2969s, 2909s, 2861s, 2725w, 1602w, 1505w, 1434s, 1385s, 1321m, 1078s, 804s, 763s, 635s, 627s cm^{-1}; Anal. Calcd for $C_{36}H_{54}Y_2$: C, 65.06; H, 8.19. Found: C, 64.26; H, 8.18. In a similar experiment using D_2, $[(C_5Me_4H)_2Y(\mu\text{-}D)]_2$ was prepared. ^1H NMR (500 MHz, cyclohexane-d_{12}): δ 6.66 (s, 4H, C_5Me_4H), 2.13 (s, 24H, C_5Me_4H), 1.92 (s, 24H, C_5Me_4H). IR: 2966s, 2907s, 2859s, 2724w, 1587w, 1435s, 1384s, 1325m, 1084s, 1045s, 1021s, 908m, 793s, 764s, 621s, 592m cm^{-1}. Specific hydride and deuteride bands could not be assigned because of the presence of numerous broad and overlapping bands in the 1150−925 and 820−720 cm^{-1} regions of each spectrum. The hydride and deuteride spectra are different in each region, but the differences do not allow identification of a specific band for a hydride stretch that is shifted in the deuteride spectrum.

$(C_5Me_4H)_2Y[N(SiMe_3)_2]$, 7. In a nitrogen-filled glovebox, Me_3SiN_3 (58 μL, 0.44 mmol) was added to a stirred pale yellow solution of $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **5**, (0.21 g, 0.22 mmol) in 10 mL of toluene. The solution immediately turned bright yellow. After the mixture was stirred for 24 h, the solution was evaporated to dryness to yield a yellow powder (76 mg). The ^1H NMR spectrum of this material revealed a mixture of compounds. Colorless crystals suitable for X-ray analysis were grown from a concentrated benzene-d_6 solution of the reaction mixture at 25 °C over the course of 24 h. The ^1H NMR spectrum of **7** was subsequently determined from an independent synthesis and by integration of the resonances of the $(C_5Me_4H)^-$ ligand in the mixture, the yield was determined to be no higher than 16%.

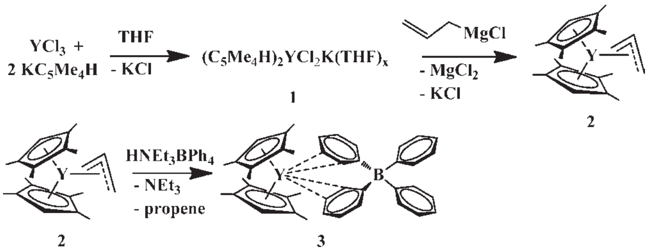
Alternative Synthesis of 7. In a nitrogen-filled glovebox, a colorless solution of $K[N(SiMe_3)_2]$ in 2 mL of toluene (0.034 g, 0.17 mmol) was added to a stirred colorless slurry of $[(C_5Me_4H)_2Y][(\mu\text{-}Ph)_2BPh_2]$, **3**, (0.12 g, 0.17 mmol) in 10 mL of toluene. After 5 min a white precipitate formed. After 24 h, the mixture was centrifuged to remove the white precipitate (presumably $KBPh_4$), and the remaining colorless solution was evaporated to dryness to yield a white powder, **7**, (0.078 g, 92%). ^1H NMR (500 MHz, benzene-d_6): δ 5.92 (s, 2H, C_5Me_5H), 1.96 (s, 12H, C_5Me_5H), 1.93 (s, 12H, C_5Me_5H), 0.14 (s, 18H, $N(SiMe_3)_2$). ^{13}C NMR (126 MHz, benzene-d_6): δ 122.15 (C_5Me_4H), 118.27 (C_5Me_4H), 114.42 (C_5Me_4H), 13.65 (C_5Me_4H), 12.25 (C_5Me_4H). IR: 2970m, 2912m, 2864m, 1480w, 1438w, 1328w, 1242s, 1023s, 870s, 822s, 776s, 746m, 705w, 667m, 603m cm^{-1}. Anal. Calcd for $C_{24}H_{44}NSi_2Y$: C, 58.63; H, 9.02; N, 2.85. Found: C, 58.60; H, 9.05; N, 2.18.

Reactivity of 5 with Phenazine, $C_{12}H_8N_2$. A yellow solution of **5** (73 mg, 0.075 mmol) in 10 mL of toluene was added to a vial containing phenazine (14 mg, 0.075 mmol). A dark red solution immediately formed. After the mixture was stirred for 30 min, the solution was evaporated to dryness to yield a dark red oily residue. The residue was triturated with hexanes and evaporated to dryness to yield a dark red microcrystalline solid [61 mg, 96% for $[(C_5Me_4H)_2Y]_2(C_{12}H_8N_2)$]. ^1H NMR (500 MHz, benzene-d_6): δ 6.07 (m, $C_{12}H_8N_2$, 4H), 5.56 (s, C_5Me_4H, 4H), 5.13 (m, $C_{12}H_8N_2$, 4H), 2.13 (s, C_5Me_4H, 24H), 2.02 (s, C_5Me_4H, 24H). ^{13}C NMR (126 MHz, benzene-d_6): δ 11.5 (C_5Me_4H), 13.3 (C_5Me_4H), 104.7 ($C_{12}H_8N_2$), 112.7 (C_5Me_4H), 119.3 (C_5Me_4H), 122.2 ($C_{12}H_8N_2$), 122.6 (C_5Me_4H), 146.8 ($C_{12}H_8N_2$). IR: 2904s, 2859s, 2727w, 1594w, 1509w, 1451s, 1383w, 1324s, 1289s, 1223w, 1116w, 1024w, 894m, 786m, 739m, 716w, 671w, 619w cm^{-1}. Anal. Calcd for $C_{48}H_{60}N_2Y_2$: C, 68.40; H, 7.18; N, 3.32.

Table 1. X-ray Data Collection Parameters for Complexes **2**, **3**, **4**, **5**, and **7**

	2	**3**	**4**	**5**	**7**
empirical formula	$C_{21}H_{31}Y$	$C_{42}H_{46}BY\cdot{}^{1}/_{2}(C_7H_8)$	$C_{27}H_{39}Y$	$C_{44}H_{68}N_2O_2Y_2\cdot 2(C_7H_8)$	$C_{24}H_{44}NSi_2Y$
Fw	372.37	696.58	452.49	1019.09	491.69
temperature (K)	153(2)	153(2)	163(2)	163(2)	103(2)
crystal system	triclinic	monoclinic	rhombohedral	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$R\bar{3}$	$C2/c$	$P2_1/m$
a (Å)	8.832(2)	14.6264(13)	15.5081(8)	15.244(3)	9.4244(3)
b (Å)	15.132(4)	14.4560(13)	15.5081(8)	13.970(3)	15.8901(6)
c (Å)	15.180(4)	17.6133(15)	16.5655(17)	25.677(6)	9.5626(3)
α (deg)	95.579(4)	90	90	90	90
β (deg)	101.882(4)	102.332(2)	90	104.864(4)	117.3923(4)
γ (deg)	102.982(4)	90	120	90	90
Volume (Å^3)	1912.5(8)	3638.2(6)	3450.3(4)	5285(2)	1271.48(7)
Z	4	4	6	4	2
ρ_{calcd} (Mg/m^3)	1.293	1.272	1.307	1.281	1.284
μ (mm^{-1})	3.045	1.634	2.545	1.281	2.398
$R1$ [$I > 2.0\sigma(I)$]	0.0354	0.0356	0.0200	0.0432	0.0279
$wR2$ (all data)	0.0880	0.0971	0.0539	0.1237	0.0728

Scheme 1



Found: C, 61.20; H, 6.31; N, 2.90. The analytical data on this sample was consistently low although the C/H/N ratio of 24.4:30.2:1 matches the 24:30:1 calculated value. This appears to be a case of incomplete combustion as has been observed in other related systems.[15]

Reactivity of 5 with Carbon Dioxide. A sealable Schlenk flask was charged with **5** (52 mg, 0.062 mmol) and a stir bar in 5 mL of benzene. The flask was attached to a high vacuum line, and the solution was degassed by three freeze−pump−thaw cycles. CO_2 (1 atm) was introduced into the system. The bright yellow solution turned pale yellow within 5 min of the addition of the CO_2. After the solution was stirred for 1 h, the solution was evaporated to dryness to yield a pale yellow powder {43 mg, 92% for $[(C_5Me_4H)_2Y]_2(C_2O_4)$}. ^{1}H NMR (500 MHz, benzene-d_6): δ 5.86 (s, $C_5Me_4\mathit{H}$, 4H), 3.59 (br s, $C_4\mathit{H}_8O$, 8H), 1.98 (s, $C_5\mathit{Me}_4H$, 24H), 1.94 (s, $C_5\mathit{Me}_5H$, 24H), 1.42 (br s, $C_4\mathit{H}_8O$, 8H). ^{13}C NMR (126 MHz, benzene-d_6): δ 168.92 (C_2O_4), 120.5 (C_5Me_4H), 118.15 (C_5Me_4H), 111.17 (C_5Me_4H), 12.18 ($C_5\mathit{Me}_4H$), 10.65 ($C_5\mathit{Me}_4H$). IR: 2961s, 2912s, 2860s, 1647s, 1564s, 1442m, 1399m, 1383m, 1024w, 790m, 621w cm^{-1}. Anal. Calcd for $C_{38}H_{52}O_4Y_2$: C, 60.80; H, 6.98. Found: C, 51.28; H, 5.79. Like the product above, the elemental analysis values were low, but the found H/C ratio, 1.35, was very close to the calculated value, 1.37.

X-ray Data Collection, Structure Solution, and Refinement for 2, 3, 4, 5, and 7. This information is available in the Supporting Information and a summary of the X-ray data collection parameters is presented in Table 1.

Results and Discussion

Precursor Synthesis. The tetramethylcyclopentadienyl yttrium precursors to $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **5**, were prepared in a manner similar to that used for the previously reported lutetium analogues.[4] Scheme 1 shows the sequential synthesis of complexes **1**−**3**.

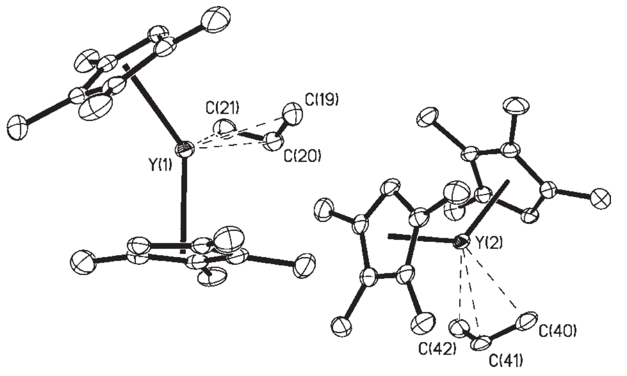


Figure 1. Thermal ellipsoid plot of $(C_5Me_4H)_2Y(\eta^3\text{-}C_3H_5)$, **2**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

The "ate" salt, $(C_5Me_4H)_2Y(\mu\text{-}Cl)_2K(THF)_x$, **1**, was prepared directly from YCl_3 and 2 equiv of KC_5Me_4H in THF in 91% yield. A similar complex, $(C_5Me_4H)Y(\mu\text{-}Cl)_2Na(Et_2O)_2$, has been previously reported to form via the ionic salt metathesis of YCl_3 with NaC_5Me_4H.[9] Complex **1** is insoluble in aliphatic and aromatic hydrocarbon solvents and therefore was characterized in THF. The elemental analysis of **1** is consistent with the unsolvated analogue, $(C_5Me_4H)_2Y(\mu\text{-}Cl)_2K$.

A slurry of the unsolvated "ate" salt, $(C_5Me_4H)_2Y(\mu\text{-}Cl)_2K$, **1**, in toluene was treated with 1 equiv of allylmagnesium chloride in THF to form $(C_5Me_4H)_2Y(\eta^3\text{-}C_3H_5)(THF)_x$. This complex was desolvated by heating for 2 days at 55 °C under vacuum (10^{-6} Torr). The resulting unsolvated allyl complex, $(C_5Me_4H)_2Y(\eta^3\text{-}C_3H_5)$, **2**, was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, elemental analysis, and X-ray crystallography, Figure 1. Structural details are discussed below.

Complex **2** was converted to the unsolvated yttrium cation, $[(C_5Me_4H)_2Y][(\mu\text{-}Ph)_2BPh_2]$, **3**, in 67% yield using 1 equiv of $[HNEt_3][BPh_4]$. Complex **3** was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, elemental analysis, and X-ray crystallography, Figure 2.

$(C_5Me_4H)_3Y$, 4. Although numerous $(C_5Me_4H)_3Ln$ complexes of the lanthanides have been reported in the literature,[4−6] the yttrium analogue had not. In contrast to

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[15] (a) Roitershtein, D.; Domingos, A.; Pereira, L. C. J.; Ascenso, J. R.; Marques, N. *Inorg. Chem.* **2003**, *42*, 7666. (b) Freedman, D.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1999**, *38*, 4400. (c) Gaunt, A. J.; Scott, B. L.; Neu, M. P. *Inorg. Chem.* **2006**, *45*, 7401.

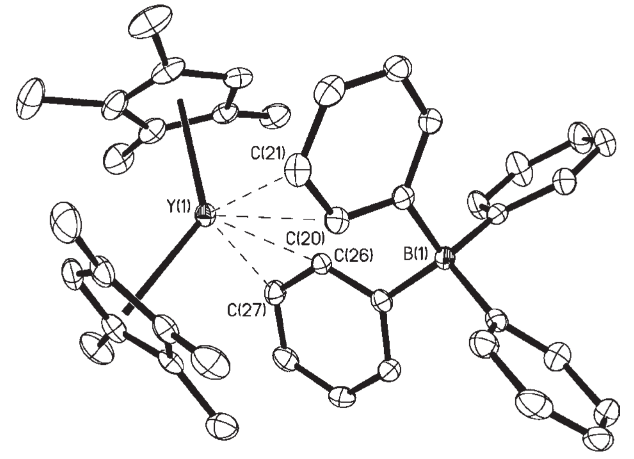
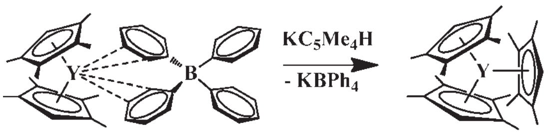


Figure 2. Thermal ellipsoid plot of [(C$_5$Me$_4$H)$_2$Y]$_2$[(μ-Ph)$_2$BPh$_2$], **3**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

the syntheses of the (C$_5$Me$_4$H)$_3$Ln complexes of the larger lanthanides, Ln = La (36%, crystalline),[5] Ce (85%),[16] Pr (78%),[5] Nd (42%, crystalline),[6] Sm (34%, crystalline),[5,6] and Tb (38%, crystalline),[5] from LnCl$_3$ and 3 equiv of KC$_5$Me$_4$H, this route with the smaller metals, Ho, Tm, and Lu, leads to the formation of (C$_5$Me$_4$H)$_2$LnCl(THF).[6] The isolation of (C$_5$Me$_4$H)$_3$Lu from the reaction of LuCl$_3$ with 3 equiv of KC$_5$Me$_4$H has been reported, but in low yield (18%).[4] Consistent with this, the direct synthesis of (C$_5$Me$_4$H)$_3$Y, **4**, by salt metathesis of YCl$_3$ with 3 equiv of KC$_5$Me$_4$H in THF was attempted and resulted in the formation of **4** in 5% yield after recrystallization. For this reason, the synthesis of **4** from **3** was examined.

Complex **4** can be synthesized from [(C$_5$Me$_4$H)$_2$Y][(μ-Ph)$_2$BPh$_2$] and KC$_5$Me$_4$H in benzene in 87% yield, eq 2, which is similar to the 94% yield for the analogous synthesis of (C$_5$Me$_4$H)$_3$Lu.[4]



3 **4** (2)

Complex **4** was fully characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, elemental analysis, and X-ray crystallography, Figure 3.

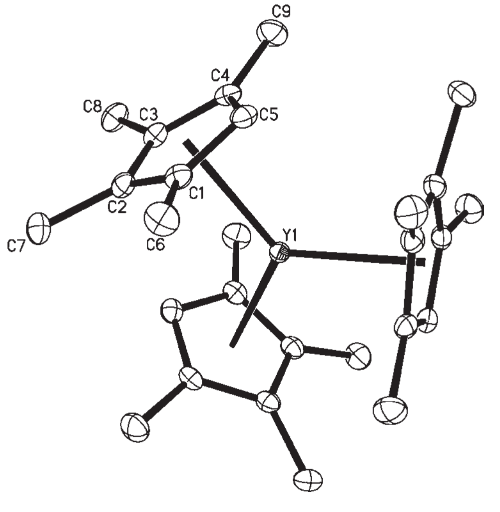
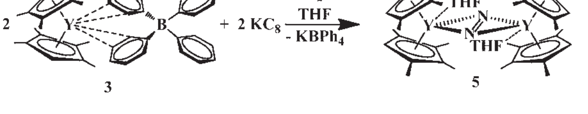


Figure 3. Thermal ellipsoid plot of (C$_5$Me$_4$H)$_3$Y, **4**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

[(C$_5$Me$_4$H)$_2$Y(THF)]$_2$(μ-η^2:η^2-N$_2$), 5. Complex **5** was synthesized using the LnZ$_2$Z′/K method[17] from [(C$_5$Me$_4$H)$_2$Y][(μ-Ph)$_2$BPh$_2$], **3**, and dinitrogen with 1.2 equiv of KC$_8$, eq 3. In contrast to the yields for the complexes described



3 **5** (3)

above, the yield of **5** (51%) was low: [(C$_5$Me$_4$H)$_2$Lu(THF)]$_2$(μ-η^2:η^2-N$_2$) is obtained analogously in 80% yield.[4] Complex **5** can also be made using the LnZ$_3$/K method from (C$_5$Me$_4$H)$_3$Y, **4**. However, the 28% yield was significantly lower than the 72% yield for the Lu analogue. The lower yields in the synthesis of **5** from both **3** and **4**, compared to those of the Lu analogue, are likely because (C$_5$Me$_4$H)$_3$Y is more accessible and present as a significant byproduct even when starting from complex **3**. Therefore, complex **5** can only be isolated as a pure substance after multiple recrystallizations that lead to a reduced isolated yield. Complex **5** was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, elemental analysis, and X-ray crystallography, Figure 4.

^{15}N NMR Spectroscopy. [(C$_5$Me$_4$H)$_2$Y(THF)]$_2$(μ-η^2:η^2-^{15}N$_2$), **5-^{15}N**, was synthesized in 31% yield from the reaction of **3** with 1.2 equiv of KC$_8$ under 1 atm of ^{15}N$_2$, which was introduced to the system using vacuum line techniques. Complex **5-^{15}N** was characterized by ^{1}H and ^{15}N NMR spectroscopy. The ^{1}H NMR spectrum was identical to that of **5**. The ^{15}N NMR spectrum of **5-^{15}N** was obtained in benzene-*d*$_6$ by collecting data for 12 h and is shown in Figure 5.

The ^{15}N NMR of **5-^{15}N** displays a triplet centered at 468 ppm (referenced to ^{15}N-MeNO$_2$) with a J_{YN} coupling constant of 5 Hz, which is in the range of other yttrium–nitrogen coupling constants reported in the literature (2–15 Hz).[18] The triplet observed in the ^{15}N NMR spectrum is consistent with a symmetric (^{15}N$_2$)$^{2-}$ moiety bound coplanar between two yttrium (I = $^1/_2$) centers as observed in the solid state. Examination of the ^{15}N NMR data available for fully characterized Ln$_2$(μ-η^2:η^2-N$_2$) complexes, Table 2, shows that the shift for **5-^{15}N** is similar to values reported for other complexes. Although the series of (C$_5$Me$_5$)$^-$, [(Me$_3$Si)$_2$N]$^-$, and (C$_5$Me$_4$H)$^-$ is only complete for lanthanum, the general trend for a given metal is a change from a higher ^{15}N chemical shift to a lower chemical shift with (C$_5$Me$_5$)$^-$ > [(Me$_3$Si)$_2$N]$^-$ > (C$_5$Me$_4$H)$^-$.

[(C$_5$Me$_4$H)$_2$Y(μ-H)]$_2$, 6. With the accessibility of the allyl complex, (C$_5$Me$_4$H)$_2$Y(η^3-C$_3$H$_5$), **2**, it was convenient to

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(16) Evans, W. J.; Rego, D. B.; Ziller, J. W. *Inorg. Chem.* **2006**, *45*, 10790.

(17) Evans, W. J.; Lee, D. S. *Can. J. Chem.* **2005**, *83*, 375.

(18) (a) Fratiello, A.; Kubo-Anderson, V.; Bolanos, E. L.; Haigh, D.; Laghaei, F.; Perrigan, R. D. *J. Magn. Reson., Ser. A* **1994**, *107*, 56. (b) Lee, S. G. *Bull. Korean Chem. Soc.* **1996**, *17*, 589.

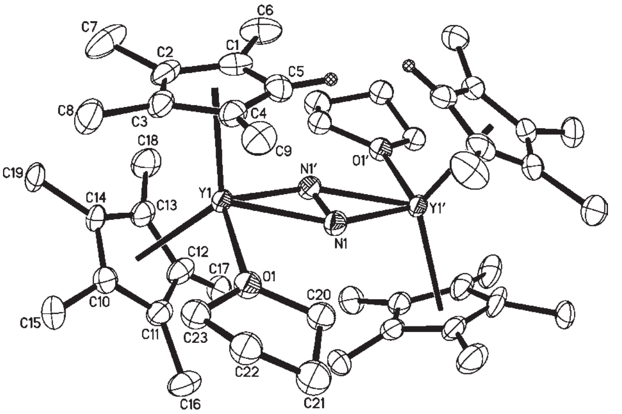

Figure 4. Thermal ellipsoid plot of [(C_5Me_4H)$_2$Y(THF)]$_2$(μ-η^2:η^2-N_2), **5**, drawn at the 50% probability level. Hydrogen atoms, except for ring hydrogens, have been omitted for clarity. Disorder in the coordinated THF molecules is not shown. The tetramethylcyclopentadienyl ring defined by atoms C(10)−C(19) was disordered such that atoms C(17) and C(19) were included with partial site-occupancy-factors to account for one methyl distributed over the two sites which gives the appearance in this diagram of $(C_5Me_5)^-$ rings.

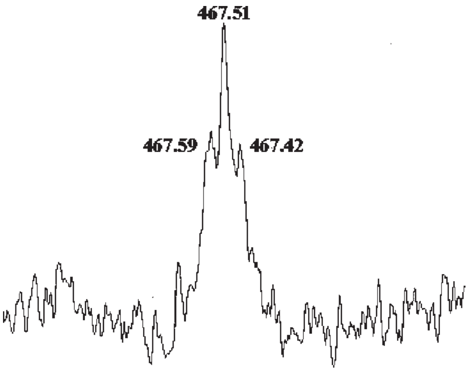

Figure 5. ^{15}N NMR spectrum (referenced to ^{15}N-nitromethane) of [(C_5Me_4H)$_2$Y(THF)]$_2$(μ-η^2:η^2-$^{15}N_2$), **5**, at 298 K.

synthesize the corresponding hydride, [(C_5Me_4H)$_2$Y(μ-H)]$_x$, **6**, by hydrogenolysis for comparison with [(C_5Me_5)$_2$Y(μ-H)]$_x$.[10] The allyl hydrogenation method is the currently favored route to [(C_5Me_5)$_2$Ln(μ-H)]$_x$ complexes.[22] The yttrium hydride complex, [(C_5Me_4H)$_2$Y(μ-H)]$_x$, **6**, was synthesized from (C_5Me_4H)$_2$Y(η^3-C_3H_5), **2**, with 1 atm of H_2 in 98% yield, eq 4. This is a higher yield than the 78% yield for the synthesis of the $(C_5Me_5)^-$ analogue by hydrogenolysis of (C_5Me_5)$_2$Y[CH(SiMe$_3$)$_2$].[10] Attempts to make **6** by the hydrogenation of complex **4** were unsuccessful.[23] Complex **6** was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, and elemental analysis. The ^{1}H NMR spectrum reported in the literature for the $(C_5Me_5)^-$ analogue, [(C_5Me_5)$_2$YH]$_x$, indicates that below room temperature this complex exists as a symmetric dimer, displaying a single hydride resonance as a triplet at 5.45 ppm (t, 2H, $^1J_{YH}$ = 37.5 Hz, 288 K).[24] ^{1}H NMR spectroscopy suggests that like the $(C_5Me_5)^-$ analogue, complex **6** exists as a symmetric dimer, [(C_5Me_4H)$_2$Y(μ-H)]$_2$, in solution based on the triplet observed for the H^- ligand at 3.82 ppm ($^1J_{YH}$ = 33 Hz).

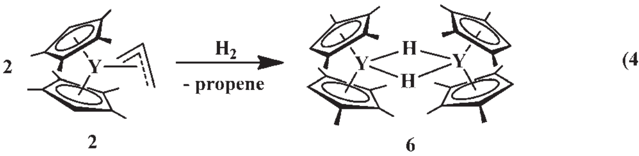

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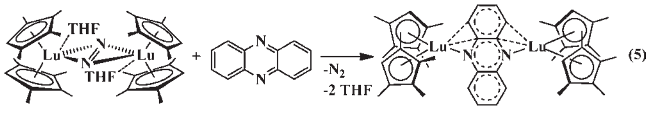
Table 2. Relative ^{15}N NMR Chemical Shifts of [Z_2Ln(THF)]$_2$(μ-η^2:η^2-N_2) Complexes

[Z_2Ln(THF)]$_2$(μ-η^2:η^2-N_2)	^{15}N NMR shift (δ)	reference
[(C_5Me_5)$_2$La(THF)]$_2$(μ-η^2:η^2-N_2)	569	2
{[(Me_3Si)$_2$N]$_2$Lu(THF)}$_2$(μ-η^2:η^2-N_2)	557	19
[(C_5Me_4H)$_2$Lu(THF)]$_2$(μ-η^2:η^2-N_2)	521	4
{[(Me_3Si)$_2$N]$_2$La(THF)}$_2$(μ-η^2:η^2-N_2)	516	20
{[(Me_3Si)$_2$N]$_2$Y(THF)}$_2$(μ-η^2:η^2-N_2)	513	21
[(C_5Me_4H)$_2$La(THF)]$_2$(μ-η^2:η^2-N_2)	495	2
[(C_5Me_4H)$_2$Y(THF)]$_2$(μ-η^2:η^2-N_2)	468	this paper

Reactivity of 5 with Reducible Substrates: Phenazine, Anthracene, and CO_2. The isolation of the reduced dinitrogen complex [(C_5Me_4H)$_2$Y(THF)]$_2$(μ-η^2:η^2-N_2), **5**, allowed for a comparative analysis of the reactivity of this complex versus the La and Lu analogues in the literature.[8] Complex **5** reacts immediately with phenazine (−0.364 V vs SCE)[25] to form a dark red solution and a single product in high yield based on the ^{1}H NMR spectrum. The ^{1}H NMR spectrum contained resonances at 6.07 and 5.13 ppm assignable to $(C_{12}H_8N_2)^{2-}$ on the basis of their similarity to 6.01 and 5.01 ppm signals in the spectrum of crystallographically characterized [(C_5Me_4H)$_2$Lu(THF)]$_2$(μ-η^3:η^3-$C_8H_{12}N_2$), eq 5.[8] Although the spectral data are consistent with formation of the yttrium analogue, that is, [(C_5Me_4H)$_2$Y]$_2$($C_8H_{12}N_2$), from the reaction between **5** and phenazine, the complex did not readily crystallize and gave incomplete combustion in elemental analysis. [(C_5Me_4H)$_2$La(THF)]$_2$(μ-η^2:η^2-N_2) also reduces phenazine, but the reaction is more complicated since an asymmetric monosolvated complex, [(C_5Me_4H)$_2$La](μ-η^4:η^2-$C_8H_{12}N_2$)[La(THF)(C_5Me_4H)], is isolated as well as the (C_5Me_4H)$_3$La ligand redistribution product that forms more readily with this large metal.[8]



In contrast to the reaction with phenazine, complex **5** does not react quantitatively with anthracene (−1.98 and −2.44 V vs SCE).[26] At room temperature, a green solution forms, but the ^{1}H NMR spectrum indicated that 25% of the starting material, **5**, remained after 2 days. Two new additional resonances were observed in the

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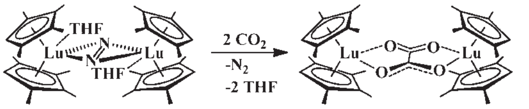
$(C_5Me_4\mathit{H})^-$ region at 6.16 and 5.84 ppm in a 1:1 ratio. For comparison, when $[(C_5Me_4H)_2La(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$[8] reacts with 1 equiv of anthracene, complete consumption of the starting material is observed. However, $[(C_5Me_4H)_2Lu(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$[8] shows no reactivity with anthracene.

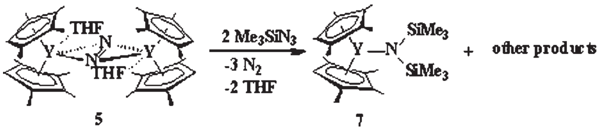
Complex **5** also reacts with CO_2 (−2.21 V vs SCE in dimethylformamide)[27] at 1 atm within 5 min to form a yellow solution. A single product is observed by ^1H NMR spectroscopy, and the ^{13}C NMR displays a resonance at 168.9 ppm, which is similar to the 168.5 ppm resonance found for the lutetium oxalate product, $[(C_5Me_4H)_2Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2O_4)$,[8] eq 6. The IR spectrum gives evidence for oxalate formation as well. A strong absorption band at 1647 cm^{-1} is consistent with the ν_{CO} of an oxalate ligand.[28] The spectroscopic data as well as the elemental analysis suggest the formation of the yttrium analogue, $[(C_5Me_4H)_2Y]_2(C_2O_4)$. In contrast, $[(C_5Me_4H)_2La(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ forms multiple reaction products upon exposure to CO_2.



(6)

On the basis of the reactivity with phenazine, anthracene, and CO_2, it can be concluded that complex **5** displays reactivity intermediate between that of $[(C_5Me_4H)_2La(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ and $[(C_5Me_4H)_2Lu(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ with these substrates.

Me_3SiN_3 Reduction. The reactivity of **5** with the azide, Me_3SiN_3, was also examined, and an unusual result was observed. Complex **5** reacts immediately with 2 equiv of Me_3SiN_3 to form a yellow solution. ^1H NMR shows a spectrum consistent with at least five different $(C_5Me_4H)^-$ environments. Colorless crystals of one of the components of the reaction mixture was obtained in low yield (16%) from this reaction and identified as $(C_5Me_4H)_2Y[N(SiMe_3)_2]$, **7**, eq 7, Figure 6. An independent synthesis of **7** from the reaction of **3** with 1 equiv of $K[N(SiMe_3)_2]$ provided the ^1H NMR spectrum of pure **7** such that it could be identified in the ^1H NMR spectrum of the reaction mixture of **5** with Me_3SiN_3. However, the other four products have yet to be identified.



(7)

Related transformations have been observed with both $U(NN'_3)$ $[NN'_3 = N(CH_2CH_2NSiMe_2Bu^t)_3]$[29] and $[\{(Et_8\text{-calix[4]tetrapyrrole})Th\}\{K(DME)\}(\eta^4\text{-}C_{10}H_8)][Li(DME)_3]$[30] with Me_3SiN_3. The thorium naphthalenide complex, $[\{(Et_8\text{-calix[4]tetrapyrrole})Th\}\{K(DME)\}(\eta^4\text{-}C_{10}H_8)][Li(DME)_3]$ undergoes reaction with 2 equiv of Me_3SiN_3 to form $[\{(Et_8\text{calix[4]-tetrapyrrole})Th\}\{N(SiMe_3)_2\}]\text{-}[Li(DME)_3]$.[30] Although the exact mechanism for this azide to amide transformation is not known, it has been proposed to occur via a two electron reduction of an azide to form an $(=NSiMe_3)^{2-}$ imido intermediate followed by the transfer of a $SiMe_3$ group from the second equiv of Me_3SiN_3 to form the $[N(SiMe_3)_2]^-$ ligand. Since $[(C_5Me_4H)_2Ln(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes have been shown to act as two electron reductants,[8] it is not unreasonable to propose that they also have the capacity to reduce an azide to an imide. If the reaction pathway proposed for thorium was to occur in the reaction of complex **5** with Me_3SiN_3, it is likely that the intermediate would be a bimetallic imido complex, since yttrium lacks the requisite 4^+ oxidation state necessary to form a monometallic metallocene imido complex.

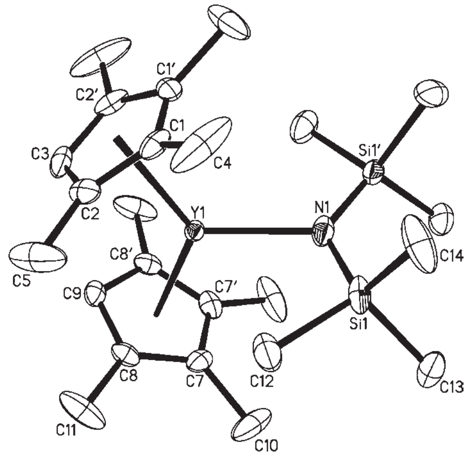


Figure 6. Thermal ellipsoid plot of $(C_5Me_4H)_2Y[N(SiMe_3)_2]$, **7**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_4H)_2Y(\eta^3\text{-}C_3H_5)$, **2**, and $(C_5Me_5)_2Y(\eta^3\text{-}C_3H_5)$, **9**.[32]

	2a	2b	9
Cnt1−Y(1)−Cnt2	134.7	134.5	138.8
Y−Cnt1	2.347	2.348	2.381
Y−Cnt2	2.334	2.341	2.362
$Y-(C_3H_5)$	2.590(3)	2.585(3)	2.582(2)
	2.594(3)	2.592(3)	2.582(2)
	2.603(3)*	2.603(3)*	2.601(2)*

* Central carbon of the $(\eta^3\text{-}C_3H_5)^-$ ligand.

Structural Analysis. Structure of $(C_5Me_4H)_2Y(\eta^3\text{-}C_3H_5)$, 2. The structure of $(C_5Me_4H)_2Y(\eta^3\text{-}C_3H_5)$ differs from the several $(C_5Me_5)_2Ln(\eta^3\text{-}C_3H_5)$ complexes previously characterized by X-ray crystallography (Ln = Nd,[22] Sm,[22,31] Tm,[22] Lu,[32] and Y,[32] **9**) in that it contains two crystallographically independent molecules in the unit cell. Select bond distances (Å) and angles (deg) of complexes **2** and **9** are presented in Table 3. The $(C_5Me_4R$ ring centroid)−Y−$(C_5Me_4R$ ring centroid) angles are 134.7°/134.5° and 138.8°, for **2** and **9**, respectively. The slightly larger angle of **9** is expected since the $(C_5Me_5)^-$ ligand provides a greater degree of steric bulk than the $(C_5Me_4H)^-$ ligand. Consistent with this, the Y−$(C_5Me_4R$ ring centroid) distances in **9**, 2.381 and 2.362 Å, are slightly longer than those observed for **2**, 2.334−2.348 Å.

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Table 4. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_4H)_2Y][(\mu\text{-Ph})_2BPh_2]$, **3**, and $[(C_5Me_4H)_2Lu][(\mu\text{-Ph})_2BPh_2]$, **10**[4]

	M = Y, **3**	M = Lu, **10**
Cnt1−M−Cnt2	132.8	133.4
M−Cnt1	2.353	2.302
M−Cnt2	2.353	2.301
M−C(20)	2.718(2)	2.668(2)
M−C(21)	2.976(2)	2.947(2)
M−C(26)	2.829(2)	2.800(2)
M−C(27)	3.223(2)	3.237(2)

Table 5. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_4H)_3Y$, **4**, $(C_5Me_4H)_3Lu$,[4] **11**, and $(C_5Me_5)_3Y$,[33] **12**

	M = Y, **4**	M = Lu, **11**	M = Y, **12**
Cnt1−M−Cnt2	120	120	120
M−Cnt	2.441	2.406	2.505
M−C(1)	2.682(1)	2.800(4)	2.884(3)
M−C(2)	2.808(1)	2.798(3)	2.776(2)
M−C(3)	2.802(1)	2.633(3)	2.725(2)
M−C(4)	2.681(1)	2.566(3)	2.725(2)
M−C(5)	2.633(1)	2.641(3)	2.776(2)

Table 6. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **5**, and $[(C_5Me_4H)_2Lu(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **13**[4]

	M = Y, **5**	M = Lu, **13**
Cnt1−M(1)−Cnt2	129.4	129.9
M(1)−Cnt1	2.416	2.369
M(1)−Cnt2	2.430	2.385
M(1)−N(1A)	2.338(3)	2.290(6)
M(1)−O(1)	2.498(8)	2.462(17)
N(1)−N(1A)	1.252(5)	1.243(12)

Table 7. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_4H)_2Y[N(SiMe_3)_2]$, **7**, and $(C_5Me_5)_2Y[N(SiMe_3)_2]$, **14**[37]

	7	**14**
Cnt1−Y−Cnt2	128.8	132.4
Y−Cnt1	2.382	2.391
Y−Cnt2	2.388	2.400
Y−N	2.258(2)	2.274(5)
Y···H(12a)	2.961	2.45
Y···H(12c)	3.064	3.00
Y···C(12)	3.251	2.97

The longest $Y-(C_3H_5)$ interaction in both complexes is the central carbon of the allyl moiety, as is typical of $(C_5Me_4R)_2Ln(\eta^3\text{-}C_3H_5)$ (R = H or Me), complexes.[4,22,31,32] These distances in **2** and **9** are similar: 2.603 Å and 2.601 Å, respectively.

Structure of $[(C_5Me_4H)_2Y][(\mu\text{-Ph})_2BPh_2]$, 3. Complex **3** is isomorphous to the lutetium analogue, $[(C_5Me_4H)_2Lu][(\mu\text{-Ph})_2BPh_2]$, **10**. As shown in Table 4, the metrical parameters in these complexes are in good agreement when the 0.042 Å difference in the 8-coordinate metal ionic radii[7] is considered. Complexes **3** and **10** display η^2-Ph interactions with two of the phenyl rings of the tetraphenylborate anion, as is typical for lanthanide metallocene tetraphenylborate complexes.[20,22] The shortest Ln−C(Ph) interactions in **3** are between Y−C(20), 2.718(2) Å, and Y−C(21), 2.976(2) Å, similar to those in **10**, where Lu−C(20) is 2.668(2) Å and Lu−C(21) is 2.947 Å.

Structure of $(C_5Me_4H)_3Y$, 4. In Table 5, the structure of **4** is compared with the lutetium analogue, $(C_5Me_4H)_3Lu$,[4] **11**, and the $(C_5Me_5)^-$ substituted complex, $(C_5Me_5)_3Y$,[33] **12**. Complexes **4**, **11**, and **12** all display trigonal planar geometries with 120° (C_5Me_4R ring centroid)−Ln−(C_5Me_4R ring centroid) bond angles. The Ln−(C_5Me_4R ring centroid) distances are 2.441, 2.406, and 2.505 Å for **4**, **11**, and **12**, respectively. The Ln−(C_5Me_4R ring centroid) distances of **4** and **11** are similar when the difference of 0.043 Å in the 9-coordinate ionic radii between Y and Lu is accounted for.[7] The significantly longer (0.1 Å) Y−(C_5Me_5 ring centroid) distance observed in **12** is typical of those observed in sterically crowded complexes. In addition, the longest Ln−C(C_5Me_4R) interaction in **4** is Y−(C2), 2.808(1) Å, where C(2) is the ring carbon bound to the hydrogen. This is also seen in **11**, with a Lu−(C4) distance of 2.800(4) Å. In complex **12**, the longest M−C(C_5Me_5) distance, Y−(C1), is 0.08 Å longer than those in **4** and **11**.

Structure of $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, 5. Structural comparisons of **5** with its isomorphous lutetium analogue, $[(C_5Me_4H)_2Lu(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **13**,[4] are given in Table 6. The N−N distances of complexes **5** and **13** are 1.252(5) and 1.243(12) Å, respectively. These N−N distances are within the range for N−N double bonds[34] and are consistent with the presence of an $(N_2)^{2-}$ ligand. In addition, the metallocene parameters for **5** are almost identical to those of **13**, Table 6, when the 0.043 Å difference in 9-coordinate atomic radii between Y^{3+} and Lu^{3+} is accounted for.[7]

The dihedral angle between the planes defined by the two ring centroids and the metal for each metallocene is 5.2° for **5**, 6.8° for **13**, and 3.6° for $[(C_5Me_4H)_2La(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$.[2] Chirik and co-workers have discussed the importance of the dihedral angles in bonding and reactivity for unsolvated $[(C_5Me_4H)_2Zr]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes.[35] Direct comparisons with **5** are more complicated because of the presence of the THF of solvation. This adds another ligand to the coordination geometry of each metal in the fully solvated form. Dissociation of THF from one or both metals prior to reaction increases the options for the dihedral angle in the reaction sequence.

Structure of $(C_5Me_4H)_2Y[N(SiMe_3)_2]$, 7. Complex **7** can be compared to that of the $(C_5Me_5)^-$ analogue, $(C_5Me_5)_2Y[N(SiMe_3)_2]$,[36] **14**, Table 7. As is common for $(C_5Me_5)_2Ln[N(SiMe_3)_2]$ complexes, **14** displays a short interaction between Y(1)···C(26) of the $[N(SiMe_3)_2]^-$ with a distance of 2.970(2) Å. This and the varied angles of 129.7(3)° and 107.1(3)° for Y(1)−N(1)−Si(1) and Y(1)−N(1)−Si(2), respectively, are indicative of an agostic interaction in **14**. In contrast, the crystal structure of **7** is symmetric such that the Y···C(12) and Y···C(12A) distances are identical at 3.251 Å. Likewise, the Y(1)−N(1)−Si(1) angles are the same: 116.37(6)°. Although **7** could be expected to display an agostic interaction similar to **14** based on the less electron donating and less sterically saturated $(C_5Me_4H)^-$ ligands, there is no evidence of this in the solid state structure. Similarly the IR does not show

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any absorption bands in the 2700−2350 cm^{-1} region where low energy C−H stretching vibrations indicative of agostic interactions are usually found.[38]

Conclusion

The successful synthesis of $(C_5Me_4H)_2Y(\mu\text{-Cl})_2K(THF)_x$, **1**, $(C_5Me_4H)_2Y(\eta^3\text{-}C_3H_5)$, **2**, $[(C_5Me_4H)_2Y][(\mu\text{-Ph})_2BPh_2]$, **3**, and $(C_5Me_4H)_3Y$, **4**, in overall yields of >65% shows that yttrium metallocene complexes display $(C_5Me_4H)^-$ chemistry like that of lutetium. The bis(tetramethylcyclopentadienyl) ligand set allows a $Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complex to be accessed with yttrium, namely, $[(C_5Me_4H)_2Y(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **5**. Complex **5** displays reactivity intermediate between that of the analogous $[(C_5Me_4H)_2Ln(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes (Ln = La, Lu), as evidenced by reaction with phenazine, anthracene, and CO_2. In addition, complex **5** reduces Me_3SiN_3 to form $(C_5Me_4H)_2Y[N(SiMe_3)_2]$, **7**, a mode of reactivity previously unknown for $Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes. The synthesis of **5**, along with $(C_5Me_4H)_3Y$, **4**, and $[(C_5Me_4H)_2Y(\mu\text{-H})]_2$, **6**, shows that $(C_5Me_4H)^-$ metallocene chemistry is fully accessible for yttrium when detailed NMR information is needed.

Acknowledgment. We thank the National Science Foundation for support of this research.

Supporting Information Available: X-ray data collection, structure solution, refinement, and X-ray diffraction details of compounds **2**, **3**, **4**, **5** and **7** (CIF, CCDC No. 772385−772389). This material is available free of charge via the Internet at http://pubs.acs.org.

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