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NH_3 and $(NH_2)^{1-}$ as Ligands in Yttrium Metallocene Chemistry

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Abstract

$(C_5Me_5)_2Y(C_3H_5)(THF)$ reacts with ammonia in THF to form the first crystallographically-characterized rare-earth metal complex with a terminal $(NH_2)^{1-}$ ligand, $(C_5Me_5)_2Y(NH_2)(THF)$, **1**. Complex **1** can be protonated with $[HNEt_3][BPh_4]$ to form $[(C_5Me_5)_2Y(NH_3)(THF)][BPh_4]$, **2**. Both complexes were characterized by X-ray crystallography which allowed a comparison of the Y-NH_2 bond length, 2.226(2) Å, with an Y-NH_3 bond length, 2.476(2) Å, in analogous coordination environments. Reactions of **2** with NaN_3 and acetone produced the known complexes $[(C_5Me_5)_2YN_3]_x$ and $[(C_5Me_5)_2Y(OCMe_2)_2][BPh_4]$, respectively, suggesting that the ammonia moiety in **2** functions as a displaceable solvate like THF.

Introduction

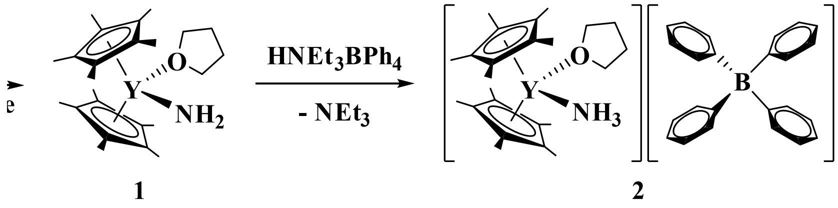
A recent study of the ammonia-ligated metallocenes $[(C_5Me_5)_2Dy(NH_3)_2][BPh_4]$ and $[(C_5Me_5)_2Dy(NH_3)(THF)][BPh_4]$, of interest as single-molecule magnets,[1] emphasized the dearth of information on ammonia-ligated organometallic complexes of the rare-earth metals and on the reactivity of ammonia with rare-earth metallocenes. This was surprising since tris(cyclopentadienyl) rare-earth metal ammonia complexes, $(C_5H_5)_3Ln(NH_3)$, have been known since the 1960s[2–5] and Sm, Gd, Dy, Ho, Er, and Yb examples were crystallographically characterized in 2006.[6] It is worth noting that for Ce, Nd, and Eu, $(C_5H_5)_3Ln(NH_3)$ complexes were not isolated and there was no mention of reactions with yttrium. The crystallographically-characterized ammonia complexes of bis(cyclopentadienyl) rare-earth metallocenes are limited to $(C_5Me_5)_2Yb(SPh)(NH_3)$,[7] $(C_5Me_5)_2Yb(TePh)(NH_3)$,[8] and $(C_5Me_5)_2Yb(THF)(NH_3)$.[9,10]

Since the ammonia ligand can be deprotonated to form $(NH_2)^{1-}$, it was also of interest in the context of examining ammonia metallocene chemistry to examine rare-earth metal $(NH_2)^{1-}$ complexes. Rare-earth metal compounds containing $(NH_2)^{1-}$ ions include salts such as $Ln(NH_2)_2$,[11–13] $Ln(NH_2)_3$,[14] and $KLn(NH_2)_3$[15] (Ln = Eu, Yb), that were identified by X-ray powder diffraction. Single crystal X-ray diffraction studies of NH_2-ligated complexes include the $K_3Ln(NH_2)_6$[16] compounds (Ln = Eu, La), the polymetallic $[Yb_5(C_4H_4N)_{12}(NH_3)_4(NH_2)]\cdot 2(C_4H_5N)$,[17] and the bridged bimetallic complexes, $[(C_5H_5)_2Ln(\mu\text{-}NH_2)]_2$ (Ln = Dy, Ho, Er, Yb),[6] $(C_5Me_5)_2Yb(\mu\text{-}NH_2)_2AlMe_2$,[18] and $[Ho_2(\mu\text{-}NH_2)_2(NH_3)_{10}](N_3)_3$.[19] To our knowledge, there is only a single molecular compound containing a rare-earth metal with a terminal amide ligand, $(C_5Me_5)_2Yb(NH_2)(NH_3)$,[18] yet no crystallographic data exists for this molecule. To remedy this deficiency, an yttrium metallocene system was investigated since Y^{3+} is diamagnetic and NMR spectroscopy could be employed for characterization. Herein we report the synthesis of the first yttrium-amide complex, $(C_5Me_5)_2Y(NH_2)(THF)$, **1**, and the subsequent protonation to $[(C_5Me_5)_2Y(NH_3)(THF)][BPh_4]$, **2**.

Results and Discussion

$(C_5Me_5)_2Y(NH_2)(THF)$. The allyl complex, $(C_5Me_5)_2Y(C_3H_5)$,[20] was chosen as the starting material since these metallocene allyls have proven to be so useful in rare-earth metal syntheses.[21–24] A solution of NH_3 in THF was added to $(C_5Me_5)_2Y(C_3H_5)$[20] as shown in Scheme

1 and crystals from the resulting solution were



Scheme 1. Synthesis of $(C_5Me_5)_2Y(NH_2)(THF)$, **1**, and $[(C_5Me_5)_2Y(NH_3)(THF)][BPh_4]$, **2**.

identified as $(C_5Me_5)_2Y(NH_2)(THF)$, **1** (Figure 1). IR spectroscopy revealed two peaks

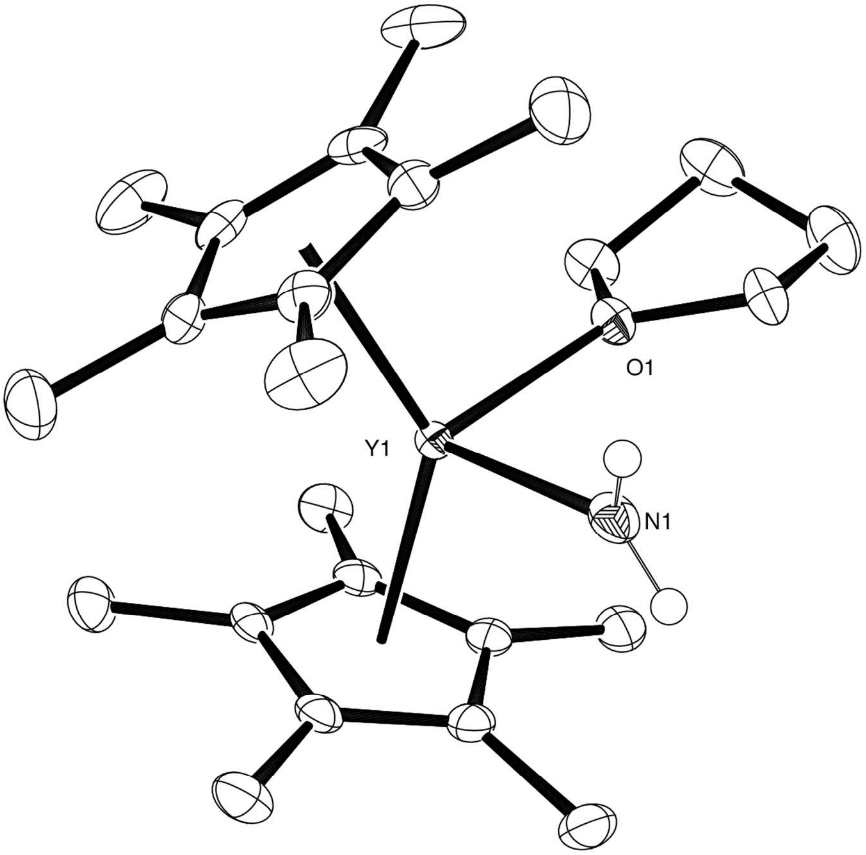


Figure 1. Thermal ellipsoid plot of $(C_5Me_5)_2Y(NH_2)(THF)$, **1**, drawn at the 50% probability level. Hydrogen atoms except those on NH_2 have been omitted for clarity.

at 3390 and 3358 cm^{-1}, consistent with the presence of a primary amide ligand.[25] This complex is a rare instance of a terminal Y–NH$_2$ bond and is the first isolated yttrium amide to be crystallographically characterized to our knowledge.[26]

[(C$_5$Me$_5$)$_2$Y(NH$_3$)(THF)][BPh$_4$]. Complex **1** was subsequently treated with [HNEt$_3$][BPh$_4$] to determine if the (NH$_2$)$^{1-}$ ligand could be protonated to form an ammonia complex. The ammonia complex, [(C$_5$Me$_5$)$_2$Y(NH$_3$)(THF)][BPh$_4$], **2**, was isolated according to Scheme 1 (Figure 2). The IR spectrum of **2** shows a broad, weak absorption at 3455 cm^{-1} and the ^{1}H NMR spectrum shows a broad resonance at δ 2.22 ppm, both indicative of an NH$_3$ group.

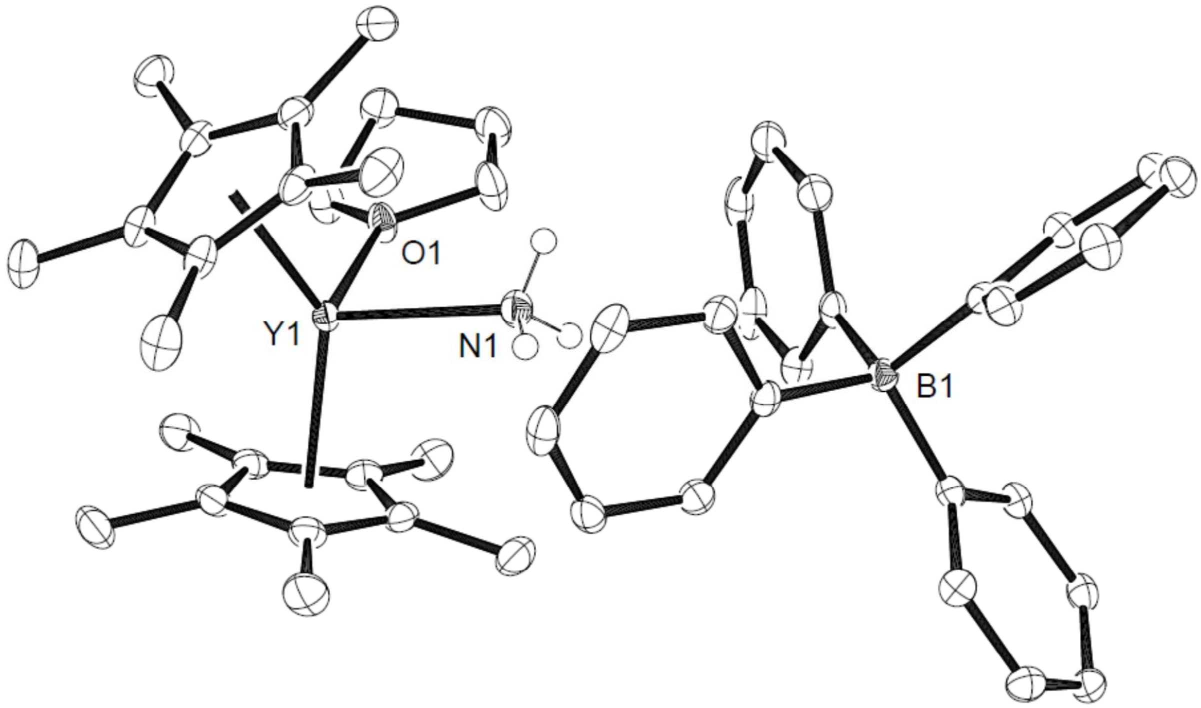


Figure 2. Thermal ellipsoid plot of [(C$_5$Me$_5$)$_2$Y(THF)(NH$_3$)][BPh$_4$]. Hydrogen atoms except those on NH$_3$ are omitted for clarity.

Structural Details. Both **1** and **2** crystallize as typical bis(cyclopentadienyl) metallocenes with two additional ligands and they are structurally similar to the methyl compound $(C_5Me_5)_2Y(CH_3)(THF)$.[27] The 2.405 Å Y-(C_5Me_5 ring centroid) distance of the neutral complex, **1**, is numerically larger than the 2.362 Å distance in the $[(C_5Me_5)_2Y(THF)(NH_3)]^{1+}$ cation although the (ring centroid–Y–ring centroid) angles, 137.8° and 138.8°, respectively, are similar. The 2.386(2) Å Y–O(THF) distance in **1** is slightly longer than the 2.353(1) Å analog measured in **2**. Protonation of the amide ligand in **1** to form the ammonia ligand in **2** lengthens the Y–N bond distance from 2.226(2) Å Y–N(NH_2) to 2.476(2) Å Y–N(NH_3) as expected for an anionic ligand compared to a neutral ligand.

Reactivity. In order to determine the parallels between reactivity of **2** and the known bis(THF) solvate, $[(C_5Me_5)_2Y(THF)_2][BPh_4]$,[28] reactions previously reported for the latter complex were carried out with **2**. The reaction of **2** and NaN_3 in THF produces a colorless solid. The IR spectrum of the resulting solid contains strong peaks at 2165 and 2117 cm^{-1}, consistent with the known complex $[(C_5Me_5)_2YN_3]_x$ made from the analogous reaction using $[(C_5Me_5)_2Y(THF)_2][BPh_4]$. The reaction of **2** with 2 equiv of acetone also generates the known complex $[(C_5Me_5)_2Y(OCMe_2)_2][BPh_4]$, identified by ^1H NMR spectroscopy. Additionally, ^1H NMR evidence of the reaction of **2** with 1 equiv of acetone suggests that acetone replaces NH_3 before THF, showing resonances that are consistent with the presence of coordinated THF and a single acetone ligand. The above reactions show that the ammonia ligand in **2** can be displaced by both $(N_3)^{1-}$ and acetone and does not react with these substrates. This reactivity matches that of $[(C_5Me_5)_2Y(THF)_2][BPh_4]$, suggesting that the NH_3 is weakly bound to the yttrium.

Table 1. Selected bond lengths (Å) and angles (°) for $(C_5Me_5)_2Y(NH_2)(THF)$, **1**, $[(C_5Me_5)_2Y(NH_3)(THF)][BPh_4]$, **2**, and $(C_5Me_5)_2Y(CH_3)(THF)$[27] (Cnt = C_5Me_5 ring centroid).

	$(C_5Me_5)_2Y(NH_2)(THF)$, **1**	$[(C_5Me_5)_2Y(NH_3)(THF)][BPh_4]$, **2**	$(C_5Me_5)_2Y(CH_3)(THF)$

Y–Cnt$_{avg}$	2.405	2.362	2.67
Y–O	2.386(2)	2.353(1)	2.379(8)
Y–X	2.226(2)	2.476(2)	2.44(2)
Cnt1–Y–Cnt2	137.8	138.8	137.0(3)
X–Y–O	91.71(8)	90.93(5)	90.3(4)

Conclusion

The synthesis of $(C_5Me_5)_2Y(NH_2)(THF)$, **1**, shows that simple amide complexes of yttrium metallocenes are accessible. Conversion of **1** to $[(C_5Me_5)_2Y(NH_3)(THF)][BPh_4]$, **2**, demonstrates that selective protonation of specific ligands in rare-earth metallocenes is viable. Since so few rare-earth metallocenes with amide ligands are known, the synthesis of **1** could provide a general route to synthesizing other rare-earth metallocene amide complexes. While the ammonia group in **2** does not affect the reactivity of the metallocene cation with azide and acetone substrates and leads to the synthesis of some known compounds, namely $[(C_5Me_5)_2YN_3]_x$ and $[(C_5Me_5)_2Y(OCMe_2)_2][BPh_4]$, the enhanced magnetic properties of $[(C_5Me_5)_2Dy(NH_3)_2][BPh_4]$[1] compared to $[(C_5Me_5)_2Dy][BPh_4]$ suggest that further exploration of this ligand could lead to new rare-earth metallocenes with desirable physical properties.

Experimental

The syntheses and manipulations described below were conducted under nitrogen atmosphere with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. Solvents were sparged with UHP argon and dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotope Laboratories) were dried over NaK alloy, degassed by three freeze-pump-thaw cycles, and vacuum transferred before use. $[HNEt_3][BPh_4]$ was prepared by literature procedures.[29] $LnCl_3$ (Ln = Y, Dy) was dried according to literature procedures by heating a mixture of the hydrated trichloride with an excess of NH_4Cl.[30,15,31–35] $K[N(SiMe_3)_2]$ (Aldrich, 95%) was purified via toluene extraction before use. C_5Me_5H was dried over molecular sieves and degassed using three freeze-pump-thaw cycles. KC_5Me_5 was synthesized by deprotonation of C_5Me_5H with $K[N(SiMe_3)_2]$.[36] NH_3 in tetrahydrofuran (THF) (Acros, 0.5 M) was degassed using three freeze-pump-thaw cycles. $(C_5Me_5)_2Y(C_3H_5)$ was synthesized by literature procedures.[20] Acetone (Fisher) was dried over 3 Å molecular sieves and degassed by three freeze-pump-thaw cycles before use. NaN_3 (Aldrich) was placed under 10^{-3} Torr for 12 h before use. ^1H NMR spectra were recorded on Bruker GN500 or CRYO500 MHz spectrometers ($^{13}C\{^1H\}$ at 125 MHz) at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. IR samples were prepared as KBr pellets and spectra were obtained on a Jasco FT/IR-4700 spectrometer. Elemental analyses were performed on a PerkinElmer series II 2400 CHNS analyzer.

$(C_5Me_5)_2Y(NH_2)(THF)$, 1. NH_3 in THF (0.50 M, 0.54 mL, 0.27 mmol) was added to a stirred solution of $(C_5Me_5)_2Y(C_3H_5)$ (100 mg, 0.26 mmol) in toluene (3 mL). The solution immediately changed from bright yellow to colorless. After the mixture was stirred for 1 h, the solvent was removed under reduced pressure to leave a colorless solid. The solid was washed with hexanes (3 □× 2 mL) and dried under reduced pressure to yield a colorless powder (82 mg, 73%). Colorless clusters of pyramidal crystals of $(C_5Me_5)_2Y(NH_2)(THF)$ suitable for X-ray diffraction were grown at −35 °C from a concentrated toluene solution over 2 d. ^1H NMR (C_6D_6): δ 3.51 (m, 4H, THF) 2.21 (s, 2H, $N\mathit{H_2}$), 2.03 (s, 30H, $C_5\mathit{Me_5}$), 1.25 (m, 4H, THF).

$^{13}C\{^1H\}$ NMR (C_6D_6): 114.7 (*C₅*Me$_5$), 113.3 (*C₅*Me$_5$), 12.4 (C_5*Me₅*). IR (cm^{-1}) 3390w, 3358w, 2957s, 2929s, 2857s, 1438m, 1380m, 1189s, 1022w, 725w, 634s, 616s, 468s. Anal. Calcd. for $C_{24}H_{40}NOY$: C, 64.42; H, 9.01; N, 3.13. Anal. Calcd. for $(C_5Me_5)_2Y(NH_2)$: C, 63.99; H, 8.59; N, 3.73. Found: C, 61.16; H, 8.34; N, 3.59. The data obtained suggest loss of THF. Low C, H, and N values were obtained even after multiple analysis attempts using different batches of samples. The found C/H/N ratios, such as $C_{20}H_{32}N$ for the data above, match that calculated and suggest incomplete combustion of the samples.[37,38]

$[(C_5Me_5)_2Y(NH_3)(THF)][BPh_4]$, 2. A slurry of $[HNEt_3][BPh_4]$ (87 mg, 0.21 mmol) in THF (2 mL) was added to $(C_5Me_5)_2Y(NH_2)(THF)$ (94 mg, 0.22 mmol) in THF (4 mL). After 20 min, volatiles were removed under reduced pressure to yield a colorless powder. The powder was washed with hexanes (3 × 2 mL) and toluene (3 × 2 mL) and then dried under reduced pressure to give as a colorless powder (142 mg, 92%). Colorless blocks of $[(C_5Me_5)_2Y(NH_3)(THF)][BPh_4]$ suitable for X-ray diffraction were grown by slow evaporation from THF at room temperature over 2 d. ^1H NMR (THF-d_8): δ 7.31 (m, 8H, B*Ph₄*), 6.90 (t, 8H, B*Ph₄*), 6.76 (t, 4H, B*Ph₄*), 3.62 (m, 4H, THF), 2.22 (s, br, 3H, N*H₃*), 1.90 (s, 30H, C_5*Me₅*), 1.77 (m, 4H, THF). $^{13}C\{^1H\}$ NMR (THF-d_8): 165.6 (B*Ph₄*), 164.8 (B*Ph₄*), 164.4 (B*Ph₄*), 121.7 (*C₅*Me$_5$), 68.0 (THF), 26.2 (THF), 10.8 (C_5*Me₅*). IR (cm^{-1}) 3455w br, 3134s, 3055s, 3001s, 1580m, 1479s, 1427m, 1390m, 1267w, 1150m, 1065w, 1032m, 840w, 742s, 706s, 605m, 476w. Anal. Calcd. for $C_{48}H_{61}OBNY$: C, 75.09; H, 8.01; N, 1.82. Found: C, 69.51; H, 7.67; N, 1.65. Low C, H, and N values were obtained even after multiple analysis attempts using different batches of samples. The found C/H/N ratios, such as $C_{48}H_{63}N$ for the data above, match that calculated and suggest incomplete combustion of the samples.[37,38]

X-ray Data Collection, Structure Determination, and Refinement. Crystallographic details for compounds $(C_5Me_5)_2Y(NH_2)(THF)$, **1**, and $[(C_5Me_5)_2Y(NH_3)(THF)][BPh_4]$, **2**, are summarized in the Supporting Information (SI).

Supporting Information Available

Crystallographic details for **1** and **2** (CCDC 1550006, 1550005). This material is available free of charge via the Internet.

Conflicts of Interest

There are no conflicts of interest to declare.

Acknowledgments

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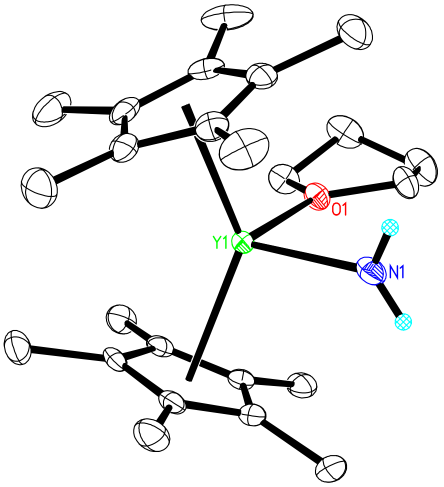

First crystallographically-characterized yttrium metallocene with a $(NH_2)^{1-}$ ligand.