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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Synthesis of a Crystalline Molecular Complex of Y^{2+}, $[(18\text{-crown-6})K][(C_5H_4SiMe_3)_3Y]$

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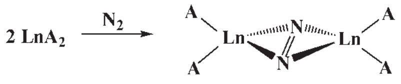
S *Supporting Information*

ABSTRACT: The La^{2+} complex $[K(18\text{-crown-6})(OEt_2)][Cp''_3La]$ (**1**) [$Cp'' = C_5H_3(SiMe_3)_2$-1,3], can be synthesized under N_2, but in the presence of KC_5Me_5, **1** reduces N_2 to the $(N{=}N)^{2-}$ product $[(C_5Me_5)_2(THF)La]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$. This suggests a dichotomy in terms of ligands that optimize isolation of reduced dinitrogen complexes versus isolation of divalent complexes of the rare earths. To determine whether the first crystalline molecular Y^{2+} complex could be isolated using this logic, Cp'_3Y (**2**) ($Cp' = C_5H_4SiMe_3$) was synthesized from YCl_3 and KCp' and reduced with KC_8 in the presence of 18-crown-6 in Et_2O at −45 °C under argon. EPR evidence was consistent with Y^{2+} and crystallization provided the first structurally characterizable molecular Y^{2+} complex, dark-maroon-purple $[(18\text{-crown-6})K][Cp'_3Y]$ (**3**).

Since the characterization of the first rare-earth dinitrogen complex, $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$,[1] prepared from the Sm^{2+} metallocene $(C_5Me_5)_2Sm$,[2] numerous complexes having the general formula $[A_2(THF)_xLn]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (A = anion; Ln = rare earth; $x = 0-2$) have been isolated with cyclopentadienyl,[1,3−10] amide,[11−14] aryloxide,[11,15,16] porphyrinogen,[17−19] and tris(pyrazolyl)borate[14] ligands. The early examples of reduced dinitrogen complexes were accessed through the reductive nature of divalent rare earth ions (Scheme 1).[1,3,4,11] However, the $LnA_3/M/N_2$ (M = alkali metal) reduction system (Scheme 2) has allowed such dinitrogen complexes to be formed from trivalent precursors as well.[5,6,9,10,12,13,20−22] This method provides "Ln^{2+}-like" reactivity to rare earth metals for which molecular Ln^{2+} ions have never been identified.

To date, isolable Ln^{2+} complexes have been shown to reduce dinitrogen only with Sm,[1,23,24] Tm,[4,14] Dy,[4] and Nd.[10] However, the $LnA_3/M/N_2$ reduction system produces reduced dinitrogen complexes for not only these metals but also La, Ce, Pr, Gd, Tb, Y, Ho, Er, Lu, and Sc. In all of the $LnA_3/M/N_2$ reactions with this second list of metals, only with yttrium has evidence been found to support the existence of short-lived divalent intermediates. Specifically, electron paramagnetic resonance (EPR) evidence for Y^{2+} in solutions of $Y[N(SiMe_3)_2]_3/KC_8$ at low temperature has been obtained, and these yttrium solutions have been found to reduce dinitrogen.[25] In this report, we describe efforts to obtain the first isolable Y^{2+} complex.

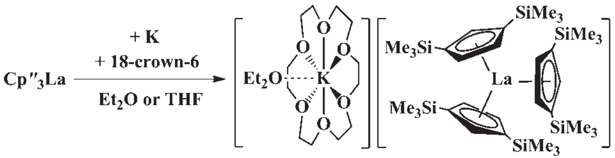
Scheme 1. Reduction of N_2 by Divalent Rare Earths (Ln = Sm, Tm, Dy, Nd)



$$2\,Ln^{2+} \longrightarrow 2\,Ln^{3+} + 2\,e^{1-}$$

$$N_2 + 2\,e^{1-} \longrightarrow (N_2)^{2-}$$

Insight into a successful approach to this target was provided by examining the dinitrogen reduction reactivity of Lappert's isolable La^{2+} complex $[K(18\text{-crown-6})(OEt_2)][Cp''_3La]$ (**1**) [$Cp'' = C_5H_3(SiMe_3)_2$-1,3], which was prepared according to eq 1.[26] Although this is a fully characterized divalent rare-earth complex, its reactivity with dinitrogen had not been previously reported. Examination of the reactivity of **1** with N_2 suggested how to optimize the isolation of divalent rare earths and their dinitrogen reduction products.



1

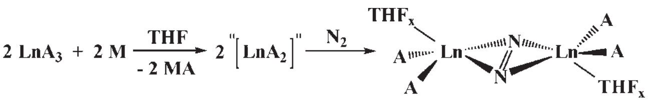
(1)

No color changes were initially observed when dark-purple tetrahydrofuran (THF) or Et_2O solutions of **1** were exposed to dinitrogen. Over 1 day (THF) or 3 days (Et_2O), the solutions became colorless, and multiple resonances were observed by ^1H NMR spectroscopy. However, elemental analysis of these products showed no detectable nitrogen. Moreover, control experiments under argon showed the same rate of color loss and gave solutions with similar ^1H NMR spectra. In addition, we found that **1** can be synthesized from Cp''_3La, K, and 18-crown-6 under a dinitrogen atmosphere! These results were surprising since (a) La^{2+} should be more reducing than Tm^{2+}, Dy^{2+}, and Nd^{2+}, which reduce dinitrogen; (b) two crystallographically characterizable $(N_2)^{2-}$ complexes of lanthanum are known, $[(C_5Me_5)_2(THF)La]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ and $[(C_5Me_4H)_2(THF)La]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$;[5] and (c) $(N_2)^{2-}$ complexes containing $(Cp'')^{1-}$ ancillary ligands (albeit with smaller metals) are known, namely, $[Cp''_2Tm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$[3] and $[Cp''_2Dy]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$,[4] which were formed from Tm^{2+} and Dy^{2+} precursors, respectively.

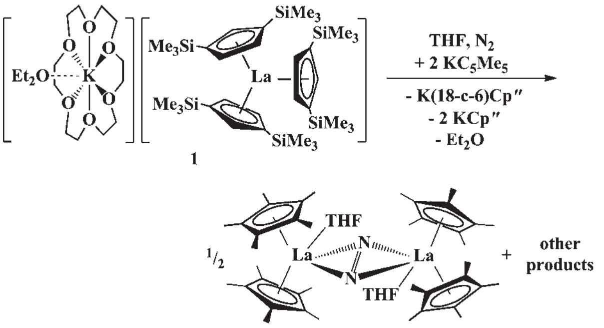
To determine whether a larger, more electron-donating[27] cyclopentadienyl ligand is required in order to isolate a reduced dinitrogen complex from La^{2+}, the reaction of **1** with N_2 was carried out in the presence of excess KC_5Me_5. The dark-purple solution of **1** in THF under these conditions changed to orange within 2 h, and $[(C_5Me_5)_2(THF)La]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$[5] and $K(18\text{-crown-6})(Cp'')$[28]

Received: August 3, 2011
Published: September 16, 2011

Scheme 2. $\mathrm{LnA_3/M/N_2}$ Reduction System with Possible $\mathrm{Ln^{2+}}$ Intermediate



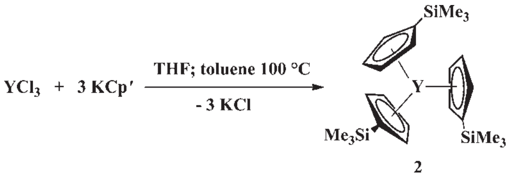
were identified by ^{1}H NMR spectroscopy (eq 2). The isolation of a $\mathrm{La^{3+}}$ complex of $\mathrm{(N{=}N)^{2-}}$ from a $\mathrm{La^{2+}}$ precursor indicates that $\mathrm{La^{2+}}$ can reduce dinitrogen to make isolable products when the proper ligands are present.



(2)

These results suggested that for lanthanum, the ideal ligands for isolating a divalent species are not optimum for isolating a dinitrogen reduction product. This is not true for all rare-earth metals, since both divalent and reduced dinitrogen complexes can be isolated with the same ligands for Nd, Sm, Dy, and Tm. However, the properties of the ancillary ligands required for stabilizing these complexes would be expected to vary depending on metal size and the stability of the divalent state. In view of the recent EPR evidence for $\mathrm{Y^{2+}}$ in solution[25] and the success of the silylcyclopentadienyl ligand class in the isolation of molecular $\mathrm{La^{2+}}$, these ligands were explored with yttrium.

Since 3 equiv of KCp″ react with $\mathrm{YCl_3}$ to form $[\mathrm{Cp''_2Y}(\mu\text{-Cl})]_2$[29,30] rather than $\mathrm{Cp''_3Y}$ and the ionic radius of nine-coordinate $\mathrm{Y^{3+}}$ (1.075 Å) is smaller than that of $\mathrm{La^{3+}}$ (1.216 Å),[31] the smaller $(\mathrm{Cp'})^{1-}$ ligand ($\mathrm{Cp' = C_5H_4SiMe_3}$) was examined with yttrium. The reaction of 3 equiv of KCp′ with $\mathrm{YCl_3}$ formed pale-yellow $\mathrm{Cp'_3Y}$ (**2**) in 90% yield (eq 3). The identity and molecular structure of **2** were determined by X-ray crystallography (Figure S2 in the Supporting Information).



(3)

The reaction of **2** with $\mathrm{KC_8}$ in the presence of 18-crown-6 in $\mathrm{Et_2O}$ under argon produced a dark-maroon-purple solution that faded to orange within 30 min at room temperature. At −45 °C, however, the solution was stable enough that dark-purple crystalline solids could be isolated after filtering the solution at −45 °C, concentrating the filtrate, and layering with pentane using Schlenk techniques at −78 °C. The EPR spectrum of these solids dissolved in $\mathrm{Et_2O}$ (Figure 1) exhibits a sharp doublet at $g_{\mathrm{iso}} = 1.991$ with a hyperfine coupling constant of 36.6 G. These parameters, which are similar to those for the EPR spectra of the dark-blue species generated by reducing $\mathrm{Y[N(SiMe_3)_2]_3}$ with $\mathrm{KC_8}$ (110 G doublet at $g_{\mathrm{iso}} = 1.976$)[25] and the $\mathrm{Y_2@C_{79}N}$ fullerene (81.2 G triplet at $g_{\mathrm{iso}} = 1.974$),[32] are consistent with a $4\mathrm{d}^1$ ion. In contrast, all other previously reported yttrium-containing radical complexes in which the unpaired electron is ligand-based have ^{89}Y coupling constants no greater than 6.3 G with g values closer to that of the free electron (2.0023).[15,16,33−37]

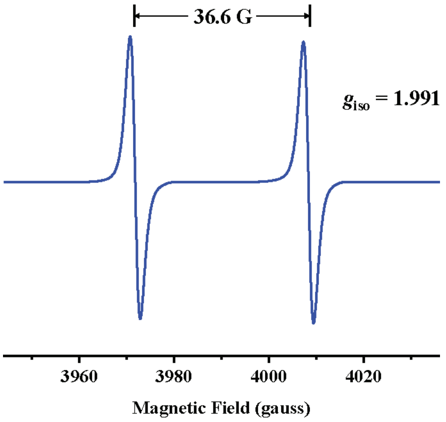
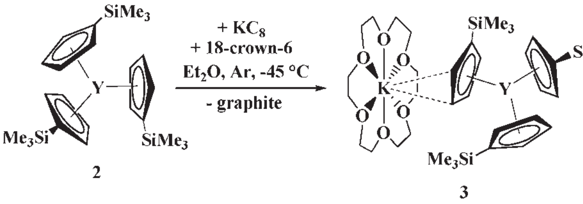


Figure 1. Room-temperature X-band EPR spectrum of **3** in $\mathrm{Et_2O}$ under argon.

Single-crystal X-ray diffraction studies of the dark-purple solids were consistent with a molecular $\mathrm{Y^{2+}}$ complex, $[(18\text{-crown-6})\mathrm{K}][\mathrm{Cp'_3Y}]$ (**3**), formed via eq 4. Analytically pure **3** was isolated in 77% yield using low-temperature Schlenk filtration and solvent manipulation.[38]



(4)

The molecular structure of **3** (Figure 2) contains a $[\mathrm{Cp'_3Y}]^{1-}$ moiety reminiscent of the $[\mathrm{Cp''_3La}]^{1-}$ anion in **1**. The potassium ion in **1** is outer-sphere, whereas in **3** the potassium is oriented toward two carbon atoms of one Cp′ ring (C18 and C19) with K−C distances of 3.079(2) and 3.055(2) Å, respectively. These are significantly shorter than the K−C(η^2-toluene) distances of 3.357−3.399 Å in $[\mathrm{K(18\text{-}crown\text{-}6)(toluene)_2}]^{1+}$ complexes[39] but slightly longer than the K−C distances in KCp′ [2.99(1)−3.04(1) Å].[40] This backside coordination of potassium does not affect the ring C−C distances in **3** within the error limits (Table S1), and the Y−C18 and Y−C19 distances [2.720(2) and 2.674(2) Å, respectively] are not unusually long in comparison with the range of all the other Y−C(Cp′) distances in the molecule [2.667(2)−2.746(2) Å]. The Y−(Cp′ ring centroid) distance of the ring containing C18 (2.419 Å) is similar to those of the other rings (2.427 and 2.433 Å).

Metal−ligand bond distances in $\mathrm{Eu^{2+}}$, $\mathrm{Yb^{2+}}$, $\mathrm{Sm^{2+}}$, $\mathrm{Tm^{2+}}$, $\mathrm{Dy^{2+}}$, and $\mathrm{Nd^{2+}}$ complexes are typically ∼0.05 to 0.2 Å larger than those in trivalent analogues.[10,31,41,42] In contrast, the 2.667(2)−2.746(2) Å range of Y−C(Cp′) distances and the 2.419−2.433 Å Y−(Cp′ ring centroid) distances in $\mathrm{Y^{2+}}$ complex **3** are only slightly larger than those in the $\mathrm{Y^{3+}}$ complex **2** [2.6605(14)−2.7174(13) and 2.403−2.409 Å, respectively]. The difference between the La−C distances in divalent **1** and those in trivalent $\mathrm{Cp''_3La}$ is similarly smaller than typically seen for complexes of di- and trivalent 4f elements.[26] Since bond distances are much less sensitive to the metal oxidation state for transition metals than

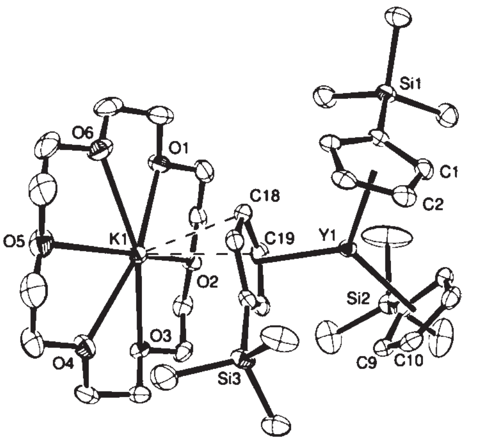
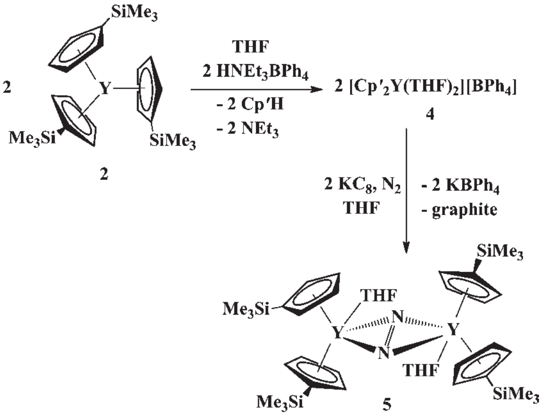


Figure 2. ORTEP[46] depiction of [(18-crown-6)K][Cp'_3Y] (**3**) with thermal ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **3**: Y1−Cnt1(C1−C5), 2.427; Y1−Cnt2(C9−C13), 2.433; Y1−Cnt3-(C17−C21), 2.419; Y1−C_{avg}, 2.707(2); K1−C18, 3.079(2); K1−C19, 3.055(2); Cnt1−Y−Cnt2, 118.7; Cnt1−Y−Cnt3, 117.8; Cnt2−Y−Cnt3, 123.1.

Scheme 3. Synthesis of [$Cp'_2(THF)Y]_2(\mu$-η^2:η^2-N_2) (5)



for the lanthanides, it is possible that the smaller difference in the lanthanum and yttrium Ln^{2+} versus Ln^{3+} cases may occur because these Ln^{2+} ions are d^1 and not f^n species: La^{2+} was found to have a $5d^1$ electron configuration,[26,43−45] and Y^{2+} is necessarily a $4d^1$ ion.

Complex **3** is easily oxidized by $AgBPh_4$ at −35 °C to reproduce the trivalent precursor **2** along with white and black precipitates presumed to be K(18-crown-6)BPh_4 and Ag^0, respectively. Before the reactivity of **3** with N_2 was compared with that of **1**, an authentic reduced dinitrogen complex of yttrium with Cp′ ligands was synthesized by the $LnA_2A'/M/N_2$ method (Scheme 3). In this synthesis, [$Cp'_2Y(THF)_2$][BPh_4] (**4**) obtained from **2** and $HNEt_3BPh_4$ was treated with KC_8 under N_2 to form [$Cp'_2(THF)Y]_2$-(μ-η^2:η^2-N_2) (**5**), which was isolated in 29% yield[47] as blue-green crystals and identified by X-ray diffraction (Figure S4 and Table S2). This yield is lower than those observed in reactions with $(C_5Me_5)^{1-}$ and $(C_5Me_4H)^{1-}$ ligands[5,6,8,20] but comparable to those of the Ln[$N(SiMe_3)_2]_3/KC_8/N_2$ reactions.[12]

Solutions of **3** changed color when exposed to N_2 at −45 °C, forming yellow-orange solutions within 30 min that yielded a tacky orange residue upon solvent removal. This material had a small yet significant nitrogen content as determined by elemental analysis (0.3%; cf. 3.1% in **5**), but no evidence of **5** was observed. These reactions were complicated by the fact that **5** was isolated as a THF adduct and **3** is not stable in the presence of THF. Neither [$(C_5Me_5)_2Y]_2(\mu$-η^2:η^2-N_2)[8] nor [$(C_5Me_4H)_2(THF)Y]_2$-(μ-η^2:η^2-N_2)[7] were observed when KC_5Me_5 and KC_5Me_4H, respectively, were added to **3** under N_2 in analogy to eq 2. It is possible that the ligand substitution reaction that is successful with lanthanum is not so facile with the smaller, more Lewis acidic yttrium.

To summarize, examination of the ligand dependence of isolating reduced dinitrogen complexes versus divalent complexes of the rare earths has led to the first crystallographically characterizable molecular complex of Y^{2+}. The existence of molecular Y^{2+} and La^{2+} complexes gives support to the possibility that the $LnA_3/M/N_2$ reduction system proceeds through divalent intermediates (Scheme 2). The ligand dependence for isolation of reduced dinitrogen versus Ln^{2+} complexes found in this study suggests that different protocols will be needed to isolate the two types of complexes. The formation of **3** means that now 10 out of the 17 rare earth elements are known to form isolable molecular Ln^{2+} compounds. In contrast, for 90 years it was thought that only Eu^{2+}, Yb^{2+}, and Sm^{2+} were stable enough to form divalent molecular species in solution. Clearly, there is still room for expansion in fundamental areas of rare earth chemistry such as the availability of the oxidation states of the metals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional experimental details; crystallographic data collection, structure solution, and refinement; and X-ray diffraction details of compounds **2**, **3**, and **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre as CCDC 836656−836658.

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■ ACKNOWLEDGMENT

We thank the U.S. National Science Foundation for support of this research and Ryan A. Zarkesh for assistance with X-ray crystallography.

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(38) Synthesis of **3**: In a glovebox, a 200 mL Schlenk flask was charged with **2** (340 mg, 0.678 mmol), KC_8 (250 mg, 1.84 mmol), 18-crown-6 (179 mg, 0.678 mmol), and a magnetic stir bar. The flask was then attached to a medium Schlenk filter frit (designed to fit in a Dewar for low-temperature filtration) that was attached to a second 200 mL Schlenk flask. The apparatus was brought out of the glovebox, attached to a Schlenk line, and placed under vacuum. Et_2O (150 mL) was vacuum-transferred onto the solids at −45 °C. The mixture immediately turned dark-maroon-purple in color. After the mixture was stirred for 3 h under argon, the apparatus was inverted and the Schlenk filter placed in a Dewar containing a MeCN slush bath. The reaction mixture was filtered into the second flask at −45 °C to remove black insoluble material. The dark-maroon-purple solution was concentrated to ∼30 mL, cooled to −78 °C, and slowly layered with pentane (50 mL), which was added via vacuum transfer. After 6 h at −78 °C, black-purple X-ray-quality crystals formed. The colorless mother liquor was decanted by cannula transfer, and the crystals were dried under vacuum to yield **3** as a dark-purple microcrystalline solid (420 mg, 77%). IR (cm^{-1}): 3712w, 3067m, 2950s, 2895s, 2827m, 2746w, 2713w, 2369w, 2084w, 2014m, 1605w, 1454m, 1403m, 1352s, 1285m, 1247s, 1183m, 1113s, 1040s, 991m, 964s, 907s, 833s, 771s, 752s, 687m, 628m, 530m. Anal. Calcd for $C_{36}H_{63}KO_6Si_3Y$: C, 53.77; H, 7.90. Found: C, 53.28; H, 8.02. UV−vis (Et_2O, −30 °C) λ_{max}/nm (ε/$M^{-1}cm^{-1}$): 402 (550), 530 (700), 700 (300sh).

(39) (a) $[K(18\text{-crown-6})(toluene)_2][Cp''_3Sm]$: Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1998**, 1843. (b) $[K(18\text{-crown-6})(\eta^2\text{-toluene})_2]\{[La(C_5H_4SiMe_2{}^tBu)_3]_2\text{-}(\mu\text{-H})\}$ and $[K(18\text{-crown-6})(\eta^2\text{-toluene})_2][(CeCp''_2)_2(\mu\text{-}\eta^6{:}\eta^6\text{-toluene})]$: Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **2000**, *19*, 2832. (c) $[K(18\text{-crown-6})(THF)(toluene)]\{Ca[N(SiMe_3)_2]_3\}$: He, X.; Allen, J. F.; Noll, B. C.; Kennedy, A. R.; Henderson, K. W. *J. Am. Chem. Soc.* **2005**, *127*, 6920.

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(47) Synthesis of **5**: In a nitrogen-filled glovebox, a solution of **4** (549 mg, 0.663 mmol) in THF (18 mL) was quickly added to KC_8 (105 mg, 0.772 mmol) while stirring. After 30 min, the mixture was filtered to remove white and black insoluble material, and the pale-green filtrate was evaporated to dryness to yield a blue-green residue. Toluene (10 mL) was added, and the mixture was stirred for 20 min, after which a colorless precipitate, presumably $KBPh_4$, was removed by filtration. Solvent was slowly removed from the filtrate under reduced pressure to form pale-blue-green X-ray-quality crystals. The crystals were rinsed with a cold 50:50 hexane/toluene mixture (1 mL, −35 °C) and dried under vacuum to yield **5** as a blue-green crystalline solid (87 mg, 29%). ^1H NMR (C_6D_6): δ 6.19 (t, $^3J_{HH}$ = 2.5 Hz, $C_5H_4SiMe_3$, 8H), 5.93 (t, $^3J_{HH}$ = 2.5 Hz, $C_5H_4SiMe_3$, 8H), 3.92 (br s, *THF*, 8H), 1.50 (br s, *THF*, 8H), 0.49 (s, $C_5H_4SiMe_3$, 36H). ^{13}C NMR (C_6D_6): δ 118.4 ($C_5H_4SiMe_3$), 111.8 ($C_5H_4SiMe_3$), 108.9 ($C_5H_4SiMe_3$), 72.2 (*THF*), 26.0 (*THF*), 1.4 ($C_5H_4SiMe_3$). IR (cm^{-1}): 3932w, 3688w, 3628w, 3078m, 2952s, 2894m, 2712w, 2361w, 2085w, 1930w, 1871w, 1715w, 1604w, 1532w, 1443m, 1402m, 1361m, 1311w, 1246s, 1178s, 1038s, 907s, 883m, 833s, 770s, 752s, 686m, 628m, 507s. Anal. Calcd for $C_{40}H_{68}N_2O_2Si_4Y_2$: C, 53.43; H, 7.62; N, 3.12. Found: C, 53.53; H, 7.70; N, 3.10.