

Alkali-Metal, Halide, and Lewis Base Free Monomeric Alkylsamarium(III) Porphyrinogen Complexes of High Stability

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Alkylsamarium(III) complexes of a dimetalated modified porphyrinogen have been synthesized that have strong structural resemblance to samarocene(III) alkyl complexes. The monomeric complexes are free of alkali metals, halides, and coordinating solvent. The methyl and (trimethylsilyl)methyl complexes have been characterized by NMR spectroscopy, X-ray crystal structure determinations, and elemental analyses. Initial reactivity studies highlight the low reactivity of the complexes.

Introduction

Alkyl complexes are among the most important organolanthanide compounds, as they are used for various organic transformations, catalytic processes, and subsequent organolanthanide syntheses.^{1,2} Progress in these areas has been dominated by complexes featuring the bis(pentamethylcyclopentadienyl) ligand set or variants based on other substitution patterns. In their simplest form such complexes have the formula $[(\eta^5\text{-C}_5\text{R}'_5)_2\text{LnR}]$, which is also the desired formulation for high activity in catalytic processes, such as alkene polymerization, as this represents the catalytically active species. However, this structural motif has only been noted for bulky alkyl derivatives, such as $[(\eta^5\text{-C}_5\text{EtMe}_4)_2\text{-SmCH}(\text{SiMe}_3)_2]$.³ For methyl complexes, Lewis base adduct formation, e.g. $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{SmMe}(\text{THF})]$ (THF = tetrahydrofuran),⁴ and electron-deficient alkyl-bridged dimerization⁵/heterobimetallic⁶ complex formation, e.g. $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Sm}(\mu_2\text{-Me})_2\text{Sm}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$ and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Er}(\mu_2\text{-Me})_2\text{Li}(\text{TMEDA})]$ (TMEDA = *N,N,N',N'*-tetramethylethylenediamine), represent the only known structural forms. Though never structurally characterized to date, alkali-metal halide incorporation, e.g. $[(\eta^5\text{-C}_5\text{R}_5)_2\text{Ln}(\mu_2\text{-Me})(\mu_2\text{-Cl})\text{Li}(\text{THF})_2]$, is conceivable

in view of the previously mentioned dimethyl Ln/Li complexes and the related dichloride complexes of the type $[(\eta^5\text{-C}_5\text{R}_5)_2\text{Ln}(\mu_2\text{-Cl})_2\text{Li}(\text{THF})_2]$.⁷ The reactivity of the last four structural types is often (or would be expected to be) greatly reduced because the coordination of substrates to the metal center is restricted.

The alkyl complexes of non-hydrocarbyl ligand systems having “bent-sandwich” structures are known only for tetrametalated porphyrinogen complexes and are limited to $[(\text{THF})_4(\text{Cl})\text{Li}_3(\text{porph-4H})\text{SmMe}]$ and $[(\text{THF})_2\text{-Li}(\mu_2\text{-Me})_2\text{Sm}(\text{porph-4H})\text{Sm}(\mu_2\text{-Me})_2\text{Li}(\text{THF})_2]$ (porph = *meso*-octaethylporphyrinogen).^{8,9} It is worth noting that these complexes retain some/all of the alkali-metal cations, halide, and associated coordination of Lewis bases arising from the metathetical exchange reactions used for their synthesis. This is due largely to the tetraanionic status of the metalated porphyrinogens and their ability to host more than one metal in the macrocycle cavity. While some of these complexes have featured the desirable terminally bound “Ln–Me” motif, the $\text{Li}_x\text{Cl}_y(\text{THF})_z$ incorporation has led to added complexities in subsequent reactivity studies. Related dimetalated 1,1-bis(2'-pyrrolyl)methane lanthanide complexes effectively controlled the retention of alkali-metal cations, but the complexes generally exist as complex oligomers (with interesting reactivity stemming from their cyclic structures).¹⁰ Terminal Sm–Me moieties have also been found for a σ -bound pyrrolide complex, $[\{2\text{-}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{-}5\text{-}t\text{-BuC}_4\text{H}_2\text{N}\}_2\text{SmMe}(\text{THF})]$,¹¹ and an arylyate complex, $[\text{Li}(\text{THF})_2][\text{Sm}(\text{O-}2,6\text{-}$

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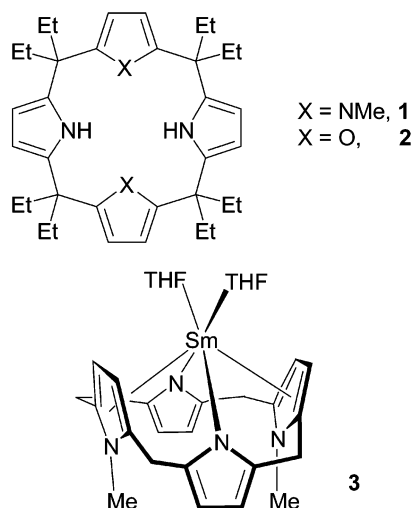
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$i\text{-Pr}_2\text{C}_6\text{H}_3)_3(\text{CH}_2\text{SiMe}_3)_2]^{12}$

We have been investigating organolanthanide complexes featuring modified porphyrinogens, including trans-*N,N'*-dimethylation (**1**) and trans difuran substitution (**2**), leading to lanthanide complexes that more closely resemble the ubiquitous lanthanocene(II) and -(III) complexes.¹³ In these complexes, the bent-metal-



locene substructure of the unmodified tetraanionic metalated porphyrinogens remains with two neutral η^5 -bound *N*-methylated pyrrole units as well as featuring σ -bound pyrroline units, as in the Sm(II) complex [(1-2H)Sm(THF)₂] (**3**). We have already noted the absence of alkali metals in complexes derived from **1**, such as **3** and the Sm(III) amide [(1-2H)SmN(SiMe₃)₂], owing to the reduced charge of the metalated macrocycle and the ability of the macrocyclic cavity to bind a single metal. In this paper, we report two new monomeric alkali-metal, halide, and Lewis base free samarium alkyl complexes of the trans-*N,N'*-dimethylated macrocyclic system, notably including a methyl derivative.

Experimental Section

General Procedures. All syntheses and manipulations of complexes were carried out under an argon atmosphere by the use of standard Schlenk techniques or in a nitrogen-filled glovebox. [(1-2H)Sm(THF)₂] (**3**) was prepared according to our literature procedure.¹³ Solvents were dried over Na or Na/K and distilled. All other chemicals were obtained from Aldrich and used as received. ¹H and ¹³C NMR spectra were recorded using a 300 MHz Varian Mercury plus spectrometer at 299.905 MHz (¹H) and 75.417 MHz (¹³C) at 298 K, internally referenced to the residual ¹H resonances of the solvents. IR spectra were recorded as Nujol mulls on NaCl plates. GC/MS spectra were obtained on a HP 5890 instrument. The CSL of the University of Tasmania or Chemical and Analytical Services Pty. Ltd., Melbourne, Australia, performed elemental analyses.

Synthesis of [(1-2H)SmMe] (4**).** To **3** (0.86 g, 1.00 mmol) dissolved in toluene (80 mL) was added a solution of *tert*-butyl chloride (0.093 g, 1.00 mmol) in THF (10 mL) dropwise with stirring, during which time the color of the solution changed from purple to light brown. Methylolithium (1.4 M in diethyl ether, 0.70 mL, 1.0 mmol) was added to the mixture at -30 °C and the solution stirred overnight at ambient temperature.

An insoluble white solid was filtered off and the solvent removed in vacuo. Recrystallization from diethyl ether led to a pure crystalline orange product (0.40 g, 54%). ¹H NMR (299.905 MHz, C₆D₆, 298 K): δ -0.56 (t, 12H, CH₂CH₃), 1.13 (m, 4H, CH₂CH₃), 1.44 (t, 12H, CH₂CH₃), 1.53 (m, 4H, CH₂CH₃), 1.95 (m, 4H, CH₂CH₃), 2.50 (m, 4H, CH₂CH₃), 2.98 (s, 4H, =CH, *N*-CH₃pyr), 3.69 (s, 6H, NCH₃), 6.76 (s, 4H, =CH, pyr), 8.94 (s, broad, 3H, SmCH₃). ¹³C NMR (75.417 MHz, C₆D₆, 298 K): δ 7.5, 9.4 (CH₂CH₃), 22.3, 32.7 (CH₂CH₃), 34.4 (NCH₃), 45.2 (CEt₂), 98.1 (CH, *N*-CH₃pyr), 102.1 (CH, pyr), 132.0 (C, *N*-CH₃pyr), 153.3 (C, pyr). Anal. Calcd for C₃₉H₅₇N₄Sm: C, 63.97; H, 7.85; N, 7.65. Found: C, 64.01; H, 7.88; N, 7.51.

Synthesis of [(1-2H)SmCH₂SiMe₃] (5**).** To **3** (0.86 g, 1.00 mmol) dissolved in toluene (80 mL) was added a solution of *tert*-butyl chloride (0.093 g, 1.00 mmol) in THF (10 mL) dropwise with stirring, during which time the color of the solution changed from purple to light brown. ((Trimethylsilyl)methyl)lithium (1.0 M in pentane, 1.0 mL, 1.0 mmol) was added to the solution and the solution stirred overnight. The solvent was removed in vacuo, and 40–60 °C petroleum ether (60 mL) was added. An insoluble white solid was filtered off and the solution concentrated in vacuo to ca. 20 mL. Recrystallization from 40–60 °C petroleum ether led to a pure crystalline orange product (0.50 g, 62%). ¹H NMR (299.905 MHz, C₆D₆, 298 K): δ -0.53 (t, 12H, CH₂CH₃), 0.97 (s, 9H, SiCH₃), 1.18 (m, 4H, CH₂CH₃), 1.44 (t, 12H, CH₂CH₃), 1.51 (m, 4H, CH₂CH₃), 1.96 (m, 4H, CH₂CH₃), 2.75 (m, 4H, CH₂CH₃), 2.94 (s, 4H, =CH, *N*-CH₃pyr), 3.50 (s, 6H, NCH₃), 6.77 (s, 4H, =CH, pyr), 9.56 (s, broad, 2H, SmCH₂). ¹³C NMR (75.417 MHz, C₆D₆, 298 K): δ 2.4 (SiCH₃), 7.5, 9.2 (CH₂CH₃), 22.1, 32.5 (CH₂CH₃), 34.1 (NCH₃), 45.2 (CEt₂), 98.4 (CH, *N*-CH₃pyr), 102.4 (CH, pyr), 133.3 (C, *N*-CH₃pyr), 153.3 (C, pyr). Anal. Calcd for C₄₂H₆₅N₄SiSm: C, 62.71; H, 8.14; N, 6.96. Found: C, 62.59; H, 8.14; N, 6.84.

Ethylene Polymerization Trials. The following conditions were applied for the attempted catalysis: 5 bar of ethylene, ambient temperature, in toluene, with/without 1000 equiv of MAO, in a Buchi glass autoclave.

X-ray Crystallography. Crystals of **4** and **5** suitable for X-ray structure determination were grown overnight by cooling of hot saturated solutions (**4**, 40–60 °C petroleum ether/diethyl ether; **5**, 40–60 °C petroleum ether) to room temperature. Data were collected on a Bruker SMART system using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods and refined using XTAL 3.7.¹⁴ For **4**, all non-H atom displacement parameter forms were refined anisotropically, except for those in a disordered pentane solvent molecule. For **5**, the asymmetric unit of **5** contains two molecules of similar geometries and a disordered pentane molecule. All discussion of the structure in this paper is based on molecule 1, as molecule 2 contains severe disorder relating to a ca. 15° rotation of the macrocyclic unit relative to the SmCH₂SiMe₃ unit, modeled as a 50%/50% site occupancy disorder of the whole macrocycle and the SiMe₃ group (the Sm–C unit being the only nondisordered portion). Only the Sm center was modeled with anisotropic displacement parameter forms in the severely disordered molecule 2 of **5**. Disorder in molecule 1 of **5** is limited to two ethyl groups (50%/50% site occupancy disorder). The disordered pentane solvent molecule in the structure of **5** was modeled with isotropic displacement parameter forms over two sites. All H atoms were included and constrained at estimated values for both **4** and **5**. The molecular structures of **4** and **5** are shown in Figures 1 and 2. Crystal data and data collection and refinement details are

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Table 1. Crystal Data and Data Collection and Refinement Details for 2 and 3

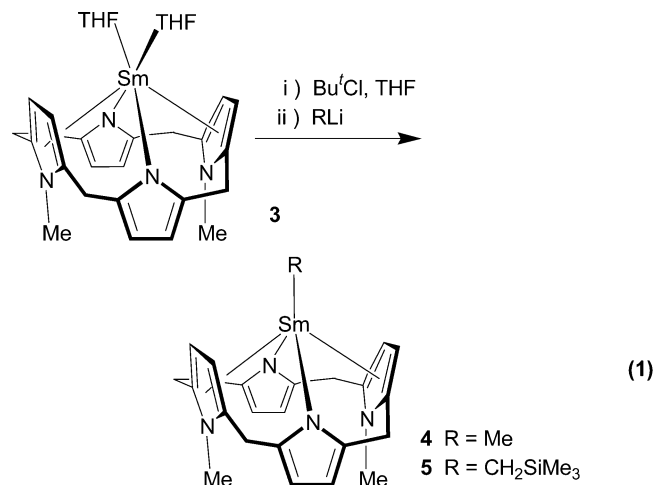
	4	5
formula	C ₃₉ H ₅₇ N ₄ Sm·C ₅ H ₁₂	C ₄₂ H ₆₅ N ₄ SiSm· 1/2C ₅ H ₁₂
fw	804.4	840.53
cryst syst	orthorhombic	triclinic
space group	<i>Pnma</i>	<i>P1</i>
color	orange	orange
<i>a</i> (Å)	14.271(1)	12.453(4)
<i>b</i> (Å)	17.676(2)	16.999(5)
<i>c</i> (Å)	16.520(1)	22.490(7)
α (deg)	90	101.202(4)
β (deg)	90	104.693(4)
γ (deg)	90	101.091(4)
<i>V</i> (Å ³)	4167(1)	4369(4)
<i>Z</i>	4	4
<i>T</i> (K)	150	150
μ (Mo K α) (cm ⁻¹)	14.42	14.05
cryst size (mm)	0.35 × 0.28 × 0.25	0.22 × 0.20 × 0.10
calcd density (Mg m ⁻³)	1.282	1.278
2 θ (max) (deg)	26.35	26.30
no. of rflns	63 093	39 895
no. of unique data	4405	17 543
no. of obsd data, <i>I</i> > 2 σ (<i>I</i>)	3813	12 410
<i>R</i> (int)	0.026	0.046
<i>R</i> 1 ^a	0.036	0.058
w <i>R</i> 2 ^b	0.056; <i>I</i> > 2 σ (<i>I</i>)	0.079; <i>I</i> > 2 σ (<i>I</i>)
GOF	1.085	1.049

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = (\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2)^{1/2}$.

given in Table 1. Further details are included in the Supporting Information.

Results and Discussion

Oxidation of the Sm(II) complex [(1-2H)Sm(THF)₂] (**3**) with 1 equiv of *tert*-butyl chloride gave the Sm(III) chloride complex,^{13,15} which was derivatized without isolation in metathetical exchange reactions with methyl lithium and ((trimethylsilyl)methyl)lithium, yielding the Sm(III) alkyl complexes **4** and **5** as orange crystalline solids in moderate yields, as shown in eq 1 (meso ethyls are not shown for clarity).



The structural assignments of **4** and **5** are based on microanalyses, ¹H and ¹³C NMR spectral data (assignments through ¹H–¹H COSY, ¹³C DEPT, and gHMBC

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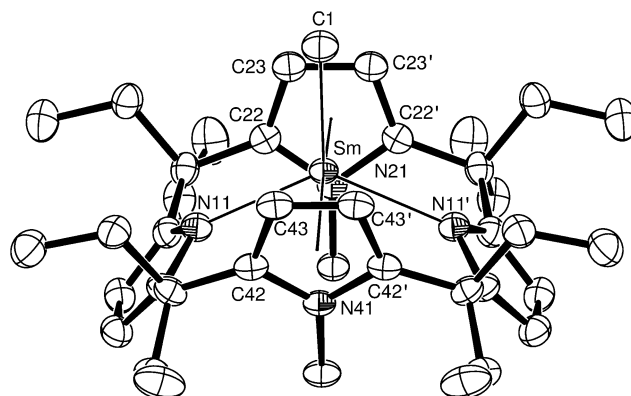


Figure 1. Molecular structure of **4** with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Sm–C1 = 2.424(5), Sm–N11 = 2.478(3), Sm–N20,N40 = 2.59₃, 2.60₉ (N20,40 are the centroids of rings 2 and 4); C1–Sm–N11 = 116.09(7), C1–Sm–N20,40 = 97.2₇, 93.8₆, N20–Sm–N40 = 168.8₆, N11–Sm–N11' = 127.82(9).

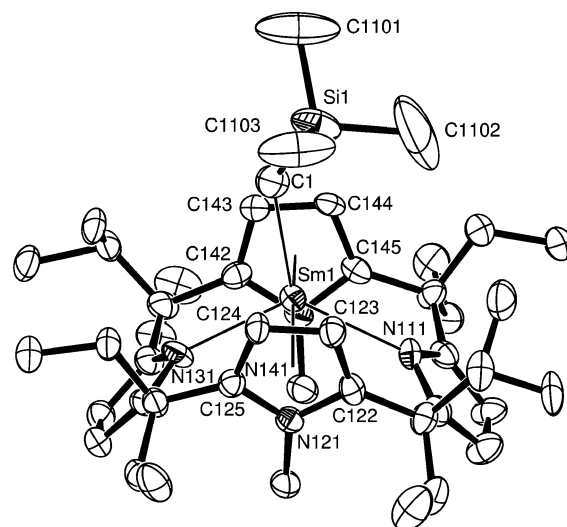


Figure 2. Molecular structure of **5** (molecule 1) with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Sm1–C1 = 2.453(7), Sm1–N111 = 2.501(5), Sm1–N131 = 2.485(6), Sm1–N120,140 = 2.60₆, 2.60₃ (N120,140 are the centroids of rings 2 and 4); C1–Sm1–N111 = 126.5(2), C1–Sm1–N131 = 109.4(2), C1–Sm1–N120,140 = 97.4₃, 95.7₆, N111–Sm1–N131 = 124.09(18), N120–Sm1–N140 = 166.7₅.

spectra: ¹³C NMR resonances for the Sm bound CH₃ and CH₂ carbons could not be identified, presumably due to the influence of the paramagnetic Sm center), and X-ray crystal structural determinations. Figures 1 and 2 show the molecular structures of **4** and **5** along with selected bond lengths and angles. Both complexes **4** and **5** adopt monomeric forms in the solid state with the Sm centers binding to the macrocycle by $\eta^5:\eta^1:\eta^5:\eta^1$ bonding modes, the macrocycle adopting a 1,3-alternate conformation (**4** possesses crystallographic *m* symmetry, with the mirror containing Sm and C1 and passing through the *N*-methylpyrrole units). The methyl and (trimethylsilyl)methyl ligands in **4** and **5**, respectively, bind to the Sm centers on the open coordination face of the metal, which is on the side of the macrocyclic cavity opposite to that blocked by the *N*-methyl substituents.

Complexes **4** and **5** feature in common the absence of

Sm-coordinated THF, which was also found in the Sm(III) nonmodified porphyrinogen complex [(THF)₄(Cl)-Li₃(porph-4H)SmMe].⁸ This differs from the metallocene analogues [(η^5 -C₅Me₅)₂Sm(Me)(THF)] and [(η^5 -C₅H₅)₂-Lu(CH₂SiMe₃)(THF)].¹⁶ The Sm–C(alkyl) distance in **4**, 2.424(5) Å, is the shortest terminal Sm–alkyl distance yet known (2.453(7) Å in **5**, to be discussed later), comparing with [(THF)₄(Cl)Li₃(porph-4H)SmMe]⁸ (2.49₈ Å), [(η^5 -C₅Me₅)₂Sm(Me)(THF)]⁴ (2.484(14) Å), and the five-coordinate complex [Li(THF)₂][Sm(O-2,6-*i*-Pr₂C₆H₃)₃(CH₂SiMe₃)₂]¹² (2.451(10) Å). The Sm–centroid distances in **4** and **5**, 2.59₃–2.60₉ Å, are long relative to those seen for decamethylsamarocene(III) complexes (e.g. 2.45₆ Å for [(η^5 -C₅EtMe₄)₂SmCH-(SiMe₃)₂]³ but similar to the pyrrolide interactions in [(THF)₄(Cl)Li₃(porph-4H)SmMe]⁸ (2.59₃ Å). This begs the question as to the significance of the η^5 interactions with the neutral pyrrole units in **4** and **5** and indeed those with the anionic pyrrolide units in tetrametalated porphyrinogen complexes themselves. That is, are **4** and **5** to be viewed as high-coordinate complexes (η^5 : η^1 : η^5 : η^1 from macrocycle + alkyl ligand) or low-coordinate complexes (η^1 : η^1 from macrocycle + alkyl ligand) in which the *N*-methylpyrrole units effectively serve as steric blockers? We are currently conducting theoretical calculations with this question in mind.

Slight differences in the structures of **4** and **5** are noted, such that the Sm center in **5** is bound to the alkyl carbon and the macrocyclic unit (both σ -N and the η^5 interactions) through slightly longer interactions than those found in **4**, corroborated by trends in the associated bond angles at the Sm centers and suggesting that the bulk of the (trimethylsilyl)methyl ligand in **5** forces a slight expulsion of the Sm center out of the macrocyclic cavity. Large variations between both C–Sm–N angles in **5**, 109.4(2) and 126.5(2)°, possibly arise from steric interactions between the (trimethylsilyl)methyl ligand and the macrocycle. The distortions do not appear to be consequent on the alkyl ligand tilting in response to any γ -H agostic interaction between the Sm center and a methyl group of the alkyl ligand (a smaller C–Si–C angle is associated with the methyl group (C1102) tending toward the Sm center, 109.1(6)°, compared with the others, 113.7(5) and 113.9(4)°). The long Sm···C and Sm···H distances of 4.38(2) and 4.0 Å associated with methyl group C1102 rule out any significant agostic interaction, which may be limited by alkyl ligand/macrocycle interactions. Increased tilting of the alkyl

ligand in **5** (i.e., further decreasing the C1–Sm1–N131 angle) would seemingly allow a stronger H-agostic interaction to form and also reduce steric interactions between the alkyl ligand and the macrocycle. Thus, in the absence of this further distortion the Sm center may not have strong tendencies to form agostic interactions such as those often noted in lanthanocene alkyl complexes. This inference may prove crucial in predicting the reactivity of this class of complex in further reactivity studies. Related to this, **4** showed no reactivity toward oligomerization or polymerization of ethylene, in contrast to samarocene complexes. The low reactivity likely relates to the Sm(III) center residing deeply within the macrocycle, giving it little opportunity to partake in the two-coordination site reactivity required for insertion-type activity toward small unsaturated molecules (cf. the Sm(II) precursor **3** that binds two THF molecules¹⁴). The promise of modified porphyrinogen complexes based on 1-2H may then be in stabilizing reactive ligands; for example, **4** does not feature the high C–H activation (and other) reactivity of [(η^5 -C₅Me₅)₂-SmMe(THF)] with respect to benzene, diethyl ether, alkenes, and alkanes.⁴ Rather, it is stable in benzene and hexane for (at least) several days.

Conclusion

The preparations of novel Sm(III) alkyl complexes free of alkali-metal cations, halides, and coordinating solvents have been achieved using a modified dianionic porphyrinogen. Access to a stable, “simple” methyl complex of the type [(nonparticipating ligand set)Ln–R] represents a significant milestone in structural simplification and control that was made possible through modification of the readily accessible porphyrinogens to better suit the lanthanide metals. We are continuing to synthesize related organolanthanide complexes based on modified porphyrinogens and other *N*-heterocyclic alternatives to the bis(cyclopentadienyl) ligand set and study their reactivity.

Acknowledgment. We thank the Australian Research Council for support of this project and Prof. F. Geoff N. Cloke (The University of Sussex) for conducting the ethylene polymerization trials.

Supporting Information Available: Tables of bond distances, bond angles, atomic coordinates, and anisotropic displacement parameters for **4** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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