

Cyclic Di- and Mixed-Valent Ytterbium Complexes Supported by Dipyrrolide Ligands

Dominique M. M. Freckmann, Tiffany Dubé, Christian D. Bérubé, Sandro Gambarotta,* and Glenn P. A. Yap

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

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The reaction of $\text{YbI}_2(\text{THF})_2$ with diphenyldipyrrolylmethanide leads to a complex reaction from which an octameric divalent Yb macrocyclic complex, [diphenyldipyrromethanediyl-Yb]₈, was obtained as a major product. A tetrameric cyclic Yb(II)-oxo complex, [(diphenyldipyrrolylmethanediyl)Yb]₄[(K(THF)₃]₂(μ-O)·2(THF), arising from solvent deoxygenation and a monomeric Yb(III) complex, Yb(diphenyldipyrrolylmethanediyl)₃[K(THF)]₃, were also isolated as byproducts of a complex reaction.

The unique characteristics of the cyclopentadienyl-based ligand system have been a significant factor in contributing to the rapid development experienced by lanthanide chemistry in the early 1980s.¹ The versatility of this ligand system is further reiterated by its ability to provide a few rare cases of low-valent lanthanide complexes. Thus, it is not surprising that attempts to reproduce the remarkable reactivity of the divalent samarocenes and ytterbocenes^{2–6} have been carried out

with alternative ligand systems.^{7–9} On this line, efforts to prepare divalent complexes of samarium started a few years ago in our laboratory by using a calix-tetrapyrrole tetranion. Attempts to prepare a simple divalent (calix-tetrapyrrole)SmLi₂ species resulted in the formation of a dinuclear complex where a dinitrogen unit has undergone a four-electron reduction.¹⁰ The isolation of this and of other related dinitrogen complexes¹¹ reiterated that polypyrrolide anions may in fact support a level of reactivity even higher than that displayed by the Cp derivatives.

With these considerations in mind, the chemistry of divalent samarium and ytterbium supported by dipyrrolide dianions, which bears some electronic and steric resemblances with the *ansa*-metallocene-type ligands, was the most obvious target for our continuing synthetic efforts.¹² However, the presence of a hard nitrogen donor atom in the five-member rings renders these anions more versatile for assembling polynuclear structures via formation of additional M–N σ-bonds. Given that low-valent lanthanides may perform only one-electron redox reactions, the presence of two or more metal centers in the same molecular frame may be desirable for performing molecular activation processes through cooperative attack on the same substrate when availability of several electrons is required. Reactivity studies carried out with this particular ligand system have so far revealed a promising feature with the formation of polynuclear clusters able to carry out four-electron reduction of dinitrogen.^{11,12}

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Another attractive characteristic of the polypyrrolide anions is their ability to retain alkali cations via both σ - and π -bonding interaction. The direct coordination of different alkali cations to the ring affects the metal redox potential, thus determining the type of reactivity and possibly allowing for the fine-tuning of the reactivity of the lanthanide center.

In an attempt to better understand the chemistry of the dipyrrolide ligand system and its ability to both assemble polynuclear structures and to tune the redox properties of low-valent lanthanide complexes, the less reducing Yb²⁺ ion was chosen for this study. Herein, we describe the formation of a novel ytterbium octameric cluster formed as part of a complex reaction.

Experimental Section

General Procedures. All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using Schlenk-type glassware in combination with a nitrogen-vacuum line. Solvents were dried by passing through a column of Al₂O₃ under an inert atmosphere prior to use, degassed in vacuo, and transferred and stored under inert atmosphere. YbI₂(THF)₂¹³ and YbCl₃(THF)₃¹⁴ were prepared according to literature procedures. Suspensions of NaH and KH in mineral oil (Aldrich) were washed with hexane, dried, and stored under nitrogen in sealed ampules. THF-*d*₆ was dried over Na/K alloy, vacuum transferred into ampules, and stored under nitrogen prior to use. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer using vacuum-sealed NMR tubes prepared inside a drybox. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls prepared inside a drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey) and corrected for underlying diamagnetism. Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400 analyzer.

Diphenyldipyrrolylmethane. A solution of benzophenone (27.0 g, 0.15 mol) and methanesulfonic acid (0.5 mL) in 99% EtOH was stirred and heated at 60–70 °C until complete dissolution. Neat pyrrole (10 mL, 0.14 mol) was added over a period of 30 min, and the mixture was stirred at 60–70 °C for 4 h, upon which the color of the solution changed from dark red to dark brown. The mixture was diluted with 99% EtOH (100 mL) and allowed to crystallize at 50 °C. A red solid was obtained, which was filtered and washed with portions of warm 99% EtOH (100 mL, 50 °C) until complete discoloration. The compound was dried in vacuo, yielding analytically pure diphenyldipyrrolylmethane (5.8 g, 19.5 mmol, 13%). Mp: 258 °C. EIMS m/e^+ : 298. IR (KBr, Nujol mull, cm⁻¹): 3412(s), 3367(s), 2954(s), 2922(vs), 2854(s), 1660(w), 1596(m), 1544(m), 1454(vs), 1409(m), 1377(vs), 1255(w), 1229(w), 1184(m), 1080(s), 1029(s), 887(m), 797(s), 733(vs), 701(vs), 624(m), 514(s). ¹H NMR (CDCl₃, 200 MHz, 25 °C) δ : 7.92 (br s, NH, 2H), 7.25 (m, CH-phenyl, 6H), 7.10 (m, CH-phenyl, 4H), 6.74 (m, CH-pyrrole, 2H), 6.17 (pseudo-quartet, CH-pyrrole, 2H), 5.93 (m, CH-pyrrole, 2H). ¹³C NMR (CDCl₃, 50.29 MHz, 25 °C) δ : 128.8 (CH-phenyl), 128.5 (CH-phenyl), 127.4 (CH-phenyl), 117.1 (CH-pyrrole), 110.2 (CH-pyrrole), 108.6 (CH-pyrrole). Quaternary C atom could not be located. Anal. Calcd (found) for C₂₁H₁₈N₂: C 84.53 (84.44), H 6.08 (5.99), N 9.39 (9.31).

1,1'-Dipyrrolylcyclohexane. A 250 mL flask was fitted with a magnetic stirrer and a dropping funnel and placed in an ice bath. Neat pyrrole (25 mL, 0.36 mol) was added to the

flask. A mixture of cyclohexanone (20 mL, 0.192 mol) and methanesulfonic acid (0.4 mL) in 99% EtOH (20 mL) was added dropwise over a period of 5 min. The resulting green solution was allowed to react overnight and cooled to -35 °C for 2 days. Colorless crystals of analytically pure *meso*-cyclohexyldipyrrolylmethane were obtained (9.2 g, 43.1 mmol, 45%). EIMS m/e^+ : 214. IR (KBr, Nujol mull cm⁻¹): 3479(m), 3398(m), 3303(m), 2924(s), 2854(s), 1562(m), 1450(s), 1411(m), 1377(m), 1288(m), 1178(m), 1047(m), 766(m), 704(m). ¹H NMR (CDCl₃, 200 MHz, 25 °C) δ : 7.66 (br s, NH, 2H), 6.60 (m, CH-pyrrole, 2H), 6.14 (multiplet, CH-pyrrole, 4H), 2.07 (m, CH₂-cyclohexyl, 4H), 1.55 (m, CH₂-cyclohexyl, 6H). ¹³C NMR (CDCl₃, 50.29 MHz, 25 °C) δ : 130.4 (quaternary C-pyrrole), 117.3 (CH-pyrrole), 108.5 (CH-pyrrole), 104.9 (CH-pyrrole), 40.5 (CH₂-cyclohexyl), 37.9 (CH₂-cyclohexyl), 28.6 (CH₂-cyclohexyl), 23.4 (CH₂-cyclohexyl). Anal. Calcd (found) for C₁₄H₁₈N₂: C 78.46 (78.41), H 8.47 (8.44), N 13.07 (13.00).

Reaction of YbI₂(THF)₂ with Diphenyldipyrrolylmethane. Isolation of (Diphenyldipyrromethanediyl)Yb₈ (1). Solid diphenyldipyrrolylmethane (1.0 g, 3.4 mmol) was added to a stirred suspension of KH (0.25 g, 6.7 mmol) in THF (100 mL). A vigorous reaction took place, and solid YbI₂(THF)₂ (1.92 g, 3.36 mmol) was added to the resulting clear solution. The color changed immediately to dark red. Stirring continued overnight, after which the reaction mixture was centrifuged, to eliminate a small amount of greenish material, concentrated to small volume (20 mL) and layered with hexane (20 mL). Dark red diamagnetic crystals of **1** separated upon standing at room temperature for 4 days (0.62 g, 0.16 mmol, 38% yield). IR (KBr, Nujol mull cm⁻¹): 3064(m), 2848(s), 1598(m), 1492(s), 1465(vs), 1416(m), 1378(s), 1260(w), 1228-(w), 1183(w), 1152(s), 1080(m), 1039(s), 978(m), 923(w), 895-(m), 852(m), 799(w), 762(vs), 743(vs), 701(vs), 657(m), 636(s). ¹H NMR (THF-*d*₆, 500 MHz, 25 °C) δ : 7.24 (m, CH-phenyl, 6H), 7.13 (m, CH-phenyl, 4H), 6.09 (br s, CH-pyrrole, 2H), 5.23 (br s, CH-pyrrole, 2H), 4.99 (br s, CH-pyrrole, 2H). ¹³C NMR (THF-*d*₆, 125.8 MHz, 25 °C) δ : 130.4 (CH-phenyl), 128.0 (CH-phenyl), 126.9 (CH-phenyl), 118.4 (CH-pyrrole), 110.3 (CH-pyrrole), 107.3 (CH-pyrrole), no resonance was found for the quaternary C. Anal. Calcd (Found) for C₁₆₈H₁₂₈N₁₆Yb₈: C 53.73 (53.58), H 3.44 (3.63), N 5.97 (5.61).

Reaction of YbI₂(THF)₂ with Diphenyldipyrrolylmethane. Isolation of [(Diphenyldipyrrolylmethanediyl)Yb]₄[K(THF)₃]₂(μ -O)-2(THF) (2). In a separate experiment identical to that described above, stirring was continued for 7 days. The solution was centrifuged, concentrated (40 mL), and layered with hexanes (30 mL). After a few days colorless and green crystals grew over a red powder. After several extractions with THF to solubilize the red powder, the red extracts were concentrated to small volume (20 mL) and layered with hexane (20 mL), upon which red crystals of **1** separated. Pure emerald-green crystals of **2** remained as an insoluble residue (0.1 g, 0.039 mmol, 5% yield). IR (Nujol mull cm⁻¹): 2923(vs), 1470(vs), 1360(vs), 1261(s), 1228(w), 1151(s), 1091(m), 1079(m), 1037(s), 894(w), 850(m), 800(s), 761(s), 742(s), 721(m), 700(s). Anal. Calcd (found) for C₁₁₆H₁₂₈N₈O₈Yb₄K₂: C 54.67 (54.19), H 5.06 (4.90), N 4.40 (4.47). The extremely low solubility prevented NMR characterization of this diamagnetic complex ($\chi_g = -342 \times 10^{-6}$ cgs).

Preparation of Yb(diphenyldipyrrolylmethanediyl)₃[K(THF)₃] (3). Method A. Colorless crystals of **3** were isolated under microscope from the crystalline mass obtained as described for the preparation of **2** and prior to THF extraction. A sufficient amount of crystals to undertake X-ray crystal structure determination and analytical and spectroscopic determination (see below) was thus obtained.

Method B. The addition of KH (0.5 g, 11.7 mmol) to a solution of diphenyldipyrrolylmethane (1.8 g, 5.9 mmol) in THF (100 mL) resulted in a vigorous reaction. After 30 min, the addition of YbCl₃(THF)₃ (1.0 g, 2 mmol) turned the color gray-beige. The reaction mixture was stirred overnight, cen-

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Table 1. Crystal Data and Structure Analysis Results

	1	2	3	4	5
formula	C ₁₆₈ H ₁₂₈ N ₁₆ Yb ₈	C ₁₆ H ₁₂₈ K ₂ N ₈ O ₉ Yb ₄	C ₇₅ H ₇₂ K ₃ N ₆ O ₃ Yb	C ₂₄₀ H ₂₇₂ I _{0.40} Li ₂ N ₁₆ O _{19.60} Yb ₈	C ₆₄ H ₈₀ N ₈ O ₃ Yb ₄
fw	3755.18	2548.62	1395.73	5144.91	1701.52
space group	tetragonal, <i>P4/n</i>	monoclinic, <i>C2/c</i>	monoclinic <i>P2(1)/n</i>	triclinic, $\bar{P}1$	monoclinic, <i>P2(1)</i>
<i>a</i> (Å)	26.859(3)	26.131(7)	13.934(2)	17.222(1)	14.183(1)
<i>b</i> (Å)	26.859(3)	17.197(5)	24.974(3)	19.127(1)	14.065(1)
<i>c</i> (Å)	24.152(3)	25.325(7)	19.565(2)	19.649(1)	14.911(1)
α (deg)				61.184(1)	
β (deg)	90	109.186(5)	107.783(2)	84.803(1)	103.209(1)
γ (deg)				74.203(1)	
volume (Å ³)	17423(3)	10748(5)	6483(1)	5450.5(7)	2895.6(4)
<i>Z</i>	4	4	4	1	2
<i>T</i> (K)	236(2)	203(2)	236(2)	233	236(2)
<i>D</i> _{calcd} (g cm ⁻³)	1.432	1.575	1.430	1.567	1.952
μ _{calcd} (cm ⁻¹)	4.296	3.586	1.689	3.519	6.454
<i>F</i> ₀₀₀	7232	5080	2860	2570	1648
<i>R</i> , <i>R</i> _w ^a	0.0483, 0.1475	0.0324, 0.0485	0.0393, 0.0661	0.0514, 0.1101	0.0319, 0.0558
GoF	1.029	1.019	1.015	1.052	1.010

$$^a R = \sum_o - F_o / \sum F_o, R_w = [(\sum(F_o - F_c)^2 / \sum F_o^2)]^{1/2}.$$

trifuged, concentrated to small volume (30 mL), and layered with hexane (30 mL). Colorless blocks of **3** separated upon standing 3 days at room temperature (0.82 g, 0.6 mmol, 30% yield). IR (Nujol mull cm⁻¹): 2923(vs), 1590(w), 1464(vs), 1414-(m), 1378(vs), 1312(w), 1281(m), 1260(w), 1242(w), 1179(w), 1141(m), 1096(w), 1075(w), 1042(s), 968(s), 894(m), 872(w), 849(w), 739(vs), 728(s), 713(s), 702(s), 658(m), 638(m), 609-(w). $\mu_{\text{eff}} = 4.34 \mu_{\text{B}}$. Anal. Calcd (found) for C₇₅H₇₂N₆O₃YbK₃: C 64.54 (64.19), H 5.20 (5.11), N 6.02 (5.47).

Preparation of [(Diphenyldipyrrolylmethanediyl)₈Yb₈(μ -O)_{1.6}(μ -I)_{0.4}][Li(THF)₄]₂·10(THF) (4**).** A solution of diphenyldipyrrolylmethanide (1.81 g, 6.1 mmol) in THF (100 mL) was treated at -20 °C with MeLi (1.4 M solution in diethyl ether, 8.5 mL). Stirring proceeded as the solution was warmed to room temperature over a 15 min period. Subsequent addition of YbI₂(THF)₂ (3.46 g, 6.1 mmol) produced a fast reaction with color change to deep red. After stirring for 20 min a red solid began to separate. Standing at room temperature for 24 h resulted in the formation of bright red crystals of **4** (1.6 g, 40% yield). IR (Nujol mull, cm⁻¹): 3080(w), 3053-(w), 2729(w), 2667(w), 1597(w), 1491(m), 1464(s), 1417(m), 1377(s), 1261(w), 1232(w), 1155(s), 1078(w), 1036(vs), 980(w), 926(w), 881(w), 850(w), 800(w), 760(vs), 742(vs), 700(vs), 660-(m), 638(m). Anal. Calcd (Found) for C₂₄₀H₂₇₂I_{0.40}Li₂N₁₆O_{19.60}Yb₈: C 56.04(54.50), H 5.33(5.24), N 4.36(4.37), I 0.99(1.13). μ_{eff} : 6.73 μ_{BM} per formula unit.

Preparation of (1,1'-Dipyrrolylcyclohexanediyl-Yb)₄(μ -O)(THF)₂ (5**). Method A.** The addition of KH (0.2 g, 5.2 mmol) to a THF solution (100 mL) of 1,1'-dipyrrolylcyclohexane (0.7 g, 2.6 mmol) resulted in a vigorous reaction. After 1 h, YbCl₃(THF)₃ (1.4 g, 2.7 mmol) was added to the slightly cloudy solution, leading to a color change to beige. Stirring was continued overnight at room temperature followed by addition of K-metal (0.14 g, 3.6 mmol). Within 4 days, the color of the reaction mixture changed to dark red. The solution was centrifuged, concentrated to small volume (30 mL), and layered with ether (30 mL). Upon standing 1 day at room temperature dark red blocks of **5** formed (0.06 g, 0.04 mmol, 6% yield).

Method B. A similar procedure as above was followed but using NaH (0.24 g, 10 mmol) and 1,1'-dipyrrolylcyclohexane (1.1 g, 5.0 mmol) in 100 mL of THF. Treatment with YbCl₃(THF)₃ (2.4 g, 4.8 mmol), followed by addition of Na-metal (0.2 g, 7.4 mmol), under the usual reaction conditions resulted in the same color changes. The solution was centrifuged and concentrated to 15 mL. Layering with ether (15 mL) and standing at room temperature for 3 days produced dark red crystals of **5** (0.2 g, 0.12 mmol, 9% yield). IR (KBr, Nujol mull cm⁻¹): 3367(w), 2917(vs), 2363(m), 1560(w), 1542(w), 1461 (vs), 1377(vs), 1302(m), 1277(m), 1264(m), 1236(w), 1195(w), 1159-(w), 1145(m), 1126(m), 1100(m), 1088(m), 1033(s), 960(m), 903-(m), 873(m), 830(w), 789(s), 743(s), 727(s), 670(w), 630(m).

Anal. Calcd (Found) for C₆₄H₈₀N₈O₃Yb₄: C 45.18 (44.58), H 4.74 (4.84), N 6.59 (6.37). $\mu_{\text{eff}} = 6.63 \mu_{\text{BM}}$ per formula unit.

X-ray Diffraction Studies. Suitable crystals were selected, mounted on thin, glass fibers using paraffin oil, and cooled to the data collection temperature. Despite repeated attempts, **4**·10(THF) consistently crystallizes as small, highly mosaic, multiple plates, and the data presented represent the results from the best efforts. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω -scans at 0°, 90°, and 180° in ϕ . Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.

No symmetry higher than triclinic was observed for **4**·10(THF). Systematic absences in the diffraction data and unit-cell parameters were consistent with *C2/c* and *Cc* for **2**·2(THF), *P2₁* and *P2₁/m* for **5**, *P4/n* and *P4/nmm* for **1**, and, uniquely, *P2₁/n* for **3**. In cases of ambiguous space group assignment, solutions were tried in available options, and packing diagrams of candidate acentric solutions were scrutinized for any overlooked centrosymmetry. Refinement in the reported space groups yielded computationally stable and chemically reasonable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on *F*². The absolute configuration parameter in **5** refined to nil, indicating that the true hand of the data had been determined.

The compound molecule of **4**·10(THF) resides on an inversion center. The compound molecule of **2**·2(THF) is located at a 2-fold rotation axis. Two symmetry-unique but chemically identical molecules are located at 4-fold rotation axes in **1**. One and five molecules of tetrahydrofuran (THF) solvent were located cocrystallized in the asymmetric units of **2**·2(THF) and **4**·10(THF), respectively.

An atomic position in **4**·10(THF) was refined as a disordered iodine/oxygen atom with a site occupancy distribution of 20/80. To conserve a favorable data/parameter ratio, only the ytterbium, nitrogen, and disordered iodine/oxygen atoms were refined anisotropically in **4**·10(THF). The phenyl groups and THF molecules in **4**·10(THF) were treated as idealized, rigid, flat, polygons with the atoms having smallest isotropic parameter per THF ring, or atoms coordinated to metal ions, assigned oxygen atom identities. All non-hydrogen atoms, except the carbon atoms in **4**·10(THF), were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion coefficients are contained in the SHEXTL 5.10 program library.

Table 2. Selected Bond Distances (Å) and Angles (deg)

	1	2	3	4	5
Yb(1)–N(3)	2.446(16)	Yb(1)–O(1) = 2.340(4)	Yb–N(1) = 2.334(3)	Yb(1)–N(4) = 2.522(11)	Yb(1)–O(2) = 2.428(7)
Yb(1)–N(1)	2.469(14)	Yb(2)–O(1) = 2.390(4)	Yb–N(2) = 2.327(3)	Yb(1)–N(1) = 2.570(10)	Yb(1)–N(1) = 2.570(8)
Yb(1)–N(4)cent ^a	2.434(15)	Yb(1)–N(1)cent = 2.518(5)	Yb–N(3) = 2.326(3)	Yb(1)–N(3)cent = 2.502(17)	Yb(1)–N(2) = 2.529(7)
Yb(1)–N(2)cent	2.431(15)	Yb(1)–N(2) = 2.560(4)	Yb–N(4) = 2.318(3)	Yb(1)–N(2)cent = 2.509(17)	Yb(1)–N(7) = 2.593(8)
Yb(1)–N(4)	2.648(13)	Yb(1)–N(4)cent = 2.629(5)	Yb–N(5) = 2.332(3)	Yb(1)–O = 2.56(2)	Yb(1)–O(1) = 2.592(7)
Yb(2)–N(4B)	2.463(14)	Yb(1)–N(4A) = 2.593(5)	Yb–N(6) = 2.336(3)	Yb(2)–O = 2.65(3)	Yb(1)–N(8)cent = 2.572(7)
Yb(2)–N(2)	2.451(15)	Yb(2)–N(1) = 2.605(5)	K(1)–O(1) = 2.649(3)	Yb(2)–N(3) = 2.634(10)	Yb(2)–N(1) = 2.431(8)
Yb(2)–N(3B)cent	2.459(15)	Yb(2)–N(2)cent = 2.544(5)	K(1)–C(10) = 3.515(3)	Yb(2)–N(6) = 2.511(10)	Yb(2)–N(2)cent = 2.414(6)
Yb(2)–N(1)cent	2.459(15)	Yb(2)–N(3) = 2.598(5)	K(1)–C(62) = 3.450(3)	Yb(3)–N(5) = 2.476(10)	Yb(2)–O(1) = 2.146(6)
N(3)–Yb(1)–N(2)cent	115.8(6)	K(1)–N(4)cent = 2.940(5)	K(1)–N(6)cent = 2.790(3)	Yb(4)–N(8) = 2.883(10)	Yb(4)–O(1) = 2.139(6)
N(3)–Yb(1)–N(4)cent	89.2(5)	K(1)–C(38)cent = 3.075(5)	K(2)–O(2) = 2.728(3)	Yb(4)–N(2A) = 2.518(9)	Yb(4)–N(6)cent = 2.406(5)
N(2)–Yb(2)–N(4B)	117.6(6)	K(1)–O(2) = 2.716(5)	K(2)–N(2) = 3.038(3)	N(4)–Yb(1)–N(3)cent = 85.7(5)	Yb(4)–N(8) = 2.443(5)
N(2)–Yb(2)–N(1)cent	87.7(5)	K(1)–O(3) = 2.685(5)	K(2)–C(2)cent = 3.186(3)	N(4)–Yb(1)–N(1) = 154.3(3)	Yb(4)–N(5) = 2.426(5)
N(2)–Yb(2)–N(3B)cent	115(6)	K(1)–O(4) = 2.720(5)	K(2)–C(36)cent = 3.193(3)	N(4)–Yb(1)–N(2)cent = 101.1(5)	Yb(4)–N(7)cent = 2.424(5)
		Yb(1)–O(1)–Yb(2A) = 179.7(9)	K(2)–N(3)cent = 3.273(3)	N(4)–Yb(1)–O = 76.3(7)	O(1)–Yb(1)–O(2) = 151.5, 7(4)
		Yb(1A)–O(1)–Yb(2) = 179.7(9)	K(3)–O(3) = 2.603(3)	Yb(2)–O–Yb(4A) = 174.5(11)	O(1)–Yb(1)–N(1) = 71.0(2)
		O(3)–K(1)–O(2) = 82.2(9)	K(3)–N(4)cent = 2.861(3)	Yb(1)–O–Yb(2) = 93.5(6)	O(1)–Yb(1)–N(2) = 85.0(2)
		O(3)–K(1)–O(4) = 79.9(9)	K(3)–C(57)cent = 3.161(3)	Yb(1)–O–Yb(4A) = 83.5(8)	O(1)–Yb(1)–N(7) = 78.8(2)
			N(1)–Yb–N(2) = 78.4(9)		Yb(4)–O(1)–Yb(2) = 178.3(4)
			N(1)–Yb–N(3) = 94.4(10)		Yb(4)–O(1)–Yb(1) = 92.2(2)
			N(1)–Yb–N(4) = 171.5(12)		Yb(2)–O(1)–Yb(1) = 89.5(2)
			N(1)–Yb–N(5) = 92.9(10)		Yb(4)–O(1)Yb(3) = 90.1(2)
			N(1)–Yb–N(6) = 91.1(10)		Yb(2)–O(1)–Yb(3) = 88.2(2)
					Yb(1)–O(1)–Yb(3) = 177.7(2)

^a Bond length or angle calculated from the ring centroid.

Results and Discussion

We have previously reported that the formation of Yb complexes of dipyrrolyl dianions is remarkably affected by the choice of the alkali counteraction and of the reaction pathway.¹⁵ While the reaction of the lithium derivatives with YbCl₃(THF)₃ followed by reduction with metallic lithium affords an octameric mixed-valence {[Ph₂C(C₄H₃N)₂]Yb}₈ (μ-Cl)₄{Li(THF)₄}₂ species featuring four bridging chloride anions in the center and two THF-solvated lithium cations in the lattice, the reaction of the sodium salt with YbI₂(THF)₂ affords a monomeric and divalent metalate, {[Ph₂C(C₄H₃N)₂]Na(THF)₂}₂Yb.

The reaction of YbI₂(THF)₂ with the *dipotassium* salt of diphenyldipyrrolylmethane discussed in this work was carried out at room temperature and in THF, forming a dark red, air-sensitive solution from which dark red blocks of the diamagnetic (diphenyldipyrrolylmethanediyl-Yb)₈ (**1**) were obtained as the major component of a crystalline mixture (Scheme 1). The NMR spectrum was not particularly informative, simply displaying the characteristic resonances of the pyrrolyl and phenyl moieties.

The solid-state crystal structure revealed an octameric macrocyclic structure (Figure 1) consisting of eight [Ph₂C(C₄H₃N)₂Yb] units arranged in a flat ring with a large interstitial space. Each diphenylmethanediyl ligand adopts the usual bridging bonding mode with each pyrrolyl ring being π-bonded to one Yb [Yb(1)–N(2) = 2.639(14) Å; Yb(1)–C(5) = 2.737(17) Å; Yb(1)–C(6) = 2.785(17) Å; Yb(1)–C(7) = 2.735(16) Å; Yb(1)–C(8) = 2.637(17) Å] and σ-bonded to the next [Yb(2)–N(2) = 2.451(15) Å]. In turn, the second Yb atom is π-bonded to the second pyrrolyl ring of the same ligand. In addition, each ytterbium is also π-bonded to a second pyrrolyl ring of another ligand and thus acts as a bridging link to assemble the macrocyclic structure. As a result, the coordination geometry around each ytterbium is bent ytterbocene-like and is determined by two π-bonded rings from two different ligands and two σ-bonded N atoms [N(1)–Yb(1)–N(3) = 117.5(5)°]. The overall macrocyclic structure is rather symmetric, in the sense that the eight Yb atoms define a nearly ideal circumference (Figure 1).

The formation of **1** is a straightforward metathesis in which two iodide anions of each Yb atom have been replaced by the dipyrrolyl dianionic ligand. The large macrocyclic structure is likely to be the result of geometry optimization as required by the particular bridging bonding mode always adopted by this class of ligands. However, it is worth mentioning that the same ligand system forms a hexameric cluster with Sm(II), which in turn is the precursor to dinitrogen fixation.¹⁶ Furthermore, the presence of two additional products in the reaction mixture indicates a more complex behavior. The first byproduct is a tetranuclear oxocluster, [(diphenyldipyrrolylmethanediyl)Yb]₄{[K(THF)₆]₂(μ-O)·2(THF)} (**2**), that was isolated in low yield as a green diamagnetic crystalline solid. Its purification was possible due to its very low solubility, allowing the

(15) Dube, T.; Freckmann, D.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 209.

(16) Ganesan, M.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 766.

Scheme 1

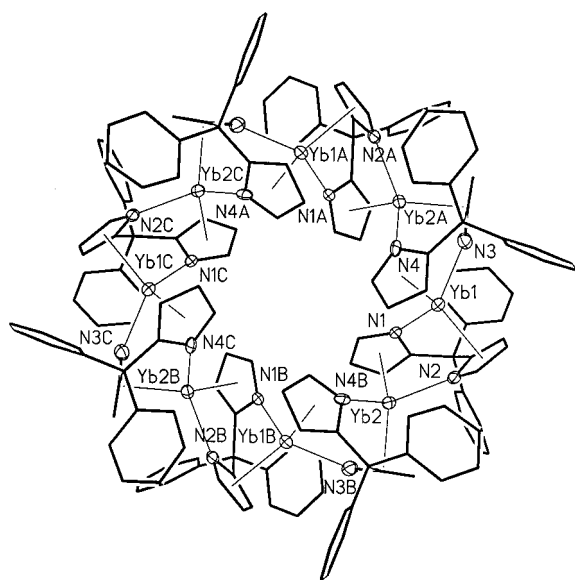
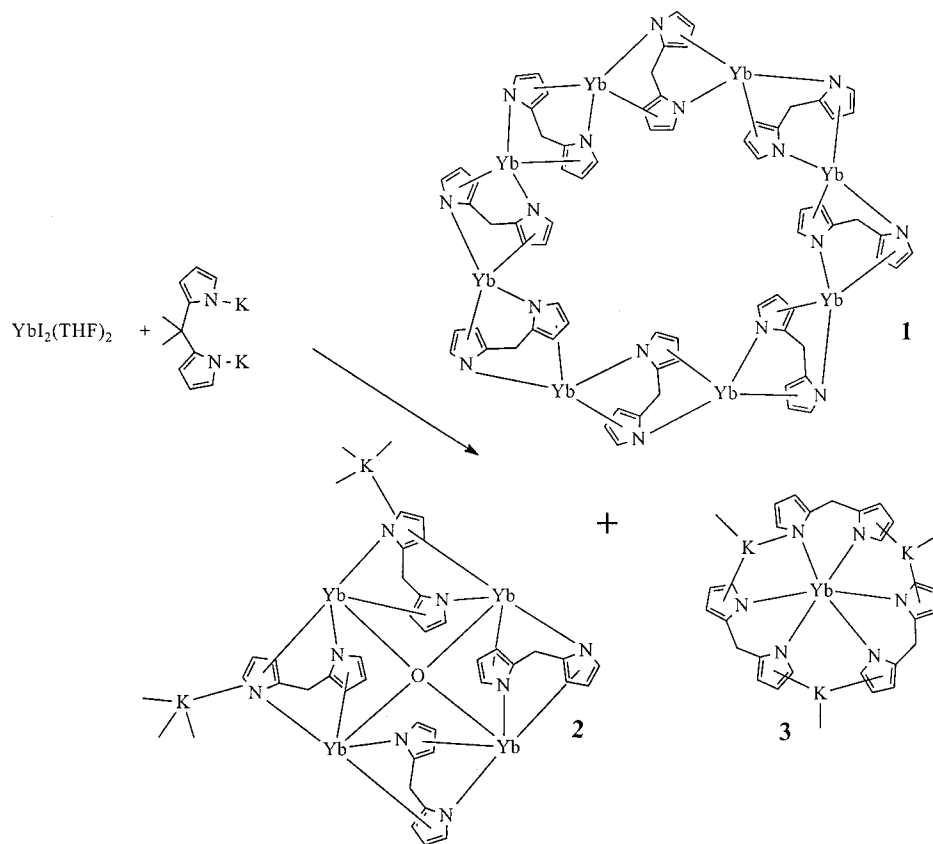


Figure 1. Partial thermal ellipsoid plot of **1**. Thermal ellipsoids are drawn at the 30% probability level.

elimination of the other two components out of the crude crystalline mass as obtained from the reaction by simply washing with THF.

The structure of **2** (Figure 2) is formed by four {[Ph-(C₄H₃N)₂]Yb} moieties forming a flat tetrametallic unit. The cavity is occupied by an oxygen atom [O(1)–Yb(1) = 2.340(4) Å; O(1)–Yb(2) = 2.390(4) Å] coplanar with the four metal atoms [Yb(1)–O(1)–Yb(2A) = 179.7(9)°; Yb(1A)–O(1)–Yb(2) = 179.7(9)°]. As usual, the ligand–metal bonding is achieved through both σ -bonding [Yb(1)–N(2) = 2.560(4) Å] and π -bonding of the pyrrolide

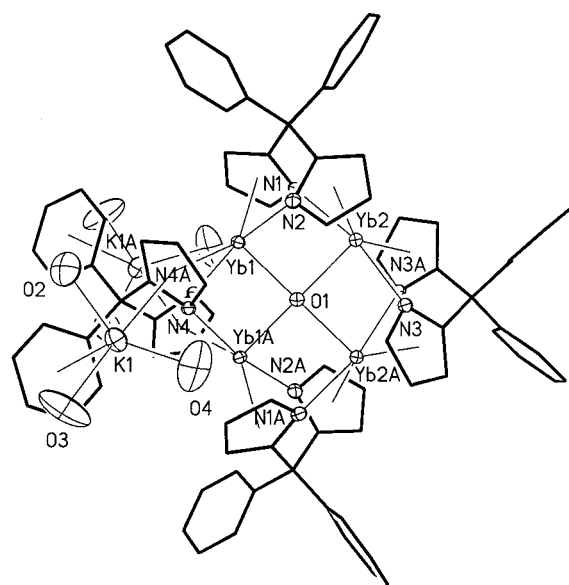


Figure 2. Partial thermal ellipsoid plot of **2**. Thermal ellipsoids are drawn at the 30% probability level. The carbon atoms of the THF molecules have been omitted for clarity.

rings, providing each ytterbium with a ytterbocene-like structure. Two potassium atoms each bonded to three THF molecules [K(1)–O(2) = 2.716(5) Å; K(1)–O(3) = 2.685(5) Å; K(1)–O(4) = 2.720(5) Å] are π -bonded to one pyrrolyl ring of the same ligand [K(1)–N(4A)_{ring centroid} = 2.940(5) Å] and to one phenyl ring [K(1)–C(33)_{ring centroid} = 3.075(5) Å].

The third compound from the same reaction mixture is a trivalent -ate Yb complex, Yb(diphenyldipyrrolyl-

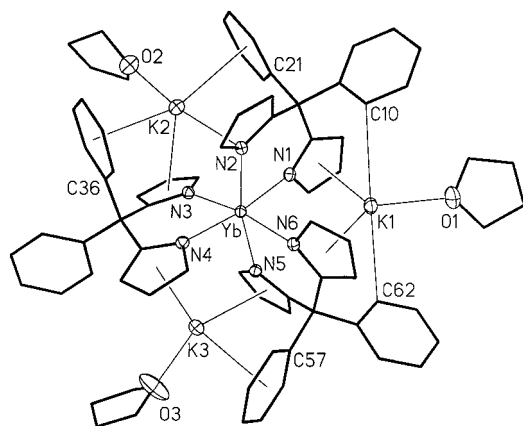
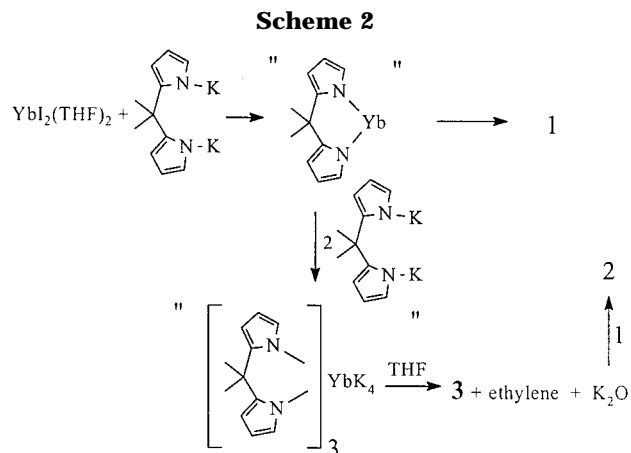


Figure 3. Partial thermal ellipsoid plot of **3**. Thermal ellipsoids are drawn at the 30% probability level.

methanediyl)₃ (**3**), whose formation implies a major molecular reorganization. Not only does it require one-electron oxidation of the metal center, but also one ligand needs to be acquired in the process. Compound **3** was rationally prepared in good yield from trivalent YbCl₃ starting material by appropriately adjusting the reaction stoichiometry.

Complex **3** is monomeric with one trivalent ytterbium atom surrounded by three σ -bonded dipyrrolyl ligands (Figure 3). Three potassium atoms each solvated by one molecule of THF complete the structure. The ytterbium atom is located in a pseudo-octahedral coordination environment [N(5)–Yb–N(2) = 167.19(11) Å; N(4)–Yb–N(1) = 171.51(11) Å; N(3)–Yb–N(6) = 169.99(11) Å]. The complex contains three chelating bidentate dipyrrolyl ligands and exhibits the usual tris-chelate structure [Yb–N(1) = 2.334(3) Å; Yb–N(3) = 2.326(3) Å; Yb–N(4) = 2.318(3) Å; Yb–N(6) = 2.336(3) Å] with N(1)N(3)N(5) forming one and N(2)N(4)N(6) the other nearly parallel triangular face. The structure also incorporates three potassium atoms, each displaying different coordination geometries. One potassium is located in the region between two of the pyrrolyl rings which define the equatorial plane around Yb. The metal appears to be symmetrically π -ligated to two rings [K(1)–N(1)_{ring centroid} = 2.800(2) Å; K(1)–N(6)_{ring centroid} = 2.790(3) Å], again forming a bent-metallocene type of structure around potassium. One molecule of THF is also bound to potassium in the region between the two rings pointing to the exterior of the molecule [K(1)–O(1) = 2.649(4) Å]. Two carbon atoms from two phenyl rings also form a curiously short K–C contact [K(1)–C(62) = 3.450(4) Å] not far from the bonding range. The second potassium atom is π -bonded to one “equatorial” pyrrolyl ring [K(2)–N(3)_{ring centroid} = 3.273(3) Å] and coordinated to the N atom of the “axial” pyrrolyl [K(2)–N(2) = 3.083(3) Å] and displays a remarkable π -coordination to two phenyl rings from two ligands [K(2)–C(2)_{ring centroid} = 3.038(3) Å; K(2)–C(36)_{ring centroid} = 3.193(3) Å]. The coordination environment of the third potassium atom appears to be different given that only one phenyl ring and two pyrrolyl rings are π -coordinated to the metal.

The formation of **2** is a reproducible event while using different batches of starting materials and implies a THF deoxygenation reaction. The oxygen abstraction from THF is a two-electron process and is accompanied by the formation of 2 equiv of ethylene. Although we could not obtain a reliable quantitative estimate of the



amount of ethylene formed during the reactions, its presence was clearly detected by GC analysis of the reaction mother liquor, thus confirming that THF deoxygenation occurred in parallel to the formation of complex **1**. A THF deoxygenation reaction requires two electrons. On the other hand, the formation of **2** is not a redox process given that the four Yb atoms have maintained the original divalent oxidation state. However, the formation of **3** gives the key to rationalize the formation of **2** (Scheme 2). Assuming a rapid reaction of the initially formed “(ligand)Yb” intermediate with the unreacted dipotassium salt, a divalent Yb(ligand)₃K₄ species may form. This intermediate must eliminate one potassium cation and one electron in order to generate **3**. The THF solvent is the possible recipient of both (two of each are necessary), forming ethylene and “K₂O”. Reaction of this species with **1** may give rise to **2**. The complexity of the overall reaction is remarkable and strongly indicates that the in situ generated low-nuclearity species (ligand)Yb has different reactivity patterns available before being stabilized into the octameric cluster structure.

In the transformations described above as well as in those reported in a previous paper,¹⁵ the nature of the alkali cation plays a fundamental role in determining the nature of the products.¹⁵ Likely, the type of interaction of the alkali cation with the pyrrolyl ring (σ - versus π -) is capable of modifying both the redox potential of the Yb atom as well as the reaction kinetics. Therefore, we have also probed the reaction of YbI₂(THF)₂ with the lithium salt of diphenyldipyrrolyl methane, which was not previously explored. The reaction proceeds in a similar manner, leading to a new complex also containing mixed-valence Yb(II)/Yb(III) and which is formulated as [(diphenyldipyrrolylmethanediyl)₈Yb₈(μ -O)_{1.6}(μ -I)_{0.4}][Li(THF)₄]₂·10THF (**4**) on the basis of the X-ray and analytical data.

The crystal structure (Figure 4) revealed an octameric and cyclic complex containing two atoms in its intermetallic space, each binding three Yb metal atoms in an overall anionic structure. Two lithium atoms, each solvated by four molecules of THF and unconnected with the octameric dianion, complete the structure. The octameric arrangement of **4** is similar to that observed in **1**. Unlike complex **1** however, the macrocycle hosts two atoms, each bridging three ytterbium atoms. The presence of the two bridging atoms causes a deformation of the macrocycle, forcing an ellipsoidal conformation (Figure 4). The two atoms have been identified as one

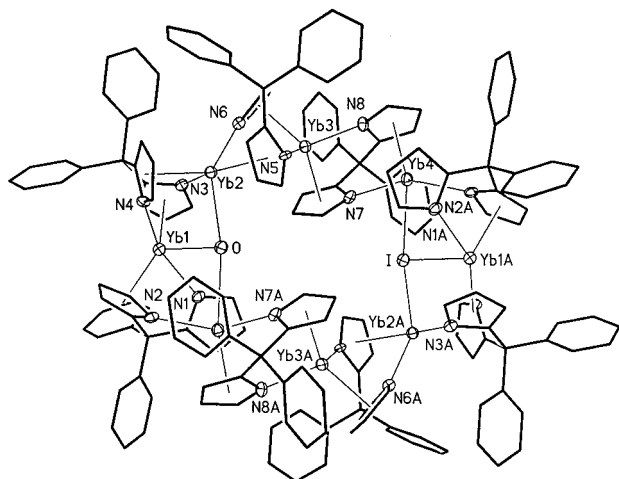


Figure 4. Thermal ellipsoid plot of the anionic part of **4**. The $\text{Li}(\text{THF})_4$ cations have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

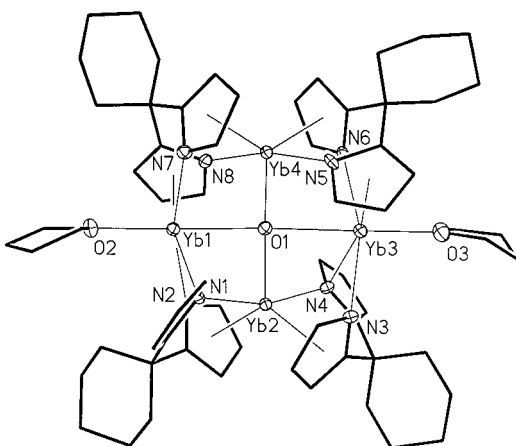


Figure 5. Thermal ellipsoid plot of **5**. Thermal ellipsoids are drawn at the 30% probability level.

oxygen and one iodine disordered over the two positions with a relative occupancy of 80% oxygen against 20% iodine. This is obviously reflected by the bond distances and angles originated by the two atoms, which are averaged and thus, by not being particularly informative, will be not commented on here. In other words, the structure may be formally regarded as the average of five identical octameric units, four of which host two oxygen atoms while the fifth is hosting two iodine anions. The valence of the Yb atoms is also averaged accordingly.

Even in this case, the oxygen atoms present in the molecular core arise from a THF deoxygenation process since the presence of ethylene could be clearly observed in the GC of the reaction mixture. The amount of ethylene observed seems to be lower than expected and, combined with the poor yield of **4**, indicates that another compound is likely to be present in the reaction mixture.

The nature of the dipyrrolyl ligand substituents is another factor also capable of substantially affecting the result of the reaction. Its ability to modify the nuclearity of the clusters is particularly apparent in the chemistry of low-valent samarium.^{11,12,15,16} In one case, the substituents also have been shown to affect the type of bonding to the lanthanide metal.^{12b} We have hence probed the effect of ligand modification in the reaction

under examination by performing the reaction with the cyclohexyldipyrrole analogue.

The reaction of this ligand with $\text{YbCl}_3(\text{THF})_3$ and subsequent reduction with either metallic potassium or sodium yielded dark crystals of (1,1'-dipyrrolylcyclohexanediyl- Yb)₄(μ -O)(THF)₂ (**5**). Despite having a core nearly identical to that of **2** the complex is a paramagnetic mixed-valent species.

Complex **5** consists of four $\{[\text{Cy}(\text{C}_4\text{H}_3\text{N})_2]\text{Yb}\}$ units arranged to form a tetrametallic planar core. One oxygen atom is located in the center of the tetrametallic structure [$\text{O}(1)-\text{Yb}(1) = 2.428(7) \text{ \AA}$; $\text{O}(1)-\text{Yb}(2) = 2.146(6) \text{ \AA}$; $\text{O}(1)-\text{Yb}(3) = 2.679(7) \text{ \AA}$; $\text{O}(1)-\text{Yb}(4) = 2.139(6) \text{ \AA}$; $\text{Yb}(4)-\text{O}(1)-\text{Yb}(1) = 92.2(2)^\circ$; $\text{Yb}(2)-\text{O}(1)-\text{Yb}(1) = 89.5(2)^\circ$; $\text{Yb}(4)-\text{O}(1)-\text{Yb}(3) = 90.1(2)^\circ$; $\text{Yb}(2)-\text{O}(1)-\text{Yb}(3) = 88.2(2)^\circ$] and is coplanar with the four metal centers [$\text{Yb}(1)-\text{O}(1)-\text{Yb}(3) = 177.7(2)^\circ$; $\text{Yb}(2)-\text{O}(1)-\text{Yb}(4) = 178.3(4)^\circ$]. Even in this case, four ligands bridge the four metal centers adopting both the σ -bonding [$\text{Yb}(1)-\text{N}(2) = 2.529(7) \text{ \AA}$; $\text{Yb}(1)-\text{N}(7) = 2.593(8) \text{ \AA}$] and π -bonding modes [$\text{Yb}(1)-\text{C}(47) = 2.771(9) \text{ \AA}$; $\text{Yb}(1)-\text{N}(1) = 2.570(8) \text{ \AA}$; $\text{Yb}(1)-\text{N}(8) = 2.607(7) \text{ \AA}$]. The usual metallocenic-type of structure around each ytterbium is realized with two π -bonded pyrrolyl rings from two different ligands. Unlike complex **2**, complex **5** retains no alkali cations in its structure, yielding a paramagnetic mixed-valent Yb(II)/Yb(III) structure.

As in the case of **2** and **4**, the central oxo-atom of **5** is generated by a THF deoxygenation process given the presence of ethylene in the GC-MS of the reaction mixture. However, different from **2**, the presence of two trivalent Yb atoms in the tetrametallic cluster easily explains the deoxygenation of THF in terms of cooperative attack of two of the four Yb atoms on the same THF molecule.

Conclusions

Attempts to form Yb(dipyrrolyl) complexes have been rewarded with the isolation of an attractive octameric structure with the eight metal centers organized in a planar ring. The particular octameric structure seems to play an important role in the stabilization of the Yb centers, since the same intermediate building block of the octamer may also undergo different reactions leading to THF deoxygenation pathways. The nature of the ligand substituents and of the alkali cation plays a fundamental role in this respect. Finally, the large octameric structure of **1** is sterically flexible and may be deformed by hosting small units. We estimate that up to five atoms may in principle be hosted in the center, but structures containing two atomic residues are in fact the more recurrent. We are actively pursuing the possibility of using complex **1** for host-guest interactions and/or multielectron redox processes.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Council of Canada (NSERC).

Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for structures **1** through **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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