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Synthesis and reactivity of *trans-N,N′*-dimethyl-*meso*-octaalkylporphyrinogen Sm(II), Eu(II) and Yb(II) complexes: Metal-based influences on the reduction of *t*-butyl-1,4-diazabuta-1,3-diene[☆]

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Sm(II), Eu(II) and Yb(II) complexes of doubly deprotonated *trans-N,N′*-dimethyl-*meso*-octaethylporphyrinogen were synthesised as tetrahydrofuran adducts (Sm and Eu, bis; Yb, mono) by metathetical exchange reactions of the dipotassium macrocyclic precursor complexes with the corresponding metal diiodides in tetrahydrofuran. The Sm and Eu complexes partially desolvate in non-coordinating solvents to give mono-tetrahydrofuran adducts. Subsequent reactions of the initial Eu(II) and Yb(II) complexes with 1,4-di-*t*-butyl-1,4-diazabuta-1,3-diene failed to yield complexes featuring the 1,4-diazabuta-1,3-diene binding to the lanthanide centres either as neutral Lewis base donors or reduced ligands, which contrasts with previous findings in the case of the analogous Sm(II) reaction. These outcomes are discussed in relation to the variety of Ln(III)–Ln(II) reduction potentials, coordination number and oxidation state dependent ionic radii of the metals and macrocycle–ancillary ligand steric interactions. The complexes were characterised by X-ray crystal structure determination, satisfactory microanalysis and NMR spectroscopy, where possible.

1. Introduction

The breadth of established reduction chemistry of organolanthanide complexes has been substantially widened in recent years. Major breakthroughs include access to the, so-called, non-traditional Ln(II) ions, and steric influences on both traditional Ln(II) metal-based reductions and ligand-based reductions of Ln(III) complexes [1]. In parallel, there has been renewed interest in the study of redox active ligands across a broad range of fundamental and applied inorganic chemistry [2]. The intersection of these contemporary research fields in the investigation of diimine complexes of the lanthanides has been of interest to a number of research groups and has led to the stabilisation of many unusual complexes and discovery of unusual reactivities [3].

The homoleptic 1,4-diazabuta-1,3-diene, R-DAB, complexes, [Ln(R-DAB)$_3$], have been the subject of on-going study with regard to formal oxidation state assignment [4]. The same ligand class has been examined in various studies of, mainly, heteroleptic lanthanocene complexes where variable neutral or reduced states of the R-DAB ligand have been reported. A non-lanthanocene example is the study of Sm and Yb complexes supported by the 1,4-bis(trimethylsilyl)cyclooctatetraenediyl dianion, affording the Sm(III) and Yb(II) complexes [{$C_8H_6(SiMe_3)_2$}Ln(R-DAB)(THF)] featuring radical anionic (for Sm(III)) and neutral (for Yb(II)) chelating R-DAB ligands (*t*-Bu-DAB and Ph-DAB, with 2,3-dimethyl substitution) [5]. Of relevance to this study, the differing reduced states of the R-DAB ligands were rationalised by the reducing strengths of the Ln(II) ions (strongest for Sm(II)). The inaccessibility of the Yb *t*-Bu-DAB complex was not discussed in this early report that lacked X-ray crystal structure determinations. More recent ytterbocene chemistry, discussed below, may indicate that steric issues play a role for the smaller Ln(II) ion in conjunction with the bulky cyclooctatetraenediyl ligand.

Interesting solvent-dependent redox activity was reported for decamethylytterbocene, with the Yb(III) complex [(C_5Me_5)$_2$Yb(*t*-Bu-DAB)] reverting to the Yb(II) complex [(C_5Me_5)$_2$Yb(THF)$_2$] and free *t*-Bu-DAB on addition of THF, Scheme 1 [6]. Central to the

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[☆] All authors dedicate this article to the memory of Prof. Dr. Herbert Schumann.

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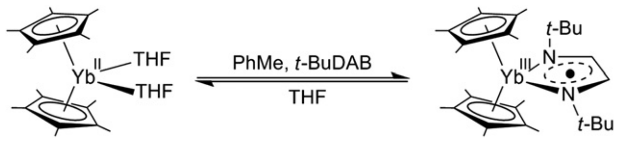


Scheme 1.

argument of steric interactions being influential on this reaction outcome is the observation that the analogous non-methylated system, $[(C_5H_5)_2Yb(t\text{-Bu-DAB})]$, is stable in the Yb(III) form in THF [7]. Significant lengthening of the Yb–N distance to the R-DAB ligand (2.390 vs 2.308 Å, average) is noted in the bulkier case, which further supports this premise. Temperature dependent solid state redox isomerism has more recently been reported for related complexes and multi-electron reductants have been developed that capitalise on these strain effects [3].

$[(C_5Me_5)_2Eu(THF)_2]$ was reported to react with *t*-Bu-DAB in toluene to give the Eu(II) complex $[(C_5Me_5)_2Eu(t\text{-Bu-DAB})]$ in which the *t*-Bu-DAB ligand bears no formal charge [8]. In contrast, the analogous reaction with C_6F_5-DAB (with 2,3-dimethyl substitution) in toluene gives the Eu(III) complex featuring the R-DAB ligand singly reduced. This complex reverts to the Eu(II) starting material upon addition of THF. The weak electron donating characteristics of the perfluorinated R-DAB ligand were implicated as a cause of the reversible redox chemistry.

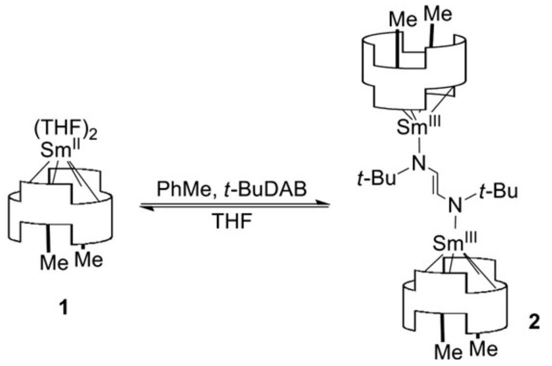
We have previously reported the synthesis and reactivity of the bis(tetrahydrofuran) adduct of the Sm(II) complex [9] of the doubly deprotonated *trans-N,N′*-dimethyl-*meso*-octaethylporphyrinogen, $(Me_2N_4)^{2-}$, that we introduced into organometallic chemistry, $[(Me_2N_4)Sm(THF)_2]$, **1**. It forms an unusual 2:1 stoichiometric complex [10] on reaction with 1,4-di-*t*-butyl-1,4-diazabuta-1,3-diene, *t*-Bu-DAB, in toluene giving the dinuclear complex $[\{(Me_2N_4)Sm\}_2(t\text{-Bu-DAB})]$, **2**. Solution and solid state characterisation of **2** were consistent with the formulation of complex **2** as a Sm(III) species possessing an uncommon dianionic *t*-Bu-DAB ligand bridging the metal centres [11]. More unusual was the solvent triggered reversal to the Sm(II) starting material and free *t*-Bu-DAB upon the addition of tetrahydrofuran, Scheme 2. Such reversible Sm(III)/Sm(II) reactivity has very rarely been reported. More typical for Sm reactivity, as established through samarocenes [12], is the reduction of R-DAB ligands with $[(C_5Me_5)_2Sm(THF)_2]$ to afford mononuclear complexes featuring the chelating, singly reduced R-DAB ligand, $[(C_5Me_5)_2Sm(R\text{-DAB})]$.

The initial finding of the reversible Sm(III)/Sm(II) reactivity with $[(Me_2N_4)Sm(THF)_2]$ **1** left many unanswered issues in relation to the range of R-DAB complexes that can be accessed, in particular a more complete understanding of the reversible Sm(III)/Sm(II) behaviour of these complexes and whether such reactivity can be exploited in novel reduction chemistry applications. In this report we have investigated the formation of analogous Eu(II) and Yb(II) complexes and their reactivity with the same R-DAB ligand. These two systems were targeted due to the, i, similar metal ionic radii but lower reduction potential of the former relative to Sm(II), and, ii, smaller metal ionic radii of the latter.

2. Experimental section

2.1. General

Unless stated, all manipulations of complexes were carried out under an argon atmosphere by the use of standard Schlenk techniques or under nitrogen in a glove box (Innovative Technologies). $[\{(Me_2N_4)K_2(THF)_2\}_n]$, $[(Me_2N_4)Sm(THF)_2]$, **1**, *t*-Bu-DAB,



Scheme 2.

$[(C_5Me_5)_2Sm]$, $EuI_2(THF)_2$ and $YbI_2(THF)_2$ were prepared according to literature procedures [10,13–16]. All other chemicals were obtained from Aldrich and used as received. ^1H and ^{13}C NMR spectra were recorded using a Varian Mercury Plus 300 spectrometer operating at 299.91 MHz (^1H) and 75.42 MHz (^{13}C). The ^1H NMR spectra were referenced to the residual ^1H resonances of chloroform-*d* (7.26), benzene-d_6 (7.15), toluene-d_8 (2.09) and THF-d_8 (1.73 or 3.75), and ^{13}C NMR spectra were referenced to the ^{13}C resonances of chloroform-*d* (77.2), benzene-d_6 (128.4), toluene-d_8 (20.4) and THF-d_8 (67.6 or 25.4). Full ^1H and ^{13}C NMR assignments of $[(Me_2N_4)Yb(THF)]$ **5** were made through gCOSY, gHMBC, gHMQC, NOESY and DEPT spectra. GC–MS spectra were performed using an HP5890 gas chromatograph equipped with an HP5790 Mass Selective Detector and a 25 m × 0.32 mm HPI column. Elemental analyses were performed by the Central Science Laboratory at the University of Tasmania (Carlo Erba EA1108 Elemental Analyser) or the Chemical and Analytical Services Pty. Ltd., Melbourne. I.R. spectra were recorded as Nujol mulls on NaCl plates using a Perkin–Elmer 1725X Fourier-transform infra-red spectrometer.

2.2. Synthesis of $[(Me_2N_4)Sm(THF)]$ **3**

Toluene (30 mL) was added to a mixture of $[(C_5Me_5)_2Sm]$ (0.17 mmol, 0.070 g) and $Li_2(Me_2N_4)$ (0.17 mmol, 0.096 g) and the mixture stirred for 5 h at 50 °C. The solution was concentrated in vacuo to 20 mL after this time and left to stand at room temperature overnight. This gave the title complex as a dark purple crystalline solid in low yield (ca. 5 mg). The ^1H NMR spectrum of the complete reaction mixture was characterised by very broad resonances spanning ca. −35 to 55 ppm ($\omega_{1/2}$ up to 400 Hz) and relatively weak resonances arising from diamagnetic impurities, including protonated macrocycle. ^1H NMR spectrum of the isolated solid of $[(Me_2N_4)Sm(THF)]$ **3** is different to this, being characterised by resonances of width and chemical shifts being intermediate between the crude reaction mixture and $[(Me_2N_4)Sm(THF)_2]$ **1**. Presumably the low yield of the mono(THF) solvate $[(Me_2N_4)Sm(THF)]$ **3** arises from incomplete desolvation of the samarocene reagent. A partial assignment is given (further assignment in the 0–10 ppm region could not be made owing to the purity of the sample obtained); ^1H NMR (298 K, C_6D_6): δ −25.6 (bs, 4H, CH_2), −9.85 (bs, 12H, CH_3), −7.83 (bs, 4H, CH_2), 12.60 (bs, 4H, =C*H*, pyrMe), 48.20 (bs, 6H, NCH_3).

2.3. Synthesis of $[(Me_2N_4)Eu(THF)_2]$ **4**

A solution of $EuI_2(THF)_2$ (0.63 mmol, 0.35 g) in THF (15 mL) was added via cannula to a suspension of $[\{(Me_2N_4)K_2(THF)_2\}_n]$ (0.63 mmol, 0.50 g) in THF (15 mL) with stirring. The colour changed from beige to yellow with the formation of pale solids. Stirring was