C–H Activation (γ-deprotonation) of a Sm(III) bis(trimethylsilyl)amide complex *via* macrocyclic stabilisation of the sodium counter ion†

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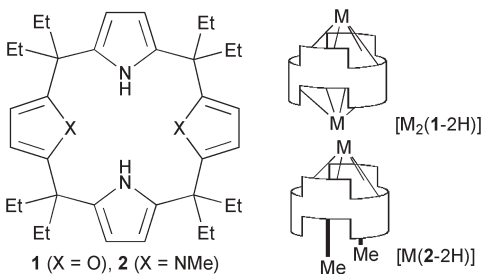
The γ-deprotonation of a samarium(III) bis(trimethylsilyl)amide complex derived from a dimetallated *trans*-dioxaporphyrinogen has been achieved through stabilisation of the counter cation within the macrocyclic cavity.

Bis(trimethylsilyl)amide is a ubiquitous ligand that has featured in many important discoveries since its popular usage was enticed by the pioneering work of Wannagat and others.[1] The anion lacks β-hydrogens, offers steric protection, the precursor amine is commercially available, as are its alkali metal complexes, and reliable syntheses of complexes spanning the periodic table exist that function as useful starting materials.

Direct reactivity on a bis(trimethylsilyl)amide ligand has only rarely been reported *via* γ-methyl deprotonation.[2] This result is surprising given that many metathetical exchange organometallic syntheses involve strong bases, such as alkyllithiums, and strong NSiMe-agostic interactions are known.[3] Most γ-methyl deprotonations appear to arise from electron deficient metal centres striving for greater coordination, *e.g.*, $[(thf)_3NaCH_2SiMe_2(Me_3Si)NYb\{N(SiMe_3)_2\}_2]$ as the product from $[Yb\{N(SiMe_3)_2\}_3]$,[3] or small molecule elimination, *e.g.*, $[\{CHSiMe_2(Me_3Si)NZrN(SiMe_3)_2\}_2]$ by the thermolysis of $[Me_2Zr\{N(SiMe_3)_2\}_2]$.[2] Insertion reactions into the M–C bond of the γ-alkylamide chelates have found many synthetic applications.[4] Related reactivity includes γ-functionalisation *via* arene elimination arising from a π-bound phenyl group and a γ-H agostic interaction of the amide in a linkage isomer of $[YbN(SiMe_3)_2(thf)BPh_4]$ giving $[YbN(SiMe_3)SiMe_2CH_2BPh_3(thf)_2]$.[5]

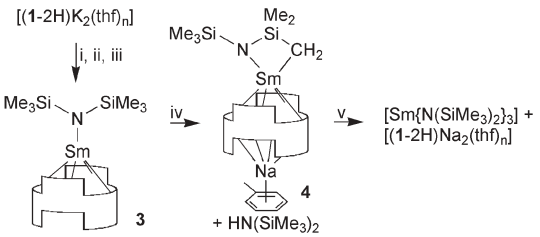


We have been investigating structural and reactivity features of complexes of deprotonated modified porphyrinogens, including *trans*-difuranyl substitution (**1**) and *trans*-*N*,*N*′-dimethylation (**2**). For example, mononuclear lanthanide complexes free of alkali metal cations were obtained for complexes derived from **2**.[6] We speculated that analogous reactions involving **1** would result in more complex chemistry by virtue of the demonstrated ability of the macrocycle's cavity to host two metals, shown schematically for the generic complexes $[M_2(\mathbf{1}\text{-}2H)]$ and $[M(\mathbf{2}\text{-}2H)]$.[7] Herein we report the reactivity under basic conditions of a samarium amide derived from **1** giving a γ-alkylamide rationalised by the macrocycle's ability to stabilise the counter cation.

Treatment of a solution of $K_2(\mathbf{1}\text{-}2H)$ in thf[7] with 1 equiv. of SmI_2 gave a green solution from which a brown complex was isolated, that we assume to be a Sm(II) complex, Scheme 1. Crystals of the Sm(II) complex analysed for a KI incorporated species $(thf)_2K(\mathbf{1}\text{-}2H)SmI$, but were unsuitable for X-ray structure determination and poor solubility prevented NMR spectroscopic characterisation. The Sm(II) complex was oxidised with I_2 and the solution reacted directly with $NaN(SiMe_3)_2$ in thf at 25 °C, affording the yellow Sm(III) amide $[(\mathbf{1}\text{-}2H)SmN(SiMe_3)_2]$, **3**, in good yield. **3** was reacted with 1 equiv. of $NaN(SiMe_3)_2$ in thf at 55 °C over 3 h to afford a red Sm(III) γ-alkylamide in good yield. The γ-alkylamide crystallised from toluene in poor yield as $[(\eta^6\text{-}C_7H_8)Na(\mathbf{1}\text{-}2H)SmN(SiMe_3)SiMe_2CH_2]$, **4**. In the presence of excess (5 equiv.) $NaN(SiMe_3)_2$, the amide **3** is deprotonated to give **4** within 5 min at 55 °C, which subsequently undergoes slow metal exchange (tending towards an equilibrium over days) giving the macrocyclic disodium complex $[(\mathbf{1}\text{-}2H)Na_2(thf)_n]$ and (presumably) $[Sm\{N(SiMe_3)_2\}_3]$, as determined by ^1H NMR spectroscopy.

Characterisation of **3** and **4** includes ^1H and ^{13}C NMR spectral, microanalytical data and X-ray crystal structure determinations.†‡ The ^1H NMR spectra of **3** and **4** differ in complexity, with **3** showing effective C_{2v} symmetry of the macrocycle, while **4** has its symmetry reduced to C_s (the mirror plane bisecting the furan units) owing to the non-fluxionality of the γ-alkylamide chelate.

The molecular structures of **3** and **4** are shown in Figs. 1 and 2. The Sm and Na (**4** only) centres bind to the macrocycle by η^5:η^1:η^5:η^1-bonding modes, which exhibit 1,3-alternate conformations. The η^1-interactions to the Sm centres are through the two O centres, while the η^5-interactions involve the pyrrolide units



Scheme 1 *Reagents and conditions*: i, SmI_2, thf; ii, I_2; iii, $NaN(SiMe_3)_2$; iv, $NaN(SiMe_3)_2$ then toluene; v, ex $NaN(SiMe_3)_2$.

† Electronic supplementary information (ESI) available: characterisation details. See http://www.rsc.org/suppdata/cc/b4/b417679k/

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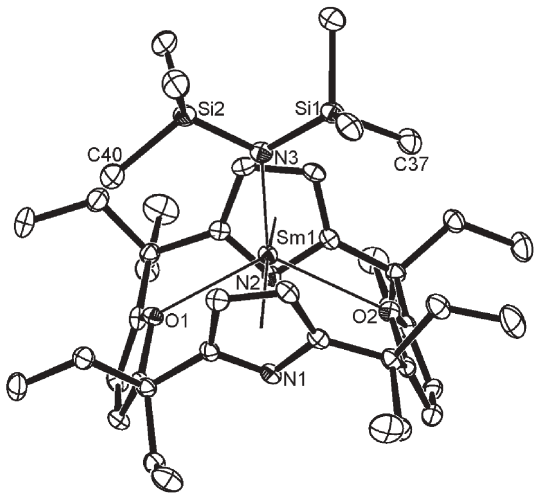

Fig. 1 Molecular structure of **3**. Selected distances and angles (deg): Sm1–O1,O2 = 2.7181(16), 2.7029(17), Sm1–η^5(N1),η^5(N2) = 2.52_6, 2.52_9, Sm1–N3 = 2.314(2), η^5(N1)–Sm1–η^5(N2) = 160.5_1.

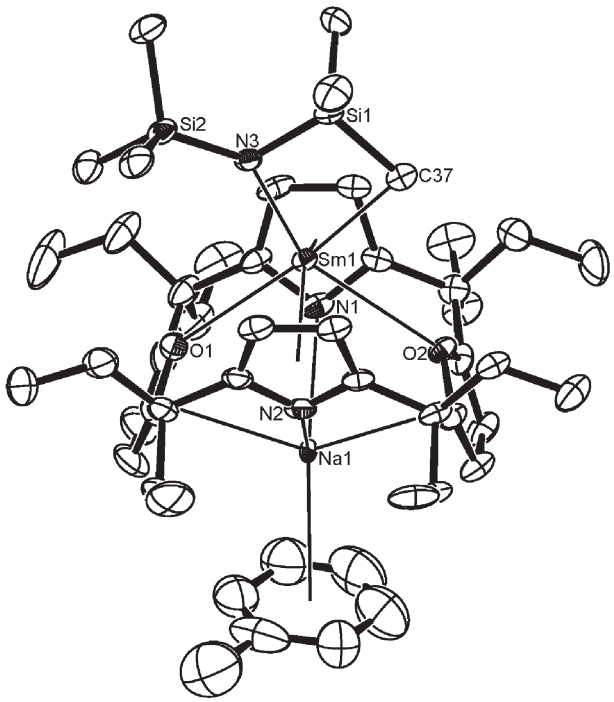

Fig. 2 Molecular structure of **4**. Selected distances (Å) and angles (deg): Sm1–O1,O2 = 3.046(2), 3.007(2), Sm1–η^5(N1),η^5(N2) = 2.59_2, 2.61_8, Sm1–N3,C37 = 2.292(2), 2.464(4), Sm1–Na1 = 3.884(3), Na1–N1,N2 = 2.782(3), 2.787(3), Na1–η^5(O1),η^5(O2) = 2.97_3, 2.99_4, Na1–η^6(C_7H_8) = 3.08_6, N3–Si1–C37 = 103.30(15), N3–Sm1–C37 = 71.77(10), η^5(N1)–Sm1–η^5(N2) = 141.4_3, Sm1–N3–Si1,Si2 = 96.43(11), 139.41(16).

(alternative models gave significantly higher *R* values). The Na centre in **4** adopts alternate bonding modes to the furanyl and pyrrolide rings (*i.e.*, Na is bound η^1- to the pyrrolides and η^5- to the furanyls). A toluene molecule is also η^6-bound to the Na centre in **4**. The γ-alkylamide in **4** chelates the Sm centre, forming a planar four membered metallo-heterocyclic (SmNSiC) ring.

The Sm(III) centre in **3** sits deeply within the macrocyclic cavity (metallocene bend angle of 160.5_1°) so that the consequent steric interactions between the macrocycle and the amide result in the approximate C_2 symmetry of the amide twisting the macrocycle (C_{2v} to C_2). These steric interactions appear to limit any further tendency of the amide to form γ-agostic interactions (Sm···C37, C40 3.51_9 and 3.67_7 Å, and associated closest Sm···H of 3.27_4 and 3.42_5 Å). Thus, we do not attribute the γ-metallation (C–H activation) of **3** to a mechanism involving γ-H agostic interactions.

We attribute the high yielding, facile metallation of **3** to the stabilisation of the Na centre within the macrocycle of **4**. This is consistent with the lack of reactivity of [(**2**-2H)SmN(SiMe$_3$)$_2$] even under more forcing conditions of a further excess of NaN(SiMe$_3$)$_2$, higher temperatures and longer reaction times.[6] In that case, the *N*-methylated porphyrinogen blocks one face of the macrocyclic cavity allowing binding of only a single metal. Na coordination in [(thf)$_3$NaCH$_2$SiMe$_2$(Me$_3$Si)NYb{N(SiMe$_3$)$_2$}$_2$], the only other structurally authenticated lanthanide γ-alkylamide derived from a bis(trimethylsilyl)amide, is *via* the bridging metallated carbon and three thf molecules.[3] γ-Deprotonations of [Ti{N(SiMe$_3$)$_2$}$_3$] in the presence of 12-crown-4 have been reported.[8] In our case, the Sm in **3** already has a high coordination number and the macrocyclic stabilisation of Na thus appears to be the sole influence driving this reaction.

In conclusion, we have established a rational γ-deprotonation of a bis(trimethylsilyl)amide complex derived from the *O*-substituted porphyrinogen **1** through stabilisation of the counter cation within the macrocyclic cavity. We are studying this effect computationally and pursuing various reactivity opportunities that the macrocycle offers in facilitating a range of unusual ligand modifications including, but not limited to, C–H activation chemistry.

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Notes and references

‡ Synthesis of **3**. Potassium metal (0.19 g, 4.8 mmol) was added to **1**, (1.09 g, 2.00 mmol) in thf (80 mL) and refluxed for 3 h. The solution was filtered to remove excess potassium metal and other insoluble impurities. SmI_2 (0.1 M in thf, 20 mL) was added dropwise to the stirred filtrate over 20 min and stirred for a further 3 h. The green solution was filtered and the filtrate concentrated *in vacuo* to *ca.* 40 mL giving a brown solid (1.42 g). To a thf solution (80 mL) of this brown solid (1.00 g), a solution of iodine (0.13 g, 0.50 mmol) in thf (20 mL) was added dropwise with stirring giving a yellow solution. Sodium bis(trimethylsilyl)amide (1.0 M in THF, 1.0 mL) was added to the stirred solution and stirring continued overnight. The solvent was removed *in vacuo* and toluene (60 mL) was added, the solution filtered and concentrated to *ca.* 20 mL giving yellow crystals of **3** (0.64 g, 75%). Synthesis of **4**. To a solution of **3** (0.50 g, 0.59 mmol) in thf (30 mL), sodium bis(trimethylsilyl)amide (1.0 M solution in THF, 0.60 mL) was added and the mixture stirred for 3 h at 55 °C. The solvent was removed *in vacuo* and toluene (10 mL) was added. The mixture was heated for 5 minutes and let stand for one week, after which time the red crystalline product precipitated and was collected (0.12 g, 20%). Crystal data for **3**: $C_{42}H_{66}N_3O_2Si_2Sm$, M = 851.51, monoclinic, a = 12.17170(10), b = 27.7942(3), c = 13.62490(10) Å, β = 113.1423(5)°, V = 4238.43(7) Å^3, space group $P2_1/n$ (no. 14), Z = 4, μ = 1.48 mm^{-1}, 52474 reflections measured, 10329 independent (R_{int} = 0.063), 7552 > 4σ(F), R = 0.032 (F > 4σ(F)), R_w = 0.072 (all data). For **4**: $C_{49}H_{73}N_3O_2NaSi_2Sm\cdot\frac{1}{2}(C_7H_8)$, M = 1012.70, triclinic, a = 11.87350(10), b = 12.4181(2), c = 18.6506(2) Å, α = 88.0740(6), β = 89.2062(6), γ = 70.8546(4)°, V = 2596.38(5) Å^3, space group $P\bar{1}$ (no. 2), Z = 2, μ = 1.23 mm^{-1}, 52007 reflections measured, 12644 independent (R_{int} = 0.064), 9343 > 4σ(F), R = 0.042 (F > 4σ(F)), R_w = 0.100 (all data). Both data sets

were collected on a Bruker KappaCCD diffractometer, T = 123 K, λ(Mo-Kα) = 0.71073 Å. CCDC 256898 (**3**) and 256899 (**4**). See http://www.rsc.org/suppdata/cc/b4/b417679k/ for crystallographic data in .cif or other electronic format.

1 U. Wannagat, *Pure Appl. Chem.*, 1969, **19**, 329; D. C. Bradley and M. H. Chisholm, *Acc. Chem. Res.*, 1976, **9**, 273; M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood Ltd, Chichester, 1980.

2 For the first structurally authenticated example, see: R. P. Planalp, R. A. Andersen and A. Zalkin, *Organometallics*, 1983, **2**, 16.

3 M. Karl, K. Harms, G. Seybert, W. Massa, S. Fau, G. Frenking and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1999, **625**, 2055.

4 For an early example, see: A. Dormond, A. El Bouadili and C. Moïse, *J. Organomet. Chem.*, 1985, **288**, C1.

5 G. B. Deacon and C. M. Forsyth, *Chem. Commun.*, 2002, 2522.

6 J. Wang, A. K. J. Dick, M. G. Gardiner, B. F. Yates, E. J. Peacock, B. W. Skelton and A. H. White, *Eur. J. Inorg. Chem.*, 2004, 1992.

7 J. Wang, M. G. Gardiner, E. J. Peacock, B. W. Skelton and A. H. White, *Dalton Trans.*, 2003, 161.

8 M. A. Putzer, J. Magull, H. Goesmann, B. Neumüller and K. Dehnicke, *Chem. Ber.*, 1996, **129**, 1401; M. A. Putzer, B. Neumüller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1087.