Low coordinate lanthanide(II) complexes supported by bulky guanidinato and amidinato ligands[†]‡

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The preparation of a series of homoleptic, four-coordinate lanthanide(II) complexes, $[Ln(Priso)_2]$ (Ln = Sm, Eu or Yb) incorporating the bulky guanidinate ligand Priso⁻ ($[(ArN)_2CNPr_2]^-$, Ar = 2,6-diisopropylphenyl) is described. X-ray crystallography shows the complexes to be isostructural and to exhibit coordination geometries midway between tetrahedral and planar. Comparisons between the geometries of the complexes and those of the bulkier systems, $[Ln(Giso)_2]$ (Giso⁻ = $[(ArN)_2CNCy_2]^-$, Cy = cyclohexyl) are discussed. Attempts to prepare the less hindered amidinate complexes, $[Ln(Piso)_2]$ (Piso⁻ = $[(ArN)_2CBu^{1}]^-$), were not successful, but did give rise to the heteroleptic complex, $[[(\kappa^1-N,\eta^6-Piso)Sm(THF)(\mu-I)_2Sm(\kappa^1-N,\eta^6-Piso)]$. Whereas the amidinate ligands in this complex chelate the samarium centre in an κ^1-N,η^6 -Ar-fashion, in the closely related complex, $[\{(\kappa^2-N,N'-Priso)Yb(THF)(\mu-I)\}_2]$, the ytterbium atoms are κ^2-N,N' -chelated by the guanidinate ligand. The facility of the planar four-coordinate complex, $[Sm(Giso)_2]$, to act as a one-electron reducing agent towards a variety of unsaturated substrates has also been explored. The complex has been shown to selectively reductively couple CS₂, *via* a C–S bond formation, to give the samarium(III) dimer, $[(Giso)_2Sm(\mu-\eta^2-:\eta^2-S_2CSCS)Sm(Giso)_2]$.

Introduction

The chemistry of amidinato and guanidinato complexes of the lanthanide metals in the +3 oxidation state has rapidly developed in recent decades.^{1,2} The interest in such compounds stems from the many applications they have found in, for example, homogeneous catalysis and as materials precursors.^{1,2} In comparison, lanthanide(II) amidinate and guanidinate complexes are rare,^{2,3} despite the significant potential they possess as one-electron reducing agents in organic and inorganic syntheses (cf. SmI₂⁴ and $SmCp_{2}^{*5}$). Rarer still are homoleptic four-coordinate examples of this compound class, the first structurally characterised representatives of which, 1-3, were reported by us in a preliminary communication in 2007.6 The coordinatively unsaturated nature of these complexes is almost certainly derived from their extremely bulky guanidinate ligands, Giso⁻ ([(ArN)₂CNCy₂]⁻, Ar = 2,6-diisopropylphenyl, Cy = cyclohexyl). Noteworthy is the fact that 1 and 2 were the first examples of complexes to exhibit planar four-coordinate lanthanide geometries,7 whereas the distorted tetrahedral ytterbium geometry exhibited by 3, had been previously described for related bulky β-diketiminate (Nacnac) complexes, [Yb(Nacnac)₂].^{8,9} In our initial report, the preparation and characterisation of the heteroleptic κ^2 -N,N'-

chelated ytterbium complex, **4**, was also detailed. Remarkably, this was found to eliminate its coordinated THF molecule in the solid state under reduced pressure to give complex **5** in which the ytterbium centre is κ^1 -N, η^6 -chelated. This process was found to be reversible.



While the origins of the differences between the coordination geometry of **3** and those of **1** and **2** are unknown, the considerably smaller Ln^{2+} ionic radius of Yb relative to those of the other two metals (values for six-coordinate Ln^{2+} : Sm^{2+} 1.19 Å, Eu^{2+} 1.17 Å, Yb^{2+} 1.02 Å¹⁰) must play a part. In addition, the substantial steric bulk of the Giso⁻ ligand presumably has an influence. In order to probe the level of this influence, it seemed appropriate to prepare analogues of **1-3**, but with marginally smaller ligand backbone substituents. The guanidinate, $Priso^-([(ArN)_2CNPri_2]^-)$, and the amidinate, $Piso^-([(ArN)_2CNBu']^-)$, were chosen for this purpose, as we have previously shown that the subtle decrease in ligand bulk in the series $Giso^- > Priso^- > Piso^-$ can lead to significant differences in the chemistry of low oxidation state s-, p- and d-block metal complexes incorporating these ligands.^{11,12}

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The results of our efforts in this direction are reported here, as is a demonstration of the use of 1 as a one-electron reducing agent.

Results and discussion

The 2:1 reactions of [K(Priso)] with THF solutions of LnI_2 (Ln = Sm, Eu or Yb) afforded low to moderate yields (ca. 30-50%) of the deeply coloured homoleptic complexes, 6-8, after recrystallisation from hexane (Scheme 1). As was the case with 1-3, there was no evidence for the coordination of THF to the metal centres of the isolated complexes, despite the reactions being carried out in that solvent. This contrasts with the 2:1 reaction of SmI₂ with the sodium salt of the smaller formamidinate ligand, Fiso-([(ArN)₂CH]⁻), which gave the octahedral samarium(II) complex, [Sm(Fiso)₂(THF)₂].^{3c} The reactions that gave 6-8 were not clean and generated significant amounts of the guanidine, PrisoH, by an unknown process. In addition, the reaction that gave 8 also led to a very low yield of the heteroleptic complex, 9 (cf. 4). Less successful were the 2:1 reactions of [K(Piso)] with LnI_2 in THF, which in no instance led to isolated complexes of the type [Ln(Piso)₂]. However, a few crystals of the heteroleptic complex, 10, were obtained from the reaction with SmI₂. A rational synthesis of 10, involving the treatment of SmI₂ with ca. one equivalent of [K(Piso)] in THF, gave an increased, but still low yield (14%) of the complex.



Scheme 1 i) 2 [K(Priso)], THF, -2 KI; ii) Ln = Sm, [K(Piso)], THF, -KI.

Due to the paramagnetic nature of 6, 7 and 10, no useful information could be obtained from their NMR spectra. The ¹H and ¹³C{¹H} NMR spectra of 8 and 9 all display very broad resonances, as was the case for the spectra of 3 and 4. Attempts to examine the origin of the signal broadening in both compounds using variable temperature NMR studies were thwarted by their low solubility in D₈-toluene below ambient temperature. However, examination of the solid state structure of 8 (*vide infra*) suggests that in this case the broadening may be due to restricted rotation of its interlocked bulky Ar groups and/or the aryl isopropyl substituents. No signals were observed in the ¹⁷¹Yb{¹H} NMR spectra of saturated samples of either complex. In comparison, signals have been reported in the spectra of closely related

Table 1 Selected bond lengths (Å) and angles (°) for 6-8 (Ln = Sm, Eu or Yb)

	6	7	8
Ln-N	2.507(2)	2.496(2)	2.376(3)
	2.515(3)	2.503(2)	2.390(3)
C–N(Ar)	1.353(3)	1.340(3)	1.341(4)
	1.332(3)	1.350(3)	1.348(4)
$C-N(Pr^i)_2$	1.397(5)	1.399(4)	1.390(5)
	1.403(5)	1.400(4)	1.397(5)
N-Ln-N	52.8(1)	53.33(9)	55.8(1)
	53.8(1)	53.96(9)	55.8(1)
(Ar)N–C–N(Ar)	113.5(3)	113.2(3)	112.0(4)
	114.3(4)	114.5(3)	114.2(4)

 $[Yb(Nacnac)_2]$ complexes in the range $\delta 2650 \pm 200$ ppm,^{8b} though these are generally very broad and sometimes not observable.

Considering the difficulties with spectroscopically characterising 6-10, the X-ray crystal structures of all complexes were determined. As compounds 6-8 are isostructural, only the molecular structure of 6 is depicted in Fig. 1, while selected metrical parameters for each complex are collected in Table 1. The dihedral angles between the CN₂Ln least squares planes in the complexes (6 46.5°, 7 47.2°, 8 47.4°) show them to have metal coordination geometries almost mid-way between planar and tetrahedral. These values differ to those of close to planar $1 (1.4^{\circ})$ and $2 (1.7^{\circ})$, and heavily distorted tetrahedral 3 (58.2°).6 Consequently, it is clear that small changes in the steric profile of the backbone substituents of the guanidinate ligand can have a substantial effect on the geometry of homoleptic lanthanide(II) complexes. That said, the effect of crystal packing forces may also be influential, given the ionic nature of the N-Ln interactions in the complexes. There appears to be delocalisation over the coordinated NCN fragments of the complexes, and their N-Ln bond distances decrease in the series Ln = Sm > Eu > Yb, as expected based on the Ln^{2+} ionic radii of the metals.



Fig. 1 Molecular structure of 6 (25% thermal ellipsoids are shown; hydrogens omitted). Symmetry operation: 'y, x, -z.

The molecular structures of **9** and **10** are shown in Fig. 2 and 3 respectively. Complex **9** possesses heavily distorted trigonal bipyramidal ytterbium centres that are symmetrically bridged by



Fig. 2 Molecular structure of 9 (25% thermal ellipsoids are shown; hydrogens omitted). Selected bond lengths (Å) and angles (°): Yb(1)-N(2) 2.364(10), Yb(1)-N(1) 2.425(9), Yb(1)-O(1) 2.427(10), Yb(1)-I(1) 3.0946(14), Yb(1)-I(1)' 3.1347(16), N(1)-C(1) 1.332(17), C(1)-N(2) 1.364(15), C(1)-N(3) 1.400(16); N(2)-Yb(1)-N(1) 55.4(3), I(1)-Yb(1)-I(1)' 89.82(3), N(1)-Yb(1)-O(1) 145.0(4), N(2)-Yb(1)-O(1) 95.4(3), O(1)-Yb(1)-I(1)' 90.1(3). Symmetry operation: '-x+1, -y+1, -z+1.



Fig. 3 Molecular structure of 10 (25% thermal ellipsoids are shown; hydrogens omitted). Selected bond lengths (Å) and angles (°): Sm(1)-N(1) 2.552(4), Sm(1)-O(1) 2.605(4), Sm(1)-I(2) 3.2945(8), Sm(1)-I(1) 3.3218(8), Sm(1)-Ar-centroid 2.697(4), I(1)-Sm(2) 3.1972(8), Sm(2)-N(3) 2.483(4), Sm(2)-I(2) 3.2207(8), Sm(2)-Ar-centroid 2.603(4), N(1)-C(1) 1.363(6), C(1)-N(2) 1.310(6), N(3)-C(34) 1.345(6), N(4)-C(34) 1.316(6); O(1)-Sm(1)-Ar-centroid 175.0(1), N(1)-Sm(1)-I(1) 143.22(10), N(1)-Sm(1)-I(2) 129.68(10), I(2)-Sm(1)-I(1) 86.416(15), N(3)-Sm(2)-I(1) 132.68(10), N(3)-Sm(2)-I(2) 127.50(10), I(1)-Sm(2)-I(2) 89.790(15), I(1)-Sm(2)-Ar-centroid 105.4(1), I(2)-Sm(2)-Ar-centroid 112.2(1), N(3)-I(1)-Sm(2)-Ar-centroid 87.7(1), N(2)-C(1)-N(1) 120.7(5), N(4)-C(34)-N(3) 120.8(5).

two iodide atoms. The coordinating NCN fragments of the compound are largely delocalised and the apical Yb(1)-N(1) distances (2.425(9) Å) are significantly longer than the equatorial Yb(1)-N(2) separations (2.364(10) Å). The compound is isostructural with **4** and is closely related to the dimeric, heteroleptic ytterbium(II) complex, [{[(Me₃Si)₂NC(NCy)₂]Yb(THF)₂(μ -I)}₂].^{3b} However, the smaller guanidinate ligand in that system allows coordination of two THF molecules at its metal centres, giving it an octahedral geometry. In contrast to **9** in which the ytterbium centres are κ^2 -*N*,*N*'-chelated, the samarium centres of **10** are κ^1 -N, η^6 -chelated by the amidinate ligand. It is unknown if this difference arises from the variations in the size of the metals, or the bulk of the ligands involved, but it is worth noting that κ^1 -N, η^6 -chelation of ytterbium(II) centres has also been observed in the THF free complex **5**.⁶ The iodide ligands of **10** effectively symmetrically bridge its two samarium centres, each of which has an η^1 -interaction with an amido centre, and an η^6 -interaction with an Ar-substituent of the Piso⁻ ligand. Moreover, the Sm(1) centre of the complex is additionally coordinated by a molecule of THF. It is likely that coordination of the other samarium atom by THF is disfavoured for steric reasons. The lengths of all interactions to each samarium atom are in the normal ranges,¹³ while the CN₂ fragments of the amidinate ligands appear to be significantly more localised than those in any of the κ^2 -N,N'-chelated complexes, **6-9**.

It has been proposed that the planar four-coordinate geometries of the samarium(II) compound 1 could lend it to use in oneelectron reductions of small unsaturated substrates that can access the "vacant" sites above and below the coordination plane of the complex.^{6,14} If this were the case, the possibility exists that the unique steric profile of the complex might lead to reduction product selectivities that differ compared to those previously observed for other lanthanide(II) reducing agents, e.g. SmI₂ and $SmCp^{*}_{2}$.^{4,5} To test these possibilities, toluene solutions of 1 were treated with a variety of substrates. No reactions occurred with Bu^tCN, Bu^tCNS, Bu^tCNO, CyN=C=NCy, PhN=NPh, Bu^tC≡P or $\{(Bu^t)N=C(H)\}_2$, despite the fact that there are many reports of Sm^{II} reductions of such substrates in the literature.^{4,5} While at first glance this may seem surprising, it should be remembered that the "vacant" Sm coordination sites of 1 are not occupied by THF, despite this being the solvent used in its preparation. Therefore, it seems logical that only substrates less sterically demanding than THF will be able to coordinate the Sm centre of 1 prior to their reduction.

One such substrate is carbon monoxide which has previously been shown to be reductively coupled by the Cp*2Sm fragment.15 In contrast, toluene solutions of compound 1 were found not react with CO at atmospheric pressure and temperatures up to 80 °C. Attention then turned to CO_2 as a linear, and potentially more reactive, substrate. Previous studies into its reactivity with [Cp*₂Sm(THF)₂] revealed that it is reductively coupled to give the oxalate complex, $[(Cp*_2Sm)_2(\mu-\eta^2:\eta^2-O_2CCO_2)]$.¹⁶ Conversely, the samarium(II) complex reacts with COS to yield a disproportionation product, $[Cp*_2Sm(\mu-\eta^2:\eta^1-S_2CO)SmCp*_2(THF)]$.¹⁶ Moreover, other very hindered samarium(II) complexes have been shown to react with CO₂ via reductive disproportionation, yielding carbonate complexes and CO.17 In the current study compound 1 was found to rapidly react with excesses of either CO₂ or COS, but these reactions were not clean and yielded GisoH as the only isolable product by an unknown process. Similarly, the fate of the samarium in these reactions is presently unknown.

The reaction of **1** with carbon disulfide, CS_2 , was found to be more controllable and under several stoichiometries (*ca.* 1 : 1, 1 : 2 or 1 : 10) led to the reductive coupling of CS_2 and the formation of the deep green complex **11** in a moderate isolated yield (55%) (Scheme 2). The reductive coupling proceeds *via* formation of an S–C bond, giving rise to the [SCSCS₂]^{2–} fragment which bridges the two Sm^{III} centres in **11**. Although reductive couplings of CS_2 have been reported on several occasions, these normally proceed *via* the formation of a C–C bond (yielding [S₂CCS₂]^{2–}),¹⁸ though a small number of C–S couplings have been observed in reactions with d-block metal complexes.¹⁹ It is possible that in the reaction



Scheme 2 i) CS₂, toluene.

with 1, the heavily sterically hindered Sm centre of the complex only allows end-on coordination of the linear CS_2 substrate, which in turn may disfavour a subsequent C–C coupling of this substrate.

As 11 is paramagnetic, no meaningful data could be obtained from its ¹H and ¹³C{¹H} NMR spectra. Accordingly, the X-ray crystal structure of 11 was determined and its molecular structure is highlighted in Fig. 4. Both of its Sm centres display distorted octahedral coordination environments. One, Sm(1), is chelated by a CS₂ fragment (*cf.* $[Cp*_2Sm(\mu-\eta^2:\eta^1-S_2CO)SmCp*_2(THF)]^{16})$, giving rise to a SmS_2C four-membered ring, while the other, Sm(2), has an η^2 -interaction with a CS moiety. Because the [SCSCS₂]²⁻ ligand of the complex is disordered over two sites, and a number of crystallographic constraints were imposed during the modelling of this disorder in the crystallographic refinement, the metrical parameters of the fragment should not be considered as fully reliable. Therefore, it is difficult to confidently discuss the degree of double bond delocalisation over the fragment. This said, the gross molecular framework of the complex is unambiguous. The Gisoligands are ordered and a meaningful discussion of their geometry is possible. As was the case with 1, the bond lengths within their NCN backbones suggest a significant degree of delocalisation. The Sm–N bond lengths in 11 (2.435 Å mean) are well within the known range, but all are considerably shorter than those in the starting material, [Sm(Giso)₂] 1 (2.546 Å mean). This is a direct result of the increase in the oxidation state of the samarium centres upon reaction.

Conclusion

In summary, a sterically bulky guanidinate ligand, Priso⁻, has been utilised in the preparation of a series of homoleptic, fourcoordinate lanthanide(II) complexes, $[Ln(Priso)_2]$ (Ln = Sm, Eu or Yb). These are isostructural and exhibit coordination geometries between those of planar $[Ln(Giso)_2]$ (Ln = Sm or Eu) and distorted tetrahedral $[Yb(Giso)_2]$, all of which bear the slightly bulkier guanidinate ligand, Giso⁻. The attempted preparations of the related complexes, $[Ln(Piso)_2]$, incorporating the smaller



Fig. 4 Molecular structure of 11 (25% thermal ellipsoids are shown; hydrogens and isopropyl groups omitted). Selected bond lengths (Å) and angles (°): Sm(1)-N(4) 2.386(5), Sm(1)-N(2) 2.416(5), Sm(1)-N(5) 2.455(5), Sm(1)-N(1) 2.486(5), Sm(1)-S(1) 2.979(10), Sm(1)-S(2) 2.998(5), N(1)-C(3) 1.356(9), N(2)-C(3) 1.360(9), N(4)-C(40) 1.365(8), N(5)-C(40) 1.363(8), Sm(2)-N(7) 2.403(5), Sm(2)-N(10) 2.416(6), Sm(2)-N(8) 2.448(6), Sm(2)-N(11) 2.473(6), Sm(2)-S(4) 2.813(8), Sm(2)-C(2) 2.444(14), N(7)-C(77) 1.369(9), N(8)-C(77) 1.355(8), N(10)-C(114) 1.360(9), N(11)-C(114) 1.364(8), S(1)-C(1) 1.710(12), C(1)-S(2) 1.682(11), C(1)-S(3) 1.778(12), C(2)-S(4) 1.605(13), C(2)-S(3) 1.720(14); N(2)-Sm(1)-N(1) 54.82(18), N(4)-Sm(1)-N(5) 55.50(19), S(1)-Sm(1)-S(2) 59.85(19), N(7)-Sm(2)-N(8) 55.11(19), N(10)-Sm(2)-N(11) 55.03(19), C(2)-Sm(2)-S(4) 34.7(3), S(2)-C(1)-S(1) 123.0(8), S(2)-C(1)-S(3) 125.0(7), S(1)-C(1)-S(3) 111.9(7), C(2)-S(3)-C(1) 113.6(6), S(4)-C(2)-S(3) 130.9(9).

amidinate, Piso⁻, were not successful. These results reveal that small changes in ligand sterics can have a significant effect on the outcome of, and the geometry of products derived from, reactions between bulky guanidinate/amidinate salts and lanthanide(II) iodides. This study has also demonstrated that while the planar complex, [Sm(Giso)₂], is generally unreactive towards unsaturated substrates, it does selectively reductively couple CS₂ via a C–S bond formation. We continue to explore the utility of bulky guanidinates for stabilising low oxidation state/low coordination number metal complexes.

Experimental section

General considerations

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon or dinitrogen. THF, hexane and toluene were distilled over potassium. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Mass spectra were recorded at the EPSRC National Mass Spectrometric Service at Swansea University. Reproducible microanalyses could not be obtained for compounds **6-9** as all consistently co-crystallised with significant amounts of PrisoH, and the complete manual separation of PrisoH from the compounds was not possible. Similarly, compound **10** cocrystallised with PisoH. IR spectra were recorded using a Nicolet

Compound	6 (hexane)	7·(hexane)	8·(hexane)	9	$10 \cdot (\text{hexane})_{0.5}$	11 \cdot (toluene) ₄
Empirical Formula	$C_{68}H_{110}N_6Sm$	C ₆₈ H ₁₁₀ N ₆ Eu	$C_{68}H_{110}N_{6}Yb$	$C_{70}H_{112}I_2N_6O_2Yb_2$	$C_{65}H_{101}I_2N_4O$	$C_{178}H_{256}N_{12}S_4Sm_2$
FW	1161.97	1163.58	1184.66	1669.54	1509.00	2992.89
T/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Cryst Syst	tetragonal	tetragonal	tetragonal	Monoclinic	Monoclinic	Monoclinic
Space Group	$P4_{1}2_{1}2$	$P4_{1}2_{1}2$	$P4_{3}2_{1}2$	$P2_{1}/c$	$P2_1/n$	$P2_{1}/c$
a/Å	14.203(2)	14.193(2)	13.983(2)	15.374(3)	16.840(3)	21.416(4)
b/Å	14.203(2)	14.193(2)	13.983(2)	10.524(2)	10.807(2)	18.051(4)
c/Å	33.354(7)	33.380(7)	33.631(7)	23.481(5)	37.239(7)	44.847(9)
α (°)	90	90	90	90	90	90
β (°)	90	90	90	105.23(3)	97.64(3)	102.99(3)
γ (°)	90	90	90	90	90	90
Vol/Å ³	6728.8(19)	6724.0(19)	6576.2(19)	3665.5(13)	6717(2)	16893(6)
Z	4	4	4	2	4	4
Density (calcd) (Mg m ⁻³)	1.147	1.149	1.197	1.513	1.492	1.177
μ (Mo-K α)/mm ⁻¹	0.914	0.974	1.464	3.422	1.492	0.790
<i>F</i> (000)	2488	2492	2520	1672	3028	6384
No. of reflections collected	11764	11408	14101	10431	20771	49987
No. of independent reflns (R_{int})	5909 (0.0317)	5891 (0.0202)	7150 (0.0234)	6079 (0.1200)	11672 (0.0428)	29126 (0.0976)
Final R_1 ($I > 2\sigma(I)$) and w R_2 indices (all data)	$R_1 = 0.0367$	$R_1 = 0.0271$	$R_1 = 0.0359$	$R_1 = 0.0872$	$R_1 = 0.0433$	$R_1 = 0.0786$
	$wR_2 = 0.0771$	$wR_2 = 0.0594$	$wR_2 = 0.0939$	$wR_2 = 0.1800$	$wR_2 = 0.0750$	$wR_2 = 0.1764$

Table 2Crystal data for compounds 6–11

510 FT-IR spectrometer as Nujol mulls between NaCl plates. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker DPX400 spectrometer and were referenced to the resonances of the solvent used. THF solutions of LnI_2 (Ln = Sm, Eu or Yb),²⁰ [K(Priso)],²¹ K[(Piso)]^{12b} and [Sm(Giso)₂]⁶ were prepared using variations of literature procedures. All other reagents were used as received.

Preparation of [Sm(Priso)₂] 6

SmI₂ (13 cm³ of a 0.1 M solution in THF, 1.30 mmol) was added to a solution of [K(Priso)] (2.50 mmol) in THF (30 cm³) at -80 °C. The mixture was slowly warmed to room temperature overnight with stirring. All volatiles were removed under reduced pressure. The residue was extracted with hexane (80 cm³), filtered, and the filtrate concentrated to *ca*. 12 cm³. Placement at -30 °C overnight afforded deep violet crystals of **6** (yield: 0.77 g, 53% based on [K(Giso)]). Mp: 210-212 °C (decomp.); IR ν/cm^{-1} (Nujol): 1612 (s), 1583 (m), 1258 (m), 1179 (m), 1109 (m), 1043 (m), 930 (m), 859 (m), 796 (m), 754 (s), 661 (m); MS/EI *m/z* (%): 464.5 (PrisoH⁺, 100).

Preparation of [Eu(Priso)₂] 7

A procedure similar to that used to prepare **6** was employed for the synthesis of orange-red crystalline **7** (yield: 46%). Mp: 201-203 °C (decomp.); IR v/cm^{-1} (Nujol): 1611 (s), 1582 (m), 1258 (m), 1154 (s), 1043 (m), 930 (m), 861 (m), 796 (s), 753 (s), 661 (m); MS/EI m/z (%): 464.5 (PrisoH⁺, 100).

Preparation of $[Yb(Priso)_2] 8$ and $[{(\kappa^2-N,N'-Priso)Yb(THF)(\mu-I)}_2] 9$

YbI₂ (80 cm³ of a 0.02 M solution in THF, 1.60 mmol) was added to a solution of [K(Priso)] (2.10 mmol) in THF (20 cm³) at -80 °C. The mixture was slowly warmed to room temperature overnight with stirring. All volatiles were then removed under reduced pressure. The residue was extracted with hexane (60 cm³) and the extract concentrated to *ca.* 30 cm³. Placement at -30 °C

overnight afforded orange-yellow crystals of 9 (yield: 0.10 g, 6% based on [K(Giso)]). Further concentration to ca. 4 cm³ and placement at -30 °C overnight gave green crystals of 8 (yield: 0.40 g, 32% based on [K(Giso)]). 8: Mp: 223-225 °C (decomp.); ¹H NMR (400.13 MHz, 300 K, C_6D_6): $\delta = 0.40$ (br, 24 H, NCH(CH₃)₂), 0.66 (br, 12 H, CH(CH₃)₂), 0.79 (br, 12 H, CH(CH₃)₂), 1.20 (br, 12 H, CH(CH₃)₂), 1.55 (br, 12 H, CH(CH₃)₂), 3.85 (br, 4 H, CH(CH₃)₂), 4.08 (br, 8 H, CH(CH₃)₂ and NCH(CH₃)₂), 7.03-7.42 (br m, 12 H, ArH); ¹³C{¹H} NMR (100.6 MHz, 300 K, C_6D_6): $\delta = 20.5$ (br, NCH(CH₃)₂), 21.3 (br, CH(CH₃)₂), 22.5 (br, CH(CH₃)₂), 23.2 (br, CH(CH₃)₂), 25.1 (br, CH(CH₃)₂), 25.5 (br, CH(CH₃)₂), 26.4 (br, CH(CH₃)₂), 46.5 (br, NCH(CH₃)₂), 120.9, 122.0, 134.4, 140.0 (br, ArC), 165.4 (br, CN_3); IR v/cm⁻¹ (Nujol): 1611 (s), 1582 (m), 1260 (m), 1108 (s), 1044 (m), 931 (m), 797 (m), 755 (m); MS/EI m/z (%): 1098.5 (M⁺, 1), 464.5 (PrisoH⁺, 100); accurate mass (EI), *m/z*: calc. for C₆₂H₉₆N₆¹⁷⁰Yb (1094.7039), found (1094.7031). **9**: Mp: 183-186 °C (decomp.); ¹H NMR (400.13 MHz, 300 K, C_6D_6): $\delta = 0.83$ (br, 24 H, NCH(CH₃)₂), 1.24 (br, 24 H, CH(CH₃)₂), 1.41 (br, 32 H, THF-CH₂ and CH(CH₃)₂), 3.65 (br, 8 H, CH(CH₃)₂), 3.77 (br, 12 H, OCH₂ and NCH(CH₃)₂), 6.80-7.22 (br, 12 H, ArH); ${}^{13}C{}^{1}H{}$ NMR (100.6 MHz, 300 K, C_6D_6): $\delta = 21.8$ (br, NCH(CH₃)₂), 23.1 (br, CH(CH₃)₂), 23.7 (br, CH(CH₃)₂), 26.8 (br, THF-CH₂), 27.9 (br, CH(CH₃)₂), 49.0 (br, NCH(CH₃)₂), 69.1 (br, OCH₂), 121.8, 123.8, 142.0, 146.4 (br, ArC), 164.5 (br, CN₃); IR v/cm⁻¹ (Nujol): 1611 (s), 1582 (m), 1260 (m), 1110 (s), 1018 (m), 861 (m), 797 (m), 755 (m); MS/EI m/z (%): 464.5 (PrisoH+, 100).

Preparation of [(κ^1 -N, η^6 -Piso)Sm(THF)(μ -I)_2Sm(κ^1 -N, η^6 -Piso)] 10

[K(Piso)] (3.10 mmol) in THF (20 cm³) was added to SmI₂ (35.5 cm³ of a 0.1 M solution in THF, 3.55 mmol) at -80 °C. The mixture was warmed to room temperature overnight with stirring. Volatiles were then removed under reduced pressure and the residue extracted with hexane (80 cm³). Concentration of the extract to *ca*. 40 cm³ and subsequent placement at -30 °C overnight

afforded deep violet crystals of **10** (yield: 0.33 g, 14%). Mp: 218-220 °C (decomp.); IR ν/cm^{-1} (Nujol): 1614 (m), 1585 (m), 1259 (m), 1155 (m), 1108 (m), 1027 (m), 926 (s), 767 (s); MS/EI m/z (%): 421.4 (PisoH⁺, 100).

Preparation of [(Giso)₂Sm(µ-η²-:η²-S₂CSCS)Sm(Giso)₂] 11

0.5 cm³ of a 1.66 M solution of CS₂ in toluene (0.81 mmol) was added to a suspension of [Sm(Giso)₂] (0.40 g, 0.32 mmol) in toluene (10 cm³) at -78 °C to give a deep green solution. The reaction mixture was warmed to 20 °C and stirred for three hours. The solution was concentrated to *ca*. 4 cm³, filtered and the filtrate stored at -30 °C to give deep green blocks of **11** (0.24 g, 55%). Mp: 131-133 °C (decomp.); IR ν/cm^{-1} (Nujol): 1612 (s), 1583 (s), 1322 (m), 1240 (m), 1013 (m), 933 (m), 894 (m), 794 (m), 778 (m); MS/EI m/z (%): 545 (GisoH⁺, 100); anal. calc. for C₁₇₈H₂₅₆N₁₂S₄Sm₂ (**11**·(toluene)₄): C 71.43, H 8.62, N 5.62%; found: C 71.31, H 8.56, N 5.49%.

X-ray crystallography

Crystals of **6-11** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97²²) using all unique data. Hydrogen atoms have been included in calculated positions (riding model) for all structures. A discussion of the crystallographic disorder encountered for the structure of **11** can be found in its CIF file in the ESI. The absolute structure parameters for **6-8** are 0.198(12), 0.009(9) and 0.182(12) respectively. Crystal data, details of data collections and refinement are given in Table 2.

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