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Redox Transmetallation Approaches to the Synthesis of Extremely Bulky Amido-Lanthanoid(II) and Calcium(II) Complexes

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Abstract

Redox transmetallation protolysis reactions between HgPh_2 , elemental metals, $M = \text{Ca, Eu, or Yb}$, and the bulky arylsilylamine $^{\text{Ph}}\text{L}^{\dagger}\text{H}$ ($\text{HN}(\text{SiPh}_3)(\text{Ar}^{\dagger})$, $\text{Ar}^{\dagger} = \text{C}_6\text{H}_2\text{Pr}^i\{\text{C}(\text{H})\text{Ph}_2\}_{2-4,2,6}$), or the borylsilylamine $^{\text{Ph}}\text{L}^{\text{B}^0}\text{H}$ ($\text{HN}(\text{SiPh}_3)\{\text{B}(\text{DipNCH})_2\}$, $\text{Dip} = \text{C}_6\text{H}_3\text{Pr}^i_{2-2,6}$) pro-ligands yielded complexes incorporating doubly deprotonated, *N,C*-chelating amido/organyl ligands, *viz.* $[\text{M}(\text{L}^{\text{H}})(\text{thf})_x]_n$, $\text{L}^{\text{H}} = ^{\text{Ph}}\text{L}^{\dagger-\text{H}}$ (**1-3**) or $^{\text{Ph}}\text{L}^{\text{B}^0-\text{H}}$ (**4-5**); $M = \text{Ca}$ (**1, 4**), Eu (**2**) or Yb (**3, 5**); $x = 0$ (**5**) or 2 (**1-4**); $n = 1$ (**1-4**) or 2 (**5**). Structural differences between **4** and **5** represent a rare divergence in the chemistry of divalent calcium and ytterbium. Utilisation of a less hindered bis(aryl) amine, $^{\text{D}}\text{L}^{\text{M}}\text{H}$ ($\text{HN}(\text{Dip})(\text{Mes})$, $\text{Mes} = \text{C}_6\text{H}_2\text{Me}_3_{2,4,6}$) in a similar reaction yielded a three-coordinate, trigonal planar ytterbium complex $[\text{Yb}(\text{D}^{\text{L}^{\text{M}}})_2(\text{thf})]$ (**6**). Direct redox transmetallation reactions between an amido-mercurial iodide $[(^{\text{Me}}\text{L}^{\dagger})\text{HgI}]$ (**7**, $^{\text{Me}}\text{L}^{\dagger} = \text{N}(\text{SiMe}_3)(\text{Ar}^{\dagger})$) and ytterbium or europium metal afforded homoleptic $[\text{Yb}(\text{MeL}^{\dagger})_2]$ (**8**) and heteroleptic $[\{\text{Eu}(\text{MeL}^{\dagger})(\mu\text{-I})(\text{thf})\}_2]$ (**9**) respectively. This study highlights the versatility of redox transmetallation pathways to amido-lanthanoid complexes, especially where such compounds are difficult to access using conventional salt metathesis pathways.

Introduction

Significant progress has been made in the field of low oxidation state lanthanoid chemistry in recent years, as evidenced by the fact that complexes containing all but one of lanthanoid metals in the +2 oxidation state are now synthetically accessible.^{1,2} The least reducing of the lanthanoid(II) ions (Sm^{2+} , Eu^{2+} , Yb^{2+} and Tm^{2+}) have been stabilised by a variety of anionic N-, C-, P- and O-donor ligand types,^{3,4} while the chemistry of the remaining atypical divalent lanthanoid ions is largely restricted to bulky cyclopentadienide coordinated systems.^{1,2,5} Given the significant potential strongly reducing lanthanoid(II) complexes have in areas such as synthesis, small molecule activation etc.,⁶ the development of a more diverse range of ligand types to stabilise such species is imperative to accelerate the development of their applications.

Mono-dentate amide ligands, such as the archetypal silyl-amide scaffold $-\text{N}(\text{SiMe}_3)_2$, have been widely utilised in lanthanoid(II and III) chemistry since the early 1970's.⁷ This is in no small part due to the favourable electronic properties of these ligands, and the ease by which they are sterically modified. A recent example of the importance of the latter property is the use of a very bulky silyl-amide in the synthesis of the first near linear bis(amido)lanthanoid(II) complexes, $[\text{M}\{\text{N}(\text{SiPr}^i_3)_2\}_2]$ ($\text{M} = \text{Sm}, \text{Eu}, \text{Yb}$ or Tm),⁸ the last of which is remarkably stable, even towards reaction with dinitrogen. Given the well documented similarities between the chemistry of Yb^{II} and Ca^{II} ,⁹ it is worth noting that the equivalent calcium complex, $[\text{Ca}\{\text{N}(\text{SiPr}^i_3)_2\}_2]$, has also been reported to have a near linear N-Ca-N fragment.¹⁰

Over the past five years we have successfully applied new classes of even bulkier silyl-amide ligands (e.g. $-\text{N}(\text{Ar}^\dagger)(\text{SiR}_3)$, $\text{Ar}^\dagger = \text{C}_6\text{H}_2\text{Pr}^i\{\text{C}(\text{H})\text{Ph}_2\}_{2-4,2,6}$; $\text{R} = \text{Me}, \text{Pr}^i$ or Ph ; and $-\text{N}\{\text{B}(\text{DipNCH})_2\}(\text{SiMe}_3)$, $\text{Dip} = \text{C}_6\text{H}_3\text{Pr}^i_{2-2,6}$)¹¹ to the stabilisation of a wide variety of, often unprecedented, low oxidation state and/or low coordinate s-,¹² p-¹³ and d-block¹⁴ metal

complex types. We believed that such amides could enable entry to novel lanthanoid(II) compound types, perhaps including complexes of the more reducing metals. Here, in a preliminary scoping study, we describe the synthesis and characterisation of a series of Eu(II), Yb(II), and related Ca(II) complexes derived from extremely bulky silyl-amide and less hindered bis(aryl) amide ligand systems. Throughout, redox transmetallation pathways, which have previously proved successful in lanthanoid and alkaline earth metal chemistry involving a variety of ligand types,¹⁵ have been employed. The outcomes of these reaction pathways depend on the ligand type, the metal involved, and the reaction conditions

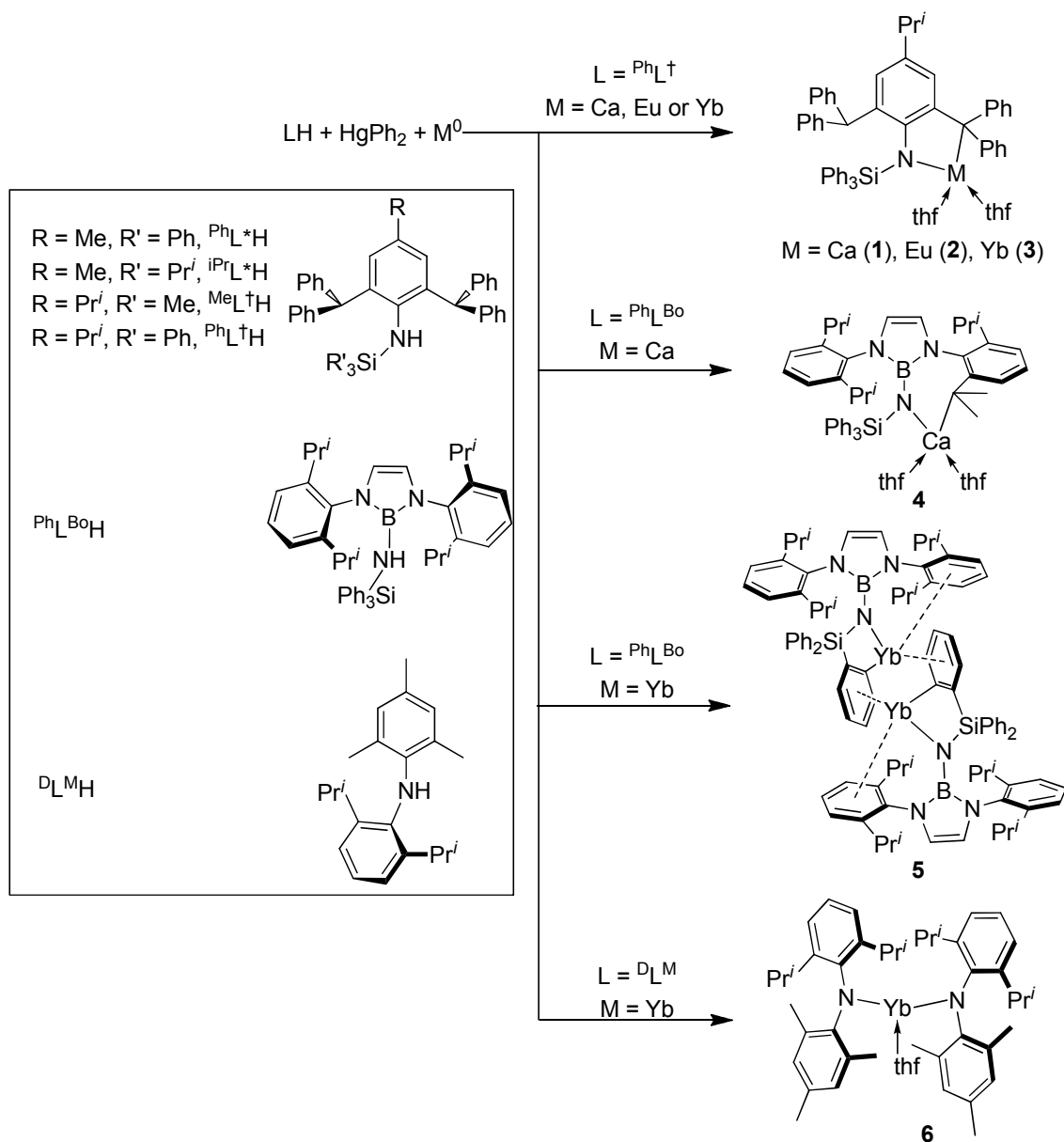
Results and Discussion

Redox transmetallation protolysis (RTP) pathways

At the outset of this study classical synthetic routes to lanthanoid(II) amides were explored, but without success. For example, salt metathesis reactions between lithium or potassium salts of a range of bulky amide ligands, including those depicted in Scheme 1, and a broad range of lanthanoid halides failed to yield isolable amido-lanthanoid products. Similarly, attempted protolysis reactions between bulky secondary amines and lanthanoid alkyls and amides, e.g. [Yb{N(SiMe₃)₂}(thf)₂], gave intractable product mixtures. To overcome these shortcomings, we shifted our attention to mercury based redox transmetallation protolysis (RTP) reactions, which have previously proved useful for the synthesis of lanthanoid complexes.¹⁵

Reactions between elemental lanthanoid metals or calcium metal, diphenylmercury and one or two equivalents of a bulky secondary amine were carried out in tetrahydrofuran in the presence of a drop of mercury at either 25 °C or 40 °C, as outlined in Scheme 1. The outcomes of these reactions were significantly dependent upon the silyl- substituents on the secondary amine reactants. For ^{Me}L[†]H and ^{iPr}L^{*}H, N-Si bond cleavage occurred, leading to free substituted aniline formation, as detected by ¹H NMR spectroscopic analyses of reaction

aliquots. In contrast, the larger amine, $^{\text{Ph}}\text{L}^{\dagger}\text{H}$, was stable to the reaction conditions employed. However, regardless of whether one or two equivalents of the amine were used, metallocyclic complexes incorporating an alkyl/amido- dianionic ligand, $[\text{M}(^{\text{Ph}}\text{L}^{\dagger-\text{H}})(\text{thf})_2]$ ($^{\text{Ph}}\text{L}^{\dagger-\text{H}} = \text{-N}(\text{SiPh}_3)(\text{C}_6\text{H}_2-4\text{-Pr}^i-6\text{-CHPh}_2-2\text{-CPh}_2\text{-})$) were isolated (M = Ca (**1**), Eu (**2**) or Yb (**3**)) in moderate to good yields (39-72%) (Scheme 1). Interestingly, attempts to form the samarium counterpart of **1-3** by an analogous route led to no reaction, even after prolonged heating of the mixture. The dianionic metallocyclic ligands of **1-3** presumably result from metallation of a weakly acidic benzyhydril CH unit (*cf.* triphenylmethane: $\text{p}K_a \sim 33$)¹⁶ by highly reactive $[\text{M}(^{\text{Ph}}\text{L}^{\dagger})(\text{Ph})(\text{thf})_n]$ intermediates. It is noteworthy that **1-3** cannot be prepared by the direct reaction of bulk metal with the secondary amine in thf. With that said, we have utilised metal vapour synthesis techniques^{13d} to prepare **3** in low yield from the reaction of calcium atoms and $^{\text{Ph}}\text{L}^{\dagger}\text{H}$ in a thf/toluene mixture.



Scheme 1. Synthesis of compounds **1-6**. Tetrahydrofuran was the reaction solvent in each case. The η^2 -Ph interactions with the metal centres in **1-3** are omitted for sake of clarity.

Complexes **1-3** are bright red in the solid state and in solution, which is most likely due to a degree of electronic delocalisation over the planar, deprotonated CAr₃ fragment of the ligand. Similar deep colours have been reported for near planar triphenylmethyl complexes of electropositive metals, e.g. [Ph₃CMg(Br)(OEt₂)₂].¹⁷ The compounds are

moderately soluble in thf and dme, but poorly soluble in hydrocarbon solvents. They are indefinitely stable in the solid state when stored under dinitrogen and show minimal decomposition when stored at room temperature as tetrahydrofuran solutions. The NMR spectroscopic data for **1** are consistent with its asymmetric structure, while those for **2** and **3** were less informative due to the paramagnetic nature of the former, and co-crystallisation with paramagnetic impurities for the latter. The solid state infrared spectra for the complexes are essentially superimposable, which suggests they have very similar structures in the solid state.

X-ray crystallographic analyses of **1-3** confirmed the complexes to be structurally very similar, hence only the molecular structure of **1** is displayed in Figure 1 (See ESI for molecular structures of **2** and **3**). The ytterbium and calcium analogues feature near identical metrical parameters (see Table 1), whilst the europium compound has slightly elongated bonds to the metal, which is consistent with the difference in ionic radii between six-coordinate europium, and calcium or ytterbium of *ca.* 0.15 Å.¹⁸ As with **2** and **3**, the metal centre in complex **1** possesses what is best described as a distorted trigonal bipyramidal geometry ($\tau = 0.83$),¹⁹ the axial positions of which are occupied by the amide nitrogen and a thf ligand, while the equatorial positions are taken up by the other thf ligand, an η^2 -phenyl interaction, and an approximately η^3 -coordinated, deprotonated benzyhydril (CPh₂) moiety. That this fragment is deprotonated is clear from the near planar C(10)C₃ fragment (Σ angles = 357°), the C(10)-Ca(1) bonding distance (2.513(2) Å; *cf.* *cis*-[Ca(CH₂Ph)₂(thf)₄] Ca-C bonds = 2.55 Å (avge.)²⁰), and the close interactions with the flanking phenyl *ipso*-carbons (C(11)-Ca(1) 2.799(2) Å and C(17)-Ca(1) 2.902(2) Å). Some degree of electronic delocalisation over the C(11)-C(10)-C(17) fragment is indicated by the shorter C-C bonds (by *ca.* 0.1 Å), relative to corresponding distances in the opposing protonated benzhydril moiety. A similar, yet more

localised, bonding situation has been observed in an aluminium complex involving benzhydryl deprotonated ${}^{\text{iPr}}\text{L}^{\dagger}$ as a bidentate dianionic ligand.^{11b}

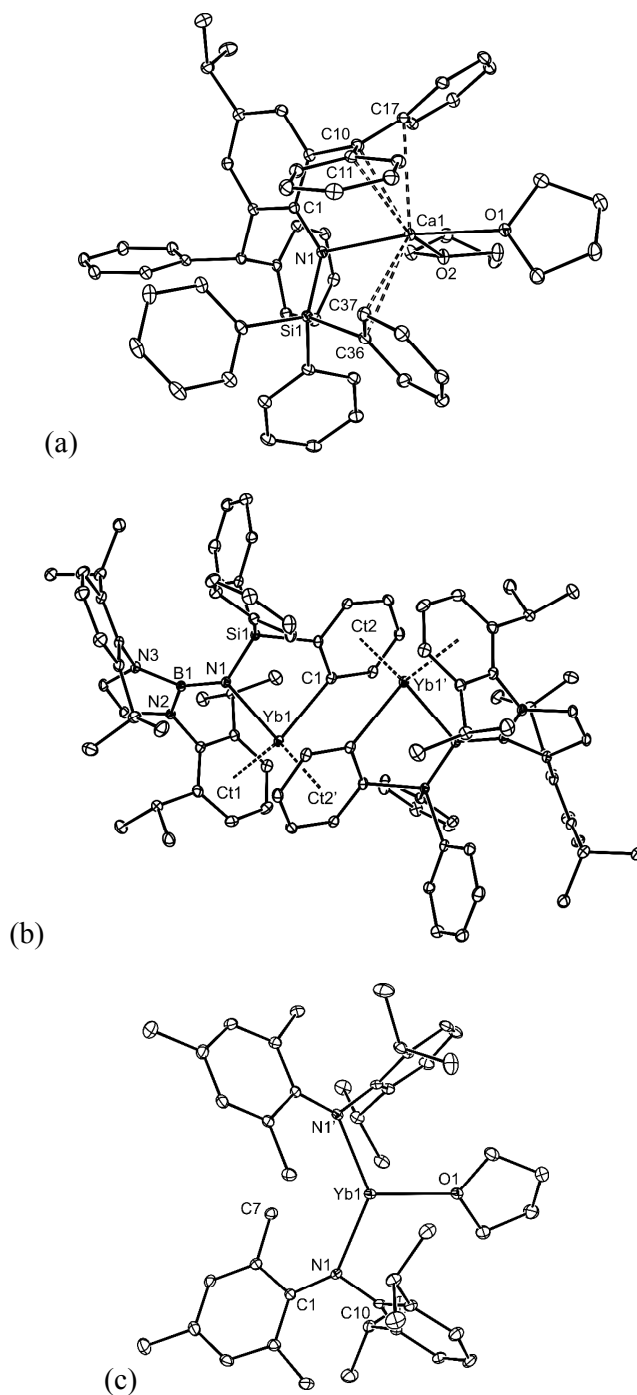


Fig. 1 Molecular structures of (a) **1**, (b) **5**, and (c) **6** (25% thermal ellipsoids; hydrogen atoms omitted). For metrical parameters of **1-3** see Table 1. Selected bond lengths (Å) and angles (°)

for **5**: Yb(1)-N(1) 2.375(3), Yb(1)-C(1) 2.481(4), Yb(1)-Ct(1) 2.664(5), Yb(1)-Ct(2) 2.519(4), N(1)-Yb(1)-C(1) 83.2(1), Ct(1)-Yb(1)-Ct(2) 123.3(1). Symmetry transformations used to generate equivalent atoms: '-x+1, -y+1, -z+1. Selected bond lengths (Å) and angles (°)

for **6**: Yb(1)-N(1) 2.315(2), Yb(1)-O(1) 2.380(3), N(1)-Yb(1)-N(1)' 134.25(10), N(1)-Yb(1)-O(1) 112.87(5), N(1)''-Yb(1)-O(1) 112.87(5). Symmetry transformations used to generate equivalent atoms: '-x+1, y, -z+1/2.

Table 1. Selected interatomic distances (Å) and angles (°) for **1-3** (M = Ca, Eu or Yb, respectively).

	1	2	3
M-N	2.3282(16)	2.47(2)	2.357(4)
M-O(1)	2.3709(15)	2.56(2)	2.443(3)
M-O(2)	2.3637(15)	2.53(2)	2.415(4)
M-CPh ₂	2.513(2)	2.63(3)	2.530(5)
N...C _{ipso} -CPh	2.799(2)	2.86(3)	2.789(5)
	2.902(2)	2.93(3)	2.937(5)
M...C _{ipso} -SiPh	2.875(2)	2.92(2)	2.888(5)
M...C _{ortho} -SiPh	3.098(2)	3.23(3)	3.046(5)
N-M-CPh ₂	73.69(6)	69.4(7)	72.72(14)
N-M-O(1)	171.32(5)	174.2(7)	171.82(12)
N-M-O(2)	91.23(5)	91.8(7)	92.38(13)
O(1)-M-O(2)	84.87(5)	85.1(8)	83.49(12)

In an attempt to circumvent ligand deprotonation processes similar to those that gave rise to **1-3**, RTP reactions were carried out between lanthanoid or calcium metal, and two secondary amines devoid of non-amine protons as acidic as the methine protons in $^{\text{Ph}}\text{L}^{\dagger}\text{H}$. The first of these was the boryl/silyl amine, $^{\text{Ph}}\text{L}^{\text{Bo}}\text{H}$, which when reacted with calcium or ytterbium in the presence of HgPh_2 , gave the structurally different ligand deprotonated metallocycles, **4** and **5**, as the only isolated products, regardless of the reaction stoichiometry employed (Scheme 1). Interestingly, despite possessing nearly identical ionic radii, ytterbium and calcium metal (1.02 Å and 1.00 Å respectively for 6 coordinate ions)⁹ produced different products in these reactions. That is, in the calcium complex an isopropyl methine carbon is deprotonated, whereas in the ytterbium compound the *ortho*-position of a phenyl ring of the triphenylsilyl moiety is metallated. However, given the relatively low isolated yields of **4** and **5**, and the absence of any NMR spectroscopic data for **5**, it cannot be ruled out that both structural motifs are generated in each reaction. Whatever the case, the mechanisms of those reactions presumably involve amido/phenyl-intermediates, " $[(^{\text{Ph}}\text{L}^{\text{Bo}})\text{MPh}(\text{thf})_n]$ ", which must be extremely reactive to deprotonate the two weakly acidic C-H sites of attack on the $^{\text{Ph}}\text{L}^{\text{Bo}}$ ligand.

It was postulated that using less basic arylmercury compounds in the RTP reactions described above might alternatively prevent ligand C-H activation processes from occurring. To this end reactions involving $[\text{Hg}(\text{C}_6\text{F}_5)_2]$, $[\text{Hg}(\text{Ph})(\text{Br})]$ or $[\text{Hg}(\text{Ph})(\text{C}_6\text{F}_5)]$,^{15a,21} ytterbium and either $^{\text{Ph}}\text{L}^{\text{Bo}}\text{H}$ or $^{\text{Ph}}\text{L}^{\dagger}\text{H}$ were carried out. All reactions resulted in complete consumption of the organomercurial but no formation of any ytterbium amide products was detected. Instead, ^{19}F NMR spectroscopic analyses of aliquots from reactions employing both $-\text{C}_6\text{F}_5$ containing mercurials, indicated the formation of $[\text{Yb}(\text{C}_6\text{F}_5)_2(\text{thf})_4]$,²² and various other fluorinated products. In the case of the reaction between $[\text{Hg}(\text{Ph})(\text{Br})]$, $^{\text{Ph}}\text{L}^{\text{Bo}}\text{H}$ and $\text{Yb}_{(\text{s})}$, a small number of crystals of the polymeric complex, $[\{\text{Yb}(\text{thf})_2(\mu\text{-Br})_2\}_\infty]$, deposited from the

filtered reaction mixture after several weeks. This complex has previously been prepared by reaction of ytterbium filings with HgBr_2 or trimethylsilyl bromide, though its solid-state structure has not previously been reported.²³ The crystal structure of the polymeric, bromide bridged complex was obtained in the current study, details of which can be found in the ESI.

The second non-benzhydryl substituted amine precursor used for the RTP reactions described here was the bulky diaryl amine $^{\text{D}}\text{L}^{\text{M}}\text{H}$.¹¹ When two equivalents of this were treated with diphenylmercury in the presence of excess ytterbium in thf, the bis(amido)ytterbium(II) complex, **6**, was produced in low-moderate isolated yields (Scheme 1). The fact that this complex, or the likely intermediate to it, $[(^{\text{D}}\text{L}^{\text{M}})\text{YbPh}(\text{thf})_n]$, is resistant to C-H activation processes is likely a result of the lower steric bulk of the amide ligand, relative to those that gave rise to metallocycles **1-5**. It is noteworthy that similar RTP reactions involving europium or calcium filings, and $^{\text{D}}\text{L}^{\text{M}}\text{H}$, were carried out, but no metal amide products were isolated from them.

Complexes **4-6** show good stability in the solid state, though **4** and **5** do decompose over several months at room temperature, under an inert atmosphere. Compound **4** is stable in C_6D_6 solutions for at least a week, which is not typical for calcium alkyls.²⁴ The ^1H NMR spectrum of the compound is consistent with its proposed unsymmetrical formulation, as evidenced by that spectrum exhibiting resonances for eight chemically inequivalent isopropyl methyl groups. The very poor solubility of **5** in aromatic solvents, and its instability in d_8 -thf solutions precluded the acquisition of meaningful NMR spectroscopic data for the compound. In contrast, compound **6** is soluble in C_6D_6 , and its ^1H NMR spectrum exhibits broadened methyl resonances that are suggestive of dynamic behaviour in solution (see below). The ^{171}Yb NMR spectrum of this complex in C_6D_6 features one sharp signal at δ 540 ppm. As a point of comparison, this resonance is considerably upfield from that for the three coordinate anionic bimetallic complex $[\text{LiYb}^{\text{II}}\{\text{N}(\text{SiMe}_3)\}_3]$ (δ 853 ppm), comparable to the signal for

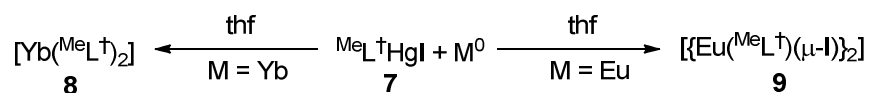
the four coordinate amide complex $[\text{Yb}^{\text{II}}\{\text{N}(\text{SiMe}_3)_2(\text{thf})_2\}]$ (δ 680 ppm), and downfield from the peak for two coordinate $[\text{Yb}^{\text{II}}\{\text{N}(\text{SiPr}'_3)_2\}_2]$ (δ 467 ppm).^{8c}

Although all of **4-6** were crystallographically characterised, the crystal structure of **4** was not of sufficient quality to publish here. With that said, refinement of that structure unambiguously confirmed the molecular connectivity shown in Scheme 1. Complex **5** (Figure 1) crystallises from toluene as a symmetrical dimer featuring two ytterbium centres possessing *pseudo*-tetrahedral coordination environments consisting of σ -covalent bonds to the amide nitrogen and a deprotonated *ortho*-carbon of the SiPh_3 group. These are in addition to two η^6 -arene interactions, one to a Dip group, and a closer η^6 -interaction to the deprotonated phenyl group of an opposing monomeric unit. As far as we are aware, this μ_2 - $\eta^1:\eta^6$ -arene bridging mode is new in organolanthanoid chemistry, but is reminiscent of η^6 -arene bridged amide and aryloxide complexes $[\text{Ln}_2\{\text{X}(2,6\text{-Pr}'_2\text{C}_6\text{H}_3)_6\}]$ ($\text{X} = \text{NH}$; $\text{Ln} = \text{La}$; $\text{X} = \text{O}$; $\text{Ln} = \text{Nd}, \text{Sm}$ or Er).²⁵

The solid-state structure of **6** (Figure 1) shows its ytterbium centre to possess a slightly distorted trigonal planar geometry. Trigonal planar lanthanoid complexes are rare, and to the best of our knowledge no other divalent, neutral monomeric lanthanoid complex with two amide and one thf ligand has been reported with such a geometry. Saying this, several anionic amide coordinated examples have been described in the literature, e.g. $[\{\text{M}(\text{solv.})_n\}\text{Ln}^{\text{II}}\{\text{N}(\text{SiMe}_3)_2\}_3]$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$; $\text{Ln} = \text{Eu}, \text{Sm}$ or Yb).²⁶ It is of note that the ytterbium coordination sphere could also include agostic interactions²⁷ with the C(7) methyl groups ($\text{C}(7)\cdots\text{Yb}(1)$ 3.120(3) Å, not shown in Figure 1) which could account for the broadening of the methyl signals in the ^1H NMR spectrum of the compound.

Direct redox transmetallation pathways

Alternative synthetic pathways were sought to try and access extremely bulky amide complexes of the lanthanoid metals. In this respect transmetallation reactions directly between a lanthanoid metal and an amido-mercury iodide were explored. Reactions between $[(^{\text{Me}}\text{L}^\dagger)\text{HgI}]$ and a slight excess of either ytterbium or europium filings in thf afforded moderate yields of the homoleptic ytterbium bis(amide) complex, **7**, and heteroleptic amido-europium iodide complex, **8** respectively (Scheme 2). Similar reactions between $[(^{\text{Me}}\text{L}^\dagger)\text{HgI}]$ and calcium, strontium, samarium and thulium metal were also attempted, however in those cases the only species detectable in ^1H NMR spectra of reaction aliquots was $^{\text{Me}}\text{L}^\dagger\text{H}$, or in the case of thulium, a mixture of $^{\text{Me}}\text{L}^\dagger\text{H}$ and $\text{Ar}^\dagger\text{NH}_2$.



Scheme 2. Synthesis of compounds **8** and **9**.

The formation of **8** is likely a result of a Schlenk-like redistribution reaction, examples of which are well known in lanthanoid chemistry.^{26d,28} The other product from such a reaction would be solvated YbI_2 , which was indeed isolated from the product mixture. While an unusual synthetic route, direct synthesis using organomercuric halides has previously been used to access bulky ytterbium triazenide chlorides,²⁹ and has in this study allowed access to bulky amido-lanthanoid complexes which are inaccessible by conventional protolysis or metathesis protocols.

The solid state structure of **8** (Figure 2) features an ytterbium centre coordinated by two $^{\text{Me}}\text{L}^\dagger$ ligands through their amido *N*-centres. In addition, one amide ligand (incorporating N(1)) exhibits an η^6 -interaction between a benzhydryl phenyl group and the ytterbium atom

(Yb(1)-Ct(1) 2.584(6) Å), while a phenyl group of the other amide (incorporating N(2)) interacts with the metal centre through one of its *ortho*-carbons (Yb(1)-C(54) 2.823(8) Å), or the C-H moiety associated with that carbon centre. These asymmetric Yb⋯aryl interactions have a significant impact on the coordination geometry of the ytterbium atom, the N-Yb-N angle of which (116.4(2)°) is significantly narrower than that in Mills and co-workers near linear [Yb{N(SiPr^{*i*})₂}₂] (N-Yb-N = 166.01(14)°), the Yb centre of which is more symmetrically coordinated by amido N-centres, and agostic interactions with C-H fragments.⁸ Also of note is the fact that the angle at Yb in **8** is narrower than that in the very bent two-coordinate system, [Yb{C(SiMe₃)₂}₂] (137.0(4) °).³⁰

Complex **9** (Figure 2) crystallises as a centrosymmetric iodide bridged dimer, with each europium additionally coordinated by an amido *N*-centre, a thf molecule, an η^6 -arene interaction to a benzhydryl phenyl group (Eu(1)-Ct(1) 2.795(3) Å), and an interaction to one *C*-centre (or its corresponding C-H unit) of another phenyl substituent (Eu(1)-C(28) 3.075(4) Å). The two bridging iodides are slightly asymmetrically coordinated to the Eu centres, which might be a reflection of the likely higher *trans*-influence of the amide centre relative to the other donor atoms (i.e. Eu(1)-I(1)_{*trans* to N} = 3.3793(4) Å vs. Eu(1)-I(1)_{*cis* to N} = 3.2456(4) Å).³¹ It is noteworthy that the magnesium analogue of **9** has been reported,¹² and while this is also an iodide bridged dimer, its magnesium centres are essentially four-coordinate as they only exhibit one η^2 -phenyl interaction each. The lower metal coordination number in this case is undoubtedly a result of the considerably smaller covalent radius of magnesium vs. that of europium.¹⁸

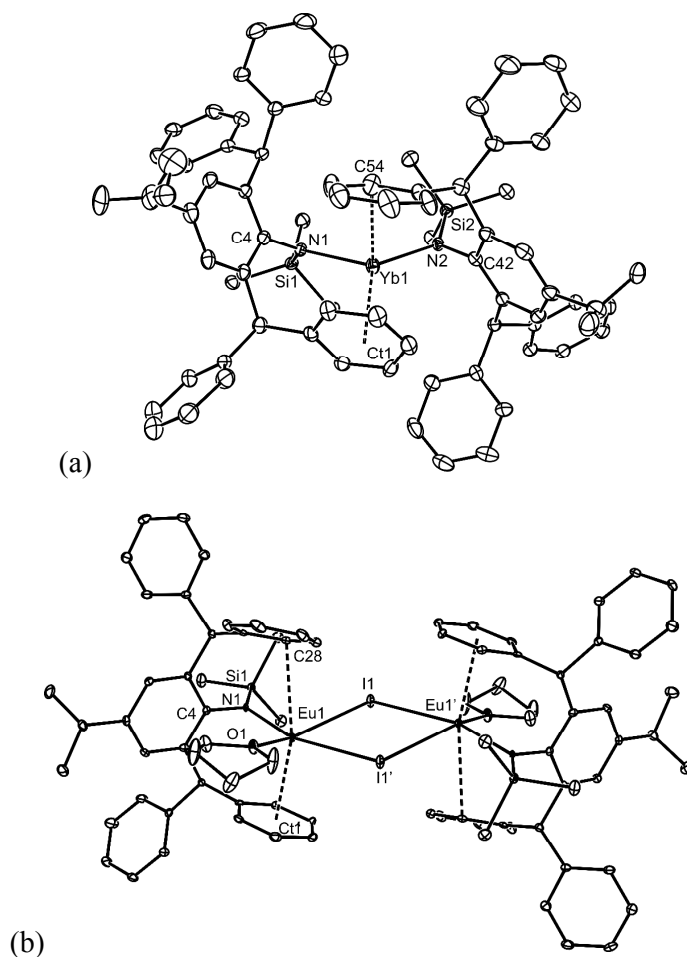


Fig. 2 Molecular structures of (a) **8** and (b) **9** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°) for **8**: Yb(1)-N(2) 2.330(5), Yb(1)-N(1) 2.338(5), Yb(1)-C(54) 2.823(8), Yb(1)-Ct(1) 2.584(6), N(2)-Yb(1)-N(1) 116.4(2), C(54)-Yb(1)-Ct(1) 104.2(2). Selected bond lengths (Å) and angles (°) for **9**: Eu(1)-N(1) 2.470(3), Eu(1)-O(1) 2.581(3), Eu(1)-C(28) 3.075(4), Eu(1)-I(1) 3.2456(4), Eu(1)-I(1)' 3.3793(4), Eu(1)-Ct(1) 2.795(4), N(1)-Eu(1)-O(1) 113.14(9), N(1)-Eu(1)-C(28) 73.92(10), O(1)-Eu(1)-C(28) 84.22(10), N(1)-Eu(1)-I(1) 88.60(7), O(1)-Eu(1)-I(1) 146.70(6), C(28)-Eu(1)-I(1) 77.81(8), N(1)-Eu(1)-I(1)' 163.25(7), O(1)-Eu(1)-I(1)' 79.87(6), I(1)-Eu(1)-I(1)' 75.22(1), Eu(1)-I(1)-Eu(1)' 104.78(1), Ct(1)-Eu(1)-N(1) 93.1(1), Ct(1)-Eu(1)-O(1) 94.7(1), Ct(1)-Eu(1)-I(1) 109.6(1). Symmetry transformations used to generate equivalent atoms: ' -x+1, -y, -z.

Conclusions

Preparations of a variety of extremely bulky amido-lanthanoid(II), and related calcium(II), complexes has been accomplished using redox transmetallation reactions, where more conventional synthetic routes have failed. In this respect, redox transmetallation protolysis reactions afforded unusual amido-metallo-cyclic complexes, **1-5**, featuring chelating, dianionic, C-H activated amido/organyl ligands. When smaller amide ligands are employed, the C-H activation processes can be circumvented and divalent amido-europium and ytterbium complexes, **6**, **8** and **9**, have been accessed by redox transmetallation protolysis and direct redox transmetallation pathways. The steric bulk of the amide ligands employed here, and their propensity to stabilise lanthanoid(II) complexes through arene interactions, suggests that they may prove useful for the synthesis of other divalent lanthanoid and lanthanoid-metal bonded systems. We are currently exploring these possibilities in our laboratory.

Experimental Section

General methods. All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Hexane, toluene, benzene and THF were distilled over molten potassium, while diethyl ether was distilled over Na/K alloy (1:1). ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{29}\text{Si}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$ and $^{171}\text{Yb}\{^1\text{H}\}$ NMR spectra were recorded on either Bruker AvanceIII 400 or DPX 300 spectrometers at 298 K and were referenced to the residual resonances of the solvent used, external SiMe_4 , $[\text{BF}_3(\text{OEt}_2)]$, or $[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{thf})_2]$ in a 9:1 tetrahydrofuran: C_6D_6 mixture. Mass spectra were collected using an Agilent Technologies 5975D inert MSD with a solid state probe. FTIR spectra were collected for solid samples as Nujol mulls on an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer.

Microanalyses were carried out at the Science Centre, London Metropolitan University. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. The compounds $\{(\text{HCNDip})_2\}\text{BNH}_2$, $^{32}\text{P}^{\text{h}}\text{L}^{\dagger}\text{H}$, $^{12}\text{D}^{\text{L}}\text{M}^{\text{H}11\text{b}}$ and $[\text{Me}^{\text{L}}\text{L}^{\dagger}\text{HgI}] \mathbf{7}^{14\text{a}}$ were prepared by literature procedures. All other reagents were used as received.

Preparation of $\text{P}^{\text{h}}\text{L}^{\text{B}0}\text{H}$. To a solution of $\{(\text{HCNDip})_2\}\text{BNH}_2$ (10.0 g, 24.9 mmol) in diethyl ether (100 mL) at $-78\text{ }^{\circ}\text{C}$ was added LiBu^n (16.3 mL, 1.6 M in hexane, 26.1 mmol) over 5 mins. The reaction mixture was removed from the cold bath and stirred at room temperature for 1.5 h. Ph_3SiCl (7.69 g, 26.1 mmol) was then added at $0\text{ }^{\circ}\text{C}$, and the resultant solution warmed to room temperature over a period of 12 h, whereupon volatiles were removed *in vacuo* and the residue extracted with hot hexane (80 mL). The extract was concentrated to *ca.* 15 mL and stored at $-30\text{ }^{\circ}\text{C}$ overnight to yield the title compound as a colourless crystalline solid (12.6 g, 73%). M.p.: $150\text{-}154\text{ }^{\circ}\text{C}$; ^1H NMR (400 MHz, C_6D_6): $\delta = 0.98$ (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.19 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 2.55 (s, 1H, NH), 3.39 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 6.04 (s, 2H, NCH), 7.00-7.35 (m, 21H, Ar-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): $\delta = 23.1$ ($\text{CH}(\text{CH}_3)_2$), 25.7 ($\text{CH}(\text{CH}_3)_2$), 28.7 ($\text{CH}(\text{CH}_3)_2$), 118.3 (NCH), 124.1, 128.1, 129.5, 135.5, 136.6, 138.9, 147.3 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): $\delta = -18.9$; $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): $\delta = 23.6$; IR ν/cm^{-1} (Nujol): 3020m (N-H str.), 1578m, 1567w, 1255m, 1190m, 1111s, 1071m, 934m, 803s, 757s, 737s, 697s; MS/EI m/z (%): 662.41 (MH^+ , 83.3), 404.32 ($\{(\text{HCNDip})_2\}\text{BNH}_2^+$, 100).

Preparation of $[\text{Ca}(\text{P}^{\text{h}}\text{L}^{\dagger}\text{H})(\text{thf})_2] (\mathbf{1})$. To a Schlenk flask charged with Ca filings (40 mg, 1.0 mmol), HgPh_2 (130 mg, 0.37 mmol) and $\text{P}^{\text{h}}\text{L}^{\dagger}\text{H}$ (265 mg, 0.37 mmol) was added a drop of mercury and 4 mL of tetrahydrofuran. This mixture was sonicated for 3 days at *ca.* $40\text{ }^{\circ}\text{C}$, and then left to stand for a day at room temperature, after which the reaction mixture was filtered

to remove excess calcium metal. The resultant clear red solution was concentrated to 1 mL *in vacuo* at 40 °C, then slowly cooled to room temperature. Overnight, red needle like crystals of **1** formed (130 mg, 39%). M.p: 187-189 °C (darkens); ^1H NMR (400 MHz, C_6D_6): δ = 1.17 (d, $^3J_{\text{H-H}} = 8$ Hz, 6H, CHCH_3), 1.26 (s, 8H, OCH_2CH_2) 2.78 (sept, $^3J_{\text{HH}} = 8$ Hz, 1H, CHCH_3), 3.06 (s, 8H, OCH_2), 6.39 (t, $^3J_{\text{HH}} = 7$ Hz, 2H, CaCPh_2 *p*-Ar-*H*), 6.58 (s, 1H, CHPh_2), 6.87 (t, $^3J_{\text{HH}} = 7$ Hz, 4H, CaCPh_2 *m*-Ar-*H*), 7.00-7.19 (m, 21H, Ar-*H*), 7.30 (d, $^3J_{\text{HH}} = 7$ Hz, 4H, CaCPh_2 *o*-Ar-*H*), 7.52 (d, $^3J_{\text{HH}} = 6$ Hz, 6H, SiPh_3 Ar-*H*); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ = 23.5 ($\text{CH}(\text{CH}_3)_2$), 24.2 (OCH_2CH_2), 32.4 ($\text{CH}(\text{CH}_3)_2$), 51.3 (CHPh_2), 61.3 (CaCPh_2) 67.4 (OCH_2), 113.0, 118.3, 123.3 125.0, 125.4 127.1, 127.1, 128.5, 129.2, 135.0, 139.8, 143.5, 145.9, 146.7 (Ar-*C*, some peaks not observed due to overlap with C_6D_6); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): δ = -38.6; IR ν/cm^{-1} (Nujol mull): 3058m, 1568m, 1414m, 1281m, 1258m, 1169m, 1098m, 1017m, 971m, 910w, 856m, 791m, 743s, 722vs; MS/EI m/z (%): 725 ($^{\text{Ph}}\text{L}^{\dagger}\text{H}^+$, 12), 259 (SiPh_3^+ , 90); anal. calc. for $\text{C}_{61}\text{H}_{61}\text{CaNO}_2\text{Si}$: C 80.66%, H 6.77%, N 1.54%; found: C 80.46%, H 6.67%, N 1.58%. N.B. crystals of **1** used for the X-ray diffraction experiment were grown from a benzene solution. N.B. compound **1** was also prepared in low yield by reaction of $^{\text{Ph}}\text{L}^{\dagger}\text{H}$ with activated calcium in thf, generated by condensation of calcium atoms in a thf/toluene matrix at 77 K using a metal vapour synthesis apparatus.^{13d}

Preparation of $[\text{Eu}(^{\text{Ph}}\text{L}^{\dagger-\text{H}})(\text{thf})_2]$ (2**).** To a Schlenk flask charged with Eu filings (120 mg, 0.79 mmol), HgPh_2 (233 mg, 0.66 mmol) and $^{\text{Ph}}\text{L}^{\dagger}\text{H}$ (477 mg, 0.66 mmol) was added a drop of mercury and 6 mL of tetrahydrofuran. This mixture was stirred for 6 days at room temperature, and then volatiles removed *in vacuo*. The residue was dissolved in toluene (15 mL), filtered, and the filtrate concentrated *in vacuo* to ca. 5 mL at 50 °C. Dark red crystals of **2** deposited upon standing overnight at room temperature (486 mg, 72%). M.p: 184-185 °C; No meaningful NMR data could be obtained for the complex due to its paramagnetic nature;

IR ν/cm^{-1} (Nujol mull): 3056w, 1570m, 1415m, 1092s, 1017s, 970w, 909w, 873m, 793s, 744m, 743m, 724vs; MS/EI m/z (%): 725 ($^{\text{Ph}}\text{L}^{\dagger}\text{H}^+$, 23), 259 (SiPh_3^+ , 100); anal. calc. for $\text{C}_{61}\text{H}_{61}\text{EuNO}_2\text{Si}$: C 71.82%, H 6.03%, N 1.37%; found: C 72.02%, H 6.16%, N 1.46%.

Preparation of $[\text{Yb}(\text{PhL}^{\dagger}\text{H})(\text{thf})_2]$ (3**).** To a Schlenk flask charged with Yb filings (431 mg, 2.5 mmol), HgPh_2 (680 mg, 1.9 mmol) and $\text{PhL}^{\dagger}\text{H}$ (1.39 g, 1.9 mmol) was added a drop of mercury and 10 mL of tetrahydrofuran. This mixture was sonicated for 3 days at *ca.* 40 °C, and then left to stand for a day, after which the reaction mixture was filtered to remove excess ytterbium metal. The resultant clear red solution was concentrated *in vacuo* to 3 mL and then 3 mL of hexane added. After standing overnight, dark red crystals of **3** had deposited (1.28 g, 64%). M.p.: 182-184°C; ^1H NMR (300 MHz, C_6D_6): δ = 1.16 (br, 6H, CHCH_3), 1.33 (br, 8H, OCH_2CH_2) 2.71 (br, 1H, CHCH_3), 3.16 (br, 8H, OCH_2) 6.37-7.84 (m, 38H Ar-*H* and CHPh_2); N.B. signals are broad due to the persistent presence of paramagnetic impurities; $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ = -46.2; no meaningful $^{13}\text{C}\{^1\text{H}\}$ or ^{171}Yb NMR data could be obtained due to the very low solubility of this complex in most organic solvents; IR ν/cm^{-1} (Nujol mull): 3058m, 1568m, 1414m, 1281m, 1170m, 1099m, 1020m, 970m, 910w, 864m, 791m, 743s, 722vs; MS/EI m/z (%): 725 ($^{\text{Ph}}\text{L}^{\dagger}\text{H}^+$, 20), 259 (SiPh_3^+ , 100); anal. calc. for $\text{C}_{61}\text{H}_{61}\text{YbNO}_2\text{Si}$: C 70.36%, H 5.90%, N 1.35%; found: C 70.16%, H 5.79%, N 1.23%.

Preparation of $[\text{Ca}(\text{PhL}^{\text{Bo-H}})(\text{thf})_2]$ (4**).** A Schlenk flask was charged with calcium filings (47 mg, 1.2 mmol), HgPh_2 (300 mg, 0.85 mmol), $\text{PhL}^{\text{Bo-H}}$ (560 mg, 0.85 mmol) and 5 mL of tetrahydrofuran. This mixture was stirred for 3 days at room temperature, during which time a brown colour developed. Volatiles were removed *in vacuo* and the residue extracted with 5 mL of toluene. The extract was concentrated to 2 mL and layered with 10 mL of hexane, then left at room temperature overnight to yield **4** as brownish-red crystals (210 mg, 35%). M.p.:

190-192 °C (darkens). ^1H NMR (300 MHz, C_6D_6): δ = 0.59 (d, $^3J_{\text{HH}} = 8$ Hz, 3H, CHCH_3), 1.05 (d, $^3J_{\text{HH}} = 8$ Hz, 3H, CHCH_3), 1.18 (br, 8H, OCH_2CH_2), 1.26 (d, $^3J_{\text{HH}} = 8$ Hz, 3H, CHCH_3), 1.33 (d, $^3J_{\text{HH}} = 8$ Hz, 3H, CHCH_3), 1.49 (d, $^3J_{\text{HH}} = 8$ Hz, 3H, CHCH_3), 1.56 (d, $^3J_{\text{HH}} = 8$ Hz, 3H, CHCH_3), 1.57 (s, 3H, CaCCH_3), 2.32 (s, 3H, CaCCH_3), 3.11 (s, 8H, OCH_2), 3.47 (sept, $^3J_{\text{HH}} = 8$ Hz, 1H, CHCH_3), 3.60 (sept, $^3J_{\text{HH}} = 8$ Hz, 1H, CHCH_3), 3.85 (sept, $^3J_{\text{HH}} = 8$ Hz, 1H, CHCH_3), 6.06 (d, 1H, $^3J_{\text{HH}} = 3$ Hz, 1H, NCH), 6.21 (d, 1H, $^3J_{\text{HH}} = 3$ Hz, 1H, NCH), 6.24 (d, $^3J_{\text{HH}} = 13$ Hz 1H, Ar-H), 6.35 (d, $^3J_{\text{HH}} = 13$ Hz 1H, Ar-H), 7.02-7.47 (m, 19H, Ar-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ = 22.3, 23.0 ($\text{CH}(\text{CH}_3)_2$), 25.2 (OCH_2CH_2), 25.9, 26.7, 27.0 ($\text{CH}(\text{CH}_3)_2$), 28.5, 28.6 ($\text{CH}(\text{CH}_3)_2$), 68.7 (OCH_2), 119.6, 121.1 (NCH), 123.0, 123.1, 124.8, 126.6, 128.9, 135.5, 136.0, 136.3, 143.1, 146.2, 147.7, 152.4 (Ar-C); N.B. not all expected signals observed due to coincidental overlaps; $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 128 MHz), δ = 23.9; IR (Nujol mull) ν/cm^{-1} : 3058m, 1568m, 1414m, 1281m, 1258m, 1169m, 1098m, 1017m, 971m, 910w, 856m, 791m, 743s, 722vs; MS/EI m/z (%): 660 ($^{\text{Ph}}\text{L}^{\text{Bo}+}$, 100), 259 (SiPh_3^+ , 23).

Preparation of $[\{\text{Yb}(\text{PhL}^{\text{Bo-H}})\}_2]$ (5**).** A Schlenk flask was charged with Yb filings (130 mg, 0.75 mmol), HgPh_2 (220 mg, 0.63 mmol) and $^{\text{Ph}}\text{L}^{\text{BoH}}$ (410 mg, 0.63 mmol). A drop of mercury and 10 mL of tetrahydrofuran were then added. This mixture was stirred for 3 days at room temperature during which time the solution became dark brown and opaque. Volatiles were removed *in vacuo* and the residue extracted with 5 mL of toluene. The extract was concentrated to 2 mL and layered with 10 mL of hexane, then left at room temperature overnight to yield **5** as black crystals (80 mg, 15%). M.p.: > 260 °C; NMR spectroscopic analyses of the compound were not possible as it was not sufficiently soluble in C_6D_6 or d_8 -toluene, and formed a complicated mixture of products when dissolved in d_8 -THF. IR ν/cm^{-1} (Nujol mull): 1600m, 1406m, 1261s, 1095s, 1019s, 865w, 800s, 700m; MS/EI m/z (%): 661

($^{\text{Ph}}\text{L}^{\text{Bo}}\text{H}^+$, 100), 403 ($\{(\text{HCNDip})_2\}\text{BNH}_2^+$, 26), 259 (SiPh_3^+ , 30); anal. calc. for $\text{C}_{88}\text{H}_{100}\text{B}_2\text{N}_6\text{Si}_2\text{Yb}_2$: C 63.45%, H 6.05%, N 5.05%; found: C 60.49%, H 6.32%, N 4.47%. N.B. The experimental carbon percentage was consistently low, as has been previously found for metal silylamide complexes, presumably due to the formation of silicon carbide.³³

Preparation of $[\text{Yb}(\text{D}^{\text{L}}\text{M})_2(\text{thf})]$ (6**).** To a Schlenk flask charged with Yb filings (200 mg, 1.56 mmol), HgPh_2 (146 mg, 0.41 mmol) and $\text{D}^{\text{L}}\text{M}\text{H}$ (244 mg, 0.82 mmol) was added a drop of mercury and 5 mL of tetrahydrofuran. This mixture was sonicated for 2 days at *ca.* 40 °C, then filtered. Volatiles were removed from the filtrate under reduced pressure, 20 mL of hexane added, and the extract concentrated *in vacuo* to 3mL. The concentrate was heated briefly at reflux and then allowed to slowly cool. Large, red-orange blocks of **6** deposited overnight (110 mg, 32%). M.p.: 164-168 °C, darkens to black; ^1H NMR (300 MHz, C_6D_6): δ = 0.95 (s, 6H, *p*-Me), 1.11 (d, $^3J_{\text{HH}} = 7$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 1.25 (m, 4H, OCH_2CH_2) 2.23 (s, 12H, *o*-Me), 2.68 (m, 4H, OCH_2), 3.32 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 6.77 (s, 4H, Ar-*H*), 7.00 (m, 2H, Ar-*H*), 7.03 (m, 4H, Ar-*H*); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ = 20.7 (*p*-Me), 22.0 (*o*-Me), 24.5 (OCH_2CH_2), 26.0 ($\text{CH}(\text{CH}_3)_2$), 28.5 ($\text{CH}(\text{CH}_3)_2$), 69.3 (OCH_2), 119.7, 124.5, 125.4, 131.5, 140.8, 151.3, 152.3 (Ar-*C*); $^{171}\text{Yb}\{^1\text{H}\}$ NMR (70 MHz, C_6D_6) δ = 540; IR (Nujol mull) ν/cm^{-1} : 3058w, 1587w, 1572sh, 1482s, 1455s, 1446s, 1363m, 1381m, 1332m, 1309m, 1232m, 1153w, 1104w, 1056m, 1034m, 1017m, 854s, 784m, 740m, 689s; MS/EI *m/z* (%): 295 ($\text{D}^{\text{L}}\text{M}\text{H}_2^+$, 100); anal. calc. for $\text{C}_{46}\text{H}_{64}\text{N}_2\text{OYb}$: C 66.24%, H 7.73%, N 3.36%; found: C 66.06%, H 7.89%, N 3.35%.

Preparation of $[\text{Yb}(\text{Me}^{\text{L}}\text{L}^\dagger)_2]$ (8**).** To a Schlenk flask charged with Yb filings (46 mg, 0.24 mmol) and $[\text{Me}^{\text{L}}\text{L}^\dagger\text{HgI}]$ (180 mg, 0.21 mmol) was added toluene (5 mL) and tetrahydrofuran (1.5 mL) at -78 °C. After stirring for 5 min a purple solution was formed. Overnight, the

majority of the ytterbium was consumed, whereupon the solution was filtered from residual ytterbium and a bright yellow powder, presumably $[\text{YbI}_2(\text{thf})_2]$. The filtrate was stored at $-30\text{ }^\circ\text{C}$ for a week, after which time purple crystals of **8** had grown (68 mg, 61%). M.p. $201\text{-}203\text{ }^\circ\text{C}$ (darkens). ^1H NMR (300 MHz, C_6D_6): $\delta = 0.49$ (s, 18H, $\text{Si}(\text{CH}_3)_3$), 1.18 (d, $^3J_{\text{HH}} = 7\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 2.73 (d, $^3J_{\text{HH}} = 7\text{ Hz}$, 2H, $\text{CH}(\text{CH}_3)_2$), 5.94 (br, 4H, CHPh_2), 6.09 (br, 4H, Ar-H) 7.02-7.82 (overlapping, 40H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): $\delta = 5.0$ ($\text{Si}(\text{CH}_3)_3$), 24.1 ($\text{CH}(\text{CH}_3)_2$), 24.7 ($\text{CH}(\text{CH}_3)_2$), 34.0 ($\text{CH}(\text{CH}_3)_2$), 53.1 (CHPh_2), 126.6, 128.6, 130.1, 138.2, 141.6, 144.9, 153.7 (Ar-C), one signal presumably obscured by solvent resonance; IR (Nujol mull) ν/cm^{-1} : 3059w, 3026w, 1598m, 1492m, 1465w, 1427s, 1388w, 1326m, 1161w, 1124m, 1075m, 1031m, 967w, 927s, 861m, 831s, 794w, 767m, 742m, 662s, 659w; MS/EI m/z (%): 467 ($\text{Ar}^\dagger\text{NH}_2^+$, 100%), 167 (CHPh_2^+ , 43%); anal. calc. for $\text{C}_{76}\text{H}_{80}\text{N}_2\text{Si}_2\text{Yb}$ C 72.99%, H 6.45%, N 2.24%; found: C 72.81%, H 6.68%, N 2.23%.

Preparation of $[\{\text{Eu}(\text{MeL}^\dagger)(\mu\text{-I})(\text{thf})_2\}_2]$ (9**).** To a Schlenk flask charged with Eu filings (150 mg, 0.99 mmol) and $[\text{MeL}^\dagger\text{HgI}]$ (320 mg, 0.34 mmol) was added thf (5 mL) at $-78\text{ }^\circ\text{C}$, then the mixture warmed to room temperature, yielding an orange suspension. The suspension was filtered, the filtrate concentrated to 1 mL, then stored at $-30\text{ }^\circ\text{C}$ overnight to yield **9** as orange crystals (80 mg, 26%). M.p. $185\text{-}188\text{ }^\circ\text{C}$ (darkens); No meaningful NMR data could be obtained for the complex due to its paramagnetic nature; IR (Nujol mull) ν/cm^{-1} : 3026w, 1598m, 1492m, 1448m, 1423m, 1388w, 1365m, 1321w, 1262m, 1232m, 1175w, 1120m, 1070m, 1029s, 924s, 859m, 830s, 769m, 745m, 708s, 698s, 662m. MS/EI m/z (%): 539 ($\text{MeL}^\dagger\text{H}^+$, 36), 467 ($\text{Ar}^\dagger\text{NH}_2^+$, 17%); anal. calc. for $\text{C}_{84}\text{H}_{96}\text{N}_2\text{Si}_2\text{Eu}_2\text{I}_2\text{O}_2$: C 56.69%, H 5.44%, N 1.57%; found: C 56.48%, H 5.41%, N 1.55%.

X-Ray Crystallography. Crystals of **1-3**, **5**, **6**, **8**, **9**, $^{\text{Ph}}\text{L}^{\dagger}\text{H}$, and $[\{\text{Yb}(\text{thf})_2(\mu\text{-Br})_2\}_\infty]$ suitable for X-ray structural determinations were mounted in silicone oil. Crystallographic measurements were carried out with either a Bruker Apex X8 diffractometer using a graphite monochromator and Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), or the MX1 beamline of the Australian Synchrotron ($\lambda = 0.7109 \text{ \AA}$).³⁴ The software package Blu-Ice³⁵ was used for synchrotron data acquisition, while the program XDS³⁶ was employed for synchrotron data reduction. All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97³⁷) using all unique data. Non-hydrogen atoms were typically refined anisotropically with hydrogen atoms included in calculated positions (riding model). Crystal data, details of data collections and refinement are given in Table S1 in the ESI.

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Supporting Information Available: Crystallographic data as CIF files for all crystal structures; further details of the crystallographic studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Redox Transmetallation Approaches to the Synthesis of Extremely Bulky Amido-Lanthanoid(II) and Calcium(II) Complexes

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TABLE OF CONTENTS ENTRY

Redox transmetallation protolysis and direct redox transmetallation reactions have been employed to access a variety of extremely bulky amido-lanthanoid(II), and related calcium(II), complexes which cannot be prepared using classical salt metathesis pathways.

