PERSPECTIVE

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Carbon bridged biphenolate ligands in rare earth chemistry

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Rare earth biphenolate species have become an increasingly studied series of complexes, owing to the diversity they offer over mononuclear aryloxide complexes, as well as their efficacy as catalysts and initiators in a range of organic transformations and polymerisation reactions. Compared to monodentate aryloxide ligands, biphenolate ligand systems are still in their infancy in rare earth coordination chemistry. In their limited use, the ligand 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (mbmpH$_2$) has been a popular candidate. This review aims to highlight the chemistry that has been explored thus far with these carbon bridged lanthanoid biphenolate systems.

1. Introduction

Alkoxide and aryloxide ligands have attracted significant attention over the last two decades, especially as bulky ligands for low coordination number lanthanoid complexes.[1–4] This attention has also led to a focus on methylene bridged biphenolate ligands, which have the propensity to act as dianionic, chelating ligands. These ligands can provide a more stereochemically rigid framework for the metal centre, offering the potential to affect stereospecific transformations, alongside reduced likelihood of redistribution reactions. Biphenolate ligand systems have been historically used to synthesise transition and main group metal coordination complexes, some of which have shown both significant, and selective catalytic activity.[5–14] Lanthanoid complexes bearing the same ligand subset also exhibit activity in a range of organic transformations. For example, biphenolate lanthanoid complexes are efficient initiators of the polymerisation of L-lactide, ε-caprolactone, and the highly stereoselective polymerisation of *rac*-lactide[13–16] as well as significant catalytic activity towards the Diels–Alder reaction of cyclopentadiene with methyl acrylate.[17] They have also been applied in sol gel methods,[1] and as feedstocks in MOCVD and ALD deposition of oxide layers.[18,19] This review does not extend to the chemistry of closely related biphenyldiolate systems (see however the work of Shibasaki[20–22] and Aspinall[23–25]).

1.1. Methylenebiphenol ligands

Methylene bridged biphenols offer a versatile, structural backbone for biphenolate chemistry. They are highly tuneable

ligands, as addition of simple alkyl substituents in the *ortho* and *para* positions can dramatically influence the coordination number, and solubility of their resulting complexes respectively. Additionally, these substituents can influence the acidity of the phenol, owing to the electron donating or withdrawing nature of the substituents. Further substitutions can be performed on the methylene bridge, altering solubility and steric properties (Fig. 1).

The primary focus of this review is the biphenol 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (mbmpH$_2$), bearing one *tert* butyl group in the *ortho* position of each phenyl ring, and one methyl group in the *para* positions (Fig. 2). The methylene bridge provides some flexibility to the ligand, and when coordinating to a metal centre can offer a wide range of coordination geometries with a variety of metals. 2,2′-Methylenebis(6-*tert*-butyl-4-methylphenol) is also commercially available making it a desirable starting material for a range of syntheses. The *ortho tert*-butyl group imposes steric demands at the metal site and also enhances solubility in low polarity solvents.

1.2. Rare earth biphenolate coordination modes

When considering the coordination of a phenolate ligand to a lanthanoid metal, there are two major influences: the steric effects of the ligand about the oxygen donor, and the ionic radius of the metal centre(s).[26–28] Fig. 3 displays some of the diverse coordination modes of the mbmp^{2-} ligand in a schematic form (free from coordinated solvent and auxiliary ligands on any main group metals for simplicity). The simplest form of divalent lanthanoid biphenolates involves two Ln(II) centres, and two mbmp^{2-} ligands, each with one terminal and one bridging oxygen atom [Ln(mbmp)]$_2$[29,30] (Fig. 3 – I). The only heterobimetallic divalent lanthanoid complex consists of a divalent samarium centre and two aluminium atoms. The samarium centre is coordinated to an mbmp^{2-} ligand through

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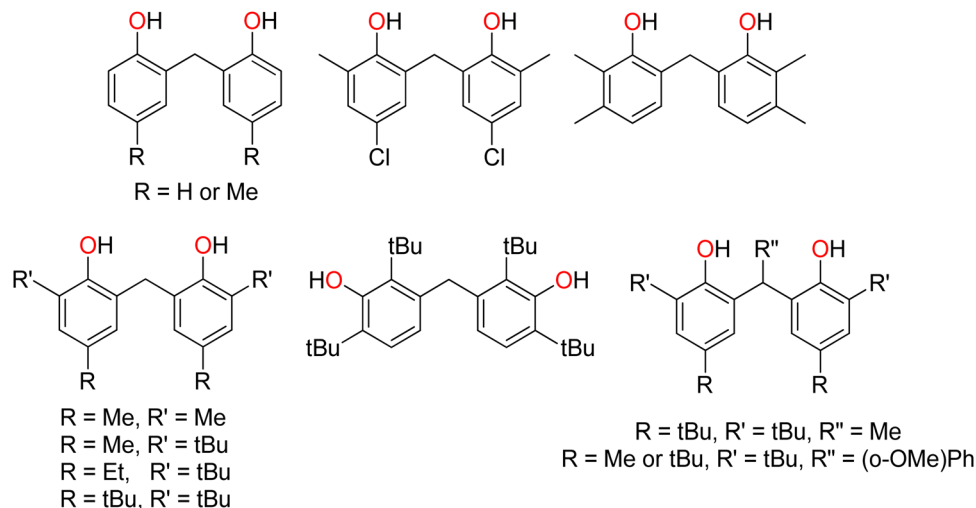
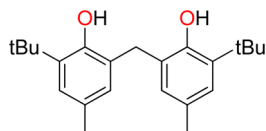Fig. 1   A range of common, substituted methylene bridged biphenol pro-ligands.

Fig. 2   2,2′-Methylenebis(6-tert-butyl-4-methylphenol) (mbmpH$_2$).

one bridging oxygen, and an η^2-intramolecular coordination of the *ipso* carbon, alongside intramolecular η^6-π-arene coordination in [Sm(mbmp)Al$_2$L$_2$][31] (L = Me) (Fig. 3 – **II**). A third coordination mode is reported where the Ln metal is coordinated to one oxygen of each ligand while the auxiliary metal coordinates to both [Ln(mbmp)$_2$M$_2$][31] (Fig. 3 – **III**).

Comparatively, the simplest trivalent complexes involve a trivalent Ln centre, ligated by two ligands, where one is fully deprotonated, and the other partially deprotonated [Ln(mbmp)-(mbmpH)][32,33] (Fig. 3 - **IV and V**). Coordination of the phenolic oxygen OH is reported in particular solvents (Fig. 3 – **IV**). Simple heteroleptic complexes have also been reported containing a trivalent Ln centre with one fully deprotonated mbmp^{2-} ligand, and an ancillary monoanionic ligand [Ln(mbmp)L][16,34–36] (L = Cp, N(SiMe$_3$)$_2$ or 3,5-dimethylpyrazolate) (Fig. 3 – **VI**). In most reported cases, the biphenolate ligand bridges between two Ln metal atoms to form a dinuclear complex such as [Ln$_2$(mbmp)$_3$][33] (Fig. 3 – **VII**), or [Ln$_2$(mbmp)$_4$M$_2$][37] (Fig. 3 – **VIII**). Less common variations involve heterobimetallic species where the auxiliary metal coordinates to the bridging phenolate oxygens such as [Ln(mbmp)$_2$M][31] (Fig. 3 – **IX**) and [Ln$_2$(mbmp)$_4$M][37,38] (Fig. 3 – **X**). Whilst displayed very generally, each example of these coordination modes is further discussed in this review in more detail.

2. Synthesis of rare earth biphenolate complexes

Several major synthetic routes are regularly employed for the synthesis of both divalent and trivalent rare earth biphenolate

complexes, including halide metathesis, protolysis, and redox transmetallation/protolysis reactions.

2.1.   Divalent lanthanoid biphenolate complexes by salt elimination metathesis

The divalent oxidation state is most readily accessible under normal conditions for the metals samarium, europium and ytterbium. Biphenolate chemistry of the rare earths in the divalent state is quite scarce, and only a few complexes have been reported. The Shen group prepared the first Eu^{2+} carbon bridged biphenolate complex[30] as a dinuclear species from a halide metathesis reaction utilising the sodium salt of mbmpH$_2$ and EuCl$_3$ in thf:hmpa (hexamethylphosphoric amide) (10:1). The resulting intermediate species was treated with Na–K alloy for reduction of the metal from Eu^{3+} to Eu^{2+} (Scheme 1).

2.2.   Divalent lanthanoid biphenolate complexes by protolysis/ligand exchange

Alternatively, the Shen group accessed divalent lanthanoid biphenolates by protolysis reactions, utilising lanthanoid silylamides ([Ln{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] where Ln = Sm, and Yb) as the lanthanoid starting material (Scheme 2).[29] Reactions were undertaken using the corresponding lanthanoid silylamide, and the protonated mbmpH$_2$ ligand in toluene at room temperature to afford [Ln(mbmp)(thf)$_n$]$_2$ (Ln = Sm, n = 3; Ln = Yb, n = 2) and crystallisation from hmpa led to [Ln(mbmp)(solv)]$_2$ (Ln = Sm, solv = (hmpa)$_2$, and Ln = Yb, solv = (hmpa)(thf)) complexes. Divalent lanthanoid complexes of mbmp^{2-} show poor solubility in thf, and thus hmpa was added as a cosolvent to crystallise the complexes.

The peralkylated aluminate samarium complex [Sm(AlMe$_4$)$_2$] reagent has also been utilised for the synthesis of the divalent samarium biphenolate complex [(AlMe$_2$)(AlMe$_4$)Sm(mbmp)] (Scheme 3).[31] This complex undergoes further reactivity with *tert*-butylisocyanate, yielding the insertion product

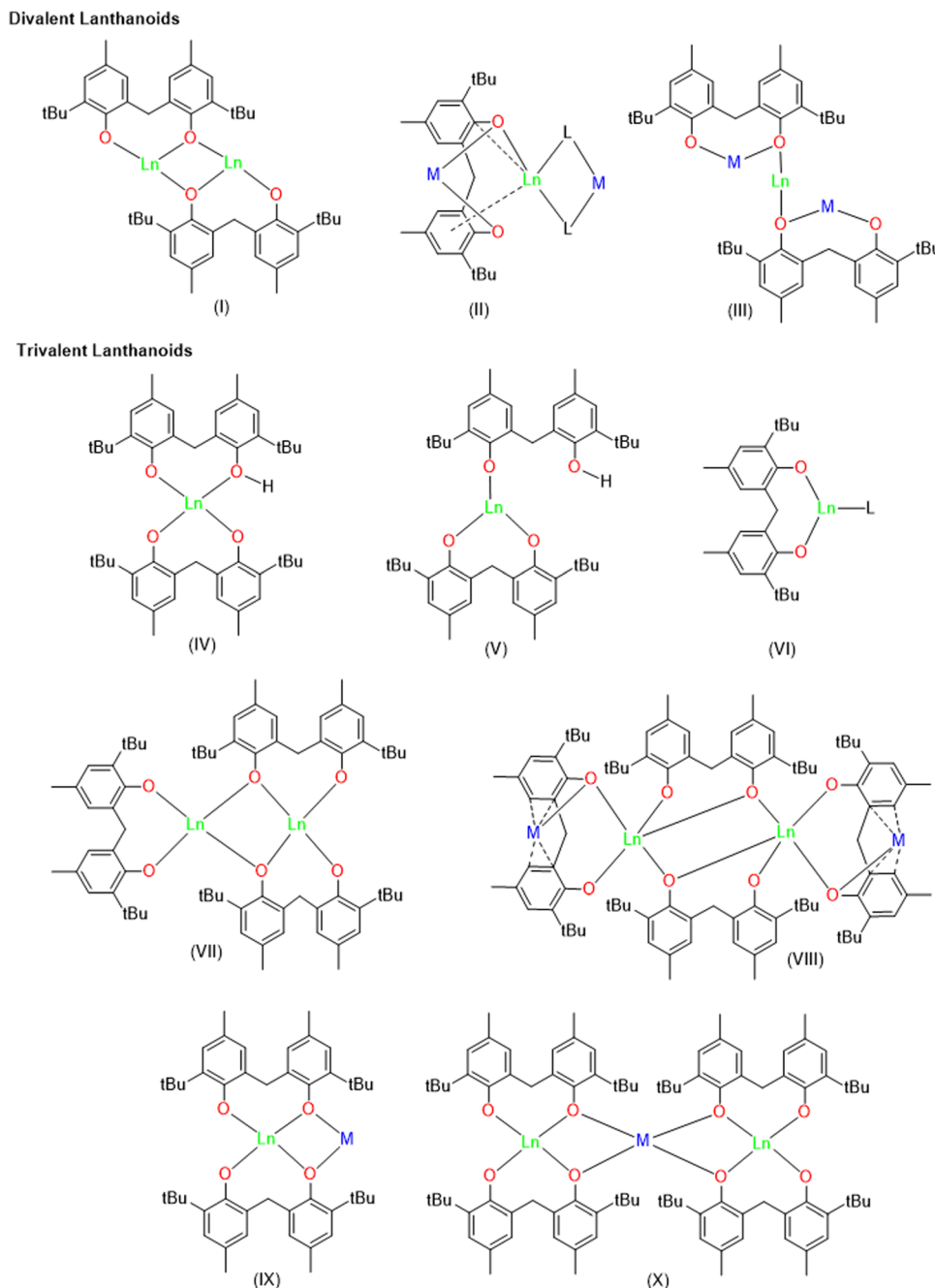**Fig. 3** A range of coordination modes of the mbmp^{2-} ligand in neutral rare earth, and rare earth/main group heterobimetallic complexes.[23–32] M represents a range of alkali metals or aluminium, where auxiliary ligands are excluded for simplicity.

[Sm{(mbmp)AlMe(^{t}BuNCO)}$_2$] with insertion into an Al–Me bond (Scheme 3).

Alternatively, when treated with azobenzene and recrystallised from thf, the samarium biphenolate aluminate undergoes oxidation and redistribution to yield [AlMe$_2$Sm(mbmp)$_2$(thf)$_2$] (Scheme 4). The use of thf as a crystallisation solvent means that the crystal structure of the complex may potentially differ to that of the actual product formed in toluene. Additionally, the fate of the reduced azobenzene, and several Al–Me$_x$ units, was not explained.

2.3. Trivalent lanthanoid biphenolate complexes by salt elimination metathesis

Much like the synthesis of divalent lanthanoid biphenolate complexes, the synthesis of trivalent lanthanoid biphenolate complexes typically involves treating the rare earth halide with the alkali metal salt of the biphenolate ligand, eliminating an alkali metal halide. One of the major drawbacks of salt metathesis reactions is the potential for incorporation of the alkali metal or halide ions into the final structure. For example, the reaction of NdCl$_3$ and LiCH$_2$SiMe$_3$ in the presence of the
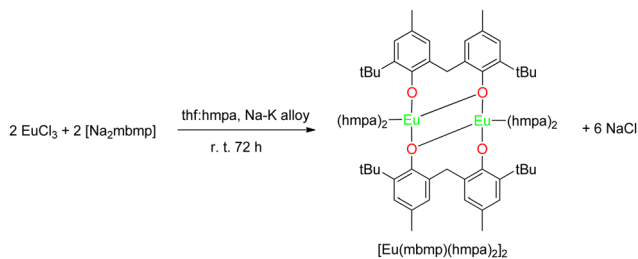
Scheme 1 Metathesis reaction, and subsequent reduction by Na–K alloy, to form [Eu(mbmp)(hmpa)$_2$]$_2$.[30]

protonated biphenol pro-ligand (bpoH$_2$) (where bpoH$_2$ = mbmpH$_2$, 6,6′-methylenebis(2,4-di-*tert*-butylphenol) (mbbpH$_2$) or 6,6′-(ethane-1,1-diyl)bis(2,4-di-*tert*-butylphenol) (edbpH$_2$)), firstly undergoes salt metathesis, then subsequent protolysis, yielding both the lithium incorporated product [Li(thf)Nd-(edbp)$_2$(thf)$_2$], and lithium chloride incorporated product [Li$_2$(thf)$_3$(μ-Cl)Nd(bpo)$_2$(thf)] (Scheme 5).[39] Attempts to avoid the ligand redistribution by reducing the reaction time and temperature to 30 minutes and 0 °C respectively were unsuccessful.

Metathesis reactions with lanthanoid halides and alkali metal salts of biphenolates can lead to either ionic, or non-ionic heterobimetallic complexes depending on the solvent system used. The Shen group exhibited this by treating LnCl$_3$ (Ln = Nd, Sm, Er and Yb) with two equivalents of Na$_2$mbmp in thf, yielding the corresponding molecular [Ln(mbmp)$_2$(thf)$_n$-Na(thf)$_2$] (Ln = Nd, Sm, n = 2, and Ln = Er, Yb, n = 1) complexes (Scheme 6).[17,40]

Of these biphenolate complexes, the Nd, Sm, and Yb hetero-bimetallics were susceptible to forming the ionic complexes [Na(dme)$_2$(thf)$_2$][Ln(mbmp)$_2$(thf)$_2$] when taken up into a mixture of toluene and dme (Scheme 7).[40]

Further variability in the products was observed when using the larger potassium salt of the biphenolate ligand for metathesis reactions with LnCl$_3$ where Ln = La, Sm, Nd, and Yb. The Sm and Yb complexes [Ln(mbmp)$_2$(thf)$_2$K(thf)$_n$] show structural similarities to their sodium analogues (Scheme 8),[37] whereas the La complex is a charge separated species with a solvated potassium cation, and a two lanthanum centred, potassium bridged anion [K(thf)$_6$][La(mbmp)$_2$(thf)$_2$(μ-K)La(mbmp)$_2$(thf)$_2$] (Scheme 9),[37] and Nd forms a large tetranuclear molecular complex [K(thf)$_2$Nd(mbmp)$_2$]$_2$ (Scheme 10).[37]

The cerium(III) biphenolate has also been synthesised by metathesis, utilising Ce(OTf)$_3$ and the lithium biphenolate salt to form the lithium cerium heterobimetallic complex [Li(thf)$_2$Ce(mbmp)$_2$(thf)$_2$] (Scheme 11).[41] The two thf molecules coordinated to the Ce^{3+} ion could be displaced by 2,2′-bipyridine, giving [Li(thf)$_2$Ce(mbmp)$_2$(bipy)], whereas addition of benzophenone displaced the coordinated thf on both the Ce^{3+} and Li$^+$ cations yielding [Li(L)Ce(mbmp)$_2$(L)$_2$] (L = benzophenone) (Scheme 11).[41]

In a similar fashion, the Shen group has performed salt elimination metathesis reactions with lanthanoid borohydrides to avoid halide inclusion. Sodium lanthanoid ionic complexes
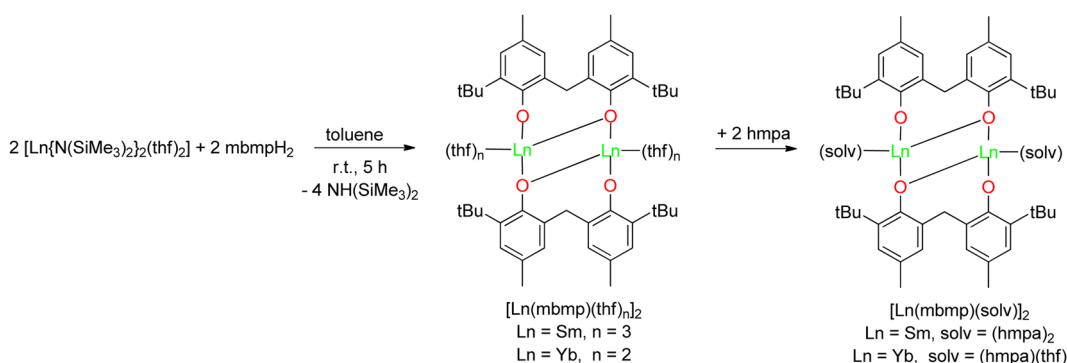

Scheme 2 Protolysis reaction to form [Ln(mbmp)(thf)$_n$]$_2$ and [Ln(mbmp)(solv)]$_2$ divalent biphenolate complexes.[29]
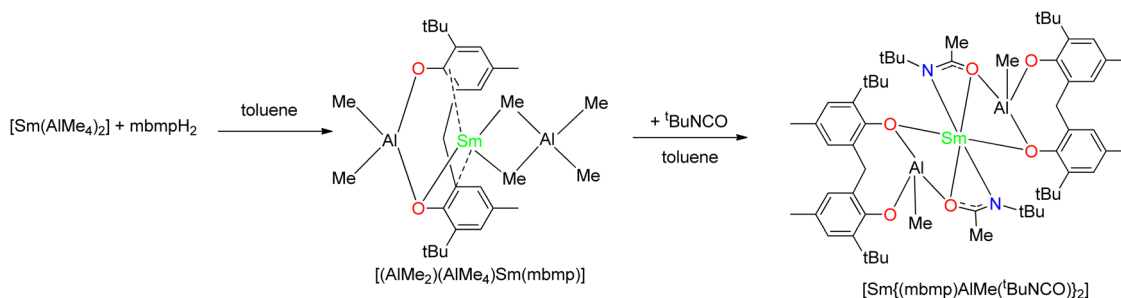
**Scheme 3** Formation of divalent samarium biphenolate heterobimetallic complexes from peralkylated aluminate samarium complex [Sm(AlMe$_4$)$_2$].[31]
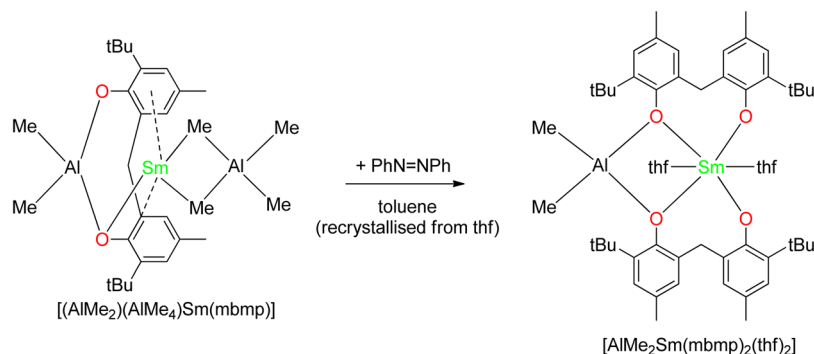
Scheme 4 Oxidation and redistribution reaction of [(AlMe₂)(AlMe₄)Sm(mbmp)] induced by azobenzene yielding [AlMe₂Sm(mbmp)₂(thf)₂].[31]
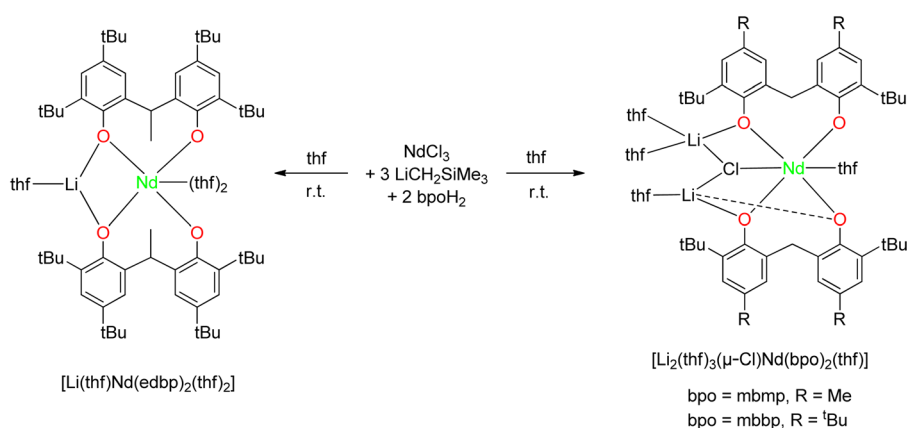
Scheme 5 Salt elimination metathesis/protolysis reactions of NdCl₃ yielding the lithium incorporated [Li(thf)Nd(edbp)₂(thf)₂], and lithium chloride incorporated [Li₂(thf)₃(μ-Cl)Nd(bpo)₂(thf)] (bpo = mbmp, and mbbp) complexes.[39]
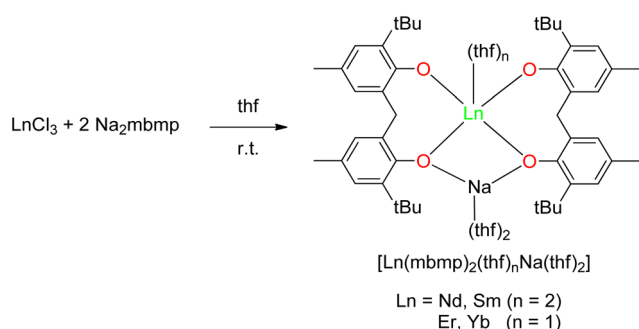
Scheme 6 Salt elimination metathesis reactions of LnCl₃ with Na₂mbmp in 1 : 2 stoichiometry, yielding sodium–lanthanoid bimetallic biphenolate complexes [Ln(mbmp)₂(thf)ₙNa(thf)₂].[17,40]

have been synthesised by treatment of [Ln(BH₄)₃(thf)₃] (Ln = Er, Yb and Sm) with Na₂edbp in dme to yield the ionic species [Na(dme)₃][Ln(edbp)₂(dme)] (Scheme 12).[42] This synthetic approach avoids the solubility issues associated with lanthanoid halide starting materials.

The Shen group has also employed metathesis with heteroleptic lanthanoid amide halide starting materials to form heteroleptic ionic biphenolate amide complexes. Treatment of [Ln{N(SiMe₃)₂}₂Cl(thf)] (Ln = Nd and Yb) with mbmpH₂ in the presence of two equivalents of *n*-butyllithium at −10 °C in thf

yielded the ionic complexes [Li(thf)₄][Ln(mbmp){N(SiMe₃)₂}₂] (Scheme 13).[34]

2.4. Trivalent lanthanoid biphenolate complexes by protolysis/ligand exchange

Synthesis of rare earth biphenolate complexes by protolysis/ligand exchange methods offers a convenient, alternative synthetic route to salt elimination metathesis methods, and eliminates the opportunity for halide and alkali metal inclusion into the final complex. The Shen group has utilised this method to synthesise simple trivalent biphenolate complexes from [LnCp₃(thf)] (Ln = Y, La and Yb) starting materials, firstly by forming the heteroleptic [Ln(mbmp)Cp(thf)ₙ] complexes by treatment of [LnCp₃(thf)] with one equivalent of mbmpH₂ in thf. Further treatment with a second equivalent of mbmpH₂ in toluene led to either [Ln(mbmp)(mbmpH)(thf)₂] (Ln = Y, Sm and Yb), or the dinuclear [La₂(mbmp)₃(thf)₃] complex (Scheme 14).[33] It has been suggested that the nuclearity of the complex is dependent on the size of the Ln³⁺ cation, with La³⁺ being considerably larger than the Y³⁺ and Yb³⁺ cations. Analogous complexes [Ln(mbmp)Cp(thf)₂] (Ln = Sm and Nd) were also synthesised by the same route, but, were not treated further with mbmpH₂ (Scheme 14).[34]

The partially deprotonated complexes of Y, Yb and Sm are of particular interest, as the protonated phenol allows for further
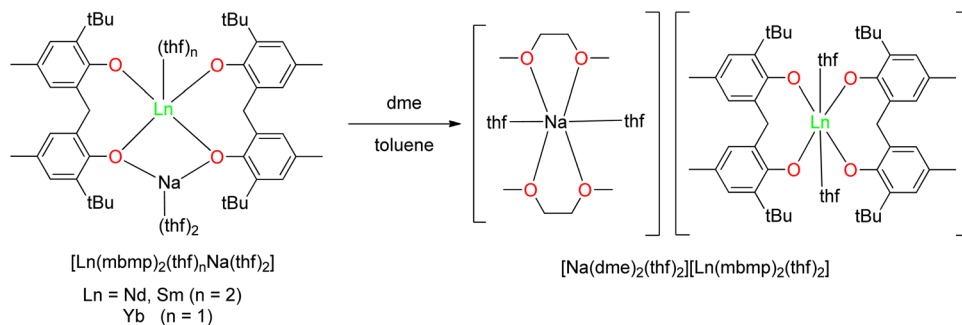
Scheme 7 Formation of ionic species [Na(dme)$_2$(thf)$_2$][Ln(mbmp)$_2$(thf)$_2$] where Ln = Nd, Sm and Yb, upon changing solvent from thf to a dme:toluene mixture.[40]
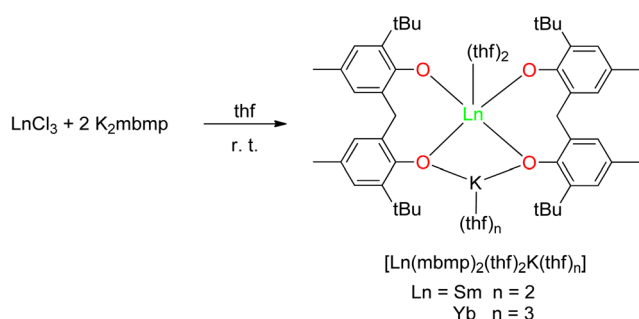
Scheme 8 Metathesis reaction of LnCl$_3$ with K$_2$mbmp to form [Ln(mbmp)$_2$(thf)$_2$K(thf)$_n$] (Ln = Sm, n = 2 and Ln = Yb, n = 3).[37]

deprotonation reactions to be undertaken quite readily. The Shen group attempted to explore this by treatment of [Ln(mbmp)(mbmpH)(thf)$_2$] complexes with basic organometallic reagents to form heterobimetallic species, but with limited success. Treatment of the above Yb complex with nBuLi resulted in formation of the desired heterobimetallic [Yb(mbmp)$_2$(thf)Li(thf)$_2$] (Scheme 15(a)). In contrast, treatment of [Yb(mbmp)(mbmpH)(thf)$_2$] with one equivalent of AlEt$_3$ resulted in redistribution, and isolation of the discrete ion pair [Yb(mbmp)(thf)$_2$(dme)][Yb(mbmp)$_2$(thf)$_2$] (Scheme 15(b)). Treatment of the [Ln(mbmp)(mbmpH)(thf)$_2$] (Ln = Y, Yb) species with ZnEt$_2$ also resulted in redistribution, yielding the dinuclear zinc biphenolate complex [Zn(mbmp)(thf)$_2$] (Scheme 15(c)).[33]
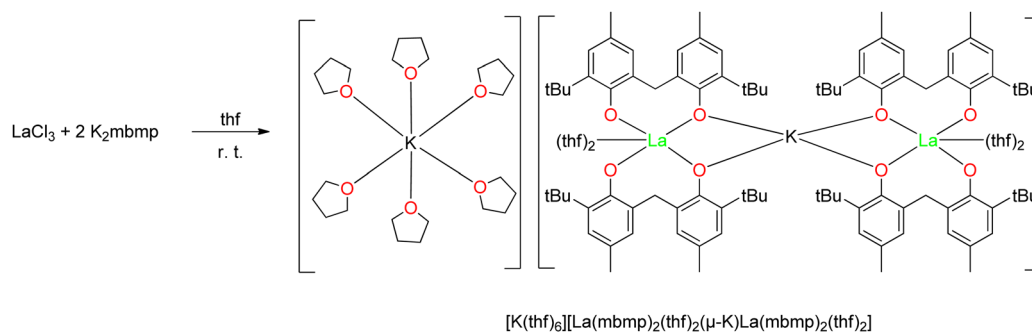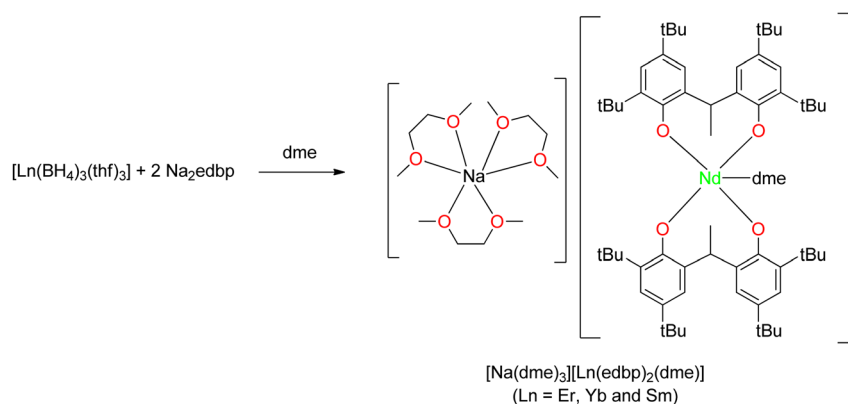

Scheme 9 Formation of the charge separated ionic species [K(thf)$_6$][La(mbmp)$_2$(thf)$_2$(μ-K)La(mbmp)$_2$(thf)$_2$].[37]
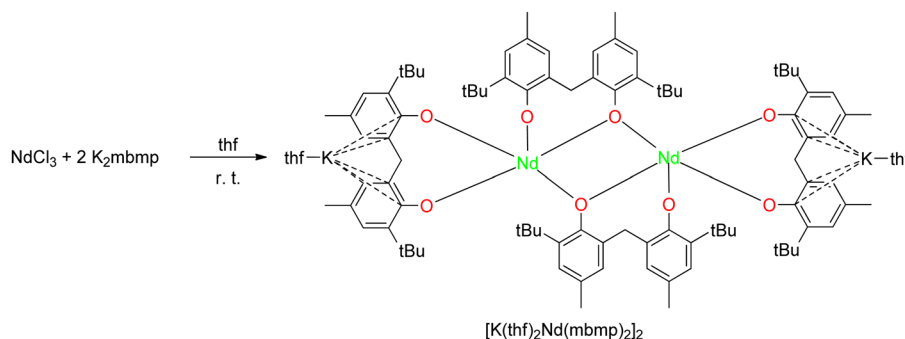
Scheme 10 Synthesis of tetranuclear Nd–K complex [K(thf)$_2$Nd(mbmp)$_2$]$_2$.[37]
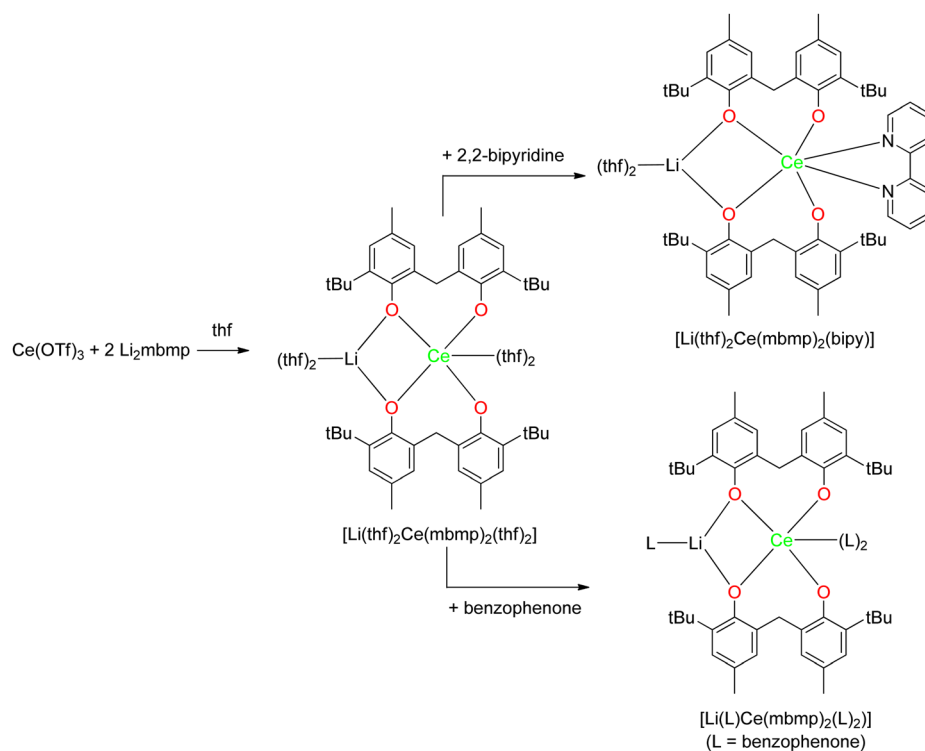
**Scheme 11** Metathesis reactions utilising Ce(OTf)$_3$ and Li$_2$mbmp giving the cerium–lithium heterobimetallic [Li(thf)$_2$Ce(mbmp)$_2$(thf)$_2$], and subsequent ligand exchange reactions (where L = benzophenone).[41]

Scheme 12 Synthesis of [Na(dme)$_3$][Ln(edbp)$_2$(dme)] (Ln = Er, Yb and Sm) from lanthanoid borohydride starting materials.[42]
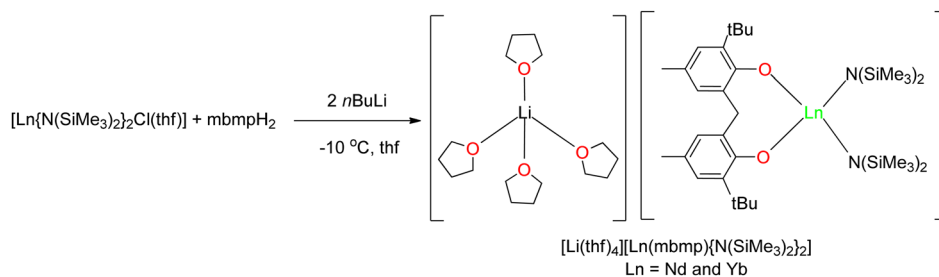
Scheme 13 Synthesis of [Li(thf)$_4$][Ln(mbmp){N(SiMe$_3$)$_2$}$_2$] by metathesis from heteroleptic lanthanoid amide halide starting materials.[34]
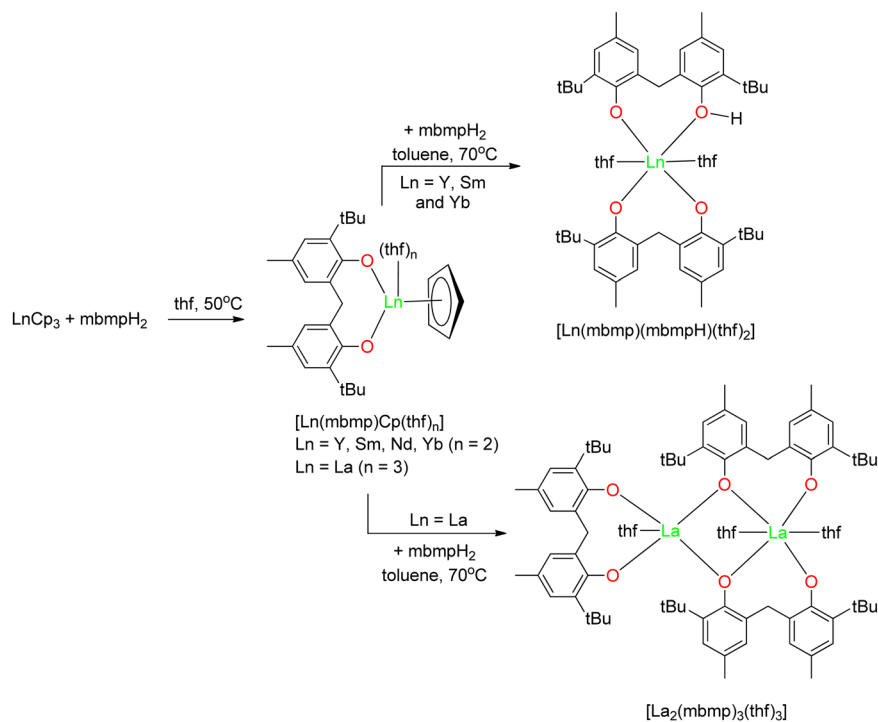
Scheme 14 Synthesis of heteroleptic [Ln(mbmp)Cp(thf)$_n$] where Ln = Y, Sm, Nd (n = 2) and La (n = 3), and subsequent treatment with mbmpH$_2$.[34]
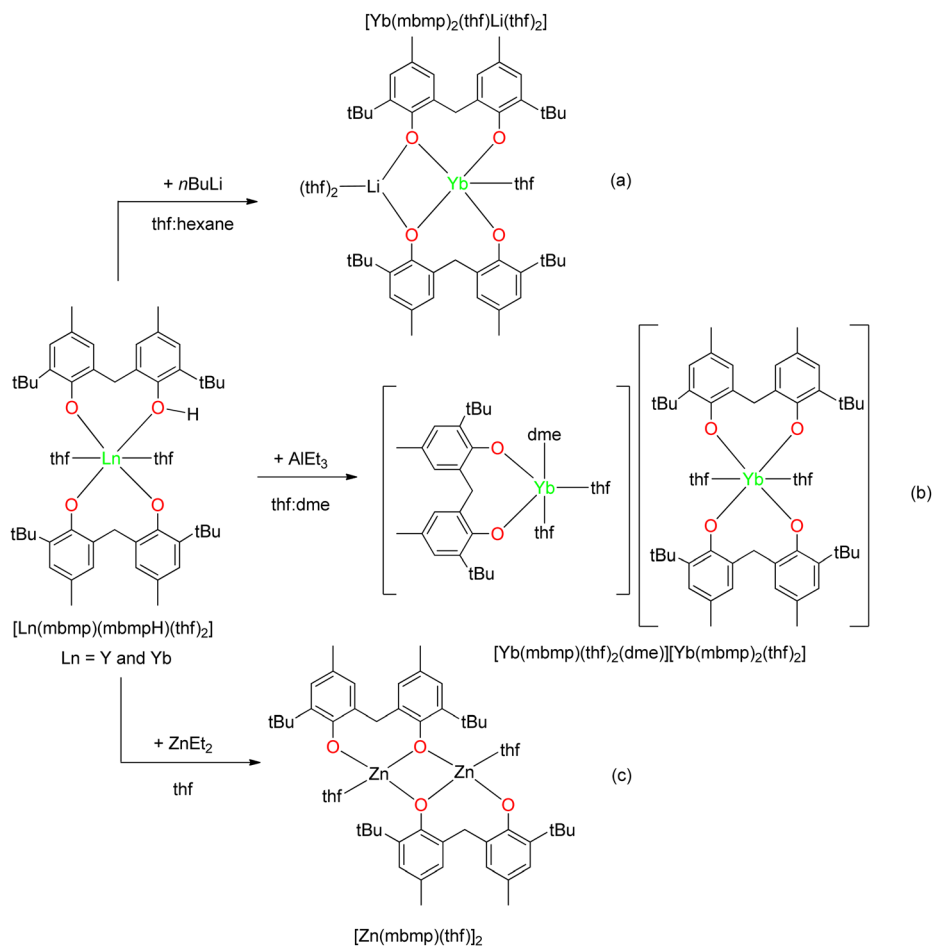
Scheme 15 Further reactivity of [Ln(mbmp)(mbmpH)(thf)$_2$] (Ln = Y and Yb) complexes with: (a) nBuLi, (b) AlEt$_3$ and (c) ZnEt$_2$.[33]
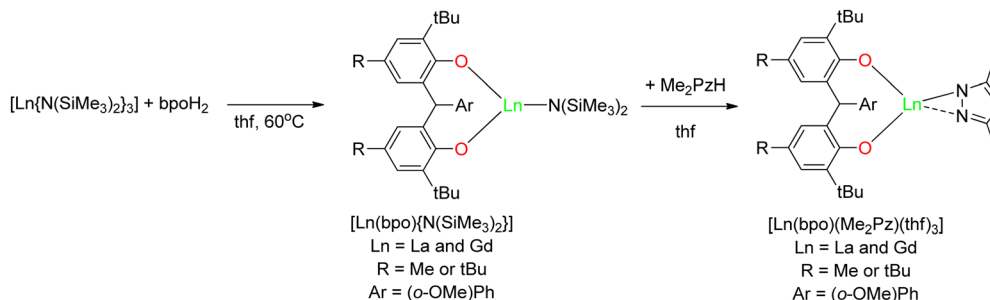
Scheme 16 Stepwise protolysis of lanthanoid silylamide starting materials with bulky biphenols (mbmpaH$_2$ and mbbpaH$_2$) and subsequent protolysis with 3,5-dimethylpyrazole.[35]

This stepwise protolysis of lanthanoid starting materials allows for facile synthesis of interesting heteroleptic complexes. The Shen group utilised a similar method to that outlined in Scheme 14 with the lanthanoid amide starting material [Ln{N(SiMe$_3$)$_2$}$_2$] (Ln = La and Gd) and the bulkier biphenols 6,6′-((2-methoxyphenyl)methylene)bis(2-(*tert*-butyl)-4-methylphenol) (mbmpaH$_2$) and 6,6′-((2-methoxyphenyl)methylene)bis(2,4-di-*tert*-butylphenol) (mbbpaH$_2$). Treatment of [Ln{N(SiMe$_3$)$_2$}$_2$] with one equivalent of biphenol (bpoH$_2$) at 60 °C led to formation of [Ln(bpo){N(SiMe$_3$)$_2$}], which could undergo further protolysis

with 3,5-dimethylpyrazole (MePzH), yielding [Ln(bpo)(Me$_2$Pz)-(thf)$_3$] (Scheme 16).[35]

Furthermore, a range of phenols and alcohols of varying steric bulk were applied in the same fashion using the [Ln(mbmp)Cp(thf)$_2$] (Ln = La, Sm, Nd and Yb) starting materials, yielding a variety of mono- and di-nuclear complexes (Scheme 17).[16,43]

Similar to the metathesis reactions previously described with heteroleptic lanthanoid amide halide starting materials (Scheme 13), these reagents can also be utilised directly for
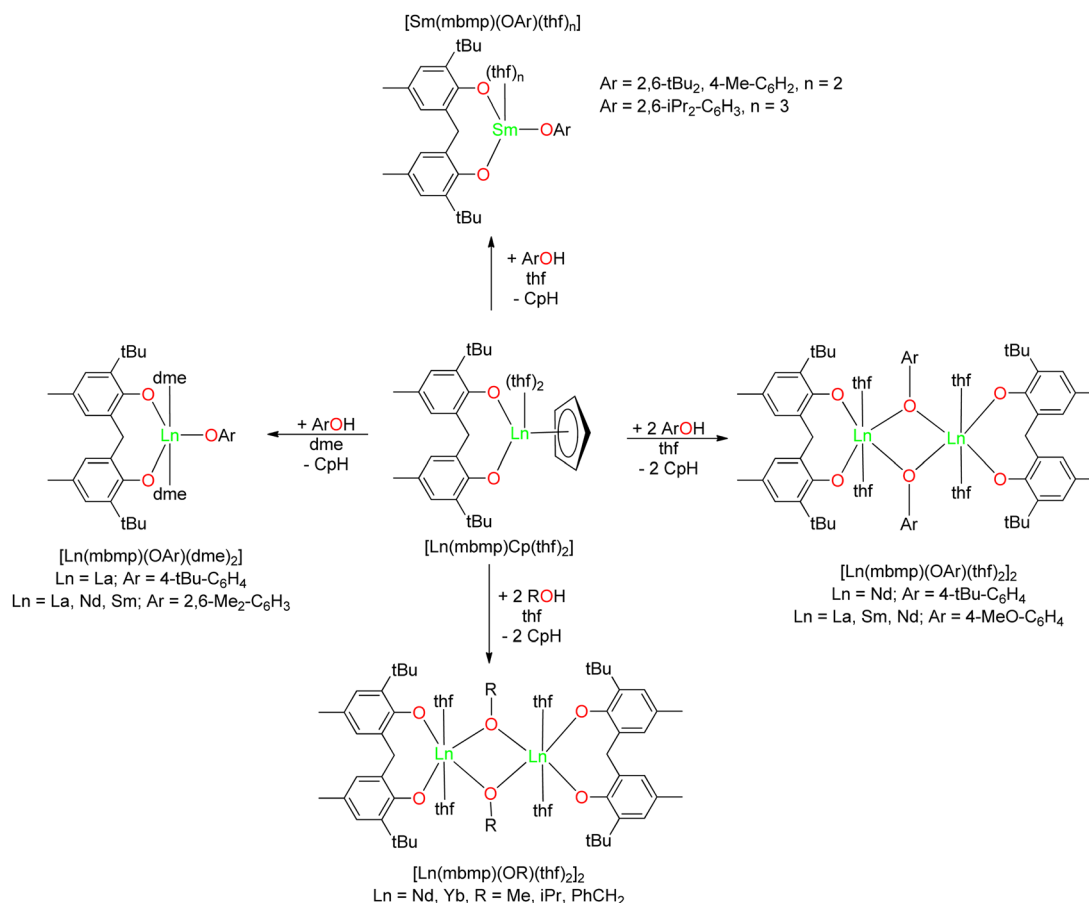
Scheme 17 Reactions of alcohols and phenols with [Ln(mbmp)Cp(thf)$_2$] yielding both mono- and di-nuclear complexes.[16,43]
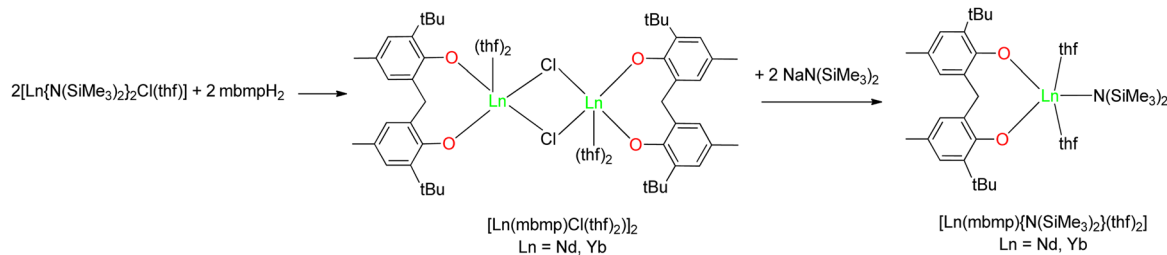
Scheme 18 Protolysis reaction of lanthanoid amide halides followed by subsequent metathesis to yield heteroleptic [Ln(mbmp){N(SiMe₃)₂}(thf)₂] (Ln = Nd and Yb) complexes.[44]

Scheme 19 Treatment of [Ln(mbmp){N(SiMe₃)₂}(thf)₂] with diisopropylcarbodiimide (iPr-N=C=N-iPr).[44]
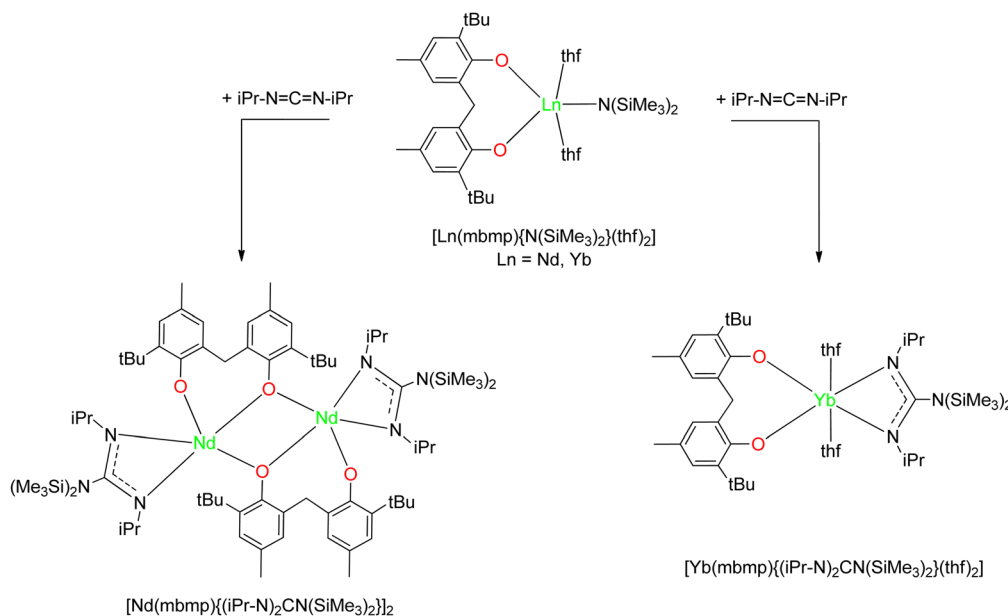
protolysis reactions owing to the basic nature of the amide ligand. The heteroleptic [Ln{N(SiMe₃)₂}₂Cl(thf)] (where Ln = Nd, and Yb) can be treated with one equivalent of mbmpH₂ to yield [Ln(mbmp)Cl(thf)₂]₂ (Scheme 18).[44] To assess the synthetic utility of the lanthanoid chloride complexes, further metathesis reactions were undertaken with NaN(SiMe₃)₂, yielding [Ln(mbmp)-{N(SiMe₃)₂}(thf)₂] (Scheme 18).[44]

Subsequent treatment of the heteroleptic silylamide complexes [Ln(mbmp){N(SiMe₃)₂}(thf)₂] (Ln = Nd and Yb) with diisopropylcarbodiimide (iPr-N=C=N-iPr) facilitated insertion into the Ln–N bonds, resulting in the heteroleptic guanidinate complexes, with the larger neodymium ion forming a dinuclear complex [Nd(mbmp){(iPr-N)₂CN(SiMe₃)₂}]₂, whilst the smaller ytterbium ion yielded the mononuclear guanidinate complex [Yb(mbmp){(iPr-N)₂CN(SiMe₃)₂}(thf)₂] (Scheme 19).[44]

In contrast, the homoleptic [Sm{N(SiMe₃)₂}₃] starting material has also been utilised alongside AlMe₃ with mbmpH₂ in toluene at 70 °C to directly synthesise the unsolvated samarium aluminium biphenolate complex [AlMe₄Sm(mbmp)]₂ (Scheme 20). Further protolysis could be achieved with another equivalent of

mbmpH₂ in toluene at 70 °C, yielding [AlMe₂Sm(mbmp)₂(thf)₂] (Scheme 20).[31]

2.5. Trivalent lanthanoid biphenolate complexes by redox transmetallation/protolysis

Until recently, salt metathesis and protolysis/ligand exchange reactions were the only two reported methods for synthesising lanthanoid biphenolate complexes. We have since synthesised a wide variety of new, simple lanthanoid biphenolate complexes, both mono- and di-nuclear in nature, utilising the redox transmetallation protolysis (RTP) reaction.[45] This process involves treatment of the lanthanoid metal in its free form with bis-(pentafluorophenyl)mercury (Hg(C₆F₅)₂) and the phenol mbmpH₂. The lanthanoid metal firstly undergoes redox transmetallation with the Hg(C₆F₅)₂, reducing the Hg²⁺ to Hg, and transferring the C₆F₅⁻ ligands to the now oxidised lanthanoid metal. This lanthanoid reagent can then readily undergo protolysis with the acidic mbmpH₂ ligand, yielding the desired lanthanoid biphenolate. This synthetic approach has been extensively applied to
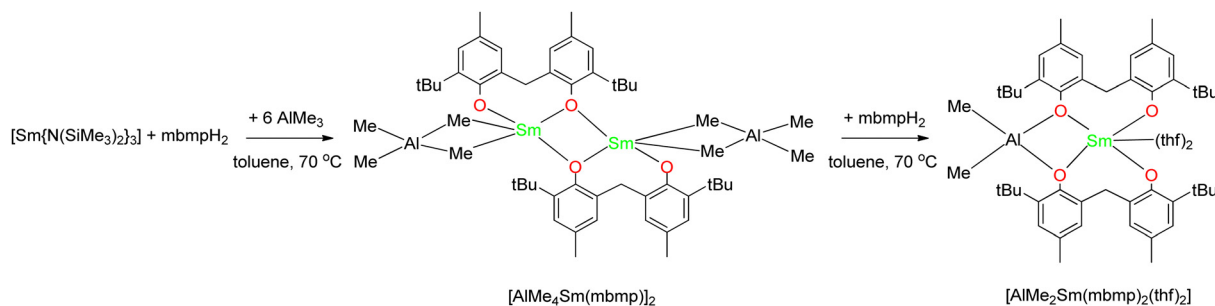
Scheme 20 Synthesis of dinuclear samarium aluminium biphenolate [AlMe₄Sm(mbmp)]₂ and subsequent protolysis.[31]

phenol pro-ligands;[45] but, no such application had been used for biphenols until recently.

A series of partially protonated lanthanoid biphenolate complexes were synthesised by RTP reactions from the free Ln metal, mbmpH₂ and Hg(C₆F₅)₂, yielding complexes of the general form [Ln(mbmp)(mbmpH)(thf)₃] (Ln = Y, Nd, Gd, Dy, Er, Tm and Lu) (Scheme 21).[32]

These complexes vary slightly from those synthesised by protolysis by the Shen group, [Ln(mbmp)(mbmpH)(thf)₂], in that the protonated phenol is not coordinated to the metal centre, and instead a third molecule of thf occupies the 6th coordination site. Recrystallisation of the yttrium complex from non-coordinating toluene led to loss of this third thf molecule, and coordination of the phenol, akin to the products reported by Shen *et al*. Formation of aluminium–lanthanoid hetero-bimetallic species was attempted by treatment of the [Ln(mbmp)-(mbmpH)(thf)₃] complexes with AlMe₃, but only the yttrium complex formed the desired bimetallic species [AlMe₂Y(mbmp)₂-(thf)₂] (Scheme 22). In all other cases only the aluminium biphenolate [AlMe(mbmp)(thf)] was isolated from the solution, except with the dysprosium analogue, where the aluminium biphenolate was isolated alongside the dinuclear dysprosium complex [Dy₂(mbmp)₃(thf)₃] (Scheme 22), suggesting that redistribution was the driving force for the aluminium biphenolate formation.[32]

When treating the [Ln(mbmp)(mbmpH)(thf)₃] (Ln = Y, Dy, Er and Lu) complexes with *n*-butyllithium as an organometallic base, they formed either a molecular complex [Li(thf)₂Ln(mbmp)₂(thf)] (Ln = Er and Lu) or an ionic complex [Li(thf)₄][Ln(mbmp)₂(thf)₂]

(Ln = Y and Dy) (Scheme 23).[38] Although the reactivities can be correlated with a change in size of the trivalent ion, a break between Y^{3+} and Er^{3+} is a surprise.

The gadolinium complex [Gd(mbmp)(mbmpH)(thf)₃] readily reacts with K{N(SiMe₃)₂} to form the heterobimetallic [K(thf)₃Gd(mbmp)₂(thf)₂] (Scheme 24).[38]

Using the same RTP approach and reaction conditions as those used for the synthesis of partially protonated [Ln(mbmp)-(mbmpH)(thf)₃] complexes (Scheme 21), dinuclear complexes of the general form [Ln₂(mbmp)₃(thf)ₙ] (Ln = Sm, Tb (*n* = 2), and Ho, Yb (*n* = 3)) are synthesised (Scheme 25).[38] Importantly, these reaction conditions left one unreacted equivalent of mbmpH₂ in solution. Whilst it was previously thought that the nuclearity of the complex was dictated by the ionic radius of the metal centre, there appears to be no correlation with these newly described species.

Whilst many of the partially protonated lanthanoid complexes were unable to form heterobimetallics by further proto-lysis with AlMe₃, these dinuclear complexes, in the presence of one equivalent of mbmpH₂, readily undergo redistribution to form a range of molecular and ionic heterobimetallic complexes when treated with organometallic bases *n*BuLi, AlMe₃, and ZnEt₂. When treated with *n*BuLi in the presence of one equivalent of mbmpH₂, [Yb₂(mbmp)₃(thf)₂] underwent redistribution to form the heterobimetallic [Li(thf)₂Yb(mbmp)₂(thf)], whereas [Ln₂(mbmp)₃(thf)ₙ₊₁] (Ln = Sm, *n* = 2, and Ln = Ho, *n* = 1) complexes gave the ionic heterobimetallic complexes [Li(thf)₄][Ln(mbmp)₂(thf)₂] (Scheme 26).[38]

Similarly, the dinuclear complexes [Ln₂(mbmp)₃(thf)₃] (Ln = Sm and Tb) in the presence of one equivalent of mbmpH₂ also underwent redistribution when treated with AlMe₃, yielding the molecular heterobimetallic species [AlMe₂Ln(mbmp)₂(thf)₂] (Ln = Sm and Tb) (Scheme 27).[38]

Further, the ytterbium complex [Yb₂(mbmp)₃(thf)₂] and one equivalent of mbmpH₂ would also undergoes a similar redistribution when treated with ZnEt₂, yielding [ZnEtYb-(mbmp)₂(thf)] (Scheme 28).[38] Interestingly, when the partially protonated [Yb(mbmp)(mbmpH)(thf)₂] species was treated with ZnEt₂ in a similar fashion, only [Zn(mbmp)(thf)₂] was isolated.[33]

Whilst the standalone biphenolate complexes of lanthanum and praseodymium were not isolated when synthesised by the RTP reaction, treatment of the reaction mixtures with
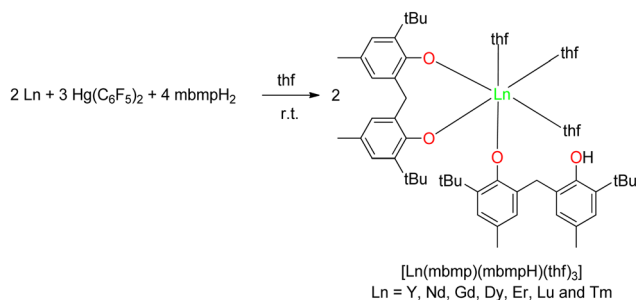
Scheme 21 Redox transmetallation protolysis reactions of lanthanoid metals with Hg(C₆F₅)₂ and mbmpH₂ yielding partially protonated [Ln(mbmp)(mbmpH)(thf)₃] (Ln = Y, Nd, Gd, Dy, Er, Lu and Tm) complexes.[32]
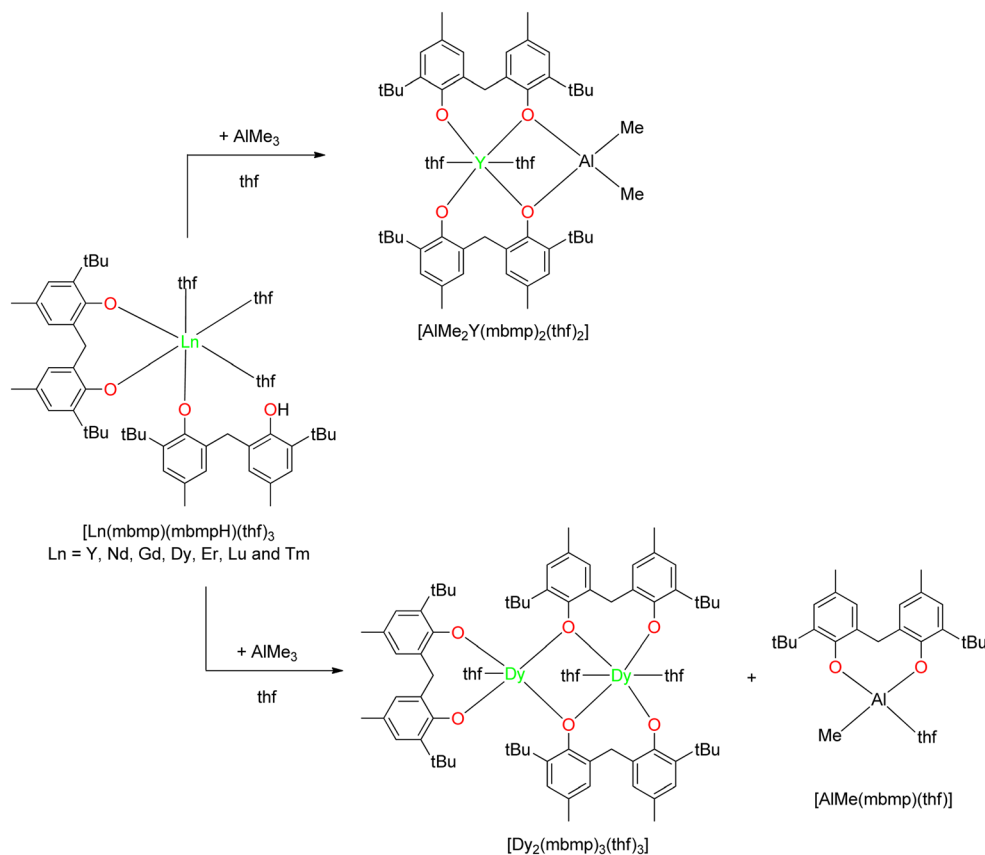
Scheme 22   Reactions of partially protonated lanthanoid biphenolate complexes [Ln(mbmp)(mbmpH)(thf)₃] with AlMe₃.[32]

organometallic bases led to isolation of heterobimetallic species. Thus, reactions of La metal with mbmpH₂ and Hg(C₆F₅)₂ in thf at room temperature did not lead to an isolable product, but when the reaction mixture was treated with nBuLi or AlMe₃, the heterobimetallics [Li(thf)₂La(mbmp)₂(thf)₂] and [La(mbmp)(thf)₅][Al(mbmp)Me₂] were isolated (Scheme 29).[38] The same reactions with Pr metal led to isolation of [Li(thf)₂-Pr(mbmp)₂(thf)₂] and [AlMe₂Pr(mbmp)₂(thf)₂] (Scheme 29).[38]

2.6.   Tetravalent lanthanoid biphenolate complexes

The chemistry of tetravalent lanthanoid biphenolates is quite limited, with only a few complexes reported. The Schelter group has synthesised cerium(IV) biphenolate complexes firstly by salt metathesis of Ce(OTf)₃ with Li₂mbmp, yielding the already discussed [Li(thf)₂Ce(mbmp)₂(thf)₂], and then oxidising this with common copper halide reagents (CuCl₂, CuBr₂) or simply with I₂, resulting in a mixture of the mononuclear Ce(mbmp)₂(thf)₂ and the heterobimetallic [Li(thf)ₙCe(mbmp)₂-(thf)X] (X = Cl, Br or I depending on the oxidant used) (Scheme 30).[41] Treatment of the mixture with 2,2-bipyridine led to isolation of the pure [Ce(mbmp)₂(bipy)] complex in good yield (Scheme 30).[41]

RTP reactions have also been used to synthesise [Ce(mbmp)₂(thf)₂] in a one pot reaction, but, with very limited yields (Scheme 31).[38]

3. Catalysis

In general, the catalytic activity of lanthanoid complexes is largely influenced by the coordination environment around the metal centre, in addition to the electronic properties of the lanthanoid metal.[44] In this aspect, biphenolate ligands have several encouraging qualities in catalytic design, as they are highly tuneable to allow for tailor-made single site catalysts, an important characteristic for controlled polymerisation reactions.[34] Historically, the biphenolate ligand has only been utilised as an ancillary ligand in lanthanoid chemistry,[40,43] but as some lanthanoid biphenolate complexes have been shown to be effective and selective catalysts in organic transformations, namely the ring-opening polymerisation of cyclic esters, they have become increasingly studied.[14,17,43,46–48]

3.1.   Divalent lanthanoid biphenolate catalysts

Owing to the limited number of divalent lanthanoid biphenolate complexes synthesised compared to their trivalent counterparts, examples of divalent biphenolate complexes as catalysts is relatively limited. Of the readily accessible divalent lanthanoid metals, samarium(II) species tend to be the most common catalysts studied, owing to their outstanding chemical reactivity with a wide range of substrates. The complex [Sm(mbmp)-(AlMe₄)(AlMe₂)] failed to act as a catalyst for the polymerisation of ethylene, even in the presence of additional activators,
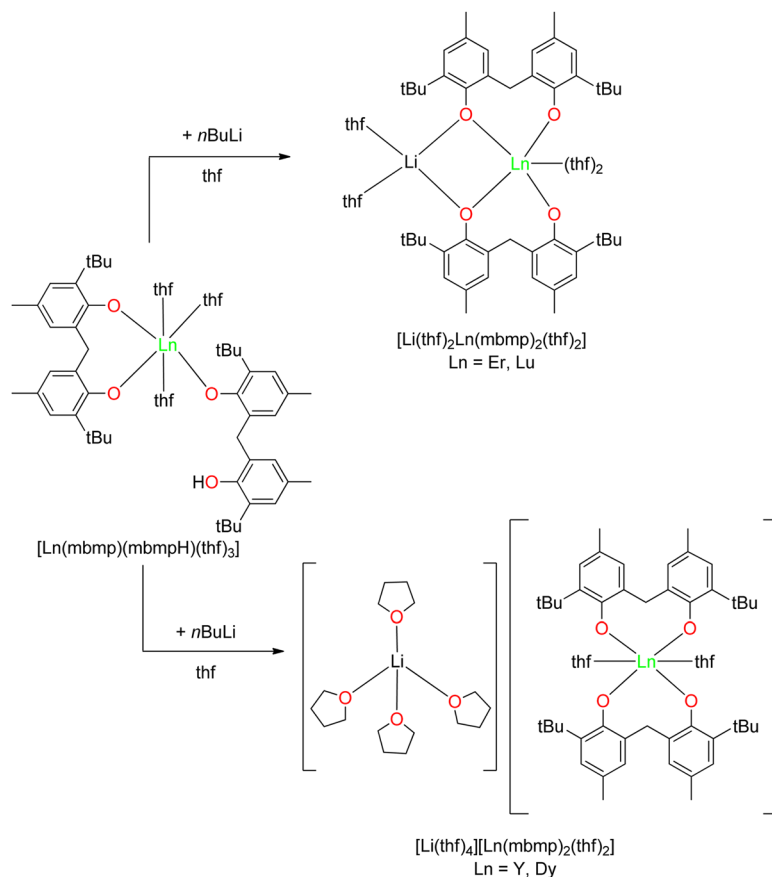
Scheme 23 Further reactivity of partially protonated lanthanoid biphenolate complexes [Ln(mbmp)(mbmpH)(thf)$_3$] with nBuLi.[38]
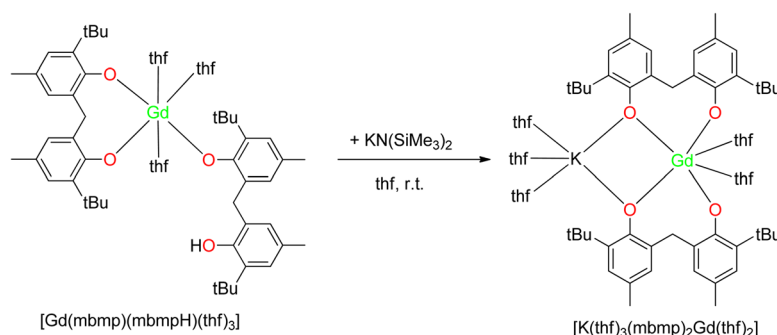
Scheme 24 Reactivity of partially protonated gadolinium biphenolate complex [Gd(mbmp)(mbmpH)(thf)$_3$] with KN(SiMe$_3$)$_2$.[38]

whereas [AlMe$_2$Sm(mbmp)(thf)$_2$] is capable of initiating polymerisation under usual Ziegler–Natta catalytic conditions (in the presence of alkyl aluminium activators).[31]

The divalent complexes [Ln(mbmp)(solv)] (Ln = Sm, solv = 2 hmpa, and Ln = Yb, solv = 1 hmpa, 1 thf) showed catalytic activity for the homo- and co-polymerisation of ε-caprolactone and 2,2-dimethyltrimethylene carbonate. These complexes were capable of catalysing the ring opening polymerisation of ε-caprolactone with moderate polydispersity indices (PDIs) (PDI < 1.80) and were also effective at catalysing the ring opening polymerisation of 2,2-dimethyltrimethylene carbonate,

and also gave polymers with relatively low PDIs (PDI < 1.55). The copolymerisation of ε-caprolactone and 2,2-dimethyltrimethylene carbonate at room temperature was also possible with these complexes, and gave random copolymers with high molecular weights, again, with relatively narrow PDIs (PDI < 1.6).[29]

3.2. Trivalent lanthanoid biphenolate catalysts

Compared to their divalent counterparts, trivalent lanthanoid biphenolate complexes have seen considerably more use. They can act as effective initiators for the ring opening
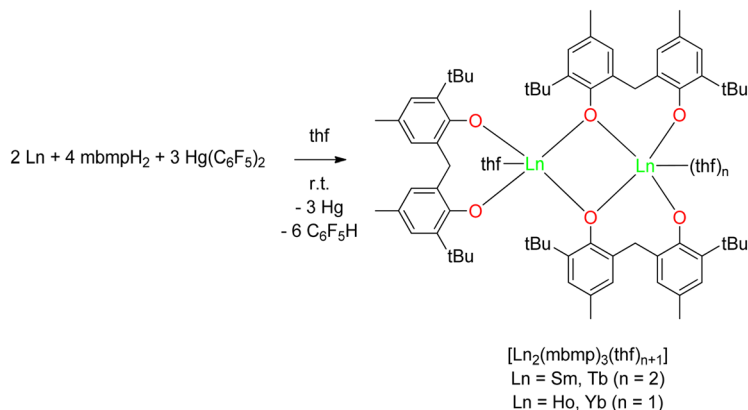
Scheme 25 Synthesis of dinuclear lanthanoid biphenolate complexes [Ln$_2$(mbmp)$_3$(thf)$_{n+1}$] (Ln = Sm, Tb (n = 2), and Ho, Yb (n = 1) complexes by RTP.[38]
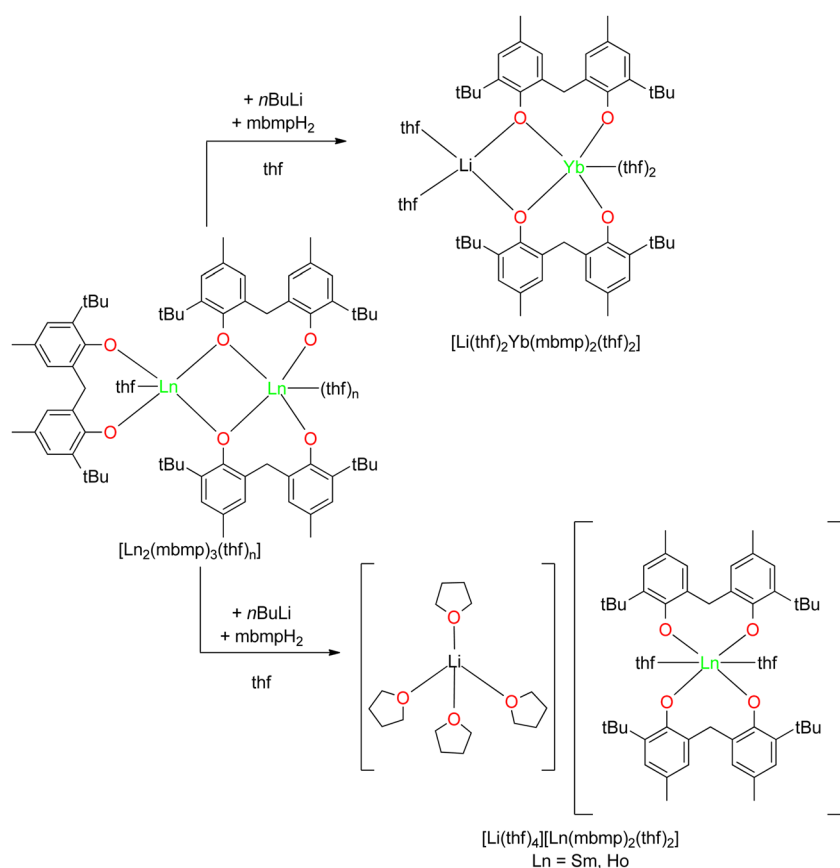

Scheme 26 Redistribution reactions of [Ln$_2$(mbmp)$_3$(thf)$_{n+1}$] (Ln = Sm (n = 2) and Ho, Yb (n = 1).[38]

polymerisation of ε-caprolactone and lactides.[49] Both molecular and ionic lanthanoid amide biphenolate complexes with the general form [Ln(mbmp){N(SiMe$_3$)$_2$}(thf)$_2$] (Ln = Nd and Yb) and [Li(thf)$_4$Ln(mbmp){N(SiMe$_3$)$_2$}$_2$] (Ln = Nd and Yb) can effectively initiate the polymerisation of ε-caprolactone, yielding high molecular weight, and low PDI polymers.[44] Of these two species, the ionic complexes are more active than the molecular complexes. It is possible that the increased activity is a result of the cooperation between the cation and anion, or

owing to the charge on the anion. These findings are in agreement with results reporting that ionic lanthanoid complexes have unique activity for the polymerisation of certain monomers, whereas the corresponding neutral lanthanoid complexes showed very low, or no activity for the same polymerisations.[27]

Complexes of the general form [Na(dme)$_3$Ln(mbmp)$_2$(dme)] (Ln = Sm, Er, Yb) have been reported as effective single component initiators for the ring opening polymerisation of
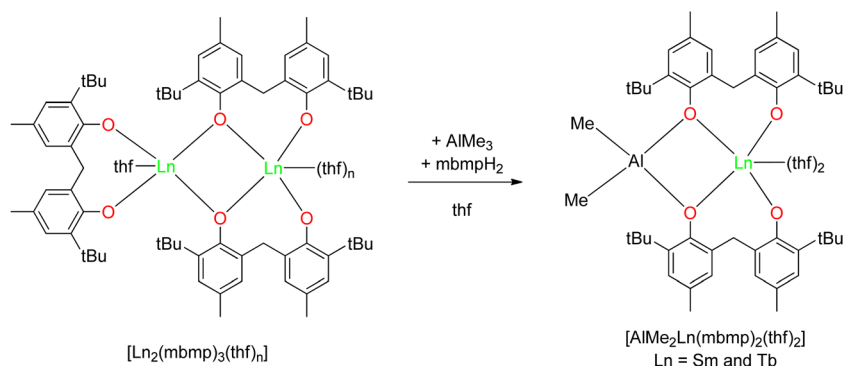
Scheme 27 Reaction of dinuclear [Ln$_2$(mbmp)$_3$(thf)$_{n+1}$] with one equivalent of mbmpH$_2$ and AlMe$_3$.[38]
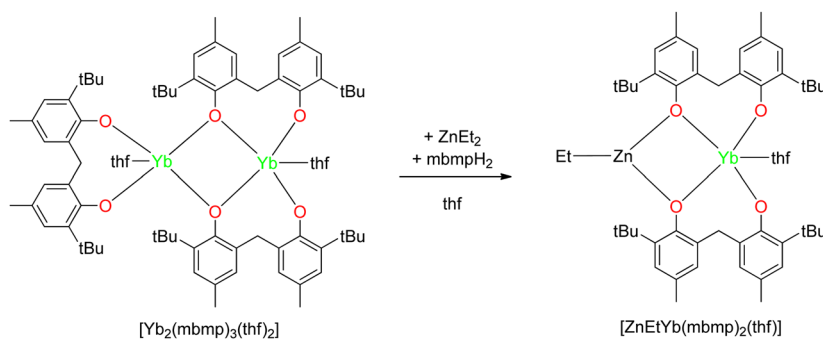
Scheme 28 Reaction of dinuclear Yb$_2$(mbmp)$_3$(thf)$_2$ with one equivalent of mbmpH$_2$ and ZnEt$_2$ yielding [ZnEtYb(mbmp)$_2$(thf)].[38]
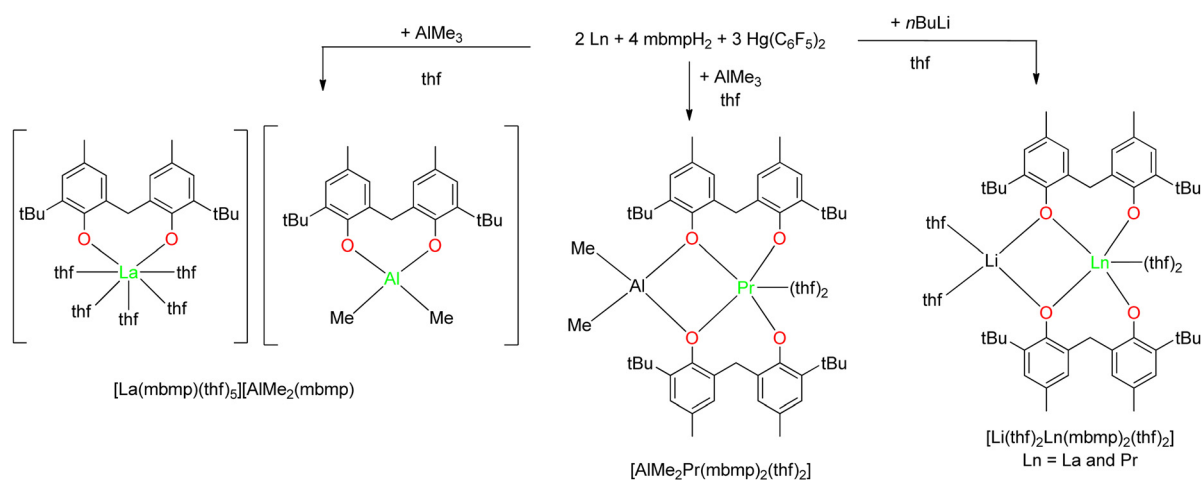

Scheme 29 Formation of lanthanum and praseodymium heterobimetallics by treatment of their reaction mixtures with AlMe$_3$ and nBuLi respectively.[38]

ε-caprolactone in toluene. It was found that an increase in temperature led to a higher degree of polymerisation, and that a larger ionic radius (Sm^{3+} > Er^{3+} > Yb^{3+}) allows for a more facile coordination process of the monomer to the lanthanoid metal centre, leading to higher polymerisation efficiency.[34]

Outside of ring opening polymerisation reactions, trivalent lanthanoid biphenolate complexes have been utilised as catalysts for the Diels–Alder reaction of cyclopentadiene

with methyl acrylate.[17] Biphenolate complexes of erbium [Er(mbmp)2(thf)Na(thf)$_2$] and samarium [Sm(mbmp)$_2$(thf)Na-(TMEDA)] in a catalytic ratio of 1:10 ([Cat.]:[Methyl acrylate] at 40 °C for 24 hours) showed significantly increased yields (91 and 92% for Er and Sm respectively) when compared to the uncatalysed reaction (67%). The use of catalysts increased stereoselectivity, heavily promoting formation of the *endo* product with both Er and Sm catalysts, increasing the *endo*:
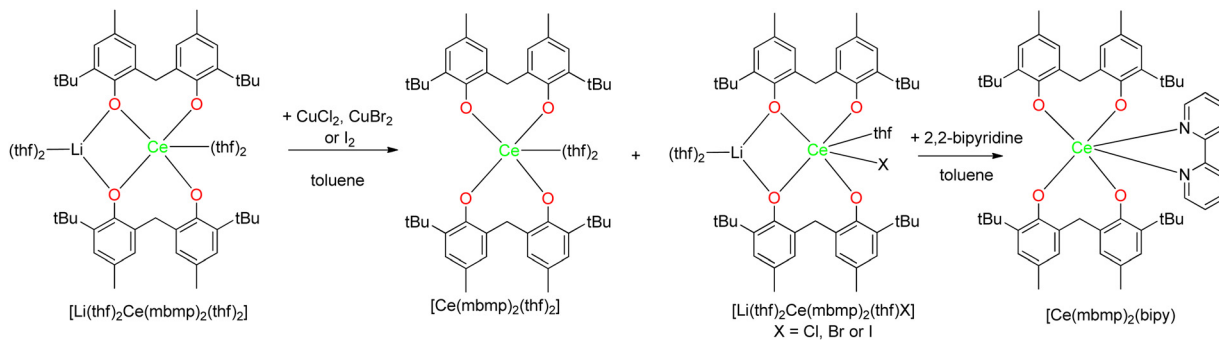
Scheme 30 Synthesis of Ce(IV) complexes by oxidation of Ce(III) species.[41]
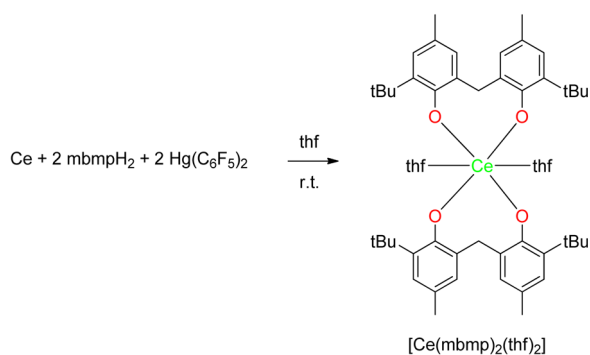
Scheme 31 Synthesis of tetravalent [Ce(mbmp)$_2$(thf)$_2$] by the RTP method.[38]

exo ratio from 2.7 for the uncatalysed reaction, to 4.1 and 4.0 respectively.

4. Conclusions and Future Perspectives

This review has aimed to provide a guide to the synthesis of a range of lanthanoid biphenolate complexes. It demonstrates the ability of these complexes to act as precursors for a wealth of heteroleptic species as well as their potential for further transformations, and the sheer diversity of the synthetic and structural capabilities of this ligand subset. With recent advances in synthetic methods for accessing both monometallic and heterobimetallic biphenolate complexes (*i.e.* with use of the RTP reaction),[32,38] there still remains significant room for expansion to target new heterobimetallic biphenolate complexes. In particular, the use of RTP reaction mixtures, without the need to isolate the rare earth biphenolate complex, to prepare heterobimetallic complexes is a major advance with considerable potential.[38]

The mbmp^{2-} ligand represents a major contender for the chemistry of rare earth biphenolate complexes, and whilst other biphenolate ligands with altered bridging groups and substituents have been employed in this chemistry, there is still significant room for extension. Lengthening the carbon bridge, incorporation of heteroatoms, or adjusting steric bulk about the phenolate donors is of interest, as variability in structure of the complexes may significantly adjust the catalytic capabilities of the complexes, and also allowing for structure–activity relationships to be established. Diversification of the biphenolate ligand systems used may also enable diversification of the auxiliary metals which can be incorporated to form a wider library of heterobimetallic complexes. Again, this variation has the potential to influence the catalytic capabilities of the bimetallic complexes formed.

Alongside these interesting future perspectives, this review outlines the strengths and limitations of these rare earth complexes as initiators and catalysts for a range of polymerisation reactions. This application has been well studied, however, extension to hydroamination and hydrosilylation reactions is yet to be explored. Outside of catalysis, these complexes may show reactivity towards small molecules, and interesting magnetism and luminescence properties. As the chemistry of rare earth biphenolate complexes is still relatively limited, they provide a myriad of opportunities for future study. The research area has been opened up, particularly by the work of Professor Qi Shen and her co-workers, and is now ready for further exploration.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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