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Chiral biarylamido/anisole complexes of yttrium in enantioselective aminoalkene hydaroamination/cyclisation

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A group of chiral, dibasic, biaryl-bridged amido proligands containing peripheral methoxyphenyl (anisole) ligation are developed for the synthesis of new amide complexes of yttrium and lanthanum. A potentially tetradentate bis(amidoanisole) system **L**^{1} gives, on reaction with [Y{N(SiMe$_2$H)$_2$}$_3$(THF)] a crystallographically-characterised bis complex [Y**L**^{1}(H**L**^{1})] presumably as a result of low steric demand, since a more bulky version **L**^{2} gives the target [**L**^{2}Y{N(SiMe$_2$H)$_2$}(THF)]. The molecular structure of the latter reveals a similar *cis*-α structure to our recently reported Schiff-base analogue. Variable-temperature NMR studies are consistent with low rigidity in the molecular structure. A potentially tridentate, amidoanisolyl/amido proligand **L**^{3} gives complexes [**L**^{3}M{N(SiMe$_2$H)$_2$}(THF)$_n$] (M = Y, n = 1; M = La, n = 2). Chiral non-racemic versions of the above complexes were tested in the hydroamination/cyclisation of 2,2′-dimethylaminopentane to the corresponding pyrrolidine. Activities were relatively low compared to recently reported examples, and ee values were in the range 20–40% despite the well-expressed chirality of the catalysts.

Introduction

It is difficult to develop effective chiral ligand environments for lanthanide-based enantioselective catalysts, essentially because the ions have large radii and their coordination spheres are highly labile.[1] The most significant progress has been made where the metal is acting principally as a Lewis acid, and it would seem that the binol[2] and pybox[3] ligands are the most generally efficient in this area. For reactions such as hydrogenation and hydroamination (*vide infra*) where the metal is required to mediate migratory insertion processes, the first enantioselective systems were Marks' C_1-symmetric (*S*)-menthylcyclopentadienyl *ansa*-metallocenes which, for example, have been shown to catalyse the hydroamination/cyclisation of aminoalkenes with ee up to 74%.[4] Last year saw a number of reports on the first enantioselective non-metallocene catalysts for this process. We have shown that chiral amino/phenoxide complexes of the lanthanides can catalyse such reactions with similar enantioselectivity to the metallocene system but with lower activity.[5] Marks and coworkers reported a thorough study of efficient bis(oxazolinato) lanthanide catalysts.[6] Collin *et al*.[7] described a bis(binaphthyldiamido) catalyst giving similar selectivity but rather higher activity than our similar mono(biaryldiamido) system.[8] Hultzsch has shown that yttrium binapholate complexes can also operate in this process.[9] It is striking that despite the efforts of these groups (and presumably others[10]) that high enantioselectivities have never been obtained in aminoalkene hydroamination/cyclisation.

In polymerisation catalysis research, diamido units (*i.e.* two R$_2$N$^-$ units) have been used as an alternative to bis(cyclopentadienyl). Reports of chiral non-racemic diamido ligands are, however, rather rare. A number of examples of 1,2-diaminocyclohexane based systems, most notably the sulfonamides,[11] have been found to catalyse the addition of dialkylzinc reagents to aldehydes with high enantioselectivity. Cloke *et al.* have reported a zirconium complex in which two amido groups are linked by the atropisomeric 2,2′-diamino-6,6′-dimethylbiphenyl backbone in **1**.[12] Gountchev and Tilley have reported an yttrium complex containing a similar ligand system that gave high enantioselectivity in the hydrosilation of norbornene.[13] Our related tetradentate N$_2$O$_2$ Schiff-bases based on diamine **1**, and the binaphthyl systems of *e.g.* Che *et al.*[14a] give chiral-at-metal complex structures,[14b] and while the middle and later transition metal complexes give highly enantioselective catalyst systems,[15] the early metal complexes suffer from decomposition *via* 1,2-migratory insertion reactions[16] and radical processes.[17] Although these reactions can be avoided almost completely in some instances,[18] we recognise that it will be difficult using Schiff-base ligands to produce complexes as durable and robust as the metallocenes.

In response to this problem we recently set out to synthesise a range of new diamido ligands based on the diamine **1**[19] with bulky and heteroatom donor aryl substituents, and the subsequent zirconium complexes.[20] In this contribution we outline our attempts to prepare yttrium complexes of this type of ligand, and describe their application to enantioselective hydroamination/cyclisation of aminoalkenes.

Results and discussion

Ligand synthesis

The group of ligands used in this study (Fig. 1) were chosen to explore the effects of varying denticity, steric demand and chelate ring size on the catalytic hydroamination reaction. We recently reported[20] the preparation of a range of N-aryl substituted biaryl diamine proligands including H$_2$**L**^{1} and H$_2$**L**^{3} from **1**[19] and the appropriate bromoarenes *via* palladium catalysed arylation.[21] These compounds are expected to act in their doubly deprotonated forms as tetradentate and tridentate ligands, respectively. Attempts to synthesise the more sterically demanding dianisole proligand H$_2$**L**^{2} by a similar protocol using 2-bromo-4,6-di-*tert*-butylanisole was unsuccessful, presumably because the bromoarene is too sterically encumbered. Instead, H$_2$**L**^{2} was synthesised efficiently using the method outlined in Scheme 1, whereby **1** was arylated under acid catalysed conditions using 2,4-di-*tert*-butylcatechol to give **2** which we found could be highly chemoselectively O-methylated. The proligand H$_2$**L**^{4} is similar to H$_2$**L**^{2} in terms of functionality, with the addition of methylene spacers between amino and anisole units. This compound was synthesised *via* tetrahydroborate reduction of the corresponding Schiff base[16] and O-methylation as for H$_2$**L**^{2}.

Complex syntheses

We have previously shown that the reaction between H$_2$**L**^{1} and Zr(NMe$_2$)$_4$ gave exclusively the monomeric C_2-symmetric N$_2$O$_2$ coordinated complex [**L**^{1}Zr(NMe$_2$)$_2$].[20] With the larger (and trivalent) yttrium metal, such a complex was rather more elusive. The reactions between racemic† H$_2$**L**^{1} and the homoleptic alkyl

† Racemic proligands were used for synthetic and structural studies. Optically-pure compounds were used in the subsequent catalytic studies.

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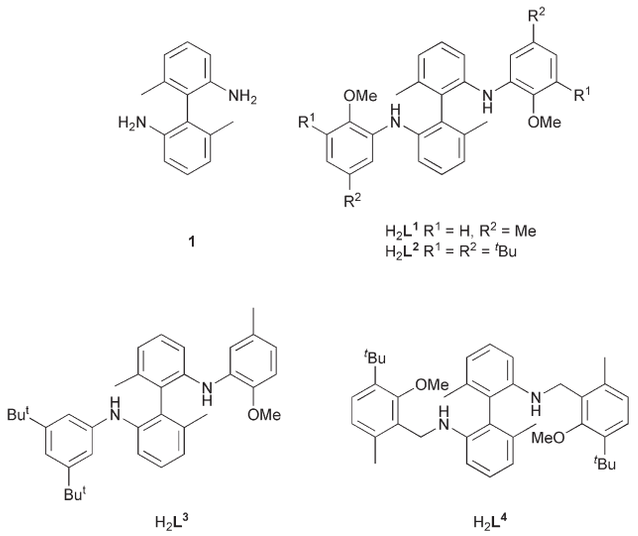
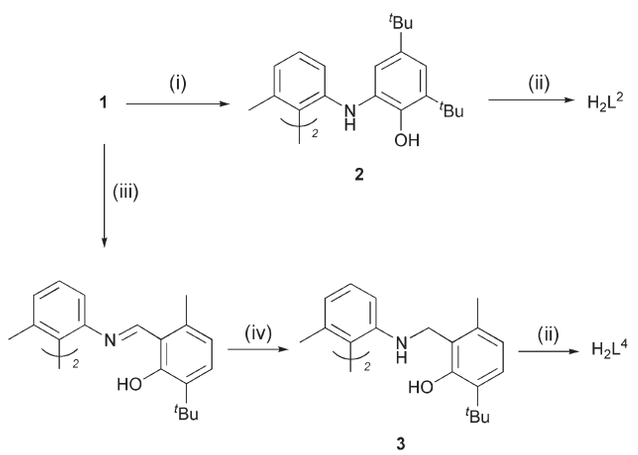


Fig. 1 Proligands used in this study.



Scheme 1 Synthesis of the aminoanisole proligands $H_2L^{2,4}$. Reagents and conditions (i) 2,4-di-*tert*-butylcatechol, acetic acid (cat.), hexane;[5] (ii) KOH/THF, MeI, 82%; (iii) 3-*tert*-butyl-6-methyl-2-hydroxybenzaldehyde;[18] (iv) $NaBH_4$/EtOH.[5]

$[Y\{CH(SiMe_3)_2\}_3]$ and amide $[Y\{N(SiMe_3)_2\}_3]$ gave mixtures of the starting material and a species $[Y\mathbf{L}^1(H\mathbf{L}^1)]$ (*vide infra*). Presumably, this results from the highly sterically shielded nature of these starting materials which renders them less reactive than the first-formed products *e.g.* $[\mathbf{L}^1Y\{CH(SiMe_3)_2\}]$. In any event it is becoming clear that the less encumbered reagents such as $[Y\{N(SiMe_2H)_2\}_3(THF)]$ are more synthetically useful, despite the presence of ligated THF.[5,8,22] Accordingly, the reaction of $H_2\mathbf{L}^1$ with $[Y\{N(SiMe_2H)_2\}_3(THF)]$ gave a mixture of what appeared (by NMR) to be *ca.* 10% $[Y\mathbf{L}^1(H\mathbf{L}^1)]$ along with the target $[\mathbf{L}^1Y\{N(SiMe_2H)_2\}(THF)_n]$. Unfortunately, the latter complex was found to be insufficiently stable for isolation.

A few crystals of the bis complex $[Y\mathbf{L}^1(H\mathbf{L}^1)]$ were isolated from one of the above reactions and the structure of this species (Fig. 2) was determined by X-ray crystallography. The complex is homochiral in that both biaryl units have the same configuration. The coordination number is seven, and the inner coordination sphere is significantly distorted from the closest regular structure, pentagonal bipyramidal, with best axial unit angle N(1)–Y(1)–N(3) of 156.39(17)° and mean deviation of the remaining five atoms from their least-squares plane of *ca.* 0.4 Å. One nitrogen atom N(4) remains in its protonated form, with a correspondingly long N(4)–Y(1) distance of 2.669(6) Å. Not surprisingly, given the unfavourable geometry for ligation of the associated anisole OMe unit, this oxygen atom is uncoordinated. The Y–N(amido) distances of 2.28–2.30 Å are unremarkable. The three Y–O(anisole) distances are in the range 2.42–2.45 Å. In the zirconium amide complex $[\mathbf{L}^1Zr(NMe_2)_2]$ the longest such distance observed was *ca.* 2.47 Å as a result of excessive ring-strain.[20] The shorter Zr–O distance was *ca.* 2.39 Å. In the yttrium compound, two of the amidoanisole chelate rings are essentially planar, and the associated O-methyl groups lie approximately in these planes. The third such chelate is significantly hinged however, with a torsion angle C(30)–O(2)–Y(1)–N(2) of *ca.* 33.4°. Correspondingly the methyl group at O(2) is oriented well out of the aryl plane. Nevertheless, the three amidoanisole bite angles are very similar at 66.70(15), 66.93(16) and 67.36(15)°.

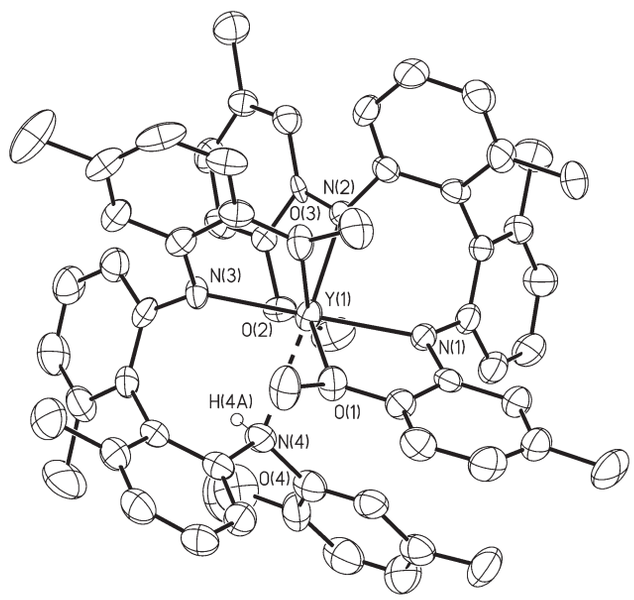


Fig. 2 Thermal ellipsoid plot of the molecular structure of $[Y\mathbf{L}^1(H\mathbf{L}^1)]$.

In the hope of isolating complexes with only one chiral ligand we turned to the more sterically demanding proligand $H_2\mathbf{L}^2$. While reactions of this compound with $[Y\{CH(SiMe_3)_2\}_3]$ and $[Y\{N(SiMe_3)_2\}_3]$ gave mixtures that appeared to contain some sort of bis complex as with $\mathbf{L}^1$, the reaction with $[Y\{N(SiMe_2H)_2\}_3(THF)]$ gave the target complex $[\mathbf{L}^2Y\{N(SiMe_2H)_2\}(THF)]$ in good yield. A corresponding lanthanum complex could not be isolated.

The asymmetric unit of $[\mathbf{L}^2Y\{N(SiMe_2H)_2\}(THF)]$ contains two independent molecules, but these have very similar geometries and metrical parameters. A thermal ellipsoid plot of the molecular structure of one is shown in Fig. 3, and a structural diagram is also given [Fig 4(a)]. The ligand $\mathbf{L}^2$ is disposed about the metal in the C_2-symmetric fashion leaving two symmetry-related sites occupied by one THF and one bis(dimethylsilyl)amido ligand. This *cis*-α orientation of the tetradentate chelate contrasts with the *cis*-β structure found for the related zirconium complex $[\mathbf{L}^1Zr(NMe_2)_2]$,[20] but since both these complexes undergo dynamic processes in solution (*vide infra*) a meaningful distinction is hard to draw.

We have recently reported the molecular structure of a biaryl bridged salicylaldimine complex of yttrium *i.e.* Fig. 4(b).[5] While this complex has an essentially octahedral coordination sphere, $[\mathbf{L}^2Y\{N(SiMe_2H)_2\}(THF)]$ [Fig. 4(a)] with one less atom in each of the NO chelates is significantly distorted from this ideal geometry. Nevertheless, the chiral ligand environment as "seen" by the auxiliary ligands is surprisingly similar for these two complexes (Fig. 4, lower). The greatest distinction arises, not surprisingly, in the presence of O-methyl groups in $[\mathbf{L}^2Y\{N(SiMe_2H)_2\}(THF)]$. The distance Y(1)–O(2) of 2.444(6) Å is within the range observed in $[Y\mathbf{L}^1_2]$ above, but the distance Y(1)–O(1) of 2.591(6) Å is significantly longer.

The ^1H NMR spectrum of $[\mathbf{L}^2Y\{N(SiMe_2H)_2\}(THF)]$ at 233 K indicates low symmetry, *e.g.* there are four sharp *tert*-butyl resonances corresponding to 9H each. This slow exchange spectrum may arise from the presence of the *cis*-β structure, or perhaps more likely one corresponding to the X-ray molecular structure above

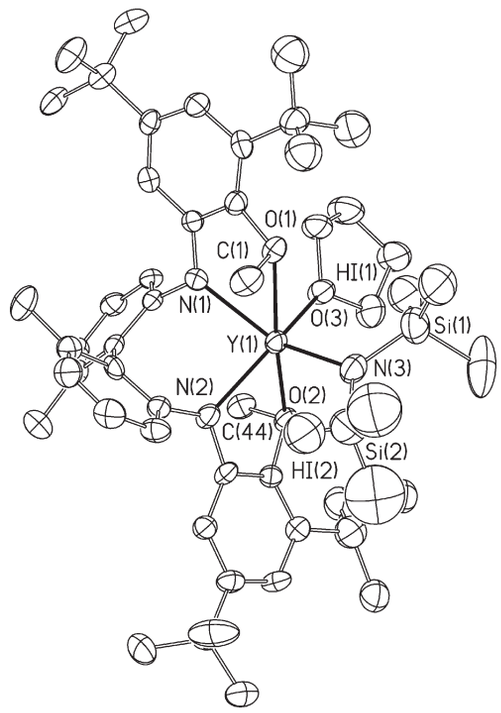


Fig. 3 Thermal ellipsoid plot of the molecular structure of [**L**^{2}Y{N(SiMe$_2$H)$_2$}(THF)].

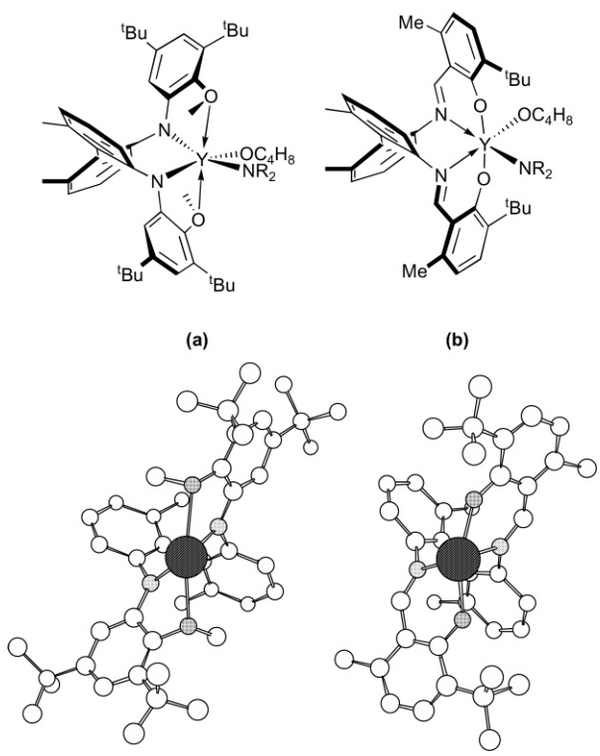


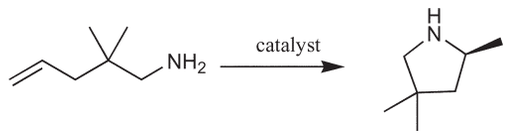
Fig. 4 ChemDraw and chem3D diagrams of the molecular structures of (a) [**L**^{2}Y{N(SiMe$_2$H)$_2$}(THF)] and (b) a related salicylaldimine complex of yttrium; the lower projections are viewed down the approximate C_2 axes.

(the low symmetry arising from unsymmetrical coordination at the two auxiliary sites).‡ At 298 K these peaks have coalesced and by 353 K two sharp resonances (each 18H) are observed. This fast exchange regime spectrum could arise from reversible coordination of the THF ligand, which we have observed in similar systems,[5] conversion between different tetradentate ligand orientations, or perhaps both. Given the rather long Y–O bond measured above, reversible decoordination of the anisole OMe group seems likely.

The reaction between H$_2$**L**^{3} and [Y{N(SiMe$_2$H)$_2$}$_3$(THF)] gave a mixture containing largely [**L**^{3}Y{N(SiMe$_2$H)$_2$}(THF)] which was isolated is moderate yield after crystallisation from pentane. A similar reaction with [La{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$] gave [**L**^{3}La{N(SiMe$_2$H)$_2$}(THF)].

The proligand H$_2$**L**^{4} undergoes very slow protonolysis with [M{N(SiMe$_2$H)$_2$}$_3$(THF)$_n$] (M = Y, La) giving less than 10% conversion after two weeks at 80 °C. Presumably this results from the relatively weak proton acidity of the mono-aryl amino units compared to those in H$_2$**L**$^{1–3}$.

Table 1 Enantioslective hydroamination/ cyclisation of 2,2′-dimethylaminopent-4-ene



Entry	Pre-catalyst	Temp/°C	Time/d	ee (%)
1	[**L**^{2}Y{Y{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$]	60	8	21
2	[**L**^{3}La{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$]	60	5	34
3	[**L**^{3}Y{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$]	60	7	40

Catalytic studies

The chiral non-racemic complexes from the above studies were tested as catalysts for the enantioselective hydroamination/ cyclisation of 2,2′-dimethylaminopentene to the corresponding pyrrolidine using an *in-situ* protocol. The di-anisole system **L**^{2} (Table 1, entry 1) is disappointingly unselective given the very favourable catalyst structure. We propose that this is a result of the fluxional nature of the coordination sphere. The lanthanum complex of the unsymmetrical **L**^{3} (entry 2) was noticeably better. Not surprisingly, given the more open coordination sphere the reaction was faster, but the ee also improved; the molecular structure of a related Zr complex of **L**^{3} displays well-expressed chirality.[20] On moving to yttrium (entry 3), the rate fell and the ee improved slightly, both commensurate with the smaller metal ion radius. Although the enantiomeric excesses obtained were modest, it should be noted that there are few catalysts for such a reaction that give a significant ee at all.

Conclusions

Highly enantioselective catalysts for the hydroamination/cyclisation of aminoalkenes have yet to be developed, and it would seem that very precise control of the metal coordination sphere is required for this to be a realistic prospect. In the attempts reported here using peripheral anisole ligation in multidentate systems, it would seem that the rigidity of the dative O-donor ligand is not sufficient for this purpose.

Experimental

All manipulations were carried out using standard Schlenk/glove-box techniques under an atmosphere of dry argon, except for the work-up procedures for the ligands, which were performed under aerobic conditions. Solvents were distilled from Na/K alloy (pentane, diethyl ether), potassium (THF) or sodium (toluene) under an atmosphere of dinitrogen. Deuterated benzene and toluene were heated to reflux *in vacuo* over potassium for three days, distilled under vacuum, degassed by three freeze–pump–thaw cycles and stored in a glove-box. The reagents [M{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$] (M = Y, La),[23] 2-methyl-4-*tert*-butylbromobenzene,[24] and the

‡ Epimerisation of the stereogenic O-centres formed on coordination of the methoxy groups to yttrium is a rather less likely source of symmetry disruption since we can see from the molecular structure that the configuration at O is strongly directed by the helicity inherent in the ligand coordination mode.

substrate 2,2-dimethylaminopent-4-ene[25] were synthesised according to literature procedures. The chiral-racemic and non-racemic ligands H**L**[1], H**L**[3], were synthesised according to our own procedures,[20] as were **1**,[19] **2** and **3**.[5]

Syntheses

(±)-HL[2]

To a stirred solution of aminophenol **2** (2.00 g, 3.22 mmol) in THF (50 ml), was added an excess of KOH pellets (0.50 g, 8.91 mmol). After stirring for *ca.* 24 h an excess of MeI (0.80 ml, 12.9 mmol) was added to the dark green solution. After stirring for a further 24 h the red solution was washed with water and extracted with diethyl ether. The solution was dried over $MgSO_4$ and the solvent was removed by rotary evaporation to yield a red oily material. Pentane (2 × 10 ml) was added and removed *in vacuo* to yield a pink solid. This solid was recrystallised from hot petroleum ether (bp 40–60 °C) to give a white solid. The supernatant was kept at 5 °C overnight to yield a further crop. Combined yield 1.71 g, 82%. Anal. Calc. for $C_{44}H_{60}N_2O_2$: C, 81.43; H, 9.32; N, 4.32. Found: C, 81.58; H, 9.25; N, 4.27%. ^{1}H NMR ($CDCl_3$, 297 K, 400 MHz): δ 1.17 (s, 18H, CMe_3), 1.24 (s, 18H, CMe_3), 2.01 (s, 6H, Ar–Me), 3.32 (s, 6H, OMe), 5.29 (s, 2H, N–H), 6.76 (d, 2H, Ar–H), 7.85 (s, 2H, Ar–H), 7.00 (d, 2H, Ar–H), 7.11 (m, 4H, Ar–H). ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K): δ 20.3 (Ar–Me_{biaryl}), 31.3 (C*Me*$_3$), 31.9 (C*Me*$_3$), 35.0 (*C*Me$_3$), 35.6 (*C*Me$_3$), 60.3 (OMe), 112.1, 117.7, 118.1, 121.7, 124.6, 128.9, 135.4, 138.6, 142.6, 142.9, 146.0, 149.7 (Ar). MS: *m*/*z* 648 (M^+), 85, 78, 62.

S(−)-HL[2]

As for (±)-H**L**[2] above. Combined yield 1.43 g, 69%. Anal. Calc. for $C_{44}H_{60}N_2O_2$: C, 81.43; H, 9.32; N, 4.32. Found: C, 81.64; H, 9.59; N, 4.15%. NMR Data as (±)-H**L**[2] above.

(±)-HL[4]

To a stirred solution of the aminophenol **3** (1.20 g, 2.12 mmol) in THF (50 ml) was added an excess of KOH pellets (0.50 g, 8.91 mmol). After stirring for 3 d an excess of MeI (0.50 ml, 8.48 mmol) was added *via* syringe to the light green solution, and the stirring was continued for a further 24 h. Water was added to the solution. The combined diethyl ether extracts (3 × 50 ml) were dried over $MgSO_4$ and the solvent was removed by rotary evaporation to yield a foamy material. A small quantity of petroleum ether (bp 40–60 °C) was added, followed by rotary evaporation to dryness. This was repeated to yield a white solid. Yield 1.19 g, 95%. Anal. Calc. for $C_{40}H_{52}N_2O_2$: C, 81.04; H, 8.84; N, 4.73. Found: C, 80.82; H, 8.98; N, 4.62%. ^{1}H NMR ($CDCl_3$, 297 K, 400 MHz): δ 1.33 (s, 18H, CMe_3), 1.86 (s, 6H, Ar–Me), 2.10 (s, 6H, Ar–Me), 3.52 (br, 2H, NH), 3.64 (s, 6H, OMe), 4.37 (m, 4H, NCH_2), 6.64 (d, 2H, Ar), 6.71 (d, 2H, Ar), 6.78 (d, 2H, Ar), 7.11 (d, 2H, Ar), 7.16 (t, 2H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K): δ 18.8 (Ar–Me), 20.1 (Ar–Me), 31.3 (C*Me*$_3$) 35.3 (*C*Me$_3$), 41.5 (NCH_2), 63.2 (OMe), 108.4, 119.6, 121.8, 125.9, 126.6, 129.2, 130.8, 137.9, 138.0, 142.5, 146.3 163.2 (Ar). MS: *m*/*z* 592 (M^+).

(±) [L[2]Y{N(SiHMe$_2$)$_2$}(THF)]

The proligand H_2**L**[2] (0.40 g, 0.62 mmol) and [Y{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$] (0.43 g, 0.68 mmol) were loaded into a Schlenk flask inside a glove box. Toluene (10 ml) was added and the reaction was stirred at 50 °C overnight during which time the solution turned yellow. The toluene was removed *in vacuo* to yield a foamy material. Pentane (2 × 10 ml) was added and removed *in vacuo* [in an attempt to remove residual toluene and HN(SiHMe$_2$)$_2$] yielding a yellow powder. Pentane was added until most of the solid had dissolved. The solution was filtered *via* cannula, concentrated and placed in a refrigerator at 0 °C for two days. A crystalline yellow precipitate formed. The supernatant was separated, concentrated and placed in the fridge for a further two days yielding a second crop. The combined material was crushed into a powder and was dried thoroughly *in vacuo* overnight to remove pentane of crystallisation (see X-ray crystallography section). Combined yield 0.43 g, 74%. Anal. Calc. for $C_{52}H_{80}N_3O_3Si_2Y$: C, 66.42; H, 8.58; N, 4.47. Found: C, 66.24; H, 8.71; N, 4.33%. ^{1}H NMR (C_6D_6, 297 K, 400 MHz): δ 0.14 (br d, 6H, SiH*Me*$_2$), 0.19 (br d, 6H, SiH*Me*$_2$), 1.31 (br, 18H, C*Me*$_3$), 1.41 (br, 18H, C*Me*$_3$), 2.14 (br, 6H, Ar–Me), 3.57 (br, 4H, THF), 3.79 (br, 6H, OMe), 4.70 (br, 2H, Si*H*Me$_2$), 6.58 (br, 2H, Ar–H), 6.9–7.25 (br, 8H, Ar–H).

(±) [L[3]Y{N(SiHMe$_2$)}(THF)]

H_2**L**[3] (0.31 g, 0.60 mmol) and [Y{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$] (0.37 g, 0.59 mmol) were loaded into a Schlenk flask inside a glove-box. Toluene (10 ml) was added and the reaction mixture was stirred at 50 °C overnight. During this time the solution turned an amber colour. The toluene was removed *in vacuo* to yield a brown foamy material. Pentane (2 × 10 ml) was added and removed *in vacuo* yielding a yellow powder. Pentane was carefully added until almost all the solid had dissolved. The solution was filtered *via* cannula, concentrated and placed in a refrigerator for 24 h yielding a crop of small pale yellow crystals. The supernatant was separated, concentrated and cooled for a further 2 d yielding a second crop. The crystalline material was dried *in vacuo* for 5 h. Combined yield 0.31 g, 64%. Anal. Calc. for $C_{44}H_{64}N_3O_2Si_2Y$: C, 65.08; H, 7.94; N, 5.17. Found: C, 64.89; H, 8.47; N, 5.02%. ^{1}H NMR (C_6D_6, 297 K, 400 MHz): δ 0.15 (d, 6H, SiH*Me*$_2$), 0.16 (br, 6H, SiH*Me*$_2$), 1.02 (br, 4H, THF), 1.45 (s, 18H, CMe_3), 2.18 (br, 6H, Ar–Me_{biaryl}), 2.27 (s, 3H, Ar–Me_{anisyl}), 3.48 (br, 4H, THF), 3.63 (s, 3H, OMe), 4.76 (br, 2H, Si*H*Me$_2$), 6.52 (m, 2H, Ar–H), 6.81 (d, 1H, Ar–H), 6.88 (d, 1H, Ar–H), 6.91 (s, 1H, Ar–H), 7.12 (m, 3H, Ar–H), 7.22 (m, 1H, Ar–H), 7.44 (m, 2H, Ar–H), 7.88 (d, 1H, Ar–H). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 3.1 (SiHMe$_2$), 21.2 (Ar–Me), 21.4 Ar–Me), 23.6 (THF), 32.2 (C*Me*$_3$), 33.5 (*C*Me$_3$) 56.1 (OMe), 71.0 (THF), 101.6, 101.9, 109.8, 110.5, 113.4, 116.6, 122.1, 123.8, 125.9, 127.77, 130.24, 133.5 139.8, 142.1 151.2 (Ar).

(±) [L[3]La{N(SiHMe$_2$)}(THF)$_2$]

The racemic proligand H_2**L**[3] (0.33 g, 0.63 mmol) and [La{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$] (0.45 g, 0.66 mmol) were loaded into a Schlenk flask inside a glove-box. Toluene (10 ml) was added and the reaction mixture was stirred at 50 °C overnight during which time the solution turned an amber colour. The product was isolated as for the analogous Y compound above. Combined yield: 0.32 g, 59%. Anal. Calc. for $C_{48}H_{72}LaN_3O_2Si_2$: C, 61.71; H, 7.77; N, 4.50. Found: C, 61.01; H, 7.42; N, 4.65%. ^{1}H NMR (C_6D_6, 297 K, 400 MHz): δ 0.26 (br, 6H, SiH*Me*$_2$), 0.35 (br, 6H, SiH*Me*$_2$), 1.30 (br, 8H, THF), 1.57 (s, 18H, C*Me*$_3$), 2.26 (br, 6H, Ar–Me), 2.43 (s, 3H, Ar–Me), 3.45 (br, 4H, THF), 3.64 (br, 4H, THF), 3.83 (s, 3H, OMe), 4.95 (br m, 2H, Si*H*Me$_2$), 6.45 (m, 1H, Ar–H), 6.57 (d, 1H, Ar–H), 6.67 (m, 2H, Ar–H), 7.04 (s, 1H, Ar–H), 7.19 (m, 3H, Ar–H), 7.36 (m, 2H, Ar–H), 7.49 (d, 1H, Ar–H), 7.75 (d, 1H, Ar–H). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 5.4 (SiHMe$_2$), 20.8 (Ar–Me), 21.1 (Ar–Me), 24.5 (THF), 32.2 (C*Me*$_3$), 38.2 (*C*Me$_3$) 54.8 (OMe), 69.0 (THF), 102.3, 105.4, 111.6, 111.9, 114.2, 119.8, 123.9, 124.4, 126.0, 128.5, 132.6, 137.1, 139.8, 146.3, 155.9 (Ar).

Catalysis

In a typical reaction approximately 10 mg of the diamine ligand under study and approximately 0.9 equivalents of the desired lanthanide amide starting material, (less than one equivalent is used to ensure complete protonolysis of lanthanide amide starting material) were loaded into a Young's tap NMR tube in a glove-box. d_8-Toluene was added and the sample was heated at 50 °C until complete protonolysis had occurred, as judged by ^{1}H NMR spectroscopy. The d_8-toluene and the amine by-product were removed *in vacuo* and d_8-toluene and 2,2-dimethylaminopentene (25–30 equivalents) were then added. The mixture was maintained at constant temperature (60 °C) until catalytic reaction was complete as judged by ^{1}H NMR spectroscopy.

Table 2 Experimental data for the X-ray diffraction studies

	$[YL^1(HL^1)]\cdot C_5H_{12}$	$[L^2Y\{N(SiMe_2H)_2\}(THF)]\cdot 0.5C_5H_{12}$
Molecular formula	$C_{65}H_{73}N_4O_4Y$	$C_{54.5}H_{86}N_3O_3Si_2Y$
Formula weight	1063.18	976.35
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	11.964(7)	11.5395(8)
b/Å	14.017(10)	20.6404(14)
c/Å	17.212(10)	26.6724(18)
α/°	91.90(4)	111.4820(10)
β/°	97.40(4)	91.202(2)
γ/°	100.67(5)	102.414(2)
V/Å^3	2808(3)	5738.4
Z	2	4
μ/mm^{-1}	1.090	1.098
Total reflections	11893	36133
Independent reflections	4516	14947
R_1, wR_2 [$I > 2\sigma(I)$]	0.0891, 0.1595	0.0690, 0.1640

For the chiral non-racemic pre-catalysts, the volatile components were vacuum transferred from NMR tube into a receiver flask and the enantiomeric excesses were determined by diastereomeric derivatization with (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (Mosher's chloride).[26] This was achieved by a modification of the procedure of Hoye[27] in which dichloromethane (1–2 ml) was added to the distillate in the reciever flask followed by addition of 1 equivalent of Mosher's chloride and triethylamine. The solution was stirred for 48 h and solvent removed *in vacuo*. The enantiomeric excess was then determined from the relative integration of the two resonances in the ^{19}F NMR ($CDCl_3$) spectra recorded at 50 °C.

Crystallography

Crystals were coated in an inert oil prior to transfer to a cold nitrogen gas stream on Bruker-AXS SMART three-circle area detector diffractometer system equipped with Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were collected with narrow (0.3° in ω) frame exposures. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections (SADABS). Reflection data for $[L^2Y\{N(SiMe_2H)_2\}(THF)]\cdot 0.5C_5H_{12}$, which contains two independent molecules in the asymmetric unit, were weak and no significant data were collected for $2\theta > 45°$. Both structures were solved by direct methods (SHELXS) with additional light atoms found by Fourier methods. For $[YL^1(HL^1)]\cdot C_5H_{12}$ the atoms of the slightly disordered pentane molecule were subject to displacement parameter restraints. Disordered *tert*-butyl groups were present in both independent molecules and were modelled and refined across two alternative positions. Both structures were refined on F^2 values for all unique data. Table 2 gives further details. All non-hydrogen atoms were refined anisotropically. The atoms Si3, C47, C48, C94, C98 and C100 of $[L^2Y\{N(SiMe_2H)_2\}(THF)]_2\cdot 0.5C_5H_{12}$ were subject to additional displacement parameter restraints. All H atoms were constrained with a riding model; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Programs used were Bruker AXS SMART (control), SAINT (integration) and SHELXTL for structure solution, refinement, and molecular graphics. Table 3 gives selected bond lengths and angles for the two compounds.

CCDC reference numbers 229165 and 229166.

See http://www.rsc.org/suppdata/dt/b4/b400799a/ for crystallographic data in CIF or other electronic format.

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Table 3 Selected bond lengths (Å) and angles (°) for $[YL^1(HL^1)]\cdot C_5H_{12}$ and $[L^2Y\{N(SiMe_2H)_2\}(THF)]\cdot 0.5C_5H_{12}$

$[YL^1(HL^1)]\cdot C_5H_{12}$		$[L^2Y\{N(SiMe_2H)_2\}(THF)]\cdot 0.5C_5H_{12}$[a]	
Y1–N1	2.295(5)	Y1–N3	2.261(8)
Y1–N2	2.284(5)	Y1–N2	2.265(8)
Y1–N3	2.302(5)	Y1–N1	2.280(7)
Y1–N4	2.669(6)	Y1–O3	2.352(6)
Y1–O1	2.445(4)	Y1–O2	2.444(6)
Y1–O2	2.451(4)	Y1–O1	2.591(6)
Y1–O3	2.418(4)	Y1–Si1	3.366(4)
		Si1–N3	1.696(9)
		Si2–N3	1.697(9)
N2–Y1–N1	86.52(17)	N3–Y1–N2	105.3(3)
N2–Y1–N3	102.53(18)	N3–Y1–N1	145.1(3)
N1–Y1–N3	156.39(17)	N2–Y1–N1	86.2(3)
N2–Y1–O3	81.68(16)	N3–Y1–O3	104.1(3)
N1–Y1–O3	93.39(16)	N2–Y1–O3	135.7(3)
N3–Y1–O3	66.93(16)	N1–Y1–O3	88.2(2)
N2–Y1–O1	139.10(16)	N3–Y1–O2	98.7(3)
N1–Y1–O1	66.70(15)	N2–Y1–O2	66.9(2)
N3–Y1–O1	93.40(16)	N1–Y1–O2	116.0(2)
O3–Y1–O1	70.30(14)	O3–Y1–O2	76.5(2)
N2–Y1–O2	67.36(15)	N3–Y1–O1	82.4(3)
N1–Y1–O2	111.49(16)	N2–Y1–O1	121.0(2)
N3–Y1–O2	92.10(16)	N1–Y1–O1	63.8(2)
O3–Y1–O2	138.01(14)	O3–Y1–O1	95.1(2)
O1–Y1–O2	150.16(13)	O2–Y1–O1	171.6(2)
N2–Y1–N4	138.70(17)	N3–Y1–Si1	27.0(2)
N1–Y1–N4	102.40(18)	N2–Y1–Si1	132.0(2)
N3–Y1–N4	85.27(18)	N1–Y1–Si1	133.9(2)
O3–Y1–N4	136.63(16)	O3–Y1–Si1	79.75(18)
O1–Y1–N4	79.34(16)	O2–Y1–Si1	104.18(16)
O2–Y1–N4	71.91(15)	O1–Y1–Si1	73.12(15)

[a] Bond lengths and angles for only one independent molecule of $[L^2Y\{N(SiMe_2H)_2\}(THF)]_2\cdot C_5H_{12}$ given. The other molecule is essentially the same.

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