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Biaryl amine ligands for lanthanide catalysed enantioselective hydroamination/cyclisation of aminoalkenes

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Abstract—Arylations of (*R*)-2,2′-diamino-6,6′-dimethylbiphenyl and the corresponding racemic compound under palladium catalysis gives a range of C_2-symmetric secondary amine proligands H_2L. The 3,5-di-*tert*-butylphenyl substituted compound reacts with the silylamides $[M\{N(SiMe_2H)_2\}_3(THF)_2]$ (M = Y, Sm, La) to produce (±)-$[ML\{N(SiMe_2H)_2\}(THF)_2]$. However, deprotonation of more sterically hindered proligands H_2L proceeded very slowly, but the reaction with the more basic akylamide $[Y(N^iPr_2)_3(THF)_2]$ gave $[YL^{1\text{-}4}(N^iPr_2)(THF)_2]$ readily. Such catalysts formed in situ from the amine proligand H_2L and metal amide, cyclised 2,2′-dimethylaminopent-4-ene to the corresponding pyrrolidine with enantiomeric excesses up to 50%. The alkylamide catalysts gave significantly faster turnover than the silylamides.

1. Introduction

The development of an effective general method for the catalytic enantioselective cyclisation of amino olefins that is of practical use in organic synthesis is an important goal, with the potential to greatly simplify the synthesis of many important nitrogen containing heterocyclic systems such as pyrrolidines and indolines. While a number of early[1] and late[2] transition metal–ligand systems have been shown to effect the cyclisation of amino-olefins and alkynes, to date the lanthanide C_1-symmetric (*S*)-menthylcyclopentadienyl *ansa*-metallocene systems, developed by Marks, provides the only reported examples of enantioselective cyclisation, with e.e.s up to 74%.[3] The synthesis of these catalysts is challenging for workers in non-specialist laboratories since rigorous exclusion of moisture is required. Also, they do not lend themselves to the use of in situ catalyst generation protocols, which have facilitated the widespread use of similarly sensitive reagents such as SmI_2. Livinghouse et al.[4] have recently shown that simple $Ln[N(SiMe_3)_2]_3$ readily catalyses the hydroamination cyclisation of aminopentene substrates, paving the way, in principle, for the application of chiral non-racemic amido ligands to an enantioselective variant of this reaction.

As part of our programme of the design and synthesis of new chiral ligand environments for early transition metals and lanthanides, we have recently reported the straightforward preparation of a range of *N*-aryl substituted biaryl diamine ligands **I** (Fig. 1, Ar = e.g. pyridyl, 2-anisolyl) from 2,2′-diamino-6,6′-dimethylbiphenyl[5] and their protonlysis reactions with $[Zr(NMe_2)]_4$.[6] We have found that members of this class of ligands undergo clean in situ metallation with certain Group 3 and lanthanide amides leading to enantioselective catalysts for aminoalkene hydroamination/cyclisation.

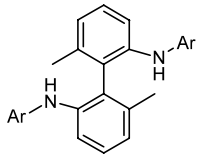

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Figure 1.

2. Results and discussion

2.1. Proligand synthesis

The synthesis of the chiral racemic and chiral non-racemic 3,5-di-*tert*-butylphenyl substituted diamine H_2L^1 via Buchwald/Hartwig amination[7] (Scheme 1) has been reported elsewhere.[6] We expected however that

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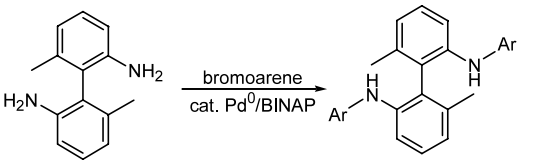


Scheme 1. Synthesis of the proligands $H_2L^{1\text{-}4}$.

2,6-disubstituted compounds might lead to greater control of the lanthanide/Group 3 element coordination sphere since similar diimino ligands lead to the most selective catalysts for e.g. alkene aziridination.[8] Unfortunately we found that the arylation of the diamine precursor did not occur at a significant rate even with 2,6-dimethylbromobenzene present. Thus we elected for a steric compromise and targeted the 2-substituted proligands H_2L^2, H_2L^3 and H_2L^4 which were synthesised successfully.

2.2. Catalyst synthesis

The NMR tube scale reaction of (±)-H_2L^1 with the metal alkyl $[Y\{CH(SiMe_3)_2\}_3]$ gave a mixture of compounds which appeared to include $[Y(L^1)(HL^1)]$ and unreacted alkyl. The THF-free yttrium triamide $Y[N(SiMe_3)_2]_3$ gave a similar mixture of products. In common with others[9] we found that the dimethylsilyl compound $[Y\{N(SiMe_2H)_2\}_3(THF)_2]$[10] gave a clean metallation product, and accordingly the reaction was scaled up to produce (±)-$[YL^1\{N(SiMe_2H)_2\}(THF)_2]$ in good yield. Similar samarium and lanthanum compounds were synthesised from $[M\{N(SiMe_2H)_2\}_3(THF)_2]$ and were isolated successfully.

Deprotonation of the sterically more hindered proligands $H_2L^{2\text{-}4}$ with $[Y\{N(SiMe_2H)_2\}_3(THF)_2]$ however proceeded very slowly (ca. 10% after 1 day), and so we looked toward lanthanide/Group 3 metal precursors with more basic amide ligands.

Aspinall has reported a convenient synthesis of $[Y(N^iPr_2)_3(THF)]$ from commercially available YCl_3 and LDA.[11] In contrast to a recent report[12] we found that Aspinall's procedure works well, although we invariably isolated the bis-THF adduct $[Y(N^iPr_2)_3(THF)_2]$. This compound was able to deprotonate not only (*R*)-H_2L^1 but also the more sterically demanding proligands (*R*)-$H_2L^{2\text{-}4}$ cleanly to give species $[YL^{1\text{-}4}(N^iPr_2)(THF)_2]$ according to NMR tube scale experiments.

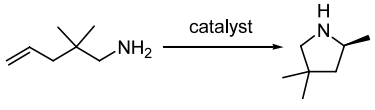
2.3. In situ catalytic hydroamination protocol

The reactions of the lanthanide/Group 3 element amides with slight excesses of the chiral non-racemic diamine proligands $H_2L^{1\text{-}4}$ were conducted as above in NMR tubes fitted with Young's type concentric PTFE stopcocks in d_8-toluene. The results of the subsequent catalytic hydroamination/cyclisations of 2,2′-dimethylaminopent-4-ene are summarised in Table 1.

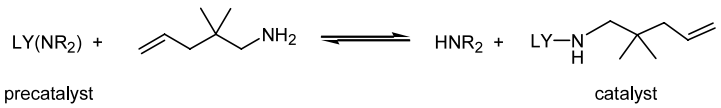
All catalysts cyclised the aminoalkene completely at ca. 3% loading, although there were large variations in rate and enantioselectivity. The metal silylamide catalysts (entries 1–3) required heating to 60°C in order to facilitate conversion of the substrate within a reasonable timescale. The rate of the reaction increased in the order Y<Sm<La and the enantiomeric excess fell from 50 to 18% in the same order. These trends are readily explained on the basis that the metal ions with the largest radii are expected to give the highest rate,[13] and their coordination spheres are expected to be most difficult to control in terms of the chiral environment.

The comparison between the yttrium silylamide and alkylamide catalysts (entries 1 and 4) is interesting; the latter is a significantly faster catalyst, taking 5 days at 35°C to complete the reaction compared to 14 days at 60°C for the former. We believe this to be a result of the relative acidities of the amines produced on precatalyst activation (Scheme 2); the silylamine $NH(SiMe_2)_2$ is expected to be at least 10 pK_a units more acidic than dialkylamines such as $NHPr^i_2$.[14] Even in the presence of an excess of substrate aminoalkene the silylamine will compete very effectively for the active site, thus lowering the effective concentration of the active catalyst in

Table 1. Catalytic enantioselective hydroamination/cyclisation of 2,2′-dimethylaminopent-4-ene



Entry	Ligand	Metal source	Temp. (°C)	Time (days)	E.e. (%)
1	H_2L^1	$[Y\{N(SiMe_2H)_2\}_3(THF)_2]$	60	14	50
2	H_2L^1	$[Sm\{N(SiMe_2H)_2\}_3(THF)_2]$	60	7	33
3	H_2L^1	$[La\{N(SiMe_2H)_2\}_3(THF)_2]$	60	7	18
4	H_2L^1	$[Y(N^iPr_2)_3(THF)_2]$	35	5	45
5	H_2L^2	$[Y(N^iPr_2)_3(THF)_2]$	35	5	20
6	H_2L^3	$[Y(N^iPr_2)_3(THF)_2]$	35	5	21
7	H_2L^4	$[Y(N^iPr_2)_3(THF)_2]$	35	5	23



Scheme 2. Protonolysis of precatalyst with substrate.

the silylamide systems (the equilibrium in Scheme 2 will lie far to the left). In contrast, the alkylamide catalyst precursors will be readily protonated by the primary amine substrate.[15] It is disappointing however that the lower temperature of the reaction in entry 4 was not accompanied by an increase in the enantiomeric excess for the catalytic reaction.

The unsymmetrically substituted ligands $L^{2,3}$ (entries 5 and 6) gave poor enantioselectivity compared to the 3,5-di-*tert*-butyl substituted L^1 (entries 1 and 4). This contrasts with a recent report by Grubbs et al.[16] that the ruthenium complexes of *N*-heterocyclic carbene ligands derived from chiral diamines and containing mono *ortho*-substituted aryl groups promotes high enantioselectivity in the ring closing metathesis reactions of achiral trienes. The unsymmetrical substitution is proposed to aid transfer of the stereochemistry of the ligand to the active site. Our attempt to marry this strategy to the apparently beneficial provision of steric bulk at the *meta* position (L^4, entry 5) did not lead to a significant increase in enantioselection.

3. Conclusions

The flexibility of lanthanide and Group 3 element coordination spheres make it notoriously difficult to generate well-defined chiral architectures that will lead to efficient enantioselective reactions.[17] While a small number of highly enantioselective lanthanide Lewis acid catalysts are known, enantioselective *organo*lanthanide systems (i.e. alkyls, hydrides and amido compounds) for which insertion processes are possible, are essentially limited[18] to Marks' chiral metallocenes mentioned above.[3] Herein we have described a method by which a well characterised enantioselective organolanthanide catalyst system can be produced using a convenient in situ protocol. While the enantioselectivity is modest (up to 50%), the principle that non-metallocene compounds can be used in this type of application is firmly established.

4. Experimental

4.1. General considerations

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 3 days, distilled under vacuum, degassed by three freeze–pump–thaw cycles and stored in a glove box. The reagents $[M\{N(SiMe_2H)_2\}_3(THF)_2]$[10] (M = Y, Sm, La), $[Y(NPr^i)_3(THF)_2]$,[11] 2-methyl-4-*tert*-butylbromobenzene,[19] (*R*)-2,2′-diamino-6,6′-dimethylbiphenyl,[5] H_2L^1 proligand[6] and 2,2-di-methylaminopent-4-ene[20] were synthesised according to literature procedures.

4.2. Proligand syntheses

4.2.1. *N*,*N*′-Bis(2-ethylphenyl)-6,6′-dimethylbiphenyl-2,2′-diamine (*R*)-(+)-H_2L^2. (*R*)-2,2′-Diamino-6,6′-dimethylbiphenyl (0.45 g, 2.12 mmol), Pd_2DBA_3 (0.039 g, 1 mol%), BINAP (0.052 g, 2 mol%) and NaO-*t*-Bu (0.57 g, 5.93 mmol) were loaded into a Schlenk flask. Toluene (50 ml) was added, followed by the 2-bromoethylbenzene (0.59 ml, 4.24 mmol). The solution was stirred at 100°C for 2 days by which time the reaction was complete as judged by TLC analysis of an aliquot. The toluene was removed in vacuo and ether was added. The resulting mixture was passed through a pad of silica and stirred over activated carbon overnight. The mixture was again passed through a pad of silica and the solvent removed on a rotary evaporator to yield a pale yellow crystalline solid. Yield 0.75 g, 85%. $[\alpha]_D^{24.2} = -147$ (*c* 0.20, $CHCl_3$); Anal. calcd for $C_{30}H_{32}N_2$: C, 85.67; H, 7.67; N, 6.66. Found: C, 85.60; H, 7.72; N, 6.51. ^{1}H NMR (C_6D_6, 297 K, 400 MHz): δ 0.88 (t, 6H, CH_2CH_3), 2.14 (s, 6H, Ar-Me), 2.35 (q, 4H, CH_2CH_3), 5.48 (s, 2H, N-H), 6.81 (m, 2H, Ar-H), 7.09 (tr, 2H, Ar-H), 7.11 (tr, 4H, Ar-H), 7.13 (m, 4H, Ar-H), 7.39 (d, 2H, Ar-H). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 12.7 (CH_2CH_3), 18.5 (Ar-Me), 23.4 (CH_2CH_3), 111.1, 120.0, 120.2, 122.2, 122.5, 125.6, 127.7, 128.2, 135.7, 137.8, 139.8, 142.7 (Ar).

4.2.2. *N*,*N*′-Bis(2-cyclohexylphenyl)-6,6′-dimethylbiphenyl-2,2′-diamine (*R*)-(+)-H_2L^3. (*R*)-2,2′-Diamino-6,6′-dimethylbiphenyl (0.50 g, 2.36 mmol), 2-bromocyclohexylbenzene (1.18 g, 4.93 mmol), Pd_2DBA_3 (0.090 g, 2 mol%), BINAP (0.123 g, 4 mol%) and NaO-*t*-Bu (0.63 g, 6.55 mmol) were loaded into a Schlenk flask. Toluene (50 ml) was added and the solution stirred at 100°C for 2 days. The toluene was removed in vacuo and ether added. The resulting mixture was passed through a pad of silica and stirred over activated carbon overnight. The mixture was again passed through a pad of silica and the solvent removed on a rotary evaporator to yield a yellow foam. Petroleum ether was twice added and then removed on a rotary evaporator to remove residual toluene. A minimal amount petroleum ether was again added to the yellow foam until it dissolved and the resulting solution kept at 5°C for 1 week to yield a crop of pale yellow crystals. A second crop was obtained similarly. Combined yield 0.90 g, 72%. $[\alpha]_D^{24.5} = -152$ (*c* 0.20,

$CHCl_3$); Anal. calcd for $C_{38}H_{44}N_2$: C, 86.31; H, 8.39; N, 5.30. Found: C, 86.25; H, 8.35; N, 5.24. ^{1}H NMR ($CDCl_3$, 297 K, 400 MHz): δ 1.06 (m, 6H, Cy-H), 1.28 (m, 4H, Cy-H), 1.43 (m, 4H, Cy-H), 1.59 (m, 6H, Cy-H), 2.00 (s, 6H, Ar-Me), 2.32 (m, 2H, Cy-H), 5.21 (s, 2H, N-H), 6.75 (d, 2H, Ar-H), 6.90 (m, 4H, Ar-H), 7.00 (tr, 2H, Ar-H), 7.10 (m, 4H, Ar-H), 7.22 (d, 2H, Ar-H). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 20.3 (Ar-Me), 26.6 (Cy-CH_2), 27.4 (Cy-CH_2), 33.6 (Cy-CH_2), 33.7 (Cy-CH_2), 38.8 (Cy-CH), 112.7, 120.6, 121.6, 123.2, 123.9, 126.6, 126.8, 128.6, 138.6, 139.5, 139.9, 142.9.

4.2.3. *N*,*N*′-Bis(2-methyl-5-*tert*-butylphenyl)-6,6′-dimethylbiphenyl-2,2′-diamine (*R*)-(+)-H_2L^4. (*R*)-2,2′-Diamino-6,6′-dimethylbiphenyl (0.50 g, 2.36 mmol), Pd_2DBA_3 (0.042 g, 1 mol%), BINAP (0.059 g, 2 mol%) and NaO-*t*-Bu (0.64 g, 6.65 mmol) were loaded into a Schlenk flask. Toluene (50 ml) was added, followed by the 2-methyl-4-*tert*-butylbromobenzene (1.07, 4.72 mmol). The solution was stirred at 100°C for 2 days. The toluene was removed in vacuo and ether added. The resulting mixture was passed through a pad of silica and stirred over activated carbon overnight. The mixture was again passed through a pad of silica and the solvent removed on a rotary evaporator to yield a pale yellow foam. Excess bromobenzene was distilled off (82°C, 0.03 mmHg). Petroleum ether was then added to dissolve the remaining oily residue and on evaporation in vacuo gave a pale yellow powder. Yield 0.93 g, 79%. $[\alpha]_D^{24.7} = -158$ (*c* 0.20, $CHCl_3$); Anal. calcd for $C_{36}H_{44}N_2$: C, 85.66; H, 8.79; N, 5.55. Found: C, 85.59; H, 8.85; N, 5.50. ^{1}H NMR ($CDCl_3$, 297 K, 400 MHz): δ 1.18 (s, 18H, CMe_3), 1.89 (s, 6H, Ar-Me), 2.04 (s, 6H, Ar-Me), 5.11 (s, 2H, N-H), 6.73 (d, 2H, Ar-H), 8.10 (d, 2H, Ar-H), 6.90 (d, 2H, Ar-H), 6.99 (d, 2H, Ar-H), 7.08 (tr, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 297 K, 100 MHz): δ 17.5 (Ar-Me), 20.3 (Ar-Me), 31.8 (CMe_3), 33.4 (CMe_3), 111.5, 119.0, 120.3, 121.2, 123.5, 125.8, 126.9, 127.9, 128.9, 130.8, 138.7, 140.3, 143.1. 150.3 (Ar).

4.3. Synthesis and isolation of catalysts

4.3.1. (±)-[YL^1{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$]. The racemic proligand H_2L^1 (0.30 g, 0.51 mmol) and [Y{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$] (0.32 g, 0.51 mmol) were loaded into a Schlenk flask inside a glove box. Toluene (10–15 ml) was added and the reaction stirred at 50°C for 3 h during which time the solution turned deep orange. The toluene was then removed in vacuo to yield a brown foamy material. Pentane (2×10 ml) was added and removed in vacuo [in an effort to remove residual toluene and $HN(SiHMe_2)_2$] yielding an orange powder. Pentane was added until most of the solid had dissolved. The solution was filtered via cannula, concentrated and kept at 0°C for 2 days. The resulting orange crystals were isolated by filtration and a second crop obtained from the supernatant. Combined yield 0.30 g, 61%. Anal. calcd for $C_{54}H_{82}N_3O_2Si_2Y$: C, 68.25; H, 8.70; N, 4.42. Found: C, 67.85; H, 8.95; N, 4.59. ^{1}H NMR (C_6D_6, 297 K, 400 MHz): δ 0.38 (d, 6H, SiHMe_2), 0.41 (d, 6H, SiHMe_2), 1.02 (br, 8H, THF), 1.43 (s, 32H, CMe_3), 2.14 (s, 6H, Ar-Me), 3.51 (br, 8H, THF), 5.25 (brm, 2H, SiHMe$_2$), 6.72 (d, 2H, Ar-H$_{biaryl}$), 6.84 (s, 2H, Ar-H), 7.00 (tr, 2H, Ar-H$_{biaryl}$), 7.12 (s, 4H, Ar-H), 7.45 (d, 2H, Ar-H$_{biaryl}$). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 2.13 (SiHMe_2), 2.23 (SiHMe_2), 20.3 (Me), 23.8 (THF), 30.6 (CMe_3), 33.8 (CMe$_3$), 69.7 (THF), 109.3, 112.2, 114.5, 121.7, 123.6, 127.5, 139.6, 148.1, 149.7, 153.4 (Ar).

4.3.2. (±)-[SmL^1{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$]. This was prepared in a similar manner to 4.3.1 using proligand H_2L^1 (0.25 g, 0.43 mmol) and [Sm{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$] (0.30 g, 0.43 mmol). Combined yield of orange crystals 0.31 g, 64%. Anal. calcd for $C_{54}H_{82}N_3O_2Si_2Sm$: C, 64.10; H, 8.17; N, 4.15. Found: C, 63.72; H, 8.34; N, 4.29.

4.3.3. (±)-[LaL^1{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$]. The racemic proligand H_2L^1 (0.28 g, 0.48 mmol) and [La{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$] (0.32 g, 0.48 mmol) were loaded into a Schlenk flask inside a glove box. Toluene (10–15 ml) was added and the reaction stirred at 50°C for 3 h during which time the solution turned amber. The toluene was removed in vacuo to yield a brown foamy material. Pentane (2×10 ml) was added and then removed in vacuo yielding a yellow powder. Heptane was carefully added until almost all of the solid had dissolved, the flask was then heated gently until the remaining solid dissolved. The flask was kept at 0°C for 2 days yielding a crop of small pale yellow crystals which were isolated by filtration. A second crop was obtained from the supernatant. Combined yield 0.25 g, 59%. Anal. calcd for $C_{54}H_{82}N_3O_2Si_2La$: C, 64.84; H, 8.26; N, 4.20. Found: C, 64.43; H, 8.15; N, 4.34. ^{1}H NMR (C_6D_6, 297 K, 400 MHz): δ 0.33 (d, 6H, SiHMe_2), 0.38 (d, 6H, SiHMe_2), 1.10 (br, 8H, THF), 1.43 (s, 36H, CMe_3), 2.15 (s, 6H, Ar-Me), 3.35 (br, 4H, THF), 3.59 (br, 4H, THF), 5.22 (brm, 2H, SiHMe$_2$), 6.72 (d, 2H, Ar-H), 6.94 (s, 2H, Ar-H), 7.00 (tr, 2H, Ar-H), 7.13 (s, 4H, Ar-H), 7.43 (d, 2H, Ar-H). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 2.18 (SiHMe_2), 20.4 (Ar-Me), 24.0 (THF), 30.6 (CMe_3), 33.8 (CMe$_3$), 68.6 (THF), 108.8, 111.4 114.5, 121.2, 123.6, 127.6, 132.3, 140.6, 147.6, 149.6, 150.7, 153.4 (Ar).

4.4. In situ protocol for catalysis

The diamine proligand $H_2L^{1\text{-}4}$ (10 mg) and the appropriate metal amide (0.8 equiv.) were loaded into an NMR tube fitted with a Young's type concentric stopcock. d_8-Toluene was added and the sample heated at 50°C until metalation of the ligand was complete (^{1}H NMR). The d_8-toluene and protonlysised amine by-product were removed in vacuo, after which 2,2-dimethylaminopent-4-ene (ca. 30 equivalents) and d_8-toluene were added. The reactions were maintained at constant temperature (Table 1) until catalytic reaction was complete.

The enantiomeric excess was determined via a modification of the procedure of Hoye.[21] Thereby, the volatile components were vacuum transferred from the NMR tube into a receiver flask. Dichloromethane (1–2 ml) was added to the distillate, followed by 1 equivalent of

(*R*) - (–) - α - methoxy - α - (trifluoromethyl)phenylacetyl chloride[22] and excess triethylamine. The solution was stirred for 48 h and the solvent removed in vacuo. The ^{19}F NMR spectrum ($CDCl_3$, 50°C) of the resultant diastereomeric mixture of amides was integrated readily, and was compared with that of the product arisen from the racemic catalyst system.

Acknowledgements

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References

1. For recent reviews, see: (a) Beller, M.; Breindl, C.; Eichberger M.; Hartung, C. G.; Seayad, J.; Thiel, O. R.; Tillack, A.; Trauthwein, H. *Synlett* **2002**, *10*, 1579; (b) Muller T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675. Selected references: (a) McGrane, P. L.; Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1992**, *114*, 5459. (b) McGrane, P. L.; Livinghouse, T. *J. Am. Chem. Soc.* **1993**, *115*, 11485; (c) Shi, Y.; Ciszewski, J. T.; Odom, A. L. *Organometallics* **2001**, *20*, 3967; (d) Cao, C.; Shi, Y.; Odom, A. L. *Org. Lett.* **2002**, *4*, 2853; (e) Ackermann, L.; Bergmann, R. G. *Org. Lett.* **2002**, *4*, 1475; (f) Burgstein, M. R.; Berberich, H.; Roesky, P. *Organometallics* **1998**, *17*, 1452.
2. (a) Ambuehl, J.; Pregosin, P. S.; Venanzi, L. M.; Ughetto, G.; Zambonelli, L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 369; (b) Ambuehl, J.; Pregosin, P. S.; Venanzi, L. M.; Consiglio, G.; Bachechi, F.; Zambonelli, L. *J. Organomet. Chem.* **1979**, *181*, 255; (c) Ambuehl, J.; Pregosin, P. S.; Venanzi, L. M.; Ughetto, G.; Zambonelli, L. *J. Organomet. Chem.* **1978**, *160*, 329; (d) Campi, E. M.; Jackson, W. R. *J. Organomet. Chem.* **1996**, *523*, 205; (e) Fukuda, Y.; Utimoto, K.; Nozaki, H. *Heterocycles* **1987**, *25*, 297; (f) Utimoto, K. *Pure Appl. Chem.* **1983**, *55*, 1845.
3. (a) Douglass, M. R.; Ogasawara, M.; Hong, S.; Metz, M. V.; Marks, T. J. *Organometallics* **2002**, *21*, 283; (b) Giardello, M. A.; Conticello, V. P.; Laurent, B.; Gagne, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241.
4. Kim, Y. K.; Livinghouse, T.; Bercaw, J. E. *Tetrahedron Lett.* **2001**, *42*, 2933.
5. Gillespie, K. M.; Sanders, C. J.; O'Shaughnessy, P.; Westmoreland, I.; Thickett, C. P.; Scott, P. *J. Org. Chem.* **2002**, *67*, 3450.
6. O'Shaughnessy, P. N.; Gillespie, K. M.; Morton, C.; Westmoreland, I.; Scott, P. *Organometallics* **2002**, *21*, 4496.
7. Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125 and references therein.
8. (a) Sanders, C. J.; Gillespie, K. M.; Bell, D.; Scott, P. *J. Am. Chem. Soc.* **2000**, *122*, 7132; (b) Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326; (c) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889.
9. Runte, O.; Priermeier, T.; Anwander, R. *Chem. Commun.* **1996**, 1385.
10. Anwander, R.; Runte, R.; Eppinger, J.; Garstberger, G.; Herdtweck, E.; Spiegler, M. *J. Chem. Soc., Dalton Trans.* **1998**, 847.
11. Aspinall, H. C.; Tillotsen, M. R. *Polyhedron* **1994**, *13*, 3229.
12. Estler, F.; Eickerling, G.; Eberhardt, H.; Anwander, R. *Organometallics* **2003**, *22*, 1212.
13. Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275.
14. Grimm, D. T.; Bartmess, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 1227 and references cited therein.
15. Armstrong, D. R.; Carstairs, A.; Henderson, K. W. *Organometallics* **1999**, *18*, 3589.
16. Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett.* **2001**, *3*, 3225.
17. Aspinall, H. C. *Chem. Rev.* **2002**, *102*, 1807.
18. It is noteworthy that the only other reported non-cyclopentadienyl organolanthanide enantioselective catalytic reaction reported use a silylated biaryldiimine ligand related to $L^{1\text{-}4}$: Gountchev, T. I.; Tilley, T. D. *Organometallics* **1999**, *18*, 5661.
19. Mallory, F. B.; Butler, K. E.; Berube, A.; Eddie, E. D.; Luzik, J.; Mallory, C. W.; Brondyke, E. J.; Hiremath, R.; Phung, N.; Carroll, P. J. *Tetrahedron* **2001**, *57*, 3715.
20. Tamaru, T.; Hojo, M.; Higashimura, H.; Yoshida, Z. *J. Am. Chem. Soc.* **1988**, *110*, 3994.
21. Hoye, T. R.; Renner, M. K. *J. Org. Chem.* **1996**, *61*, 2056.
22. Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.