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Chiral-at-metal organolanthanides: enantioselective aminoalkene hydroamination/cyclisation with non-cyclopentadienyls†

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Chiral non-racemic complexes [ML{N(SiMe$_2$H)$_2$}(thf)] (M = Y, La, H_2L = salicylaldimine ligands derived from 2,2′-diamino-6,6′-dimethylbiphenyl) are found not to be effective catalysts for the intramolecular hydroamination of aminoalkenes, but new amino/phenoxide ligand designs without reducible functional groups led to long-lived and enantioselective catalysts.

The lability of group 3 and lanthanide element–ligand bonds and the flexibility of their coordination geometries make these elements highly suitable for use in catalysis, but these factors also make it difficult to generate well-defined chiral architectures that will lead to efficient enantioselective reactions. It has been pointed out that the number of truly effective chiral ligands in lanthanide coordination chemistry is severely limited.[1] For *organo*lanthanide systems‡ the chiral cyclopentadienyls, particularly Marks' planar chiral menthyl and neomenthyl Cp complexes[2] are essentially peerless, and while several groups worldwide are working on the synthesis of new chiral organolanthanide complexes, actual enantioselective catalyses are exceptionally rare.[3] It is becoming clear that for organolanthanides to be successful in this type of application there is a requirement that the chirality of the system is exceptionally well expressed in the active sites. This presents a major challenge to lanthanide chemists.[1]

Polydentate Schiff base ligands have been used in a wide range of metal-catalysed reactions,[4] and well defined complexes of these ligands with lanthanide and group 3 elements have been reported.[5] Chiral salicylaldimines[6] such as H_2L^1 and similar binaphthyls[7] coordinate to transition metals giving chiral-at-metal[8] structures. We envisioned this type of structure could lead to enantioselective organolanthanide catalysts for aminoalkene hydroamination,[2] particularly since they give stereoselective ring-opening polymerisation of *meso*-lactide.[9]

Treatment of H_2L^1 with [M{N(SiMe$_2$H)$_2$}$_3$(THF)$_2$] (M = Y, La)[5a] led to clean formation of [ML^1{N(SiMe$_2$H)$_2$}(THF)] (M = Y, La). (Figure 1). Both complexes mediated the cyclisation of 2,2-dimethylaminopent-4-ene at 70° (Table 1 entries 1, 2), but conversion ceased after a few turnovers. Since this catalytic reaction involves the intermediacy of a metal alkyl species,[2c] we conjectured that the catalyst could be decomposing by 1,2-migratory insertion at an imine unit.[5b] We have recently shown how a similar reaction in group 4 complexes can be prevented by use of the 6-methylsalicylaldimine unit in L^2.[6d] Accordingly, the complexes [ML^2{N(SiMe$_2$H)$_2$}(THF)] (M = Y, La) were prepared, and while significantly better conversions were obtained in hydroamination/cyclisation, the reaction was very slow (Table 1, entries 3, 4).

The molecular structure of the complex [YL^2{N(SiMe$_2$H)$_2$}(THF)] (Figure 1) is similar to that observed in our group 4 metal complexes in that the Schiff base is disposed with C_2 symmetry about the metal in the rare *cis*-α orientation. The chirality arising from the biaryl unit is thus very well expressed in the (potentially) active sites at the metal, and this encouraged us to investigate alternative methods of generating this type of architecture with ligands that do not contain reactive electrophilic groups. This problem has been noted by Evans.[5d]

The new chiral aminophenoxido proligand (*S*)-H_2L^3 was prepared conveniently and in high yield as shown in Scheme 2. The diamine (*S*)-**1**[10] reacted with 3,5-di-*tert*-butylcatechol under acid catalysed conditions to give **2** directly.§ The N–H groups in this compound were efficiently methylated using LiBu^n/MeI to give H_2L^3. Protonolysis reactions with the metal amides gave [ML^3{N(SiMe$_2$H)$_2$}(THF)$_2$] (M = Y, Sm, La).

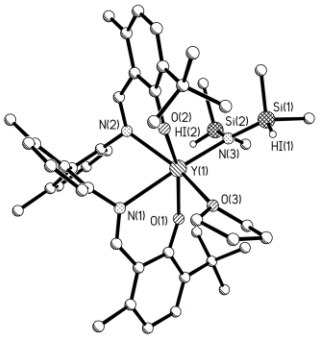
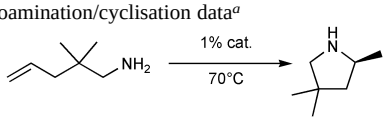


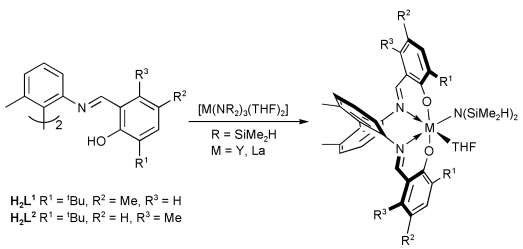
Fig. 1 Molecular structure of [YL^2{N(SiMe$_2$H)$_2$}(THF)].

Table 1 Hydroamination/cyclisation data[a]



Entry	Catalyst	M	*t*/h	Conv./%	ee/%
1	[ML^1{N(SiMe$_2$H)$_2$}(THF)]	Y	24[b]	12	—
2		La		9	—
3	[ML^2{N(SiMe$_2$H)$_2$}(THF)]	Y	24[c]	45	—
4		La		49	—
5		Y	72	100	5
6	[ML^3{N(SiMe$_2$H)$_2$}(THF)$_2$]	Sm	44	100	0
7		La	40	100	0
8		Y	24	100	11
9	[ML^4{N(SiMe$_2$H)$_2$}(THF)$_2$]	Sm	30	100	27
10		La	40	100	61

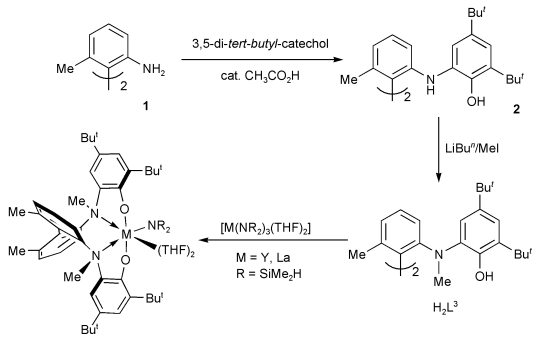
[a] All reactions were performed in C_6D_6 at 70 °C in presence of *ca* 1% catalyst. [b] No further turnover was observed after this time. [c] Very slow, but catalysis still occurring after 4 weeks.



Scheme 1 Synthesis of Schiff base complexes.

† Electronic supplementary information (ESI) available: complete experimental procedures and characterising data for all ligands and complexes, crystal data for [YL^2{N(SiMe$_2$H)$_2$}(THF)] and [SmL^4{N(SiMe$_2$H)}]. See http://www.rsc.org/suppdata/cc/b3/b305105f/

DOI: 10.1039/b305105f

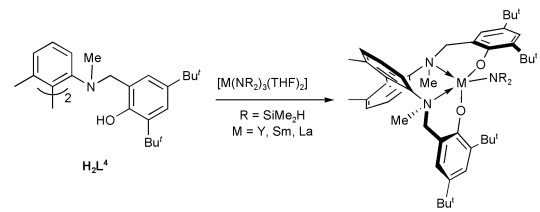


Scheme 2 Synthetic route to aminophenols H_2L^3 and metal complexes.

A further novel chiral ligand (*S*)-H_2L^4 (Scheme 3) was prepared *via* reduction of the corresponding Schiff-base and *N*-methylation as before. The subsequent complexes [ML^4{N(Si-$Me_2H)_2$}$(THF)_2$] (M = Y, Sm, La) were accessible. NMR spectra indicate that the complexes are C_2 symmetric on this timescale in the presence of THF. In the case of the Y compound, prolonged drying *in vacuo* removed the majority of THF and a single diastereomeric C_1 symmetric system was observed by NMR spectroscopy. The structure of the THF-free samarium complex (Figure 2) indicates that the biaryl unit has predetermined in this case a (*S*)-Λ-*cis*-β_1 structure[6c,8] consistent with the NMR data. Notably, the stereogenic NMe units have opposite absolute configurations. One amido SiH group is involved in an agostic Si–H–Sm interaction.[11]

All of the above complexes of L^{3-4} are catalysts for hydroamination/cyclisation of dimethylaminopentene at 70 °C, giving complete conversion of the substrate (Table 1, entries 5–10). In the case of the L^3 complexes we were surprised to find that the products were essentially racemic. This situation was not improved significantly by operating the catalysts at lower temperatures. In contrast, the complexes of L^4 gave significant enantiomeric excess in this reaction, and in the case of the lanthanum complex [ML^4{N($SiMe_2H$)] the selectivity is comparable with the best result thus far obtained by Marks using the C_1 symmetric (*S*)-menthylcyclopentadienyl *ansa*-metallocene system,[2] although the activity is somewhat lower.

Hence it appears that (i) the Schiff base ligands $L^{1,2}$ are too reactive to support this type of reaction, and (ii) while the L^3 system is chemically robust, the chirality of the biaryl unit is poorly communicated to the prochiral reagent, probably as a result of insufficient chelate "reach-around". In contrast L^4 provides a non-cyclopentadienyl environment for enantioselective organolanthanide catalysis.‡ It is worth noting that the *cis*-β structure adopted by complexes of L^4 is analogous to that of the ruthenium complexes of *e.g.* L^1 which give exceptionally high stereoselectivity in catalytic alkene cyclopropanation.[6c] We believe that the chiral-at-metal architecture is the origin of the selectivity in both cases; as in the case of planar-chiral cyclopentadienyl systems,[2] the chirality is strongly expressed in the active site.



Scheme 3 Synthetic route to aminophenols H_2L^3 and metal complexes.

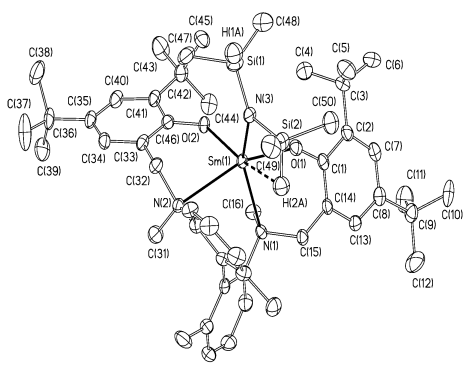


Fig. 2 Molecular structure of (*S*)-Λ-*cis*-β_1-[SmL^4{N($SiMe_2H$)}]

PS thanks EPSRC and BP Chemicals for support of this work.

Notes and references

‡ The distinction between lanthanide coordination complexes and organolanthanides (broadly alkyls, hydrides and amido compounds) is important since in the former all catalyses are expected to be Lewis acid processes, whereas in the latter there exists the possibility of other reactions such as migratory insertion.

§ Our development of this reaction type will be reported elsewhere.

Electronic Supplementary Information (ESI) available.†

Crystal data: $C_{46}H_{64}N_3O_3Si_2Y$, *M* = 852.09, monoclinic, *a* = 15.92(2), *b* = 17.51(3), *c* = 16.80(2) Å, *β* = 95.16(13), *U* = 4666(12) Å^3, *T* = 180(2) K, space group *P*2(1)/*a*, *Z* = 4, μ(Mo–Kα) = 1.341 mm^{-1}, 20959 reflections measured, 6070 unique (R_{int} = 0.3134). The final *R*1 = 0.1607 [*I* > 2σ (*I*)]. CCDC 210134. $C_{57}H_{92}N_3O_2Si_2Sm$, *M* = 1057.87, triclinic, *a* = 11.1290(13), *b* = 14.1565(17), *c* = 19.349(2) Å, *α* = 101.030(2), *β* = 101.798(3), *γ* = 94.828(3), *U* = 2904.7(6) Å^3, *T* = 180(2) K, space group *P*1, *Z* = 2, μ(Mo–Kα) = 1.092 mm^{-1}, 28296 reflections measured, 9141 unique (R_{int} = 0.0661). The final *R*1 = 0.0524 [*I* > 2σ (*I*)]. CCDC 211979. See http://www.rsc.org/suppdata/cc/b3/b305105f/ for crystallographic data in .cif or other electronic format.

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