

# Lanthanide complexes derived from (*R*)-1,1'-binaphthyl-2,2'-bis(neopentylamine) – {Li(THF)<sub>4</sub>}{Ln[(*R*)-C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>(C<sub>10</sub>H<sub>22</sub>)<sub>2</sub>] (Ln = Sm, Yb) – novel catalysts for enantioselective intramolecular hydroamination†

Jacqueline Collin,<sup>\*a</sup> Jean-Claude Daran,<sup>b</sup> Emmanuelle Schulz<sup>a</sup> and Alexander Trifonov<sup>\*c</sup>

<sup>a</sup> Laboratoire de Catalyse Moléculaire, ICMMO, Université Paris-Sud, 91405 Orsay, France

<sup>b</sup> Laboratoire de Chimie de Coordination, 205 route de Narbonne, 31077 Toulouse, France

<sup>c</sup> G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinia 49, 603600 Nizhny Novgorod GSP-445, Russia. E-mail: jacollin@icmo.u-psud.fr; Fax: 33 (0) 1 69154680; Tel: 33 (0) 1 69154740

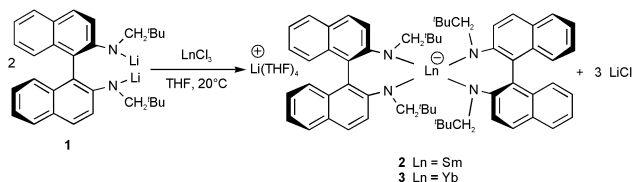
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The complexes {Li(THF)<sub>4</sub>}{Ln[(*R*)-C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>(C<sub>10</sub>H<sub>22</sub>)<sub>2</sub>] (Ln = Sm, Yb) have been synthesized, fully characterized and found to be efficient and enantioselective catalysts for intramolecular hydroamination of 1-(aminomethyl)-1-allylcyclohexane.

Catalytic formation of carbon–nitrogen bonds resulting in amines has not been much developed yet, in spite of its potential.<sup>1</sup> Lanthanide alkyl and amido metallocene complexes Cp<sub>2</sub>LnR (Cp = Cp\*, Me<sub>2</sub>Si[(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>)(*t*-BuN)], (CH<sub>2</sub>-1-C<sub>9</sub>H<sub>6</sub>)<sub>2</sub>) proved to be efficient catalysts for intramolecular hydroamination–cyclisation of primary aminoolefins<sup>2</sup> affording useful synthetic pathways to various nitrogen-containing heterocycles. Catalysis of this reaction by non-cyclopentadienyl lanthanide complexes Ln[N(TMS)<sub>2</sub>]<sub>3</sub> (Ln = Nd, Y) has been recently described.<sup>3</sup> The catalysts *in situ* prepared by reaction of the latter precursors with chelating diamines afforded rate enhancements and improved diastereoselectivities.<sup>4</sup> The first enantioselective intramolecular cyclisation of aminoolefins catalysed by lanthanide(III) metallocene alkyl and amido complexes coordinated by chiral ansa bis(cyclopentadienyl) ligands has been described by Marks.<sup>5</sup> When the present work has been undertaken, no example of enantioselective intramolecular hydroamination catalysed by non-cyclopentadienyl lanthanide complexes was reported.<sup>6</sup> The recent publications on the use of chiral ligands derived from 2,2'-diamino-6,6'-dimethylbiphenyl for the enantioselective cyclisation of 2,2-dimethylaminopent-4-ene,<sup>7</sup> prompted us to report our first results on a new family of structurally defined lanthanide amides {Li(THF)<sub>4</sub>}{Ln[(*R*)-C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>(C<sub>10</sub>H<sub>22</sub>)<sub>2</sub>] (Ln = Sm, Yb) as catalysts for enantioselective intramolecular hydroamination–cyclisation of 1-(aminomethyl)-1-allylcyclohexane.

Although a large variety of enantioselective catalytic reactions with numerous metals including lanthanides involves binaphthol as chiral ligand,<sup>8</sup> no lanthanide catalyst based on a binaphthyl diamine ligand has been reported, as far as we know. Complexes **2** and **3** have been synthesized by metathetic reactions of anhydrous LnCl<sub>3</sub> (Ln = Sm, Yb) in THF at ambient temperature, with two equivalents of Li<sub>2</sub>[(*R*)-C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>(C<sub>10</sub>H<sub>22</sub>)] (**1**) (Scheme 1).<sup>9</sup> In order to eliminate LiCl

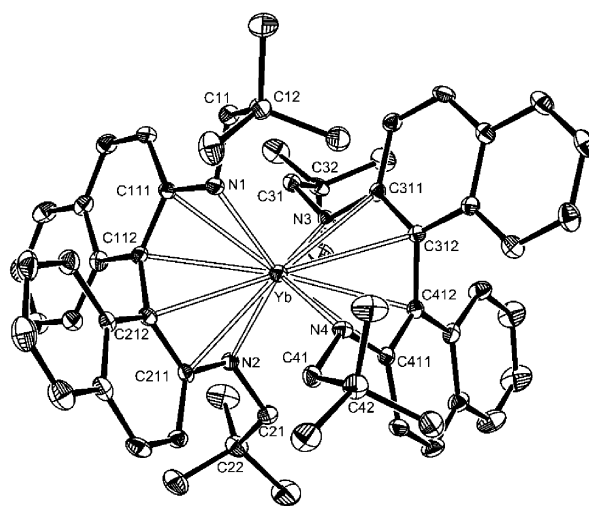


**Scheme 1** Synthesis of the complexes {Li(THF)<sub>4</sub>}{Ln[(*R*)-C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>(C<sub>10</sub>H<sub>22</sub>)<sub>2</sub>] (Ln = Sm, Yb).

† Electronic supplementary information (ESI) available: full characterisation. See <http://www.rsc.org/suppdata/cc/b3/b310954b/>

formed in the reactions, THF was evaporated *in vacuo* and solid residues were extracted with toluene. Evaporation of toluene and recrystallization of the products from a mixture of THF–hexane at 20 °C resulted in isolation of complexes **2** and **3** in 55 and 62% yield, respectively. Complex **2** is orange and **3** is a reddish-brown paramagnetic crystalline solid. They are soluble in THF, sparingly soluble in toluene and nearly insoluble in hexane.

X-Ray diffraction studies of **2** and **3** have revealed these compounds to be isostructural ionic complexes.‡ They are both composed of a discrete cation Li(THF)<sub>4</sub><sup>+</sup> and a discrete complex anion {Ln[(*R*)-C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>(C<sub>10</sub>H<sub>22</sub>)<sub>2</sub>]}<sup>-</sup>. The Ln atoms coordinated by four nitrogen atoms adopt a distorted tetrahedral geometry (Fig. 1). Vicinal bulky neopentyl groups are *trans*-oriented. The Yb–N bond lengths in **3** are noticeably longer than those normally reported for neutral ytterbium amido complexes,<sup>10a,b</sup> and are comparable to the distances in the sterically hindered complex (MeC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>YbNPh<sub>2</sub>(THF)<sup>10c</sup> and in the related ionic complex [Li(THF)<sub>4</sub>][Yb(NPh<sub>2</sub>)<sub>4</sub>].<sup>10d</sup> The values of the Sm–N bond distances in **2** are close to that in the complex Cp\*<sub>2</sub>SmNPh(THF),<sup>10e</sup> but substantially shorter than those in the complex of trivalent samarium Cp\*<sub>2</sub>Sm(bipy).<sup>10f</sup> The short contacts between the lanthanide atoms and the carbon atoms in *ipso*- and *ortho*-positions to the amido groups in **2** and **3**, comparable to the Ln–C bond distances in the arene complexes Yb(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)(AlCl<sub>4</sub>)<sub>3</sub><sup>11a</sup> and Sm(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)(AlCl<sub>4</sub>)<sub>3</sub>,<sup>11b</sup>



**Fig. 1** Molecular view of complex **3** with atom labelling scheme. Ellipsoids at 30%. Selected bond lengths (Å): Yb–N(3) 2.232(3); Yb–N(4) 2.255(2); Yb–N(1) 2.271(3); Yb–N(2) 2.286(3); Yb–C(211) 2.684(3); Yb–C(411) 2.718(3); Yb–C(212) 2.724(4); Yb–C(111) 2.736(4); Yb–C(311) 2.741(3); Yb–C(112) 2.812(4); Yb–C(412) 2.832(4); Yb–C(312) 2.849(3).

probably result from  $\eta^2$ -interaction of the Ln(III) atoms with the aromatic rings of the binaphthyl ligand.

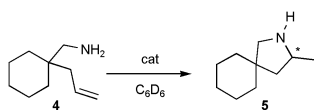
We have tested these novel lanthanide chiral complexes in the intramolecular hydroamination reaction of 1-(aminomethyl)-1-allylcyclohexane **4**.<sup>12</sup> This transformation allows the preparation of a new spirocyclic pyrrolidine **5**, a structure that can be found in numerous steroidal alkaloids of the conessine or conanine series.

1-(Aminomethyl)-1-allylcyclohexane **4** was first successfully cyclised in the presence of 5 mol% Sm[N(TMS)<sub>2</sub>]<sub>3</sub> at room temperature in benzene (entry 1, Table 1) to afford the spiro compound **5** (100%, 24 h). Derivatizing the spiropyrrolidine **5** into the corresponding Mosher amide afforded a method of determination of the diastereomeric excess (*i.e.* the related enantiomeric excess) by GC analysis. Related reactions using chiral catalysts **2** and **3** were directly performed as NMR tube scale reactions to supply the kinetics of the transformation. The samarium complex **2** allowed the cyclisation to be achieved in 2 h (20 °C) with a catalyst ratio of 12 mol% and yielded compound **5** with 26% enantiomeric excess (entry 2). Decreasing the catalyst ratio (5 mol%) afforded the desired product with similar yield and enantiomeric excess (entry 3), indicating a high activity of this type of catalyst compared to Sm[N(TMS)<sub>2</sub>]<sub>3</sub>. The presence of the chelating diamine induces hence in this transformation a remarkable ligand accelerating effect.

A series of experiments was analogously run with the chiral ytterbium catalyst **3**, leading as a whole to a more active and selective catalysis (see entry 4, 41% ee). Here too, decreasing the catalyst ratio, did not affect neither the conversion, nor the enantiomeric excess (entry 5). This experiment was realized at a larger scale, leading to isolated pure product **5** in 55% yield.<sup>13</sup> Analogous transformations were performed in deuterated toluene to allow a decrease in the temperature of the reaction. The catalytic system proved to be, in this solvent, as active and enantioselective as in C<sub>6</sub>D<sub>6</sub> (entry 6). A decrease in the temperature enhanced the enantiomeric excess up to 47% (at 0 °C) and 53% (at -20 °C), however led to dramatic diminution in activity.

New non cyclopentadienyl chiral lanthanide complexes have been synthesized and showed high activity for enantioselective intramolecular hydroamination of an aminopentene derivative. Studies are currently in progress in our laboratories to extend

**Table 1** Hydroamination–cyclisation of 1-(aminomethyl)-1-allylcyclohexane **4**



	Catalyst	T/°C	Cat. ratio (mol%)	Time/h	GC yield (%)	ee (%)
1	SmR <sub>3</sub> <sup>a,b</sup>	25	5	24	100	—
2	<b>2</b> <sup>b</sup>	25	12	2	84	26
3	<b>2</b> <sup>b</sup>	25	5	2	78	24
4	<b>3</b> <sup>b</sup>	25	6.6	1	91	41
5	<b>3</b> <sup>b</sup>	25	3.5	1.5	87	41
6	<b>3</b> <sup>c</sup>	25	6	0.5	94	40
7	<b>3</b> <sup>c</sup>	0	6	17	81	47
8	<b>3</b> <sup>c</sup>	-20	6	24	13	53

<sup>a</sup> SmR<sub>3</sub> = Sm[N(TMS)<sub>2</sub>]<sub>3</sub>. <sup>b</sup> C<sub>6</sub>D<sub>6</sub>. <sup>c</sup> C<sub>7</sub>D<sub>8</sub>.

this new family of enantioselective catalysts and widen the scope of substrates.

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## Notes and references

‡ *Crystal data*: {Li(THF)<sub>4</sub>}{Sm[(R)-C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>(C<sub>10</sub>H<sub>22</sub>)<sub>2</sub>]} (**2**): C<sub>76</sub>H<sub>100</sub>Li<sub>4</sub>N<sub>4</sub>O<sub>4</sub>Sm, *M* = 1290.89, orthorhombic, *a* = 11.1019(7), *b* = 25.0568(14), *c* = 25.2362(14) Å, *U* = 7020.2(7) Å<sup>3</sup>, *T* = 180 K, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (no. 19), *Z* = 4,  $\mu$ (Mo–K $\alpha$ ) = 0.886 mm<sup>-1</sup>, 53 629 reflections measured, 14 301 unique (*R*<sub>int</sub> = 0.069) which were used in all calculations. The final *R* and *wR*(*F*<sup>2</sup>) were 0.0512 and 0.0900 respectively (all data), Flack's parameter = 0.001(9), CCDC 216530.

*Crystal data*: {Li(THF)<sub>4</sub>}{Yb[(R)-C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>(C<sub>10</sub>H<sub>22</sub>)<sub>2</sub>]} (**3**): C<sub>76</sub>H<sub>100</sub>Li<sub>4</sub>N<sub>4</sub>O<sub>4</sub>Yb, *M* = 1313.58, orthorhombic, *a* = 11.0896(6), *b* = 24.9395(12), *c* = 25.1973(11) Å, *U* = 6968.8(6) Å<sup>3</sup>, *T* = 180 K, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (no. 19), *Z* = 4,  $\mu$ (Mo–K $\alpha$ ) = 1.392 mm<sup>-1</sup>, 51 786 reflections measured, 13 754 unique (*R*<sub>int</sub> = 0.061) which were used in all calculations. The final *R* and *wR*(*F*<sup>2</sup>) were 0.0388 and 0.0657 respectively (all data), Flack's parameter = 0.035(5), CCDC 216529. See <http://www.rsc.org/suppdata/cc/b3/b310954b/> for crystallographic data in .cif or other electronic format.

- (a) T. E. Muller and M. Beller, *Chem. Rev.*, 1998, **98**, 675–703; (b) M. Nobis and B. Driessen-Hölscher, *Angew. Chem., Int. Ed.*, 2001, **40**, 3983–3984; (c) G. A. Molander and J. A. Romero, *Chem. Rev.*, 2002, **102**, 2161–2185.
- (a) M. R. Gagné, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 275–294; (b) S. Tian, V. M. Arredondo, C. L. Stern and T. J. Marks, *Organometallics*, 1999, **18**, 2568–2570; (c) G. A. Molander and E. D. Dowdy, *J. Org. Chem.*, 1998, **63**, 8983–8988; (d) G. A. Molander, E. D. Dowdy and S. K. Pack, *J. Org. Chem.*, 2001, **66**, 4344–4347; (e) A. T. Gilbert, B. L. Davis, T. J. Emge and R. D. Broene, *Organometallics*, 1999, **18**, 2125–2132.
- Y. K. Kim and T. Livinghouse, *Tetrahedron Lett.*, 2001, **42**, 2933–2935.
- Y. K. Kim and T. Livinghouse, *Angew. Chem. Int. Ed.*, 2002, **41**, 3645–3647.
- (a) M. A. Giardello, V. P. Conticello, L. Brard, M. R. Gagné and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10241–10254; (b) M. R. Douglass, M. Ogasawara, S. Hong, M. V. Metz and T. J. Marks, *Organometallics*, 2002, **21**, 283–292; (c) S. Hong and T. J. Marks, *J. Am. Chem. Soc.*, 2002, **124**, 7886–7887.
- P. W. Roesky and T. Muller, *Angew. Chem., Int. Ed.*, 2003, **42**, 2708–2710.
- (a) P. N. O'Shaughnessy and P. Scott, *Tetrahedron: Asymm.*, 2003, **14**, 1979–1983; (b) P. N. O'Shaughnessy, P. D. Knight, C. Morton, K. M. Gillespie and P. Scott, *Chem. Commun.*, 2003, 1770–1771.
- H. C. Aspinall, *Chem. Rev.*, 2002, **102**, 1807–1850.
- C. Drost, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1996, 3595–3601.
- (a) M. Nimeyer, *Z. Anorg. Allg. Chem.*, 2002, **628**, 647–657; (b) H. C. Aspinall, D. C. Bradley, M. B. Hirsthouse, K. D. Sales, N. P. C. Walker and B. Hussain, *J. Chem. Soc., Dalton Trans.*, 1989, 623–626; (c) Y. Wang, Q. Shen, F. Xue and K. Yu, *J. Organometal. Chem.*, 2000, **598**, 359–364; (d) W.-K. Wong, L. Zhang, F. Xue and T. C. Mak, *Polyhedron*, 1997, **16**, 345–347; (e) W. J. Evans, G. Kociok-Koehn, V. S. Leong and J. W. Ziller, *Inorg. Chem.*, 1992, **31**, 3592–3600; (f) W. J. Evans and D. K. Drummond, *J. Am. Chem. Soc.*, 1989, **111**, 3329–3335.
- (a) H. Liang, Q. Shen, J. Guan and Y. Lin, *J. Organometal. Chem.*, 1994, **474**, 117–122; (b) F. A. Cotton and W. Schwotzer, *Organometallics*, 1987, **6**, 1275–1280.
- N. De Kimpe, D. De Smaele, A. Hofkens, Y. Dejaegher and B. Kesteleyn, *Tetrahedron*, 1997, **53**, 10803–10816.
- This new compound has been fully characterized, see ESI.