Supplementary informations

Lanthanide complexes derived from (*R*)-1,1'-binaphthyl-2,2'-bis(neopentylamine) - {Li(THF)$_4$} {Ln[(*R*)-$C_{20}H_{12}N_2(C_{10}H_{22})$]$_2$} (Ln = Sm, Yb) - novel catalysts for enantioselective intramolecular hydroamination.

Jacqueline Collin*[a], Jean-Claude Daran[b], Emmanuelle Schulz[a], Alexander Trifonov *[c]

[a] *Laboratoire de Catalyse Moléculaire, ICMMO, Université Paris-Sud, 91405 Orsay, France*

[b] *Laboratoire de Chimie de Coordination, 205 route de Narbonne, 31077 Toulouse, France*

[c] *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

Experimental .

General comments

All manipulations were carried out under an argon atmosphere using standard Schlenk or glove box techniques. THF, C_6D_6 and C_7D_8 were distilled from sodium benzophenone ketyl, hexane and toluene from CaH_2. All solvents were degassed by three freeze-pump–thaw cycles and stored in the glove box. $Sm[N(TMS)_2]_3$ was prepared by the literature procedure.[1]Bruker AM 250, and Bruker DRX 400 NMR spectrometers, (operating at 250, and 400 MHz respectively) were used for recording the NMR spectra. Infrared spectra were recorded as Nujol mulls using NaCl or CsI plates on a Perkin-Elmer 1000 FT-IR spectrometer and are reported in cm^{-1}. Optical rotations were measured with a Perkin-Elmer 341 polarimeter.

Syntheses

{Li(THF)$_4$} {Sm[(*R*)-$C_{20}H_{12}N_2(C_{10}H_{22})$]$_2$} 2. $SmCl_3$ (0.036 g, 0.140 mmol) was slowly added to a solution of 0.122 g (0.280 mmol) of **1** in 5 mL of THF at 20°C under vigorous stirring. The reaction mixture was stirred for 3 h, THF evaporated *in vacuo* and the resulted solid extracted with toluene (15 mL). The extracts were filtered, toluene was evaporated and the solid residue was dissolved in 2 mL of THF. Slow condensation of hexane in the THF solution at 20°C resulted in 0.100 g (55 %) of **2** as orange crystals. ^{1}H NMR (C_6D_6, 20°C, δ): 9.39 (bs, 2H), 8.70 (bs, 2H), 7.96 (bs, 2H), 7.79 (bs, 2H), 7.54 (bs, 2H), 7.34 (bs, 2H), 7.12 (bs, 2H), 6.87 (bs, 2H), 5.24 (bs, 4H), 4.64 (bs, 4H), 3.64, (bs, 16H), 2.53 (bs, 4H), 1.47 (bs, 16H), 1.05 (bs, 4H), 0.87 (bs, 18H), 0.32 (bs, 18H). ^{13}C NMR (C_6D_6, 20°C, δ): 145.63,

134.71, 129.93, 126.81, 124.48, 124.20, 122.23, 121.26, 119.70, 114.22, 112.01, 110.64, 68.09, 61.50, 53.36, 31.21, 29.10, 28.57, 27.24, 25.77. IR (CsI, Nujol, cm^{-1}) : 3050(w), 1597(m), 1499(m), 1335(m), 1261(m), 1194(w), 1096(s), 1040(s), 1022(s), 886(m), 807(s), 744(s). Anal. Calcd for $C_{76}H_{100}LiN_4O_4Sm$: C 70.71; H 7.80; Found: C 70.04; H 7.36.

í Li(THF)$_4$ý í Yb[(*R*)-C$_{20}$H$_{12}$N$_2$(C$_{10}$H$_{22}$)]$_2$ý 3. $YbCl_3$ (0.064 g, 0.229 mmol) was slowly added to a solution of 0.200 g (0.458 mmol) of **1** in 5 mL of THF at 20°C under vigorous stirring. The reaction mixture was stirred for 3 h, THF evaporated *in vacuo* and the resulted solid was extracted with toluene (15 mL). The extracts were filtered, toluene was evaporated and the solid residue was dissolved in 2 mL of THF. Slow condensation of hexane in the THF solution at 20°C resulted in 0.186 g (62 %) of **3** as reddish-brown crystals. IR (CsI, Nujol, cm^{-1}) : 3050(w), 1608(s), 1538(m), 1496(s), 1336(m), 1282(m), 1151(s), 1094(s), 1042(s), 887(m), 810(s), 744(s). Anal. Calcd for $C_{76}H_{100}LiN_4O_4Yb$: C 69.49; H 7.67; Found: C 68.88; H 7.87.

NMR-scale hydroamination-cyclisation of 1-(aminomethyl)-1-allylcyclohexane 4 and determination of enantiomeric excesses

Inside the glove box a solution of 20 mg (0.131 mmol) of 1-(aminomethyl)-1-allyl-cyclohexane **4** in 0.5 mL C_6D_6 or C_7D_8 dried on molecular sieves was added to complex **2** or **3** (see Table 1 for catalytic ratio) charged in an NMR tube equipped with a teflon stopcock. After disappearance of the olefinic protons monitored by NMR, CH_2Cl_2 was added and the amine **5** was transformed in the corresponding amide by reaction with Mosher chloride.[2] The reaction mixture was diluted with 2 mL CH_2Cl_2 and treated with 100 µl of Et_3N, 20 mg of DMAP and 30 µl of (*R*)-(-)-α-methoxy- α–(trifluoromethyl)phenylacetyl chloride. After 2 h stirring at room temperature the mixture was washed with saturated NH_4Cl solution and extracted by CH_2Cl_2. After drying, the crude product dissolved in ether was injected on a GC capillary column DB-1, (80°C - 10°C/min - 200°C - 10 min - 10°C/min - 250°C - 10 min, injector (250°C), detector (250°C)). Retention times of diastereoisomeric amides formed by reaction with the cyclised amine 3-methyl-2-aza-spiro[4,5]decane **5** and of the amide formed by reaction with the non reacted 1-(aminomethyl)-1-allyl-cyclohexane **4** are respectively 21.6 min, 22.4 min, 23.15 min. Enantiomeric excesses of methyl-2-aza-spiro[4,5]decane and GC yields in the cyclised product were determined by integration of these three peaks.

Preparative enantioselective hydroamination-cyclisation of 1-(aminomethyl)-1-allyl-cyclohexane

Inside the glove box a solution of 101 mg (0.654 mmol) of 1-aminomethyl-1-allyl-cyclohexane in 1 mL C_6D_6 dried on molecular sieves is added on 34 mg (0.026 mmol) of complex **3** in 2 mL C_6D_6. After 3h stirring at room temperature, the solvent is evaporated and the residue is distillated in Kugelrohr apparatus (b. p. $_{20\ mm\ Hg}$ = 144°C) to afford the spiropyrrolidine **5** in 55% yield. ^{1}H NMR ($CDCl_3$, 20°C, δ): 3.08 (m, 1H), 2.71 (d, 1H, *J* = 11 Hz), 2.52 (d, 1H, *J* = 11 Hz), 2.14 (bs, 1H), 1.69 (dd, 1H, *J* = 11 Hz, *J* = 7 Hz), 1.32 (m, 10H), 1.07 (d, 3H, *J* = 7 Hz), 0.93 (dd, 1H, *J* = 10 Hz, *J* = 9 Hz). ^{13}C NMR ($CDCl_3$, 20°C, δ): 59.30, 54.42, 47.84, 44.37, 39.00, 37.62, 26.46, 24.24, 24.06, 21.71. IR (NaCl, CCl_4 cm^{-1}) : 3854(w), 3747(w), 3672(w), 3650(w), 3630(w), 2928(s), 2856(m), 1450(w), 1376(w). MS electrospray $M+H^+$ 154.2, 100% $[\alpha]_D^{20}$ = + 17 (*c* 2.3, $CHCl_3$), for 40 % enantiomeric excess.

1 D. C. Bradley, J. S. Ghotra and F. A. Hart, *J. Chem. Soc. Dalton Trans.*, 1973, 1021-1023.
2 J. A. Dale, D. L. Dull and H. S. Mosher, *J. Org. Chem.,* 1969, **34**, 2543-2549.