Stereoselective synthesis of ring C-hexasubstituted trianglamines†

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The addition of organolithium reagents to the trianglimine derived from (*R*,*R*)-1,2-diaminocyclohexane and terephthalaldehyde gave the corresponding trianglamine with complete stereocontrol and the *R* configuration of all six newly formed stereocenters. The structure of the hexaphenyl-substituted macrocyle was determined by X-ray crystallographic study. The new trianglamines were tested as ligands in enantioselective catalytic reactions.

Introduction

Chiral perazamacrocycles and their metal complexes have found applications in biomedical research, diagnosis, anion sensing, molecular recognition, enantiomeric discrimination, asymmetric catalysis, and materials chemistry.[1]

The condensation of enantiopure 1,2-diaminocyclohexane with aromatic dialdehydes allows for the preparation of symmetric polyimine macrocycles, which incorporate equal amounts of both reaction partners and whose size can be tuned by the proper choice of experimental conditions, such as the use of a metal template, temperature and solvent. Although the [2+2] cyclocondensation products are generally thermodynamically favoured, the formation of the [3+3] hexaiminomacrocycles, called trianglimines, is favored by the rigidity of both reaction partners.[2] Reduction of the imine functions afforded the corresponding perazamacrocyles containing secondary amine groups (trianglamines). Compound **1**, and the reduced analogue **2** derived from terephthalaldehyde, are typical examples of such compounds.[3]

Although ring substituents can be easily introduced at the nitrogen atoms of the secondary amines,[4] alkylation of the imine moieties in macrocyclic polyimines has never been described. This would also be an alternative procedure to introduce lateral functionalities in the macromolecules and expand their potential for a variety of applications. Owing to the relatively poor electrophilicity of the imine function, we envisioned that the use of strong nucleophiles, such as organometallic reagents, would allow the achievement of this goal (Scheme 1).

Results and discussion

With this aim, we performed the addition of organolithium reagents to the trianglimine **1**, using our previous experience and knowledge concerning the addition of organolithium reagents to the diimines derived from (*R*,*R*)-1,2-diaminocyclohexane and aromatic aldehydes.[5] We were pleased to observe that, regardless of the nature of the organolithium reagent (methyl, *n*-butyl, phenyl), a single diastereomer was produced in excellent yields in the reactions affording **3a–c** (Table 1). In fact, traces of different diastereomers could not be detected by NMR analyses of the crude reaction mixtures. The C_3-symmetry of these compounds was evident in their ^{1}H-NMR spectra. On the other hand the addition of the corresponding Grignard reagents proved to be unsuccessful, as no reaction was observed (MeMgBr, PhMgBr), or a complex mixture was obtained with low conversion (allylMgCl).

Table 1 Synthesis of compounds **3a–c** from macrocyclic hexaimine **1**

RM	Product	Yield (%)
MeLi	**3a**	98 (89)[a]
n-BuLi	**3b**	94 (86)[b]
PhLi[c]	**3c**	97 (92)[a]

[a] After crystallization (MeOH). [b] After column chromatography. [c] No reaction occurred upon addition of PhMgBr in the same conditions.

Based on our previous studies,[5] the *R* configuration of all the newly formed stereocenters was assumed. Later, this and the C_3 symmetry, was confirmed by the X-ray crystallographic study of the Ph-substituted compound **3c** (Fig. 1).† In the crystal the molecules stack along [001] creating columns with the channels filled with acetonitrile molecules (see ESI†). The structure of this compound displays alternating up and down spatial position of the phenyl substituents around the almost planar ring. The stereochemical outcome can be explained by the preferred attack of the nucleophile to the less hindered face

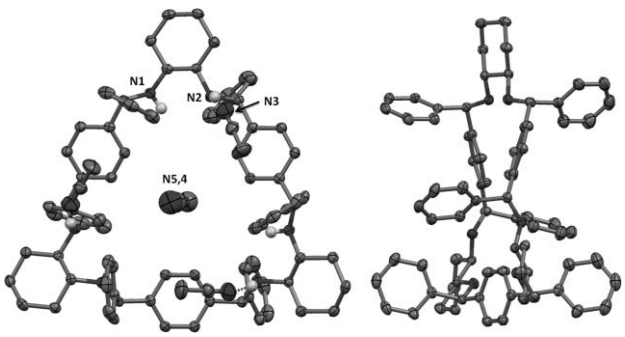

Fig. 1 Views of the molecular structure of **3c·4(CH$_3$CN) solvate**; the C-bound H-atoms have been omitted for clarity.

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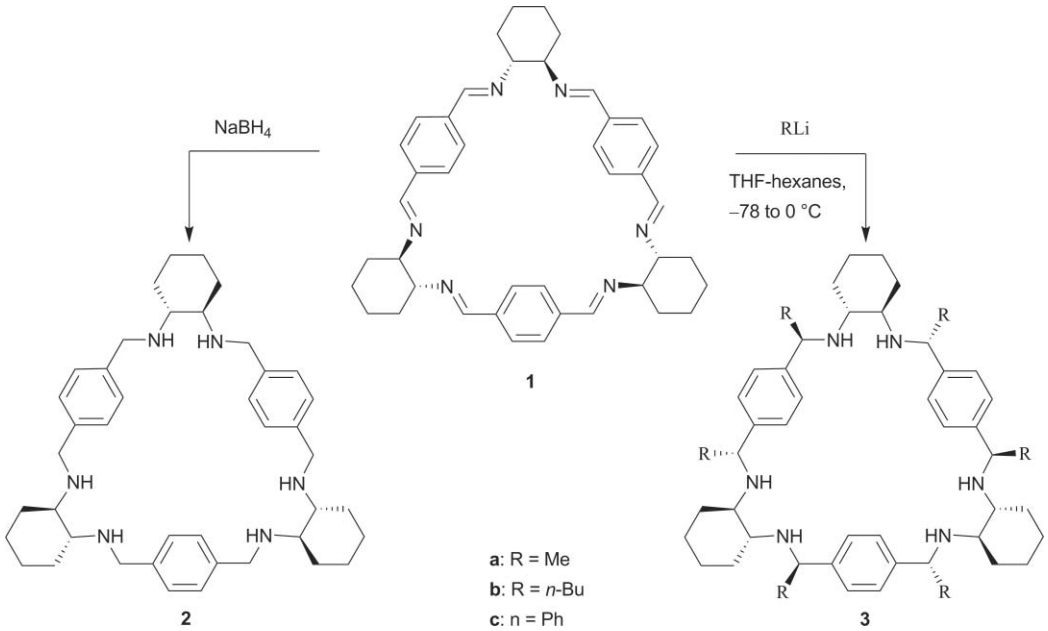
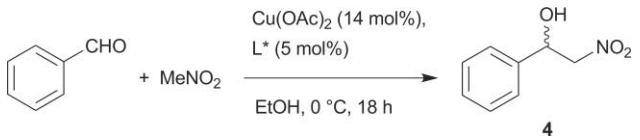


Scheme 1 Stereoselective synthesis of hexasubstituted trianglamines.

of each imine group, *i.e. syn* to the C1-H and C2-H hydrogen atoms of the cyclohexane rings. The complete diastereoselectivity is probably due to the rigidity of the substrate in the first step, and, after each individual step, by the stereochemistry of the previously introduced substituents.

It should be underlined that this communication is the first report on C–C bond forming organometallic reactions performed on macrocyclic polyimines. Instead, reduction of the macrocyclic polyimine **1** by sodium borodeuteride has been reported affording the quasi-enantiomeric d_6-derivatives of compound **2** with complete diastereoselectivity.[6] Also relevant to the present communication is the report on the reduction of the bisketimine moiety of the $MnCl_2$-complex of a pentaazamacrocycle derived from 2,6-diacetylpyridine and an ethylene-tethered bis[(*S*,*S*)-1,2-diaminocyclohexane]: the sense of asymmetric induction and the degree of diastereoselectivity were found dependent on the type of reduction (Pd-catalyzed hydrogenation with ammonium formate *vs.* borohydride addition).[7]

Owing to the ability of compound **2** to act as a ligand in metal-catalyzed enantioselective organic synthesis,[8,9] we were interested to verify if the stereocontrolled introduction of substituents in the macrocyclic ring would modify the coordination behavior of the ligand towards the metal center, so affecting and hopefully improving the enantioselectivity in the catalytic process. Therefore, the macrocylic ligands **3** were tested in two typical reactions where the unsubstituted ligand **2** displayed moderate enantioselectivity, namely, the $Cu(OAc)_2$-catalyzed Henry reaction[10,11] between nitromethane and benzaldehyde (Scheme 2)[8] and the reduction



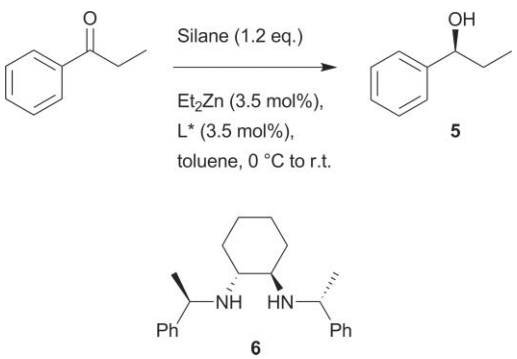
Scheme 2 Enantioselective catalytic Henry reaction.

Table 2 Copper-catalyzed enantioselective Henry reaction

Ligand	Yield of **4**[a]	Configuration	E.e. (%)[b]
3a	78 (76)[c]	*R*	46
3c	74 (72)[c]	*S*	19
2	93	*R*	84
ent-**2**[d]	96 (78)[c]	*S*	82

[a] Calculated by ^{1}H NMR. [b] Calculated by HPLC analysis on chiral column Chiralpak OD. [c] Yield of isolated, pure product (%). [d] Data taken from the literature,[8] obtained using *ent*-**2**-$Cu(OAc)_2$ (3 mol%), 10 equiv. $MeNO_2$ and no solvent.

of acetophenone by silanes (Scheme 3). The outcomes of these reactions are reported in Tables 2 and 3, respectively.



Scheme 3 Enantioselective catalytic reduction of propiophenone.

The reactions between nitromethane and benzaldehyde performed in the presence of ligand **3a** and **3c** were not satisfactory, considering that the use of the unsubstituted ligand **2** in the same experimental conditions provided a better yield and enantioselectivity for product **4**.[12] It is surprising, however, that **3c** provided the opposite sense of asymmetric induction as compared to **3a**

Table 3 Zinc-catalyzed enantioselective reduction of propiophenone

Ligand	Silane	Yield (%) of **5**[a]	E.e. (%)[b]
3a	PMHS	71	60
3a	Et_3SiH	11	60
3a	Ph_2SiH_2	94	64
3b	Ph_2SiH_2	89	54
3c	Ph_2SiH_2	86	25
3a	Ph_2SiH_2[c]	93	66
3a	Ph_2SiH_2[d]	91	67
3a	Ph_2SiH_2[e]	90	67
3a	Ph_2SiH_2[f]	92	71
2	PMHS[g]	70	86
2	Ph_2SiH_2	71	83
2	Ph_2SiH_2[d]	73	74
2	Ph_2SiH_2[f]	70	78
6	PMHS[a]	90	83
6	Ph_2SiH_2	93	83

[a] After chromatographic purification. [b] Calculated by HPLC analysis on a chiral column Chiralpak OD. [c] 7.0 mol% of Et_2Zn was used. [d] 10.5 mol% of Et_2Zn was used. [e] 1.5 mol% of **3a** and 4.5 mol% of Et_2Zn were used. [f] 10.5 mol% of Et_2Zn was used starting from −78 °C. [g] Data taken from the literature.[9] [h] Data taken from the literature,[9] where the use of *ent*-**6** gave (*R*)-**5**.

and **2**, affording product **4** with the *S* configuration and very low enantioselectivity.

Similar results were obtained in the reduction of propiophenone by different silanes in the presence of catalytic amounts of diethylzinc and ligands **3a–c**. By using the methyl-substituted ligand **3a**, the effect of the nature of the reducing agent was examined under identical experimental conditions: 1.2 equiv. reducing agent and 3.5 mol% of either Et_2Zn and ligand. It was observed that higher yield and e.e. of (*S*)-1-phenylpropanol **5** were obtained using diphenylsilane (94%, 64% e.e.) with respect to polymethylhydrogensiloxane (PMHS, 71%, 60% e.e.) and triethylsilane (11%, 60% e.e.).

Successively, the role of the macrocyclic ring substituent was investigated with the n-butyl and phenyl-substituted macrocycles **3b** and **3c**, respectively, with Ph_2SiH_2 as the reducing agent. The adverse effect of the increased size on the enantioselectivity was assessed: in fact, the e.e. of (*S*)-1-phenylpropanol **5** decreased: **3a**, 64% e.e.; **3b**, 54% e.e.; **3c**: 25%. Further experiments were carried out using the best performing ligand **3a** and vaying the amounts of Et_2Zn: two- and three-fold increases of the amount of Et_2Zn allowed the enhancement of the e.e. to 66% and 67%, respectively, and the same 67% e.e. was obtained even reducing the amounts of Et_2Zn (4.5 mol%) and ligand **3a** (1.5 mol%). Finally, a slightly better 71% e.e. and 92% yield of **5** was obtained by performing the reduction at −78 °C and allowing the mixture to slowly reach room temperature.

A comparison was then made between the unsubstituted macrocyclic ligand **2** and the methyl-substituted analogue **3a**, using Ph_2SiH_2. It was shown that **2** provided a higher level of enantioselectivity (83% e.e.), which was only slightly lower than that reported in the literature[9] using PMHS as the reducing agent (86% e.e.).

To understand the importance of the ligand macrocyclic structure on the stereocontrol, these results should also be compared with those previously obtained with the open ligand **6**,[5,13] whose skeleton is a fragment of the macrocyclic ligand **3a**. Although a higher yield of 1-phenylpropanol **5** was obtained with ligand **6** using PMHS, a higher e.e. was obtained with the open ligand **2** (86% *vs.* 83%). In our hands, working with ligand **6** and Ph_2SiH_2 the yield of **5** could be increased to 93%, but the same level of enantioselectivity (83% e.e.) was obtained.

The lower enantioselectivity exhibited by the macrocyclic ligand **3a** (e.e. ≤71%) with respect to the analogous acyclic ligand **6** (83% e.e.) might be explained by its markedly reduced ability to undergo rotation around the benzylic C*–N bonds, contrary to **6** which can assume the most stable conformation in the transition state.

In conclusion, the introduction of ring substituents in the macrocyclic ligand caused a diminished enantioselectivity in the hydrosilylation of propiophenone as well as in the Henry reaction. In the latter case inversion of the sense of asymmetric induction was observed with the macrocyclic ligand bearing the more bulky substituent. Therefore, it is conceivable that the diastereomeric macrocyclic ligands with the same configuration of the cyclohexanediamine moieties but the opposite configuration of the substituted stereocenters can give more satisfactory performances. Hence, attempts will be made to prepare the hexamethyl derivative through the reduction of the precursory macrocyclic hexaketimine derived from 1,4-diacetylbenzene. The introduction of functionalized or heteroaromatic substituents would also increase the interest for such macrocycles for their potential use in the wide field of supramolecular chemistry.

Experimental

General Information

Melting points are uncorrected. Optical rotations were measured on a digital polarimeter in a dm cell and $[\alpha]^D$-values are given in 10^{-1} deg cm^3 g^{-1}. ^{1}H NMR spectra were recorded on Varian Mercury and Gemini instruments for samples in $CDCl_3$ which was stored over Mg: ^{1}H chemical shifts are reported in ppm relative to $CHCl_3$ (δ_H 7.27), *J*-values are given in Hz. Infrared spectra were recorded on a Nicolet FT-380 spectrometer and IR assignments are reported in wave numbers (cm^{-1}). MS spectra were taken at an ionising voltage of 70 eV on a Agilent Technologies 5975 spectrometer with GLC injection (using HP-5 column, 30 m, ID 0.25 mm). Molecular weights were determined on an Agilent Technologies MS 1100 instrument. Analytical high performance liquid chromatography (HPLC) was performed on Agilent Technologies 1200 instrument equipped with a variable wave-length UV detector, using a Daicel Chiralpak OD column (0.46 cm I.D. x 25 cm). HPLC grade isopropanol and *n*-hexane were used as the eluting solvents. Chromatographic separations were performed on columns of SiO_2 (Merck, 230–400 mesh) at medium pressure. All the organic, inorganic and organometallic reagents and anhydrous solvents were purchased from Aldrich. The products **1**,[3] **2**,[3a] **5**,[14] **6**,[5,15] were previously described.

Synthesis of imine 1

To the suspension of (*R*,*R*)-1,2-diaminocyclohexane L-tartrate (2.35 g, 8.9 mmol) in MeOH (25 mL), terephtalaldehyde (1.19 g, 8.9 mmol) and triethylamine (3.10 mL, 22.3 mmol) were added. The reaction mixture was stirred for 48 h and the solvent was evaporated at reduced pressure. A saturated aqueous solution of $NaHCO_3$ (20 mL) was added and the organic material was

extracted with dichloromethane (3 × 30 mL). The collected organic layers were washed with brine (20 mL), dried over Na_2SO_4 and concentrated to leave a white solid, which was crystallized from AcOEt to give pure **1** (1.77 g, 2.8 mmol, 94%).

Organometallic additions to imine 1. Typical procedure

Phenyllithium (0.5 M in Et_2O, 14.1 mL, 7.06 mmol) was added to a magnetically stirred solution of the imine **1** (0.500 g, 0.78 mmol) in THF (20 mL) cooled at −78 °C. After 60 min the reaction mixture was slowly warmed up until room temperature was reached and stirring was continued for 24 h. The mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (10 mL) at 0 °C, then the organic material was extracted with ethyl acetate (3 × 30 mL). The collected ethereal layers were washed with brine (20 mL), dried over Na_2SO_4 and concentrated to leave a white solid, which was crystallized from MeOH to give pure **3c** (0.792 g, 0.72 mmol, 92%).

3a

White solid; 89% (0.509 g, 0.69 mmol) from 0.78 mmol (0.500 g) of **1**; mp 87–88 °C (from MeOH); $[\alpha]_{20}^{D}$ −150.4 (*c* 0.99 in $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3228, 3301, 2962, 2925, 2854, 1448, 1367, 1125, 1059, 1016, 932, 757; δ_H (200 MHz; $CDCl_3$) 0.92–1.12 (6 H, m), 1.25 (18 H, d, *J* 6.4), 1.74–1.88 (m, 6 H), 2.21 (6 H, m), 2.49 (6 H, m), 4.01 (6 H, q, *J* 6.4), 7.37 (12 H, s); δ_C (50 MHz; $CDCl_3$) 22.2, 24.9, 31.2, 52.8, 57.1, 126.5, 145.9; *m*/*z* (ES) 734.0 (40%, [M + H]$^+$), 367.5 (100, [1/2 M + H]$^+$); 245.4 (21, [1/3 M + H]$^+$).

3b

Yellow slurry oil; 86% (0.525 g, 0.53 mmol) from 0.62 mmol (0.400 g) of **1**; $[\alpha]_{20}^{D}$ −54.6 (*c* 1.10 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 3302, 2854, 2928, 2856, 1581, 1464, 1377, 1266, 1123, 833, 735; δ_H (400 MHz; $CDCl_3$) 0.77 (18 H, t, *J* 7.1), 1.00–1.26 (42 H, m), 1.44 (6 H, m), 1.67–1.84 (12 H, m), 2.04 (6 H, d, *J* 11.3), 2.48 (6 H, m), 3.78 (6 H, dd, *J* 3.3 and 8.2), 7.26 (12 H, s); δ_C (50 MHz; $CDCl_3$) 13.9, 22.7, 24.6, 28.0, 31.1, 35.5, 56.8, 58.4, 127.1, 143.7; *m*/*z* (ES) 985.7 (21%, [M + H]$^+$), 493.4 (89, [1/2 M + H]$^+$); 329.3 (100, [1/3 M + H]$^+$).

3c

White crystals, mp 136–137 °C (from MeOH); $[\alpha]_{20}^{D}$ −13.4 (*c* 0.50 in $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3442, 3319, 3083, 3059, 3023, 2925, 2853, 1599, 1507, 1492, 1452, 1106, 1027, 855, 811, 742, 700, 608; δ_H (400 MHz; $CDCl_3$) 0.90 (6 H, m), 1.02 (6 H, m), 1.58 (6 H, d, *J* 7.9), 2.14 (6 H, d, *J* 11.7), 2.28 (12 H, m), 5.02 (6 H, s), 7.07 (16 H, dd, *J* 2.4 and 3.7), 7.34 (6 H, d, *J* 2.0), 7.36 (6 H, d, *J* 3.7), 7.43 (14 H, s); δ_C (100 MHz; $CDCl_3$) 24.6, 30.3, 57.5, 62.5, 126.7, 127.1, 127.3, 128.5, 143.0, 144.0; *m*/*z* (ES) 1106.3 (21%, [M + H]$^+$), 553.8 (100, [1/2 M + H]$^+$); 369.5 (40, [1/3 M + H]$^+$).

Enantioselective Henry reaction. Typical procedure

To a solution of $Cu(AcO)_2 \cdot H_2O$ (0.010 g, 0.048 mmol) in EtOH (3 mL), **2** (0.010 g, 0.016 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. Benzaldehyde (33 μL, 0.32 mmol) and nitromethane (087 μL, 1.60 mmol) were added at −20 °C at the reaction was slowly warmed at 0 °C. After 20 h the reaction mixture was filtered on a small amount of silica and washed with MeOH. Column chromatography (SiO_2, cyclohexane/AcOEt, 9 : 1) gave (*R*)-**4**: 0.046 g (86%); 84% e.e. was determined by chiral HPLC (Chiralpak OD; 2-propanol/hexane 1 : 9, 1.0 mL min^{-1}.; 214 nm): retention times 11.5 min (*S*, minor enantiomer) and 13.8 min (*R*, major enantiomer).

Enantioselective hydrosilylation reaction. Typical procedure

Et_2Zn (1.0 M in toluene, 68 μL, 0.07 mmol) was slowly added to a solution of **3a** (0.050 g, 0.07 mmol) in toluene (2 mL). After 30 min propiophenone (252 μL, 1.89 mmol) and diphenyl silane (419 μL, 2.27 mmol) were added at 0 °C and the reaction was warmed at room temperature. After 4 h a 1 M solution of NaOH in MeOH (1 mL) was slowly added at 0 °C and the mixture was stirred for 30 min. The organic phase was extracted with Et_2O (3 ×10 mL). The organic layer was dried over Na_2SO_4 and the solvents were evaporated to dryness. Column chromatography (SiO_2, cyclohexane/AcOEt, 9 : 1) gave (*S*)-**5**: 0.165 g (94%); 64% e.e. was determined by chiral HPLC (Chiralpak OD; 2-propanol/hexane 1 : 99 to 5 : 95 in 10 min., 0.5 mL min^{-1}.; 214 nm): retention times 20.7 min (*R*, minor enantiomer) and 21.4 min (*S*, major enantiomer).

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