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The synthesis of tetradentate salens derived from (3*R*,4*R*)-*N*-substituted-3,4-diaminopyrrolidines and their application in the enantioselective trimethylsilylcyanation of aromatic aldehydes

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ABSTRACT

The in situ formed Ti(IV) complexes of pyrrolidine-based chiral salen ligands derived from natural L-tartaric acid were evaluated as catalysts in the enantioselective trimethylsilylcyanation of aromatic aldehydes. The different activity and selectivity of the catalysts in the formation of the products were found to be dependent on the *N*-substituent of the pyrrolidine.

1. Introduction

The enantioselective trimethylsilylcyanation of aldehydes catalyzed by titanium complexes is a convenient process for synthesizing optically active cyanohydrins. These chiral products have great synthetic interest as precursors of molecules with other important functional groups, such as α-hydroxyacids, α-hydroxyketones, primary and secondary β-hydroxyamines, α-aminonitriles, and α-hydroxyesters. Titanium, vanadium, and aluminum metals have been successfully used as Lewis acids in these reactions and structurally diverse chiral ligands have proven to be efficient in this enantioselective process.[1–6] Oguni's pioneering work with Schiff bases[7–9] led to the development of many ligands of this type for the enantioselective trimethylsilylcyanation of aldehydes.[10–16]

Our research has focused on various types of enantioselective catalysis, particularly for the alkylation and cyanation of aldehydes.[17–19] We have been especially interested in the synthesis of chiral salens from the condensation of chiral diamines with different backbones with substituted salicylaldehydes. The structural characteristics of these ligands make them appropriate for both the alkylation and trimethylsilylcyanation of aldehydes, allowing a convenient multiple application of these chiral ligands in enantioselective transformations. In this sense, we herein report the results of the trimethylsilylcyanation of several aromatic aldehydes using chiral salens prepared from the condensation of three different *N*-substituted-3,4-diaminopyrrolidines with 3,5-di-*t*-butylsalycylaldehdye and 2-hydroxy-1-naphthaldehyde.

2. Results and discussion

2.1. Synthesis of chiral salen ligands

The 3,4-diaminopyrrolidines **2a**–**2c** were prepared from natural L-tartaric acid and a primary amine (benzylamine, cyclohexylamine and aniline) according to previously described procedures[19,20] (Scheme 1). The subsequent reaction of **2a**–**2c** with the aldehydes under ultrasound irradiation gave **3a**–**3c** and **4a**–**4c** in very good yields.

2.2. Enantioselective trimethylsilylcyanation

Using benzaldehyde as the model substrate, the titanium(IV) complexes of chiral salens **3b**, **3c** and **4b**, **4c** were evaluated as catalysts in the enantioselective trimethylsilylcyanation reaction and compared with the results for **3a** and **4a**, which were previously prepared and tested in this catalytic process.[19]

The reactions were carried out in dichloromethane with titanium tetraisopropoxide and trimethylsilylcyanide, in a N_2 atmosphere for 24 h at −30 °C (Scheme 2). The Ti/ligand/aldehyde/TMSCN ratio used was 1:1.1:5:10.

The catalytic experimental results are summarized in Table 1. The catalysts were found to be very active, giving almost quantitative conversions under these reaction conditions, with the exception of **3c** and **4c**, which gave slightly lower conversions. The ee of the products varied according to the structure of each particular ligand, with the most selective being the 3,5-di-*t*-butylsalicylaldehyde derivatives of the *N*-benzyl and *N*-cyclohexylpyrrolidines **3a** and **3b**, which gave the corresponding cyanosilylethers with ees of 88% and 82%, respectively. The 2-hydroxynaphthaldehdye derived salens **4a**–**4c** gave conversions similar to their 3,5-di-*t*-butylsalicylaldehyde counterparts, although the product ee were low for the three *N*-substituted derivatives.

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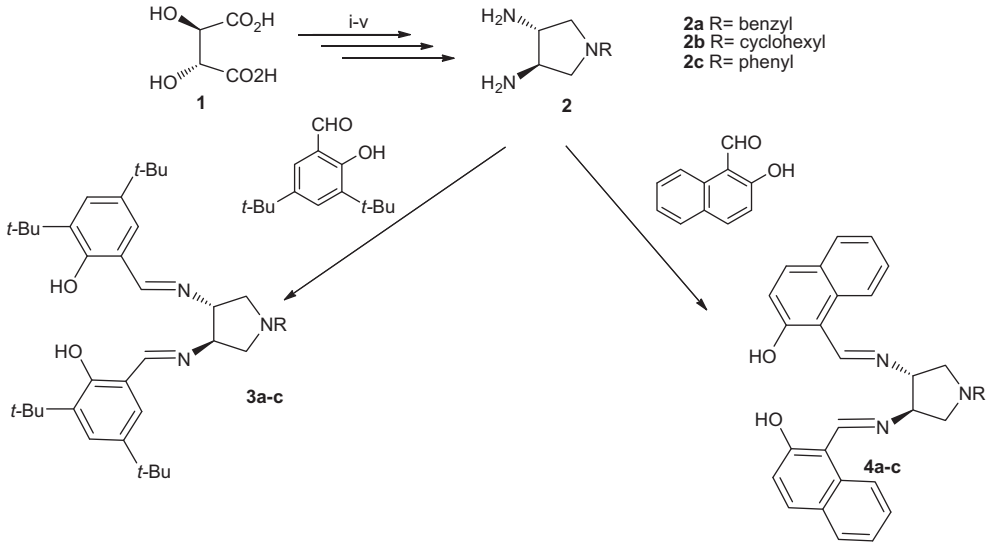
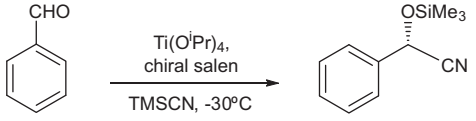
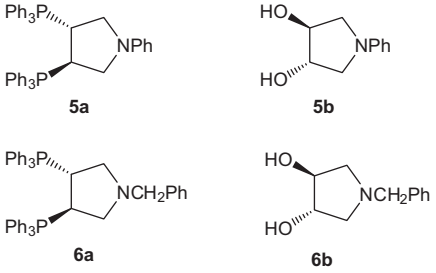


Scheme 1. Reagents and conditions: (i) RNH_2, xylene, reflux; (ii) AcCl, reflux; (iii) $LiAlH_4$, ether, reflux; (iv) DEAD/PPh_3, HN_3, rt; (v) H_2, Pd/C 10%.



Scheme 2.



Scheme 3.

Table 1
Enantioselective trimethylsilylcyanation of benzaldehyde in the presence of titanium complexes of ligands **3** and **4**[a]

Entry	Salen	Conversion[b] (%)	ee[c] (%)
1	**3a**	>99	88 (*S*)
2	**3b**	>99	82 (*S*)
3	**3c**	87	15 (*S*)
4	**4a**	97	30 (*S*)
5	**4b**	>99	40 (*S*)
6	**4c**	79	20 (*S*)

[a] Reaction on a 2 mmol scale in 5 mL of dry CH_2Cl_2 at −30 °C, 24 h (molar ratio of Ti/ligand/aldehyde/TMSCN of 1:1.1:5:10).
[b] Determined by GC.
[c] Of the silylether, determined by chiral GC.

In an attempt to explain our best results with the 3,5-di-*t*-butylsalicylaldehyde derived salens and taking into account the apparent structural similarities of ligands **3a**–**3c**, that is, the steric properties of the *N*-substituents, the results observed for **3c** might be considered to be unexpected. However, similar trends in behavior have previously been observed by us with analogous diphosphines **5a** and **6a** and the corresponding diols **5b** and **6b** (Scheme 3) when used in enantioselective transfer hydrogenation and alkylation reactions.[21,22]

The structure of diphosphine **5a** determined by X-ray crystallography and its comparison with the structures of analogous *N*-substituted pyrrolidine diphosphines[21,23–27] including **6a**, resulted in significant explanatory differences. Crystallography results revealed the coplanarity of the pyrrolidine and *N*-phenyl rings in **5a** due to the sp^2 character of the nitrogen atom in this structure, a unique characteristic compared to other structural analogues where the nitrogen atom is sp^3 hybridized. This is apparently responsible for the low discrimination observed with this ligand compared to **6a**.

Considering a similar situation in the salen ligands, the Ti(IV)-**3c** complex should exhibit a greater planarity than the Ti(IV)-**3a** and Ti(IV)-**3b** complexes, with the different geometries justifying the ee of the trimethylsilylcyanation products.

In order to determine the best solvent for the trimethysilylcyanations with our salen ligands, we tested a set of the most frequently used solvents.[3,10] Our study was carried out with our most efficient ligand **3a** using benzaldehyde as the substrate. With all of the solvents used, except for ethyl ether, conversions greater than 97%. The ee of the products were slightly lower in chloroform and acetonitrile, 78% and 77% respectively, than in dichloromethane. When ethyl ether and toluene were used, the enantiomeric excesses of the products were very low, 12% and 40% ee, respectively. We thus concluded that the best solvent for the trimethysilylcyanations with our ligands was dichloromethane (Table 2).

Using our most efficient ligands **3a** and **3b**, we extended our studies to a wide range of substituted benzaldehydes. The results are summarized in Tables 3 and 4.

No significant differences in activity were observed between the two catalytic systems studied. All substrates, with the exception of *para*-bromobenzaldehyde, gave reaction products with conversions greater than 93%.

The structural characteristics of the ligand, as well as the steric and electronic properties of the aromatic aldehyde substrate, were determining factors in the enantioselectivity of the trimethylsilylcyanation reaction products.[8,10,11]

Table 2
Enantioselective trimethylsilylcyanation of benzaldehyde with Ti-**3a**, using different solvents[a]

Solvent	Conversion[b] (%)/ee[c] (%)
Dichloromethane	>99/88 (*S*)
Chloroform	97/78 (*S*)
Acetonitrile	98/77 (*S*)
Toluene	98/12 (*S*)
Ethyl ether	82/40 (*S*)

[a] Reaction on a 2 mmol scale in 5 mL of dry solvent at −30 °C, 24 h (molar ratio of Ti/ligand/aldehyde/TMSCN of 1:1.1:5:10).
[b] Determined by GC.
[c] Of the silylether, determined by chiral GC.

Table 3
Enantioselective trimethylsilylcyanation of various aromatic aldehydes in the presence of the titanium complex of **3a**[a]

Entry	Aldehyde	Conversion[b] (%)	ee[c] (%)
1	Benzaldehyde	>99	88 (*S*)
2	*p*-Methylbenzaldehyde	96	62 (*S*)
3	*p*-Chlorobenzaldehyde	>99	91 (*S*)
4	*p*-Bromobenzaldehyde	85	86 (*S*)
5	*o*-Chlorobenzaldehyde	94	66 (*S*)
6	*m*-Methylbenzaldehyde	95	87 (*S*)
7	*o*-Methylbenzaldehyde	99	73 (*S*)

[a] Reaction on a 2 mmol scale in 5 mL of dry CH_2Cl_2 at −30 °C, 24 h (molar ratio of Ti/ligand/aldehyde/TMSCN of 1:1.1:5:10).
[b] Determined by GC.
[c] Of the silylether, determined by chiral GC.

Table 4
Enantioselective trimethylsilylcyanation of various aromatic aldehydes in the presence of the titanium complex of **3b**[a]

Entry	Aldehyde	Conversion[b] (%)	ee (%)
1	Benzaldehyde	>99	82 (*S*)
2	*p*-Methylbenzaldehyde	95	86 (*S*)
3	*p*-Chlorobenzaldehyde	93	86 (*S*)
4	*p*-Bromobenzaldehyde	88	81 (*S*)
5	*o*-Chlorobenzaldehyde	94	57 (*S*)
6	*m*-Methylbenzaldehyde	97	92 (*S*)
7	*o*-Methylbenzaldehyde	97	76 (*S*)

[a] Reaction on a 2 mmol scale in 5 mL of dry CH_2Cl_2 at −30 °C, 24 h (molar ratio of Ti/ligand/aldehyde/TMSCN of 1:1.1:5:10).
[b]Determined by GC.
[c]Of the silylether, determined by chiral GC.

With our catalytic system, the lowest selectivities (below 76% ee) were obtained when *ortho*-substituted substrates were used. This may be attributed to the steric properties of the substrate. On the other hand, benzaldehyde as well as *meta*- and *para*-substituted benzaldehydes gave reaction products with higher ee values, varying from 80% to 92%.

From the aromatic aldehydes studied, no direct relationship was observed between the electronic properties of the substrate and the ee of the reaction products. In the presence of **3a**, the highest ee was obtained with electron-deficient *para*-chlorobenzaldehyde (91%), while electron-rich *para*-methylbenzaldehyde gave the product with the lowest ee. Benzaldehyde, *meta*-methylbenzaldehyde, and *para*-bromobenzaldehyde gave cyanosilylation products with very similar, intermediate ee values. Conversely, with **3b**, the highest ee was observed with electron-rich *meta*-methylbenzaldehyde (92%), with no significant difference being observed between electron-rich *para*-methylbenzaldehyde and electron-deficient *para*-chlorobenzaldehyde. Benzaldehyde and *para*-bromobenzaldehyde gave products with slightly lower, albeit identical, ee.

3. Conclusion

Chiral salens **3a**–**c** and **4a**–**c** were prepared according to previously established procedures. The Ti(IV) complexes of these ligands were used in the trimethylsilylcyanation of a series of substituted benzaldehydes and showed conversions greater than 93% and selectivities of up to 92% ee, in the presence of **3a** and **3b** with two sterically demanding *t*-butyl substituents on each aldehyde moiety of the salen ligand. These *N*-benzyl and *N*-cyclohexyl derivatives showed greater activity and selectivity than their *N*-phenyl counterpart **3c**. The differences may be explained by comparing the geometry of the ligands and their corresponding complexes, a tendency that has previously been observed and explained when structurally analogous pyrrolidine diphosphines and diols were used in other catalytic transformations.

4. Experimental

4.1. General procedures

All solvents were dried prior to use following standard procedures. Titanium tetraisopropoxide was obtained from Aldrich and distilled prior to use; trimethylsilylcyanide was obtained from Fluka. Benzaldehyde was distilled prior to use and stored over 4 Å molecular sieves. Other aldehydes and reagents were used as commercially obtained.

Melting points were determined using a Leitz–Wetzler 799 microscope with a heated plate (values are uncorrected). Optical rotations were measured with an Optical Activity AA-5 polarimeter. NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. TMS was used as the internal standard, chemical shifts are referred in δ and coupling constants, *J*, in Hz. Infrared spectra were recorded on a Thermo Scientific Nicolet 6700 FTIR (solids were processed as KBr pellets). Elemental Analysis was carried out on a Fisons Instruments EA-1108 CHNS-O apparatus.

Sonication was performed in a Bandelin Sonorex RK100H cleaning bath with a frequency of 35 Hz and a nominal power of 80/160 W.

Trimethylsilylcyanation reactions were carried out under an inert N_2 atmosphere using standard Schlenk-type techniques. Catalytic experiments were repeated in order to confirm the reproducibility of the results. Enantiomeric excesses were determined using a chiral γ-cyclodextrin capillary column (FS-Lipodex-E, 25 m, 0.25 i.d.) from Machery-Nagel, on an Agilant 7820A instrument. The absolute configuration of the major enantiomer was determined by comparison of the specific rotation with literature values and by NMR with a derivatizing agent.[7,8,28–30] HRMS spectra were recorded on a Finnigan MAT95 S Instrument.

(3*R*,4*R*)-*N*′,*N*″-Bis[3′,5′-di-*t*-butylsalicylidene]-*N*-benzyl-3,4-diaminopyrrolidine **3a** and (3*R*,4*R*)-*N*′,*N*″-bis[2′-hydroxynaphthylidene]-*N*-benzyl-3,4-diaminopyrrolidine **4a** were prepared according to our previously described procedure.[19,2]

4.2. Ligand synthesis

4.2.1. (3*R*,4*R*)-*N*-Cyclohexyl-3,4-diaminopyrrolidine 2b

The compound was prepared from the corresponding diazide, according to the procedure described in the literature.[31] Product characterization is in agreement with that described in the literature.[32] ^{1}H NMR ($CDCl_3$): 1.20–1.28 (m, 5H); 1.62–1.64 (m, 1H); 1.70–1.80 (m, 2H); 1.83–1.96 (m, 2H); 2.38–2.45 (m, 1H); 2.81–

2.84 (m, 2H); 3.23 (dd, 2H, *J* 5.0, 10.6); 3.69 (br s, 4H); 4.11–4.16 (m, 2H).

4.2.2. (3*R*,4*R*)-*N*-Phenyl-3,4-diaminopyrrolidine 2c

The compound was prepared from the corresponding diazide, according to the procedure described in the literature.[31] Product characterization is in agreement with that described in the literature.[32] ^{1}H NMR ($CDCl_3$): 2.99 (dd, 2H, *J* 5.4, 8.6); 3.15 (m, 2H); 3.63 (m, 2H); 6.51 (d, 2H, *J* 8.0); 6.68 (t, 1H, *J* 7.2); 7.22 (t, 1H, *J* 8.0).

4.2.3. General procedure for the synthesis of chiral salens

The diamine (1.5 mmol) was dissolved in 5 mL of dry dichloromethane in a 25 mL Erlenmeyer flask and the aldehyde (3 mmol) was added, followed by activated silica (0.900 g). The mixture was placed in an ultrasound bath until the reaction was complete, as monitored by TLC (approximately 30 min). The silica was filtered off and washed with dichloromethane. The combined organic phases were dried over anhydrous sodium sulfate, filtered, and evaporated. The product was isolated by crystallization from the appropriate solvent, to give the title compound.

4.2.4. (3*R*,4*R*)-*N*′,*N*″-Bis[3′,5′-di-*t*-butylsalicylidene]-*N*-cyclohexyl-3,4-diaminopyrrolidine 3b

The product was crystallized from ethanol/water, yield 65%. Mp 165–167 °C. $[\alpha]_D^{25} = -320$ (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): 1.26–1.34 (m, 23H); 1.47 (s, 18H); 1.61–1.70 (m, 1H); 1.75–1.87 (m, 2H); 1.91–2.04 (m, 2H); 2.18–2.25 (m, 1H); 2.98–3.09 (m, 2H); 3.18–3.29 (m, 2H); 3.95–4.02 (m, 2H); 7.06 (s, 2H); 7.40 (s, 2H); 8.33 (s, 2H); 13.50 (s, 2H). ^{13}C NMR ($CDCl_3$): 25.81, 25.91, 26.90, 30.35, 32.22, 32.36, 35.03, 35.94, 58.76, 64.13, 75.65, 118.51, 127.21, 128.12, 137.52, 141.12, 158.85, 167.54. IR (cm^{-1}): 2954, 1626, 1596, 1469, 1441, 1362, 1251, 1173, 877, 827, 804, 773, 645. LC–MS: *m*/*z* (ESI^+): 616 $(M+1)^+$ Elemental analysis: $C_{40}H_{61}N_3O_2{\cdot}H_2O$ calcd C, 75.78; H, 10.02; N, 6.63. Found: C, 75.80; H, 9.78; N, 6.38.

4.2.5. (3*R*,4*R*)-*N*′,*N*″-Bis[3′,5′-di-*t*-butylsalicylidene]-*N*-phenyl-3,4-diaminopyrrolidine 3c

The product was crystallized from ethanol/water, yield 64%. Mp 212–214 °C. $[\alpha]_D^{25} = -350$ (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): 1.27 (s, 18H); 1.44 (s, 18H); 3.65–3.67 (m, 2H); 3.83–3.7 (m, 2H); 4.16–4.18 (m, 2H); 6.61 (d, 2H, *J* 8.0); 6.75 (t, 1H, *J* 7.2); 7.07 (s, 2H); 7.28 (t, 2H, *J* 8.0); 7.39 (s, 2H); 8.42 (s, 2H); 13.26 (s, 2H). ^{13}C NMR ($CDCl_3$): 29.46, 31.45, 34.15, 35.06, 53.35, 73.68, 111.68, 116.57, 117.58, 126.50, 127.60, 129.35, 136.73, 140.44, 147.11, 157.95, 167.85. IR (cm^{-1}): 2961, 1629, 1595, 1503, 1477, 1440, 1361, 1250, 804, 773, 750, 729, 693. LC–MS: *m*/*z* (ESI^+): 610 $(M+1)^+$; Elemental analysis: $C_{40}H_{55}N_3O_2$ calcd C, 78.77; H, 9.09; N, 6.89. Found: C, 78.65; H, 9.09; N, 6.75.

4.2.6. (3*R*,4*R*)-*N*′,*N*″-Bis[2′-hydroxynaphthylidene]-*N*-cyclohexyl-3,4-diaminopyrrolidine 4b

The product was crystallized from ethanol, yield 68%. Mp 190–192 °C. $[\alpha]_D^{25} = -305$ (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): 1.21–1.39 (m, 5H); 1.60–1.66 (m, 1H); 1.74–1.88 (m, 2H); 1.89–2.02 (m, 2H); 2.23–2.37 (m, 1H); 3.02 (dd, 2H, *J* 6.0, 9.6); 3.34 (dd, 2H, *J* 6.8, 9.6); 4.13–4.18 (m, 2H); 7.07 (d, 2H, *J* 9.2); 7.24–7.28 (m, 2H); 7.39–7.43 (m, 2H); 7.66 (d, 2H, *J* 8.0); 7.76 (d, 2H, *J* 9.2); 7.89 (d, 2H, *J* 8.4); 9.02 (s, 2H); 14.80 (br s, 2H). ^{13}C NMR ($CDCl_3$): 25.61, 25.69, 26.92, 32.17, 58.22, 63.29, 73.26, 108.64, 119.62, 122.95, 124.09, 127.91, 128.84, 130.03, 133.90, 137.00, 160.51, 170.46. IR (cm^{-1}): 2965, 1626, 1544, 1346, 1314, 863, 834, 753. HRMS (ESI): calcd for $C_{32}H_{33}N_3O_2$ $[M]^+$ 491.2573; found $[MH]^+$ 492.2634.

4.2.7. (3*R*,4*R*)-*N*′,*N*″-Bis[2′-hydroxynaphthylidene]-*N*-phenyl-3,4-diaminopyrrolidine 4c

The product was crystallized from ethanol, yield 68%. Mp 225–227 °C. $[\alpha]_D^{25} = -620$ (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): 3.75 (dd, 2H, *J* 7.4, 9.2); 4.02 (dd, 2H, *J* 6.8, 9.2); 4.34–4.40 (m, 2H); 7.11 (d, 2H, *J* 9.0); 7.26–7.35 (m, 2H); 7.40–7.44 (m, 2H); 7.68 (d, 2H, *J*8.0); 7.78 (d, 2H, *J* 9.0); 7.94 (d, 2H, *J* 8.4); 9.20 (s, 2H); 14.79 (br s, 2H). ^{13}C NMR ($CDCl_3$): 54.01, 73.34, 109.08, 112.65, 117.91, 119.89, 121.62, 124.30, 128.26, 128.84, 130.02, 130.32, 133.58, 136.55, 147.74, 162.67, 167.29. IR (cm^{-1}): 3049, 1628, 1596, 1508, 1477, 1293, 840, 829, 748, 693. HRMS (ESI): calcd for $C_{32}H_{27}N_3O_2$ $[M]^+$ 485.2103; found $[MH]^+$ 486.2177.

4.3. General procedure for trimethylsilylcyanation

To a solution of the chiral salen ligand (0.44 mmol) in dry dichloromethane (5 mL), $Ti(O^iPr)_4$ (0.40 mmol, 0.12 mL) was added under an inert atmosphere at room temperature. The resulting mixture was stirred overnight and subsequently cooled to −30 °C. The aldehyde (2 mmol) and trimethylsilylcyanide (4 mmol, 0.54 mL) were added and the reaction stirred for 24 h at −30 °C.

Next, hexane was added and the precipitated solids were filtered off. Conversions and the ee of the resulting cyanosilylethers were determined by chiral gc analysis.

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