

Titanium and ruthenium binaphthyl Schiff base complexes as catalysts for asymmetric trimethylsilylcyanation of aldehydes

Xiang-Ge Zhou, Jie-Sheng Huang, Po-Hung Ko, Kung-Kai Cheung and Chi-Ming Che *

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

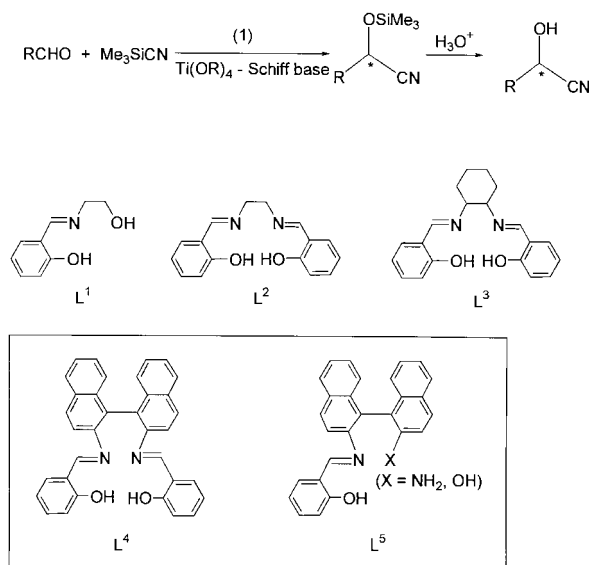
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Investigations on the catalytic behaviour of titanium complexes formed *in situ* from $Ti(OPr^i)_4$ and a variety of Schiff bases, mainly the binaphthyl derivatives 2,2'-bis(3-R¹-5-R²-2-hydroxybenzylideneamino)-1,1'-binaphthyl, toward the asymmetric trimethylsilylcyanation of some aromatic and aliphatic aldehydes demonstrated that the titanium complex of the binaphthyl Schiff base with R¹ = R² = Bu^t is one of the best catalysts for such a process, with an enantiomeric excess (e.e.) as high as 96% obtained for *m*-tolualdehyde. Crystal structure determination of a nitrosylruthenium complex, $[Ru^{II}(L)(NO)Cl]$ (L is the dianion of the binaphthyl Schiff base with R¹ = R² = Cl), revealed that the complex assumes a *cis*- β configuration with the binaphthyl moiety having a dihedral angle of 70.2°. After treatment with AgPF₆, the ruthenium complex also exhibited a good catalytic property for the trimethylsilylcyanation of benzaldehyde albeit with a lower e.e. (24%).

The synthesis of optically active cyanohydrins, a type of versatile reagent in organic synthesis and good precursors to some important insecticides and medicinals,¹⁻³ *via* asymmetric trimethylsilylcyanation of aldehydes catalysed by metal complexes with chiral auxiliary ligands constitutes an area of increasing interest.⁴⁻²¹ Among such catalysts reported so far are the complexes of titanium,⁴⁻¹⁸ magnesium,^{10,19} zinc,¹⁰ lanthanum,²⁰ and yttrium.²¹ The $Ti(OR)_4$ -Schiff base systems (Scheme 1)

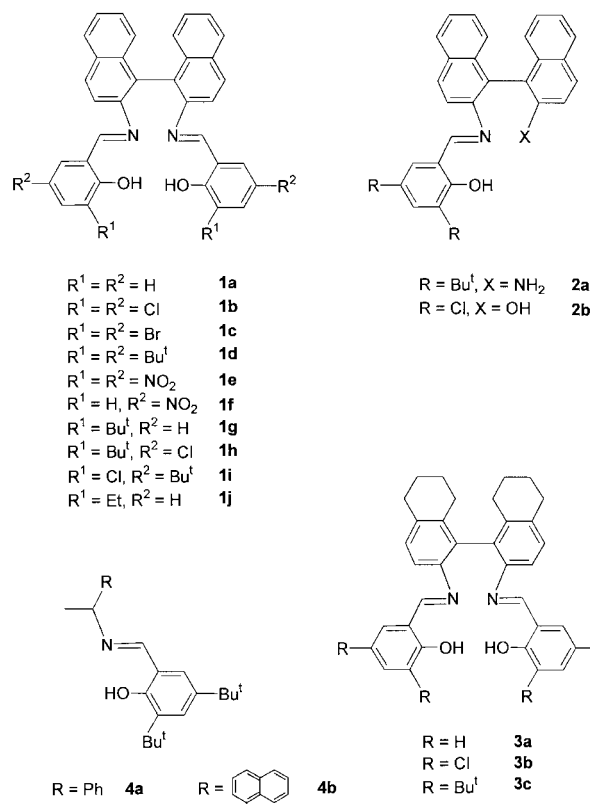
shown that the L⁴-type Schiff bases, 2,2'-bis(3-R¹-5-R²-2-hydroxybenzylideneamino)-1,1'-binaphthyl, co-ordinate with metal ions in a manner considerably different from that of L²- or L³-type Schiff bases,^{24,25} suggesting that they might have a different interaction with the substrates upon ligation to metal ions. When this work was just started there were no reports on reaction (1) involving binaphthyl Schiff bases. Very recently, a report appeared which concerned the (*S*) isomer of unsubstituted L⁴ with only low to moderate enantiomeric excesses (e.e.s) (12.7–67.5%).¹⁶

Herein we describe an extensive study on reaction (1) by using a series of L⁴ and L⁵ derivatives (1 and 2 respectively), along with other types of Schiff bases 3 and 4. Interestingly, excellent e.e. (up to 96%) could be obtained by introducing



Scheme 1 Asymmetric trimethylsilylcyanation of aldehydes with Me₃SiCN catalysed by titanium Schiff base complexes. The types of Schiff bases which have been extensively studied (L¹–L³) are indicated. The inset shows the main types of Schiff bases involved in this work (L⁴ and L⁵).

first developed by Oguni and co-workers in 1991⁸ have received special attention.⁸⁻¹⁶ Extensive studies on these systems by employing a variety of Schiff bases derived from L¹,⁸⁻¹⁰ L²,^{12,13} and L³^{11,13-15} revealed that the enantioselectivity of reaction (1) is highly dependent on the type of Schiff base used. Our interest in the derivatives of L⁴ and L⁵ containing a binaphthyl group was stimulated by the fact that ligands bearing binaphthyl groups exhibit many advantages in asymmetric synthesis, as described in some depth elsewhere.^{22,23} Moreover, we have



bulky electron donating substituents on L⁴. In addition, we first extended reaction (1) to a ruthenium complex, which contains the dianion of **1b**. The crystal structural determination of [Ru^{II}(**1b** - 2H)(NO)Cl], the first isolated ruthenium binaphthyl Schiff base complex, is also described.

Experimental

Instrumentation

The ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 300 FT-NMR spectrometer (300 MHz). Chemical shifts (δ in ppm) are reported relative to tetramethylsilane (TMS). The UV-visible spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer, infrared spectra on a Shimadzu-470 spectrometer, FAB mass spectra on a Finnigan MAT 95 spectrometer, electrospray mass spectrum on a Finnigan LCQ quadrupole ion trap mass spectrometer and CD spectra on a JASCO spectrophotometer. The GC analyses were carried out on an HP 5890 series II system equipped with an HP 5890A flame ionization detector and an HP 3395 integrator. A capillary column containing β -cyclodextrin was used to analyse the cyanohydrins after derivatization. All melting points are uncorrected. Elemental analyses were performed by Butterworth Laboratories Ltd. or Institute of Chemistry, Chinese Academy of Sciences.

Materials

Acetonitrile and dichloromethane were distilled over calcium hydride, benzene, tetrahydrofuran, and toluene over sodium-benzophenone. Acetone and methanol (AR, Merck) were used as received. All aldehydes except those indicated as follows were freshly distilled before use. 3,5-Dichlorosalicylaldehyde, 3,5-dibromosalicylaldehyde, 5-nitrosalicylaldehyde, trimethylsilyl cyanide, (S)-(-)-1-(1-naphthyl)ethylamine, (S)-(-)- α -methylbenzylamine, AgPF₆ (all Aldrich products), and (R)- and (S)-2,2'-diamino-1,1'-binaphthyl (BINAM) (both Fluka products) were used as received. Racemic BINAM,²⁶ the ligands **1a**-**1f**^{25,27,28} and **2b**,²⁹ and the complex [Ru^{II}(NO)Cl₃(PPh₃)₂]³⁰ were all prepared by the literature methods.

Preparations

(R)-5,5',6,6',7,7',8,8'-Octahydro-1,1'-binaphthyl-2,2'-diamine [(R)-H₈BINAM]. This compound was prepared by a procedure analogous to that for its diol analogue.³¹ A mixture of (R)-BINAM (200 mg), PtO₂ (20 mg), and glacial acetic acid (20 ml) was stirred in a 50 ml autoclave under hydrogen (3 atm) at room temperature for 3 d. After releasing the hydrogen gas and removing solid by filtration, the mixture was neutralized with 10% NaHCO₃ solution (200 ml) followed by extraction with chloroform (3 \times 30 ml). The solvent of the organic layer dried with Na₂SO₄ was then removed by evaporation to give a crude product, which was purified by column chromatography. Yield: 83%. [α]_D²⁰ = +133 (c 1.0, pyridine), mp 210 °C. HRMS: *m/z* 292.1935 (M⁺) (calc. for C₂₀H₂₄N₂: 292.1939). IR (KBr, cm⁻¹): 3456, 3365, 2925, 1609, 1479, 1442, 1300, 1286, 826 and 808. ¹H NMR (CDCl₃, 300 MHz): δ 6.90 (d, 2 H, *J* = 8.2, aryl H), 6.60 (d, 2 H, *J* = 8.1 Hz, aryl H), 3.31 (s, 4 H, NH₂), 2.70 (m, 4 H, CH₂), 2.22 (t, 4 H, *J* = 6.02 Hz, CH₂) and 1.67 (m, 8 H, CH₂). ¹³C NMR (CDCl₃, 300 MHz): δ 141.5, 136.2, 129.2, 127.7, 122.0, 113.1, 29.4, 27.0, 23.4 and 23.2.

General procedure for Schiff bases **1g**, **1j**, **2a** and **3c**

The compound (R)-BINAM (284 mg, 0.1 mmol) and the corresponding salicylaldehyde (1.05 equivalents for **2a** and 2.1 equivalents for the others) were dissolved in ethanol-acetic acid (7:1 v/v, 20 ml) and stirred at 60 °C for 2 h. Upon removal of solvent, the residue was recrystallized from dichloromethane-ethanol.

(R)-2,2'-Bis(3-tert-butyl-2-hydroxybenzylideneamino)-1,1'-binaphthyl **1g**. Yield: 72%. [α]_D²⁰ = -289.5 (c 0.3, CHCl₃), mp 184–187 °C (Found: C, 83.03; H, 6.60; N, 4.16. C₂₁H₂₀NO requires C, 83.44; H, 6.62; N, 4.63%). MS: *m/z* 604 (M⁺), 589 (M⁺ - CH₃) and 547 (M⁺ - C₄H₉). HRMS: *m/z* 604.3058 (M⁺) (calc. for C₄₂H₄₀N₂O₂: 604.3089). ¹H NMR (CDCl₃, 300 MHz): δ 12.9 (s, 2 H, OH), 8.6 (s, 2 H, CH=N), 8.05 (d, 2 H, *J* = 8.80, Ph), 7.95 (d, 2 H, *J* = 8.15, aryl H), 7.58 (d, 2 H, *J* = 8.80, aryl H), 6.90–7.5 (m, 10 H, aryl H), 6.67 (t, 2 H, *J* = 7.62 Hz, aryl H) and 1.2 (s, 18 H, Bu^t). ¹³C NMR (CDCl₃, 300 MHz): δ 162.2, 160.5, 143.8, 137.3, 133.4, 132.6, 130.3, 129.8, 129.3, 128.2, 126.9, 126.6, 125.6, 123.4, 118.9, 117.6, 117.1, 34.7 and 29.0.

(R)-2,2'-Bis(3-ethyl-2-hydroxybenzylideneamino)-1,1'-binaphthyl **1j**. Yield: 78%. [α]_D²⁰ = -448.0 (c 0.66, CHCl₃), mp 223–225 °C (Found: C, 83.01; H, 5.78; N, 4.83. C₁₉H₁₆NO requires C, 83.21; H, 5.83; N, 5.10%). MS: *m/z* 548 (M⁺). ¹H NMR (CDCl₃, 300 MHz): δ 12.3 (s, 2 H, OH), 8.55 (s, 2 H, CH=N), 8.05 (d, 2 H, *J* = 7.50, aryl H), 7.93 (d, 2 H, *J* = 7.35, aryl H), 6.90–7.50 (m, 12 H, aryl H), 6.68 (t, 2 H, *J* = 7.45 Hz, aryl H), 2.5 (q, 4 H, CH₂CH₃) and 1.1 (t, 6 H, CH₂CH₃). ¹³C NMR (CDCl₃, 300 MHz): δ 162.9, 158.9, 144.6, 133.3, 132.4, 132.1, 131.9, 129.9, 128.6, 128.2, 126.8, 126.5, 125.6, 124.6, 118.6, 118.2, 117.8, 22.5 and 13.5.

(R)-2-Amino-2'-(3,5-di-tert-butyl-2-hydroxybenzylideneamino)-1,1'-binaphthyl **2a**. Yield: 63%. [α]_D²⁰ = -4.5 (c 0.378, CHCl₃), mp 89–90 °C (Found: C, 82.79; H, 7.44; N, 5.53. C₃₅H₃₆N₂O·0.5H₂O requires C, 82.51; H, 7.27; N, 5.50%). MS: *m/z* 500 (M⁺). ¹H NMR (CDCl₃, 300 MHz): δ 11.6 (s, 1 H, OH), 8.65 (s, 1 H, CH=N), 6.9–8.1 (m, 14 H, aryl H), 1.25 (s, 9 H, Bu^t) and 1.24 (s, 9 H, Bu^t). ¹³C NMR (CDCl₃, 300 MHz): δ 163.1, 158.7, 144.8, 143.1, 142.2, 140.3, 133.1, 130.2, 129.9, 129.7, 128.6, 128.4, 128.1, 127.9, 127.6, 127.3, 126.9, 126.84, 126.82, 124.3, 122.8, 122.5, 118.7, 118.5, 118.3, 112.9, 35.3, 34.6, 31.8 and 29.7.

(R)-2,2'-Bis(3,5-di-tert-butyl-2-hydroxybenzylideneamino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl **3c**. Yield: 68%. [α]_D²⁰ = +47.5 (c 1.15, CHCl₃), mp 202–204 °C (Found: C, 83.16; H, 9.15; N, 3.50. C₂₅H₃₂NO requires C, 82.87; H, 8.84; N, 3.86%). HRMS: *m/z* 724.4963 (M⁺) (calc. for C₅₀H₆₄N₂O₂: 724.4968). ¹H NMR (CDCl₃, 300 MHz): δ 13.1 (s, 2 H, OH), 8.5 (s, 2 H, CH=N), 7.3 (d, 2 H, *J* = 2.5, aryl H), 7.12 (d, 2 H, *J* = 5.3, aryl H), 7.08 (d, 2 H, *J* = 2.5, aryl H), 7.0 (d, 2 H, *J* = 5.3 Hz, aryl H), 2.8–2.9 (m, 4 H, CH₂), 2.3–2.6 (m, 4 H, CH₂), 1.7–1.9 (m, 8 H, CH₂), 1.33 (s, 18 H, Bu^t) and 1.24 (s, 18 H, Bu^t). ¹³C NMR (CDCl₃, 300 MHz): δ 162.5, 160.2, 145.1, 141.5, 138.5, 137.6, 136.0, 130.9, 128.9, 128.1, 120.1, 116.1, 36.8, 35.9, 33.3, 32.8, 31.8, 31.0, 25.0 and 24.7.

General procedure for Schiff bases **1h, **1i**, **3a**, **3b**, and **4****. A mixture of the corresponding chiral amine (0.1 mmol) and substituted salicylaldehyde (1.05 equivalents for **4** and 2.1 equivalents for the others) in ethanol (20 ml) was refluxed for 2 h. After concentrating the solution to 5 ml, the product precipitated was collected by filtration and washed with cold methanol.

(R)-2,2'-Bis(3-tert-butyl-5-chloro-2-hydroxybenzylideneamino)-1,1'-binaphthyl **1h**. Yield: 78%. [α]_D²⁰ = -327.9 (c 0.372, CHCl₃), mp 214–215 °C (Found: C, 74.82; H, 5.59; N, 3.87. C₂₁H₁₉ClNO requires C, 74.88; H, 5.64; N, 4.16%). MS: *m/z* 673 (M⁺). ¹H NMR (CDCl₃, 300 MHz): δ 12.9 (s, 2 H, OH), 8.5 (s, 2 H, CH=N), 8.08 (d, 2 H, *J* = 8.85, aryl H), 7.97 (d, 2 H, *J* = 8.23, aryl H), 7.59 (d, 2 H, *J* = 8.87, aryl H), 7.2–7.5 (m, 6 H, aryl H), 7.12 (d, 2 H, *J* = 2.52, aryl H), 6.99 (d, 2 H, *J* = 2.57 Hz, aryl H) and 1.15 (s, 18 H, Bu^t). ¹³C NMR (CDCl₃, 300 MHz): δ 160.7, 159.0, 143.1, 139.6, 133.2, 132.8, 129.9, 129.6, 128.8, 128.2, 127.1, 126.5, 125.9, 122.4, 119.5, 116.6, 34.9 and 28.8.

(R)-2,2'-Bis(5-tert-butyl-3-chloro-2-hydroxybenzylideneamino)-1,1'-binaphthyl **1i**. Yield: 80%. [α]_D²⁰ = -375.0 (c 0.36, CHCl₃), mp 159–160 °C (Found: C, 74.86; H, 5.61; N, 4.22.

C₂₁H₁₉ClNO requires C, 74.88; H, 5.64; N, 4.16%). MS: 673 (M⁺). ¹H NMR (CDCl₃, 300 MHz): δ 12.5 (s, 2 H, OH), 8.65 (s, 2 H, CH=N), 8.08 (d, 2 H, *J* = 8.58, aryl H), 7.95 (d, 2 H, *J* = 8.13, aryl H), 7.70–7.90 (m, 2 H, aryl H), 7.59 (d, 2 H, *J* = 8.78 Hz, aryl H), 7.05–7.5 (m, 8 H, aryl H) and 1.22 (s, 18 H, Bu^t). ¹³C NMR (CDCl₃, 300 MHz): δ 163.3, 154.2, 143.7, 142.0, 133.2, 132.6, 130.5, 130.2, 129.0, 128.3, 127.3, 127.0, 126.4, 125.9, 120.7, 119.5, 117.4, 34.0 and 31.2.

(*R*)-2,2'-Bis(2-hydroxybenzylideneamino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl **3a**. Yield: 82%. [α]_D²⁰ = −202.8 (c 0.80, CHCl₃), mp 180–181 °C (Found: C, 82.06; H, 6.43; N, 5.00. C₁₇H₁₆NO requires C, 81.60; H, 6.40; N, 5.60%). HRMS: *m/z* 500.2465 (M⁺) (calc. for C₃₄H₃₂N₂O₂: 500.2463). ¹H NMR (CDCl₃, 300 MHz): δ 12.3 (s, 2 H, OH), 8.53 (s, 2 H, CH=N), 6.7–7.3 (m, 12 H, aryl H), 2.7–3.0 (m, 4 H, CH₂), 2.1–2.4 (m, 4 H, CH₂) and 1.6–1.9 (m, 8 H, CH₂).

(*R*)-2,2'-Bis(3,5-dichloro-2-hydroxybenzylideneamino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl **3b**. Yield: 85%. [α]_D²⁰ = −213.7 (c 1.0, CHCl₃), mp 139–140 °C (Found: C, 64.33; H, 4.32; N, 4.06. C₁₇H₁₄Cl₂NO requires C, 63.95; H, 4.38; N, 4.38%). HRMS: *m/z* 636.0853 (M⁺) (calc. for C₃₄H₂₈Cl₄N₂O₂: 636.0905). ¹H NMR (CDCl₃, 300 MHz): δ 12.9 (s, 2 H, OH), 8.4 (s, 2 H, CH=N), 7.31 (d, 2 H, *J* = 2.5, aryl H), 7.21 (d, 2 H, *J* = 8.2, aryl H), 7.15 (d, 2 H, *J* = 2.5, aryl H), 7.10 (d, 2 H, *J* = 8.2 Hz, aryl H), 2.75–3.0 (m, 4 H, CH₂), 2.2–2.3 (m, 4 H, CH₂) and 1.6–1.9 (m, 8 H, CH₂). ¹³C NMR (CDCl₃, 300 MHz): δ 158.4, 155.7, 142.5, 138.2, 136.1, 133.7, 132.1, 129.9, 129.5, 122.9, 122.5, 120.5, 114.7, 29.9, 27.6, 23.0 and 22.7.

(*S*)-1-(3',5'-Di-*tert*-butyl-2'-hydroxybenzylideneamino)-1-phenylethane **4a**. Yield: 74%. [α]_D²⁰ = +119.6 (c 0.726, CHCl₃), mp 93–94 °C (Found: C, 81.88; H, 9.32; N, 3.97. C₂₃H₃₁NO requires C, 81.90; H, 9.19; N, 4.15%). MS: *m/z* 337 (M⁺), 322 (M⁺ − CH₃), 294 (M⁺ − C₃H₇) and 280 (M⁺ − C₄H₉). ¹H NMR (CDCl₃, 300 MHz): δ 13.8 (s, 1 H, OH), 8.42 (s, 1 H, CH=N), 7.07–7.62 (m, 7 H, aryl H), 4.52 (q, 1 H, CHN=), 1.62 (d, 3 H, CH₃, *J* = 6.54 Hz), 1.45 (s, 9 H, Bu^t) and 1.29 (s, 9 H, Bu^t). ¹³C NMR (CDCl₃, 300 MHz): δ 172.2, 165.6, 151.7, 147.7, 144.3, 136.2, 134.8, 134.6, 134.2, 133.6, 125.5, 76.2, 42.7, 41.8, 39.1, 37.1 and 32.6.

(*S*)-1-(3',5'-Di-*tert*-butyl-2'-hydroxybenzylideneamino)-1-naphthylethane **4b**. Yield: 76%. [α]_D²⁰ = +272.9 (c 0.812, CHCl₃), mp 129–130 °C (Found: C, 84.03; H, 8.57; N, 3.44. C₂₇H₃₃NO requires C, 83.68; H, 8.58; N, 3.61%). MS: *m/z* 387 (M⁺), 372 (M⁺ − CH₃) and 344 (M⁺ − C₃H₇). ¹H NMR (CDCl₃, 300 MHz): δ 14.0 (s, 1 H, OH), 8.44 (s, 1 H, CH=N), 7.02–8.14 (m, 9 H, aryl H), 5.4 (q, 1 H, CHN=), 1.78 (d, 3 H, CH₃, *J* = 6.55 Hz), 1.47 (s, 9 H, Bu^t) and 1.27 (s, 9 H, Bu^t). ¹³C NMR (CDCl₃, 300 MHz): δ 164.9, 158.1, 140.1, 139.7, 136.7, 133.9, 130.5, 129.0, 127.7, 126.9, 126.2, 126.1, 125.7, 125.5, 123.9, 123.1, 117.9, 63.8, 35.1, 34.1, 31.5, 29.5 and 24.5.

[Ru^{II}(1b − 2H)(NO)Cl] **5**. A mixture of compound **1b** (250 mg, 0.40 mmol) and NaH (150 mg, 6.25 mmol) was stirred in thf (20 ml) for 15 min until evolution of hydrogen ceased. The mixture was filtered and evaporated to dryness. To the residue was added toluene (35 ml) and [Ru^{II}(NO)Cl₃(PPh₃)₂] (290 mg, 0.38 mmol). The mixture was refluxed for 12 h, then filtered to remove any insoluble material. After removal of the solvent under vacuum, the crude product was purified by chromatography on an alumina column with diethyl ether–light petroleum (bp 40–60 °C) (1 : 4) followed by dichloromethane as eluent. The brown band was collected and the solvent removed under vacuum. Upon addition of methanol, the desired product was precipitated out as a brown solid. Yield: 35% (Found: C, 51.78; H, 2.98; N, 5.05. C₃₄H₁₈Cl₅N₃O₃Ru requires C, 51.35; H, 2.27; N, 5.29%). IR (cm^{−1}): 1851 and 1602. ¹H NMR (CDCl₃, 300 MHz): δ 8.17 (1 H, d, *J* = 8.58), 8.04 (1 H, d, *J* = 8.25), 7.98 (1 H, s), 7.92 (1 H, d, *J* = 8.25 Hz), 7.88 (1 H, d, *J* = 8.2), 7.81 (1 H, s), 7.65 (1 H, d, *J* = 8.58), 7.58 (1 H, m), 7.52 (1 H, d, *J* = 2.8), 7.51 (1 H, m), 7.41 (1 H, d, *J* = 2.8), 7.40 (1 H,

m), 7.27 (1 H, m), 7.20 (1 H, d, *J* = 8.25), 7.18 (1 H, d, *J* = 8.9), 7.13 (1 H, d, *J* = 2.64), 6.94 (1 H, d, *J* = 2.70) and 6.88 (1 H, d, *J* = 8.58 Hz). MS: *m/z* 795 (M⁺), 760 (M⁺ − Cl) and 730 (M⁺ − Cl − NO).

Crystallography

Crystal data of 5·CH₂Cl₂. C₃₄H₁₈Cl₅N₃O₃Ru·CH₂Cl₂, *M* = 879.80, triclinic, space group *P*1 (no. 2), *a* = 11.555(5), *b* = 12.807(4), *c* = 13.347(4) Å, *a* = 81.70(3), *β* = 72.34(3), *γ* = 83.89(3)°, *V* = 1753(2) Å³, *Z* = 2, *D*_c = 1.666 g cm^{−3}, *μ*(Mo-Kα) = 10.21 cm^{−1}.

Single crystals of complex 5·CH₂Cl₂ suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into a dichloromethane solution of **5**. Data were collected at 25 °C on a Rigaku AFC7R diffractometer with graphite monochromatized Mo-Kα radiation (*λ* = 0.71073 Å). Upon averaging the 4840 reflections measured, 4574 unique reflections were obtained (*R*_{int} = 0.042); 3085 with *I* > 3σ(*I*) were considered observed and used in the structural analysis. Convergence for 442 variable parameters by least squares refinement for 3085 reflections with *I* > 3σ(*I*) was reached at *R* = 0.040 and *R'* = 0.050. Selected bond distances and angles are listed in Table 1.

CCDC reference number 186/1584.

See <http://www.rsc.org/suppdata/dt/1999/3303/> for crystallographic files in .cif format.

Asymmetric trimethylsilylcyanation of aldehydes

Catalysed by titanium complexes: general procedure. To a solution of binaphthyl Schiff base (0.55 mmol) in dichloromethane (2.5 ml) in a dry Schlenk tube was added Ti(OPrⁱ)₄ (0.5 mmol) at room temperature. The mixture was stirred for 2 h, then cooled to −78 °C. Freshly distilled aldehyde (2.50 mmol) and an excess of trimethylsilyl cyanide (6.60 mmol) were sequentially added through a syringe. The whole mixture was stirred for 36 or 120 h at this temperature and then poured into a mixture of 1 mol dm^{−3} HCl (30 ml) and ethyl acetate (100 ml) and stirred vigorously for 6 h at room temperature. The mixture was then extracted with ethyl acetate (50 ml × 3), and the combined extracts were washed with saturated NaHCO₃ and brine and dried over Na₂SO₄. After column chromatography on silica gel, oil or solid products could be obtained.

Catalysed by ruthenium complexes. This was carried out by the same procedure as for the titanium case except that complex **5** and the complex formed after treatment of **5** with AgPF₆ were used instead of the titanium complexes formed from Ti(OPrⁱ)₄ and Schiff bases.

Procedure for the AgPF₆ treatment of complex 5 (all operations under argon). To a solution of complex **5** (79 mg, 0.1 mmol) in acetonitrile (15 ml) in a Schlenk flask protected from light was added AgPF₆ (25 mg, 0.1 mmol). The mixture was stirred for 2 h, resulting in an off-white precipitation, probably due to the formation of AgCl. The mixture was then filtered through Celite. After removal of the solvent under vacuum, the residual solid was directly used for the trimethylsilylcyanation reaction.

Determination of enantiomeric excess of cyanohydrin products. Except for 2-hydroxy-3-phenylpropanenitrile, a product from phenylacetaldehyde, which was determined by ¹H NMR after derivatization from *α*-methoxy-*α*-(trifluoromethyl)phenylacetic acid (MTPA),⁹ all cyanohydrins were analysed by GC with a chiral column after derivatization by trifluoroacetic anhydride (TFAA). The procedure for the preparation of the TFAA ester was as follows: to a solution of cyanohydrin (10 mg) in ethyl acetate (1 ml) was added TFAA (1 ml). The mixture was refluxed for 30 min with a drying tube. After cooling, the organic layer was washed by brine and dried by Na₂SO₄. The product was obtained upon removal of solvent.

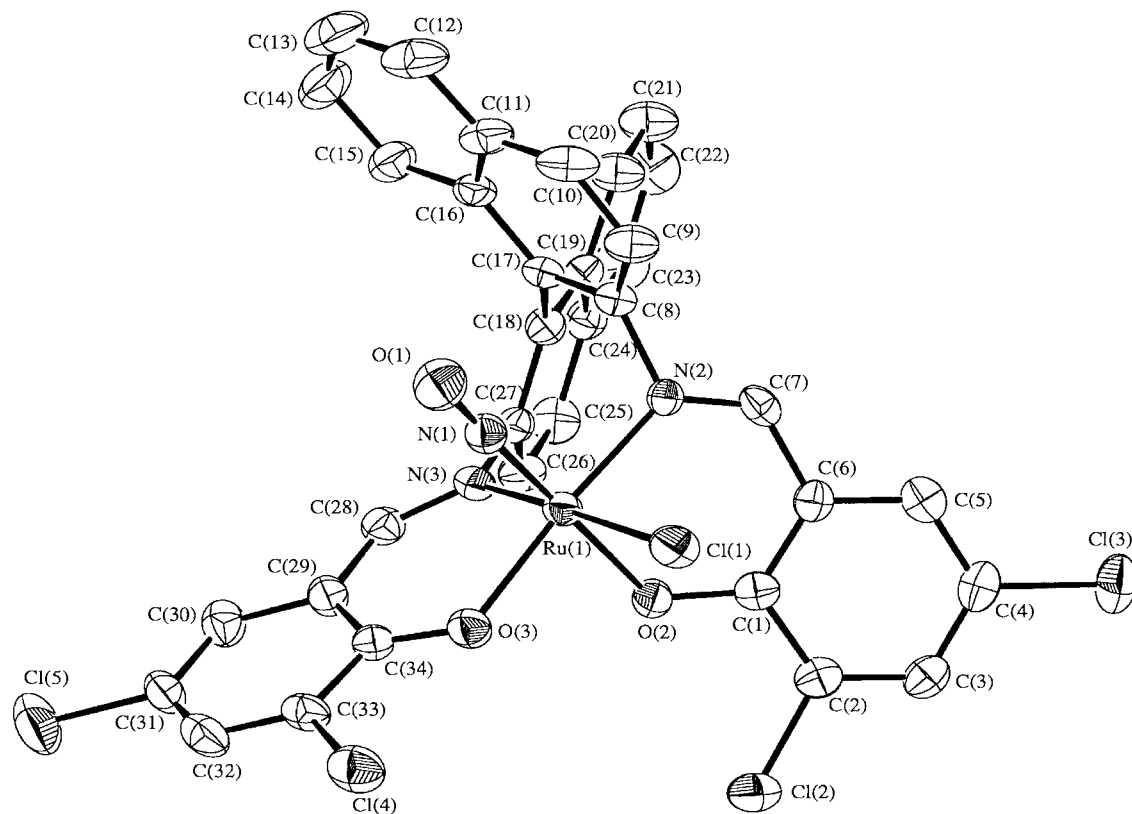


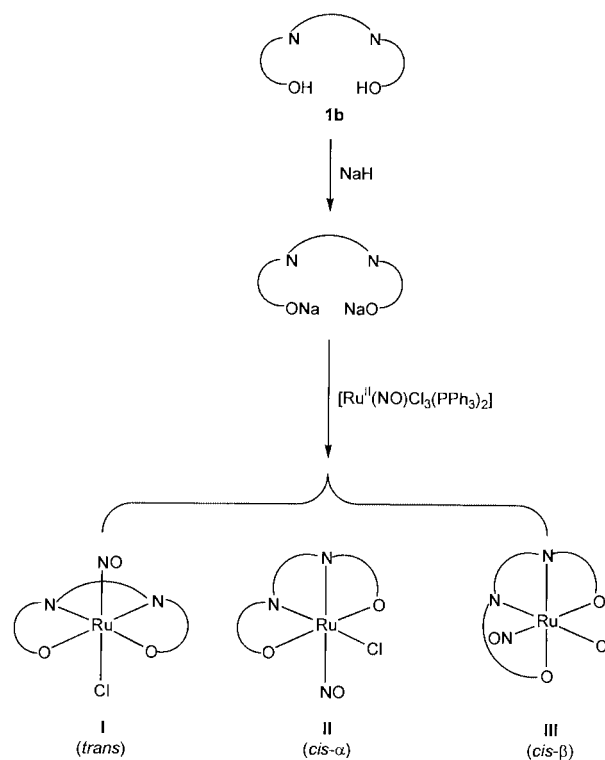
Fig. 1 Molecular structure of complex **5**. Hydrogen atoms are omitted. Thermal ellipsoids are drawn at 40% probability level.

Characterization of cyanohydrin products. All the products were identified by comparison of their spectral data with those reported in the literature.^{9,32}

Results and discussion

The binaphthyl Schiff bases employed in this work were exclusively prepared by a one-pot reaction of the corresponding amine with salicylaldehyde or its derivatives. It has been demonstrated that this type of Schiff base readily forms stable complexes with a variety of transition metals;^{24,25,28} three such complexes have been structurally characterized.^{24,25} In the literature there are a good number of reports on titanium–Schiff base complexes formed *in situ* by treating $\text{Ti}(\text{OPr}^i)_4$ with derivatives of $\text{L}^1\text{--L}^3$ ^{8–15} and L^5 ^{29,33,34} none of which has been isolated. The titanium complexes in this work were all generated in a similar manner through reaction of $\text{Ti}(\text{OPr}^i)_4$ with *ca.* 1 equivalent Schiff base in dichloromethane. Attempts to isolate and characterize these complexes proved difficult. Therefore, in all cases, the complex formed *in situ* was used to perform the subsequent trimethylsilylcyanation reactions.

In contrast, a ruthenium complex with the dianion of compound **1b** has been isolated. Treatment of $[\text{Ru}^{\text{II}}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ with the sodium salt of **1b** (formed *in situ* through reaction of **1b** with sodium hydride) in toluene resulted in formation of complex **5** in 35% yield (Scheme 2). Complex **5** may have a total of three geometric isomers, which are depicted in Scheme 2. The *trans* isomer **I** should be disfavoured by the binaphthyl Schiff base, as observed for manganese and iron analogues.²⁴ The structure of **5** determined by X-ray crystallography (Fig. 1) corresponds to isomer **III** of *cis-β* configuration, in which the two phenoxy rings are *cis* to each other with a dihedral angle of $62.9(2)^\circ$. The same configuration has also been observed in the structures of the manganese and iron analogues.²⁴ The dihedral angle between the two naphthylene rings is 70.2° , which is smaller than the corresponding angles of $85.5(3)$ and



Scheme 2

$72.1(1)^\circ$ previously reported for the manganese and iron analogues, respectively.²⁴ Apparently, the binaphthyl moiety is quite flexible in forming complexes with metal ions. The Ru–N (NO), Ru–N(2), Ru–N(3), and Ru–O(3) distances (1.724(7), 2.046(6), 2.075(6), and 2.040(5) Å respectively) (Table 1) are all slightly longer than but comparable to the corresponding distances in $[\text{Ru}(\text{salen})(\text{NO})(\text{H}_2\text{O})]^+$ (salen =

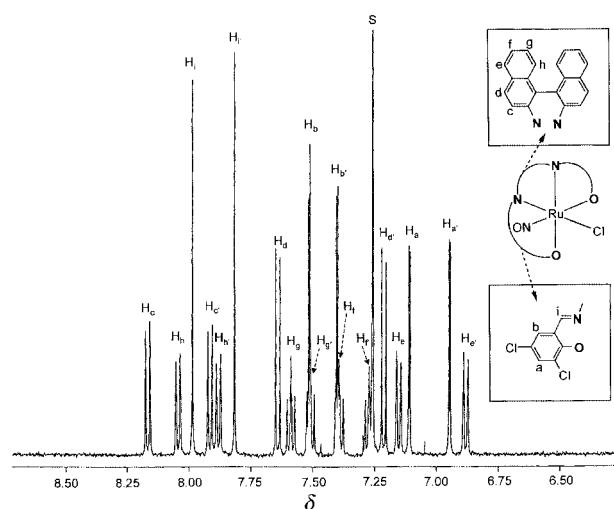


Fig. 2 The ^1H NMR spectrum (300 MHz) of complex **5** in CDCl_3 .

N,N' -bis(salicylidene)ethylenediamine dianion)³⁵ whose configuration is similar to that of the *trans* isomer **1**. However, the Ru–O(2) bond (1.974(5) Å) *trans* to the NO group is significantly shorter than the Ru–O (salen) bond in $[\text{Ru}(\text{salen})\text{-(NO)}(\text{H}_2\text{O})]^+$. The Ru–N–O angle is 174.7(6)°, indicating a basically linear NO^+ group, consistent with the observed high ν_{NO} stretching frequency (1851 cm^{-1}).

The UV-VIS spectrum of complex **5** in chloroform is almost featureless, exhibiting a weak broad band spanning the region 375–500 nm. The ^1H NMR spectrum shows well resolved peaks typical of a diamagnetic species, as depicted in Fig. 2. Since **5** has no element of symmetry, the two halves of the binaphthyl Schiff base, each having 9 different protons, are non-equivalent, consistent with a total of 18 discernible signals of equal intensity in the spectrum. The assignment of the signals was based on their multiplicity and ^1H – ^1H COSY measurements.

Trimethylsilylcyanation of benzaldehyde catalysed by titanium Schiff base complexes

All the reactions were carried out in dichloromethane at -78°C with 20 mol% titanium complexes formed *in situ* through reaction of $\text{Ti}(\text{OPr}^i)_4$ with the corresponding Schiff bases. These conditions are similar to the optimum ones found by Oguni and co-workers⁹ for L^1 -type Schiff bases. Table 2 summarizes the chemical yields and e.e.s of the reactions.

It can be seen from Table 2 that the tetradentate binaphthyl Schiff bases **1** are generally superior to the bi- and tri-dentate ligands **4** and **2b** respectively. For example, by using both the bidentate ligands **4**, only 29–38 e.e. (entries 18, 17) were obtained. In contrast, the use of **1** results in an excellent enantioselectivity, *ca.* 90% e.e. (entries 4, 5, 8), although their complexes with titanium exhibited a lower catalytic activity than those of the tridentate ligands **2** (reaction (1) was completed within 120 h for **1** but only 36 h for **2**).

For the Schiff bases **1**, those of the (*R*) configuration preferably led to (*S*) products and *vice versa*. It is evident that the nature of the substituents R^1 and R^2 on the phenyl groups strongly influences the enantioselectivity. First, substituents of larger steric hindrance led to a higher e.e. When both R^1 and R^2 were Bu^t groups an e.e. as high as 93% was obtained (entries 4, 5). Secondly, the substituent *ortho* to the hydroxy group (R^1) had a larger effect on the enantioselectivity. For a given $\text{R}^2 = \text{H}$, changing R^1 along the sequence $\text{H} \rightarrow \text{Et} \rightarrow \text{Bu}^t$ increased the e.e. from 38 to 75 to 86% (entries 1, 11, 8). However, when $\text{R}^1 = \text{Bu}^t$, a change of R^2 from H to Bu^t didn't cause a remarkable increase in e.e. (entries 8, 4). Thirdly, electron withdrawing substituents caused a significant decrease in both chemical yield

Table 1 Selected bond distances (Å) and angles (°) for complex **5**· CH_2Cl_2

Ru(1)–N(1)	1.724(7)	N(1)–O(1)	1.157(7)
Ru(1)–Cl(1)	2.365(2)	N(2)–C(7)	1.271(9)
Ru(1)–N(2)	2.046(6)	N(2)–C(8)	1.458(8)
Ru(1)–N(3)	2.075(6)	N(3)–C(27)	1.449(9)
Ru(1)–O(2)	1.974(5)	N(3)–C(28)	1.299(9)
Ru(1)–O(3)	2.040(5)	C(1)–O(2)	1.319(8)
		C(34)–O(3)	1.295(8)
N(1)–Ru(1)–Cl(1)	90.0(2)	N(2)–Ru(1)–N(3)	89.9(2)
N(1)–Ru(1)–N(2)	94.2(2)	N(3)–Ru(1)–O(3)	91.1(2)
N(1)–Ru(1)–N(3)	95.9(3)	O(3)–Ru(1)–Cl(1)	89.6(1)
N(1)–Ru(1)–O(3)	91.0(2)	Ru(1)–N(1)–O(1)	174.7(6)
O(2)–Ru(1)–Cl(1)	87.0(2)	N(1)–Ru(1)–O(2)	176.8(3)
O(2)–Ru(1)–N(2)	86.8(2)	N(3)–Ru(1)–Cl(1)	174.0(2)
O(2)–Ru(1)–N(3)	87.1(2)	N(2)–Ru(1)–O(3)	174.6(2)
O(2)–Ru(1)–O(3)	87.9(2)	Ru(1)–O(2)–C(1)	124.6(4)
N(2)–Ru(1)–Cl(1)	88.9(2)	Ru(1)–O(3)–C(34)	125.0(4)

Table 2 Enantioselective trimethylsilylcyanation of benzaldehyde^a

Entry	Schiff base (configuration)	e.e. (%) ^b (configuration) ^c	Yield (%) ^d
1	1a (<i>R</i>)	38 (<i>S</i>)	76
2	1b (<i>R</i>)	47 (<i>S</i>)	53
3	1c (<i>R</i>)	81 (<i>S</i>)	60
4	1d (<i>R</i>)	93 (<i>S</i>)	92
5	1d (<i>S</i>)	93 (<i>R</i>)	94
6	1e (<i>R</i>)		no reaction
7	1f (<i>R</i>)	35 (<i>S</i>)	53
8	1g (<i>R</i>)	86 (<i>S</i>)	82
9	1h (<i>R</i>)	75 (<i>S</i>)	73
10	1i (<i>R</i>)	51 (<i>S</i>)	63
11	1j (<i>R</i>)	75 (<i>S</i>)	85
12	2a (<i>R</i>)	66 (<i>S</i>)	98
13	2b (<i>R</i>)	34 (<i>S</i>)	82
14	3a (<i>R</i>)	68 (<i>S</i>)	85
15	3b (<i>R</i>)	37 (<i>S</i>)	42
16	3c (<i>R</i>)	24 (<i>S</i>)	54
17	4a (<i>S</i>)	38 (<i>S</i>)	75
18	4b (<i>S</i>)	29 (<i>S</i>)	68

^a All reactions were carried out in dichloromethane using 20 mol% of catalyst based on benzaldehyde at -78°C for 36 h for tridentate ligands **2a, 2b** and 120 h for the others). ^b Determined by GC with a chiral β -cyclodextrin column after derivatization by TFAA. ^c The configurations of the products were determined by comparison of the sign of optical rotation values with those in the literature. ^d Isolated yield or determined by NMR analysis.







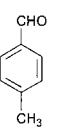
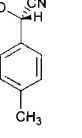


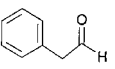
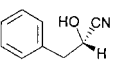
and e.e. For example, for a given $\text{R}^1 = \text{Bu}^t$, changing R^2 along the sequence $\text{Bu}^t \rightarrow \text{H} \rightarrow \text{Cl}$ resulted in a decrease in e.e. from 93 to 86 to 75% (entries 4, 8, 9). When both R^1 and $\text{R}^2 = \text{NO}_2$, no reaction was observed (entry 6). It is noteworthy that, when both R^1 and R^2 changed along the sequence $\text{H} \rightarrow \text{Cl} \rightarrow \text{Br}$, the e.e. increased from 38 to 47 to 81% (entries 1–3). It is likely that, in these cases, the steric effect is a dominating factor.

In attempting further to improve both the enantioselectivity and catalytic activity, we synthesized a novel type of tetradentate Schiff base **3**, analogous to but even more sterically demanding than the corresponding **1**. The results obtained with these novel ligands are also listed in Table 2. Unexpectedly, only low to moderate e.e.s (24–68%) were obtained (entries 14–16). Therefore, the best Schiff base for reaction (1) in our case is **1d**.

Trimethylsilylcyanation of other aldehydes catalysed by $\text{Ti}(\text{OPr}^i)_4$ –**1d**

Under the same conditions, reaction (1) catalysed by $\text{Ti}(\text{OPr}^i)_4$ –**1d** was also performed for other aldehydes, both aliphatic and aromatic. The results are summarized in Table 3. As can be seen, substituted benzaldehydes with electron donating groups

Table 3 Asymmetric catalytic trimethylsilylcyanation of other aldehydes^a

Aldehydes	Product	e.e. (%) (configuration)	Yield (%)
		42 (<i>S</i>) ^b	75
		51 (<i>S</i>) ^b	82
		95 (<i>S</i>) ^b	87
		88 (<i>S</i>) ^b	82
		96 (<i>S</i>) ^b	75
		71 (<i>S</i>) ^b	63

^a The experimental conditions are identical with those described in Table 2. ^b Determined by GC with a chiral β -cyclodextrin column after derivatization by TFAA. ^c Determined by ¹H NMR after derivatization by MTPA.

were trimethylsilylcyanated with excellent e.e.s. The highest e.e. (96%) was achieved in the case of *m*-tolualdehyde. The aliphatic aldehydes and aromatic aldehydes with electron withdrawing substituents, however, resulted in lower e.e. values. This is different from the Ti(OPrⁱ)₄-tridentate Schiff base system developed by Oguni and co-workers,⁹ which proved best for some alkyl aldehydes.

Trimethylsilylcyanation of benzaldehyde catalysed by ruthenium binaphthyl Schiff base complexes

Attempts were made to extend reaction (1) to complex **5** in the case of benzaldehyde. The reaction was performed in dichloromethane at -78 °C for 60 h, a condition similar to that in the titanium cases. However, at the end of the reaction very little desired product was detected. This might be due to the fact that the ruthenium centre in **5** is both electronically and coordinatively saturated, lacking labile sites for substrate activation. With this in mind, we treated **5** with AgPF₆, intending to remove the chloride ion through precipitation of AgCl. Indeed, after the treatment, complex **5** exhibited a good catalytic property, leading to formation of 2-hydroxy-2-phenylacetonitrile in 90% yield, but a rather low e.e. (24%) was obtained. Since the Schiff base ligand in **5** assumes (*S*) configuration, the product of (*R*) configuration was preferably formed, similar to the cases of titanium.

On the mechanism of asymmetric trimethylsilylcyanation of aldehydes catalysed by titanium and ruthenium complexes

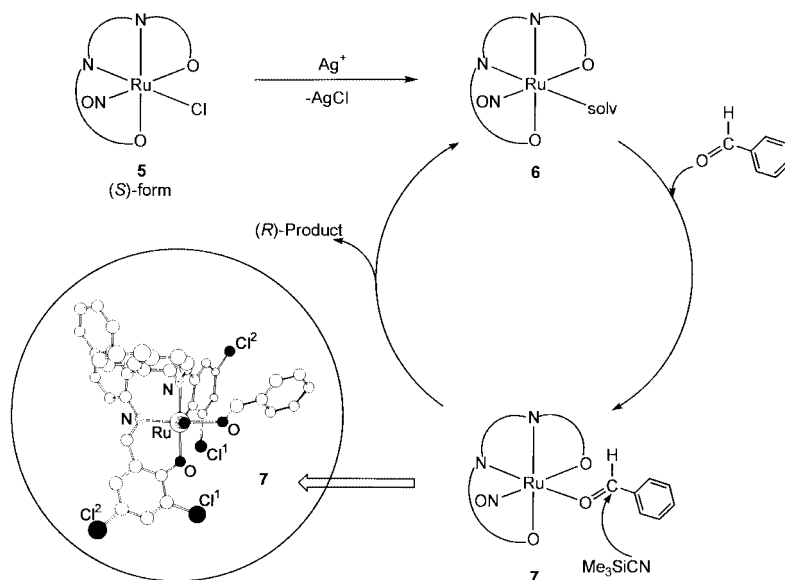
The mechanism for reaction (1) involving L¹-type tridentate Schiff bases has been discussed by Oguni and co-workers⁹ in some detail. A five-co-ordinate mononuclear titanium complex, identified by ¹³C NMR, FAB MS and molecular weight measurements, is the active species, which could bind an alde-

hyde molecule and thus enhance its reactivity toward attack by cyanide group. The steric hindrance mainly provided by the substituents on L¹ accounts for the enantioselectivity of the reaction. However, for tetradentate Schiff bases such as derivatives of L² and L³, the mechanism of reaction (1) is essentially unclear, although it was proposed that the first step in the catalytic cycle might be the binding of cyanide anion rather than an aldehyde molecule to the active titanium complexes.^{11,16}

In our case, the trimethylsilylcyanation of benzaldehyde with Me₃SiCN catalysed by AgPF₆-treated ruthenium complex **5** most likely proceeds by a mechanism (Scheme 3) analogous to that proposed by Oguni and co-workers.⁹ As described above, complex **5** itself exhibited almost no catalytic activity toward the reaction, consistent with the fact that the electronically saturated **5** lacks ligands that are sufficiently labile to be replaced by an aldehyde molecule. Treatment of **5** with AgPF₆ would remove the chloride anion and generate **6** bearing a "vacant" site. Reaction of this type has been well demonstrated by Bosnich and co-workers³⁵ in the case of [Ru(salen)(NO)Cl]. Complex **6** should be able to bind benzaldehyde and form the intermediate **7**, rendering the aldehyde more readily attacked by Me₃SiCN. On the basis of the structure of **5** and assuming that the Ru–O distance and Ru–O–C angle of the ruthenium–benzaldehyde moiety are *ca.* 2.1 Å and 125° respectively, we built a model structure for **7**, which is inset in Scheme 3 as viewed along the ON–Ru–O axis. The phenyl group of the aldehyde should favour the indicated orientation in order to minimize its repulsive interaction with both Cl¹ atoms. Owing to the steric hindrance of the rigid phenolate group to the *re* face of the aldehyde, the *si* face of the aldehyde should be more readily attacked by Me₃SiCN, generating the product mainly of the (*R*) configuration, consistent with the result described above.

With regard to the titanium catalysts containing derivatives of L⁴, we found that, in the absence of these catalysts, no reaction could be observed between aldehyde and Me₃SiCN even for several days. This indicates that the titanium complexes must be able to activate the substrates. In order to get some information on the nature of the titanium complexes, we studied an equimolar mixture of Ti(OPrⁱ)₄ and **1b** in dichloromethane by electrospray MS, which revealed a prominent cluster peak at *m/z* = 734.9 corresponding to [Ti(**1b** – 2H)(OPrⁱ)⁺]. The peak due to [Ti(**1b** – 2H)(OPrⁱ)⁺] (*m/z* = 794.8) also appeared but was rather weak. There were no peaks in the higher *m/z* region. From this measurement, it is highly possible that the equimolar reaction of Ti(OPrⁱ)₄ with **1b** in dichloromethane led to formation of the mononuclear species [Ti(**1b** – 2H)(OPrⁱ)₂] **8** with concomitant formation of two equivalents of isopropyl alcohol. This might also be the case for other L⁴ derivatives.

Since all the structurally characterized metal complexes with the dianion of compound **1b** assume the *cis*- β configuration (see above), and the total size of two OPrⁱ groups is comparable to that of the acac ligand in [Mn(**1b** – 2H)(acac)]₂,²⁴ the titanium complex **8** most reasonably has a structure analogous to that of **5**. However, as a direct substitution of the OPrⁱ group in **8** by aldehyde should be difficult, the mechanism for reaction (1) catalysed by **8** might be rather complicated. The following are possibilities. First, dissociation of **8** in solution could generate a five-co-ordinate species [Ti(**1b** – 2H)(OPrⁱ)⁺] **9** bearing a "vacant" co-ordination site, which might function as the active species for the trimethylsilylcyanation in a manner similar to that of the ruthenium complex **6** as depicted in Scheme 3. This is consistent with the observation that the (*S*)-form Schiff base preferably resulted in formation of the (*R*) product, and *vice versa* (Table 2). Evidently, larger substituents on L⁴, such as R¹ and R² of **1**, would give a higher enantiomeric excess, and those closer to the titanium centre (R¹) would have a considerably larger effect. Secondly, the coordinated OPrⁱ group in **8** could react with Me₃SiCN to form [Ti(**1b** – 2H)(OPrⁱ(CN))] **10** or [Ti(**1b** – 2H)(CN)₂] **11** with concomitant formation of Me₃Si-



Scheme 3

OPr^d , similar to the case reported by Nakai and co-workers¹⁷ for a chiral binaphthol-titanium complex bearing OPr^d groups. The activated cyanide group in complexes **10** and **11** could then react with aldehyde to effect the cyanation process. Moreover, any five-co-ordinate species resulting from the dissociation of complexes **10** and **11** may catalyse reaction (1) by a mechanism analogous to that depicted in Scheme 3.

Conclusion

Titanium complexes formed *in situ* from reaction of $\text{Ti}(\text{OPr}^d)_4$ with tetradentate binaphthyl Schiff bases, 2,2'-bis(3- R^1 -5- R^2 -2-hydroxybenzylideneamino)-1,1'-binaphthyl, are efficient catalysts for the asymmetric trimethylsilylcyanation of aromatic aldehydes with trimethylsilyl cyanide. The enantiomeric selectivity of such reactions markedly increases with the steric hindrance of R^1 but decreases with the electron withdrawing ability of both R^1 and R^2 . Excellent e.e.s (93–96%) could be obtained with $\text{R}^1 = \text{R}^2 = \text{Bu}^t$ in the cases of benzaldehyde and *o*- or *m*-tolualdehyde. The mononuclear nitrosyl ruthenium complex $[\text{Ru}^{\text{II}}(\text{L})(\text{NO})\text{Cl}]$ (L = the dianion of the above Schiff base with $\text{R}^1 = \text{R}^2 = \text{Cl}$), which has been isolated and structurally characterized, also exhibits good catalytic property toward the trimethylsilylcyanation of benzaldehyde after treatment with AgPF_6 , albeit in a lower e.e. (24%).

Acknowledgements

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