Synthesis, structure, and catalytic activity of group 4 complexes with new chiral biaryl-based NO$_2$ ligands

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ABSTRACT

A new series of chiral bis-ligated group 4 complexes have been prepared from the reaction between M(NMe$_2$)$_4$ (M = Ti, Zr) and C_1-symmetric biaryl-based NO$_2$ ligands, (R)-2-(mesitoylamino)-2′-methoxy-1,1′-binaphthyl (1H), (R)-2-(mesitoylamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (2H), (S)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(mesitoylamino)-2′-methoxy-1,1′-binaphthyl (3H), (R)-2-(3,5-di-*tert*-butyl-2-hydroxyphenylmethyleneamino)-2′-methoxy-1,1′-binaphthyl (4H), (R)-2-(3-*tert*-butyl-2-hydroxyphenylmethyleneamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (5H), which are derived from (R)-2-amino-2′-methoxy-1,1′-binaphthyl, (R)-2-amino-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl or (S)-5,5′,6,6′,7,7′,8,8′-octahydro-2-amino-2′-methoxy-1,1′-binaphthyl. Treatment of M(NMe$_2$)$_4$ with 2 equiv. of mesitoylamides 1H, 2H or 3H gives, after recrystallization from a toluene or *n*-hexane solution, the bis-ligated chiral titanium amides (1)$_2$Ti(NMe$_2$)$_2$ (6), (2)$_2$Ti(NMe$_2$)$_2$ (8), (3)$_2$Ti(NMe$_2$)$_2$ (10), and zirconium amides (1)$_2$Zr(NMe$_2$)$_2$ (7), (2)$_2$Zr(NMe$_2$)$_2$ (9), (3)$_2$Zr(NMe$_2$)$_2$ (11), respectively, in good yields. Under similar reaction conditions, treatment of M(NMe$_2$)$_4$ with 2 equiv. of Schiff base ligands 4H or 5H gives, after recrystallization from a toluene solution, the chiral bis-ligated titanium complex {(R)-2-[3,5-(Me$_3$C)$_2$-2-O-C$_6$H$_2$CH(NMe$_2$)N]-2′-(MeO)-1,1′-C$_{20}$H$_{12}$}$_2$Ti (12) and zirconium complex {(R)-2-[3-Me$_3$C-2-O-C$_6$H$_3$CH(NMe$_2$)N]-2′-(MeO)-1,1′-(6-Me-C$_6$H$_3$)$_2$}(5)ZrNMe$_2$ (13), respectively, in good yields. All new compounds have been characterized by various spectroscopic techniques, and elemental analyses. The solid-state structures of compounds 1H, 6, 8, 9, 12 and 13 have further been confirmed by X-ray diffraction analyses. The titanium and zirconium amides are active catalysts for the asymmetric hydroamination/cyclization of aminoalkenes, affording cyclic amines in moderate to excellent yields with good ee values.

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1. Introduction

Chiral group 4 metal complexes have been widely studied in the past decades [1–14]. Among these, the development of group 4 metal catalysts for intramolecular asymmetric alkene hydroamination has received growing attention in recent years [11–14], because the hydroamination is a highly atom economical process in which an amine N–H bond is added to an unsaturated carbon–carbon bond leading to the formation of nitrogen heterocycles that are prevalent in naturally occurring and/or biologically active molecules. To date, the chiral group 4 metal catalysts have been shown promising for this transformation [15–30], however, successful catalysts affording significant enantioselectivity (>90% ee) are still scarcely reported, and those high enantioselective inductions are observed only for one or two substrates [20,21,30]. Thus, the development of new chiral group 4 metal catalysts for asymmetric alkene hydroamination is a desirable and challenging goal.

In recent years, 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN) as its (R) or (S) enantiomer has been modified to give variants which bear appropriate structural and electronic features for intended specific reactions, and its derivatives have exhibited good to excellent enantioselectivities in a number of asymmetric transformations [31–33]. However, few examples of chiral early transition metal catalysts based on NOBIN have been reported [31–33]. More recently, we have developed a series of early transition metal complexes based on chiral NOBIN, and found they are useful catalysts in the polymerization of methyl methacrylate (MMA), the ring-opening polymerization of *rac*-lactide, and the hydroamination/cyclization of the aminoalkenes [34–37]. In our endeavors to further explore the chiral NOBIN ligand system, and in our previous study we found that the group 4 complexes with chiral biaryl-based mesitoylamidate ligands [25,30] are more effective chiral catalysts for asymmetric hydroamination/cyclization than other ligated catalysts [24,28,29], we therefore have recently extended our research work to new chiral C_1-symmetric versatile mesitoylamide ligands, (R)-2-(mesitoylamino)-2′-methoxy-1,1′-binaphthyl (1H) and (S)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(mesitoylamino)-2′-methoxy-1,1′-binaphthyl (3H),

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each ligand contains two σ-donating oxygen atoms and one σ-donating nitrogen atom that can act in a bidentate or tridentate fashion. Herein, we report the synthesis and properties of the new chiral ligands, their use in the coordination chemistry of titanium(IV) and zirconium(IV), and the applications of the resulting complexes as catalysts for the asymmetric hydroamination/cyclization of aminoalkenes. For better understanding and comparison, the new ligands (R)-2-(mesitoylamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (**2**H), (R)-2-(3,5-di-tert-butyl-2-hydroxyphenylmethyleneamino)-2′-methoxy-1,1′-binaphthyl (**4**H) and (R)-2-(3-tert-butyl-2-hydroxyphenylmethyleneamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (**5**H) will be also included in this contribution.

2. Experimental

2.1. General methods

Group 4 complexes and catalytic reactions were performed under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. (R)-2-Amino-2′-methoxy-1,1′-binaphthyl [37], (R)-2-amino-2′-methoxy-6,6′-dimethyl-1, 1′-biphenyl [37], (S)-5,5′,6,6′,7,7′,8,8′-octahydro-2-amino-2′-methoxy-1,1′-binaphthyl [37], 2,2-dimethylpent-4-enylamine [38], 2,2′-dimethylhex-5-enylamine [38], and 1-(aminomethyl)-1-allyl-cyclohexane [39] were prepared according to literature methods. All chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co., and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 and 100 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

2.2. Preparation of (R)-2-(mesitoylamino)-2′-methoxy-1,1′-binaphthyl (1H)

Mesitoyl chloride (0.91 g, 5.0 mmol) was mixed with (R)-2-amino-2′-methoxy-1,1′-binaphthyl (1.50 g, 5.0 mmol) in dry toluene (30 mL). Pyridine (2 mL, 25.3 mmol) was added, and the solution was refluxed for two days. The solvent was removed and the residue was decomposed with H$_2$O (20 mL) and extracted with ethyl acetate (20 mL × 3) and washed with brine (20 mL). The combined organic layers were dried with anhydrous Na$_2$SO$_4$ and the solvent was removed under reduced pressure to give a white solid, which was further purified by flash column chromatography (n-hexane/ethyl acetate = 10:1) to give **1**H as a white solid. Colorless crystals suitable for X-ray structure analysis were grown from a toluene solution at room temperature. Yield: 1.78 g (80%). M.p.: 148–150 °C. ^{1}H NMR (CDCl$_3$): δ 8.62 (d, J = 8.8 Hz, 1H, aryl), 8.05 (d, J = 9.0 Hz, 1H, aryl), 7.99 (d, J = 9.0 Hz, 1H, aryl), 7.93 (d, J = 8.2 Hz, 1H, aryl), 7.86 (d, J = 8.1 Hz, 1H, aryl), 7.42 (m, 2H, aryl), 7.34 (m, 1H, aryl), 7.23 (m, 2H, aryl), 7.10 (d, J = 8.5 Hz, 1H, aryl), 7.05 (d, J = 8.5 Hz, 1H, aryl), 7.00 (s, 1H, NH), 6.68 (s, 2H, aryl), 3.74 (s, 3H, OCH$_3$), 2.18 (s, 3H, CH$_3$), 1.94 (s, 6H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 168.8, 154.9, 138.5, 134.8, 134.3, 134.1, 133.8, 133.1, 131.4, 130.8, 129.2, 128.6, 128.1, 128.0, 127.4, 126.3, 125.7, 125.0, 124.8, 124.1, 124.0, 123.1, 121.9, 117.1, 113.3, 56.3, 21.0, 18.6. IR (KBr, cm^{-1}): v 3399 (s), 3056 (w), 2956 (m), 1682 (s), 1612 (s), 1596 (s), 1488 (s), 1426 (s), 1351 (s), 1266 (s), 1251 (s), 1082

(s), 815 (s), 749 (s). Anal. Calc. for C$_{31}$H$_{27}$NO$_2$: C, 83.57; H, 6.11; N, 3.14. Found: C, 83.53; H, 6.03; N, 3.18%.

2.3. Preparation of (R)-2-(mesitoylamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (2H)

This compound was prepared as a white solid from the reaction of mesitoyl chloride (0.91 g, 5.0 mmol) with (R)-2-amino-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (1.14 g, 5.0 mmol) in the presence of pyridine (2 mL, 25.3 mmol) in dry toluene (30 mL) at reflux and purification by flash column chromatography (n-hexane/ethyl acetate = 10:1) using a similar procedure as in the synthesis of **1**H. Yield: 1.70 g (91%). M.p.: 52–54 °C. ^{1}H NMR (CDCl$_3$): δ 8.28 (d, J = 8.2 Hz, 1H, aryl), 7.38 (t, J = 7.9 Hz, 1H, aryl), 7.27 (m, 1H, aryl), 7.15 (d, J = 7.5 Hz, 1H, aryl), 6.92 (d, J = 7.5 Hz, 1H, aryl), 6.81 (m, 4H, NH and aryl H), 3.69 (s, 3H, OCH$_3$), 2.26 (s, 3H, CH$_3$), 2.18 (s, 6H, CH$_3$), 1.97 (s, 3H, CH$_3$), 1.96 (s, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 168.6, 156.8, 138.6, 138.5, 137.2, 135.7, 135.2, 134.3, 129.3, 128.6, 128.2, 127.9, 126.2, 124.3, 122.9, 119.5, 108.5, 55.5, 21.0, 19.9, 19.6, 18.8. IR (KBr, cm^{-1}): v 3397 (s), 3061 (w), 2920 (m), 1680 (s), 1579 (s), 1513 (s), 1465 (s), 1410 (s), 1292 (s), 1256 (s), 1080 (s), 799 (s). Anal. Calc. for C$_{25}$H$_{27}$NO$_2$: C, 80.40; H, 7.29; N, 3.75. Found: C, 80.34; H, 7.38; N, 3.73%.

2.4. Preparation of (S)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(mesitoylamino)-2′-methoxy-1,1′-binaphthyl (3H)

This compound was prepared as a white solid from the reaction of mesitoyl chloride (0.91 g, 5.0 mmol) with (S)-5,5′,6,6′,7,7′,8,8′-octahydro-2-amino-2′-methoxy-1,1′-binaphthyl (1.54 g, 5.0 mmol) in the presence of pyridine (2 mL, 25.3 mmol) in dry toluene (30 mL) at reflux and purification by flash column chromatography (n-hexane/ethyl acetate = 10:1) using a similar procedure as in the synthesis of **1**H. Yield: 1.84 g (81%). M.p.: 56–58 °C. ^{1}H NMR (CDCl$_3$): δ 8.02 (d, J = 8.3 Hz, 1H, aryl), 7.09 (d, J = 8.3 Hz, 1H, aryl), 6.96 (d, J = 8.4 Hz, 1H, aryl), 6.66 (m, 4H, NH and aryl H), 3.56 (s, 3H, OCH$_3$), 2.75 (m, 2H, CH$_2$), 2.64 (m, 2H, CH$_2$), 2.16 (s, 3H, CH$_3$), 2.06 (s, 6H, CH$_3$), 1.98 (m, 4H, CH$_2$), 1.68–1.51 (m, 8H, CH$_2$). ^{13}C NMR (CDCl$_3$): δ 167.5, 153.4, 137.3, 136.0, 134.8, 134.7, 133.3, 133.2, 131.6, 129.4, 128.9, 127.8, 127.6, 127.1, 122.9, 118.7, 107.6, 54.4, 28.7, 28.3, 28.2, 26.2, 26.1, 22.2, 22.0, 21.9, 20.0, 17.8. IR (KBr, cm^{-1}): v 3395 (s), 2926 (s), 2855 (w), 1680 (s), 1593 (s), 1504 (s), 1479 (s), 1440 (s), 1260 (s), 1085 (s), 803 (s). Anal. Calc. for C$_{31}$H$_{35}$NO$_2$: C, 82.08; H, 7.78; N, 3.09. Found: C, 81.92; H, 7.68; N, 3.13%.

2.5. Preparation of (R)-2-(3,5-di-tert-butyl-2-hydroxyphenyl-methyleneamino)-2′-methoxy-1,1′-binaphthyl (4H)

3,5-Di-tert-butyl-2-hydroxybenzaldehyde (2.34 g, 10.0 mmol) was mixed with (R)-2-amino-2′-methoxy-1,1′-binaphthyl (2.99 g, 10.0 mmol) in dry toluene (50 mL). A few 4 Å molecular sieves were added, and the solution was warmed up to 70 °C and kept for two days at this temperature. The solution was filtered and the solvent was removed under reduced pressure. The residue was purified by recrystallization from an n-hexane solution to give **4**H as a yellow solid. Yield: 3.40 g (66%). M.p.: 190–192 °C. ^{1}H NMR (C$_6$D$_6$): δ 13.57 (s, 1H, OH), 8.38 (s, 1H, CH=N), 7.98 (d, J = 9.0 Hz, 1H, aryl), 7.88 (m, 3H, aryl), 7.69 (d, J = 8.4 Hz, 1H, aryl), 7.55 (d, J = 2.4 Hz, 1H, aryl), 7.43 (d, J = 8.4 Hz, 1H, aryl), 7.31 (m, 3H, aryl), 7.23 (d, J = 7.2 Hz, 1H, aryl), 7.14 (m, 2H, aryl), 6.99 (d, J = 2.4 Hz, 1H, aryl), 3.44 (s, 3H, OCH$_3$), 1.55 (s, 9H, CH$_3$), 1.37 (s, 9H, CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 162.4, 159.1, 155.1, 144.1, 139.9, 137.0, 134.5, 134.4, 133.1, 130.1, 129.8, 129.6, 129.3, 128.4, 127.6, 127.4, 127.1, 127.0, 126.9, 126.8, 125.9, 125.5, 123.8, 120.4, 118.9, 117.7, 113.7, 55.8, 35.2, 34.2, 31.6, 29.5. IR (KBr, cm^{-1}): v 3432

(m), 3054 (w), 2957 (s), 1623 (s), 1610 (s), 1578 (s), 1508 (s), 1465 (s), 1250 (s), 1171 (s), 1084 (s), 804 (s), 746 (s). *Anal.* Calc. for $C_{36}H_{37}NO_2$: C, 83.85; H, 7.23; N, 2.72. Found: C, 83.96; H, 7.28; N, 2.73%.

2.6. Preparation of (R)-2-(3-tert-butyl-2-hydroxyphenyl-methyleneamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (5H)

This compound was prepared as a yellow solid from the reaction of 3-*tert*-butyl-2-hydroxybenzaldehyde (1.78 g, 10.0 mmol) with (R)-2-amino-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (2.27 g, 10.0 mmol) in the presence of 4 Å molecular sieves in dry toluene (50 mL) at 70 °C and purification by recrystallization from an *n*-hexane solution using a similar procedure as in the synthesis of **4**H. Yield: 3.14 g (81%). M.p.: 118–120 °C. ^{1}H NMR (C_6D_6): δ 13.82 (s, 1H, O*H*), 8.33 (s, 1H, C*H*=N), 7.32 (m, 1H, aryl), 7.22 (m, 1H, aryl), 7.18 (d, *J* = 7.6 Hz, 1H, aryl), 7.12 (m, 1H, aryl), 7.01 (d, *J* = 7.6 Hz, 1H, aryl), 6.96 (d, *J* = 7.6 Hz, 1H, aryl), 6.90 (d, *J* = 7.6 Hz, 1H, aryl), 6.79 (t, *J* = 7.6 Hz, 1H, aryl), 6.70 (d, *J* = 8.2 Hz, 1H, aryl), 3.34 (s, 3H, OC*H₃*), 2.17 (s, 3H, C*H₃*), 2.08 (s, 3H, C*H₃*), 1.59 (s, 9H, C*H₃*). ^{13}C NMR (C_6D_6): δ 162.1, 161.3, 157.0, 147.1, 138.3, 137.7, 137.5, 133.7, 130.6, 130.2, 129.3, 128.6, 128.5, 127.4, 122.9, 119.6, 118.1, 115.6, 108.6, 55.1, 35.1, 29.5, 20.0, 19.8. IR (KBr, cm^{-1}): ν 3434 (m), 3000 (m), 2955 (s), 2918 (m), 2827 (m), 1625 (s), 1610 (s), 1569 (s), 1467 (s), 1429 (s), 1255 (s), 1201 (s), 1114 (s), 1086 (s), 754 (s). *Anal.* Calc. for $C_{26}H_{29}NO_2$: C, 80.59; H, 7.54; N, 3.61. Found: C, 80.66; H, 7.48; N, 3.63%.

2.7. Preparation of (1)₂Ti(NMe₂)₂ (6)

A toluene solution (10 mL) of **1**H (0.45 g, 1.0 mmol) was slowly added into a toluene solution (10 mL) of Ti(NMe₂)₄ (0.11 g, 0.5 mmol) with stirring at room temperature. The solution was stirred at room temperature for one day. The solution was filtered and the solvent was removed under reduced pressure. The resulting red solid was recrystallized from a toluene solution to give **6** as red crystals. Yield: 0.38 g (75%). M.p.: 246–248 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.94 (d, *J* = 8.8 Hz, 2H, aryl), 7.86 (m, 4H, aryl), 7.76 (m, 4H, aryl), 7.10 (m, 8H, aryl), 6.91 (t, *J* = 7.5 Hz, 2H, aryl), 6.67 (s, 4H, aryl), 6.34 (s, 2H, aryl), 5.99 (s, 2H, aryl), 3.60 (s, 12H, NMe₂), 3.28 (s, 6H, OC*H₃*), 2.11 (s, 6H, C*H₃*), 1.98 (s, 6H, C*H₃*), 1.67 (s, 6H, C*H₃*). ^{13}C NMR (C_6D_6): δ 180.6, 155.2, 142.8, 137.4, 136.6, 135.4, 134.1, 132.9, 131.7, 129.7, 129.1, 128.9, 128.2, 127.4, 127.2, 127.0, 126.3, 126.0, 125.9, 125.8, 125.4, 124.4, 122.2, 119.5, 112.6, 55.2, 47.3, 20.9, 20.7, 20.2. IR (KBr, cm^{-1}): ν 2963 (m), 1652 (s), 1592 (s), 1447 (s), 1260 (vs), 1083 (vs), 1020 (vs), 799 (s). *Anal.* Calc. for $C_{66}H_{64}N_4O_4Ti$: C, 77.33; H, 6.29; N, 5.47. Found: C, 77.18; H, 6.48; N, 5.45%.

2.8. Preparation of (1)₂Zr(NMe₂)₂ (7)

This compound was prepared as yellow microcrystals from the reaction of **1**H (0.45 g, 1.0 mmol) with Zr(NMe₂)₄ (0.14 g, 0.5 mmol) in toluene (20 mL) at room temperature and recrystallization from a toluene solution by a similar procedure as in the synthesis of **6**. Yield: 0.37 g (70%). M.p.: 196–198 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.96 (m, 2H, aryl), 7.85 (m, 4H, aryl), 7.75 (t, *J* = 7.2 Hz, 4H, aryl), 7.14 (m, 8H, aryl), 6.90 (t, *J* = 7.2 Hz, 2H, aryl), 6.66 (s, 4H, aryl), 6.34 (s, 2H, aryl), 5.97 (s, 2H, aryl), 3.35 (s, 6H, OC*H₃*), 3.28 (s, 12H, NMe₂), 2.17 (s, 6H, C*H₃*), 1.98 (s, 6H, C*H₃*), 1.51 (s, 6H, C*H₃*). ^{13}C NMR (C_6D_6): δ 181.9, 155.0, 141.9, 137.6, 136.4, 135.3, 134.1, 132.6, 131.7, 129.7, 129.1, 128.9, 128.3, 128.2, 127.4, 127.2, 127.0, 126.4, 126.2, 125.8, 125.4, 124.5, 122.3, 119.4, 112.9, 55.5, 42.0, 21.0, 20.8, 20.7. IR (KBr, cm^{-1}): ν 2962 (m), 1675 (s), 1609 (s), 1594 (s), 1502 (s), 1425 (s), 1260 (s),

1085 (s), 1020 (s), 799 (s). *Anal.* Calc. for $C_{66}H_{64}N_4O_4Zr$: C, 74.19; H, 6.04; N, 5.24. Found: C, 74.05; H, 6.21; N, 5.23%.

2.9. Preparation of (2)₂Ti(NMe₂)₂ (8)

This compound was prepared as red crystals from the reaction of **2**H (0.37 g, 1.0 mmol) with Ti(NMe₂)₄ (0.11 g, 0.5 mmol) in toluene (20 mL) at room temperature and recrystallization from a toluene solution by a similar procedure as in the synthesis of **6**. Yield: 0.32 g (72%). M.p.: 196–198 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.54 (d, *J* = 5.5 Hz, 2H, aryl), 7.43 (s, 2H, aryl), 7.11 (s, 2H, aryl), 7.01 (d, *J* = 7.6 Hz, 2H, aryl), 6.93 (d, *J* = 7.2 Hz, 2H, aryl), 6.53 (m, 2H, aryl), 6.49 (m, 2H, aryl), 6.46 (m, 2H, aryl), 3.62 (s, 12H, NMe₂), 3.09 (s, 6H, OC*H₃*), 2.16 (s, 6H, C*H₃*), 2.08 (s, 12H, C*H₃*), 1.94 (s, 12H, C*H₃*). ^{13}C NMR (C_6D_6): δ 181.7, 157.8, 144.2, 137.4, 133.3, 131.8, 129.0, 128.3, 128.2, 127.7, 127.6, 127.2, 126.4, 126.2, 124.6, 122.1, 107.4, 54.4, 47.9, 20.8, 20.7, 20.6, 20.3. IR (KBr, cm^{-1}): ν 2961 (m), 2921 (m), 1653 (s), 1609 (s), 1575 (s), 1464 (s), 1260 (s), 1081 (s), 1020 (s), 944 (s), 796 (s). *Anal.* Calc. for $C_{54}H_{64}N_4O_4Ti$: C, 73.62; H, 7.32; N, 6.36. Found: C, 73.58; H, 7.44; N, 6.33%.

2.10. Preparation of (2)₂Zr(NMe₂)₂ (9)

This compound was prepared as yellow crystals from the reaction of **2**H (0.37 g, 1.0 mmol) with Zr(NMe₂)₄ (0.14 g, 0.5 mmol) in toluene (20 mL) at room temperature and recrystallization from a toluene solution by a similar procedure as in the synthesis of **6**. Yield: 0.32 g (70%). M.p.: 202–204 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.51 (d, *J* = 7.8 Hz, 2H, aryl), 7.13 (m, 4H, aryl), 7.04 (m, 2H, aryl), 6.93 (d, *J* = 6.7 Hz, 2H, aryl), 6.48 (m, 2H, aryl), 6.42 (m, 2H, aryl), 6.36 (m, 2H, aryl), 3.17 (s, 12H, NMe₂), 3.06 (s, 6H, OC*H₃*), 2.06 (s, 18H, C*H₃*), 1.83 (s, 12H, C*H₃*). ^{13}C NMR (C_6D_6): δ 182.4, 157.6, 143.1, 137.7, 137.6, 133.3, 132.2, 129.1, 128.3, 128.2, 127.7, 127.6, 126.5, 126.4, 125.2, 122.3, 107.5, 54.6, 42.3, 22.8, 21.2, 20.6, 20.2. IR (KBr, cm^{-1}): ν 2921 (m), 1676 (s), 1609 (s), 1577 (s), 1508 (s), 1465 (s), 1390 (s), 1259 (s), 1079 (s), 1021 (s), 947 (s), 773 (s). *Anal.* Calc. for $C_{54}H_{64}N_4O_4Zr$: C, 70.17; H, 6.98; N, 6.06. Found: C, 70.05; H, 6.81; N, 6.13%.

2.11. Preparation of (3)₂Ti(NMe₂)₂ (10)

This compound was prepared as red microcrystals from the reaction of **3**H (0.45 g, 1.0 mmol) with Ti(NMe₂)₄ (0.11 g, 0.5 mmol) in toluene (20 mL) at room temperature and recrystallization from an *n*-hexane solution by a similar procedure as in the synthesis of **6**. Yield: 0.42 g (80%). M.p.: 130–132 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.51 (d, *J* = 8.2 Hz, 2H, aryl), 7.15 (d, *J* = 7.6 Hz, 2H, aryl), 7.06 (m, 4H, aryl), 6.5 (m, 2H, aryl), 6.40 (m, 2H, aryl), 3.58 (s, 12H, NMe₂), 3.03 (s, 6H, OC*H₃*), 2.85 (m, 4H, C*H₂*), 2.60 (m, 4H, C*H₂*), 2.27 (m, 4H, C*H₂*), 2.20 (s, 6H, C*H₃*), 2.02 (s, 6H, C*H₃*), 2.01 (s, 6H, C*H₃*), 1.85 (m, 4H, C*H₂*), 1.60 (m, 16H, C*H₂*). ^{13}C NMR (C_6D_6): δ 183.0, 155.7, 142.0, 137.6, 135.7, 135.5, 133.6, 132.9, 131.4, 129.0, 128.9, 128.6, 128.3, 126.5, 125.4, 124.4, 107.6, 54.3, 48.3, 29.9, 29.7, 27.5, 25.6, 23.6, 22.9, 21.1, 20.9, 20.8, 20.5. IR (KBr, cm^{-1}): ν 2922 (m), 1680 (s), 1591 (s), 1495 (s), 1446 (s), 1259 (s), 1085 (s), 1034 (s), 798 (s). *Anal.* Calc. for $C_{66}H_{80}N_4O_4Ti$: C, 76.13; H, 7.74; N, 5.38. Found: C, 76.05; H, 7.62; N, 5.33%.

2.12. Preparation of (3)₂Zr(NMe₂)₂ (11)

This compound was prepared as yellow microcrystals from the reaction of **3**H (0.45 g, 1.0 mmol) with Zr(NMe₂)₄ (0.14 g, 0.5 mmol) in toluene (20 mL) at room temperature and recrystallization from an *n*-hexane solution by a similar procedure as in the synthesis of **6**. Yield: 0.45 g (84%). M.p.: 142–144 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.61 (d, *J* = 8.2 Hz, 2H, aryl), 7.24 (d, *J* = 7.6 Hz, 2H, aryl),

7.14 (m, 4H, aryl), 6.79 (m, 2H, aryl), 6.56 (m, 2H, aryl), 3.34 (s, 12H, NMe₂), 2.93 (s, 6H, OCH₃), 2.89–2.69 (m, 12H, CH₂), 2.30 (m, 4H, CH₂), 2.26 (s, 6H, CH₃), 2.24 (s, 6H, CH₃), 2.10 (s, 6H, CH₃), 1.89–1.64 (m, 16H, CH₂). ^{13}C NMR (C₆D₆): δ 180.3, 155.6, 140.8, 137.6, 137.3, 137.2, 135.8, 133.5, 133.4, 133.3, 131.7, 129.1, 128.8, 126.2, 125.4, 124.8, 107.7, 54.4, 43.0, 29.9, 27.5, 27.0, 23.8, 23.5, 23.2, 22.9, 22.8, 20.8, 20.7. IR (KBr, cm^{-1}): ν 2923 (m), 1675 (s), 1583 (s), 1496 (s), 1477 (s), 1448 (s), 1258 (s), 1084 (s), 1002 (s), 799 (s). *Anal.* Calc. for C₆₆H₈₀N₄O₄Zr: C, 73.09; H, 7.43; N, 5.17. Found: C, 73.05; H, 7.21; N, 5.23%.

2.13. Preparation of {(R)-2-[3,5-(Me₃C)₂-2-O-C₆H₂CH(NMe₂)N]-2'-(MeO)-1,1'-C₂₀H₁₂}₂Ti (**12**)

This compound was prepared as red crystals from the reaction of **4**H (0.52 g, 1.0 mmol) with Ti(NMe₂)₄ (0.11 g, 0.5 mmol) in toluene (20 mL) at room temperature and recrystallization from a toluene solution by a similar procedure as in the synthesis of **6**. Yield: 0.35 g (60%). M.p.: 178–180 °C (dec.). ^{1}H NMR (C₆D₆): δ 7.95–7.85 (m, 4H, aryl), 7.78–7.66 (m, 4H, aryl), 7.57 (m, 2H, aryl), 7.49 (m, 4H, aryl), 7.46 (m, 4H, aryl), 7.05 (m, 4H, aryl), 6.71 (m, 4H, aryl), 5.77 (s, 2H, aryl), 4.77 (s, 2H, CH), 3.67 (s, 6H, OCH₃), 2.22 (s, 12H, NMe₂), 1.81 (s, 18H, C(CH₃)₃), 1.59 (s, 18H, C(CH₃)₃). ^{13}C NMR (C₆D₆): δ 160.8, 159.1, 155.6, 155.5, 150.9, 150.4, 141.2, 140.0, 134.6, 134.3, 133.7, 133.6, 132.0, 130.0, 126.6, 125.6, 124.7, 124.3, 120.3, 87.6, 56.6, 43.7, 35.2, 34.3, 31.9, 29.8. IR (KBr, cm^{-1}): ν 2962 (m), 2915 (m), 2850 (m), 1578 (m), 1349 (s), 1260 (s), 1197 (s), 1082 (s), 1054 (s), 1018 (s), 800 (s). *Anal.* Calc. for C₇₆H₈₄N₄O₄Ti: C, 78.33; H, 7.27; N, 4.81. Found: C, 78.18; H, 7.48; N, 4.75%.

2.14. Preparation of {(R)-2-[3-Me₃C-2-O-C₆H₃CH(NMe₂)N]-2'-(MeO)-1,1'-(6-Me-C₆H₃)₂}(**5**)ZrNMe₂ (**13**)

This compound was prepared as yellow crystals from the reaction of **5**H (0.39 g, 1.0 mmol) with Zr(NMe₂)₄ (0.14 g, 0.5 mmol) in toluene (20 mL) at room temperature and recrystallization from a toluene solution by a similar procedure as in the synthesis of **6**. Yield: 0.33 g (70%). M.p.: 212–214 °C (dec.). ^{1}H NMR (C₆D₆): δ 8.47 (s, 1H, CH=N), 7.45–7.34 (m, 4H, aryl), 6.99–6.77 (m, 4H, aryl), 6.72–6.56 (m, 6H, aryl), 6.48 (t, J = 7.6 Hz, 2H, aryl), 6.43 (d, J = 8.2 Hz, 2H, aryl), 4.92 (s, 1H, CH), 3.26 (s, 6H, ZrNMe₂), 3.00 (s,

6H, OCH₃), 2.42 (s, 6H, NMe₂), 2.18 (s, 6H, CH₃), 1.86 (s, 6H, CH₃), 1.39 (s, 18H, C(CH₃)₃). ^{13}C NMR (C₆D₆): δ 162.3, 157.6, 151.9, 140.4, 139.4, 138.4, 134.2, 129.9, 129.0, 127.5, 127.3, 127.0, 126.3, 124.1, 123.8, 123.5, 117.4, 107.7, 87.9, 54.7, 45.2, 44.3, 35.2, 30.0, 21.1, 20.7. IR (KBr, cm^{-1}): ν 2948 (m), 2772 (w), 1623 (w), 1594 (s), 1546 (s), 1465 (s), 1424 (s), 1319 (s), 1250 (s), 1189 (s), 1080 (s), 1027 (s), 938 (s), 868 (s), 756 (s). *Anal.* Calc. for C₅₆H₆₈N₄O₄Zr: C, 70.62; H, 7.20; N, 5.88. Found: C, 70.45; H, 7.21; N, 5.83%.

2.15. General procedure for asymmetric hydroamination/cyclization

In a nitrogen-filled glove box, precatalyst (0.016 mmol), C₆D₆ (0.7 mL), and aminoalkene (0.16 mmol) were introduced sequentially into a Young NMR tube equipped with Teflon screw cap. The reaction mixture was subsequently kept at 120 °C to achieve hydroamination, and the reaction was monitored periodically by ^{1}H NMR spectroscopy. The cyclic amine was vacuum transferred from the Young NMR tube into a 25 mL Schlenk flask which contained 31 mg (0.16 mmol) of (S)-(+)-O-acetylmandelic acid. The resulting mixture was stirred at room temperature for 2 h and the volatiles were removed *in vacuo*. The resulting diastereomeric salt was then dissolved in CDCl₃ and the enantiomeric excesses were determined by ^{1}H NMR spectroscopy [38].

Table 2
Selected bond distances (Å) and bond angles (°) for compounds **6**, **8**, **9**, **12** and **13**.

Compound	**6** (Ti)	**8** (Ti)	**9** (Zr)	**12** (Ti)	**13** (Zr)
M–N (av.)	2.027(6)	2.021(1)	2.300(2)	2.122(2)	2.260(1)
M–N(1)	2.155(4)	2.125(1)	2.278(2)	1.954(2)	2.373(1)
M–N(2)	2.141(4)	2.143(1)	2.283(2)	2.247(2)	2.139(1)
M–N(3)	1.904(6)	1.907(1)	2.052(2)	2.006(2)	2.482(1)
M–N(4)	1.907(6)	1.909(1)	2.044(2)	2.282(2)	2.048(1)
M–O (av.)	2.136(5)	2.131(1)	2.224(2)	1.901(2)	2.047(1)
M–C (av.)	2.525(6)	2.536(2)	2.670(2)		
Sum angles of N	N(3):	N(3):	N(3):	N(1):	N(2):
	359.5(6)	359.3(1)	360.0(2)	350.7(2)	357.8(1)
	N(4):	N(4):	N(4):	N(3):	N(4):
	359.9(6)	360.0(1)	359.5(2)	354.6(2)	359.2(2)
Torsion (aryl–aryl)	69.1(6)	73.3(1)	69.7(2)	82.8(2)	83.5(1)
	71.9(6)	69.3(1)	71.3(2)	89.0(2)	84.5(1)

Table 1
Crystal data and experimental parameters for compounds **1H**, **6**, **8**, **9**, **12** and **13**.

Compound	**1H**	**6**	**8**	**9**	**12**	**13**
Formula	C₃₁H₂₇NO₂	C₆₆H₆₄N₄O₄Ti	C₅₄H₆₄N₄O₄Ti	C₅₄H₆₄N₄O₄Zr	C₇₆H₈₄N₄O₄Ti	C₅₆H₆₈N₄O₄Zr
Formula weight	445.54	1025.11	880.99	924.31	1165.37	952.36
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	P2₁2₁2₁	P12₁1	P2₁2₁2₁	P2₁2₁2₁	P2₁2₁2₁	P2₁2₁2₁
a (Å)	8.023(2)	15.071(3)	9.344(2)	9.224(1)	16.181(5)	15.270(2)
b (Å)	17.250(3)	9.199(2)	19.234(4)	19.226(2)	36.786(1)	15.260(1)
c (Å)	20.727(4)	19.282(4)	26.737(5)	27.295(3)	12.400(1)	21.788(2)
β (°)	90	94.83(2)	90	90	90	90
V (Å³)	2868.5(10)	2663.7(10)	4805.5(17)	4840.3(9)	7380.3(4)	5077.2(9)
Z	4	2	4	4	4	4
D_calc. (g cm^{-3})	1.032	1.278	1.218	1.268	1.049	1.246
Size (mm)	0.26 × 0.24 × 0.22	0.22 × 0.20 × 0.12	0.28 × 0.26 × 0.22	0.16 × 0.14 × 0.10	0.26 × 0.22 × 0.18	0.26 × 0.20 × 0.18
F(0 0 0)	944	1084	1880	1952	2488	2016
2θ Range (°)	3.94–55.70	4.60–135.98	3.04–55.76	3.66–55.80	2.74–55.76	20.01–55.78
No. of reflections collected	29 063	17 328	27 672	36 281	50 397	58 779
No. of unique reflections (R_int)	3839(0.0481)	8386(0.0777)	11 344(0.0275)	11 436(0.0528)	17 339(0.0437)	11 478(0.0417)
No. of observed reflections	3443	5869	10 035	10 489	15 207	11 324
Absorbed corrections (T_max, T_min)	0.99, 0.98	0.81, 0.69	0.95, 0.94	0.97, 0.96	0.97, 0.96	0.95, 0.93
R	0.049	0.079	0.033	0.038	0.056	0.027
R_w	0.138	0.175	0.078	0.083	0.148	0.061
wR² (all data)	0.142	0.228	0.081	0.086	0.154	0.061
Goodness-of-fit (GOF)	1.19	1.09	1.03	1.04	1.03	1.06

2.16. X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Rigaku Saturn CCD diffractometer at 113(2) K using graphite monochromated Mo Kα radiation (λ = 0.71 075 Å) or Cu Kα radiation (λ = 1.54 187 Å). An empirical absorption correction was applied using the SADABS program [40]. All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package [41]. All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for **1**H, **6**, **8**, **9**, **12** and **13** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Synthesis and characterization of ligands

The C_1-symmetric mesitoylamide ligands, (R)-2-(mesitoylamino)-2′-methoxy-1,1′-binaphthyl (**1**H), (R)-2-(mesitoylamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (**2**H) and (S)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(mesitoylamino)-2′-methoxy-1,1′-binaphthyl (**3**H), are readily prepared in good yields by treatment of mesitoyl chloride with 1 equiv. of (R)-2-amino-2′-methoxy-1,1′-binaphthyl, (R)-2-amino-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl or (S)-5,5′,6,6′,7,7′,8,8′-octahydro-2-amino-2′-methoxy-1,1′-binaphthyl, respectively, in the presence of an excess of pyridine in toluene at reflux, after purification by flash column chromatography (Schemes 1–3). The C_1-symmetric Schiff base ligands, (R)-2-(3,5-di-tert-butyl-2-hydroxyphenylmethyleneamino)-2′-methoxy-1,1′-binaphthyl (**4**H), (R)-2-(3-tert-butyl-2-hydroxyphenylmethyleneamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (**5**H), are also readily prepared in good yields by condensation of the starting materials (R)-2-amino-2′-methoxy-1,1′-binaphthyl, (R)-2-amino-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl with 1 equiv. of 3,5-di-tert-butyl-2-hydroxybenzaldehyde or 3-tert-butyl-2-hydroxybenzaldehyde, respectively, in the presence of molecular sieves in toluene at 70 °C, followed by recrystallization from an n-hexane solution (Schemes 1 and 2).
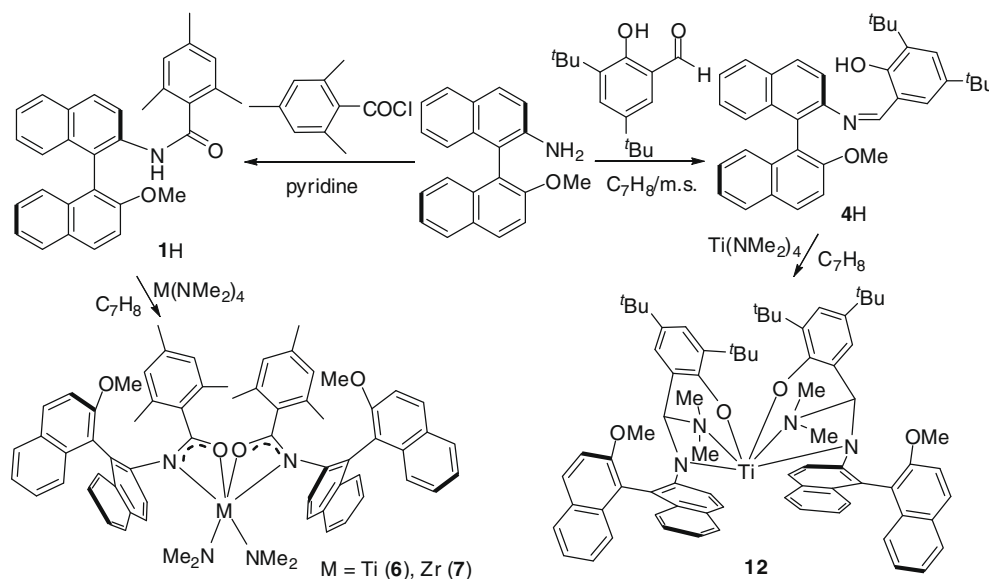
All the new ligands are air-stable, and soluble in CH_2Cl_2, $CHCl_3$, toluene, benzene, and n-hexane. They have been fully characterized by various spectroscopic techniques and elemental analyses. Their ^{1}H and ^{13}C NMR spectra indicate that they are non-symmet-rical on the NMR timescale, which are consistent with their C_1-symmetric structures. The infrared spectra of these compounds exhibit peaks corresponding to aromatic stretches in addition to N–H stretches at about 3390 cm^{-1}, and strong C=O stretches at about 1680 cm^{-1} for **1**H, **2**H and **3**H, and O–H stretches at about 3430 cm^{-1}, and strong C=N stretches at about 1620 cm^{-1} for **4**H and **5**H. The solid-state structure of compound **1**H has been further confirmed by X-ray diffraction analysis.
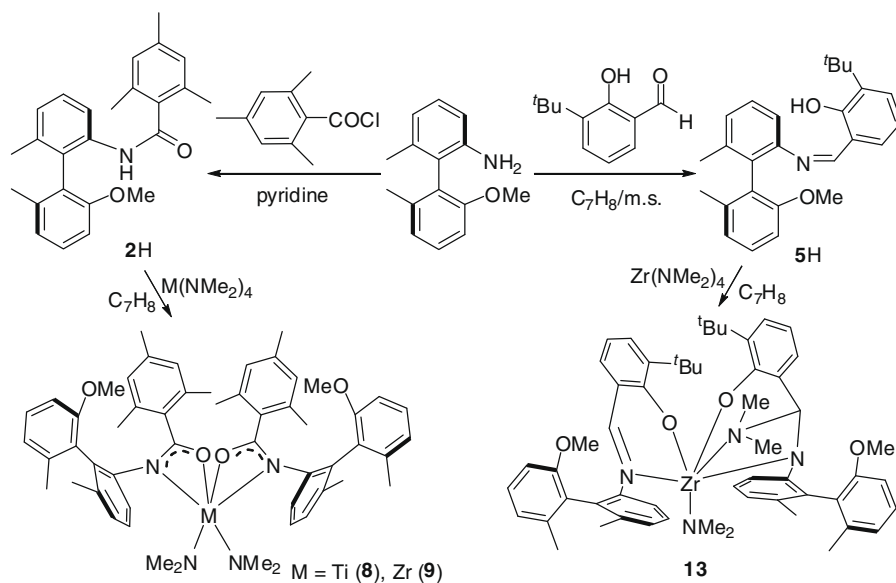
The single-crystal X-ray diffraction analysis shows that the binaphthyl groups of the compound **1**H arrange in a staggered geometry (Fig. 1). The twisting between the naphthyl rings of torsion angle is 77.9(3)°, which is smaller than that found in 2-amino-2′-hydroxy-1,1′-binaphthyl (87.9(1)°) [42].

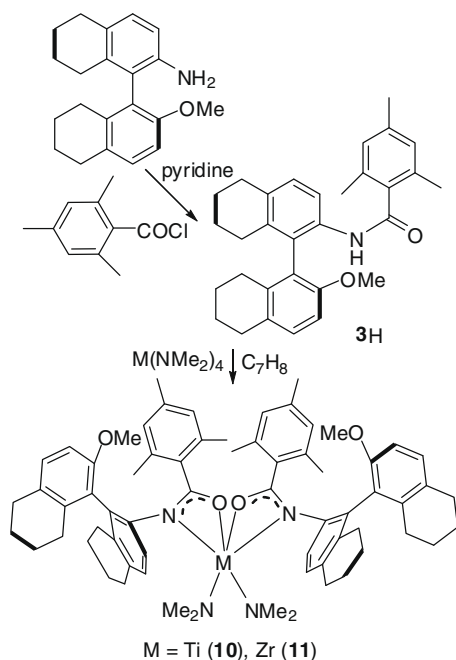### 3.2. Synthesis and characterization of complexes

Group 4 metal amide complexes can be efficiently prepared via amine elimination reaction between M(NMe$_2$)$_4$ and protic reagents. For example, treatment of M(NMe$_2$)$_4$ with 2 equiv. of mesitoylamides, (R)-2-(mesitoylamino)-2′-methoxy-1,1′-binaphthyl (**1**H), (R)-2-(mesitoylamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (**2**H) or (S)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(mesitoylamino)-2′-methoxy-1,1′-binaphthyl (**3**H) gives, after recrystallization from a toluene or n-hexane solution, the bis-ligated chiral titanium amides (**1**)$_2$Ti(NMe$_2$)$_2$ (**6**), (**2**)$_2$Ti(NMe$_2$)$_2$ (**8**), (**3**)$_2$Ti(NMe$_2$)$_2$ (**10**), and zirconium amides (**1**)$_2$Zr(NMe$_2$)$_2$ (**7**), (**2**)$_2$Zr(NMe$_2$)$_2$ (**9**), (**3**)$_2$Zr(NMe$_2$)$_2$ (**11**), respectively, in good yields (Schemes 1–3). Our previous work has shown that interaction between the Schiff base ligand (R)-2-(pyrrol-2-ylmethyleneamino)-2′-methoxy-1,1′-binaphthyl and M(NMe$_2$)$_4$ (M = Ti, Zr) gives the bis-ligated amides [(R)-1,1′-C$_{20}$H$_{12}$-2′-(MeO)-2-(NCH-2-C$_4$H$_3$N)]$_2$M(NMe$_2$)$_2$ [37]. However, under similar reaction conditions, treatment of Ti(NMe$_2$)$_4$ with 2 equiv. of the Schiff base ligand (R)-2-(3,5-di-tert-butyl-2-hydroxyphenylmethyleneamino)-2′-methoxy-1,1′-binaphthyl (**4**H) does not lead to the expected bis-ligated amide complex (**4**)$_2$Ti(NMe$_2$)$_2$, instead, a chiral bis-ligated titanium complex {(R)-2-[3,5-(Me$_3$C)$_2$-2-O-C$_6$H$_2$CH(NMe$_2$)N]-2′-(MeO)-1,1′-C$_{20}$H$_{12}$}$_2$Ti (**12**) has been isolated in 60% yield (Scheme 1), where {(R)-2-[3,5-(Me$_3$C)$_2$-2-O-C$_6$H$_2$CH(NMe$_2$)N]-2′-(MeO)-1,1′-C$_{20}$H$_{12}$}$^{2-}$ is a tridentate ligand resulting from the insertion of the anion Me$_2$N$^-$ at the imine unit of **4**H. The 1,2-migratory inser-
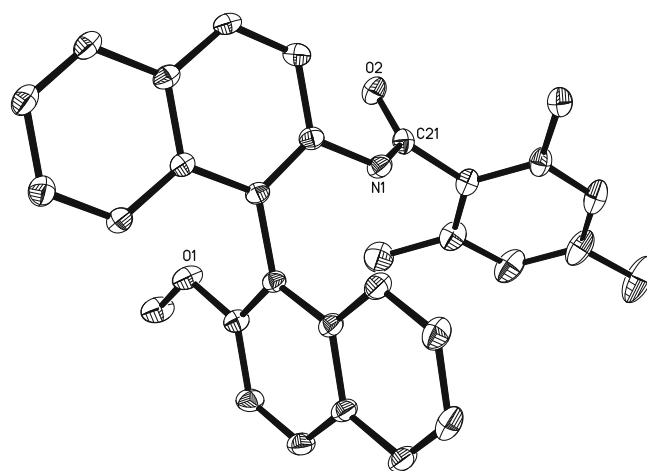

Scheme 1.

Scheme 2.

Scheme 3.

Fig. 1. Molecular structure of **1**H (thermal ellipsoids drawn at the 35% probability level).

tion of the anion Me$_2$N$^-$ at the imine unit has been also observed in the reaction between the Schiff base ligand (R)-2-(3-tert-butyl-2-hydroxyphenylmethyleneamino)-2′-methoxy-6,6′-dimethyl-1, 1′-biphenyl (**5**H) and Zr(NMe$_2$)$_4$, results in the isolation of the complex {(R)-2-[3-Me$_3$C-2-O-C$_6$H$_3$CH(NMe$_2$)N]-2′-(MeO)-1,1′-(6-Me-C$_6$H$_3$)$_2$}(**5**)ZrNMe$_2$ (**13**) in 70% yield (Scheme 2).

These complexes are stable in dry nitrogen atmosphere, while they are very sensitive to moisture. They are soluble in organic solvents such as THF, DME, pyridine, toluene, and benzene, and only slightly soluble in n-hexane. They have been characterized by various spectroscopic techniques, and elemental analyses. The ^{1}H NMR spectra of **6**–**11** support that the ratio of amino group NMe$_2$ and ligand anion **1**, **2** or **3** is 1:1, supporting the formation of the

bis-ligated complexes **6**–**11**. Unlike the titanium amides **6**, **8** and **10**, the ^{1}H NMR spectrum of **12** does not exhibit a singlet resonance at about 3.60 ppm attributable to the TiNMe$_2$ groups, while a singlet resonance appears at about 2.22 ppm attributable to the RNMe$_2$ groups, supporting the formation of the bis-ligated complex **12**. The ^{1}H NMR spectrum of **13** exhibits two singlet resonances with the ratio of 1:1 at about 3.26 ppm and 2.42 ppm attributable to the ZrNMe$_2$ and RNMe$_2$ groups, respectively, supporting the formation of the mixed-bis-ligated complex **13**. These results are consistent with their ^{13}C NMR spectra. The solid-state structures of the complexes **6**, **8**, **9**, **12** and **13** have further been confirmed by X-ray diffraction analyses.

The single-crystal X-ray diffraction analyses confirm that **8** and **9** are isostructural. In each molecule of (**1**)$_2$Ti(NMe$_2$)$_2$ or (**2**)$_2$M(NMe$_2$), the substituted MeO group is far away from the metal center, and the M^{4+} is σ-bound to two nitrogen atoms and two oxygen atoms from the two ligands **1**, or **2** and two nitrogen atoms from amino groups NMe$_2$ in a distorted-octahedron geometry (Figs. 2 and 3) with the average distance of Ti–N (2.027(6) Å) for
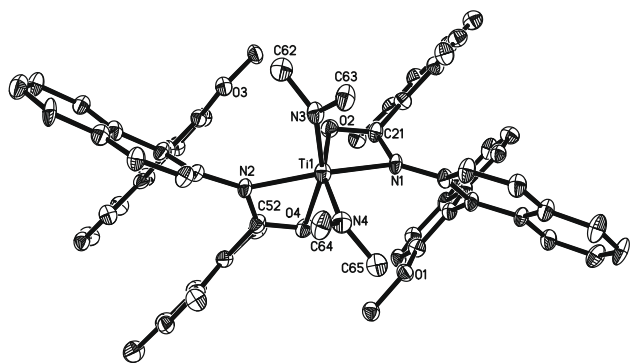
Fig. 2. Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level).
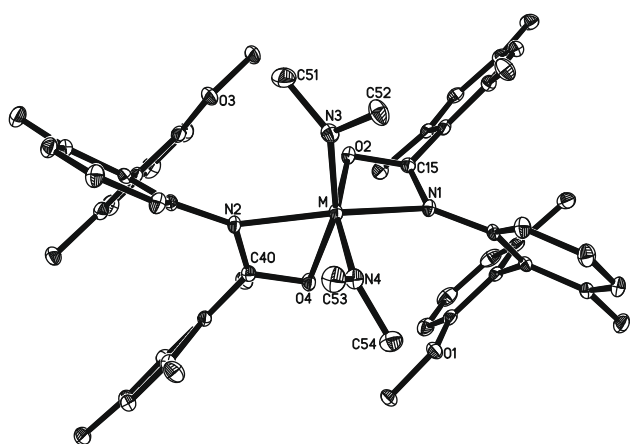

Fig. 3. Molecular structure of **8** (M = Ti) and **9** (M = Zr) (thermal ellipsoids drawn at the 35% probability level).

Fig. 4a. Molecular structure of **12** (thermal ellipsoids drawn at the 35% probability level).
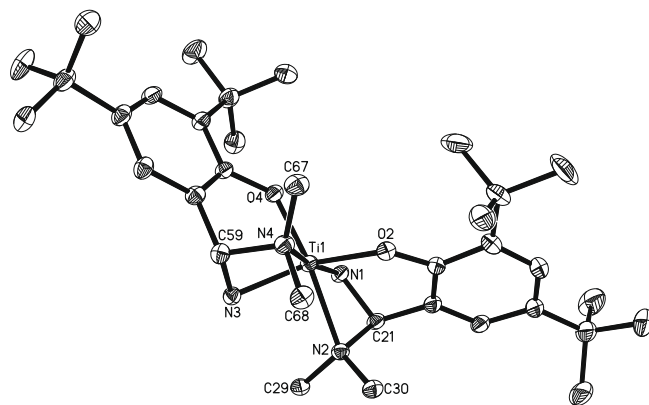
Fig. 4b. Core structure of **12** (thermal ellipsoids drawn at the 35% probability level).

6, Ti–N (2.021(1) Å) for **8**, Zr–N (2.300(2) Å) for **9**, respectively, and the average distance of Ti–O (2.136(5) Å) for **6**, Ti–O (2.131(1) Å) for **8**, Zr–O (2.224(2) Å) for **9**, respectively. The short M–N(3) and M–N(4) bond distances (1.904(6) and 1.907(6) Å for **6**, 1.907(1) and 1.909(1) Å for **8**, 2.052(2) and 2.044(2) Å for **9**) and the planar geometry around the N(3) and N(4) nitrogen atoms indicate that the nitrogen atoms with sp^2 hybridization are engaged in N(p$_\pi$) → M(d$_\pi$) interactions. These structural data are very close to those found in the literatures [43–49]. The aryl rings are twisted by 69.1(6)° and 71.9(6)° for **6**, 73.3(1)° and 69.3(1)° for **8**, 69.7(2)° and 71.3(2)° for **9**, which are comparable to those found in **1**H (77.9(3)°), [(R)-1,1′-C$_{20}$H$_{12}$-2′-(MeO)-2-(NCH-2-C$_4$H$_3$N)]$_2$Ti(NMe$_2$)$_2$ (89.7(9)° and 87.2(9)°) [37], [(R)-(6-Me-C$_6$H$_3$)$_2$-2′-(MeO)-2-(NCH-2-C$_4$H$_3$N)]$_2$Ti(NMe$_2$)$_2$ (78.2(4)° and 86.4(4)°) [37] and [(R)-(6-Me-C$_6$H$_3$)$_2$-2′-(MeO)-2-(NCH-2-C$_4$H$_3$N)]$_2$Zr(NMe$_2$)$_2$ (84.9(4)° and 89.7 (4)°) [37].

The solid-state structure of **12** shows that the Ti^{4+} is σ-bound to four nitrogen atoms and two oxygen atoms from two ligand anions {(R)-2-[3,5-(Me$_3$C)$_2$-2-O-C$_6$H$_2$CH(NMe$_2$)N]-2′-(MeO)-1,1′-C$_{20}$H$_{12}$}$^{2-}$ in a distorted-octahedron geometry (Fig. 4a and b) with the average distance of Ti–N (2.122(2) Å) and the average distance of Ti–O (1.901(2) Å). The short Ti–N(1) and Ti–N(3) bond distances (1.954(2) and 2.006(2) Å) and the planar geometry around the N(1) and N(3) nitrogen atoms indicate that both nitrogen atoms with sp^2 hybridization are engaged in N(p$_\pi$) → Ti(d$_\pi$) interactions. The twisting between the binaphthyl rings of torsion angles are 82.8(2)° and 89.0(2)°, which are larger than those found in **1**H (77.9(3)°) and **6** (69.1(6)° and 71.9(6)°).
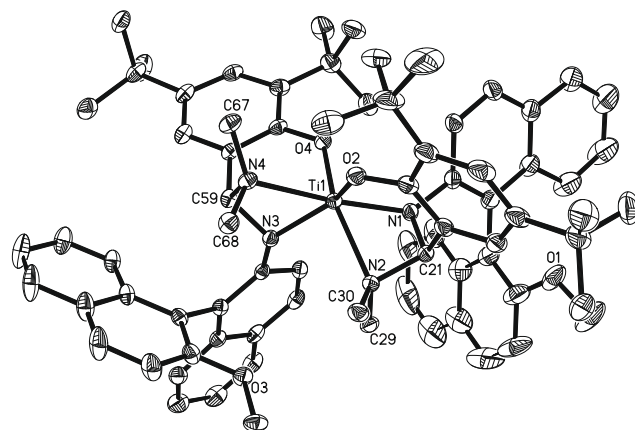
The solid-state structure of **13** shows that the Zr^{4+} is σ-bound to two nitrogen atoms and one oxygen atom from the anion {(R)-2-[3-Me$_3$C-2-O-C$_6$H$_3$CH(NMe$_2$)N]-2′-(MeO)-1,1′-(6-Me-C$_6$H$_3$)$_2$}$^{2-}$, and two nitrogen atoms and one oxygen atom from the ligand **5** in a distorted-octahedron geometry (Fig. 5) with the average distance of Zr–N (2.260(1) Å) and the average distance of Zr–O (2.047(1) Å). The short Zr–N(2) and Zr–N(4) bond distances (2.139(1) and 2.048(1) Å) and the planar geometry around the N(2) and N(4) nitrogen atoms indicate that both nitrogen atoms with sp^2 hybridization are engaged in N(p$_\pi$) → Zr(d$_\pi$) interactions. The twisting between the binaphthyl rings of torsion angles are 83.5(1)° and 84.5(1)°, which are larger than those found in **8** (73.3(1)° and 69.3(1)°) and **9** (69.7(2)° and 71.3(2)°).

3.3. Asymmetric hydroamination/cyclization

To evaluate the catalytic ability of the complexes **6–13**, the asymmetric hydroamination/cyclization of unactivated terminal aminoalkenes has been tested under the conditions given in Table 3. The results of the hydroamination/cyclization of 2,2-dimethyl-pent-4-enylamine clearly show that the zirconium amidates are active catalysts for this transformation (Table 3, entries 2, 4 and 6), and the complex **7** shows more effective catalyst for this asymmetric transformation with a good enantioselectivity (up to 61%; Table 3, entry 2). When more bulky ligand **3** is used, the ee value decreases significantly (Table 3, entry 6). However, when the Ti^{4+} ion is used (Table 3, entry 1), the ee value increases slightly (up to 68%) but the rate decreases. Complex **13** can medi-
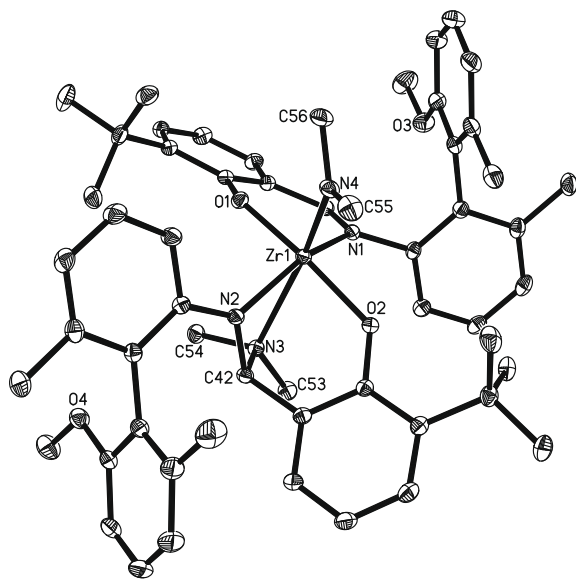
Fig. 5. Molecular structure of **13** (thermal ellipsoids drawn at the 35% probability level).

ate the cyclization of 2,2-dimethylpent-4-enylamine (Table 3, entry 8), but the conversion ceases after 1 or 2 days due to the decomposition by the intermediacy of the metal alkyl species *via* 1,2-migratory insertion at the imine unit [50]. Under similar reaction conditions, no detectable hydroamination activity is observed for titanium complex **12** even heated at 120 °C for one week, and none of the complexes described above is effective catalyst for the cyclization of 1-aminopent-4-ene into 2-methylpyrrolidine, presumably due to a lack of a Thorpe–Ingold effect [51,52] from the unsubstituted aminoalkene, and none of the catalysts is effective catalyst for the cyclization of aminoalkenes containing secondary amine groups such as the substrate 1-(N-methylamino)-2,2-dimethylpent-4-ene into the corresponding heterocycles, which is in agreement with the amine elimination followed by [2+2] cycloaddition mechanism postulated by Berg-

man and others [19,20,22]. Substrate **15a** reacts fast but the ee values are moderate (Table 3, entries 9–14). The formation of six-membered ring can also be performed with our amidate catalysts (Table 3, entries 15–20), and a moderate enantioselectivity (up to 25%), mediated by the catalyst **6**, has been obtained (Table 3, entry 15). Our results show that the bis-ligated amidate group 4 complexes are more effective chiral catalysts for the asymmetric hydroamination/cyclization than those ligated by Schiff base ligands [37], but less than those coordinated by C_2-symmetric bis-amidate ligands [20,21,30]. Although the enantiomeric excesses obtained remain moderate to good, it should be noted that there are only few group 4 catalysts for these reactions that give a significant ee (>90%) at all [20,21,30].

4. Conclusions

In conclusion, a new series of chiral bis-ligated group 4 metal complexes have been readily prepared from the reactions between M(NMe$_2$)$_4$ (M = Ti, Zr) and chiral C_1-symmetric ligands, **1**H, **2**H, **3**H, **4**H and **5**H, and the bis-ligated amidate complexes have been shown more effective chiral catalysts for asymmetric hydroamination/cyclization than those ligated by Schiff base ligands [37]. When changes are made from pyrrol-2-ylmethyleneamino group to mesitoylamino group, and to phenylmethyleneamino group, the ligands (R)-2-(pyrrol-2-ylmethyleneamino)-2'-methoxy-1,1'-binaphthyl [37], (R)-2-(mesitoylamino)-2'-methoxy-1,1'-binaphthyl (**1**H) and (R)-2-(3,5-di-*tert*-butyl-2-hydroxyphenylmethyleneamino)-2'-methoxy-1,1'-binaphthyl (**4**H) exhibit different reactivity patterns. For example, reaction of the Schiff base ligand (R)-2-(pyrrol-2-ylmethyleneamino)-2'-methoxy-1,1'-binaphthyl or amidate ligand **1**H with Ti(NMe$_2$)$_4$ gives the bis-ligated titanium amides [(R)-1,1'-C$_{20}$H$_{12}$-2'-(MeO)-2-(NCH-2-C$_4$H$_3$N)]$_2$Ti(NMe$_2$)$_2$ [37] and (**1**)$_2$Ti(NMe$_2$)$_2$ (**6**), respectively, while reaction of the Schiff base ligand **4**H with Ti(NMe$_2$)$_4$ affords a bis-ligated complex {(R)-2-[3,5-(Me$_3$C)$_2$-2-O-C$_6$H$_2$CH(NMe$_2$)N]-2'-(MeO)-1,1'-C$_{20}$H$_{12}$}$_2$Ti (**12**) in which the amide complex is decomposed by the dimethylamino *via* 1,2-migratory insertion at the imine unit of **4**H. The Schiff base ligated titanium amide [(R)-1,1'-C$_{20}$H$_{12}$-2'-(MeO)-2-(NCH-2-C$_4$H$_3$N)]$_2$Ti(NMe$_2$)$_2$ shows no catalytic activity for the enantioselective hydroamination/cyclization reaction [37], while the

Table 3
Enantioselective hydroamination/cyclization of aminoalkenes.[a]

Entry	Catalyst (M)	Substrate	Product	Time (h)	Conv. (%)[b]	ee (%)[c]
1	**6** (Ti)	**14a**	**14b**	48	93	68
2	**7** (Zr)			24	100	61
3	**8** (Ti)			48	96	51
4	**9** (Zr)			24	100	43
5	**10** (Ti)			48	86	46
6	**11** (Zr)			24	100	38
7	**12** (Ti)			160	N.R.	N.A.
8	**13** (Zr)			48	24	15
9	**6** (Ti)	**15a**	**15b**	36	100	52
10	**7** (Zr)			16	100	43
11	**8** (Ti)			36	100	46
12	**9** (Zr)			16	100	39
13	**10** (Ti)			36	100	42
14	**11** (Zr)			16	100	36
15	**6** (Ti)	**16a**	**16b**	48	98	25
16	**7** (Zr)			24	100	20
17	**8** (Ti)			48	100	24
18	**9** (Zr)			24	100	21
19	**10** (Ti)			48	90	23
20	**11** (Zr)			24	100	19

[a] Conditions: C$_6$D$_6$ (0.70 mL), aminoalkene (0.16 mmol), catalyst (0.016 mmol), at 120 °C.
[b] Determined by ^{1}H NMR based on *p*-xylene as the internal standard. N.R., no reaction.
[c] Determined by ^{1}H NMR of its diastereomeric (S)-(+)-O-acetylmandelic acid salt [38]. N.A., not applicable.

titanium amidate ($\mathbf{1}$)$_2$Ti(NMe$_2$)$_2$ (**6**) does, and in some cases, the corresponding heterocyclic products have been obtained with good ee values (up to 68%) by this modified chiral 2-amino-2′-hydroxy-1,1′-binaphthyl ligand. Although the titanium amidates show more enantioselective than zirconium amidates for the hydroamination/cyclization reaction, they exhibit less effective catalytic activity than zirconium amidates. How to fully optimize both the rate and selectivity remains a question for the asymmetric hydroamination. We are planning to synthesize similar tridentate or bidentate chiral biaryl embedded in a C_1-symmetric chiral scaffold in order to obtain more effective and stereoselective chiral ligands (including 3,3′-substituted NOBIN) and to utilize those novel chiral ligands in this transformation and other catalytic asymmetric reactions. Work along these lines is in progress.

Acknowledgements

Appendix A. Supplementary data

CCDC 760930, 760931, 760932, 760933, 760934, and 760935 contain the supplementary crystallographic data for **1**H, **6**, **8**, **9**, **12** and **13**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.03.014.

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