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Synthesis, structure, and catalytic activity of titanium(IV) and zirconium(IV) amides with chiral biphenyldiamine-based ligands

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ABSTRACT

A new series of titanium(IV) and zirconium(IV) amides have been prepared from the reaction between $M(NMe_2)_4$ (M = Ti, Zr) and C_2-symmetric ligands, (*R*)-2,2′-bis(pyridin-2-ylmethylamino)-6,6′-dimethyl-1,1′-biphenyl (**2**H_2), (*R*)-2,2′-bis(pyrrol-2-ylmethyleneamino)-6,6′-dimethyl-1,1′-biphenyl (**3**H_2), (*R*)-2,2′-bis(diphenylphosphinoylamino)-6,6′-dimethyl-1,1′-biphenyl (**4**H_2), (*R*)-2,2′-bis(methanesulphonylamino)-6,6′-dimethyl-1,1′-biphenyl (**5**H_2), (*R*)-2,2′-bis(*p*-toluenesulphonylamino)-6,6′-dimethyl-1,1′-biphenyl (**6**H_2), and C_1-symmetric ligands, (*R*)-2-(diphenylthiophosphoramino)-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl (**7**H) and (*R*)-2-(pyridin-2-ylamino)-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl (**8**H), which are derived from (*R*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl. Treatment of $M(NMe_2)_4$ with 1 equiv. of N_4-ligand, **2**H_2 or **3**H_2 gives, after recrystallization from an *n*-hexane solution, the chiral zirconium amides (**2**)$Zr(NMe_2)_2$ (**9**), (**3**)$Zr(NMe_2)_2$ (**11**), and titanium amide (**3**)$Ti(NMe_2)_2$ (**10**), respectively, in good yields. Reaction of $Zr(NMe_2)_4$ with 1 equiv of diphenylphosphoramide **4**H_2 affords the chiral zirconium amide (**4**)$Zr(NMe_2)_2$ (**12**) in 85% yield. Under similar reaction conditions, treatment of $Ti(NMe_2)_4$ with 1 equiv. of sulphonylamide ligand, **5**H_2 or **6**H_2 gives, after recrystallization from a toluene solution, the chiral titanium amides (**5**)$Ti(NMe_2)_2{\cdot}0.5C_7H_8$ (**13**$\cdot 0.5C_7H_8$) and (**6**)$Ti(NMe_2)_2$ (**15**), respectively, in good yields, while reaction of $Zr(NMe_2)_4$ with 1 equiv. of **5**H_2 or **6**H_2 gives the bis-ligated complexes, $(\mathbf{5})_2Zr$ (**14**) and $(\mathbf{6})_2Zr$ (**16**). Treatment of $M(NMe_2)_4$ with 2 equiv. of diphenylthiophosphoramide ligand **7**H or N_3-ligand **8**H gives, after recrystallization from a benzene solution, the bis-ligated chiral zirconium amides $(\mathbf{7})_2Zr(NMe_2)_2$ (**17**) and $(\mathbf{8})_2Zr(NMe_2)_2$ (**19**), and bis-ligated chiral titanium amide $(\mathbf{8})_2Ti(NMe_2)_2$ (**18**), respectively, in good yields. All new compounds have been characterized by various spectroscopic techniques, and elemental analyses. The solid-state structures of complexes **10**, **12**, **13**, and **17**–**19** have further been confirmed by X-ray diffraction analyses. The zirconium amides are active catalysts for the asymmetric hydroamination/cyclization of aminoalkenes, affording cyclic amines in good to excellent yields with moderate ee values, while the titanium amides are not.

1. Introduction

Ligand modification plays a key role in developing new catalyst precursors for asymmetric synthesis. To meet the requirements of different purposes, a large number of chiral ligands have been developed. Among these, the nitrogen-containing ligands have received increasing attention in recent years due to their high complex stability and good availability in enantiomerically pure form, which are advantageous for practical applications [1–5]. Although a variety of chiral nitrogen-containing ligands have been studied, the development of new N-ligands for asymmetric transformations is still a desirable goal. In recent years, we have therefore developed a series of chiral nitrogen-containing multidentate ligands, and their Ir(I), Rh(I), Ti(IV), Ag(I), Cu(II), Zr(IV) and lanthanide complexes are useful catalysts for a wide range of transformations [6–21], and we found that the group 4 metal amides based on chiral binaphthyl-backbones are effective catalysts for the asymmetric hydroamination/cyclization, in which good enantioselectivities (up to 72% ee) have been obtained [19–21]. In our endeavors to further explore the chiral biaryl ligand system, we have recently extended our research work to biphenyl-backbones, including C_2-symmetric ligands, (*R*)-2,2′-bis(pyridin-2-ylmethylamino)-6,6′-dimethyl-1,1′-biphenyl (**2**H_2), (*R*)-2,2′-bis(pyrrol-2-ylmethyleneamino)-6,6′-dimethyl-1,1′-biphenyl (**3**H_2), (*R*)-2,2′-bis(diphenylphosphinoylamino)-6,6′-dimethyl-1,1′-biphenyl (**4**H_2), (*R*)-2,2′-bis(methanesulphonylamino)-6,6′-dimethyl-1,1′-biphenyl (**5**H_2), and (*R*)-2,2′-bis(*p*-toluenesulphonylamino)-6,6′-dimethyl-1,1′-biphenyl (**6**H_2), and C_1-symmetric ligands, (*R*)-2-(diphenylthiophosphoramino)-2′-

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(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl (**7**H) and (*R*)-2-(pyridin-2-ylamino)-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl (**8**H), which are derived from (*R*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl. Herein, we report the synthesis and properties of the 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 complex [(*R*)-(6-MeC_6H_3)$_2$-2-{NCO(2,4,6-$Me_3C_6H_2$)}$_2$]-$Zr(NMe_2)_2$ (**20**) [22–24] will be also discussed in this contribution.

2. Experimental

2.1. General methods

All experiments 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*)-2,2′-Diamino-6,6′-dimethyl-1,1′-biphenyl (>98% ee) [25], (*R*)-2-amino-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl [21], $M(NMe_2)_4$ [26], 2,2-dimethylpent-4-enylamine [27], 2,2′-dimethylhex-5-enylamine [27], and 1-(aminomethyl)-1-allylcyclohexane [28] 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)-2,2′-bis(pyridin-2-ylmethylamino)-6,6′-dimethyl-1,1′-biphenyl (**2**H_2)

Modified method [29]. Pyridine-2-carboxaldehyde (1.07 g, 10.0 mmol) was mixed with (*R*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl (1.06 g, 5.0 mmol) in dry toluene (25 mL). A few 4 Å molecular sieves were added, and the solution was warmed up to 70 °C and kept for 2 days at this temperature. The solution was filtered and the solvent was removed under reduced pressure. The resulting yellow oily residue (crude **1**) was dissolved in methanol (40 mL), $NaBH_4$ (2.00 g, 52.6 mmol) was added in small portions at 0 °C, then the solution was warmed up to 50 °C and kept for 2 h at this temperature. The solvent was removed and the residue was decomposed with H_2O (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_2SO_4 and the solvent was removed under reduced pressure to give a yellow oil, which was further purified by flash column chromatography (hexane/ethyl acetate = 4:1) to give **2**H_2 as a colorless oil. Yield: 1.36 g (69%). ^{1}H NMR ($CDCl_3$): δ 8.38 (d, J = 4.6 Hz, 2H, aryl), 7.38 (m, 2H, aryl), 7.15 (d, J = 7.8 Hz, 2H, aryl), 7.02 (m, 4H, aryl), 6.61 (d, J = 7.4 Hz, 2H, aryl), 6.37 (d, J = 8.1 Hz, 2H, aryl), 4.34 (m, 4H, CH_2), 1.90 (s, 6H, CH_3); protons of N*H* were not observed. These spectroscopic data are in agreement with those reported in the literature [29].

2.3. Preparation of (R)-2,2′-bis(pyrrol-2-ylmethyleneamino)-6,6′-dimethyl-1,1′-biphenyl (**3**H_2)

Modified method [29]. Pyrrole-2-carboxaldehyde (0.95 g, 10.0 mmol) was mixed with (*R*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl (1.06 g, 5.0 mmol) in dry toluene (25 mL). A few 4 Å molecular sieves were added, and the solution was warmed up to 70 °C and kept for 2 days at this temperature. The solution was filtered and the solvent was removed under reduced pressure. The resulting red oily residue was washed with cold *n*-hexane (30 mL × 3) to give **3**H_2 as a red solid. Yield: 1.15 g (63%). M.p.: 70–72 °C. ^{1}H NMR ($CDCl_3$): δ 7.97 (s, 2H, N=C*H*), 7.23 (m, 2H, aryl), 7.08 (m, 2H, aryl), 6.83 (m, 4H, aryl), 6.50 (m, 2H, aryl), 6.22 (m, 2H, aryl), 2.01 (s, 6H, CH_3); protons of N*H* were not observed. These spectroscopic data are in agreement with those reported in the literature [29].

2.4. Preparation of (R)-2,2′-bis(diphenylphosphinoylamino)-6,6′-dimethyl-1,1′-biphenyl (**4**H_2)

Diphenylphosphinoyl chloride (2.37 g, 10.0 mmol) was mixed with (*R*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl (1.06 g, 5.0 mmol) in dry toluene (30 mL). Pyridine (2 mL, 25.3 mmol) was added, and the solution was refluxed for 2 days. The solvent was removed and the residue was decomposed with H_2O (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_2SO_4 and the solvent was removed under reduced pressure to give a white solid, which was further purified by flash column chromatography (hexane/ethyl acetate = 2:1) to give **4**H_2 as a white solid. Yield: 2.91 g (95%). M.p.: 174–176 °C. ^{1}H NMR ($CDCl_3$): δ 7.68–7.57 (m, 8H, aryl), 7.42–7.38 (m, 2H, aryl), 7.34–7.27 (m, 6H, aryl), 7.17–7.09 (m, 6H, aryl), 7.00 (t, J = 7.8 Hz, 2H, aryl), 6.84 (d, J = 7.5 Hz, 2H, aryl), 5.11 (d, J = 10.2 Hz, 2H, N*H*), 1.98 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 137.2, 131.7, 131.1, 130.4, 130.3, 130.2, 127.7, 125.5, 123.1, 114.7, 18.9. IR (KBr, cm^{-1}): ν 3371 (s), 3052 (w), 1581 (s), 1463 (s), 1438 (s), 1372 (m), 1206 (s), 1122 (s), 1040 (m), 964 (m), 848 (m), 722 (s), 697 (s). Anal. Calc. for $C_{38}H_{34}N_2O_2P_2$: C, 74.50; H, 5.59; N, 4.57. Found: C, 74.29; H, 5.62; N, 4.50%.

2.5. Preparation of (R)-2,2′-bis(methanesulphonylamino)-6,6′-dimethyl-1,1′-biphenyl (**5**H_2)

This compound was prepared as a white solid from the reaction of methanesulphonyl chloride (1.15 g, 10.0 mmol) with (*R*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl (1.06 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 (hexane/ethyl acetate = 4:1) using a similar procedure as in the synthesis of **4**H_2. Yield: 1.82 g (99%). M.p.: 112–114 °C. ^{1}H NMR ($CDCl_3$): δ 7.44 (d, J = 8.2 Hz, 2H, aryl), 7.31 (t, J = 8.0 Hz, 2H, aryl), 7.06 (d, J = 7.4 Hz, 2H, aryl), 5.88 (s, 2H, N*H*), 2.98 (s, 6H, SO_2CH_3), 1.87 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 138.5, 135.5, 130.2, 126.6, 124.2, 115.9, 40.4, 19.8. IR (KBr, cm^{-1}): ν 3449 (m), 3274 (m), 2928 (w), 1582 (s), 1464 (s), 1377 (s), 1320 (vs), 1156 (vs), 1037 (s), 973 (s), 857 (s), 783 (s). Anal. Calc. for $C_{16}H_{20}N_2O_4S_2$: C, 52.15; H, 5.47; N, 7.60. Found: C, 51.87; H, 5.15; N, 7.47%.

2.6. Preparation of (R)-2,2′-bis(p-toluenesulphonylamino)-6,6′-dimethyl-1,1′-biphenyl (**6**H_2)

This compound was prepared as a white solid from the reaction of *p*-toluenesulphonyl chloride (1.91 g, 10.0 mmol) with (*R*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl (1.06 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 (hexane/ethyl acetate = 5:1) using a similar procedure as in the synthesis of **4**H_2. Yield: 2.58 g (99%). M.p.: 150–152 °C. ^{1}H NMR ($CDCl_3$): δ 7.59–7.57 (m, 4H, aryl), 7.48 (d, J = 8.2 Hz, 2H, aryl), 7.20 (m, 6H, aryl), 6.92 (d, J = 7.6 Hz, 2H, aryl), 5.68 (s, 2H, N*H*), 2.33 (s, 6H,

CH_3), 1.50 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 144.5, 138.1, 136.0, 135.2, 129.9, 129.8, 127.3, 126.2, 123.4, 115.7, 21.6, 19.3. IR (KBr, cm^{-1}): ν 3331 (s), 2921 (m), 1598 (s), 1462 (s), 1385 (s), 1327 (s), 1164 (s), 1091 (s), 1034 (s), 959 (s), 847 (s). Anal. Calc. for $C_{28}H_{28}N_2O_4S_2$: C, 64.59; H, 5.42; N, 5.38. Found: C, 64.67; H, 5.20; N, 5.38%.

2.7. Preparation of (R)-2-(diphenylthiophosphoramino)-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl (7H)

This compound was prepared as a white solid from the reaction of diphenylthiophosphinic chloride (1.26 g, 5.0 mmol) with (*R*)-2-amino-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl (1.20 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 (hexane/ethyl acetate = 50:1) using a similar procedure as in the synthesis of **4**H_2. Yield: 1.62 g (71%). M.p.: 48–50 °C. ^1H NMR ($CDCl_3$): δ 7.74 (m, 2H, aryl), 7.60 (m, 2H, aryl), 7.34 (m, 1H, aryl), 7.26 (m, 3H, aryl), 7.20 (m, 4H, aryl), 6.92 (m, 2H, aryl), 6.81 (m, 2H, aryl), 5.37 (d, J = 8.6 Hz, 1H, N*H*), 2.39 (s, 6H, NMe_2), 1.95 (s, 3H, CH_3), 1.91 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 150.5, 137.2, 136.2, 133.6, 132.6, 130.2, 130.1, 129.9, 129.7, 127.1, 126.9, 126.6, 125.9, 122.6, 116.0, 114.4, 42.2, 18.9, 18.8. IR (KBr, cm^{-1}): ν 3360 (m), 2940 (m), 1580 (s), 1463 (s), 1437 (s), 1289 (s), 1104 (s), 966 (s), 720 (s). Anal. Calc. for $C_{28}H_{29}N_2PS$: C, 73.66; H, 6.40; N, 6.14. Found: C, 73.67; H, 6.47; N, 5.89%.

2.8. Preparation of (R)-2-(pyridin-2-ylamino)-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl (8H)

(*R*)-2-Amino-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl (1.20 g, 5.0 mmol), tris(dibenzylideneacetone)dipalladium ($Pd_2(DBA)_3$; 50.3 mg, 1.1 mol%), 1,3-bis(diphenylphosphino)propane (DPPP; 42.5 mg, 2 mol%), and ^tBuONa (680 mg, 7.0 mmol) were loaded into a Schlenk flask with stirring. Toluene (50 mL) was added followed by addition of 2-bromopyridine (0.78 mL, 8.0 mmol) via syringe. The solution was stirred at 80 °C for 2 days. The solvent was removed under reduced pressure to give a pale yellow oil, which was further purified by flash column chromatography (hexane/ethyl acetate = 50:1) to give **8**H as a colorless oil. Yield: 1.54 g (97%). ^1H NMR (C_6D_6): δ 8.22 (m, 2H, aryl), 7.31 (t, J = 7.8 Hz, 1H, aryl), 7.23 (t, J = 7.8 Hz, 1H, aryl), 7.04 (m, 2H, aryl), 6.95 (m, 2H, aryl), 6.79 (s, 1H, N*H*), 6.51 (d, J = 8.1 Hz, 1H, aryl), 6.42 (m,1H, aryl), 2.42 (s, 6H, NMe_2), 2.11 (s, 3H, CH_3), 2.02 (s, 3H, CH_3). ^{13}C NMR (C_6D_6): δ 156.7, 152.7, 148.8, 138.9, 138.3, 137.5, 137.1, 130.9, 128.8, 124.7, 124.4, 117.9, 116.7, 114.7, 108.7, 43.5, 20.3, 20.0. IR (KBr, cm^{-1}): ν 3397 (m), 2943 (m), 1604 (s), 1582 (s), 1513 (s), 1464 (vs), 1440 (vs), 1318 (s), 1150 (s), 985 (w), 768 (s). Anal. Calc. for $C_{21}H_{23}N_3$: C, 79.46; H, 7.30; N, 13.24. Found: C, 79.35; H, 7.61; N, 13.34%.

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

A toluene solution (10 mL) of **2**H_2 (0.20 g, 0.5 mmol) was slowly added to a toluene solution (10 mL) of $Zr(NMe_2)_4$ (0.14 g, 0.5 mmol) with stirring at room temperature. The solution was stirred at room temperature for 1 day. The solution was filtered and the solvent was removed under reduced pressure. The resulting orange solid was recrystallized from an *n*-hexane solution to give **9** as orange microcrystals. Yield: 0.23 g (80%). M.p.: 124–126 °C (dec.). ^1H NMR (C_6D_6): δ 8.23 (d, J = 4.8 Hz, 2H, aryl), 7.24 (m, 2H, aryl), 7.11 (d, J = 7.7 Hz, 2H, aryl), 6.90 (m, 4H, aryl), 6.54 (d, J = 7.4 Hz, 4H, aryl), 5.09 (d, J = 18.8 Hz, 2H, CH_2), 4.69 (d, J = 18.8 Hz, 2H, CH_2), 3.05 (s, 12H, $Zr(NMe_2)_2$), 2.32 (s, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 167.2, 155.7, 148.2, 136.8, 136.1, 134.8, 126.6, 121.7, 120.7, 120.5, 119.9, 62.5, 43.8, 20.6. IR (KBr, cm^{-1}): ν 2921 (w), 2747 (m), 1564 (s), 1438 (s), 1216 (s), 1109 (s), 1015 (s), 931 (s), 754 (s). Anal. Calc. for $C_{30}H_{36}N_6Zr$: C, 63.01; H, 6.35; N, 14.70. Found: C, 62.83; H, 6.25; N, 14.40%.

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

This compound was prepared as red microcrystals from the reaction of **3**H_2 (0.18 g, 0.5 mmol) with $Ti(NMe_2)_4$ (0.11 g, 0.5 mmol) in toluene (20 mL) and recrystallization from an *n*-hexane solution by a similar procedure as in the synthesis of **9**. Yield: 0.13 g (50%). M.p.: 128–130 °C (dec.). ^1H NMR (C_6D_6): δ 7.70 (m, 2H, aryl), 7.19 (m, 4H, aryl), 7.04 (d, J = 7.7 Hz, 2H, aryl), 6.91 (t, J = 7.7 Hz, 2H, aryl), 6.83 (m, 2H, aryl), 6.47 (m, 2H, aryl), 3.41 (s, 12H, $Ti(NMe_2)_2$), 2.01 (s, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 159.2, 149.3, 137.9, 137.8, 133.1, 127.3, 127.0, 120.3, 116.8, 112.5, 47.3, 20.1. IR (KBr, cm^{-1}): ν 2948 (m), 1560 (s), 1433 (m), 1389 (s), 1292 (s), 1260 (s), 1091 (s), 1031 (s), 944 (s), 799 (s). Anal. Calc. for $C_{28}H_{32}N_6Ti$: C, 67.20; H, 6.44; N, 16.79. Found: C, 67.15; H, 6.24; N, 16.69%. Few red crystals suitable for X-ray diffraction analysis were picked up from the mixture.

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

This compound was prepared as orange microcrystals from the reaction of **3**H_2 (0.18 g, 0.5 mmol) with $Zr(NMe_2)_4$ (0.14 g, 0.5 mmol) in toluene (20 mL) and recrystallization from an *n*-hexane solution by a similar procedure as in the synthesis of **9**. Yield: 0.20 g (75%). M.p.: 128–130 °C (dec.). ^1H NMR (C_6D_6): δ 7.60 (m, 2H, aryl), 7.33 (m, 2H, aryl), 7.13 (m, 2H, aryl), 6.92 (m, 4H, aryl), 6.62 (m, 2H, aryl), 6.49 (m, 2H, aryl), 3.27 (s, 12H, $Zr(NMe_2)_2$), 2.03 (s, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 158.9, 146.7, 138.7, 137.7, 136.2, 131.6, 128.1, 127.3, 119.7, 118.7, 112.3, 41.6, 21.8. IR (KBr, cm^{-1}): ν 2959 (w), 1558 (s), 1432 (m), 1389 (s), 1288 (s), 1259 (s), 1032 (s), 934 (m), 732 (s). Anal. Calc. for $C_{28}H_{32}N_6Zr$: C, 61.84; H, 5.93; N, 15.45. Found: C, 61.64; H, 5.83; N, 15.32%.

2.12. Preparation of (4)Zr(NMe2)2 (12)

This compound was prepared as yellow microcrystals from the reaction of **4**H_2 (0.31 g, 0.5 mmol) with $Zr(NMe_2)_4$ (0.14 g, 0.5 mmol) in toluene (20 mL) and recrystallization from a benzene solution by a similar procedure as in the synthesis of **9**. Yield: 0.34 g (85%). M.p.: 250–252 °C (dec.). ^1H NMR (C_6D_6): δ 7.95 (m, 4H, aryl), 7.28 (m, 4H, aryl), 7.20 (m, 4H, aryl), 7.05–6.89 (m, 12H, aryl), 6.76 (m, 2H, aryl), 3.39 (s, 12H, $Zr(NMe_2)_2$), 1.79 (s, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 144.3, 136.3, 134.5, 133.4, 132.4, 131.4, 131.0, 126.7, 124.6, 124.1, 42.6, 20.3. IR (KBr, cm^{-1}): ν 2961 (m), 2924.6 (m), 1589 (s), 1432 (s), 1364 (s), 1309 (m), 1260 (s), 1117 (vs), 1044 (vs), 932 (m), 788 (s), 719 (vs). Anal. Calc. for $C_{42}H_{44}N_4O_2P_2Zr$: C, 63.85; H, 5.61; N, 7.09. Found: C, 63.75; H, 5.53; N, 7.21%. Few yellow crystals suitable for X-ray diffraction analysis were picked up from the mixture.

2.13. Preparation of (5)Ti(NMe2)2 (13)

This compound was prepared as red microcrystals from the reaction of **5**H_2 (0.18 g, 0.5 mmol) with $Ti(NMe_2)_4$ (0.11 g, 0.5 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **9**. Yield: 0.20 g (78%). M.p.: 230–232 °C (dec.). ^1H NMR (C_6D_6): δ 7.58 (d, J = 7.9 Hz, 2H, aryl), 7.12 (t, J = 7.7 Hz, 2H, aryl), 6.93 (d, J = 7.6 Hz, 2H, aryl), 3.40 (s, 12H, $Ti(NMe_2)_2$), 2.15 (s, 6H, CH_3), 1.91 (s, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 139.8, 137.4, 134.7, 129.0, 125.4 125.1, 45.5, 39.9, 19.6. IR (KBr, cm^{-1}): ν 2862 (m), 1445 (s), 1298 (vs), 1276 (vs), 1137 (vs), 1062 (s), 936 (s), 870 (vs), 807 (s). Anal. Calc. for $C_{20}H_{30}N_4O_4S_2Ti$: C, 47.81; H, 6.02; N, 11.15. Found: C, 47.72; H,

5.87; N, 11.35%. Few red crystals suitable for X-ray diffraction analysis were picked up from the mixture, which was identified as **13**·0.5C_7H_8.

2.14. Preparation of (**5**)$_2$Zr (**14**)

This compound was prepared as yellow microcrystals from the reaction of **5**H_2 (0.18 g, 0.5 mmol) with Zr(NMe_2)$_4$ (0.14 g, 0.5 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **9**. Yield: 0.11 g (55%). M.p.: 260–262 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.09 (d, J = 8.0 Hz, 4H, aryl), 7.17 (t, J = 7.8 Hz, 4H, aryl), 6.99 (d, J = 7.5 Hz, 4H, aryl), 2.25 (s, 12H, CH_3), 1.99 (s, 12H, CH_3). ^{13}C NMR (C_6D_6): δ 139.7, 136.8, 132.9, 129.0, 128.3, 124.6, 40.0, 19.8. IR (KBr, cm^{-1}): ν 2852 (m), 1567 (m), 1449 (s), 1277 (s), 1077 (m), 1040(s), 948 (m), 867 (s), 749(m). Anal. Calc. for $C_{32}H_{36}N_4O_8S_4Zr$: C, 46.64; H, 4.40; N, 6.80. Found: C, 46.99; H, 3.96; N, 7.12%.

2.15. Preparation of (**6**)Ti(NMe_2)$_2$ (**15**)

This compound was prepared as red microcrystals from the reaction of **6**H_2 (0.26 g, 0.5 mmol) with Ti(NMe_2)$_4$ (0.11 g, 0.5 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **9**. Yield: 0.21 g (63%). M.p.: 174–176 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.79 (d, J = 7.9 Hz, 2H, aryl), 7.30 (d, J = 8.0 Hz, 4H, aryl), 7.10 (t, J = 7.7 Hz, 2H, aryl), 6.73 (d, J = 7.5 Hz, 2H, aryl), 6.56 (d, J = 8.0 Hz, 4H, aryl), 3.52 (s, 12H, Ti(NMe_2)$_2$), 1.87 (s, 6H, CH_3), 1.36 (s, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 141.8, 139.9, 138.9, 138.5, 135.1, 128.9, 128.3, 127.6, 127.3, 124.6, 46.1, 20.7, 19.5. IR (KBr, cm^{-1}): ν 2854 (w), 1447 (m), 1274 (s), 1088 (s), 1041 (m), 933 (m), 868 (s), 734 (s). Anal. Calc. for $C_{32}H_{38}N_4O_4S_2Ti$: C, 58.71; H, 5.85; N, 8.56. Found: C, 58.61; H, 5.82; N, 8.46%.

2.16. Preparation of (**6**)$_2$Zr (**16**)

This compound was prepared as yellow microcrystals from the reaction of **6**H_2 (0.26 g, 0.5 mmol) with Zr(NMe_2)$_4$ (0.14 g, 0.5 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **9**. Yield: 0.16 g (55%). M.p.: > 300 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.61 (d, J = 7.9 Hz, 4H, aryl), 7.57 (d, J = 8.2 Hz, 8H, aryl), 7.25 (t, J = 7.8 Hz, 4H, aryl), 6.78 (d, J = 7.5 Hz, 4H, aryl), 6.44 (d, J = 8.2 Hz, 8H, aryl), 1.67 (s, 12H, CH_3), 1.49(s, 12H, CH_3). ^{13}C NMR (C_6D_6): δ 142.6, 140.2, 137.7, 137.6, 137.5, 133.7, 129.1, 128.9, 128.3, 125.2, 20.7, 19.5. IR (KBr, cm^{-1}): ν 2919 (w), 1568 (m), 1450 (s), 1283 (s), 1111 (s), 1074 (s), 1023 (s), 1008 (s), 865 (s), 798 (s), 730 (s). Anal. Calc. for $C_{56}H_{52}N_4O_8S_4Zr$: C, 59.60; H, 4.64; N, 4.96. Found: C, 59.53; H, 4.38; N, 4.87%.

2.17. Preparation of (**7**)$_2$Zr(NMe_2)$_2$ (**17**)

This compound was prepared as yellow crystals from the reaction of **7**H (0.23 g, 0.5 mmol) with Zr(NMe_2)$_4$ (0.07 g, 0.25 mmol) in toluene (20 mL) and recrystallization from a benzene solution by a similar procedure as in the synthesis of **9**. Yield: 0.17 g (63%). M.p.: 210–212 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.63 (m, 4H, aryl), 7.27–7.07 (m, 10H, aryl), 6.99 (m, 10H, aryl), 6.82 (m, 4H, aryl), 6.70 (m, 4H, aryl), 2.73 (s, 12H, Zr(NMe_2)$_2$), 2.40 (s, 6H, CH_3), 1.89 (s, 6H, CH_3), 1.66 (s, 12H, NMe_2). ^{13}C NMR (C_6D_6): δ 150.9, 149.7, 138.8, 134.7, 134.6, 134.4, 132.2, 131.2, 129.0, 128.3, 126.4, 125.4, 124.3, 122.7, 118.6, 116.0, 43.8, 42.7, 20.4, 20.0. IR (KBr, cm^{-1}): ν 2865 (m), 1574 (m), 1434 (s), 1234 (vs), 1105 (s), 1042 (s), 1024 (s), 931 (s), 849 (s), 796 (s), 743 (s). Anal. Calc. for $C_{60}H_{68}N_6P_2S_2Zr$: C, 66.08; H, 6.29; N, 7.71. Found: C, 66.21; H, 6.15; N, 7.65%.

2.18. Preparation of (**8**)$_2$Ti(NMe_2)$_2$ (**18**)

This compound was prepared as red crystals from the reaction of **8**H (0.16 g, 0.5 mmol) with Ti(NMe_2)$_4$ (0.06 g, 0.25 mmol) in toluene (20 mL) and recrystallization from a benzene solution by a similar procedure as in the synthesis of **9**. Yield: 0.13 g (70%). M.p.: 238–240 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.10 (d, J = 5.0 Hz, 2H, aryl), 7.54 (d, J = 7.8 Hz, 2H, aryl), 7.35 (t, J = 7.6 Hz, 2H, aryl), 7.09 (m, 4H, aryl), 6.94 (d, J = 7.4 Hz, 2H, aryl), 6.89 (t, J = 8.2 Hz, 2H, aryl), 6.81 (d, J = 7.9 Hz, 2H, aryl), 6.21 (d, J = 8.7 Hz, 2H, aryl), 5.94 (t, J = 6.2 Hz, 2H, aryl), 2.75 (s, 12H, Ti(NMe_2)$_2$), 2.15 (s, 6H, CH_3), 2.05 (s, 6H, CH_3), 2.00 (s, 12H, NMe_2). ^{13}C NMR (C_6D_6): δ 168.2, 153.0, 150.3, 142.3, 138.8, 138.1, 137.1, 136.4, 136.0, 128.3, 127.4, 127.3, 125.9, 125.0, 117.9, 107.2, 107.0, 45.6, 43.3, 20.6, 20.1. IR (KBr, cm^{-1}): ν 2802 (w), 1593 (s), 1467 (s), 1439 (s), 1355 (s), 1295 (s), 1020 (m), 940 (m), 759 (s), 732 (s). Anal. Calc. for $C_{46}H_{56}N_8Ti$: C, 71.86; H, 7.34; N, 14.57. Found: C, 72.11; H, 7.06; N, 14.58%.

2.19. Preparation of (**8**)$_2$Zr(NMe_2)$_2$ (**19**)

This compound was prepared as orange crystals from the reaction of **8**H (0.16 g, 0.5 mmol) with Zr(NMe_2)$_4$ (0.07 g, 0.25 mmol) in toluene (20 mL) and recrystallization from a benzene solution by a similar procedure as in the synthesis of **9**. Yield: 0.15 g (74%). M.p.: 261–263 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.84 (m, 2H, aryl), 7.33 (m, 4H, aryl), 7.08 (m, 4H, aryl), 6.94 (d, J = 7.4 Hz, 2H, aryl), 6.85 (m, 4H, aryl), 6.23 (d, J = 8.8 Hz, 2H, aryl), 5.89 (t, J = 6.2 Hz, 2H, aryl), 2.52 (s, 12H, Zr(NMe_2)$_2$), 2.12 (s, 6H, CH_3), 2.05 (s, 6H, CH_3), 2.03 (s, 12H, NMe_2). ^{13}C NMR (C_6D_6): δ 169.2, 152.9, 148.4, 142.6, 138.7, 138.0, 137.3, 137.0, 135.0, 128.3, 127.3, 125.8, 125.3, 125.0, 117.6, 107.9, 107.6, 43.2, 41.1, 20.4, 19.9. IR (KBr, cm^{-1}): ν 2930 (w), 1596 (s), 1463 (s), 1438 (s), 1296 (s), 930 (s), 764 (s), 733 (s). Anal. Calc. for $C_{46}H_{56}N_8Zr$: C, 68.02; H, 6.95; N, 13.80. Found: C, 67.82; H, 6.85; N, 13.76%.

2.20. General procedure for asymmetric hydroamination/cyclization

In a nitrogen-filled glove box, precatalyst (0.016 mmol), C_6D_6 (0.7 mL), and aminoalkene (0.16 mmol) were introduced sequentially into a J. 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 J. 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 $CDCl_3$ and the enantiomeric excesses were determined by ^{1}H NMR spectroscopy [27].

2.21. 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 = 0.71070 Å). An empirical absorption correction was applied using the SADABS program [30]. All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package [31]. All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for **10**, **12**, **13**, and **17–19** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 1
Crystal data and experimental parameters for compounds **10**, **12**, **13**, and **17–19**.

Compound	**10**	**12**	**13**·0.5C_7H_8	**17**	**18**	**19**
Formula	$C_{28}H_{32}N_6Ti$	$C_{42}H_{44}N_4O_2P_2Zr$	$C_{23.5}H_{34}N_4O_4S_2Ti$	$C_{60}H_{68}N_6P_2S_2Zr$	$C_{46}H_{56}N_8Ti$	$C_{46}H_{56}N_8Zr$
Formula weight	500.50	789.97	548.57	1090.48	768.89	812.21
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P12/n1$	$P12/c1$	$P\bar{1}$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.685(1)	20.435(2)	9.605(1)	12.687(1)	14.846(3)	14.856(2)
b (Å)	11.784(1)	10.781(1)	9.842(1)	14.226(1)	15.661(3)	15.638(2)
c (Å)	11.984(1)	19.361(2)	15.707(2)	15.850(2)	18.290(4)	18.287(2)
α (°)	90	90	73.44(1)	90	90	90
β (°)	108.50(1)	115.85(1)	80.63(1)	90.08(3)	90	90
γ (°)	90	90	69.56(1)	90	90	90
V (Å^3)	1297.1(2)	3838.7(6)	1330.2(3)	2860.4(5)	4252.4(15)	4248.5(8)
Z	2	4	2	2	4	4
$D_{calc.}$ (g/cm^3)	1.281	1.367	1.370	1.266	1.201	1.270
μ (Mo Kα)$_{calc}$ (mm^{-1})	0.358	0.411	0.515	0.364	0.243	0.300
Size (mm)	0.22 × 0.16 × 0.14	0.22 × 0.20 × 0.18	0.26 × 0.20 × 0.16	0.22 × 0.18 × 0.14	0.26 × 0.24 × 0.22	0.36 × 0.34 × 0.30
F(0 0 0)	528	1640	578	1144	1640	1712
2θ Range (°)	4.74–55.74	4.22–54.58	4.54–55.74	2.86–54.20	3.42–56.00	3.54–55.74
Number of reflections collected	15 917	25 985	16 664	26 776	21 964	41 654
Number of unique reflections [R_{int}]	3088 (0.0532)	8405 (0.0448)	6298 (0.0244)	10 511 (0.0634)	9594 (0.0303)	10 124 (0.0336)
Number of observed reflections	2861	7250	5421	9438	9323	9811
Absorbed corrections (T_{max}, T_{min})	0.95, 0.93	0.93, 0.92	0.92, 0.88	0.95, 0.92	0.95, 0.94	0.92, 0.90
R	0.053	0.044	0.034	0.032	0.042	0.026
wR	0.119	0.111	0.086	0.056	0.100	0.061
wR_2 (all data)	0.131	0.117	0.089	0.058	0.101	0.062
Goodness-of-fit (GOF)	1.15	1.05	1.04	0.90	1.09	1.03

Table 2
Selected bond distances (Å) and bond angles (°) for compounds **10**, **12**, **13**, and **17–19**.

Compound	**10** (Ti)	**12** (Zr)	**13** (Ti)	**17** (Zr)	**18** (Ti)	**19** (Zr)
M–N (av.)	2.109(2)	2.171(2)	1.961(1)	2.171(3)	2.098(2)	2.209(1)
M–N (NMe_2)	1.903(2)	2.071(2)	1.861(1)	2.035(3)	1.912(2)	2.029(1)
	1.903(2)	2.071(2)	1.879(1)	2.052(3)	1.913(2)	2.043(1)
M–X (av.)		M–O	M–O	Zr–S		
		2.249(2)	2.194(1)	2.754(1)		
		Zr–P	Ti–S	Zr–P		
		2.912(1)	2.797(1)	3.106(1)		
Sum angles of N (NMe_2)	359.9(2)	359.7(2)	358.7(1)	359.5(3)	356.9(2)	356.6(2)
	359.9(2)	359.7(2)	359.8(1)	359.1(3)	359.5(2)	359.9(2)
Torsion (aryl–aryl)	67.8(3)	72.1(2)	68.5(2)	85.4(5)	71.7(2)	71.0(2)
				81.6(5)	71.1(2)	70.7(2)

3. Results and discussion

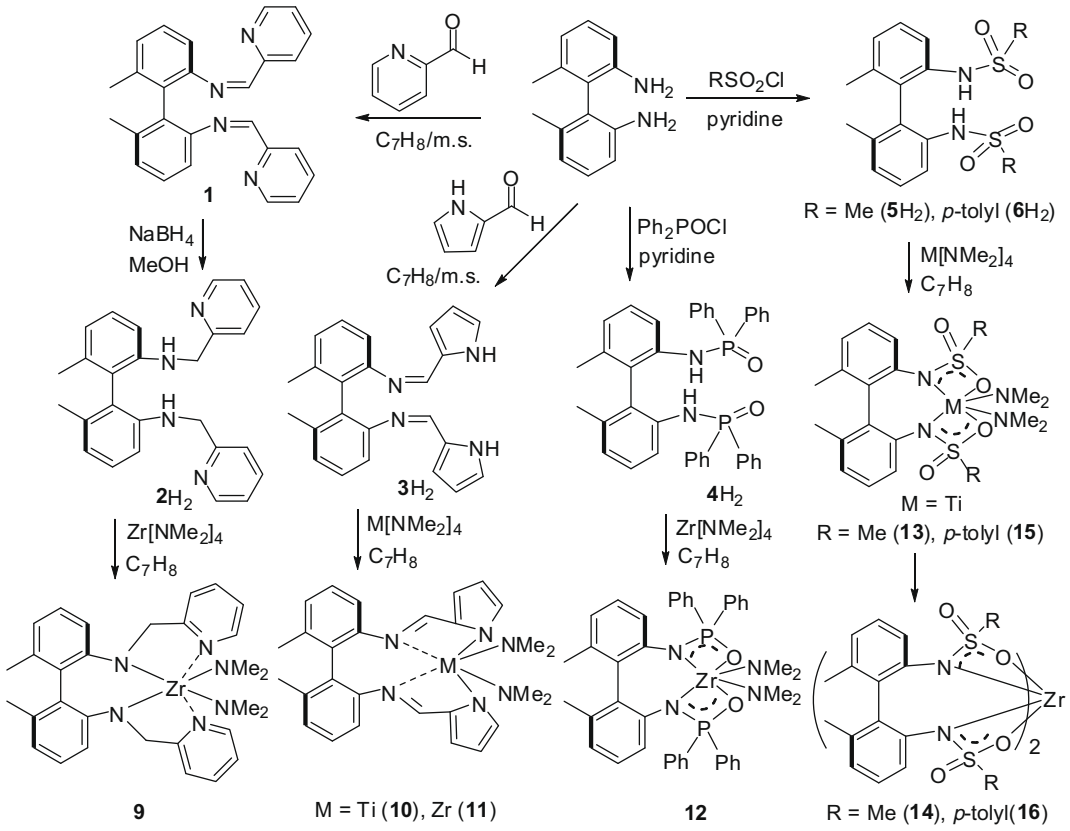
3.1. Synthesis and characterization of ligands

The C_2-symmetric pyridine ligand, (*R*)-2,2′-bis(pyridin-2-ylmethylamino)-6,6′-dimethyl-1,1′-biphenyl (**2**H_2), is readily prepared in 69% yield by condensation of the starting material (*R*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl with 2 equiv. of pyridine-2-carboxaldehyde in the presence of molecular sieves in toluene at 70 °C, followed by reduction with an excess of $NaBH_4$ in methanol (Scheme 1). Of course, the C_2-symmetric Schiff base ligand, (*R*)-2,2′-bis(pyrrol-2-ylmethyleneamino)-6,6′-dimethyl-1,1′-biphenyl (**3**H_2), is also readily prepared in 63% yield by condensation of (*R*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl with 2 equiv. of pyrrole-2-carboxaldehyde in the presence of molecular sieves in toluene at 70 °C (Scheme 1). Treatment of (*R*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl with 2 equiv. of diphenylphosphinoyl chloride, methanesulphonyl chloride, or *p*-toluenesulphonyl chloride in the presence of an excess of pyridine in toluene at reflux gives, after purification by flash column chromatography, (*R*)-2,2′-bis(diphenylphosphinoylamino)-6,6′-dimethyl-1,1′-biphenyl (**4**H_2), (*R*)-2,2′-bis(methanesulphonylamino)-6,6′-dimethyl-1,1′-biphenyl (**5**H_2), and (*R*)-2,2′-bis(*p*-toluenesulphonylamino)-6,6′-dimethyl-1,1′-biphenyl (**6**H_2), respectively, in good yields (Scheme 1). Under similar reaction conditions, reaction of (*R*)-2-(amino)-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl with 1 equiv. of diphenylthiophosphinic chloride in the presence of an excess of pyridine in toluene at reflux, after purification by flash column chromatography, gives C_1-symmetric ligand, (*R*)-2-(diphenylthiophosphoramino)-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl (**7**H) in 71% yield (Scheme 2). Treatment of (*R*)-2-(amino)-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl with an excess of 2-bromopyridine in the presence of catalytic amount of tris(dibenzylideneacetone)dipalladium ($Pd_2(DBA)_3$) and 1,3-bis(diphenylphosphino)propane (DPPP) in toluene at 80 °C, after purification by flash column chromatography, gives C_1-symmetric N_3-ligand, (*R*)-2-(pyridin-2-ylamino)-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl (**8**H) in 97% yield (Scheme 2).

All ligands are air-stable, and are soluble in CH_2Cl_2, $CHCl_3$, toluene and benzene, and slightly soluble in *n*-hexane. They have been fully characterized by various spectroscopic techniques, and elemental analyses. The ^{1}H and ^{13}C NMR spectra of **2**H_2, **3**H_2, **4**H_2, **5**H_2 and **6**H_2 indicate that they are symmetrical on the NMR timescale, which are consistent with their C_2-symmetric structures. And the ^{1}H and ^{13}C NMR spectra of **7**H and **8**H confirm that they are non-symmetrical on the NMR timescale 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 3360 cm^{-1}.

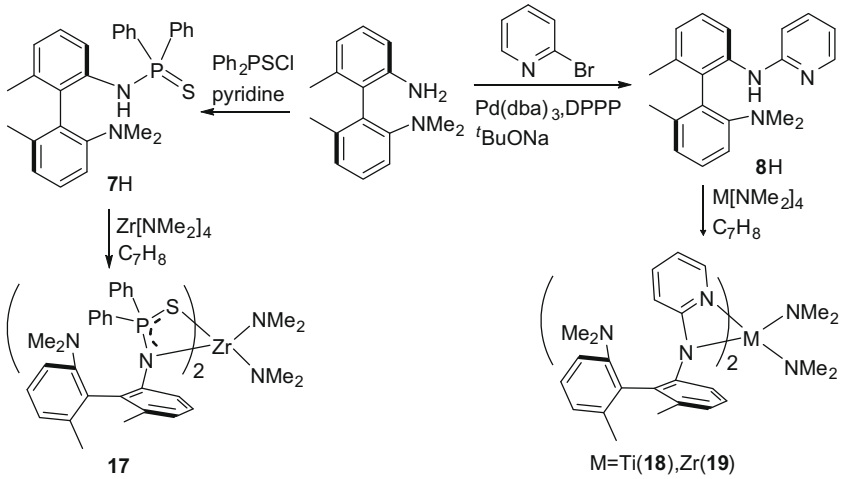
3.2. Synthesis and characterization of complexes

Group 4 metal amide complexes can be efficiently prepared via amine elimination reaction between M(NMe_2)$_4$ and protic reagents [32–43]. It is rational to propose that the acidic proton in the ligands **2**H_2, **3**H_2, **4**H_2, **5**H_2, **6**H_2, **7**H and **8**H would allow the similar amine elimination to occur between **2**H_2, **3**H_2, **4**H_2, **5**H_2, **6**H_2, **7**H or **8**H and metal amides. In fact, treatment of M(NMe_2)$_4$ with 1 equiv. of N_4-ligand, (*R*)-2,2′-bis(pyridin-2-ylmethylamino)-6,6′-dimethyl-1,1′-biphenyl (**2**H_2) or (*R*)-2,2′-bis(pyrrol-2-ylmethyleneamino)-



Scheme 1.

6,6′-dimethyl-1,1′-biphenyl ($\mathbf{3}H_2$) gives, after recrystallization from an *n*-hexane solution, the chiral zirconium amides ($\mathbf{2}$)$Zr(NMe_2)_2$ (**9**), ($\mathbf{3}$)$Zr(NMe_2)_2$ (**11**), and titanium amide ($\mathbf{3}$)$Ti(NMe_2)_2$ (**10**), respectively, in good yields (Scheme 1). Reaction of $Zr(NMe_2)_4$ with 1 equiv. of diphenylphosphoramide (*R*)-2,2′-bis(diphenylphosphinoylamino)-6,6′-dimethyl-1,1′-biphenyl ($\mathbf{4}H_2$) affords, after recrystallization from a benzene solution, the chiral zirconium amide ($\mathbf{4}$)$Zr(NMe_2)_2$ (**12**) in 85% yield (Scheme 1). Under similar reaction conditions, treatment of $Ti(NMe_2)_4$ with 1 equiv. of sulphonylamide ligand, (*R*)-2,2′-bis(methanesulphonylamino)-6,6′-dimethyl-1,1′-biphenyl ($\mathbf{5}H_2$) or (*R*)-2,2′-bis(*p*-toluenesulphonylamino)-6,6′-dimethyl-1,1′-biphenyl ($\mathbf{6}H_2$) gives, after recrystallization from a toluene solution, the chiral titanium amides ($\mathbf{5}$)$Ti(NMe_2)_2{\cdot}0.5C_7H_8$ (**13**$\cdot 0.5C_7H_8$), ($\mathbf{6}$)$Ti(NMe_2)_2$ (**15**), respectively, in good yields (Scheme 1), while reaction of $Zr(NMe_2)_4$ with 1 equiv. of $\mathbf{5}H_2$ or $\mathbf{6}H_2$ does not give the expected complex ($\mathbf{5}$)$Zr(NMe_2)_2$ or ($\mathbf{6}$)$Zr(NMe_2)_2$, instead, the bis-ligated complexes, $(\mathbf{5})_2Zr$ (**14**) and $(\mathbf{6})_2Zr$ (**16**), have been isolated, respectively, in good yields (Scheme 1). Under similar reaction conditions, treatment of $Zr(NMe_2)_4$ with 2 equiv. of diphenylthiophosphoramide ligand, (*R*)-2-(diphenylthiophosphoramino)-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl (**7**H)



Scheme 2.

gives, after recrystallization from a benzene solution, the bis-ligated chiral zirconium amide (**7**)$_2$Zr(NMe$_2$)$_2$ (**17**) in 63% yield (Scheme 2). Reaction of M(NMe$_2$)$_4$ with 2 equiv. of N$_3$-ligand (*R*)-2-(pyridin-2-ylamino)-2′-(dimethylamino)-6,6′-dimethyl-1,1′-biphenyl (**8**H) also gives, after recrystallization from a benzene solution, the bis-ligated chiral titanium amide (**8**)$_2$Ti(NMe$_2$)$_2$ (**18**), and zirconium amide (**8**)$_2$Zr(NMe$_2$)$_2$ (**19**), respectively, in good yields (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 **9**, **10**, **11**, **12**, **13** and **15** support that the ratio of amino group NMe$_2$ and ligand anion **2**, **3**, **4**, **5** or **9** is 2:1, and establish that half toluene molecule for **13** co-crystallized. Unlike the zirconium amides **9**, **11** and **12**, the ^{1}H NMR spectra of **14** and **16** do not exhibit a singlet resonance at about 3.30 ppm attributable to the NMe$_2$ groups, supporting the formation of the bis-ligated complexes **14** and **16**. The ^{1}H NMR spectra of **17**, **18** and **19** support that the ratio of amino group NMe$_2$ and ligand anion **7** or **8** is 1:1, supporting the formation of the bis-ligated complexes **17**, **18** and **19**. These results are consistent with their ^{13}C NMR spectra. The solid-state structures of the complexes **10**, **12**, **13** and **17–19** have further been confirmed by X-ray diffraction analyses.

The solid-state structure of **10** shows that the Ti^{4+} is σ-bound to four nitrogen atoms from the ligand anion **3** and two nitrogen atoms from amino groups NMe$_2$ in a distorted-octahedron geometry (Fig. 1) with the average distance of Ti–N (2.109(2) Å). The short Ti–N(3) and Ti–N(3A) bond distances (1.903(2) and 1.903(2) Å) and the planar geometry around the N(3) and N(3A) nitrogen atoms indicate that both nitrogen atoms with sp^2 hybridization are engaged in N(p_π) → Ti(d_π) interactions. These structural data are close to those found in [(*R*)-C$_{20}$H$_{12}$(NCHC$_4$H$_3$N)$_2$]Ti(NMe$_2$)$_2$ [20]. The twisting between the phenyl rings of torsion angle is 67.8(3)°.

The solid-state structure of **12** shows that there are two molecules (**4**)Zr(NMe$_2$)$_2$ in the lattice. In each molecule of (**4**)Zr(NMe$_2$)$_2$, the Zr^{4+} is σ-bound to two nitrogen atoms and two oxygen atoms from the ligand **4** and two nitrogen atoms from amino groups NMe$_2$ in a distorted-octahedron geometry (Fig. 2) with the average distance of Zr–N (2.171(2) Å) and the average distance of Zr–O (2.249(2) Å), respectively. The short distances of Zr–NMe$_2$ (2.071(2) and 2.071(2) Å) and the planar geometry around the nitrogen atoms of N(2) and N(2A) indicate that the nitrogen atoms with sp^2 hybridization are engaged in N(p_π) → Zr(d_π) interactions. The twisting between the phenyl rings of torsion angle is 72.1(2)°, which is slightly larger than that found in **10** (67.8(3)°).

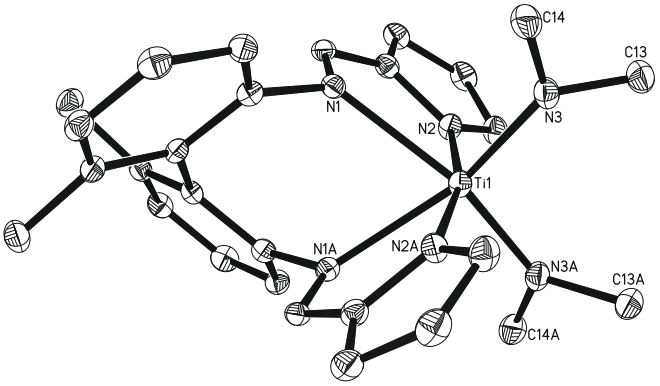


Fig. 1. Molecular structure of **10** (thermal ellipsoids drawn at the 35% probability level).

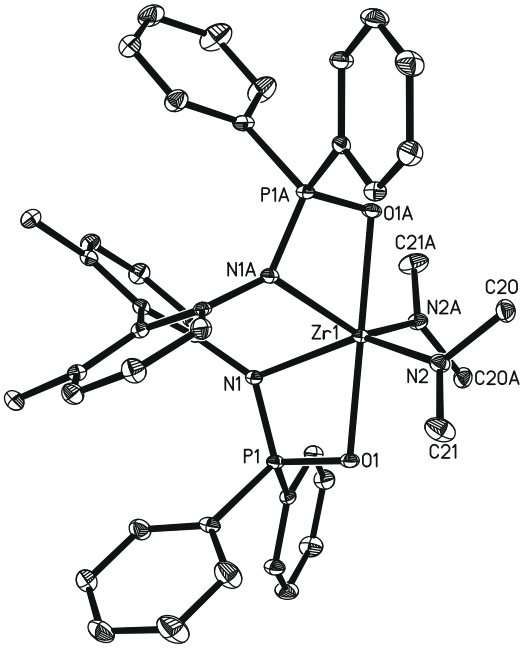


Fig. 2. Molecular structure of **12** (thermal ellipsoids drawn at the 35% probability level).

The solid-state structure of **13** shows that there are two molecules (**5**)Ti(NMe$_2$)$_2$ and one solvate benzene in the lattice. In each molecule of (**5**)Ti(NMe$_2$)$_2$, the Ti^{4+} is σ-bound to two nitrogen atoms and one oxygen atom from the ligand **5** and two nitrogen atoms from amino groups NMe$_2$ in a distorted-trigonal–bipyramidal geometry (Fig. 3) with the average distance of Ti–N (1.961(1) Å) and the distance of Ti–O (2.194(1) Å), respectively. The short distances of Ti–NMe$_2$ (1.861(1) and 1.879(1) Å) and the planar geometry around the nitrogen atoms of N(3) and N(4) indicate that the nitrogen atoms with sp^2 hybridization are engaged in N(p_π)→Ti(d_π) interactions. The twisting between the phenyl rings of torsion angle is 68.5(2)°, which is comparable to those found in **10** (67.8(3)°) and **12** (72.1(2)°).

The solid-state structure of **17** shows that the substituted Me$_2$N group is far away from the metal center, and the Zr^{4+} is σ-bound to

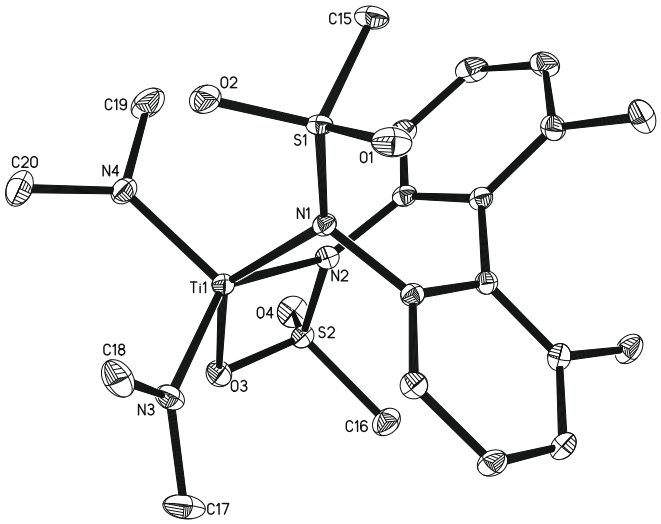


Fig. 3. Molecular structure of **13** (thermal ellipsoids drawn at the 35% probability level).

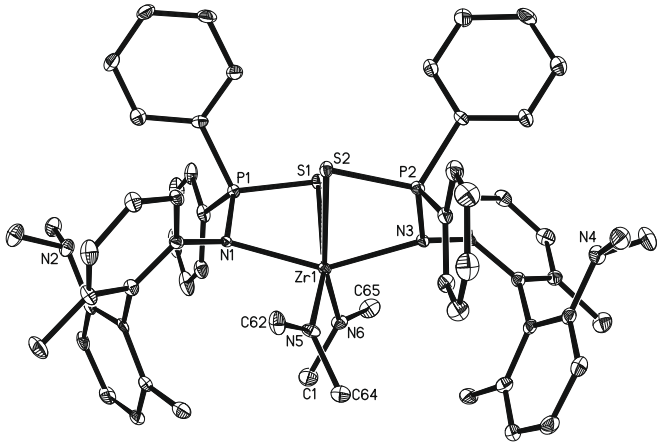


Fig. 4. Molecular structure of **17** (thermal ellipsoids drawn at the 35% probability level).

two nitrogen atoms and two sulfur atoms from the two ligands **7** and two nitrogen atoms from amino groups NMe_2 in a distorted-octahedron geometry (Fig. 4) with the average distance of Zr–N (2.171(3) Å) and the average distance of M–S (2.754(1) Å). The short Zr–N(5) and Zr–N(6) bond distances (2.035(3) and 2.052(3) Å) and the planar geometry around the N(5) and N(6) nitrogen atoms indicate that the nitrogen atoms with sp^2 hybridization are engaged in $N(p_\pi) \rightarrow Zr(d_\pi)$ interactions. The twisting between the phenyl rings of torsion angles are 85.4(5) and 81.6(5)°, which are close to those found in [(*R*)-2-(Ph_2PON)-2′-(Me_2N)-(6-MeC_6H_3)$_2$]$_2$Zr(NMe_2)$_2$ (85.4(3) and 86.8(3)°) [21].

The single-crystal X-ray diffraction analysis shows that **18** and **19** are isostructural. In each molecule (**8**)$_2$M(NMe_2)$_2$, the substituted Me_2N group is far away from the metal center, and the M^{4+} is σ-bound to four nitrogen atoms from the two ligands **8** and two nitrogen atoms from amino groups NMe_2 in a distorted-octahedron geometry (Fig. 5) with the average distance of M–N (2.098(2) Å) for Ti and (2.209(1) Å) for Zr, respectively. The short distances of M–NMe_2 1.912(2) and 1.913(2) Å for Ti and 2.029(1) and 2.043(1) Å for Zr and the planar geometry around the nitrogen atoms N(7) and N(8) indicate that the nitrogen atoms with sp^2 hybridization are engaged in $N(p_\pi) \rightarrow M(d_\pi)$ interactions. The twisting between the phenyl rings of torsion angle is 71.7(2)° and 71.1(2)° for **18** and 71.0(2)° and 70.7(2)° for **19**, which are smaller than those found in **17** (85.4(5)° and 81.6(5)°).

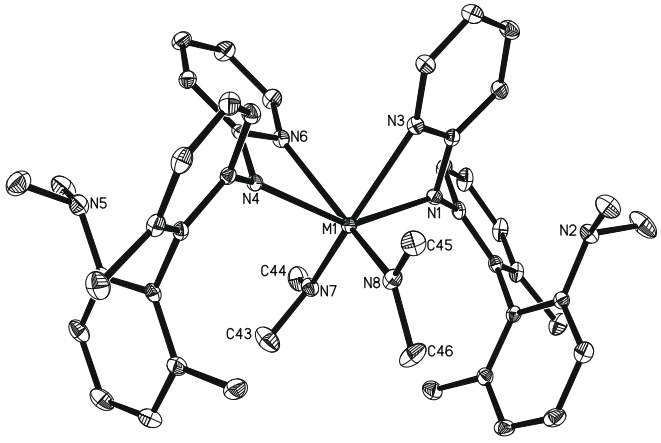


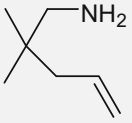
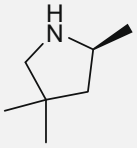
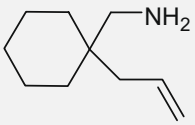
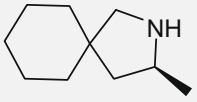
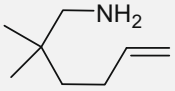
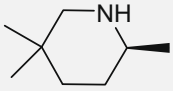
Fig. 5. Molecular structure of **18** (M = Ti) and **19** (M = Zr) (thermal ellipsoids drawn at the 35% probability level).

3.3. Asymmetric hydroamination/cyclization

To examine the catalytic ability of the complexes **9–19**, the asymmetric hydroamination/cyclization of unactivated terminal aminoalkenes has been evaluated under the conditions given in Table 3. The results of the hydroamination/cyclization of 2,2-dimethylpent-4-enylamine clearly show that the zirconium amides are active catalysts for this transformation (Table 3, entries 1, 3, 4, 9 and 11), and the mono-ligated complex **11** shows the most effective catalyst for this transformation, but the enantioselectivity is moderate (only up to 21%; Table 3, entry 3). When more bulky ligand **4** is used, both the rate and ee value decrease significantly (Table 3, entry 4). However, the bis-ligated complex **17** gives a noticeably better ee value (38%; Table 3, entry 9), but the rate is slow. When the less bulky ligand **8** is used, the rate increases while the ee value decreases slightly (Table 3, entry 11). Under similar reaction conditions, no detectable hydroamination activity is observed for titanium complexes **10**, **13**, **15** and **18** (Table 3, entries 2, 5, 7 and 10), and bis-ligated zirconium complexes **14** and **16** (Table 3, entries 6 and 8) even heated at 120 °C for one week, and none of the complexes described above is effective catalysts for the cyclization of 1-aminopent-4-ene into 2-methylpyrrolidine, presumably due to a lack of a Thorpe–Ingold effect [44,45] from the unsubstituted aminoalkene. Substrate **22a** reacts fast but the ee values are moderate (Table 3, entries 13–17). We are pleased to find that the formation of six-membered ring can also be performed with our zirconium catalysts (Table 3, entries 18–22), and a moderate enantioselectivity (up to 24%), mediated by the catalyst **17**, has been obtained (Table 3, entry 21). The catalytic activities of the bis-ligated zirconium complexes **17** and **19** are more effective than C_2-symmetric zirconium amides **9**, **11** and **12**, but less than bis(amidate) zirconium amide [(*R*)-(6-MeC_6H_3)$_2$-2-{NCO(2,4,6-$Me_3C_6H_2$)}$_2$]Zr(NMe_2)$_2$ (**20**) (Table 3, entry 12) [22]. Although the enantiomeric excesses obtained remain moderate, it should be noted that there are only few group four catalysts for these reactions that give a significant ee (>90%) at all [19–23,46–53].

The stereochemical outcome of the asymmetric hydroamination/cyclization of aminoalkene **21a** catalyzed by C_2-symmetric zirconium amides can be rationalized by the transition state pictures (Fig. 6) similar to those proposed by Hultzsch and others [23,54], which may well explain the experimental observations that the substituted groups on the biphenyl backbone have considerable influence on the enantioselectivity of the catalysts and the configuration of the resulting products. For example, the more sterically unfavorable interactions between the carbon chain of the substrate and the mesitoylamido groups of complex [(*R*)-(6-MeC_6H_3)$_2$-2-{NCO(2,4,6-$Me_3C_6H_2$)}$_2$]Zr(NMe_2)$_2$ (**20**) lead to the product 2,4,4-trimethylpyrrolidine with a significantly preferentially (up to 93% ee) with (*S*)-configuration (Table 3, entry 12) [22,23], while the less sterically unfavorable interactions between the carbon chain of the substrate and the diphenylphosphinoylamido groups of complex **12** result in a poor enantioselectivity (only up to 6.8% ee; Table 3, entry 4), indicating that highly enantioselective catalyst for this transformation requires very precise control of the metal coordination sphere. The enantioselectivity induced by C_2-symmetric zirconium amides could be roughly ruled out, however, it is difficult to draw a conclusion from the different enantioselectivity between the bis-ligated zirconium complexes and the C_2-symmetric zirconium amides. For example, the bis-ligated diphenylphosphoramidate [(*R*)-2-(Ph_2PON)-2′-(Me_2N)-(6-MeC_6H_3)$_2$]$_2$Zr(NMe_2)$_2$ [21] is more selective than C_2-symmetric diphenylphosphoramidate **12**, while the bis-ligated mesitoylamidate [(*R*)-2-{NCO(2,4,6-$Me_3C_6H_2$)}-2′-(Me_2N)-(6-MeC_6H_3)$_2$]$_2$Zr(NMe_2)$_2$ [21] is less selective than the C_2-symmetric mesitoylamidate [(*R*)-(6-MeC_6H_3)$_2$-2-{NCO(2,4,6-$Me_3C_6H_2$)}$_2$]Zr(NMe_2)$_2$ (**20**) [22]. Although the reasons for the different enantioselectivity between the bis-ligated zirconium

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

Entry	Catalyst (M)	Substrate	Product	Time (h)	Conv. (%)[b]	Ee (%)[c]
1	**9** (Zr)			24	96	24 (*S*)[d]
2	**10** (Ti)			160	NR	NA
3	**11** (Zr)			24	100	21 (*S*)[d]
4	**12** (Zr)			24	86	6.8 (*S*)[d]
5	**13** (Ti)			160	NR	NA
6	**14** (Zr)			160	NR	NA
7	**15** (Ti)	**21a**	**21b**	160	NR	NA
8	**16** (Zr)			160	NR	NA
9	**17** (Zr)			24	92	38 (*S*)[d]
10	**18** (Ti)			160	NR	NA
11	**19** (Zr)			24	100	32 (*S*)[d]
12	(*R*)-**20** (Zr)[e]			3	>98	93 (*S*)
13	**9** (Zr)			16	100	19
14	**11** (Zr)			16	100	17
15	**12** (Zr)			16	93	8.9
16	**17** (Zr)			16	100	28
17	**19** (Zr)	**22a**	**22b**	16	94	24
18	**9** (Zr)			24	100	18
19	**11** (Zr)			24	100	16
20	**12** (Zr)			24	95	11
21	**17** (Zr)			24	100	24
22	**19** (Zr)	**23a**	**23b**	24	100	20

[a] *Conditions:* C_6D_6 (0.70 mL), aminoalkene (0.16 mmol), catalyst (0.016 mmol), at 120 °C.
[b] Determined by ^1H NMR based on *p*-xylene as the internal standard. NR = no reaction.
[c] Determined by ^1H NMR of its diastereomeric (*S*)-(+)-*O*-acetylmandelic acid salt [27]. NA = not applicable.
[d] Absolute configuration of the major enantiomer was assigned by the comparison of optical rotation with literature data [54].
[e] See Refs. [22,23].

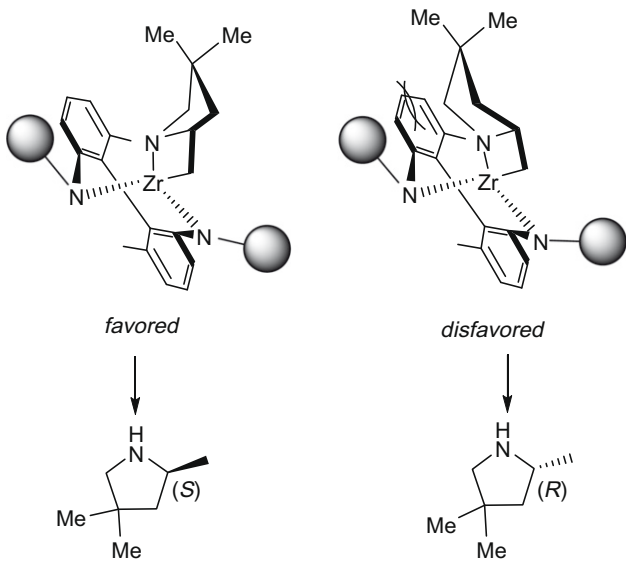


Fig. 6. Proposed transition states.

complexes (**17** and **19**) and the C_2-symmetric zirconium amides (**9**, **11** and **12**) are not clear at this time, the coordination environment around the metal center seems to be a major reason for this different olefin switch approach. Further computational investigation of the ligand architecture for this transformation is currently underway.

4. Conclusions

In conclusion, a new series of chiral titanium(IV) and zirconium(IV) amides have been prepared from the reactions between $M(NMe_2)_4$ (M = Ti, Zr) and chiral ligands, **2**H_2, **3**H_2, **4**H_2, **5**H_2, **6**H_2, 7H and **8**H. The zirconium amides have displayed good to excellent catalytic activity for the asymmetric hydroamination/cyclization of representative aminoalkenes, while the titanium amides have not. The bis-ligated zirconium complexes **17** and **19** are more effective chiral catalysts for the enantioselective hydroamination/cyclization reaction than C_2-symmetric zirconium amides **9**, **11** and **12**, but less than bis(amidate) zirconium amide [(*R*)-(6-MeC_6H_3)$_2$-2-{$NCO(2,4,6\text{-}Me_3C_6H_2)$}$_2$]$Zr(NMe_2)_2$ (**20**) [22–24]. How to fully optimize both the rate and selectivity remains a question for asymmetric hydroamination, it seems that very precise control of the metal coordination sphere is required for this transformation to be a realistic prospect. Our ligand set using peripheral biphenyl-based N_4, N_3 or N_2O_2-ligand in multidentate systems does not provide a successful suitable coordination sphere to achieve a significant enantioselectivity, however, this modification should significantly expand the range of possibilities in designing catalysts not only for hydroamination but also for many other reactions [1–4]. Further optimization of the ligand architecture to improve the enantiomeric excess for this transformation and the exploration of these catalysts toward other types of transformations are still underway.

Acknowledgements

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Appendix A. Supplementary material

CCDC 749372, 749373, 749374, 749375, 749376, and 749377 contain the supplementary crystallographic data for **10**, **12**, **13**,

17, **18** and **19**. 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.2009.12.008.

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