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Synthesis, structure, and catalytic activity of titanium complexes with chiral biaryl Schiff-base ligands

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ABSTRACT

A series of chiral organo-titanium complexes have been prepared from the reaction between Ti(O^iPr)$_4$ and chiral biaryl Schiff-base ligands **1**H_2–**12**H. The steric demand of the ligand plays an important role in the formation of the titanium complexes. For example, treatment of ligand **1**H_2 with 1 equiv of Ti(O^iPr)$_4$ in toluene at room temperature gives, after recrystallization from a toluene solution, the chiral bis-ligated titanium complex (**L1**)$_2$Ti (**14**). While under similar reaction conditions, the more bulky ligands **2**H_2, **4**H_2, and **6**H_2 form the mono-ligated titanium complexes (**L2**)Ti(O^iPr)$_2$ (**15**), (**L4**)Ti(O^iPr)$_2$ (**19**), and (**L6**)Ti(O^iPr)$_2$ (**22**), respectively, in good yields. The mono-ligated titanium alkoxides can be converted to bis-ligated complex *via* ligand redistribution reaction. For one instance, treatment of mono-ligated complex (**L2**)Ti(O^iPr)$_2$ (**15**) in benzene at 60 °C results in the isolation of the bis-ligated complex (**L2**)$_2$Ti (**16**) in 92% yield. All titanium complexes have been characterized by various spectroscopic techniques and elemental analyses. The solid-state structures of complexes **14**–**21**, **23**, **24** and **29** have further been confirmed by X-ray diffraction analyses. The titanium complexes are active catalysts for the asymmetric hydrophosphonylation of aromatic aldehydes with moderate enantioselectivities.

1. Introduction

Hydrophosphonylation is an economical process in which a dialkyl phosphite is added to carbonyl or imine compounds (Pudovik reaction), leading to the formation of the α-hydroxy or α-amino phosphonates that are found in numerous biologically and pharmacologically active compounds [1–5]. Therefore, it is not surprising that recent efforts have focused on the development of chiral catalysts for the asymmetric hydrophosphonylation of aldehydes [6–10]. Since the pioneering work of Shibuya and co-workers in 1993 [11,12], many chiral catalysts based on lanthanide [12–17], aluminum [18–26], titanium [11,15,16,27–33] and late transition metals [34,35] have extensively been studied. Among these, the chiral titanium catalysts have been identified as very promising candidates for this transformation [11,15,16,27–33]. However, even within this class, successful catalysts affording significant stereoselectivity are rare [31]. Thus, the development of new chiral titanium catalysts for the enantioselective hydrophosphonylation is still a desirable and challenging goal.

Recently, we have developed a series of chiral biaryl-based multi-dentate ligands, and their Zr(IV), V(IV), Ta(V), Rh(III), Ir(III), Ni(II) and lanthanide complexes that are useful catalysts for a wide range of transformations [36–62]. Furthermore we demonstrated that the biaryl-based bis-ligated lanthanide amides [(*S*)-2-Me_2N-$C_{20}H_{12}$-2′-(NCHC_4H_3N)]$_2$LnN($SiMe_3$)$_2$ with C_1-symmetric N_3-ligand are more effective chiral catalysts for the enantioselective hydroamination/cyclization reaction than those [(*R*)-$C_{20}H_{12}$(NCHC_4H_3N)$_2$]-LnN($SiMe_3$)$_2$(thf) (Ln = Sm, Y, Yb) with C_2-symmetric N_4-ligands [39,41]. In our ongoing research, we are now focusing on the preparation of the type of bis-ligated catalysts coordinated by chiral C_1-symmetric tridentate ligands. In our endeavor to further explore the biaryl-backbones, we have recently extended our work to chiral C_1-symmetric ligands, **1**H_2–**6**H_2 and **7**H (Fig. 1), in which can bind in tridentate fashion. In the literatures, binaphthyl-based salicyaldimine NOO-type titanium complexes have been shown that they are efficient chiral cataysts for the asymmetric aldol additions [63–66] and hetero-Diels–Alder reactions [67,68], in which excellent enantioselectivities have been obtained. In this paper, we report on some observations concerning the coordination chemistry of the ligands **1**H_2–**6**H_2 and **7**H (Fig. 1), which are derived from (*R*)-2-amino-2′-hydroxy-1,1′-binaphthyl or (*R*)-2-amino-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl, with titanium isopropoxide, and the use of the resulting complexes as catalysts in asymmetric hydrophosphonylation. For comparison, the C_2-symmetric ligands **8**H_2–**11**H_2 and C_1-symmetric ligand **12**H (Fig. 1), which are derived from (*R*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl or

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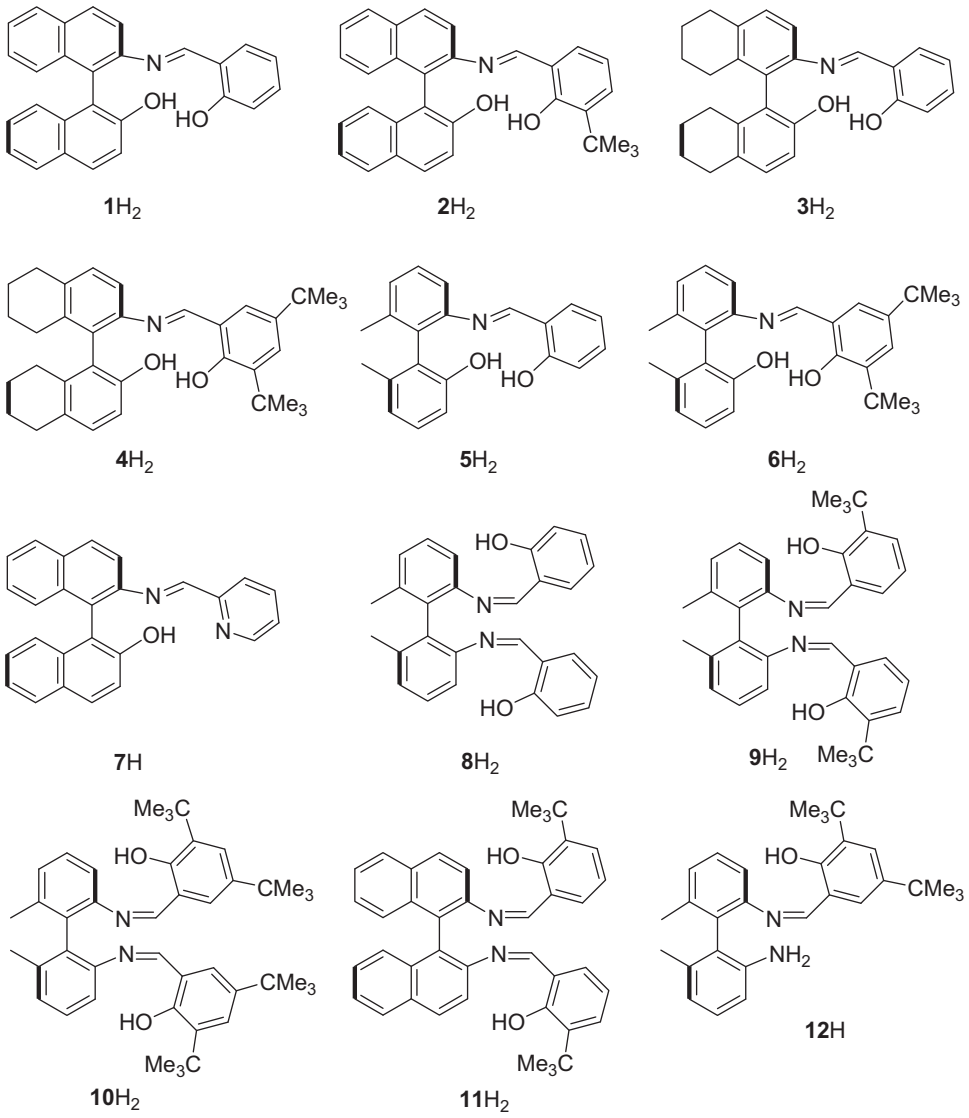


Fig. 1. Chiral Schiff-base ligands.

(*R*)-2,2′-diamino-1,1′-binaphthyl, respectively, will also be included in this contribution.

2. Experimental

2.1. General methods

Titanium complexes and catalytic reactions were performed under an atmosphere of dry dinitrogen with rigorous 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′-hydroxy-1,1′-binaphthyl [40], (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-amino-2′-hydroxy-1,1′-binaphthyl [40], (*R*)-2-amino-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl [40], (*R*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl [56], (*R*)-2,2′-diamino-1,1′-binaphthyl [56], **9**H_2 [56], **10**H_2 [56] and **11**H_2 [56] were prepared according to the literature methods. All chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co., and were used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer. ^{1}H NMR spectra were recorded on a Bruker AV 400 spectrometer. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents. HPLC analyses were conducted on a Shimadzu Series SPD-20A with UV–Vis detector using a Chiralcel AS-H or AD-H or OD-H column (length: 25 cm, inner diameter: 4.6 mm, particle size: 5 μm). Retention time was given in minutes. 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 **1**H_2

Modified method [69]. Salicylaldehyde (1.22 g, 10.0 mmol) was mixed with (*R*)-2-amino-2′-hydroxy-1,1′-binaphthyl (2.85 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 filtrate was concentrated to 10 mL. Yellow microcrystals **1**H_2 were isolated when this solution was kept at −20 °C for two days. Yield: 3.31 g (85%). M.p.: 120–122 °C. ^{1}H NMR (C_6D_6): δ 12.45 (s, 1H, O*H*), 8.23 (s, 1H, C*H*=N), 7.83 (m, 2H, aryl), 7.74 (m, 2H, aryl), 7.57 (d, J = 8.4 Hz, 1H, aryl), 7.36 (m, 1H, aryl), 7.28

(m, 2H, aryl), 7.17 (m, 2H, aryl), 7.11 (m, 2H, aryl), 6.96–6.83 (m, 3H, aryl), 6.62 (t, J = 7.2 Hz, 1H, aryl), 4.73 (s, 1H O*H*). These spectroscopic data were in agreement with those reported in the literature [69].

2.3. Preparation of **2**H_2

Modified method [67]. 3-*tert*-Butylsalicylaldehyde (1.78 g, 10.0 mmol) was mixed with (*R*)-2-amino-2′-hydroxy-1,1′-binaphthyl (2.85 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 column chromatography (*n*-hexane/ethyl acetate = 5:1) to give **2**H_2 as a yellow solid. Yield: 4.09 g (92%). M.p.: 86–88 °C. ^{1}H NMR (C_6D_6): δ 13.28 (s, 1H, O*H*), 8.31 (s, 1H, C*H*=N), 7.80 (m, 4H, aryl), 7.62 (d, J = 8.4 Hz, 1H, aryl), 7.38 (d, J = 8.9 Hz, 1H, aryl), 7.22 (m, 5H, aryl), 7.12 (m, 2H, aryl), 6.87 (d, J = 7.5 Hz, 1H, aryl), 6.71 (t, J = 7.6 Hz, 1H, aryl), 4.52 (br s, 1H, O*H*), 1.45 (s, 9H, CH_3). These spectroscopic data were in agreement with those reported in the literature [67].

2.4. Preparation of **3**H_2

This compound was prepared as a yellow solid from the reaction of salicylaldehyde (1.22 g, 10.0 mmol) with (*R*)-5,5′,6,6′,7,7′,8,8′-*octahydro*-2-amino-2′-hydroxy-1,1′-binaphthyl (2.93 g, 10.0 mmol) in dry toluene (50 mL) in the presence of 4 Å molecular sieves at 70 °C and recrystallization from a solvent mixture of toluene and *n*-hexane (1:4) by a similar procedure as in the synthesis of **1**H_2. Yield: 3.38 g (85%). M.p.: 162–164 °C. ^{1}H NMR (C_6D_6): δ 12.72 (s, 1H, O*H*), 8.32 (s, 1H, C*H*=N), 7.07 (t, J = 8.4 Hz, 2H, aryl), 7.01 (m, 2H, aryl), 6.93 (d, J = 8.2 Hz, 1H, aryl), 6.88 (d, J = 8.2 Hz, 1H, aryl), 6.70 (m, 2H, aryl), 4.26 (br s, 1H, O*H*), 2.80 (m, 4H, CH_2), 2.64 (m, 2H, CH_2), 2.40 (m, 2H, CH_2), 1.77–1.59 (m, 8H, CH_2). IR (KBr, cm^{-1}): ν 3412 (m), 2929 (s), 1617 (s), 1590 (s), 1493 (s), 1469 (s), 1453 (s), 1277 (s), 1205 (s), 1152 (s), 936 (s), 807 (s), 757 (s). *Anal.* Calc. for $C_{27}H_{27}NO_2$: C, 81.58; H, 6.85; N, 3.52. Found: C, 81.61; H, 6.82; N, 3.56%.

2.5. Preparation of **4**H_2

This compound was prepared as a yellow solid from the reaction of 3,5-di-*tert*-butylsalicylaldehyde (2.34 g, 10.0 mmol) with (*R*)-5,5′,6,6′,7,7′,8,8′-*octahydro*-2-amino-2′-hydroxy-1,1′-binaphthyl (2.93 g, 10.0 mmol) in dry toluene (50 mL) in the presence of 4 Å molecular sieves at 70 °C and purified by flash column chromatography (*n*-hexane/ethyl acetate = 5:1) using a similar procedure as in the synthesis of **2**H_2. Yield: 4.13 g (81%). M.p.: 92–94 °C. ^{1}H NMR (C_6D_6): δ 13.46 (s, 1H, O*H*), 8.37 (s, 1H, C*H*=N), 7.62 (d, J = 1.8 Hz, 1H, aryl), 7.11 (m, 3H, aryl), 6.95 (m, 2H, aryl), 4.26 (s, 1H, O*H*), 2.87 (m, 2H, CH_2), 2.75 (m, 2H, CH_2), 2.63 (m, 2H, CH_2), 2.44 (m, 2H, CH_2), 1.84 (m, 4H, CH_2), 1.64 (s, 9H, CH_3), 1.62 (m, 4H, CH_2), 1.41 (s, 9H, CH_3). IR (KBr, cm^{-1}): ν 3435 (m), 2955 (s), 2930 (s), 2859 (s), 1617 (s), 1594 (s), 1473 (s), 1438 (s), 1249 (s), 1171 (s), 1025 (s), 806 (s). *Anal.* Calc. for $C_{35}H_{43}NO_2$: C, 82.47; H, 8.50; N, 2.75. Found: C, 82.51; H, 8.52; N, 2.76%.

2.6. Preparation of **5**H_2

This compound was prepared as an orange solid from the reaction of salicylaldehyde (1.22 g, 10.0 mmol) with (*R*)-2-amino-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl (2.13 g, 10.0 mmol) in dry toluene (50 mL) in the presence of 4 Å molecular sieves at 70 °C and recrystallization from a solvent mixture of toluene and *n*-hexane (10:1) by a similar procedure as in the synthesis of **1**H_2. Yield: 2.66 g (84%). M.p.: 120–122 °C. ^{1}H NMR (C_6D_6): δ 12.67 (s, 1H, O*H*), 8.21 (s, 1H, C*H*=N), 7.17 (m, 2H, aryl), 7.09 (d, J = 7.5 Hz, 1H, aryl), 7.01 (m, 3H, aryl), 6.92 (d, J = 7.6 Hz, 1H, aryl), 6.86 (d, J = 8.1 Hz, 1H, aryl), 6.81 (d, J = 7.9 Hz, 1H, aryl), 6.69 (m, 1H, aryl), 4.32 (s, 1H, O*H*), 2.07 (s, 3H, CH_3), 2.03 (s, 3H, CH_3). These spectroscopic data were in agreement with those reported in the literature [70].

2.7. Preparation of **6**H_2

This compound was prepared as an orange solid from the reaction of 3,5-di-*tert*-butylsalicylaldehyde (2.34 g, 10.0 mmol) with (*R*)-2-amino-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl (2.13 g, 10.0 mmol) in dry toluene (50 mL) in the presence of 4 Å molecular sieves at 70 °C and purified by flash column chromatography (*n*-hexane/ethyl acetate = 5:1) using a similar procedure as in the synthesis of **2**H_2. Yield: 3.65 g (85%). M.p.: 75–77 °C. ^{1}H NMR (C_6D_6): δ 13.29 (s, 1H, O*H*), 8.28 (s, 1H, C*H*=N), 7.62 (d, J = 1.9 Hz, 1H, aryl), 7.21 (t, J = 7.7 Hz, 2H, aryl), 7.10 (d, J = 8.4 Hz, 2H, aryl), 6.92 (d, J = 7.4 Hz, 1H, aryl), 6.86 (t, J = 7.0 Hz, 2H, aryl), 4.54 (br s, 1H, O*H*), 2.09 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.62 (s, 9H, CH_3), 1.40 (s, 9H, CH_3). These spectroscopic data were in agreement with those reported in the literature [70].

2.8. Preparation of **7***H*

This compound was prepared as a yellow solid from the reaction of pyridine-2-carboxaldehyde (1.07 g, 10.0 mmol) with (*R*)-2-amino-2′-hydroxy-1,1′-binaphthyl (2.85 g, 10.0 mmol) in dry toluene (50 mL) in the presence of 4 Å molecular sieves at 70 °C and recrystallization from a toluene solution by a similar procedure as in the synthesis of **1**H_2. Yield: 2.99 g (80%). M.p.: 180–182 °C. ^{1}H NMR (C_6D_6): δ 8.62 (s, 1H, C*H*=N), 7.88 (s, 1H, aryl), 7.61 (m, 2H, aryl), 7.52 (m, 5H, aryl), 7.24 (d, J = 8.0 Hz, 1H, aryl), 7.10–6.95 (m, 5H, aryl), 6.56 (t, J = 6.8 Hz, 1H, aryl), 6.24 (m, 1H, aryl); the proton of the O*H* group was not observed. These spectroscopic data were in agreement with those reported in the literature [69].

2.9. Preparation of **8**H_2

This compound was prepared as an orange solid from the reaction of salicylaldehyde (2,44 g, 20.0 mmol) with (*R*)-2,2′-diamino-6,6′-dimethyl-1,1-biphenyl (2.12 g, 10 mmol) in dry toluene (50 mL) in the presence of 4 Å molecular sieves at 70 °C and purified by flash column chromatography (*n*-hexane/ethyl acetate = 5:1) using a similar procedure as in the synthesis of **2**H_2. Yield: 3.36 g (80%). M.p.: 185–187 °C. ^{1}H NMR (C_6D_6): δ 12.65 (s, 2H, O*H*), 8.17 (s, 2H, N=C*H*), 7.18 (m, 4H, aryl), 6.87 (m, 4H, aryl), 6.78 (m, 4H, aryl), 6.54 (m, 2H, aryl), 2.00 (s, 6H, CH_3). These spectroscopic data were in agreement with those reported in the literature [71].

2.10. Preparation of **12***H*

A drop of H_2O was added to a toluene (5 mL) solution of **10**H_2 (0.65 g, 1 mmol). The solution was warmed up to 65 °C and kept for one hour at this temperature. Solvent was removed, and the residue was purified by flash column chromatography (*n*-hexane/ethyl acetate = 5:1) to give **12**H as a bright yellow solid. Yeild: 0.41 g (95%). M.p.: 93–95 °C. ^{1}H NMR (C_6D_6): δ 13.40 (s, 1H, O*H*), 8.24 (s, 1H, N=C*H*), 7.46 (s, 1H, aryl), 7.13 (m, 4H, aryl), 6.75 (m, 2H, aryl), 6.37 (s, 1H, aryl), 2.96 (s, 2H, N*H*), 2.03 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.53 (s, 9H, CH_3), 1.25 (s, 9H, CH_3). IR (KBr, cm^{-1}): ν 3439 (s), 3420 (s), 3346 (s), 2957 (s), 2905 (s), 2867 (s), 1618 (s), 1568 (s), 1460 (s), 1441 (s), 1360 (s), 1250 (s), 1175 (s), 945 (s), 790 (s). *Anal.* Calc. for $C_{29}H_{36}N_2O$: C, 81.27; H, 8.47; N,

6.54. Found: C, 81.24; H, 8.46; N, 6.44%. This compound could also be prepared in 40% yield by condensation of 3,5-di-*tert*-butylsalicylaldehyde with 1 equiv of (*R*)-2,2′-diamino-6,6′-dimethylbiphenyl in the presence of 4 Å molecular sieves in dry toluene at 70 °C, and purification by flash column chromatography (*n*-hexane/ethyl acetate = 5:1) by a similar procedure as in the synthesis of **2**H_2.

2.11. Preparation of (**L1**)$_2$Ti (**14**)

A toluene solution (10 mL) of **1**H_2 (0.39 g, 1.0 mmol) was slowly added to a toluene solution (10 mL) of Ti(O^{i}Pr)$_4$ (0.28 g, 1.0 mmol) with stirring at room temperature. The resulting yellow solution was stirred at room temperature for one day. The solution was filtered, and the filtrate was concentrated to about 2 mL. Yellow microcrystals **14** were isolated when this solution was kept at room temperature for three days. Yield: 0.29 g (70%). M.p.: 120–122 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.77 (s, 2H, N=C*H*), 7.68 (m, 2H, aryl), 7.56 (m, 4H, aryl), 7.35 (m, 6H, aryl), 6.99 (m, 10H, aryl), 6.66 (m, 2H, aryl), 6.32 (m, 6H, aryl), 5.74 (m, 2H, aryl); these spectroscopic data were in agreement with those reported in the literature [72]. IR (KBr, cm^{-1}): ν 2962 (s), 1598 (s), 1460 (s), 1422 (s), 1260 (s), 1091 (s), 1020 (s), 870 (s), 799 (s). *Anal.* Calc. for $C_{54}H_{34}N_2O_4Ti$: C, 78.83; H, 4.17; N, 3.40. Found: C, 78.85; H, 4.16; N, 3.34%. Yellow crystals **14**·C_7H_8·DME suitable for X-ray structural analysis were grown from a solvent mixture of toluene and DME (10:1).

2.12. Preparation of (**L2**)Ti(O^{i}Pr)$_2$ (**15**)

This compound was prepared as yellow crystals from the reaction of **2**H_2 (0.45 g, 1.0 mmol) with Ti(O^{i}Pr)$_4$ (0.28 g, 1.0 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **14**. Yield: 0.40 g (65%). M.p.: 140–142 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.92 (s, 1H, C*H*=N), 7.79 (m, 2H, aryl), 7.64 (d, *J* = 10.2 Hz, 1H, aryl), 7.58 (m, 2H, aryl), 7.47 (d, *J* = 8.8 Hz, 1H, aryl), 7.41 (d, *J* = 8.4 Hz, 1H, aryl), 7.29 (d, *J* = 7.5 Hz, 1H, aryl), 7.25 (t, *J* = 7.5 Hz, 1H, aryl), 7.10 (t, *J* = 7.2 Hz, 1H, aryl), 7.04 (m, 2H, aryl), 6.98 (t, *J* = 7.4 Hz, 1H, aryl), 6.49 (t, *J* = 7.6 Hz, 1H, aryl), 6.42 (d, *J* = 6.5 Hz, 1H, aryl), 5.27 (m, 1H, OC*H*), 4.74 (m, 1H, OC*H*), 1.61 (s, 9H, CH_3), 1.58 (d, *J* = 6.0 Hz, 3H, CH_3), 1.56 (d, *J* = 6.0 Hz, 3H, CH_3), 1.30 (d, *J* = 6.0 Hz, 3H, CH_3), 1.27 (d, *J* = 6.0 Hz, 3H, CH_3). IR (KBr, cm^{-1}): ν 2962 (s), 1606 (m), 1586 (m), 1548 (m), 1455 (m), 1260 (s), 1090 (s), 1018 (s), 799 (s). *Anal.* Calc. for $C_{37}H_{39}NO_4Ti$: C, 72.90; H, 6.45; N, 2.30. Found: C, 72.85; H, 6.46; N, 2.34%.

2.13. Preparation of (**L2**)$_2$Ti (**16**)

A benzene solution (2 mL) of **15** (61 mg, 0.1 mmol) was warmed up to 60 °C and kept for one hour at this temperature. Yellow crystals, which were identified as (**L2**)$_2$Ti (**16**) by X-ray diffraction analysis, were isolated in 92% yield (43 mg) after this solution was stood at room temperature for one day. M.p.: 266–268 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.51 (s, 2H, C*H*=N), 8.12 (m, 2H, aryl), 7.63 (m, 2H, aryl), 7.38 (m, 4H, aryl), 7.08 (m, 10H, aryl), 6.81 (m, 6H, aryl), 6.70 (m, 2H, aryl), 6.48 (m, 2H, aryl), 6.28 (m, 2H, aryl), 1.42 (s, 18H, CH_3). IR (KBr, cm^{-1}): ν 2959 (s), 1603 (m), 1584 (m), 1541 (m), 1449 (m), 1408 (m), 1260 (s), 1089 (s), 1019 (s), 798 (s). *Anal.* Calc. for $C_{62}H_{50}N_2O_4Ti$: C, 79.65; H, 5.39; N, 3.00. Found: C, 79.55; H, 5.46; N, 2.94%.

2.14. Preparation of (**L3**)Ti(O^{i}Pr)$_2$·(**L3**)$_2$Ti (**17**·**18**)

A toluene solution (10 mL) of **3**H_2 (0.40 g, 1.0 mmol) was slowly added to a toluene solution (10 mL) of Ti(O^{i}Pr)$_4$ (0.28 g, 1.0 mmol) with stirring at room temperature. The resulting yellow solution was stirred at room temperature for one day. The solution was filtered, and the filtrate was concentrated to about 2 mL. Yellow crystals, which were identified as **17**·**18** by X-ray diffraction analysis, were isolated after this solution was kept at room temperature for three days. Yield: 0.28 g (60%). M.p: 170–172 °C (dec.). **17**: ^{1}H NMR (C_6D_6): 8.01 (s, 1H, N=C*H*), 7.08–5.80 (m, 8H, aryl), 5.24 (m, 1H, OC*H*), 4.75 (m, 1H, OC*H*), 2.69–1.25 (m, 28H, CH_2 and CH_3). **18**: ^{1}H NMR (C_6D_6): 8.15 (s, 2H, N = C*H*), 7.08–5.80 (m, 16H, aryl), 2.69–1.25 (m, 32H, CH_2). IR (KBr, cm^{-1}): ν 2962 (s), 1606 (s), 1542 (m), 1439 (s), 1260 (s), 1092 (s), 1018 (s), 799 (s). *Anal.* Calc. for $C_{87}H_{89}N_3O_8Ti_2$: C, 74.62; H, 6.41; N, 3.00. Found: C, 74.65; H, 6.46; N, 2.96%. The ^{1}H NMR spectrum of the mixture **17**·**18** could not be assigned unambiguously, but on the basis of the analogous complexes **15** and **16**, their C*H* = N groups were assigned, which showed that the ratio of **17**/**18** is 1:1.

2.15. Preparation of (**L4**)Ti(O^{i}Pr)$_2$ (**19**)

This compound was prepared as yellow crystals from the reaction of **4**H_2 (0.51 g, 1.0 mmol) with Ti(O^{i}Pr)$_4$ (0.28 g, 1.0 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **14**. Yield: 0.55 g (82%). M.p.: 182–184 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.19 (s, 1H, N=C*H*), 7.56 (s, 1H, aryl), 7.14 (d, *J* = 8.2 Hz, 1H, aryl), 7.09 (d, *J* = 7.9 Hz, 1H, aryl), 6.94 (d, *J* = 7.9 Hz, 1H, aryl), 6.89 (d, *J* = 8.2 Hz, 1H, aryl), 6.85 (s, 1H, aryl), 5.32 (m, 1H, OC*H*), 4.80 (m, 1H, OC*H*), 2.74 (m, 4H, CH_2), 2.44 (m, 2H, CH_2), 2.30 (m, 2H, CH_2), 1.65 (s, 9H, CH_3), 1.59 (d, *J* = 6.1 Hz, 3H, CH_3), 1.55 (d, *J* = 6.1 Hz, 3H, CH_3), 1.46 (m, 8H, CH_2), 1.29 (d, *J* = 6.1 Hz, 3H, CH_3), 1.19 (s, 9H, C(CH_3)$_3$), 1.08 (d, *J* = 6.1 Hz, 3H, CH_3). IR (KBr, cm^{-1}): ν 2960 (s), 2922 (s), 1556 (s), 1469 (s), 1258 (s), 1113 (s), 1018 (s), 988 (s), 810 (s). *Anal.* Calc. for $C_{41}H_{55}NO_4Ti$: C, 73.09; H, 8.23; N, 2.08. Found: C, 73.15; H, 8.25; N, 2.04%.

2.16. Preparation of (**L5**)Ti(O^{i}Pr)$_2$·(**L5**)$_2$Ti (**20**·**21**)

This compound was prepared as yellow crystals from the reaction of **5**H_2 (0.32 g, 1.0 mmol) with Ti(O^{i}Pr)$_4$ (0.28 g, 1.0 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **17**·**18**. Yield: 0.24 g (63%). M.p.: 185–187 °C (dec.). **20**: ^{1}H NMR (C_6D_6): δ 7.99 (s, 1H, N=C*H*), 7.10 (m, 1H, aryl), 7.06 (m, 1H, aryl), 7.02 (m, 1H, aryl), 6.94 (m, 3H, aryl), 6.75 (m, 1H, aryl), 6.66 (m, 3H, aryl), 5.29 (m, 1H, OC*H*), 4.80 (m, 1H, OC*H*), 2.16 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 1.62 (br s, 6H, CH_3), 1.16 (br s, 6H, CH_3). **21**: ^{1}H NMR (C_6D_6): δ 7.85 (s, 2H, N=C*H*), 7.41 (m, 2H, aryl), 7.00 (m, 4H, aryl), 6.88 (m, 4H, aryl), 6.80 (m, 4H, aryl), 6.62 (m, 4H, aryl), 6.51 (m, 2H, aryl), 2.25 (s, 6H, CH_3), 1.91 (s, 6H, CH_3). IR (KBr, cm^{-1}): ν 2962 (s), 1604 (m), 1439 (m), 1260 (s), 1091 (s), 1019 (s), 798 (s). *Anal.* Calc. for $C_{69}H_{65}N_3O_8Ti_2$: C, 71.44; H, 5.65; N, 3.62. Found: C, 71.45; H, 5.56; N, 3.64%. The ^{1}H NMR spectrum of the mixture **20**·**21** could not be assigned unambiguously, but according to the analogous complexes **15** and **16**, their C*H*=N groups were assigned, which showed that the ratio of **20**/**21** is 1:1.

2.17. Preparation of (**L5**)$_2$Ti (**21**)

A benzene solution (2 mL) of mixture **20**·**21** (232 mg, 0.2 mmol) was warmed up to 60 °C and kept for one hour at this temperature. Yellow microcrystals were isolated in 90% yield (183 mg) after this solution was kept at room temperature for two days. M.p.: 280–282 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.85 (s, 2H, N=C*H*), 7.41 (m, 2H, aryl), 7.00 (m, 4H, aryl), 6.88 (m, 4H, aryl), 6.80 (m, 4H, aryl), 6.62 (m, 4H, aryl), 6.51 (m, 2H, aryl), 2.25 (s, 6H, CH_3), 1.91 (s, 6H, CH_3). IR (KBr, cm^{-1}): ν 2964 (s), 1607 (s), 1544 (s), 1430 (s),

1376 (s), 1260 (s), 1093 (s), 1019 (s), 796 (s). *Anal.* Calc. for $C_{42}H_{34}N_2O_4Ti$: C, 74.34; H, 5.05; N, 4.13. Found: C, 74.35; H, 5.09; N, 4.04%.

2.18. Preparation of (**L6**)Ti(O^{i}Pr)$_2$ (**22**)

This compound was prepared as yellow microcrystals from the reaction of **6**H$_2$ (0.43 g, 1.0 mmol) with Ti(O^{i}Pr)$_4$ (0.28 g, 1.0 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **14**. Yield: 0.44 g (74%). M.p.: 180–182 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.00 (s, 1H, N=C*H*), 7.56 (d, *J* = 2.0 Hz, 1H, aryl), 7.12 (s, 1H, aryl), 7.06 (m, 2H, aryl), 6.98 (t, *J* = 7.6 Hz, 1H, aryl), 6.84 (d, *J* = 7.2 Hz, 1H, aryl), 6.75 (s, 1H, aryl), 6.62 (d, *J* = 7.2 Hz, 1H, aryl), 5.34 (m, 1H, OC*H*), 4.88 (m, 1H, OC*H*), 2.17 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 1.70 (s, 9H, CH_3), 1.64 (d, *J* = 6.2 Hz, 3H, CH_3), 1.61 (d, *J* = 6.2 Hz, 3H, CH_3), 1.27 (s, 9H, CH_3), 1.22 (d, *J* = 6.00 Hz, 3H, CH_3), 1.13 (d, *J* = 6.00 Hz, 3H, CH_3). IR (KBr, cm^{-1}): *v* 2956 (s), 1560 (m), 1445 (s), 1260 (s), 1098 (s), 1016 (s), 801 (s). *Anal.* Calc. for $C_{35}H_{47}NO_4Ti$: C, 70.82; H, 7.98; N, 2.36. Found: C, 70.85; H, 7.92; N, 2.34%.

2.19. Preparation of (**L7**)$_2$Ti(O^{i}Pr)$_2$ (**23**)

This compound was prepared as yellow crystals from the reaction of **7**H (0.37 g, 1.0 mmol) with Ti(O^{i}Pr)$_4$ (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 **14**. Yield: 0.27 g (61%). M.p.: 125–127 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.68 (s, 1H, N=C*H*), 8.55 (s, 1H, N=C*H*), 7.84 (m, 8H, aryl), 7.57 (m, 6H, aryl), 7.45 (m, 6H, aryl), 7.21 (m, 6H, aryl), 6.82 (m, 4H, aryl), 6.70 (m, 2H, aryl), 5.45 (m, 1H, OC*H*), 4.67 (m, 1H, OC*H*), 1.36 (br s, 6H, CH_3), 1.16 (d, *J* = 6.0 Hz, 3H, CH_3), 1.06 (d, *J* = 6.0 Hz, 3H, CH_3). IR (KBr, cm^{-1}): *v* 2961 (s), 1612 (m), 1451 (m), 1260 (s), 1090 (s), 1017 (s), 799 (s). *Anal.* Calc. for $C_{58}H_{48}N_4O_4Ti$: C, 76.31; H, 5.30; N, 6.14. Found: C, 76.29; H, 5.36; N, 6.12%.

2.20. Preparation of (**L7**)$_3$Ti(O^{i}Pr) (**24**)

This compound was prepared as yellow crystals from the reaction of **7**H (0.56 g, 1.5 mmol) with Ti(O^{i}Pr)$_4$ (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 **14**. Yield: 0.39 g (63%). M.p.: 110–112 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.64 (s, 1H, N=C*H*), 8.51 (s, 1H, N=C*H*), 8.42 (s, 1H, N=C*H*), 7.84 (m, 12H, aryl), 7.60 (m, 11H, aryl), 7.11 (m, 14H, aryl), 6.93 (m, 4H, aryl), 6.74 (m, 4H, aryl), 6.46 (m, 3H, aryl), 5.47 (m, 1H, OC*H*), 1.27 (br s, 3H, CH_3), 1.17 (br s, 3H, CH_3). IR (KBr, cm^{-1}): *v* 2962 (s), 1607 (m), 1581 (m), 1260 (s), 1093 (s), 1019 (s), 799 (s). *Anal.* Calc. for $C_{81}H_{58}N_6O_4Ti$: C, 79.27; H, 4.76; N, 6.85. Found: C, 79.25; H, 4.76; N, 6.84%.

2.21. Preparation of (**L12**)Ti(O^{i}Pr)$_3$ (**25**)

This compound was prepared as yellow microcrystals from the reaction of **12**H (0.43 g, 1.0 mmol) with Ti(O^{i}Pr)$_4$ (0.28 g, 1.0 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **14**. Yield: 0.44 g (67%). M.p.: 116–118 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.01 (d, *J* = 8.0 Hz, 1H, aryl), 7.90 (s, 1H, N=C*H*), 7.55 (d, *J* = 2.8 Hz, 1H, aryl), 7.27 (t, *J* = 7.6 Hz, 1H, aryl), 7.04 (d, *J* = 7.2 Hz, 1H, aryl), 6.74 (t, *J* = 7.6 Hz, 1H, aryl), 6.71 (d, *J* = 2.4 Hz, 1H, aryl), 6.47 (d, *J* = 7.6 Hz, 1H, aryl), 6.16 (d, *J* = 8.4 Hz, 1H, aryl), 4.94 (m, 3H, OC*H*), 3.93 (s, 2H, NH_2), 2.0 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 1.67 (s, 9H, CH_3), 1.26 (s, 9H, CH_3), 1.24 (s, 9H, CH_3), 1.21 (s, 9H, CH_3). IR (KBr, cm^{-1}): *v* 3455 (m), 2952 (s), 1601 (m), 1355 (s), 1261 (s), 1094 (s), 1019 (s), 800 (s). *Anal.* Calc. for $C_{38}H_{56}N_2O_4Ti$: C, 69.92; H, 8.65; N, 4.29. Found: C, 69.90; H, 8.66; N, 4.34%.

2.22. Preparation of (**L8**)Ti(O^{i}Pr)$_2$ (**26**)

This compound was prepared as yellow microcrystals from the reaction of **8**H$_2$ (0.42 g, 1.0 mmol) with Ti(O^{i}Pr)$_4$ (0.28 g, 1.0 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **14**. Yield: 0.40 g (68%). M.p.: 155–157 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.64 (s, 2H, N=C*H*), 7.22 (d, *J* = 6.4 Hz, 2H, aryl), 7.05 (t, *J* = 7.2 Hz, 4H, aryl), 6.90 (d, *J* = 4.8 Hz, 2H, aryl), 6.81 (d, *J* = 6.8 Hz, 2H, aryl), 6.62 (d, *J* = 6.4 Hz, 2H, aryl), 6.43 (m, 2H, aryl), 4.96 (m, 2H, OC*H*), 1.79 (s, 6H, CH_3), 1.29 (br s, 6H, CH_3), 1.22 (br s, 6H, CH_3). IR (KBr, cm^{-1}): *v* 2961 (s), 1607 (s), 1535 (m), 1442 (s), 1260 (vs), 1089 (s), 1017 (s), 798 (s). *Anal.* Calc. for $C_{34}H_{36}N_2O_4Ti$: C, 69.86; H, 6.21; N, 4.79. Found: C, 69.84; H, 6.26; N, 4.74%.

2.23. Preparation of (**L9**)Ti(O^{i}Pr)$_2$ (**27**)

This compound was prepared as yellow microcrystals from the reaction of **9**H$_2$ (0.53 g, 1.0 mmol) with Ti(O^{i}Pr)$_4$ (0.28 g, 1.0 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **14**. Yield: 0.58 g (83%). M.p.: 140–142 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.64 (s, 2H, N=C*H*), 7.30 (d, *J* = 6.4 Hz, 2H, aryl), 7.18 (d, *J* = 7.6 Hz, 2H, aryl), 6.92 (t, *J* = 8.0 Hz, 2H, aryl), 6.75 (d, *J* = 7.2 Hz, 2H, aryl), 6.58 (d, *J* = 7.2 Hz, 2H, aryl), 6.49 (t, *J* = 7.6 Hz, 2H, aryl), 4.67 (m, 2H, OC*H*), 1.80 (s, 6H, CH_3), 1.71 (s, 18H, CH_3), 1.12 (d, *J* = 6.0 Hz, 6H, CH_3), 1.08 (d, *J* = 6.4 Hz, 6H, CH_3). IR (KBr, cm^{-1}): *v* 2970 (s), 1605 (s), 1544 (s), 1403 (s), 1298 (s), 1260 (s), 1089 (s), 1008 (s), 795 (s). *Anal.* Calc. for $C_{42}H_{52}N_2O_4Ti$: C, 72.40; H, 7.52; N, 4.02. Found: C, 72.35; H, 7.46; N, 4.04%.

2.24. Preparation of (**L10**)Ti(O^{i}Pr)$_2$ (**28**)

This compound was prepared as yellow microcrystals from the reaction of **10**H$_2$ (0.64 g, 1.0 mmol) with Ti(O^{i}Pr)$_4$ (0.28 g, 1.0 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **14**. Yield: 0.63 g (78%). M.p.: 175–177 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.70 (s, 2H, N=C*H*), 7.23 (d, *J* = 7.6 Hz, 2H, aryl), 7.18 (d, *J* = 7.6 Hz, 2H, aryl), 6.96 (m, 2H, aryl), 6.85 (m, 2H, aryl), 6.53 (m, 2H, aryl), 4.66 (m, 2H, OC*H*), 1.80 (s, 6H, CH_3), 1.78 (s, 18H, CH_3), 1.17 (s, 18H, CH_3), 1.10 (d, *J* = 6.0 Hz, 6H, CH_3), 1.05 (d, *J* = 6.0 Hz, 6H, CH_3). IR (KBr, cm^{-1}): *v* 2964 (s), 1533 (s), 1430 (s), 1387 (s), 1260 (s), 1097 (s), 1016 (s), 799 (s). *Anal.* Calc. for $C_{50}H_{68}N_2O_4Ti$: C, 74.24; H, 8.47; N, 3.46. Found: C, 74.25; H, 8.46; N, 3.34%.

2.25. Preparation of (**L11**)Ti(O^{i}Pr)$_2$ (**29**)

This compound was prepared as yellow crystals from the reaction of **11**H$_2$ (0.60 g, 1.0 mmol) with Ti(O^{i}Pr)$_4$ (0.28 g, 1.0 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **14**. Yield: 0.48 g (62%). M.p.: 96–98 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.98 (s, 2H, N=C*H*), 7.80 (d, *J* = 7.6 Hz, 2H, aryl), 7.73 (d, *J* = 8.0 Hz, 2H, aryl), 7.70 (m, 4H, aryl), 7.22 (d, *J* = 7.2 Hz, 2H, aryl), 6.89 (t, *J* = 7.6 Hz, 2H, aryl), 6.82 (d, *J* = 8.4 Hz, 2H, aryl), 6.73 (d, *J* = 7.2 Hz, 2H, aryl), 6.61 (t, *J* = 7.6 Hz, 2H, aryl), 4.96 (m, 2H, OC*H*), 1.72 (s, 18H, CH_3), 1.14 (d, *J* = 6.0 Hz, 6H, CH_3), 1.09 (d, *J* = 6.0 Hz, 6H, CH_3). IR (KBr, cm^{-1}): *v* 2959 (s), 1604 (m), 1547 (m), 1454 (m), 1384 (s), 1260 (s), 1087 (s), 1016 (s), 799 (s). *Anal.* Calc. for $C_{48}H_{52}N_2O_4Ti$: C, 74.99; H, 6.82; N, 3.64. Found: C, 74.95; H, 6.86; N, 3.62%.

Table 1
Crystal data and experimental parameters for compounds **14–19**.

Compound	**14**·C_7H_8·DME	**15**	**16**	**17**·**18**	**19**
Formula	$C_{65}H_{52}N_2O_6Ti$	$C_{74}H_{78}N_2O_8Ti_2$	$C_{62}H_{50}N_2O_4Ti$	$C_{87}H_{89}N_3O_8Ti_2$	$C_{41}H_{55}NO_4Ti$
Formula weight	1004.99	1219.18	934.94	1400.41	673.76
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$
a (Å)	11.451(1)	11.732(3)	13.487(1)	13.272(1)	10.021(2)
b (Å)	15.465(1)	20.372(5)	18.250(2)	18.675(2)	10.796(2)
c (Å)	28.495(2)	13.555(3)	26.636(2)	15.438(2)	34.202(5)
α (°)	90	90	90	90	90
β (°)	90	95.24(1)	90	107.91(1)	90
γ (°)	90	90	90	90	90
V (Å^3)	5046.0(7)	3226.1(13)	6556.1(10)	3640.9(6)	3700.1(11)
Z	4	2	4	2	4
D_{calc} (g/cm^3)	1.323	1.255	0.947	1.277	1.209
Size (mm)	0.35 × 0.26 × 0.22	0.26 × 0.24 × 0.20	0.32 × 0.28 × 0.24	0.35 × 0.28 × 0.23	0.34 × 0.18 × 0.16
F(000)	2104	1288	1960	1480	1448
2θ range (°)	3.88–50.50	3.48–55.80	3.06–55.74	3.54–50.50	5.16–144.90
No. of reflections collected	25550	32252	48341	18511	30605
No. of unique reflections (R_{int})	9127 (0.0611)	14935 (0.0301)	15524 (0.0381)	12619 (0.0379)	7042 (0.0461)
No. of observed reflections	7646	12707	14499	10715	6375
Absorbed corrections (T_{max}, T_{min})	0.95, 0.92	0.94, 0.92	0.96, 0.95	0.94, 0.91	0.71, 0.51
R	0.045	0.041	0.048	0.055	0.030
R_w	0.095	0.086	0.141	0.124	0.070
$wR2$ (all data)	0.101	0.088	0.145	0.133	0.071
Goodness-of-fit	1.02	1.02	1.12	1.06	1.01
Flack χ	−0.01(2)	−0.01(1)	0.05(2)	−0.01(2)	0.01(1)

Table 2
Crystal data and experimental parameters for compounds **20**·**21**, **23**, **24** and **29**.

Compound	**20**·**21**	**23**·**THF**	**24**	**29**
Formula	$C_{69}H_{65}N_3O_8Ti$	$C_{58}H_{48}N_4O_4Ti$	$C_{81}H_{58}N_6O_4Ti$	$C_{48}H_{52}N_2O_4Ti$
Formula weight	1160.04	912.90	1227.23	768.82
Crystal system	monoclinic	hexagonal	orthorhombic	orthorhombic
Space group	$P2_1$	$P6_5$	$P2_12_12_1$	$C222_1$
a (Å)	12.960(1)	25.644(1)	14.426(4)	18.434(3)
b (Å)	12.081(1)	25.644(1)	17.398(4)	18.468(3)
c (Å)	19.156(2)	14.326(1)	34.210(8)	24.873(4)
α (°)	90	90	90	90
β (°)	91.36(1)	90	90	90
γ (°)	90	120	90	90
V (Å^3)	2998.3(4)	8158.3(5)	8586(4)	8468(3)
Z	2	6	4	8
D_{calc} (g/cm^3)	1.285	1.115	0.949	1.206
Size (mm)	0.43 × 0.20 × 0.13	0.40 × 0.20 × 0.20	0.24 × 0.22 × 0.20	0.30 × 0.28 × 0.22
F(000)	1216	2868	2560	3264
2θ range (deg)	3.84–55.20	3.66–50.00	2.62–55.74	4.42–50.50
No. of reflections collected	18075	40525	69473	20,867
No. of unique reflections [$R_{(int)}$]	12757 (0.0499)	9548 (0.0564)	20430 (0.0992)	7631 (0.0333)
No. of observed reflections	9274	6177	13858	7399
Absorbed corrections (T_{max}, T_{min})	0.96, 0.87	0.96, 0.92	0.97, 0.96	0.95, 0.93
R	0.064	0.062	0.069	0.029
R_w	0.117	0.171	0.145	0.064
$wR2$ (all data)	0.132	0.188	0.157	0.065
Goodness-of-fit	1.03	1.12	1.01	1.09
Flack χ	−0.03(2)	−0.02(3)	0.07(2)	0.01(2)

2.26. General procedure for asymmetric hydrophosphonylation of aromatic aldehydes

In a nitrogen-filled glove box, titanium complex (0.05 mmol) was dissolved in toluene or THF (1.0 mL). Aldehyde (0.5 mmol) and dimethyl phosphite (0.65 mmol) were added successively into the solution at 20 °C. After the solution was stirred at this temperature for 48 h, solvent was removed. CH_2Cl_2 (10 mL) and 2 M $NaHCO_3$ (10 mL) were added and stirred for 0.5 h, then extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with brine (20 mL) and dried with anhydrous Na_2SO_4, then filtered. The solvent was removed, and the resulting residue was further purified by flash column chromatography on silica gel (acetone/*n*-hexane 1:5–1:1). Enantiomeric excesses were determined by HPLC analysis using a Chiralcel AS-H or AD-H or OD-H column.

2.26.1. Dimethyl hydroxyl (phenyl) methylphosphonate [25]

HPLC (AS-H, 254 nm, hexane/2-propanol = 80:20, 0.8 mL/min): t_R = 11.0 and 13.0 min. ^{1}H NMR ($CDCl_3$): δ 7.48 (m, 2H, Ph), 7.35 (m, 3H, Ph), 5.05 (d, J = 10.8 Hz, 1H, C*H*), 3.70 (d, J = 10.4 Hz, 3H, CH_3), 3.66 (d, J = 10.4 Hz, 3H, CH_3); the proton of the O*H* group was not observed.

2.26.2. Dimethyl hydroxyl (4-chlorophenyl) methylphosphonate [25]

HPLC (AS-H, 254 nm, hexane/2-propanol = 80:20, 0.8 mL/min): t_R = 14.6 and 17.9 min. ^{1}H NMR ($CDCl_3$): δ 7.42 (d, J = 8.4 Hz, 2H,

Table 3
Selected bond distances (Å) and bond angles (°) for compounds **14**–**21**, **23**, **24** and **29**.

*Compound **14***			
Ti(1)–O(1)	1.863(2)	Ti(1)–O(2)	1.890(2)
Ti(1)–O(3)	1.867(2)	Ti(1)–O(4)	1.880(2)
Ti(1)–N(1)	2.238(2)	Ti(1)–N(2)	2.219(2)
O(1)–Ti(1)–O(2)	96.22(9)	O(1)–Ti(1)–O(3)	102.46(8)
O(1)–Ti(1)–O(4)	94.70(9)	O(2)–Ti(1)–O(3)	93.82(8)
O(2)–Ti(1)–O(4)	161.09(8)	O(3)–Ti(1)–O(4)	98.84(8)
O(1)–Ti(1)–N(1)	85.31(8)	O(1)–Ti(1)–N(2)	171.93(8)
O(2)–Ti(1)–N(1)	79.85(8)	O(2)–Ti(1)–N(2)	87.23(8)
O(3)–Ti(1)–N(1)	170.55(9)	O(3)–Ti(1)–N(2)	84.54(8)
O(4)–Ti(1)–N(1)	85.72(9)	O(4)–Ti(1)–N(2)	80.10(8)
N(2)–Ti(1)–N(1)	88.13(8)	torsion (aryl–aryl)	58.5(3), 64.0(3)
*Compound **15***			
Ti(1)–O(1)	1.889(2)	Ti(1)–O(2)	1.879(2)
Ti(1)–O(3)	1.775(2)	Ti(1)–O(4)	1.792(2)
Ti(1)–N(1)	2.211(2)	O(1)–Ti(1)–O(2)	129.17(7)
O(1)–Ti(1)–O(3)	96.68(7)	O(1)–Ti(1)–O(4)	114.98(7)
O(2)–Ti(1)–O(3)	93.64(7)	O(2)–Ti(1)–O(4)	111.55(7)
O(3)–Ti(1)–O(4)	100.85(8)	O(1)–Ti(1)–N(1)	83.10(6)
O(2)–Ti(1)–N(1)	80.58(7)	O(3)–Ti(1)–N(1)	172.15(8)
O(4)–Ti(1)-N(1)	86.28(7)	Torsion (aryl–aryl)	68.0(2)
*Compound **16***			
Ti(1)–O(1)	1.865(2)	Ti(1)–O(2)	1.893(2)
Ti(1)–O(3)	1.858(2)	Ti(1)–O(4)	1.901(2)
Ti(1)–N(1)	2.220(2)	Ti(1)–N(2)	2.230(2)
O(1)–Ti(1)–O(2)	96.34(7)	O(1)–Ti(1)–O(3)	104.61(7)
O(1)–Ti(1)–O(4)	94.83(7)	O(2)–Ti(1)–O(3)	92.77(7)
O(2)–Ti(1)–O(4)	162.34(7)	O(3)–Ti(1)–O(4)	97.60(7)
O(1)–Ti(1)–N(1)	86.03(7)	O(1)–Ti(1)–N(2)	169.57(7)
O(2)–Ti(1)–N(1)	79.30(7)	O(2)–Ti(1)–N(2)	88.00(7)
O(3)–Ti(1)–N(1)	167.48(7)	O(3)–Ti(1)–N(2)	84.59(7)
O(4)–Ti(1)–N(1)	87.89(7)	O(4)–Ti(1)–N(2)	78.85(7)
N(1)–Ti(1)–N(2)	85.46(7)	Torsion (aryl–aryl)	59.3(2), 64.4(2)
*Compound **17**·**18***			
Ti(1)–O(1)	1.857(3)	Ti(1)–O(2)	1.918(3)
Ti(1)–O(3)	1.853(3)	Ti(1)–O(4)	1.943(3)
Ti(1)–N(1)	2.197(3)	Ti(1)–N(2)	2.188(3)
Ti(2)–O(5)	1.865(3)	Ti(2)–O(6)	1.859(3)
Ti(2)–O(7)	1.766(3)	Ti(2)–O(8)	1.811(3)
Ti(2)–N(3)	2.294(3)	O(1)–Ti(1)–O(2)	163.37(11)
O(1)–Ti(1)–O(3)	98.77(11)	O(1)–Ti(1)–O(4)	88.88(11)
O(2)–Ti(1)–O(3)	91.84(11)	O(2)–Ti(1)–O(4)	83.93(11)
O(3)–Ti(1)–O(4)	164.76(11)	O(1)–Ti(1)–N(1)	84.69(11)
O(1)–Ti(1)–N(2)	97.19(11)	O(2)–Ti(1)–N(1)	81.49(11)
O(2)–Ti(1)–N(2)	96.54(12)	O(3)–Ti(1)–N(1)	95.90(12)
O(3)–Ti(1)–N(2)	84.52(11)	O(4)–Ti(1)–N(1)	97.92(11)
O(4)–Ti(1)–N(2)	81.45(11)	N(1)–Ti(1)–N(2)	177.99(12)
O(5)–Ti(2)–O(6)	129.51(14)	O(5)–Ti(2)–O(7)	111.36(15)
O(5)-Ti(2)–O(7)	95.26(14)	O(6)–Ti(2)–O(7)	114.32(16)
O(6)–Ti(2)-O(8)	95.27(15)	O(7)–Ti(2)–O(8)	102.05(17)
O(5)–Ti(2)-N(3)	82.00(12)	O(6)–Ti(2)–N(3)	81.57(12)
O(7)–Ti(2)–N(3)	85.11(14)	O(8)–Ti(2)–N(3)	172.85(15)
torsion (aryl–aryl)	**17**: 63.2(4)**18**: 64.4(4), 68.4(4)		
*Compound **19***			
Ti(1)–O(1)	1.864(1)	Ti(1)–O(2)	1.882(1)
Ti(1)–O(3)	1.801(1)	Ti(1)–O(4)	1.783(1)
Ti(1)–N(1)	2.269(1)	O(1)–Ti(1)–O(2)	124.07(6)
O(1)–Ti(1)–O(3)	113.05(6)	O(1)–Ti(1)–O(4)	96.76(6)
O(2)–Ti(1)–O(3)	117.70(6)	O(2)–Ti(1)–O(4)	96.25(6)
O(3)–Ti(1)–O(4)	99.97(7)	O(1)–Ti(1)–N(1)	85.67(6)
O(2)–Ti(1)–N(1)	79.04(5)	O(3)–Ti(1)–N(1)	82.71(6)
O(4)–Ti(1)–N(1)	175.28(6)	torsion (aryl–aryl)	71.0(2)
*Compound **20**·**21***			
Ti(1)–O(1)	1.846(3)	Ti(1)–O(2)	1.900(3)
Ti(1)–O(3)	1.879(3)	Ti(1)–O(4)	1.852(3)
Ti(1)–N(1)	2.230(3)	Ti(1)–N(2)	2.251(3)
Ti(2)–O(5)	1.895(4)	Ti(2)–O(6)	1.865(3)
Ti(2)–O(7)	1.777(3)	Ti(2)–O(8)	1.787(3)
Ti(2)–N(3)	2.246(4)	O(1)–Ti(1)–O(2)	98.71(12)
O(1)–Ti(1)–O(3)	93.99(11)	O(1)–Ti(1)–O(4)	99.86(11)
O(2)–Ti(1)–O(3)	159.17(11)	O(2)–Ti(1)–O(4)	94.20(11)
O(3)–Ti(1)–O(4)	99.84(12)	O(1)–Ti(1)–N(1)	86.06(11)
O(1)–Ti(1)–N(2)	173.72(12)	O(2)–Ti(1)–N(1)	79.49(11)

O(2)–Ti(1)–N(2)	86.40(11)	O(3)–Ti(1)–N(1)	85.01(12)
O(3)–Ti(1)–N(2)	80.09(11)	O(4)–Ti(1)–N(1)	172.00(12)
O(4)–Ti(1)–N(2)	83.32(11)	N(1)–Ti(1)–N(2)	91.32(11)
O(5)–Ti(2)–O(6)	132.65(14)	O(5)–Ti(2)–O(7)	110.93(16)
O(5)–Ti(2)–O(8)	92.73(18)	O(6)–Ti(2)–O(7)	112.12(15)
O(6)–Ti(2)–O(8)	96.93(16)	O(7)–Ti(2)–O(8)	101.84(16)
O(5)–Ti(2)–N(3)	80.90(15)	O(6)–Ti(2)–N(3)	82.93(13)
O(7)–Ti(2)–N(3)	86.51(13)	O(8)–Ti(2)–N(3)	170.95(17)
torsion (aryl–aryl)	**20**: 60.7(4)**21**: 64.1(4), 58.0(4)		
*Compound **23***			
Ti(1)–O(1)	1.952(3)	Ti(1)–O(2)	1.892(3)
Ti(1)–O(3)	1.824(3)	Ti(1)–O(4)	1.790(3)
Ti(1)–N(1)	2.298(3)	Ti(1)–N(2)	2.270(3)
O(1)–Ti(1)–O(2)	159.83(13)	O(1)–Ti(1)–O(3)	96.52(13)
O(1)-Ti(1)–O(4)	91.47(14)	O(2)–Ti(1)–O(3)	98.11(14)
O(2)–Ti(1)–O(4)	98.09(13)	O(3)–Ti(1)–O(4)	104.88(14)
O(1)–Ti(1)-N(1)	88.19(12)	O(1)–Ti(1)–N(2)	74.92(12)
O(2)–Ti(1)–N(1)	78.88(12)	O(2)–Ti(1)-N(2)	86.10(12)
O(3)–Ti(1)–N(1)	86.75(13)	O(3)–Ti(1)–N(2)	155.50(14)
O(4)–Ti(1)–N(1)	168.33(14)	O(4)–Ti(1)–N(2)	98.34(14)
N(1)–Ti(1)–N(2)	70.31(12)	torsion (aryl–aryl)	62.3(4), 69.2(4)
*Compound **24***			
Ti(1)–O(1)	1.907(2)	Ti(1)–O(2)	1.856(2)
Ti(1)–O(3)	1.909(2)	Ti(1)–O(4)	1.768(2)
Ti(1)–N(1)	2.255(3)	Ti(1)–N(2)	2.280(3)
O(1)–Ti(1)–O(2)	97.81(10)	O(1)–Ti(1)–O(3)	160.10(9)
O(1)–Ti(1)–O(4)	94.25(11)	O(2)–Ti(1)–O(3)	97.88(10)
O(2)–Ti(1)–O(4)	104.39(10)	O(3)–Ti(1)–O(4)	93.63(10)
O(1)–Ti(1)–N(1)	76.99(10)	O(1)–Ti(1)–N(2)	85.67(10)
O(2)–Ti(1)–N(1)	156.31(10)	O(2)–Ti(1)–N(2)	86.58(10)
O(3)–Ti(1)–N(1)	83.74(10)	O(3)–Ti(1)–N(2)	83.13(10)
O(4)–Ti(1)–N(1)	99.07(10)	O(4)–Ti(1)–N(2)	168.92(11)
N(1)–Ti(1)–N(2)	70.09(10)	torsion (aryl–aryl)	63.9(3), 83.2(3), 87.6(3)
*Compound **29***			
Ti(1)–O(1)	1.931(2)	Ti(1)–O(2)	1.945(2)
Ti(1)–O(3)	1.778(2)	Ti(1)–O(4)	1.777(2)
Ti(1)–N(1)	2.277(2)	Ti(1)–N(2)	2.269(2)
O(1)–Ti(1)–O(2)	165.35(7)	O(1)–Ti(1)–O(3)	94.72(8)
O(1)–Ti(1)–O(4)	93.69(8)	O(2)–Ti(1)–O(3)	94.66(8)
O(2)–Ti(1)–O(4)	94.60(8)	O(3)–Ti(1)–O(4)	105.65(8)
O(1)–Ti(1)–N(1)	80.15(8)	O(1)–Ti(1)–N(2)	88.94(8)
O(2)-Ti(1)–N(1)	88.49(7)	O(2)–Ti(1)–N(2)	78.91(8)
O(3)–Ti(1)–N(1)	90.75(7)	O(3)–Ti(1)–N(2)	162.99(7)
O(4)–Ti(1)–N(1)	162.96(8)	O(4)–Ti(1)–N(2)	90.64(7)
N(1)–Ti(1)–N(2)	73.49(7)	torsion (aryl–aryl)	65.3(2)

Ph), 7.35 (d, J = 8.4 Hz, 2H, Ph), 5.04 (d, J = 10.8 Hz, 1H, C*H*), 3.73 (d, J = 6.0 Hz, 3H, CH_3), 3.70 (d, J = 6.0 Hz, 3H, CH_3), 2.03 (br s, 1H, O*H*).

2.26.3. Dimethyl hydroxyl (4-nitrophenyl) methylphosphonate [25]

HPLC (AS-H, 254 nm, hexane/2-propanol = 80:20, 0.8 mL/min): t_R = 25.4 and 29.9 min. ^{1}H NMR ($CDCl_3$): δ 8.25 (d, J = 8.5 Hz, 2H, Ph), 7.68 (d, J = 7.0 Hz, 2H, Ph), 5.21 (d, J = 12.2 Hz, 1H, C*H*), 3.76 (t, J = 10.3 Hz, 6H, CH_3), 1.64 (br s, 1H, O*H*).

2.26.4. Dimethyl hydroxyl (4-methoxyphenyl) methylphosphonate [25]

HPLC (AS-H, 254 nm, hexane/2-propanol = 80:20, 0.8 mL/min): t_R = 25.9 and 39.9 min. ^{1}H NMR ($CDCl_3$): δ 7.41 (d, J = 8.8 Hz, 2H, Ph), 7.23 (d, J = 8.8 Hz, 2H, Ph), 4.99 (d, J = 10.0 Hz, 1H, C*H*), 3.81 (s, 3H, CH_3), 3.72 (d, J = 10.4 Hz, 3H, CH_3), 3.66 (d, J = 10.4 Hz, 3H, CH_3), 3.22 (br s, 1H, O*H*) .

2.26.5. Dimethyl hydroxyl (o-tolyl) methylphosphonate [73]

HPLC (AS-H, 210 nm, hexane/2-propanol = 5:1, 0.5 mL/min): t_R = 21.5 and 31.9 min. ^{1}H NMR ($CDCl_3$): δ 7.64 (d, J = 7.6 Hz, 1H, Ph), 7.23 (m, 2H, Ph), 7.16 (m, 1H, Ph), 5.29 (d, J = 10.8 Hz, 1H, C*H*), 3.71 (d, J = 10.4 Hz, 3H, CH_3), 3.64 (d, J = 10.4 Hz, 3H, CH_3), 3.21 (br s, 1H, O*H*), 2.38 (s, 3H, CH_3).

2.26.6. Dimethyl hydroxyl (2-fluorophenyl) methylphosphonate [73]

HPLC (AS-H, 210 nm, hexane/2-propanol = 3:1, 0.5 mL/min): t_R = 18.1 and 25.0 min. ^{1}H NMR ($CDCl_3$): δ 7.68 (t, J = 7.5 Hz, 1H, Ph), 7.30 (m, 1H, Ph), 7.20 (t, J = 7.5 Hz, 1H, Ph), 7.05 (t, J = 9 Hz, 1H, Ph), 5.43 (d, J = 11.2 Hz, 1H, C*H*), 4.53 (br s, 1H, O*H*), 3.80 (d, J = 10.6 Hz, 3H, CH_3), 3.67 (d, J = 10.6 Hz, 3H, CH_3).

2.26.7. Dimethyl hydroxyl (p-tolyl) methylphosphonate [73]

HPLC (AS-H, 210 nm, hexane/2-propanol = 5:1, 1.0 mL/min): t_R = 14.2 and 18.4 min. ^{1}H NMR ($CDCl_3$): δ 7.37 (d, J = 6.4 Hz, 2H, Ph), 7.19 (d, J = 7.9 Hz, 2H, Ph), 5.01 (d, J = 10.4 Hz, 1H, C*H*), 3.72 (d, J = 10.4 Hz, 3H, CH_3), 3.67 (d, J = 10.3 Hz, 3H, CH_3), 2.57 (br s, 1H, O*H*), 2.35 (s, 3H, CH_3).

2.26.8. Dimethyl hydroxyl (2-methoxyphenyl) methylphosphonate [31]

HPLC (AD-H, 215 nm, hexane/2-propanol = 90:10, 1.0 mL/min): t_R = 15.6 and 16.6 min. ^{1}H NMR ($CDCl_3$): δ 7.50 (d, J = 7.6 Hz, 1H, Ph), 7.30 (t, J = 8.0 Hz, 1H, Ph), 7.00 (t, J = 7.5 Hz, 1H, Ph), 6.91 (d, J = 8.3 Hz, 1H, Ph), 5.4 (d, J = 12.1 Hz, 1H, C*H*), 3.87 (s, 3H, CH_3), 3.78 (d, J = 10.4 Hz, 3H, CH_3), 3.62 (d, J = 10.4 Hz, 3H, CH_3), 3.14 (br s, 1H, O*H*).

2.26.9. Dimethyl hydroxy (2-chlorophenyl) methylphosphonate [31]

HPLC (AD-H, 215 nm, hexane/2-propanol = 90:10, 1.0 mL/min): t_R = 9.7 and 10.7 min. ^{1}H NMR ($CDCl_3$): δ 7.74 (d, J = 7.7 Hz, 1H, Ph), 7.36 (m, 2H, Ph), 7.28 (m, 1H, aryl), 5.60 (d, J = 11.8 Hz, 1H, C*H*), 3.80 (d, J = 10.4 Hz, 3H, CH_3), 3.67 (d, J = 10.4 Hz, 3H, CH_3); the proton of the O*H* group was not observed.

2.26.10. Dimethyl hydroxyl (3-chlorophenyl) methylphosphonate [31]

HPLC (OD-H, 215 nm, hexane/2-propanol = 90:10, 1.0 mL/min): t_R = 11.0 and 14.1 min. ^{1}H NMR ($CDCl_3$): δ 7.51 (s, 1H, Ph), 7.36 (d, J = 4.7 Hz, 1H, Ph), 7.30 (d, J = 4.9 Hz, 2H, Ph), 5.04 (d, J = 4.8 Hz, 1H, C*H*), 3.74 (d, J = 6.4 Hz, 3H, CH_3), 3.72 (d, J = 6.4 Hz, 3H, CH_3); the proton of the O*H* group was not observed.

2.26.11. Dimethyl hydroxyl (4-fluorophenyl) methylphosphonate [31]

HPLC (OD-H, 215 nm, hexane/2-propanol = 90:10, 1.0 mL/min): t_R = 11.7 and 14.5 min. ^{1}H NMR ($CDCl_3$): δ 7.46 (m, 2H, Ph), 7.08 (t, J = 8.6 Hz, 2H, Ph), 5.04 (d, J = 10.3 Hz, 1H, C*H*), 3.71 (t, J = 10.5 Hz, 6H, CH_3), 2.26 (br s, 1H, O*H*).

2.26.12. Dimethyl hydroxyl (naphthalene-1-yl)methylphosphonate [31]

HPLC (OD-H, 254 nm, hexane/2-propanol = 90:10, 1.0 mL/min): t_R = 20.0 and 26.5 min. ^{1}H NMR ($CDCl_3$): δ 8.08 (d, J = 8.2 Hz, 1H, aryl), 7.88 (m, 3H, aryl), 7.55 (m, 3H, aryl), 5.90 (d, J = 11.3 Hz, 1H, C*H*), 3.71 (d, J = 10.4 Hz, 3H, CH_3), 3.54 (d, J = 10.4 Hz, 3H, CH_3), 2.54 (br s, 1H, O*H*).

2.27. X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Rigaku Saturn CCD or on a Bruker SMART CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54187 Å). An empirical absorption correction was applied using the SADABS program [74]. All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package [75]. All hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for complexes **14**–**21**, **23**, **24** and **29** are summarized in Tables 1 and 2. Selected bond lengths and angles are listed in Table 3.

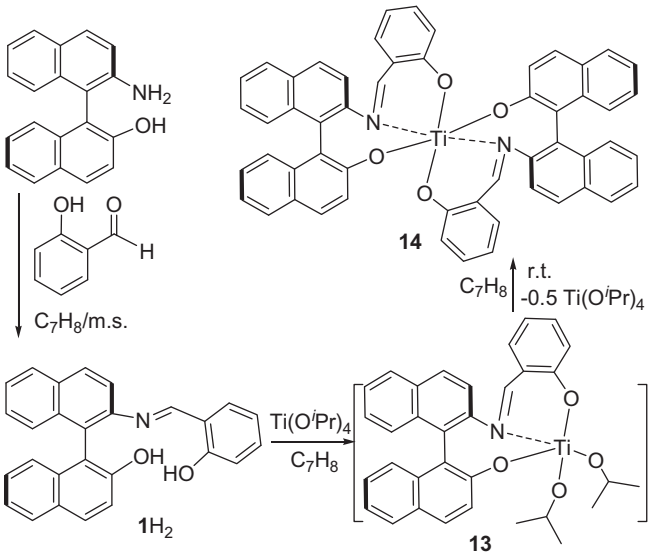
3. Results and discussion

3.1. Synthesis and characterization of ligands

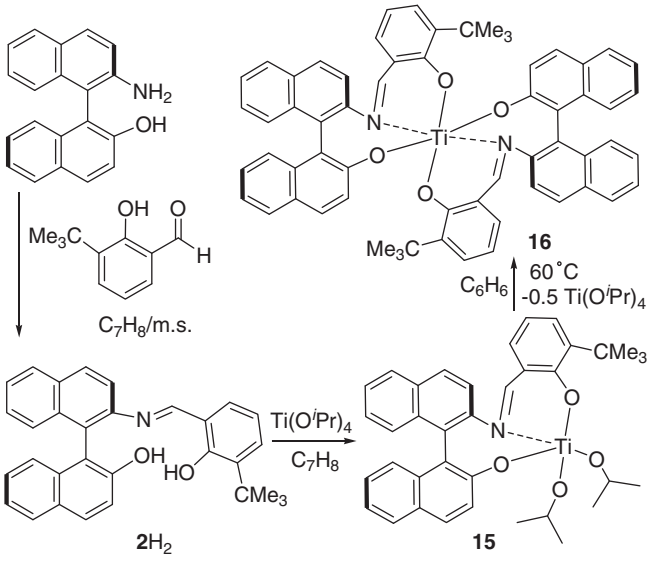
Condensation of (*R*)-2-amino-2′-hydroxy-1,1′-binaphthyl, (*R*)-5,5′, 6,6′,7,7′,8,8′-octahydro-2-amino-2′-hydroxy-1,1′-binaphthyl,(*R*)-2-amino-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl, (*R*)-2,2′-diamino-6, 6′-dimethyl-1,1′-biphenyl or (*R*)-2,2′-diamino-1,1′-binaphthyl with 1 or 2 equiv of salicylaldehyde, 3-*tert*-butylsalicylaldehyde, 3,5-di-*tert*-butylsalicylaldehyde or pyridine-2-carboxaldehyde in toluene in the presence of molecular sieves at 70 °C gives, the C_1-symmetric Schiff-base ligands **1**H$_2$–**7**H (Schemes 1–7), and C_2-symmetric Schiff-base ligands **8**H$_2$–**11**H$_2$ (Schemes 8–11), respectively, in good yields. These Schiff base ligands are stable in dry air atmosphere, but they degrade in the presence of moisture. For example, treatment of **11**H$_2$ with a drop of H_2O in toluene at 60 °C for one hour leads to the isolation of the C_1-symmetric Schiff-base ligand **12**H in 95% yield (Scheme 11). Compounds **1**H$_2$ **–12**H are very soluble in CH_2Cl_2, $CHCl_3$, toluene and benzene, but only slightly soluble in *n*-hexane. The new ligands **3**H$_2$, **4**H$_2$ and **12**H have been fully characterized by various spectroscopic techniques and elemental analyses. Their ^{1}H NMR spectra indicate that they are unsymmetrical on the NMR timescale, which are consistent with their C_1-symmetric structures. Their IR spectra exhibit peaks corresponding to aromatic stretches in addition to O–H stretches at about 3420 cm^{-1}, and strong C=N stretches at about 1617 cm^{-1}.

3.2. Synthesis and characterization of titanium complexes with C_1-symmetric ligands

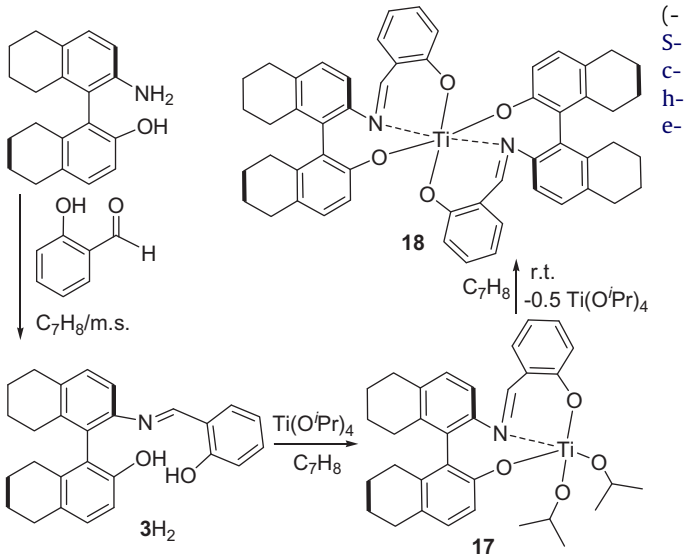
Titanium complexes can be efficiently prepared *via* alcohol elimination reaction between Ti(O^{i}Pr)$_4$ and protic reagents. For example, treatment of Ti(O^{i}Pr)$_4$ with 1 equiv of **1**H$_2$ in toluene gives the bis-ligated titanium complex (**L1**)$_2$Ti (**14**) in 70% yield (Scheme 1), and no mono-ligated complex (**L1**)Ti(O^{i}Pr)$_2$ (**13**) was isolated. However, under similar reaction conditions, treatment of Ti(O^{i}Pr)$_4$ with 1 equiv of **2**H$_2$, **3**H$_2$ or **4**H$_2$ gives, after recrystallization from a toluene solution, the mono-ligated complex (**L2**)Ti(O^{i}Pr)$_2$ (**15**), a mixture of mono-ligated complex (**L3**)Ti(O^{i}Pr)$_2$ (**17**) and bis-ligated complex (**L3**)$_2$Ti (**18**), and mono-ligated complex (**L4**)Ti(O^{i}Pr)$_2$ (**19**), respectively, in good yields



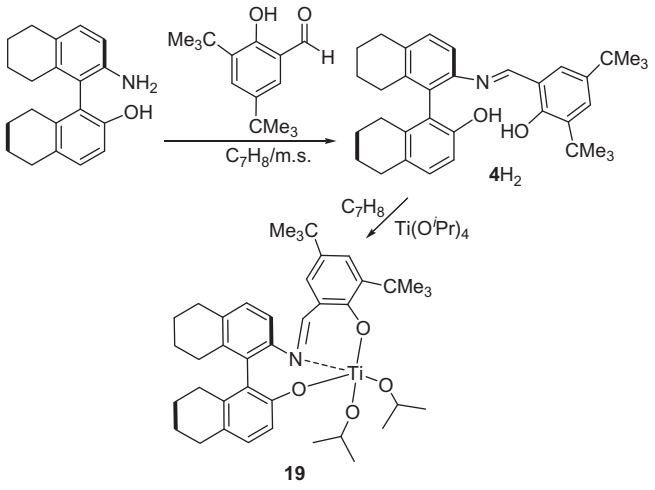
Scheme 1. Synthesis of complex **14**.



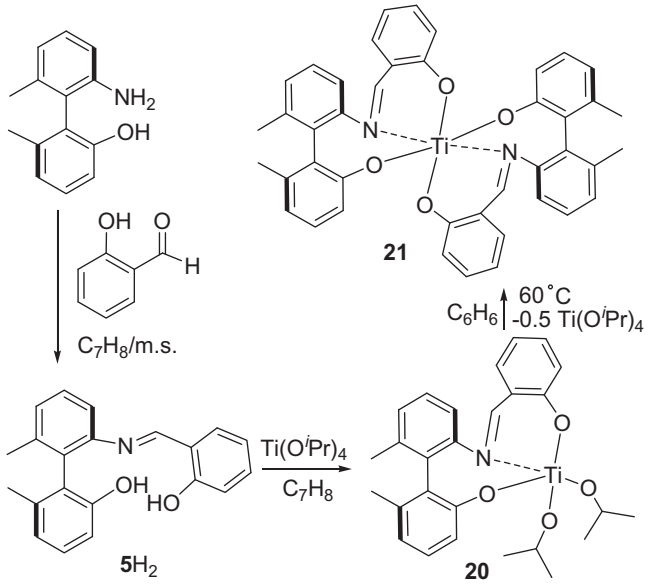
Scheme 2. Synthesis of complexes **15** and **16**.



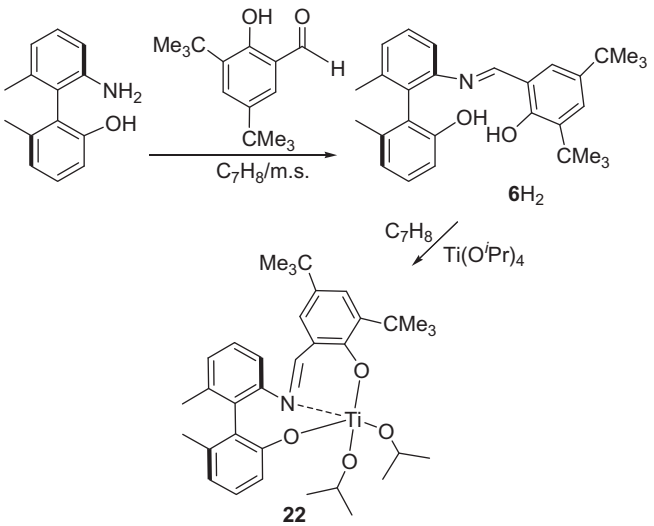
Scheme 3. Synthesis of complexes **17** and **18**.



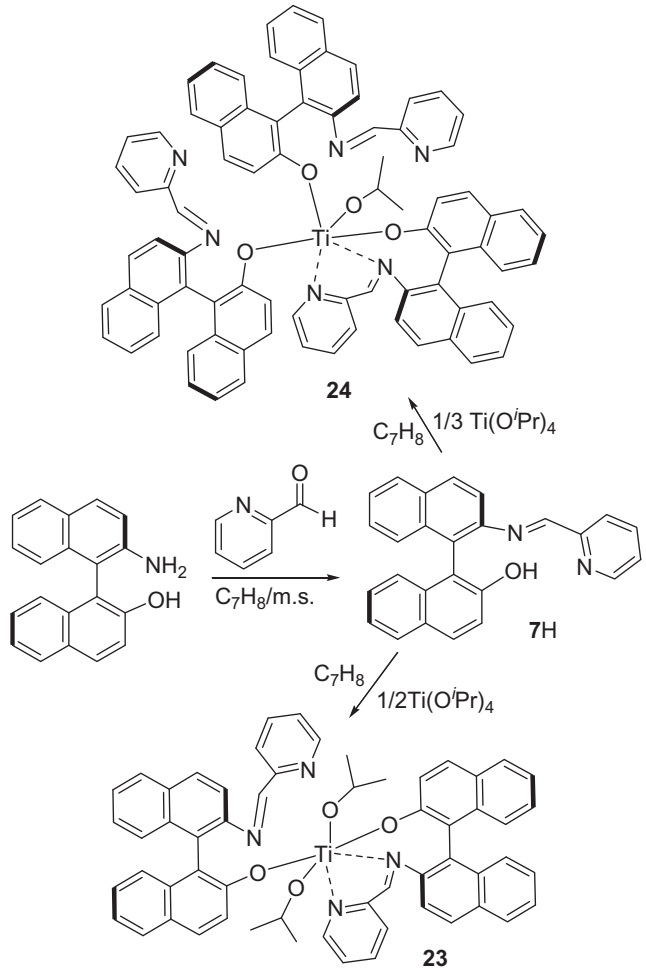
Scheme 4. Synthesis of complex **19**.



Scheme 5. Synthesis of complexes **20** and **21**.

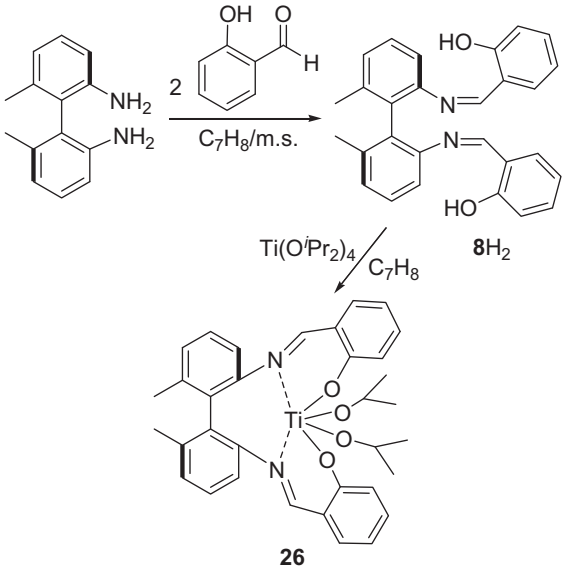


Scheme 6. Synthesis of complex **22**.

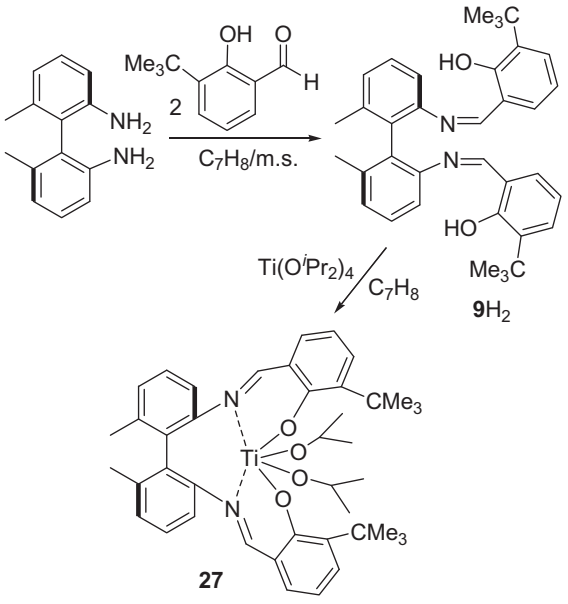


Scheme 7. Synthesis of complexes **23** and **24**.

mes 2–4). The observed reactivity differences are most likely due to the different steric demand of these ligands. A similar result is also observed between ligand $\mathbf{5}H_2$ and $\mathbf{6}H_2$, in which $\mathbf{5}H_2$ gives a mixture of mono-ligated complex (**L5**)Ti(O^iPr)$_2$ (**20**) and bis-ligated complex (**L5**)$_2$Ti (**21**) (Scheme 5), while $\mathbf{6}H_2$ gives the mono-ligated



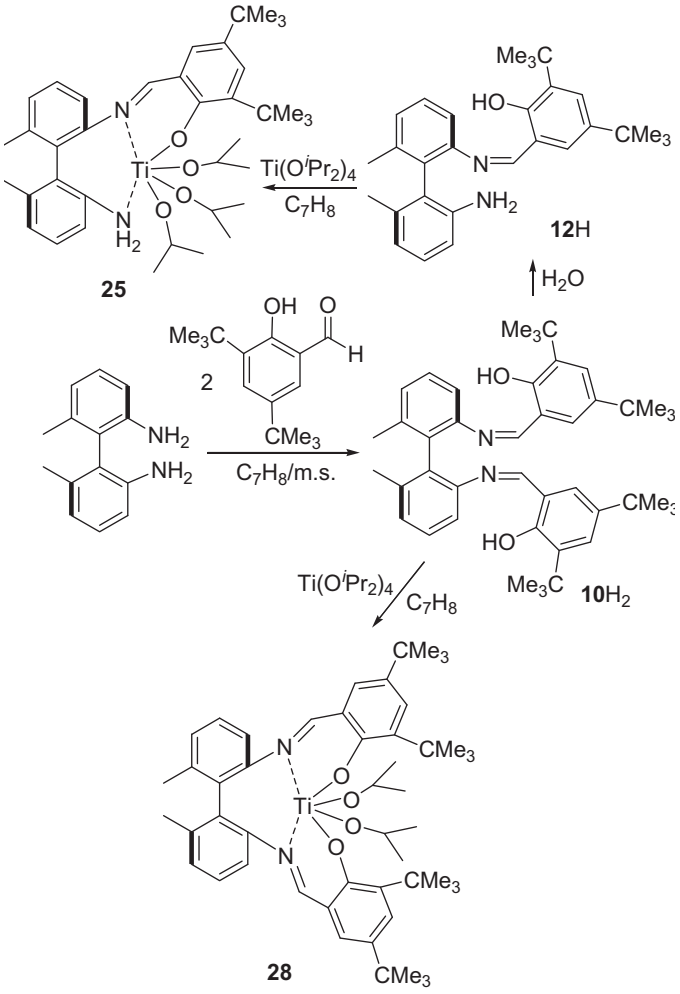
Scheme 8. Synthesis of complex **26**.



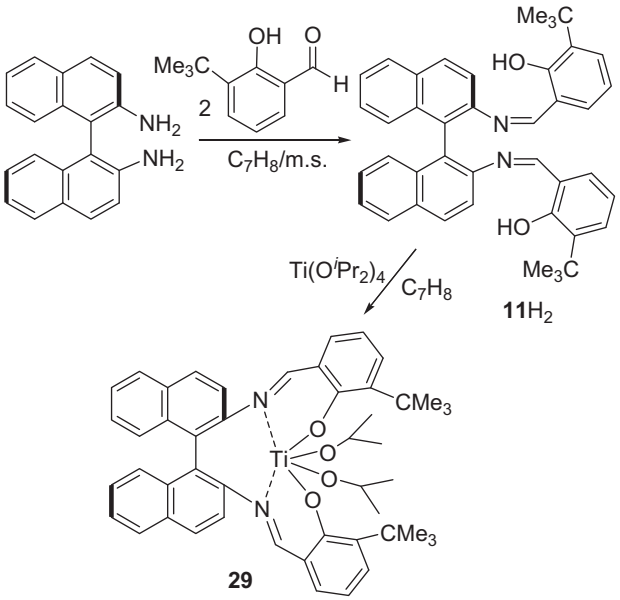
Scheme 9. Synthesis of complex **27**.

complex (**L6**)Ti(O^{i}Pr)$_2$ (**22**) (Scheme 6). The mono-ligated titanium alkoxides can be converted to the bis-ligated complex *via* ligand redistribution reaction. For example, treatment of mono-ligated complex (**L2**)Ti(O^{i}Pr)$_2$ (**15**) or (**L5**)Ti(O^{i}Pr)$_2$ (**20**) at 60 °C gives the bis-ligated complexes (**L2**)$_2$Ti (**16**) and (**L5**)$_2$Ti (**21**), respectively, in good yields (Schemes 2 and 5). Reaction of Ti(O^{i}Pr)$_4$ with 2 or 3 equiv of ligand **7**H gives the bis-ligated complex (**L7**)$_2$Ti(O^{i}Pr)$_2$ (**23**) and the tris-ligated complex (**L7**)$_3$Ti(O^{i}Pr) (**24**), respectively, in good yields (Scheme 7), presumably because of the flexibility of the ligand **7**. Under similar reaction conditions, treatment of ligand **12**H with 1 equiv of Ti(O^{i}Pr)$_4$ gives a mono-ligated complex (**L12**)Ti(O^{i}Pr)$_3$ (**25**) in 67% yield (Scheme 10).

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 support that the ratio of isopropoxyl group O^{i}Pr and



Scheme 10. Synthesis of complexes **25** and **28**.



Scheme 11. Synthesis of complex **29**.

ligand anion is 2:1 for complexes **15** and **19**, 1:1 for **23**, 1:3 for **24**, and 3:1 for **25**, respectively. The solid-state structures of com-

plexes **14**–**21**, **23** and **24** have further been confirmed by X-ray diffraction analyses.

The single-crystal X-ray diffraction analyses show that there is one molecule (**L3**)Ti(O^{i}Pr)$_2$ (**17**) and one molecule (**L3**)$_2$Ti (**18**), one molecule (**L5**)Ti(O^{i}Pr)$_2$ (**20**) and one molecule (**L5**)$_2$Ti (**21**), in the lattice. In each molecule (**L1**)$_2$Ti (**14**), (**L2**)$_2$Ti (**16**), (**L3**)$_2$Ti (**18**), and (**L5**)$_2$Ti (**21**), the Ti^{4+} ion is six coordinate and σ-bound to four oxygen atoms and two nitrogen atoms from the two ligands **1**, **2**, **3** and **5**, respectively, in a distorted-octahedral geometry (Figs. 2–5), in which the two nitrogen atoms in **14**, **16** and **21** adopt a *cis* configuration while those of **18** are situated in *trans* configuration, presumably because of the steric effect of the ligand. The average distance of Ti–OAr is 1.875(2) Å for **14**, 1.879(2) Å for **16**, 1.893(3) Å for **18**, and 1.869(3) Å for **21**, respectively, and the average distance of Ti–N is 2.229(2) Å for **14**, 2.225(2) Å for **16**, 2.241(3) Å for **18**, and 2.241(3) Å for **21**, respectively. These crystal data are comparable to those found in *rac*-(**L1**)$_2$Ti and (*S*)-(**L1**)$_2$Ti [72]. The twisting between the biaryl rings of torsion angles are 58.5(3)° and 64.0(3)° for **14**, 59.3(2)° and 64.4(2)° for **16**, 64.4(4)° and 68.4(4)° for **18**, and 64.1(4)° and 58.0(4)° for **21**, respectively.

The single-crystal X-ray diffraction analyses show that in each molecule (**L2**)Ti(O^{i}Pr)$_2$ (**15**), (**L3**)Ti(O^{i}Pr)$_2$ (**17**), (**L4**)Ti(O^{i}Pr)$_2$ (**19**), and (**L5**)Ti(O^{i}Pr)$_2$ (**20**), the Ti^{4+} ion is five coordinate and σ-bound to two oxygen atoms from two isopropoxyl groups (O^{i}Pr) and two oxygen atoms and one nitrogen atom from the one ligand **2**, **3**, **4** and **5**, respectively, in a distorted-trigonal–bipyramidal

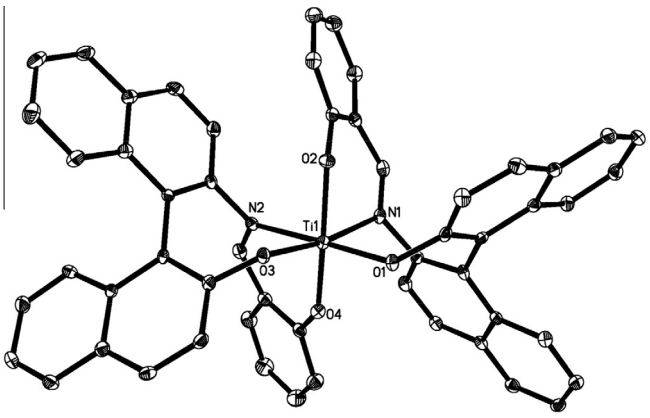


Fig. 2. Molecular structure of **14** (thermal ellipsoids drawn at the 35% probability level).

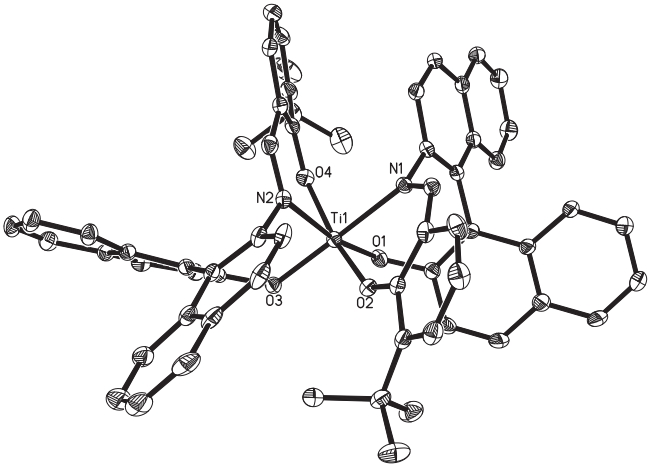


Fig. 3. Molecular structure of **16** (thermal ellipsoids drawn at the 35% probability level).

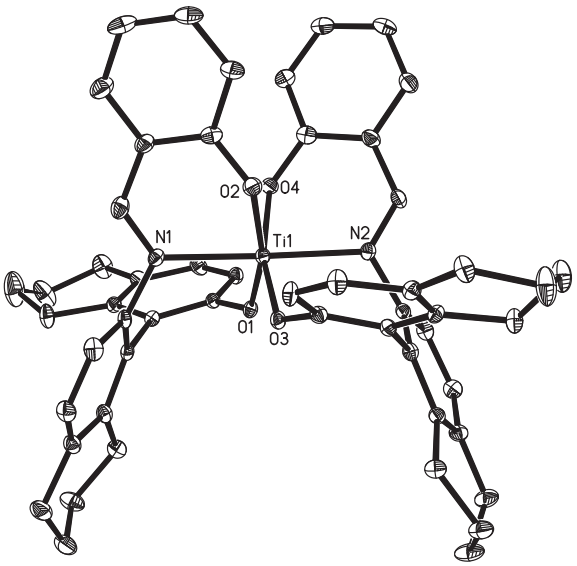


Fig. 4. Molecular structure of **18** in the co-crystallized complexes **17**·**18** (thermal ellipsoids drawn at the 35% probability level).

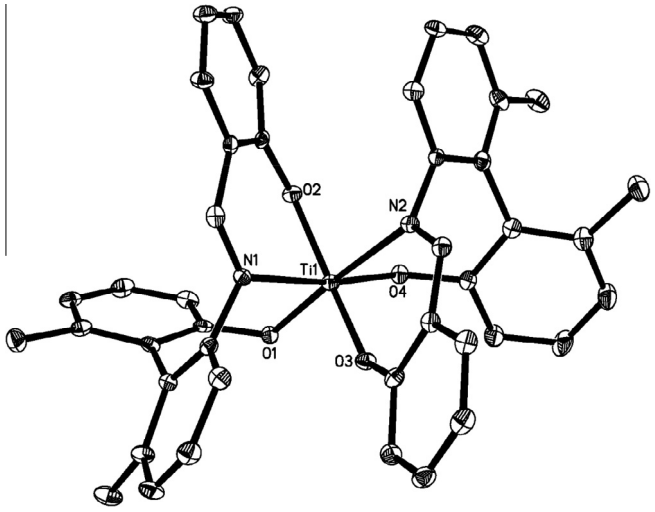


Fig. 5. Molecular structure of **21** in the co-crystallized complexes **20**·**21** (thermal ellipsoids drawn at the 35% probability level).

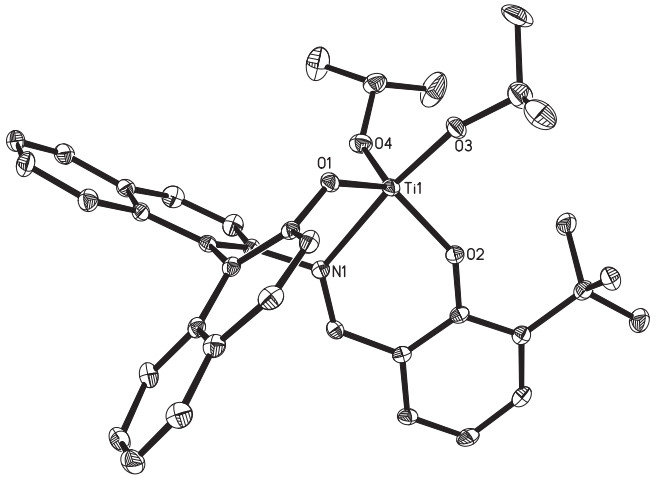


Fig. 6. Molecular structure of **15** (thermal ellipsoids drawn at the 35% probability level).

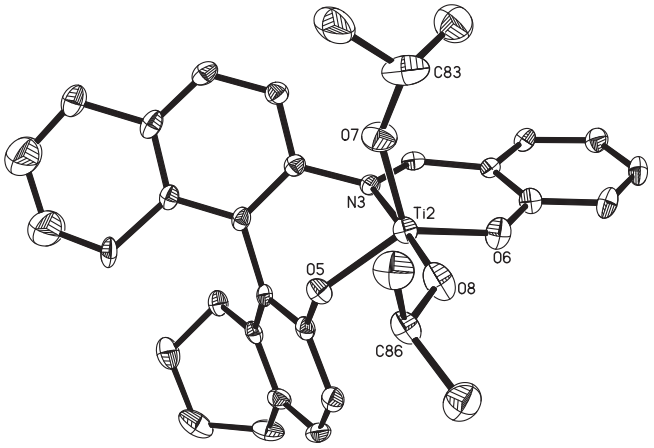


Fig. 7. Molecular structure of **17** in the co-crystallized complexes **17**·**18** (thermal ellipsoids drawn at the 35% probability level).

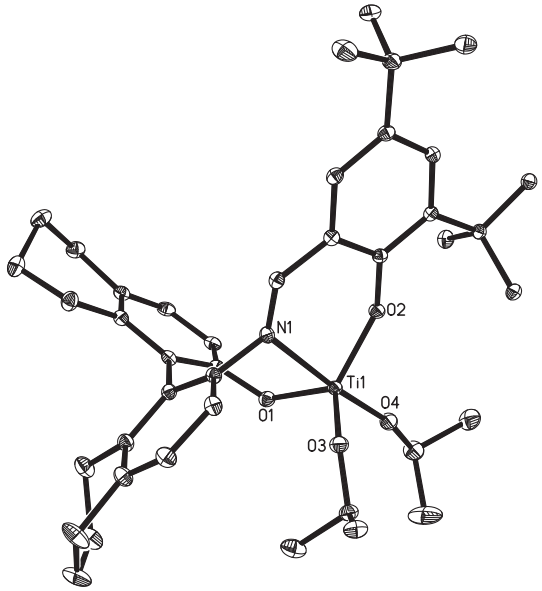


Fig. 8. Molecular structure of **19** (thermal ellipsoids drawn at the 35% probability level).

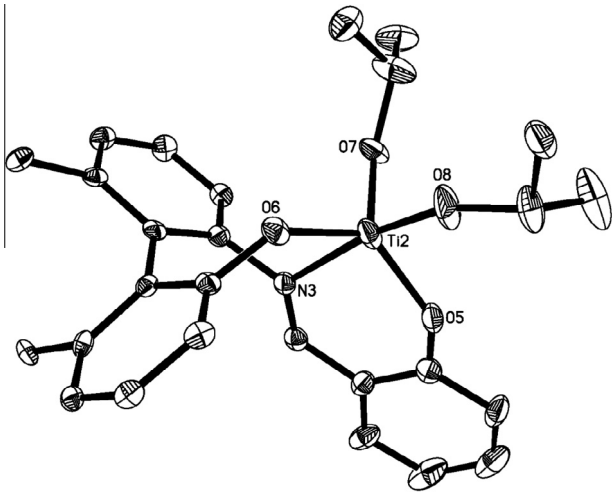


Fig. 9. Molecular structure of **20** in the co-crystallized complexes **20**·**21** (thermal ellipsoids drawn at the 35% probability level).

geometry (Figs. 6–9), in which the nitrogen atom and one isopropoxyl group (O^iPr) are situated on the axial position. The average distance of Ti–OAr is 1.884(2) Å for **15**, 1.862(3) Å for **17**, 1.873(1) Å for **19**, and 1.880(4) Å for **20**, respectively, which are slightly longer than the average distance of Ti–O^iPr in **15** (1.784(2) Å), **17** (1.789(3) Å), **19** (1.792(1) Å), and **20** (1.782(3) Å). The distance of Ti–N is 2.211(2) Å for **15**, 2.294(3) Å for **17**, 2.269(1) Å for **19**, and 2.246(4) Å for **20** respectively. The biaryl rings are twisted by 68.0(2)° for **15**, 63.2(4)° for **17**, 71.0(2)° for **19**, and 60.7(4)° for **20**, respectively. These structural data are comparable to those found in **14**, **16**, **18** and **21** (Table 3).

The molecular structure of **23** shows that the Ti^{4+} ion is six coordinate and σ-bound to two oxygen atoms from two isopropoxyl groups (O^iPr) and two oxygen atoms and two nitrogen atoms from

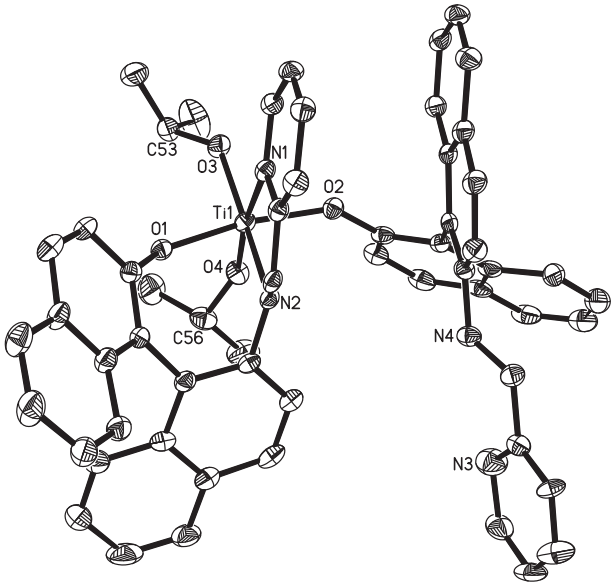


Fig. 10. Molecular structure of **23** (thermal ellipsoids drawn at the 35% probability level).

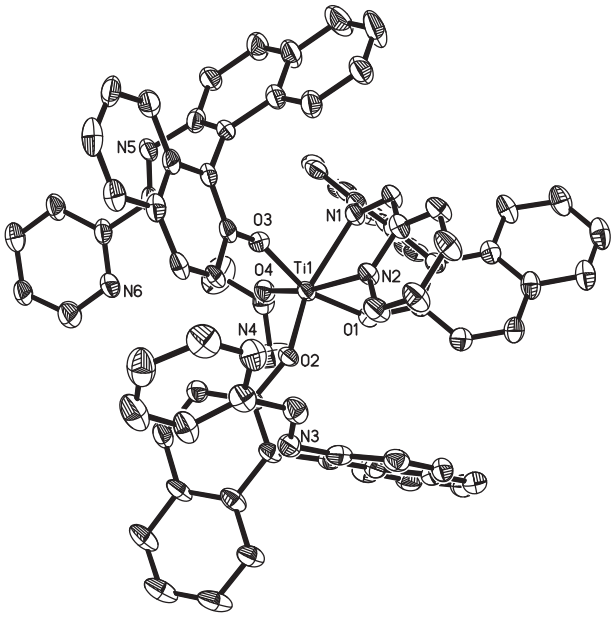


Fig. 11. Molecular structure of **24** (thermal ellipsoids drawn at the 35% probability level).

the two ligands **7** in a distorted-octahedral geometry (Fig. 10), in which the two nitrogen atoms (N(1) and N(2)) are situated in *cis* configuration and the other nitrogen atoms (N(3) and N(4)) are not coordinated to the Ti^{4+} ion. The average distance of Ti–OAr is 1.922(3) Å, which is slightly longer than that of Ti–O^{i}Pr (1.807(3) Å). The average distance of Ti–N is 2.284(3) Å. These structural data are comparable to those found in complexes **14**–**21** (Table 3). The torsion angles between the binaphthyl rings are 62.3(4)° and 69.2(4)°, which are close to those found in **14**, **15** and **16** (Table 3).

The molecular structure of **24** shows that the Ti^{4+} ion is six coordinate and σ-bound to one oxygen atom from one isopropoxyl group (O^{i}Pr) and three oxygen atoms from the three ligands **7** and two nitrogen atoms from one pyridinylmethylimido group of one ligand **7** in a distorted-octahedral geometry (Fig. 11), in which the two nitrogen atoms (N(1) and N(2)) are situated in *cis* configuration and the other two pyridinylmethylimido groups of the other two ligands **7** are not coordinated to the Ti^{4+} ion. The average distance of Ti–OAr is 1.891(2) Å, which is slightly longer than the distance of Ti–O^{i}Pr (1.768(2) Å). The average distance of Ti–N is 2.268(3) Å. The twisting between the binaphthyl rings of torsion angles are 63.9(3)°, 83.2(3)° and 87.6(3)°. These structural data are comparable to those found in complex **23**.

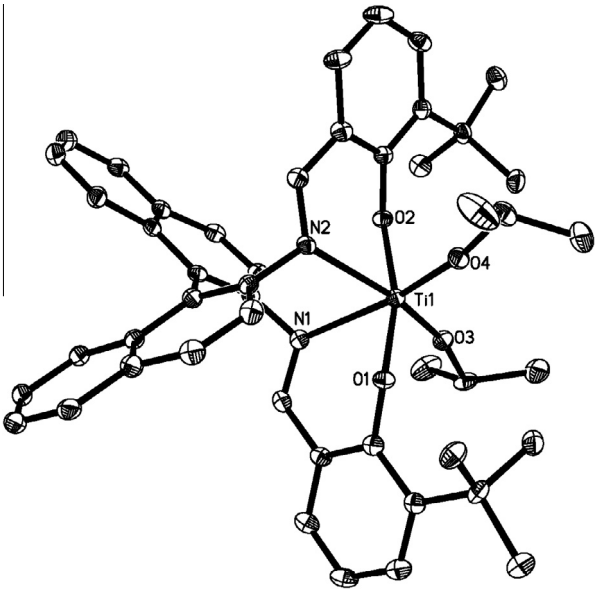
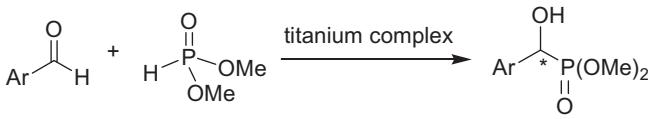


Fig. 12. Molecular structure of **29** (thermal ellipsoids drawn at the 35% probability level).

3.3. Synthesis and characterization of titanium complexes with C_2-symmetric ligands

Simultaneously, we have also prepared a series of chiral titanium complexes with C_2-symmetric ligands **8**H_2–**11**H_2. Treatment of Ti(O^{i}Pr)$_4$ with 1 equiv of **8**H_2, **9**H_2, **10**H_2 or **11**H_2 in toluene gives, after recrystallization from a toluene solution, the mono-ligated complex (**L8**)$_2$Ti(O^{i}Pr)$_2$ (**26**), (**L9**)$_2$Ti(O^{i}Pr)$_2$ (**27**), (**L10**)$_2$Ti(O^{i}Pr)$_2$

Table 4
Enantioselective hydrophosphonylation of aromatic aldehydes catalyzed by titanium complexes.[a]



Entry	Complex	Ar	Solvent	Temp. (°C)	Yield[b] (%)	ee (%)[c]
1	**14**	Ph	toluene	20	90	20
2	**15**	Ph	toluene	20	95	7.6
3	**16**	Ph	toluene	20	90	22
4	**19**	Ph	toluene	20	96	7.2
5	**21**	Ph	toluene	20	88	27
6	**22**	Ph	toluene	20	96	7.7
7	**23**	Ph	toluene	20	91	18
8	**24**	Ph	toluene	20	84	6.3
9	**25**	Ph	toluene	20	90	5.0
10	**26**	Ph	toluene	20	90	5.3
11	**27**	Ph	toluene	20	85	6.7
12	**28**	Ph	toluene	20	90	5.9
13	**29**	Ph	toluene	20	87	7.8
14	**21**	Ph	CH_2Cl_2	20	90	30
15	**21**	Ph	Et_2O	20	91	24
16	**21**	Ph	THF	20	94	45
17	**21**	Ph	THF	10	78	47
18	**21**	Ph	THF	0	42	49
19	**21**	1-naphthyl	THF	20	91	48
20	**21**	2-$CH_3C_6H_4$	THF	20	86	53
21	**21**	2-FC_6H_4	THF	20	82	47
22	**21**	2-$MeOC_6H_4$	THF	20	88	56
23	**21**	2-ClC_6H_4	THF	20	87	66
24	**21**	3-ClC_6H_4	THF	20	89	61
25	**21**	4-ClC_6H_4	THF	20	95	40
26	**21**	4-FC_6H_4	THF	20	90	45
27	**21**	4-$NO_2C_6H_4$	THF	20	95	41
28	**21**	4-$MeOC_6H_4$	THF	20	86	42
29	**21**	4-$CH_3C_6H_4$	THF	20	84	44

[a] All reactions were carried on a 0.5 mmol scale with 10 mol% of complex and 1.3 equiv of dimethyl phosphate, solvent 1.0 mL, time 48 h.
[b] Isolated yields.
[c] Enantiomeric excess was determined by chiral HPLC.

(**28**) and (**L11**)$_2$Ti(O^{i}Pr)$_2$ (**29**), respectively, in good yields (Schemes 8–11). These complexes are stable in dry nitrogen atmosphere, while they are 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. Their ^{1}H NMR spectra indicate that the complexes are symmetrical on the NMR timescale, and support that the ratio of isopropoxyl group O^{i}Pr and ligand anion **8**, **9**, **10** or **11** is 2:1. The solid-state structure of complex **29** has been further confirmed by X-ray diffraction analysis.

The molecular structure of **29** shows that the Ti^{4+} ion is six coordinate and σ-bound to two oxygen atoms from two isopropoxyl groups (O^{i}Pr) and two oxygen atoms and two nitrogen atoms from the one ligand **11** in a distorted-octahedral geometry (Fig. 12), in which the two nitrogen atoms are situated in *cis* configuration. The average distance of Ti–OAr is 1.938(2) Å, which is slightly longer than that of Ti–O^{i}Pr (1.778(2) Å). The average distance of Ti–N is 2.273(2) Å. The twisting between the binaphthyl rings of torsion angle is 65.3(2)°. These structural data are comparable to those found in complexes **14** and **15** (Table 3).

3.4. Asymmetric hydrophosphonylation of aldehydes

To examine the catalytic potential of these complexes toward the asymmetric reactions, hydrophosphonylation of aromatic aldehydes with dimethyl phosphite have been tested under the conditions given in Table 4.

The titanium complexes **14**–**16**, **19**, and **21**–**29** are efficient catalysts for hydrophosphonylation of aromatic aldehydes with dimethyl phosphate in toluene, however, the enantiomeric excess is low (Table 4, entries 1–13). The bis-ligated complex **21** shows the highest enantioselectivity for this transformation, but only a moderate ee value (27%) has been obtained (Table 4, entry 5). When C_2-symmetric ligands **8–11** are used, the different enantioselectivity between the bis-ligated C_2-symmetric complexes and mono-ligated C_2-symmetric complexes is observed (Table 4, entries 1, 3, 5, 10–13), but rather poor enantioselectivities (only up to 7.8% ee) mediated by complexes **26**–**29** have been obtained. Solvent has a notable effect on the enantioselectivity (Table 4, entries 5, 14–16), and a moderate enantioselectivity (45% ee) has been obtained in THF. The enantioselectivity can be slightly improved by lowering the temperature but the rate decreases (Table 4, entries 16–18). When various aromatic aldehydes are used (Table 4, entries 19–29), the steric hindrance has a noticeable effect on the enantioselectivity, and 2-chlorobenzaldehyde gives the best enantioselectivity with 66% ee (Table 4, entry 23), but the electronic effect on the enantioselectivity is not noticed. The titanium complexes **14**–**16**, **19**, and **21**–**29** can promote the asymmetric hydrophosphonylation of aromatic aldehydes, however, these complexes showed either no activity or rather poor activity for hydrophosphonylation of aliphatic aldehydes or ketones such as valeraldehyde and acetophenone, in which *racemic* products with low conversions (<5%) were detected under similar reaction conditions, presumably because of the electronic effect of the substrates.

4. Conclusions

A series of chiral titanium complexes have been prepared from the reaction between Ti(O^{i}Pr)$_4$ and chiral biaryl Schiff-base ligands **1**H$_2$-**12**H. The titanium complexes have displayed good catalytic activity for the asymmetric hydrophosphonylation of representative aromatic aldehydes. The steric demand of the ligand plays an important role in the formation of the titanium complexes and their reactivity. For example, treatment of ligand **1**H$_2$ with 1 equiv of Ti(O^{i}Pr)$_4$ in toluene at room temperature gives the chiral bis-ligated titanium complex (**L1**)$_2$Ti (**14**), while under similar reaction conditions the more bulky ligands **2**H$_2$, **4**H$_2$, and **6**H$_2$ form the mono-ligated titanium complexes (**L2**)Ti(O^{i}Pr)$_2$ (**15**), (**L4**)Ti(O^{i}Pr)$_2$ (**19**), and (**L6**)Ti(O^{i}Pr)$_2$ (**22**), respectively. Overall the bis-ligated complex titanium complexes are more effective chiral catalysts for the enantioselective hydrophosphonylation reaction than the C_1 and C_2-symmetric mono-ligated titanium complexes, *e.g.*, the bis-ligated complex **14** shows an increased enantioselectivity in the hydrophosphonylation reaction, and a moderate ee value (up to 20%) has been obtained, while the mono-ligated C_1-symmetric complex **15** and C_2-symmetric complex **29** do not. Although our ligand set using peripheral biaryl-based NO_2 or N_2O_2-ligand in multidentate systems does not provide a suitable coordination sphere to achieve a significant enantioselectivity (ee > 90%) for hydrophosphonylation, the present results should significantly expand the range of possibilities in designing catalysts not only for hydrophosphonylation but also for many other reactions [76–85]. 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 922365, 922366, 922367, 922368, 922369, 922370, 922373, 922374, and 922379 contains the supplementary crystallographic data for **14**, **15**, **16**, **17**·**18**, **19**, **20**·**21**, **23**, **24**, and **29**. 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 http://dx.doi.org/10.1016/j.ica.2013.04.008.

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