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Synthesis, Structure, and Catalytic Activity of Ti^{IV} and Zr^{IV} Complexes Derived from (*R*)-2,2′-Diamino-1,1′-binaphthyl-Based N_4-Donor Ligands

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Reaction of (*R*)-bis(pyrrol-2-ylmethyleneamino)-1,1′-binaphthyl (**1**H_2) or (*R*)-*N*,*N*′-bis(pyridin-2-ylmethyl)-1,1′-binaphthyl-2,2′-diamine (**2**H_2) with $Zr(NMe_2)_4$ (1 equiv.) gives chiral zirconium amides **1**-$Zr(NMe_2)_2$·C_7H_8 (**4**·C_7H_8) or **2**-$Zr(NMe_2)_2$ (**6**) in good yields, respectively. Under similar conditions, **1**H_2 reacts with $Ti(NMe_2)_4$ (1 equiv.) to give chiral titanium amide **1**-$Ti(NMe_2)_2$·C_6H_6 (**3**·C_6H_6), whereas treatment of **2**H_2 with $Ti(NMe_2)_4$ (1 equiv.) leads to the isolation of bis(ligated) product $(\mathbf{2})_2$-Ti·C_7H_8 (**5**·C_7H_8) in 74 % yield. All complexes were characterized by various spectroscopic techniques, elemental analysis, and X-ray diffraction analysis. Zirconium amides **4** and **6** are active catalysts for the asymmetric hydroamination/cyclization of aminoalkenes, and cyclic amines were obtained in good-to-excellent yields with moderate *ee* values (up to 59 %); titanium amides **2** and **5** were not active under the reaction conditions.

Introduction

Hydroamination is a highly atom-economical process in which an amine N–H bond adds to an unsaturated carbon–carbon bond to form nitrogen heterocycles, which can be found in numerous biologically active compounds.[1] Therefore, it is not surprising that recent efforts have focused on the development of chiral catalysts for intramolecular asymmetric alkene hydroamination.[2–10] Since the pioneering work of Marks in 1992,[3a,3b] many chiral catalysts based on lanthanide metals, main group metals, group 4 metals, and late-transition metals have been widely studied,[2–10] but only a small number of highly enantioselective reactions (>90%*ee*) have been reported.[7a,9c,9e,10e–10g] Thus, the development of new catalysts for asymmetric alkene hydroamination is a desirable and challenging goal. In recent years, we have developed a series of chiral non-Cp multidentate ligands, and it was shown that their Ir^{I}, Rh^{I}, Ti^{IV}, Ag^{I}, Zn^{II}, and lanthanide complexes are useful catalysts for a wide range of transformations.[11] In our endeavors to further explore the coordination chemistry of the chiral (*R*)-bis(pyrrol-2-ylmethyleneamino)-1,1′-binaphthyl (**1**H_2) and (*R*)-*N*,*N*′-bis(pyridin-2-ylmethyl)-1,1′-binaphthyl-2,2′-diamine (**2**H_2) N_4-ligands, we recently extended our research work to titanium(IV) and zirconium(IV) chemistry.[12] In the only other literature report featuring ligand **2**H_2, it was shown that its Ru^{II} complex is a useful catalyst for the asymmetric hydrogenation of aromatic ketones, although this complex was not isolated.[13] In this paper, we report on some observations concerning the chemistry of ligands **1**H_2 and **2**H_2 with titanium(IV) and zirconium(IV) amides and the use of the resulting complexes as catalysts in asymmetric hydroamination/cyclization reactions.

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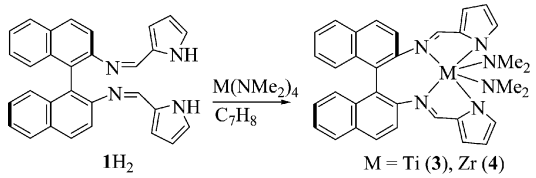
Results and Discussion

Synthesis

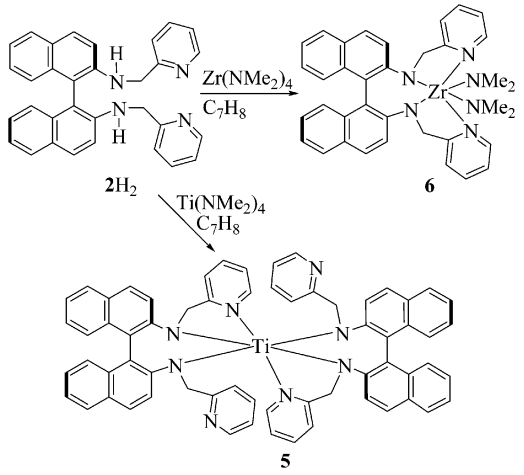
Group 4 metal amide complexes can be efficiently prepared by amine elimination of $M(NMe_2)_4$ with protic reagents.[14] It is rational to propose that two acidic protons in ligands **1**H_2 and **2**H_2 would allow a similar amine elimination reaction to occur between **1**H_2 or **2**H_2 and metal amides. In fact, treatment of **1**H_2 or **2**H_2 with $Zr(NMe_2)_4$ (1 equiv.) gives desired chiral zirconium amides **1**-$Zr(NMe_2)_2$·C_7H_8 (**4**·C_7H_8) (Scheme 1) or **2**-$Zr(NMe_2)_2$ (**6**) (Scheme 2), respectively, in good yields. Under similar conditions, the reaction of **1**H_2 with $Ti(NMe_2)_4$ (1 equiv.) gives chiral titanium amide **1**-$Ti(NMe_2)_2$·C_6H_6 (**3**·C_6H_6) (Scheme 1). However, treatment of **2**H_2 with $Ti(NMe_2)_4$



1H_2 M = Ti (**3**), Zr (**4**)

Scheme 1. Synthesis of complexes **3** and **4**.

(1 equiv.) does not yield expected compound **2**-Ti(NMe_2)$_2$; instead, bis(ligated) product (**2**)$_2$-Ti·C_7H_8 (**5**·C_7H_8) was isolated in 74% yield (Scheme 2).



Scheme 2. Synthesis of complexes **5** and **6**.

These complexes are stable in a dry-nitrogen atmosphere, but they are very sensitive to moisture. They are soluble in organic solvents such as THF, DME, pyridine, toluene, and benzene, and they are only slightly soluble in *n*-hexane. They were characterized by various spectroscopic techniques, elemental analysis, and X-ray diffraction analysis. The ^{1}H NMR spectra of **3**, **4**, and **6** support that the ratio of the NMe_2 amino group and ligand anion **1** or **2** is 2:1; analysis also established that one benzene molecule for **3** and one toluene molecule for **4** per ligand anion **1**, respectively, cocrystallized in the lattice. The ^{1}H NMR spectrum of **5** confirmed that the ratio of toluene and ligand anion **2** is 1:2. The ^{13}C NMR spectra are consistent with these conclusions.

Molecular Structures

Complexes **3**–**6** were characterized by single-crystal X-ray diffraction analysis. Selected bond lengths and angles are listed in Table 1. Single-crystal X-ray diffraction analysis showed that there are two **1**-M(NMe_2)$_2$ molecules and two solvate benzene molecules for **3** and two solvate toluene molecules for **4** in the lattice. In each **1**-M(NMe_2)$_2$ molecule, the M^{4+} is σ bound to four nitrogen atoms from ligand anion **1** and two nitrogen atoms from the NMe_2 groups in a distorted-octahedron geometry (Figures 1 and 2); the average distance are M–N 2.104(2) Å for Ti and 2.234(5) Å for Zr. The short distances of M–NMe_2 [Ti–N5 1.890(2) Å, Ti–N6 1.895(2) Å for Ti and Zr–N5 2.038(5) Å, Zr–N6 2.041(5) Å for Zr] and the planar geometry around the N5 and N6 atoms indicate that both sp^2-hybridized nitrogen atoms are engaged in N(p_π)→M(d_π) interactions. These structural data are very close to those found in the literature.[14] The twisting between the naphthylene rings has a torsion angle of 71.2(2)° for Ti and 67.7(5)° for Zr, which are comparable to those found in **1**-YCl(dme) [70.1(3)°] and **1**-Y[N($SiMe_3$)$_2$](thf) [67.3(4)°].[11f]

Table 1. Selected bond lengths [Å] and bond angles [°] for **3**–**6**.

Compound **3**·C_6H_6			
Ti1–N1	2.278(2)	Ti1–N2	2.286(2)
Ti1–N3	2.143(2)	Ti1–N4	2.129(2)
Ti1–N5	1.890(2)	Ti1–N6	1.895(2)
N1–Ti1–N2	72.70(8)	N1–Ti1–N3	73.73(8)
N2–Ti1–N4	72.81(8)	N5–Ti1–N6	101.99(10)
C31–N5–C32	111.3(2)	C31–N5–Ti1	124.75(19)
C32–N5–Ti1	123.39(19)	C33–N6–C34	110.1(2)
C33–N6–Ti1	122.84(19)	C34–N6–Ti1	127.0(2)
torsion (aryl–aryl)	71.2(2)		
Compound **4**·C_7H_8			
Zr1–N1	2.291(5)	Zr1–N2	2.377(4)
Zr1–N3	2.377(4)	Zr1–N4	2.280(4)
Zr1–N5	2.038(5)	Zr1–N6	2.041(5)
N1–Zr1–N2	70.01(15)	N2–Zr1–N3	72.33(13)
N3–Zr1–N4	69.47(14)	N5–Zr1–N6	108.1(2)
C31–N5–C32	112.5(6)	C31–N5–Zr1	126.4(5)
C32–N5–Zr1	120.8(5)	C33–N6–C34	114.8(6)
C33–N6–Zr1	117.4(5)	C34–N6–Zr1	127.3(5)
torsion (aryl–aryl)	67.7(5)		
Compound **5**·C_7H_8			
Ti1–N1	2.072(4)	Ti1–N2	1.976(4)
Ti1–N3	2.315(4)	Ti1–N5	2.018(4)
Ti1–N6	1.969(4)	Ti1–N7	2.294(4)
N1–Ti1–N2	97.32(15)	N1–Ti1–N3	74.67(13)
N5–Ti1–N6	96.12(16)	N5–Ti1–N7	73.72(16)
C34–N5–C53	114.6(4)	C34–N5–Ti1	120.1(3)
C53–N5–Ti1	123.2(3)	C44–N6–C59	114.6(3)
C44–N6–Ti1	119.5(3)	C59–N6–Ti1	117.4(3)
torsion (aryl–aryl)	62.8(3)		
	67.2(3)		
Compound **6**			
Zr1–N1	2.2155(19)	Zr1–N1A	2.2155(19)
Zr1–N2	2.4204(19)	Zr1–N2A	2.4204(19)
Zr1–N3	2.0866(19)	Zr1–N3A	2.0866(19)
N1–Zr1–N1A	83.08(9)	N1–Zr1–N2	69.25(7)
N3–Zr1–N3A	113.72(12)	C18–N3–C17	111.6(2)
C17–N3–Zr1	126.30(19)	C18–N3–Zr1	121.94(19)
torsion (aryl–aryl)	66.5(2)		

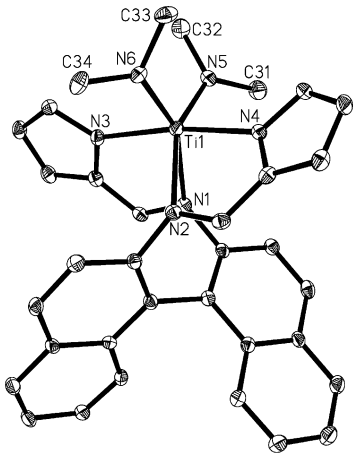


Figure 1. Molecular structure of **3** (thermal ellipsoids drawn at the 35% probability level).

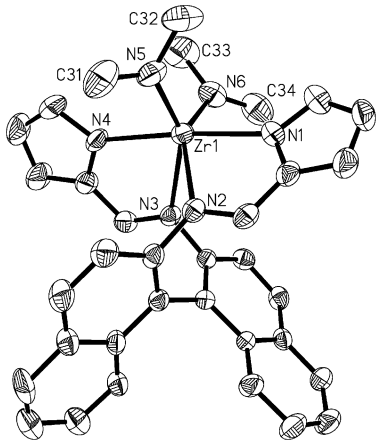


Figure 2. Molecular structure of **4** (thermal ellipsoids drawn at the 35% probability level).

Single-crystal X-ray diffraction analysis of **5** revealed that there are two molecules of **5** and two toluene solvent molecules in the lattice. In each molecule of **5**, the Ti^{4+} is σ bound to the six nitrogen atoms from two ligand anions **2** in a distorted-octahedron geometry (Figure 3) with an average distance of Ti–N 2.107(4) Å, which is close to that found in **3** [2.104(2) Å]. The twisting between the naphthylene rings occurs with torsion angles of 62.8(3) and 67.2(3)°, which are smaller than that found in **3** [71.2(2)°].

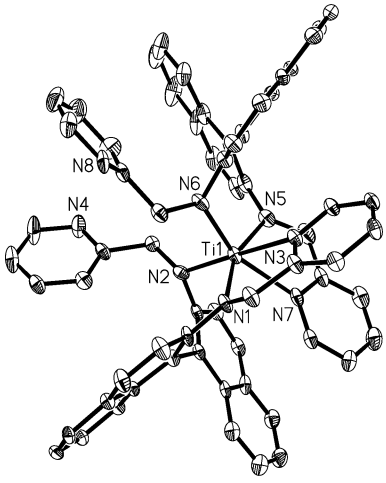


Figure 3. Molecular structure of **5** (thermal ellipsoids drawn at the 35% probability level).

The solid-state structure of **6** shows that the Zr^{4+} is σ bound to four nitrogen atoms from ligand anion **2** and two nitrogen atoms from the NMe_2 groups in a distorted-octahedron geometry (Figure 4) with an average distance of Zr–N 2.2408(19) Å. The short Zr–N3 and Zr–N3A bond lengths [2.0866(19) and 2.0866(19) Å, respectively] and the planar geometry around the N3 and N3A atoms indicate that both sp^2-hybridized nitrogen atoms are engaged in $N(p_\pi) \rightarrow Zr(d_\pi)$ interactions. The twisting between the naphthylene rings has a torsion angle of 66.5(2)°. These structural data are close to those found in **4**.

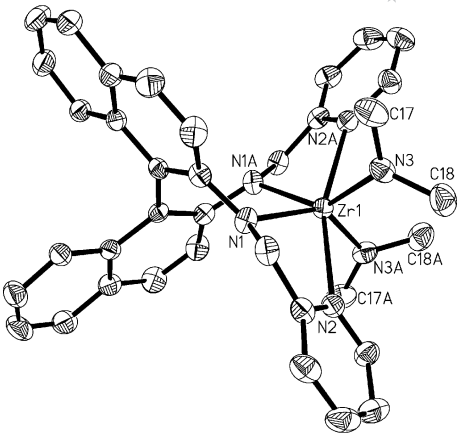
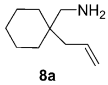
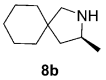


Figure 4. Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level).

Asymmetric Hydroamination/Cyclization

To examine the catalytic ability of complexes **3**–**6**, the asymmetric hydroamination/cyclization of unactivated terminal aminoalkenes was tested under the conditions given in Table 2. The results of the hydroamination/cyclization of 2,2-dimethylpent-4-enylamine show that the zirconium amides are active catalysts for this transformation (Table 2, Entries 2 and 4). Complex **4** gives a noticeably better *ee* value (59%; Table 2, Entry 2), whereas complex **6** shows poor enantioselectivity (only 14%) for this transformation. Under similar reaction conditions, no detectable hydroamination activity was observed for titanium complexes **3** and **5**, even at 120 °C for one week (Table 2, Entries 1 and 3). The reaction of substrate **8a** was fast, but the *ee* values were low (Table 2, Entries 5 and 6). We were encouraged to find that formation of a six-membered ring could also be performed with our zirconium catalysts (Table 2, Entries 7 and 8), and that the reaction, mediated by catalyst **6**, proceeded with moderate enantioselectivity (up to 49%; Table 2, Entry 8). It can be concluded that the rate of cycli-

Table 2. Enantioselective hydroamination/cyclization of aminoalkenes.[a]

Entry	Catalyst (M)	Substrate	Product	Time [h]	Conv. [%][b]	*ee* [%][c]
1	**3** (Ti)			160	N.R.	N.A.
2	**4** (Zr)			80	87	59
3	**5** (Ti)	**7a**	**7b**	160	N.R.	N.A.
4	**6** (Zr)			80	96	14
5	**4** (Zr)			80	100	14
6	**6** (Zr)	**8a**	**8b**	80	100	18
7	**4** (Zr)			80	80	21
8	**6** (Zr)	**9a**	**9b**	80	85	49

[a] Conditions: C_6D_6 (0.70 mL), aminoalkene (0.16 mmol), catalyst (0.016 mmol), at 120 °C. [b] Determined by ^1H NMR spectroscopy on the basis of tetramethylsilane (TMS) as the internal standard. [c] Determined by ^1H NMR spectroscopy of its diastereomeric (*S*)-(+)-*O*-acetylmandelic acid salt on the basis of tetramethylsilane (TMS) as the internal standard.[6,8g]

zation of the aminoalkenes follows the order 5 > 6, which is consistent with classical, stereoelectronically controlled, cyclization processes. Our results show that the catalytic activities of zirconium amides **4** and **6** resemble those of zirconium bis(amido) catalysts,[10d] whereas the enantiomeric excesses of the resulting cyclic amines are similar to those obtained with bis(phenolate).[10a] Although the enantiomeric excesses obtained are moderate, it should be noted that there are only a few catalysts available that give significant *ee* values for these reactions.

Conclusions

A series of chiral organotitanium(IV) and organozirconium(IV) amide complexes was synthesized from the reaction of $M(NMe_2)_4$ (M = Ti, Zr) with chiral N_4 ligands, (*R*)-bis(pyrrol-2-ylmethyleneamino)-1,1′-binaphthyl (**1**H_2) and (*R*)-*N*,*N*′-bis(pyridin-2-ylmethyl)-1,1′-binaphthyl-2,2′-diamine (**2**H_2). Their use as catalysts in asymmetric hydroamination/cyclization reactions was studied. The zirconium amides showed good-to-excellent catalytic activity in the reactions of representative aminoalkenes, whereas the titanium amides did not.

By changing the pyrrol-2-ylmethylene group to a pyridin-2-ylmethyl one, ligands **1**H_2 and **2**H_2 exhibited different reactivity patterns. For example, reaction of $Ti(NMe_2)_4$ with **1**H_2 gave expected complex **1**-$Ti(NMe_2)_2$ (**3**), whereas that of **2**H_2 afforded bis(ligated) complex (**2**)$_2$-Ti (**5**). Zirconium complex **4** (with ligand anion **1**) showed moderate enantioselectivity (up to 59%*ee*) for the asymmetric hydroamination/cyclization of 2,2-dimethylpent-4-enylamine, whereas zirconium complex **6** (with ligand anion **2**) did not, which might indicate that very precise control of the metal coordination sphere is required for this asymmetric transformation to be a realistic prospect. Our ligand set, which involves a peripheral binaphthylene unit coupled to pyrrole or pyridine ligation in multidentate systems, does not provide sufficient rigidity of the dative N-donor ligand to achieve this goal; however, in contrast to the chiral biphenyl-based N_2O_2 ligand system,[10e,f] the present results should significantly expand the range of possibilities that can be used in the design of catalysts not only for hydroamination but also for many other reactions.[12] Further exploration of these catalysts towards other types of transformations and the optimization of the ligand architecture to improve the enantiomeric excess for this transformation are still underway.

Experimental Section

General Methods: All experiments were performed under an atmosphere of dry nitrogen with rigid exclusion of air and moisture by using standard Schlenk or cannula techniques, or the experiments were performed in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. (*R*)-Bis(pyrrol-2-ylmethyleneamino)-1,1′-binaphthyl (**1**H_2),[11f] (*R*)-*N*,*N*′-bis(pyridin-2-ylmethyl)-1,1′-binaphthyl-2,2′-diamine (**2**H_2),[11c] $M(NMe_2)_4$,[15] 2,2-dimethylpent-4-enylamine,[6] 2,2′-dimethylhex/5-enylamine,[6] and 1-(aminomethyl)-1-allylcyclohexane[8a] 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 with an Avatar 360 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker AV 500 spectrometer at 500 and 125 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents or protons of tetramethylsilane [TMS; contained 1% (v/v) in C_6D_6], which are internal standards, for proton and carbon chemical shifts. Melting points were measured with an X-6 melting point apparatus and are uncorrected. Elemental analyses were performed with a Vario EL elemental analyzer.

1-Ti(NMe$_2$)$_2$·C$_6$H$_6$ (3·C$_6$H$_6$): A toluene solution (10 mL) of **1**H_2 (0.22 g, 0.5 mmol) was slowly added to a toluene solution (10 mL) of $Ti(NMe_2)_4$ (0.11 g, 0.5 mmol) with stirring at room temperature. The solution was warmed to 60 °C and kept for 1 d at this temperature. The solution was filtered, and the solvent was removed under reduced pressure. The resulting red solid was recrystallized from a benzene solution to give **3**·C_6H_6 as red crystals. Yield: 0.29 g (90%). M.p. 143–145 °C (dec.). ^1H NMR (500 MHz, C_6D_6): δ = 7.70 (m, 4 H, C*H*=N and aryl H), 7.60 (m, 4 H, aryl H), 7.50 (m, 2 H, aryl H), 7.28 (m, 4 H, aryl H), 7.18–7.15 (m, 8 H, aryl and pyrrolyl H), 6.43 (d, *J* = 1.6 Hz, 2 H, pyrrolyl H), 6.13 (d, *J* = 3.4 Hz, 2 H, pyrrolyl H), 3.52 [s, 12 H, N(C*H*$_3$)$_2$] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 159.9, 148.5, 138.0, 137.9, 134.4, 131.8, 128.6. 128.5, 128.3, 128.1, 127.1, 126.7, 124.9, 122.7, 117.5, 112.8 (aryl C), 47.3 [N(*C*H$_3$)$_2$] ppm. IR (KBr): $\tilde{\nu}$ = 2962 (s), 2923 (m), 2850 (m), 1592 (w), 1567 (vs), 1504 (s), 1390 (s), 1260 (s), 1036 (vs), 804 (s) cm^{-1}. $C_{40}H_{38}N_6Ti$ (650.64): calcd. C 73.84, H 5.89, N 12.92; found C 73.55, H 5.78, N 12.71.

1-Zr(NMe$_2$)$_2$·C$_7$H$_8$ (4·C$_7$H$_8$): This compound was prepared by a similar procedure to that described for **3**·C_6H_6. Orange crystals were obtained from the reaction of **1**H_2 (0.22 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. Yield: 0.30 g (86%). M.p. 170–172 °C (dec.). ^1H NMR (500 MHz, C_6D_6): δ = 7.55–7.33 (m, 10 H, C*H*=N and aryl H), 7.15–7.10 (m, 7 H, aryl H), 7.04 (m, 4 H, aryl and pyrrolyl H), 6.26 (m, 2 H, pyrrolyl H), 6.10 (d, *J* = 2.7 Hz, 2 H, pyrrolyl H), 3.21 [s, 12 H, N(C*H*$_3$)$_2$], 2.10 (s, 3 H, $C_6H_5CH_3$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 160.7, 147.2, 139.9, 138.9, 134.4, 132.1, 129.3, 129.2, 128.9, 128.5, 128.3, 127.7, 127.1, 127.0, 125.6, 125.3, 123.0, 120.4, 113.8 (aryl C), 42.7 [N(*C*H$_3$)$_2$], 21.4 ($C_6H_5CH_3$) ppm. IR (KBr): $\tilde{\nu}$ = 2961 (s), 2923 (m), 2850 (m), 1599 (s), 1575 (vs), 1392 (s), 1286 (s), 1260 (s), 1037 (vs), 800 (s) cm^{-1}. $C_{41}H_{40}N_6Zr$ (708.02): calcd. C 69.55, H 5.68, N 11.87; found C 69.72, H 5.66, N 11.68.

(2)$_2$-Ti·C$_7$H$_8$ (5·C$_7$H$_8$): This compound was prepared by a similar procedure to that described for **3**·C_6H_6. Red crystals were obtained from the reaction of **2**H_2 (0.23 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. Yield: 0.20 g (74%; base on ligand **2**H_2). M.p. 108–110 °C (dec.). ^1H NMR (500 MHz, C_6D_6): δ = 8.19 (d, *J* = 9.0 Hz, 2 H, aryl H), 7.98 (m, 4 H, aryl H), 7.80 (d, *J* = 8.7 Hz, 2 H, aryl H), 7.69 (d, *J* = 8.4 Hz, 2 H, aryl H), 7.54 (d, *J* = 7.8 Hz, 2 H, aryl H), 7.50 (d, *J* = 5.3 Hz, 2 H, aryl H), 7.29–7.08 (m, 13 H, aryl H), 7.01 (d, *J* = 8.6 Hz, 2 H, aryl H), 6.86 (m, 2 H, aryl H), 6.68 (d, *J* = 7.9 Hz, 2 H, aryl H), 6.50 (m, 2 H, aryl H), 6.34 (m, 4 H, aryl H), 6.22 (m, 2 H, aryl H), 6.11 (d, *J* = 16.7 Hz, 2 H, aryl H), 5.61 (t, *J* = 6.3 Hz, 2 H, aryl H), 5.52 (d, *J* = 5.2 Hz, 2 H, NC*H*$_2$), 5.49 (s, 2 H, NC*H*$_2$), 4.75 (d, *J* = 20.4 Hz, 2 H, NC*H*$_2$), 4.32–4.20 (m, 2 H, NC*H*$_2$), 2.23 (s, 3 H, $C_6H_5CH_3$) ppm. ^{13}C NMR

(125 MHz, C_6D_6): δ = 161.6, 161.2, 156.6, 150.2, 149.2, 148.4, 148.0, 136.0, 135.7, 135.1, 128.5, 128.4, 128.3, 128.2, 128.1, 127.4, 127.3, 126.9, 125.7, 122.5, 122.3, 120.3, 120.2, 120.1, 118.8, 114.2 (aryl C), 64.5 (N*C*H_2), 62.6 (N*C*H_2), 49.0 (N*C*H_2), 21.2 (C_6H_5*C*H_3) ppm; other carbon resonances overlapped. IR (KBr): $\tilde{\nu}$ = 3053 (m), 2961 (m), 2920 (m), 1614 (s), 1590 (s), 1503 (s), 1422 (s), 1325 (s), 1260 (s), 1091 (s), 806 (s) cm^{-1}. $C_{71}H_{56}N_8Ti$ (1069.13): calcd. C 79.76, H 5.28, N 10.48; found C 79.64, H 5.36, N 10.24.

2-Zr(NMe$_2$)$_2$ (6): This compound was prepared by a similar procedure to that described for **3**·C_6H_6. Orange crystals were obtained from the reaction of **2**H_2 (0.23 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. Yield: 0.24 g (76%). M.p. 158–160 °C (dec.). ^{1}H NMR (500 MHz, C_6D_6): δ = 8.24 (d, J = 5.2 Hz, 2 H, aryl H), 7.82 (m, 4 H, aryl H), 7.59 (d, J = 8.4 Hz, 4 H, aryl H), 7.21 (t, J = 7.3 Hz, 2 H, aryl H), 7.11 (t, J = 7.9 Hz, 2 H, aryl H), 6.78 (t, J = 7.5 Hz, 2 H, aryl H), 6.52 (t, J = 6.2 Hz, 2 H, aryl H), 6.27 (d, J = 7.8 Hz, 2 H, aryl H), 5.10 (d, J = 19.2 Hz, 2 H, NCH_2), 4.61 (d, J = 19.2 Hz, 2 H, NCH_2), 3.04 [s, 12 H, N(CH_3)$_2$] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 166.8, 154.2, 147.9, 136.9, 135.2, 129.6, 128.3, 127.3, 127.1, 126.7, 125.5, 124.9, 122.2, 120.8, 120.6 (aryl C), 62.5 (N*C*H_2), 43.8 [N(*C*H_3)$_2$] ppm. IR (KBr): $\tilde{\nu}$ = 3046 (w), 2919 (m), 2757 (s), 1607 (s), 1588 (s), 1499 (s), 1421 (s), 1332 (s), 1260 (s), 1017 (vs), 930 (s), 804 (s) cm^{-1}. $C_{36}H_{36}N_6Zr$ (643.94): calcd. C 67.15, H 5.64, N 13.05; found C 67.48, H 5.48, N 12.87.

General Procedure for the Asymmetric Hydroamination/Cyclization Reaction: The cyclization of 2,2-dimethylpent-4-enylamine (**7a**) catalyzed by catalyst **4** is representative (Table 2, Entry 2). In a nitrogen-filled glovebox, **1**-Zr(NMe$_2$)$_2$·C_7H_8 (**4**·C_7H_8; 11.3 mg, 0.016 mmol), C_6D_6 [0.7 mL; contains 1% (v/v) TMS], and 2,2-dimethylpent-4-enylamine (**7a**; 18 mg, 22.6 μL, 0.16 mmol) were introduced sequentially into a J. Young NMR tube equipped with a 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. After heating for 80 h, 87% conversion (based on TMS) from 2,2-dimethylpent-4-enylamine to 2,4,4-trimethylpyrrolidine (**7b**) was determined. ^{1}H NMR (500 MHz, C_6D_6): δ = 3.10 (m, 1 H, NC*H*), 2.64 (m, 1 H, NC*H*H), 2.50 (m, 1 H, NCH*H*), 1.50 (m, 1 H, CH*H*), 1.18 (br. s, 1 H, N*H*), 1.07 (d, J = 6.2 Hz, 3 H, CH_3), 0.98 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3) ppm. These data were in agreement with those reported in the literature.[6,8g] The cyclic amine 2,4,4-trimethylpyrrolidine (**7b**) was vacuum transferred from the J. Young NMR tube into a 25-mL Schlenk flask, which contained (*S*)-(+)-*O*-acetylmandelic acid (31 mg, 0.16 mmol). This transfer was quantitated by washing the NMR tube with a small amount of $CDCl_3$. The resulting mixture was stirred at room temperature for 2 h, and the volatiles were then removed in vacuo. The resulting diastereomeric salt was then dissolved in $CDCl_3$, and the enantiomeric excess was determined by ^{1}H NMR spectroscopy (59%*ee*). ^{1}H NMR (500 MHz, $CDCl_3$) (major isomer): δ = 7.50 (d, J = 7.2 Hz, 2 H, aryl H), 7.31–7.24 (m, 3 H, aryl H), 5.74 (s, 1 H, C*H*OAc), 3.52 (m, 1 H, NC*H*), 2.84 (d, J = 11.4 Hz, 1 H, NC*H*H), 2.68 (q, J = 11.0 Hz, 1 H, NCH*H*), 2.13 (s, 1 H, CH_3CO), 1.65 (m, 1 H, CHCH_2), 1.27 (t, J = 11.4 Hz, 1 H, CHCH_2), 1.22 (d, J = 6.5 Hz, 3 H, NHCH_3), 1.05 (s, 1 H, CH_3), 0.96 (s, 1 H, CH_3) ppm. ^{1}H NMR (500 MHz, $CDCl_3$) (minor isomer): δ = 7.50 (d, J = 7.2 Hz, 2 H, aryl H), 7.31–7.24 (m, 3 H, aryl H), 5.74 (s, 1 H, C*H*OAc), 3.35 (m, 1 H, NC*H*), 2.84 (d, J = 11.4 Hz, 1 H, NC*H*H), 2.68 (q, J = 11.0 Hz, 1 H, NCH*H*), 2.13 (s, 1 H, CH_3CO), 1.65 (m, 1 H, CHCH_2), 1.27 (t, J = 11.4 Hz, 1 H, CHCH_2), 1.15 (d, J = 6.5 Hz, 3 H, NHCH_3), 1.05 (s, 1 H, CH_3), 0.96 (s, 1 H, CH_3) ppm. These data were in agreement with those reported in the literature.[6,8g]

X-ray Crystallography: Single-crystal X-ray diffraction measurements were carried out with a Rigaku Saturn CCD diffractometer at 113(2) K by using graphite monochromated Mo-K_α radiation (λ = 0.71070 Å). An empirical absorption correction was applied by using the SADABS program.[16] All structures were solved by direct methods and refined by full-matrix least-squares on F^2 with the use of the SHELXL-97 program package.[17] All hydrogen atoms were

Table 3. Crystal data and experimental parameters for compounds **3**–**6**.

Compound	**3**·C_6H_6	**4**·C_7H_8	**5**·C_7H_8	**6**
Formula	$C_{40}H_{38}N_6Ti$	$C_{41}H_{40}N_6Zr$	$C_{71}H_{56}N_8Ti$	$C_{36}H_{36}N_6Zr$
Formula weight	650.66	708.01	1069.14	643.93
Crystal system	orthorhombic	orthorhombic	monoclinic	trigonal
Space group	$P2_12_12$	$C222_1$	$P12_11$	$P3_221$
a [Å]	22.910(1)	9.878(1)	15.263(6)	11.591(1)
b [Å]	30.511(1)	20.895(3)	19.815(8)	11.591(1)
c [Å]	9.661(1)	35.945(4)	21.584(9)	20.734(3)
α [°]	90	90	90	90
β [°]	90	90	102.88(1)	90
γ [°]	90	90	90	120
V [Å^3]	6752.7(4)	7419.1(17)	6363(4)	2412.5(5)
Z	8	8	4	3
$D_{calcd.}$ [g cm^{-3}]	1.280	1.268	1.116	1.330
μ [mm^{-1}]	0.292	0.333	0.180	0.376
Size [mm]	0.12 × 0.10 × 0.08	0.24 × 0.20 × 0.16	0.20 × 0.20 × 0.20	0.24 × 0.20 × 0.18
F(000)	2736	2944	2240	1002
2θ range [°]	3.20 to 55.74	3.90 to 52.82	3.42 to 50.00	4.06 to 52.86
No. of reflections, collected	64197	21150	47836	13630
No. of unique reflections	15991 (R_{int} = 0.0689)	7605 (R_{int} = 0.0388)	20129 (R_{int} = 0.0590)	3312 (R_{int} = 0.0377)
No. of observed reflections	15991	7605	20129	3312
Abs_{corr} (T_{max}, T_{min})	0.98, 0.97	1.00, 0.69	0.96, 0.80	0.94, 0.92
R	0.053	0.052	0.069	0.027
R_w	0.115	0.132	0.166	0.057
R_{all}	0.067	0.081	0.078	0.038
Gof	1.04	1.06	1.08	1.09

geometrically fixed by using the riding model. The crystal data and experimental data for **3**–**6** are summarized in Table 3. Selected bond lengths and angles are listed in Table 1.

CCDC-663456 (for **3**), -663457(for **4**), -663458 (for **5**), and -663459 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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