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Synthesis, structure, and catalytic activity of group 4 complexes with new chiral binaphthyldiamine-based ligands

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ABSTRACT

Five group 4 metal complexes (**1**)$_2$Zr(NMe$_2$)$_2$ (**5**), (**2**)$_2$Ti(NMe$_2$)$_2$ (**6**), (**2**)$_2$Zr(NMe$_2$)$_2$ (**7**), (**3**)$_2$Zr (**8**) and (**4**)$_2$Ti(NMe$_2$)$_2$ (**9**) have been readily prepared from the reaction between M(NMe$_2$)$_4$ (M = Ti, Zr) and chiral binaphthyldiamine-based ligands, (*R*)-2,2′-bis(diphenylthiophosphoramino)-1,1′-binaphthyl (**1**H$_2$), (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-2,2′-bis(diphenylthiophosphoramino)-1,1′-binaphthyl (**2**H$_2$), (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-2,2′-bis(methanesulphonylamino)-1,1′-binaphthyl (**3**H$_2$), and C_1-symmetric ligand, (*R*)-2-(mesitylenesulphonylamino)-2′-(dimethylamino)-1,1′-binaphthyl (**4**H). All the complexes have been characterized by various spectroscopic techniques, elemental analyses and X-ray diffraction analyses. The zirconium amides are active catalysts for the asymmetric hydroamination/cyclization of aminoalkenes, affording cyclic amines in good yields with moderate ee (enantiomeric excess) values.

Chiral group 4 metal complexes based on non-Cp multidentate ligands have received growing attention in the past decades [1–13]. One of the initial driving forces for this work is the interest in the development of catalysts for intramolecular asymmetric alkene hydroamination [10–13], because the hydroamination is a highly atomic economical process in which an amine N–H bond is added to an unsaturated carbon–carbon bond leading to the formation of nitrogen heterocycles that are found in numerous biologically and pharmacologically active compounds. Although chiral catalysts based on group 4 metals for asymmetric alkene hydroamination have been intensively studied in recent years [14–24], only a small number of highly enantioselective reactions (>90% ee) have been reported [19,20]. Thus, the development of new group 4 metal catalysts for asymmetric alkene hydroamination is a desirable and challenging goal. Recently, we have developed a series of Zr(IV) and lanthanide complexes with chiral biaryl-based nitrogen-containing multidentate ligands, and found that they are effective catalysts for the asymmetric hydroamination/cyclization, in which excellent enantioselectivities (up to 93% ee) have been obtained [25–34]. In our endeavors to further explore the chiral biaryl ligand system, we have recently extended our research work to new ligands, (*R*)-2,2′-bis(diphenylthiophosphoramino)-1,1′-binaphthyl (**1**H$_2$), (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-2,2′-bis(diphenylthiophosphoramino)-1,1′-binaphthyl (**2**H$_2$), (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-2,2′-bis(methanesulphonylamino)-1,1′-binaphthyl (**3**H$_2$), and C_1-symmetric ligand, (*R*)-2-(mesitylenesulphonylamino)-2′-(dimethylamino)-1,1′-binaphthyl (**4**H), which are derived from (*R*)-2,2′-diamino-1,1′-binaphthyl. We report herein the synthesis and properties of the chiral ligands, their use in the coordination chemistry of titanium(IV) and zirconium(IV), and the applications of the resulting complexes as catalysts for the asymmetric hydroamination/cyclization of aminoalkenes.

Treatment of the starting material (*R*)-2,2′-diamine-1,1′-binaphthyl or (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-2,2′-diamine-1,1′-binaphthyl with 2 equiv of diphenylthiophosphinic chloride or methanesulphonyl chloride in the presence of an excess of pyridine in toluene at reflux gives, after purification by flash column chromatography, the C_2-symmetric ligands, (*R*)-2,2′-bis(diphenylthiophosphoramino)-1,1′-binaphthyl (**1**H$_2$), (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-2,2′-bis(diphenylthiophosphoramino)-1,1′-binaphthyl (**2**H$_2$) and (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-2,2′-bis(methanesulphonylamino)-1,1′-binaphthyl (**3**H$_2$), respectively, in good yields (Schemes 1–2). Of course, the C_1-symmetric ligand, (*R*)-2-(mesitylenesulphonylamino)-2′-(dimethylamino)-1,1′-binaphthyl (**4**H), is also readily prepared in 84% yield by reaction of (*R*)-2-amino-2′-(dimethylamino)-1,1′-binaphthyl with 1 equiv of mesitylenesulphonyl chloride in the presence of an excess of pyridine in toluene at reflux, followed by purification with flash column chromatography (Scheme 3). All new ligands are air-stable, and are soluble in CH_2Cl_2, $CHCl_3$, toluene and benzene, and slightly soluble in *n*-hexane. They have been fully characterized by various spectroscopic techniques, and elemental analyses. The ^{1}H and ^{13}C NMR spectra of **1**H$_2$, **2**H$_2$ and **3**H$_2$ indicate that they are symmetrical on the NMR timescale, which are consistent with their C_2-symmetric structures. And the ^{1}H and ^{13}C NMR spectra of **4**H confirm that it is non-symmetrical on the NMR timescale consistent with its C_1-symmetric structure. The infrared spectra of these compounds exhibit peaks corresponding to aromatic stretches in addition to N–H stretches at about 3300 cm^{-1}.

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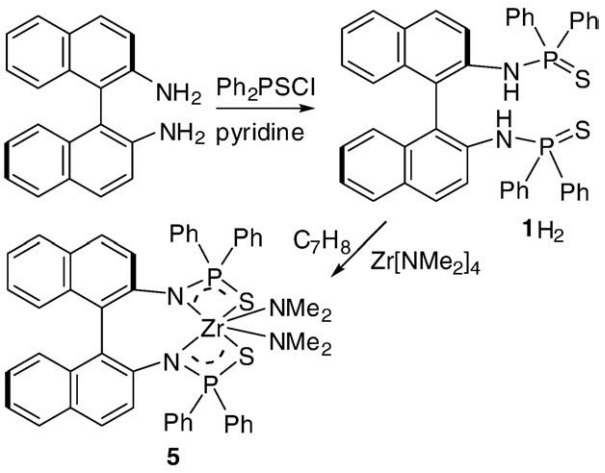
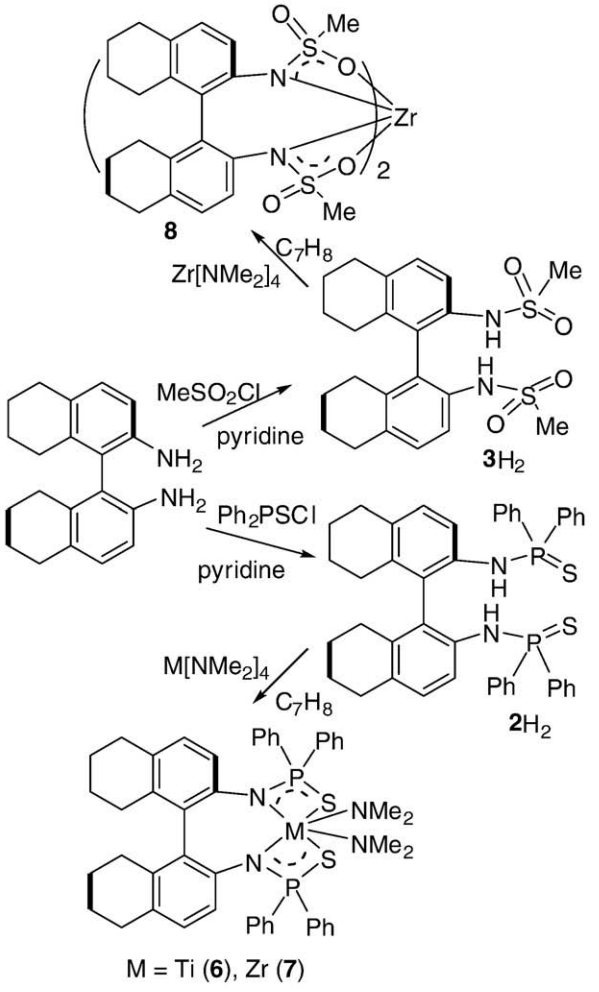
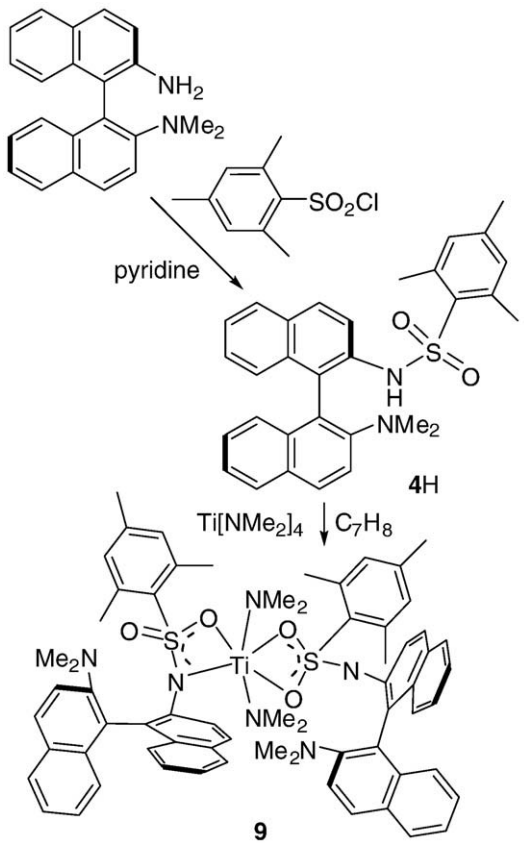


Scheme 1.

Group 4 metal amide complexes can be efficiently prepared via amine elimination reaction between $M(NMe_2)_4$ and protic reagents. For example, treatment of $M(NMe_2)_4$ with 1 equiv of (*R*)-2,2′-bis(diphenylthiophosphoramino)-1,1′-binaphthyl (**1**H_2) or (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-2,2′-bis(diphenylthiophosphoramino)-1,1′-binaphthyl (**2**H_2) gives, after recrystallization from a toluene, benzene or *n*-hexane solution, the zirconium amides (**1**)$_2$Zr$(NMe_2)_2$ (**5**) and



Scheme 2.



Scheme 3.

(**2**)$_2$Zr$(NMe_2)_2\cdot C_6H_6\cdot C_6H_{12}$ (**7**$\cdot C_6H_6\cdot C_6H_{12}$), and titanium amide (**2**)$_2$Ti$(NMe_2)_2\cdot 0.5C_7H_8$ (**6**$\cdot 0.5C_7H_8$), respectively, in good yields (Schemes 1–2), while reaction of $Zr(NMe_2)_4$ with 1 equiv of (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-2,2′-bis(methanesulphonylamino)-1,1′-binaphthyl (**3**H_2) does not give the expected complex (**3**)Zr$(NMe_2)_2$, instead, a bis-ligated complex, (**3**)$_2$Zr$\cdot C_6H_6$ (**8**$\cdot C_6H_6$), has been isolated in 72% yield (Scheme 2). Under similar reaction conditions, treatment of $Ti(NMe_2)_4$ with 2 equiv of (*R*)-2-(mesitylenesulphonylamino)-2′-(dimethylamino)-1,1′-binaphthyl (**4**H) gives, after recrystallization from a benzene solution, the bis-ligated chiral titanium amide (**4**)$_2$Ti$(NMe_2)_2\cdot C_6H_6$ (**9**$\cdot C_6H_6$) in 73% yield (Scheme 3). These complexes are stable in dry nitrogen atmosphere, while they are very sensitive to moisture. They are soluble in organic solvents such as THF, DME, pyridine, toluene, and benzene, and only slightly soluble in *n*-hexane. They have been characterized by various spectroscopic techniques and elemental analyses. The ^{1}H NMR spectra of **5–7** support that the ratio of amino group NMe_2 and ligand anion **1**or **2** is 2:1, supporting the formation of the mono-ligated complexes **5–7**. Unlike the zirconium amides **5** and **7**, the ^{1}H NMR spectrum of **8** does not exhibit a singlet resonance at about 3.25 ppm attributable to the NMe_2 groups, supporting the formation of the bis-ligated complex **8**. The ^{1}H NMR spectrum of **9** supports that the ratio of amino group NMe_2 and ligand anion **4** is 1:1, supporting the formation of the bis-ligated complex **9**. These results are consistent with their ^{13}C NMR spectra. The solid-state structures of these complexes have further been confirmed by X-ray diffraction analyses [35].

The single-crystal X-ray diffraction analyses show that there are two molecules (**1**)Zr$(NMe_2)_2$ for **5**, and one molecules (**2**)Zr$(NMe_2)_2$ and one solvated benzene molecule and one *n*-hexane molecule for **7** in the lattice. In each molecule of (**1**)Zr$(NMe_2)_2$ (**5**) or (**2**)Zr$(NMe_2)_2$ (**7**), the Zr^{4+} is σ-bound to two nitrogen atoms and two sulfur atoms from the ligands **1** or **2** and two nitrogen atoms from amino groups NMe_2 in a distorted-octahedron geometry (Fig. 1) with the average

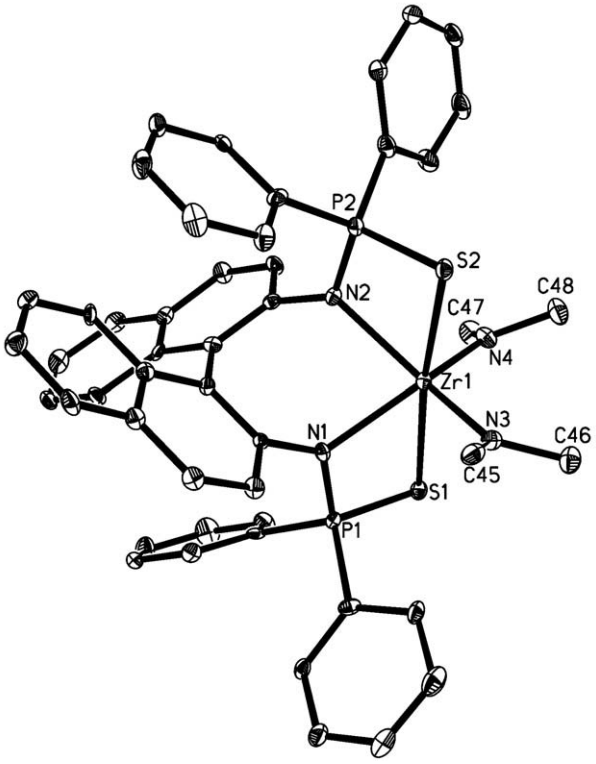


Fig. 1. Molecular structure of **5** (thermal ellipsoids drawn at the 35% probability level).

distance of Zr–N is 2.156(5) Å for **5**, and 2.153(1) Å for **7**, respectively. The average distance of Zr–S is 2.776(2) Å for **5**, and 2.774(1) Å for **7**, respectively. The short distances of Zr–NMe_2 2.050(5) and 2.066(5) Å for **5**, and 2.035(1) and 2.063(1) Å for **7**, respectively, and the planar geometry around the nitrogen atoms of NMe_2 groups indicate that both nitrogen atoms with sp^2 hybridization are engaged in $N(p_\pi) \rightarrow Zr(d_\pi)$ interactions. The torsion angle between the naphthyl ring is 65.5

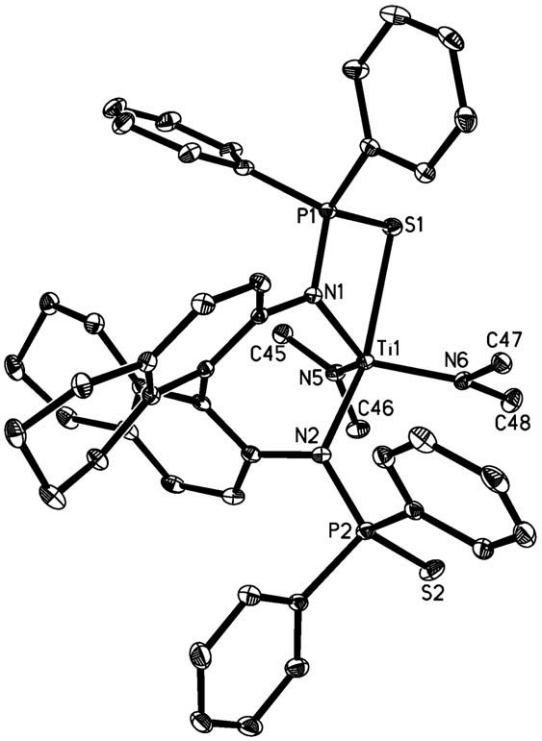


Fig. 2. Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level).

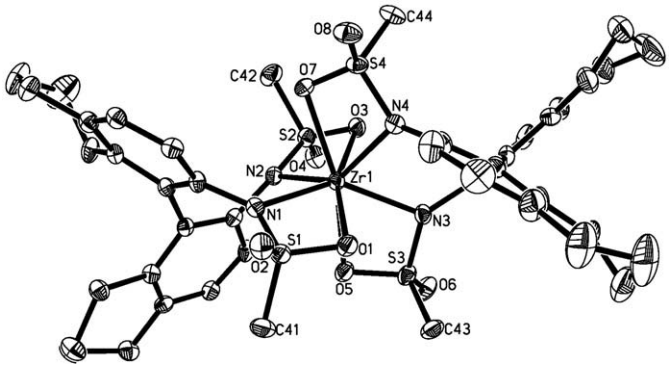


Fig. 3. Molecular structure of **8** (thermal ellipsoids drawn at the 35% probability level).

(5)° for **5**, and 69.4(1)° for **7**, respectively, which is comparable to that found in $[(R)\text{-}C_{20}H_{12}(NCHC_4H_3N)_2]Zr(NMe_2)_2$ (67.7(5)°) [25].

The single-crystal X-ray diffraction analyses show that there are two molecules (**2**)$Ti(NMe_2)_2$ (**6**) and one solvated toluene molecule in the lattice. In each molecule of (**2**)$Ti(NMe_2)_2$ (**6**), the Ti^{4+} is σ-bound to two nitrogen atoms and one sulfur atom from the ligand **2** and two nitrogen atoms from amino groups NMe_2 in a distorted-trigonal-bipyramidal geometry (Fig. 2) with the average distance of Ti–N (1.981(2) Å) and the distance of Ti–S (2.673(1) Å). The short distances of Ti–NMe_2 (1.874(2) and 1.883(2) Å) and the planar geometry around the nitrogen atom of NMe_2 indicate that the nitrogen atoms with sp^2 hybridization are engaged in $N(p_\pi) \rightarrow Ti(d_\pi)$ interactions. The twist between the naphthyl rings of torsion angle is 66.9(2)°, which is smaller than that found in **7** (69.4(1)°).

The single-crystal X-ray diffraction analyses show that there are two molecules $(\mathbf{3})_2Zr$ and two solvated benzene molecules in the lattice. In each molecule of $(\mathbf{3})_2Zr$ (**8**), the Zr^{4+} is σ-bound to four nitrogen atoms and four oxygen atoms from the two ligands **3** in a distorted-dodecahedron geometry (Fig. 3) with the average distance of Zr–N 2.206(6) Å and the average distance of Zr–O 2.300(5) Å. The torsion angles between the naphthyl rings are 66.4(9) and 76.2(9), which are comparable to that found in **7** (69.4(1)°).

The single-crystal X-ray diffraction analyses show that there is one molecule $(\mathbf{4})_2Ti(NMe_2)_2$ and one solvated benzene molecule in the lattice. In the molecule of $(\mathbf{4})_2Ti(NMe_2)_2$, the substituted Me_2N groups are far away from the metal center, and the Ti^{4+} is σ-bound to one nitrogen atom and three oxygen atoms from the two ligands **4** and two nitrogen atoms from amino groups NMe_2 in a distorted-octahedron geometry (Fig. 4) with the average distance of Ti–N

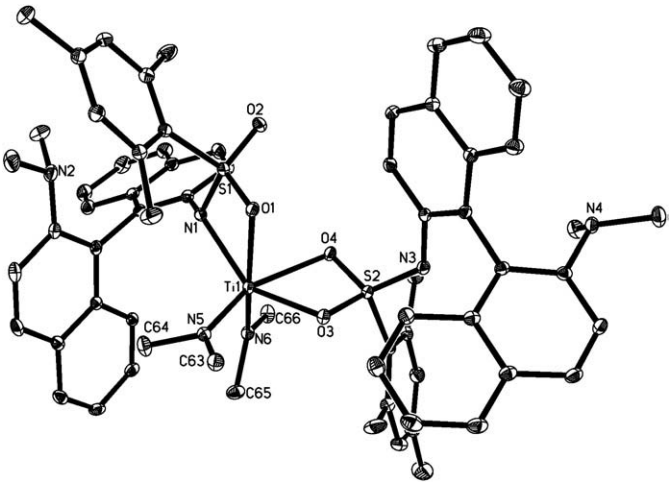
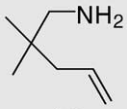
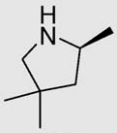
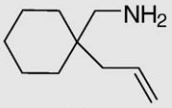
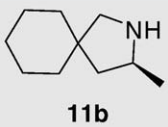
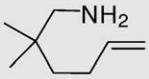
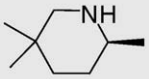


Fig. 4. Molecular structure of **9** (thermal ellipsoids drawn at the 35% probability level).

Table 1
Enantioselective hydroamination/cyclization of aminoalkenes.[a]

Entry	Catalyst (M)	Substrate	Product	Time (h)	Conv. (%)[b]	ee (%)[c]
1	**5** (Zr)			48	100	37
2	**6** (Ti)			160	N.R.	N.A.
3	**7** (Zr)			48	90	30
4	**8** (Zr)			160	N.R.	N.A.
5	**9** (Ti)	**10a**	**10b**	48	45	26
6	**5** (Zr)			48	100	30
7	**7** (Zr)			48	100	28
8	**9** (Ti)	**11a**	**11b**	48	87	26
9	**5** (Zr)			48	100	24
10	**7** (Zr)			48	100	16
11	**9** (Ti)	**12a**	**12b**	48	37	21

[a] Conditions: C_6D_6 (0.70 mL), aminoalkene (0.16 mmol), catalyst (0.016 mmol), at 120 °C.
[b] Determined by ^{1}H NMR based on *p*-xylene as the internal standard. N.R. = no reaction.
[c] Determined by ^{1}H NMR of its diastereomeric (*S*)-(+)-*O*-acetylmandelic acid salt. N.A. = not applicable.

(1.971(1) Å) and the average distance of Ti–O (2.175(1) Å). The short distances of Ti–NMe_2 (1.873(1) and 1.891(1) Å) and the planar geometry around the N(5) and N(6) nitrogen atoms indicate that both nitrogen atoms with sp^2 hybridization are engaged in $N(p_\pi) \rightarrow Ti(d_\pi)$ interactions. The torsion angles between the naphthyl rings are 80.3 (1) and 72.8(1)°, which are comparable to that found in (*S*)-2-amino-2′-(dimethylamino)-1,1′-binaphthyl (86.0(2)°) [26].

To evaluate the catalytic ability of the complexes **5**–**9**, the asymmetric hydroamination/cyclization of unactivated terminal aminoalkenes has been tested under the conditions given in Table 1. The results of the hydroamination/cyclization of **10a** clearly show that the complexes **5**, **7** and **9** are active catalysts for this transformation (Table 1, entries 1, 3 and 5), and the complex **5** shows more effective catalyst for this asymmetric transformation with a moderate enantioselectivity (up to 37%; Table 1, entry 1). When more bulky ligand **2** is used, both the rate and ee value decrease slightly (Table 1, entry 3). The titanium complex **9** can mediate the cyclization of 2,2-dimethylpent-4-enylamine (Table 1, entry 5), but the rate is slow, presumably due to the smaller metal ion radius. Under similar reaction conditions, no detectable hydroamination activity is observed for titanium complex **6** and bis-ligated zirconium complex **8** even heated at 120 °C for one week (Table 1, entries 2 and 4), and none of the complexes described above is effective catalysts for the cyclization of 1-aminopent-4-ene into 2-methylpyrrolidine, presumably due to a lack of a Thorpe–Ingold effect [36,37] from the unsubstituted aminoalkene. Substrate **11a** reacts fast but the ee values are moderate (Table 1, entries 6–8). The formation of a six-membered ring can also be performed with our complexes **5**, **7** and **9** (Table 1, entries 9–11), and a moderate enantioselectivity (up to 24%), mediated by the catalyst **5**, has been obtained (Table 1, entry 9). Although the enantiomeric excesses obtained remain moderate, it should be noted that there are only a few group 4 catalysts for these reactions that give a significant ee (>90%) at all [19,20].

In conclusion, a new series of chiral group 4 metal complexes have been readily prepared from the reactions between $M(NMe_2)_4$ (M = Ti, Zr) and chiral binaphthyldiamine-based ligands, **1**H_2, **2**H_2, **3**H_2 and **4**H. The amides **5**, **7** and **9** have displayed good catalytic activity for the asymmetric hydroamination/cyclization of representative aminoalkenes although the enantiomeric excesses remain moderate. Our ligand set using peripheral binaphthyl-based N_2S_2, N_2O_2 or N_2O-ligand in multidentate systems does not provide a successful suitable coordination sphere to achieve an excellent enantioselectivity, however, this ligand modification has shown a certain ability in stereodirecting the asymmetric hydroamination/cyclization, and the present results should expand the range of possibilities in designing catalysts not only for hydroamination but also for many other reactions [1–9]. 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 data

CCDC 762015, 762016, 762017, 762018 and 762019 contain the supplementary crystallographic data for **5**, **6**, **7**, **8** and **9**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambrige CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.03.015.

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