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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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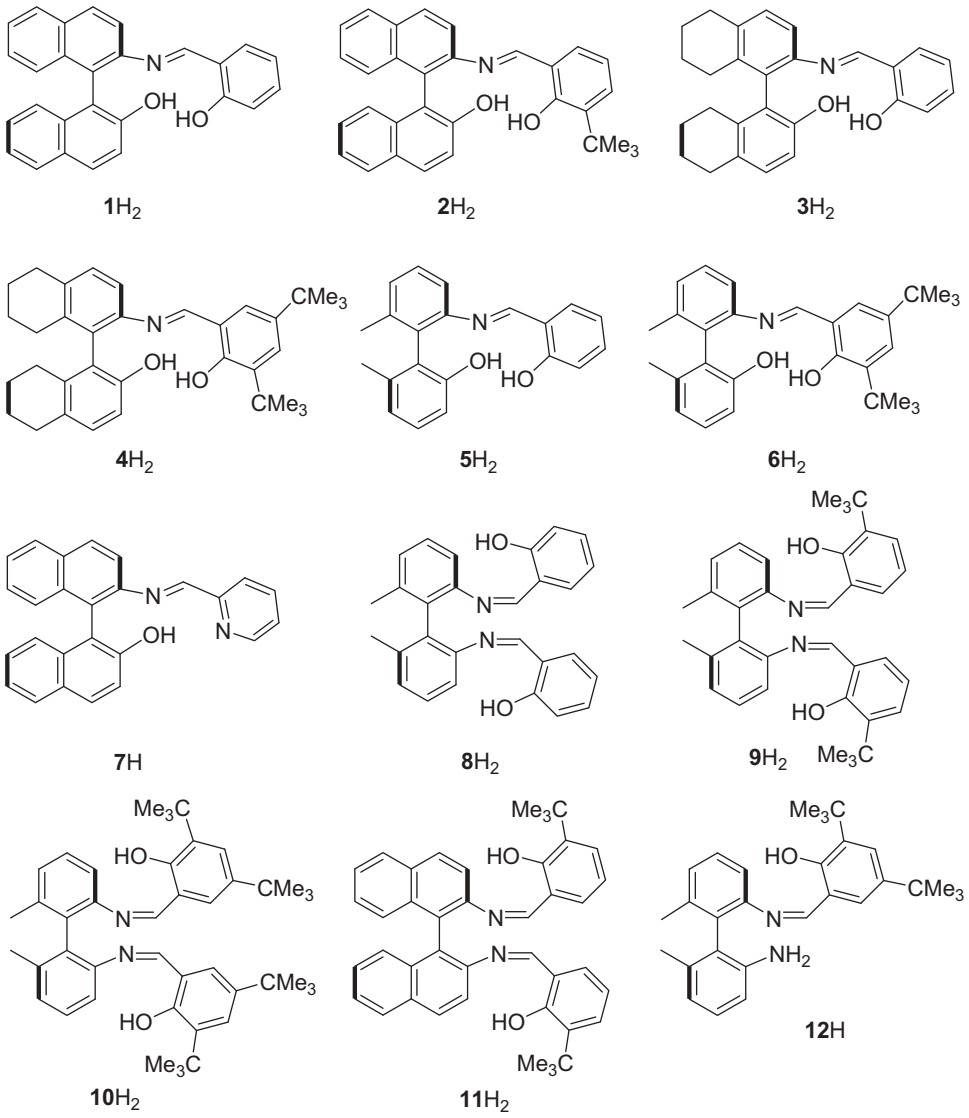

Fig. 1. Chiral Schiff-base ligands.

(*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