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Synthesis and characterization of TiL_2 complexes with tridentate (ONO) (*S*)-NOBIN Schiff-base ligands

Sanmitra Barman, John Desper, Christopher J. Levy *

Department of Chemistry, Kansas State University, 213 CBC Bldg., Manhattan, KS 66506, USA

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ABSTRACT

Tridentate (ONO) C_1-symmetric Schiff base ligands were synthesized by the condensation of (*S*)-2-amino-2′-hydroxy-1,1′-binaphthyalene with 4-hydroxy-3-phenanthrenecarboxaldehyde or 1-hydroxybenz[*a*]anthracene-2-carboxaldehyde. C_2-symmetric titanium(IV) Schiff base complexes, TiL_2, were synthesized and characterized with these ligands. The complex with the benz[*a*]anthryl unit crystallizes in a facial coordination mode, *OC*-6-1′3′-*C*, whereas complex with phenanthryl unit crystallizes in a meridional mode, *OC*-6-22′-*A*. A comparison between the complexes and the ligands were done in solution using circular dichroism spectroscopy. Preliminary catalytic studies showed that these complexes can catalyze asymmetric carbonyl-ene addition reactions of 2-methoxypropene with aromatic aldehydes with moderate selectivity. The ligands and complexes were characterized by NMR, HRMS, single crystal X-ray diffraction and CD spectroscopy.

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1. Introduction

Carbon–carbon bond formation by asymmetric aldol additions and carbonyl-ene reactions are widely used in organic synthesis and the pharmaceutical industry. These transformations are effective for producing chiral β-hydroxy aldehydes or β-hydroxy ketones [1], and considerable effort has been directed to the development of new organo- and transition metal catalysts for a variety of important substrates [2]. Effective catalysts for aldol and related hetero-ene reactions based on Ti(IV) Lewis acids with NOBIN (2-amino-2′-hydroxy-1,1′-binaphthyl) derived Schiff-base ligands were first developed by Carreira (Scheme 1) [3]. The titanium complex (*R*)-**2** derived from ligand (*R*)-**1** is sufficiently electrophilic to activate aldehydes towards the addition of weak nucleophiles such as 2-methoxypropene under mild conditions. Subsequently, the NOBIN moiety has received considerable interest as the chiral component of asymmetric catalysts [4]. Despite their significance, few transition-metal NOBIN complexes have been structurally characterized [5,6]. Herein we report two new NOBIN-based Schiff-base ligands with extended aromatic sidearms containing phenolate-type donors in phenanthryl or benz[*a*]anthryl ring structures. TiL_2 X-ray structures are reported and catalytic activity is examined for the addition of 2-methoxypropene to aryl aldehydes.

2. Materials and methods

All reactions were performed under dry nitrogen or argon unless otherwise noted. Solvents were stored over drying agents, degassed prior to use, and vacuum-transferred into reaction mixtures. Toluene and THF were dried over sodium benzophenone ketyl, ethanol was dried over magnesium, and CH_2Cl_2 was dried over calcium hydride. The aldehydes used in the catalytic runs were freshly distilled before use. The 2-methoxy propene was passed through basic alumina to remove any acidic impurities and was then distilled. The aldehyde precursors, 4-hydroxy-3-phenanthrenecarbox-aldehyde and 1-hydroxybenz[*a*]anthracene-2-carboxaldehyde were synthesized by procedures we have reported previously [7]. (*S*)-NOBIN was synthesized from *rac*-BINOL in 98% ee using literature methods [8].

CD spectra were collected on a JASCO 720 spectropolarimeter. Solution samples for this technique was prepared using dried spectroscopic grade THF, at concentrations that ranged between 1.5 and 2.5×10^{-5} M. A 1.00 cm path length quartz cell was employed for the analysis. ^1H and ^{13}C NMR spectra were obtained on a Varian Unity 400 MHz (for ^1H) spectrometer employing residual solvent protons or TMS as internal standards. Crystallographic data was collected using either a Bruker SMART 1000 CCD or a Bruker-AXS SMART APEX CCD. All mass spectra were recorded Bruker Daltonics HCT Ultra ESI-Ion Trap Mass Spectrometer. IR spectra were taken of neat samples using a Nicolet 380 FT-IR spectrometer with ZnSe ATR attachment. Single point energies for minimized geometries

* Corresponding author. Tel.: +1 (785) 532 6688; fax: +1 (785) 532 6666.
E-mail address: clevy@ksu.edu (C.J. Levy).

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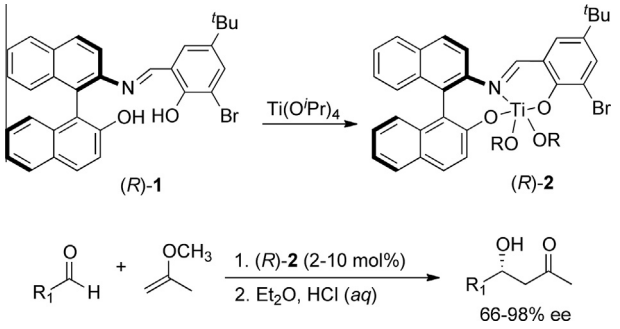


Scheme 1. Carreira's Ti(IV)-NOBIN catalyst for the asymmetric hetero-ene addition of 2-methoxypropene to aromatic, aliphatic and acetylinic aldehydes.

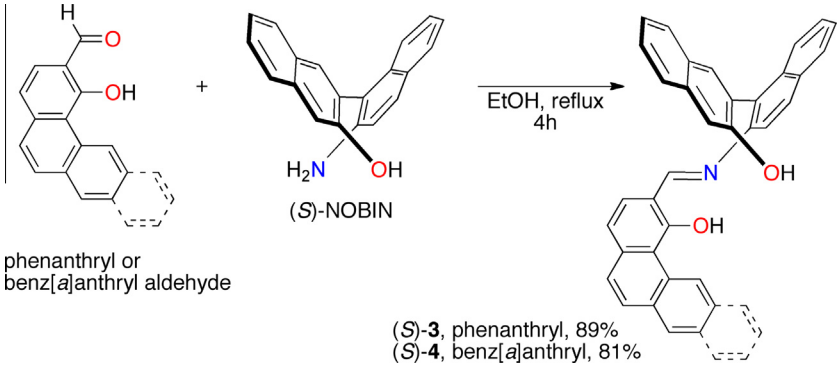
were calculated using GAUSSIAN 09 with the B3LYP density functional and the STO3G (d,p) basis set. Input files were generated using Arguslab.

2.1. (S)-3, (S)-2-hydroxy-1,1′-binaphthyl-2′-imine-phenanthrene-1-ol

A mixture of 0.0936 g (0.351 mmol) of (*S*)-NOBIN and 0.115 g (0.422 mmol) of 2-phenanthraldehyde-1-ol were refluxed in absolute ethanol (15 mL) under argon for 10 h. The mixture was hot filtered, washed with hot ethanol, and the orange solid was dried *in vacuo*. Yield of (*S*)-**3**: 0.210 g, 89% from (*S*)-NOBIN. Melting point = 201 °C; $[\alpha]_D$ (20 °C) = +124 (*c* = 1.04, THF). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.88 (s, 1H, OH); 7.12–7.14 (d, 1H, *J* = 3.4 Hz, CH); 7.26 (m, 2H, CH); 7.34–7.42 (d, 1H, *J* = 3.8 Hz, CH); 7.35 (dt, 2H, *J* = 1.8 Hz, CH); 7.36–7.42 (d, 1H, *J* = 2.8 Hz, CH); 7.42 (dt, 2H, *J* = 1.8 Hz, CH); 7.49 (d, 1H, *J* = 2.8 Hz, CH); 7.53 (m, 2H, CH); 7.56 (m, 2H, CH); 7.64 (dt, 2H, *J* = 1.8 Hz, CH); 7.75–7.77 (d, 1H, *J* = 3.8 Hz, CH); 7.83 (m, 2H, CH); 7.95–7.97 (d, 2H, *J* = 3.4 Hz, CH); 8.03 (t, 1H, *J* = 2.8 Hz, CH); 8.16–8.18 (d, 2H, *J* = 3.4 Hz, CH); 8.84 (s, 1H, CH); 9.43–9.46 (d, 1H, *J* = 3.4 Hz, CH); 14.97 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 115.14, 115.82, 117.24, 118.82, 123.74, 124.72, 125.10, 126.04, 126.63, 127.08, 127.25, 127.99, 128.32, 129.11, 129.78, 130.66, 131.00, 131.50, 132.52, 132.87, 133.79, 133.87, 137.16, 137.46, 143.72, 151.33, 160.96, 165.50. TOF-MS (*m*/*z*): $[M]^+$ Calcd for $C_{35}H_{23}O_2N_1$ 490.181, found 490.022. *Anal.* Calc. for $C_{35}H_{23}O_2N_1$: C, 85.87; H, 4.74; N, 2.86. Found: C, 85.10; H, 4.15; N, 2.13%.

2.2. (S)-4, (S)-2-hydroxy-1,1′-binaphthyl-2′-imine-benz[a] anthracene-1-ol

A mixture of 0.100 g (0.351 mmol) of (*S*)-NOBIN and 0.115 g (0.422 mmol) of 2-benz[*a*]anthraldehyde-1-ol were refluxed in



Scheme 2. Synthesis of ligands (*S*)-**3** and *S*-(**4**) by condensation.

Table 1
Crystal data and experimental parameters for structures.

Compound[a]	(*S*)-**4**	Ti[(*S*)-**3**]$_2$	Ti[(*S*)-**4**]$_2$
Empirical Formula	$C_{39}H_{25}NO_2$	$(C_{35}H_{21}NO_2)_4Ti_2\ (C_2H_6O)_4$	$(C_{39}H_{23}NO_2)_2Ti\ (C_2H_6O)_4$
M	539.60	2230.18	1307.34
Crystal system	triclinic	orthorhombic	orthorhombic
a (Å)	8.5983(8)	16.0470(7)	15.5874(14)
b (Å)	10.8846(12)	22.6153(10)	17.2424(16)
c (Å)	14.7524(15)	31.1102(15)	24.5188(17)
α (°)	94.397(4)	90.00	90.00
β (°)	97.974(4)	90.00	90.00
γ (°)	103.422(4)	90.00	90.00
Unit cell vol. (Å^3)	1321.4(2)	11290.1(9)	6589.8(10)
Space group	*P*1	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)
Z	2	4	4
T (K)	120(2)	120(2)	120(2)
Radiation	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	0.083	0.211	0.194
N	21393	130183	59496
N_{ind}	7555	29692	17538
R_{int}	0.1090	0.1457	0.1901
R_1[a] ($I > 2\sigma(I)$)	0.0719	0.0756	0.0807
wR_2[a] ($I > 2\sigma(I)$)	0.1420	0.1424	0.1480
R_1 (all data)	0.1622	0.1618	0.2059
wR_2 (all data)	0.1719	0.1726	0.1977
Goodness-of-fit (GOF)	1.001	1.004	1.037
Flack parameter		0.03(2)	−0.01(4)

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$ and $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)]\}^{1/2}$.

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