

Chiral dinuclear vanadium(v) catalysts for oxidative coupling of 2-naphthols†‡

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Preparation and structural analysis of chiral dinuclear vanadium(v) catalysts with high catalytic activity for the oxidative coupling of 2-naphthols are described.

Optically pure BINOL and its derivatives are used as chiral auxiliaries and ligands for a wide range of asymmetric syntheses.¹ In light of the important applications of these compounds, catalytic asymmetric preparation of BINOLs has continued to attract the attention of many researchers.² Asymmetric oxidative coupling of 2-naphthols using a chiral vanadium catalyst is one of the most useful methods for the synthesis of optically pure BINOL derivatives.³ The vanadium-mediated couplings, which occur *via* a favorable one-electron phenolic oxidation, generally proceed under mild reaction conditions and tolerate many functional groups, with the further advantage that only water is formed as a side product. Ung and co-workers found that the activity of catalysts could be improved by the addition of a Lewis or Brønsted acid,^{3a,b} resulting in the production of BINOL with moderate to good enantioselectivity. Barhate and Chen found that a high oxygen pressure dramatically enhanced the reaction rate but led to a significant drop in ee for the coupling product.^{3c} Although chiral vanadium catalysts give good enantioselectivity in the coupling, 2 to 15 days are required for complete reaction due to the low catalyst activities. Development of active vanadium complexes with high enantiocontrol remains a challenge. In this paper, we present chiral dinuclear vanadium(v) complexes, (*R_a,S,S*)-**2**, as highly active catalysts for asymmetric coupling of 2-naphthols (Fig. 1).

Our work has been focused on developing bifunctional enantioselective catalysts which can promote carbon–carbon bond forming reactions *via* a dual activation mechanism.⁴ We have previously reported on the chiral dinuclear vanadium(IV) complex (*R_a,S,S*)-**1** for oxidative coupling of 2-naphthols.^{4a} Simultaneous activation of two molecules of 2-naphthol by two vanadium metals in the chiral template led to smooth enantioselective homocoupling. Characterization using HRMS-FAB, FT-IR and electron spin resonance (ESR) spec-

trosopy revealed that (*R_a,S,S*)-**1** was a paramagnetic vanadium(IV) complex. During further investigation, single crystals suitable for X-ray analysis were obtained as an adduct of NaOH by recrystallization of (*R_a,S,S*)-**1** from MeOH–Et₂O–H₂O in the presence of NaOAc. The binding energy of V 2p_{3/2} for the crystals was determined to be 516.9 eV by X-ray photoelectron spectroscopy (XPS), which is attributed to V(v).^{5a} The X-ray crystal structure (ESI†) suggested that the complex had been oxidized to a distorted octahedral vanadium(v) species with one extra hydroxide for each vanadium center (V1–O3, 1.747(5) Å) (Fig. 2).^{5b,6} The hydroxide is *anti* to the imine nitrogen. The V=O (V1–O2, 1.602(8) Å) bond is *syn* to the *tert*-butyl groups in the template. The (*R*)-BINOL derivative lies about a twofold axis. The sodium cation is coordinated by the oxygen atoms of two carboxylic groups (Na1–O4, 2.393(5) Å) on the (*S*)-*tert*-leucine regions. The coordination of oxygen to several sodium cations results in helical molecular aggregation within the crystal (see ESI†).

To determine the oxidation state of the vanadium after preparation from (*R_a,S,S*)-**1**, superconducting quantum interference device (SQUID) analyses were performed on the dinuclear vanadium complexes using VOSO₄ and V₂O₅ as standards for the vanadium(IV) and vanadium(V) samples, respectively (Fig. 3).⁷ The magnetic susceptibility of (*R_a,S,S*)-**1** prepared under air was 5 emu mol⁻¹ at 5 K and 5 T (curve c). In contrast, the vanadium complex prepared under Ar gave a value of 28 emu mol⁻¹ (curve b). The magnetic susceptibility of the single crystals obtained by recrystallization, as shown in Fig. 2, was 0 emu mol⁻¹, clearly indicating a vanadium(V) species (curve d). These results suggest the dinuclear vanadium(IV) complex is readily oxidized to afford the vanadium(V) species during preparation under air.

When the single crystals (Fig. 2) were used as the catalyst for the oxidative coupling of 2-naphthol, no catalytic activity was

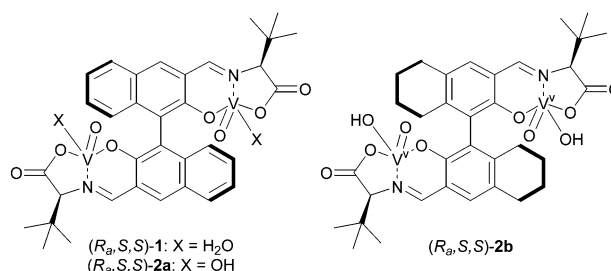


Fig. 1 Dinuclear vanadium complexes for the oxidative coupling of 2-naphthols.

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‡ Electronic supplementary information (ESI) available: Experimental section and crystallography. See DOI: 10.1039/b717068h

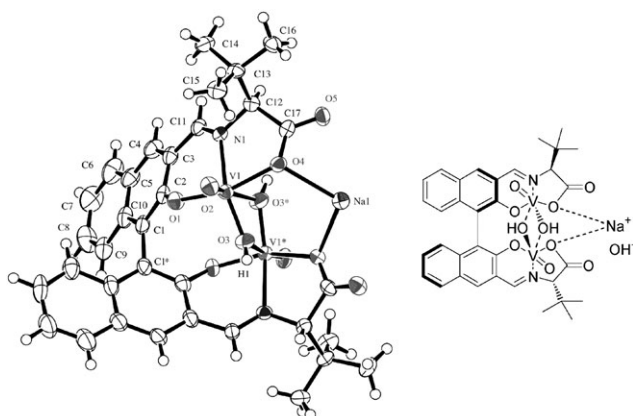


Fig. 2 Structure of the dinuclear vanadium(v) complex (R_a,S,S)-**2a**·NaOH. A counter anion OH^- , the hydrogen atom of which has not been determined, is omitted for clarity.

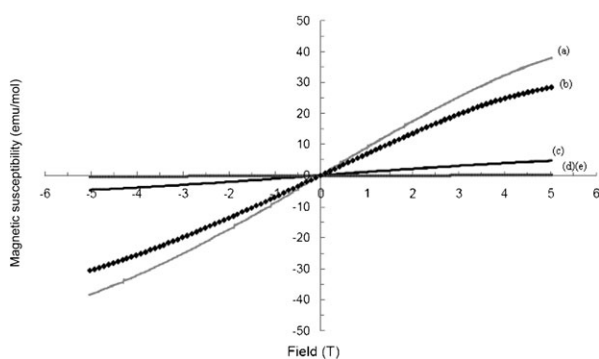


Fig. 3 SQUID magnetometer plot of magnetic susceptibility for vanadium under a magnetic field at 5 K for (a) VOSO_4 , (b) (R_a,S,S)-**1** (prepared under Ar), (c) (R_a,S,S)-**1** (prepared under air), (d) single crystals (R_a,S,S)-**2a**·NaOH obtained by recrystallization of (R_a,S,S)-**1** from $\text{MeOH-Et}_2\text{O-H}_2\text{O}$ containing NaOAc, and (e) V_2O_5 .

observed due to low solubility in CH_2Cl_2 . However, the addition of 1 equiv. of 5 M HCl aq. to the sodium cation on the crystal gave a homogeneous solution. To the above



Scheme 1 Preparation of dinuclear vanadium(v) complex (R_a,S,S)-**2a**.

Table 1 Coupling reaction of 2-naphthol catalyzed by vanadium(v) complexes

Entry	Catalyst (5 mol%)	Atmosphere	$T/^\circ\text{C}$	t/h	Yield ^a (%)	Ee ^b (%)
1	(R_a,S,S)- 2a	O_2	30	24	Quant.	71
2	(R_a,S,S)- 2a	Air	30	24	96	85
3	(R_a,S,S)- 2a	Air	0	72	Quant.	90
4 ^c	(S)- 3	O_2	30	24	46	61

^a Isolated yield. ^b Determined by chiral HPLC. ^c 10 mol% of (S)-**3** was used.

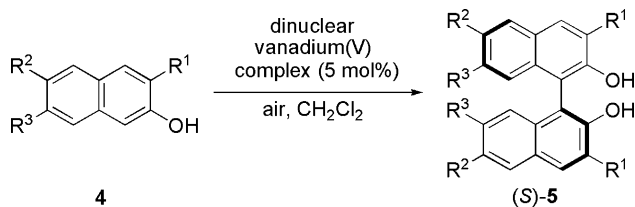
homogeneous solution, containing 5 mol% of the dinuclear vanadium(v) complex, was added 2-naphthol under air, providing (S)-BINOL in 90% yield with 83% ee after 24 h.

To determine the exact catalytic activity of the dinuclear vanadium(v) catalyst, (R_a,S,S)-**2a** was prepared from VOCl_3 , (R)-3,3'-diformyl-2,2'-dihydroxy-1,1'-binaphthyl⁸ and (S)-*tert*-leucine as shown in Scheme 1. (R_a,S,S)-**2a** was characterized by ^1H , ^{13}C , ^{51}V NMR, FT-IR, MS, and elemental analysis. Since the couplings were catalyzed by (R_a,S,S)-**2a** with reaction rates 2.3 times those of (R_a,S,S)-**1**,^{9a} the vanadium(iv) complex is likely a precatalyst.^{9b,c} Next, (R_a,S,S)-**2a** was applied to the coupling of 2-naphthol under various reaction conditions (Table 1). In all reactions, no byproducts

Table 2 Coupling reaction of 2-naphthols catalyzed by dinuclear vanadium(v) complexes (R_a,S,S)-**2**

Entry	Catalyst	Substrate	$T/^\circ\text{C}$	t/h	Yield ^a (%)	Ee ^b (%)
1	(R_a,S,S)- 2a	4a , $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$	0	72	5a , Quant.	90
2	(R_a,S,S)- 2a	4b , $\text{R}^1 = \text{R}^3 = \text{H}$, $\text{R}^2 = \text{Bn}$	0	72	5b , 91	90
3	(R_a,S,S)- 2a	4c , $\text{R}^1 = \text{R}^3 = \text{H}$, $\text{R}^2 = \text{Ph}$	30	36	5c , Quant.	86
4	(R_a,S,S)- 2a	4d , $\text{R}^1 = \text{R}^3 = \text{H}$, $\text{R}^2 = \text{Br}$	30	48	5d , 83	81
5	(R_a,S,S)- 2a	4e , $\text{R}^1 = \text{R}^2 = \text{H}$, $\text{R}^3 = \text{OMe}$	30	24	5e , 98	89
6	(R_a,S,S)- 2a	4f , $\text{R}^1 = \text{R}^2 = \text{H}$, $\text{R}^3 = \text{OCH}_2\text{CHCH}_2$	30	24	5f , Quant.	87
7	(R_a,S,S)- 2a	4g , 9-phenanthrol	0	24	5g , 94	84
8	(R_a,S,S)- 2a	4h , $\text{R}^1 = \text{OMe}$, $\text{R}^2 = \text{R}^3 = \text{H}$	30	240	5h , 35	48
9	(R_a,S,S)- 2a	4i , $\text{R}^1 = \text{CO}_2\text{Me}$, $\text{R}^2 = \text{R}^3 = \text{H}$	30	240	5i , 10	4
10	(R_a,S,S)- 2b	4a	0	72	5a , 56	97
11	(R_a,S,S)- 2b	4b	0	72	5b , 69	97
12	(R_a,S,S)- 2b	4c	30	72	5c , Quant.	93
13	(R_a,S,S)- 2b	4d	30	48	5d , 31	78
14	(R_a,S,S)- 2b	4e	0	72	5e , 67	93
15	(R_a,S,S)- 2b	4f	0	72	5f , 45	87
16	(R_a,S,S)- 2b	4g	0	24	5g , 84	77

^a Isolated yield. ^b Determined by chiral HPLC.



were observed. The reaction under O₂ afforded (*S*)-BINOL in quantitative yield with 71% ee (entry 1). Although the reaction rate was slightly decreased under air, (*S*)-BINOL was obtained in 96% yield with higher enantioselectivity (85% ee) than that produced under O₂ (entry 2). Lowering the temperature to 0 °C (entry 3) led to an increase in the selectivity to 90% ee (entry 3). The reaction rate of mononuclear vanadium(v) catalyst (*S*)-**3** was quite low in comparison with that of (*R_a,S,S*)-**2a** when using 10 mol% of (*S*)-**3** (entry 4). The higher reaction rate and enantioselectivity obtained using the complex (*R_a,S,S*)-**2a** as compared to those obtained using (*S*)-**3** can be attributed to the simultaneous activation of two molecules of 2-naphthol to form BINOL.^{9a}

We then examined the coupling reaction of various 2-naphthol derivatives. These results are summarized in Table 2. Electron donating and withdrawing substituents at the C6, C7 positions of 2-naphthol resulted in coupling products with good enantioselectivities. Although 9-phenanthrol was found to be an adequate substrate (entry 7), appending a substituent at the C3 position (R¹ = OMe, CO₂Me) led to the corresponding products with diminished yield and ee (entries 8 and 9). These C3 substituted 2-naphthols barely approach vanadium on the catalyst due to steric hindrance. The best outcome in terms of enantioselectivity was achieved using the dinuclear vanadium(v) complex (*R_a,S,S*)-**2b** bearing a H8-BINOL backbone (Fig. 1).¹⁰ (*S*)-BINOLs were obtained in 97% ee when using (*R_a,S,S*)-**2b** (entries 14 and 15). In conclusion, we have developed chiral dinuclear vanadium(v) catalysts with high catalytic activity for the oxidative coupling of 2-naphthols. Large-scale application of the dinuclear vanadium(v) catalysts is currently in progress. After preparation of this manuscript, a paper by Gong and co-workers was published, in which dinuclear vanadium(v) catalysts bearing a V–O–V linkage were employed for the synthesis of BINOLs. These catalysts were found to promote oxidative coupling of 2-naphthols with high enantioselectivity.¹¹

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- The pre-edge peak position (5468.0 eV) of the crystal, as determined by X-ray absorption near edge structure (XANES) analysis, is comparable to that of the dinuclear vanadium(v) complex (*R_a,S,S*)-**2a** (5468.0 eV) and the mononuclear vanadium(v) complex (*S*)-**3** (5468.0 eV).
- The magnetic susceptibilities of VOSO₄ and V₂O₅ as vanadium(IV) and (V) standards are 38 and 0 emu mol⁻¹, respectively.
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- (a) Catalysis of 2-naphthol coupling by complexes (*R_a,S,S*)-**1**, (*R_a,S,S*)-**2a** and (*S*)-**3** obeyed second-order kinetics for up to about 15 h. The calculated rate constants for the coupling reactions using (*R_a,S,S*)-**1**, (*R_a,S,S*)-**2a** and (*S*)-**3** as catalysts were $k_{(R_a,S,S)-1} = 0.1738 \text{ M}^{-1} \text{ h}^{-1}$, $k_{(R_a,S,S)-2a} = 0.4000 \text{ M}^{-1} \text{ h}^{-1}$, and $k_{(S)-3} = 0.0850 \text{ M}^{-1} \text{ h}^{-1}$, respectively; (b) an induction period was observed when (*R_a,S,S*)-**1** was used for the coupling of 2-naphthols. The % ee of the product increases during the course of the reaction when using (*R_a,S,S*)-**1**, from 38% ee at 4% conversion to 86% ee at 14% conversion, while the % ee of the product stays nearly constant (83–85% ee) when using (*R_a,S,S*)-**2a**; (c) in the coupling of 2-naphthol using 5 mol% of (*R_a,S,S*)-**2a** under Ar, BINOL was formed in only 9% yield after 48 h due to prevention of regeneration of the active vanadium(v) complex from the inactive vanadium(IV) complex in the absence of air. Purging the above solution with air led to the reaction occurring smoothly, producing BINOL in a total yield of 99%.
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