Dinuclear chiral vanadium catalysts for oxidative coupling of 2-naphthols *via* a dual activation mechanism

Shinobu Takizawa, Tomomi Katayama and Hiroaki Sasai*

This review describes our recent efforts in the development of chiral dinuclear vanadium complexes that work as dual activation catalysts for the oxidative coupling of 2-naphthols. The dinuclear vanadium(IV) complex (R_a,S,S)-**1a** was prepared by complexation of $VOSO_4$ with the Schiff base derived from (R)-3,3'-diformyl-2,2'-dihydroxy-1,1'-binaphthyl (**15**) and (S)-*tert*-leucine. Since the dinuclear vanadium(IV) complex was found to be readily oxidized to afford a corresponding vanadium(V) species during preparation in air, a new synthetic procedure using $VOCl_3$ has been applied towards dinuclear vanadium(V) complexes (R_a,S,S)-**2** and (R_a,S,S)-**3**. To the best of our knowledge, (R_a,S,S)-**1a**, **2** and **3** show considerably higher catalytic activity than previously reported vanadium complexes for the oxidative coupling of 2-naphthols.

1. Introduction

Asymmetric catalysis provides chemists with new and powerful tools for the efficient preparation of optically active molecules. The design and development of high performance catalysts are of ongoing interest in organic chemistry.[1] These catalysts, in combination with reaction-promoting functionalities, are considered state of the art in recent stereoselective syntheses. Dual activation by bi- or multi-functional catalysts leads to high reaction rates and appropriate positions for reaction substrates resulting in excellent asymmetric induction, and promises to offer potential gains in efficacy over mono-functional catalysts.[2] For effective dual activation of substrates such as a nucleophile and an electrophile, a balance between acidic and basic functionalities in the catalyst is required (Fig. 1, Type A). For instance in an acid–base type

*The Institute of Scientific and Industrial Research (ISIR), Osaka University, Mihogaoka, Ibaraki-shi, Osaka 567-0047, Japan.
E-mail: sasai@sanken.osaka-u.ac.jp; Fax: +81-6-6879-8469;
Tel: +81-6-6879-8465*

catalyst, the self-quenching reaction of acidic and basic sites on the catalyst can lead to inactivation. On the contrary, a chiral complex with two identical metal centers in one molecule, which could activate two substrates simultaneously in a homolytic coupling reaction of 2-naphthols, would enhance the reaction rate with high enantiocontrol (Type B).[3] To achieve the dual activation concept in an oxidative coupling reaction, we have designed and developed the catalysts (R_a,S,S)[4]-**1a**, **2** and **3** possessing two active sites attached to a binaphthyl-derived skeleton, which take advantage of activation entropy. Activation entropy strongly contributes to oxidative coupling after two molecules of 2-naphthol are complexed with the dinuclear vanadium catalyst.[5]

2. Chiral vanadium catalysts for oxidative coupling of 2-naphthols

Optically pure BINOLs have been successfully used as chiral ligands and auxiliaries for highly stereoselective reactions.[6] For this reason, the synthesis of optically pure BINOLs has continued

Dr Shinobu Takizawa was born in 1971 and received his BC and MS from Toyama Medical and Pharmaceutical University. He was a JSPS fellow (1999–2000) and received his PhD in 2000 from Osaka University. He became an Assistant Professor at Osaka University in 2000. Since 2006, he has been staying at the Scripps Research Institute (TSRI) as a Research Associate. He received the Daiichi Pharmaceutical Co. Ltd. Award in Synthetic Organic Chemistry, Japan, in 2000.

Ms Tomomi Katayama was born in 1983 and received her MS in 2007 from Osaka University.

Prof. Dr Hiroaki Sasai was born in 1956 and received his PhD in 1985 from Keio University. After three years at Sagami Chemical Research Center as a Researcher he joined Prof. Shibasaki's group at Hokkaido University. In 1992, he moved to the University of Tokyo, and in 1997 he was promoted to the Professor of Chemistry at the ISIR, Osaka University. He was a recipient of 1995 Pharmaceutical Society of Japan Award for Young Scientists and The Fluka Prize "Reagent of the Year 1996". In 2006 he received The Chemical Society of Japan Award for Creative Work and the Ichimura Science Award.
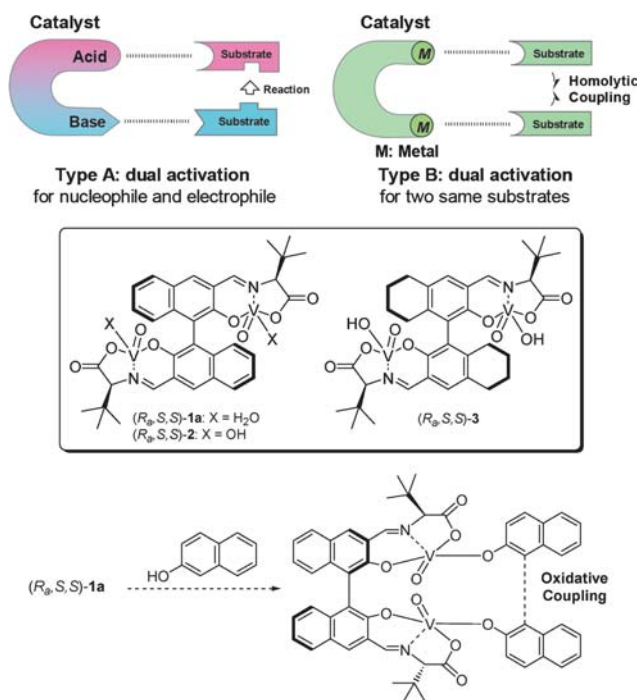
Fig. 1 Dinuclear vanadium complex with dual activation system in oxidative coupling of 2-naphthols.
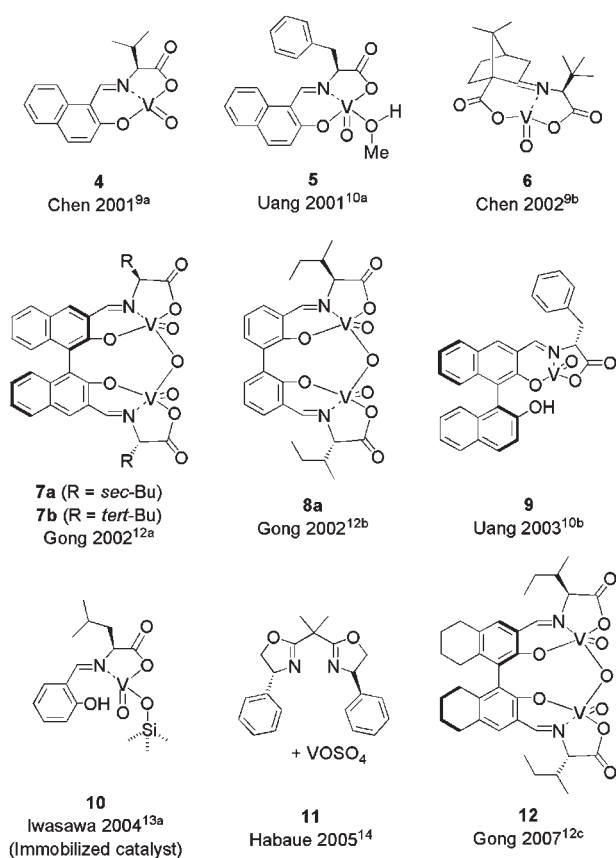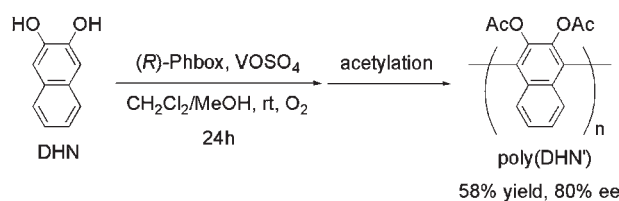

Fig. 2 Chiral vanadium catalysts for the oxidative coupling of 2-naphthols.

Scheme 1 Asymmetric oxidative coupling polymerization of 2,3-dihydroxynaphthalene (DHN) promoted by the catalyst 11 derived from VOSO₄ and (R)-Phbox.

to attract the attention of many researchers.[7] The asymmetric oxidative coupling of 2-naphthols with a chiral vanadium catalyst provides one of the simplest routes to prepare optically pure BINOLs. Vanadium-mediated couplings proceed under mild reaction conditions and tolerate many functional groups, with the further advantage that only water is formed as a side product. In 1969, Carrick first reported that VCl_4 and $VOCl_3$ catalyzed the coupling reaction of 2-naphthols to produce racemic BINOLs.[8] In 2001, Chen[9a] and Uang[10a] independently reported the first efficient asymmetric vanadium(IV) catalysts 4 and 5 for oxidative coupling of 2-naphthols which are prepared from vanadyl sulfate, aldehydes and (S)-amino acids[11] (Fig. 2). Chen investigated the effect of oxygen pressure to improve the coupling yields. The coupling rate of 2-naphthol using catalyst 6[9b] was greatly enhanced by more than six times under an oxygen pressure of 8.8 atm, though a significant drop in ee for BINOL was observed from 84 to 54% ee. Uang found that the activity of catalysts 5 and 9 could be improved by the addition of Lewis[10a] or Brønsted acids.[10b] Gong reported highly enantioselective dinuclear vanadium catalysts 7a–b, 8a and 12 possessing a V–O–V linkage.[12] The self-dimerized vanadium complexes 10 on SiO_2 were developed by Iwasawa for the oxidative coupling of 2-naphthol.[13] Habaue explored the asymmetric oxidative coupling polymerization of 2,3-dihydroxynaphthalene (DHN) promoted by catalyst 11 prepared from (R)-Phbox and vanadyl sulfate (Scheme 1).[14] The enantioselectivity during the polymerization was estimated to be 80% ee, though catalyst 11 gave (R)-BINOL with 4% ee when using 2-naphthol as a substrate. Although the vanadium catalysts as shown in Fig. 2 exhibited good enantioselectivity for the coupling of 2-naphthols, the catalytic activity was moderate (Table 1).

Development of active vanadium complexes with high enantiocontrol remains a challenge.
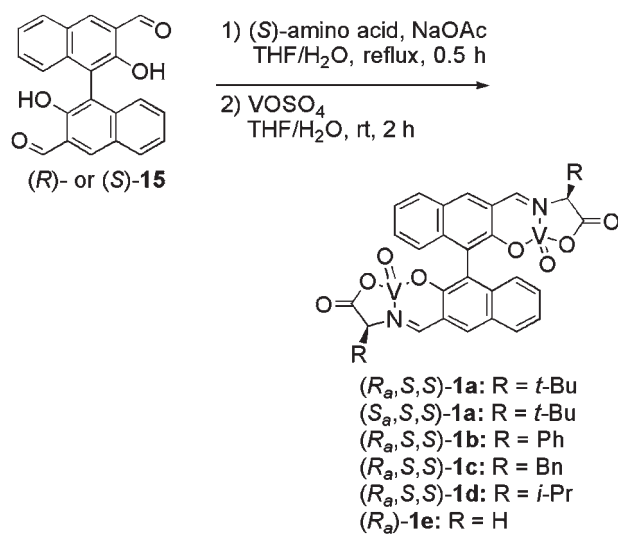
3. Chiral dinuclear vanadium(IV) complexes for oxidative coupling of 2-naphthol

In order to create a dual activation system in an oxidative coupling reaction, dinuclear vanadium(IV) complexes were prepared from vanadyl sulfate, (R)- or (S)-3,3′-diformyl-2,2′-dihydroxy-1,1′-binaphthyl (15) and amino acids (Scheme 2). Since NMR spectroscopy is not suitable for the paramagnetic vanadium(IV) species, FAB-HRMS, electron spin resonance (ESR) spectroscopy and FT-IR analyses were used to characterize 1. ESR of (R_a,S,S)-1a showed eight peaks which can be assigned to a vanadium(IV) species (Fig. 3). The oxidative coupling reactions of 2-naphthol by catalysts 1 were carried out in CH_2Cl_2 at 30 °C for 24 h under oxygen (Table 2). Among the catalysts we studied, (R_a,S,S)-1a possessing tert-butyl groups exhibited an extremely high catalytic activity in the oxidative coupling of 2-naphthol (entry 1). No byproduct was observed in any reaction. Since the diastereomeric
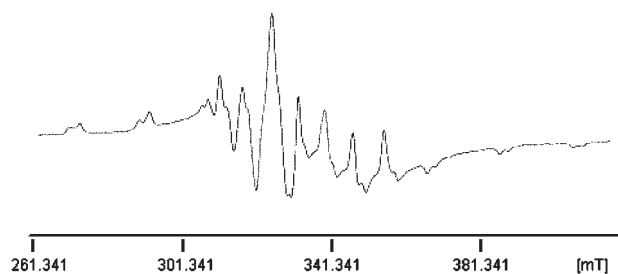
Table 1 Oxidative coupling of 2-naphthol mediated by chiral vanadium catalysts

Catalyst (mol%)	Atmosphere (1 atm)	Solvent	Temp./°C	Time/h	Yield (%)	Ee (%)
4 (10)	O_2	CCl_4	0	144	94	62 (R)
5 (2)[a]	O_2	$CHCl_3$	Rt	24	82	51 (R)
6 (3)	O_2	CCl_4	40–45	168	99	84 (S)
7a (10)	O_2	CCl_4	0	144	93	83 (R)
7b (10)	O_2	CCl_4	0	192	63	71 (R)
8a (10)	O_2	CCl_4	0	168	89	89 (R)
9 (5)	O_2	$CHCl_3$	Rt	17	93	54 (R)
10 (3)	Air	Toluene	−10	264	93	90 (R)
11 (10)	O_2	CH_2Cl_2–MeOH (7 : 1)	Rt	144	27	4 (R)
12 (5)	Air	CCl_4	0	96	58	60 (R)

[a] 2 mol% of TMSCl was added.

Scheme 2 Preparation of dinuclear vanadium(IV) complexes **1**.

Fig. 3 ESR spectrum of (R_a,S,S)-**1a** in CH_2Cl_2 at −120 °C.

phenyl–phenyl or phenyl–naphthyl unit, were also prepared, though their reaction rates were decreased compared to (R_a,S,S)-**1a** (entries 7 and 8). In the case of the complexes (S,S)-**16** and **17**, the equilibrium between matched and mismatched conformations reduced the reaction rate. These results revealed that the two *tert*-leucine derived moieties in the catalyst affect the enantiocontrol of the coupling and the binaphthyl backbone assists in aligning the two molecules of 2-naphthol with each other for the oxidative coupling.
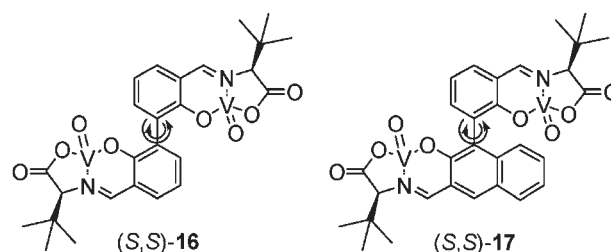
An insufficient amount of vanadyl sulfate leads to the formation of vanadium(IV) complex **18** which bears only one vanadium metal in the catalyst molecule. An attempt to deliberately prepare complex **18** for comparison of its catalytic activity with that of (R_a,S,S)-**1a** resulted in a switch of the major product enantiomer to (R)-BINOL with 13% ee (Table 3, entry 1). To prevent the formation of a mononuclear vanadium catalyst, 4 equiv. of vanadyl sulfate was used (entry 3). The excess vanadyl sulfate can be filtered off after complex formation. Although the reaction rate promoted by (R_a,S,S)-**1a** was slightly decreased under air, (S)-BINOL was obtained with higher enantioselectivity than that produced under oxygen (entry 4). In either CCl_4 or $CHCl_3$, the reaction mixture was heterogeneous and (S)-BINOL was obtained in low yields with moderate enantioselectivity (entries 6 and 7). In $(CH_2Cl)_2$, the coupling reaction proceeded smoothly to

catalyst (S_a,S,S)-**1a** was less active (entry 2), (R_a,S,S)-**1a** constitutes a *matched pair* and (S_a,S,S)-**1a** would be a *mismatched pair*[15] for the oxidative coupling of 2-naphthol. The tropos-type[16] complexes (S,S)-**16** and **17**, with free rotation of either the

Table 2 Enantioselective coupling of 2-naphthol promoted by chiral dinuclear vanadium(IV) catalysts

$$13a \xrightarrow[\text{O}_2(1atm),CH_2Cl_2,30\ °C,\ 24\ h]{\text{Catalyst}(5mol\%)} 14a$$

Entry	Catalyst	Yield (%)	Ee (%)
1	(R_a,S,S)-**1a**	83	83 (S)
2	(S_a,S,S)-**1a**	9	2 (R)
3	(R_a,S,S)-**1b**	21	Rac
4	(R_a,S,S)-**1c**	30	8 (R)
5	(R_a,S,S)-**1d**	52	66 (S)
6	(R_a)-**1e**	6	Rac
7	(S,S)-**16**	57	81 (S)
8	(S,S)-**17**	63	81 (S)

Table 3 Activity of the catalyst derived from various amounts of VOSO$_4$, (R)-**15** and (S)-tert-leucine

Entry	Amount of VOSO$_4$[a]/ mol equiv.	Atmosphere	Solvent	Amount of catalyst (mol%)	Time/h	Yield (%)	Ee (%)
1	1	O$_2$	CH$_2$Cl$_2$	5	24	15	13 (R)
2	2	O$_2$	CH$_2$Cl$_2$	5	24	64	78 (S)
3	4	O$_2$	CH$_2$Cl$_2$	5	24	83	83 (S)
4	4	Air	CH$_2$Cl$_2$	5	24	76	91 (S)
5	4	Air	CH$_2$Cl$_2$	1	168	99	90 (S)
6	4	Air	CCl$_4$	5	24	42	36 (S)
7	4	Air	CHCl$_3$	5	24	40	63 (S)
8	4	Air	(CH$_2$Cl)$_2$	5	24	99	89 (S)

[a] Numbers shows molar equiv. to the diformyl compounds.

afford (S)-BINOL with similar enantiocontrol to that mediated in CH$_2$Cl$_2$ (entry 8).

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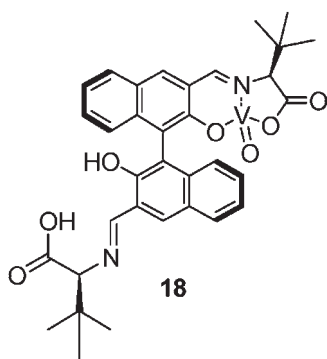
4. Confirmation of the oxidative state of vanadium in the catalyst

During further characterization, single crystals suitable for X-ray analysis were obtained by recrystallization of (R_a,S,S)-**1a** from MeOH–Et$_2$O–H$_2$O in the presence of NaOAc as an interfusion form in the complexation as shown in Scheme 2.[17] The binding energy of V 2p$_{3/2}$ for the crystals is 516.9 eV by X-ray photoelectron spectroscopy (XPS), which is attributed to V(v).[18] The complex was oxidized to a distorted octahedral vanadium(v) species with one extra hydroxide to each vanadium center [V1–O3, 1.747(5) Å] (Fig. 4a).[19] The hydroxyl group 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 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 a helical molecular aggregation within the crystal (Fig. 4b and 4c). To determine the oxidative state of vanadium after complex formation to yield (R_a,S,S)-**1a**, superconducting quantum interference device (SQUID) analyses were carried out on the dinuclear vanadium complexes.[20] The magnetic susceptibility of (R_a,S,S)-**1a** prepared under air was 5 emu mol^{-1} at 5 K in 5 T. In contrast, the vanadium complex prepared under argon gave a value of 28 emu mol^{-1}. The magnetic susceptibility of the single crystals obtained by the recrystallization, as shown in Fig. 4, exhibited 0 emu mol^{-1}, clearly indicating a vanadium(v) species. These results suggest the dinuclear vanadium(IV) complex is readily oxidized to afford a vanadium(v) species during preparation in air. When single crystals (Fig. 4) were used as the catalyst for the oxidative coupling of 2-naphthol, no catalytic activity was observed. This may be attributed to the low solubility in CH$_2$Cl$_2$. However, the addition of 1 equiv. of 5 N HCl aq. to the sodium in the crystal gave a homogeneous solution.[21] To the 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.

5. Kinetic analysis of vanadium complexes in the coupling reaction

In order to clarify the dual activation mechanism in the dinuclear vanadium catalyst (R_a,S,S)-**1a**, mononuclear vanadium(IV) complex (S)-**19** was prepared. In the kinetic analysis (Fig. 5), the amount of (S)-**19** used was twice that of (R_a,S,S)-**1a** because
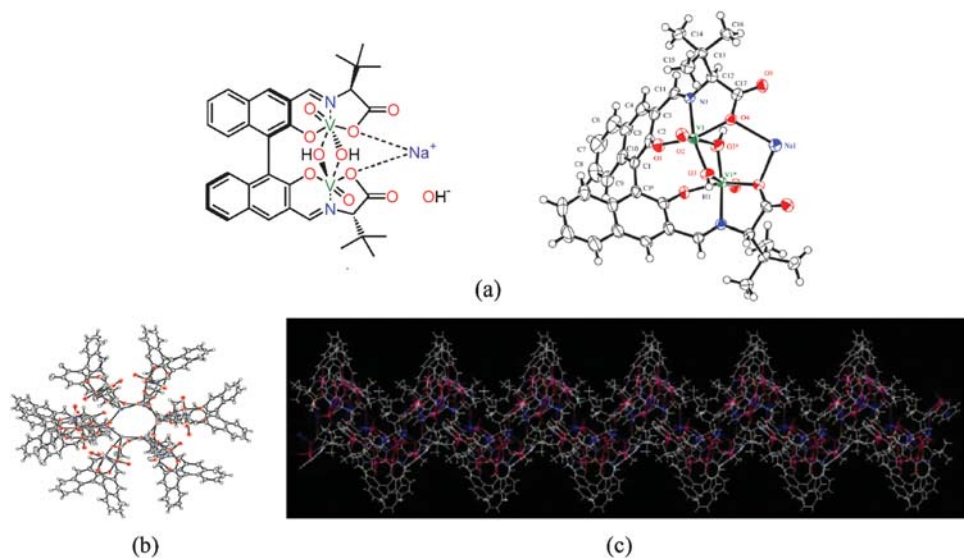
Fig. 4 (a) Structure of the dinuclear vanadium(v) complex (R_a,S,S)-**2** NaOH. A counter anion OH⁻, the hydrogen atom of which has not been determined, is omitted for clarity. (b) Top view. (c) Side view (ref. 3*b*).

(S)-**19** has only one active center. The catalysis by (R_a,S,S)-**1a** and (S)-**19** obeyed second-order kinetics up to about 15 h. The mononuclear complex (S)-**19** had quite low activity and gave almost racemic BINOL. The calculated rate constants for the coupling reactions were $k_{(R_a,S,S)\text{-}1a} = 0.1738$ M⁻¹h⁻¹ and $k_{(S)\text{-}19} = 0.0036$ M⁻¹h⁻¹. The coupling rate in the presence of 5 mol% of the dinuclear complex (R_a,S,S)-**1a** was shown to be up to 48.3 times faster than that using 10 mol% of the mononuclear complex (S)-**19**. Calculations based on Arrhenius and Eyring plots indicated that the activation energies of catalysts (R_a,S,S)-**1a** and (S)-**19** were $\Delta E_{(R_a,S,S)\text{-}1a} = 0.74$ kcal mol⁻¹ and $\Delta E_{(S)\text{-}19} = 23$ kcal mol⁻¹. The activation entropy and enthalpy of catalyst (R_a,S,S)-**1a** were $\Delta S^{\ddagger}_{(R_a,S,S)\text{-}1a} = -7.8 \times 10^{-2}$ kcal mol⁻¹ K⁻¹ and $\Delta H^{\ddagger}_{(R_a,S,S)\text{-}1a} = 0.16$ kcal mol⁻¹, and those of (S)-**19** were $\Delta S^{\ddagger}_{(S)\text{-}19} = -1.5 \times 10^{-2}$ kcal mol⁻¹ K⁻¹, and $\Delta H^{\ddagger}_{(S)\text{-}19} = 21$ kcal mol⁻¹, respectively. The *lower activation entropy* using

(R_a,S,S)-**1a** compared to (S)-**19** is attributed to the dual activation of two 2-naphthol molecules in one chiral complex to produce BINOL. The *higher activation enthalpy* using (S)-**19** compared to (R_a,S,S)-**1a** is due to the intermolecular radical–radical coupling of reaction intermediates after complexation of (S)-**19** with 2-naphthol. To realize the most powerful dual activation catalyst in the oxidative coupling, dinuclear vanadium(v) complex (R_a,S,S)-**2** and mononuclear vanadium(v) complex (S)-**20** were also prepared by a use of VOCl₃ as vanadium(v) source. The coupling of 2-naphthol was catalyzed by (R_a,S,S)-**2** with reaction rates enhanced 2.3 times faster than that of (R_a,S,S)-**1a**. The dinuclear vanadium(IV) complex is likely a precatalyst.[22] Interestingly, not only the reaction rate but also the enantioselectivity of mononuclear vanadium(v) complex (S)-**20** was significantly higher than that of mononuclear vanadium(IV) complex (S)-**19**. In addition, an induction period was observed when using (S)-**20**.[23]
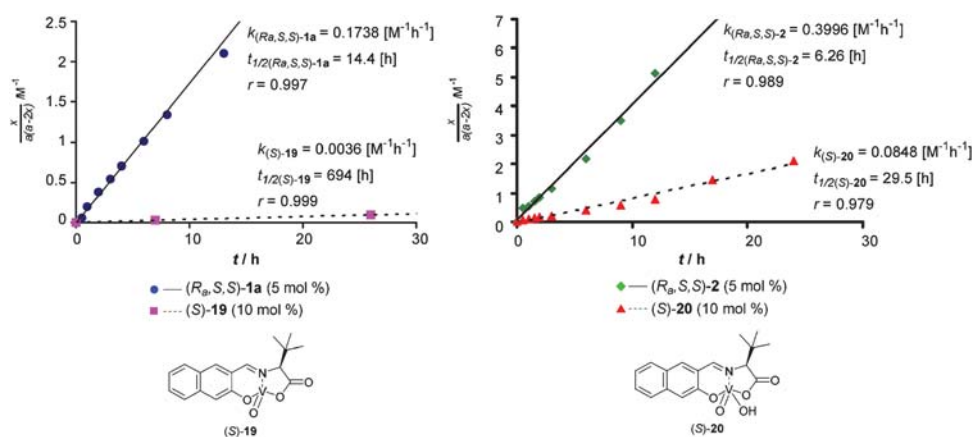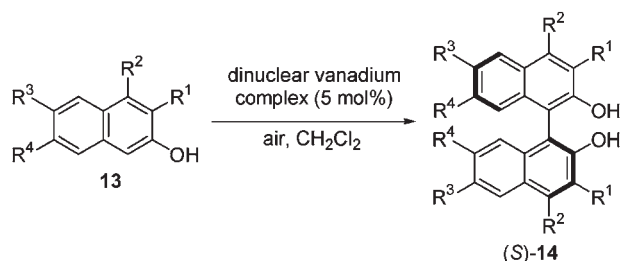

Fig. 5 Kinetic analysis of either mononuclear vanadium or dinuclear vanadium catalyst-mediated oxidative coupling reactions of 2-naphthol; a = initial concentration of 2-naphthol (0.2 M), x = concentration of BINOL.

Table 4 Coupling reaction of 2-naphthols catalyzed by dinuclear vanadium complexes

| Entry	Vanadium complex	Substrate	Temp./°C	Time/h	Product and yield (%)	Ee (%)
1	(R_a,S,S)-**1a**	$R^1 = R^2 = R^3 = R^4 = H$, **13a**	30	24	**14a**, 76	91
2	(R_a,S,S)-**2**	**13a**	0	72	**14a**, quant.	90
3	(R_a,S,S)-**3**	**13a**	0	72	**14a**, 56	97
4	(R_a,S,S)-**1a**	$R^1 = R^2 = H$, $R^3 = OMe$, $R^4 = H$, **13b**	30	24	**14b**, quant.	86
5	(R_a,S,S)-**2**	**13b**	30	24	**14b**, 98	89
6	(R_a,S,S)-**1a**	$R^1 = R^2 = H$, $R^3 = Br$, $R^4 = H$, **13c**	30	48	**14c**, 43	68
7	(R_a,S,S)-**2**	**13c**	30	48	**14c**, 83	81
8	(R_a,S,S)-**3**	**13c**	30	48	**14c**, 31	78
9	(R_a,S,S)-**1a**	$R^1 = CO_2Me$, $R^2 = R^3 = R^4 = H$, **13d**	30	240	**14d**, trace	—
10	(R_a,S,S)-**2**	**13d**	30	240	**14d**, 10	4
11	(R_a,S,S)-**1a**	$R^1 = H$, $R^2 = Br$, $R^3 = R^4 = H$, **13e**	30	48	**14e**, 35	86
12	(R_a,S,S)-**1a**	$R^1 = R^2 = H$, $R^3 = Me$, $R^4 = H$, **13f**	0	72	**14f**, 62	92
13	(R_a,S,S)-**1a**	$R^1 = R^2 = H$, $R^3 = OMOM$, $R^4 = H$, **13g**	0	72	**14g**, 83	89
14	(R_a,S,S)-**1a**	$R^1 = R^2 = H$, $R^3 = OBn$, $R^4 = H$, **13h**	30	24	**14h**, 94	89
15	(R_a,S,S)-**2**	**13h**	0	72	**14h**, 94	80
16	(R_a,S,S)-**1a**	$R^1 = R^2 = H$, $R^3 = Bn$, $R^4 = H$, **13i**	0	72	**14i**, 91	93
17	(R_a,S,S)-**2**	**13i**	0	72	**14i**, 91	90
18	(R_a,S,S)-**3**	**13i**	0	72	**14i**, 69	97
19	(R_a,S,S)-**1a**	$R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = H$, **13j**	30	24	**14j**, 82	88
20	(R_a,S,S)-**2**	**13j**	30	36	**14j**, quant.	86
21	(R_a,S,S)-**3**	**13j**	30	72	**14j**, quant.	93
22	(R_a,S,S)-**1a**	$R^1 = R^2 = R^3 = H$, $R^4 = OMe$, **13k**	30	24	**14k**, 55	86
23	(R_a,S,S)-**2**	**13k**	30	24	**14k**, 98	86
24	(R_a,S,S)-**3**	**13k**	0	72	**14k**, 67	93
25	(R_a,S,S)-**1a**	$R^1 = R^2 = R^3 = H$, $R^4 = OMOM$, **13l**	0	72	**14l**, 51	92
26	(R_a,S,S)-**1a**	$R^1 = R^2 = R^3 = H$, $R^4 = OCH_2CHCH_2$, **13m**	30	24	**14m**, 71	87
27	(R_a,S,S)-**2**	**13m**	30	24	**14m**, quant.	87
28	(R_a,S,S)-**3**	**13m**	0	72	**14m**, 45	87
29	(R_a,S,S)-**1a**	9-Phenanthrol, **13n**	0	24	**14n**, 84	77
30	(R_a,S,S)-**2**	**13n**	0	24	**14n**, 94	84
31	(R_a,S,S)-**3**	**13n**	0	24	**14n**, 84	77
32	(R_a,S,S)-**1a**	$R^1 = OMe$, $R^2 = R^3 = R^4 = H$, **13o**	30	240	**14o**, 35	45
33	(R_a,S,S)-**2**	**13o**	30	240	**14o**, 35	48
34	(R_a,S,S)-**1a**	5,6,7,8-Tetrahydro-2-naphthol, **13p**	30	120	**14p**, 12	13
35	(R_a,S,S)-**2**	**13p**	30	120	**14p**, 26	14
36	(R_a,S,S)-**2**	**13a**	30	24	**14a**, 96	85
37	(S_a,S,S)-**2**	**13a**	30	24	**14a**, 15	47
38	(S)-**20**[a]	**13a**	30	24	**14a**, 37	81

[a] 10 mol% of catalyst was used.

6. Dinuclear vanadium complexes catalyzed oxidative coupling reaction of 2-naphthols

To elucidate the generality of the dual activation concept in oxidative coupling of 2-naphthols, the C3, C4, C6 or C7 substituted 2-naphthols were investigated with dinuclear vanadium complexes (Table 4). 2-Naphthol bearing electron donating or withdrawing groups at the C4 (R^2), C6 (R^3) and C7 (R^4) positions resulted in coupling products with high enantioselectivities (entries 4–8 and 11–28). 9-Phenanthrol was found to be an adequate substrate (entries 29–31), although appending a substituent at the C3 position ($R^1 = CO_2Me$, OMe) led to the corresponding product with diminished yield and ee (entries 9, 10, 32 and 33). These C3-substituted 2-naphthols barely approach vanadium on the catalyst due to steric hindrance. The dinuclear vanadium complexes mediated coupling of 5,6,7,8-tetrahydro-2-naphthol to afford H8-BINOL[24] for the first time, though with low chemical yields and low enantioselectivities (entries 34 and 35). In terms of enantioselectivity, the best result was achieved by using dinuclear vanadium(v) complex (R_a,S,S)-**3**, which was prepared from VOCl$_3$, (R)-3, 3'-diformyl-H8-BINOL and (S)-*tert*-leucine. (S)-BINOLs were obtained in 97% ee when using (R_a,S,S)-**3** (entries 3 and 18).

## 7. Reaction mechanism of chiral dinuclear complex-mediated coupling

In the coupling of 2-naphthol using 5 mol% of (R_a,S,S)-**2** under Ar, BINOL was formed with only 9% yield after 48 h due to no re-oxidation of the vanadium(IV) complex in the absence of air. After introducing air to the reaction vessel, the catalytic cycle sufficiently resumed to produce BINOL in 99% yield. The cross-couplings of **13a** with **13d**, and **13b** with **13c** catalyzed by (R_a,S,S)-**2** afforded only homolytic coupling products **14** and no cross-coupling product was observed in any case (**14a** and **14d**: quant. (83% ee) and 0% yield; **14b** and **14c**: 98% yield (86% ee) and 21% yield (68% ee), respectively). The complex (R_a,S,S)-**2** mediated coupling might include neither a simple radical–radical nor a radical–anion
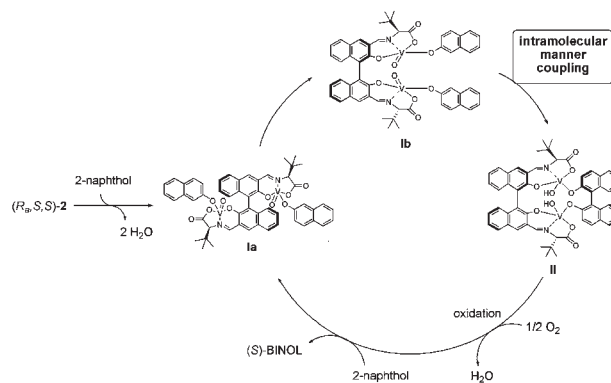
Scheme 3 Plausible mechanism for (R_a,S,S)-**2** catalyzed oxidative coupling reaction.

Table 5 Preparation and catalytic activity of dinuclear vanadium(IV) catalysts (R_a,S,S)-**1a**, (S,S)-**16**, dinuclear vanadium(V) catalysts (R_a,S,S)-**2**, (R_a,S,S)-**3** and Gong's catalysts **7**, **8**, **12**

| Catalyst | Preparation of complex | | | Catalytic activity | |
	Vanadium source (mol eq)[a]	Solvent for complexation	Characterization	Optimized reaction conditions	Coupling of **13a**
(R_a,S,S)-**1a**	VOSO$_4$xH$_2$O, x = 3–5 (4.0)[b]	THF/H$_2$O	IR, HRMS(FAB), ESR	Cat. 5 mol% 30 °C, air, CH$_2$Cl$_2$ 24 h	76% yield, 91% ee (S)
(R_a,S,S)-**2**	VOCl$_3$ (4.0)	CH$_2$Cl$_2$	^{1}H-, ^{13}C-, ^{51}V-NMR, IR, HRMS(ESI), X-ray crystallography and elemental analysis, SQUID, XANES, XPS	Cat. 5 mol% 0 °C, air, CH$_2$Cl$_2$ 72 h	quant, 91% ee (S)
(S,S)-**16**	VOSO$_4$xH$_2$O, x = 3–5 (4.0)[b]	THF/H$_2$O	IR, HRMS(FAB), ESR	Cat. 2.5 mol% 30 °C, air, CH$_2$Cl$_2$ 72 h	84% yield, 92% ee (S)
(R_a,S,S)-**3**	VOCl$_3$ (4.0)	CH$_2$Cl$_2$	1H-, ^{13}C-NMR, IR, HRMS(ESI)	Cat. 5 mol% 0 °C, air, CH$_2$Cl$_2$ 72 h	56% yield, 97% ee (S)
(R_a,S,S)-**7a**[12]	VOSO$_4$·3H$_2$O (2.0)	EtOH/THF/H$_2$O	^{51}V-NMR, IR, HRMS(ESI)	Cat. 10 mol% 0 °C, O$_2$, CCl$_4$ 144 h	93% yield, 83% ee (R)
(R_a,S,S)-**7b**[12]	VOSO$_4$·3H$_2$O (2.0)	EtOH/THF/H$_2$O	IR, HRMS(ESI)	Cat. 10 mol% 0 °C, O$_2$, CCl$_4$ 192 h	63% yield, 71% ee (R)
(S,S)-**8a**[12]	VOSO$_4$·3H$_2$O (2.2)	EtOH/THF/H$_2$O	^{1}H-, ^{13}C-, ^{51}V-NMR, IR, HRMS(ESI), elemental analysis	Cat. 10 mol% 0 °C, O$_2$, CCl$_4$ 168 h	89% yield, 89% ee (R)
(S,S)-**8b**[12]	VOSO$_4$·3H$_2$O (2.2)	EtOH/THF/H$_2$O	IR, HRMS(ESI)	Cat. 10 mol% 0 °C, O$_2$, CCl$_4$ 168 h	56% yield, 79% ee (R)[26]
(R_a,S,S)-**12**[12]	VOSO$_4$·3H$_2$O (2.2)	EtOH/THF/H$_2$O	IR, HRMS(ESI)	Cat. 5 mol% 0 °C, air, CCl$_4$ 96 h	58% yield, 60% ee (R)
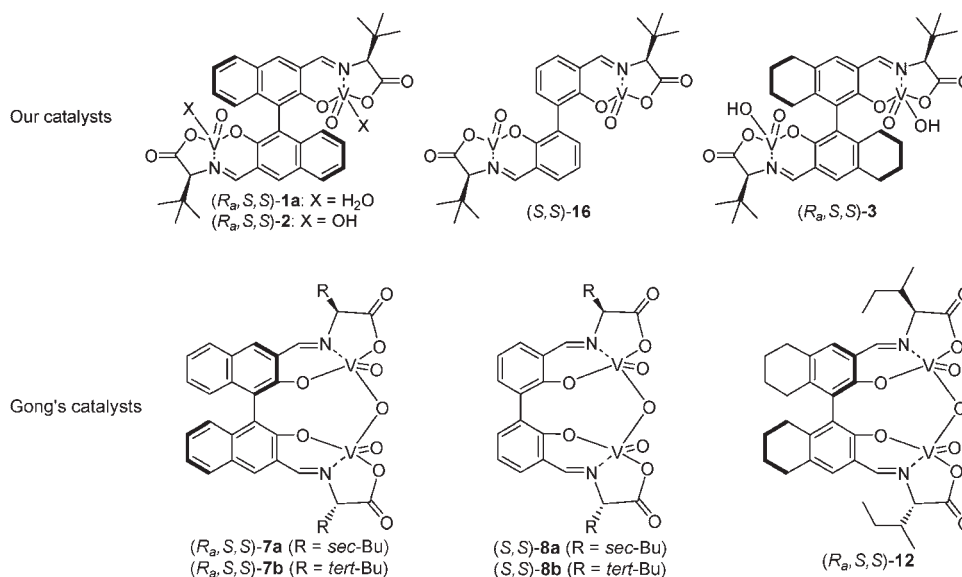
[a] Numbers show molar equiv. to the diformyl compounds. [b] 99.99% VOSO$_4$·xH$_2$O, x = 3–5 (Aldrich, product no. 204862) was used.

Table 6 Catalyst activities in the oxidative coupling of 2-naphthol under Gong's optimized conditions[12]

$$13a \xrightarrow[\text{O}_2, \text{CCl}_4, \, 0\,^{\circ}\text{C}]{\text{Catalyst (10 mol\%)}} 14a$$

Entry	Chiral catalyst	Time/h	Yield (%)	Ee (%)
1[a]	(R_a,S,S)-**1a**	192	16	8
2[a]	Gong's catalyst **7b** (according to Gong's procedure)[b]	192	7–42	39–60
3[a]	(R_a,S,S)-**2**	72	70	76
4[a]	Gong's result using **7b** (ref. 12)	192	63	71

[a] Heterogeneous. [b] Gong's catalyst **7b** was prepared from (R)-**15** (1 mol equiv), (S)-*tert*-leucine (2.0 mol equiv) and VOSO$_4$ (2.0 mol equiv).[12]

Table 7 Coupling reaction of 2-naphthols catalyzed by dinuclear vanadium(v) complexes

$$13 \xrightarrow[\text{solvent, } 0\,^{\circ}\text{C}]{\text{dinuclear vanadium(V) complex (10 mol\%)}} 14$$

Entry	Catalyst	Atmosphere	Solvent	Substrate	Time/h	Yield (%)	Ee (%)
1	(R_a,S,S)-**2**	O$_2$	CH$_2$Cl$_2$	**13a**	72	**14a**, quant.	90 (S)
2	(R_a,S,S)-**2**	O$_2$	(CH$_2$Cl)$_2$	**13a**	72	**14a**, 49	67 (S)
3[a]	(R_a,S,S)-**2**	O$_2$	Toluene	**13a**	72	**14a**, 33	64 (R)
4[a]	(R_a,S,S)-**2**	O$_2$	CCl$_4$	**13a**	72	**14a**, 70	76 (R)
5[a]	(R_a,S,S)-**2**	O$_2$	CCl$_4$	**13c**	219	**14c**, 52	91 (R)
6[a]	(R_a,S,S)-**2**	O$_2$	CCl$_4$	**13d**	240	**14d**, trace	—
7[a]	(R_a,S,S)-**2**	O$_2$	CCl$_4$	**13j**	195	**14j**, 23	73 (R)
8[a]	(R_a,S,S)-**2**	O$_2$	CCl$_4$	**13k**	144	**14k**, 48	95 (R)
9[a]	(R_a,S,S)-**2**	O$_2$	CCl$_4$	**13o**	240	**14o**, trace	—
10[a]	(R_a,S,S)-**3**	O$_2$	CCl$_4$	**13a**	76	**14a**, 85	78 (R)
11	(R_a,S,S)-**12**[b]	Air	CCl$_4$	**13a**	96	**14a**, 58	60 (R)
12[a]	(R_a,S,S)-**3**	O$_2$	CCl$_4$	**13c**	168	**14c**, 84	83 (R)
13	(R_a,S,S)-**12**[b]	Air	CCl$_4$	**13c**	48	**14c**, 82	86 (R)
14[a]	(R_a,S,S)-**3**	O$_2$	CCl$_4$	**13k**	167	**14k**, 98	90 (R)
15	(R_a,S,S)-**12**[b]	Air	CCl$_4$	**13k**	48	**14k**, 94	92 (R)

[a] Heterogeneous. [b] Reported by Gong *et al.* using 5 mol% of the catalyst. See ref. 12*c*.

coupling, in contrast to Gong's dinuclear vanadium(v) catalyzed coupling for which radical–radical cross-coupling is observed.[12] All of these results are in agreement with an intramolecular manner of coupling as shown in Scheme 3. Dinuclear vanadium(v) complex (R_a,S,S)-**2** reacts with two molecules of 2-naphthol resulting in **Ia**. The C1 positions of the 2-naphthol molecules approach each other by the rotation of the binaphthyl axis yielding **Ib**, which is then intramolecularly coupled after a single electron transfer to a vanadium(v) species. After the enolization of the coupling product and oxidation of the vanadium(iv) species **II**, the vanadium(v) species was regenerated[25] and (S)-BINOL was released. Since the catalytic activity of (R_a,S,S)-**2** is significantly higher than that of diastereomeric complex (S_a,S,S)-**2** and mononuclear complex (S)-**20** (Table 4, entries 36–38), intermolecular manner couplings proceed as a minor pathway.

8. Comparison of our dinuclear vanadium(iv) and (v) catalysts with Gong's catalysts

Although we independently developed dinuclear vanadium(iv) catalysts and dinuclear vanadium(v) catalysts for enantioselective oxidative coupling of 2-naphthols,[3] the preparation procedure for

dinuclear vanadium(iv) catalysts is similar to that of Gong's catalysts[12] except for the use of 2.0–2.2 equiv. of vanadyl sulfate in EtOH–THF–H$_2$O for the complexation. Even though the absolute configurations of the components of the catalysts are the same, the absolute configurations of the major products were opposite to each other (Table 5). Since Gong carried out the coupling reaction in CCl$_4$ at 0 °C under oxygen, we examined the (R_a,S,S)-**1a** catalyzed reaction under the same conditions to compare the new character of our catalysts (Table 6). A large difference was observed between our catalysts and Gong's catalysts: (R_a,S,S)-**1a** and 2-naphthol had limited solubility in CCl$_4$ at 0 °C, and the coupling product was obtained in quite low yield and low enantioselectivity (entry 1). The use of Gong's catalyst **7b** that we prepared according to his procedure[12] provided poorly reproducible outcomes (entry 2). Finally we realized the absolute configuration of the major products was switched by choosing CCl$_4$ when using the dinuclear vanadium(v) catalyst.[26] However (R_a,S,S)-**2** showed much higher activity than that of Gong's catalyst **7b** (entries 3 and 4). The reason for a switch of enantioselectivity in the (R_a,S,S)-**2**-mediated coupling by the choice of solvent is not clearly understood at the moment, but may involve the generation of oligomeric dinuclear complexes with different asymmetric induction abilities

from that of the monomeric dinuclear complex (R_a,S,S)-**2**.[27,28] As a result, reactions run in CH_2Cl_2 or $(CH_2Cl)_2$ provided (*S*)-configuration of BINOLs (Table 7, entries 1 and 2), and for all reactions run in CCl_4 or toluene gave (*R*)-BINOLs (entries 3–10, 12 and 14).

Conclusion

Our recent work on the development of dual activation catalysis for the homolytic coupling of 2-naphthols promoted by dinuclear vanadium complexes was reviewed. Chiral dinuclear vanadium(IV) complex (R_a,S,S)-**1a** and vanadium(V) complexes **2** and **3** simultaneously activate two molecules of 2-naphthols to afford (*S*)-BINOLs in high yield with high enantioselectivity.

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20 The magnetic susceptibilities of $VOSO_4$ and V_2O_5 as vanadium(iv) and (v) standards are 38 and 0 emu mol^{-1}, respectively.

21 The ^{1}H-NMR chart of the vanadium(v) species causing form the addition of 1 equiv. of 5 N HCl aq. to the sodium cation on the crystal was same as that of (R_a,S,S)-**2**.

22 An induction period was observed when dinuclear vanadium(iv) complex (R_a,S,S)-**1a** was used for the coupling of 2-naphthol. The %ee of the product increased during the course of the reaction when using (R_a,S,S)-**1a** from 38% ee at 4% conversion to 86% ee at 14% conversion while the %ee of the product remained nearly constant (83–85% ee) when using (R_a,S,S)-**2**.

23 The %ee of the product increased during the course of the reaction catalyzed by (S)-**20**; from 26% ee at 2% conversion to 77% ee at 19% conversion. In general a mononuclear vanadium(v) complex tends to form a dimeric complex by self-assembly. This induction period might arise due to the monomerization in the reaction media.

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