

COMMUNICATION

Vanadium-catalysed regioselective hydroboration of epoxides for synthesis of secondary alcohols

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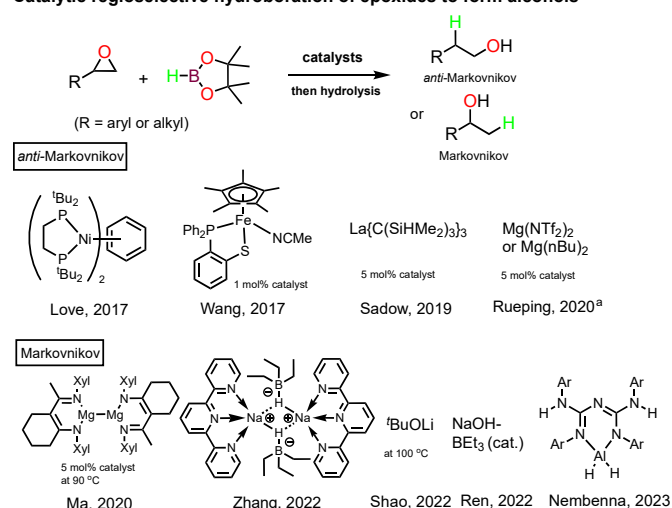
Regioselective epoxide ring-opening through hydroboration catalysed by a vanadium(III) dialkyl complex supported by a redox-active terpyridine ligand is reported. Secondary alcohols were obtained in high yields via effective Markovnikov hydroboration of terminal epoxides, showcasing a new catalytic application of an earth-abundant vanadium(III) complex.

The synthesis of alcohols has continued to receive great attention from organic chemists due to the widespread applications of alcohols and hydroxyl-containing compounds in many fields, including natural product synthesis, pharmaceuticals, agrochemicals and functional materials.¹ Among many protocols developed for alcohol synthesis, the direct reduction of epoxides through a ring-opening reaction provides an efficient pathway leading to regioselective formation of linear (anti-Markovnikov) and branched (Markovnikov) alcohols in which the regioselectivity could be precisely controlled with appropriate catalysts and reaction conditions.² In this regard, transition metal catalyzed hydrogenation of terminal epoxides with molecular H₂ was first developed with good regioselectivities in terms of primary or secondary alcohols.²⁻⁴ However, this methodology suffers from high H₂ pressure and temperature and often poor product selectivity.²⁻⁴ More recently, the hydroboration of epoxides with pinacolborane (HBpin) has emerged as an alternative efficient method that avoids the use of hydrogen gas. Excellent regioselectivity control has been achieved using a diverse group of catalysts made from transition metals, rare earth, and main group metals (Scheme 1).⁵⁻¹⁰

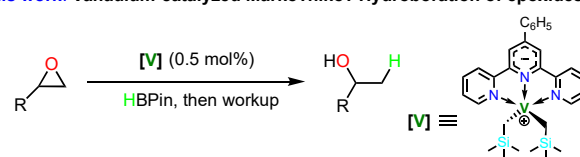
In 2017, the Love group reported a Ni(0) complex with a diphosphine ligand that catalysed the anti-Markovnikov hydroboration of a few styrenyl epoxides, albeit with low efficiency.⁵ In the same year, Wang and coworkers introduced a more effective, cooperative Fe-thiolate catalyst for the hydroboration of a range of

Previous work:

Catalytic regioselective hydroboration of epoxides to form alcohols



This work: Vanadium-catalyzed Markovnikov Hydroboration of epoxides



Scheme 1. The state-of-the-art of metal-catalysed regioselective hydroboration of epoxides and the results presented in this work. ^a Divergent regioselectivities were reported.

aryl epoxides with complete anti-Markovnikov selectivity.⁶ Later on, a simple lanthanide complex, La{C(SiHMe₂)₃}₃, was found to be active for the hydroboration of styrene oxide to give the anti-Markovnikov product.⁷ The Rueping group reported that Mg(NTf₂)₂ and Mg(nBu)₂ catalyze regiodivergent C-O bond cleavage for a large scope of epoxides, giving primary or secondary alcohols.⁸ A few more catalyst systems for Markovnikov epoxide hydroboration have been developed in the past three years, and all are focused on main group metals. For instance, the Ma group characterized a series of dinuclear magnesium(I) complexes containing Mg-Mg bonds that are active for Markovnikov hydroboration of epoxides at 90 °C.⁹ In 2022, our group

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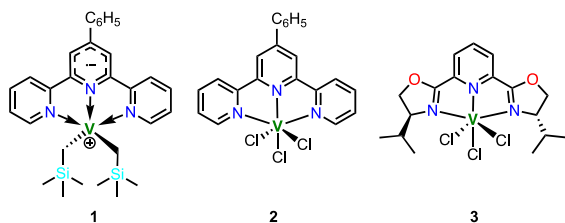
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reported terpyridine-ligated alkali metal triethylborohydrides (Li, Na or K) as highly efficient catalysts for the synthesis of secondary alcohols using both aryl and aliphatic epoxides.¹⁰ The simple lithium salt, ^tBuOLi was found to behave as a catalyst for hydroboration of several terminal epoxides at 100 °C to afford secondary alcohols, while it is also effective for the hydroboration of esters.¹¹ The Ren group later reported a NaOH/BET₃ system effective for the hydroboration of a broad range of epoxides with complete Markovnikov selectivity.¹² In a recent work by Nembenna and coworkers, an aluminum dihydride catalyst supported by a N, N'-chelated conjugated bis-guanidinate ligand enabled the hydroboration of epoxides with high regioselectivity for primary alcohols at 70 °C.¹³ In addition, rather early pioneering work by Brown and Yoon has revealed the existence of catalytic activity of NaBH₄ for anti-Markovnikov BH₃ addition to epoxides.¹⁴

Among the catalysts described above, little progress has been made using transition metals as catalysts for hydroboration of epoxides except for the initial contributions based on Ni and Fe catalysts.^{5,6} In continuation of our efforts using earth-abundant metal catalysts with terpyridine (tpy)-type ligands for hydroboration reactions,¹⁵ we have recently developed highly active and versatile vanadium(III) catalysts (such as **1**, Scheme 2) supported by redox-noninnocent tpy ligands for the reduction of a range of carbonyl compounds, esters and amides through hydroboration and hydrosilylation, and the hydroboration of alkynes.^{16,17} Though it is the sixth most abundant transition metal in the earth's crust and has long explored in some homogeneous transformations, mostly in oxidation processes,¹⁸ vanadium has rarely been applied to the catalytic reduction compared to other transition metals.¹⁹ In this work, we further extend the utilization of the well-defined vanadium complex (**1**) as a catalyst for the hydroboration of epoxides with high regioselectivity for the synthesis of secondary alcohols.



Scheme 2. The structures of V^{III}-NNN complexes studied in this work.

To start the catalytic testing, we were interested to compare the catalytic activity of vanadium dialkyl **1** with two vanadium chloride precursors, **2** and **3** (Scheme 2). As previously reported, complex **1** could be synthesized in one step from **2** by alkylation with an excess amount of LiCH₂SiMe₃. We were unable to obtain the X-ray structure of **2** due to its poor solubility in common organic solvents, which made it challenging to grow crystals, while **1** has been fully characterized. Complex **3** was synthesized by reacting the commercial pyBOX ligand with equimolar VCl₃ in THF. The resulting light brown product is well soluble in CH₂Cl₂ or CHCl₃, and partially soluble in THF, which allows for the formation of good quality single crystals from a dilute THF solution. The X-ray structural analysis confirms the formation of a mononuclear hexa-coordinate V^{III} complex as expected (Fig. 1). Complex **3** crystallises in the chiral orthorhombic space group *P*2₁2₁2₁. The ORTEP diagram show that the V^{III} ion is coordinated to the N₃ cavity of the ligand and further surrounded by three chloride ions to give a saturated coordination environment while adopting a pseudooctahedral geometry. The

oxazole rings are co-planar with the central pyridinyl ring (the dihedral angles between rings are 0.49° and 4.37°, respectively). The V-N bond lengths range from 2.1160(19) to 2.1423(18) Å, which are slightly longer than those in complex **1** (which range from 1.9643(15) – 2.1193 (16) Å). One THF molecule cocrystallises in the asymmetric unit.

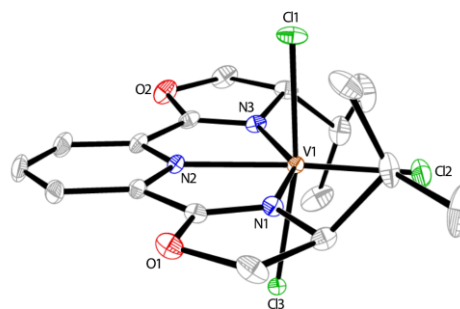


Fig. 1. The ORTEP diagram of the independent molecular cation of **3** with atomic displacement parameters drawn at the 30% probability level. The H atoms and co-crystallised THF molecule are omitted for clarity.

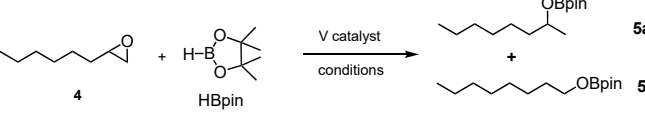
Next, we examined the catalytic activity of vanadium complexes **1-3** for the hydroboration of a model compound, 1,2-epoxyoctane, with HBpin. The results of condition screening are summarized in Table 1. Initially, we carried out the reaction between 1,2-epoxyoctane and HBpin using **1-3** as the catalysts (0.5 mol%), respectively, at ambient temperature (entries 1-3, Table 1). It was pleasing to find out that **1** was the most active catalyst for the regioselective hydroboration of 1,2-epoxyoctane with a 98% yield and 50:1 ratio of regioisomers, **5a** and **5a'**, as determined by GC analysis. This is consistent with the demonstrated activity of **1** for hydroboration of various unsaturated bonds.^{16,17} Although **2** and **3** show less catalytic activity and poor regioselectivity, we were interested to see whether the results could be improved as they are stable and easy to synthesize. Thus, a base additive such as potassium *tert*-butoxide (KO^tBu) was used when **3** was chosen as the catalyst (entry 4). It was found that the regioselectivity was significantly improved (30:1), while the yield was slightly increased. Other base additives did not show better performance (entries 5-7). Various solvents were added to the reaction using **3**/KO^tBu as catalyst, yet no improved results were obtained (entries 8-11). It was also found that the yields were significantly lower when the reaction was conducted in a solvent even using **1** as a catalyst (entries 12 and 13). Finally, control experiments were carried out in the absence of catalyst or in air, however neither showed reactivity (entries 14 and 15). Lowering the loading amount of **1** to 0.1 mol% decreased the yield to 72% (entry 16), while retaining the same regioselectivity.

Since enantiopure complex **3** was used as a precatalyst above and the reaction proceeded with a moderate yield of boronate ester **5a**, we were interested to examine whether enantioselective catalysis could be realized using **3**. Thus, the hydroboration of racemic styrene oxide (**4n**, Scheme 3) was performed in the presence of **3** (0.5 mol%) and KO^tBu (2 mol%) as a catalyst in THF (see ESI for details). The desired alcohol **5n** was then isolated after workup and its enantiomeric excess (ee) was determined to be 0%, indicating that the asymmetric catalysis did not occur.

As catalyst **1** (0.5 mol%) was found to be the best-performing catalyst without any additive under neat conditions, we examined the scope of epoxides using **1** under the conditions described above (entry 1, Table 1) and the results are summarized in Scheme 3. Aliphatic terminal epoxides were readily converted to the corresponding secondary alcohols (**5a-c**) with high isolated yields and

excellent Markovnikov selectivity through **1**-catalysed hydroboration followed by hydrolysis during workup. A terminal alkene was found to remain intact during the hydroboration reaction. Likewise, 1,2-epoxycyclohexane experienced complete hydroboration at room temperature. In general, terminal epoxides containing arylether groups are suitable substrates for the synthesis of functionalized secondary alcohols (**5e-k**) with complete regioselective control, although in some cases elevated temperature (70 °C) was required for complete conversion. In addition, glycidol bearing triethoxysilyl or furyl groups proceeded equally well at room temperature to afford **5l** and **5m** in good yield, respectively. Finally, styrene epoxides

Table 1. Screening of reaction conditions for hydroboration of 1,2-epoxyoctane with HBpin.^a



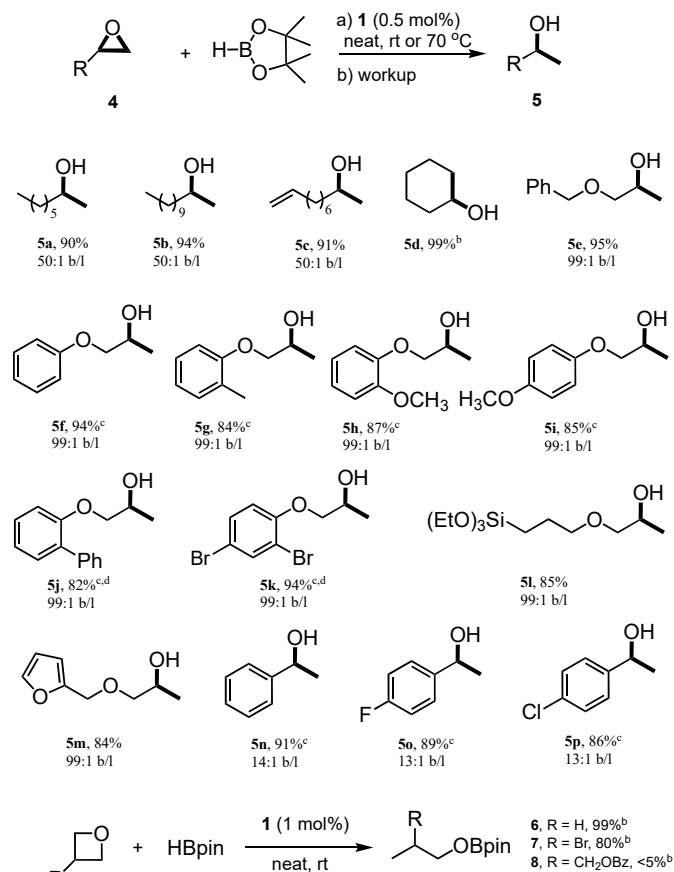
entry	catalyst	additive	solvent	Yield (%) ^b	5a/5a' ^c
1	1	-	-	98	50:1
2	2	-	-	30	5:1
3	3	-	-	32	4:1
4	3	KO ^t Bu	-	48	30:1
5	3	K ₂ CO ₃	-	25	30:1
6	3	KOH	-	40	50:1
7	3	NaO ^t Bu	-	38	50:1
8	3	KO ^t Bu	toluene	<5	-
9	3	KO ^t Bu	Et ₂ O	25	30:1
10	3	KO ^t Bu	CH ₂ Cl ₂	<5	-
11	3	KO ^t Bu	THF	55	50:1
12	1	-	THF	36	40:1
13	1	-	Et ₂ O	22	35:1
14	none	-	-	0	-
15 ^d	1	-	-	<2	-
16 ^e	1	-	-	72	50:1

^a Conditions: 1,2-epoxyoctane (1.0 mmol), HBpin (1.2 mmol), catalyst (0.5 mol%), additive (2 mol%) and solvent (0.5 mL), rt, 16 h, N₂. ^b Yield of **5a** + **5a'** products determined by GC analysis using hexamethylbenzene as an internal standard. ^c Ratio determined by GC analysis. ^d Reaction run in the air. ^e Reaction run using 0.1 mol% of **1**.

were employed and complete hydroboration was achieved at 70 °C, while the regioselectivity dropped to ~13:1 (**5n-p**). It is interesting to note that oxetanes such as trimethyl oxide and 3-bromooxetane were effectively hydroborated to afford boronate esters **6** and **7** in high yields, respectively, at room temperature as determined by GC analysis. However, 3-((benzyloxy)methyl)oxetane was found to be almost inactive under the same conditions. To demonstrate the applicability of this method, a gram-scale experiment has been conducted for the synthesis of product **5e**. Thus, when 10 mmol of **4e** was reacted with HBpin under standard conditions, 1.5 g product **5e** was isolated as the only product in 90% yield (Scheme 3 and ESI). Furthermore, when enantiopure styrene oxide (**S**)-**4n** (98% ee) was employed as a substrate under optimal conditions using **1** as a catalyst, alcohol **5n** was isolated with high enantiopurity (98% ee), indicating the complete retention of its stereochemistry (Scheme 4 and ESI).

Scheme 3. **1**-catalysed Markovnikov hydroboration of various

epoxides.^a



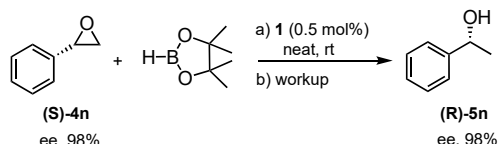
^a Conditions: **1** (0.5 mol%), epoxide (1.0 mmol) and HBpin (1.2 mmol), neat, 25 °C, 16 h, N₂. Yields are given for isolated products and b/l is determined by GC analysis for the boronate ester precursors. ^b Yield of the boronate esters determined by GC analysis using hexamethylbenzene as an internal standard.

^c Reactions run at 70 °C. ^d Reactions run in THF (0.5 mL).

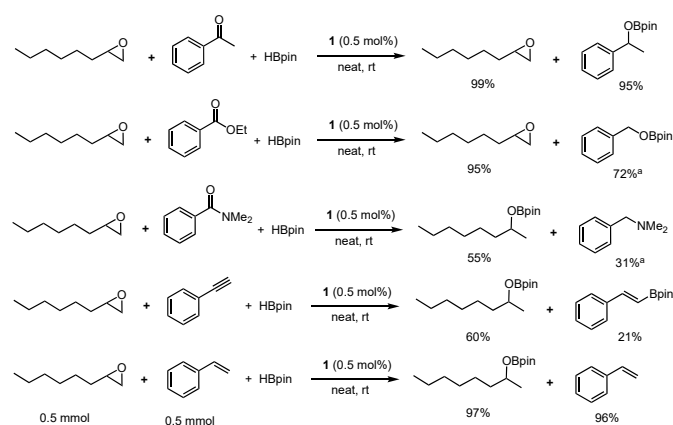
It should be mentioned that some limitation of substrates with the current method has been observed for several epoxide substrates containing other reducible functional groups such as ketone, ester, amide and nitro groups, which led to either decomposition of substrates or complex mixtures of hydroborated products under standard catalytic conditions. In addition, the internal epoxide, trans-stilbene oxide is not a suitable substrate for the current method, as no desired alcohol product has been isolated after two independent attempts. To ascertain the functional group tolerance, intermolecular competing experiments were performed to understand the chemoselectivity of vanadium-catalysed hydroboration, and the results are illustrated in Scheme 5. When a mixture of 1,2-epoxyoctane with ketone or ester was subject to the catalytic reactions with **1** at room temperature, hydroboration selectively occurred with the ketone or ester to afford boronate esters with good to high yield, while the epoxide remained almost intact. This is consistent with the fact that **1** was an active catalyst for the hydroboration of ketones and esters.¹⁶ Furthermore, we examined the reaction using *N,N*-dimethylbenzamide as a competing reducible substrate, and the result revealed both partial hydroboration of epoxide and the deoxygenation reduction of amide, indicating poor chemoselectivity in this case. Chemicals with nonpolar unsaturated bonds such as alkene and alkyne were also used as competing substrates with epoxide. It was found that

epoxide showed slightly better reactivity than phenylacetylene and excellent chemoselectivity over styrene.

Comparing to other catalysts enabling regioselective hydroboration of epoxides reported thus far,⁵⁻¹³ the current vanadium catalyst which features the first early transition-metal catalyst for Markovnikov-selective epoxide hydroboration shows higher reactivity (i.e. lower catalyst loading and milder conditions) than those containing main-group metals, except the dimeric NaHBET₃/tpy complex.¹⁰ However, the substrate scope and functional group tolerance for the current vanadium catalyst are not as good as those known catalysts.⁸⁻¹³

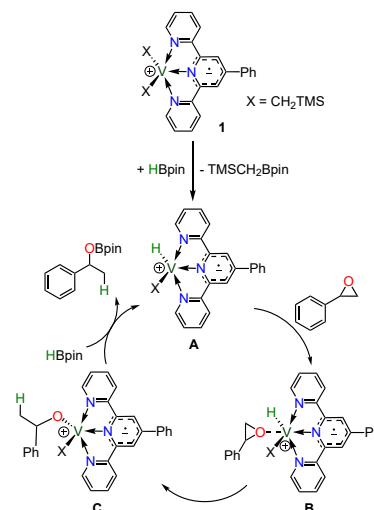


Scheme 4. Catalytic test with enantiopure styrene oxide for determination of enantiomeric excess of the alcohol product. Enantioselectivity of **5n** was determined by ¹H NMR using the Mosher ester method (ESI).



Scheme 5. Intermolecular competing experiments between 1,2-epoxyoctane and other reducible substrates for chemoselective hydroboration catalysed by **1**. HBpin (0.6 mmol) was used unless otherwise stated. Yields were determined by GC analysis using hexamethylbenzene as an internal standard. ^a HBpin (1 mmol) was used.

Based on previous reports^{16,17} and the current results, a plausible mechanism that may operate for the regioselective hydroboration of epoxides is proposed (Scheme 6). As evidenced previously, vanadium complex **1** would first react readily with HBpin to generate a vanadium hydride species (**A**) by releasing TMSCH₂Bpin from the reaction.¹⁶ Then an epoxide substrate such as styrene oxide is likely to coordinate with the V³⁺ center to give complex **B**, which would experience facile 1,3-hydride shift by attacking the less substituted carbon of oxirane, affording intermediate **C** regioselectively. **C** would further react with one equivalent of HBpin to regenerate the active catalyst **A**, while releasing the desired hydroborated product and completing the catalytic cycle.



Scheme 6. Proposed mechanism for the V-catalysed hydroboration of epoxides.

Conclusions

In conclusion, we report a facile epoxide ring-opening hydroboration reaction catalysed by an active vanadium dialkyl complex supported by a redox-active terpyridine ligand. A range of secondary alcohols have been selectively synthesized from terminal epoxides under mild conditions utilizing the V^{III} catalyst at a low catalyst loading. The chemoselectivity of this method was explored to demonstrate the catalyst tolerance with various reducible functional groups. This work extends the catalytic applications of underexplored trivalent vanadium complexes in the regioselective hydroboration of challenging substrates.

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Author contributions

G. Z. and S. Z. conceived and supervised the project. H. Z., Q. T. and S. A. performed experimental studies. M. C. N. conducted the X-ray crystallographic analysis. All authors analysed the data and wrote the article.

Conflicts of interest

There are no conflicts of interest to declare.

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