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Asymmetric $NaBH_4$ 1,4-Reduction of C3-Disubstituted 2-Propenoates Catalyzed by a Diamidine Cobalt Complex

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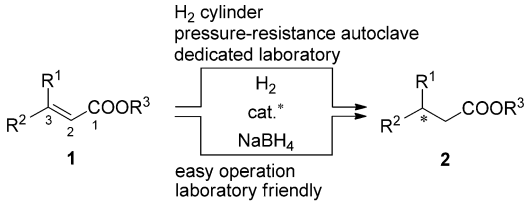
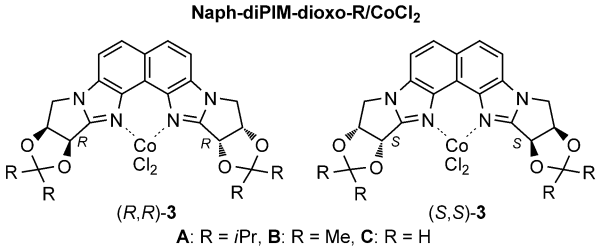
A new Co complex of a unique diamidine ligand catalyzes asymmetric $NaBH_4$ reduction of C3-disubstituted (*E*)- and (*Z*)-2-propenoates, including C3-oxygen- and nitrogen-substituted substrates with high enantioselectivity. Analysis by X-ray diffraction, ^1H NMR spectroscopy, ring-opening radical-clock and D-labeling reactions, and the structure/selectivity relationship suggest that a mechanism of CoH-involved non-single-electron transfer 1,4-addition differentiates the C2 enantioface. Involvement of CoH species has been supported by quantitative isolation of a new type of $CoH_2(BH_3)_2$ complex.

Asymmetric 1,4-reduction of α,β-unsaturated carboxylic esters is an important and versatile unit operation in multistep syntheses of natural products and pharmaceuticals.[1] In particular, stereo- and olefin-selective reduction of C3-disubstituted 2-propenoates **1**, yielding the saturated prenyl-type motif **2** has considerable importance (Scheme 1). Asymmetric hydrogenation has been the major approach to this reduction since 1987, when the first success using $Ru(OCOCH_3)_2$(binap) (binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) was reported.[2,3] Two years later, Pfaltz and co-workers reported an excellent chiral Co semicorrin catalyst affecting asymmetric 1,4-reduction of α,β-unsaturated carboxylic esters by $NaBH_4$;[4] however, this development did not result in a significant advance in the field.[5] This may be due to the lower atom efficiency, as well as the higher E factor, of $NaBH_4$ compared with that of the H_2 system. However, hydrogenation often requires a high-pressure-resistance stainless autoclave in a dedicated laboratory with specialized techniques for manipulating the air-sensitive catalyst precursor. By contrast, the operational simplicity of $NaBH_4$ reduction makes experiments very easy, enabling not only small-scale reactions, but also industrial-scale production.[6] Reconsidering the advantages, we have reinvestigated the $NaBH_4$ reduction of **1** with the $CoCl_2$ complexes (*R*,*R*)- and (*S*,*S*)-**3**, as a step towards the development of the utility of our chiral diamidine sp^2N ligand, Naph-diPIM-dioxo-R.[7]



Scheme 1. Asymmetric 1,4-reduction of C3-disubstituted 2-propenoates.



The substrate (*E*)-**1a** was selected as the standard, and the concentrations were set to [(*E*)-**1a**] = 250 mM, [(*R*,*R*)-**3**] = 2.5 mM, and [$NaBH_4$] = 500 mM. The complex (*R*,*R*)-**3** was prepared by mixing $CoCl_2$ and (*R*,*R*)-Naph-diPIM-dioxo-R (R = *i*Pr, Me, and H) in CH_3OH at 25 °C for 1 h, followed by concentration (see below). To the cooled CH_2Cl_2 suspension of $NaBH_4$ containing (*R*,*R*)-**3A** and (*E*)-**1a**, CH_3OH at 0 °C was added to achieve a 1:1 CH_3OH/CH_2Cl_2 solvent system. After 1 h at 25 °C, the yield and enantiomeric ratio (*er*) of the product **2a** were analyzed.[8] The results are shown in Table 1. The standard conditions quantitatively afforded **2a** with an *R*/*S* *er* of >99:1. Switching the chirality of the catalyst to (*S*,*S*)-**3A** gave almost enantiopure (*S*)-**2a**. The concentration of (*R*,*R*)-**3A** could be reduced from 2.5 mM to 0.125 mM (substrate/catalyst (S/C) ratio of 2000) without loss of enantioselectivity. A 1:1 CH_3OH/CH_2Cl_2 solvent system with the Co complex provided the best results of the conditions investigated.[8] Replacement of *i*Pr in Naph-diPIM-dioxo-R with Me ((*S*,*S*)-**3B**) resulted in a reduction of the *er* to 2:98; this decrease in *er* was more significant with (*S*,*S*)-**3C** (R = H). Bisoxazoline ligands, **L1** and **L2**, and BINAP (**L3**), which are recognized as privileged ligands,[9] were not effective in this particular reaction.

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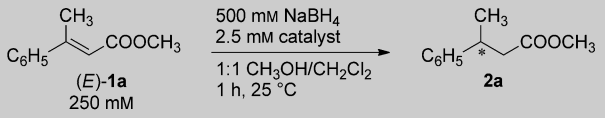
Table 1. Co-catalyzed asymmetric $NaBH_4$ 1,4-reduction.



Catalyst	S/C	NMR yield [%]	*R/S*
(*R,R*)-**3 A**	100	>99	>99:1
(*S,S*)-**3 A**	100	>99	1:>99
(*R,R*)-**3 A**[a]	2000	88	99:1
(*R,R*)-**3 A**[b]	10000	53	91:9
(*S,S*)-**3 B**	100	>99	2:98
(*S,S*)-**3 C**	100	>99	10:90
L1/$CoCl_2$	100	54	42:58
L2/$CoCl_2$	100	35	35:65
L3/$CoCl_2$	100	9	70:30

[a] [(*R,R*)-**3 A**] = 0.125 mM; 7 h. [b] [(*E*)-**1 a**] = 1 M; [$NaBH_4$] = 2 M; [(*R,R*)-**3 A**] = 0.1 mM; 24 h.

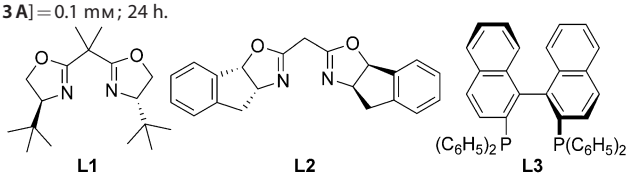
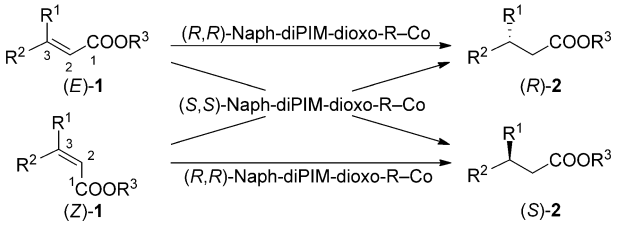


Table 2. (*R,R*)-Naph-diPIM-dioxo-*i*Pr–Co-catalyzed asymmetric $NaBH_4$ 1,4-reduction of C3-disubstituted methyl 2-propenoates.[a]

Entry	Substrate	R^1	R^2	Yield [%][b]	Product *er*[c]	Config.
1[d]	(*E*)-**1 a**	CH_3	C_6H_5	98	99:1	*R*
2	(*E*)-**1 b**	C_2H_5	C_6H_5	93	98:2	*R*
3	(*E*)-**1 c**	*i*-C_3H_7	C_6H_5	92	98:2	*S*
4	(*E*)-**1 d**	*c*-C_3H_5	C_6H_5	98	>99:1	–[e]
5[f]	(*E*)-**1 e**	*t*-C_4H_9	C_6H_5	<5	–	–
6[f]	(*E*)-**1 f**	C_6H_5	4-$CH_3OC_6H_4$	95[g]	94:6	*S*
7	(*E*)-**1 g**	C_6H_5	4-$CF_3C_6H_4$	97	92:8	–[e]
8	(*E*)-**1 h**	CH_3	$C_6H_5(CH_2)_2$	94	99:1	*S*
9	(*E*)-**1 i**	CH_3	*c*-C_6H_{11}	90	97:3	–[e]
10	(*E*)-**1 j**	CH_3	*t*-C_4H_9	72	98:2	–[e]
11	(*Z*)-**1 a**	C_6H_5	CH_3	90	99:1	*S*
12	(*Z*)-**1 h**	$C_6H_5(CH_2)_2$	CH_3	93	99:1	*R*
13[h,i]	(*Z*)-**1 k**	CH_3CONH	C_6H_5	89	97:3	*R*
14[h,i]	(*Z*)-**1 l**	CH_3CONH	CH_3	86	98:2	–[e]
15[h,i]	(*Z*)-**1 m**	TBDMSO	CH_3	98	>99:1[j]	*R*

[a] Unless specified otherwise, all reactions were carried out in 1:1 CH_3OH/CH_2Cl_2 under conditions on a 0.5 mmol scale; [**1**] = 250 ± 10 mM; [$NaBH_4$] = 500 mM; [(*R,R*)-**3A**] = 2.5 mM; 25 °C; 1 h. [b] Isolated yield. [c] Chiral HPLC or GC analyses of the product **2**, or ^1H NMR analyses of the diastereomeric amides derived from **2**.[8] [d] 50 mmol scale; S/C = 1000. [e] Not determined. [f] 28 h. [g] ^1H NMR yield. [h] Ethyl esters (R^3 = C_2H_5) were used in 1:1 C_2H_5OH/CH_2Cl_2. [i] 3 h. [j] Determined by chiral HPLC analysis after desilylation.[8]

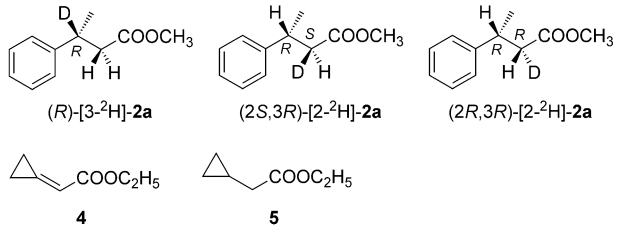
As summarized in Table 2, the Naph-diPIM-dioxo-*i*Pr–Co complex (*R,R*)-**3 A** exhibited a high level of enantio-differentiating ability in the reduction of C3-disubstituted 2-propenoates with alkyl, aryl, and heteroatom substitution patterns. The C3-CH_3 substituent of **1 a** could be replaced by a primary or secondary alkyl group, but no reaction occurred with **1 e**, which possessed a *tert*-butyl group (entries 1–5). The C3-diaryl substituted substrates **1 f** and **1 g** were reduced with reasonable enantioselectivity (entries 6 and 7). The C3-dialkyl-substituted substrates **1 h–j** were efficiently reduced to give the corresponding saturated products with high enantioselectivities, even with a *tert*-butyl substituent (entries 8–10). With the diastereomeric substrates (*Z*)-**1 a** and (*Z*)-**1 h**, the enantioselectivity was reversed without any negative effect on the *er* (entries 11 and 12). The present asymmetric catalysis could be also applied to C3-heterosubstituted **1**. Thus, C3-CH_3CONH-substituted ethyl cinnamate **1 k** and crotonate **1 l** were quantitatively reduced to the corresponding β-amino acid derivatives with *R/S* ratios of >97:3 (entries 13 and 14).[10] The *tert*-butyldimethylsilyl (TBDMS)-protected enol of a β-keto ester, **1 m**, was also reduced with a *R/S er* of >99:1 (entry 15). The esters of tiglic acid and angelic acid were found to be poor substrates.[8] The stereochemical outcome obtained by the substrate-structure/enantioface-selectivity relationship (Table 2) is outlined in Scheme 2, and implies that the Naph-diPIM-dioxo-*i*Pr–Co species differentiates the C2 enantiofaces at a certain stage of the catalysis. Both *R* and *S* enantiomers are accessible either by changing the geometry of the olefin or by switching the chirality of the catalysts.



Scheme 2. General rule of enantioface selection. $R^2 > CH_2CO_2R^3 > R^1$.

We assume that the Naph-diPIM-dioxo-*i*Pr–CoH_n (n = 1 or 2) species is generated by the action of $NaBH_4$ on the $Co^{II}Cl_2$ precursor,[11] and that the hydride is delivered to C3 of **1** in a 1,4-addition manner by a two-electron-transfer mechanism, rather than by single-electron transfer (SET), to generate the corresponding Co enolate,[4g,12] as suggested by the following four observations. i) The reaction of (*E*)-**1 a** with (*R,R*)-**3 A** under standard conditions using $NaBD_4$/1:1 CH_3OH/CH_2Cl_2 gave (*R*)-[3-^2H]-**2 a** as the sole product within the error range, and under the conditions of $NaBH_4$/1:1 CH_3OD/CH_2Cl_2 gave (2*S*,3*R*)-[2-^2H]-**2 a** and (2*R*,3*R*)-[2-^2H]-**2 a** in a 1:1 ratio. ii) The electronic effect on the reactivity observed for (*E*)-**1 f**/(*E*)-**1 g** (Table 2, entries 6 and 7) is in agreement with a 1,4-addition mechanism. iii) Both the SET mechanism[13] and H addition onto the C2 atom can be excluded by the fact that the C3-cyclopropyl-substituted substrate **1 d** (Table 2, entry 4) and ethyl 2-cyclopropylideneacetate (**4**) are quantitatively converted to the corresponding 1,4-reduction products **5** without cleavage of the cyclopropyl ring. iv) A Co hydride complex, $CoH_2(BH_3)_2$((*R,R*)-Naph-diPIM-dioxo-*i*Pr), with the same catalyst performance as that of (*R,R*)-**3 A**, was quantitatively prepared by reaction of the $CoCl_2$ precursor

(*R*,*R*)-**3 A** with a 2 mol amount of $NaBH_4$ in dimethoxyethane (DME).[8,14]



Considering these results together with the molecular structures of (*R*,*R*)-**3 A** and $CoH_2(BH_3)_2$((*R*,*R*)-Naph-diPIM-dioxo-*i*Pr) complexes in the crystals (Figure 1),[8,15] the enantioface of **1** is

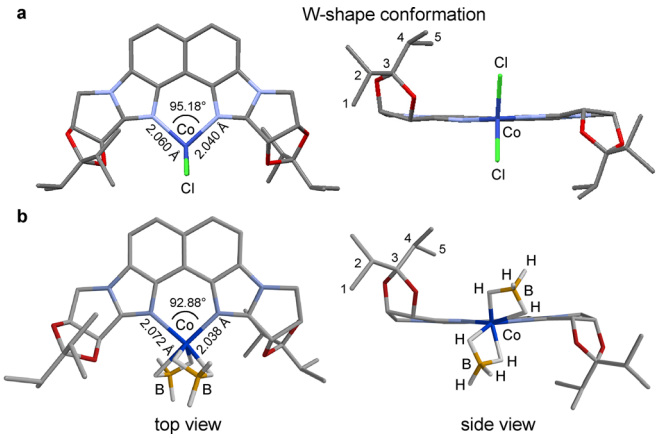
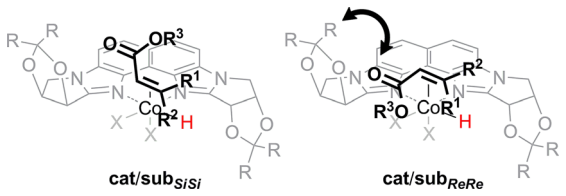


Figure 1. Molecular structures of a) $CoCl_2$((*R*,*R*)-Naph-diPIM-dioxo-*i*Pr)·thf ((*R*,*R*)-3 A·thf) (thf omitted) and b) $CoH_2(BH_3)_2$((*R*,*R*)-Naph-diPIM-dioxo-*i*Pr)·ether (ether omitted). Hydrogen atoms on Co and B were located by Fourier differences and isotropically refined.

thought to be selected by the catalyst/substrate complexes **cat/sub**$_{SiSi}$ and **cat/sub**$_{ReRe}$ (R^2>=CHCO$_2$R^3> R^1; X = H, H(BH$_3$), Cl, solvent, substrate, product). The CoH species would interact with the C2=C3 bond of **1** in parallel to the Co–H bond. In this case, **cat/sub**$_{SiSi}$ is more stereo-complementary than **cat/sub**$_{ReRe}$, which is affected by steric repulsion from the dioxolane ring of the *R*,*R* ligand, yielding (*R*)-**2** (R^2 > $CH_2CO_2R^3$ > R^1) as the major product. The higher enantioselectivity achieved with **3 A** can be ascribed to the W-shape conformation of the five-carbon system of the two *i*Pr groups (Figure 1, side view), which extend a methyl group toward the reaction site. Swapping R^1 and R^2 leads to formation of the enantiomeric product, because only the *Si* C2 enantioface is recognized by (*R*,*R*)-**3 A**. Neither the configuration nor the valency of Co[11] is clear, and the involvement of a CoH/BH_3 bridged species[11d] cannot be excluded. Nevertheless, by assuming **cat/sub**$_{SiSi}$ and **cat/sub**$_{ReRe}$, the stereochemical outcome in Scheme 2 can be well explained. A detailed mechanistic study is now underway.

In summary, we have developed a high-performance molecular asymmetric catalyst for the 1,4-reduction of various C3-disubstituted 2-propenoates by $NaBH_4$. The success of this catalyst is ascribed to the following characteristics of Naph-diPIM-dioxo-R, which differ from those of conventional sp^{2}N-based bidentate ligands: i) high σ-donating ability derived from two amidine units fixed to the same side on the highly rigid and planar ligand, enhancing the hydride properties of the CoH species; ii) an almost 90° bite angle to stabilize the CoH complex; iii) an extended π-conjugated system to accept the back donation from the low-valence CoH species; and iv) clear chirality constructed by the C2-*i*Pr-substituted dioxolane rings pointing up and down on the core 5,5,6,6,5,5 ring system. The reaction pathway, as well as the mechanism of enantioface selection, has been assumed on the basis of the substrate-structure/enantioselectivity relationship, deuterium-labeling experiments, radical-clock experiments, and X-ray crystallographic analysis of a new type of $CoH_2(BH_3)_2$ complex. The present method is operationally simple, and will provide organic synthetic chemists with a powerful tool for the multistep syntheses of natural products and pharmaceuticals.



Experimental Section

A solution of (*R*,*R*)-**3 A** (5.00 mM in CH_3OH, 10.0 mL, 50.0 μmol) was added to a 1000 mL Young-type Schlenk flask and concentrated in vacuo, leaving a blue solid in the tube. $NaBH_4$ (3.78 g, 100 mmol), CH_2Cl_2 (100 mL), and (*E*)-methyl 3-phenylbut-2-enoate ((*E*)-**1 a**) (8.81 g, 50.0 mmol) were then added. After cooling the mixture to 0 °C, CH_3OH (100 mL) was slowly added. After removal from the ice bath, the mixture was stirred at RT for 1 h. After this time the reaction was quenched by the addition of 1 M aqueous HCl (200 mL) and extracted by CH_2Cl_2 (3×100 mL). The aqueous layer was concentrated to half its volume and extracted by CH_2Cl_2 (3×100 mL). The combined organic layers were concentrated to give a crude product (9.25 g, >99%), which was dissolved in diethyl ether and passed through a short silica gel column (5 cmϕ×10 cm; 25 g; eluent; ether). The filtrate was concentrated to give (*R*)-methyl 3-phenylbutanoate ((*R*)-**2 a**) (8.72 g, 98% yield) with a 99:1 *R*/*S* *er* as a colorless oil ($[\alpha]_D^{25} = -29.4$ (c = 1.0 in $CHCl_3$)).

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Keywords: asymmetric catalysis · carboxylic esters · cobalt · reduction · sodium borohydride

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[14] The ^{1}H NMR signals resonated at unusual chemical shifts because of the magnetic properties of the complex, but one set of signals was observed.

[15] CCDC 1049568 ((*R*,*R*)-**3 A**·thf) and CCDC 1049569 ($CoH_2(BH_3)_2$((*R*,*R*)-Naph-diPIM-dioxo-*i*Pr)·ether) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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