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Asymmetric Synthesis of *O*-Acetylcyanohydrins by Reaction of Aldehydes with NaCN/KCN Catalyzed by Recyclable Chiral Dimeric Titanium(IV)/Vanadium(V) Salen Complexes

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Keywords: Cyanohydrins / Catalysis / Dimeric Ti^{IV}/V^{V} salen complexes

The efficient catalytic asymmetric addition of an inexpensive and nonvolatile cyanide source such as NaCN or KCN and acetic anhydride to various aldehydes was catalyzed by recyclable dimeric Ti^{IV} and V^{V} chiral salen complexes at –20 °C. High chiral induction (96 % *ee*) in the *O*-acetylcyanohydrin was obtained in the case of 2-fluorobenzaldehyde, and the results achieved with sodium cyanide are quite comparable to those with potassium cyanide. The chiral V^{V} salen complex was found to be the most efficient recyclable catalyst reported so far in the literature, and was better than the Ti^{IV} salen system. Both the catalysts were recovered after the first use and recycled effectively four times.

Introduction

Chiral cyanohydrins are versatile building blocks for pharmaceuticals, agrochemicals and specialty materials bearing optically active multifunctional groups such as amino alcohols, hydroxy acids, and amino acids.[1,2] A number of synthetic methods have been reported for the synthesis of chiral cyanohydrins employing enzymes,[3] synthetic peptides,[4] organocatalysts[5] and metal complexes,[6–11] the latter being the most widely used over the last decades.[6–11] Most of these hydrocyanation reactions utilized trimethylsilyl cyanide (TMSCN) as a source of cyanide to achieve *O*-(trimethylsilyl)cyanohydrins. However, *O*-(trimethylsilyl)cyanohydrins are labile and readily undergo hydrolysis to form cyanohydrins that are prone to racemization. In addition, cyanohydrins are frequently prepared at very low temperatures while using toxic, highly volatile and expensive hydrogen cyanide or trimethylsilyl cyanide. It is therefore advantageous from synthetic and economic points of view to obtain chemically *O*-protected chiral cyanohydrins using an inexpensive and nonvolatile source of cyanide e.g., potassium cyanide or sodium cyanide, under milder conditions. In this direction, very efficient catalysts based on bimetallic Ti–O–Ti and V^{V}=O complexes were reported by Belokon et al. using potassium cyanide as a cyanide source to give high *ee* up to 92% at –42 °C.[12] As chiral ligands are expensive, the recycling of chiral catalysts is highly desirable. Recently, many efforts have been made to develop recyclable metal complexes using organic or inorganic supports[13] and ionic liquids[14] as reaction media where expensive and volatile trimethylsilyl cyanide was used as source of cyanide. We have reported the development of recyclable polymeric and dimeric chiral salen complexes for enantioselective epoxidation and hydrolytic kinetic resolution of terminal epoxides.[15] Herein we are extending the application of dimeric salen ligands by synthesizing titanium(IV) and vanadium(V) complexes **1** and **2**, respectively, for the asymmetric addition of nonvolatile and inexpensive sodium cyanide and potassium cyanide to various aldehydes in the presence of acetic anhydride at –20 °C. Quantitative yield (99%) of *O*-acetylcyanohydrin with high chiral induction (*ee* up to 96%) was achieved in the case of 2-fluorobenzaldehyde. Remarkably, with our methodology, comparable yields and chiral inductions in the products were achieved with sodium cyanide and potassium cyanide. We also observed that the V^{V} salen complex was the most efficient recyclable catalyst reported so far in the literature, and was a better catalyst than the Ti^{IV} salen complex.

Results and Discussion

The synthesis of dimeric salen ligand **1′** (Figure 1) and its precursors was carried out as described in reference.[15a] The complexation of the dimeric salen ligand (**1′**) with $V(O)SO_4 \cdot 5H_2O$ for catalyst **2** (Figure 2) was carried out in ethanol, while catalyst **1** was generated in situ by the interaction of equimolar quantities of the chiral salen ligand with $Ti(OiPr)_4$ (Figure 3). These catalysts, **1** and **2**, were characterized by ^1H NMR, optical rotation, IR, UV/Vis and CHN microanalysis (see data given in Exp. Sect.). The

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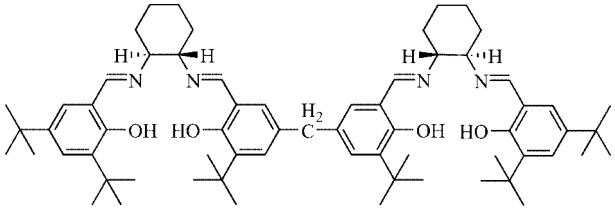
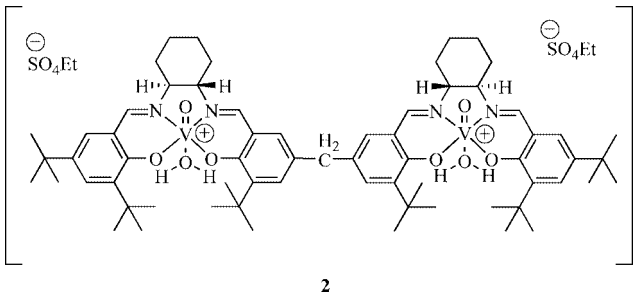
formation of Ti–O–Ti complex **1** generated in situ was confirmed by recording the solution IR of the parent complex $TiL(OiPr)_2$ and after interaction with 1 equiv. water, which forms catalyst **1** or species **A** (Scheme 1). The emergence of a new band at 702 cm^{-1} indicates the formation of the Ti–O–Ti complex. This band was absent in the complex $TiL(OiPr)_2$ prior to the addition of water.[17] Catalyst **1** in solution was found to be in the *cis*-β-configuration, confirmed by ^{1}H-NMR, which gives two sets of azomethine protons at δ = 7.80 and 8.18 ppm. These results are in consonance with earlier reports.[12e,18] Further, we have also observed a slight positive nonlinear correlation (Figure 4) of the *ee* of catalyst **1** and the *ee* of **4a** that supports the existence of the *cis*-β-configuration in catalyst **1**.[18a]



1'

Figure 1. Structure of the ligand **1′**.

Catalysts **1** and **2** were used for the asymmetric addition of cyanide by using sodium cyanide and potassium cyanide as nonvolatile and inexpensive cyanide sources to various aldehydes namely, benzaldehyde (**3a**), 4-methoxybenzaldehyde (**3b**), 3-methoxybenzaldehyde (**3c**), 2-methoxybenzaldehyde (**3d**), 4-chlorobenzaldehyde (**3e**), 4-bromobenzaldehyde (**3f**), 4-fluorobenzaldehyde (**3g**) and 2-fluorobenzaldehyde (**3h**) in the presence of acetic anhydride at –20 °C, as shown in Table 1 and Table 2. Initially, we conducted the



2

Figure 2. Structure of catalyst **2**.

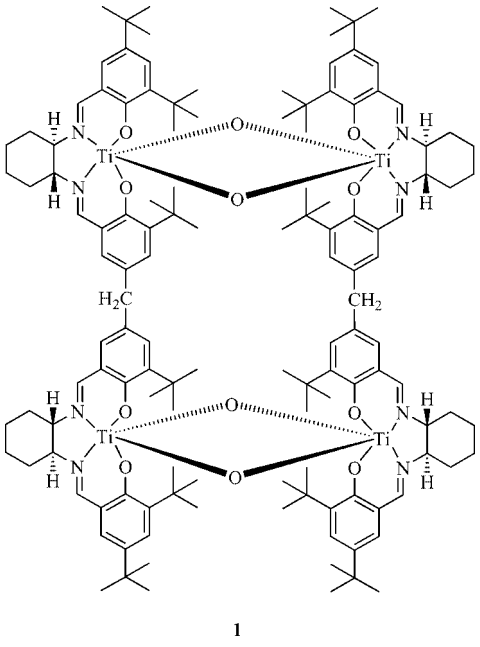


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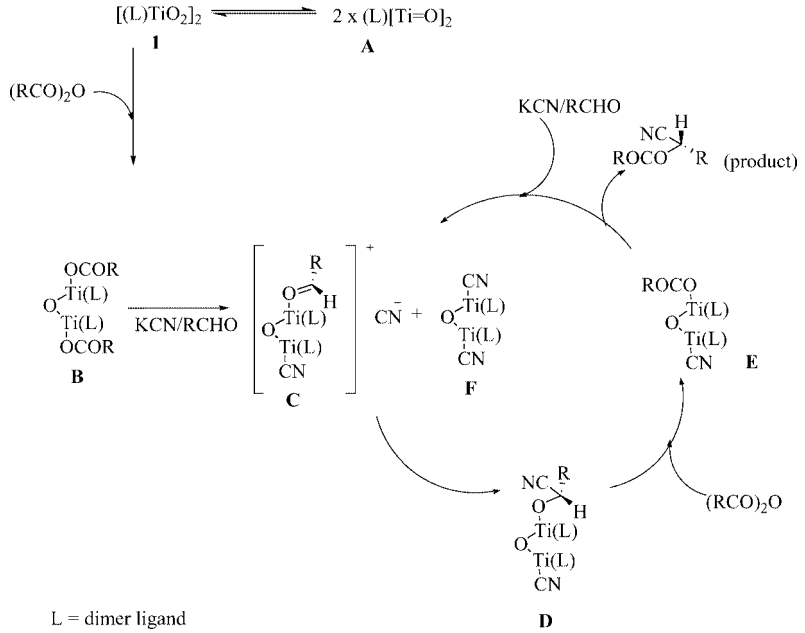
Figure 3. Structure of catalyst **1**.



L = dimer ligand

Scheme 1. Probable mechanism for catalytic cycle of the asymmetric cyanation reaction.

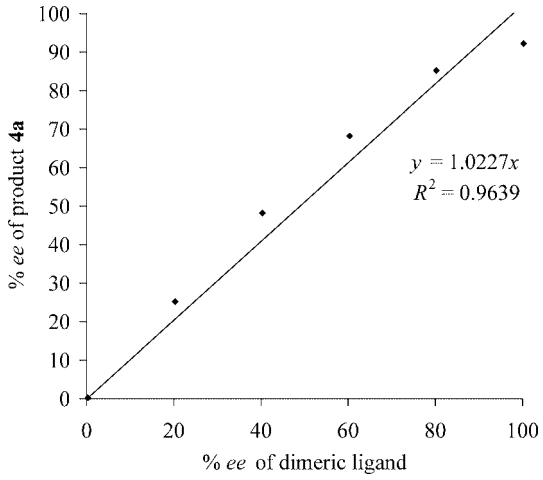
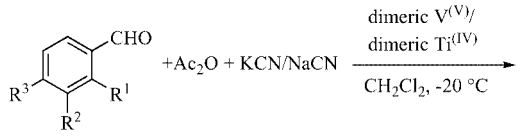
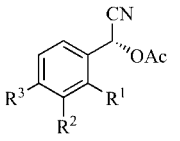


Figure 4. Nonlinearity effect of the catalyst **1**.

experiments with benzaldehyde as a model substrate using NaCN/KCN as source of cyanide. ^{1}H and ^{13}C NMR confirmed that product **4a** was obtained exclusively, with no formation of enolizable product (see data given in the Exp. Sect.). It can be seen that the present catalytic protocol is quite general for the range of substrates used in the present study. However, the substituents on the benzaldehyde derivatives had some influence on the reactivity and enantioselectivity of the reactions. While excellent conversions to *O*-acetylcyanohydrin (yields up to 98–99%) (Table 1, entries 1, 2, 9–16 and Table 2, entries 17, 18, 25–32) were obtained for most of the aldehydes with both the catalysts in 8–10 h, methoxy-substituted aldehydes (Table 1, entries 3–8 and Table 2, entries 19–24) gave relatively lower conversions to *O*-acetylcyanohydrin (conversion 90–93%). The lower conversions for 4-methoxybenzaldehyde were also observed with BINOLAM-Ti^{IV} complexes.[9j] The best enantioinduction (96% *ee*) and quantitative yield of *O*-acetylcyanohydrin was obtained for 2-fluorobenzaldehyde using KCN as the cyanide source with catalyst **2** (Entry 16). The chiral induction in the *O*-acetylcyanohydrins utilizing the catalysts **1** and **2** followed this sequence: F-benzaldehyde > benzaldehyde > Cl-benzaldehyde > Br-benzaldehyde > MeO-benzaldehyde, as shown in Figure 5. The overall performance of the V^V chiral salen complex **2** was found to be the most efficient recyclable system reported in literature so far, better than the Ti^{IV} salen complex in terms of reactivity and enantioselectivity. Further, the results obtained with sodium cyanide as the cyanide source are fairly comparable with those of KCN in terms of reactivity and enantioselectivity, which is an important finding, considering that the former is far less toxic than the latter. On conducting the cyanation reaction with an aliphatic aldehyde such as valeraldehyde using catalyst **2** in the presence of KCN and acetic anhydride at –20 °C, 87% conversion with 91% *ee* of *O*-acetylcyanohydrin was achieved in 8 h. Furthermore, these results are quite superior to the reported linear polymeric salen V^V and linear salen Ti^{IV} catalysts.[6d] This may be due to an increase in active catalytic sites which are working in a cooperative manner.[15,16]

Table 1. Enantioselective synthesis of *O*-acetylcyanohydrins from various aldehydes, potassium cyanide and acetic anhydride catalyzed by dimeric chiral Ti^{IV} and V^V complexes.





4a-h

3a: R^1 = H, R^2 = H, R^3 = H
3b: R^1, R^2 = H, R^3 = OMe
3c: R^1 = H, R^2 = OMe, R^3 = H
3d: R^1 = OMe, R^2 = H, R^3 = H
3e: R^1 = H, R^2 = H, R^3 = Cl
3f: R^1 = H, R^2 = H, R^3 = Br
3g: R^1 = H, R^2 = H, R^3 = F
3h: R^1 = F, R^2 = H, R^3 = H

Entry	Substrate	Conversion [%][a]	*ee* [%][b,d]
1 (2)	**3a**	99[e] (99)[f]	92 (93)[c]
3 (4)	**3b**	91[e] (90)[f]	88 (90)
5 (6)	**3c**	92[e] (93)[f]	89 (89)
7 (8)	**3d**	90[e] (92)[f]	89 (90)
9 (10)	**3e**	99[e] (99)[f]	90 (93)
11 (12)	**3f**	99[e] (99)[f]	90 (92)
13 (14)	**3g**	99[e] (99)[f]	91 (94)
15 (16)	**3h**	99[e] (99)[f]	95 (96)

[a] The conversion was determined based on G. C. integral area. [b] The *ee* was determined by using Chiralpak HPLC OD and AD columns. [c] Values in parentheses are for catalyst **2**. [d] The absolute configuration was assigned by comparison with literature data, and was found to be *S*.[12b] [e] Conversion for catalysts **1**. [f] Conversion for catalysts **2**.

Table 2. Enantioselective synthesis of *O*-acetylcyanohydrins from various aldehydes, sodium cyanide and acetic anhydride catalyzed by dimeric complexes **1** and **2**.

Entry	Substrate	Conversion [%][a]	*ee* [%][b,d]
17 (18)	**3a**	99[e] (99)[f]	89 (90)[c]
19 (20)	**3b**	90[e] (90)[f]	87 (88)
21 (22)	**3c**	91[e] (93)[f]	86 (88)
23 (24)	**3d**	90[e] (91)[f]	85 (87)
25 (26)	**3e**	98[e] (99)[f]	89 (91)
27 (28)	**3f**	99[e] (99)[f]	88 (90)
29 (30)	**3g**	98[e] (99)[f]	90 (92)
31 (32)	**3h**	98[e] (99)[f]	91 (93)

[a] The conversion was determined based on G. C. integral area. [b] The *ee* was determined by using Chiralpak HPLC OD and AD columns. [c] Values in parentheses are for catalyst **2**. [d] The absolute configuration was assigned by comparison with literature data found to be *S*.[12b] [e] Conversion for catalysts **1**. [f] Conversion for catalysts **2**.

It has been reported that the reactivity and enantioselectivity of *O*-acetylcyanohydrin formation using chiral Ti^{IV} salen complexes is solvent-dependent.[6d] Thus, the effect of solvent using the complexes **1** and **2** on the asymmetric addition of KCN and acetic anhydride to benzaldehyde was carried out, and the results are shown in Table 3. Good conversion (80–82%) and high *ee* (85–87%) were achieved when 1,2-dichloroethane (entries 35, 36) was used as the solvent, while in cases of toluene and THF, the conversions

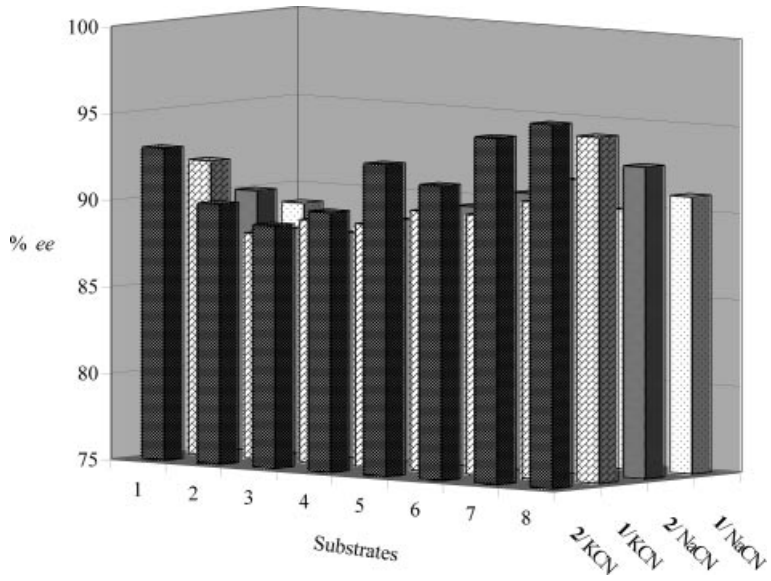


Figure 5. 3D view showing % *ee* vs. aldehydes (1) **3a**, (2) **3b**, (3) **3c**, (4) **3d**, (5) **3e**, (6) **3f**, (7) **3g**, (8) **3h** using the catalysts **1** and **2** with KCN and NaCN.

(40–53%) and enantioselectivities (68–71% *ee*) were not high (Entries 37–40). Of all the solvents used, dichloromethane was found to be the solvent of choice (Entries 33, 34), and it showed better results than the previously reported chiral cross-linked polymeric salen complexes with Ti^{IV}.[6d]

Table 3. Effect of solvents on conversion and *ee* of *O*-acetylcyanohydrin using benzaldehyde as a representative substrate, with KCN and catalysts **1** and **2**.

Entry	Solvent	Conversion [%][a]	*ee* [%][b]
33 (34)	dichloromethane	99 (99)	92 (93)[c]
35 (36)	1,2-dichloroethane	80 (82)	85 (87)
37 (38)	toluene	40 (43)	70 (71)
39 (40)	tetrahydrofuran	50 (53)	67 (68)

[a] The conversion was determined based on G. C. integral area. [b] The *ee* was determined by using Chiralpak HPLC OD columns. [c] Results in parentheses are for catalyst **2**.

Complexes **1** and **2** were also used to examine the influence of catalyst loading and temperature variation on the formation of *O*-acetylcyanohydrin using benzaldehyde as the substrate and KCN as the cyanide source. The results are given in Table 4, where the best conversion (99%) and *ee* (92–93%) were achieved at –20 °C with 5 mol-% (with respect to the salen unit) of the complexes **1** and **2** (Entries 41, 42). On reducing the catalyst loading from 5 mol-% to 2 mol-% there is decrease in conversion to 90–92% (Entries 43, 44) with similar *ee* (91–92%). On further decreasing the catalyst loading (1 mol-%), there is further decrease in conversion and *ee* (Entries 45, 46). Furthermore, the increase in reaction temperature had an adverse effect on the yield and enantioselectivity of the product (entries 47–50). These observations are in consonance with those reported earlier.[6d]

Table 4. Effects of loading and temperature on conversion and *ee* of *O*-acetylcyanohydrin using benzaldehyde as a representative substrate, with KCN and catalysts **1** and **2**.

Entry	Catalyst loading [mol-%]	Temp. [°C]	Conversion [%][a]	*ee* [%][b]
41 (42)	5	–20	99 (99)	92 (93)[c]
43 (44)	2	–20	90 (92)	91 (92)
45 (46)	1	–20	78 (80)	90 (92)
47 (48)	5	–8	88 (89)	70 (71)
49 (50)	5	room temp.	89 (91)	60 (61)

[a] The conversion was determined based on G. C. integral area. [b] The *ee* was determined by using Chiralpak HPLC OD column. [c] Values in parentheses are for catalyst **2**.

A plausible mechanism for the formation of *O*-acetylcyanohydrin is shown in Scheme 1. Catalyst **1** is activated by the addition of acetic anhydride to give bis-acetate **B**, which on reaction with KCN/NaCN in the presence of an aldehyde gives species **C**. The nucleophilic attack by the CN group on the partially coordinated aldehydic carbon to species **D** takes place, which facilitates the acylation of the titanium-bound cyanohydrin to give the *O*-acetylcyanohydrin product. This titanium complex **E** either reacts with cyanide to give bis-cyanide species **F**, or reacts with aldehyde to form species **C**, which further continues the catalytic cycle. It has been reported[18] that the catalytic cycle in the case of the V^V salen complex proceeds in an intramolecular manner via the formation of a *cis*-β V^V salen species in the same manner as reported[12b,18] for the Ti (salen) di-μ-oxo complex.

Catalyst recycling studies were carried out by precipitating the catalyst by the addition of hexane to the post-catalytic reaction mixture. To the recovered catalyst, fresh substrates and reactants were supplied in similar manner as in

the case of fresh catalyst. The data for four-time use of the same catalyst is given in Table 5. The activity of the recycled catalysts gradually decreased upon successive use, possibly due to some physical loss of the catalyst with retention of enantioselectivity. The recyclability of this catalytic system has advantages over previously reported linear and cross-linked polymeric V^V and Ti^{IV} salen complexes.

Table 5. Enantioselective synthesis of the *O*-acetylcyanohydrin with benzaldehyde, potassium cyanide and acetic anhydride catalyzed by recovered dimeric chiral Ti^{IV} and V^V complexes.

Run	1	2	3	4
Time (h)	8 (8)	10 (9)	12 (10)	14 (12)
Conversion [%][a]	99 (99)[c]	98 (99)	90 (92)	88 (90)
ee [%][b]	92 (93)	92 (93)	92 (93)	92 (93)

[a] The conversion was determined based on G. C. integral area. [b] The *ee* was determined by using Chiralpak HPLC OD column. [c] Values in parentheses are for catalyst **2**.

Conclusions

Chiral dimeric titanium(IV) and vanadium(V) salen complexes were used for the asymmetric addition of non-volatile and inexpensive sodium cyanide and potassium cyanide as cyanide sources to various aldehydes in the presence of acetic anhydride at –20 °C. Excellent yields (99%) of *O*-acetylcyanohydrin and high chiral induction (up to 96% *ee*) were achieved in the case of 2-fluorobenzaldehyde, and the results achieved with sodium cyanide are quite comparable to those of potassium cyanide. The V^V salen complex also turned to be the most efficient recyclable system reported so far in the literature. Both the catalysts were recovered after their first use and recycled four times effectively.

Experimental Section

Vanadyl sulfate hydrate (Loba Chemie, India), titanium tetraisopropoxide (Aldrich), KCN (Merck), NaCN (Robert Johnson), benzaldehyde (**3a**), 4-methoxybenzaldehyde (**3b**), 3-methoxybenzaldehyde (**3c**), 2-methoxybenzaldehyde (**3d**), 4-chlorobenzaldehyde (**3e**), 4-bromobenzaldehyde (**3f**), 4-fluorobenzaldehyde (**3g**), and 2-fluorobenzaldehyde (**3h**) were purchased from Aldrich Chemicals and were used as received. Dimeric chiral salen ligand **1′** was synthesized by the reported method.[15a] All the solvents were dried by standard procedures,[19] distilled and stored under nitrogen. Thin-layer chromatography was performed using aluminum TLC sheets precoated with silica gel having a florescent UV indicator. NMR spectra were obtained with a Bruker F113V spectrometer (200 MHz and 50 MHz for ^1H and ^{13}C respectively) and are referenced internally with TMS. FTIR spectra were recorded on a Perkin–Elmer Spectrum GX spectrophotometer in a KBr window. High-resolution mass spectra were obtained with LC-MS (Q-TOF) LC (Waters), or MS (Micromass) instruments. For product purification, flash chromatography was performed using silica gel 60–200 mesh purchased from s. d. Fine-Chemicals Limited, Mumbai (India). Enantiomeric excess (*ee*) were determined by HPLC (Shimadzu SCL-10AVP) using Daicel Chiralpak OD and AD chiral columns with 2-propanol/hexane as eluent. Optical rotations were measured with a Digipol 781 Automatic Polarimeter (Rudolph Instruments).

Synthesis of Vanadium(V) Complex (2): The ligand **1′** (0.499 g, 0.504 mmol) was dissolved in ethanol/CH_2Cl_2 (3:2, 15 mL), to which an aqueous solution of vanadyl sulfate hydrate (0.255 g, 1.008 mmol in 2 mL water) was added dropwise under an inert atmosphere at room temperature. The resulting solution was refluxed for 4 h and then cooled to room temperature with stirring for 2 h while opening the side arm of the reaction flask. The solvent was completely evaporated, and the residue was dissolved in CH_2Cl_2 (10 mL), washed with water (3 × 5 mL) and then with brine. The organic layer was dried with anhydrous Na_2SO_4, filtered and evaporated to give the V^V complex. Yield, 0.385 g, 68.02%. Melting point: d. 200 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.82 (t, J = 7.2, 6 H), 1.33 (s, 18 H), 1.42 (s, 36 H), 1.6–2.3 (m, 16 H), 3.41 (q, J = 7.2, 4 H), 3.81 (m, 2 H), 3.92 (s, 2 H), 4.25 (m, 2 H), 7.48 (s, 2 H), 7.53 (s, 2 H), 7.68 (s, 2 H), 7.73 (s, 2 H), 8.52 (s, 2 H), 8.73 (s, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 3435, 2958, 2868, 2359, 1650, 1613, 1538, 1465, 1437, 1389, 1361, 1317, 1269, 1253, 1227, 1171, 1028, 982, 929, 834, 770, 748, 711, 643, 563 cm^{-1}. $C_{69}H_{102}N_4O_{16}S_2V_2^{+2}$ (1409.6): calcd. C 58.79, H 7.29, N 3.97; found C 58.85, H 7.32, N 3.99. λ_{max} (ε): 252 (33915), 352 (12681), 421 (4114), 633 (1592). $[\alpha]_D^{27}$ = –860 (c = 0.01, $CHCl_3$). TOF-MS (ESI+): m/z 1160.4 $[M+H]^+$.

Procedure for Ti^{IV} Dimeric Salen-Catalyzed Asymmetric *O*-Acetylcyanation of Aldehyde: A solution of ligand **1′** (98.0 mg, 0.099 mmol) and titanium tetraisopropoxide (58.0 μL, 0.198 mmol) in dry CH_2Cl_2 (2 mL) was stirred at room temperature under nitrogen for 2 h. H_2O (3.6 μL, 0.20 mmol) was added, and the reaction mixture was again stirred at room temperature for 3 h. The resulting yellow solution was cooled to –20 °C, and CH_2Cl_2 (2 mL), *t*BuOH (0.2 mL, 2.09 mmol), H_2O (20 μL, 1.11 mmol), benzaldehyde (0.202 mL, 1.98 mmol) and Ac_2O (0.748 mL, 7.92 mmol) were added in that sequence. Solid KCN (0.515 g, 7.92 mmol) was then added in small fractions over a period of 2 h with vigorous stirring, followed by the addition of CH_2Cl_2 (3 mL). After the completion of the reaction (8–10 h, determined byTLC), the reaction mass was washed with water (3 × 5 mL) and brine. The organic layer was separated and dried with anhydrous Na_2SO_4. The solution was filtered, evaporated and the *O*-acetylcyanohydrin product was purified by flash column chromatography on silica gel (eluted with hexane/ethyl acetate = 95:5). The enantiomeric excess of *O*-acetylcyanohydrin was determined by HPLC analysis. Catalyst **1**. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.05 (s, 36 H), 1.22 (s, 36 H), 1.31 (s, 36 H), 2.5–2.6 (m, 32 H), 3.92 (s, 2 H), 3.94 (s, 2 H), 4.0–4.1 (m, 8 H), 6.97 (s, 4 H), 7.05 (s, 4 H), 7.24 (s, 4 H), 7.43 (s, 4 H), 7.80 (s, 4 H), 8.18 (s, 4 H) ppm. ^{13}C (50 MHz, $CDCl_3$): δ = 24.3, 24.7, 28.0, 29.3, 30.2, 30.3, 31.4, 34.0, 35.0, 35.2, 40.7, 41.0, 65.2, 69.4, 121.3, 125.0, 127.1, 128.4, 128.8, 137.1, 138.2, 139.0, 139.5, 157.0, 161.4 ppm. IR (KBr): $\tilde{\nu}$ = 1624, 702 cm^{-1}. $[\alpha]_D^{27}$ = –320 (c = 0.01, $CHCl_3$). $C_{130}H_{176}N_8O_{12}Ti_4$ (2234.3): calcd. C 69.88, H 7.94, N 5.02; found C 69.10, H 7.97, N 5.01. TOF-MS (ESI+): m/z = 2235.8 $[M+H]^+$.

Procedure for Vanadium(V) Dimeric Salen-Catalyzed Asymmetric *O*-Acetylcyanation of Aldehyde: V^V-salen catalyst **2** was dissolved in CH_2Cl_2 (3 mL) and the solution was cooled to –20 °C. CH_2Cl_2 (2 mL), *t*BuOH (0.2 mL, 2.09 mmol), H_2O (20 μL, 1.11 mmol), benzaldehyde (0.202 mL, 1.98 mmol) and Ac_2O (0.748 mL, 7.92 mmol) were added to the solution in that order. The addition of KCN (0.515 g, 7.92 mmol) was done slowly during 2 h, followed by addition of CH_2Cl_2 (3 mL). After the reaction was completed (as detected by TLC), the reaction mass was washed with water

(3 × 5 mL) followed by brine, and the organic layer was separated and dried with anhydrous Na_2SO_4. The solution was filtered, evaporated and the *O*-acetylcyanohydrin product was purified by flash column chromatography on silica gel (eluted with hexane/ethylacetate = 95:5). The enantiomeric excess of *O*-acetylcyanohydrin was determined by HPLC analysis. **4a**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.11 (s, 3 H), 6.38 (s, 1 H), 7.40–7.52 (m, 5 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.8, 63.3, 116.7, 128.3, 129.7, 130.8, 132.3, 169.4 ppm. $[a]_D^{27}$ = –30.5 (*c* = 1, CH_2Cl_2) ppm. TOF-MS (ESI+): *m*/*z* = 160.2 $[M+H]^+$.

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