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Vanadium(V) Salen Complex Catalyzed Highly Enantioselective Cyanoformylation of Aldehydes in the Presence of Imidazole as a Cocatalyst

Noor-ul H. Khan,*[a] Santosh Agrawal,[a] Rukhsana I. Kureshy,[a] Sayed H. R. Abdi,[a] K. Jeya Prathap,[a] and Raksh V. Jasra[a]

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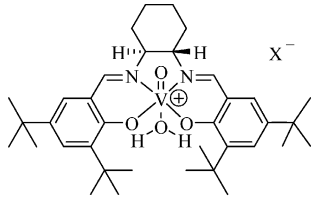
Highly enantioselective cyanoformylation of aldehydes catalyzed by V^V chiral salen complex by using ethyl cyanoformate as a source of cyanide was accomplished in the presence of several cocatalysts. Excellent yields and *ee* values for the resulting cyanohydrin carbonates were achieved when imidazole was used as a cocatalyst at –20 °C. The *ee* value of the cyanohydrin carbonate of 2-naphthaldehyde was further improved to >99% by recrystallization.

Introduction

The enantioselective synthesis of cyanohydrins through carbonyl compounds is a topic of current interest because the resulting optically pure cyanohydrins can be transformed into versatile synthetic building blocks with no loss in optical purity.[1] They also play an important role in the preparation of a wide range of pharmaceuticals, agrochemicals, and insecticides.[2] To achieve high chiral induction in cyanohydrins various catalytic systems for the enantioselective cyanation of aldehydes and ketones were used with KCN, NaCN, trimethylsilyl cyanide (TMSCN), and HCN as sources for cyanide.[3,4] Among these catalytic systems, a V^V salen complex showed impressive enantioinduction in the product *O*-trimethylsilyl cyanohydrins with TMSCN[3e–3h] as a cyanide source; however, *O*-trimethylsilyl cyanohydrins are not so stable and readily undergo hydrolysis to form cyanohydrins that are prone to racemization. Recently, attempts were made to utilize various other sources of cyanide, for example, cyanoformate esters (ROCOCN), acetyl cyanide, diethyl cyanophosphonate, and benzoyl cyanide to synthesize optically pure cyanohydrins with different catalytic systems.[5–10] Belokon et al.[6b] reported a Ti^{IV} salen complex as an efficient catalyst (5 mol-%) for cyanoformylation of aldehydes at –40 °C in 6–48 h with high conversions and *ee* values. Later, Moberg et al.[8a] reported an improvement over this catalytic system by conducting the cyanoformylation of aldehydes in the presence of various Lewis bases. The presence of triethylamine as a Lewis base significantly cut the reaction time (4–12 h) with similar enantioselectivities. Feng et al.[10c] also tried the same reaction but in the presence of 2-propanol/chloroform mixture as a solvent at –20 °C; however, the reaction took 10–92 h and only moderate to high conversions and *ee* values were obtained. With our interest in enantioselective cyanation of aldehydes and ketones, we previously reported Ti^{IV}, V^V, and Mn^{III} metal complexes with dimeric and polymeric salen ligands as catalysts with different cyanide sources.[11] In the present manuscript we explored the catalytic efficacy of V^V salen complex **1** (Figure 1)[3f] in the enantioselective cyanation of aldehydes by using ethyl cyanoformate as a source of cyanide in combination with various cocatalysts. Excellent yields and *ee* values for the cyanohydrin carbonate of hydrocinnamaldehyde were achieved with this catalyst in the presence of imidazole as a cocatalyst. Further, in the case of solid products such as the cyanohydrin carbonate of 2-naphthaldehyde, the *ee* was improved to >99% upon recrystallization. Notably, the carbonate products are more stable towards unwanted hydrolysis that takes place in the case of cyanohydrin trimethylsilyl ethers.



Complex **1** X = $EtSO_4$
Complex **2** X = Cl

Figure 1. Structure of complexes **1** and **2**.

Results and Discussion

Our systematic study started with the asymmetric cyanoformylation of benzaldehyde (**2a**) by using chiral V^V salen

[a] Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSMCRI, CSIR), Bhavnagar- 364 002, Gujarat, India
Fax: +91-0278-2566970
E-mail: khan2593@yahoo.co.in
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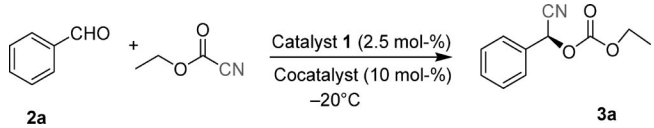
complexes **1** and **2** as catalysts at –20 °C in dichloromethane. However, even after 48 h there was no product formation (Table 1, Entries 1 and 2). When the same reaction was conducted in the presence of imidazole as a cocatalyst (Table 1, Entries 3 and 4), excellent conversion (96%) into the cyanohydrin carbonate in 93%*ee* was achieved with catalyst **1**. We further explored the role of other cocatalysts, viz., KCN, LiOH, 2,6-lutidine, pyridine, 2-methylimidazole, and triethylamine with catalyst **1** (Table 1, Entries 5–10) in the cyanoformylation of benzaldehyde as a model substrate. Very good to excellent yield of cyanohydrin carbonate was achieved except for pyridine where there was no product formation in 24 h (Table 1, Entry 8). The use of LiOH and triethylamine as cocatalysts in the cyanoformylation reaction severely affected the enantioselectivity, though the latter cocatalyst tremendously accelerated the reaction (Table 1, Entry 10). Among all the cocatalysts used in the present study, imidazole was found to be the most efficient in terms of high chiral induction and product yield (Table 1, Entry 3). Therefore, our subsequent studies for asymmetric cyanoformylation were carried out with chiral V^V salen complex **1** as a catalyst and imidazole as a cocatalyst. In order to get the optimal reaction conditions we carried out asymmetric cyanoformylation of benzaldehyde (**2a**) for 18 h at various temperatures and loadings of the catalyst, cocatalyst, and ethyl cyanoformate. The results are summarized in Table 2. At first the catalyst loading was varied over a range of 1 to 7.5 mol-% keeping the cocatalyst loading at 10 mol-% at –20 °C (Table 2, Entries 1–4). It is evident from the results that 2.5 mol-% catalyst loading is optimum (Table 2, Entry 2) at –20 °C. At –40 °C, there was an improvement in the enantioselectivity, although marginal, but there was a concomitant decrease in the product yield (Table 2, Entry 5). By raising the temperature from –20 to 0 °C and to room temperature, the yields of the cyanohydrin carbonates were increased, but at the expense of the enantioselectivities (Table 2, Entries 6 and 7). Therefore, for the rest of the catalytic experiments –20 °C was taken as the optimum temperature (Table 2, Entry 2). We next optimize the loadings of the cocatalyst and ethyl cyanoformate by keeping the other parameters constant (Table 2, Entries 8–12). It is emerged that 10 mol-% cocatalyst loading with 200 mol-% ethyl cyanoformate is optimum (Table 2, Entry 2).

We also evaluated the catalytic activity of V^V salen complex **1** for the cyanoformylation of benzaldehyde (**2a**) under the above-optimized reaction conditions in various solvents, for example, 1,2-dichloroethane (1,2-DCE), dichloromethane (DCM), chloroform ($CHCl_3$), tetrahydrofuran (THF), toluene, and acetonitrile (CH_3CN) (Table 2, Entries 2, 13–17). Out of all the solvents used, DCM was found to be the best solvent for this system (Table 2, Entry 2).

Under the above-optimized reaction conditions the scope of this protocol for the cyanoformylation reaction was further extended to a variety of aromatic and aliphatic aldehydes. Data in Table 3 is indicative of applicability of this protocol over a range of substrates where good to excellent isolated yields (80–97%) and *ee* values (76–97%) for the products were achieved in 18–48 h. Surprisingly, the electronic factors of different substituents on the substrate did not have much effect on the yield and selectivity of the product. However, reactions of benzaldehyde and aromatic aldehydes with smaller substituents at the 2- and 3-positions were fast (Table 3, Entries 1–4) relative to the aromatic aldehydes having bulkier groups in the same positions (24–48 h; Table 3, Entries 6, 7, 9, 10). In general, 4-substituted aromatic aldehydes reacted slowly (24–60 h; Table 3, Entries 5,

Table 1. Effect of cocatalysts on the asymmetric addition of ethyl cyanoformate to benzaldehyde at –20 °C.[a]



2a **3a**

Entry	Complex	Cocatalyst	Time [h]	Yield [%][b]	*ee* [%][c]
1	V^V $EtSO_4$	–	48	–	–
2	V^V Cl	–	48	–	–
3	V^V $EtSO_4$	imidazole	18	96	93
4	V^V Cl	imidazole	18	92	90
5	V^V $EtSO_4$	KCN	18	91	92
6	V^V $EtSO_4$	LiOH	18	93	03
7	V^V $EtSO_4$	2,6-lutidine	36	89	93
8	V^V $EtSO_4$	pyridine	24	–	–
9	V^V $EtSO_4$	2-methylimidazole	12	95	90
10	V^V $EtSO_4$	triethylamine	08	95	09

[a] All reactions were carried out at –20 °C by using catalyst (0.031 mmol), benzaldehyde (0.62 mmol), ethyl cyanoformate (1.24 mmol), cocatalyst (0.062 mmol) in dry DCM (0.8 mL). [b] Isolated yield. [c] The *ee* values were determined by using a chiracel OD column.

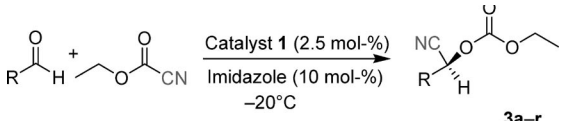
Table 2. Effect of catalyst loading, cocatalyst loading, temperature, and solvent variation for the synthesis of the cyanohydrin carbonate of benzaldehyde.[a]

Entry	Solvent	Catalyst [mol-%]	Cocatalyst loading [mol-%]	*T* [°C]	Yield[b] [%]	*ee*[c] [%]
1	DCM	1	10	–20	92	86
2	DCM	2.5	10	–20	96	93
3	DCM	5	10	–20	96	93
4	DCM	7.5	10	–20	96	95
5	DCM	2.5	10	–40	85	96
6	DCM	2.5	10	0	91	84
7	DCM	2.5	10	r.t.	93	80
8	DCM	2.5	5	–20	86	88
9	DCM	2.5	15	–20	96	93
10[d]	DCM	2.5	10	–20	89	90
11[e]	DCM	2.5	10	–20	96	93
12[f]	DCM	2.5	10	–20	96	93
13	$CHCl_3$	2.5	10	–20	90	89
14	1,2-DCE	2.5	10	–20	87	82
15	THF	2.5	10	–20	68	70
16	CH_3CN	2.5	10	–20	79	72
17	toluene	2.5	10	–20	70	73

[a] All reactions were carried out by using catalyst **1**, aldehyde (0.62 mmol), ethyl cyanoformate (1.24 mmol). [b] Isolated yield. [c] The *ee* values were determined by using a chiracel OD column. [d] By using 160 mol-% of ethyl cyanoformate. [e] By using 240 mol-% of ethyl cyanoformate. [f] By using 320 mol-% of ethyl cyanoformate.

8,11–13). In the case of α, β-unsaturated aldehydes high yields and *ee* values were achieved in 24–48 h (Table 3, Entries 14 and 15). Aliphatic aldehydes bearing an aromatic ring in the alkyl chain, such as hydrocinnamaldehyde, gave the highest *ee* value of 97% with 92% isolated yield within 24 h (Table 3, Entry 16), whereas aliphatic aldehydes with no such functionality gave moderate yields and *ee* values (Table 3, Entries 17 and 18). For all catalytic runs in which the V^V salen complex possessed (*R*) stereochemistry, the cyanohydrin carbonate product was obtained as the (*S*) enantiomer. Further, the cyanohydrin carbonate of 2-naphthaldehyde was obtained as a white solid, which upon recrystallization (hexane/DCM, 60:40) gave a product with 99%*ee*. The high *ee* value was probably due the preferential homochiral aggregation of the product, which crystallized out first to leave behind racemic product with less pronounced heterochiral aggregation in the solution.[12]

Table 3. Synthesis of cyanohydrin carbonates of various aldehydes by using the V^V salen complex under optimum reaction conditions.[a]



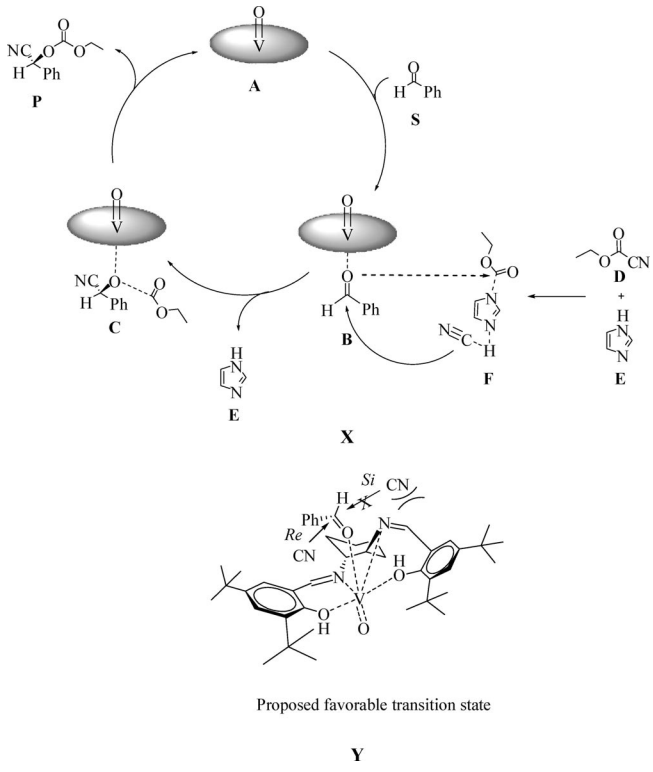
2a–r **3a–r**

Entry	Substrate	Time [h]	Yield[b] [%]	*ee*[c] [%]
1	benzaldehyde (**2a**)	18	95	93
2	2-naphthaldehyde (**2b**)	18	93	95(>99)[d]
3	2-methoxybenzaldehyde (**2c**)	18	96	91
4	3-methylbenzaldehyde (**2d**)	18	97	94
5	4-methylbenzaldehyde (**2e**)	24	91	90
6	2-methoxybenzaldehyde (**2f**)	24	90	96
7	3-methoxybenzaldehyde (**2g**)	48	89	89
8	4-methoxybenzaldehyde (**2h**)	60	90	93
9	2-ethoxybenzaldehyde (**2i**)	48	92	93
10	2-benzyloxybenzaldehyde (**2j**)	48	93	96
11	4-fluorobenzaldehyde (**2k**)	48	95	93
12	4-chlorobenzaldehyde (**2l**)	48	80	85
13	4-bromobenzaldehyde (**2m**)	48	90	91
14	(*E*)-cinnamaldehyde (**2n**)	24	91	92
15	crotonaldehyde (**2o**)	48	91	90[e]
16	hydrocinnamaldehyde (**2p**)	24	92	97
17	isovalerladehyde (**2q**)	24	89	76[f]
18	hexanal (**2r**)	24	82	83[f]

[a] All reactions were carried out by using catalyst **1** (2.5 mol-%), aldehyde (0.62 mmol), ethyl cyanoformate (1.24 mmol), imidazole (10 mol-%) as cocatalyst at –20 °C. [b] Isolated Yield. [c] The *ee* values were determined by using OD and OD-H chiral columns. [d] The *ee* value was obtained by recrystallization. [e] The *ee* value was determined by using an AD chiral column. [f] The *ee* value was determined by using a GC chiral G-TA column.

Mechanism

To understand the probable mechanism of the catalytic reaction (Scheme 1, **X**) we carried out a series of experiments with catalyst **1** with benzaldehyde as the substrate (**S**) and imidazole (**E**) as a cocatalyst by using ethyl cyanoformate (**D**) as a cyanide source. The reaction was monitored by UV/Vis spectrophotometry and ^{1}H and ^{13}C NMR spectroscopy. During the catalytic run **D** first reacts with imidazole to form an intermediate species with a probable structure **F** (Scheme 1), as evidenced by the emergence of new sets of peaks at δ = 8.125, 7.438, 7.038 ppm in the ^{1}H NMR spectrum (Figure 2). Similar changes were also observed in the ^{13}C NMR (Figure 3) and UV/Vis spectra (spectrum is given in the Supporting Information). Species **F** is likely to react with intermediate **B** [formed by the interaction of **S** with **1**(**A**)] to form species **C**, which eventually gives product



Scheme 1. Probable mechanism for cyanoformylation of aldehydes (**X**) and proposed working model for enantioselection (**Y**).

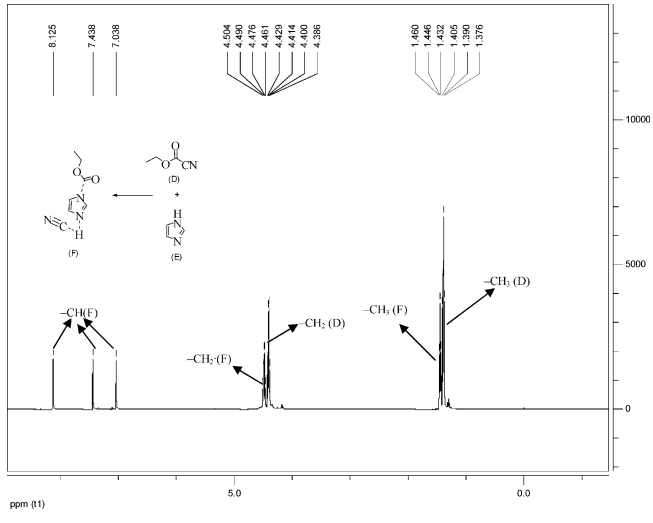


Figure 2. ^{1}H NMR spectrum of a mixture of ethyl cyanoformate and imidazole in $CDCl_3$.

P. On the basis of the X-ray structure of the vanadium salen complex reported by Belokon et al.,[3f] the potential transition state was generated where the attack of cyanide through the less hindered *Re* face is favored to form the (*S*) enantiomer in excess (Scheme 1, **Y**).

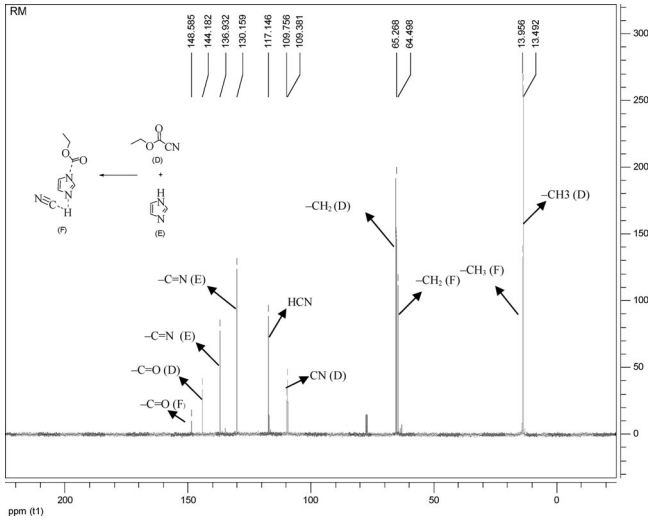


Figure 3. ^{13}C NMR spectrum of a mixture of imidazole and ethyl cyanoformate in $CDCl_3$.

Conclusions

We carried out an efficient enantioselective cyanoformylation of various aromatic and aliphatic aldehydes by using V^V chiral salen complex **1** as a catalyst with ethyl cyanoformate as a source of cyanide in the presence of imidazole as a cocatalyst. Excellent yields and enantioselectivities up to 97% for the product cyanohydrin carbonate were achieved at –20 °C. The chiral purity of the cyanohydrin carbonate of naphthaldehyde was further improved to >99% by recrystallization.

Experimental Section

General: Vanadyl sulfate hydrate (Loba Chemie, India), imidazole, LiOH, triethylamine (s. d. Fine-Chem. India), KCN (Merck), 2,6 lutidine, 2-methylimidazole, ethyl cyanoformate, benzaldehyde (**2a**), 2-naphthaldehyde (**2b**), 2-methoxybenzaldehyde (**2f**), 3-methoxybenzaldehyde (**2g**), 4-methoxybenzaldehyde (**2h**), 2-ethoxybenzaldehyde (**2i**), 2-benzyloxybenzaldehyde (**2j**), 4-fluorobenzaldehyde (**2k**), 4-chlorobenzaldehyde (**2l**), 4-bromobenzaldehyde (**2m**), (*E*)-cinnamaldehyde (**2n**), crotonaldehyde (**2o**), hydrocinnamaldehyde (**2p**), isovaleraldehyde (**2q**), and hexanal (**2r**) were purchased from Aldrich Chemicals and 2-methylbenzaldehyde (**2c**), 3-methylbenzaldehyde (**2d**), and 4-methylbenzaldehyde (**2e**) were purchased from Merck chemicals and used as received. All the solvents were dried by standard procedures,[13] distilled, and stored under nitrogen. Chiral salen ligand viz., (1*R*,2*R*)-*N*,*N*′-bis[3,5-bis(*tert*-butyl)salicylidene]cyclohexane-1,2-diamine was synthesized by the reported method.[14] NMR spectra were obtained with a Bruker F113V spectrometer (500 and 125 MHz for ^1H and ^{13}C, respectively) and are referenced internally with TMS. FTIR spectra were recorded with a Perkin–Elmer Spectrum GX spectrophotometer in KBr window. High-resolution mass spectra were obtained with LC–MS (Q-TOFF), LC (Waters), MS (Micromass) instruments. For the product purification flash chromatography was performed by using silica gel 60–200 mesh purchased from s. d. Fine-Chem. Limited Mumbai (India). Enantiomeric excesses (*ee*) of the products were determined by HPLC (Shimadzu SCL-10AVP) by using Daicel Chiralpak AD and OD chiral columns with 2-propanol/hexane as the eluent. Optical rotations were measured with a Digipol 781 Automatic Polarimeter Rudolph Instruments.

Complex 1: Complex **1** was synthesized by the reported procedure.[3f] A solution of (1*R*,2*R*)-*N*,*N*′-bis[3,5-bis(*tert*-butyl)salicylidene]cyclohexane-1,2-diamine (2.7 mmol, 1.5 g) in THF (20 mL) and vanadyl sulfate hydrate (2.7 mmol, 0.69 g) in hot ethanol (30 mL) were mixed. The resulting solution was heated at reflux for 2 h under an inert atmosphere and then cooled to room temperature. The reaction mass was further allowed to stir for an additional 12 h while opening the side arm of the reaction flask for autooxidation. The solvent was completely evaporated, and the residue was dissolved in DCM (15 mL) and washed with water (3 × 5 mL) and brine. The organic layer was dried with anhydrous Na_2SO_4, and the complex was purified by column chromatography to afford a dark-green solid.

Complex 2: Complex **2** was synthesized by the reported procedure.[3c] A solution of (1*R*,2*R*)-*N*,*N*′-bis[3,5-bis(*tert*-butyl)salicylidene]cyclohexane-1,2-diamine (0.91 mmol, 0.5 g) in THF (20 mL) and $VOCl_3$ (1.38 mmol, 0.13 mL) were mixed. The resulting solution was stirred at room temperature for 30 min, and the solvent was then evaporated. The product was purified by column chromatography to afford a dark-green solid.

Typical Experimental Procedure for the Enantioselective Cyanoformylation of Aldehydes: A solution of V^V salen complexes **1** and **2** (0.015 mmol) and the appropriate aldehyde (0.62 mmol) in dry CH_2Cl_2 (0.8 mL) was stirred for 10 min at room temperature under a N_2 atmosphere. To this solution was added imidazole (4 mg, 0.062 mmol), and the solution was cooled to –20 °C. To this cooled solution was dropwise added ethyl cyanoformate (77 μL, 0.78 mmol) over a period of 5 min. The reaction was monitored on TLC. After completion of the reaction the product was purified by flash column chromatography on a silica gel column (hexane/ethyl acetate, 90:10). The purified products were characterized by ^1H and ^{13}C NMR spectroscopy, and the spectra were in agreement with the reported values.[6d,10d]

Supporting Information (see footnote on the first page of this article): Characterization data and HPLC and GC profiles of the cyanohydrin carbonate products.

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