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Enantioselective cyanosilylation of aldehydes catalyzed by Mn(salen) complex/triphenyl phosphine oxide

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The activation of chiral Mn(salen) complexes with Ph_3PO has been found to provide a good strategy for the asymmetric cyanosilylation of aldehydes. Aromatic aldehydes have been converted into the corresponding cyanohydrin trimethylsilylether in yields up to 95% and ee up to 67% using 0.25 mol% chiral Mn(salen) complex in combination with 10 mol% of achiral Ph_3PO as additive. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: cyanosilylation; aldehydes; Mn(salen); enantioselectivity

INTRODUCTION

Design and synthesis of chiral metal complexes for asymmetric cyanosilylation of carbonyl compounds is of current interest in synthetic chemistry. The cyanohydrins produced are very useful synthetic intermediates for homochiral products, pharmaceutical compounds and natural products.[1–8] Chiral metal salen complexes are useful catalysts for a variety of asymmetric transformations[9–14] including cyanosilylation reactions.[15,16] The advent and successful employment of chiral Mn(salen) complexes for asymmetric epoxidation of unfunctionlized olefins devised by Jacobsen[17] and Katsuki[18] are the starting point for catalysis by various metal salen complexes. There are various reports available on the catalytic utility of chiral Mn(salen) complexes.

Gaquere *et al*. studied the directing role of tert-pentyl group on epoxidation using Mn(salen) complexes.[19] Optically active α-hydroxy ketones were prepared with high enantioselectivity by the catalytic oxidation of (*E*)-enol phosphates using Mn(salen) complex.[20] Choudary *et al*. prepared heterogeneous Mn(salen) complex through covalent attachment of salen ligand on silica gel via a chloropropyl spacer and subsequent complexation with Mn(salen).[21] We reported the catalytic activity of Al(salen)[22,23] and Mn(salen)[24,25] complexes in the asymmetric synthesis of cyanohydrins by dual activation. The concept of dual activation has been pioneered by Shibasaki's group. They reported enantioselective catalytic additions of TMSCN to various ketones utilizing bifunctional ligand and $Ti(OiPr)_4$ or the lanthanide complexes.[26–28] We report here the catalytic activity of Katsuki's catalyst (**1**, Fig. 1) for the cyanosilylation of aldehydes.

EXPERIMENTAL

Materials and instruments

In all cases the ^1H NMR (200 MHz) spectra were recorded with Varian Gemini 2000 spectrophotometer. Chemical shifts are reported in ppm in $CDCl_3$ with tetramethylsilane as internal standard. ^{13}C NMR data were collected on a Varian Unity Inova 400 (100 MHz) spectrophotometer at a field of 9.34 T. Enantionmeric excess was determined by HPLC analysis on Chiracel OD column in comparisons with authentic racemates. HRMS analysis was carried on a Hewlett-Packard 5890A gas chromatograph/Jeol JMS–DX303 mass spectrometer by chemical ionization with methane as the flow gas. Analytical high-performance liquid chromatography (HPLC) was performed on a Shimadzu HPLC (LC 10-AD-VP) using the indicated chiral column. All data was in accordance with literature values. The absolute configurations were determined by optical rotation.[22,24,29–31]

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The catalyst, Mn(salen) {(1*S*,2*S*)-*N*,*N*′-Bis[(*R*)-2-hydroxy-2′-phenyl-1,1′-binaphthyl-3-ylmethylene]-1,2-diphenyl-ethylenedaminato manganses(III)acetate; M.F is $C_{70}H_{49}MnN_2O_4$}, aldehdyes and Ph_3PO were purchased from Aldrich.

Preparation of cyanohydrin trimethylsilylether

To 0.25 mol% of the catalyst **1**, $POPh_3$ (10 mol%), TMSCN (2.4 equiv) and THF (1 ml) were added and stirred at 0 °C in a 10 ml round-bottom flask. To this mixture aldehyde (1 mmol) was added drop-wise using a syringe pump. The reaction mixture was stirred continuously under the conditions mentioned in Table 1 and progress of the reaction was followed by TLC. The reaction mixture was purified by silicagel flash chromatography using EtOAc–hexane (1 : 9) mixture as eluent. The silylethers thus obtained were identified by ^1H and ^{13}C NMR and HRMS data, which are consistent with the structure. The chiral enationmeric excess of cyanohydrins was determined by Chiral HPLC column (Daicel Chiral cel OD).

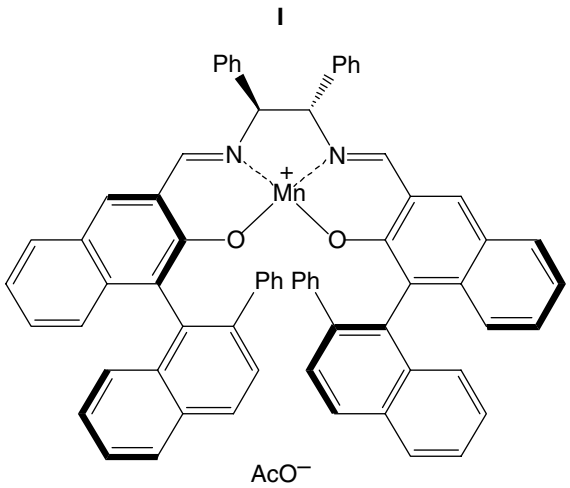


Figure 1. Katsuki's catalyst.

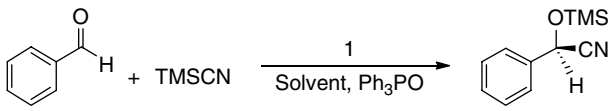
2-Phenyl-2-(trimethylsilyloxy)acetonitrile (Table 2, entry 1)

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.257$ (s, 9H), 5.52 (s, 1H), 7.42–7.47 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.32$, 63.59, 119.12, 126.29, 128.87, 129.27, 136.18. HRMS(M^+)[32] calcd for $C_{11}H_{15}NOSi$: 205.0923; found: 205.0912. *S* enantiomer in 65% ee. HPLC (Daicel Chiralcel OD, ^{i}PrOH–*n*-hexane = 0.5 : 99.5; flow rate = 0.5 ml/min) 22.4 and 23.3 min.

2-(4-Methylphenyl)-2-(trimethylsilyloxy) acetonitrile (entry 2)

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.142$ (s, 9H), 2.29 (s, 3H), 5.49 (s, 1H), 7.18 (d, 2H) 7.25 (d, 2H) ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.28$, 55.78, 63.87, 114.66, 119.47, 127.58, 128.78, 160.23. HRMS(M^+)[32] calcd for $C_{12}H_{17}NOSi$: 219.1079; found: 219.1069. *S* enantiomer in 56% ee. HPLC (Daicel Chiralcel OD,^{i}PrOH–*n*-hexane = 0.5 : 99.5; flow rate = 0.5 ml/min) 29.2 and 31.4 min.

Table 1. Cyanosilylation of benzaldehyde under various conditions[a]



Entry	**1** (mol%)	Ph_3PO (mol%)	Solvent (1 ml)	Temperature (0 °C)	Time (h)	Yield[b] (%)	ee[c] (%)
1	0.1	10	MC	RT	6	90	25
2	0.25	10	MC	RT	3	95	35
3	0.5	10	MC	RT	1.5	90	25
4	1	10	MC	RT	0.5	95	22
5	0.25	20	MC	RT	5	85	30
6	0.25	30	MC	RT	5	75	28
7	0.5	0	MC	RT	1.5	65	20
8	0.25	10	—	RT	12	50	15
9	0.25	10	THF	RT	8	90	51
10	0.25	10	$CHCl_3$	RT	8	85	30
11	0.25	10	MeCN	RT	20	—	—
12	0.25	10	THF	0	80	80	65
13	0.25	10	THF	−10	10 days	65	55
14	0.25	10	THF	−20	14 days	65	30
15	0.25	10	THF	−40	—	—	—
16	—	10	MC	RT	10	—	—

[a] 0.25 mol% of Mn(salen) and 10 mol% Ph_3PO were used. [b] Isolated yield. [c] ee determined from chiral HPLC column.

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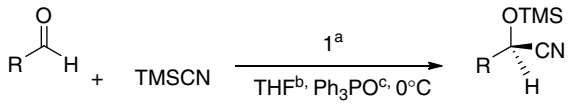
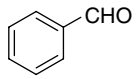
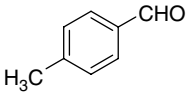
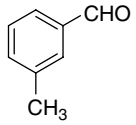
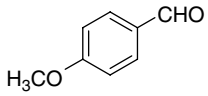
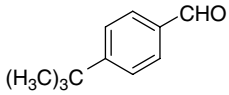
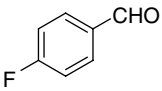
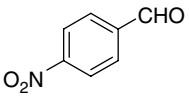
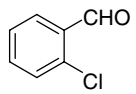
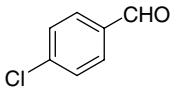
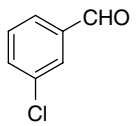
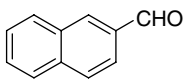
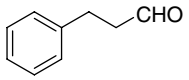
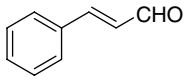
Table 2. Cyanosilylation of various aldehydes



Entry	Substrate	Time (h)	Yield (%)[d]	ee (%)[e]	R or S[f]
1		80	80	65	S
2		70	80	56	S
3		75	90	11	S
4		75	75	53	S
5		60	93	45	S
6		60	85	39	S
7		30	95	43	S
8		40	92	30	S
9		45	89	20	S
10		72	83	52	S
11		45	80	67	S
12		35	84	67	S
13		46	88	44	S

[a] 0.25 mol% of Mn(salen) complex as catalyst. [b] 1 ml of THF as the solvent. [c] 10 mol% of Ph_3PO as the additive. [d] Isolated yield. [e] ee was determined from chiral HPLC column. [f] Absolute configuration were determined by optical rotation method.

2-(3-Methyl phenyl)-2(trimethylsilyloxy) acetonitrile (entry 3)

^{1}H NMR ($CDCl_3$, 200 MHz): $\delta \doteq 0.232$ (s, 9H), 5.45 (s, 1H), 2.38 (s, 3H) 7.26–7.28 (m, 4H) ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.123$, 21.46, 63.72, 119.21, 123.41, 126.93, 128.74, 130.02, 136.07, 138.74 HRMS (M^+) calcd for $C_{12}H_{17}NOSi$: 219.1077; found: 220.1087. *S* enantiomer in 11% ee. HPLC (Daicel Chiralcel OD, ^{i}PrOH–*n*-hexane = 0.5 : 99.5; flow rate = 0.5 ml/min) 40.7 and 43.1 min.

2-(4-Methoxyphenyl)-2-(trimethylsilyloxy) acetonitrile (entry 4)

^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.38$ (s, 9H), 3.83 (s, 3H), 5.44 (s, 1H), 6.96 (d, 2H), 7.42 (d, 2H) ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.26$, 55.34, 63.34, 114.25, 119.32, 127.93, 128.46, 160.33. HRMS(M^+)[32] calcd for $C_{12}H_{17}NO_2Si$: 235.1029; found: 236.1032. *S* enantiomer in 53% ee. HPLC (Daicel Chiralcel OD, ^{i}PrOH–*n*-hexane = 0.5 : 99.5; flow rate = 0.5 ml/min) 36.1 and 39.3 min.

2-(4-*tert*-Butylphenyl)-2-(trimethylsilyloxy) acetonitrile (entry 5)

^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.23$ (s, 9H), 1.32 (s, 9H), 5.38 (s, 1H), 7.09–7.21 (m, 4H). ^{13}C NMR($CDCl_3$, 100 MHz): $\delta = -0.39$, 31.12, 34.52, 63.33, 119.28, 125.73, 126.04, 133.19, 152.47. HRMS(M^+)[32] calcd for $C_{15}H_{23}NOSi$: 261.1549; found: 262.1552. *S* enantiomer in 45% ee. HPLC (Daicel Chiralcel OD, ^{i}PrOH–*n*-hexane = 0.5 : 99.5; flow rate = 0.5 ml/min) 22.1 and 35.8 min.

2-(4-Fluorophenyl)-2-(trimethylsilyloxy) acetonitrile (entry 6)

^{1}H NMR ($CDCl_3$, 200 MHz): $\delta \doteq 0.286$ (s, 9H), 5.52 (s, 1H), 7.14 (d, 2H), 7.36 (d, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.28$, 65.02, 118.35, 129.25, 130.54, 162.12. HRMS(M^+)[32] calcd for $C_{11}H_{14}FNOSi$: 223.0829; found: 223.0835. *S* enantiomer in 39% ee. HPLC (Daicel Chiralcel OD, ^{i}PrOH–*n*-hexane = 0.5 : 99.5 flow = 0.5 ml/min) 25.5 and 26.3 min.

2-(4-Nitrophenyl)-2-(trimethylsilyloxy) acetonitrile (entry 7)

^{1}H NMR ($CDCl_3$, 200 MHz): $\delta \doteq 0.286$ (s, 9H), 5.62 (s, 1H), 7.78 (d, 2H), 8.32 (d, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.28$, 65.02, 118.35, 124.25, 139.54, 147.12. HRMS(M^+) calcd for $C_{11}H_{14}N_2O_3Si$: 250.0774; found: 250.0782. *S* enantiomer in 43% ee. HPLC (Daicel Chiralcel OD, ^{i}PrOH–*n*-hexane = 0.5/99.5; flow rate = 0.5 ml/min) 28.2 and 33.7 min.

2-(2-Chlorophenyl)-2-(trimethylsilyloxy) acetonitrile (entry 8)

^{1}H NMR ($CDCl_3$, 200 MHz): $\delta \doteq 0.286$ (s, 9H), 5.62 (s, 1H), 7.26 (m, 3H), 7.72 (t, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.28$, 65.02, 118.35, 126.25, 128.54, 129.8, 130.12, 131.9, 134.1 HRMS(M^+) calcd for $C_{11}H_{14}ClNOSi$: 239.0536; found: 239.0542. *S* enantiomer in 30% ee. HPLC (Daicel Chiralcel OD,

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^{i}PrOH–*n*-hexane = 0.5/99.5 flow rate = 0.5 ml/min) 22.5 and 23.9 min.

2-(4-Chlorophenyl)-2-(trimethylsilyloxy) acetonitrile (entry 9)

^{1}H NMR ($CDCl_3$, 200 MHz): $\delta \doteq 0.286$ (s, 9H), 5.62 (s, 1H), 7.38 (d, 2H), 7.42 (d, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.28$, 65.02, 118.35, 128.25, 130.54, 131.8, 133.12. HRMS(M^+)[32] calcd for $C_{11}H_{14}ClNOSi$: 239.0533; found 239.0589. *S* enantiomer in 20% ee. HPLC (Daicel Chiralcel OD, ^{i}PrOH–*n*-hexane = 0.5 : 99.5; flow rate = 0.5 ml/min) 31.6 and 37.4 min.

2-(3-Chlorophenyl)-2-(trimethylsilyloxy) acetonitrile (entry 10)

^{1}H NMR ($CDCl_3$, 200 MHz): $\delta \doteq 0.286$ (s, 9H), 5.62 (s, 1H), 7.24 ~ 7.55 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.28$, 65.02, 118.35, 126.95, 128.14, 128.8, 129.42, 133.9, 135.1 HRMS(M^+) calcd for $C_{11}H_{14}ClNOSi$: 239.0531; found: 239.0542. *S* enantiomer in 52% ee. HPLC (Daicel Chiralcel OD, ^{i}PrOH–*n*-hexane = 0.5 : 99.5; flow rate = 0.5 ml/min) 26.1 and 29.9 min.

2-(Naphthalene-1-yl)-2-(trimethylsilyloxy) acetonitrile (entry 11)

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.063$ (s, 9H), 5.72 (s, 1H), 7.53–7.61 (m, 3H) 7.85–7.94 (m, 3H), 8.02–8.04 (d, 1H) ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -16.35$, 64.04, 118.75, 126.33, 127.1, 127.39, 127.92, 128.44, 129.54, 132.54, 133.05, 133.83. HRMS(M^+) calcd for $C_{15}H_{17}NOSi$: 255.1079; found: 256.1089. *S* enantiomer in 67% ee. HPLC (Daicel Chiralcel OD, ^{i}PrOH–*n*-hexane = 0.5 : 99.5; flow rate = 0.5 ml/min) 30.0 and 31.8 min.

4-Phenyl-2-(trimethylsilyloxy)butanenitrile (entry 12)

^{1}H NMR ($CDCl_3$, 200 MHz): $\delta \doteq 0.286$ (s, 9H), 4.21 (s, 1H), 2.14 (t, 2H), 2.53 (t, 2H), 7.29–7.41 (m, 5H) ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.28, 28.31, 36.13, 60.02, 119.35, 126.15, 128.14, 128.82, 142.02$. HRMS($M^+$) calcd for $C_{13}H_{19}NOSi$: 233.1234; found: 234.1247. *S* enantiomer in 55% ee. HPLC (Daicel Chiralcel OD, ^{i}PrOH–*n*-hexane = 0.5 : 99.5; flow rate = 0.5 ml/min) 8.7 and 10.9 min.

4-Phenyl-2-(trimethylsilyloxy)but-3-enenitrile (entry 13)

^{1}H NMR ($CDCl_3$, 200 MHz): $\delta \doteq 0.286$ (s, 9H), 4.91 (m, 1H), 6.25 (m, 1H), 6.65 (d, 1H), 7.22–7.41 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.28$, 64.42, 118.42, 127.91, 128.51, 128.55, 136.45. HRMS(M^+) calcd for $C_{13}H_{17}NOSi$: 231.1079; found: 231.1085. *S* enantiomer in 44% ee. HPLC (Daicel Chiralcel OD, ^{i}PrOH–*n*-hexane = 0.5 : 99.5; flow rate = 0.5 ml/min) 18.1 and 22.3 min.

Trimethyl silanecarbonitrile (TMSCN)

^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.354$. ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 1.98, 126.97$.

A mixture of trimethyl silanecarbonitrile and triphenyl phosphine oxide (TMSCN +Ph_3PO)

^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.067, 0.371$ (s, 9H), 7.41–7.71 (m, 15H). ^{13}C NMR ($CDCl_3$, 100 MHz): 1.38, 1.985, 127.00, 128.319, 128.440,131.890,131.988.

RESULTS AND DISCUSSION

The optimization of the variables of the reaction of benzaldehyde with TMSCN was examined by employing Mn(salen) as catalyst and Ph_3PO as the additive. Initially the effect of quantity of catalyst on the cyanosilylation of benzaldehyde was examined (entries 1–4, Table 1). The loading was varied from 0.1 to 1 mol%. With 0.25 mol% of the catalyst, the yield and ee were 95 and 35%, respectively, for a reaction time of 3 h. With increasing the catalyst loading from 0.25 to 1 mol%, the reaction time was reduced from 3 to 0.5 h at the cost of ee. Here ee was reduced from 35 to 22% without reducing the yield (entries 2 and 4). In all the cases the loading of additive was 10 mol%. When the amount of additive was increased from 10 to 30 mol%, the yield and ee were reduced (entries 2, 5 and 6). Therefore 10 mol% is the optimal additive quantity. In the absence of additive (entry 7), the reaction went off with reduced yield (65%) and ee (20%). In the absence of solvent, the reaction took a longer time for completion and the yield and ee were tremendously reduced (entry 8). The effect of solvent on cyanosilylation of benzaldehyde was compared (entries 2, 9, 10 and 11). In addition to MC, THF, $CHCl_3$ and MeCN were tested. Among these solvents the best result was obtained with THF (entry 9). The influence of temperature on the cyanosilylation of benzaldehyde was also examined (entries 2, 12, 13, 14 and 15). The best result was obtained at 0 °C. Therefore entry 12 of Table 1 is considered as the optimal conditions for the cyanosilylation reactions.

Mn(salen) catalyzed cyanosilylations were explored for a variety of aldehydes utilizing the conditions of entry 12 of Table 1. Table 2 summarizes the results obtained under the optimized conditions. The aromatic aldehydes are converted into the corresponding cyanohydrin trimethylsilylether in excellent isolated yields with moderate to good ee at 0 °C. The experimental results indicated that *para* substitutents on aromatic ring (entries 2, 4, 5, 6, 7 and 9) did not reveal any consistent electronic effects. Electron-donating *p-tert*-butyl (entry 5) and electron-withdrawing *p*-nitro groups (entry 7) exhibited excellent yields (93 and 95% respectively) with similar moderate ee (45 and 43% respectively). We also compared the influence *o*-, *p*-, and *m*-chlorosubstituted benzaldehyde on the cyanosilylation reaction (entry 8, 9 and 10). The reaction of *o*-chlorobenzaldehyde was completed for 40 h with a yield of 92% and a reduced ee of 30%. *m*-Chlorobenzaldehyde took a much longer time to complete the reaction with reduced yield (83%) but increased ee (52%). *p*-Chlorobenzaldehyde took a reaction time of 45 h with a

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yield of 89% and a reduced ee of 20%. *m*-Chlorobenzaldehyde achieved the highest ee despite the longest reaction time of the three chlorobenzaldehydes. *p*-Methyl group produced higher ee (56%) compared with *m*-methyl group (11%) (entries 2 and 3). The electron-donating methyl group appeared to reduce the ee (compare ee of entries 1–3). 2-Naphthaldehyde took 45 h to complete the reaction with a yield of 80% and ee of 67% (entry 11). This is the best ee obtained among all the entries. Cinnamaldehyde was predominantly converted into 1,2 adducts with a yield of 88% and ee of 44%, leaving the olefinic function intact (entry 13).

The mechanism of the cyanosilylation reaction by Mn(salen) is proposed as follows. A double activation process occurs through the catalysis of both the chiral Lewis acid and achiral Lewis base. The Mn atom of chiral Mn(salen) complex is used to activate carbonyl oxygen for the formation of the Si–O bond. Ph_3PO acts as a N≡C group to be transferred to the carbon atom of the carbonyl. The chirality of the Mn(salen) controls the direction of approach of both groups to give the more S form of cyanohydrin trimethyl ether. The following results support the proposed mechanism. There was no reaction in the absence of Mn(salen) (Table 1, entry 16) and the reaction was less productive without Ph_3PO (Table 1, entry 7). In the presence of 10 mol% Ph_3PO, the reaction gave about 90% yield and 25% ee whereas without Ph_3PO the reaction gave only 65% yield within the same time. Direct evidence for the coordination between Ph_3PO and TMSCN was obtained from ^1H NMR (200 MHz, $CDCl_3$) studies. The chemical shift of free TMSCN was located at $\delta = 0.354$. However, in the presence of Ph_3PO a new signal appeared at $\delta = 0.067$ as a result of condensed electron density around the silicon atom caused by the coordination of TMSCN to Ph_3PO. This coordination was also supported by the ^{13}C spectra of TMSCN and Ph_3PO. There was a new peak observed at $\delta = 1.38$ besides the chemical shift of TMSCN at $\delta = 1.985$. These results indicate that Ph_3PO acts as a base for the activation of TMSCN. Therefore the cyanosilylation of aldehdyes by Mn(salen) occurs through a double activation process in which Mn(salen) acts as Lewis acid and Ph_3PO acts as a Lewis base.

CONCLUSION

A double activation catalysis by **1**/Ph_3PO has been developed for the enantioselective cyanosilylation of various aldehydes. Under optimized conditions, most aromatic aldehydes are converted into the corresponding cyanohydrin trimethylsilylethers in 80–95% yields and in 11–67% ee. Overall the cyanosilylation reaction takes place under comparatively mild reaction conditions in terms of temperature and low catalyst loading.

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