Niobium Fluoride (NbF_5): A Highly Efficient Catalyst for Solvent-Free Cyanosilylation of Aldehydes

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Abstract: An efficient method for the addition of trimethylsilylcyanide (TMSCN) to aldehydes using dispersed NbF_5 as the catalyst is described. Cyano transfer from TMSCN to aldehydes occurs within 10 minutes at room temperature in the presence of 0.5 mol% of NbF_5 under solvent-free conditions giving cyanohydrins in excellent yields of over 95%. These conditions are extremely mild, simple and tolerate various functional groups.

Key words: aldehydes, catalysis, green chemistry, cyanohydrins, solvent-free

The catalytic addition reaction of trimethylsilylcyanide to carbonyl compounds is an area of great interest due to the synthetic versatility of cyanohydrins. These can be elaborated into a variety of useful synthetic building blocks such as α-hydroxy acids, α-hydroxy aldehydes, 1,2-diols, and α-amino alcohols.[2] A variety of catalysts can be used[3,4] including Lewis acids, Lewis bases, metal alkoxides, bifunctional catalysts and inorganic salts. Many metal complexes have been employed as Lewis acids for the addition of hydrogen cyanide (HCN) or TMSCN to aldehydes and ketones including magnesium, zirconium, titanium, aluminium, yttrium, lanthanum, samarium, vanadium and gadolinium complexes containing mono- or polydentate ligands.[5] Metal halides, such as $AlCl_3$, $BiBr_3$, InX_3, $LnCl_3$ (where Ln = La, Ce, Sm), $MgBr_2$, $SnCl_4$, $TiCl_4$, and ZnI_2 are known to be Lewis acidic catalysts used in the cyanosilylation of aldehydes.[6] Lithium chloride acts as an active and simple catalyst in the cyanosilylation of aldehydes and ketones.[7]

$P(RNCH_2CH_2)N$, a non-ionic strong base has been used as a catalyst in the cyanosilylation of aldehydes and ketones.[8] Tetramethylguanidine was successfully employed as an effective catalyst in the cyanosilylation of ketones.[9] Very recently, *N*-heterocyclic carbenes (NHC) were reported in the activation of TMSCN.[10,11] In recent years, several optically active catalysts used in the asymmetric synthesis of cyanohydrins have been reported in the literature.[12] Recently we have reported the cyanosilylation of aldehydes and ketones utilizing several chiral[13] and achiral[14] catalysts.

The heterogenization of inorganic reagents and catalysts in organic reactions is a very important area in 'green' or 'sustainable chemistry'.[15] One of the major goals is to facilitate easy separation of the final reaction mixture. This feature can lead to improved processing steps, better process economics and also environmentally friendly industrial manufacturing.

Numerous reactions have been carried out in solvents including dichloromethane, acetonitrile and tetrahydrofuran. However, due to the current challenges in developing solvent-free and environmentally-benign synthetic systems, we would like to report a novel method for the cyanation of aldehydes using TMSCN in the presence of dispersed NbF_5 under solvent-free conditions.

Niobium(V) has strong oxophilicity and can promote Lewis acid mediated reactions such as the Diels–Alder reaction, allylation of aldehydes and others.[16] We have used these properties of NbF_5 in the silylcyanation of aldehydes and the results are described here.

The catalytic activity of NbF_5 was tested using benzaldehyde as a model substrate. NbF_5 exhibited excellent activity under solvent-free conditions. When a mixture of benzaldehyde (1 mmol) and TMSCN (1.2 equiv) was treated with various amounts of NbF_5 (0.1–10 mol%) at room temperature, the cyanide addition occurred in relatively short reaction times (Table 1, entries 1–5). The amount of catalyst appeared to be an important parameter in the reduction of reaction time. The reaction took place more rapidly with larger quantities of catalyst (Table 1, entry 1 and 2). Using 0.5 mol% of NbF_5 proved to be the optimal amount and gave excellent yields (96%) at room temperature under solvent-free conditions (Table 1, entry 4). A further reduction in catalytic loading meant that longer reaction times were needed. However, the NbF_5-cataylzed system is still an excellent method in terms of reaction time as an effective reaction can take place using only 0.1 mol% of catalyst in 25 minutes and 93% yield. Other recently reported cyanosilylation reactions under solvent-free conditions took four hours and gave a 99% yield.[9] The catalytic efficiency decreased when the reaction was conducted in organic solvents (Table 1, entries 6–8).

These results clearly indicate that low catalyst loading and solvent-free conditions are optimal in the activation of TMSCN with NbF_5. 20 mol% of $BiCl_3$,[3m] 5 mol% of $Cu(OTf)_2$[3d] or 20 mol% of *N*-methylmorpholine *N*-oxide (NMO)[14c] was required in the presence of organic solvents to promote complete conversion of benzaldehyde to the corresponding trimethylsilylated cyanohydrin.

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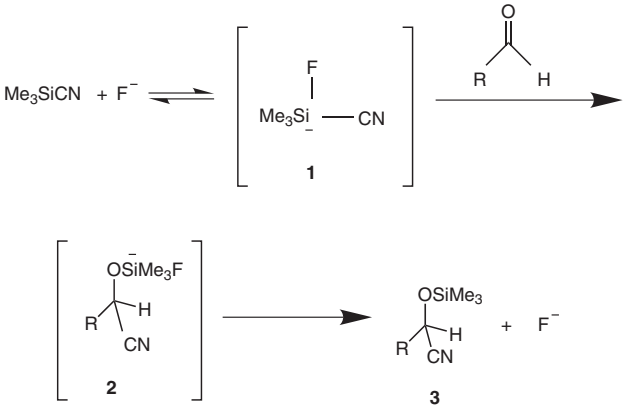
Table 1 Cyanosilylation of Benzaldehyde under Various Conditions

Entry	Catalyst (mol%)	Solvent	Time (min)	Yield (%)
1	10	–	5	98
2	5	–	5	98
3	1	–	10	96
4	0.5	–	10	96
5	0.1	–	25	93
6	0.5	CH_2Cl_2[a]	20	95
7	0.5	THF[a]	45	87
8	0.5	$CHCl_3$[a]	90	80

[a] 1 mmol of benzaldehyde was used in these studies.

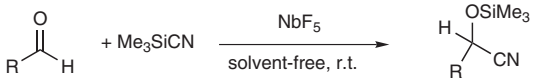
The scope of the NbF_5 method was examined using a number of representative aldehydes with 0.5 mol% catalyst loading (Table 2). Aromatic, aliphatic, cyclic and heterocyclic aldehydes underwent NbF_5-catalyzed cyanosilylation in excellent yields. Unsubstituted and substituted benzaldehydes (Table 2, entries 1–5) underwent very smooth silylcyanation in over 95% yield. Naphthaldehyde (Table 2, entry 6) gave the corresponding silylethers in excellent yield. As a comparison, methyltriphenyl phosphoniumiodide,[3g] $LiClO_4$,[3n] and NHC[11]-catalyzed cyanosilylation of naphthaldehyde required longer reaction times (30 min–24 h) as well as higher catalyst loading (1–100 mol%). The nature of the substituents on the aromatic ring seems to have no major effect on the reaction time and yields. The branched and cyclic aliphatic aldehydes (Table 2, entries 7–10) were converted into the corresponding cyanohydrin silylethers in excellent yield.

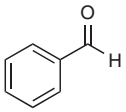
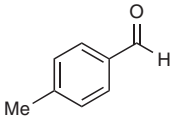
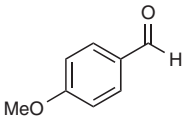
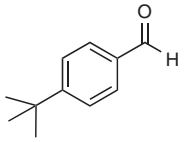
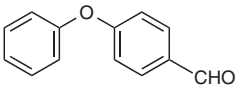
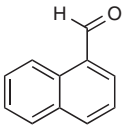
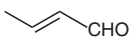
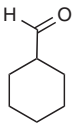
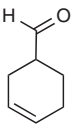
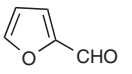
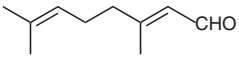


Scheme 1

Acid-sensitive aldehydes, such as 2-furfuraldehyde, react smoothly without any decomposition or polymerization under the reaction conditions (Table 2, entry 11). Further-

Table 2 Cyanosilylation of Aldehydes Using NbF_5[a]



Entries	Substrate	Time (min)	Yield (%)[b]
1		10	96[c]
		3 h	95[17]
		24 h	75[3g]
		3 h	81[3d]
		4 h	99[9]
		30	100[3n]
2		10	96
		12 h	80[3d]
3		10	95
		30	69[14]
		4 h	95[17]
		24	85[3g]
		1 h	94[7]
4		10	98
5		10	97
6		10	98
		30	94[14]
		24 h	86[3g]
7	$(Me)_2$-CH-CHO	10	97
		30	90[3n]
8		10	97
9		10	96
		2 h	90[7]
10		10	95
11		10	96
		24 h	97[3g]
		3 h	75[3d]
		6 h	88[18]
		45	94[3n]
12		10	96
		4.5 h	90[17]

[a] 0.5 mol% NbF_5 used.
[b] Isolated yield.
[c] Reproducibility is good.

more, it should be noted that the branched aliphatic aldehyde, citral, was transformed into the corresponding silylether in excellent yield (Table 2, entry 12).

NbF_5 is superior in the activation of TMSCN when compared with other recently reported achiral catalytic systems used in the silylcyanation of aldehydes. The present system has given excellent yields with comparatively short reaction times. It is also worthwhile to note that the addition reaction of TMSCN to aldehydes was achieved without any additive. As shown in Table 2, our catalytic system requires considerably less catalyst loading when compared to previous studies.[3d,g,n,9,7,14,17]

We have started to test the cyanosilylation of ketones using NbF_5. Using acetophenone as the substrate, the cyanosilylation reaction took 20 minutes and gave a 96% yield. The difference in structure between aldehydes and ketones appeared to lengthen the reaction time from 10 minutes (aldehydes) to 20 minutes (acetophenone). Further results for the cyanosilylation of ketones will be published later.

A possible mechanism for the reaction is as follows. The formation of hypervalent silicate **1** is formed from the addition of F^- ions to TMSCN. **1** then reacts with the aldehyde to generate complex **2** which upon fragmentation provides the corresponding silylether **3** and F^- ions (Scheme 1).

In summary, we have described the use of a readily available metal salt (NbF_5) that effectively promotes the cyanosilylation of aldehydes with low and dispersed catalytic loading under mild conditions. This NbF_5-catalyzed reaction may contribute to the development of green chemistry because of its solvent free-conditions. Furthermore, the procedure tolerates a wide variety of substrates. Efforts to extend NbF_5 catalysis to other organic transformations are ongoing. Further investigations to clarify the reaction mechanism and to recover and reuse the catalyst are in progress.

Cyanosilylation of Aldehydes; Typical Procedure

A mixture of benzaldehyde (2 mmol), dispersed NbF_5 (1 mol%) and TMSCN (2.4 equiv) was stirred for 10 min at r.t. in a 10 mL round bottom flask. Then 0.5 mL of CH_2Cl_2 was added and the mixture was stirred for less than 10 min. Purification by silica gel flash column chromatography (hexanes–EtOAc, 9:1) gave the desired 2-phenyl-2-(trimethylsilyloxy)acetonitrile as a colorless oil (96%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.25 (s, 9 H), 5.52 (s, 1 H), 7.42–7.47 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.33, 63.59, 119.12, 126.29, 128.87, 129.27, 136.18.

2-(4-Methylphenyl)-2-(trimethylsilyloxy)acetonitrile (Table 2, Entry 2)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.22 (s, 9 H), 2.35 (s, 3 H), 5.45 (s, 1 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 7.37 (d, *J* = 7.8 Hz 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.25, 55.78, 63.87, 114.66, 119.47, 127.88, 128.77, 160.23.

2-(4-Methoxyphenyl)-2-(trimethylsilyloxy)acetonitrile (Table 2, Entry 3)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.21 (s, 9 H), 3.82 (s, 3 H), 5.43 (s, 1 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 7.38 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.23, 55.34, 63.34, 114.25, 119.32, 127.93, 128.46, 160.33.

2-(4-*tert*-Butylphenyl)-2-(trimethylsilyloxy)acetonitrile (Table 2, Entry 4)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.24 (s, 9 H), 1.32 (s, 9 H), 5.46 (s, 1 H), 7.29–7.42 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.39, 31.10, 34.52, 63.32, 119.18, 125.73, 126.04, 133.19, 152.37.

2-(4-Phenoxyphenyl)-2-(trimethylsilyloxy)acetonitrile (Table 2, Entry 5)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.22 (s, 9 H), 5.46 (s, 1 H), 6.99–7.13 (m, 5 H), 7.31–7.44 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.26, 63.18, 117.50, 118.75, 119.48, 120.42, 124.04, 124.94, 28.02, 128.41, 129.92, 130.73, 131.98, 156.38, 158.84.

HRMS (EI): *m/z* calcd for $C_{17}H_{19}NO_2Si$: 297.1185; found: 297.1181.

2-(Naphthalen-1-yl)-2-(trimethylsilyloxy)acetonitrile (Table 2, Entry 6)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.23 (s, 9 H), 6.05 (s, 1 H), 7.45–7.70 (m, 3 H), 7.85–7.95 (m, 3 H), 8.23 (d, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.29, 63.4, 118.45, 122.37, 125.62, 125.01, 126.3, 128.3, 131.01, 133.45, 136.12.

3-Methyl-2-(trimethylsilyloxy)butanenitrile (Table 2, Entry 7)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.2 (s, 9 H), 0.88–1.05 (m, 6 H), 1.94–1.96 (m, 1 H), 4.16 (d, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.34, 17.68, 33.92, 67.28, 119.94.

2-(Trimethylsilyloxy)pent-3-enenitrile (Table 2, Entry 8)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.20 (s, 9 H), 1.79 (d, *J* = 2.4 Hz, 3 H), 4.90 (d, *J* = 8.4 Hz, 1 H), 5.51–5.62 (m, 1 H), 5.93–6.04 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.39, 17.16, 61.91, 118.55, 126.06, 130.98.

Cyclohexyl(trimethylsilyloxy)acetonitrile (Table 2, Entry 9)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.26 (s, 9 H), 1.18–1.29 (m, 5 H), 1.68–1.88 (m, 6 H), 4.15 (d, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.335, 25.47, 26.09, 28.15, 28.21, 42.98, 66.55, 119.39.

Cyclohex-3-enyl(trimethylsilyloxy)acetonitrile (Table 2, Entry 10)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.23 (s, 9 H), 1.60–2.12 (m, 7 H), 4.27 (m, 1 H), 5.70 (s, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.67, 23.72, 24.26, 26.48, 65.59, 119.07, 124.72, 126.75.

2-Furanyl(trimethylsilyloxy)acetonitrile (Table 2, Entry 11)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.22 (s, 9 H), 5.55 (s, 1 H), 6.41–6.43 (m, 1 H), 6.55–6.57 (m, 1 H), 7.28–7.48 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.43, 57.41, 109.70, 110.78, 117.11, 143.84, 148.20.

HRMS (EI): *m/z* calcd for $C_9H_{13}NO_2Si$: 195.0715; found: 195.0712.

4,8-Dimethyl-2-(trimethylsilyloxy)nona-3,7-dienenitrile (Table 2, Entry 12)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.22 (s, 9 H), 1.62 (s, 3 H), 1.70–1.80 (m, 6 H), 2.10–2.12 (m, 4 H), 5.09–5.13 (m, 2 H), 5.31–5.33 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.12, 16.76, 17.65, 23.18, 25.83, 39.13, 58.42, 119.50, 120.59, 123.14, 133.04, 142.82.

HRMS (EI): *m/z* calcd for $C_{14}H_{25}NOSi$: 251.1705; found: 251.1713.

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