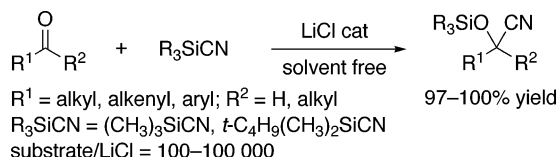# Lithium Chloride: An Active and Simple Catalyst for Cyanosilylation of Aldehydes and Ketones

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R[1] = alkyl, alkenyl, aryl; R[2] = H, alkyl
R$_3$SiCN = (CH$_3$)$_3$SiCN, *t*-C$_4$H$_9$(CH$_3$)$_2$SiCN
substrate/LiCl = 100–100 000

97–100% yield

LiCl acts as a highly effective catalyst for cyanosilylation of various aldehydes and ketones to the corresponding silylated cyanohydrins. The reaction proceeds smoothly with a substrate/catalyst molar ratio of 100–100 000 at 20–25 °C under solvent-free conditions. α,β-Unsaturated aldehydes are completely converted to the 1,2-adducts. The cyanation products can be isolated by direct distillation of the reaction mixture.

Cyanosilylation of carbonyl compounds is an efficient procedure for the synthesis of silylated cyanohydrins, which are readily converted to useful functionalized compounds, such as α-hydroxy carbonyl compounds and β-amino alcohols.[1,2] Liquid (CH$_3$)$_3$SiCN (bp 118 °C) reacts with aldehydes in the presence of a catalytic amount of Lewis acids[3,4] or nucleophilic compounds[5,6] to afford the desired adducts. Recently reported chiral Lewis acid–Lewis base combined catalysts have been successfully applied to the asymmetric reaction.[7]

Metal halides, such as AlCl$_3$,[3b,5a] BiBr$_3$,[3l] BF$_3$,[3f] InX$_3$ (X = Br,[3o] F[3m]), LnCl$_3$ (Ln = La, Ce, Sm),[3e] MgBr$_2$,[3f] SnCl$_4$,[3f] R$_2$SnCl$_2$ (R = *n*-C$_4$H$_9$, C$_6$H$_5$),[3j] TiCl$_4$,[3f] and ZnI$_2$,[3a] are known to be Lewis acidic catalysts for cyanosilylation of aldehydes. However, no report has described the catalytic properties of LiCl, one of the simplest metal halides, for this reaction.[8] We here report an efficient and facile procedure for cyanosilylation of aldehydes and some ketones catalyzed by LiCl with a substrate-to-catalyst molar ratio (S/C) as high as 100 000 under solvent-free conditions. A series of silylated cyanohydrins can be isolated by direct distillation.

First, the catalytic activity of simple alkaline salts was tested in the reaction of benzaldehyde (**1a**) and (CH$_3$)$_3$-SiCN in a 1:1 ratio at 20–25 °C. As shown in Table 1, LiCl exhibited excellent catalytic activity under solvent-free conditions. The reaction with an S/C of 10 000 [**1a** (72.7 g, 678 mmol), (CH$_3$)$_3$SiCN (68.0 g, 685 mmol), LiCl (2.5 mg, 59 µmol)] was completed within 1 h, affording the cyanation product **2a** in 100% yield (entry 2). A THF solution of LiCl could be used for this reaction [**1a** (1.07 g, 10.1 mmol), (CH$_3$)$_3$SiCN (1.02 g, 10.3 mmol), LiCl (29.5 mM in THF, 34 µL, 1.0 µmol)] without loss of catalytic activity (entry 3). Turnover frequency (TOF), defined as moles of product per mole of catalyst per hour, reached

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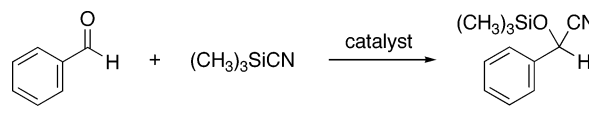
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TABLE 1. Cyanosilylation of Benzaldehyde (1a)[a]

entry	catalyst	method[b]	S/C[c]	solvent[d]	yield (%)[e]
1	LiCl	A	50000	neat	56
2	LiCl	B	10000[f]	neat	100
3	LiCl	A	10000	neat	100
4	LiCl	A	50000	CH$_2$Cl$_2$[g]	<0.3
5	LiCl	A	50000	THF[g]	7
6	LiCl	A	10000	toluene[g]	7
7	NaCl	B	20	neat	1
8	KCl	B	20	neat	0.3
9	CsCl	B	20	neat	22
10	LiF	A	10000	neat	<0.3
11	LiBr	A	10000	neat	86
12	LiI	A	10000	neat	98
13	LiClO$_4$	A	10000	neat	2.5
14[h]	–	–	–	neat	<0.3

[a] Unless otherwise stated, reactions were conducted using 10 mmol of **1a** and 1 equiv of (CH$_3$)$_3$SiCN in the presence of catalyst at 20−25 °C for 1 h. [b] A: Catalyst was added as a 29.5 mM solution of THF. B: Catalyst was added as a solid. [c] Substrate/catalyst molar ratio. [d] Neat: Reaction was conducted under solvent-free conditions. [e] Determined by GC or ^{1}H NMR analysis. [f] Reaction using 72.7 g (678 mmol) of **1a**. [g] [**1a**] = 1.0 M. [h] Reaction without catalyst.
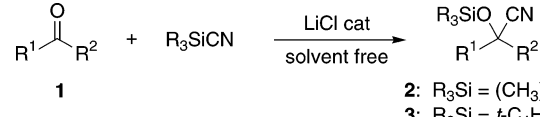
28 000 at an S/C of 50 000 (entry 1). Thus, LiCl is one of the most active metal halide catalysts so far reported.[3] The catalytic efficiency was decreased when the reaction was conducted in organic solvents ([**1a**] = 1.0 M), such as CH$_2$Cl$_2$, THF, and toluene (entries 4−6). Insoluble NaCl and KCl are totally ineffective for this reaction (entries 7 and 8).[9,10] The TOF of the reaction with CsCl was only 4 (entry 9). The activities of LiBr and LiI were comparable to that of LiCl (entries 11 and 12), while LiF gave no adduct under the same conditions (entry 10). The reaction in the presence of LiClO$_4$ with an S/C of 10 000, which is known as a promoter of cyanosilylation of aldehydes and ketones, resulted in only 2.5% conversion (entry 13).[11] These results clearly indicate that the combination of a lithium cation and a halide anion, Cl$^-$, Br$^-$, or I$^-$, is crucial for obtaining high catalytic activity.

A series of carbonyl compounds **1** reacted with cyanotrialkylsilanes in the presence of LiCl under solvent-free conditions at room temperature to give the cyanation products, **2** and **3**, in excellent yield as shown in Table 2. The obtained products were isolated at >98% purity (^{1}H NMR analysis) by direct distillation of the reaction mixture. No extraction or chromatogram separation was necessary (see Experimental Section). The LiCl catalyzed the reaction of **1a** and (CH$_3$)$_3$SiCN with an S/C of 100 000, affording **2a** in 99% yield after 48 h. The sterically hindered t-C$_4$H$_9$(CH$_3$)$_2$SiCN can be used as a cyanation reagent. Reaction of ortho- or para-substituted benzaldehydes by electron-attracting Cl or CF$_3$, **1c, d**, and **f**, and (CH$_3$)$_3$SiCN in a 1:1 ratio with LiCl (S/C = 10 000) was completed within 40 min.

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TABLE 2. Cyanosilylation of Aldehydes and Ketones[a]

2: R$_3$Si = (CH$_3$)$_3$Si
3: R$_3$Si = t-C$_4$H$_9$(CH$_3$)$_2$Si

a: R^1 = C$_6$H$_5$; R^2 = H
b: R^1 = 4-CH$_3$C$_6$H$_4$; R^2 = H
c: R^1 = 2-ClC$_6$H$_4$; R^2 = H
d: R^1 = 4-ClC$_6$H$_4$; R^2 = H
e: R^1 = 4-CH$_3$OC$_6$H$_4$; R^2 = H
f: R^1 = 4-CF$_3$C$_6$H$_4$; R^2 = H
g: R^1 = 2-naphthyl; R^2 = H
h: R^1 = (E)-C$_6$H$_5$CH=CH; R^2 = H
i: R^1 = (E)-n-C$_5$H$_{11}$CH=CH; R^2 = H
j: R^1 = n-C$_7$H$_{15}$; R^2 = H
k: R^1 = cyclo-C$_6$H$_{10}$; R^2 = H
l: R^1 = t-C$_4$H$_9$; R^2 = H
m: R^1 = C$_6$H$_5$; R^2 = CH$_3$
n: R^1 = n-C$_4$H$_9$; R^2 = n-C$_4$H$_9$

1	R$_3$Si	S/C[b]	time (h)	yield of 2 or 3 (%)[c]
1a[d]	(CH$_3$)$_3$Si	10000	1	100 (94)
1a[e]	(CH$_3$)$_3$Si	100000	48	99 (f)
1a	t-C$_4$H$_9$(CH$_3$)$_2$Si	10000	5	100 (96)
1b	(CH$_3$)$_3$Si[g]	5000	5	100 (98)
1c	(CH$_3$)$_3$Si	10000	0.5	100 (93)
1c	t-C$_4$H$_9$(CH$_3$)$_2$Si	10000	1	100 (93)
1d	(CH$_3$)$_3$Si	10000	0.6	100 (97)
1e	(CH$_3$)$_3$Si[g]	5000	6	100 (97)
1f	(CH$_3$)$_3$Si	10000	0.5	100 (98)
1g	(CH$_3$)$_3$Si	10000	0.4	100 (96)
1h	(CH$_3$)$_3$Si	10000	3	97 (88)[h]
1h	t-C$_4$H$_9$(CH$_3$)$_2$Si	10000	8	100 (93)[h]
1i	(CH$_3$)$_3$Si	10000	22	99 (98)[h]
1j	(CH$_3$)$_3$Si	10000	0.5	100 (95)
1k	(CH$_3$)$_3$Si	10000	0.5	100 (94)
1l	(CH$_3$)$_3$Si	10000	0.2	100 (98)
1l	t-C$_4$H$_9$(CH$_3$)$_2$Si	10000	2	100 (90)
1m[i]	(CH$_3$)$_3$Si[g]	1000	6	81 (f)
1m[i]	(CH$_3$)$_3$Si[g]	100	3	100 (96)
1n[i]	(CH$_3$)$_3$Si[g]	1000	6	80 (f)
1n[i]	(CH$_3$)$_3$Si[g]	100	2.5	100 (94)

[a] Unless otherwise stated, reactions were conducted using 10 mmol of **1** and one equiv of R$_3$SiCN in the presence of LiCl added as a THF solution (24−60 mM), at 20−25 °C under solvent-free conditions. [b] Substrate/catalyst molar ratio. [c] Determined by GC or ^{1}H NMR analysis. The isolated yield is indicated in parentheses. [d] Reaction using 10.8 g (101 mmol) of **1a** with LiCl added as a 0.31 M THF solution. [e] Reaction using 5.3 g (50 mmol) of **1a**. [f] Not isolated. [g] 1.3 equiv of (CH$_3$)$_3$SiCN was used. [h] No conjugated addition product was observed by ^{1}H NMR analysis. [i] Use of 5 mmol of **1** with LiCl added as a THF solution (0.20−0.22 M).

4-Methyl and 4-methoxybenzaldehydes, **1b** and **e**, were less reactive than the simple benzaldehyde **1a**. The reactions in the presence of a 1.3 equiv of (CH$_3$)$_3$SiCN with an S/C of 5000 were completed in 6 h. The cyanation of 2-naphthalenecarbaldehyde (**1g**) with an S/C of 10 000 was completed in 25 min. Cinnamaldehyde (**1h**) and 2-octenal (**1i**) were predominantly converted to the 1,2-adducts, **2h, i**, and **3h**, leaving the olefinic function intact.[2] No conjugated addition product was observed. Even higher efficiency was achieved in the cyanation of aliphatic aldehydes. Reaction of n-octanal (**1j**) and (CH$_3$)$_3$-SiCN with LiCl (S/C = 10 000) was completed in 30 min. Cyclohexanecarbaldehyde (**1k**) reacted in the same way. Notably, sterically congested pivalaldehyde (**1l**) was completely converted to the cyanation product **2l** in only 10 min (TOF = 60 000 h^{-1}). The reaction with t-C$_4$H$_9$-(CH$_3$)$_2$SiCN was completed in 2 h. LiCl was also effective for cyanosilylation of less reactive ketones. A turnover number of 810 in 6 h was achieved in the reaction of acetophenone (**1m**), an aromatic ketone, with an S/C of 1000 (Table 2). When the reaction was conducted with
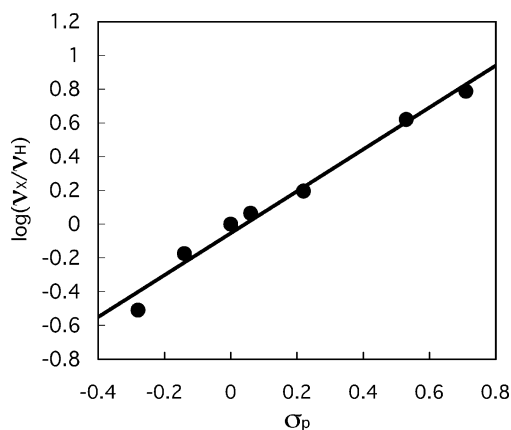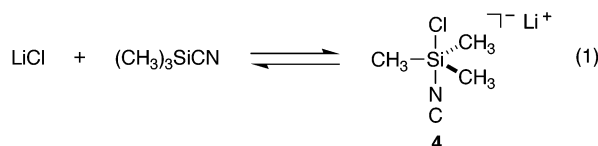
FIGURE 1. Hammett plots for cyanosilylation of *p*-substituted benzaldehydes catalyzed by LiCl.

an S/C of 100, the desired cyanation product **2m** was obtained in 100% yield. Reaction of 5-nonanone (**1n**), an aliphatic ketone, afforded the adduct **2n** in the same way.

The electronic effect of para substituents of benzaldehydes on the rate of the LiCl-catalyzed cyanosilylation was examined by competition experiments using an equimolar mixture of **1a** and a series of para-substituted aldehydes. The initial rates of reaction of the substituted benzaldehyde (v_X) and the parent aldehyde (v_H) were calculated from three or four experiment sets. When the relative rates were plotted against the σ_P constant,[12] a linear relationship with a ρ value of +1.24 was obtained as shown in Figure 1. This result clearly indicates the nucleophilic property of the reactive species.

LiCl is a soluble inorganic salt in several organic polar compounds and acts as a source of nucleophilic Cl⁻.[13] When LiCl behaves as a nucleophilic catalyst,[5,6] Li[(CH₃)₃-SiCl(NC)] (**4**), a pentavalent silicon compound, is a probable reactive species (eq 1).[14] A ¹³C NMR experiment

$$\text{LiCl} \quad + \quad (CH_3)_3SiCN \quad \rightleftharpoons \quad \begin{bmatrix} CH_3 - \underset{\underset{C}{\overset{|}{N}}}{\overset{Cl}{\underset{|}{Si}}} \cdots^{CH_3}_{CH_3} \end{bmatrix}^- Li^+ \quad (1)$$

4

supported this hypothesis (see the Supporting Information). A 1:1 mixture of LiCl and (CH₃)₃SiCN in THF-d_8 solution at 25 °C indicated a new methyl signal at δ 1.93

with decrement of the original signal of (CH₃)₃SiCN at δ −2.07. No peak of (CH₃)₃SiCl at δ 3.02 was observed. This result was consistent with the measurement of a mixture of 18-crown-6, KCN, and (CH₃)₃SiCN, indicating a methyl signal at δ 1.91. The 18-crown-6/KCN combination is known as the representative nucleophilic catalyst for cyanosilylation of carbonyl compounds[5a] and epoxides,[14b] and the pentavalent [(CH₃)₃Si(NC)₂]⁻ was proposed to be the reactive species based on the spectroscopic and theoretical studies.[14]

In conclusion, LiCl is an active, inexpensive, and simple catalyst for cyanosilylation of aldehydes and ketones. The reaction can be conducted with an S/C as high as 100 000 under solvent-free conditions. A series of synthetically useful silylated cyanohydrins are obtainable by direct distillation of the reaction mixture.

Experimental Section

Experimental Procedure for Reaction of Benzaldehyde (1a) and (CH₃)₃SiCN (S/C = 10 000). LiCl (130.3 mg, 3.07 mmol) and THF (10 mL) were placed in a 15-mL two-necked flask, and the mixture was sonicated for 10 min and used as a catalyst stock solution. Aldehyde **1a** (10.76 g, 101.4 mmol) and (CH₃)₃SiCN (11.40 g, 114.9 mmol) were placed in a 50-mL two-necked flask, and the mixture was stirred at 20 °C under Ar. The catalyst solution (33 μL, 10.1 μmol) was added to the mixture, and the reaction proceeded exothermically. After stirring for 1 h, the reaction mixture was distilled to give 2-phenyl-2-trimethylsilyloxyacetonitrile (**2a**) (19.55 g, 94%), bp 92−94 °C/2.0 mmHg. The yield determined by GC was 100%. *Caution: (CH₃)₃SiCN must be used in a well-ventilated hood due to its high toxicity.*

Supporting Information Available: Procedures of cyanosilylation of aldehydes and ketones, GC and NMR behavior of products and LiCl with (CH₃)₃SiCN, and kinetic experiments for the Hammett plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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