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Highly efficient trialkylsilylcyanation of aldehydes, ketones and imines catalyzed by a nucleophilic *N*-heterocyclic carbene

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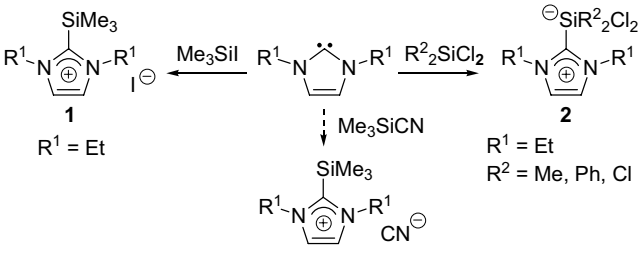
Abstract—The synthetic utility of *N*-heterocyclic carbenes was demonstrated by the trialkylsilylcyanation of aldehydes, ketones and imines. In the presence of a catalytic amount of **3a**, the reactions with Me_3SiCN proceeded smoothly to give the corresponding cyanohydrin trimethylsilyl ethers or amino nitrile derivatives in good to excellent yields.

In the past few years, nucleophilic *N*-heterocyclic carbenes have been utilized not only as a ligand for metal salts,[1] but also as an organocatalyst[2] for the benzoin condensation,[3] Stetter reaction[4] and the transesterification between esters and alcohols.[5,6] Recently, in our and other laboratories, the chiral carbene catalysts generated from the corresponding imidazolium salts were also independently found to effectively catalyze the enantioselective acylation of secondary alcohols to give the highly enantiomerically enriched alcohols.[7] To date, however, the applicability of *N*-heterocyclic carbenes as a nucleophilic organocatalyst for other transformation reactions has not been fully investigated.[8] For example, *N*-heterocyclic carbenes were already reported to react with trimethylsilyl iodide or polychlorosilanes to afford the corresponding ionic 2-(trimethylsilyl)imidazolium salt **1** or pentavalent silicon species **2**, respectively (Scheme 1).[9] To the best of our knowledge, however, these types of silicon–carbene complexes have rarely been utilized in organic transformations.[10] Accordingly, we are interested in the possibility of activating Me_3SiCN by complexation with nucleophilic *N*-heterocyclic carbenes as a Lewis base. Very recently, Song reported the study of trimethylsilylcyanation of aldehydes and ketones catalyzed by nucleophilic *N*-heterocyclic carbenes,[11] and this report prompted us to disclose our own result on the synthetic utility of carbenes. In this letter, we describe a new application of the *N*-heterocyclic carbene as a highly efficient Lewis base catalyst



Scheme 1.

for the trimethylsilylcyanation of aldehydes, ketones and imines.[12–14] One of the most characteristic features of this catalyst system is the ability to provide sterically congested cyanohydrin trimethylsilyl ethers with relatively low catalyst loadings. The resulting products can be readily converted into a variety of important synthetic intermediates, including α-hydroxy acids,[15] β-amino alcohols,[16] α-amino acids[17] and 1,2-diamines.[18]

The requisite carbene catalysts **3** were generated in situ by the treatment of the corresponding imidazolium salts with potassium *tert*-butoxide in THF at room temperature.[19,20] Thus, in the presence of 10 mol % of *N*-heterocyclic carbene **3a**, acetophenone was treated with 2 equiv of Me_3SiCN in THF at 0 °C for 1 h, and the desired cyanohydrin trimethylsilyl ether was obtained in an excellent yield (Table 1, entry 1).[21] Interestingly, the combination of commercially available thiazolium salt **4** with triethylamine, which would generate an *N*,*S*-heterocyclic carbene,[22] exhibited a very low catalytic activity (entry 2). *N*-Heterocyclic carbene **3** as a

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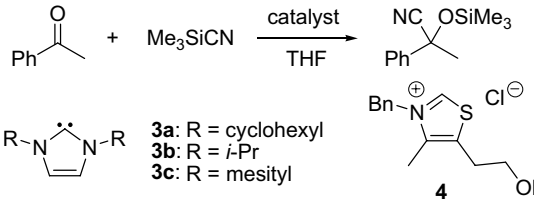
Table 1. Lewis base-catalyzed trimethylsilylcyanation of acetophenone[a]



Entry	Catalyst	(mol %)	Conditions (°C, h)	Yield[b] (%)
1	**3a**	10	0, 1	97
2[c]	**4**/Et_3N	10	rt, 24	15
3	$KOBu^t$	10	rt, 24	26
4	PBu_3	10	rt, 24	0
5	DABCO	10	rt, 24	5
6	DMAP	10	rt, 24	0
7	DBU	10	0, 1.5	90
8[d]	DBU	1	0, 1	12
9[d]	**3a**	1	0, 0.5	99
10[d]	**3b**	1	0, 0.5	95
11[d]	**3c**	1	0, 0.5	97

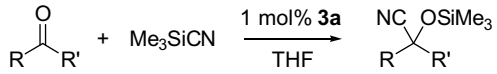
[a] Unless otherwise specified, acetophenone (0.2 mmol) was treated with 2 equiv of Me_3SiCN in the presence of a catalyst in 2 mL of THF under the given reaction conditions under an argon atmosphere.
[b] Isolated yield.
[c] Catalyst was generated by treatment of **4** with 10 equiv of triethylamine.
[d] Reaction performed with acetophenone (1.0 mmol) and 1.2 equiv of Me_3SiCN in 5 mL of THF.

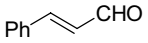
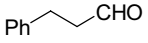
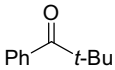
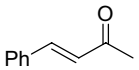
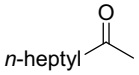
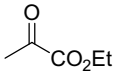
nucleophilic organocatalyst was then evaluated by comparison with other Lewis base catalysts in the trimethylsilylcyanation of acetophenone. The reaction with 10 mol % of $KOBu^t$ at room temperature for 24 h afforded the addition product in 26% yield (entry 3). The use of tributylphosphine, DABCO or DMAP gave poor results (entries 4–6); in contrast, the reaction using DBU gave a high yield of the product (entry 7). While the use of a catalyst level as low as 1 mol % of DBU resulted in a significant decrease in yield (entry 8), 1 mol % of *N*-heterocyclic carbene **3a** was enough to achieve an excellent yield (entry 9). Additionally, other *N*-heterocyclic carbenes **3b** and **3c** were also found to show similar catalytic activity (entries 10 and 11).

With these initial results in hand, we next investigated the efficiency of *N*-heterocyclic carbene **3a** in the reactions of various aldehydes and ketones, and the results are summarized in Table 2. Aromatic, olefinic and aliphatic aldehydes as well as ketones were found to be suitable substrates. In general, trimethylsilylcyanation of the carbonyl compounds proceeded to give the corresponding cyanohydrin trimethylsilyl ether in good to excellent isolated yields. It should be noted that only the 1,2-addition products were observed with the α,β-unsaturated aldehyde and ketone (entries 2 and 6). The present method was also applicable to the sterically congested ketones[23] (entries 5 and 9) and an enolizable ketone, such as ethyl pyruvate (entry 10).

The present reaction system is also applicable to a more sterically demanding trialkylsilyl cyanide.[24] Indeed, in

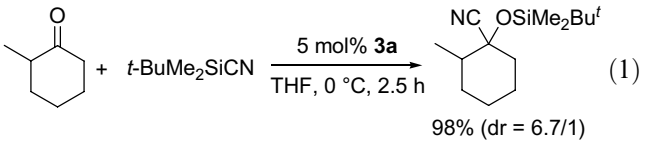
Table 2. Trimethylsilylcyanation of various aldehydes and ketones catalyzed by carbene **3a**[a]

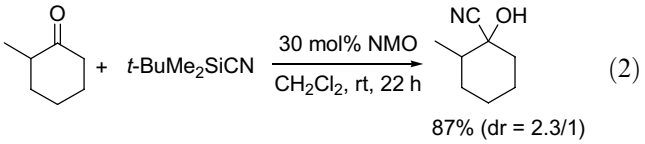


Entry	Substrate	Conditions (°C, h)	Yield[b] (%)
1	PhCHO	0, 0.5	89[c]
2		0, 0.5	99[c]
3		0, 0.5	99[c]
4		0, 0.5	99
5		0, 1	87
6		0, 1; rt, 1	93
7		0, 1	90
8		0, 2; rt, 2	99
9		0, 0.5	99
10		0, 1	89

[a] An aldehyde or a ketone (1 mmol) was treated with 1.2 equiv of Me_3SiCN in the presence of carbene **3a** in 5 mL of THF under the given reaction conditions under an argon atmosphere.
[b] Isolated yield.
[c] Isolated yield of the cyanohydrin after hydrolysis with 2 N HCl.

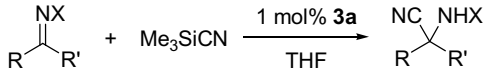
the presence of 5 mol % of **3a**, the reaction of 2-methylcyclohexanone with *t*-$BuMe_2SiCN$ proceeded smoothly to give the sterically congested cyanohydrin *t*-butyldimethylsilyl ether in excellent yield (Eq. 1). In sharp contrast, the reaction using 30 mol % of *N*-methylmorpholine-*N*-oxide (NMO) as a catalyst under the reported conditions provided the cyanohydrin exclusively (Eq. 2).[12i]

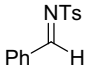
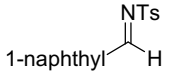
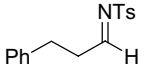
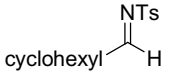
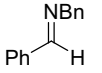
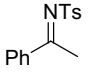
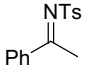
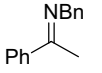
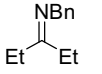




N-Heterocyclic carbene **3a** also proved to be a reasonably effective catalyst for the cyanation of *N*-sulfonyl imines derived from various aldehydes (Table 3, entries

Table 3. Trimethylsilylcyanation of various imines catalyzed by carbene **3a**[a]



Entry	Substrate	Conditions (°C, h)	Yield[b] (%)
1		rt, 4	92
2		rt, 2	92
3		rt, 3.5	83
4		rt, 5	82
5		rt, 6	25
6		rt, 12	2
7[c]		rt, 1.5	49
8		rt, 4	76
9		rt, 2	69

[a] An imine (1 mmol) was treated with 1.2 equiv of Me_3SiCN in the presence of carbene **3a** in 2–3 mL of THF under the given reaction conditions under an argon atmosphere.
[b] Isolated yield.
[c] Use of 10 mol % of **3a**.

1–4).[24–26] However, attempted cyanation of an *N*-benzyl imine from benzaldehyde resulted in the formation of the product in low yield (entry 5). Although the cyanation of an *N*-sulfonyl imine derived from acetophenone gave only trace amounts of the corresponding amino nitrile (entry 6), employment of **3a** at a high catalyst loading (10 mol %) afforded the product in moderate yield (entry 7). In comparison, the reaction of an *N*-benzyl ketimine of acetophenone provided the desired amino nitrile in 76% yield, even with 1 mol % of **3a** (entry 8). The present reaction was also applicable to an *N*-benzyl ketimine of aliphatic pentan-3-one (entry 9). These reactions proceeded under neutral and mild conditions without using Lewis acid or hazardous HCN, either of which is usually required in catalytic Strecker reaction, except for a few examples.[14] In this respect, our catalyst system would provide an alternative method for the synthesis of amino nitriles.

In conclusion, we have demonstrated that the *N*-heterocyclic carbene efficiently catalyzes the trialkylsilylcyanation of various aldehydes, ketones and imines with Me_3SiCN to give the corresponding addition products in good to excellent yields. Further investigations aimed at the elucidation of the precise mechanism and the scope of this reaction are currently underway.

Acknowledgments

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20. General procedure for the preparation of *N*-heterocyclic carbene catalyst: A solution of 1,3-dicyclohexylimidazolium tetrafluoroborate (3.2 mg, 0.01 mmol) in freshly distilled THF (5 mL) was carefully degassed with argon at −78 °C. To the solution was added a 1.0 M THF solution of potassium *tert*-butoxide (10 μL, 0.01 mmol) dropwise at room temperature. After being stirred for 0.5 h, the catalyst solution was used for the following reactions without further purification.
21. General procedure for the trimethysilylcyanation of ketones with trimethylsilyl cyanide by an *N*-heterocyclic carbene catalyst: To a solution of *N*-heterocyclic carbene catalyst (0.01 mmol) in 5 mL of THF was added a ketone (1 mmol) and trimethylsilyl cyanide (1.2 mmol) dropwise at 0 °C. The reaction mixture was stirred under the conditions as indicated in Table 2. The resulting mixture was then treated with aqueous saturated NH_4Cl and basified with aqueous saturated $NaHCO_3$. After ethereal extraction, the organic layer was dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (cooled by dry ice) (ethyl acetate/hexane = 1:50–1:10 as eluent) to give the corresponding cyanohydrin trimethylsilyl ether.
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23. 2,2-Dimethyl-1-(trimethylsilyloxy)cyclohexanecarbonitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.96–1.90 (1H, m, (TMSO)(CN)CCH_2), 1.83–1.76 (1H, m, (TMSO)(CN)-CCH_2), 1.71–1.65 (1H, m, –CH_2CH_2CH_2–), 1.61–1.39 (5H, m, –CH_2CH_2CH_2–), 1.11 (3H, s, CH_3), 0.96 (3H, s, CH_3), 0.23 (9H, s, (CH_3)$_3$SiO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.3, 76.7, 38.5, 35.5, 34.7, 25.4, 22.2, 20.6, 1.3; IR (neat) 2953, 2938, 1252, 1173, 1123, 1086, 978, 914, 889, 886, 843, 754 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{12}H_{23}NNaOSi$: 248.1441 ([M+Na]$^+$). Found: 248.1441 ([M+Na]$^+$).
24. None of these results were mentioned in the previous paper, see Ref. 11.
25. 2-Tosylamino-2-phenylacetonitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (2H, d, J = 8.4 Hz, SO_2Ar–H), 7.44–7.34 (7H, m, Ar–H), 5.46 (1H, d, J = 9.2 Hz, PhC*H*CN), 5.26 (1H, d, J = 9.2 Hz, TsN*H*), 2.45 (3H, s, SO_2Ph–CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 135.9, 132.0, 129.9, 129.8, 129.3, 127.2, 127.0, 116.2, 48.2, 21.8; IR (neat) 3292, 1331, 1157, 1088, 1070, 937, 903, 745, 669, 590 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{15}H_{14}N_2NaO_2S$: 309.0668 ([M+Na]$^+$). Found: 309.0667 ([M+Na]$^+$).
26. 2-Benzylamino-2-phenylpropanenitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (2H, d, J = 8.4 Hz, NHCH_2Ar–H), 7.43–7.24 (8H, m, Ar–H), 3.86 (1H, d, J = 12.6 Hz, NHCH_2Ph), 3.54 (1H, d, J = 12.6 Hz, NHCH_2Ph), 1.76 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 138.8, 128.7, 128.4, 128.3, 128.0, 127.2, 125.3, 121.1, 60.4, 49.5, 31.3; IR (neat) 1493, 1447, 1152, 1074, 1026, 762, 737, 696, 567 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{16}H_{17}N_2$: 237.1386 ([M+H]$^+$). Found: 237.1382 ([M+H]$^+$).