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Efficient and selective aldehyde cyanosilylation catalyzed by Mg-Li bimetallic complex

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ABSTRACT

A NCN-pincer ligand-based Mg-Li bimetallic complex $[\text{NCN-MgBr}_2][\text{Li(THF)}_4]$ **1** has been employed as an efficient catalyst for cyanosilylation of a wide range of aldehydes with trimethylsilyl cyanide (TMSCN) at room temperature in $CDCl_3$. In addition, catalyst **1** shows a good tolerance towards various functional groups such as amide, acid, ester, heterocyclic and alkene etc. The chemoselective cyanosilylation of aldehydes over ketones was also achieved under these conditions.

1. Introduction

The reductions of unsaturated organic compounds are the important transformations in organic chemistry. They generally involve the hydroamination, hydrophosphination, hydroboration and hydrosilylation of C=C, C=O or C=N etc unsaturated bonds [1–4]. The catalytic cyanosilylation reaction of carbonyl compounds was one of these high-value transformations [5]. Up to now, a number of catalyst have been employed for the cyanosilylation reaction of carbonyl compounds to obtain the cyanohydrins derivatives which can be further converted into α-hydroxy acids, α-amino acids, β-amino alcohols etc. The catalytic carbonyl cyanosilylation is usually achieved by the use of transition metal and lanthanide metal complexes [6,7]. Recently, the main group metal catalyzed cyanosilylation of carbonyl compounds has attracted increasing attention, particularly for aluminium, alkali and alkaline earth metal complexes [8]. For example, Sen group successively reported that an organocalcium iodide complex and three simple lithium compounds have been used as efficient catalysts for cyanosilylation reaction of a variety of aldehydes and ketones with TMSCN under ambient conditions without the need of any co-catalyst quite recently [9]. Meanwhile, our group also independently reported a low-valent magnesium(I)-catalyzed cyanosilylation reaction of a wide range of carbonyl compounds under mild conditions [10].

It was well known that tridentate ligands such as NCN-pincer ligands have been proved as an appropriate choice of ligands to accomplish a well-defined metal-ligand bonding in the catalytic system [11]. In contrast to the wide application in transition metal complexes, main group compounds supported by pincer ligands received less attention and relatively few examples of catalytic application have been reported [12]. In 2008, Cui and co-workers prepared the first aryldiimine NCN-pincer stabilized rare earth metal dichlorides which can be used as good co-catalysts for the highly *cis*-1,4 selective polymerization of dienes [13]. Recently, our group also reported a NCN-pincer ligand-based magnesiate complex $[\text{NCN-MgBr}_2][\text{Li(THF)}_4]$ **1** as an efficient and selective catalyst for hydroboration of carbonyl compounds [14].

To our surprise, few bimetal catalyzed cyanosilylation of carbonyl compounds has been reported hitherto. To the best of our knowledge, there is only one example of bimetal catalyzed cyanosilylation, that is, Nagendran et al. explored the catalytic cyanosilylation of carbonyl compounds using germylene stabilized platinum(II) dicyanide lately [6d]. The bimetallic complexes generally have a synergistic effect on catalysis. Based on the previously obtained positive results of bimetal complexes in the

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catalytic hydrosilylation and hydroboration of carbonyl compounds by our group [14,15], to expand the catalytic potential of the bimetal complex, we extend Mg-Li bimetallic complex **1** to the catalytic cyanosilylation of carbonyl compounds. Herein, we report a NCN-pincer ligand-based Mg-Li bimetallic complex (**1**) catalyzed cyanosilylation of a variety of aldehydes under mild conditions.

2. Results and discussion

Initially the catalytic cyanosilylation of benzaldehyde with TMSCN was investigated. Reaction of benzaldehyde (1.0 equiv.) and TMSCN (1.0 equiv.) with bimetallic catalyst **1** (2 mol % and 5 mol %) at room temperature for 15 min in $CDCl_3$ resulted in 73% and 87% yields, respectively (entries 1–2, Table 1). Increasing the reaction time to 30 min lead to a slightly high yield (77% and 91%) (entries 3–4, Table 1). When TMSCN was increased from 1.0 to 1.5 equivalent, however, the quantitative conversion was observed in 15 min with 2 mol% catalyst loading of **1** (entry 5, Table 1). Compared with the aforementioned Ge-Pt bimetallic complex catalyzed cyanosilylation of benzaldehyde [6d], the Mg-Li bimetallic complex **1** showed a slightly high activity (**Mg-Li**: 15 min, 25 °C, 2 mol% catalyst, 99% yield *VS* **Ge-Pt**: 90 min, 50 °C, 1 mol% catalyst, 99% yield). A blank reaction of benzaldehyde and 1.5 equiv. of TMSCN without catalyst only gave trace yield after 48 h (entry 6, Table 1). We also tested the solvent effect (entries 7–8, Table 1). The protic MeOH only gave 83% yield. The corresponding solvent-free experiment has been done as well (entry 9, Table 1).

With the optimized reaction conditions in hand, a variety of aliphatic and aromatic aldehydes were screened (Table 2). The cyanosilylation of 1-pentanal, 5-chloropentanal and cyclohexyl aldehydes with 2 mol% catalyst loading of complex **1** all afforded the corresponding cyanohydrin trimethylsilyl ethers in 99% yields in 15 min at room temperature (entries 1–3, Table 2). Compared with benzaldehyde, however, the cyanosilylation of aromatic aldehydes with electron-donating or electron-withdrawing groups such as -Me, -NMe_2, -OMe, -NO_2, -F or -Cl required a slightly longer reaction time ($\leq$3 h) to get the quantitative conversion (entries 5–14, Table 2). Similarly, the reaction of α, β-unsaturated cinnamaldehyde or even sterically bulky 9-anthraldehyde can also be completed to give 99% yield in 3 h (entries 15–16, Table 2). Under the same reaction conditions, heterocyclic aldehyde 2-thiophenecarboxaldehyde could be cleanly converted into the corresponding cyanohydrin trimethylsilyl ether in 2 h, however, the cyanosilylation of 3-pyridinecarboxaldehyde took only half an hour (entries 17–18, Table 2). The *N*-(4-formylphenyl) acetamide, 4-formylphenyl acetate and 2-formylbenzoic acid were selectively and exclusively cyanosilylated on the aldehyde substituent and retained the amide, ester and acid group intact (entries 19–21, Table 2). For dicarbonyl substrate 2-bromoisophthalaldehyde, when it was treated with equimolar TMSCN at room temperature, a mixture of the monocyanosilylated and dicyanosilylated products were observed in 7:3 M ratio with the full consumption of trimethylsilyl cyanide in 6 h monitored by ^1H NMR spectroscopy. Hence 2.5 equiv. TMSCN was used to get dicyanosilylated product in 99% yield within 2 h (entry 22, Table 2).

Encouraged by the above aldehyde cyanosilylation results, we further investigate the cyanosilylation of ketones. As expected, the cyanosilylation of aromatic ketones catalyzed by bimetallic complex **1** displayed a lower reactivity than that of aldehydes due to the steric effect. For example, an initial reaction of acetophenone and 1.5 equiv. TMSCN with 5 mol% catalyst loading of **1** at room temperature for 48 h generated only 70% conversion. The cyanosilylation of aromatic ketones with electron-withdrawing substituents such as 4-nitroacetophenone and 4-acetylbenzonitrile also showed a similar reactivity (79% and 73% yield, respectively) under same reaction conditions (5 mol% catalyst **1**, rt, 48 h). To further investigate the selectivity of catalyst **1**, an intramolecular reaction of 4-acetyl benzaldehyde with 1.5 equivalent of TMSCN in the presence of 2 mol% catalyst **1** was performed. Only the aldehyde moiety of 4-acetyl benzaldehyde was selectively cyanosilylated in quantitative yield and the ketone group retained intact (entry 23, Table 2).

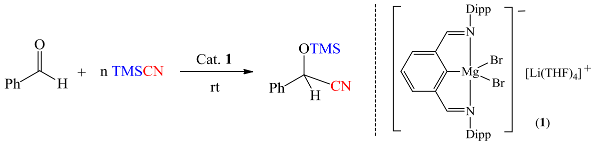
3. Conclusions

In summary, we have demonstrated that the Mg-Li bimetallic complex **1** was employed as an efficient and chemoselective catalyst for the cyanosilylation of a wide range of aldehydes in a relative cheaper and unpurified $CDCl_3$ at room temperature although less effective to ketones. Catalyst **1** showed high functional group tolerance towards amide, ester and acid ect. The chemoselectivity of the aldehyde over ketone was achieved through the intramolecular cyanosilylation of 4-acetyl benzaldehyde.

4. Experimental section

All air-sensitive compounds were carried out using standard

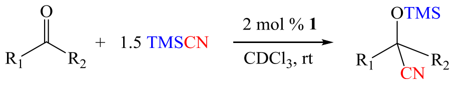
Table 1
Optimization of cyanosilylation of benzaldehyde.

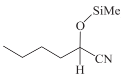
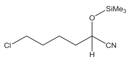
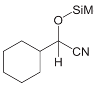
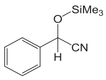
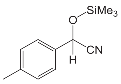
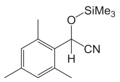
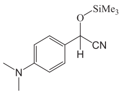
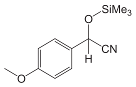
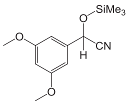
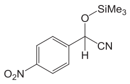
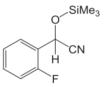
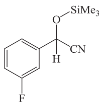
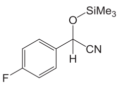
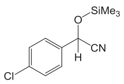
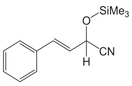
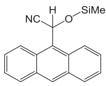
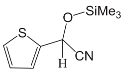
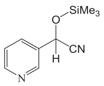
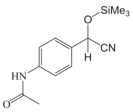
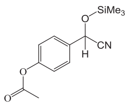
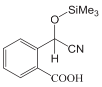
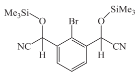
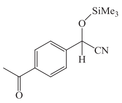


Entry	n	Cat (mol%)	Solvent	Time	Yield (%)[a]
1	1.0	2	$CDCl_3$	15 min	73
2	1.0	5	$CDCl_3$	15 min	87
3	1.0	2	$CDCl_3$	30 min	77
4	1.0	5	$CDCl_3$	30 min	91
5	1.5	2	$CDCl_3$	15 min	99
6	1.5	none	$CDCl_3$	48 h	trace
7	1.5	2	MeOD	2 h	83
8	1.5	2	THF-d8	2 h	95
9	1.5	2	–	2 h	97

[a] The reaction was monitored by ^1H NMR spectroscopy.

Table 2
Cyanosilylation of aldehydes catalyzed by **1**.



Entry	Product	Time	Yield (%)[a]	Entry	Product	Time	Yield (%)[a]
1		15min	99(85[d])	2		15min	99
3		15min	99	4		15min	99(90[d])
5		15min	99	6		30min	99
7		30min	99	8		3 h	99
9		3 h	99	10		30min	99
11		1 h	99	12		1 h	99
13		1 h	99	14		1 h	99
15		3 h	99	16		3 h	99
17		2 h	99	18		30min	99
19		30min	99	20		2 h	99
21[b]		3 h	96	22[c]		2 h	99
23		2 h	99				

[a] The reaction was monitored by ^{1}H NMR spectroscopy.
[b] TMSCN (1 equiv.).
[c] TMSCN (2.5 equiv.).
[d] Isolated yield.

Schlenk-line or glovebox techniques under high-purity argon. Diethyl ether, toluene, THF and hexane were dried and distilled from molten sodium. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 25 °C with a Bruker Avance III 600 MHz spectrometer and were referenced to the resonances of the solvent used. Catalyst **1** was prepared according to literature procedure [14]. Other reagents were used as received.

4.1. General procedure for catalytic cyanosilylation of aldehydes

In a glove box, catalyst **1** (2 mol%) was added to a solution of aldehydes (0.25 mmol) and Me_3SiCN (1.5 equiv.) at room temperature in a common NMR tube, which was charged with $CDCl_3$ (0.5 mL). The progress of the reaction was monitored by ^{1}H NMR and ^{13}C NMR. Two examples were selected to give the isolated yield: after evaporation of $CDCl_3$ solvent, the resulting viscous liquid was treated with acidic water (HCl) and was purified by flash column chromatography to give pure products.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jorganchem.2018.08.019.

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