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The cyanosilylation of prochiral aldehydes catalyzed by lanthanide complexes

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Abstract

A new series of silylene-bridged rare-earth complexes involving fluorenyl are shown to be the very efficient Lewis acidic catalysts, giving cyanotrimethylsilyl ethers of aldehydes >99% conversion.

Keywords: Silylene-bridged rare-earth complexes involving fluorenyl; Lewis acidic catalysts; Cyanotrimethylsilyl ethers

1. Introduction

Rare-earth organometallic complexes are the most important catalysts in polymerization of alkenes [1–3] and organic reactions [4,5]. I have recently succeeded in developing the new family Lewis acid catalysts **1**–**5**, and could demonstrate that complex **5** is the most general catalyst for the cyanosilylation of aldehydes.

Chiral cyanohydrins from aldehydes and ketones are highly versatile synthetic intermediates which can be easily converted into a wide variety of important synthetic intermediates including chiral α-hydroxy acids, α-amino acids, and β-amino alcohols. As we all know that they are very important in medical synthesis and natural products synthesis such as L-biotin [6], 20S-amptothecin [7] synthesis, etc. For these reasons, there has been intense research activity in this area in recent years. Shibasaki first put forward bifunctional catalyst concept [8–10], he and co-workers developed many heterodifunctional metallic complexes, later, Jacobsen [11], Garcia [12–14], and Nakai [15] have developed many catalysts in cyanosilylation of aldehydes.

Recently, Corey [16] develops a series of rare-earth trichloride as Lewis acidic catalysts in cyanosilylation of aldehydes. Inspired by the pioneering works, I used five rare-earth organometallic complexes as catalysts, of many products in 3 h, they could get the nearly 100% conversions.

2. Experimental

2.1. General procedures [17]

All cyanosilylation reactions were performed using chloroform as solvent, ligands and lanthanum complexes were synthesized, reactions were monitored by thin-layer chromatography using 0.25 mm E. Merck silica gel-coated glass plates (60F-254) using UV light to visualize the course of reaction. Flash column chromatography was performed using E. Merck silica gel (60, particle size 0.02–0.03 mm). Chemical conversion was obtained by ^{1}H NMR, ^{13}C NMR. ^{1}H and ^{13}C NMR spectra were obtained using either a Bruker AM-300 or a AM-500 spectrometer. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. Infrared spectra were recorded on a Mattson Galaxy Series FTIR 3000

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Spectrometer. High-resolution mass spectra were obtained on a MASPEC.

2.2. Preparation of bis(9-fluorenyl)(methyl)-(phenyl)silane [18]

Ten grams (60.24 mmol) of dry fluorene and 2 g (288.33 mmol) of lithium were added under free-water and free-oxygen condition in a dry 100 ml Schlenk flask. They were dissolved in 100 ml of dry THF. The yellow mixture was stirred for 48 h, and it is to be used.

4.9 ml (30.12 mmol) of dichloro(methyl)(phenyl)silane was added dropwise at room temperature to the flask containing a THF solution of fluorenyllithium. After the condition was complete, the reaction mixture was stirred for an additional 24 h. The solvent was removed under vacuum and the residue was treated with 30 ml of *n*-hexane, the crude product was washed by *n*-hexane to afford white solid. m.p.: 208–212 °C; $C_{33}H_{26}Si$, found (calc., %):C, 88.02% (88.00%); H, 5.79% (5.78%). ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C), δ (ppm) = 7.71–7.77 (d, 6H, aromH), 7.30–7.33 (t, 8H, aromH), 7.15–7.18 (t, 2H, aromH), 7.09–7.10 (t, 1H, aromH), 6.85–6.88 (t, 2H, aromH), 6.49–6.51 (t, 2H, aromH), 4.64 (s, 2H, H-9, Flu), −0.32 (s, 3H, CH_3); ^{13}CNMR: −10.001, 39.623, 120.109, 120.186, 124.603, 125.700, 125.750, 126.262, 126. 295, 126.773, 129.266, 134.076, 141.044, 141.159, 144.397, 144.440. MS: *m*/*z* 450 [M^+, 4.66%].

2.3. Preparation of (methyl)(phenyl)silylene-bis(9-fluorenyl)lithium

A certain amount of 2 g (288.18 mmol) of lithium and 1 g (2.22 mmol) of bis(9-fluorenyl)(methyl)(phenyl)silane were diluted with 30 ml dry THF under argon in a 100 ml Schlenk flask. The stirred solution was cool down to 0 to −5 °C. The resulting green solution was stirred for 48 h, and it is to be used.

2.4. Preparation of (methyl)(phenyl)silylene-bis(9-fluorenyl)yttrium chloride

A solution of rare-earth trichlorine was cooled down to 0 to −5 °C and bis(9-fluorenyl)(methyl)(phenyl)silylene lithium was added dropwise under argon. The resulting yellow mixture was stirred for 48 h and then was allowed to warm up to room temperature. The resulting solution was concentrated in vacuum to about 20 ml. By addition of 30 ml of *n*-hexane, solid precipitated out which was recrystallized in THF/*n*-hexane. It was washed twice with THF/*n*-hexane and dried in vacuum gave complex **1** as a white crystals (72% yield). HRMS (EI): 657.1306, Yb% 25.98 (26.33%), IR (KBr, cm^{-1}) ν3065.4, 2962.6, 2925.9, 2835.2, 1632.1, 1457.3, 1428.7, 1261.3, 790.0, 737.7, 403.3, 390.7. Anal. Calc. for $CH_3PhSi(C_{13}H_9)_2$ YbCl: C, 59.97%; H, 3.64%. Found: C, 60.32%, H3.68%.

2.5. Preparation of (methyl)(phenyl)silylene-bis(9-fluorenyl)dysprosium chloride

Following the procedure described in Section 2.4. Complex **2** as a white crystals (80%yield). HRMS (EI): 646.6505, Dy% 25.98 (25.13%); IR (KBr, cm^{-1}) ν 3069.1, 2961.1, 2924.1, 2851.2, 1634.6, 1476.3, 1428.2, 1260.9, 1098.0, 1028.2, 872.9, 798.6, 1098.0, 1028.2, 872.9, 798.6, 437.4. Anal. Calc. for $CH_3PhSi(C_{13}H_9)_2$ DyCl: C, 60.97%; H, 3.67%. Found: C, 61.30%, H:3.71%.

2.6. Preparation of (methyl)(phenyl)silylene-bis(9-fluorenyl)praseodymium chloride

Following the procedure described in Section 2.4. Complex **3** as yellow crystals (75% yield). HRMS (EI): 625.0642, Pr% 21.98 (22.54%); IR (KBr, cm^{-1}) ν 3066.0, 3047.7, 2956.6, 2923.2, 2852.1, 1646.2, 1615.9, 1516.7, 1448.7, 1427.8, 1114.8, 1020.2, 983.7, 738.5, 484.2, 442.7. Anal. Calc. for $CH_3PhSi(C_{13}H_9)_2$ PrCl:C, 63.23%; H, 3.77%. Found: C, 63.42%; H, 3.87%.

2.7. Preparation of (methyl)(phenyl)silylene-bis(9-fluorenyl)samarium chloride

Following the procedure described in Section 2.4. Complex **4** as yellow crystals (90% yield). HRMS (EI): 634.0565, Sm% 23.59 (23.70%); IR (KBr, cm^{-1}) ν 3068.1, 2962.7, 1635.3, 1475.6, 1446.8, 1260.9, 1098.8, 1027.7, 790.6, 484.3, 443.5. Anal. Calc. for $CH_3PhSi(C_{13}H_9)_2$ SmCl: C, 62.51%, H, 3.62%. Found: C, 62.47%; H, 3.81%.

2.8. Preparation of (methyl)(phenyl)silylene-bis(9-fluorenyl)neodymium chloride

Following the procedure described in Section 2.4. Complex **5** as yellow crystals (86% yield). HRMS (EI): 627.9565, Nd% 22.31 (22.96%); IR (KBr, cm^{-1}) ν 3067.9, 2961.2, 2923.5, 1634.7, 1476.7, 1260.6, 1049.1, 1028.1, 789.1, 789.8, 737.8, 481.8, 430.5. Anal. Calc. for $CH_3PhSi(C_{13}H_9)_2$ NdCl: C, 62.98%; H, 3.79%. Found: C, 63.08%; H, 3.84%.

2.9. Preparation of α-(trimethylsilyoxyl)-phenylacetonitrile

$CH_3PhSi(C_{13}H_9)_2$ LnCl 0.015 mmol was dissolved in $CHCl_3$ phenyl aldehyde (1 mmol) and TMSCN (297 μl, 2.2 mmol) was successively added at room temperature. After 0.5 h, the reaction was quenched. Further purification was performed by silica gel. ^{1}H NMR (300 MHz, $CDCl_3$) 7.39–7.39 (t, 0.9 Hz, 2H), 7.31–7.34 (m, 3H), 5.43 (s, 1H), 0.16 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 148.0, 129.4, 128.9, 124.3, 115.8, 62.9, −0.26.

2.10. Preparation of α-(trimethylsilyoxyl)-o-methyloxylphenylacetonitrile

Following the procedure described in Section 2.9. ^{1}H NMR (300 MHz, $CDCl_3$) 7.57–7.61 (d, 11.4 Hz, 1H), 7.28–7.36 (t, 5.8 Hz, 1H), 6.99–7.07 (t, 0.9 Hz, 1H), 6.89–6.92 (d, 11.7 Hz, 1H), 5.80 (s, 1H), 3.75 (s, 3H), 0.158 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$) 162.5, 130.2, 126.9, 126.7, 124.6, 120.5, 110.3, 57.9, 55.2, −2.18.

2.11. Preparation of α-(trimethylsilyoxyl)-o-fluorophenylacetonitrile

Following the procedure described in Section 2.9. ^{1}H NMR (300 MHz, $CDCl_3$) 7.17–7.20 (d, 9 Hz, 2H) 7.04–7.08 (d, 12 Hz, 2H), 5.70 (s, 1H), 0.098 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 162.6, 131.3, 128.3, 127.1, 124.7, 115.7, 115.2, 57.5, −1.95.

2.12. Preparation of α-(trimethylsilyoxyl)-o-nitrophenylacetonitrile

Following the procedure described in Section 2.9. ^{1}H NMR (300 MHz, $CDCl_3$) 8.03–8.16 (d, 10.5 Hz, 1H), 7.94–7.98 (d, 12 Hz, 1H), 7.62–7.71 (t, 2.7 Hz, 1H), 7.54–7.58 (t, 5.4 Hz, 1H), 6.15 (s, 1H), 0.31 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 134.9, 132.4, 130.6, 128.8, 127.6, 125.7, 118.2, 60.5, −1.54.

2.13. Preparation of α-(trimethylsilyoxyl)-p-methyloxylphenylacetonitrile

Following the procedure described in Section 2.9. ^{1}H NMR (300 MHz, $CDCl_3$) 7.38–7.42 (d, 12 Hz, 2H), 6.94–6.96 (d, 8 Hz, 2H), 5.45 (s, 1H), 3.83 (s, 3H), 0.23 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 161.3, 129.8, 128.4, 127.8, 119.2, 114.4, 114.1, 113.7, 63.2, 55.2, −0.40.

2.14. Preparation of α-(trimethylsilyoxyl)-p-fluorophenylacetonitrile

Following the procedure described in Section 2.9. ^{1}H NMR (300 MHz, $CDCl_3$) 8.09–8.12 (d, 10.5 Hz, 1H), 7.94–7.98 (d, 11.7 Hz, 1H), 7.71–7.73 (t, 3.3 Hz, 1H), 7.54–7.58 (t, 9 Hz, 1H), 6.16 (s, 1H), 0.31 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 161.4, 130.8, 128.4, 128.3, 118.9, 116.2, 115.9, 63.3, −0.33.

2.15. Preparation of α-(trimethylsilyoxyl)-p-chlorophenylacetonitrile

Following the procedure described in Section 2.9. ^{1}H NMR (300 MHz, $CDCl_3$) 7.38–7.40 (d, 6 Hz, 2H), 7.21–7.27 (d, 3 Hz, 2H), 5.48 (s, 1H), 0.245 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 134.9, 131.8, 128.7, 128.4, 127.4, 126.6, 118.7, 62.5, −2.67.

2.16. Preparation of α-(trimethylsilyoxyl)-p-nitrophenylacetonitrile

Following the procedure described in Section 2.9. ^{1}H NMR (300 MHz, $CDCl_3$) 8.28–8.38 (d, 2H), 7.67–7.77 (d, 2H), 5.62 (s, 1H), 0.38 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 143.8, 130.8, 127.3, 126.9, 123.8, 123.3, 117.9, 62.3, −2.16.

2.17. Preparation of α-(trimethylsilyoxyl)-1-naphthylacetonitrile

Following the procedure described for 2.9. ^{1}H NMR (300 MHz, $CDCl_3$) 7.84–7.88 (d, 12 Hz, 2H), 7.18–7.54 (m, 5H), 6.09 (s, 1H), 0.32 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$) 133.7, 130.4, 129.6, 128.8, 126.9, 126.2, 125.5, 124.9, 122.9, 122.1, 118.9, 62.8, −0.36.

3. Results and discussion

Rare-earth organometallic complexes are prepared from bis(9-fluorenyl)(methyl)(phenyl)silylene lithium with $LnCl_3$ in THF under argon, they were characterized by MS, IR and elemental analysis, the concrete procedure and data can be seen in Asian J. Chem. [17,18]. The synthesis routes as follows:

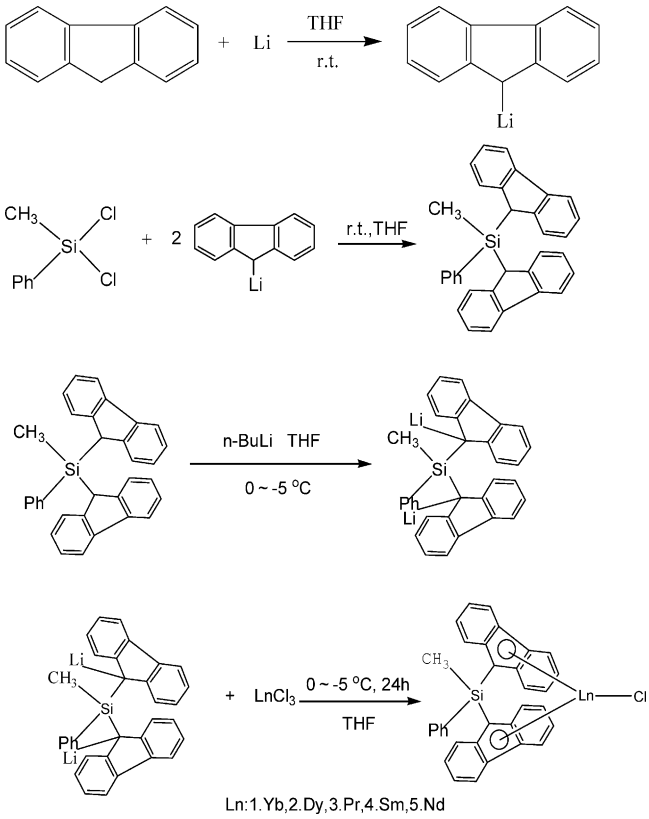
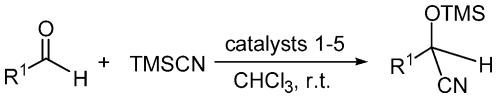


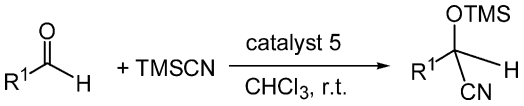
Table 1
The effect of different Ln^{3+} to cyanosilylation of phenyl aldehyde[a]



Entry	Catalyst	Time (h)	Conversion (%)[b]
1	$CH_3PhSi(C_{13}H_9)_2YbCl$	0.5	44
2	$CH_3PhSi(C_{13}H_9)_2DyCl$	0.5	89
3	$CH_3PhSi(C_{13}H_9)_2PrCl$	0.5	91
4	$CH_3PhSi(C_{13}H_9)_2SmCl$	0.5	32
5	$CH_3PhSi(C_{13}H_9)_2NdCl$	0.5	>99
6	$NdCl_3$	1.5	74
7	No	1.5	0
8	$CH_3PhSi(C_{13}H_9)_2$	1.5	0

[a] The temperature is at 25 °C,$CHCl_3$ solvent.
[b] The conversion (%) was given by ^1H NMR (300 MHz, $CDCl_3$).

Table 2
Cyanosilylation of aldehydes catalyzed by catalyst 5[a]



Entry	R^1	Time (h)	Conversion (%)[b]
1	C_6H_5	0.5	>99
2	2-$OCH_3C_6H_4$	3	>99
3	2-FC_6H_4	1	81
4	2-$NO_2C_6H_4$	1	>99
5	4-$OCH_3C_6H_4$	3	>99
6	4-FC_6H_4	3	>99
7	4-ClC_6H_4	3	>99
8	4-$NO_2C_6H_4$	3	>99
9	1-Naphthyl	1	61
9	1-Naphthyl	5	90

[a] The temperature is at 25 °C,$CHCl_3$ solvent.
[b] The conversion (%) was given by ^1H NMR (300 MHz, $CDCl_3$).

In this study, I first use rare-earth trichloride as catalyst in freshly purified chloroform (0.015 M), TMSCN and phenylaldehyde were added in room temperature, but it was not nearly dissolved in $CHCl_3$, maybe this is the poor performance in reactivity, 1.5 h later, no reaction, this prompted me to use the complexes **1**–**5** that I have synthesized, they all dissolved in solvent, and the reaction rate is greatly improved, 1 h later, of one product (entry 3), the yield is getting nearly 100%. The effects of different Ln^{3+} are as follows: $Nd^{3+} > Pr^{3+} > Dy^{3+} > Yb^{3+} > Sm^{3+}$, the results are listed in Table 1.

At the same time, I compared silylene-bridged catalyst $CH_3PhSi\ (C_{13}H_9)_2$ and no catalyst, the results were found that after 1.5 h, no reactivity.

The mechanism of cyanosilylation can be proposed that one pair isolated electron in oxygen atom of C=O bond, could complex with the Ln^{3+}, so the catalysts greatly actived substrates, the reactivity became very high, and leading to the smooth reaction.

A range of aldehydes underwent efficient reaction under these conditions, including electron-deficient and electron-rich substrates, and they were all displayed high reactivity. The results can be seen in Table 2.

From Table 2, no matter the electron-deficient and electron-rich substrates, the conversions are very high after 3 h, but as to the entry 9, 5 h later, the conversion has not gotten to 100%, so the steric factor is the main reason for the reactivity.

4. Conclusion

In summary, the first example of the highly Lewis acidic catalysts in cyanosilylation of aldehydes to give stable cyanotrimethylsilyl ethers has been reported in excellent yields at room temperature and with broad substrate generality. Further efforts are being directed toward the cyanosilylation of ketones, separation the planar chiral complexes and application to cyanosilylation of prochiral ketones and aldehydes. This study clearly demonstrates that the structure of the complexes and different rare-earth ions can greatly change the yield. Silylene-bridged ligands and no catalyst will lead the slow reaction or no reaction. All in all, no matter the electron-deficient and electron-rich substrates, the steric factor is the main reason for the reactivity.

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