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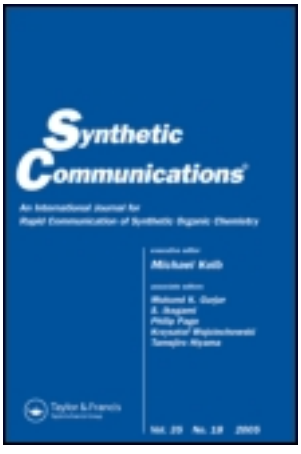

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Research on the Cyanosilylation of Prochiral Aldehydes Catalyzed by Alkyldimethoxyl Silylene-Bridged Lanthanide Complexes

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Abstract: A series of novel silylene-bridged Ln-O rare earth complexes are very efficient Lewis acidic catalysts in cyanosilylation of aldehydes, giving some cyano trimethylsilyl ethers of aldehydes in >99% yields.

Keywords: Cyanosilylation of aldehydes, cyano trimethylsilyl ethers, Lewis acidic catalysts, novel silylene-bridged Ln-O rare earth complexes

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With the development of chemistry, rare earth organometallic complexes are becoming more important in polymerization and organic reactions.[1–4] Chiral cyanohydrins are important synthetic intermediates including chiral α-hydroxyacids, α-amino acids, and β-amino alcohols, and they are also applied in natural products such as (S)-oxybutynin,[5] (20S)-camptothecin[6] synthesis, and so forth. Many chemists such as Corey,[7] Jacobsen,[8] Shibasaki,[9–12] Garcia,[13–15] and Nakai[16] have made great contributions to this field.

Alkyldimethoxyl silane, the electronic donors in Ln-O complexes, have been widely used as the catalysts in industry. We have tried the cyanosilylation of aldehydes using the rare earth complexes involving cyclopropenyl and got satisfactory results. To enrich the pool of catalysts, we employed these six ligands[17] and lanthanide complexes (Fig. 1) for further research.

The first step is screening the ligand-Dy complexes with dichloromethane solvent at room temperature; after 1 h, it was found that **4a** had achieved the product formation in 94.1% yield (Table 1). From this table, we can see that the alkyl groups have some effects on the reaction, and the steric factor may be the reason. No catalysts and ligands lead to a low reaction. With the rare earth ion optimization, $Dy^{3+} > Sm^{3+} > Nd^{3+} > La^{3+} > Pr^{3+}$, **4a** in 2 h >99%, but thus can properly reduce the reaction time to 1 h, and still result in 94% yield (Table 2).

We propose that the mechanism of cyanosilylation of aldehydes is that Ln^{3+} could complex with the one pair of isolated electrons in the oxygen atom of C═O bond and the reactivities of the substrates are greatly actived by the complexes, leading to the smooth reaction.

Catalyst **4a** proved to be general for the high activity including electron-deficient and electron-rich substrates. The results are in entries 1–10, Table 3.

From Table 3, as to the 4-position aromatic aldehydes, the electron-deficient substrates are proved to have poor reactivity after 2.5 h. Their electron-rich counterparts are better in reactivity. The conversion of 2-position substitution substrates are better than that of 4-position substitution substrates, even through the 2-position are electron deficient.

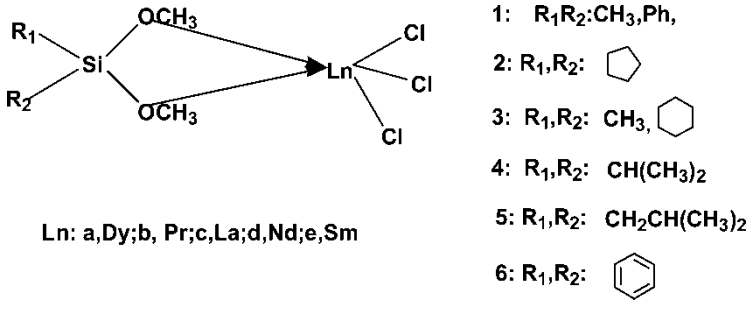
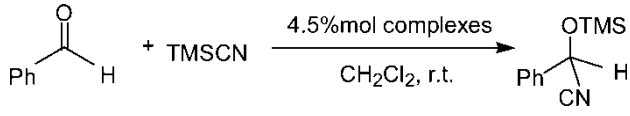


Figure 1. Lanthanide complexes.

Table 1. Ligand-complexes optimization[a]



Catalyst	Time (h)	Yield (%)[b]
1a	1	80.0
2a	1	46.9
3a	1	60.2
4a	1	94.1
5a	1	71.9
6a	2	80.1
$LaCl_3$	2	5.57
$DyCl_3$	2	59.6
No catalyst	2	0.30
Ligand 4	2	0.48
4a	2	>99
4a	1	94.1

[a]The temperature is 30°C, CH_2Cl_2 solvent.
[b]The yield (%) was given by ^{1}H NMR (300 MHz, $CDCl_3$).

This follows the chemical theory and fully shows the results of P-π conjugate effects (entries 2–5), electron effects (entries 2–9), and steric effects (entry 2).

In conclusion, the highly Ln-O complexes as the catalysts in cyanosilylation of aldehydes give stable cyano trimethylsilyl ethers in excellent yields at room temperature and with broad substrate generality. Further efforts are being developed toward the determination of the structure of complexes (cultivating the single crystals of the complexes), application to cyanosilylation of prochiral ketones, and some other alkene polymerization reactions.

Table 2. Rare earth opatimization[a]

Catalyst	Time (h)	Yield (%)[b]
4a	2h	>99
4a	1h	94.1
4b	2h	46.2
4c	2h	73.5
4d	2h	83.0
4e	2h	89.9

[a]The temperature is 30°C, CH_2Cl_2 solvent.
[b]The yield (%) was given by ^{1}H NMR (300 MHz, $CDCl_3$).

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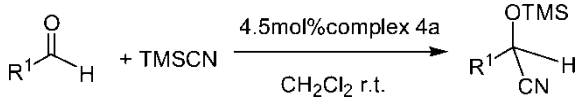
Table 3. Cyanosilylation of aldehydes catalyzed by rare earth complex 4a[a]



Entry	R^1	Time (h)	Yield (%)[b]
1	C_6H_5	1	94.1
2	2-$OCH_3C_6C_4$	2.5	93.0
3	2-$BrCH_3C_6H_4$	2.5	>99
4	2-FC_6H_4	2.5	>99
5	2-$NO_2C_6H_4$	2.5	>99
6	4- $OCH_3C_6H_4$	2.5	>99
7	4- BrC_6H_4	1	79.4
7	4- BrC_6H_4	2.5	83.6
8	4-$ClCH_3C_6H_4$	1	83.8
8	4-ClC_6H_4	2.5	91.3
9	4- $NO_2C_6H_4$	2.5	65.9
10	Naphthyl	2.5	90.5

[a]The temperature is 30°C, CH_2Cl_2 solvent.
[b]The yield (%) was given by ^{1}H NMR (300 MHz, $CDCl_3$).

EXPERIMENTAL

General Procedures

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) with 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 were obtained by ^{1}H NMR,^{13}C NMR. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker AM-300 spectrometer. The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d = doublet, t = triplet, and m = multiplet. Infrared spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer. High-resolution mass spectra were obtained on a MASPEC.

Preparation of Diphenyl Dimethoxyl Silane (Method A)

A 250-mL Schlenk flask, equipped with a pressure-equalizing dropping funnel, was charged with a solution of dichlorine silane (10 mL, 50 mmol) of dry methanol (30 mL) in 20 ml of benzene. The dropping funnel was charged with 25 mL of benzene and 8 mL of pyridine, and this was added

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dropwise to the flask at about $-5-0$ °C while stirring; after 20 min, white pyridine hydrochloric acid was obtained. The mixture was allowed to warm up to room temperature and was refuxed at 70–80°C for 5 h. The mixture was carefully filtered at room temperature, and the solvent was evaporated in vacuo using a rotary evaporator, then washed with 10 mL of H_2O, extracted with 2×30 mL CH_2Cl_2, and dried with $NaSO_4$ to yield 9.0 g (36.8 mmol, 71%). ^{1}H NMR (300 MHz,$CDCl_3$, 27°C), δ(ppm) = 7.66–7.69 (m, 5H, aromH), 7.31–7.66 (m, 5H, aromH), 3.59 (s,6H). ^{13}C NMR 50.93, 51.00, 127.81, 127.93, 127.98, 130.20, 130.28, 130.35, 130.45, 134.076, 134.45, 134.64, 134.70, 134.88.

Preparation of Diisobutyl Dimethoxyl Silane

We followed the procedure previously described (method A). Bp: 72°C (10 mm Hg),^{1}H NMR (300 MHz, $CDCl_3$, 27°C), δ (ppm) = 3.51 (m, 6H), 1.81–1.90 (m, 2H), 0.96–0.98 (d, 6.58 Hz, 2H), 0.61–0.64 (7.05 Hz, 4H). ^{13}C NMR 23.06 ($\times$2), 23.96 ($\times$2), 26.17 ($\times$4), 50.16 ($\times$2).

Cyclohexyl Methyl Dimethoxyl Silane

Method A. Bp:196–198°C ^{1}H NMR (300 MHz, $CDCl_3$, 27°C), δ (ppm) = 3.45 (s, 6H), 1.66–1.68 (m, 5H), 1.10–1.19 (m,5H), -0.004 to -0.0021 (s,3H). ^{13}C NMR -7.89, 24.78, 26.70, 26.90, 27.61, 27.79, 50.39 ($\times$2).

Diisopropyl Dimethoxyl Silane

Method A. Bp:164°C (740 mm Hg), ^{1}H NMR (300 MHz, $CDCl_3$, 27°C), δ (ppm) = 3.56 (s, 6H), 1.48–1.83 (m, 2H), 1.05–1.06 (d, 2.53 Hz, 12H), ^{13}C NMR 11.91 ($\times$2), 17.38 ($\times$4), 50.99 ($\times$2).

Dicyclopentyl Dimethoxy Silane

Method A. Bp:120°C (6 mmHg), ^{1}H NMR (300 MHz,$CDCl_3$, 27°C), δ (ppm) = 3.61 (s, 6H), 1.82–1.84 (m, 2H), 1.65–1.66 (m, 2H), 1.52–1.58 (m, 4H), 1.08–1.12 (m, 2H). ^{13}C NMR 23.55 ($\times$2), 26.99 ($\times$4), 27.70 ($\times$4), 50.99 ($\times$2).

Methyl, Phenyl Dimethoxy Silane

Method A. Bp: 106–108°C (10 mm Hg), ^{1}H NMR (300 MHz, $CDCl_3$, 27°C), δ (ppm) = 7.61–7.64 (m, 2H, aromH), 7.35–7.41 (m, 3H, aromH), 3.56 (s,6H), 0.36 (s, 3H). ^{13}C NMR -5.13, 127.99 ($\times$2), 130.23, 133.94, 134.05.

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Preparation of α-(Trimethylsilyoxyl)-phenylacetonitrile (Method B)

To a solution of rare earth trichlorine (11.2 mg), ligand diisopropyl dimethoxyl silane (7.8 mg) was added dropwise under argon. The resulting white mixture was stirred for 2 h at room temperature. The resulting solution was concentrated in vacuum and dried to give complex **4a**, which was dissolved in 1 mL of CH_2Cl_2. Phenyl aldehyde (1 mmol) and TMSCN (0.2 ml, 2.2 mmol) were successively added at room temperature. After 2.5 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.

α-(Trimethylsilyoxyl)-o-methyloxylphenylacetonitrile

We followed the procedure described in the previous paragraph (method B).^{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.

α(Trimethylsilyoxyl)-o-fluorophenylacetonitrile

Method B. ^{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, 6$CDCl_3$) 162.6, 131.3, 128.3, 127.1, 124.7, 115.7,115.2, 57.5, −1.95.

α-(Trimethylsilyoxyl)-o-nitrophenylacetonitrile

Method B. ^{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.

α-(Trimethylsilyoxyl)-p-methyloxylphenylacetonitrile

Method B. ^{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.

α-(Trimethylsilyoxyl)-p-fluorophenylacetonitrile

Method B. ^{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.

α-(Trimethylsilyoxyl)-p-chlorophenylacetonitrile

Method B. ^{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.

α-(Trimethylsilyoxyl)-p-nitrophenylacetonitrile

Method B. ^{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.

α-(Trimethylsilyoxyl)-1-naphthylacetonitrile

Method B. ^{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.

α-(Trimethylsilyoxyl)-1-p-bromophenylacetonitrile

Method B. ^{1}H NMR(300 MHz, $CDCl_3$) 7.49–7.50 (m, 2H), 7. 29–7.34 (m, 2H), 5.41 (s, 1H), 0.093 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$) 135.4, 132.2, 128.3, 128.0, 124.0, 123.6, 118.8, −0.19. HRMS: calcd. for $C_{11}H_{14}SiNO81Br$: 85.0008, found: 284.9986.

α-(Trimethylsilyoxyl)-1-o-bromophenylacetonitrile

Method B. ^{1}H NMR (300 MHz, $CDCl_3$) 7.64–7.66 (m, 1H), 7.48–7.51 (m, 1H), 7. 31–7.35 (m,1H), 7.18–7.20 (m, 1H), 0.060 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 135.5, 133.1, 130.9, 128.6, 128.2, 121.8, 118.4, −0.21.

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