Research Article

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Studies on cyanosilylation reaction catalyzed by Ln–N complexes

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A novel family of Ln–N complexes was synthesized by two methods and as the Lewis acidic catalysts in application to the cyanosilylation of prochiral ketones and aldehydes, which gave yields >99% of some cyano trimethylsilyl ethers from the wide range of aldehyde substrates and moderate yields from the ketone substrates at room temperature using 20 mol% catalyst loadings.

Keywords: Ln–N complexes; Lewis acidic catalysts; cyanosilylation of prochiral ketones and aldehydes; cyano trimethylsilyl ethers

Introduction

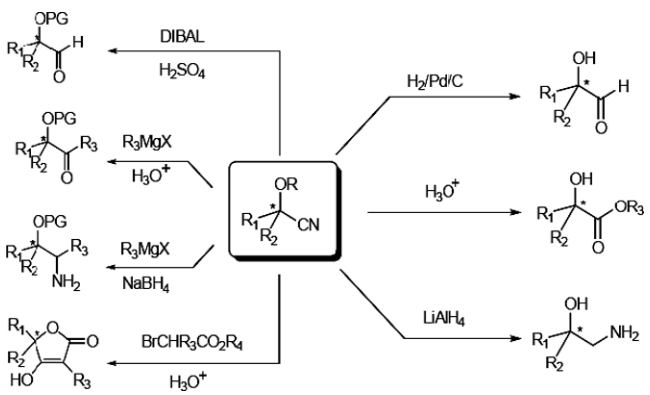
The first Ln–N complex was reported in 1963;[1] later, Ln–N complexes were widely used as the catalysts in many organic reactions, such as in hydroamination reaction, Tishchenko reaction, hydrosilylation reaction, polymerization and hydrophosphination reaction.[2–5]

The products, cyanohydrins, are intermediates for the synthesis of pharmaceuticals[6] (Scheme 1). The use of lanthanide chlorides as catalysts for cyanoation was first reported a long time ago by Vougioukas and Kagan;[7] this work was followed by studies on catalysis with lanthanide complexes.[8]

The recent progress on cyanosilylation reaction can be outlined as follows:

1. The Shibasaki group first synthesized a bifunctional asymmetric catalyst;[9–11] for example, they used BINOL as the chiral backbone, which contains aluminum and phosphone oxide. This catalyst displayed high Lewis acidity and Lewis basicity in a catalytic enantioselective cyanosilylation of aldehydes and the ketones.
2. Deng and Jacobsen and co-workers[12–14] also developed a series of catalysts for this reaction, their main feature being their basicity. For example, Deng used DABCO and DHQ_2(AQN), and Jacobsen employed thiourea, and both obtained satisfactory results.
3. Corey[15,16] used chiral oxazalineborolidinium as the powerfully Lewis acidic catalysts, and Feng's[17–19] group devised bifunctional, Ti-based, inorganic/organic salt catalysts for this reaction. All these catalysts displayed their special catalyst effects in the cyanosilylation reaction realm.

Our group has been inspired to use the Lewis acidic catalysts for cyanosilylation, and to study further improved catalysts effiency.[20,8b]



Scheme 1. Many products as the cyanohydrins precursors.

Experimental

Materials and instruments

All cyanosilylation reactions were performed using chloroform as solvent; 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 the reaction. Flash column chromatography was performed using E. Merck siliga gel (60, particle size 0.02–0.03 mm). Chemical conversions were obtained by ^{1}H NMR, ^{13}C NMR; ^{1}H and ^{13}C NMR spectra were obtained using a Bruker AM-300spectrometer. The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. Infrared spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer. High-resolution mass spectra were obtained on a MicroGCT-MS, EI ionization. TMSCN, $LnCl_3$, ligand, ketones and aldehydes were purchased from Aldrich.

General procedure of Scheme 1

n-BuLi (0.18 cm^3, 1.6 M, 0.106 mmol) was added in a dropwise fashion to a solution of 2-aminopyridine (0.010g, 0.106 mmol)

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in ether 5 mL at 0 °C. To the solution was added dropwise $NdCl_3$ (0.106 mmol,) forming a yellow solution and a white LiCl precipitate. Filtration afforded a yellow solution, and reduced *in vacuo*.

General procedure of Scheme 2

n-BuLi (0.18 cm^3, 1.6 M, 0.106 mmol) was added in a dropwise fashion to a solution of 2-aminopyridine (0.01 g, 0.106 mmol) in ether 5 ml at 0 °C. To the solution was added dropwise $LnCl_3$ (0.0503 mmol) forming a yellow solution and a white LiCl precipitate. Filtration afforded a yellow solution, and reduced *in vacuo*.

General procedure of Scheme 3

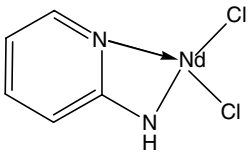
Pyridine (0.05 ml) was added in a dropwise fashion to a solution of 2-aminopyridine (0.01 g, 0.106 mmol) in CH_2Cl_2 5 ml at 0 °C. To the solution was added dropwise $LnCl_3$ (0.106 mmol) forming a white solution and a white pyridine hydrochlorine salt precipitate. Filtration afforded a yellow solution, and reduced *in vacuo*.

General procedure of Scheme 4

Pyridine (0.05 ml) was added in a dropwise fashion to a solution of 2-aminopyridine (0.01 g, 0.106 mmol) in CH_2Cl_2 5 mL at 0 °C. To the solution was added dropwise $LnCl_3$ (0.0503 mmol), forming a white solution and a white pyridine hydrochlorine salt precipitate. Filtration afforded a yellow solution, and reduced *in vacuo*.

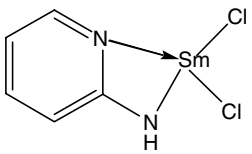
Data for the complexes

1a, *1 : 1 Nd–N complex*



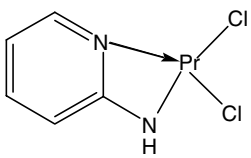
IR: 3443, 3072, 1261, 1093, 1020, 857, 799, 774, 737, 404; HRMS: calculated for [M] $C_5H_5N_2Cl_2$142Nd: 304.8907, found 304.8942.

1b, *1 : 1 Sm–N complex*



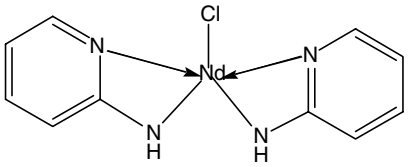
IR: 3462, 3017, 1261, 1043, 844, 773, 737, 408; HRMS: calculated [M] for $C_5H_5N_2Cl_2$152Sm 314.9027, found 314.9040.

1c, *1 : 1 Pr–N complex*



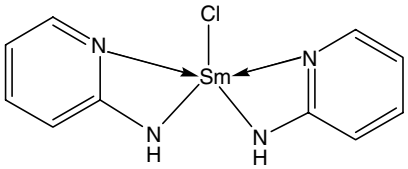
IR: 3459, 3019, 1272, 1047, 859, 774, 738, 409; HRMS: calculated [M] for $C_5H_5N_2Cl_2$141Pr: 303.8906, found 303.8936.

2a, *2 : 1 Nd–N complex*



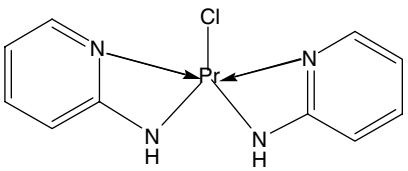
IR: 3406, 3070, 1263, 1088, 891, 785, 740, 417; HRMS: calculated [M] for $C_{10}H_{10}N_4Cl$ 142Nd: 362.9671, found 362.9662.

2b, *2 : 1 Sm–N complex*



IR: 3446, 3072, 1277, 1140, 856, 768, 738, 406 HRMS: calculated [M] for $C_{10}H_{10}N_4Cl$152Sm: 372.9791, found 372.9810.

2c, *2 : 1 Pr–N complex*



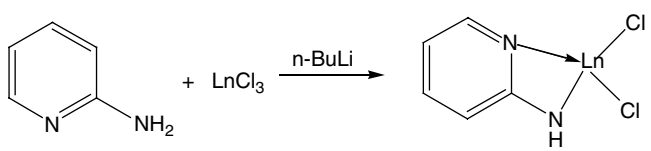
IR: 3460, 3017, 1261, 1094, 1046, 775, 738, 703, 408; HRMS: calculate [M] for $C_{10}H_{10}N_4Cl$ 141Pr: 361.9671, found 361.9699.

General procedure of Nd 1 : 1 complex-catalyzed addition of TMSCN to acetophone

Nd 1 : 1 complexes 0.0836 mmol was dissolved in 1 ml CH_2Cl_2, acetophone 0.05 ml (0.418 mmol) and trimethylsilyl cyanide (TMSCN) 0.1 ml (1.1 mmol) were successively added at room temperature. After 12 h, the reaction was quenched. Further purification was performed by silica gel. The title compound was obtained as a colorless oil, yield = 62.9%, ^{1}H NMR (300 MHz, $CDCl_3$): 7.44–7.47 (m, 3H), 7.24–7.32 (m, 2H), 1.76 (s, 3H), 0.079 (s, 9H). ^{13}C NMR (75MHz, $CDCl_3$): 141.9, 128.6(×2), 124.5(×2), 121.5, 71.5, 22.6 and −1.0.

2-(Trimethylsilyoxy)- 2-(2′-flurophenyl) propanenitrile

The title compound was obtained as a colorless oil, yield = 53.2%, ^{1}H NMR (300 MHz, $CDCl_3$) : 7.73–7.76 (m, 1H), 7.37–7.38 (m, 1H),



Ln: a, Sm; b, Pr; c, Nd

Scheme 2. 1 : 1 Complex synthetic route.

7.21–7.22 (m, 1H), 7.09–7.19 (m, 1H), 1.97 (s, 3H), 0.29 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$):1.23(×3), 30.98, 116.55, 116.73, 120.81, 124.38, 126.82, 130.78, 130.85.

2-(Trimethylsilyoxy)-2-(2′-methoxyphenyl)-propanenitrile

The title compound was obtained as a colorless oil, yield = 55.5%, ^{1}H NMR (300 MHz, $CDCl_3$) : 7.44–7.48 (m, 1H), 7.23–7.29 (m, 1H), 6.85–6.95 (m, 2H), 3.83 (s, 3H), 1.83 (s, 3H), 0.23 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 1.28(×3), 30.09, 55.53, 68.53, 111.63, 120.56, 125.72, 129.80(×2), 157.9;

2-(Trimethylsilyoxy)- 2-(2′-methylphenyl)propanenitrile

Yield = 18.7%, ^{1}H NMR (300 MHz, $CDCl_3$) : 7.53–7.58 (m, 1H), 7.18–7.27 (m, 3H), 2.55 (s, 3H), 1.94 (s, 3H), 0.077 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 1.09(×3), 20.68, 30.51, 71.68, 121.62, 125.29, 125.97, 128.66, 132.64, 135.50, 138.41.

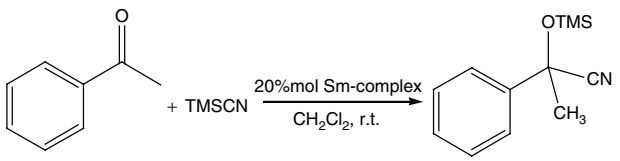
2-(Trimethylsilyoxy)-2-(4′-methylphenyl)-propanenitrile

Yield = 54.4%; ^{1}H NMR (300 MHz, $CDCl_3$): 7.33–7.37 (m, 2H), δ 7.09–7.17 (m, 2H), 2.28 (s, 3H), 1.18 (s, 3H), 0.068 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 1.00(×3), 20.98, 33.45, 71.44, 121.67, 124.51(×2), 129.19(×2), 138.43, 139.03.

2-(Trimethylsilyoxy)-2-(4′-bromophenyl)propanenitrile

Yield = 18.9%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42–7.46 (d, J = 13.5 Hz, 2H), 7.31–7.35 (d, J = 12.6 Hz, 2H), 1.74 (s, 3H), −0.002 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 1.00(×3), 33.42, 71.02, 115.87, 121.07, 122.66, 126.30(×2), 131.73(×2), 141.19.

Table 1. The effect of ligand ratio to $SmCl_3$[a]



Entry	Catalyst	Time (h)	Yield (%)[b]
1	1 : 1 complex	10	64.6
2	2 : 1 complex	10	53.8

[a] 2 mol% catalyst was added to a mixture of TMSCN (2.2 equiv.) and acetophone (0.418 mmol, 1 equiv.) at room temperature. [b] Isolated yield.

2-(Trimethylsilyoxy)-2-(4′-chlorophenyl)propanenitrile

Yield = 7.1%; the physical and spectral data were identical to those previously reported for this compound. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13–8.16 (m, 2H), 7.61–7.64 (m, 2H), 7.33–7.36 (m, 2H), 1.75 (s, 3H), 0.12 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 0.96(×3), 33.42, 70.96, 121.12, 126.00, 128.75(×2), 134.5(×2), 140.64.

General procedure of Sm 2 : 1 complex-catalyzed addition of TMSCN to benzaldehyde

Sm 2 : 1 complex 0.106 mmol was dissolved in 1 ml CH_2Cl_2; phenyl aldehyde 0.05 ml (0.5 mmol) and trimethylsilyl cyanide (TMSCN) 0.1 ml (1.1 mmol) were successively added at room temperature. After 8 h, the reaction was quenched. Further purification was performed by silica gel, yield = 99.7%, ^{1}H NMR (300 MHz, $CDCl_3$) 7.56–7.59 (m, 0.9 Hz, 2H), 7.31–7.34 (m, 3H), 5.43 (s, 1H), 0.16 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 136.1, 128.8(×2), 126.2(×2), 119.1, 63.5, −0.39(×3).

2-(2-Furyl-phenyl)-2-(trimethylsilyloxy)acetonitrile

Yield = 99.4%, ^{1}H NMR (300 MHz, $CDCl_3$) 7.56–7.57 (m, 0.9 Hz, 1H), 7.29–7.31 (m, 1H), 7.14–7.1 (m, 1H), 6.99–7.03 (m, 1H), 5.69 (s, 1H), 0.16 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 160.92, 158.24, 131.38, 131.30, 128.45, 128.42, 124.81, 124.81, 124.77, 123.96, 123.83, 118.34, 115.79, 115.59, 57.73, 57.68, 22.65, 22.60, 14.09, −0.45.

2-(2-Bromophenyl)-2-(trimethylsilyloxy)acetonitrile

Yield = 99.5%, ^{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.

2-(2-Nitrophenyl)-2-(trimethylsilyloxy)acetonitrile

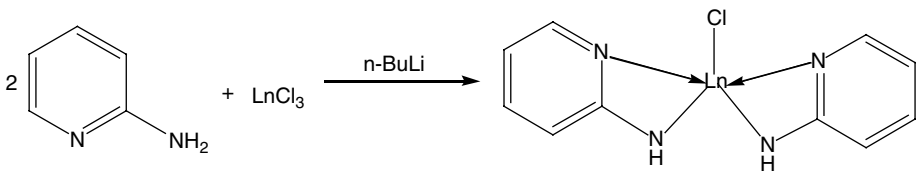
Yield = 99.9%, ^{1}H NMR (300 MHz, $CDCl_3$) 8.28–8.30 (d, J = 6.72 Hz, 2H), 7.34–7.56 (d, J = 6.36 Hz, 2H), 5.68 (s, 1H), 0.15 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$), 148.50, 142.49, 130.58, 127.47, 124.36, 124.19, 118.44, 62.20, 30.97, 29.23, 1.25(×3).

2-(4-Bromophenyl)-2-(trimethylsilyloxy)acetonitrile

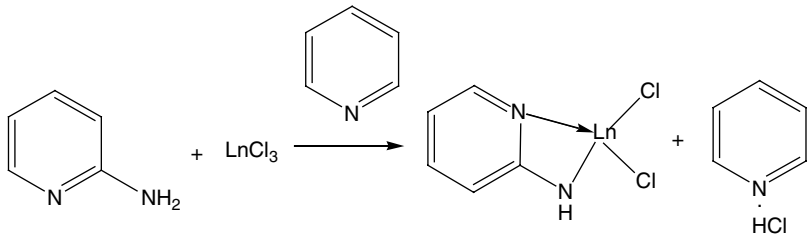
Yield = 98.0%, ^{1}H NMR (300 MHz, $CDCl_3$) 7.53–7.55 (m, 2H), 7.33–7.36 (m, 2H), 5.44 (s, 1H), 0.24 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 135.45, 132.19, 128.02, 123.56, 118.78, 63.11, 29.76, −0.21.

2-(4-Clorophenyl)-2-(trimethylsilyloxy)acetonitrile

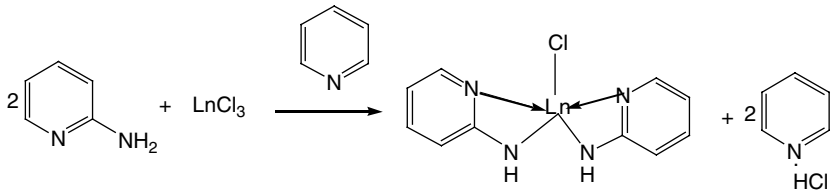
Yield = 98.4%, ^{1}H NMR (300 MHz, $CDCl_3$) 7.40–7.41 (m, 4H), 5.46 (s, 1H), 0.23 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 135.47, 134.95, 129.28, 127.8, 118.87, 63.10, 29.79, −0.18.



Scheme 3. 2 : 1 complex synthetic route.



Scheme 4. 1 : 1 complex improved synthetic route.



Scheme 5. 2 : 1 complex improved synthetic route.

2-(4-Nitrophenyl)-2-(trimethylsilyloxy)acetonitrile

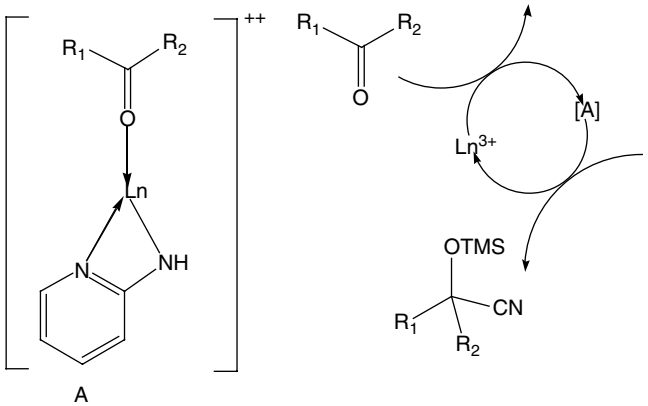
Yield = 97.0%, ^{1}H NMR (300MHz, $CDCl_3$) 8.28–8.30 (m, 2H), 7.66–7.69 (dd, J = 0.48, 0.51, 2H), 5.59 (s, 1H), 0.28 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 143.0, 127.28, 124.36, 118.26, 62.85, 31.06, 29.86, −0.15.

α-(Trimethylsilyoxyl)-1-naphthylacetonitrile

Yield = 95.2%, ^{1}H NMR (300 MHz, $CDCl_3$) 8.16–8.18 (m, 1H), 7.88–7.91 (m, 2H), 7.69–7.71 (m, 1H), 7.25–7.61 (m, 4H), ^{13}C NMR (75 MHz, $CDCl_3$) 134.06, 131.47, 130.53, 129.05, 127.08, 126.39, 125.53, 125.17, 123.14, 119.16, 62.78, 29.78, −0.09(×3).

Results and Discussion

Based on a full literature investigation, we devised the synthetic routes of the complexes (Schemes 2 and 3). They were prepared from 2-aminopyridine reacting with *n*-butyllithium in anhydrous ether, after 2 h adding $LnCl_3$(Sm, Pr, Nd) according to the molar ratio 1 : 1 and 1 : 2. The complexes were all characterized by MS and IR.



Scheme 6. The proposed mechanism.

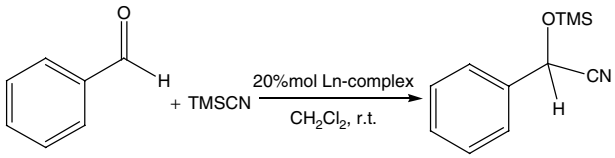
We gradually discovered that, when synthesizing the catalysts with *n*-butyllithium, the yield is not high. We decided to adopt the second synthetic route (Schemes 4 and 5).

Schemes 4 and 5 employed a certain amount of pyridine, which can form pyridinehydrochlorine salts in preparation of the catalysts. This method can greatly improve the yield. The same structures of the complexes were also proved after comparison of MS and IR data.

In the catalytic process, under equal conditions, with a reaction time of 10 h, dichloromethane as the solvent, at room temperature, the catalyst effect with **1b** was better than that with **2b**. The results can be seen in Table 1.

Then the same conditions were tested with different solvents such as ether, toluene and THF. The optimum choice was CH_2Cl_2 for 3 h and, because $SmCl_3$ was used up in the process, the optimum condition for prochiral acetophene was 20 mol% Nd 1 : 1 complex at room temperature and CH_2Cl_2 solvent. We continued to study the reactivities of the catalysts with cyanosilylation of prochiral

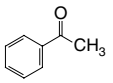
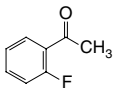
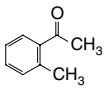
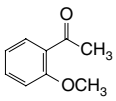
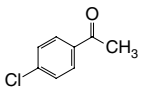
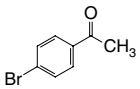
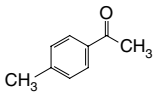
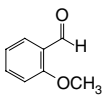
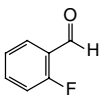
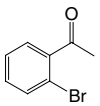
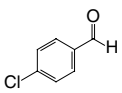
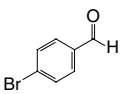
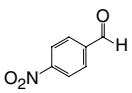
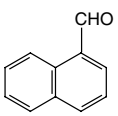
Table 2. The effect of different rare earth ions[a]



Entry	Catalyst	Time (h)	Yield (%)[b]
1	1 : 1 Nd–ligand	4	7.5
2	2 : 1 Nd–ligand	4	21.3
3	1 : 1 Sm–ligand	4	26.9
4	2 : 1 Sm–ligand	4	46.4
5	1 : 1 Pr–ligand	4	28.8
6	2 : 1 Pr–ligand	4	23.0
7	2 : 1 Sm–ligand	8	99.7

[a] 20 mol% catalyst was added to a mixture of TMSCN (2.2 equiv.) and acetophone (0.0418 mmol, 1 equiv.) at room temperature. [b] Isolated yield.

Table 3. Cyanosilylation of different ketones and aldehydes

Entry	Catalyst	Substrate	Time (h)	Yield (%)[a]
1	Nd 1 : 1		12	62.9
2	Nd 1 : 1		15	53.2
3	Nd1 : 1		15	18.7
4	Nd1 : 1		15	55.5
5	Nd1 : 1		15	7.1
6	Nd1 : 1		15	18.9
7	Nd1 : 1		15	54.4
8	Sm2 : 1		8	99.9
9	Sm2 : 1		8	99.4
10	Sm2 : 1		8	99.5
11	Sm2 : 1		8	99.9
12	Sm2 : 1		8	98.4
13	Sm2 : 1		8	98.0
14	Sm2 : 1		8	97.0
15	Sm2 : 1		8	95.2

[a] 20 mol% of catalyst is added to a mixture of TMSCN (2.2 equiv.), aldehydes (0.05 mmol, 1 equiv.) and ketones (0.0418 mmol) at room temperature. [b] Isolated yield.

aldehydes. The first step was screening the rare earth ions, see Table 2.

Complexes **1a, 1b, 1c, 2a, 2b** and **2c** were used for studying their reactivities. Their catalytic activities were discovered to be as follows: **2b** > **1c** > **1b** > **2c** > **2a** > **1a**. **2b** catalyst showed the best activity; the yields achieved nearly >99% when the reaction time was prolonged to 8 h.

Encouraged by the result obtained for acetophone and benzaldehyde in the presence of 20 mol% **1a** and **2b**, the cyanosilylation of prochiral aromatic ketones and aldehydes proceeded well under the optimized reaction conditions. From Table 3, we obtained the following conclusions:

(1) the longer reaction time, the higher yield of the products;
(2) ketones and aldehydes with the electron-donor and electron-withdrawing substitute gave a lower yield than acetophone and benzaldehyde (entries 2–14);
(3) ketones and aldehydes with the donor-electron gave a higher yield than withdraw-electron substitutes (entries 2–14);
(4) ketones and aldehydes with 2-substitute gave higher yields than those with 4-substitute;
(5) entry 15 is naphthaldehyde; because the naphthyl ring is relatively bigger than phenyl ring, and for its steric hindrance, it gave the relatively lower yield than the others.

All in all, no matter what the kind of substituted group was, the stereoscopic effect was an important factor in determining the reactivities.

The mechanism can be proposed that the rare earth ions activated the ketones and aldehydes; take 1 : 1 Ln–N complex as example – it formed the transition state A, and this continuely constituted the catalytic cycle (Scheme 6).

Conclusion

In summary, we reported two kinds of Ln–N complexes, studied carefully their catalytic application to cyanosilylation reaction, and proposed the mechanism. Further efforts towards the other catalytic applications of the complexes are underway.

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