ORGANOMETALLICS

Synthesis, Characterization, and Reactivity of Lanthanide Amides Incorporating Neutral Pyrrole Ligand. Isolation and Characterization of Active Catalyst for Cyanosilylation of Ketones

Fenhua Wang,^{†,§} Yun Wei,[†] Shaowu Wang,^{*,†,‡} Xiancui Zhu,[†] Shuangliu Zhou,[†] Gaosheng Yang,[†] Xiaoxia Gu,[†] Guangchao Zhang,[†] and Xiaolong Mu[†]

[†]Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, Institute of Organic Chemistry, School of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, P. R. China

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China

[§]College of Biological and Chemical Engineering, Anhui Polytechnic University, Wuhu, Anhui 241000, P. R. China

Supporting Information

ABSTRACT: A series of lanthanide amido complexes incorporating a neutral pyrrole ligand were synthesized and characterized, and their catalytic activities were studied. Treatment of $[(Me_3Si)_2N]_3Ln(\mu-Cl)Li(THF)_3$ with 1 equiv of $[(2,5-Me_2C_4H_2N)CH_2CH_2]_2NH(1)$ in toluene afforded the corresponding lanthanide amides with the formula $[\eta^5:\eta^1-(2,5-Me_2C_4H_2N)CH_2CH_2]_2NLn[N(SiMe_3)_2]_2$ (Ln = La (2), Nd (3)). Reaction of 2 or 3 with *N,N'*-dicyclohexylcarbodiimide (CyN=C=NCy) gave the carbodiimide selectively inserted into the appended Ln–N bond products formulated as CyNC{ $[N,N-(2,5-Me_2C_4H_2N)CH_2CH_2]_2N$ NCyLn $[N-(SiMe_3)_2]_2$ (Ln = La (4), Nd (5)). Reactions of the lanthanide amides with Me_3SiCN were also examined. A mixed reaction



of $[(Me_3Si)_2N]_3La(\mu-Cl)Li(THF)_3$, $[(2,5-Me_2C_4H_2N)CH_2CH_2]_2NH$ (1), and Me_3SiCN in toluene at room temperature produced the novel cyano bridged dinuclear lanthanum complex $\eta^5:\eta^1:\eta^3-[(2,5-Me_2C_4H_2NCH_2CH_2)_2N]La[N(SiMe_3)_2](\mu-CN)La[N(SiMe_3)_2]_3$ (6). The stoichiometric reactions of lanthanide amides 2 or 3 with Me_3SiCN produced the novel trinuclear lanthanum and neodymium complexes $\{(\eta^5:\eta^1-[(2,5-Me_2C_4H_2NCH_2CH_2)_2N]Ln[N(SiMe_3)_2](\mu-CN)\}_3$ (Ln = La (7), Nd (8)) through selective σ -bond metathesis reaction of the terminal Ln-N (N(SiMe_3)_2) bond with the Si-C bond of Me_3SiCN. On the basis of the stoichiometric reactions of complexes 2, or 3 with Me_3SiCN , complexes 2, 3, 4, 5, 7, and 8 as catalysts for cyanosilylation of ketones were investigated. Results indicated that these complexes displayed a high catalytic activity on addition of Me_3SiCN to ketones, and the activity of the complexes has the order of $7 \sim 8 > 2 \sim 3 \sim 4 \sim 5$. Thus, complex 7 or 8 was proposed as the active catalyst in the catalytic reaction for the precatalysts of 2 and 3.

INTRODUCTION

Cyanosilylation of carbonyl compounds is an efficient procedure for the synthesis of silylated cyanohydrins, which could be readily converted to synthetic and medicinal applicable functional compounds, such as α -hydroxy carbonyl compounds and β -amino alcohols.¹ Therefore, many efforts have been devoted to the development of synthesis for cyanohydrins. As a consequence, a number of catalysts including Lewis acids,² Lewis bases,³ and two-center catalysis⁴ have been reported for the catalytic cyanosilylation of carbonyl compounds using TMSCN. In recent years, several lanthanide compounds, such as triflates,⁵ lanthanide chlorides,⁶ and organometallic derivatives,⁷ have been used as catalysts for the addition of TMSCN to carbonyl compounds. Additionally, asymmetric versions for the catalytic cyanosilylations with lanthanide compounds have been developed.⁸ Although

different lanthanide compounds as precatalysts for catalytic cyanosilylation of carbonyl compounds were developed, less attention has been paid to isolate and characterize the active catalyst for the catalytic reaction.

It is documented that pyrrolyl ligands have been proved to be alternatives to cyclopentadienyl bonding with metal in an η^5 mode in one way, and the pyrrolyl ligands can bond with metal in an η^1 mode as donor ligand as well.⁹ It has been demonstrated that lanthanide complexes containing pyrrolide ligands having different structures displayed various reactivities with regard to polymerization of ε -caprolactone, methyl methacrylate, lactide, and isoprene,¹⁰ reduction of N₂,¹¹ and hydroamination of unsaturated bonds.¹² We have reported that

Received: September 7, 2014 Published: December 26, 2014



lanthanide amido complexes were able to catalyze additions of the N-H bond of the amines to carbodiimides,¹³ and hydrophosphonylations of aldehydes, unactivated ketones, and aldimines.¹⁴ The π -bonded neutral pyrrole rare-earth metal complexes incorporating a multipyrrolyl moiety or appended with a cyclopentadienyl anion have been reported.¹⁵ Recently, we reported a series of lanthanide amides containing a neutral pyrrole ligand in the constrained geometry architecture. These types of complexes exhibited a high activity with a high chemo- and regioselectivity on the catalytic addition of dialkyl phosphite to α,β -unsaturated carbonyl derivatives.¹⁶ As part of our continuous work on lanthanide amido complexes with a neutral pyrrole ligand, we herein report the synthesis and reactivity of rare-earth metal amides with neutral pyrrole ligands, together with their application as catalysts for cyanosilylation of ketones. The active catalyst was for the first time isolated and characterized, and the mechanism for the catalytic reaction was proposed on the basis of kinetic study.

RESULTS AND DISCUSSION

Synthesis and Characterization of Lanthanide Amides Incorporating Neutral Pyrrole Ligand. In an attempt to search for the synthesis and catalytic activity of neutral pyrrole supported sandwiched-type lanthanide complexes, a neutral pyrrole ligand $[(2,5-Me_2C_4H_2N)CH_2CH_2]_2NH$ (1) was prepared. Treatment of $[(Me_3Si)_2N]_3Ln(\mu-Cl)Li(THF)_3$ (Ln = La, Nd) with 1 equiv of $[(2,5-Me_2C_4H_2N)CH_2CH_2]_2NH$ (1) in toluene at 80 °C for 24 h afforded the rare-earth metal amido complexes $[\eta^{5}:\eta^{1}-(2,5-Me_2C_4H_2N)CH_2CH_2]_2NLn[N-(SiMe_3)_2]_2$ (Ln = La (2), Nd (3)) (Scheme 1) in good isolated yields.

X-ray analyses revealed that complexes 2 and 3 are isostructural organolanthanide bisamido complexes containing a neutral pyrrole ligand, and a representative structure diagram is shown in Figure 1. In complexes 2 and 3, the rare-earth metal



Figure 1. Representative molecular structure of complexes 2 and 3; hydrogen atoms are omitted for clarity.

adopts a distorted pseudotetrahedral geometry; only one neutral pyrrole is coordinated to the rare-earth metal ion in an η^5 mode and another neutral pyrrole is far away from the rare-earth metal ion. From Table 1, we can see that the usual

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of Complexes 2-3

	2	3
Ln(1)-N(1)	3.155(3)	3.118(4)
Ln(1)-C(1)	3.076(3)	3.019(4)
Ln(1)-C(2)	3.050(4)	2.987(4)
Ln(1)-C(3)	3.161(4)	3.102(4)
Ln(1)-C(4)	3.239(4)	3.194(4)
$Ln(1)-Pyr_{av}$	3.136(2)	3.084(4)
Ln(1)-Pyr _{cent}	2.910(2)	2.853(3)
Ln(1)-N(2)	2.336(2)	2.276(3)
Ln(1)-N(4)	2.386(2)	2.327(2)
Ln(1) - N(5)	2.400(2)	2.341(2)
Pyr_{cent} -Ln(1)-N(2)	81.1(1)	82.2(1)
Pyr_{cent} -Ln(1)-N(4)	140.7(1)	139.2(1)
Pyr_{cent} -Ln(1)-N(5)	102.3(1)	103.2(1)
N(2)-Ln(1)-N(4)	104.0(1)	103.2(1)
N(4)-Ln(1)-N(5)	109.0(1)	109.8(1)
C(8)-N(2)-Ln(1)	123.5(2)	122.3(3)

consequence of the contraction of the ionic radius of the Ln³⁺ ions is reflected by Ln–N(2) distances of 2.336(2) Å in **2**, and 2.276(3) Å in **3**. The similar results can be found in the Ln–Pyr_{cent} distances of 2.910(2) Å in **2**, and 2.853(3) Å in **3**. The Ln–Pyr_{cent} distances of **2** and **3** are longer than the corresponding values in the structures of $[\eta^5:\eta^1-(N-C_6H_5N-CH_2CH_2)(2,5-Me_2C_4H_2N)]Ln[N(SiMe_3)_2]_2$ (2.847(5) Å for La–Pyr_{cent} and 2.793(3) Å for Nd–Pyr_{cent}).¹⁶

Reactivity of the Lanthanide Amido Complexes. Recently, insertions of carbodiimides into the lanthanideligand bonds have been extensively studied. $^{17}\ {\rm To}\ {\rm gain}\ {\rm more}$ insight into the selectivity of the above complexes with different Ln-N bonds (appended Ln-N and terminal Ln-N bonds), reactions of complexes 2 or 3 with N,N'-dicyclohexylcarbodiimide (Scheme 1) were studied. It was found that the reaction 2 or 3 with N,N'-dicyclohexylcarbodiimide produced complexes 4 and 5 through the carbodiimide selectively inserting into the appended Ln-N bond. The central metal in complexes 4 and 5 is coordinated by a monoanionic guanidinate ligand and two $N(SiMe_3)_2$ (Figure 2). The bond distances of C23–N4 and C23-N5 of the guanidinate group are approximately equivalent, but significantly shorter than the C-N single bond distances, indicating electrons delocalization within N-C-N of the guanidinate unit. The Ln-N4 and Ln-N5 distances, 2.475(2) and 2.489(2) Å in 4, 2.430(2) and 2.420(2)



Figure 2. Representative molecular structure of complexes 4 and 5; all hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): (4) La1–N4, 2.475(2); La1–N5, 2.489(2); La1–N6, 2.367(2); La1–N7, 2.375(2); C23–N4, 1.331(3); C23–N5, 1.332(3); N5–C23–N4, 115.6(2). (5) Nd1–N4, 2.429(19); Nd1–N5, 2.419(19); Nd1–N6, 2.310(2); Nd1–N7, 2.320(2); C23–N4, 1.334(3); C23–N5, 1.335(3); N5–C23–N4, 115.4(2).

Å in 5, are between the values observed for the Ln-N single bond distance and the Ln-N donor bond distance.^{16,18}

The cyano bridged lanthanide complexes were previously reported by reductions of samarium(II) complexes with cyclohexyl isocyanide and *tert*-butyl isocyanide,¹⁹ or by reactions of sterically crowded complexes (C_5Me_5)₃Ln (Ln = Sm, Pr, La) with *tert*-butyl isocyanide or Me₃SiCN;²⁰ these reactivities involve reduction of C–C or C–Si bonds. Reactions of dimeric isocyanotrimethylsilyl amido complexes { $(C_5Me_5)_2$ -La[μ -N(SiMe₃)NC]}₂ with Me₃SiCN,²¹ or reactions of (C_5Me_5)₂CeI with NⁿBu₄CN,²² or reaction of (C_5Me_5)₂SmCH-(SiMe₃)₂ with N-benzylidene(trimethylsilyl)amine with 20 psi H₂ at 90 °C also produced the cyanide bridged lanthanide complexes.²³ However, the reactivity of lanthanide amides supported by neutral pyrrole ligands with Me₃SiCN has not been developed to date.

A mixed reaction of $[(Me_3Si)_2N]_3La(\mu-Cl)Li(THF)_3$ with $[(2,5-Me_2C_4H_2NCH_2CH_2)_2N]$ (1) and Me_3SiCN was first tested, and a novel cyano bridged dinuclear lanthanum complex $\eta^5:\eta^1:\eta^3-[(2,5-Me_2C_4H_2NCH_2CH_2)_2N]La[N(SiMe_3)_2](\mu-CN)-La[NSi(Me_3)_2]_3$ (6) was isolated (Scheme 2). The result indicated that a σ -bond metathesis reaction between the La-N $[(N(SiMe_3)_2]$ bond and Me_3SiCN could happen. Stoichiometric reactions of **2** or **3** with Me_3SiCN were then carried out with isolation of the novel cyano bridged neutral pyrrole supported trinuclear complexes 7 and 8 formulated as $\{(\eta^5:\eta^1-[(2,5-Me_2C_4H_2NCH_2CH_2)_2N]Ln[(NSiMe_3)_2](\mu-CN)\}_3$ (Ln = La, Nd) (Scheme 3).

X-ray analysis revealed that complex 6 is a dinuclear complex having a CN ligand in bridged ways bonding with metals

(Figure 3). The La–CN–La is almost linearly with La(1)– C(23)–N(5) and La(2)–N(5)–C(23) angles of 174.9(3)° and 176.9(3)°. The bond distances of La–Pyr(1) [N(1), C(2)– C(4)] range from 2.984(4) to 3.179(3) Å with an average distance 3.084(3) Å. These values are considered to represent an η^5 bonding mode of the neutral pyrrole ligand with lanthanum ion. The corresponding distances of 3.436(3) Å for La(1)–N(3), 3.429(3) Å for La(1)–C(11) in La–Pyr(2) [N(3), C(11)–C(14)] are significantly longer than those distances of 3.152(3) Å for La(1)–C(12), 2.980(3) Å for La(1)–C(13), and 3.168(3) Å for La(1)–C(14), indicating that the neutral Pyr(2) bonded with the metal in an η^3 mode. To our best knowledge, it represents the first example of a cyano bridged dinuclear lanthanide complex incoporating the neutral pyrrole ligand bonded with metal in $\eta^5:\eta^1:\eta^3$ modes.

Complexes 7 and 8 crystallize as trimers, composed of LLnN(SiMe₃)₂ units bridged by the cyanide ligand (Figure 4). The bond distances of La–Pyr(1) [N(1), C(2)–C(4)] range from 2.972(4) to 3.146(3) Å in 7, indicating the η^{5} bonding mode of this neutral pyrrole to the metal ion, and another pyrrole is far away from the rare-earth metal. A similar result was found in complex 8. The seven-coordinate Ln³⁺ ions are ligated by one neutral pyrrole, one amido ligand, one appended amido group, and two cyanide ligands. The 1.145(4) Å of N(5)–C(23) (CN group) in 7 is comparable to the corresponding average distances of 1.164(4) Å in [(C₅Me₅)₂-La(μ -CN)(NC-SiMe₃)]₃, and 1.147(6) Å in [(C₅Me₅)₂La(μ -CN)(Me₃SiCH₂NC)]₃.²¹ The angles of La(1)–C(23)–N(5) and La(2)–N(5)–C(23) in 7 are 162.1(4)° and 177.0(1)°, approaching linearity, and the analogous angles of 163.5(4)° and 175.9(4)° in 8 are found.

Catalytic Additions of Trimethylsilylcyanide to Ketones Catalyzed by Lanthanide Amides Incorporating Neutral Pyrrole Ligand. As evidenced by the above results of stoichiometric reactions of lanthanide amido complexes with Me₃SiCN, the addition of Me₃SiCN to acetophenone was first investigated in the presence of 1 mol % of complex 2 (Table 2). The yields of the product can be improved from 48% to 97% by prolonging the reaction time from 0.5 to 2 h (Table 2, entries 1-3). It is found that the cvanosilvlation of acetophenone could also be accomplished in toluene at room temperature within 2 h, producing the product in 95% yield with a 0.1 mol % catalyst loading (Table 2, entry 4). However, further decreasing the catalyst loadings to 0.05 mol % led to a low yield of product (entry 5). It is found that complex 2 displayed a similar catalytic activity in toluene, THF, or n-hexane (see Table 2, entries 4, 6, 7, 8), indicating solvents suitability of the catalyst. It was interesting to find that a high yield of product was also obtained under solvent-free conditions (entry 9). Then, the following catalytic reactions were performed using 0.1 mol % of rare-earth metal complexes, at room temperature under solvent-free conditions for 2 h.





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Figure 3. Molecular structure of complex 6; hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): La1–N1, 3.179(3); La1–C1, 3.153(3); La1–C2, 3.027(3); La1–C3, 2.984(4); La1–C4, 3.080(3); La1–N3, 3.436(3); La1–C11, 3.429(3); La1–C12, 3.152(3); La1–C13, 2.980(3); La1–C14, 3.168(3); La1–C12, 3.152(3); La1–C13, 2.980(3); La1–C14, 3.168(3); La1–Pyr_{cent}(1), 2.855(3); La1–C23, 2.659(3); C23–N5, 1.158(5); N5–C23–La1, 176.9(3); C23–N5–La2, 174.9(3).



Figure 4. Representative molecular structure of complexes 7 and 8; all hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): (7) La1–C1, 3.146(4); La1–C2, 3.062(4); La1–C3, 2.973(4); La1–C4, 2.997(3); La1–N1, 3.104(3); La1–C23, 2.624(3); C23–N5, 1.145(4); La1–Pyr_{cent}(1), 2.826(3); N5–C23–La1, 162.1(4); C23–N5–La2, 177.0(1). (8) Nd1–C1, 2.965(4); Nd1–C2, 2.925(4); Nd1–C3, 3.019(4); Nd1–C4, 3.133(5); Nd1–N1, 3.087(3); Nd1–C23, 2.574(4); C23–N5, 1.140(4); Nd1–Pyr_{cent}(1), 2.972(4); N5–C23–Nd1, 163.5(4); C23–N5–Nd2, 175.9(4).

Table 2. Cyanosilylation of Acetophenone Catalyzed by Complex 2 under Various Conditions a

	\bigcirc	Me + Me ₃	SiCN <u>C</u> i	Me ₃ SiO	< ^{CN} Me
entry	cat.	loading (mol %)	time (h)	solvent	yield $(\%)^b$
1	2	1	0.5	toluene	48
2	2	1	1	toluene	70
3	2	1	2	toluene	97
4	2	0.1	2	toluene	95
5	2	0.05	2	toluene	80
6	2	0.1	2	hexane	95
7	2	0.1	2	diethyl ether	89
8	2	0.1	2	THF	96
9	2	0.1	2	solvent free	98
^a React	ion co	onditions: acetor	henone (S	.0 mmol). TN	MSCN (6.0

mmol), solvent (2 mL) or solvent free, room temperature. ^bIsolated yields.

Under the optimized reaction conditions, we next examined the substrate scope of the cyanosilylation reaction, and the results are presented in Table 3. As shown in the table, the optimized catalytic system worked excellently for aliphatic ketones and alicyclic ketones (entries 1-5). Next, the scope of the substrates were expanded to various aromatic ketones. The phenyl ring with substituents having electron-donating groups, such as CH₃, CH₃O, and NH₂, produced the cyanosilylation products in good to excellent yields (89–98%, entries 7–12) regardless of the ortho- or para-substituents. The phenyl ring with substituents having electron-withdrawing groups, such as Cl and Br, have a little influence on the outputs of the reaction (entries 13–16), but strong electron-withdrawing groups, such as NO₂ and F, produced the products in moderate yields. When conjugated ketones such as 4-phenyl acetophenone, benzophenone, or chalcone were employed in the reactions, the cyanohydrins were also isolated in moderate yields (entries 21, 22, and 24). These results indicated that the catalysts displayed a high catalytic activity on addition of Me₃SiCN to ketones with a wide substrates scope under mild conditions.

Kinetic Study of the Catalytic Reaction. A kinetic study for the reaction of TMSCN with acetophenone catalyzed by different catalysts under the above conditions was carried out. Figure 5 shows the yields of cyanohydrins versus reaction time. From the figure, we can get following information: (1) The catalytic reactions are very fast, and all catalysts surveyed can Table 3. Results of Cyanosilylation of Ketones with TMSCN by Catalyst 2^{a}

^1	$\bigcup_{R^2}^{O} + Me_3SiCN = \frac{0.1 \text{ mol } 9}{\text{ solvent}}$	6 Cat. Me₃Si ► -free R ¹	
entry	ketone	product	yield (%) ^b
1	CH ₃ COCH ₃	9a	99
2	CH ₃ CH(CH ₃)CH ₂ COCH ₃	9b	98
3	CH ₃ CH ₂ COCH ₂ CH ₃	9c	98
4	cyclohexanone	9d	98
5	cyclopentanone	9e	99
6	C ₆ H ₅ COCH ₃	9f	98
7	2-MeC ₆ H ₄ COCH ₃	9g	89
8	2- H ₂ NC ₆ H ₄ COCH ₃	9h	91
9	3-MeOC ₆ H ₄ COCH ₃	9i	97
10	4-MeC ₆ H ₄ COCH ₃	9j	98
11	4-MeOC ₆ H ₄ COCH ₃	9k	97
12	2,5-(MeO) ₂ C ₆ H ₃ COCH ₃	91	90
13	3-ClC ₆ H ₄ COCH ₃	9m	98
14	3-BrC ₆ H ₄ COCH ₃	9n	96
15	4-BrC ₆ H ₄ COCH ₃	90	97
16	2,4-Cl ₂ C ₆ H ₃ COCH ₃	9p	89
17	4-FC ₆ H ₄ COCH ₃	9q	81
18	2-O ₂ NC ₆ H ₄ COCH ₃	9r	73
19	3-O ₂ NC ₆ H ₄ COCH ₃	9s	80
20^{c}	4-O ₂ NC ₆ H ₄ COCH ₃	9t	78
21	4-PhC ₆ H ₄ COCH ₃	9u	75
22	PhCOPh	9v	78
23	(E)-PhCH=CHCOCH ₃	9w	89
24	(E)-PhCH=CHCOPh	9x	70

^{*a*}Reaction conditions: acetophenone (5.0 mmol), TMSCN (6.0 mmol), catalyst loading (0.1 mol %), solvent free, room temperature. ^{*b*}Isolated yields. ^{*c*}The product of this reaction was characterized by X-ray.



Figure 5. Plot of the yield of cyanohydrins versus reaction time by different catalysts. The reaction was performed by treating acetophenone (5.0 mmol) with TMSCN (6.0 mmol) at room temperature under solvent-free conditions.

catalyze the reaction to reach a high isolated yield of products in less than 180 min. (2) Complexes 7 and 8 have similar catalytic activities, which are higher than those of complexes 2-5, and the $[(Me_3Si)_2N]_3La(\mu-Cl)Li(THF)_3$ displayed the lowest activity. (3) The differences in catalytic activities can be mainly attributed to ligand effects; complexes 2 and 3 have an electron-rich neutral pyrrole bonding with the metals. The differences in catalytic activities between 7 or 8, and 2, or 3 can be explained by the evidence that 2 or 3 should react with TMSCN at first to produce the "Ln-CN" motif, which was then transferred acetophenone to produce the final product, in other words, the catalytic reactions catalyzed by 2 or 3 require a initiation step to produce the "Ln-CN" motif. Thus, complex 7 or 8 was proposed as the active catalyst for the precatalyst 2 or 3 in the catalytic cycle. For preparation convenience (7 and 8 should be prepared by further reaction), complex 2 was selected as the catalyst for the above study of the scope of the cyanosilylation reaction of ketones.

¹H NMR Probe the Catalytic Reaction. Complexes 7 and 8 containing the "Ln-CN" motif displayed the highest catalytic activity (Figure 5) on addition of Me₃SiCN to ketones, which was proposed as the active catalyst for the precatalyst 2 or 3 in the catalytic cycle. In order to get more support for the catalytic mechanism, the reaction of 7 with acetophenone was monitored by ¹H NMR spectroscopy in THF- d_8 at room temperature. When 7 was reacted with excess acetophenone for 30 min, the clear resonances of the methyl proton resonances appeared at about 2.59 and 1.85 ppm (see the Supporting Information), which can be assigned as the methyl protons of the coordinated acetophenone (intermediate A as indicated in Scheme 4) and the methyl protons after the addition of the CN group to carbonyl (intermediate B as indicated in Scheme 4).

Scheme 4. Proposed Mechanism for the Catalytic Reactions



We have tried several times to prepare the complexes of the type LRE(CN)₂ by reactions of 7 or 8 with Me₃SiCN, but no such kinds of complexes could be isolated. Then, the catalytic reaction was simulated in a NMR tube with excess Me₃SiCN in THF- d_8 at room temperature. The resonances of the methyl proton of acetophenone had almost disappeared after 30 min, showing that acetophenone nearly quantitatively converted into the catalytic product, but the methyl protons of N(SiMe₃)₂ and

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excess Me₃SiCN were found (see the Supporting Information), which indicated that the $N(SiMe_3)_2$ group in 7 or 8 did not transfer to CN in the catalytic cycle.

On the basis of these experimental results, a plausible pathway of the catalytic reaction is proposed as follows (Scheme 4): interaction of catalyst with cyanotrimethylsilane Me_3SiCN produced the active catalyst 7 or 8, which coordinated by ketone to afford intermediate A, resulting in greater electron deficiency on the carbon atom of ketone after the O atom of ketone coordinated with the metal. Addition of the CN group to carbonyl carbon gave intermediate B, which then interacted with cyanotrimethylsilane to produce the final products and the active catalyst, finishing a catalytic cycle.

CONCLUSION

In summary, we have described the synthesis, characterization, and reactivity of new lanthanide complexes with a neutral pyrrole ligand. Reactivity studies showed that the complexes have different reactivity patterns depending on the steric and electronic properties of the substrates. Reactions of the neutral pyrrole complexes with carbodiimide produced the insertion product through the appended amido group of the supporting neutral pyrrole ligand. Reactions of the lanthanide amides with Me₃SiCN afforded the novel neutral pyrrole ligand supported cyanide bridged dinuclear lanthanum complex and cyanide bridged trinuclear complexes through σ -bond metathesis of the terminal Ln-N (N(SiMe₃)₂) bond with Me₃SiCN. They represent the first example of cyanide bridged organolanthanide complexes supported by neutral pyrrole ligands. All the new complexes displayed a high catalytic activity on addition of Me₃SiCN to ketones with a wide substrates scope and very good solvents compatibility and a low catalyst loading (0.1 mol %) under mild conditions. Results of kinetic study indicated the cyanide bridged trinuclear complexes 7 and 8 have similar catalytic activities, which are higher than those of complexes 2-5 and $([(Me_3Si)_2N]_3La(\mu-Cl)Li(THF)_3)$. The trinuclear cyanide bridged complexes were proposed as the active catalyst in the catalytic cycle on the basis of kinetic and probing experimental results. It represents the first example of lanthanide cyanide as catalyst for the catalytic addition of Me₃SiCN to ketones. This work implies that, although different precatalysts for the catalytic addition of Me₃SiCN to ketones were developed, the active catalysts and catalytic mechanism for the reaction may be different, as evidenced by the results of reactions of different lanthanide amides with Me₃SiCN producing different cyanide bridged complexes (complexes 6, 7, or 8); it still remains to be investigated. Further investigations in this field using organolanthanide complexes are now in progress.

EXPERIMENTAL SECTION

General Procedure. All synthesis and manipulations of air- and moisture-sensitive materials were performed under dry argon and an oxygen-free atmosphere using standard Schlenk techniques or in a glove-box. All solvents were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. $[(Me_3Si)_2N]_3Ln(\mu-Cl)Li(THF)_3$ (Ln = La, Nd) were prepared according to literature methods.²⁴ Elemental analyses data were obtained on a PerkinElmer 2400 Series II elemental analyzer. ¹H NMR and ¹³C NMR spectra for analyses of compounds were recorded on a Bruker AV-300 NMR spectrometer (300 MHz for ¹H; 75 MHz for ¹³C) and a Bruker AV-500 NMR spectrometer (500 MHz for ¹H; 125 MHz for ¹³C). Chemical shifts (δ) were reported in ppm. J values are reported in Hz. IR spectra were recorded on a Shimadzu FTIR-8400s

spectrometer (KBr pellet). Mass spectra were performed on a Micromass GCT–MS spectrometer.

Preparation of (2,5-Me₂C₄H₂NCH₂CH₂)₂NH (HL). Diethylenetriamine (5.2 g, 0.05 mol), acetonylacetone (11.4 g, 0.10 mol), and sufficient toluene were placed in a round-bottom flask with a water separator and refluxed overnight. The water produced during the reaction was removed as a toluene azeotrope. The toluene was removed in vacuo after the reaction was completed. Recrystallization of crude product from hexane and ethyl acetate (1:2) gave the product (HL) (11.0 g, 85% yield). mp: 76–78 °C. ¹H NMR (300 MHz, CDCl₃): δ 5.76 (s, 4H, pyr), 3.84 (m, 4H, CH₂pyr), 2.80 (m, 4H, CH₂NCH₂), 2.22 (s, 12H, CH₃). ¹³C NMR (75.0 MHz, CDCl₃): δ 127.9, 105.6, 50.3, 44.0, 12.9. IR (KBr pellets, cm⁻¹): ν 3311 (s), 3093 (s), 2887 (m), 2825 (m), 2735 (w), 2690 (w), 1672 (m), 1573 (s), 1517 (s), 1406 (s), 1298 (s), 1122 (s), 1002 (m), 839 (m), 765 (m), 688 (m). *m*/*z*: calcd for C₁₆H₂₆N₃ (M + H⁺) 260.2126; Found: 260.2126.

Preparation of $[\eta^5:\eta^1-(2,5-Me_2C_4H_2NCH_2CH_2)_2N]La[N (SiMe_3)_2]_2$ (2). To a toluene solution (20 mL) of $[(Me_3Si)_2N]_3La$ - $(\mu$ -Cl)Li(THF)₃ (1.05 g, 1.20 mmol) was slowly added the toluene solution (10.0 mL) of (2,5-Me₂C₄H₂NCH₂CH₂)₂NH (HL) (0.31 g, 1.20 mmol). The reaction mixture was stirred at room temperature for 6 h, it was then stirred at 80 °C for 24 h. The solvent was evaporated and the solid was extracted with hexane $(2 \times 15 \text{ mL})$. The extraction was combined and concentrated to about 10 mL. Pale yellow crystals were obtained upon standing the solution at 0 °C for several days (0.67 g, 78%). mp: 184–187 °C. ¹H NMR (300 MHz, C₆D₆): δ 5.95 (s, 4H, pyr), 3.19 (t, J = 6.0 Hz, 4H, CH₂), 3.18 (t, J = 6.0 Hz, 4H, CH₂), 2.00 (s, 12H, CH₃), 0.35 (s, 36H, CH₃). ¹³C NMR (75.0 MHz, C_6D_6): δ 129.4, 106.8, 53.4, 44.5, 12.9, 5.1. IR (KBr pellet, cm⁻¹): ν 3311 (s), 3093 (m), 2887 (m), 2825(m), 1672 (w), 1573 (w), 1517 (s), 1467 (s), 1406 (s), 1292 (w), 1213 (m), 1122 (s), 1018 (m), 852 (m), 765 (s), Anal. Calcd for C₂₈H₆₀LaN₅Si₄: C, 46.83; H, 8.42; N, 9.75, Found: C, 46.79; H, 8.34; N, 9.64.

Preparation of $[η^5:η^1-(2,5-Me_2C_4H_2NCH_2CH_2)_2N]Nd[N-(SiMe_3)_2]_2$ (3). This compound was isolated as blue crystals in 75% (0.57 g) yield by treatment of $[(Me_3Si)_2N]_3Nd(\mu-CI)Li(THF)_3$ (0.93 g, 1.05 mmol) with $(2,5-Me_2C_4H_2NCH_2CH_2)_2NH$ (0.27 g, 1.05 mmol) following the procedures similar to those used for preparation of 2. mp: 175–178 °C. IR (KBr pellets, cm⁻¹): ν 3068 (w), 2929 (s), 2852 (s), 1612 (m), 1587 (m), 1552 (m), 1504 (s), 1446 (s), 1348 (m), 1255 (s), 1236 (m), 1166 (s), 1083 (s), 933 (s), 889 (s), 837 (m), 754 (s), 696 (m). Anal. Calcd for $C_{28}H_{60}N_5NdSi_4$: C, 46.49; H, 8.36; N, 9.68. Found: C, 46.31; H, 8.30; N, 9.45.

Preparation of CyNC{[*N*,*N*-(2,5-Me₂C₄H₂N)CH₂CH₂]₂N}NCyLa-[N(SiMe₃)₂]₂ (4). To a 20 mL toluene solution of 2 (0.43 g, 0.6 mmol) was added *N*,*N'*-dicyclohexylcarbodiimide (0.12 g, 0.6 mmol) in room temperature. After it was stirred for 30 min, the reaction mixture was slowly warmed to 50 °C and stirred for 12 h. The solvent was removed under vacuum to give an orange powder. Recrystallization of the powder from hexane gave 4 as pale yellow crystals. Yield: 0.432 g (78%). mp: 83–84 °C. ¹H NMR (500 MHz, C₆D₆): δ 6.14 (s, 4H, pyr), 3.67–3.64 (m, 4H, CH₂), 3.15–3.11 (m, 4H, CH₂), 2.22 (s, 12H, CH₃), 1.84–1.25 (m, 22H, C₆H₁₁), 0.46 (s, 36H, CH₃). ¹³C NMR (125.7 MHz, C₆D₆): δ 167.5, 126.6, 106.9, 56.2, 50.2, 42.2, 38.6, 26.3, 12.7, 4.1. IR (KBr pellet, cm⁻¹): ν 2850 (m), 2360 (m), 2339 (m), 1633 (m), 1404 (m), 1313 (s), 1300 (s), 1016 (s), 754 (s). Anal. Calcd for C₄₁H₈₂LaN₇Si₄: C, 53.27; H, 8.94; N, 10.61, Found: C, 53.14; H, 9.14; N, 10.69.

Preparation of CyNC{[*N*,*N*-(**2**,**5**-Me₂C₄H₂N)CH₂CH₂]₂N}-NCyNd[N(SiMe₃)₂]₂ (**5**). Using the procedure described for 4, the reaction of 3 (0.49 g, 0.68 mmol) and *N*,*N*'-dicyclohexylcarbodiimide (0.14 g, 0.68 mmol) in toluene afforded **5** as blue crystals. Yield: 0.467 g (74%). mp: 80–82 °C. IR (KBr pellets, cm⁻¹): ν 2924 (w), 2850 (m), 1631 (w), 1521 (s), 1448 (s), 1406 (w), 1290 (s), 1180 (s), 1139 (s), 1016 (m), 933 (m), 887 (m), 842 (m), 754 (w). Anal. Calcd for C₄₁H₈₂N₇NdSi₄: C, 52.97; H, 8.89; N, 10.55. Found: C, 52.95; H, 9.26; N, 10.61.

Preparation of $[\eta^5:\eta^1:\eta^3-(2,5-Me_2C_4H_2NCH_2CH_2)_2N]La[N-(SiMe_3)]_2(\mu-CN)La[N(SiMe_3)_2]_3$ (6). A Schlenk flask was charged

with $[(Me_3Si)_2N]_3La(\mu-Cl)Li(THF)_3$ (1.77 g, 2.00 mmol), (2,5-Me_2C_4H_2NCH_2CH_2)_2NH (0.26 g, 1.00 mmol), toluene solution (30 mL), and TMSCN (0.125 mL, 1.00 mmol). The mixture was stirred at room temperature for 4 h, the solvent was evaporated under reduced pressure, and the residues were extracted with hexane (15 mL). Crystals were obtained upon standing the solution at 0 °C for several days (0.48 g, 53%). mp: 90–92 °C. ¹H NMR (500 MHz, toluene-*d*₈): δ 5.92 (s, 4H, pyr), 3.32–3.30 (m, 4H, CH₂), 2.25–2.08 (m, 4H, CH₂), 2.08 (s, 12H, CH₃), 0.08 (s, 72H, CH₃). ¹³C NMR (125 MHz, toluene-*d*₈): δ 129.1, 128.2, 106.4, 50.2, 43.9, 12.7, 2.6. IR (KBr pellets, cm⁻¹): 3290 (s), 2953 (s), 2816 (m), 2081 (s), 1571 (s), 1517 (m), 1463 (m), 1408 (w), 1301 (w), 1251 (w), 1182 (m), 1126 (s), 1004 (s), 933 (w), 889 (m), 842 (m), 765 (s). Anal. Calcd for C₄₁H₉₆La₂N₈Si₈: C, 40.91; H, 8.04; N, 9.31. Found: C, 40.77; H, 8.28; N, 9.16.

Preparation of {[η^5 : η^1 -(2,5-Me₂C₄H₂NCH₂CH₂)₂N]La[N-(SiMe₃)₂](μ-CN)}₃ (7). To a 20 mL toluene solution of 2 (0.73 g, 1.01 mmol) was added TMSCN (0.126 mL, 1.01 mmol) at room temperature. After it was stirred for 4 h, the solvent was removed under vacuum to give a viscous oil. It was extracted with hexane (15 mL) and was obtained as yellow crystals (0.400 g, 68%). mp: 118–120 °C. ¹H NMR (500 MHz, toluene- d_8): δ 6.03 (s, 12H, pyr), 3.31–3.30 (m, 12H, CH₂), 3.05–3.03 (m, 12H, CH₂), 2.20 (s, 36H, CH₃), 0.32 (d, 54H, CH₃). ¹³C NMR (75 MHz, THF- d_8): δ 129.1, 127.6, 106.1, 51.2, 44.8, 12.8, 2.8. IR (KBr pellets, cm⁻¹): 2945 (m), 2887 (m), 2823 (s), 1517 (s), 1467 (m), 1406 (m), 1365 (s), 1300 (m), 1251 (s), 1182 (s), 1124 (s), 1018 (m), 933 (m), 887 (s), 840 (m). Anal. Calcd for C₆₉H₁₂₆N₁₅La₃Si₆: C, 47.33; H, 7.25; N, 12.00. Found: C, 46.94; H, 7.53; N, 11.75.

Preparation of {[$η^5:η^1-(2,5-Me_2C_4H_2NCH_2CH_2)_2N$]Nd[N-(SiMe_3)_2](μ-CN)}₃ (8). The synthesis of 8 was carried out in the same way as that for the synthesis of 7, but 3 (0.79 g, 1.10 mmol) and TMSCN (0.137 mL, 1.10 mmol) was used. Yield: 0.48 g (75%). mp: 110–112 °C. IR (KBr pellets, cm⁻¹): 3290 (m), 3099 (m), 2954 (w), 2726 (s), 2113 (s), 1517 (s), 1463 (m), 1406 (w), 1365 (m), 1301 (m), 1253 (m), 1215 (s), 1182 (s), 1058 (s), 1018 (s), 844 (m). Anal. Calcd for C₆₉H₁₂₆N₁₅Nd₃Si₆: C, 46.90; H, 7.19; N, 11.89. Found: C, 46.94; H, 7.21; N, 11.80.

General Experimental Procedure for Cyanosilylation of Ketones. Under an argon atmosphere, an oven-dried 20.0 mL Schlenk flask equipped with a magnetic stir bar was charged with the acetophenone (0.58 mL, 5 mmol) and catalyst 2 (3.4 mg, 0.005 mmol). TMSCN (0.75 mL, 6 mmol) was added, and the resulting mixture was stirred under solvent-free conditions for 2 h. After completion, the crude product was purified by column chromatography on silica gel using ether/petroleum ether (1/20, V/V) as an eluent. The desired 2-trimethylsilyloxy-2-phenylpropanenitrile was obtained as a colorless oil (1.07 g, 98% yield).

Crystal Structure Determinations. Suitable crystal of complexes **2–8** was each mounted in a sealed capillary. Diffraction was performed on a Burker SMART CCD area detector diffractometer using graphite-monochromated Mo–K α radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using the SADABS program.²⁵ All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.²⁶ CCDC numbers 994786–994792 for complexes **2–8** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac. uk/data request/cif.

ASSOCIATED CONTENT

Supporting Information

Full experimental details, characterization data for new compounds, crystallographic data and refinements for complexes 2–8, and X-ray crystallographic files, in CIF format, for structure determination of complexes 2–8. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: swwang@mail.ahnu.edu.cn (S.W.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was co-supported by the National Natural Science Foundation of China (Grant Nos. 21432001, 21372010, 21202002, 21372009), the National Basic Research Program of China (2012CB821604), and grants from Anhui Normal University.

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