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Synthesis, structure, and catalytic activity of rare-earth metal amides with a neutral pyrrolyl-functionalized indolyl ligand

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The reactions of neutral pyrrolyl-functionalized indole with rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ produced the rare-earth metal complexes $[(Me_3Si)_2N]_2RE([\eta^1: \mu\text{-}\eta^2\text{-}3\text{-}(2\text{-}(N\text{–}CH_3)C_4H_3NCH{=}N\text{–}CH_2CH_2)C_8H_5N])(\mu\text{-}Cl)Li(THF)$ (RE = Er, Y) having indolyl ligand η^1 bonded to rare-earth metal ion and η^2 bonded to lithium ion. The catalytic activities of these lanthanide amido complexes for addition of terminal alkynes to aromatic nitriles were explored. Results reveal that these complexes displayed a good catalytic activity for the addition reaction under mild conditions.

terminal alkyne, aromatic nitrile, ynone, rare-earth metal

1 Introduction

Conjugated ynones are important building blocks widely found in bioactive and synthetic materials [1–4] and are important synthons in synthetic chemistry especially for syntheses of heterocylic compounds [5–9]. Development of synthetic methods for the prepration of an ynones system based on transition metal-catalyzed cross-coupling reactions has attracted much attention, and several successful methods are documented. Original works started from reactions of aryl derivatives and terminal alkynes under CO atmosphere in the presence of palladium catalysts. The aryl halides were used in the reactions from the very beginning; aryl triflates or aryl amines were developed as substrates [10–17]. The method by which alkynyl carboxylic acids reacted with aryl iodides under a CO atmosphere in the presence of a palladium catalyst through decarboxylative coupling is noteworthy [18]. Another method started from reactions of terminal alkynes and acyl chlorides with employment of a palladium catalyst system [19–25]. Corrosive acyl chlorides or strictly prepared carbon monoxide as substrates, as well as indispensable stoichiometric amounts of bases, should be used in this method. A method for avoiding the use of bases was developed, based on an iron-catalyst system for the coupling reactions between the silylated alkynes and acyl chlorides for the preparation of ynones [26], but this reaction requires low temperature (–15 °C), and must be carried out in toxic $MeNO_2$. The direct additions of terminal alkynes to aromatic nitriles to produce conjugated ynones in the presence of lanthanide amides as catalysts were reported very recently [27, 28]; to date, these are only two reports based on rare-earth metal catalysts. Thus the need to development of new rare-earth catalysts for the preparation of conjugated ynones by reaction of aromatic nitriles with terminal alkynes remains.

Because electronic and steric properties of the amido

Dedicated to Professor Qian Changtao on the occasion of his 80th birthday.
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ligand can be easily tuned, trivalent rare-earth-metal amido complexes have been reported to show broaden applications in catalytic transformations of unsaturated compounds [29–37] or as catalysts in synthetic chemistry [38–44]. Recently, due to their bonding capability, functionalized pyrroles and indoles have received particular attention as versatile ligands in rare-earth metal chemistry, and are anticipated as alternatives to cyclopentadienyl or indenyl ligands [45–49]. In our recent studies, we found that reactions of different functionalized pyrroles or indoles with rare-earth metal amides displayed different bonding modes and different reactivities. Reactions of 3-*t*-butylimino-functionalized indole with rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Yb, Y) produced novel rare-earth metal complexes containing an unusual indolyl-1,2-dianion bonded to the metals in a novel η^1:(μ_2-η^1:η^1) mode through imino-directed C–H bond activation [50]. In addition, the reaction of $[(Me_3Si)_2N]_3Ln^{III}(\mu\text{-}Cl)Li(THF)_3$ with 2 equiv. of $3\text{-}(CyNHCH_2)C_8H_5NH$ in toluene produced the amino-coordinate-lithium bridged bis(indolyl) lanthanide amides $[\mu\text{-}\{[\eta^1:\eta^1:\eta^1:\eta^1\text{-}3\text{-}(CyNHCH_2)Ind]_2Li\}RE[N(SiMe_3)_2]_2]$ (Cy = cyclohexyl, Ind = Indolyl) [51]. Recently, we found that reaction of 2-(2,6-diisopropylphenylaminomethylene) indole $2\text{-}(2,6\text{-}{}^iPr_2C_6H_3NHCH_2)C_8H_5NH$ with europium amide $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ afforded a novel europium(II) complex formulated as $\{[\mu\text{-}\eta^6:\eta^1:\eta^1\text{-}2\text{-}(2,6\text{-}{}^iPr_2C_6H_3N{=}CH)C_8H_5N]Eu[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3N{=}CH)\text{-}C_8H_5N]\}_2$ and having a bridged indolyl ligand in novel μ-η^6: η^1:η^1 hapticities with the reduction of europium(III) to europium(II), oxidation of the amino to imino groups. In addition, reactivity studies led to findings of novel bonding modes of the indolyl ligands with europium(II) metal [52]. We also found that reactions of *N*-((1*H*-pyrrol-2-yl)-methylene)-2-(1*H*-indol-3-yl)-ethanamine $3\text{-}(2\text{-}C_4H_3NHCH{=}NCH_2CH_2)$ C_8H_5NH with rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Yb, Er, Dy, Eu, Y) afforded a series of novel trinuclear rare-earth metal amido complexes that incorporate indolyl ligand in μ-η^5:η^1 bonding modes and a μ_3-O group [37]. Here we report the synthesis of the trivalent rare-earth-metal amido complexes supported by neutral pyrrolyl-functionalized indolyl ligand and their catalytic activity of addition of terminal alkynes to nitriles.

2 Experimental

2.1 General information

All syntheses and manipulations of air- and moisture-sensitive materials were performed under a purified Ar atmosphere using standard Schlenk techniques or in a glovebox. Hexane, toluene, and THF were refluxed and distilled from sodium benzophenone ketyl under Ar prior to use. All alkynes and nitriles were predried, recrystallized or redistilled before use. Other reagents were used as commercial ones without further purification unless otherwise noted. $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Yb, Dy, Er, Y) were prepared according to literature methods [53, 54]. The ligand $3\text{-}(2\text{-}(N\text{–}CH_3)C_4H_3NCH{=}NCH_2CH_2)\text{–}C_8H_5NH$ (**1**) and the complexes (**2** for Yb, and **3** for Dy) were also prepared according to literature methods [37]. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-300 NMR spectrometer (300 MHz for ^{1}H; 75.0 MHz for ^{13}C in C_6D_6 for lanthanide complexes and in $CDCl_3$ for organic compounds. Chemical shifts (δ) were reported in ppm and relative to TMS. IR spectra were recorded on a Shimadzu FTIR-8400s spectrometer (KBr pellet). Elemental analyses data were obtained on a Perkin-Elmer 2400 Series II elemental analyzer for CHN analysis. Melting points were determined in sealed capillaries without correction. High-resolution mass spectra (HRMS) were obtained on an Agilent 6200 MS instrument.

2.2 Synthesis of the complexes

*$[(Me_3Si)_2N]_2Er([\eta^1:\mu\text{-}\eta^2\text{-}3\text{-}(2\text{-}(N\text{–}CH_3)C_4H_3NCH{=}N\text{–}CH_2\text{–}CH_2)C_8H_5N])(\mu\text{-}Cl)Li(THF)$ (**4**)*

To a toluene (10.0 mL) solution of $3\text{-}(2\text{-}(N\text{–}CH_3)C_4H_3\text{-}NCH{=}NCH_2CH_2)C_8H_5NH$ (0.253 g, 1.00 mmol) we added a toluene (20.0 mL) solution of $[(Me_3Si)_2N]_3Er(\mu\text{-}Cl)Li\text{-}(THF)_3$ (0.908 g, 1.00 mmol) at room temperature and obtained a clear light-brown solution. As the reaction mixture was heated at 75 °C for 36 h, the color gradually changed to a darker brown. The solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (2 × 15.0 mL). The combined extractions were concentrated to about 10.0 mL. Pink crystals were obtained at room temperature overnight (0.664 g, 78% yield), m.p. 173–178 °C. ν_{max} (KBr, cm^{-1}): 2929 s, 2881 s, 1633 s, 1535 m, 1512 s, 1388 m, 1226 s, 1215 s, 1147 s, 1068 w, 935 w. Found: C, 45.05; H, 7.04; N, 7.97. Calc. for $C_{32}H_{60}ClLiN_5OSi_4Er$: C, 45.07; H, 7.09; N, 8.21%.

*$[(Me_3Si)_2N]_2Y([\eta^1:\mu\text{-}\eta^2\text{-}3\text{-}(2\text{-}(N\text{–}CH_3)C_4H_3NCH{=}N\text{–}CH_2\text{–}CH_2)C_8H_5N])(\mu\text{-}Cl)Li(THF)$ (**5**)*

This compound was isolated as colorless crystals in 73% yield by treatment of a toluene (10.0 mL) solution of ligand **1** (0.253 g, 1.00 mmol) with $[(Me_3Si)_2N]_3Y(\mu\text{-}Cl)Li\text{-}(THF)_3$ (0.830 g, 1.00 mmol) following procedures similar to the preparation of **4**. m.p. 177–181 °C (dec.). ν_{max} (KBr, cm^{-1}): 2934 s, 2878 s, 1631 s, 1541 m, 1509 s, 1383 m, 1233 s, 1224 s, 1139 s, 1061 w, 927 w. Found: C, 50.48; H, 8.12; N, 8.90. Calc. for $C_{32}H_{60}ClLiN_5OSi_4Y\cdot0.25C_6H_{14}$: C, 50.55; H, 8.04; N, 8.80%. δ_H (300 MHz, C_6D_6, ppm): 8.44 (m, 1H), 7.85 (m, 1H), 7.39–7.34 (m, 1H), 7.20–7.06 (m), 6.91 (s), 6.66 (s), 3.97 (m, 3H), 3.47 (s, 2H), 3.08 (m, 2H), 2.47, 1.82 (m, 4H), 1.63–0.91 (hexane), 0.65 (s), 0.27 (s), 0.07 (s). ^{13}C NMR (75 MHz, C_6D_6, ppm): δ_C 146.1, 146.0, 129.2, 125.2, 125.2, 124.5, 120.9, 120.5, 66.5, 36.95, 36.4, 21.6, 17.0, 16.6, 1.4.

2.3 X-ray structure determination and refinement

A suitable crystal of complexes **2–5** was mounted in a sealed capillary. Diffraction was performed on a Bruker SMART APEX II CCD area detector diffractometer (Bruker AXS GmbH, Germany) using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), temperature 293(2) K, and ϕ- and ω-scan technique. An empirical absorption correction was applied using the SADABS program [55]. All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package (Bruker AXS Inc., USA) [56]. The hydrogen atom coordinates were calculated with SHELXTL using an appropriate riding model with varied thermal parameters. During refinement, constraints are used because of the presence of well-known disordered groups such as THF, ethylene group and terminal methyl group. All disordered parts based on ideal structures were restrained by using DFIX, DELU, or SIMU instructions to make the geometrical configurations and the displacement parameters more reasonable. The residual electron densities were of no chemical significance. Crystal data and details of the data collection and structure refinements are given in Table 1. CCDC 988915 and 988916 for **4** and **5** contain the supplementary crystallographic data for this paper. Please note that these data can be obtained free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif), and are also given in the Supporting Information online.

2.4 General experimental procedure for the addition of alkyne to nitrile

A 25.0 mL Schlenk tube under dried Ar was charged with complex **4** (42.6 mg, 0.05 mmol), alkynes (5 mmol), and solvent-free or toluene (3.0 mL). Benzonitrile (1 mmol) was then added to the mixture. The resulting mixture was stirred at 40 °C for 36 h and then quenched with 0.5 mol/L H_2SO_4, extracted with diethyl ether, dried over anhydrous sodium sulfate, and filtered. After the solvent was removed under reduced pressure, the final products were further purified by flash column chromatography to afford the desired products. Flash column chromatography was performed over silica gel (300–400 mesh) using a mixture of petroleum ether (30–60 °C) and ethyl acetate (15:1, 10:1) as effluent.

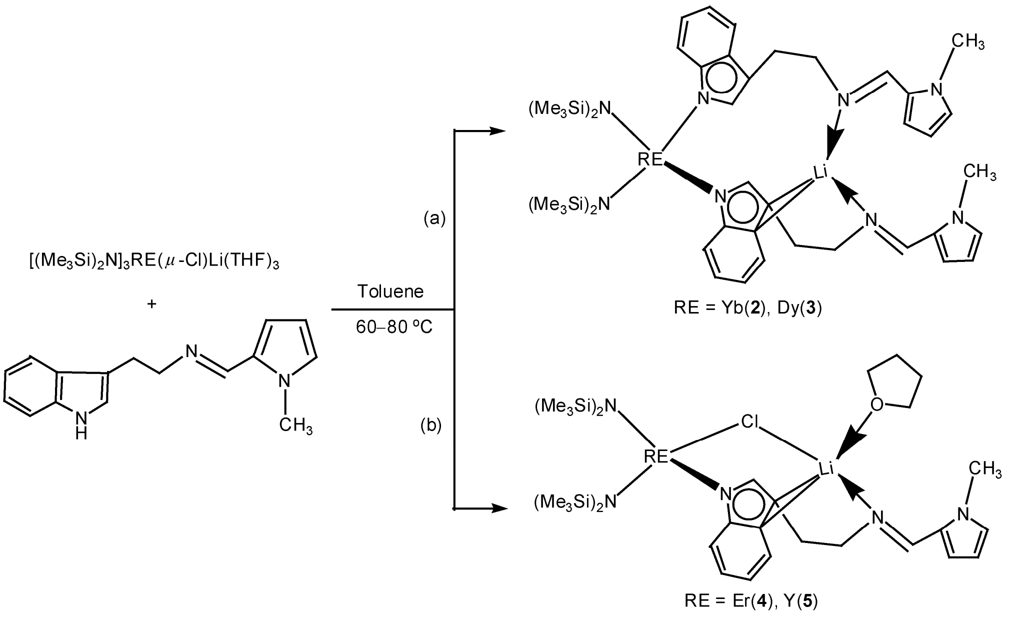
Table 1 Crystallographic data for complexes **4** and **5**

Compounds	**4**	**5**
Formula	$C_{32}H_{60}ClErLiN_5OSi_4$	$C_{35}H_{67}ClYLiN_5OSi_4$
Formula wt	852.86	817.60
Cryst system	triclinic	monoclinic
Space group	$P-1$	$P2_1/n$
a (Å)	13.198(3)	16.2287(12)
b (Å)	17.905(4)	15.9464(12)
c (Å)	21.327(4)	18.3705(14)
α (°)	105.859(2)	90
β (°)	94.948(3)	92.9840(10)
γ (°)	102.857(2)	90
Volume (Å^3)	4667.9(17)	4747.6(6)
Z	4	4
D_{calcd} (g/cm^3)	1.214	1.144
μ (mm^{-1})	1.984	1.415
F(000)	1756	1740
θ range (°)	1.33 to 26.00	1.63 to 27.00
Limiting indices	$-16 \leqslant h \leqslant 15$ $-22 \leqslant k \leqslant 22$ $-23 \leqslant l \leqslant 26$	$-20 \leqslant h \leqslant 20$ $-20 \leqslant k \leqslant 20$ $-23 \leqslant l \leqslant 21$
Reflections collected/unique	35026/17916 [R(int) = 0.0428]	39164/10310 [R(int) = 0.0712]
Data/restraints/parameters	17916/38/785	10310/18/447
GOF	1.020	1.039
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0671 $wR2$ = 0.1909	$R1$ = 0.0531 $wR2$ = 0.1090
R indices (all data)	$R1$ = 0.1175 $wR2$ = 0.2092	$R1$ = 0.1375 $wR2$ = 0.1390
Largest diff. peak/hole (e/Å^3)	0.973 and −1.196	0.473 and −0.300

3 Results and discussion

3.1 Synthesis and characterization of rare-earth metal complexes

In our previous study, reactions of neutral pyrrolyl-functionalized indole ($2\text{-}(3\text{-}C_8H_5NHCH_2CH_2N{=}CH)C_4H_3NCH_3$) (**1**) with $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Yb, Dy) in toluene afforded the hetero-nuclear bimetallic complexes $(\eta^1{:}\eta^1\text{-}[\eta^1\text{-}3\text{-}(2\text{-}(N\text{–}CH_3)C_4H_3N\text{–}CH{=}NCH_2CH_2)C_8H_5N]Li[\mu\text{-}\eta^2{:}\eta^1\text{-}3\text{-}(2\text{-}(N\text{–}CH_3)C_4H_3NCH{=}N\text{–}CH_2CH_2)C_8H_5N])RE\text{-}[N(SiMe_3)_2]_2$ (RE = Yb(**2**), Dy(**3**)) (Scheme 1, path (a)) [37]. However, by further expansion of this reaction to rare-earth metal Er and Y, different hetero-nuclear bimetallic complexes $[(Me_3Si)_2N]_2RE([\eta^1{:}\mu\text{-}\eta^2\text{-}3\text{-}(2\text{-}(N\text{–}CH_3)C_4H_3NCH{=}NCH_2CH_2)C_8H_5N])(\mu\text{-}Cl)Li(THF)$ (RE = Er(**4**), Y(**5**)) (Scheme 1, path (b)) were obtained. With treatment of **1** with 0.5 equiv. of $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Er, Y) under the same conditions, the same bimetallic complexes **4** and **5** were isolated. Adding excess amount of ligand had no influence on the coordination method. These results imply that different ionic radii of rare-earth metals had an effect on the coordination patterns of these types of rare-earth complex. Complexes **4** and **5** are sensitive to air and moisture, but remain stable for months in an inert at



Scheme 1 Preparation of complexes.

mosphere. They are soluble in polar solvents but hardly soluble in nonpolar solvents. All complexes were characterized by elemental analyses, as well as IR and X-ray analyses. The representative molecular structure of complexes **4** and **5** are shown in Figure 1, Figures S1 and S2 (see the Supporting Information online).

X-ray analyses revealed that complexes **4** and **5** are isostructural hetero-nuclear structures. In complexes **4** and **5**, the rare-earth metal ion coordinated with one nitrogen atom of the indolyl ring, two nitrogen atoms of N(SiMe$_3$)$_2$ group, and a bridged chloride, to form a distorted tetrahedral geometry. The molecular structure was stabilized by a bridged chloride and the lithium ion adoption of another triangular pyramid. In **2** and **3**, however, the rare-earth metal ion coordinated with two nitrogen atoms from the indolyl ring and two nitrogen atoms from the N(SiMe$_3$)$_2$ groups, to form a distorted tetrahedral geometry. The lithium ion occupying the apical position of another triangular pyramid stablized the molecular structure [37]. The selected bond lengths and angles of complexes **4** and **5** are listed in Table 2.

As seen in Table 2, the average distances between a rare-earth metal ion and an N atom of an indolyl ring, 2.301(6) Å in **4** and 2.280(3) Å in **5**, are slightly shorter than **2** (2.257(3) Å) and **3** (2.315(7) Å) [37]; this difference can be explained by taking into consideration the change in the ionic radii of the RE(III) ions. The average distances between a rare-earth metal ion and an N atom in the N(SiMe$_3$)$_2$ group, which are 2.2305(6) Å in **4** and 2.221(3) Å in **5**, are also slightly shorter than **2** (2.2035(3) Å) and **3** (2.252(7) Å) [37]; this difference can also be explained by taking into consideration the change in the ionic radii of the RE(III) ions. The above deviation perhaps results from the different electronic effects and coordination environments of rare-earth metal

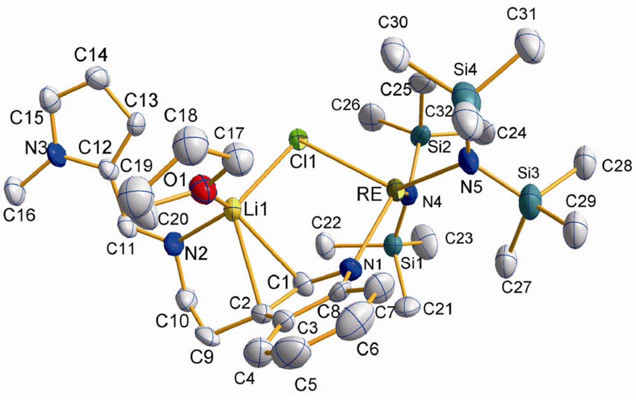


Figure 1 Molecular structural representation of complexes **4** and **5**. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **4** and **5**

Compounds	4	5
RE(1)–Cl(1)	2.6180(18)	2.6212(12)
RE(1)–N(1)	2.301(6)	2.280(3)
RE(1)–N(4)	2.232(6)	2.214(3)
RE(1)–N(5)	2.229(6)	2.228(3)
Li(1)–C(1)	2.502(14)	2.459(9)
Li(1)–C(2)	2.522(14)	2.582(9)
Li(1)–N(2)	2.043(14)	2.051(7)
Li(1)–Cl(1)	2.366(13)	2.422(7)
Li(1)–O(1)	1.911(15)	1.864(8)
N(1)–RE(1)–Cl(1)	87.41(14)	87.67(8)
N(4)–RE(1)–Cl(1)	101.16(14)	121.32(8)
N(5)–RE(1)–Cl(1)	118.60(16)	102.88(8)
N(4)–RE(1)–N(1)	114.1(2)	107.75(11)
N(5)–RE(1)–N(1)	108.7(2)	111.64(11)
N(5)–RE(1)–N(4)	121.9(2)	120.78(10)

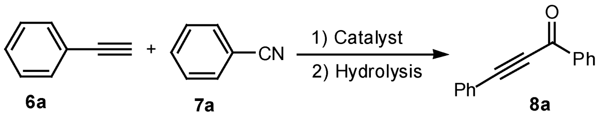
ions. The distances between a lithium ion and an α-position carbon atom in an indolyl ring of 2.502(14) and 2.459(9) Å in complexes **4** and **5**, respectively, are slightly shorter than between a lithium ion and a β-position carbon atom of 2.522(14) and 2.582(9) Å. The distances between a lithium ion and a β-position carbon atom of an indolyl ring are comparable to $[\mu\text{-}\{[\eta^1:\eta^1:\eta^1:\eta^1\text{-}3\text{-}(CyNHCH_2)\text{-}Ind]_2Li\}Ln[N(SiMe_3)_2]_2]$ (Cy = cyclohexyl, Ind = Indolyl, Ln = Sm (2.531(4) Å), Eu (2.522(9) Å), Dy (2.534(11) Å), and Yb (2.528(8) Å)) [51].

3.2 Catalytic addition of alkyne to nitrile

The addition reaction of phenylacetylene (**6**) to benzonitrile (**7**) was first examined as a model reaction using rare-earth metal amido complexes **2**–**5** as catalysts; the results are summarized in Table 3. Here we see that all of these complexes can catalyze this addition reaction to afford conjugated ynones at room temperature under solvent-free conditions or in polar solvents. In loading 5 mol% catalyst under solvent-free conditions, complex **4** showed the highest activity for this reaction (Table 3, entry 6). We also found that the yield of product decreased at elevated temperature (Table 3, entries 6 and 8–10) and the maximum yield was obtained at 40 °C (Table 3, entry 8). The addition reaction cannot proceed in hexane, probably due to the insolubility of the catalysts in hexane (Table 3, entry 20). The highest yield can be obtained under solvent-free conditions rather than in polar solvents (Table 3, entries 16, 18 and 19). Therefore, we further explored the addition reaction was using complex **4** as a catalyst (5 mol%) at 40 °C under solvent-free conditions. The yield increased with the increase of the molar ratio of alkyne to nitrile; the ratio of 5:1 proved to be the optimum choice (Table 3, entry 13). The excess amount of acetylene can be easily recovered.

Next, we examined the substrate scope and limitation of this methodology (Table 4). The location of the substituent on the phenyl ring of alkyne and nitrile had a significant effect on this reaction. For example, the reaction of phenylacetylene with *ortho*-substituted benzonitrile hardly gave the desired product under the given conditions (Table 4, entries 4 and 5), bearing either an electron-donating substituent or an electron-withdrawing substituent. The addition of *o*-fluorophenylacetylene to benzonitrile could provide corresponding product in lower yield (Table 4, entry 14), perhaps because of the steric effect of the *ortho*-substituent groups. As for the electronic properties of aromatic alkynes and nitrile, there were scarcely any effects on the yields of ynones (Table 4, entries 1–7, 9, 12, and 13). Aliphatic alkynes and benzonitrile proceeded smoothly to produce the desired products in moderate yields (Table 4, entry 15). However, the heteroaromatic alkyne and the aliphatic nitriles

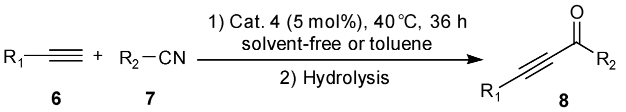
Table 3 Optimizations of the reaction conditions



Entry	Catalyst	Catalyst loading (mol%)	Time (h)	T (°C)	**6a/7a**	Solvent	Yield (%) [a]
1	**3**	1	24	r.t.	1:1	solvent-free	trace
2	**3**	2.5	24	r.t.	1:1	solvent-free	42
3	**3**	5	24	r.t.	1:1	solvent-free	47
4	**3**	10	24	r.t.	1:1	solvent-free	49
5	**2**	5	24	r.t.	1:1	solvent-free	48
6	**4**	5	24	r.t.	1:1	solvent-free	53
7	**5**	5	24	r.t.	1:1	solvent-free	27
8	**4**	5	24	40	1:1	solvent-free	56
9	**4**	5	24	60	1:1	solvent-free	21
10	**4**	5	24	0	1:1	solvent-free	33
11	**4**	5	24	40	2:1	solvent-free	60
12	**4**	5	24	40	3:1	solvent-free	69
13	**4**	5	24	40	5:1	solvent-free	71
14	**4**	5	24	40	8:1	solvent-free	72
15	**4**	5	12	40	5:1	solvent-free	41
16	**4**	5	36	40	5:1	solvent-free	74
17	**4**	5	48	40	5:1	solvent-free	68
18	**4**	5	36	40	5:1	THF	52
19	**4**	5	36	40	5:1	toluene	66
20	**4**	5	36	40	5:1	hexane	trace

a) Isolated yield based on nitrile.

Table 4 The addition of alkynes to nitriles catalyzed by complex **4** a)



Entry	R_1	R_2	Solvent	Product	Yield (%) b)
1	Ph	Ph	solvent-free	**8a**	74
2	Ph	4-MeC_6H_4	solvent-free	**8b**	73
3	Ph	3-MeC_6H_4	solvent-free	**8c**	70
4	Ph	2-MeC_6H_4	solvent-free	–	no reaction
5	Ph	2-$O_2NC_6H_4$	solvent-free	–	no reaction
6	Ph	4-$F_3CC_6H_4$	solvent-free	**8d**	72
7	Ph	4-ClC_6H_4	solvent-free	**8e**	68
8	Ph	*n*-Pr	solvent-free	–	no reaction
9	4-FC_6H_4	Ph	toluene	**8f**	71
10	4-FC_6H_4	4-MeC_6H_4	toluene	**8g**	69
11	4-FC_6H_4	4-$F_3CC_6H_4$	toluene	**8h**	72
12	4-MeC_6H_4	Ph	solvent-free	**8i**	67
13	3-MeC_6H_4	Ph	solvent-free	**8j**	66
14	2-FC_6H_4	Ph	solvent-free	**8k**	41
15	*n*-Bu	Ph	solvent-free	**8l**	61
16	2-thienyl	Ph	solvent-free	–	no reaction

a) The molar ratio of terminal alkynes to aromatic nitriles is 5:1; b) isolated yield based on nitrile.

hardly produced the target product under the given conditions (Table 4, entries 8 and 16).

4 Conclusions

We found that different central rare-earth metals had different coordination modes with the indolyl group in the reactions of neutral pyrrolyl-functionalized indoles with the rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$. These complexes exhibited a catalytic activity for the addition of terminal alkynes to aromatic nitriles to produce the corresponding ynones in moderate to good yields. The catalytic reaction is well suited for a wide range of terminal alkynes and aromatic nitriles under environmentally benign conditions. The influence of the steric effects of aromatic alkynes and aromatic nitriles was more powerful than the influence of the electronic properties on this reaction. These advantages of these complexes imply the potential applications of other rare-earth metal amides in this field. Further works on catalytic properties of other rare-earth metal amides are now in progress.

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