

Influence of Schiff Base and Lanthanide Metals on the Synthesis, Stability, and Reactivity of Monoamido Lanthanide Complexes Bearing Two Schiff Bases

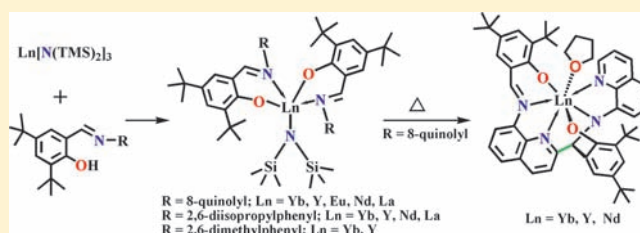
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S Supporting Information

ABSTRACT: The monoamido lanthanide complexes stabilized by Schiff base ligand $L_2LnN(TMS)_2$ ($L = 3,5\text{-Bu}^t\text{-2-(O)-C}_6\text{H}_2\text{CH=N-8-C}_9\text{H}_6\text{N}$, Ln = Yb (1), Y (2), Eu (3), Nd (4), and La (5)) were synthesized in good yields by the reactions of $Ln[N(TMS)_2]_3$ with 1.8 equiv of HL in hexane at room temperature. It was found that the stability of 1–5 depends greatly on the size of the lanthanide metals with the increasing trend of $Yb \approx Y < Nd < La$. The amine elimination of $Ln[N(TMS)_2]_3$ with the bulky bidentate Schiff base HL' ($L' = 3,5\text{-Bu}^t\text{-2-(O)-C}_6\text{H}_2\text{CH=N-2,6-Pr}^i\text{-C}_6\text{H}_3$) afforded the monoamido lanthanide complexes $L'_2LnN(TMS)_2$ (Ln = Yb (9), Y (10), Nd (11), and La (12)). While the amine elimination with the less bulky Schiff base HL'' ($L'' = 3,5\text{-Bu}^t\text{-2-(O)-C}_6\text{H}_2\text{CH=N-2,6-Me}_2\text{-C}_6\text{H}_3$) yielded the desired monoamido complexes with the small metals of Y and Yb, $L''_2LnN(TMS)_2$ (Ln = Yb (13) and Y (14)), and the more stable tris-Schiff base complexes with the large metals of La and Nd, yielded L'''_3Ln as the only product. Complexes 1–14 were fully characterized including X-ray crystal structural analysis. Complexes 1–5, 10, and 14 can serve as the efficient catalysts for addition of amines to carbodiimides, and the catalytic activity is greatly affected by the lanthanide metals with the active sequence of $Yb < Y < Eu \approx Nd \approx La$.



INTRODUCTION

A contemporary theme in modern lanthanide and yttrium chemistry is the design of new ligand environments of lanthanide complexes which are capable of supporting lanthanide (Ln^{3+}) ions exhibiting high activity.¹ Accordingly, noncyclopentadienyl ligand sets have recently attracted considerable interest because of their easy tailorability with respect to steric demand and electronic properties. Schiff bases, one of the widely utilized noncyclopentadienyl ligands in coordination chemistry of transition and lanthanide metals,² have the obvious advantages of ease of synthesis, low cost, a hard donor atom framework, and tunable steric and electronic effects. However, the structurally characterized amido lanthanide complexes supported by Schiff base ligands are rare,³ although various amido lanthanide complexes stabilized by noncyclopentadienyl ligands, such as β -diketiminates,⁴ guanidates,⁵ benzamidates,^{5a,b,6} diamido-ligands,⁷ bridged bisphenolate,⁸ have been synthesized and found many important catalytic applications including organic transformations and various types of polymerization. To date, only the monoamido lanthanide complexes stabilized by salen-type ligands are well-known.³

Recently, we have reported the synthesis of the first mono-amido complexes of Sm and Nd bearing two monoanionic Schiff-

base ligands L^1 ($L^1 = 3,5\text{-Bu}^t\text{-2-(O)-C}_6\text{H}_2\text{CH=N-2-C}_3\text{H}_4\text{N}$),⁹ and the related complexes of Y and Yb with the ligands L ($L = 3,5\text{-Bu}^t\text{-2-(O)-C}_6\text{H}_2\text{CH=N-8-C}_9\text{H}_6\text{N}$).¹⁰

To gain insight into the potential of the Schiff bases as ancillary ligands in stabilizing Ln -amido active groups, we continue to study the synthesis, stability, and reactivity of monoamido lanthanide complexes using the following three Schiff bases, L , L' ($L' = 3,5\text{-Bu}^t\text{-2-(O)-C}_6\text{H}_2\text{CH=N-2,6-Pr}^i\text{-C}_6\text{H}_3$) and L'' ($L'' = 3,5\text{-Bu}^t\text{-2-(O)-C}_6\text{H}_2\text{CH=N-2,6-Me}_2\text{-C}_6\text{H}_3$), since their use in stabilizing amido lanthanide complexes has remained relatively unexplored. It was found that the synthesis of monoamido lanthanide complexes was largely influenced by the Schiff base ligand and the size of the lanthanide metals. Using ligands L and L' , the desired monoamido lanthanides complexes including the large metals of La and Nd and the small metals of Y and Yb can be facilely synthesized in good yields, while by use of L'' , the related complexes can be prepared only when the lanthanide metals are small ones of Y and Yb. In contrast, the homoleptic tris-Schiff base complexes L'''_3Ln were isolated as the only products when the large metals of La and Nd were used. The

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stability of these monoamido lanthanide complexes were found to depend greatly on the Schiff base ligand and the size of the lanthanide metals. Here we would like to report the results. Their catalytic activity for addition of amines to carbodiimides is also included.

EXPERIMENTAL SECTION

Materials and Methods. Standard Schlenk techniques and a Vacuum Atmospheres N₂-filled glovebox were used throughout the isolation and handling of all metal complexes. Tetrahydrofuran, toluene, and *n*-hexane were dried and distilled from sodium benzophenone ketal under argon prior to use. Ln[N(TMS)₂]₃ was prepared according to the literature procedure.¹¹ ¹H NMR and ¹³C NMR spectra were recorded on a 300 MHz or 400 MHz instrument and processed using the NUTS software. Elemental analyses were performed by direct combustion using a Carlo-Erba EA 1110 instrument. The IR spectra were recorded on a Magna-IR 550 spectrometer as KBr pellets. All yields of lanthanide complexes were calculated based on ligands and were of crystallized yield only for the first time.

L₂EuN(TMS)₂·THF·C₆H₁₄ (**3**). A solution of the Eu[N(TMS)₂]₃ (1.19 g, 1.88 mmol) in *n*-hexane was added as fast as possible in one portion to a stirring slurry of ligand HL (1.22 g, 3.38 mmol) in *n*-hexane at room temperature. The reaction mixture was stirred for 2 h. The volatiles were removed under reduced pressure, and the residue was extracted with about 5 mL of *n*-hexane; removing the *n*-hexane solution by centrifugation led to orange solids. The solids were crystallized from toluene or a mixture of tetrahydrofuran and *n*-hexane at 0 °C. Complex **3** was isolated as orange crystals after several days. Yield: 0.91 g (45%). IR (KBr, cm⁻¹): 2956(s), 2904(m), 2869(m), 1610(s), 1600(s), 1531(s), 1502(s), 1463(m), 1425(s), 1383(m), 1360(w), 1314(w), 1254(s), 1233(m), 1161(s), 1085(w), 1064(w), 931(m), 840(m), 793(m), 755(w), 744(w); Anal. Calcd for C₆₄H₉₄N₅O₃Si₂Eu (1189.58): C, 64.61; H, 7.97; N, 5.89. Found: C, 63.82; H, 7.02; N, 5.99.

L₂NdN(TMS)₂·0.5THF (**4**). The synthesis of complex **4** was carried out in the same way as that described for complex **3**, but HL (1.23 g, 3.40 mmol) and Nd[N(TMS)₂]₃ (1.18 g, 1.89 mmol) were used. The orange crystals were isolated. Yield: 1.01 g (56%). IR (KBr, cm⁻¹): 2954(s), 2903(m), 2869(m), 1609(s), 1599(s), 1528(s), 1501(s), 1462(m), 1424(s), 1382(m), 1359(w), 1314(w), 1250(s), 1231(s), 1159(s), 1084(w), 1063(w), 932(m), 839(m), 792(m), 754(w), 744(w); Anal. Calcd for C₅₆H₇₆N₅O_{2.5}Si₂Nd (1059.64): C, 63.47; H, 7.23; N, 6.61. Found: C, 63.17; H, 6.87; N, 5.83.

L₂LaN(TMS)₂·0.5THF (**5**). The synthesis of complex **5** was carried out in the same way as that described for complex **3**, but HL (2.12 g, 6.10 mmol) and La[N(TMS)₂]₃ (2.10 g, 3.39 mmol) were used. The orange crystals were isolated. Yield: 2.02 g (63%). ¹H NMR (400 MHz, C₆D₆): δ 9.28 (br, 2 H), 8.30 (s, 2 H), 7.60 (s, 2 H), 7.55–7.40 (m, 2 H), 7.23 (s, 2 H), 7.16–7.11 (m, 4 H, overlapping), 7.01–6.98 (m, 2 H), 6.78 (br, 2 H), 1.37 and 1.30 (s and br, 36 H), –0.03 (s, 18 H); ¹³C NMR (101 MHz, C₆D₆): 168.90, 167.08, 151.50, 150.68, 144.12, 140.04, 137.81, 135.77, 129.46, 128.41, 128.18, 128.14, 127.94, 124.89, 122.92, 121.48, 118.63, 35.41, 34.10, 31.78, 30.06, 5.38; IR (KBr, cm⁻¹): 2955(s), 2904(m), 2871(m), 1611(s), 1599(s), 1531(s), 1502(s), 1461(m), 1426(s), 1382(m), 1360(w), 1314(w), 1251(s), 1232(s), 1160(s), 1084(w), 1065(m), 932(m), 838(m), 793(m), 754(w), 744(w); Anal. Calcd for C₅₆H₇₆N₅O_{2.5}Si₂La (1054.31): C, 63.79; H, 7.27; N, 6.64. Found: C, 64.61; H, 7.12; N, 5.60.

L_{(N, O, O)′}³⁻Nd(THF)·THF (**6**). The complex **4** (0.59 g, 0.56 mmol) was dissolved in about 10 mL of tetrahydrofuran (THF) and sealed in the reaction bottle, then heated in the reaction system to 70 °C. And the color of the solution changed from orange to deep-red gradually. After 5 days, the volatiles were removed under reduced pressure, and the residues were washed with about 10 mL of *n*-hexane at 3 times. The

solids were crystallized from a mixture of tetrahydrofuran and *n*-hexane at room temperature. Complex **6**, together with Complex **4** (orange crystals), was obtained as deep-red crystals after several days. IR (KBr, cm⁻¹): 2954(s), 2904(m), 2869(m), 1611(s), 1588(s), 1530(m), 1504(w), 1470(s), 1428(s), 1394(w), 1360(w), 1312(w), 1230(s), 1160(s), 1079(w), 835(m), 797(w), 745(w); Anal. Calcd for C₅₆H₆₉N₄O₄Nd (1006.39): C, 66.83; H, 6.91; N, 5.57. Found: C, 66.38; H, 7.06; N, 5.99.

L′₂YbN(TMS)₂ (**9**). A solution of the ligand HL′ (1.08 g, 2.75 mmol) in tetrahydrofuran was slowly added to a stirred solution of Yb[N(TMS)₂]₃ (0.95 g, 1.45 mmol) in tetrahydrofuran over 2 h at –50 °C. The reaction mixture was stirred for another 2 h. The volatiles were removed under reduced pressure, and the residues were crystallized from a mixture of tetrahydrofuran and *n*-hexane at about 0 °C. The complex **9** was isolated as light yellow crystals after several days. Yield: 0.61 g (40%). IR (KBr, cm⁻¹): 2961(s), 2870(m), 1622(s), 1584(s), 1536(m), 1465(s), 1438(s), 1393(w), 1363(m), 1324(w), 1246(s), 1162(s), 1108(w), 1044(w), 980(w), 933(w), 862(w), 840(w), 799(w), 762(w), 720(w), 639(m), 555(m), 504(s); Anal. Calcd for C₆₀H₉₄N₃O₂Si₂Yb (1118.60): C, 64.42; H, 8.47; N, 3.76. Found: C, 64.68; H, 8.26; N, 4.01.

L′₂YN(TMS)₂ (**10**). The synthesis of complex **10** was carried out in the same way as that described for complex **9**, but HL′ (1.21 g, 3.07 mmol) and Y[N(TMS)₂]₃ (0.93 g, 1.63 mmol) were used. The light yellow crystals were isolated. Yield: 0.64 g (41%). ¹H NMR (400 MHz, C₆D₆): δ 7.96 (d, 2 H), 7.67 (d, 2 H), 7.22–7.17 (m, 4 H), 7.06–7.03 (m, 2 H), 6.81–6.80 (d, 2 H), 3.55–3.44 (m, 2 H), 2.85–2.74 (m, 2 H), 1.63 (d, 6 H), 1.26 (s, 18 H), 1.17 (s, 18 H), 1.16 (d, 6 H), 1.06 (d, 6 H), 0.64 (d, 6 H), 0.41 (s, 18 H); ¹³C NMR (101 MHz, C₆D₆): 177.06, 165.28, 165.24, 151.72, 141.68, 141.19, 139.12, 138.19, 133.58, 131.51, 127.11, 125.27, 124.41, 122.93, 35.81, 33.91, 31.57, 31.31, 29.54, 29.21, 23.51, 23.38, 6.56, 6.29; IR (KBr, cm⁻¹): 2961(s), 2870(m), 1623(s), 1584(s), 1536(m), 1463(s), 1435(s), 1395(w), 1362(m), 1324(m), 1250(s), 1161(s), 1107(w), 1044(w), 976(m), 933(m), 840(m), 799(w), 763(m), 720(w), 639(m), 555(m), 505(s); Anal. Calcd for C₆₀H₉₄N₃O₂Si₂Y (1034.47): C, 69.66; H, 9.16; N, 4.06. Found: C, 69.98; H, 9.06; N, 4.17.

L′₂NdN(TMS)₂ (**11**). The synthesis of complex **11** was carried out in the same way as that described for complex **9**, but HL′ (1.02 g, 2.58 mmol) and Nd[N(TMS)₂]₃ (0.85 g, 1.36 mmol) were used. The light green crystals were isolated. Yield: 0.82 g (58%). IR (KBr, cm⁻¹): 2962(s), 2869(m), 1622(s), 1585(s), 1534(w), 1463(m), 1438(m), 1396(w), 1362(m), 1324(w), 1250(s), 1158(s), 1108(w), 1044(w), 976(w), 933(w), 840(w), 798(w), 761(w), 720(w), 638(m), 555(m), 505(s); Anal. Calcd for C₆₀H₉₄N₃O₂Si₂Nd (1089.80): C, 66.12; H, 8.69; N, 3.86. Found: C, 66.01; H, 8.56; N, 3.77.

L′₂LaN(TMS)₂ (**12**). The synthesis of complex **12** was carried out in the same way as that described for complex **9**, but HL′ (0.64 g, 1.63 mmol) and La[N(TMS)₂]₃ (0.53 g, 0.85 mmol) were used. The orange crystals were isolated. Yield: 0.56 g (63%). ¹H NMR (400 MHz, C₆D₆): δ 7.89 (s, 2 H), 7.62 (d, 2 H), 7.14–7.09 (m, 4 H), 7.04–7.00 (m, 2 H), 6.81–6.79 (d, 2 H), 3.47–3.36 (m, 2 H), 2.95–2.84 (m, 2 H), 1.62 (d, 6 H), 1.26 (s, 18 H), 1.16 (d, 6 H), 1.15 (s, 18 H), 1.05 (d, 6 H), 0.79 (d, 6 H), 0.34 (s, 18 H); IR (KBr, cm⁻¹): 2961(s), 2870(m), 1622(s), 1584(s), 1540(s), 1462(m), 1437(s), 1397(w), 1362(m), 1325(m), 1253(s), 1162(s), 1107(w), 1043(w), 976(w), 933(w), 841(m), 800(w), 763(w), 720(w), 639(w), 555(m), 505(m); Anal. Calcd for C₆₀H₉₄N₃O₂Si₂La (1084.47): C, 66.45; H, 8.74; N, 3.88. Found: C, 66.88; H, 9.01; N, 4.14.

L′′₂YbN(TMS)₂ (**13**). The synthesis of complex **13** was carried out in the same way as that described for complex **9**, but HL′′ (0.87 g, 2.58 mmol) and Yb[N(TMS)₂]₃ (0.89 g, 1.36 mmol) were used. The orange crystals were isolated. Yield: 0.71 g (55%). IR (KBr, cm⁻¹): 2957(s), 2870(m), 1623(s), 1586(s), 1537(s), 1467(m), 1435(s), 1393(w),

Table 1. Crystallographic Data for Complexes 3–6

	3	4	5	6
formula	C ₆₄ H ₉₄ N ₅ O ₃ Si ₂ Eu	C ₅₆ H ₇₆ N ₅ O _{2.5} Si ₂ Nd	C ₅₆ H ₇₆ N ₅ O _{2.5} Si ₂ La	C ₅₆ H ₆₉ N ₄ O ₄ Nd
mol wt	1189.58	1059.64	1054.31	1006.39
temp (K)	223(2)	223(2)	223(2)	223(2)
λ (Å)	0.71075	0.71075	0.71075	0.71075
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	C2/c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
cryst size (mm)	0.40 × 0.15 × 0.10	0.38 × 0.20 × 0.12	0.60 × 0.15 × 0.08	0.80 × 0.25 × 0.10
<i>a</i> (Å)	18.600(2)	13.2593(13)	13.429(2)	14.0041(16)
<i>b</i> (Å)	24.731(3)	24.940(2)	24.942(4)	17.7799(17)
<i>c</i> (Å)	16.632(2)	17.4422(17)	17.499(3)	22.603(3)
α (deg)	90	90	90	90
β (deg)	120.696(3)	103.183(3)	103.522(5)	101.853(3)
γ (deg)	90	90	90	90
<i>V</i> (Å ³)	6578.6(13)	5616.0(9)	5698.3(15)	5507.9(10)
<i>Z</i> (Å ³), <i>D</i> _{calcd} (g/mL)	4, 1.201	4, 1.253	4, 1.229	4, 1.214
μ (mm ⁻¹)	1.034	1.011	0.835	0.987
<i>F</i> (000)	2512	2220	2208	2100
θ range (deg)	3.03–25.50	3.01–25.50	3.00–25.50	3.08–25.50
total no. of rflns	16888	28893	28858	27699
no. of indep rflns	6095	10410	10588	10200
<i>R</i> _{int}	0.0694	0.0954	0.1244	0.0599
GOF	1.116	1.197	1.092	1.114
R1, wR2 (<i>I</i> > 2 σ (<i>I</i>))	0.0666, 0.1497	0.0897, 0.1307	0.1277, 0.2828	0.0882, 0.2167
R1, wR2 (all data)	0.0850, 0.1600	0.1307, 0.1447	0.2076, 0.3399	0.1112, 0.2358

1362(w), 1325(w), 1251(s), 1161(s), 1094(w), 1060(w), 984 (w), 884(w), 841(s), 768(w), 639(w), 505(s); Anal. Calcd for C₅₂H₇₈N₃O₂·Si₂Yb (1006.39): C, 62.06; H, 7.81; N, 4.18. Found: C, 61.85; H, 7.86; N, 4.08.

L'₂YN(TMS)₂ (**14**). The synthesis of complex **14** was carried out in the same way as that described for complex **9**, but HL'' (0.82 g, 2.43 mmol) and Y[N(TMS)₂]₃ (0.72 g, 1.26 mmol) were used. The orange crystals were isolated. Yield: 0.74 g (66%). ¹H NMR (400 MHz, C₆D₆): δ 7.77 (d, 2 H), 7.63 (d, 2 H), 6.97–6.85 (m, 6 H), 6.83 (d, 2 H), 2.18 (br, 12 H), 1.38 (d, 18 H), 1.23 (s, 18 H), 0.20 (s, 18 H); ¹³C NMR (101 MHz, C₆D₆): 176.64, 152.70, 139.44, 137.83, 130.88, 130.82, 129.52, 126.20, 123.13, 35.56, 34.08, 31.59, 30.17, 20.72, 5.44; IR (KBr, cm⁻¹): 2958(s), 2871(m), 1624(s), 1587(m), 1535(m), 1470(m), 1438(m), 1394(w), 1362(w), 1324(w), 1250(s), 1159(s), 1093(w), 1059(w), 981(w), 886(w), 842(m), 768(m), 640(w), 504(s); Anal. Calcd for C₅₂H₇₈N₃O₂Si₂Y (922.26): C, 67.72; H, 8.53; N, 4.56. Found: C, 67.48; H, 8.46; N, 4.43.

General Procedure for the Reaction of Amines with Carbodiimides Catalyzed by the Amido Complexes 1–5, 10, and 14. A 10 mL Schlenk tube under dried argon was charged with the related lanthanide amido complexes (0.01 equiv), amines, and carbodiimides. The resulting mixture was stirred at 40 or 100 °C for the desired time, as shown in Table 7 and Table 8. After the reaction was completed, the reaction mixture was hydrolyzed with water, extracted with dichloromethane (3 × 10 mL), dried over anhydrous Na₂SO₄, and filtered. Then the solvent was removed under reduced pressure, and the final products were further purified by recrystallization from *n*-hexane.

X-ray Crystallography. Crystals suitable for X-ray diffraction of complexes 3–6 and 9–14 were sealed in a thin-walled glass capillary filled with argon for structural analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector in the ω scan mode using Mo K α radiation (λ = 0.71073 and 0.71075 Å). The diffracted intensities

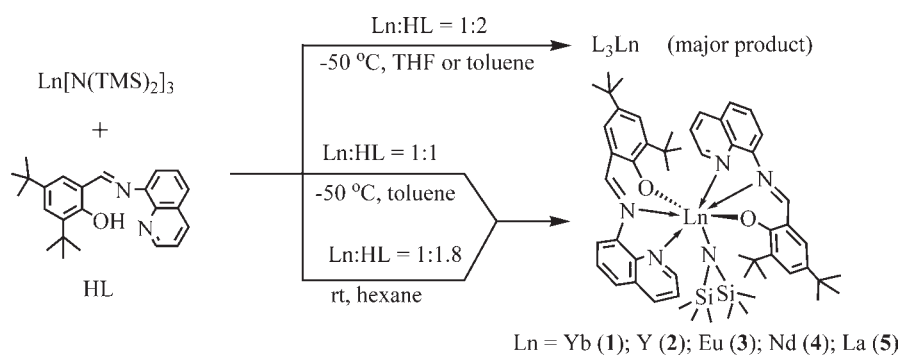
were corrected for Lorentz-polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 1 and Table 2. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. The structures were refined using SHELXL-97 programs.

RESULTS AND DISCUSSION

Synthesis and Molecular Structures of L₂LnN(TMS)₂ (L = 3,5-Bu^t-2-(O)-C₆H₂CH=N-8-C₉H₆N; Ln = Yb (1), Y (2), Eu (3), Nd (4), and La (5)): the Influence of the Size of Lanthanide Metals. Recently, we have reported the synthesis and molecular structures of L₂LnN(TMS)₂ (Ln = Yb (1) and Y (2)) by amine elimination reaction between the corresponding amido complexes Ln[N(TMS)₂]₃ and the proligand HL in a molar ratio of 1:1 at –50 °C.¹⁰ The harsh condition (low reaction temperature) and the low yield of the amido complex by this procedure is undesired. Accordingly, efforts to improve the synthesis of these monoamido complexes were made including the choice of molar ratio of substrates, reaction temperature, and solvent. However, increasing the molar ratio from 1:1 to 1:2 led to the undesired homoleptic tris-Schiff base complexes L₃Ln as the major product for both metals (Scheme 1), indicating that the monoamido complex formed in the reaction solution under the conditions will gradually react with HL to convert to the homoleptic byproduct. This may be attributed to the instability of the low coordinated monoamido complex,

Table 2. Crystallographic Data for Complexes 9–14

	9	10	11	12	13	14
formula	C ₆₀ H ₉₄ N ₃ O ₂ Si ₂ Yb	C ₆₀ H ₉₄ N ₃ O ₂ Si ₂ Y	C ₆₀ H ₉₄ N ₃ O ₂ Si ₂ Nd	C ₆₀ H ₉₄ N ₃ O ₂ Si ₂ La	C ₅₂ H ₇₈ N ₃ O ₂ Si ₂ Yb	C ₅₂ H ₇₈ N ₃ O ₂ Si ₂ Y
mol wt	1118.60	1034.47	1089.80	1084.47	1006.39	922.26
temp (K)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)
λ (Å)	0.71075	0.71073	0.71073	0.71075	0.71075	0.71075
cryst syst	tetragonal	tetragonal	tetragonal	tetragonal	orthorhombic	orthorhombic
space group	<i>P</i> 4 ₃ 2 ₁ 2	<i>P</i> 4 ₃ 2 ₁ 2	<i>P</i> 4 ₃ 2 ₁ 2	<i>P</i> 4 ₃ 2 ₁ 2	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
cryst size (mm)	0.80 × 0.40 × 0.40	0.40 × 0.38 × 0.25	0.40 × 0.40 × 0.30	0.40 × 0.30 × 0.20	0.44 × 0.28 × 0.20	0.60 × 0.30 × 0.20
<i>a</i> (Å)	12.8009(11)	12.7298(7)	12.6488(18)	12.6732(7)	13.3661(5)	13.3775(11)
<i>b</i> (Å)	12.8009(11)	12.7298(7)	12.6488(18)	12.6732(7)	17.9742(8)	18.0251(16)
<i>c</i> (Å)	37.601(4)	37.972(3)	38.283(8)	38.391(3)	22.0690(9)	22.185(2)
α (deg)	90	90	90	90	90	90
β (deg)	90	90	90	90	90	90
γ (deg)	90	90	90	90	90	90
<i>V</i> (Å ³)	6161.4(10)	6153.2(6)	6124.9(17)	6166.1(6)	5302.0(4)	5349.6(8)
<i>Z</i> (Å ³), <i>D</i> _{calcd} (g/mL)	4, 1.206	4, 1.117	4, 1.182	4, 1.168	4, 1.261	4, 1.145
μ (mm ⁻¹)	1.597	1.027	0.927	0.771	1.848	1.173
<i>F</i> (000)	2356	2232	2316	2304	2100	1976
θ range (deg)	3.12–25.50	3.12–25.50	3.11–25.50	3.10–25.50	3.05–25.50	3.05–25.50
total no. of rflns	14071	19523	17147	21496	22171	23885
no. of indep rflns	5475	5682	5664	5734	9746	9881
<i>R</i> _{int}	0.0586	0.0632	0.0450	0.0969	0.0431	0.0756
GOF	1.113	1.048	1.091	1.098	1.049	1.052
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0659, 0.1437	0.0672, 0.1619	0.0373, 0.0743	0.0582, 0.1244	0.0392, 0.0652	0.0693, 0.1188
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0737, 0.1489	0.0811, 0.1705	0.0407, 0.0763	0.0738, 0.1394	0.0422, 0.0666	0.0922, 0.1290

Scheme 1. Amine Elimination Reaction of Ln[N(TMS)₂]₃ with HL

which tends to transfer to the more stable homoleptic Schiff base complex.

Raising the reaction temperature from -50 °C to room temperature resulted remarkably in the decrease in the yield of monoamido complexes and even no monoamido complexes of Y and Yb could be obtained, but the complexes bearing a novel [N,O,O] trianionic ligand were isolated via the further transformation of the in situ formed monoamido complexes by metalation reaction, because of the instability of these monoamido lanthanides complexes in THF or toluene solution.¹⁰ On the basis of the poor solubility of the monoamido lanthanide complex in *n*-hexane, we thought that it might be possible to drive the reaction to the pathway to a monoamido complex by removing the monoamido complex formed immediately from the reaction solution as precipitates using *n*-hexane, instead of toluene, as the solvent. Thus, the reaction of Yb[N(TMS)₂]₃

with HL in a molar ratio of 1:1.8 at -50 °C in *n*-hexane was then tried. Addition of an *n*-hexane solution of Yb[N(TMS)₂]₃ as fast as possible into a suspension of HL in *n*-hexane with stirring, and then stirring for another 2 h resulted in the color change of the suspension from red to yellow gradually. Removing the mother liquid by centrifugation and crystallization from toluene at 0 °C gave yellow crystals which were characterized to be the target complex L₂YbN(TMS)₂ (1) in good yield. Given that the monoamido complex in the solid state is much more stable than that in a solution, the same reaction was then tested at room temperature. Indeed the monoamido complex 1 could also be isolated in almost the same yield as that obtained at -50 °C (Scheme 1). By the optimal reaction conditions, the molar ratio of 1 to 1.8 (Ln[N(TMS)₂]₃ to HL); room temperature and fast addition of Ln[N(TMS)₂]₃ into HL, *n*-hexane as the solvent, the monoamido lanthanides complexes including

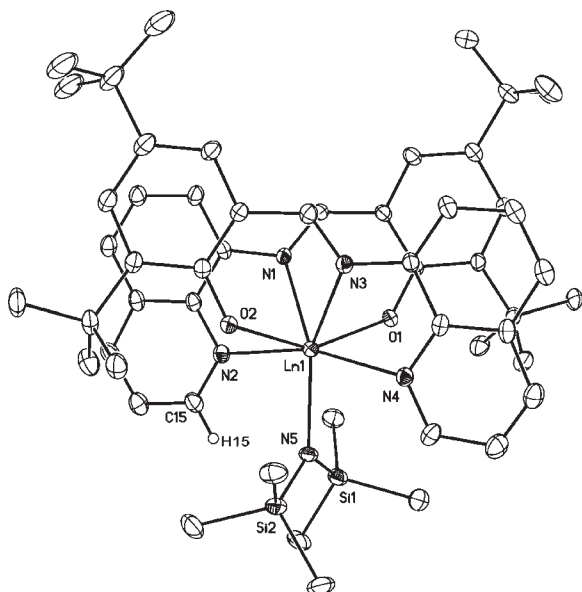


Figure 1. ORTEP diagram of the molecular structures of complexes 3–5 (Ln = Eu (3), Nd (4), La (5)). Thermal ellipsoids are drawn at 20% probability level. All hydrogen atoms except for H(15), disordered *tert*-butyl groups and noncoordinating THF and hexane molecules are omitted for clarity.

Y, Eu, Nd, and La, could be prepared facily in high yields (Scheme 1).

Complexes 1–5 are highly soluble in the usual organic solvents (THF, benzene, and toluene), but almost insoluble in *n*-hexane. Complexes 1–5 were fully characterized by elemental analysis, IR, ^1H NMR, and ^{13}C NMR for 5 and X-ray crystal structural analysis.

Molecular Structures of 3–5. Single crystals of complexes 3–5 suitable for X-ray diffraction analysis were obtained by recrystallization from a toluene solution or a mixture of THF and *n*-hexane at 0 °C. Complex 3 contains one THF and one *n*-hexane molecules in the unit cell as a THF and a hexane solvate $3 \cdot \text{THF} \cdot \text{hexane}$, while both complexes 4 and 5 crystallized as half a THF solvate $4 \cdot 0.5\text{THF}$ and $5 \cdot 0.5\text{THF}$. The molecular structures of 3–5 are shown in Figure 1 as 3–5 are isostructural. Selected bond distances and angles are given in Table 3. The solid-state structure of each of them consists of discrete, mononuclear $\text{L}_2\text{LnN}(\text{TMS})_2$ complexes with Ln metal bonded to the four nitrogen and two oxygen atoms of the two ligands and one nitrogen atom of the amido group in a manner similar to those observed for 1 and 2 reported previously.¹⁰ Each seven-coordinate Ln metal best approximates a pentagonal bipyramidal geometry with the O (1) and O (2) atoms occupying the axis positions. The N (1), N (2), N (5), N (4), and N (3) atoms are nearly coplanar with sums of the bond angles of 368.54° for 3, 365.87° for 4, and 366.6° for 5. The two planes of O (1), N (1), N (2) and O (2), N (3), N (4) atoms from the two ligands are nearly parallel with the dihedral angles of 11.031°, 11.647°, and 4.844°, respectively. The bond angles of O (1)–Ln (1)–O (2) are highly distorted from the ideal value of 180° to 146.9(2)° for 3, 141.52(16)° for 4, and 139.8(3)° for 5. These values, together with the values reported for complexes 1 and 2,¹⁰ indicated that the larger the ionic radius of the lanthanide atom is, the larger the bond angle O (1)–Ln (1)–O (2) distorts. The bond distances including Ln (1)–O (Schiff base), Ln (1)–N (imine), and Ln

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complexes 3–5

	3	4	5
Bond Lengths			
Ln (1)–O (1)	2.247(4)	2.280(4)	2.317(9)
Ln (1)–O (2)	2.247(4)	2.295(5)	2.339(8)
Ln (1)–N (1)	2.537(5)	2.553(6)	2.616(10)
Ln (1)–N (2)	2.635(5)	2.698(6)	2.752(11)
Ln (1)–N (3)	2.537(5)	2.561(5)	2.623(10)
Ln (1)–N (4)	2.635(5)	2.723(6)	2.768(11)
Ln (1)–N (5)	2.375(7)	2.433(5)	2.488(11)
N (5)···H (15)	2.7812	2.8526	2.9051
Bond Angles			
O (2)–Ln (1)–O (1)	146.9(2)	141.52(16)	139.8(3)
N (1)–Ln (1)–N (2)	62.57(15)	61.12(17)	59.9(3)
N (3)–Ln (1)–N (1)	75.3(2)	74.57(17)	74.0(3)
N (5)–Ln (1)–N (2)	84.05(11)	83.81(18)	85.2(3)
N (5)–Ln (1)–N (4)	84.05(11)	85.37(18)	87.5(3)
N (3)–Ln (1)–N (4)	62.57(15)	61.00(18)	60.0(3)

(1)–N (5) (amido) follow the increase trend, $1 < 2 < 3 < 4 < 5$, with the increase of the Ln (III) ion radius.

It is noteworthy that the distances between the N (5) atom of the $-\text{N}(\text{TMS})_2$ group and the H (15) atom of one quinoline ring for complexes 3–5 (2.7812 Å for 3, 2.8526 Å for 4, 2.9051 Å for 5) are longer than the sum of van der Waals radius of N and H atoms ($r_{\text{N}} = 1.55 \text{ Å}$, $r_{\text{H}} = 1.20 \text{ Å}$), which are different from those found in 1 and 2; the related distances in 1 and 2 are shorter than 2.75 Å. This may be the reason for why complexes 1 and 2 with smaller metals are much more unstable and easy to decompose via metalation reaction.

Influence of the Size of Lanthanide Metals on the Stability of Complexes 1–5. It is worthy of notice that the stability of these monoamido complexes is largely influenced by the size of the central metals. For example, complexes 1 and 2 with smaller ionic radius (Y and Yb) are unstable in solution and convert to the corresponding complexes with the $[\text{N}_2\text{O}_2\text{O}]$ trianionic ligand via metalation reaction completely at 40 °C for only 2 days, and slow conversion was also found even at ambient temperature.¹⁰ In contrast, 5 with the largest lanthanide metal La is quite stable; no such a conversion was observed even at 70 °C for 10 days. However, the slow transformation of 4 in solution was observed at heating to 70 °C for 5 days, and a mixture of the product 6, which are the analogues to Y and Yb derivatives reported by the same reaction pathway,¹⁰ and the starting materials 4 could be isolated at about 2:1 molar ratio (Scheme 2). Evidently, steric effect controls the C–H bond activation processes: decreasing the size of the central metal creates compression at the metal center, which is alleviated upon elimination of a metal-bound amido group via abstracting an activated hydrogen atom from one of the quinoline rings of the ligand.

The formation of complex 6 was further confirmed by X-ray single crystal structural analysis. Its molecular structure is shown in Figure 2. The selected bond distances and angles are listed in Table 4. The coordination geometry around the seven-coordinate Nd metal by the newly formed $[\text{N}_2\text{O}_2\text{O}]$ trianionic ligand via the formation of a new C (15)–C (31) bond and one THF molecule can be described as a distorted pentagonal bipyramid, which is similar to those of Y and Yb partners reported previously.

Scheme 2. Influence of the Size of the Metals on the Stability of Complexes 1–5

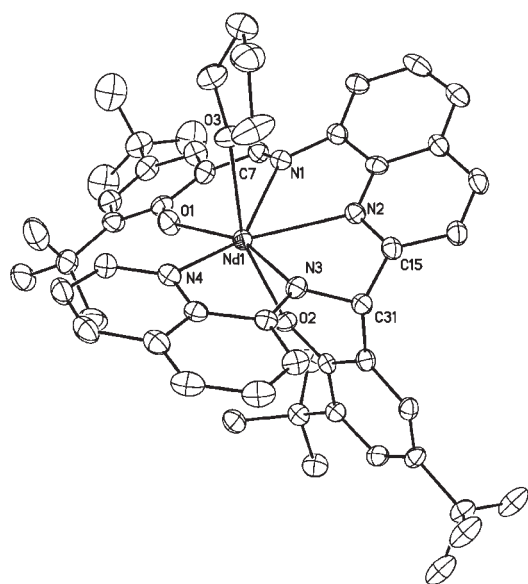
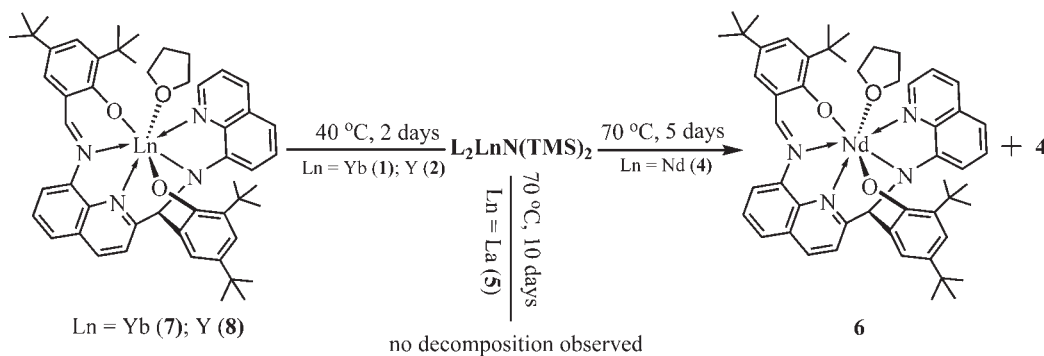


Figure 2. ORTEP diagram of the molecular structure of complex **6**. Thermal ellipsoids are drawn at 20% probability level. All hydrogens and disordered *tert*-butyl groups and noncoordinating THF molecules are omitted for clarity.

Synthesis of $L'_2\text{LnN(TMS)}_2$ ($L' = 3,5\text{-Bu}^t\text{-2-(O)-C}_6\text{H}_2\text{CH}=\text{N-2,6-Pr}^i\text{-2-C}_6\text{H}_3$; Ln = Yb (9**), Y (**10**), Nd (**11**), and La (**12**)) and $L''_2\text{LnN(TMS)}_2$ ($L'' = 3,5\text{-Bu}^t\text{-2-(O)-C}_6\text{H}_2\text{CH}=\text{N-2,6-Me}_2\text{-C}_6\text{H}_3$; Ln = Yb (**13**) and Y (**14**)): Influence of Schiff Base Ligands and Lanthanide Metals.** To address the influence of Schiff base ligand on the synthesis, stability, and reactivity of monoamido lanthanide complexes, the bidentate Schiff bases L' and L'' were chosen, as they have not yet been used as ancillary ligand for stabilizing a monoamido lanthanide complex.

The reaction of $\text{Y}[\text{N(TMS)}_2]_3$ with 2 equiv of proligand HL' was conducted. The reaction proceeded immediately at $-50\text{ }^\circ\text{C}$ in THF to afford the monoamido complex $L'_2\text{YN(TMS)}_2$ (**10**), with the concomitant release of 2 equiv of bis(dimethylsilyl) amine (Scheme 3).

Further study revealed that complex **10** could also be prepared by the salt metathesis reaction of $L'_2\text{YCl}$, which was formed in situ by the reaction of YCl_3 with 2 equiv of NaL' in THF, with NaN(TMS)_2 in THF at room temperature (Scheme 3). The facile synthesis of **10** prompted us to extend the utility of the ligand in stabilizing monoamido complexes with other

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex **6**

6			
Bond Lengths			
Nd (1)–O (1)	2.277(6)	Nd (1)–N (3)	2.411(7)
Nd (1)–O (2)	2.219(5)	Nd (1)–N (4)	2.598(7)
Nd (1)–O (3)	2.545(6)	N (3)–C (31)	1.456(10)
Nd (1)–N (1)	2.622(6)	N (1)–C (7)	1.288(10)
Nd (1)–N (2)	2.511(6)	C (15)–C (31)	1.500(11)
Bond Angles			
O (2)–Nd (1)–O (3)	159.7(2)	N (2)–Nd (1)–N (3)	66.2(2)
O (1)–Nd (1)–N (1)	72.1(2)	N (3)–Nd (1)–N (4)	63.9(2)
N (1)–Nd (1)–N (2)	63.9(2)	O (1)–Nd (1)–N (4)	97.4(2)

lanthanide metals. The amine elimination reaction was used for this purpose. It was pleasing to note that all the reactions of the lanthanide amidos including $\text{Yb}[\text{N(TMS)}_2]_3$, $\text{Nd}[\text{N(TMS)}_2]_3$, and $\text{La}[\text{N(TMS)}_2]_3$, respectively, with HL' in a molar ratio of 1:2 at $-50\text{ }^\circ\text{C}$ in THF went smoothly and afforded the corresponding monoamido complexes $L'_2\text{LnN(TMS)}_2$ (Ln = Yb (**9**), Nd (**11**), La (**12**)) in good yields (Scheme 3).

For the less bulky bidentate ligand HL'' , the situation is quite different. Treatment of the amido complexes of $\text{Yb}[\text{N(TMS)}_2]_3$ and $\text{Y}[\text{N(TMS)}_2]_3$ with HL'' in a 1:2 molar ratio at $-50\text{ }^\circ\text{C}$ in THF afforded the desired monoamido complexes of $L'_2\text{YbN(TMS)}_2$ (**13**) and $L'_2\text{YN(TMS)}_2$ (**14**), respectively, in good yields (Scheme 4). However, attempts to prepare the analogues of the larger metals such as La and Nd metals following the procedure used for **13** and **14** were unsuccessful. Instead, the homoleptic tris-Schiff base lanthanide complexes $L''_3\text{Ln}$ were formed with the concomitant release of 3 equiv of free amine for both cases (Scheme 4). It is likely that the larger ionic radius of La and Nd metals account for the apparent instability of relatively low-coordinate species, thus resulting in the formation of homoleptic Schiff base complexes.

Complexes **9–14** are well soluble in THF and toluene, but insoluble in *n*-hexane. It was noted that all the amido complexes **9–14** are quite stable either in the solid state or in a solution. Neither metalation reaction nor migration of the amido group for all the cases was observed, as revealed by the ^1H NMR spectrum, even elevated temperature to $80\text{ }^\circ\text{C}$ in C_6D_6 for complexes **10** and **14**, no matter if the substituents at the 2, 6-positions of the phenyl ring are methyl or isopropyl groups. This may be because

Scheme 3. Synthesis of Complexes 9–12

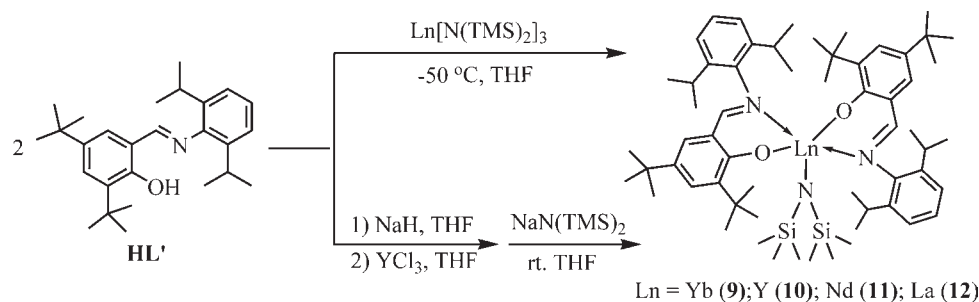
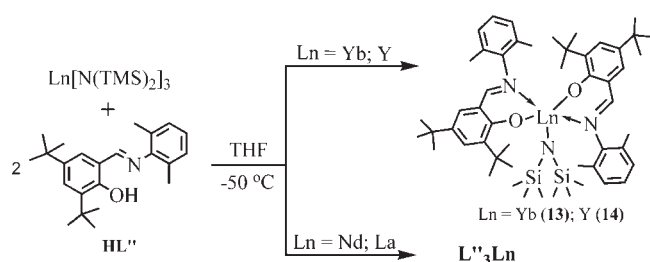
Scheme 4. Amine Elimination Reaction of $\text{Ln}[\text{N}(\text{TMS})_2]_3$ with HL'' 

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complexes 9–12

	9	10	11	12
Bond Lengths				
Ln (1)–O (1)	2.110(6)	2.154(3)	2.236(2)	2.277(4)
Ln (1)–N (1)	2.414(8)	2.463(4)	2.586(3)	2.658(5)
Ln (1)–N (2)	2.189(11)	2.245(6)	2.340(4)	2.403(7)
Bond Angles				
O (1)–Ln (1)–O (1A)	150.8(3)	149.54(18)	146.41(13)	143.7(2)
N (1)–Ln (1)–N (2)	122.35(17)	122.85(9)	123.57(7)	124.39(11)
N (1)–Ln (1)–N (N1A)	115.3(3)	114.29(18)	112.86(13)	111.2(2)

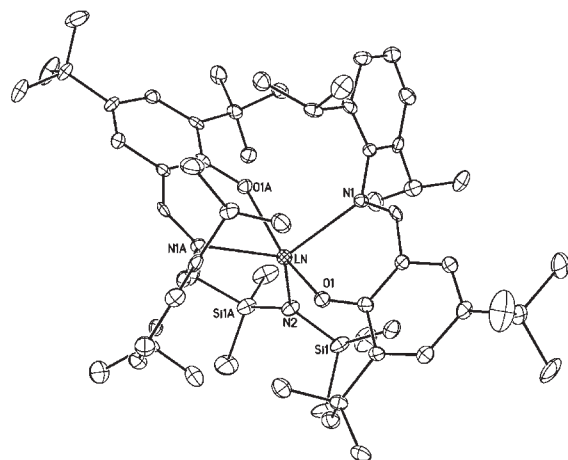
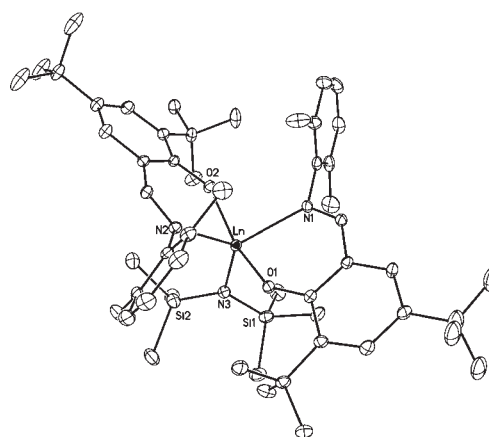


Figure 3. ORTEP diagram of the molecular structures of complexes 9–12 (Ln = Yb (9), Y (10), Nd (11), and La (12)). Thermal ellipsoids are drawn at 20% probability level. All hydrogens are omitted for clarity.

the free rotation of the C–C bond makes the methyl groups occupy an optimal position away from the metal-bound amido group.

Molecular Structures of Complexes 9–14. The five-coordinated monoamido complexes of lanthanides supported by bismonoanionic Schiff base ligands, which have been structurally characterized, are rare, although this kind of amido complexes bearing a salen-type ligand are well-known.³ Therefore, the molecular structures of 9–14 are determined by X-ray crystallography.

The molecular structures of complexes 9–12 are shown in Figure 3, as they are isostructural. The important bond distances and angles are listed in Table 5. Each complex adopts a distorted

Figure 4. ORTEP diagram of the molecular structures of complexes 13–14 (Ln = Yb (13), Y (14)). Thermal ellipsoids are drawn at 20% probability level. All hydrogens and disordered *tert*-butyl groups are omitted for clarity.

trigonal bipyramidal arrangement by two bidentate salicylaldimine ligands and one amido group around the five-coordinate metal. The N (1), N (2), N (1A) atoms occupy the equatorial positions, and are nearly coplanar with sums of the bond angles of 360° for 9, 359.99° for 10, 360° for 11, and 359.98° for 12. The O (1) and O (1A) atoms occupy the axis positions, and the bond angles of O (1)–Y (1)–O (1A) are distorted from the ideal value of 180° to 150.8(3)° for 9, 149.54(18)° for 10, 146.41(13)° for 11, and 143.7(2)° for 12.

The Ln–O (Schiff base) bond distances (2.110(6) Å for 9, 2.154(3) Å for 10, 2.236(2) Å for 11, and 2.277(4) Å for 12) and the Ln–N (imine) bond lengths (2.414(8) Å for 9, 2.463(4) Å

Table 6. Selected Bond Distances (Å) and Angles (deg) for Complexes 13–14

	13	14		13	14
Bond Lengths					
Ln (1)–O (1)	2.113(3)	2.140(3)	Ln (1)–N (1)	2.420(4)	2.467(4)
Ln (1)–O (2)	2.096(3)	2.132(4)	Ln (1)–N (2)	2.411(4)	2.446(5)
			Ln (1)–N (3)	2.219(4)	2.245(4)
Bond Angles					
O (1)–Ln (1)–O (2)	154.59(14)	153.03(16)	N (2)–Ln (1)–N (3)	120.57(14)	120.59(15)
N (1)–Ln (1)–N (3)	123.98(14)	124.17(16)	N (1)–Ln (1)–N (2)	115.45(14)	115.24(15)

Table 7. Reaction of Aniline with *N,N'*-Diisopropylcarbodiimide Catalyzed by Complexes 1–5, 10, and 14^a

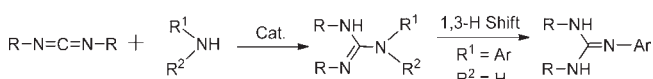
entry	cat.	time/h	yield (%) ^b
1	5	1	97
2	4	1	95
3	3	1	96
4	2	1	75
5	1	1	65
6	10	1	73
7	14	1	77

^aThe reaction was performed by treating 1.02 equiv of aniline with 1 equiv of *N,N'*-diisopropylcarbodiimide; the catalyst's loading was 1%; 40 °C. ^b Isolated yield.

for **10**, 2.586(3) Å for **11**, and 2.658(5) Å for **12**) compare well with each other when the differences in ionic radius among the lanthanide metals are considered. The values are also consistent with the corresponding bond distances in other reported Schiff base complexes on taking into account the difference in ionic radius among the different coordination numbers of lanthanide metals. However, The Y (1)–N (2) (amido) bond distance in **10** (2.245(6) Å) is slightly longer than 2.204(4) Å found in the five-coordinated Schiff base amido complex Y(DIP₂-pyr)₂N-(TMS)₂,^{3k} this may be because of the more open coordination sphere around the central metal with a bridged ligand than that bearing two unbridged ligands. This value is also about 0.03 Å longer than the seven-coordinated tridentate Schiff base amido complex **2** (2.338(3) Å),¹⁰ when the difference in ionic radius between five- and seven-coordinated Y metal is considered.

X-ray crystallographic analyses of **13** and **14** revealed their monomeric structures (Figure 4), which are similar to those for **9–12**. The selected bond distances and angles are listed in Table 6. In both complexes, the central metal is coordinated in a distorted trigonal bipyramidal geometry, in which O (1) and O (2) atoms from the two Schiff base ligands occupy the axis positions, and the bond angles O (1)–Ln (1)–O (2) are distorted from the ideal value of 180° to 154.59(14)° for **13** and 153.03(16)° for **14**. The N (1), N (2) atoms from the two Schiff base ligands and N (3) atom from the -N(TMS)₂ group occupy the equatorial positions, and are nearly coplanar with sums of the bond angles of 360° for **13** and **14**. The average bond distances of Ln–O (Schiff base) (2.104 Å for **13**, 2.136 Å for **14**), Ln–N (imine) (2.416 Å for **13** and 2.456 Å for **14**), and Ln–N (amido) (2.219(4) Å for **13** and 2.245 Å for **14**) compare well with the corresponding values found in **9–12**.

Catalytic Activity of 1–5, 10, and 14 for Addition of Amines to Carbodiimides. To access the influence of the Schiff base and central metals on reactivity of monoamido

Table 8. Results of Reactions of Different Amines with Carbodiimides Catalyzed by Complex 4^a

entry	R	R ¹ R ² NH	time (h)	product	yield (%) ^b
1	ⁱ Pr		1	1	91
2	Cy		1	2	96
3	ⁱ Pr		1	3	99
4	Cy		1	4	99
5	ⁱ Pr		1	5	99
6	Cy		1	6	98
7	ⁱ Pr		1	7	95
8	Cy		1	8	98
9	ⁱ Pr		5	9	98
10	Cy		6	10	93
11	ⁱ Pr		2	11	96 ^c
12	ⁱ Pr		4	12	94 ^c
13	ⁱ Pr		2	13	95 ^c
14	ⁱ Pr		24	14	97 ^d

^aThe reaction was performed by treating 1.02 equiv of amines with 1 equiv of carbodiimides; the catalyst's loading was 1%. ^b Isolated yield. ^c 1.5 equiv of DIC was used. ^d Temperature is 100 °C.

complexes of lanthanides, addition of aniline to *N,N'*-diisopropylcarbodiimide was tested using a catalytic amount of 0.01 equiv at 40 °C under solvent-free condition as a template reaction. As shown in Table 7, all the complexes can serve as a catalyst to yield the corresponding guanidine in good to excellent yields. It is noted that almost no differences in activity are observed among the amido complexes with various Schiff base ligands (Table 7, entries 4, 6, 7). However, the activity is largely influenced by the central metals with the active sequence of La ≈ Nd ≈ Eu > Y > Yb (Table 7, entry 1–5).

Therefore, **4** was selected as the catalyst for the examination of the following guanylation of various amines. Representative

results are summarized in Table 8. As shown in Table 8, a wide range of substituted anilines could be used for this reaction. The reaction was not influenced by either electron-withdrawing or electron-donating substituents or the position of the substituents at the phenyl ring. When the substituents on the phenyl ring are CH₃-, Cl-, and F-, excellent yields of the corresponding guanidine can be isolated from the reactions of related amine with carbodiimides at 40 °C (Table 8, entries 3–8, 11, 13). When the substituents on the phenyl ring are CH₃O- group, excellent yields of the guanidines (Table 8, entries 9, 10, 12) could be obtained at 40 °C, when the reaction time was extended. While the reaction of 2,6-dimethylaniline with *N,N'*-Diisopropylcarbodiimide required 24 h at 100 °C with 97% isolated yields of guanidine (Table 8, entry 14).

CONCLUSION

In conclusion, we have described the synthesis and molecular structures of a series of monoamido complexes of lanthanides bearing two Schiff base ligands by amine elimination reaction. The synthesis and stability of monoamido complexes of lanthanides supported by two Schiff base ligands are largely influenced by the ligands and the size of the central metals. By ligand and solvent choice, it is possible to isolate monoamido complexes of lanthanide metals including Yb, Y, Nd, and La in good yields. An intramolecular C–H bond activation of a quinoline ring in **4** with the ligand L by a metal bound amido group and subsequent attack of the newly formed aryl species at the imine group of the second ligand occurs. Evidently, steric effect controls the processes. All the amido complexes **1–5**, **10**, and **14** presented here were found to be efficient catalysts for addition of amines to carbodiimides.

ASSOCIATED CONTENT

S Supporting Information. X-ray crystallographic data of complexes **3–6** and **9–14** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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