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Syntheses, Structure, and Properties of Mixed Cp−Amidinate Rare-Earth-Metal(III) Complexes

Jun-Feng Liu,[†,‡] Fu-Xing Pan,[†,‡] Shuang Yao,[†] Xue Min,[†,‡] Dongmei Cui,[§] and Zhong-Ming Sun*[,†]

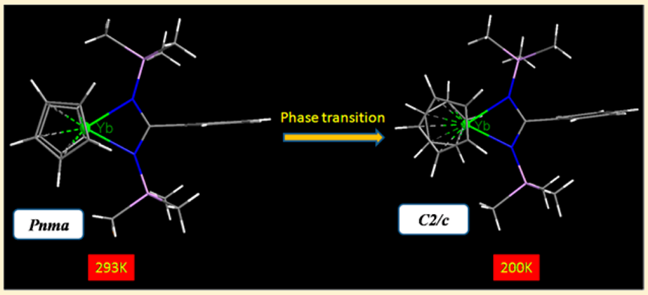
[†]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, People's Republic of China

[‡]University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

[§]Changchun Institute of Applied Chemistry, State Key Laboratory of Polymer Physics and Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, People's Republic of China

Supporting Information

ABSTRACT: A family of mixed Cp−amidinate rare-earth-metal(III) complexes [$Cp_2L^1LnPhCN$] (Ln = Y (**1**), La (**2**), Sm (**3**), Eu (**4**), Gd (**5**), Tb (**6**), Dy (**7**); L^1 = PhC-($NSiMe_3$)$_2$), [Cp_2L^1Ln] (Ln = Er (**8**), Yb (**9**)), and [Cp_2L^2Ln] (Ln = Y (**10**), Eu (**11**), Gd (**12**), Tb (**13**), Dy (**14**), Er (**15**); L^2 = N(*t*-Bu)C(Ph)N($SiMe_3$)) were synthesized by treatment of Cp_3Ln with lithium amidinates. The phase transition has been observed for compounds **5** and **9** at low temperature (200 K). Single-crystal structural analyses reveal that compounds **1**, **3**, **4**, **5b**, **6**, **7**, **9b**, and **10**−**15** contain two staggered Cp rings. In contrast, two eclipsed Cp rings were observed in compounds **2**, **5a**, **8**, and **9a**. Moreover, the luminescent properties of complex **6** and magnetic properties of complex **7** were also investigated.



INTRODUCTION

Over the past decades, organolanthanide chemistry has attracted considerable attention in materials science due to their unique properties in single-molecule magnets (SMMs),[1] catalytic transformations,[2,3]and atomic layer deposition (ALD) and metal−organic chemical vapor deposition (MOCVD) processes.[2,4] Amidinate ligands [$R^1NC(R^3)NR^2$]$^-$ (L^-; R^1, R^2 = H, alkyl, cycloalkyl, aryl, trimethylsilyl; R^3 = H, alkyl, aryl) are very popular in the synthesis of lanthanide complexes because of their versatile steric and electronic properties, which can be easily tuned by changing various groups on R^1, R^2, and R^3.[5] Edelmann and co-workers made pioneering contributions in the rare-earth-metal chemistry of amidinate ligands.[5] In general, the rare-earth-metal amidinate complexes can be obtained by the reactions between amidinate ligands and rare-earth-metal precursors. Alternatively, the Junk group also synthesized rare-earth-metal amidinate complexes using elemental rare-earth metals, organomercury reagents, and formamidinate ligands [$R^1NC(H)NR^2$] (LH) as reactants.[6] Some of the divalent rare-earth-metal amidinate complexes have the unique properties of reduction to cleave the E−E bond in the diaryl dichalcogenides REER (R = aryl; E = Se, Te),[7] activate C−X bonds,[6f,h] and reduce carbodiimides.[6e] In addition, the catalytic activities of the trivalent rare-earth-metal amidinate complexes were also studied,[5b−d,l,8] such as the Tishchenko reaction,[6d] polymerization of olefins[9] and dienes,[10] intramolecular hydroamination/cyclization reactions,[11] and ring-opening polymerization of *rac*-lactide.[12]

On the other hand, reactions based on tris(cyclopentadienyl) rare-earth-metal(III) species Cp_3Ln have aroused longstanding interest in the synthesis of mixed ligand supported organic rare-earth-metal complexes,[13] which often exhibit unique chemical reactivities and magnetic properties.[1b,c,14] Alcohol,[15] thiol,[15h,16] hydroxylaminato,[17] and amino[14,18] ligands have been widely used to prepare new organic rare-earth-metal compounds,[2a−p,13] in which the cyclopentadienyl Cp ring can be easily substituted by these ligands mentioned above. Generally, the majority of the obtained target complexes have di- or trinuclear frameworks and the O or N atoms in the ligand can serve as bridging atoms. In addition, various rare-earth/aluminum heterobimetallic complexes have been reported by Roesky and co-workers using Cp_3Ln and the aluminum monohydroxide L′AlOH(Me) (L′ = CH(CMeNAr)$_2$, Ar = 2,6-$^iPr_2C_6H_3$) as precursors.[19] The new class of rare-earth/aluminum heterobimetallic compounds as catalysts is very effective for the polymerization of ε-caprolactone. Recently, the functionalization of rare-earth metallocenes was investigated through the reactions of Cp_3Ln with various unsaturated molecules.[20,21] For example, the reaction of Cp_3Y with $^iPrN{=}C{=}N^iPr$ in toluene gave rise to an amidino-substituted cyclopentadienyl yttrium complex, as a result of Ln−Cp bond insertion and subsequent isomerization.[21a]

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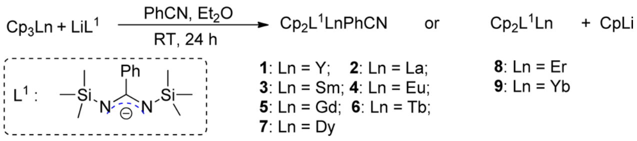
In comparison with the above achievements of rare-earth-metal complexes, only a few studies on the chemistry of rare-earth-metal complexes containing a mixed cyclopentadienyl−amidinate (Cp-amidinate) ligand have been reported,[22,23] and the utilization of the mixed Cp−amidinate rare-earth-metal complexes in materials chemistry remains unexplored.[2a−p,5] Herein, we describe the synthesis and characterization of mixed Cp−amidinate rare-earth-metal complexes starting from the simple Cp_3Ln and alkali-metal salt of amidinate precursors (Schemes 1 and 2). Furthermore, a phase transformation occurring in the crystal structures has been observed when the temperature is changed. In addition, the luminescent properties of complex **6** and magnetic properties of complex **7** have also been investigated in this contribution.

■ RESULTS AND DISCUSSION

Synthesis and Structure of Mixed Cp−Amidinate Rare-Earth-Metal(III) Complexes 1−9. As shown in Scheme 1, to a solution of LiL^1 and PhCN in Et_2O was added the appropriate Cp_3Ln species at ambient temperature to give rise to the corresponding $Cp_2L^1LnPhCN$ (Ln = Y (**1**), La (**2**), Sm (**3**), Eu (**4**), Gd (**5**), Tb (**6**), Dy (**7**)). Interestingly, analogous reactions led to Cp_2L^1Ln (Ln = Er (**8**), Yb (**9**)) under similar conditions.

Scheme 1. Synthesis of Mixed Cp−Amidinate Rare-Earth-Metal(III) Complexes 1−9



The X-ray diffraction analysis of single crystals of complexes **1**−**4**, **5a**, **6**−**8**, and **9a** was carried out at room temperature, and the corresponding data of the compounds **5b** and **9b** were also obtained at low temperature (Tables S1 and S2, Supporting Information) (compound **5** has a phase transition at low temperature; compounds **5a**,**b** are identical and are obtained at room and low temperature, respectively; compound **9** is similar to compound **5**). The X-ray structure characterizations for complexes **1**−**7** indicate that these compounds are isostructural and adopt the same triclinic space group $P\bar{1}$. The corresponding data of compounds **8** and **9a** show that they are also isostructural and crystallize in the orthorhombic crystal system with the space group *Pnma*, while compound **9b** adopts monoclinic space group *C*2/*c*.

Figure 1 shows representative features of the isostructural complexes **1**−**7** in which each central metal atom is coordinated by one amidinate ligand, two cyclopentadienyl rings, and one neutral benzonitrile molecule. The two cyclopentadienyl rings of complexes **1**, **3**, **4**, **5b**, **6**, and **7** were staggered, while an eclipsed conformation was observed in complexes **2** and **5a**.

Compound **1**, shown in Figure 1, was collected as colorless crystals in 46% yield. This complex contains two staggered cyclopentadienyl rings. The Y−N(2) length is 2.393(3) Å and is shorter than that of Y−N(1) (2.410(3) Å). As expected, the distance between the metal center and the nitrogen atom in the benzonitrile molecule is 2.526(4) Å (Y−N(3)), slightly longer than those of Y−N(1) and Y−N(2). The C−N distances of the delocalized N−C−N ligand are similar (N(1)−C(1) 1.333(4) Å and N2−C1 1.340(4) Å). The N(1)−Y−N(2) and N(1)−C(1)−N(2) angles are 57.09(10) and 118.3(3)°, respectively.

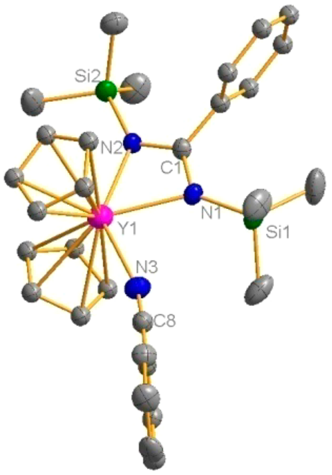


Figure 1. ORTEP representation of complex **1** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Similar to the case for compound **1**, compound **2** was also obtained as colorless crystals in 51% yield. The feature of compound **2** is that the two cyclopentadienyl rings are arranged in an eclipsed orientation with respect to each other (Figure S1, Supporting Information). Unlike the case for compound **1**, the distances of La−N(1) and La−N(2) in compound **2** are equal (La−N(1) 2.521(3) Å and La−N(2) 2.526(3) Å). The La−N(3) distance in compound **2** is 2.679(3) Å, which is longer than the Y−N(3) bond length in compound **1**. The N−C distances of the amidinate ligand in compound **2** are also similar (N(1)−C(1) 1.327(5) Å and N(2)−C(1) 1.333(4) Å). The N(1)−La−N(2) bite angle (54.07(10)°) is decreased in comparison to that in compound **1**, but the acute N(1)−C(1)−N(2) bite angle of the amidimate ligand in compound **2** (119.1(3)°) is slightly larger than that in compound **1**.

The structures of complexes **3**, **4**, **5a**, **6** and **7** are more similar to that of complex **1** on account of bearing two staggered cyclopentadienyl rings. Due to the lanthanide contraction effect, the corresponding Ln−N(1)/N(2) bond lengths slightly decrease with the reduction of the metal ion radius in compounds **3**, **4**, **5b**, **6** and **7** (Figure 2A). On the other hand, the N(1)−Ln−N(2) angles for compounds **3**, **4**, **5b**, and **7** slightly increase with the reduction of the lanthanide ion radius (Figure 2B). However, a particular exception occurs in compound **6**, in which the N(1)−Tb−N(2) angle is smaller than those of compounds **5b** and **7** (Figure 2B).

It is interesting and noteworthy that the two cyclopentadienyl rings of complex **5** adopt a staggered conformation at low temperature (**5b**) (Figure S5, Supporting Information), while they are eclipsed at room temperature (**5a**) (Figure S4, Supporting Information). This phenomenon indicates that compound **5** has a phase transition at low temperature (Figure 3). To the best of our knowledge, this behavior has not been documented in mixed Cp−amidinate rare-earth-metal complexes. The phase transition phenomenon is also reflected on the corresponding cell parameters, with the cell volume reduced at a ratio of 4.2% (Table S1, Supporting Information). The Ln−N(1)/N(2) distances in compound **5a** containing two staggered rings (Gd−N(1) 2.526(4) Å and Gd−N(2) 2.529(4) Å) are not only longer than corresponding values of compound

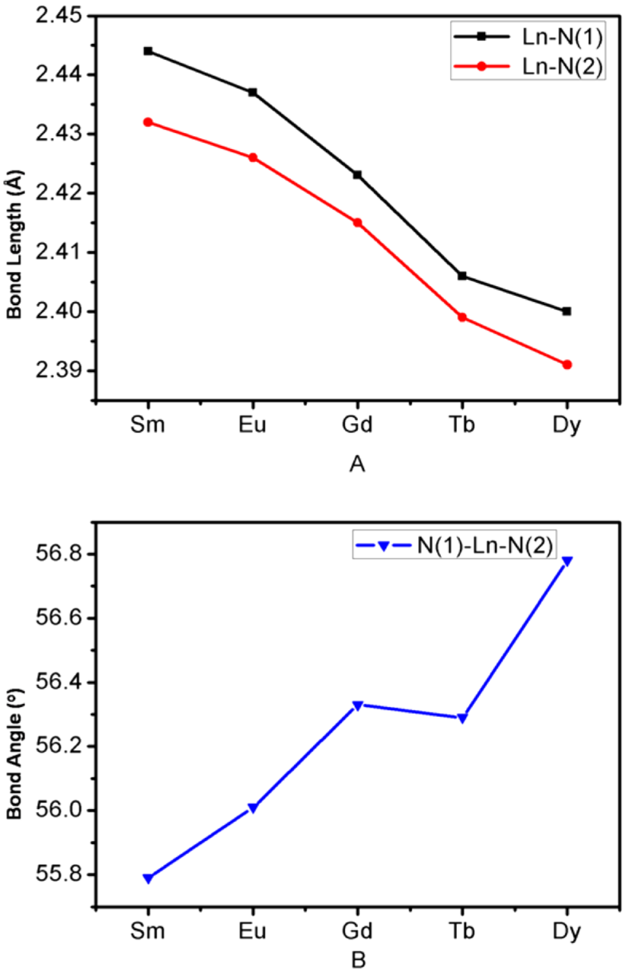


Figure 2. Ln−N(1)/N(2) distances (A) and N(1)−Ln−N(2) angles (B) of compounds **3** (Sm), **4** (Eu), **5b** (Gd), **6** (Tb), and **7** (Dy).

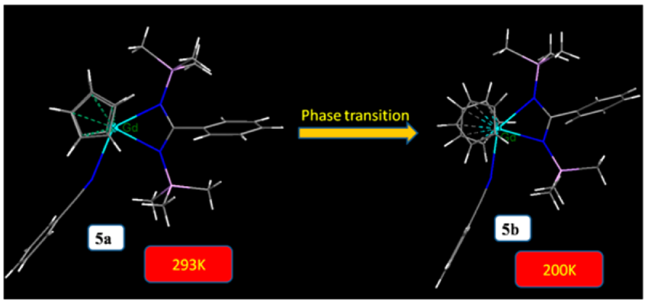


Figure 3. Phase transition of complex **5**.

5b containing two staggered rings (Figure S8, Supporting Information) but also longer than those of compound **3** (Sm−N(1) 2.444(3) Å and Sm−N(2) 2.432(4) Å). However, the N(1)−Ln−N(2) angle of 53.83(13)° in compound **5a** is smaller than the corresponding angles of compounds **3**, **4**, **5b**, **6**, and **7** (Figure 2B). On the other hand, the data of compounds **2** and **5a** with regard to Ln−N(1)/N(2) bond lengths and N(1)−Ln−N(2) angles are very similar because of two eclipsed rings exist in both complexes.

Compound **3** was confirmed by NMR spectroscopy. In the ^{1}H NMR spectrum, only one signal was observed at low field for the two cyclopentadienyl rings (^{1}H NMR δ 10.72 ppm). The signals for chemical shifts of the aromatic protons appear as multiplets between 10.50 and 6.52 ppm. Moreover, a single peak at −3.48 ppm is attributed to the characteristic $SiMe_3$ resonance.

In comparison to compounds **1**−**7**, the features of compounds **8** (Figure S8, Supporting Information), **9a** (Figure S9, Supporting Information) and **9b** (Figure 4) are the loss of benzonitrile ligand and adoption of a more highly symmetric space group. Obviously, there is not enough room for compounds **8** and **9** to accommodate the coordination of other ligands due to the smaller ionic radii of Er^{3+} and Yb^{3+}. Similar to the case for compounds **2** and **5a**, compounds **8** and **9a** contain two eclipsed cyclopentadienyl rings. The Ln−N distances of compound **8** (Er−N(1) 2.309(4) Å and Er−N(2) 2.315(5) Å) are slightly longer than those of compound **9a** (Yb−N(1) 2.289(4) Å and Yb−N(2) 2.303(4) Å). Their N(1)−Ln−N(2) angles are similar (58.96(17)° (**8**) and 59.75(14)° (**9a**)). Interestingly, the phase transition phenomenon is also observed in compounds **9a**,**b** when the temperature is changed (Figure 5). In comparison to compound **9a**, compound **9b** contains two staggered cyclopentadienyl rings and adopts a lower space group (monoclinic group *C*2/*c*). The bond lengths and bond angle of compound **9b** (Yb−N(1) 2.285(4) Å, Yb−N(2) 2.296(4) Å, and N(1)−Yb−N(2) 59.55(14)°) are similar to those of compound **9a**. Moreover, due to the paramagnetism of the ytterbium atom, only broad signals were observed in the ^{1}H NMR spectrum of compound **9**.[7c,11b]

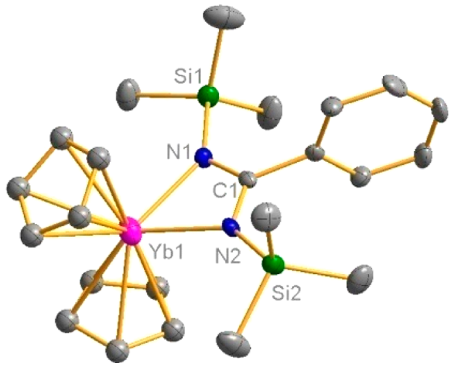


Figure 4. ORTEP representation of complex **9b** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

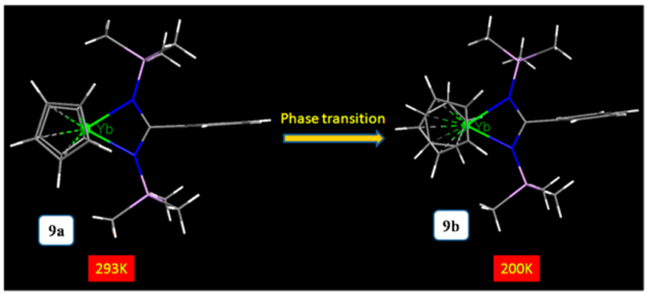
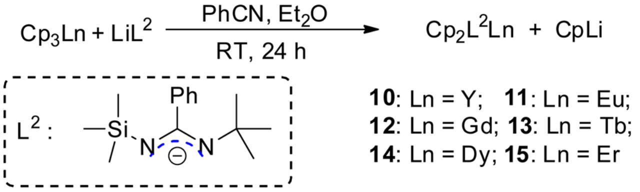


Figure 5. Phase transition of complex **9**.

Synthesis and Structure of Mixed Cp−Amidinate Rare-Earth-Metal(III) Complexes 10−15. As shown in Scheme 2, treatment of LiL^2 and PhCN in Et_2O with the appropriate Cp_3Ln species at ambient temperature gave

Scheme 2. Synthesis of Complexes 10−15



Cp_2L^2Ln (Ln = Y (**10**), Eu(**11**), Gd (**12**), Tb (**13**), Dy (**14**), Er (**15**)), respectively. The X-ray crystal structures for complexes **10**−**15** indicate that these compounds are isostructural and adopt the same monoclinic space group $P2_1$ (Tables S2 and Table S3, Supporting Information).

Figure 6 shows a feature of the isostructural compounds **10**−**15** in which two atoms (Si and C) of ligand L^2 are jointly occupied. Similar to the case for compounds **8** and **9**, compounds **10**−**15** also have no benzonitrile ligand. Moreover, although the two cyclopentadienyl rings in compounds **10**−**15** are staggered, they are very close to eclipsed. Similar to the case for compound **1**, the Y−N(1) length (2.315(4) Å) is longer than that of Y−N(2) (2.305(5) Å) in compound **10**. The Y−N distances in compound **10** are shorter than those in compound **1**, but the N(1)−Y−N(2) bite angle (58.4(2)°) in compound **10** is larger than that of compound **1**. Additionally, the Ln−N(1) distances and the N(1)−Ln−N(2) bite angles for compounds **11**−**15** display the trends similar to those found in compounds **3**, **4**, **5a**, **6**, and **7**. However, the Tb−N(2) bond length (2.354(5) Å) is the longest in compounds **11**−**15**.

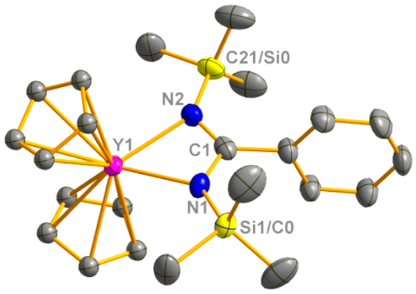


Figure 6. ORTEP representation of complex **10** with the probability ellipsoids drawn at the 30% level. Partial hydrogen atoms are omitted for clarity.

Phase Transition Behavior. Thirty years ago, some rare-earth-metal complexes bearing two eclipsed cyclopentadienyls,[13,15a,b,16a,18c,21c,23a,24] pentamethylcyclopentadienyls (C_5Me_5),[13,25] and other substituted cyclopentadienyls[13,26] have been observed previously by different research groups. However, the eclipsed ring phenomenon occurring in rare-earth-metal complexes has been almost entirely attributed to the result of steric hindrance. In our investigation of the mixed Cp−amidinate rare-earth-metal(III) complexes, the phase transition of eclipsed cyclopentadienyl rings and staggered cyclopentadienyl rings depend on the temperature, which is similar to the case for ferrocene.[27] For example, the eclipsed cyclopentadienyl rings in compound **5a** are observed at ambient temperature; in contrast, compound **5b** with staggered cyclopentadienyl rings is more stable at low temperature. Interestingly, as the phase transition occurs, compounds **9a**,**b** adopt a higher symmetry space group (orthorhombic group *Pnma*) and lower symmetry space group (monoclinic group *C*2/*c*), respectively.

Fluorescent Properties. It is well-known that the rare-earth-metal compounds play an important role in materials chemistry, due to their distinctive and excellent luminescent performance. Recently, a few works on the luminescent properties of rare-earth-metal amidinate complexes have been documented.[28] In 2011, the luminescent properties of a divalent europium silaamidinate complex were reported by Pan and co-workers.[28] In the divalent lanthanide complex, the emission peak at 528 nm can be contributed to the 4f−5d transition of Eu^{2+}. We report here the fluorescent properties of the mixed Cp−amidinate trivalent terbium complex. The emission spectrum of $[Cp_2L^1TbPhCN]$ (**6**) was measured. The characteristic transitions for the Tb^{3+} ion were observed at 493, 547, 590, and 623 nm, which can be attributed to $^5D_4 \rightarrow {}^7F_J$ (J = 6−3) (Figure 7). Among these transitions, the green emission at 547 nm ($^5D_4 \rightarrow {}^7F_5$) is the most prominent. Unfortunately, in contrast to compound **6**, the characteristic transitions for the Tb^{3+} and Eu^{3+} ions were not observed in the compounds $[Cp_2L^2Tb]$ (**13**), $[Cp_2L^1EuPhCN]$ (**4**), and $[Cp_2L^2Eu]$ (**11**).[29]

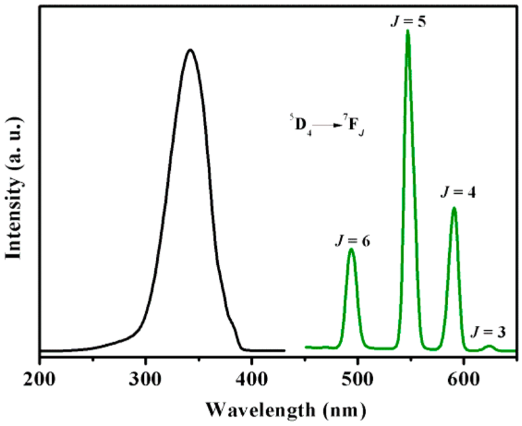


Figure 7. Excitation (black, λ_{em} 547 nm) and emission spectra (green, λ_{ex} 341 nm) of complex **6** as solid samples.

Magnetic Properties. Considering the magnetic properties of Ln^{3+} ions,[1] the temperature dependence of the magnetic susceptibility $\chi_m T$ for compound **7** were measured in the temperature range 2−300 K under an applied field of 1000 Oe using polycrystalline samples (Figure S21, Supporting Information). For compound **7**, the value of $\chi_m T$ is 14.51 cm^3 K mol^{-1} at 300 K, which is close to the expected value of 14.17 cm^3 K mol^{-1} for a single Dy^{3+} ion ($^6H_{15/2}$, $S = {}^5/_2$, $L = 5$, $g = {}^4/_3$).[30] Upon cooling, the value of $\chi_m T$ for compound **7** slowly increases to reach a maximum of 14.99 cm^3 K mol^{-1} at 50 K and then rapidly decreases to a minimum value of 11.60 cm^3 K mol^{-1} at 2 K. These magnetic behaviors are attributed to crystal-field effects such as thermal depopulation of the Dy^{3+} Stark sublevels.[30] Alternating current (ac) susceptibility measurements for compound **7** were carried out under zero direct current (dc) field with an ac field of 3 Oe with oscillating frequencies. As shown in Figure S23 (Supporting Information), compound **7** exhibits frequency-dependent out-of-phase signals without maxima, suggesting the presence of slow magnetic relaxation at low temperature, which is due to extremely efficient quantum tunneling of the magnetization within the lowest Kramers doublet.

■ CONCLUSION

A family of mixed Cp−amidinate rare-earth-metal(III) complexes were prepared in a one-step reaction using Cp_3Ln and lithium salts of the amidinate ligands as precursors. There are two staggered Cp rings in compounds **1**, **3**, **4**, **5b**, **6**, **7**, **9b**, and **10**−**15**, whereas compounds **2**, **5a**, **8**, and **9a** contain two eclipsed Cp rings. Interestingly, a phase transformation occurring in the crystal structures for compounds **5** and **9** has been observed when the temperature is changed. Moreover, the luminescent and magnetic properties of compounds **6** and **7** were also investigated.

■ EXPERIMENTAL SECTION

Materials, Syntheses, and Characterization. All manipulations were carried out under a purified nitrogen atmosphere using modified Schlenk techniques or in a N_2 gas glovebox unless otherwise indicated. Et_2O, *n*-hexane, and THF were distilled under a nitrogen atmosphere from sodium benzophenone prior to use. Cp_3Ln (Ln = Y, La, Sm, Eu, Gd, Tb, Dy, Er, Yb),[31] Li[CPh$(NSiMe_3)_2$],[5a,32] and Li[N(*t*-Bu)C(Ph)N$(SiMe_3)$][33] were prepared by literature methods. Benzonitrile and lithium bis(trimethylsilyl)amide were purchased from Alfa Aesar and Sigma-Aldrich, respectively. They were directly used without further purification. The deuterated solvent C_6D_6 was dried over activated molecular sieves (4 Å) and vacuum-transferred before use. NMR spectra were recorded on a Bruker 400 MHz spectrometer at 298 K. The elemental analyses of C, H, and N in the solid samples were carried out on a VarioEL analyzer. IR spectra were obtained on a Nicolet 6700 instrument in the range 4000−650 cm^{-1}. The luminescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The photomultiplier tube (PMT) voltage was 400 V, the scan speed was 1200 nm/min, and the slit width of excitation and emission is 5.0 nm. Temperature-dependent magnetic susceptibility data were recorded on a Quantum Design MPMS-XL SQUID magnetometer under an applied field of 1 kOe over the temperature range 2−300 K.

Synthesis of Complexes 1−9. To a mixture of Li[CPh$(NSiMe_3)_2$] (LiL^1; 0.25 mmol) and benzonitrile (PhCN; 0.25 mmol) in 5 mL of Et_2O was added Cp_3Ln (0.20 mmol) at room temperature, and the mixture was stirred for 24 h. After filtration, the resulting solution was stored at ambient temperature for several days to obtain the desired compounds.

Complex 1. Yield: 54 mg (46%) as colorless crystals. ^1H NMR (400 MHz, C_6D_6): δ 7.01−6.98 (m, 5H, Ph), 6.89−6.87 (m, 2H, Ph), 6.80 (t, J_{H-H} = 7.6 Hz, 1H, Ph), 6.64 (t, J_{H-H} = 8.0 Hz, 2H, Ph), 6.25 (s, 10H, Cp), −0.14 (s, 18H, $SiMe_3$). Anal. Calcd for **1**, $C_{30}H_{38}N_3Si_2Y$ (M_r = 585.72): C, 61.51; H, 6.55; N, 7.18. Found: C, 61.45; H, 6.60; N, 7.20.

Complex 2. Yield: 65 mg (51%) as colorless crystals. Anal. Calcd for **2**, $C_{30}H_{38}N_3Si_2La$ (M_r = 635.72): C, 56.68; H, 6.04; N, 6.61. Found: C, 56.61; H, 6.10; N, 6.65. IR data (cm^{-1}): 3060 (w), 2952 (w), 2893 (w), 2229 (w), 1634 (m), 1567 (m), 1498 (w), 1450 (m), 1428 (w), 1363 (w), 1321 (w), 1251 (m), 1237 (m), 1209 (m), 1122 (w), 950 (m), 892 (w), 823 (m), 779 (w), 750 (m), 699 (m), 664 (m).

Complex 3. Yield: 84 mg (65%) as yellow crystals. ^1H NMR (400 MHz, C_6D_6): δ 10.72 (s, 10H), 10.49 (d, J_{H-H} = 7.2 Hz, 2H, Ph), 8.11 (t, J_{H-H} = 7.2 Hz, 2H, Ph), 7.91 (t, J_{H-H} = 7.2 Hz, 1H, Ph), 6.73−6.63 (m, 5H, Ph), −3.478 (s, 18H, $SiMe_3$). Anal. Calcd for **3**, $C_{30}H_{38}N_3Si_2Sm$ (M_r =647.16): C, 55.67; H, 5.93; N, 6.49. Found: C, 55.27; H, 5.97; N, 6.53. IR data (cm^{-1}): 3071 (w), 2937 (w), 2853 (w), 1627 (m), 1607 (m), 1590 (m), 1566 (m), 1449 (m), 1439 (m), 1363 (w), 1247 (w), 1237 (m), 1128 (w), 1012 (w), 946 (w), 889 (w), 842 (m), 825 (m), 748 (m), 725 (w), 701 (m), 666 (w).

Complex 4. Yield: 86 mg (66%) as red crystals. Anal. Calcd for **4**, $C_{30}H_{38}N_3Si_2Eu$ (M_r = 648.77): C, 55.54; H, 5.92; N, 6.49. Found: C, 55.49; H, 5.95; N, 6.53.

Complex 5. Yield: 80 mg (61%) as yellowish crystals. Anal. Calcd for **5**, $C_{30}H_{38}N_3Si_2Gd$ (M_r = 654.06): C, 55.09; H, 5.87; N, 6.43. Found: C, 55.02; H, 5.90; N, 6.46. IR data (cm^{-1}): 3061 (w), 2950 (w), 2896 (w), 2254 (m),1642 (m), 1608 (w),1596 (m), 1565 (m), 1489 (w), 1446 (m), 1408 (s), 1247 (s), 1013 (w), 1003 (w), 988 (m), 951 (w), 918 (w), 825 (s), 745 (s), 697 (w), 681 (w).

Complex 6. Yield: 67 mg (51%) as yellowish crystals. Anal. Calcd for **6**, $C_{30}H_{38}N_3Si_2Tb$ (M_r = 655.73): C, 54.95; H, 5.85; N, 6.41. Found: C, 54.87; H, 5.90; N, 6.45. IR data (cm^{-1}): 3062 (w), 2950 (w), 2896 (w), 2229 (w),1640 (m), 1594 (w),1565 (m), 1492 (w), 1451 (m), 1430 (m), 1366 (w), 1242 (m), 1051 (w), 1014 (w), 952 (w), 921 (w), 892 (w), 825 (m), 750 (m), 698 (m), 666 (w).

Complex 7. Yield: 75 mg (57%) as yellow crystals. Anal. Calcd for **7**, $C_{30}H_{38}N_3Si_2Dy$ (M_r = 659.31): C, 54.65; H, 5.82; N, 6.37. Found: C, 54.68; H, 5.86; N, 6.41. IR data (cm^{-1}): 3065 (w), 2952 (w), 2895 (w), 2250 (w),1643 (m), 1597 (w),1567 (w), 1498 (w), 1446 (w), 1401 (m), 1364 (w), 1245 (s), 1050 (w), 1014 (w), 1002 (w), 988 (w), 954 (w), 917 (w), 891 (w), 826 (s), 745 (m), 698 (m), 681 (w).

Complex 8. Yield: 51 mg (45%) as yellow-brown crystals. Anal. Calcd for **8**, $C_{23}H_{33}N_2Si_2Er$ (M_r = 560.95): C, 49.24; H, 5.94; N, 5.00. Found: C, 49.30; H, 5.84; N, 5.11. IR data (cm^{-1}): 3082 (w), 2950 (w), 2893 (w), 1645 (m), 1594 (w), 1563 (w), 1499 (w), 1409 (s), 1261 (w), 1242 (s), 1072 (w), 1032 (w), 1005 (s), 995 (m), 963 (w), 918 (w), 888 (w), 827 (s), 751 (s), 701 (m), 685 (w).

Complex 9. Yield: 71 mg (63%) as yellow-brown crystals. Anal. Calcd for **9**, $C_{23}H_{33}N_2Si_2Yb$ (M_r = 566.73): C, 48.74; H, 5.88; N, 4.94. Found: C, 48.80; H, 5.84; N, 4.87. IR data (cm^{-1}): 3082 (w), 2953 (w), 2894 (w), 1644 (m), 1593 (w),1562 (w), 1498 (w), 1420 (s), 1409 (s), 1262 (w), 1242 (s), 1073 (w), 1032 (w), 1004 (m), 993 (m), 959 (w), 918 (w), 828(m), 742 (m), 702 (w), 686 (w).

Synthesis of Complexes 10−15. To a mixture of Li[N(*t*-Bu)C(Ph)N$(SiMe_3)$] (LiL^2; 0.25 mmol) and benzonitrile (PhCN; 0.25 mmol) in 5 mL of Et_2O was added Cp_3Ln (0.20 mmol) at room temperature, and the mixture was stirred for 24 h. After filtration, the resulting solution was stored at ambient temperature for several days to obtain the desired compounds.

Complex 10. Yield: 40 mg (43%) as colorless crystals. ^1H NMR (400 MHz, C_6D_6): δ 7.04−6.99 (m, 3H, Ph), 6.92−6.90 (m, 2H, Ph), 6.27 (s, 10H, Cp), 0.90 (s, 9H, CMe_3), −0.17 (s, 9H, $SiMe_3$). Anal. Calcd for **10**, $C_{24}H_{33}N_2SiY$ (M_r = 466.52): C, 61.79; H, 7.14; N, 6.01. Found: C, 61.56; H, 7.23; N, 6.08.

Complex 11. Yield: 54 mg (51%) as red crystals. Anal. Calcd for **11**, $C_{24}H_{33}N_2SiEu$ (M_r = 529.57): C, 54.43; H, 6.29; N, 5.29. Found: C, 54.39; H, 6.31; N, 5.33. IR data (cm^{-1}): 3083 (w), 2955 (w), 2897 (w), 1612 (w), 1599 (w), 1572 (w), 1525 (w), 1489 (w), 1452 (w), 1368 (m), 1241 (m), 1076 (w), 1038 (w), 1011 (w), 962 (w), 914 (w), 829 (m), 746 (m), 700 (w), 667 (w).

Complex 12. Yield: 60 mg (56%) as yellowish crystals. Anal. Calcd for **12**, $C_{24}H_{33}N_2SiGd$ (M_r = 534.86): C, 53.89; H, 6.23; N, 5.24. Found: C, 53.85; H, 6.27; N, 5.28. IR data (cm^{-1}): 3082 (w), 2953 (w), 2899 (w), 1611 (w), 1599 (w), 1574 (w), 1524 (m), 1492 (w), 1463 (w), 1450 (m), 1369 (m), 1244 (m), 1154 (w), 1076 (w), 1042 (w), 1011 (m), 919 (w), 870 (w), 827 (w), 754 (m), 703 (w), 668 (w).

Complex 13. Yield: 58 mg (54%) as yellowish crystals. Anal. Calcd for **13**, $C_{24}H_{33}N_2SiTb$ (M_r = 536.53): C, 53.72; H, 6.21; N, 5.22. Found: C, 53.68; H, 6.24; N, 5.27. IR data (cm^{-1}): 3085 (w), 2959 (m), 2899 (w), 1611 (w), 1596 (w), 1574 (w), 1528 (m), 1491 (w), 1465 (w), 1451 (m), 1382 (m), 1244 (m), 1155 (w), 1075 (w), 1040 (w), 1011 (m), 984 (w), 921 (w), 870 (w), 828 (m), 757 (m), 703 (m), 666 (w).

Complex 14. Yield: 64 mg (59%) as yellowish crystals. Anal. Calcd for **14**, $C_{24}H_{33}N_2SiDy$ (M_r = 540.11): C, 53.37; H, 6.17; N, 5.19. Found: C, 53.31; H, 6.20; N, 5.23. IR data (cm^{-1}): 3081 (w), 2956 (m), 2899 (w), 1612 (m), 1600 (m), 1574 (w), 1524 (m), 1490 (w), 1460 (w), 1444 (w), 1392 (w), 1365 (m), 1238 (m), 1127 (w), 1050 (w), 1013 (w), 988 (w), 920 (w), 825 (m), 748 (m), 701 (m), 666 (w).

Complex 15. Yield: 40 mg (37%) as yellow-brown crystals. Anal. Calcd for **15**, $C_{24}H_{33}N_2SiEr$ (M_r = 544.87): C, 52.90; H, 6.12; N, 5.14. Found: C, 52.85; H, 6.16; N, 5.19.

X-ray Crystal Structure Determination. Suitable crystals of compounds **1**−**15** were covered in mineral oil (Aldrich). Crystallographic data were collected at 200 or 293 K on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data processing was accomplished with the SAINT program.[34] The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL-97.[35] All non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculations. A summary of the crystallographic data for complexes **1**−**15** is given in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF files giving X-ray crystallographic data, a summary of crystal data for compounds **1**−**15**, ORTEP representation of compounds **3**−**8**, **9a**, and **11**−**15**, luminescence measurements of compounds **4**, **11**, and **13**, magnetic measurements of compound **7**, and ^{1}H NMR spectra of compounds **1**, **3** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for Z.-M.S.: szm@ciac.ac.cn.

Notes

The authors declare no competing financial interest.

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