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Synthesis, Structure, and Reactivity of Lanthanide Complexes Incorporating Indolyl Ligands in Novel Hapticities

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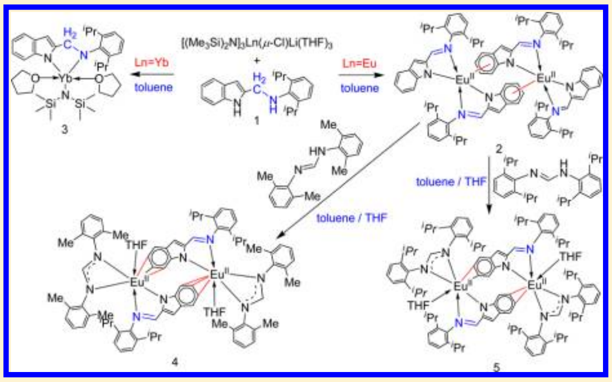
Supporting Information

ABSTRACT: The chemistry of interactions of 2-(2,6-diisopropylphenylaminomethylene)indole ligand (**1**) with europium and ytterbium amides is described. Reaction of 2-(2,6-diisopropylphenylaminomethylene)indole 2-(2,6-i-$Pr_2C_6H_3NHCH_2)C_8H_5NH$ (**1**) with europium amide $[(Me_3Si)_2N]_3Eu^{III}(\mu\text{-}Cl)Li(THF)_3$ afforded a novel europium(II) complex formulated as $\{[\mu\text{-}\eta^6{:}\eta^1{:}\eta^1\text{-}2\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3N{=}CH)C_8H_5N]Eu[2\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3N{=}CH)C_8H_5N]\}_2$ (**2**), having a bridged indolyl ligand in the novel μ-$\eta^6{:}\eta^1{:}\eta^1$ hapticities with the reduction of europium(III) to europium(II) and the oxidation of amino to imino group. Reaction of 2-(2,6-diisopropylphenylaminomethylene)indole 2-(2,6-i-$Pr_2C_6H_3NHCH_2)C_8H_5NH$ (**1**) with ytterbium(III) amide $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(THF)_3$ produced the only deprotonated ytterbium(III) complex formulated as $[2\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3NCH_2)C_8H_5N]Yb[N(SiMe_3)_2](THF)_2$ (**3**), having an η^1 hapticity indolyl ligand. Reaction of **2** with formamidine $[(2,6\text{-}Me_2C_6H_3)NCHNH(C_6H_3Me_2\text{-}2,6)]$ produced $\{[\mu\text{-}\eta^3{:}\eta^1{:}\eta^1\text{-}2\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3N{=}CH)C_8H_5N]Eu[(2,6\text{-}Me_2C_6H_3)NCHN(C_6H_3Me_2\text{-}2,6)](THF)\}_2$ (**4**), which has a bridged indolyl ligand in the novel μ-$\eta^3{:}\eta^1{:}\eta^1$ hapticities, whereas the reaction of **2** with the more sterically bulky formamidine $[(2,6\text{-}i\text{-}Pr_2C_6H_3)NCHNH(C_6H_3i\text{-}Pr_2\text{-}2,6)]$ afforded complex $\{[\mu\text{-}\eta^2{:}\eta^1{:}\eta^1\text{-}2\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3N{=}CH)C_8H_5N]Eu[(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}CHN(C_6H_3i\text{-}Pr_2\text{-}2,6)](THF)\}_2$ (**5**), having the indolyl ligand in the novel μ-$\eta^2{:}\eta^1{:}\eta^1$ hapticities. The results represent the first example of organometallic complexes having indolyl ligands in the novel μ-$\eta^6{:}\eta^1{:}\eta^1$, μ-$\eta^3{:}\eta^1{:}\eta^1$, and μ-$\eta^2{:}\eta^1{:}\eta^1$ bonding modes with metal.



INTRODUCTION

Over the past decades, tremendous research efforts have been devoted to the development of noncyclopentadienyl ancillary ligand systems capable of stabilizing organometallic complexes while provoking novel reactivity.[1−6] Among those cyclopentadienyl alternatives, many similar nitrogen-containing systems such as various modified amido ligands,[2] cyclic pyrrolyl,[3] carbazolyl,[4] pyrazolyl,[5] and aromatic indolyl[6] ligands have proved to be versatile. It has been demonstrated that indole is an electron-rich aromatic compound, and the indolyl compounds widely used in transition metal chemistry[7] are intriguing ligands because they have a propensity to bind with metal in the η^1 mode ultilizing the electron-rich nitrogen atom,[6a] and they can also bind in the η^3 fashion via the nitrogen atom and the fused carbons of indolyl ring,[6a] in the η^5 manner through the five-membered heterocyclic ring that is most common for cyclopentadienyl ligands,[8a] in an η^6 mode through the benzo ring,[8b,c] and in a μ_2-$\eta^1{:}\eta^1$ bonding mode with iron[8d] (see Chart 1). Recently, an η^1 and an unusual $\eta^1{:}(\mu_2\text{-}\eta^1{:}\eta^1)$ bonding mode of novel indolyl-1,2-dianion ligand with rare-earth metals were reported by our group[8e,f] (see Chart 1).

Among the divalent lanthanides, the most accessible divalent oxidation state is Eu^{2+}. Pioneer works demonstrated that europium(II) complexes displayed unique catalytic, photophysical, and magnetic properties of Eu^{2+} and spurred a great deal of research with the findings of some novel bonding modes and applications. For example, Deacon reported novel bonding modes of the pyrazolate ligands to Eu(II) in complexes including the η^2, μ-$\eta^5{:}\eta^2$, and μ-$\eta^2{:}\eta^2$ fashions.[9a] Hitzbleck and co-workers have also reported a μ-$\eta^5{:}\eta^1$ mode to Eu(II) with the bridging 3,5-diisopropylpyrazolate ligand.[9b] In addition, the π-arene interactions of the phenyl-, biphenyl-, or terphenyl-containing ligands bonded with Eu(II) via the benzo ring including the η^1, η^3, η^5, $\eta^4{:}\eta^2{:}\eta^1$, $\eta^1{:}\eta^6{:}\eta^3$, μ-$\eta^6{:}\eta^1$, and η^6 fashion were also reported.[10a−g] Recently, we have reported the indenyl ligand bonded to the central metal europium through the benzo ring with η^4 hapticity.[2f] However, the μ-$\eta^6{:}\eta^1{:}\eta^1$, μ-$\eta^3{:}\eta^1{:}\eta^1$, and μ-$\eta^2{:}\eta^1{:}\eta^1$ coordination modes via both the benzo and five-membered heterocycle rings of indolyl group with transition metals remain scarce.

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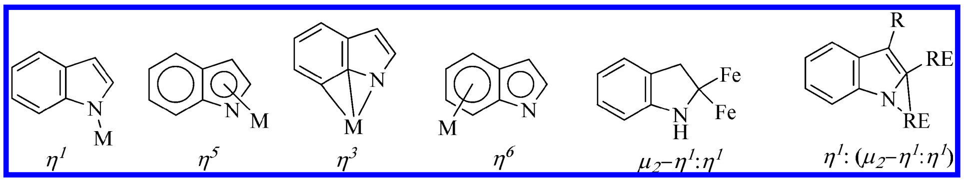
Chart 1. Reported Bonding Modes of the Indolyl Ligand with Transition Metals

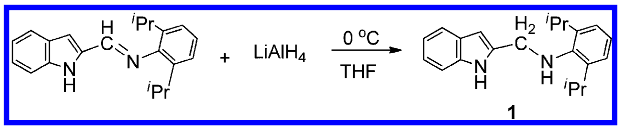


As part of our continuous work on the chemistry of lanthanide complexes with functionalized indolyl ligand systems, we have studied the reactivity of lanthanide amides $[(Me_3Si)_2N]_3Ln^{III}(\mu\text{-}Cl)Li(THF)_3$ (Ln = Eu, Yb) with 2-(2,6-i-$Pr_2C_6H_3NHCH_2$)-C_8H_5NH (**1**), resulting in the isolation and characterization of lanthanide complexes having an indolyl ligand in novel μ-η^6:η^1:η^1 hapticities. Furthermore, the reactivity of the novel europium(II) complex was also examined. In this paper, we report the results.

■ RESULTS AND DISCUSSION

Synthesis of 2-(2,6-*i*-$Pr_2C_6H_3NHCH_2$)C_8H_5NH (1). Treatment of 2-(2,6-i-$Pr_2C_6H_3N{=}CH$)C_8H_5NH with 3 equiv of $LiAlH_4$ in diethyl ether yielded, after workup, 2-(2,6-i-$Pr_2C_6H_3NHCH_2$)C_8H_5NH (**1**) in 95% yield (Scheme 1). The compound was fully characterized by NMR spectra.

Scheme 1. Synthesis of 2-(2,6-Diisopropylphenylaminomethylene)indole



Interactions of 2-(2,6-Diisopropylphenylaminomethylene)-indole Ligand (1) with $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ and the Synthesis and Characterization of Novel Indolyl Lanthanide Complexes. Treatment of europium(III) amide $[(Me_3Si)_2N]_3$-$Eu(\mu\text{-}Cl)Li(THF)_3$ with 1 or 2 equiv of 2-(2,6-i-$Pr_2C_6H_3NHCH_2$)-C_8H_5NH (**1**) in toluene at 80 °C produced a novel europium(II) complex {[μ-η^6:η^1:η^1-2-(2,6-i-$Pr_2C_6H_3N{=}CH$)C_8H_5N]Eu-[2-(2,6-i-$Pr_2C_6H_3N{=}CH$)C_8H_5N]}$_2$ (**2**) as deep red crystals in a moderate yield (Scheme 2). Complex **2** is extremely sensitive to air and moisture. It is readily soluble in common organic solvents such as THF, toluene, and n-hexane. It was characterized by spectroscopic and elemental analyses, and its structure was elucidated by X-ray diffraction study.

The structure of **2** is displayed in Figure 1, and the selected bond lengths and angles are given in Table 1. X-ray analyses revealed that complex **2** is a dinuclear europium(II) complex having two indolyl ligands in bridged ways bonding with metals in novel μ-η^6:η^1:η^1 hapticities and two terminal indolyl ligands bonding with metals in η^1:η^1 fashions. It represents the first example of an organometallic complex that has the indolyl ligand bonded with metal in μ-η^6:η^1:η^1 modes.

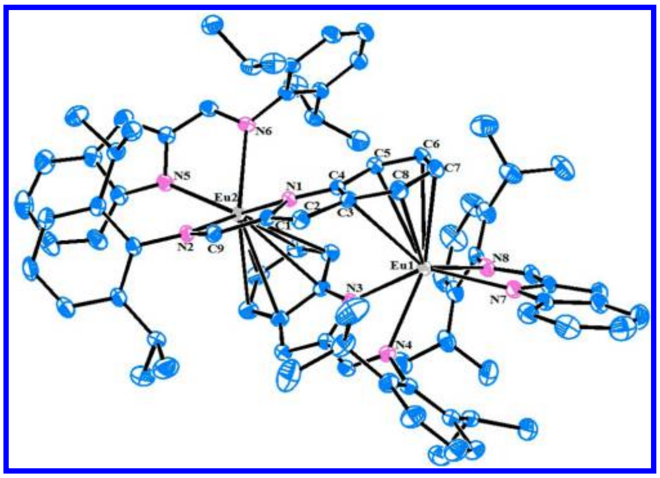


Figure 1. ORTEP diagram of the molecular structure of complex **2** (ellipsoids at 15% probability level). All hydrogen atoms are omitted for clarity.

The most important feature of complex **2** lies in the μ-η^6:η^1:η^1 coordination of the indolyl ligand with the metal. The Eu(1)−C (C_6 ring, [C(3)−C(8)]) bond distances range from 2.921(3) to

Scheme 2. Synthesis of Complexes 2 and 3

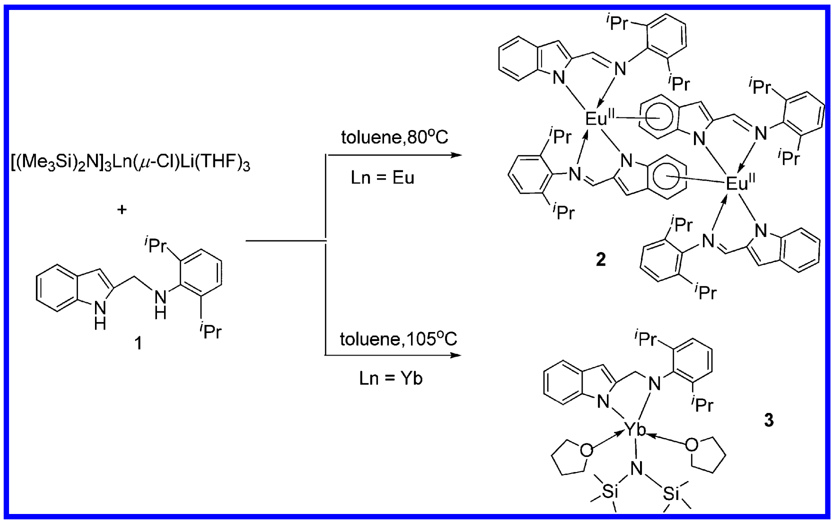


Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of Complexes 2−5

	2	4	5	3
Eu(1)−C(3)	3.132(3)	3.385(5)	3.530(8)	
Eu(1)−C(4)	3.130(3)	3.377(5)	3.501(7)	
Eu(1)−C(5)	3.063(3)	3.171(5)	3.273(8)	
Eu(1)−C(6)	2.951(3)	3.037(5)	3.042(9)	
Eu(1)−C(7)	2.921(3)	3.086(6)	3.081(10)	
Eu(1)−C(8)	3.033(3)	3.273(5)	3.305(10)	
C(9)−N(2)	1.276(4)	1.263(5)	1.250(11)	1.475(6)
Eu(1)−N(1)			2.512(6)	
Eu(1)−N(2)			2.789(7)	
Eu(1)−N(3)	2.581(3)	2.544(4)	2.576(7)	
Eu(1)−N(4)	2.620(2)	2.761(4)	2.671(7)	
Eu(1)−N(7)	2.508(3)	2.612(4)		
Eu(1)−N(8)	2.614(3)	2.592(4)		
Eu(1)−O(1)		2.593(4)	2.583(7)	
Yb(1)−N(1)				2.279(5)
Yb(1)−N(2)				2.145(4)
Yb(1)−N(3)				2.249(4)
Yb(1)−O(1)				2.317(4)
Yb(1)−O(2)				2.330(4)
N(7)−Eu(1)−N(3)	142.84(8)	96.27(13)		
N(8)−Eu(1)−N(4)	121.57(8)	152.12(13)		
N(7)−Eu(1)−N(4)	92.25(8)	99.60(12)		
N(1)−Eu(1)−N(3)			108.0(2)	
N(4)−Eu(1)−N(2)			99.70(19)	
N(3)−Eu(1)−O(1)		146.20(15)	102.2(3)	
O(1)−Eu(1)−N(4)		80.96(14)	95.5(2)	
N(3)−Yb(1)−N(1)				147.87(16)
N(3)−Yb(1)−O(1)				89.25(15)
O(1)−Yb(1)−O(2)				155.23(17)

3.132(3) Å (with an average Eu(1)−C distance of 3.038(3) Å) in **2** (Table 1). These values are considered to represent a significant *π*-arene−Eu interaction that is entirely consistent with the Eu−C distances in the complexes of Eu metals with neutral *π* arenes, such as the average Eu−C distance of 3.002(18) Å found in the η^6-*π*-arene europium(II) complex $[Eu(C_6Me_6)(AlCl_4)_2]_4$,[10f] the average Eu−C distance of 3.065(3) Å in η^6-*π*-arene complexes $Eu^{II}(SAr^*)_2$ ($Ar^* = 2,6\text{-}Trip_2C_6H_3$ with $Trip = 2,4,6\text{-}i\text{-}Pr_3C_6H_2$),[10g] and the average Eu−C distance of 3.105(3) Å for Eu−*π*-(*μ*-Ph_2) in $(C_5Me_5)Eu(\mu\text{-}\eta^6{:}\eta^1\text{-}Ph)_2BPh_2$,[10e] when the differences in Eu^{2+} ionic radius with different coordination numbers were taken into account.[11] Therefore, the bonding of the indolyl ligand with the metal in **2** is best described as the $\mu\text{-}\eta^6{:}\eta^1{:}\eta^1$ mode on the basis of these structural parameters.

Furthermore, an X-ray diffraction study of the structure of **2** also indicates that the ligands in complex **2** are the imino-functionalized indolyl ligands with a C(9)−N(2) bond distance of 1.276(4) Å, which is normally observed for a C═N double bond. It is also found that the central europium metals are in the oxidation state of +2. The facts suggest that a redox reaction occurred in the interaction of $2\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3NHCH_2)\text{-}C_8H_5NH$ (**1**) with $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ resulting in the isolation of the europium(II) and imino-functionalized indolyl complex **2**. This result is similar to our previous findings of the redox chemistry between the europium(III) amide $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ and the pyrrolyl-functionalized secondary amines leading to oxidative dehydrogenation of the secondary amines to imino groups and reduction of europium(III) to europium(II).[3d] Similarly, the reduction of Eu^{3+} to Eu^{2+} has been previously observed with $C_5Me_5^-$,[10f] $C_8H_8^{2-}$,[12] and $C_9H_6^-$.[13]

Analogous reaction of $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ with 1 equiv of **1** in toluene at 105 °C produced ytterbium(III) amido complex $[\eta^1{:}\eta^1\text{-}2\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3NCH_2)C_8H_5N]Yb[N(SiMe_3)_2](THF)_2$ (**3**) as dark red crystals (Scheme 2). A difference from the above reaction for the preparation of complex **2** (the europium case) was observed; the N(2)−C(9) bond distance of 1.471(5) Å found in complex **3** is normally observed for a C−N single bond (see Table 1), indicating that no redox reaction occurred even though the reaction was carried out at elevated temperature. The difference in the reactivity between europium(III) and ytterbium(III) amide with the same ligand (**1**) can be ascribed to the difference in the reduction potentials of the Eu^{3+}/Eu^{2+} and Yb^{3+}/Yb^{2+} couples, reported to be −0.35 and −1.15 V (versus NHE), respectively.[14] This result is in accordance with our previous report.[3d] X-ray diffraction showed that compound **3** is a five-coordinate trivalent ytterbium complex containing an amido-appended indolyl ligand bonding with Yb in an $\eta^1{:}\eta^1$ fashion, two THF molecules, and an amido ligand $[N(SiMe_3)_2]$, adopting a distorted trigonal bipyramid geometry (Figure 2) with three nitrogen atoms occuping the equatorial positions and two oxygen atoms from the THF molecule situated at the axial positions [O(1)−Yb−O(2) (155.23(17) °]. The Yb−N distances in **3** are within the range 2.145(4)−2.279(5) Å (Table 1), which are comparable to the range 2.152(6)−2.343(6) Å reported in the related pyrrolyl complex $[\{(\mu\text{-}\eta^5{:}\eta^1){:}\eta^1\text{-}2\text{-}[(2,6\text{-}i\text{-}Pr_2C_6H_3)\text{-}NCH_2]C_4H_3N\}Yb\{N(SiMe_3)_2\}]_2$.[3f] The corresponding average Yb−N distance of 2.221 Å found in **3** is also comparable to the value 2.232 Å found in $[\mu\text{-}\{[\eta^1{:}\eta^1\text{-}3\text{-}(CyNHCH_2)C_8H_5N]_2Li(THF)\}Yb\text{-}[N(SiMe_3)_2]_2]$,[8f] allowing for ionic radii difference.

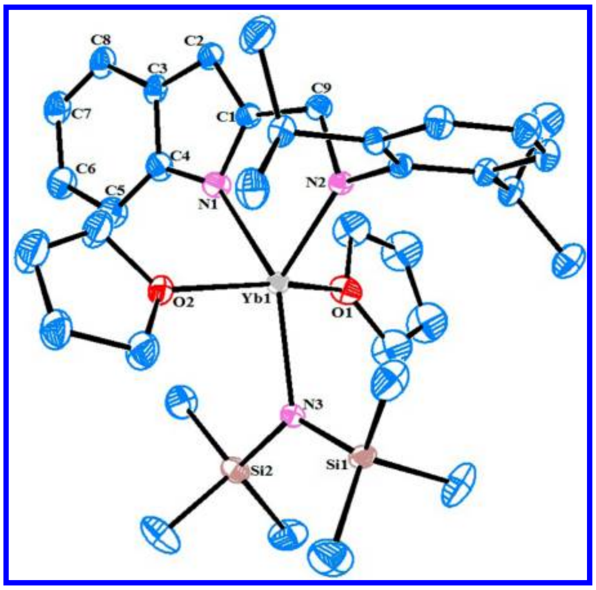
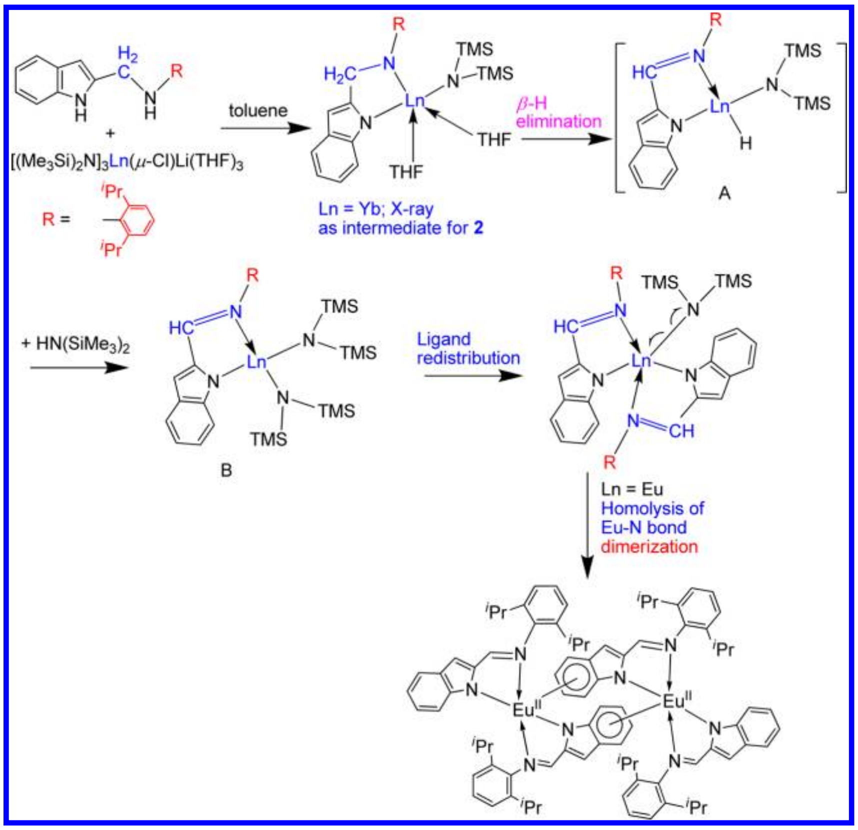


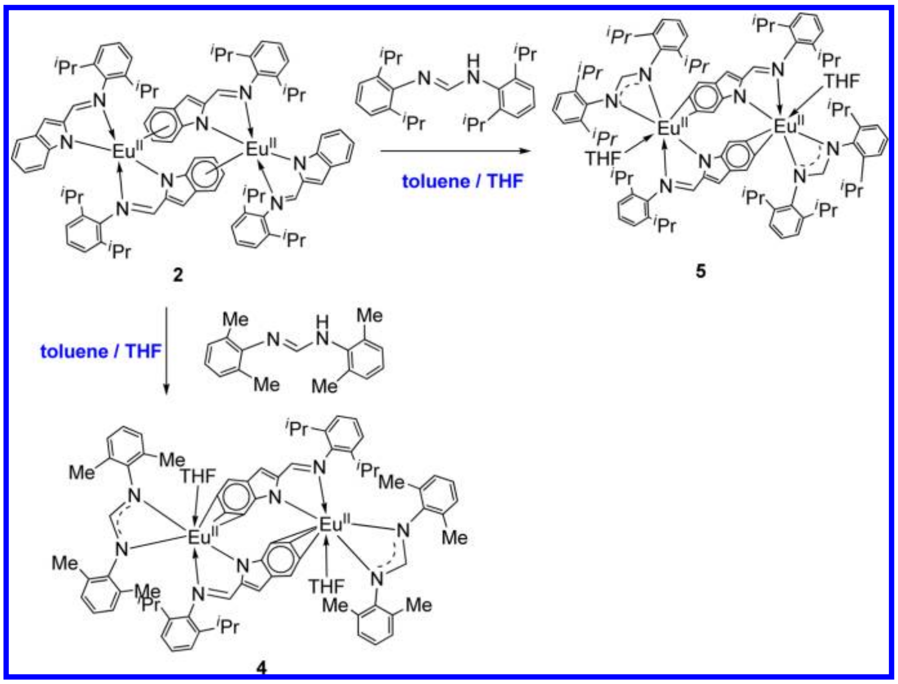
Figure 2. ORTEP diagram of the molecular structure of complex **3** (ellipsoids at 15% probability level). All hydrogen atoms are omitted for clarity.

Not only are different results obtained between the reactions of europium amide and the ytterbium amide $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Eu, Yb) with 2-amino-functionalized indole $[2\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3NHCH_2)C_8H_5NH]$ (**1**), but also the results are different than those of reactions of 3-amino-functionalized

Scheme 3. Proposed Pathway for the Formation of Complex 2



Scheme 4. Reaction of Complex 2 with Formamidines



indole with rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = different rare-earth metal), which produced the only indole deprotonation complexes.[8f] The results are also different than our previous finding that reactions of 3-imino-functionalized indole with $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Y, Yb) resulted in an unusual 1,2-dianionic indolyl ligand.[8e] These results indicated that reactions of different indoles having substituents at the 2- or 3-positions with rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ displayed different reactivities and different bonding modes of the indolyl ligands.

Isolation of complex **3** suggested that it may serve as an intermediate in the formation of complex **2**. This intermediate underwent β-H elimination[3d,f] to produce the intermediate **A**, which has the imino-functionalized indolyl ligand, which then reacted with amine $HN(SiMe_3)_2$ to give the diamido intermediate **B**. The intermediate **B** underwent ligand redistribution followed by homolysis of Eu−N bond[2f,15] and dimerization to produce the final novel europium(II) complex **2** (Scheme 3).

Reactivity of Novel Indolyl Europium(II) Complex 2 with Formamidines (Form). Amidines are useful ligands and important substrates for metal-based reactivity studies, and a number of rare-earth metal amidinates have been reported.[1,16] Although the bonding mode of amidines with lanthanides is observed to be primarily η^2, Hamidi and co-workers have recently reported an example of $[La\{\eta^1(N){:}\eta^6(Ar)\text{-}Me_2CH_2FormAlMe_3\}(AlMe_3)(AlMe_4)][La(Me_2CH_2FormAlMe_3)(AlMe_3)(AlMe_4)](C_6H_{14})_{1.5}(AlMe_4)_2](C_7H_8)_{1.5}$ in which amidinato appended arene ligand coordinated to the lanthanum center in η^1(N):η^6(arene) manners.[17] Given the coordination diversities of amidines and indolyl ligands, the reactions of the novel europium(II) complex **2** with formamidines that have different substituents ArNCHNHAr (Ar = 2,6-$Me_2C_6H_3$; 2,6-*i*-$Pr_2C_6H_3$) were examined to see if these would make variations of the bonding mode of the indolyl or amidine ligands to the central metal in complex **2**.

As shown in Scheme 4, the reaction of **2** with 2 equiv of $[(2,6\text{-}Me_2C_6H_3)NCHNH(C_6H_3Me_2\text{-}2,6)]$ in toluene with the addition of a drop of THF produced a novel europium(II) complex formulated as $\{[\mu\text{-}\eta^3{:}\eta^1{:}\eta^1\text{-}2\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3N{=}CH)C_8H_5N]Eu[(2,6\text{-}Me_2C_6H_3)NCHN(C_6H_3Me_2\text{-}2,6)](THF)\}_2$ (**4**), whereas treatment of complex **2** with 2 equiv of a sterically bulky formamidine $[(2,6\text{-}i\text{-}Pr_2C_6H_3)NCHNH(C_6H_3i\text{-}Pr_2\text{-}2,6)]$ afforded a novel europium(II) complex formulated as $\{[\mu\text{-}\eta^2{:}\eta^1{:}\eta^1\text{-}2\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3N{=}CH)C_8H_5N]Eu[(2,6\text{-}i\text{-}Pr_2C_6H_3)NCHN(C_6H_3i\text{-}Pr_2\text{-}2,6)](THF)\}_2$ (**5**). The molecular structures demonstrated that the bridged indolyl ligands in complex **2** still remained in complexes **4** and **5** (Figures 3 and 4), but the bonding modes were changed, and the terminal indolyl ligands in complex **2** were replaced by the formamidinato ligands. Selected bond lengths and angles of complexes **4** and **5** are given in Table 1.

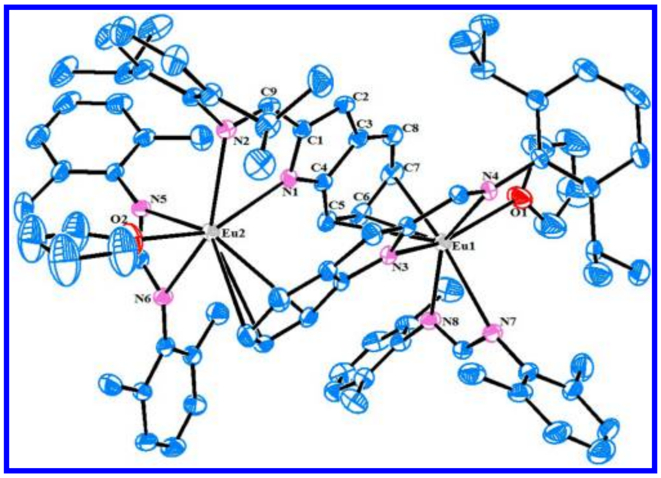


Figure 3. ORTEP diagram of the molecular structure of complex **4** (ellipsoids at 15% probability level). All hydrogen atoms are omitted for clarity.

X-ray analyses revealed that the Eu(1)−C distances in complex **4** are in the range 3.037(5)−3.386(5) Å, and the corresponding distances of Eu(1)−C(5) of 3.170(5) Å, Eu(1)−C(6) of 3.037(5) Å, Eu(1)−C(7) of 3.086(6) Å (with an average Eu(1)−C distance of 3.098(6) Å) are significantly shorter than the other distances of Eu(1)−C(3) of 3.385(5) Å, Eu(1)−C(4) of 3.377(5) Å, and Eu(1)−C(8) of 3.273(5) Å. The average value of 3.098(6) Å of the three Eu(1)−C distances can be compared to the mean Eu−C distance of 3.038(3) Å found in complex **2**, indicating the bonding modes of the bridged indolyl ligands have changed from the μ-η^6:η^1:η^1 to the μ-η^3:η^1:η^1 mode. A similar change was found in complex **5** by comparing the distances of Eu(1)−C(6) of 3.042(9) Å and Eu(1)−C(7) of 3.081(10) Å with the other distances of Eu(1)−C(3) of 3.530(8) Å, Eu(1)−C(4) of 3.501(7) Å, Eu(1)−C(5) of 3.273(8) Å, and Eu(1)−C(8) of 3.305(10) Å, indicating that the bonding modes of the bridged indolyl ligands were changed to the μ-η^2:η^1:η^1 mode, suggesting steric effects on the bonding for the different substituents (*i*-Pr and Me) on the formamidinato ligands. Another reason for the difference in bonding modes of the bridged indolyl ligands between **2** and **4** or **5** may be THF coordination.

CONCLUSIONS

Reactions of a 2-amino-functionalized indole with lanthanide amides $[(Me_3Si)_2N]_3Ln^{III}(\mu\text{-}Cl)Li(THF)_3$ (Ln = Eu, Yb) were studied with the findings of different reactivity patterns and the first example of a dinuclear Eu(II) complex incorporating bridged indolyl ligand in novel μ-η^6:η^1:η^1 hapticities. Reactivity studies of the novel europium(II) complex led to the discovery of bonding modes of the bridged indolyl ligands changing from the novel μ-η^6:η^1:η^1 to the μ-η^3:η^1:η^1 or the μ-η^2:η^1:η^1, depending on the steric effects of the formamidinate ligands and coordination of THF. The results represent the first report on the indolyl ligands bonding with rare-earth metal in these ways. This work together with previous works in this field implies that there would be versatile reactivities of indolyl ligands with rare-earth metals complexes, and also, there would be different bonding modes of the indolyl ligands with rare-earth metals. Further works on the chemistry of rare-earth metal complexes with different indolyl ligands are now in progress.

EXPERIMENTAL SECTION

General Methods. All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and in an oxygen-free atmosphere using standard Schlenk techniques or in a glovebox. All solvents were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. $[(Me_3Si)_2N]_3Ln^{III}(\mu\text{-}Cl)Li(THF)_3$ (Ln = Eu, Yb),[15d,18] 2-(2,6-*i*-$Pr_2C_6H_3N{=}CH)C_8H_5NH$,[19] and formamidines 2,6-$R_2C_6H_3N{=}CHNHC_6H_3R_2$-2,6 (R = CH_3, *i*-Pr)[20] were prepared according to literature methods. Elemental analyses data were obtained on a PerkinElmer 2400 Series II elemental analyzer. ^1H NMR and ^{13}C NMR spectra were run on a Bruker AV-300 NMR spectrometer (300 MHz for ^1H; 75.0 MHz for ^{13}C) with $CDCl_3$ (for organic compounds) as a solvent and internal standard. Chemical shifts (δ) were reported in parts per millin (ppm). *J* values are reported in hertz (Hz). IR spectra were run on a Shimadzu FTIR-8400s spectrometer (KBr pellets). HRMS measurements were conducted with an Agilent 6220 ESI-TOF mass spectrometer. Melting points were determined in sealed capillaries and are uncorrected.

Preparation of 2-(2,6-*i*-$Pr_2C_6H_3NHCH_2)C_8H_5NH$ (1). $LiAlH_4$ (3.52 g, 90.0 mmol) was suspended in Et_2O (30 mL), and a solution of 2-(2,6-*i*-$Pr_2C_6H_3N{=}CH)C_8H_5NH$[19] (9.12 g, 30.0 mmol) in Et_2O (30 mL) was added dropwise at 0 °C. The reaction mixture was stirred overnight at room temperature; then it was hydrolyzed. The organic layer was separated, and the white residue was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$ followed by filtration. Removal of solvent under a vacuum gave the objective compound as an off-white solid (8.72 g) in 95% yield. The product was subsequently recrystallized from the mixture of hexane and ethyl acetate. Mp: 97−98 °C. ^1H NMR

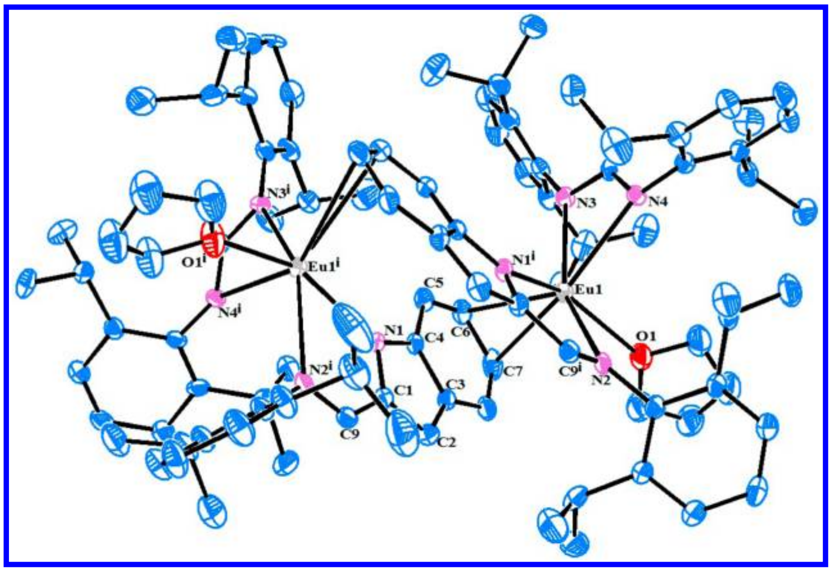


Figure 4. ORTEP diagram of the molecular structure of complex **5** (ellipsoids at 15% probability level). All hydrogen atoms are omitted for clarity.

Table 2. Experimental Data for the X-ray Diffraction Studies of Complexes 2−5

	2	3	4	5
formula	$C_{84}H_{91}Eu_2N_8$	$C_{35}H_{58}N_3O_2Si_2Yb$	$C_{84}H_{100}Eu_2N_8O_2$	$C_{100}H_{132}Eu_2N_8O_2$
fw	1516.58	782.06	1557.64	1782.06
T (K)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
crystal system	monoclinic	monoclinic	monoclinic	tetragonal
space group	$C2/c$	$P2_1/n$	$P2_1/c$	$P4_32_12$
a (Å)	40.057(6)	10.6005(8)	17.1270(11)	13.0633(6)
b (Å)	16.650(2)	32.236(2)	15.5956(10)	13.0633(6)
c (Å)	26.106(4)	11.9390(9)	35.030(2)	65.076(5)
α (deg)	90	90	90	90
β (deg)	106.721(2)	109.7180(10)	99.5680(10)	90
γ (deg)	90	90	90	90
V (Å^3)	16 675(4)	3840.6(5)	9226.7(10)	11 105.2(11)
Z	8	4	4	4
D_{calcd} (mg m^{-3})	1.209	1.353	1.121	1.066
μ (mm^{-1})	1.534	2.529	1.389	1.162
F(000)	6224	1612	3208	3720
θ range (deg)	1.48−27.60	1.92−27.64	1.43−25.00	1.59−27.50
reflections collected/unique	71 301/19 168	33 049/8878	64 835/16 255	95 512/12 708
R (int)	0.0370	0.0256	0.0653	0.0727
goodness-of-fit on F^2	1.009	1.000	1.039	1.022
R_1, wR_2 [$I > 2\sigma(I)$]	0.0355, 0.0719	0.0438, 0.1603	0.0466, 0.0772	0.0720, 0.1714
R_1, wR_2 (all data)	0.0642, 0.0786	0.0511, 0.1690	0.0994, 0.0843	0.0957, 0.1825
largest diff. peak and hole (e Å^{-3})	+0.928 and −0.456	+0.637 and −2.715	+0.522 and −0.796	+1.031 and −1.228

(300 MHz, $CDCl_3$): δ 8.43 (s, 1H, —N*H*—), 7.60 (d, J = 7.47 Hz, 1H, indole—Ar—*H*), 7.38 (d, J = 7.68 Hz, 1H, indole—Ar—*H*), 7.18−7.11 (m, 5H, Ar—*H*), 6.42 (s, 1H, —NH—C═C*H*—), 4.22 (s, 2H, —C*H*$_2$—NH—), 3.30 (t, 2H, —C*H*$(CH_3)_2$), 1.21 (12H, —C*H*$_3$). ^{13}C NMR (75.0 MHz, $CDCl_3$): δ 142.8 (aromatic *C*—NH—), 142.4, 136.0, 100.1 (indole C of 2-pyrrole), 137.4, 128.4, 124.6, 123.8, 121.8, 120.4, 119.9, 110.8 (aromatic C), 49.3 (—CH_2—NH), 27.9 (—$CH(CH_3)_2$), 24.4 (CH_3). HRMS (ESI) m/z: calcd for $C_{21}H_{25}N_2^+$, 305.2012; found, 305.2011. IR (KBr pellets, cm^{-1}) ν: 3435 (s), 2955 (m), 1614 (s), 1589 (m), 1554 (m), 1456 (s), 1413 (m), 1286 (m), 1195 (m), 1064 (m), 1051 (m), 792 (s), 764 (m), 744 (s), 636 (s).

Preparation of {[μ-η^6:η^1:η^1-2-(2,6-*i*-$Pr_2C_6H_3N$═CH)C_8H_5N]Eu-[2-(2,6-*i*-$Pr_2C_6H_3N$═CH)C_8H_5N]}$_2$ (2). A Schlenk flask was charged with **1** (0.31 g, 1.00 mmol), $[(Me_3Si)_2N]_3Eu^{III}(\mu\text{-Cl})Li(THF)_3$ (0.89 g, 1.00 mmol), and toluene (30 mL). The reaction mixture was stirred overnight at 80 °C. The solvent was removed under a vacuum, and the dark red residue was extracted with *n*-hexane and filtered. The hexane solution was cooled to 5 °C. Dark red crystals that were suitable for X-ray diffraction were obtained from the solution after a few days (0.18 g, 46%). Mp (sealed): 239−240 °C under Ar. Anal. Calcd for $C_{84}H_{91}Eu_2N_8$: C, 66.52; H, 6.05; N, 7.39. Found: C, 65.64; H, 6.68; N, 6.77. IR (KBr pellet, cm^{-1}) ν: 3048 (w), 2961 (m), 1632 (s), 1614 (s), 1587 (m), 1460 (m), 1435 (m), 1234 (w), 1178 (w), 1130 (m), 1098 (w), 933 (w), 816 (m), 802 (m), 770 (m), 739 (s), 660 (m).

Preparation of [η^1:η^1-2-(2,6-*i*-$Pr_2C_6H_3NCH_2$)C_8H_5N]Yb[N-$(SiMe_3)_2$](THF)$_2$ (3). The complex **3** was prepared following procedures similar to those used for the synthesis of **2** by running the reaction at 105 °C, using 0.31 g of **1** (1.00 mmol), 0.91 g of $[(Me_3Si)_2N]_3Yb(\mu\text{-Cl})Li(THF)_3$ (1.00 mmol), and 30 mL of toluene. The reaction yielded dark red crystals of **3** (0.62 g, 79%). Mp (sealed): 295 °C (decomp) under Ar. Anal. Calcd for $C_{35}H_{58}N_3O_2Si_2Yb$: C, 53.75; H, 7.48; N, 5.37. Found: C, 53.64; H, 7.30; N, 5.25. IR (KBr pellet, cm^{-1}) ν: 3024 (m), 2955 (s), 2870 (m), 2828 (m), 1925 (w), 1881 (w), 1456 (s), 1414 (m), 1383 (m), 1362 (m), 1319 (m), 1286 (m), 1196 (m), 1065 (m), 1051 (m), 993 (m), 793 (s), 748 (s), 630 (s).

Preparation of $\{[\mu\text{-}\eta^3\text{:}\eta^1\text{:}\eta^1\text{-2-(2,6-}i\text{-}Pr_2C_6H_3N{=}CH)C_8H_5N]Eu[(2,6\text{-}Me_2C_6H_3N{=}CHN(C_6H_3Me_2\text{-2,6})](THF)\}_2$ (4). A Schlenk flask was charged with **2** (1.51 g, 1.00 mmol), $2,6\text{-}Me_2C_6H_3N{=}CHNH(C_6H_3Me_2\text{-}2,6)$ (0.50 g, 2.00 mmol), and toluene (30 mL) with the addition of a drop of THF. The reaction mixture was stirred at 80 °C for 10 h. The red-brown solution was evaporated to dryness and extracted with *n*-hexane. Orange-red crystals that were suitable for X-ray diffraction were obtained upon crystallization from hexane at 5 °C after a few days (0.75 g, 48%). Mp (sealed): 182−183 °C under Ar. Anal. Calcd for $C_{84}H_{100}Eu_2N_8O_2$: C, 64.77; H, 6.47; N, 7.19. Found: C, 64.41; H, 6.77; N, 6.80. IR (KBr pellet, cm^{-1}) ν: 3061 (m), 2959 (s), 1651 (s), 1630 (s), 1589 (m), 1466 (m), 1433 (m), 1369 (m), 1296 (m), 1250 (w), 1202 (m), 1126 (m), 1094 (w), 897 (w), 864 (w), 798 (m), 764 (m), 735 (m), 667 (m).

Preparation of $\{[\mu\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1\text{-2-(2,6-}i\text{-}Pr_2C_6H_3N{=}CH)C_8H_5N]Eu[(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}CHN(C_6H_3i\text{-}Pr_2\text{-2,6})](THF)\}_2$ (5). A Schlenk flask was charged with **2** (1.51 g, 1.00 mmol), $2,6\text{-}i\text{-}Pr_2C_6H_3N{=}CHNH(C_6H_3i\text{-}Pr_2\text{-}2,6)$ (0.72 g, 2.00 mmol), and toluene (30 mL) with the addition of a drop of THF. The reaction mixture was stirred at 80 °C for 10 h. The red-brown solution was evaporated to dryness and extracted with *n*-hexane. Orange-red crystals that were suitable for X-ray diffraction were obtained upon crystallization from hexane at 5 °C after a few days (0.98 g, 55%). Mp (sealed): 218−219 °C under Ar. Anal. Calcd for $C_{100}H_{132}Eu_2N_8O_2$: C, 67.40; H, 7.47; N, 6.29. Found: C, 67.51; H, 7.90; N, 6.25. IR (KBr pellet, cm^{-1}) ν: 3047 (m), 2960 (s), 2870 (m), 1631 (s), 1614 (s), 1587 (m), 1460 (m), 1435 (m), 1382 (m), 1336 (m), 1319 (m), 1234 (m), 1178 (m), 1130 (m), 1097 (m), 1058 (w), 987 (w), 933 (m), 895 (w), 868 (m), 816 (m), 770 (m), 739 (s), 660 (m).

X-ray Crystallographic Analysis. Single crystals of complexes **2**−**5** suitable for X-ray diffraction studies were mounted in glass capillaries and sealed under argon. Diffraction was performed on a Burker SMART CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). An empirical absorption correction was applied using the *SADABS* program.[21] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.[22] All hydrogen atoms were refined using a riding model. Crystal data and details of the data collection are given in Table 2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization spectra for compound **1**, crystallographic information files (CIF), and selected bond distances (Å) and angles (deg) of complexes **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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