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Synthesis of a Naphthalene-Bridged Bis(guanidinato)ytterbium(II) Complex and an Unexpected Pathway in Its Reaction with CH_3CN, p-$ClC_6H_4CH_2CN$, and Ph_2CHCN

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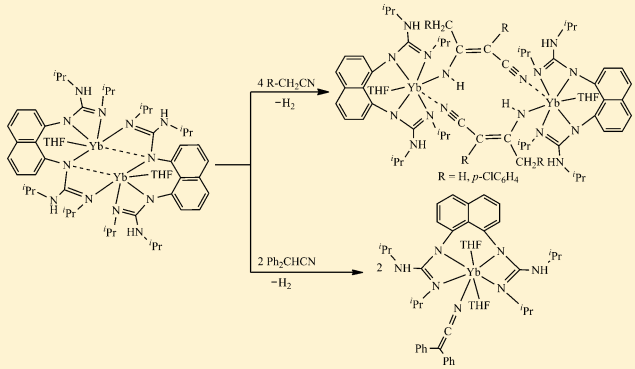
Supporting Information

ABSTRACT: A novel binuclear ytterbium(II) complex supported by a naphthalene-bridged bis(guanidinate) ligand, [Yb(μ-L)(THF)]$_2$ (**1**; L = 1,8-$C_{10}H_6${NC(N^{i}Pr)(NH^{i}Pr)}$_2$), was synthesized by the reduction reaction of [Yb(L)Cl(THF)$_2$] with Na/K alloy in THF and structurally characterized. The reactions of **1** with CH_3CN and p-$ClC_6H_4CH_2CN$ resulted in the formation of the corresponding binuclear (crotononitrileamido)ytterbium(III) complexes [Yb(L)(μ-(N,N')-N(H)C(Me)=C(H)C≡N)(THF)]$_2$ (**2**) and [Yb(L)-(μ(N,N')-N(H)C($CH_2C_6H_4$-p-Cl)=C(C_6H_4-p-Cl)C≡N)-(THF)]$_2$ (**3**) via metalation of the nitrile, followed by insertion of a second nitrile molecule. Treatment of **1** with the bulkier Ph_2CHCN afforded the mononuclear (keteniminato)ytterbium-(III) complex [Yb(L)(N=C=CPh_2)(THF)$_2$] (**4**) by deprotonation of Ph_2CHCN. The molecular structures of **2**–**4** have been determined.



INTRODUCTION

Divalent lanthanide complexes have been found to have a diverse range of reactivity toward small molecules as one-electron reducing agents.[1] Their ability to reduce a number of organic and inorganic molecules has proven to be synthetically very useful for organometallic chemistry and organic synthesis as well.[2] As a result, the activation and transformation of small molecules mediated by divalent lanthanide complexes has become one of the most attractive topics in organolanthanide chemistry.[3] Nitriles are of interest not only for their wide utilities in organic synthesis[4] but also for their widespread reactivity shown in lanthanide metal (Ln) based reactivity studies. For example, insertion reactions of nitrile into Ln−H, Ln−C, and Ln−N bonds[5] and C−H bond activation of acetonitrile by trivalent lanthanide alkyl complexes[6] have been known for many years. The double-insertion reaction of benzonitrile into Ln−H bonds of tetranuclear Lu and Y polyhydride complexes can also take place.[7] The pioneering work by Evans and his group demonstrated that the reaction of the divalent samarium complex [Sm(C_5Me_5)$_2$(THF)$_2$] with Me_3CCN led to reductive C−C bond cleavage of Me_3CCN with the formation of a samarium(III) cyanide complex.[8] The same reaction mode of Me_3CCN was also realized with a dimetalated N,N'-dimethyl-substituted samarium(II) porphyrinogen complex.[9] Interestingly, a novel reductive pathway of acetonitrile, acetonitrile coupling to 2,4-diimino-3-methyl-3-aminopentane, was achieved by use of the strong reducing agents LnI_2 (Ln = Dy, Tm).[10]

The reactivity of a divalent lanthanide complex has been known to depend strongly on the ancillary ligands. Bridged bis(guanidinate) dianions are one of the accessible non-cyclopentadienyl ligand sets and have proven the ability to provide a useful coordination environment for stabilizing various trivalent lanthanide derivatives.[6b,11] However, no example for the use of these ligands in divalent lanthanide chemistry was observed. To extend their applications, we investigated the synthesis of a divalent ytterbium complex with this ligand and its reactivity toward nitriles. Here we wish to describe the synthesis of the novel binuclear naphthalene-bridged bis(guanidinato)ytterbium(II) complex [Yb(μ-L)-(THF)]$_2$ (L = 1,8-$C_{10}H_6${NC(N^{i}Pr)(NH^{i}Pr)}$_2$) (**1**) and an alternative reductive mode of CH_3CN, p-$ClC_6H_4CH_2CN$, and Ph_2CHCN by **1**, which resulted in the formation of (crotononitrileamido)ytterbium(III) complexes for CH_3CN and p-$ClC_6H_4CH_2CN$ and a (keteniminato)ytterbium(III) complex for Ph_2CHCN via metalation of nitriles. The molecular structures of **1**–**4** are also described.

RESULTS AND DISCUSSION

Synthesis and Molecular Structure of 1. The reaction of [Yb(L)Cl(THF)$_2$], which was synthesized by the procedure reported,[12] with Na/K alloy at a molar ratio of 1/1.3 in THF at

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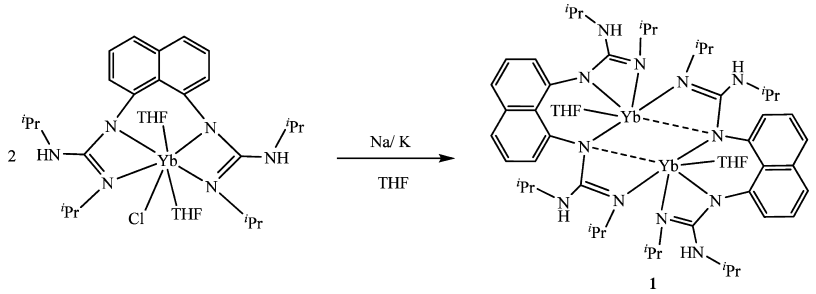
Scheme 1. Synthesis of 1



room temperature afforded complex **1** as black crystals in 60% yield upon crystallization from a mixture of THF and hexane (Scheme 1). The crystals are very sensitive to air and moisture. They are soluble in THF and toluene but not soluble in hexane.

Elemental analysis of the crystals is consistent with the formula. The ^{1}H NMR spectra of **1** in C_6D_6 clearly showed the expected set of signals corresponding to the ligand L and THF, indicating **1** being a diamagnetic Yb(II) complex.

The binuclear structure of **1** was further confirmed by an X-ray diffraction analysis, as shown in Figure 1 with selected bond

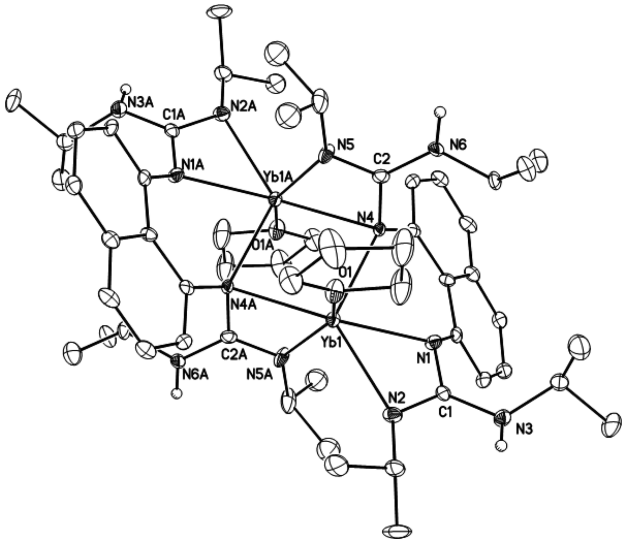


Figure 1. ORTEP drawing of **1** with 30% probability ellipsoids. Hydrogen atoms (except those on the nitrogen atoms) are omitted for clarity. Selected bond distances (Å) and angles (deg): Yb(1)−N(1) = 2.352(7), Yb(1)−N(2) = 2.476(8), Yb(1)−N(4) = 2.427(7), Yb(1)−N(4A) = 2.598(6), Yb(1)−N(5A) = 2.454(7), N(1)−C(1) = 1.344(11), N(2)−C(1) = 1.315(11), N(3)−C(1) = 1.375(11), N(4)−C(2) = 1.360(10), N(5)−C(2) = 1.319(11), N(6)−C(2) = 1.371(11); N(1)−Yb(1)−N(2) = 55.1(2), N(4A)−Yb(1)−N(5A) = 53.1(2), N(4A)−Yb(1)−N(4) = 91.9(2), Yb(1A)−N(4)−Yb(1) = 88.1(2).

distances and bond angles. Complex **1** crystallizes in the monoclinic space group $P2_1/n$ with a crystallographic inversion center located at the center of the Yb(1)−N(4)−Yb(1A)−N(4A) plane. The two metals are connected together by the two bridging guanidinate species from the two L ligands, and both L groups here adopt a μ-η^1:η^2:η^2 coordination fashion. Each metal center is six-coordinate and is bound to five nitrogen atoms of the three guanidinate groups and one oxygen atom from a THF molecule. The coordination geometry is a pseudotrigonal pyramid, if all the guanidinate groups are considered to be point donors located at the central carbon atoms. The bond parameters within Yb(1)−N(1)−C(1)−N(2) unit match those of related Yb(II) complexes supported by nonbridging guanidinate[13] or amidinate ligands.[14] The average Yb−$N_{\mu\text{-guanidinate}}$ bond distance (2.494 Å) is about 0.079 Å longer than that for the Yb−$N_{\text{guanidinate}}$ bonds (2.415 Å). The three C−N bond distances of each guanidine group (C(1)−N(1) = 1.344(11) Å, N(2)−C(1) = 1.315(11) Å, N(3)−C(1) = 1.375(11) Å) indicate that the π electron of the C═N double bond is not delocalized within the CN_3 unit. The same bonding type is also found in complexes with the severely sterically bulky amidinate or guanidinate ligands.[15]

Reactions of 1 with CH_3CN and *p*-$ClC_6H_4CH_2CN$: Syntheses and Molecular Structures of the (Crotononitrileamido)ytterbium(III) Complexes [Yb(L)(*μ*-(*N*,*N*′)-N(H)C(Me)═C(H)C≡N)(THF)]$_2$ (2) and [Yb(L)(*μ*-(*N*,*N*′)-N(H)C($CH_2C_6H_4$-*p*-Cl)═C(C_6H_4-*p*-Cl)C≡N)(THF)]$_2$ (3). Addition of a 4-fold molar excess of CH_3CN into a solution of **1** in THF at room temperature resulted in a rapid color change to red, indicative of the oxidation of Yb(II). From the resulting solution, an unexpected Yb(III) complex bearing a crotononitrileamide ligand, **2**, was isolated as pale yellow crystals in 62% yield (Scheme 2).

Complex **2** is readily soluble in THF and toluene but sparingly soluble in hexane. It is sensitive to air and moisture but thermally stable.

Elemental analysis of the crystals is consistent with the formula of **2**. The paramagnetic properties of **2** corroborate the trivalent state of ytterbium. The IR spectrum of **2** shows the obvious absorptions at about 3340 and 2190 cm^{-1}, which are assigned to N−H and C≡N stretching vibrations, respectively.[6a,b,16]

Crystallization of **2** by slow cooling of the solution in THF resulted in single crystals of the THF solvate **2**·2THF that were suitable for crystal structure analysis. An X-ray diffraction study revealed that **2** is a dimer, in which the two units of LYb are connected together by two bridges of newly formed crotononitrileamide groups (Figure 2). Each metal center is seven-coordinate by two guanidinate groups in a η^2 fashion, two crotononitrileamide groups, and one THF molecule in a distorted trigonal bipyramid, if each guanidinate group is considered to be a point donor located at the central carbon atom. The two carbon atoms (C(1) and C(2)) from the ligand L and the N(8A) atom occupy equatorial positions, while oxygen atom O(1) and N(7) are located at axial positions with an O(1)−Yb(1)−N(7) angle of 166.44(13)°.

The shortening of the N(7)−C(26) (1.313(6) Å), C(26)−C(27) (1.393(7) Å), and C(27)−C(28) bonds (1.389(7) Å) and elongation of the C(28)−N(8) bond (1.162(2) Å) indicate considerable charge delocalization within the crotononitrilea-

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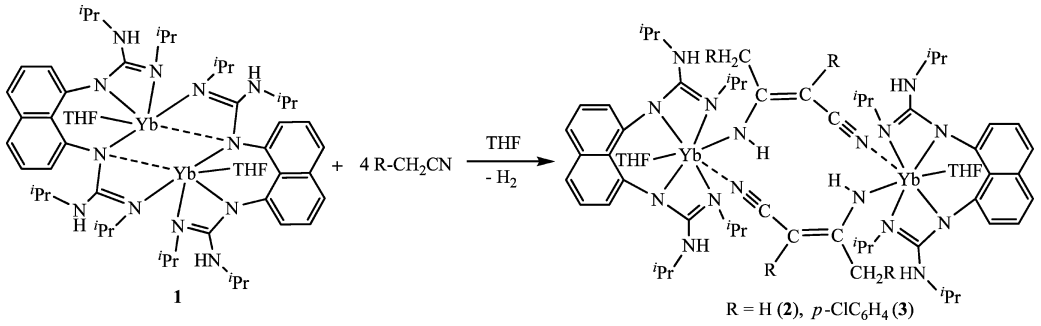
Scheme 2. Reactions of 1 with CH_3CN and p-$ClC_6H_4CH_2CN$



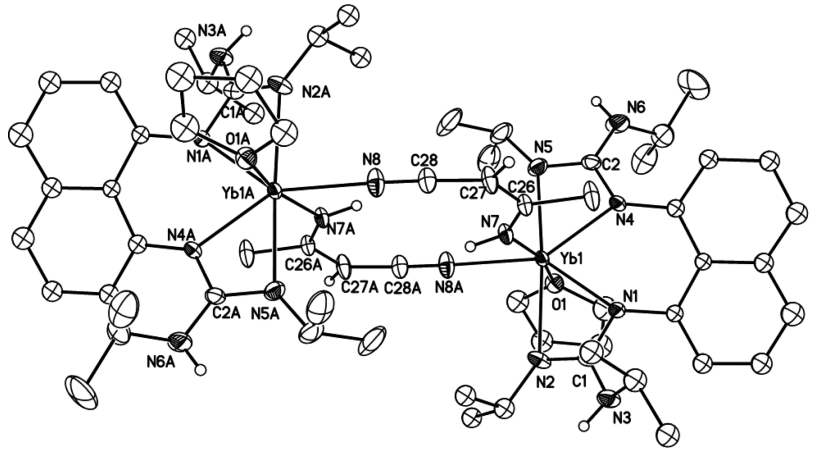


Figure 2. ORTEP drawing of **2** with 30% probability ellipsoids. Hydrogen atoms (except those on C27, C27A, and the nitrogen atoms) and free THF molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Yb(1)−N(1) = 2.251(4), Yb(1)−N(2) = 2.451(4), Yb(1)−N(4) = 2.272(3), Yb(1)−N(5) = 2.383(4), Yb(1)−N(7) = 2.323(4), Yb(1)−N(8A) = 2.391(4), Yb(1)−O(1) = 2.373(3), N(7)−C(26) = 1.313(6), N(8)−C(28) = 1.153(6), C(26)−C(27) = 1.393(7), C(27)−C(28) = 1.389(7), N(1)−C(1) = 1.364(6), N(2)−C(1) = 1.309(7), N(3)−C(1) = 1.373(6), N(4)−C(2) = 1.357(6), N(5)−C(2) = 1.322(7), N(6)−C(2) = 1.374(6); O(1)−Yb(1)−N(7) = 166.44(13), N(7)−Yb(1)−N(8A) = 81.98(13), C(28)−N(8)−Yb(1A) = 170.9(4), N(2)−C(1)−N(1) = 111.8(4), N(2)−C(1)−N(3) = 125.3(4), N(1)−C(1)−N(3) = 122.8(5), N(5)−C(2)−N(4) = 111.5(4), N(5)−C(2)−N(6) = 124.4(5), N(4)−C(2)−N(6) = 124.0(5), N(7)−C(26)−C(27) = 126.6(4), C(28)−C(27)−C(26) = 121.1(4), N(8)−C(28)−C(27) = 177.6(6).

mide group. Moreover, the metal atom bound to N(7) is in a position *cis* to the CH_3 group of the crotononitrileamide group, in a way similar to that in the complexes $[Y\{Me_2Si(NCMe_3)(OCMe_3)\}_2(\mu(N,N')\text{-}N(H)C(Me)=C(H)C\equiv N)]_2$ and $[Sm\{^iPr(Me_3Si)NC(N^iPr)N(CH_2)_3NC(N^iPr)N(SiMe_3)^iPr\}\{\mu(N,N')\text{-}N(H)C(Me)=C(H)C\equiv N)(THF)\}]_2$ reported previously.[6a,b]

Although the formation of a crotononitrileamidolanthanide(III) complex from the reaction of a trivalent lanthanide alkyl complex with CH_3CN is known, the same result obtained with a divalent lanthanide complex had not been observed before this study was initiated. Thus, the reaction of **1** with p-$ClC_6H_4CH_2CN$ was further investigated to see the generality. The reaction went smoothly under the same conditions as those for the reaction with CH_3CN, and a color change of the reaction solution from dark green to red was observed rapidly. After workup, the analogous complex **3** could be obtained as orange crystals in 65% yield (Scheme 2). Complex **3** was fully characterized, including an IR spectrum, elemental analysis, and X-ray crystal structure analysis. The IR spectrum of **3** shows the obvious absorptions at about 3338 and 2187 cm^{-1} assigned to N−H and C≡N stretching vibrations ,respectively,[6a,b,16] indicative of a crotononitrileamide group. Complex **3** crystallizes in the monoclinic space group $P2_1/n$ with two free toluene molecules in the unit cell. Complex **3** has a dimeric structure with two crotononitrileamide bridges. The molecular structure of **3** is quite similar to that of **2**. The bond parameters of the units of [LYb] and [(crotononitrileamido)Yb] are comparable with those found in **2** (Figure 3).

Dehydrogenation−reduction of propene, butene, and allylbenzene as well as cyclopentadiene by $[Sm(C_5Me_5)_2(THF)_2]$ has been well documented.[17] Thus, the reaction of **1** with CH_3CN or p-$ClC_6H_4CH_2CN$ might first lead to the ytterbium intermediate A via metalation of nitrile and then afford **2** or **3** by the insertion of a second molecule of CH_3CN or p-$ClC_6H_4CH_2CN$ into the Yb−C bond of A, followed by a 1,3-H shift, as shown in Scheme 3.

Reaction of 1 with Ph_2CHCN: Synthesis and Molecular Structure of the (Keteniminato)ytterbium(III) Complex $[Yb(L)(N{=}C{=}CPh_2)(THF)_2]$ (4). The reactivity of main-group-metal and transition-metal complexes with Ph_2CHCN has recently attracted great attention, and a deprotonation reaction of Ph_2CHCN can take place to form keteniminate species.[18] In contrast, the chemical reactivity of this substrate with lanthanide complexes has not been demonstrated. Moreover, no well-defined (keteniminato)lanthanide complex has been reported until now. The above results prompted us to further study the reaction between **1** and Ph_2CHCN to understand the influence of nitrile on the reaction outcome. Thus, the reaction of **1** with Ph_2CHCN was then conducted in

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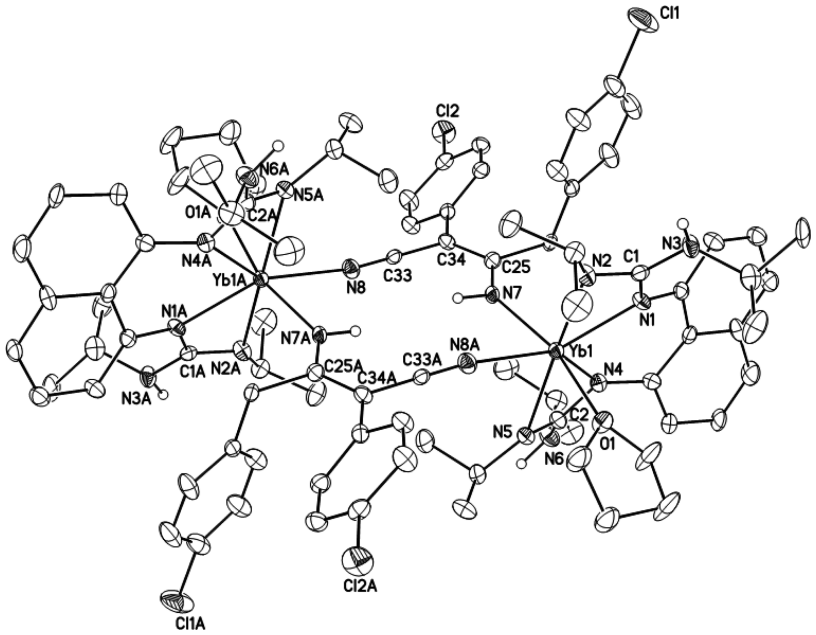
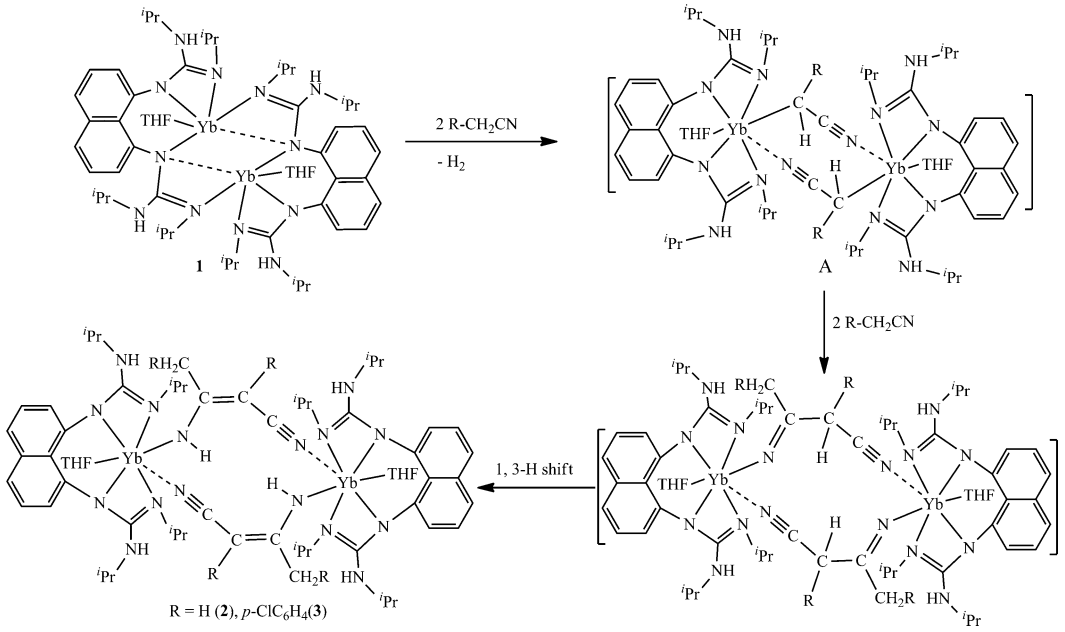


Figure 3. ORTEP drawing of **3** with 30% probability ellipsoids. Hydrogen atoms (except those on the nitrogen atoms) and free toluene molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Yb(1)−N(1) = 2.251(4), Yb(1)−N(2) = 2.383(8), Yb(1)−N(4) = 2.271(8), Yb(1)−N(5) = 2.422(8), Yb(1)−N(7) = 2.326(7), Yb(1)−N(8A) = 2.428(8), Yb(1)−O(1) = 2.367(7), N(7)−C(25) = 1.325(12), N(8)−C(33) = 1.134(12), C(25)−C(34) = 1.395(13), C(33)−C(34) = 1.404(13), N(1)−C(1) = 1.352(12), N(2)−C(1) = 1.325(13), N(3)−C(1) = 1.393(13), N(4)−C(2) = 1.346(12), N(5)−C(2) = 1.320(13), N(6)−C(2) = 1.394(13); N(7)−Yb(1)−N(8A) = 79.9(3), C(33)−N(8)−Yb(1A) = 165.4(8), N(2)−C(1)−N(1) = 113.3(9), N(2)−C(1)−N(3) = 123.1(9), N(1)−C(1)−N(3) = 123.5(9), N(5)−C(2)−N(4) = 113.2(9), N(5)−C(2)−N(6) = 123.9(9), N(4)−C(2)−N(6) = 122.8(9), N(7)−C(25)−C(34) = 126.5(8), C(25)−C(34)−C(33) = 116.1(8), N(8)−C(33)−C(34) = 179.2(10).

Scheme 3. Possible Reaction Pathway for the Formation of 2 and 3



THF at room temperature. Replacement of the CH_3CN (*p*-$ClC_6H_4CH_2CN$) with Ph_2CHCN in the reaction also gave a color change from dark green to red, signifying oxidation of the Yb(II) center to Yb(III). Indeed, crystallization of the product from solution afforded the expected keteniminate complex $[Yb(L)(N{=}C{=}CPh_2)(THF)_2]$ (**4**) as light yellow crystals in 57% yield (Scheme 4). Complex **4** should result from the deprotonation reaction of Ph_2CHCN by **1** directly. In comparison with the results obtained from the reactions with CH_3CN and *p*-$ClC_6H_4CH_2CN$, it can be supposed that the insertion reaction of the second nitrile molecule into the Yb−C bond of the metalation product formed in situ is very sensitive to the steric bulk of the nitrile, and the substitution of the two hydrogen atoms in CH_3CN by two phenyl groups makes the insertion reaction of the second Ph_2CHCN impossible due to the steric hindrance (Scheme 4).

Complex **4** is readily soluble in THF and toluene but sparingly soluble in hexane. The paramagnetic properties of **4**

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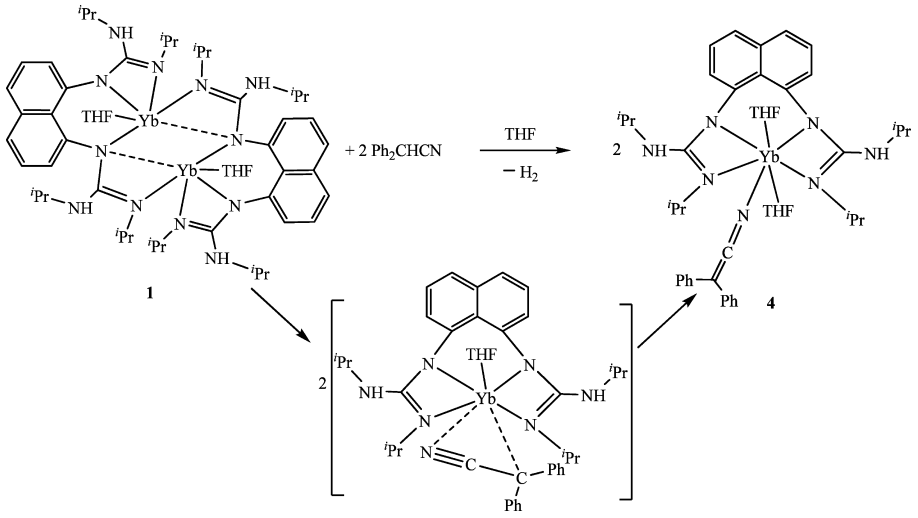
Scheme 4. Reaction of 1 with Ph_2CHCN



indicate the trivalent state of ytterbium. The IR spectrum shows a strong absorption at about 2111 cm^{-1} assigned to the N═C═C stretching mode, as observed for the metal keteniminate complexes reported.[18] This is a shift of nearly 130 cm^{-1} in comparison to Ph_2CHCN (2240 cm^{-1} (C≡N)), indicating the conversion of the triple bond to a C═N double bond. The identity of **4** was unequivocally established by an X-ray structure determination.

Complex **4** crystallizes in the monoclinic space group $P2_1/c$ with one THF molecule in the unit cell. The molecular structure of **4** is shown in Figure 4 with selected bond distances and angles. The metal center in **4** is bound to two guanidinate groups in a η^2 fashion, one almost linear keteniminate fragment, and two THF molecules. The metal center is seven-coordinate and adopts a pseudo-trigonal-bipyramidal geometry if the guanidinate groups are considered to be point donors located at the central carbon atoms.

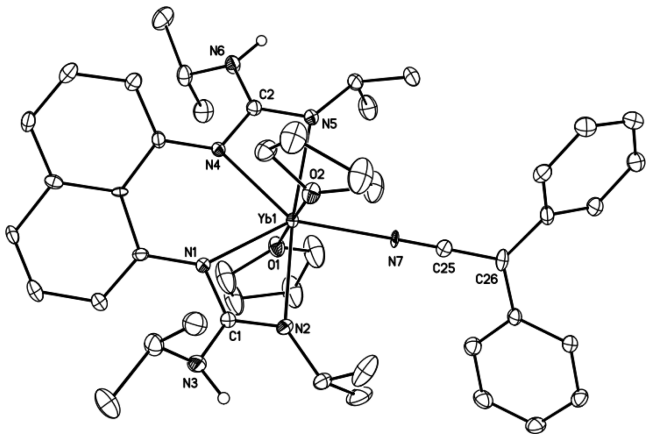


Figure 4. ORTEP diagram of complex **4**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except those on the nitrogen atoms) and a free THF molecule are omitted for clarity. Selected bond distances (Å) and angles (deg): Yb(1)–N(1) = 2.268(5), Yb(1)–N(2) = 2.400(5), Yb(1)–N(4) = 2.278(4), Yb(1)–N(5) = 2.401(5), Yb(1)–N(7) = 2.356(4), Yb(1)–O(1) = 2.334(4), Yb(1)–O(2) = 2.325(4), N(7)–C(25) = 1.165(7), C(25)–C(26) = 1.386(8), N(1)–C(1) = 1.358(7), N(2)–C(1) = 1.325(7), N(3)–C(1) = 1.383(8), N(4)–C(2) = 1.359(7), N(5)–C(2) = 1.324(7), N(6)–C(2) = 1.371(7); O(1)–Yb(1)–O(2) = 178.57(16), C(25)–N(7)–Yb(1) = 178.4(5), N(7)–Yb(1)–O(1) = 87.98(16), N(2)–C(1)–N(1) = 112.4(5), N(2)–C(1)–N(3) = 124.1(5), N(1)–C(1)–N(3) = 123.5(5), N(5)–C(2)–N(4) = 112.1(5), N(5)–C(2)–N(6) = 124.6(5), N(4)–C(2)–N(6) = 123.3(5), N(7)–C(25)–C(26) = 178.9(7).

The bond distance of Yb(1)–N(7), 2.356(4) Å, can be described as an Yb–N single bond, which is comparable with the Yb–N distance in related Yb(III) amide complexes.[19] The heteroallene type of the keteniminate ligand in **4** is demonstrated by the shortening of the C(25)–C(26) bond (1.384(8) Å) and elongation of the N(7)–C(25) bond (1.165(7) Å) in comparison with those bonds in $Ph_2CHC{\equiv}N$ (1.470 and 1.147 Å, respectively). Moreover, the C(26)–C(25)–N(7) angle in the $Ph_2C{=}C{=}N$ unit is 179.0(7)°, indicating that the CCN fragment is almost linear. A similar bond allocation can also be observed in the Li–, Mg–, and transition-metal–keteniminate complexes reported.[18]

The bond parameters of the part of Yb attached to the guanidinate group are comparable with those found in **2** and **3**.

Although the synthesis of a dimeric (cyanomethyl)lanthanoid complex has been reported by the reaction of $[La(C_5Me_5)_2\{CH(SiMe_3)_2\}]$ with CH_3CN, the bonding of the CCN unit in that complex is best described as intermediate between a *C*-metalated structure and an *N*-metalated keteniminate form.[6c] To best of our knowledge, complex **4** is the first structurally characterized lanthanide complex with a terminal keteniminate ligand.

CONCLUSION

In summary, a novel Yb(II) complex supported by the naphthalene-bridged bis(guanidinate) ligand **1** was synthesized and structurally characterized. The reactivity of **1** toward CH_3CN, *p*-$ClC_6H_4CH_2CN$, and Ph_2CHCN was studied, and an alternative reductive mode of nitriles was presented: reactions of **1** with CH_3CN and *p*-$ClC_6H_4CH_2CN$ both led to the formation of (crotonitrileamido)ytterbium(III) complexes **2** and **3**, while, the reaction with Ph_2CHCN afforded the (keteniminato)ytterbium(III) complex **4**. This study provides evidence that metalation of heteroatomic substrates containing active C–H bonds by divalent lanthanide complexes is quite possible. Further investigationd of the reactivity of lanthanide(II) complexes toward small molecules are ongoing in our laboratory.

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Table 1. Crystal Data and Refinement Parameters for 1−4

	1	2·2THF	3·2C_7H_8	4·THF
empirical formula	$C_{56}H_{88}N_{12}O_2Yb_2$	$C_{72}H_{114}N_{16}O_4Yb_2$	$C_{102}H_{126}Cl_4N_{16}O_2Yb_2$	$C_{50}H_{70}N_7O_3Yb$
formula wt	1307.46	1613.87	2096.07	990.17
cryst size (mm)	0.60 × 0.50 × 0.30	0.78 × 0.35 × 0.30	0.30 × 0.20 × 0.20	0.45 × 0.38 × 0.28
temp (K)	223(2)	220(2)	293(2)	200(2)
wavelength λ (Å)	0.71075	0.71073	0.71075	0.71070
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
unit cell dimens				
a (Å)	13.641(5)	9.7383(3)	14.372(4)	13.1512(3)
b (Å)	15.473(6)	13.1396(3)	21.107(5)	15.0219(4)
c (Å)	13.537(5)	17.0112(5)	16.541(4)	24.6389(7)
α (deg)	90	71.884(2)	90	90
β (deg)	90.516(13)	77.899(2)	90.723(6)	97.087(3)
γ (deg)	90	70.021(2)	90	90
V (Å^3)	2409.0(4)	1931.23(9)	5017(2)	4830.4(2)
Z	2	1	2	4
D_{calc} (g cm^{-3})	1.520	1.388	1.387	1.362
F(000)	1328	830	2148	2052
θ (deg)	3.03−25.50	3.18−25.50	1.71−25.50	3.09−25.50
abs coeff (mm^{-1})	3.304	2.462	2.015	1.984
max, min transmission	0.370, 0.214	1.000, 0.431	0.6887, 0.5832	0.6066, 0.4689
largest diff peak, hole (Å^{-3})	1.231, −2.426	0.827, −1.067	0.929, −2.218	3.086, −1.219
no. of collected/unique rflns	23052/5301	36997/7189	41605/9308	27419/8969
R(int)	0.0923	0.0304	0.0787	0.0241
goodness of fit on F^2	1.099	1.051	1.212	1.090
final R indices ($I > 2\sigma(I)$]	R1 = 0.0538, wR2 = 0.1433	R1 = 0.0335, wR2 = 0.0859	R1 = 0.0707, wR2 = 0.2158	R1 = 0.0449, wR2 = 0.1153
R indices (all data)	R1 = 0.0796, wR2 = 0.1817	R1 = 0.0381, wR2 = 0.0891	R1 = 0.0949, wR2 = 0.2455	R1 = 0.0623, wR2 = 0.1209

EXPERIMENTAL SECTION

All manipulations and reactions described below were carried out under a purified argon atmosphere using standard Schlenk or glovebox techniques. Solvents were degassed and distilled from sodium benzophenone ketyl under argon before use. The ^{1}H and ^{13}C NMR spectra were recorded in a C_6D_6 solution for complex **1** on a Unity Varian spectrometer. Elemental analysis was 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.

[Yb(μ-L)(THF)]$_2$ (1). Into a solution of Na/K alloy (0.146 g, 5.95 mmol) in toluene (10 mL) was added a solution of [Yb(L)Cl(THF)$_2$] (3.48 g, 4.58 mmol) in THF (30 mL). The reaction mixture was stirred for 48 h at room temperature. The solvent was evaporated under vacuum to dryness and extracted with toluene followed by centrifugation to remove the NaCl. The volume of the extract was reduced to 5 mL, and then hexane (6 mL) was added. Cooling the solution to 0 °C afforded complex **1** as black crystals (1.80 g, 60%). Anal. Calcd for $C_{56}H_{88}N_{12}O_2Yb_2$ (1307.46): C, 51.44; H, 6.73; N, 12.85. Found: C, 51.12; H, 6.76; N, 12.69. ^{1}H NMR (400 MHz, C_6D_6): δ 7.50 (2H, d, $^3J_{HH}$ = 7.2 Hz, Ar), 7.42 (2H, t, $^3J_{HH}$ = 7.4 Hz, Ar), 7.25 (6H, m, Ar), 6.82 (2H, d, $^3J_{HH}$ = 6.0 Hz, Ar), 4.02 (2H, m, $CH(CH_3)_2$), 3.73 (2H, d, $^3J_{HH}$ = 10.0 Hz, NH), 3.64 (10H, m, α-CH_2 THF and $CH(CH_3)_2$), 3.44 (2H, d, $^3J_{HH}$ = 8.4 Hz, NH), 3.33 (2H, m, $CH(CH_3)_2$), 3.13 (2H, m, $CH(CH_3)_2$), 1.40 (8H, m, β-CH_2 THF), 1.26 (12H, m, CH_3), 1.05 (12H, m, CH_3), 0.96 (6H, d, $^3J_{HH}$ = 4.8 Hz, CH_3), 0.87 (6H, d, $^3J_{HH}$ = 4.4 Hz, CH_3), 0.69 (6H, d, $^3J_{HH}$ = 4.4 Hz, CH_3), 0.55 (6H, d, $^3J_{HH}$ = 4.8 Hz, CH_3). ^{13}C NMR (75 MHz, C_6D_6): δ 161.4 (CN_3), 158.3 (CN_3), 149.9 (Ar), 148.9 (Ar), 139.8 (Ar), 128.3 (Ar), 126.1 (Ar), 125.0 (Ar), 124.1 (Ar), 121.7 (Ar), 113.6 (Ar), 108.6 (Ar), 70.1 (α-CH_2 THF), 45.7 ($CH(CH_3)_2$), 45.2 ($CH(CH_3)_2$), 44.4 ($CH(CH_3)_2$), 43.9 ($CH(CH_3)_2$), 26.3 (β-CH_2 THF), 25.6 (CH_3), 25.1 (CH_3), 25.0 (CH_3), 24.2 (CH_3), 24.0 (CH_3), 23.9 (CH_3), 23.3 (CH_3), 22.4 (CH_3). IR (KBr, cm^{-1}): 3332 (m), 2969 (m), 2873 (w), 1627 (s), 1573 (s), 1546(s), 1369 (w), 1384 (w), 1207 (s), 1153 (s), 821 (w), 763 (m), 624 (m), 555 (m).

[Yb(L)(μ(*N*,*N*′)-N(H)C(Me)═C(H)C≡N)(THF)]$_2$·2THF (2). To a toluene solution (20 mL) of **1** (1.57 g, 1.20 mmol) was slowly added acetonitrile (4.80 mL, 1 M in THF). The solution changed from black to red. The resulting solution was stirred overnight at room temperature. After the clear solution was concentrated, pale yellow crystals of **2** (1.20 g, yield 62%) were isolated at room temperature. Anal. Calcd for $C_{72}H_{114}N_{16}O_4Yb_2$ (1613.87): C, 53.58; H, 7.06; N, 13.88. Found: C, 53.86; H, 7.33; N, 13.42. IR (KBr, cm^{-1}): 3340 (m), 2969 (m), 2931 (w), 2873 (w), 2190 (m), 1631 (s), 1612 (s), 1569 (s), 1461 (s), 1384 (m), 1238 (s), 1157 (s), 863 (w), 821 (m), 763 (m), 636 (m), 555 (m).

[Yb(L)(μ(*N*,*N*′)-N(H)C($CH_2C_6H_4$-*p*-Cl)═C(C_6H_4-*p*-Cl)C≡N)(THF)]$_2$·2C_7H_8 (3). The synthesis of complex **3** was carried out as described for complex **2**, but *p*-$C_6H_4CH_2CN$ (6.0 mL, 1 M in THF) and **1** (1.96 g, 1.5 mmol) were used. Orange crystals of complex **3** were obtained from a THF/*n*-hexane solution (2.04 g, 65%) at room temperature. Anal. Calcd for $C_{102}H_{126}Cl_4N_{16}O_2Yb_2$ (2096.07): C, 58.44; H, 6.01; N, 10.68. Found: C, 58.13; H, 6.33; N, 10.42. IR (KBr, cm^{-1}): 3338 (m), 2969 (m), 2931 (w), 2869 (w), 2187 (m), 1619 (s), 1581 (s), 1538 (m), 1492 (m), 1384 (m), 1228 (vs), 1157 (vs), 1014 (w), 829 (m), 802 (w), 767 (m), 636 (m), 624 (m), 555 (m).

[Yb(L)(N═C═CPh$_2$)(THF)$_2$]·THF (4). The synthesis of complex **4** was carried out as described for complex **2**, but Ph_2CHCN (0.64 g, 3.30 mmol) and **1** (2.15 g, 1.65 mmol) were used. Light yellow crystals of complex **4** were obtained from a THF/*n*-hexane solution (1.86 g, 57%) at room temperature. Anal. Calcd for $C_{50}H_{70}N_7O_3Yb$ (990.17): C,, 60.64; H, 7.07; N, 9.90%. Found: C, 60.26; H, 7.48; N, 10.23. IR (KBr, cm^{-1}): 3432 (m), 2973 (m), 2111 (m), 1634 (m), 1613 (m), 1576 (m), 1384 (m), 1319 (m), 1244 (s), 1213(s), 1155 (s), 816 (w), 760 (m), 636 (m), 625 (m), 555 (m), 504 (s).

X-ray Crystallography. Crystals of complexes **1**−**4** suitable for X-ray diffraction were sealed in thin-walled glass capillaries filled under argon. Diffraction data were collected on a Agilent Xcalibur CCD area detector in the ω scan mode using Mo Kα radiation for complexes **2** (λ = 0.71073 Å) and **4** (λ = 0.71070 Å) and on a Rigaku Saturn CCD area detector in the ω scan mode using Mo Kα radiation (λ = 0.71075

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Å) for complexes **1** and **3**. 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. 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 with anisotropic displacement coefficients. 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. Some static disorders were found in the structures and taken into account during the refinement. In particular, the naphthalene rings, isopropyl groups, and coordinated THF molecules of complex **2** were found to be disordered over two positions and were refined with occupancies of 0.50. The structures were solved and refined using SHELXL-97 programs. CCDC 922084 (for **1**), 922085 (for **2**), 926758 (for **3**), and 926759 (for **4**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving X-ray crystallographic data for complexes **1**−**4**. 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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