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Versatile Reactivity of β-Diketiminato-Supported Yttrium Dialkyl Complex toward Aromatic N-Heterocycles

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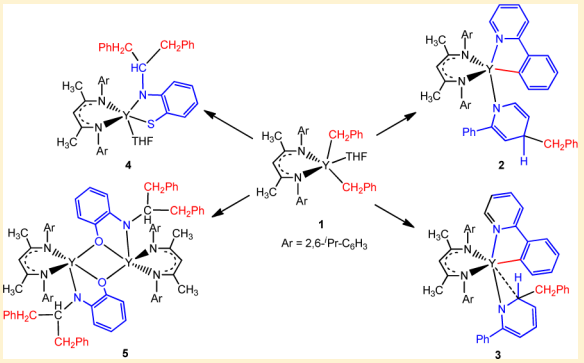
Supporting Information

ABSTRACT: The reactions of β-diketiminatoyttrium dialkyl complex $LY(CH_2Ph)_2(THF)$ (**1**, L = $[\{N(2,6\text{-}^iPr_2C_6H_3)C(Me)\}_2CH]^-$) with a series of aromatic N-heterocycles such as 2-phenylpyridine, benzothiazole, and benzoxazole were studied and displayed discrete reactivity including C−H activation, C−C coupling, ring-opening/insertion, and dearomatization. The reaction of **1** with 2-phenylpyridine in 1:2 molar ratio in THF at 30 °C for 14 days afforded a structurally characterized metal complex, $LY(\eta^2\text{-}N,C\text{-}C_5H_4NC_6H_4\text{-}2)[C_5H_4N(CH_2Ph\text{-}4)Ph]$ (**2**), in 73% isolated yield, indicating the occurrence of phenyl ring $C(sp^2)$−H activation and pyridine ring 1,4-addition/dearomatization. However, when this reaction was done at 5 °C for 7 days, it gave the pyridine ring 1,2-addition product $LY(\eta^2\text{-}N,C\text{-}C_5H_4NC_6H_4\text{-}2)[C_5H_4N(CH_2Ph\text{-}2)Ph]$ (**3**) in 54% isolated yield. Further investigations revealed that complex **2** is the thermodynamic controlled product and complex **3** is the kinetically controlled product; **3** converted slowly into **2**, as confirmed by ^1H NMR spectroscopy. The equimolar reaction of **1** with benzothiazole or benzoxazole produced two C−C coupling/ring-opening/insertion products, $LY[\eta^2\text{-}S,N\text{-}SC_6H_4NCH(CH_2Ph)_2](THF)$ (**4**) and $\{LY[\mu\text{-}\eta^2\text{:}\eta^1\text{-}O,N\text{-}OC_6H_4NCH(CH_2Ph)_2]\}_2$ (**5**), in 84% and 78% isolated yields, respectively.



INTRODUCTION

Aromatic N-heterocycles are important and ubiquitous organic small molecules with some pharmacological activity and have been widely applied in organic/medicinal synthesis[1] and organometallic[2] and material chemistry.[3] Classical metal-mediated activations of these aromatic N-heterocycles are metalation, viz., deprotonation of the $C(sp^2)$−H bond at the *ortho* position of their aromatic ring to form a new metal−carbon bond while preserving aromaticity.[4] The ring and aromaticity of these molecules survive during these processes.[4a−g] However, some selective functionalization of these heterocycles destroys their aromaticity or planar ring structure (viz., dearomatization or ring-opening). Recently, some examples of ring-opening and/or dearomatization of aromatic N-heterocycles mediated by metal complexes including magnesium,[5] calcium,[6] titanium,[7] rhenium,[8] group 3,[9] and uranium[10] displayed some nice reaction chemistry and novel structures. However, the reactivity of rare-earth dialkyl complexes toward aromatic N-heterocycles has been little studied so far.[4f,11]

Rare-earth-metal dialkyl complexes bearing a monoanionic ancillary ligand ($LLnR_2$) have occupied a central place in the organometallic chemistry of these elements during the last decades, since the presence of two highly reactive σ-bonded hydrocarbon ligands may impart their rare-earth-metal complexes with a marked reactivity that is difficult or impossible to achieve from the corresponding monoalkyls. These complexes not only serve as excellent catalysts for the polymerization of a variety of olefins[12] but also are useful precursors for the synthesis of a wide range of rare-earth-metal derivatives such as rare-earth-metal polyhydrides,[13] rare-earth-metal terminal imido complexes,[14] and rare-earth-metal carbene complexes.[15] Our recent interest is in the investigation on reactivity of rare-earth dialkyl complexes toward unsaturated substrates, and we found that they can cleave the C═S double bond of isothiocyanate, activate the $C(sp^3)$−H bond of a benzyl group,[16] and activate 1-methylbenzimidazole with a three-component combination and ring-opening beyond C−H activation under mild conditions.[11b] In this contribution, we report a yttrium dialkyl complex with β-diketiminato ligand mediated activations of a series of aromatic N-heterocycles including 2-phenylpyridine, benzothiazole, and benzoxazole and reveal various chemical transformations such as C−H activation, C−C coupling, ring-opening/insertion, and dearomatization.

RESULTS AND DISCUSSION

The β-diketiminato yttrium dialkyl complex $LY(CH_2Ph)_2(THF)$ (**1**, L = $[\{N(2,6\text{-}^iPr_2C_6H_3)C(Me)\}_2CH]^-$) was prepared through a modified literature method[17] with a higher yield; namely, $LYCl_2(THF)_2$ was reacted with 2 equiv of KCH_2Ph. After workup, **1** was isolated in 68% yield as a pale yellow crystalline solid. The reaction of **1** with 2 equiv of 2-

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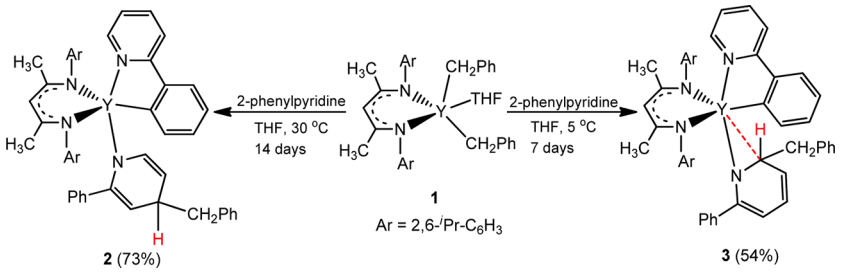
Scheme 1. Reactions of β-Diketiminatoyttrium Dialkyl Complex with 2-Phenylpyridine



phenylpyridine in THF at 30 °C for 14 days afforded complex **2** (LY(η^2-*N*,*C*-$C_5H_4NC_6H_4$-2)[$C_5H_4N(CH_2Ph$-4)Ph]) in 73% isolated yield, as shown in Scheme 1, indicating that a phenyl ring C−H activation at the *ortho* position and pyridine ring 1,4-addition and dearomatization occurred in this reaction. However, complex **1** reacted with 2 equiv of 2-phenylpyridine in THF at 5 °C for 7 days to give another product, **3** (LY(η^2-*N*,*C*-$C_5H_4NC_6H_4$-2)[$C_5H_4N(CH_2Ph$-2)Ph]), in 54% isolated yield. The formation of **2** and **3** indicated that two benzyl groups of **1** can not only activate the C(sp^2)−H bond of the phenyl ring at the *ortho* position but also dearomatize the pyridine ring through one benzyl group addition at the *para* or *ortho* positions of the pyridine skeleton. These results are different from the observations of other rare-earth-metal alkyl complexes with pyridines. For example, the reaction of the yttrium monoalkyl complexes with a 1,1′-ferrocenylene-diamide (NN^{fc})[9g] or ene-diamido[18] ligand with 2-phenylpyridine gave the *ortho*-phenyl ring C−H activation products. The lutetium dialkyl or trialkyl complexes reacted with 2,2′:6′,2″-terpyridine (tpy) to afford the one alkyl group 1,2-addition at the *ortho* position of the central pyridine ring products.[11a] The reaction of NN^{fc}-supported rare-earth-metal (Sc and Lu) monoalkyl complexes with 2,2′-bipyridine afforded a alkyl-transfer product at the *para* position of the pyridine ring.[9f] To the best of our knowledge, no examples of rare-earth-metal complex mediated dearomatization of pyridines to give the two alkyl-transfer products (viz., alkyl group 1,2- or 1,4-addition at the *ortho* or *para* position of the pyridine ring) have been reported.

Both **2** and **3** were characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. Their important bond parameters are compiled in Figures 1 and 2, respectively. The single-crystal diffraction analysis results showed that the central metal Y^{3+} ion is bound with a η^2-β-diketiminato ligand, a η^2-*N*,*C*-$C_5H_4NC_6H_4$-2 unit, and one terminal nitrogen from the dearomatized pyridine (dihydropyridine, DHP) ring to form a distorted square pyramidal geometry in **2**. The Y1−N3 and Y1−C36 bond distances (2.504(6) and 2.480(8) Å) are in the range expected for the Y−N and Y−C bond interaction with partial single and donor bond character. The unique character of **2** is the loss of aromaticity of DHP, as evidenced by the deviations in its bond length and planarity. For example, the bond distances for C43−C42 (1.543(11) Å) and C43−C44 (1.489(10) Å) are consistent with single bonds to the newly formed quaternary carbon atom. The next four contiguous bonds in the ring have bond distances of 1.329(8) Å (C44−C45), 1.405(8) Å (C45−N4), 1.426(8) Å (N4−C41), and 1.304(10) Å (C41−C42) and show obvious double-, single-, single-, and double-bond characters. The short Y1−N4 bond length (2.232(6) Å) compares well with those found in other structurally characterized yttrium amide complexes, indicating that the $C_5H_4N(CH_2Ph$-4)Ph-2 unit is a monoanionic ligand.

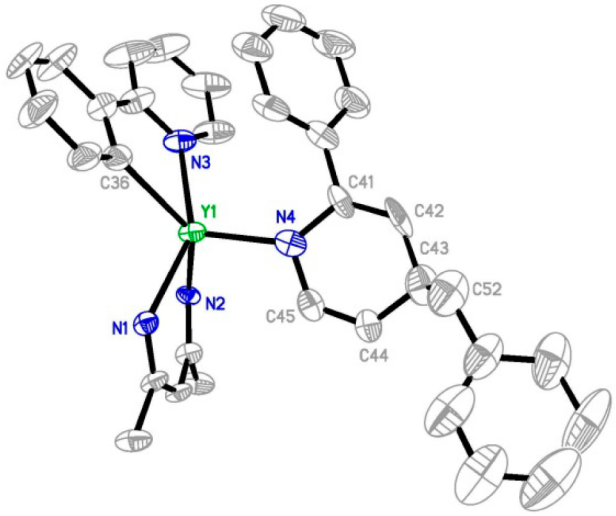


Figure 1. Molecular structure of **2** with thermal ellipsoids at 30% probability. 2,6-Diisopropylphenyl groups of the β-diketiminato ligand and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−N4 2.232(6), Y1−N2 2.369(5), Y1−N1 2.383(5), Y1−C36 2.480(8), Y1−N3 2.504(6), N4−C41 1.426(8), N4−C45 1.405(8), C41−C42 1.304(10), C42−C43 1.543(11), C43−C44 1.489(10), C44−C45 1.329(8), N4−Y1−N2 101.59(19), N4−Y1−N1 100.89(19), N2−Y1−N1 78.48(18), N4−Y1−C36 123.7(2), N2−Y1−C36 134.5(2), N1−Y1−C36 95.0(2), N4−Y1−N3 110.9(2), N2−Y1−N3 94.31(19), N1−Y1−N3 148.24(19), C36−Y1−N3 68.0(2), C45−N4−C41 111.1(6), C45−N4−Y1 114.3(5), C41−N4−Y1 133.8(5), C42−C41−N4 124.5(9), C41−C42−C43 125.7(9), C44−C43−C52 114.3(8), C44−C43−C42 105.7(7), C52−C43−C42 110.0(9), C45−C44−C43 123.5(8), C44−C45−N4, 127.6(8).

The assigned signals of the ^1H and ^{13}C NMR spectra are in agreement with the dearomatized nature of the pyridine ligand, in which four broad peaks at δ = 6.87 ppm (buried in the peaks of Ar groups), δ = 4.44, 4.72, and δ = 3.95 ppm are assigned to the C*H* resonances of the DHP ring and five peaks at δ = 141.5, 126.0, 100.0, 99.4, and 38.7 ppm are assigned to the *C* resonances of the DHP ring.

The structure of **3** (Figure 2) is similar to that of **2** except for the position of the benzyl group on the pyridine ring. Moreover, there is a weak Y···C interaction between the Y^{3+} ion and the *ortho* carbon atom of the DHP ring (Y1−C41 2.986(10) Å). The bond parameters of the DHP ring (Figure 2, bottom) also reveal the dearomatization of this pyridine ring through alkyl transfer. Complex **3** has also been characterized by ^1H and ^{13}C NMR spectroscopy, which was in agreement with its solid-state structure. However, all attempts to secure assignment of the DHP hydrogens by ^1H−^1H COSY failed, and the assignment of the "b/d" signals followed the Kipplinger results.[11a]

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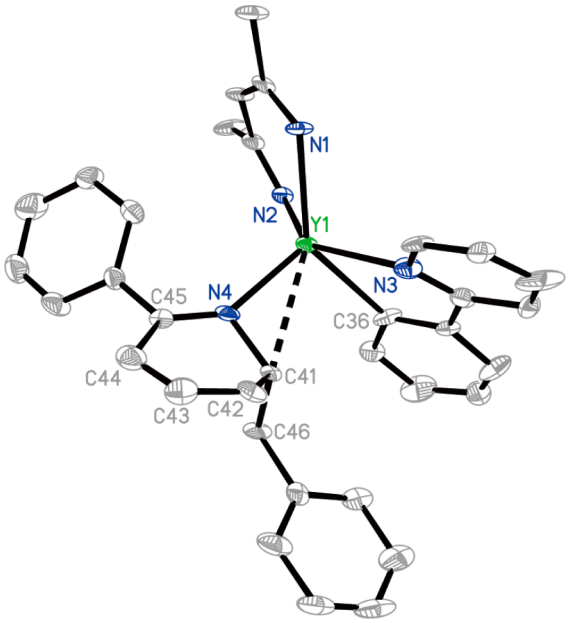
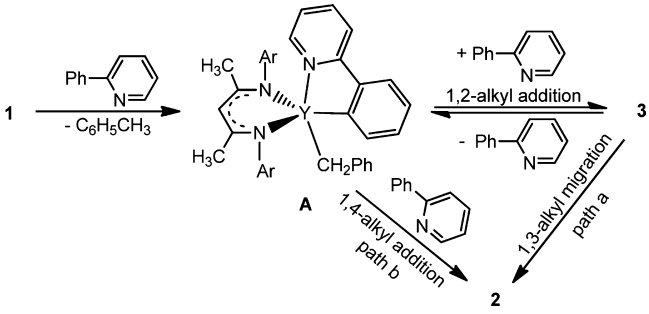


Figure 2. Molecular structure of **3** with thermal ellipsoids at 30% probability. 2,6-Diisopropylphenyl groups of the β-diketiminato ligand and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−N4 2.257(9), Y1−N2 2.370(8), Y1−N1 2.430(8), Y1−C36 2.456(11), Y1−N3 2.506(10), Y1−C41 2.986(10), N4−C45 1.318(13), N4−C41 1.540(13), C41−C42 1.462(15), C41−C46 1.578(13), C42−C43 1.352(17), C43−C44 1.463(18), C44−C45 1.383(16), N4−Y1−N2 117.4(3), N4−Y1−N1 116.1(3), N2−Y1−N1 78.4(3), N4−Y1−C36 103.7(4), N2−Y1−C36 94.4(3), N1−Y1−C36 138.4(4), N4−Y1−N3 100.8(3), N2−Y1−N3 140.7(3), N1−Y1−N3 93.4(3), C36−Y1−N3 66.6(3), N4−Y1−C41 30.3(3), N2−Y1−C41 137.4(3), N1−Y1−C41, 132.5(3), C36−Y1−C41 79.1(4), N3−Y1−C41 74.9(3), C41−N4−Y1 102.0(6), C45−N4−C41 113.1(8), N4−C41−C46 106.9(8), C42−C41−Y1, 130.8(6), C42−C41−N4 109.7(9), C42−C41−C46 112.5(9), N4−C41−Y1 47.7(4), C46−C41−Y1 115.9(7), C43−C42−C41 119.3(11), C42−C43−C44 119.2(12), C45−C44−C43 115.6(13), N4−C45−C44 126.3(12).

Recently, Okuda et al. reported dearomatization of pyridines in a calcium allyl complex and confirmed that the *ortho*-allylated product can be used as an intermediate to transfer into the *para*-allylated product by NMR spectroscopy and the DFT calculation method.[6a] This result encouraged us to examine the formation mechanism of **2** and **3**. So a series of ^{1}H NMR experiments on the transformation between **2** and **3** have been carried out: (1) The *in situ* reaction of **1** with 2 equiv of 2-phenylpyridine in C_6D_6 at room temperature for 7 days produced **2** and **3** in about 2:3 molar ratio, and after 20 days the reaction gave **2** and **3** in about 9:1 molar ratio. (2) When complex **3** was kept in C_6D_6 at room temperature for 24 h, about 10% of **2** could be determined by ^{1}H NMR spectroscopy, accompanied by about 40% of alkyl group dissociation product (alkyl intermediate LY(η^2-*N*,*C*-$C_5H_4NC_6H_4$-2)CH_2Ph, **A**) and neutral 2-phenylpyridine. These mixtures were heated at 30 °C for 7 days to give **2**, **3**, and **A** in about 4:2:4 molar ratio, confirmed by ^{1}H NMR spectroscopy. (3) The equimolar reaction of **1** and 2-phenylpyridine in C_6D_6 at room temperature for 7 days gave complex **3** (about 20% yield) and original materials, accompanied by a small amount of the alkyl intermediate **A**. These NMR experimental results indicated that **2** is a thermodynamically controlled product, complex **3** is the kinetically controlled product, and **3** can slowly turn into **2** by heating or by prolonging the reaction time.

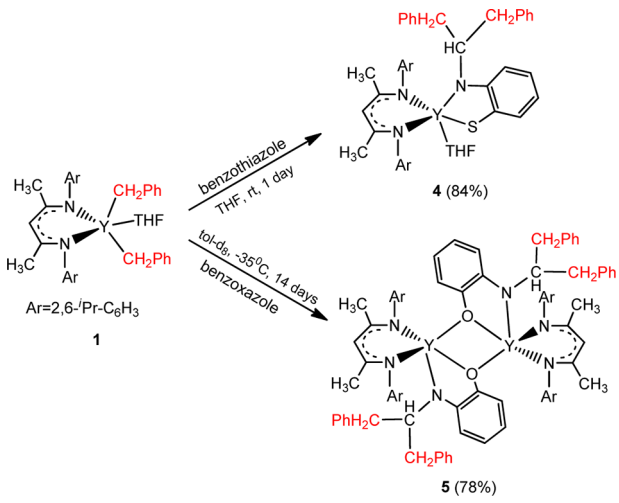
On the basis of the observations described above, we propose a possible mechanism for the formation of **2** and **3**, which is displayed in Scheme 2. Complex **1** first reacts with one 2-phenylpyridine molecule to form intermediate **A** through C(sp^2)−H activation at the C2 position of the phenyl group of the 2-phenylpyridine moiety, accompanied by the elimination of a toluene molecule. Then the benzyl group of **A** adds to the C═N double bond of the second 2-phenylpyridine molecule to afford **3**. The formation of **2** may proceed via two different pathways: one is that **3** directly turns into **2** by 1,3-alkyl migration (path a); the other is that **3** first dissociates to produce **A** and 2-phenylpyridine; then **A** reacts with 2-phenylpyridine to form **2** through the pyridine ring 1,4-addition (path b). Due to the existence of the equilibrium between **3** and the alkyl intermediate **A**, we cannot exclude path b. It should be noted that attempts to clarify the mechanism of formation of complexes **2** and **3** by D-labeling experiments proved uninformative, possibly due to the complex nature of the reaction and poor quality of the ^{2}H NMR spectra of the products obtained.

Scheme 2. Plausible Mechanism for the Formation of 2 and 3



To further explore the reactivity of rare-earth dialkyl complexes and extend the scope of N-heterocycles, the reactions of complex **1** and benzothiazole or benzoxazole were also investigated. As shown in Scheme 3, the reaction of

Scheme 3. Synthesis of Compounds 4 and 5 from Compound 1



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complex **1** with 1 equiv of benzothiazole in THF at ambient temperature for 24 h afforded the alkyl addition and thiazole ring-opening product LY[η^2-*S*,*N*-$SC_6H_4NCH(CH_2Ph)_2$]-(THF) (**4**) in 84% isolated yield. It should be noted that the formation of **4** is independent of the reaction stoichiometry; namely, the reaction of **1** with benzothiazole in 1:2 molar ratio under the same conditions also gave **4** and the residual benzothiazole. Complex **4** was also structurally characterized by single-crystal X-ray diffraction analysis and showed that it is a solvated monomer (Figure 3). The C36−N3, C36−C37, and C36−C44 bonds (1.464(8), 1.540(10), and 1.515(10) Å, respectively) are a standard C−N or C−C single bond. The distances of the Y1−S1 and Y1−N3 bonds (2.605(2) and 2.170(5) Å, respectively) are also classical Y−S or Y−N σ bonds and are comparable to the corresponding values found in other lanthanide sulfenyl or amido complexes such as [*o*-$Me_2NC_6H_4CH_2C(NC_6H_4{}^iPr_2$-2,6)$_2$]Lu($CH_2C_6H_4NMe_2$-*o*)-($SCH_2C_6H_4NMe_2$-*o*)(THF) (Lu−S = 2.641(1) Å)[19a] and {$Me_2Si(C_5Me_4)$(NPh)}Y(THF){^{t}BuNC(C≡CPh)N^{t}Bu} (Y−N3 2.285(5) Å).[19b] The newly formed bidentate substituted 2-aminothiophenolate ligand is dianionic and bonded to a Y^{3+} center with a monoanionic β-diketiminato ligand. The ^{1}H NMR spectrum of **4** also shows that one hydrogen is attached to the C36 atom, confirmed by a multiple peak at δ = 4.83 ppm assignable to the NC*H*($CH_2Ph)_2$ group. The benzyl protons $CH_2C_6H_5$ have two sets of signals. The first set is a doublet, δ = 3.61 (J = 13.6 Hz), and the second set overlaps with the $CHMe_2$ signals at δ 3.14.

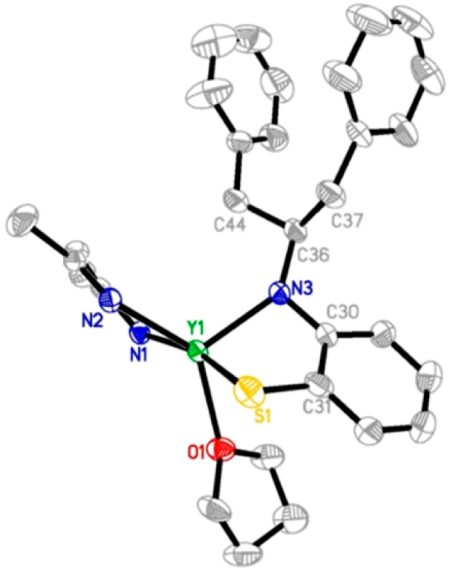

Figure 3. Molecular structure of **4** with thermal ellipsoids at 30% probability. 2,6-Diisopropylphenyl groups of the β-diketiminato ligand and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−N3 2.170(5), Y1−N2 2.338(5), Y1−O1 2.365(5), Y1−N1 2.366(5), Y1−S1 2.605(2), N3−C30 1.380(8), S1−C31 1.772(8), C30−C31 1.425(10), N3−C36 1.464(8), C36−C37 1.540(10), C36−C44 1.515(10), N3−Y1−N2 111.8(2), N3−Y1−O1 110.58(19), N2−Y1−O1 137.30(17), N3−Y1−N1 111.25(19), N2−Y1−N1 79.92(18), O1−Y1−N1 89.83(18), N3−Y1−S1 80.88(16), N2−Y1−S1 95.86(14), O1−Y1−S1 85.62(13), N1−Y1−S1 167.87(13), S1−Y1−C31 36.86(16), C30−N3−C36 119.4(5), C30−N3−Y1 102.3(4), C36−N3−Y1 137.7(4), C31−S1−Y1 81.3(3), N3−C30−C31 120.4(6), C30−C31−S1 123.4(6), C44−C36−C37 112.4(6).

The formation of **4** clearly indicated that a benzothiazole ring-opening and three-component combination, including two benzyl groups and one benzothiazole unit, occurred in the reaction of LY($CH_2Ph)_2$(THF) with benzothiazole. This result is also different from the observation in the reaction of the known Tp^{Me2}-supported yttrium dialkyl complex with benzothiazole.[11b] The latter gave the carbon−carbon coupling, thiazole ring-opening, and toluene elimination product [Tp^{Me2}Y(μ-η^1:η^2-SC_6H_4NCH═CHPh-2)THF]$_2$. This might be attributed to the differences of the steric hindrance and electric charge density around the center metal Y^{3+} ion in the two dialkyl complexes. The lower steric hindrance and electronic delocalization of the β-diketiminato ligand L in LY($CH_2Ph)_2$THF increase the nucleophilicity of the benzyl ligands toward the C2 atom of the thiazole ring, leading to the dual carbon−carbon coupling product **4**.

This N-heterocycle ring-opening and dual carbon−carbon coupling phenomenon has also been observed in the reaction of LY($CH_2Ph)_2$THF with benzoxazole. The equimolar reaction of LY($CH_2Ph)_2$THF with benzoxazole in toluene-d_8 at −35 °C afforded complex **5** ({LY[μ-η^2:η^1-(O,N)-OC_6H_4NCH-($CH_2Ph)_2$]}$_2$) in 78% isolated yield (Scheme 3). It should be noted that when this reaction was carried out in THF or toluene at ambient temperature, the starting materials were fully consumed. However, the red solid material obtained from the reaction was insoluble in common organic solvents such as THF, toluene, and hexane, which prevented further characterization; consequently satisfactory ^{1}H and ^{13}C NMR spectra for complex **5** could not be obtained. The solid-state structure of **5** was further confirmed by the single-crystal X-ray diffraction analysis and indicated that complex **5** is a solvent-free dimer (Figure 4). The two Y ions are surrounded by one β-diketiminato ligand, a 2-aminophenolate ligand, and a bridging oxygen atom (O1) from the other 2-aminophenolate ligand in the dimer. The six atoms Y1, N3, O1A, Y1A, N3A, and O1 form an interlinked tricyclic structure via two bridged oxygen atoms. The Y1−O1A and Y1−N3 bond distances are 2.295(4) and 2.271(4) Å, respectively, and are in the range of the normal Y−O or Y−N σ bonds. Moreover, the N3−C30, C30−C31, and C30−C38 bonds (1.470(7), 1.552(8), and 1.557(8) Å, respectively) are classical C−N and C−C single bonds. These bond parameters also indicated that the newly formed 2-aminophenolate ligands are dianionic.

CONCLUSION

This work has provided a complementary study on rare-earth-metal dialkyl complex mediated activation of some aromatic N-heterocycles such as 2-phenylpyridine and benzothiazole/benzoxazole and revealed various chemical bond transformations including C−H activation, C−C coupling, ring-opening, or dearomatization of these aromatic N-heterocyclic species. These results are different from those observed in reactions of the known rare-earth mono-, di-, and trialkyl complexes with these N-heterocycles,[4f,9,11,18] indicating that the ancillary ligands in metal complexes also play a vital role in metal-mediated activation of aromatic N-heterocycles.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under a dry and inert atmosphere either using standard Schlenk techniques or under a nitrogen atmosphere in an MBraun glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox

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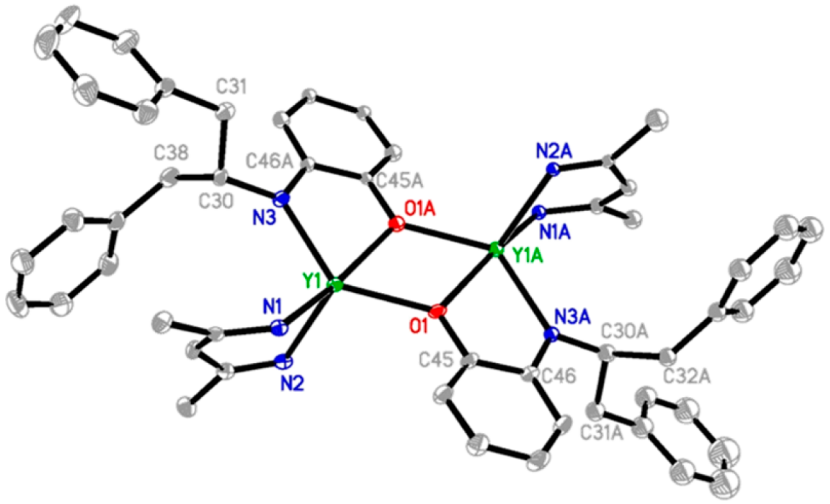
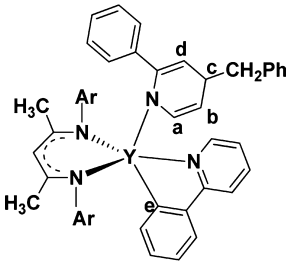


Figure 4. Molecular structure of **5** with thermal ellipsoids at 30% probability. 2,6-Diisopropylphenyl groups of the β-diketiminato ligand and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−N3 2.271(4), Y1−O1 2.277(4), Y1−O1A 2.295(4), Y1−N1 2.352(4), Y1−N2 2.361(4), O1−Y1A 2.295(4), N3−C30 1.470(7), C30−C31 1.552(8), C30−C38 1.567(8), N3−C46A 1.394(7), O1−C45 1.395(6), C45−C46 1.408(8), C46−N3A 1.394(7), N3−Y1−O1 136.43(14), N3−Y1−O1A 72.12(14), O1−Y1−O1A 67.55(14), N3−Y1−N1 104.38(15), O1−Y1−N1 108.04(14), O1A−Y1−N1 160.50(14), N3−Y1−N2 102.86(15), O1−Y1−N2 109.06(14), O1A−Y1−N2 116.16(14), N1−Y1−N2 83.33(14), C46A−N3−C30 116.7(4), C46A−N3−Y1, 115.9(3), C45−O1−Y1 132.7(3), C45−O1−Y1A 114.8(3), Y1−O1−Y1A 112.46(14).

atmosphere were monitored by an O_2/H_2O Combi-Analyzer (MBraun) to ensure both were always below 1 ppm. The THF, toluene, and *n*-hexane solvents were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. $LY(CH_2Ph)_2(THF)$ (**1**) were prepared according to slightly modified literature methods.[17] 2-Phenylpyridine, benzothiazole, and benzoxazole were purchased from Aldrich and were used without purification. Elemental analyses for C, H, and N were carried out on a Rapid CHN-O analyzer. ^1H and ^{13}C NMR data were obtained on a Brüker DMX-400 NMR spectrometer (400 MHz for ^1H; 100 MHz for ^{13}C, Ar = C_6H_3, C_6H_4, or C_6H_5). Infrared spectra were recorded on a Nicolet Avatar-360 FT-IR spectrometer with samples prepared in Nujol mulls.

Synthesis of LY(η^2-*N,C*-$C_5H_4NC_6H_4$-2)[$C_5H_4N(CH_2Ph$-4)Ph] (2). A 10 mL THF solution of 2-phenylpyridine (0.155 g, 1.0 mmol) was added to a 15 mL THF solution of **1** (0.382 g, 0.5 mmol) at ambient temperature, and the mixture was heated at 30 °C for 14 days. Then the solution was evaporated to dryness under vacuum and washed by *n*-pentane (2 × 5 mL), and 5 mL of toluene was added to the residue. Then diffusion of *n*-pentane to the concentrated toluene solution gave pale yellow crystals of **2**. Yield: 0.331 g (73%). ^1H NMR (400 MHz, C_6D_6, RT): δ 7.52−7.00 (m, 14H, *H*-Ar), 6.98−6.81 (m, 3H, *H*-Ar and a), 6.74−6.60 (m, 1H, *H*-Ar), 6.54−6.35 (m, 2H, *H*-Ar), 6.33−6.13 (m, 3H, *H*-Ar), 6.01−5.83 (m, 2H, *H*-Ar), 5.16 (s, 1H, −CC*H*C−), 4.72 (br, 1H, b), 4.44 (two isolated broad peaks, 1H, d), 4.06 (br, 1H, −C*H*Me$_2$), 3.95 (br, 1H, c), 3.33 (br, 1H, −C*H*Me$_2$), 3.03 (br, 3H, −C*H*Me$_2$ and −CH_2Ph), 2.75 (br, 1H, −C*H*Me$_2$), 1.96−1.79 (m, 3H, −CH*Me*$_2$), 1.78−1.46 (m, 12H, −CHC(*Me*)N− and −CH*Me*$_2$), 1.45−1.30 (m, 3H, −CH*Me*$_2$), 1.12 (d, J = 5.6 Hz, 3H, −CH*Me*$_2$), 0.82 (d, J = 5.6 Hz, 3H, −CH*Me*$_2$), 0.68 (d, J = 5.6 Hz, 3H, −CH*Me*$_2$), 0.54 (d, J = 5.6 Hz, 3H, −CH*Me*$_2$). ^{13}C NMR (100 MHz, C_6D_6, RT): δ 188.8 (d, J_{Y-C} = 48.2 Hz, e), 167.5 (−NC(Me)−), 167.1 (−NC(Me)−), 163.8, 147.2, 146.3, 145.3, 144.8, 144.4, 143.7, 142.9, 141.5, 140.4, 138.7, 137.1, 130.2, 129.6, 128.5, 128.3, 128.1, 127.5, 126.2 (*C*-Ar), 126.0 (a), 125.8, 125.6, 125.3, 125.0, 124.6, 124.3, 123.0, 122.7, 119.3, 118.2 (*C*-Ar), 100.0 (b), 99.4 (d), 98.2 (−CCHC−), 50.6 (−CH_2Ph), 38.7 (c), 30.3 (−CHMe$_2$), 28.7 (−CHMe$_2$), 28.4 (−CHMe$_2$), 27.7 (−CHMe$_2$), 25.8 (−CH*Me*$_2$), 25.3 (−CHC(*Me*)N−), 24.9 (−CH*Me*$_2$), 24.8 (−CH*Me*$_2$), 24.5 (−CHC(*Me*)N−), 24.4 (−CH*Me*$_2$), 24.1 (−CH*Me*$_2$), 23.8 (−CH*Me*$_2$), 23.0 (−CH*Me*$_2$), 21.1 (−CH*Me*$_2$). Anal. Calcd (%) for $C_{58}H_{65}N_4Y$: C 76.80, H 7.22, N 6.18. Found: C 76.54, H 7.16, N 6.42. IR (Nujol): 3167 m, 3058 m, 2725 s, 1947 w, 1806 w, 1623 m, 1581 m, 1552 s, 1329 s, 1276 s, 1223 m, 1174 m, 1101 m, 1074 m, 1058 m, 1023 m, 965 m, 935 m, 983 m, 896 w, 848 w, 785 m, 757 m, 743 s, 698 m, cm^{-1}.



Synthesis of LY(η^2-*N,C*-$C_5H_4NC_6H_4$-2)[$C_5H_4N(CH_2Ph$-2)Ph] (3). A cooled 10 mL THF solution of 2-phenylpyridine (0.155 g, 1.0 mmol) was added to a cooled 15 mL THF solution of **1** (0.382 g, 0.5 mmol) at 5 °C, and the mixture was stirred at that temperature for 7 days. Then the solution was evaporated to dryness under vacuum and washed by *n*-hexane (2 × 5 mL), 5 mL of toluene was added to the residue, and then diffusion of *n*-hexane to the concentrated toluene solution gave yellow crystals of **3**. Yield: 0.245 g (54%). ^1H NMR (400 MHz, C_6D_6, RT): δ 7.82 (s, 2H, *H*-Ar), 7.49 (m, 4H, *H*-Ar), 7.28 (s, 4H, *H*-Ar), 7.11−6.86 (m, 8H, *H*-Ar), 6.75−6.20 (m, 6H, *H*-Ar or c), 6.14(s, 1H, *H*-Ar or c), 5.98 (s, 1H, b or d), 5.63 (br, 1H, b or d), 5.19 (s, 1H, −CC*H*C−), 4.34 (two broad peaks, 1H, a), 3.44 (br, 1H, −CH_2Ph), 3.21 (br, 1H, −C*H*Me$_2$), 3.06 (br, 2H, −C*H*Me$_2$), 2.93 (br, 1H, −C*H*Me$_2$), 2.36 (br, 1H, −CH_2Ph), 1.66 (s, 3H, −CHC(*Me*)N−), 1.55 (s, 3H, −CHC(*Me*)N−), 1.39 (d, J = 5.6 Hz, 3H, −CH*Me*$_2$), 1.31 (br, 3H, −CH*Me*$_2$), 1.19−0.96 (m, 9H, −CH*Me*$_2$), 0.90 (d, J = 5.6 Hz, 3H, −CH*Me*$_2$), 0.58 (br, 6H, −CH*Me*$_2$). ^{13}C NMR (100 MHz, C_6D_6, RT): δ 187.8 (d, J_{Y-C} = 50.6 Hz, e), 168.2 (−NC(Me)−), 167.2 (−NC(Me)−), 164.1, 152.2, 149.6, 147.2, 146.7, 146.0, 145.8, 145.1, 143.7, 142.2, 139.1, 138.6, 138.1, 137.6, 136.0, 129.9, 128.8, 128.6, 128.2, 126.9, 126.4, 126.0, 125.9, 125.6, 124.9, 124.6, 124.2, 124.0, 123.8, 123.0, 122.4, 121.6, 120.1 (*C*-Ar), 119.1 (d), 119.0, 118.7, 116.9 (*C*-Ar), 107.3 (c), 99.3 (−CCHC−), 98.0 (a), 49.3 (b), 40.2 (−CH_2Ph), 29.8 (−CHMe$_2$), 29.0 (−CHMe$_2$), 28.1 (−CHMe$_2$), 26.4 (−CH*Me*$_2$), 25.7 (−CHC(*Me*)N−), 25.0 (−CH*Me*$_2$), 24.4 (−CH*Me*$_2$), 24.2 (−CH*Me*$_2$), 22.4 (−CH*Me*$_2$). Anal. Calcd (%) for $C_{58}H_{65}N_4Y$: C 76.80, H 7.22, N 6.18. Found: C 76.57, H 7.09, N 6.33. IR (Nujol): 3167 w, 3055 m, 2725 w, 2671 w,

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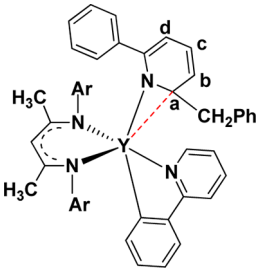
1944 w, 1876 w, 1815 w, 1800 w, 1597 m, 1569 m, 1597 m, 1308 s, 1276 m, 1258 s, 1169 s, 1156 w, 1109 s, 1072 m, 1056 m, 1019 s, 977 m, 932 m, 915 s, 841 s, 795 s, 776 m, 748 s, 700 s, 675 s, 642 s, cm^{-1}.



^{1}H NMR Experiments. (1) Reaction of **1** with 2 equiv of 2-phenylpyridine: 2-phenylpyridine (0.0155 g, 0.1 mmol in 0.3 mL of C_6D_6, 2 equiv) was added to a solution of **1** (0.0382 g, 0.05 mmol in 0.5 mL of C_6D_6) in a J-Young NMR tube. The progress of the reaction was monitored using ^{1}H NMR spectroscopy. The molar ratio of **2** to **3** is 2:3 over the course of 7 days. After 20 days the reaction gave **2** and **3** in about 9:1 molar ratio. (2) Compound **3** (0.0362 g in 0.8 mL of C_6D_6) was dissolved in C_6D_6 at room temperature in a J. Young tube. The progress of the reaction was monitored using ^{1}H NMR spectroscopy. About 10% of **2** accompanied by 40% LY(η^2-*N,C*-$C_5H_4NC_6H_4$-2)CH_2Ph(A) and neutral 2-phenylpyridine was detected by ^{1}H NMR spectroscopy over the course of 24 h. The mixture was heated at 30 °C in C_6D_6 in a J. Young tube, and the molar ratio of **2**, **3**, and **A** was 4:2:4 over the course of 7 days. (3) Equimolar 2-phenylpyridine to 2-phenylpyridine (8 mg in 0.3 mL of C_6D_6) was added to a solution of **1** (0.0382 g, 0.05 mmol in 0.5 mL of C_6D_6) in a J-Young NMR tube. The progress of the reaction was monitored using ^{1}H NMR spectroscopy. After 7 days, the ^{1}H NMR spectrum showed mostly starting materials, about 20% of complex **3** accompanied by a small amount of intermediate **A**.

Synthesis of LY[η^2-(S,N)-$SC_6H_4NCH(CH_2Ph)_2$](THF) (4). A 10 mL THF solution of benzothiazole (0.068 g, 0.5 mmol) was added slowly to a stirred THF solution (15 mL) of **1** (0.382 g, 0.5 mmol). The mixture was left to stir for 24 h at room temperature; then the solution was evaporated to dryness under vacuum and washed with *n*-hexane (2 × 10 mL). The slurry was filtered, and a yellow solid was obtained. Yellow crystals of **4** suitable for X-ray analysis were obtained by recrystallization from THF (2−3 mL) at room temperature. Yield: 0.376 g (84%). ^{1}H NMR (400 MHz, C_6D_6, RT): δ 7.63 (d, J = 7.6 Hz, 1H, *H*-Ar), 7.20−7.12 (m, 6H, *H*-Ar), 7.11−6.94 (m, 12H, *H*-Ar), 6.64 (t, J = 7.0 Hz, 1H, *H*-Ar), 4.94 (s, 1H, −CC*H*C−), 4.83 (br m, 1H, −NC*H*$(CH_2Ph)_2$), 3.70 (br s, 2H, −C*H*Me_2), 3.61 (d, J = 13.6 Hz, 2H, −NCH($CH_2Ph)_2$), 3.46 (br s, 4H, THF), 3.14 (m, 4H, −NCH($CH_2Ph)_2$ and −C*H*Me_2), 1.52 (t, 12H, −CHC(*Me*)N− and −CH*Me*$_2$), 1.35 (d, J = 5.6 Hz, 6H, −CH*Me*$_2$), 1.25 (br d, 10H, −CH*Me*$_2$ and THF), 1.08 (d, J = 6.0 Hz, 6H, −CH*Me*$_2$). ^{1}H NMR (500 MHz, C_7D_8, 0 °C): δ 7.55 (d, J = 8.0 Hz, 1H, *H*-Ar), 7.15−7.09 (m, 7H, *H*-Ar), 7.09−7.03 (m, 7H, *H*-Ar), 7.00−6.98 (m, 2H, *H*-Ar), 6.97−6.92 (m, 2H, *H*-Ar), 6.63 (t, J = 7.5 Hz, 1H, *H*-Ar), 4.92 (s, 1H, −CC*H*C−), 4.78 (br m, 1H, −NC*H*$(CH_2Ph)_2$), 3.71 (m, 2H, −C*H*Me_2), 3.56 (s, 2H, −NCH($CH_2Ph)_2$), 3.14 (m, 4H, −NCH-($CH_2Ph)_2$ and −C*H*Me_2), 2.89 (br s, 4H, THF), 1.54 (s, 6H, −CHC(*Me*)N−), 1.51 (d, J = 6.5 Hz, 6H, −CH*Me*$_2$), 1.37 (d, J = 6.5 Hz, 6H, −CH*Me*$_2$), 1.27 (d, J = 6.5 Hz, 6H, −CH*Me*$_2$), 1.08 (d, J = 6.5 Hz, 6H, −CH*Me*$_2$), 0.79 (br s, 4H, THF). ^{13}C NMR (100 MHz, C_6D_6, RT): δ 167.3 (−NC(Me)−), 146.9, 145.3, 143.6, 141.1, 137.5, 129.4, 128.8,127.8, 125.5, 125.3, 124.7, 124.0, 122.9, 119.4, 118.8 (*C*-Ar), 97.8 (−CCHC−), 69.4 (br, THF), 63.0 (−NCH($CH_2Ph)_2$), 44.7 (−NCH($CH_2Ph)_2$), 29.4 (−CHMe$_2$), 28.6 (−CHMe$_2$), 25.4 (−CH*Me*$_2$), 25.2 (br, THF), 24.7 (−CHC(*Me*)N−), 24.5 (−CH*Me*$_2$), 24.0 (−CH*Me*$_2$). Anal. Calcd (%) for $C_{54}H_{68}N_3OSY$: C 72.38, H 7.65, N 4.69. Found: C 72.21, H 7.49, N 4.88. IR (Nujol): 3057 m, 2725 w, 2671 w, 1937 w, 1864 w, 1800 w, 1646 w, 1604 m, 1568 m, 1520 s, 1496 s, 1310 s, 1261 s, 1168 m, 1128 m, 1099 m, 1077 m, 1058 m, 1031 m, 1018 m, 1005 m, 960 m, 928 m, 866 m, 841 m, 789 s, 759 s, 743 s, 696 s, cm^{-1}.

Synthesis of {LY[μ-η^2:η^1-(O,N)-$OC_6H_4NCH(CH_2Ph)_2$]}$_2$ (5). A cooled toluene-d_8 solution (0.5 mL) of benzoxazole (0.024 g, 0.2 mmol) was added quickly to a cooled toluene-d_8 solution (2 mL) of **1** (0.153 g, 0.2 mmol). The color of the solution quickly changed from yellow to red, and yellow crystals of **5** were harvested after the solution was kept for 14 days at −35 °C. Yield: 0.126 g (78%). Anal. Calcd (%) for $C_{100}H_{120}N_6O_2Y_2$: C 74.33, H 7.49, N 5.20. Found: C 74.44, H 7.56, N 5.11. IR (Nujol): 3058 m, 2725 w, 1941 w, 1870 w, 1796 w, 1585 m, 1518 m, 1314 m, 1256 m, 1193 m, 1169 m, 1117 m, 1063 m, 1022 m, 925 m, 889 m, 840 m, 792 m, 699 m, cm^{-1}. No satisfactory ^{1}H and ^{13}C NMR spectra of **5** could be obtained due to poor solubility in normal deuterated solvents such as C_6D_6, C_7D_8, and C_4D_8O.

X-ray Data Collection, Structure Determination, and Refinement. Suitable single crystals of complexes **2**−**6** were sealed under nitrogen in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Brüker SMART Apex CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz−polarization effects and empirical absorption with the SADABS program.[20] The structures were solved by the direct method using the SHELXL-97 program.[21] All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in the refinement. All calculations were performed using the SHELXL program. A summary of the crystallographic data and selected experimental information are listed in Table S1

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, text, tables, and figures giving crystal data and processing parameters, selected NMR spectra, and additional experimental details. 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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