ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

Unexpected C−H Bond Activation Promoted by Bimetallic Lanthanide Amido Complexes Bearing a META-Phenylene-Bridged Bis(β-diketiminate) Ligand

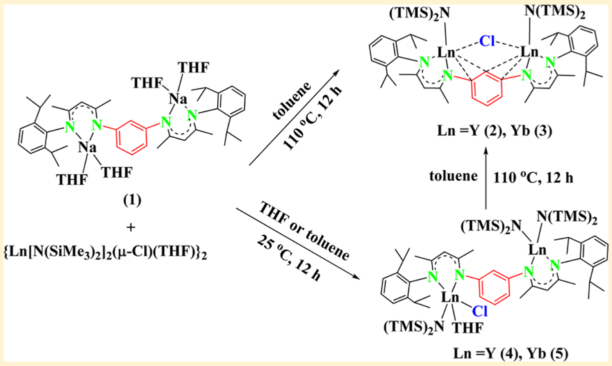
Song Sun,[†] Qiu Sun,[†] Bei Zhao,*[,†] Yong Zhang,[†] Qi Shen,[†] and Yingming Yao*[,†,‡]

[†]Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou 215123, People's Republic of China

[‡]The Institute of Low Carbon Economy, Suzhou 215123, People's Republic of China

S *Supporting Information*

ABSTRACT: Treatment of META-$[Na(THF)_2]_2$ (**1**; META = $\{[2,6\text{-}{}^iPr_2C_6H_3NC(Me)C(H)C(Me)N]^-\}_2$-(*m*-phenylene)] with 1 equiv of $\{Ln[N(SiMe_3)_2]_2(\mu\text{-Cl})(THF)\}_2$ (Ln = Y, Yb) in toluene at 110 °C afforded bimetallic lanthanide amido complexes bridged by a chloride and a phenyl group, $\{Ln[N(SiMe_3)_2]\}_2(META')(\mu\text{-Cl})$ (Ln = Y (**2**), Yb (**3**)), which formed via unexpected C−H bond activation of the arene ring. However, the same reactions carried out in both THF and toluene at room temperature gave the bimetallic lanthanide amido−chloro complexes $\{Ln[N(SiMe_3)_2]_2\}META\{Ln[N(SiMe_3)_2]Cl(THF)\}$ (Ln = Y (**4**), Yb (**5**)). When they were heated to 110 °C in toluene, complexes **4** and **5** were converted to complexes **2** and **3** via amine elimination. All of these complexes were confirmed by elemental analysis, FT-IR, and X-ray structure analysis and by NMR analysis in the cases of complexes **1**, **2**, and **4**.



■ INTRODUCTION

In recent years, the design and synthesis of bimetallic complexes supported by binucleating ligands have received considerable attention, due to their wide application in homogeneous catalysis. Such chemistry has been developed on the basis of the notion of the presence of cooperative effects between the two metal centers and/or nuclearity effects.[1] To date, a number of bimetallic complexes of main-group and transition metals supported by well-defined binucleating ligands have been reported.[2] In comparison with their monometallic analogues, these complexes indeed have demonstrated promising catalytic activities and/or selectivities in the polymerization of olefins,[2g,h,j−l,o] the copolymerization of epoxide with CO_2,[2a,e,f,m] and a series of organic transformations.[2c,d,n] For example, Marks et al. reported that a series of bimetallic titanium (Ti_2) and zirconium (Zr_2) complexes supported by "constrained geometry" ligands have shown obvious bimetallic cooperative effects in olefin polymerization.[1b,3] However, the cooperative effects of bimetallic lanthanide complexes in organolanthanide chemistry remains largely unexplored, due to the fact that the synthesis of covalently linked binuclear lanthanide complexes is more challenging.[4]

During the past 10 years, β-diketiminate ligands have been widely used in organolanthanide and organolanthanoid chemistry to stabilize lanthanide complexes, because these ligand systems are easily available and their steric and electronic properties are tunable.[5] Numerous organolanthanide β-diketiminate complexes have been prepared, and some of them have exhibited exciting catalytic activities and/or selectivities for the polymerization of lactones and lactides[6] and conjugated dienes.[7] Phenylene-bridged bis(β-diketiminate) groups, as one type of β-diketiminate ligand, are useful dinucleating ligands to stabilize bimetallic organometallic complexes. Recently, Harder et al. reported that the bimetallic calcium and zinc phenylene-bridged bis(β-diketiminate) complexes are efficient catalysts for the copolymerization of cyclohexene oxide and CO_2. Moreover, the META-phenylene-bridged zinc complexes are superior to the PARA-phenylene-bridged analogues for this copolymerization, which was attributed to the cooperative effects in these binuclear catalysts.[8] However, the phenylene-bridged bis(β-diketiminate) ligands have not been used in organolanthanide chemistry to our knowledge. Herein, we introduce such ligands into this area. During the synthesis of lanthanide amido complexes stabilized by a META-phenylene-bridged bis(β-diketiminate) ligand, we found an unexpected C−H bond activation of the arene ring promoted by the bimetallic complexes.

Received: January 10, 2013
Published: March 12, 2013

dx.doi.org/10.1021/om400018b | *Organometallics* 2013, 32, 1876−1881

EXPERIMENTAL SECTION

General Procedures. All of the manipulations were performed under an argon atmosphere, using standard Schlenk techniques. Anhydrous $LnCl_3$, $HN(TMS)_2$, and NaH are commercially available. $HN(SiMe_3)_2$ was dried over CaH_2 for 4 days and distilled before use. Tetrahydrofuran (THF), toluene, and hexane were dried and freed of oxygen by refluxing over sodium/benzophenone ketyl and distilled prior to use. The ligand META-H_2 (=[2,6-$^iPr_2C_6H_3NHC(Me)C(H)$-$C(Me)N]_2$-(*m*-phenylene),[8] $NaN(TMS)_2$, and $\{Ln[N(SiMe_3)_2]_2(\mu\text{-}Cl)(THF)\}_2$ (Ln = Y, Yb)[9] were prepared according to the published procedures. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The FT-IR spectra were recorded with a Nicolet-550 FT-IR spectrometer as KBr pellets. The ^1H NMR spectra were recorded in a C_6D_6 or d_8-THF solution for complexes **1**, **2**, and **4** with a Unity Varian-300 or Unity Varian-400 spectrometer. Because of their paramagnetism, no resolvable NMR spectra for complexes **3** and **5** were obtained. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges.

Synthesis of META-[Na(THF)$_2$]$_2$ (1). A THF solution of META-H_2 (50 mL, 14.77 g, 25.00 mmol) was added to a suspension of NaH (1.20 g, 50.00 mmol) in 20 mL of THF. The resulting mixture was heated to reflux for about 6 h. The dissolved portion was removed by centrifugation, the solvent was removed under vacuum, and hexane was added to extract the product. Red crystals were obtained from the concentrated hexane solution at room temperature (20.78 g, 90%). Mp: 157−159 °C. IR (KBr, cm^{-1}): 3063 (m), 2960 (s), 2867 (s), 1626 (s), 1588 (s), 1553 (s), 1440 (s), 1382 (s), 1325 (m), 1278 (s), 1178 (s), 1100 (w), 865 (s), 758 (s). ^1H NMR (C_6D_6, 400 MHz): 7.15−7.17 (m, 8H, $CH_{\text{N-aryl}}$, overlapped with C_6D_6), 7.08−7.11 (m, 3H, $CH_{\text{N-aryl}}$), 6.65 (s, 1H, $CH_{\text{N-aryl}}$), 4.60 (s, 1H, CH_3CNCH), 3.45 (m, 16H, THF-α-CH_2), 3.13 (s, 4H, $CH(CH_3)_2$), 1.38 (s, 16H, THF-β-CH_2), 1.24−1.28 (m, 36H, CH_3CN + $CH(CH_3)_2$). ^{13}C NMR (C_6D_6, 100 MHz): δ 23.93 (CH_3CN), 24.13 ($CH(CH_3)_2$), 25.43 (THF-β-CH_2), 26.06 ($CH(CH_3)_2$), 67.79 (THF-α-CH_2), 93.56 (CH_3CNCH), 117.86 ($CH_{\text{N-aryl}}$), 122.28 ($CH_{\text{N-aryl}}$), 123.22 (CH_{Naryl}), 129.12 (CH_{Naryl}), 139.51 (CH_{Naryl}), 147.52 ($C{=}N$), 150.31 ($C{=}N$), 155.98 ($C{=}N$), 161.71 ($C{=}N$). Anal. Calcd for $C_{56}H_{84}N_4Na_2O_4$: C, 72.85; H, 9.17; N, 6.07. Found: C, 72.52; H, 9.43; N, 5.88.

Synthesis of {Y[N(SiMe$_3$)$_2$]}$_2$(META′)(μ-Cl) (2). To a toluene solution of $\{Y[N(SiMe_3)_2]_2(\mu\text{-}Cl)(THF)\}_2$ (1.03 g, 1.00 mmol) was added a toluene solution of META-$[Na(THF)_2]_2$ (6.10 mL, 1.00 mmol). The mixture was stirred at 110 °C for about 48 h. The precipitate that formed was removed by centrifugation, and the solvent was evaporated completely under reduced pressure. Hexane (1 × 3 mL) was added to precipitate the product. Colorless crystals were obtained from a mixture of hexane and toluene (6/4 v/v) at 25 °C overnight (0.59 g, 53%). Mp: 219−222 °C dec. IR (KBr, cm^{-1}): 3054 (m), 2960 (s), 2862 (m), 1625 (s), 1595 (s), 1553 (s), 1492 (s), 1434 (s), 1381 (s), 1368 (m), 1277 (s), 1178 (m), 1026 (w), 842 (w), 758 (m). ^1H NMR (C_6D_6, 300 MHz): 7.43 (m, 2H, $CH_{\text{N-aryl}}$), 7.16 (s, 5H, $CH_{\text{N-aryl}}$ + overlapped with C_6D_6), 6.77 (d, 2H, $CH_{\text{N-aryl}}$), 4.95 (s, 2H, CH_3CNCH), 3.28−3.37 (m, 4H, $CH(CH_3)_2$), 2.27 (s, 6H, CH_3CN), 1.61 (s, 6H, CH_3CN), 1.39−1.48 (d, 12H, $CH(CH_3)_2$), 1.05−1.12 (d, 12H, $CH(CH_3)_2$), 0.02 (s, 36H, $SiMe_3$). ^{13}C NMR (d_8-THF, 100 MHz): δ 5.14 ($Si(CH_3)_3$), 5.59 ($Si(CH_3)_3$), 23.56 ($CH(CH_3)_2$), 25.07 ($CH(CH_3)_2$), 25.60 ($CH(CH_3)_2$), 25.87 ($CH(CH_3)_2$), 27.07 (CH_3CN), 28.99 ($CH(CH_3)_2$), 29.59 ($CH(CH_3)_2$), 101.99 (CH_3CNCH), 118.08 ($CH_{\text{N-aryl}}$), 125.20 ($CH_{\text{N-aryl}}$), 125.61 (CH_{Naryl}), 126.94 (CH_{Naryl}), 133.51 (CH_{Naryl}), 143.90 (CH_{Naryl}), 144.44 (CH_{Naryl}), 146.81 (CH_{Naryl}), 154.27 (CH_{Naryl}), 158.83 ($C{=}N$), 168.07 ($C{=}N$). Anal. Calcd for $C_{52}H_{87}ClN_6Si_4Y_2$: C, 55.67; H, 7.82; N, 7.49. Found: C, 55.93; H, 7.98; N, 7.35.

Synthesis of {Yb[N(SiMe$_3$)$_2$]}$_2$(META′)(μ-Cl) (3). The synthesis of complex **3** was carried out in the same way as that described for complex **2**, but $\{Yb[N(SiMe_3)_2]_2(\mu\text{-}Cl)(THF)\}_2$ (1.20 g, 1.00 mmol) was used instead of $\{Y[N(SiMe_3)_2]_2(\mu\text{-}Cl)(THF)\}_2$. Hexane (2 × 3 mL) was added to precipitate the product. Red crystals were obtained from a solution of hexane and toluene (5/5 v/v) at 25 °C overnight (0.77 g, 60%). Mp: 221−223 °C dec. IR (KBr, cm^{-1}): 3055 (m), 2962 (s), 2860 (m), 1625 (s), 1593 (s), 1550 (s), 1493 (s), 1434 (s), 1380 (s), 1367 (m), 1267 (s), 1176 (m), 1024 (w), 843 (w), 769 (m). Anal. Calcd for $C_{52}H_{87}ClN_6Si_4Yb_2$: C, 48.41; H, 6.80; N, 6.51. Found: C, 48.73; H, 6.35; N, 6.76.

Synthesis of {Y[N(SiMe$_3$)$_2$]$_2$}META{Y[N(SiMe$_3$)$_2$]Cl(THF)} (4). To a THF solution of $\{Y[N(SiMe_3)_2]_2(\mu\text{-}Cl)(THF)\}_2$ (1.03 g, 1.00 mmol) was added a THF solution of META-$[Na(THF)_2]_2$ (6.10 mL, 1.00 mmol). The mixture was stirred overnight at 25 °C. The precipitate that formed was removed by centrifugation, and the solvent was evaporated completely under reduced pressure. Hexane (3 × 3 mL) was added to precipitate the product. Colorless crystals were obtained from a mixture of hexane and toluene (6/1 v/v) at 25 °C overnight (0.63 g, 46%). Mp: 253−257 °C dec. IR (KBr, cm^{-1}): 3060 (m), 2960 (s), 2866 (m), 1625 (s), 1593 (m), 1552 (s), 1492 (m), 1435 (s), 1380 (s), 1363 (m), 1278 (m), 1178 (w), 933 (s), 841 (m), 757 (m). ^1H NMR (d_8-THF, 400 MHz): 7.34 (m, 1H, $CH_{\text{N-aryl}}$), 7.20 (m, 8H, $CH_{\text{N-aryl}}$), 6.68 (s, 1H, $CH_{\text{N-aryl}}$), 5.40 (s, 1H, CH_3CNCH), 5.09 (s, 1H, CH_3CNCH), 3.62 (m, 4H, THF-α-CH_2), 3.25−2.91 (m, 4H, $CH(CH_3)_2$), 2.14 (s, 3H, CH_3CN), 1.96 (s, 3H, CH_3CN), 1.79−1.77 (m, 7H, CH_3CN+THF-β-CH_2), 1.66 (s, 3H, CH_3CN $CH(CH_3)_2$), 1.34 (d, 12H, $CH(CH_3)_2$), 1.14 (d, 12H, $CH(CH_3)_2$), 0.25 (m, 54H, $SiMe_3$). ^{13}C NMR (d_8-THF, 100 MHz): δ 5.48 ($SiMe_3$), 25.08 (THF-β-CH_2), 26.06 ($CH(CH_3)_2$), 26.14 ($CH(CH_3)_2$), 26.29 (CH_3CN), 26.55 (CH_3CN), 26.75 ($CH(CH_3)_2$), 68.39 (THF-α-CH_2), 96.46 (CH_3CNCH), 99.83 (CH_3CNCH), 123.13 ($CH_{\text{N-aryl}}$), 125.06 ($CH_{\text{N-aryl}}$), 125.58 (CH_{Naryl}), 126.68 (CH_{Naryl}), 127.02 (CH_{Naryl}), 129.82 (CH_{Naryl}), 143.03 ($CH_{\text{N-aryl}}$), 146.22 ($CH_{\text{N-aryl}}$), 146.54 (CH_{Naryl}), 150.21 ($C{=}N$), 151.61 ($C{=}N$), 167.89 ($C{=}N$), 168.87 ($C{=}N$). Anal. Calcd for $C_{62}H_{114}ClN_7OSi_6Y_2$: C, 54.94; H, 8.48; N, 7.23. Found: C, 54.65; H, 8.57; N, 7.06.

Synthesis of {Yb[N(SiMe$_3$)$_2$]$_2$}META{Yb[N(SiMe$_3$)$_2$]Cl(THF)} (5). The synthesis of complex **5** was carried out in the same way as that described for complex **4**, but $\{Yb[N(SiMe_3)_2]_2(\mu\text{-}Cl)(THF)\}_2$ (1.20 g, 1.00 mmol) was used instead of $\{Y[N(SiMe_3)_2]_2(\mu\text{-}Cl)(THF)\}_2$. Red crystals were obtained from a mixture of hexane and toluene (7/2 v/v) at 25 °C in a few days (0.61 g, 40%). Mp: 249−252 °C dec. IR (KBr, cm^{-1}): 3058 (m), 2963 (s), 2876 (m), 1627 (s), 1595 (m), 1552 (s), 1489 (m), 1436 (s), 1380 (s), 1364 (m), 1276 (m), 1178 (w), 928 (s), 843 (m), 756 (m). Anal. Calcd for $C_{62}H_{114}ClN_7OSi_6Yb_2$: C, 48.87; H, 7.54; N, 6.43. Found: C, 48.51 ; H, 7.69; N, 6.21.

X-ray Crystallography. Suitable single crystals of complexes **2**−**5** were sealed in a thin-walled glass capillary for the determination of single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo Kα radiation (λ = 0.71070 Å). The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in STable 1 (Supporting Information).

The structures were solved by direct methods and refined by full-matrix least-squares procedures on the basis of $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELXL-97 programs.

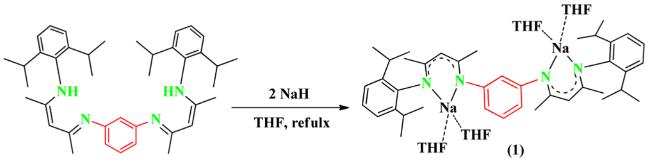
RESULTS AND DISCUSSION

The amine elimination reaction of lanthanide amido complexes with a preligand is a popular method for the synthesis of new lanthanide complexes. However, a ^1H NMR monitoring reaction between $Y[N(SiMe_3)_2]_3$ and *m*-phenylene-bridged bis(β-diketimine) (META-H_2) revealed that this reaction did not occur in C_6D_6 at 70 °C, as the methyl signal of the free $HN(SiMe_3)_2$ at δ 0.10 ppm is very weak, even after the reaction time was elongated to 72 h (SFigures 2−5, Supporting

Information). Therefore, we attempted to synthesize the desired lanthanide amido complexes via a metathesis reaction.

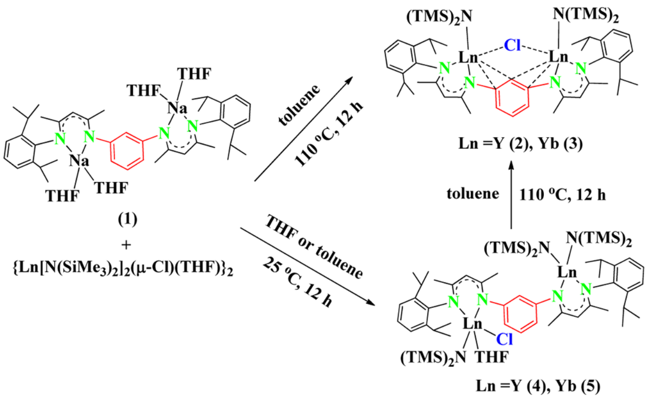
The preligand META-H_2 reacted with NaH in THF under reflux, after workup, to give red crystals from hexane in a good isolated yield. Elemental analysis and NMR characterization revealed that the formula of this compound is META-$[Na(THF)_2]_2$. X-ray diffraction analysis confirmed that the product is the bimetallic sodium bis(β-diketiminate) complex META-$[Na(THF)_2]_2$ (**1**), as shown in Scheme 1. However, the crystal data of compound **1** are relatively poor, and only the framework was obtained.

Scheme 1



Treatment of $\{Ln[N(SiMe_3)_2]_2(\mu\text{-Cl})(THF)\}_2$ (Ln = Y, Yb) with 1 equiv of compound **1** in toluene at 110 °C, after workup, gave colorless (for Y, **2**) and red (for Yb, **3**) crystals in good isolated yields. In the ^1H NMR spectrum of complex **2** (in C_6D_6), in addition to the signals for the *m*-phenylene-bridged bis(β-diketiminate) ligand, there is a slightly broad singlet at δ 0.02 ppm, which can be assigned to the amido groups $-N(SiMe_3)_2$. Its integration amounts to only 36 H, which is less than the 72 H in the desired complex META-$\{Y[N(SiMe_3)_2]_2\}_2$ (SFigure 6, Supporting Information). Further X-ray structure determination confirmed that complexes **2** and **3** were not the desired lanthanide bisamido complexes but the novel bimetallic lanthanide amido complexes bridged by a chloride and a phenyl group $\{Ln[N(SiMe_3)_2]\}_2(META')(\mu\text{-Cl})$ (Ln = Y (**2**), Yb (**3**)), in which an unexpected C−H bond activation of the phenyl group occurred, as shown in Scheme 2.

Scheme 2



When the same reactions were conducted in THF at room temperature, colorless (for Y, **4**) and red (for Yb, **5**) crystals were isolated from concentrated toluene/hexane solutions in 46% and 40% isolated yields, respectively. In the ^1H NMR spectrum of complex **4** (in d_8-THF), the signal of the amido groups $-N(SiMe_3)_2$ appeared at δ 0.09−0.25 ppm as a broad multiplet, which is different from that in complex **2**. In addition, the integration of this peak revealed that there are 54 H for the amido group, which was also less than the 72 H in the desired yttrium amido complex META-$\{Y[N(SiMe_3)_2]_2\}_2$ (SFigure 8, Supporting Information). Further X-ray structure determination confirmed that complexes **4** and **5** were the bimetallic lanthanide amido−chloro complexes $\{Ln[N(SiMe_3)_2]_2\}$-META$\{Ln[N(SiMe_3)_2]Cl(THF)\}$, (Ln = Y (**4**), Yb (**5**)) (Scheme 2). It was found that the reaction media do not influence these reactions at room temperature. Complexes **4** and **5** can also be obtained in toluene at room temperature. It seems that the ionic radii play a key role on the formation of a bimetallic lanthanide bis(amido) complex, because the complex META-$\{Nd[N(SiMe_3)_2]_2\}_2$ can be isolated.[10]

A further study revealed that complexes **4** and **5** can be converted to complexes **2** and **3** under suitable conditions, and the reaction media and temperature have a significant influence on this transformation. An NMR monitoring reaction revealed that the ^1H NMR spectrum had no obvious change when complex **4** was dissolved in d_8-THF in a J. Young valve NMR tube, even after the sample was heated to 70 °C for about 3 days (SFigure 9, Supporting Information). However, part of complex **4** was converted to complex **2** when complex **4** in C_6D_6 was heated to 70 °C for about 3 days, as evidenced by a new resonance at 0.02 ppm assignable to the amido groups in complex **2** (SFigure 10, Supporting Information). After the toluene solution of complex **4** was heated to 110 °C for 12 h, toluene was evaporated completely under reduced pressure, and C_6D_6 was added. The ^1H NMR spectrum revealed that the transformation was complete, and only one singlet appeared at δ 4.95 ppm for the two protons of CH_3CNCH, in comparison with the two singlets at δ 5.40 and 5.09 ppm in complex **4**, indicating that the chemical environments of the two protons of CH_3CNCH in the two β-diketiminate units of complex **2** are the same. Furthermore, the broad multiplet at δ 0.09−0.25 ppm almost disappeared, and a doublet appeared at 0.01 and 0.03 ppm, which is similar to that of complex **2** (SFigure 11, Supporting Information). These results indicated that complexes **4** and **5** were the intermediates and that complexes **2** and **3** formed from complexes **4** and **5** via an unexpected C−H bond activation of the arene ring along with the release of $HN(TMS_2)_2$ at high reaction temperature.

The possible pathway for the formation of the C−H bond activation product is postulated in Scheme 3. Although the two central metals in complexes **4** and **5** are located at opposite sides of the bridge plane to avoid steric congestion, the two metals could adjust to be on the same side at raised temperature, which is favorable for elimination of $HN(SiMe_3)_2$, and to form a bridged chloride bond. It is noteworthy that the C−H bond activation cannot occur in the monometallic complex **6** (see the Supporting Information for details for the synthesis of complex **6**) (Chart 1) under the same conditions. These results demonstrate that the bimetallic structure plays a key role in the C−H bond activation reaction in these complexes and provide experimental evidence for cooperative effects in a bimetallic system.

The definitive molecular structures of complexes **2**−**5** were provided by single-crystal X-ray structure diffraction. Complexes **2** and **3** are isostructural, and the molecular structure of complex **2** is shown in Figure 1, along with selected bond lengths and angles. Complex **2** has a C_2-symmetric bimetallic structure, and the two yttrium atoms are connected by one chlorine atom and a phenyl group. The bridging phenyl ring adopts an η^3 coordination mode, which is different from the η^1 coordination mode in the monometallic lanthanide β-diketiminate complexes obtained via C−H bond activation

Scheme 3

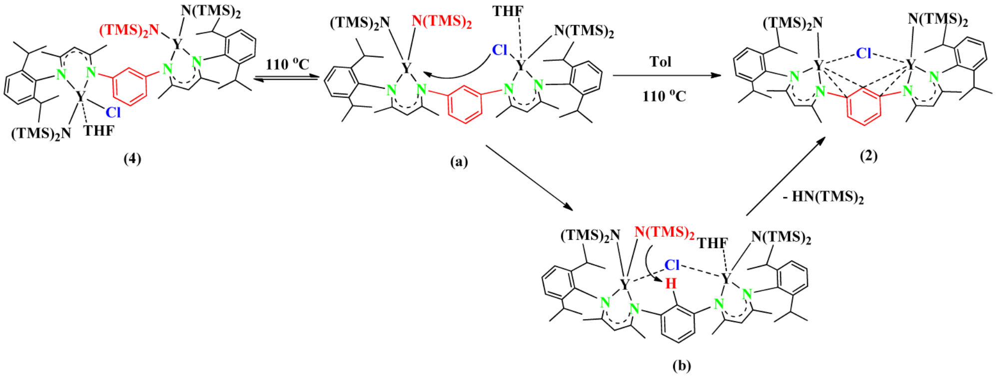
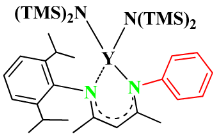


Chart 1



(6)

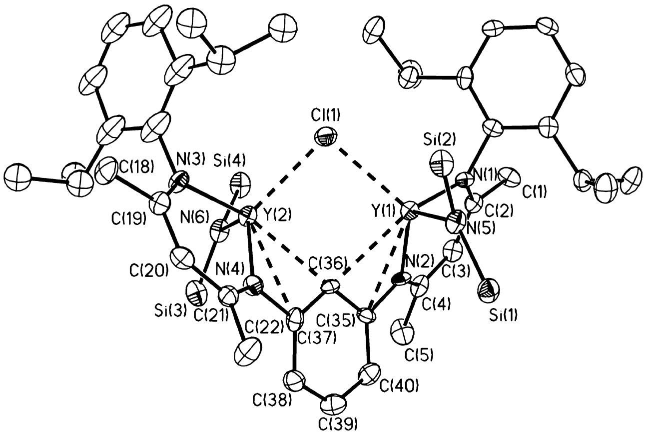


Figure 1. ORTEP diagram of complex **2** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−N1 = 2.350(5), Y1−N2 = 2.272(4), Y1−N5 = 2.232(5), Y1−C36 = 2.589(5), Y1−Cl1 = 2.6359(18), Y1−Y2 = 3.8248(12), Y2−N6 = 2.237(5), Y2−N4 = 2.281(5), Y2−N3 = 2.352(5), Y2−C36 = 2.560(5), Y2−Cl1 = 2.6285(18); C36−Y1−Cl1 = 85.03(12), C36−Y2−Cl1 = 85.77(13).

reported by Chen et al. and Cui et al., respectively.[11a,b] In complex **2**, each of the yttrium atoms is six-coordinated with two nitrogen atoms from the N,N-chelating β-diketiminate unit, a $-N(SiMe_3)_2$ group, two carbon atoms from the bridged phenyl, and a chlorine atom. The coordination geometry can be best described as a distorted trigonal bipyramid. The bond lengths of Y1−C36 and Y2−C36 are 2.589(5) and 2.560(5) Å, respectively, which are obviously shorter than that of 2.798(2) Å in $[Yb\{\eta^5\text{-}C_{13}H_8C(=N[2,6\text{-}^iPr_2C_6H_3])\text{-}CH_2NHC_6H_3(2,6\text{-}^iPr_2C_6H_3)\}_2(THF)]$ reported by Trifonov et al..[12] However, these bond lengths are apparently longer than the values in the lanthanide alkyl complexes supported by a pyridyl-1-azaallyl dianionic ligand (2.396(3) Å)[11b] and anilido phosphinimine ligands (2.435(5) Å).[11a] Although one carbon atom (C(36)) is anionic and the bridging phenylene group in complexes **2** and **3** adopts an η^3 coordination mode, the C(35)−C(36) and C(36)−C(37) bond lengths are 1.414(8) and 1.389(8) Å, respectively, which are in the range for normal benzene rings. The Y1−Cl1 and Y2−Cl1 bond lengths are 2.6285(18) and 2.6359(18) Å, respectively, which are also similar to the bridged Ln−Cl bond lengths reported in the literature.[4c] Additionally, the distance between the two yttrium atoms is 3.8248(12) Å, which falls in the range of two metal centers in close proximity (3.5−6.0 Å) that may in some cases lead to enhanced substrate activation or to a more stabilized reaction center.[2n] The Cl(1), Y(1), C(36), and Y(2) atoms are coplanar, and the dihedral angle between this plane and the bridging phenylene plane defined by C(35)−C(40) is 45.19(1)°.

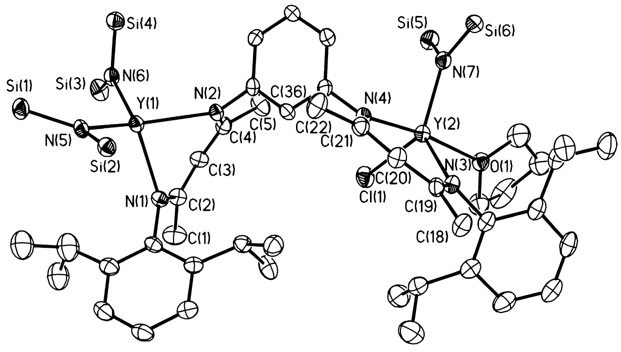


Figure 2. ORTEP diagram of complex **4** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−N1 = 2.306(4), Y1−N2 = 2.344(4), Y1−N5 = 2.260(4), Y1−N6 = 2.233(4), Y2−N3 = 2.373(4), Y2−N4 = 2.343(4), Y2−N7 = 2.228(4), Y2−O1 = 2.389(3), Y2−Cl1 = 2.5363(14); N7−Y2−O1 = 89.14(14), N7−Y2−Cl1 = 120.56(11), O1−Y2−Cl1 = 87.99(9), N3−Y2−Cl1 = 110.75(10).

Complexes **4** and **5** are also isostructural, and the molecular structure of complex **4** is shown in Figure 2, along with selected bond lengths and angles. In complex **4**, two yttrium atoms are situated at opposite sides of the bridging phenyl plane to reduce steric repulsion. The coordination environments around the two yttrium atoms are inequivalent. One is four-coordinated with two nitrogen atoms from the N,N-chelating β-diketiminate unit and two nitrogen atoms from two $(Me_3Si)_2N-$ groups, and the coordination geometry can be described as a distorted tetrahedron. The other yttrium atom is five-coordinated with two nitrogen atoms from the N,N-chelating β-diketiminate unit, one nitrogen atom from the $(Me_3Si)_2N-$ group, one chlorine atom, and one oxygen atom from a THF molecule to form a distorted square pyramid. The distance between the two yttrium atoms is 8.2143(14) Å, which is decidely longer than that in complex **2**.

Further attempts to elucidate the reactivity of complexes **2** and **3** were carried out but were unsuccessful. For example, we recently reported that the dianionic lanthanide *β*-diketiminate complexes can react with borate to give cationic lanthanide amido complexes.[13] Zhou et al. found that the insertion of carbodiimide into the Ln−C bond of the lanthanide *γ*-alkylamide chelate formed via C−H activation can occur smoothly.[14] However, no cationic species were detected from the reaction of complex **2** with borate ($[\mathrm{Ph_3C}][[\mathrm{B(C_6F_5)_4}]$ or $[\mathrm{PhNMe_2H}][[\mathrm{B(C_6F_5)_4}])$. The insertion reactions of complex **2** with a series of unsaturated molecules, such as carbodiimines, were also carried out, but no reaction was observed. These results indicated that complexes **2** and **3** are rather inert.

■ CONCLUSION

In conclusion, an unexpected C−H bond activation of an arene ring was observed in a bimetallic system, and the novel bimetallic lanthanide amido complexes bridged by a chloride and a phenyl group $\{\mathrm{Ln[N(SiMe_3)_2]}\}_2(\mathrm{META'})(\mu\text{-Cl})$ (Ln = Y (**2**), Yb (**3**)) were isolated and characterized. Moreover, the bimetallic lanthanide amido−chloro complexes supported by a META-phenylene-bridged bis(*β*-diketiminate) ligand $\{\mathrm{Ln[N(SiMe_3)_2]_2}\}\mathrm{META}\{\mathrm{Ln[N(SiMe_3)_2]Cl(THF)}\}$ (Ln = Y (**4**), Yb (**5**)) were synthesized at room temperature, which have been proven to be the intermediates in the formation of complexes **2** and **3**. These results provided experimental evidence for cooperative effects in a bimetallic system. The investigation of the reactivity of complexes **2** and **3** is still ongoing in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files and a table giving crystallographic data for **2**−**5**, text giving experimental details for **6**, and figures giving NMR spectra and an ORTEP diagram for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Y.Y.: fax, (86)512-65880305; tel, (86)512-65882806; e-mail, yaoym@suda.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (Grants 21174095, 21172165, and 21132002), the PAPD, and the Qing Lan Project is gratefully acknowledged.

■ REFERENCES

(1) (a) Gavrilova, A. L.; Bosnich, B. *Chem. Rev.* **2004**, *104*, 349. (b) Li, H.; Marks, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15295. (c) Ritleng, V.; Chetcuti, M. J. *Chem. Rev.* **2007**, *107*, 797. (d) Singh, S.; Roesky, H. W. *Dalton Trans.* **2007**, 1360.

(2) (a) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2003**, *125*, 11911. (b) McNevin, M. J.; Hagadorn, J. R. *Inorg. Chem.* **2004**, *43*, 8547. (c) Trost, B. M.; Fettes, A.; Shireman, B. T. *J. Am. Chem. Soc.* **2004**, *126*, 2660. (d) Matsunaga, S.; Yoshida, T.; Morimoto, H.; Kumagai, N.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, *126*, 8777. (e) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S.; Yun, H.; Lee, H.; Park, Y. W. *J. Am. Chem. Soc.* **2005**, *127*, 3031. (f) Xiao, Y. L.; Wang, Z.; Ding, K. L. *Macromolecules* **2006**, *39*, 128. (g) Amin, S. B.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 2938. (h) Rodriguez, B. A.; Delferro, M.; Marks, T. J. *Organometallics* **2008**, *27*, 2166. (i) Arbaoui, A.; Redshaw, C.; Hughes, D. L. *Chem. Commun.* **2008**, 4717. (j) Guo, N. C.; Stern, L.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 2246. (k) Motta, A.; Fragalà, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 3974. (l) Rodriguez, A.; Delferro, M.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5902. (m) Buchard, A.; Kember, M. R.; Sandeman, K. G.; Williams, C. K. *Chem. Commun.* **2011**, *47*, 212. (n) Ho, J. H. H.; Choy, S. W. S.; Macgregor, S. A.; Messerle, B. A. *Organometallics* **2011**, *30*, 5978. (o) Weberski, M. P.; Chen, C.; Delferro, M.; Zuccaccia, C.; Macchioni, A.; Marks, T. J. *Organometallics* **2012**, *31*, 3773. (p) Li, W. Y.; Wu, W. T.; Wang, Y. R.; Yao, Y. M.; Zhang, Y.; Shen, Q. *Dalton Trans.* **2011**, *40*, 11378. (q) Li, W. Y.; Yao, Y. M.; Zhang, Y.; Shen,, Q. *Chin. J. Chem.* **2012**, *30*, 609.

(3) (a) Li, H.; Li, L.; Marks, T. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 4937. (b) Li, H.; Li, L.; Schwartz, D. J.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 14756. (c) Li, H.; Stern, C. L.; Marks, T. J. *Macromolecules* **2005**, *38*, 9015.

(4) (a) Wang, J. F.; Cai, T.; Yao, Y. M.; Zhang, Y.; Shen, Q. *Dalton Trans.* **2007**, 5275. (b) Yuen, H. F.; Marks, T. J. *Organometallics* **2008**, *27*, 155. (c) Zhang, Z. J.; Xu, X. P.; Sun, S.; Yao, Y. M.; Zhang, Y.; Shen, Q. *Chem. Commun.* **2009**, 7414. (d) Wang, J. F.; Yao, Y. M.; Zhang, Y.; Shen, Q. *Inorg. Chem.* **2009**, *48*, 744. (e) Yuen, H. F.; Marks, T. J. *Organometallics* **2009**, *28*, 2423. (f) Li, W. Y.; Zhang, Z. J.; Yao, Y. M.; Zhang, Y.; Shen, Q. *Organometallics* **2012**, *31*, 3499.

(5) (a) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031. (b) Hayes, P. G.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 2132. (c) Piers, W. E.; Emslie, D. J. H. *Coord. Chem. Rev.* **2002**, *233*−*234*, 131. (d) Hayes, P. G.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2003**, *125*, 5622. (e) Gibson, V. C.; Spitzmesser, K. *Chem. Rev.* **2003**, *103*, 283. (f) Mirica, L. M.; Ottenwaelder, X. T.; Stack, D. P. *Chem. Rev.* **2004**, *104*, 1013. (g) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618. (h) Bonnet, F.; Visseaux, M.; Barbier-Baudry, D.; Vigier, E.; Kubicki, M. *Chem. Eur. J.* **2004**, *10*, 2428. (i) Lauterwasser, F.; Hayes, P. G.; Brase, S.; Piers, W. E.; Schafer, L. L. *Organometallics* **2004**, *23*, 2234. (j) Zhang, Z. C.; Cui, D. M.; Liu, X. L. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6810. (k) Xu, X.; Xu, X.; Chen, Y. F.; Sun, J. *Organometallics* **2008**, *27*, 758. (l) Lu, E.; Gan, W.; Chen, Y. F. *Organometallics* **2009**, *28*, 2318. (m) Chu, J.; Lu, E.; Liu, Z.; Chen, Y. F.; Leng, X.; Song, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 1. (n) Lu, E.; Chen, Y. F.; Leng, X. *Organometallics* **2011**, *30*, 5433.

(6) (a) Xue, M. Q.; Yao, Y. M.; Shen, Q.; Zhang, Y. *J. Organomet. Chem.* **2005**, *690*, 4685. (b) Yao, Y. M.; Zhang, Z. Q.; Peng, H. M.; Zhang, Y.; Shen, Q.; Lin, J. *Inorg. Chem.* **2006**, *45*, 2175. (c) Sanchez-Barba, L. F.; Hughes, D. L.; Humphrey, S. M.; Bochmann, M. *Organometallics* **2005**, *24*, 3792. (d) Chen, H. X.; Liu, P.; Yao, H. S.; Zhang, Y.; Yao, Y. M.; Shen, Q. *Dalton Trans.* **2010**, *39*, 6877.

(7) Li, D. F.; Li, S. H.; Cui, D. M.; Zhang, X. Q. *Organometallics* **2010**, *29*, 2186.

(8) Piesik, D. F. J.; Range, S.; Harder, S. *Organometallics* **2008**, *27*, 6178.

(9) (a) Aspinall, H.; Bradley, D.; Hursthouse, M.; Sales, K.; Walker, N.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1989**, 623. (b) Karl, M.; Seybert, G.; Massa, W.; Agarwal, S.; Greiner, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1405. (c) Niemeyer, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 647.

(10) Sun, S.; Nie, K.; Tan, Y. F.; Zhao, B.; Zhang, Y.; Shen, Q.; Yao, Y. M. *Dalton Trans.* **2013**, *42*, 2870.

(11) (a) Liu, B.; Cui, D. M.; Ma, J.; Chen, X. S.; Jing, X. B. *Chem. Eur. J.* **2007**, *13*, 834. (b) Lu, E. L.; Gan, W.; Chen, Y. F. *Dalton Trans.* **2011**, *40*, 2366.

(12) Trifonov, A. A.; Fedorova, E. A.; Fukin, G. K.; Druzhkov, N. O.; Bochkarev, M. N. *Angew. Chem., Int. Ed.* **2004**, *43*, 5045.

(13) Liu, P.; Zhang, Y.; Yao, Y. M.; Shen, Q. *Organometallics* **2012**, *31*, 1017.
(14) Han, F.; Zhang, J.; Yi, W.; Zhang, Z.; Yu, J.; Weng, L.; Zhou, X. *Inorg. Chem.* **2010**, *49*, 2793.