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Reactivity of Tp^{Me2}-Supported Yttrium Alkyl Complexes toward Aromatic N-Heterocycles: Ring-Opening or C=C Bond Formation Directed by C–H Activation

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Abstract: Unusual chemical transformations such as three-component combination and ring-opening of N-heterocycles or formation of a carbon–carbon double bond through multiple C–H activation were observed in the reactions of Tp^{Me2}-supported yttrium alkyl complexes with aromatic N-heterocycles. The scorpionate-anchored yttrium dialkyl complex [$Tp^{Me2}Y(CH_2Ph)_2(THF)$] reacted with 1-methylimidazole in 1:2 molar ratio to give a rare hexanuclear 24-membered rare-earth metallomacrocyclic compound [$Tp^{Me2}Y(\mu$-*N*,*C*-Im)(η^2-*N*,*C*-Im)]$_6$ (**1**; Im = 1-methylimidazolyl) through two kinds of C–H activations at the C2- and C5-positions of the imidazole ring. However, [$Tp^{Me2}Y(CH_2Ph)_2(THF)$] reacted with two equivalents of 1-methylbenzimidazole to afford a C–C coupling/ring-opening/C–C coupling product [$Tp^{Me2}Y\{\eta^3$-(*N*,*N*,*N*)-N-$(CH_3)C_6H_4NHCH{=}C(Ph)CN(CH_3)C_6H_4NH\}$] (**2**). Further investigations indicated that [$Tp^{Me2}Y(CH_2Ph)_2(THF)$] reacted with benzothiazole in 1:1 or 1:2 molar ratio to produce a C–C coupling/ring-opening product $\{(Tp^{Me2})Y[\mu$-η^2:η^1-$SC_6H_4N(CH{=}CHPh)](THF)\}_2$ (**3**). Moreover, the mixed Tp^{Me2}/Cp yttrium monoalkyl complex [$(Tp^{Me2})CpYCH_2Ph(THF)$] reacted with two equivalents of 1-methylimidazole in THF at room temperature to afford a trinuclear yttrium complex [$Tp^{Me2}CpY(\mu$-*N*,*C*-Im)]$_3$ (**5**), whereas when the above reaction was carried out at 55 °C for two days, two structurally characterized metal complexes [$Tp^{Me2}Y(Im$-$Tp^{Me2})$] (**7**; *Im*-Tp^{Me2} = 1-methylimidazolyl-Tp^{Me2}) and [Cp_3Y(HIm)] (**8**; HIm = 1-methylimidazole) were obtained in 26 and 17% isolated yields, respectively, accompanied by some unidentified materials. The formation of **7** reveals an uncommon example of construction of a C=C bond through multiple C–H activations.

Introduction

C–N cleavage of aromatic N-heterocycles is a challenging process that attracts much interest because it is not only significant for understanding hydro-denitrogenation processes (HDN),[1] but can also provide a new strategy for the construction of novel structural organometallic complexes.[2–5] Examples of homogenous systems that mediate ring-opening of these heterocycles are mainly based on early-transition-metal complexes and usually require the presence of multiple bonds to the metals.[3] Rhenium-mediated ring-opening of N-heterocycles employing external bases or electrophilic regents are also known.[4] Recently, Diaconescu et al. reported that rare-earth metal monoalkyl and uranium dialkyl complexes with a 1,1′-ferrocenylene-diamide ligand can initiate C–N cleavage of 1-methylimidazole under heating.[5] However, little is known of the reactivity of rare-earth dialkyl complexes towards aromatic N-heterocycles.[6] On the other hand, metal-mediated inactive C–H bond activation [including C(sp^3)–H and C(sp^2)–H bonds] has become a productive research field in organic and organometallic chemistry,[7] and this approach serves as one of the most powerful tools for the construction of carbon–carbon or carbon–heteroatom bonds.[8] However, only one or two C(sp^2 or sp^3)–H bond is activated (the latter was also termed cross-dehydrogenative-coupling, CGC) and forms a new carbon–carbon or carbon–heteroatom single bond in most cases.[7d,9] Examples of multiple C–H bond activations for the construction of carbon–carbon or carbon–heteroatom double bonds are rare.[10]

Recently, we have been investigating the reactivity of yttrium derivatives with the tri(3,5-dimethylpyrazolyl)borate (Tp^{Me2}) ligands[11] toward small molecules,[12] and found that [$(Tp^{Me2})CpYCH_2Ph(THF)$] can activate benzonitrile to give the imine-enamine tautomer products after insertion,[12a] and [$Tp^{Me2}Y(CH_2Ph)_2(THF)$] can cleave the C=S bond of isothiocyanate, or activate the C(sp^3)–H bond of the benzyl group.[12c] Herein, we would like to report the reactivity of yttrium dialkyl complex [$Tp^{Me2}Y(CH_2Ph)_2(THF)$] toward N-heterocycles such as 1-methylimidazole, 1-methylbenzimidazole, and benzothiazole under mild conditions, and disclose their unusual reaction behavior, including three-component combination and ring-opening beyond C–H activation. Moreover, we also display a rare example of the construction C=C bonds through multiple C–H activations.

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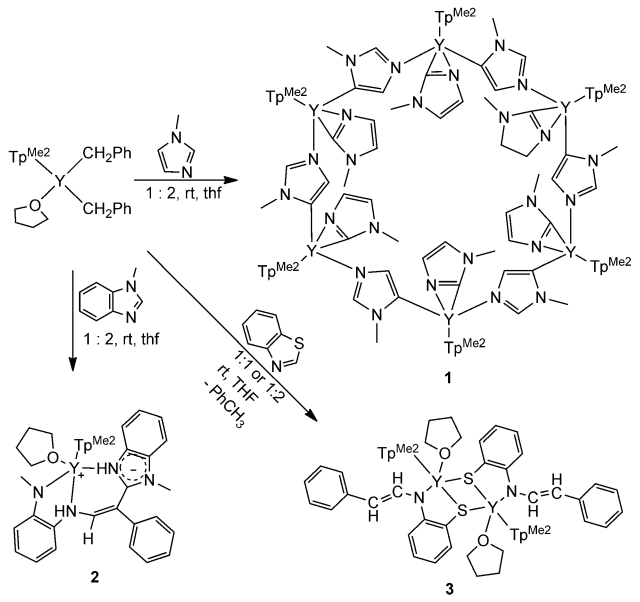


Scheme 1. Reactions of scorpionate-anchored yttrium dialkyl complex with some N-heterocycles.

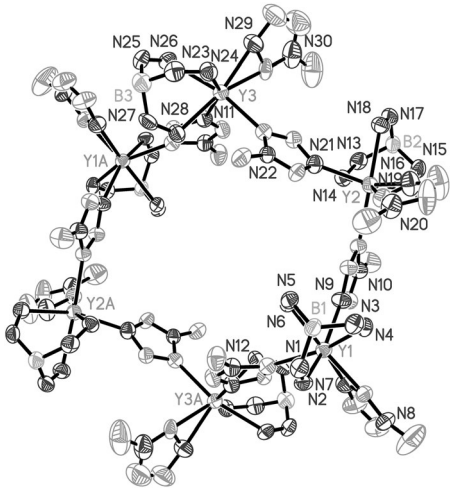


Figure 1. Molecular structure of **1** with thermal ellipsoids at 30% probability level. Carbon atoms on Tp^{Me2} in **1** and all hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Y1–N7 2.319(6), Y1–C18 2.363(7), Y1–N9 2.414(4), Y1–C25 2.439(6), Y2–N19 2.298(6), Y2–C45 2.364(6), Y2–N14 2.489(5), Y2–C21 2.461(5), Y3–N29 2.311(6), Y3–C28 2.322(7), Y3–N11 2.392(5), Y3–C48 2.443(6); C25-Y1-N9 105.30(17), C21-Y2-N14 86.90(17), C48-Y3-N11 104.02(17). Symmetry transformations used to generate equivalent atoms: $-x+1$, $-y+2$, $-z+1$.

Results and Discussion

The reaction of $[Tp^{Me2}Y(CH_2Ph)_2(THF)]$ with two equivalents of 1-methylimidazole in THF at room temperature afforded a double C–H activation product $[Tp^{Me2}Y(\eta^2\text{-N,C-Im})(\mu\text{-Im})]_6$ (**1**; Im = 1-methylimidazolyl) in 93% isolated yield, as shown in Scheme 1. It should be noted that the formation of complex **1** is independent of the reaction stoichiometry; the equimolar reaction of $[Tp^{Me2}Y(CH_2Ph)_2(THF)]$ with 1-methylimidazole under the same conditions also gave complex **1** and the original material $[Tp^{Me2}Y(CH_2Ph)_2(THF)]$. We also investigated the reaction of $[Tp^{Me2}Y(CH_2Ph)_2(THF)]$ with 1-methylimidazole in a 1:3 molar ratio in toluene at 100 °C for two days, however, only complex **1** was obtained. No further transformations involving **1** occurred under the reaction conditions. This result differs from that observed in the reaction of uranium dibenzyl complex with 1-methylimidazole in $[D_8]$toluene at 100 °C, in which C–N cleavage of 1-methylimidazole was initiated and further cascade reactions followed.[5b]

Complex **1** was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography (Figure 1), confirming that **1** is a hexanuclear yttrium complex with a C_{2v} symmetrical 24-membered metallo-macrocyclic structure. Each yttrium atom is bound with a κ_3-Tp^{Me2} ligand, a η^2-*N,C*-imidazolyl ring, and two μ-imidazolyl rings. The average Y–N and Y–C bond distances from the bridging imidazolyl rings are 2.432(5) and 2.448(6) Å, respectively [Y–N 2.392(5)–2.489(5) Å; Y–C 2.439(6)–2.461(5) Å]. The average Y–N and Y–C bond distances [2.309(6) and 2.350(7) Å] from the η^2-*N,C*-imidazolyl rings are significantly shorter than those of the Y–N and Y–C bond from the bridging imidazolyl rings, and are in the range of Y–C and Y–N σ and donor bonds. These bond parameters revealed that two different C–H bonds of 1-methylimidazolyl units were activated in **1**: one being the C–H bond at the C2-position from the chelating imidazolyl ring, and the second being the C–H bond at the C5-position from the bridging imidazolyl ring. Consistent with this observation, the ^{1}H NMR spectrum of **1** shows two group signals that can be assigned to the C–H resonances of 1-methylimidazolyl: one from the chelating imidazolyl moiety ($\delta = 7.48$, 7.14, and 3.61 ppm), assigned to 4-, 5-H, and *Me*-Im in a 1:1:3 ratio, and the second from the bridging imidazolyl moiety ($\delta = 7.18$, 6.87, and 3.53 ppm), assigned to 2-, 4-H, and *Me*-Im in a 1:1:3 ratio.

The reaction of $[Tp^{Me2}Y(CH_2Ph)_2(THF)]$ with two equivalents of 1-methylbenzimidazole in THF at room temperature gave a nonclassical ionic-type complex $[Tp^{Me2}Y\{\eta^3\text{-}(N,N,N)\text{-}N\text{-}(CH_3)C_6H_4NHCH{=}C(Ph)CN(CH_3)C_6H_4NH\}]$ (**2**) in 79% isolated yield, indicating that a continuous carbon–carbon coupling, ring-opening and carbon–carbon coupling process occurred (Scheme 1). The structure of complex **2** was also characterized by single-crystal X-ray diffraction analysis (Figure 2). The C1–C8 bond [1.455(7) Å] is clearly indicative of a C–C single bond, whereas the lengths of the C8–C9 and C9–N3 bonds [1.356(7) and 1.324(6) Å, respectively] are between the C–C and C–N single and double bonds, revealing the delocalization character of the π electrons of the C8=C9 bond. Moreover, the bond angles around C8 and C9 are consistent with sp^2 hybridization. The lengths of the Y–N1 and Y–N3 [2.473(4) and 2.371(4) Å, respectively] bonds are significantly longer than that of the Y–N4 bond [2.275(5) Å], with the latter being a classical Y–N σ bond. The newly formed tridentate substituted benzimidazolyl ligand is dianionic, bonded to an Y^{3+} center with a monoanionic Tp^{Me2} ligand, and the observed bond lengths in the tridentate substituted benzimidazolyl ligand indicate charge delocalization. The ^{1}H NMR spectrum of **2** also indicated that only one hydrogen is localized near the C9 atom, which was con-

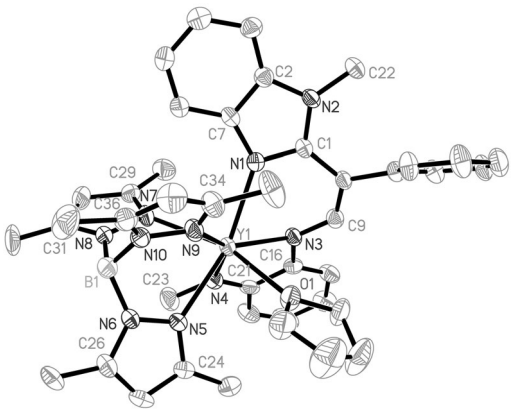


Figure 2. Molecular structure of **2** with thermal ellipsoids at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Y1–N1 2.473(4), Y1–N3 2.371(4), Y1–N4 2.275(5), Y1–O1 2.461(3), N1–C1 1.353(5), N2–C1 1.360(6), C1–C8 1.455(7), C8–C9 1.356(7), C9–N3 1.324(6), N3–C16 1.430(6); N1-C1-N2 110.8(4), N1-C1-C8 125.8(5), N2-C1-N8 123.4(4), C1-C8-C9 122.3(4), C1-C8-C10 119.6(5), C9-C8-C10 118.0(5).

firmed by a single peak at $\delta = 7.83$ ppm assignable to the C=*CH* group. Two single peaks at $\delta = 4.50$ and 4.24 ppm were assigned to the resonances of NH (N1-H and N3-H).

The formation of **2** clearly indicated that a 1-methylbenzimidazole ring-opening and three-component combination including a benzyl group and two 1-methylbenzimidazole moieties occurred in the reaction of $[Tp^{Me2}Y(CH_2Ph)_2(THF)]$ with 1-methylbenzimidazole.[13] This result is also significantly different from that of the known rare-earth monoalkyl or uranium dibenzyl complexes with 1-methylimidazole or 1-methylbenzimidazole.[9a,b] The latter usually gave the imidazole ring-opening and/or coupling species, and no alkyl group was involved in the framework of the final product. To understand the process involved in the formation of **2**, the equimolar reaction of $[Tp^{Me2}Y(CH_2Ph)_2(THF)]$ with 1-methylbenzimidazole under the same conditions was also performed, however, only the original material $[Tp^{Me2}Y(CH_2Ph)_2(THF)]$ and **2** were isolated, which was partially attributable to fast carbon–carbon coupling between the ring-opening intermediate **D** with a second 1-methylbenzimidazole (Scheme 2). To our delight, the equimolar reaction of $[Tp^{Me2}Y(CH_2Ph)_2(THF)]$ with benzothiazole gave $\{[Tp^{Me2}Y(\mu\text{-}\eta^1\text{:}\eta^2\text{-}SC_6H_4NCH{=}CHPh\text{-}o)THF]_2\}$ (**3**; 86% isolated yield). The formation of complex **3** was also independent of the reaction stoichiometry. The ^1H and ^{13}C NMR spectra and structural determination (Figure 3) reveal that a novel dianionic ligand $[SC_6H_4NCH{=}CHPh\text{-}o]^{2-}$ in **3** was constructed through a carbon–carbon coupling and ring-opening process. In its ^1H NMR spectrum, the NC*H*=C*H*Ph fragments were observed as two doublets at $\delta = 8.13$ and 5.80 ppm with $J = 16$ Hz, and its ^{13}C NMR spectrum displayed two resonances at $\delta = 160.5$ and 115.7 ppm, which were assigned to the NCH=*C*HPh units. The N7–C7 bond length [1.392(5) Å] is consistent with a single bond, whereas the C7–C8 bond length [1.334(5) Å] reveals substantial double-bond character. The Y–N1 [2.365(3) Å] and Y–S1 [2.704(1) Å] bonds are also in the range of Y–N and Y–S σ bonds. These structural data also indicate the $SC_6H_4NCH{=}CHPh\text{-}o$ ligand is dianionic. The bond parameters of the Tp^{Me2} ligands and phenyl rings are in the normal range.

The formation of **3** provides credible proof that the carbon–carbon coupling of benzyl with 1-methylbenzimidazole and its ring-opening (i.e., to form **D**; Scheme 2) probably occurs prior to carbon–carbon coupling of **D** with a second 1-methylbenzimidazole molecule. However, because the sequence between carbon–carbon coupling of benzyl with 1-methylbenzimidazole and its ring-opening process remained unclear, we reacted $[Tp^{Me2}Y(CH_2Ph)_2(THF)]$ with two equivalents of 1-methylbenzimidazole in THF at room temperature for 3 h, and then added

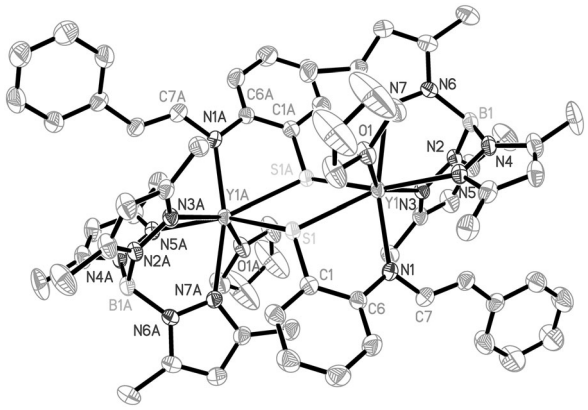
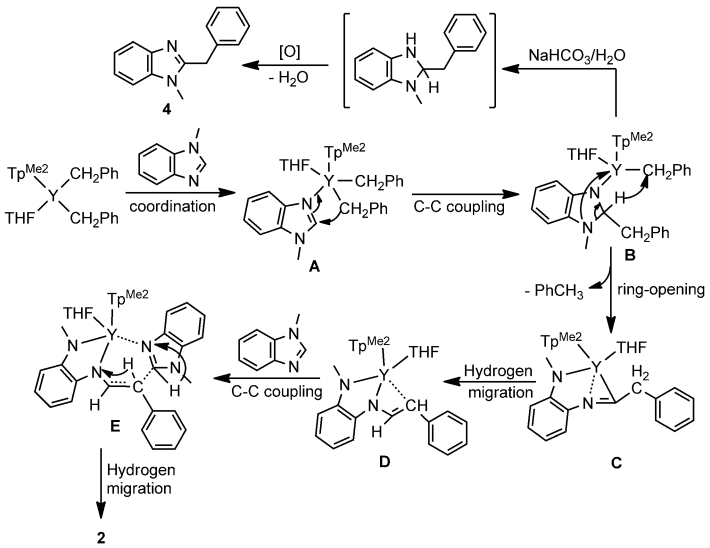


Figure 3. Molecular structure of **3** with thermal ellipsoids at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Y1–N1 2.365(3), Y1–S1 2.7040(12), Y1–S1A 2.8738(13), Y1–O1 2.461(3), N1–C7 1.392(5), C7–C8 1.334(5); C8-C7-N1 127.0(4), C8-C7-H7 116.5, N1-C7-H7 116.5, C7-C8-C9 127.0(4), C7-C8-H8 116.5, C9-C8-H8 116.5. Symmetry transformations used to generate equivalent atoms: $-x+1$, $-y+1$, $-z+1$.



Scheme 2. Plausible mechanism for the formation of **2**.

an aqueous water solution of saturated $NaHCO_3$, and stirred the mixture for 30 min. After workup, 2-benzyl-1-methylbenzimidazole **4** [$PhCH_2C{=}NC_6H_4N(CH_3)$] was isolated in 73% yield (based on Y metal), which was confirmed by ^1H NMR spectroscopic and X-ray crystallographic analyses. In the ^1H NMR spectrum of **4**, two single peaks at $\delta = 4.35$ and 3.59 ppm were assigned to the resonances of CH_2 of the benzyl group and the NCH_3 unit in a 2:3 ratio, and three multiple peaks at $\delta = 7.22$–7.81 ppm were assigned to the resonances of the phenyl ring protons of the C_6H_4 and C_6H_5 moieties. In the crystal structure of **4** (Figure 4), the averaged bond lengths [N1–C1 1.308(2),

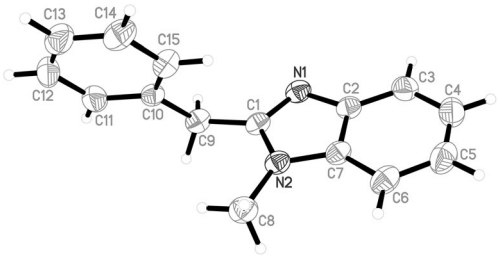


Figure 4. Molecular structure of **4** with thermal ellipsoids at 30% probability level. Selected bond lengths [Å] and bond angles [°]: N1–C1 1.308(2), N2–C1 1.367(2), N1–C2 1.382(2), N2–C7 1.375(3), C2–C7 1.393(2), C1–C9 1.480(2), C9–C10 1.516(2); N1-C1-N2 113.01(13), N1-C1-C9 124.10(14), N2-C1-C9 122.88(14), C1-N1-C2 104.97(13) C1-N2-C7 106.60(12) N1-C2-C7 110.07(15) N2-C7-C2 105.35(14).

N2–C1 1.367(2), N1–C2 1.382(2), N2–C7 1.375(3), C2–C7 1.393(2) Å] and the sum of bond angles of 540° [N1-C1-N2 113.01(13), C1-N1-C2 104.97(13), C1-N2-C7 106.60(12), N1-C2-C7 110.07(15), N2-C7-C2 105.35(14)] in the N1-C1-N2-C7-C2 ring indicated that **4** is also an aromatic N-heterocyclic molecule. We therefore conclude that the carbon–carbon coupling of benzyl with 1-methylbenzimidazole probably occurs prior to ring-opening of 1-methylbenzimidazole.

On the basis of the observations described above, we propose a possible mechanism for the formation of **2**, displayed in Scheme 2. One 1-methylbenzimidazole molecule is first coordinated with the yttrium center to form intermediate **A**. Then, **A** transforms into **B** through carbon–carbon coupling between the benzyl group and the 1-methylbenzimidazole molecule. Ring-opening of benzimidazolyl occurs to give intermediate **C**, accompanied by elimination of one toluene molecule. Intermediate **D** is formed from **C** through a 1,2-hydrogen migration process. A second carbon–carbon coupling between **D** and a second 1-methylbenzimidazole occurs to yield **E**. The final product **2** is formed by 1,3- and 1,2-hydrogen migration events.

To further explore the reactivity of rare-earth alkyl complexes toward these N-heterocycles, we also investigated the reactions of mixed Tp^{Me2}/Cp yttrium monoalkyl complex [$(Tp^{Me2})CpYCH_2Ph(THF)$][14] with 1-methylimidazole or 1-methylbenzimidazle. As shown in Scheme 3, [$(Tp^{Me2})CpYCH_2Ph(THF)$] reacted with two equivalents of 1-methylimidazole in THF at room temperature to afford a trinuclear metallo-macrocyclic complex with bridging 1-methylimidazolyl ligands [{$Tp^{Me2}CpY(\mu$-*N*,*C*-Im)}$_3$] (**5**; 62% isolated yield), whereas it reacted with two equivalents of 1-methylbenzimidazole under the same conditions to give a monomer with C–H activation at the C2-position [$(Tp^{Me2})CpY(HBIm)(\eta^2$-*N*,*C*-BIm)] (**6**; 72% isolated yield, BIm = 1-methylbenzimidazolyl). When the above two reactions were carried out at 55 °C for two days, the latter still gave complex **6**, but the former afforded two structurally characterized metal complexes [$Tp^{Me2}Y(Im$-$Tp^{Me2})$] (**7**; *Im*-Tp^{Me2} = 1-methyl-imidazolyl-Tp^{Me2}) and [$Cp_3Y(HIm)$] (**8**; HIm = 1-methylimidazole) in 26 and 17% isolated yields (based on Y metal), respectively, accompanied by some unidentified materials.

Complexes **5**–**8** were also characterized by elemental analysis, ^1H and ^{13}C NMR spectroscopy, and single-crystal X-ray analysis. The crystal structure depicted in Figure 5 reveals that **5** possesses a trinuclear 12-membered metallomacrocyclic structure. The quality of the crystallographic data for **5** was rather

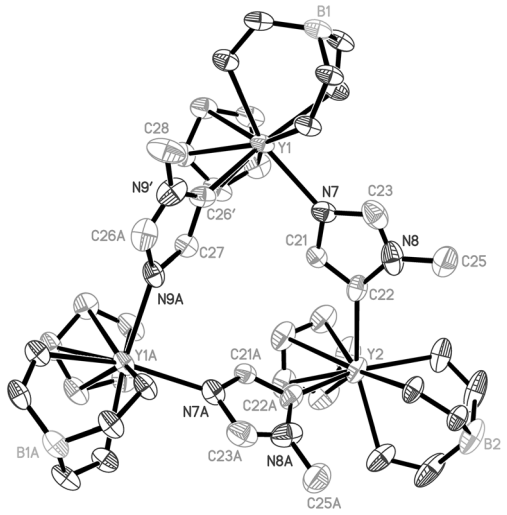
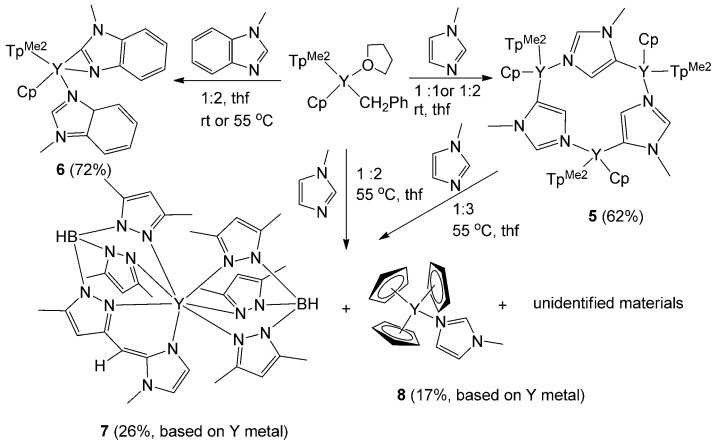


Figure 5. Molecular structure of **5** with thermal ellipsoids at 30% probability level. Carbon atoms on Tp^{Me2} in **5** and all hydrogen atoms are omitted for clarity.



Scheme 3. Synthesis of compounds **5**–**8** form yttrium monoalkyl complex.

poor [with the value of R on the high side, $R_1 = 0.0822$, $wR_2 = 0.2362$], thus the bond distances and bond angles for **5** will not be discussed. However, the overall structure of **5** was clearly determined, and indicated that the three 1-methylimidazolyl groups adopt a μ_2-bonding mode, and each edge of the triangular metal framework is almost equally bridged by one 1-methylimidazolyl group. The C–H activation of the imidazolyl group was also confirmed by the ^{1}H NMR spectrum of **5**, which displayed only three resonances at $\delta = 6.94$, 6.74, and 3.65 ppm, assignable to the C*H* of C2 and C4 atoms and the N-*Me* of the 1-methylimidazolyl groups, in addition to the assignable peaks at $\delta = 5.82$ ppm for C_5H_5, and the peaks at $\delta = 5.63$, 2.35, and 2.29 ppm for 4*H*-Tp^{Me2}, 3- and 5-*Me*-Tp^{Me2}.

The results of the structural determination (Figure 6) show that complex **6** is a solvent-free monomer and that the central

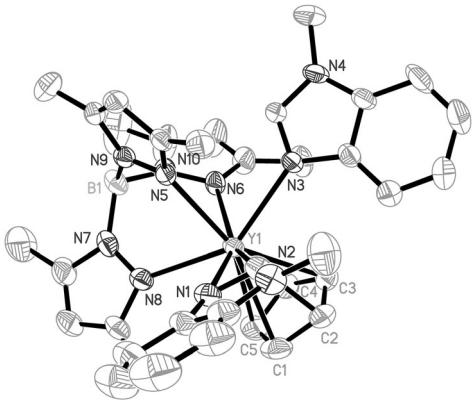


Figure 6. Molecular structure of **6** with thermal ellipsoids at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Y1–N1 2.356(4), Y1–C6 2.410(5), Y1–N3 2.509(3), N1–C6 1.335(5), N2–C6 1.387(5).

metal atom, Y^{3+}, is bonded to one κ_3-Tp^{Me2} ligand, one η^5-Cp group, one η^2-*N*,*C*-1-methylbenzimidazolyl ligand, and a neutral 1-methylbenzimidazole molecule. The Y1–N1 and Y1–C6 distances of 2.356(4) and 2.410(5) Å, respectively, are in the range expected for the Y–N and Y–C bond interaction with partial single and donor bond character. The Y1–N3 distance of 2.509(3) Å is also a normal Y–N donor bond. The ^{1}H NMR spectrum of **6** contains a characteristic single peak at $\delta = 7.21$ ppm that was assigned to the C2–H resonance from the neutral 1-methylbenzimidazole molecule ($C_6H_4NC\mathit{H}NCH_3$).

X-ray crystallographic analysis (Figure 7) and ^{1}H, ^{13}C NMR spectra of **7** confirmed that a new C=C bond was formed through carbon–carbon coupling between the 1-methylimidazolyl moiety and one methyl group of a Tp^{Me2} ligand. In **7**, the yttrium atom is surrounded by seven nitrogen atoms, and the newly formed imidazolyl-substituted Tp^{Me2} ligand is coordinated with the central metal in a κ_4-bonding mode. The C1–C5 and C5–C6 [1.366(10) and 1.405(10) Å] bond lengths are significantly shorter than that of the C–C single bond (1.50 Å), indicating delocalized double- and single-bond characters. The Y–N1 length [2.417(6) Å] is also comparable to the other Y–N bond lengths in the *Im*-Tp^{Me2} ligand [Y1–N4 2.390(5), Y1–N6 2.450(6), and Y1–N8 2.439(6) Å]. These bond data indicate that

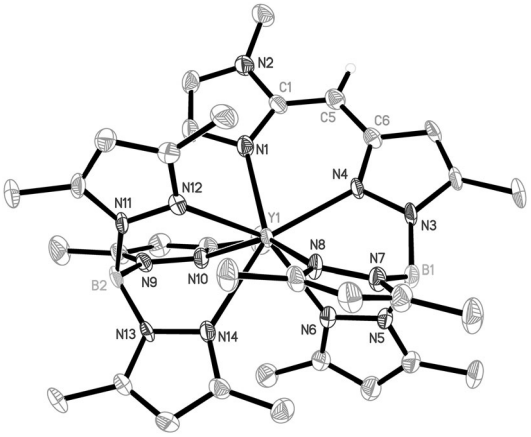


Figure 7. Molecular structure of **7** with thermal ellipsoids at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Y1–N1 2.417(6), Y1–N4 2.390(5), Y1–N6 2.450(6), Y1–N8 2.439(6), N1–C1 1.352(9), N2–C1 1.375(9), C1–C5 1.366(10), C5–C6 1.405(10); N1-C1-N2 108.6(6), C5-C1-N2 123.4(7), N1-C1-C5 128.1(7), C1-C5-C6 125.0(7), C1-C5-H5 117.5, C6-C5-H5 117.5.

the newly formed *Im*-Tp^{Me2} ligand is dianionic. In the ^{1}H NMR spectrum of **7**, four single peaks at $\delta = 6.28$, 2.18, 2.14, and 2.11 ppm are assigned to the resonances of 4H-Tp^{Me2}, 3- and 5-*Me*-Tp^{Me2} in the Tp^{Me2} ligand, respectively. Two single peaks at $\delta = 5.85$ and 5.77 ppm are assigned to the resonance of 4H-*Im*-Tp^{Me2} in a 2:1 ratio, and three single peaks at $\delta = 2.55$, 2.48, and 2.44 ppm are assigned to the resonances of *Me*-Tp^{Me2}-*Im* in a 6:6:3 ratio. The chelating 1-methylimidazolyl group shows three signals at $\delta = 6.92$, 6.53, and 2.31 ppm assignable to 4-, 5-H, and *Me*-Im in a 1:1:3 ratio. Moreover, a characteristic C-H resonance at $\delta = 6.44$ ppm was also observed that could be assigned to the methenyl moiety C5H. Deprotonation of one methyl group is common, however, double deprotonation of one methyl group to construct a C=C bond has not been reported so far.[15,16] The formation of **7** implied at least three C–H bonds [one C(sp^2)-H and two C(sp^3)–H bonds] were activated during this process, but the detailed mechanism is presently unclear.[17]

The overall structure of **8** (Figure 8) is very similar to that of [Cp_3Y(THF)], when the coordinated 1-methylimidazole mole-

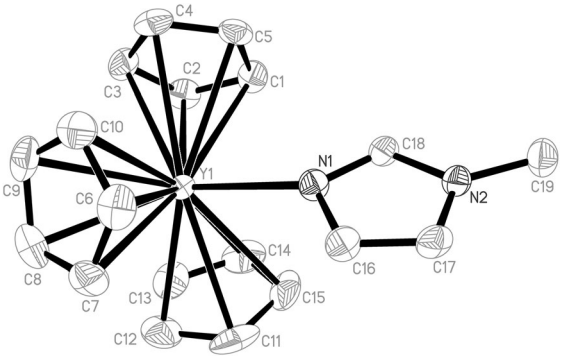


Figure 8. Molecular structure of **8** with thermal ellipsoids at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Y1–N1 2.481(4), N1–C18 1.321(6), N2–C18 1.341(6).

cule in **8** replaces the THF molecule. The yttrium atom carries three Cp groups and one nitrogen atom from a neutral 1-methylimidazole moiety. The Y1–N1 distance is 2.448(9) Å, and is thus a standard Y–N donor bond. The Y–C(Cp) distances are in the normal range observed for lanthanide metallocenes.

Conclusion

We have shown that Tp^{Me2}-supported rare-earth dibenzyl complexes mediate three-component combination and ring-opening of 1-methylbenzimidazole and activates the C–H bonds at the C2 and C5-position of 1-methylimidazole to construct a rare hexanuclear rare-earth metallomacrocyclic compound.[18] Moreover, we also reveal an uncommon example of the construction of a C=C bond through multiple C–H activations. This study provides new insights into the activation of N-heterocycles in rare-earth alkyl complexes.

Experimental Section

General Methods

All reactions were carried out under a dry and inert atmosphere using either standard Schlenk techniques or under a nitrogen atmosphere in a 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 atmosphere were monitored by an O_2/H_2O Combi-Analyzer (MBRAUN) to ensure both were always below 1 ppm. THF, toluene, *n*-hexane were heated to reflux and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. [Tp^{Me2}Y-$(CH_2Ph)_2$(THF)],[12c] and [Tp^{Me2}CpYCH_2Ph(THF)][14] were prepared according to the literature. 1-Methylimidazole, 1-methylbenzimidazole, and benzothiazole were purchased from Aldrich and were used without purification. Elemental analyses for C, H and N were carried out with a Rapid CHN-O analyzer. ^{1}H and ^{13}C NMR data were obtained with a Bruker DMX-400 NMR spectrometer (400 MHz for ^{1}H; 100 MHz for ^{13}C).

Synthesis of [$Tp^{Me2}Y(\mu$-N,C-$NC_3H_2NCH_3)(\eta^2$-N,C-$NC_3H_2NCH_3)]_6$ (1)

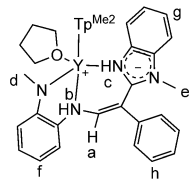
Method A: In a glovebox, a solution of 1-methylimidazole (0.082 g, 1.00 mmol) in THF (5 mL) was added slowly to a solution of [$Tp^{Me2}Y(CH_2Ph)_2$THF] (0.320 g, 0.50 mmol) in THF (15 mL), and the resulting mixture was stirred overnight at RT. The solution was evaporated to dryness under vacuum, and washed with *n*-hexane (2×10 mL), THF (20 mL) was added to the residue, and then diffusion of *n*-hexane into the concentrated THF solution gave colorless crystals of **1**. Yield: 0.255 g (93%); ^{1}H NMR(400 MHz, [D_8]THF, RT): δ = 7.42 (s, 6H; $C_3H_2N_2CH_3$), 7.18 (s, 6H; $C_3H_2N_2CH_3$), 7.14 (s, 6H; $C_3H_2N_2CH_3$), 6.87 (s, 6H; $C_3H_2N_2CH_3$), 5.64 (s, 18H; 4H-Tp^{Me2}), 3.61 (s, 18H; $C_3H_2N_2CH_3$), 3.53 (s, 18H; $C_3H_2N_2CH_3$), 2.48 (s, 36H; CH_3 of Tp^{Me2}), 2.45 (s, 18H; CH_3 of Tp^{Me2}), 2.37 (s, 18H; CH_3 of Tp^{Me2}), 2.30 ppm (s, 36H; CH_3 of Tp^{Me2}); ^{13}C NMR (100 MHz, [D_8]THF, RT): δ = 181.57 (s, 2-*C*-Im ring), 170.17 (s, 2-*C*-Im ring), 149.85 (s, 3-*C*-Pz), 145.26 (s, 3-*C*-Pz), 138.37 (s, 5-*C*-Pz), 129.48 (s, 5-*C*-Im ring), 128.72 (s, 5-*C*-Im ring), 125.86 (s, 4-*C*-Im ring), 105.58 (s, 4-*C*-Pz), 35.82 (s, $C_3H_2N_2CH_3$), 37.24 (s, $C_3H_2N_2CH_3$), 35.82 (s, $C_3H_2N_2CH_3$), 13.10 (s, 3-*Me*-Pz), 12.94 ppm (s, 5-*Me*-Pz); elemental analysis calcd (%) for $C_{138}H_{192}B_6N_{60}Y_6$: C 50.38, H 5.88, N 25.55; found: C 50.61, H 5.96, N 25.37.

Method B: In a glovebox, a solution of 1-methylimidazole (0.041 g, 1 equiv) in THF (2 mL) was added slowly to a solution of [$Tp^{Me2}Y$-$(CH_2Ph)_2$THF] (0.320 g, 0.50 mmol) in THF (15 mL), and the resulting mixture was stirred overnight at RT. The resulting mixture was worked up as described in Method A, to give colorless crystals of **1** (0.074 g, 27% isolated yield based on Y metal). The mother liquid was then evaporated to dryness under vacuum, and the residue was partially dissolved in toluene (15 mL), then the toluene solution was evaporated slowly in a glovebox to afford the original material [$Tp^{Me2}Y(CH_2Ph)_2$THF] as colorless crystals. Yield: 0.035 g (11% based on Y metal).

Method C: In a glovebox, a solution of 1-methylimidazole (0.123 g, 3 equiv) in THF (2 mL) was added slowly to a solution of [$Tp^{Me2}Y$-$(CH_2Ph)_2$THF] (0.320 g, 0.50 mmol) in THF (15 mL), then the mixture was removed from the glovebox, and stirred at 100 °C for 48 h. The resulting mixture was worked up as described in Method A, to give colorless crystals of **1** (0.175 g, 64% isolated yield based on Y metal).

Synthesis of [$Tp^{Me2}Y\{\eta^3$-(*N*,*N*,*N*)-$N(CH_3)C_6H_4NHCH$=$C(Ph)CN$-(CH_3)C_6H_4NH\}$] (2)

Method A: In a glovebox, a mixture of [$Tp^{Me2}Y(CH_2Ph)_2$THF] (0.320 g, 0.50 mmol) and 1-methylbenzimidazole (0.132 g, 1.00 mmol) in THF (15 mL) was stirred at RT for 24 h, then the solution was concentrated to dryness under vacuum. Toluene (10 mL) was added to the residue, and then diffusion of *n*-hexane into the concentrated toluene solution gave red crystals of **2** (0.320 g, 79%). ^{1}H NMR(400 MHz, [D_8]THF, RT): δ (see Scheme 4 for numbering) = 7.83 (s, 1H; *a*) 7.60–7.14 (m, 10H; *f*, *g* or *h*), 6.50–6.30 (m, 3H; *f*, *g* or *h*), 5.66 (s, 2H; 4H-Tp^{Me2}), 5.52 (s, 1H; 4H-Tp^{Me2}), 4.50 (s, 1H; *b* or *c*), 4.24 (s, 1H; *b* or *c*), 3.77 (s, 3H; *e*), 2.67 (s, 3H; *d*), 2.64 (s, 3H; CH_3 of Tp^{Me2}), 2.42 (s, 6H; CH_3 of Tp^{Me2}), 2.33 (s, 6H; CH_3 of Tp^{Me2}), 2.08 ppm (s, 3H; CH_3 of Tp^{Me2}); ^{13}C NMR (100 MHz, [D_8]THF, RT): δ = 153.80 (s, C_6H_4NHCH=$C(C_6H_5)C_7H_5$-N_2CH_3), 151.39 (s, 3-*C*-Pz), 149.51 (s, 3-*C*-Pz), 145.78 (s, 3-*C*-Pz), 143.40 (s, 5-*C*-Pz), 137.89 (s, 5-*C*-Pz), 137.15 (s, 5-*C*-Pz), 130.38 (s, C_6H_4 or C_6H_5), 129.17 (s, C_6H_4 or C_6H_5), 127.89 (s, C_6H_4 or C_6H_5), 127.09 (s, C_6H_4 or C_6H_5), 122.13 (s, C_6H_4 or C_6H_5), 121.67 (s, C_6H_4 or C_6H_5), 119.80 (s, C_6H_4 or C_6H_5), 119.17 (s, C_6H_4 or C_6H_5), 114.36 (s, C_6H_4NHCH=*C*-$(C_6H_5)C_7H_5N_2CH_3$), 109.54 (s, 4-*C*-Pz), 106.15 (s, 4-*C*-Pz), 68.03 (s, THF), 34.86 (s, NCH_3), 34.40 (s, NCH_3), 26.18 (s, THF), 13.64 (s, 3-*Me*-Pz), 13.00 (s, 5-*Me*-Pz); elemental analysis calcd (%) for $C_{42}H_{52}BN_{10}OY$: C 62.08, H 6.45, N 17.24; found: C 62.27, H 6.52, N 17.06.



Scheme 4. Complex **2** numbering system.

Method B: In a glovebox, a solution of 1-methylbenzimidazole (0.066 g, 1 equiv) in THF (5 mL) was slowly added to a solution of [$Tp^{Me2}Y(CH_2Ph)_2$THF] (0.320 g, 0.50 mmol) in THF (15 mL) at RT. After stirring overnight, the resulting mixture was worked up as described in Method A. Two crystals, **2** (red) and [$Tp^{Me2}Y$-$(CH_2Ph)_2$THF] (colorless), were obtained from the crystalline samples, which were identified by single-crystal X-ray diffraction analysis.

Synthesis of [{(Tp^{Me2})Y[μ-η²:η¹-$SC_6H_4N(CH{=}CHPh)$](THF)}$_2$] (3)

Method A: In a glovebox, a solution of benzothiazole (0.068 g, 0.50 mmol) in THF (5 mL) was slowly added to a solution of [$Tp^{Me2}Y(CH_2Ph)_2THF$] (0.320 g, 0.50 mmol) in THF (15 mL) at RT. After stirring overnight, the resulting mixture was worked up as described for **2**, to give green crystals of **3** that were isolated from the solution. Yield: 0.301 g (88%). ^{1}H NMR (400 MHz, C_6D_6, RT): $\delta =$ 8.13 (d, $J = 16$ Hz, 2H; NC*H*CHC$_6$H$_5$), 6.93–7.08 (m, 18H; C$_6$H$_5$ and C$_6$H$_4$), 5.80 (d, $J = 16$ Hz, 2H; NCHC*H*C$_6$H$_5$), 5.47 (s, 6H; 4H-Tp^{Me2}), 3.57 (s, 8H; O(C*H*$_2$CH$_2$)$_2$), 2.28 (s, 18H; C*H*$_3$ of Tp^{Me2}), 2.10 (s, 18H; C*H*$_3$ of Tp^{Me2}), 1.39 ppm (s, 8H; O(CH$_2$C*H*$_2$)); ^{13}C NMR (100 MHz, [D$_8$]THF, RT): $\delta = 160.45$ (s, NCHCHC$_6$H$_5$), 151.35 (s, 3-*C*-Pz), 150.65 (s, 3-*C*-Pz), 149.46 (s, 3-*C*-Pz), 146.47 (s, 5-*C*-Pz), 145.99 (s, 5-*C*-Pz), 140.59 (s, 5-*C*-Pz), 130.09 (s, C$_6$H$_4$ or C$_6$H$_5$), 128.56 (s, C$_6$H$_4$ or C$_6$H$_5$), 128.41 (s, C$_6$H$_4$ or C$_6$H$_5$), 126.21 (s, C$_6$H$_4$ or C$_6$H$_5$), 124.39 (s, C$_6$H$_4$ or C$_6$H$_5$), 115.69 (s, NCH*C*HC$_6$H$_5$), 106.53 (s, 4-*C*-Pz), 105.57 (s, 4-*C*-Pz), 68.02 (s, THF), 26.13 (s, THF), 13.74 (s, 3-*Me*-Pz), 12.99 ppm (s, 5-*Me*-Pz); elemental analysis calcd (%) for $C_{66}H_{82}B_2N_{14}O_2S_2Y_2$: C 57.99, H 6.05, N 14.34; found: C 58.13, H 6.16, N 14.14.

Method B: In a glovebox, a solution of benzothiazole (0.136 g, 2 equiv) in THF (5 mL) was slowly added to a solution of [$Tp^{Me2}Y(CH_2Ph)_2THF$] (0.320 g, 0.50 mmol) in THF (15 mL) at RT. After stirring overnight, the resulting mixture was worked up as described for **2**, to give green crystals of **3** that were isolated from the solution. Yield: 0.280 g (82%).

Synthesis of 1-methyl(2-benzyl)benzimidazole $C_6H_5CH_2C{=}N\text{-}C_6H_4N(CH_3)$ (4)

In a glovebox, a mixture of [$Tp^{Me2}Y(CH_2Ph)_2THF$] (0.320 g, 0.50 mmol) and 1-methylbenzimidazole (0.132 g, 1.00 mmol) in THF (15 mL) was stirred at RT for 3 h. An aqueous solution of saturated $NaHCO_3$ (5 mL) was added and the reaction mixture was stirred for 30 min. All undissolved solids were removed, and the aqueous layer was extracted with *n*-hexane (2×5 mL). The organic layer (including the organic layer and the extracted *n*-hexane solution) was dried with anhydrous Na_2SO_4, and slowly volatilized in air to afford **4** (0.081 g, 73% based on Y metal) as colorless crystals. ^{1}H NMR (400 MHz, C_6D_6, RT): $\delta = 7.81$ (m, 1H; C$_6$H$_4$), 7.22–7.33 (m, 8H; C$_6$H$_5$ and C$_6$H$_4$), 4.35 (s, 2H; C*H*$_2$Ph), 3.59 (s, 3H; NC*H*$_3$); elemental analysis calcd (%) for $C_{15}H_{14}N_2$: C 81.05, H 6.34, N 12.60; found: C 80.79, H 6.26, N 12.81.

Synthesis of [{Tp^{Me2}CpY(μ-N,C-$NC_3H_2NCH_3$)}$_3$] (5)

In a glovebox, a solution of 1-methylimidazole (0.082 g, 1.00 mmol) in THF (5 mL) was added slowly to a solution of [$Tp^{Me2}CpYCH_2Ph$-(THF)] (0.307 g, 0.50 mmol) in THF (15 mL) at RT. After stirring overnight, the resulting mixture was worked up as described in **1**, to give colorless crystals of **5** that were isolated from the solution. Yield: 0.165 g (62%). ^{1}H NMR (400 MHz, [D$_8$]THF, RT): $\delta = 6.94$ (s, 3H; C$_3$*H*$_2$N$_2$CH$_3$), 6.74 (s, 3H; C$_3$*H*$_2$N$_2$CH$_3$), 5.82 (s, 15H; C$_5$*H*$_5$), 5.63 (s, 9H; 4H-Tp^{Me2}), 3.65 (s, 9H; C$_3$H$_2$N$_2$C*H*$_3$), 2.35 (s, 27H; C*H*$_3$ of Tp^{Me2}), 2.29 ppm (s, 29H; C*H*$_3$ of Tp^{Me2}); ^{13}C NMR (100 MHz, [D$_8$]THF, RT): $\delta = 189.46$ (s, 2-*C*-Im ring), 150.49 (s, 3-*C*-Pz), 143.98 (s, 5-*C*-Pz), 124.91 (s, 4-*C*-Im ring), 123.60 (s, 5-*C*-Im ring), 109.47 (s, C$_5$H$_5$), 106.41 (s, 4-*C*-Pz), 35.61 (s, C$_3$H$_2$N$_2$*C*H$_3$), 13.73 (s, 3-*Me*-Pz), 13.32 ppm (s, 5-*Me*-Pz); elemental analysis calcd (%) for $C_{72}H_{96}B_3N_{24}Y_3$: C 54.16, H 6.06, N 21.05; found: C 54.33, H 6.17, N 20.76.

Synthesis of [$Tp^{Me2}CpY(\eta^2\text{-}N,C\text{-}N{=}CC_6H_4NCH_3)(N{=}CHC_6H_4NCH_3)$] (6)

In a glovebox, a solution of 1-methylbenzimidazole (0.1322 g, 1.00 mmol) in THF (5 mL) was added slowly to a solution of [$Tp^{Me2}CpYCH_2Ph(THF)$] (0.307 g, 0.50 mmol) in THF (15 mL) at RT. After stirring overnight, the resulting mixture was worked up as described in **2**, to give colorless crystals of **6**·0.5C$_7$H$_8$ that were isolated from the solution. Yield: 0.273 g (72%). ^{1}H NMR (400 MHz, [D$_8$]THF, RT): $\delta = 7.43$ (d, 2H; C$_6$H$_4$), 7.23 (s, 1H; C$_6$H$_4$NC*H*NCH$_3$), 7.19 (m, 4H; C$_6$*H*$_4$), 6.95 (m, 1H; C$_6$*H*$_4$), 6.90 (m, 1H; C$_6$*H*$_4$), 5.99 (s, 5H; C$_5$*H*$_5$), 5.88 (s, 1H; 4H-Tp^{Me2}), 5.79 (s, 1H; 4H-Tp^{Me2}), 5.52 (s, 1H; 4H-Tp^{Me2}), 3.77 (s, 3H; NC*H*$_3$), 3.73 (s, 3H; NC*H*$_3$), 2.50 (s, 3H; C*H*$_3$ of Tp^{Me2}), 2.41 (s, 9H; C*H*$_3$ of Tp^{Me2}), 2.34 (s, 3H; C*H*$_3$ of Tp^{Me2}), 2.29 ppm (s, 3H; C*H*$_3$ of Tp^{Me2}); ^{13}C NMR (100 MHz, [D$_8$]THF, RT): $\delta =$ 194.19 (s, C$_6$H$_4$*N*CNCH$_3$), 175.21 (s, C$_6$H$_4$NCHNCH$_3$), 150.88 (s, 3-*C*-Pz), 143.96 (s, 3-*C*-Pz), 142.16 (s, 5-*C*-Pz), 135.32 (s, 5-*C*-Pz), 129.47 (s, C$_6$H$_4$), 128.71 (s, C$_6$H$_4$), 123.08 (s, C$_6$H$_4$), 122.30 (s, C$_6$H$_4$), 120.94 (s, C$_6$H$_4$), 120.13 (s, C$_6$H$_4$), 119.86 (s, C$_6$H$_4$), 116.55 (s, C$_6$H$_4$), 110.46 (s, C$_5$H$_5$), 109.97 (s, C$_5$H$_5$), 108.97 (s, C$_5$H$_5$), 106.72 (s, 4-*C*-Pz), 33.07 (s, C$_6$H$_4$NCN*C*H$_3$), 30.67 (s, C$_6$H$_4$NCHN*C*H$_3$), 13.82 (s, 3-*Me*-Pz), 13.36 ppm (s, 5-*Me*-Pz); elemental analysis calcd (%) for $C_{79}H_{90}B_2N_{20}Y_2$: C 62.46, H 5.97, N 18.44; found: C 62.25, H 5.85, N 18.68.

Synthesis of [$Tp^{Me2}Y$(*Im*-Tp^{Me2})] (7; *Im*-Tp^{Me2} = 1-methyl-imidazolyl-Tp^{Me2}) and [Cp_3Y(HIm)] (8; HIm = 1-methylimidzaloe)

In a glovebox, a solution of 1-methylimidazole (0.082 g, 1.00 mmol) in THF (5 mL) was added slowly to a solution of [$Tp^{Me2}CpYCH_2Ph$-(THF)] (0.307 g, 0.50 mmol) in THF (15 mL) at RT, then the mixture was removed from the glovebox, and stirred at 55 °C for 48 h. The solution was evaporated to dryness under vacuum, and washed with *n*-hexane (2×10 mL). Toluene (20 mL) was added to the residue (partial dissolution), and the undissolved solids (in toluene) were collected by filtration. Diffusion of *n*-hexane into the clear toluene solution gave colorless crystals of **7**. Yield: 0.099 g (26%, based on Y metal). ^{1}H NMR (400 MHz, C_6D_6, RT): $\delta = 6.92$ (s, 1H; H-Im ring), 6.53 (s, 1H; H-Im ring), 6.44 (s, 1H; C5-*H*), 6.28 (s, 3H; 4H-Tp^{Me2}), 5.85 (s, 2H; 4H -Tp^{Me2}-*Im*), 5.77 (s, 1H; 4H -Tp^{Me2}-*Im*), 2.55 (s, 6H; C*H*$_3$ of Tp^{Me2}-*Im*), 2.48 (s, 6H; C*H*$_3$ of Tp^{Me2}-*Im*), 2.44 (s, 3H; C*H*$_3$ of Tp^{Me2}-*Im*), 2.31 (s, 3H; *Me*-Im ring), 2.18 (s, 3H; C*H*$_3$ of Tp^{Me2}), 2.14 (s, 6H; C*H*$_3$ of Tp^{Me2}), 2.11 ppm (s, 9H; C*H*$_3$ of Tp^{Me2}); ^{13}C NMR (100 MHz, C_6D_6, RT): $\delta = 167.03$ (s, 2-*C*-Im ring), 150.11 (s, 3-*C*-Pz), 147.27 (s, 3-*C*-Pz), 146.89 (s, 3-*C*-Pz), 143.39 (s, 3-*C*-Pz), 138.27 (s, 5-*C*-Pz), 137.94 (s, 5-*C*-Pz), 129.92 (s, 4-*C*-Im ring), 125.78 (s, 5-*C*-Im ring), 119.85 (s, 4-*C*-Pz of Tp^{Me2}-*Im*), 103.74 (s, 4-*C*-Pz of Tp^{Me2}), 67.83 (s, *C*5), 32.04 (s, *C*H$_3$-Im ring), 14.38 (s, *Me*-Pz), 14.17 (s, *Me*-Pz), 14.03 (s, *Me*-Pz), 13.58 (s, *Me*-Pz), 13.12 ppm (s, *Me*-Pz); elemental analysis calcd (%) for $C_{34}H_{47}B_2N_{14}Y$: C 53.56, H 6.21, N 25.72; found: C 53.43, H 6.14, N 25.86.

THF (10 mL) was added to the undissolved solids (in toluene) and the mixture was stirred overnight. These solids were also not completely dissolved in the THF solution. After filtration (the residue was collected), the clear THF solution was placed in a freezer at −35 °C, whereupon colorless crystals of **8** formed after several days. Yield: 0.031 g (17%, based on Y metal). ^{1}H NMR (400 MHz, [D$_8$]THF, RT): $\delta = 7.80$ (s, 1H; C$_3$*H*$_3$N$_2$CH$_3$), 7.09 (s, 2H; C$_3$*H*$_3$N$_2$CH$_3$), 5.74 (s, 15H; C$_5$*H*$_5$), 3.75 ppm (s, 3H; C$_3$H$_3$N$_2$C*H*$_3$); elemental analysis calcd (%) for $C_{19}H_{21}N_2Y$: C 62.30, H 5.78, N 7.65; found: C 62.48, H 5.84, N 7.48. No useful ^{13}C NMR spectrum of **8** was obtained due to its low solubility in [D$_8$]THF.

The undissolved solids (in THF) were hydrolyzed by the addition of an aqueous solution of saturated $NaHCO_3$. The mixture was worked up as described in **4**, to give three organic products 1-methylimidazole, 3,5-dimethylpyrazole, and cyclopentadiene, the identities of which were confirmed by GC/MS spectroscopy.

X-ray data collection, structure determination and refinement

Suitable single crystals of complexes **1**–**8** were sealed under nitrogen in Lindemann glass capillaries for X-ray structure analysis. Diffraction data were collected with a Bruker SMART Apex CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption with SADABS program.[19] The structures were solved by direct methods using the SHELXL-97 program.[20] 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 by using the SHELXL program. A summary of the crystallographic data and selected experimental information are listed in Tables 1 and 2. CCDC-951557 (**1**), -951564 (**2**), -951558 (**3**), -951559 (**4**), -951560 (**5**), -951561 (**6**), -951562 (**7**), and -951563 (**8**) contain the 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. Due to the poor quality of data for compound **5**, it was appropriate to leave most of the atoms as isotropic because only the overall connectivity was reliable. The diffraction intensity was too weak in the remote sets during the crystal data collection because of the poor crystal quality of **5**.

Table 1. Crystal and data collection parameters of complexes **1**–**4**.

	1	**2**	**3**	**4**
formula	$C_{138}H_{192}B_6N_{60}Y_6$	$C_{42}H_{52}BN_{10}OY$	$C_{66}H_{82}B_2N_{14}O_2S_2Y_2$	$C_{15}H_{14}N_2$
molecular weight	3289.84	812.65	1367.02	222.28
crystal color	colorless	colorless	colorless	colorless
crystal dimension [mm]	0.20×0.12×0.10	0.15×0.10×0.06	0.20×0.15×0.10	0.18×0.12×0.10
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	$P1$	$P\bar{1}$	$P\bar{1}$	$P21/c$
unit cell dimensions				
a [Å]	16.206(7)	11.924(4)	11.828(4)	8.661(4)
b [Å]	19.041(8)	12.269(4)	12.274(4)	19.052(8)
c [Å]	21.430(9)	17.650(6)	14.901(6)	7.320(3)
α [°]	112.196(5)	98.647(6)	114.290 (3)	90
β [°]	101.770(6)	100.926(5)	105.627(5)	94.550(5)
γ [°]	106.071(6)	97.732(5)	98.013(4)	90
V [Å^3]	5518(4)	2470.8(15)	1820.0(11)	1204.2(9)
Z	1	2	1	4
ρ_{calcd} [g cm^{-3}]	0.990	1.092	1.247	1.226
μ [mm^{-1}]	1.608	1.218	1.694	0.073
F (000)	1704	852	712	472
radiation (λ=0.710730 Å)	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
T [K]	293(2)	293(2)	293(2)	293(2)
scan type	ω-2θ	ω-2θ	ω-2θ	ω-2θ
θ range [°]	1.39 to 25.00	1.703 to 25.010	1.61 to 26.01	2.14 to 25.50
h,k,l range	$-19 \le h \le 8$ $-19 \le k \le 22$ $-23 \le l \le 25$	$-14 \le h \le 14$ $-12 \le k \le 14$ $-20 \le l \le 18$	$-12 \le h \le 14$ $-13 \le k \le 15$ $-18 \le l \le 17$	$-10 \le h \le 9$ $-15 \le k \le 23$ $-6 \le l \le 8$
no. of reflections measured	23002	10306	8285	5134
no. of unique reflections	19103 [R(int) = 0.0573]	8549 [R(int) = 0.0975]	6984 [R(int) = 0.0364]	2239 [R(int) = 0.0408]
completeness to θ	98.2 % (θ=25.00)	95.6 % (θ=25.242)	97.2 % (θ=25.01)	100.0 % (θ=25.50)
max. and min. transmission	0.8558 and 0.7392		0.8489 and 0.7281	0.9927 and 0.9869
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/ parameters	19103/7/980	8549/6/508	6984/12/407	2239/0/156
goodness-of-fit on F^2	0.723	0.859	0.950	1.005
final R indices [$I>2\sigma$ (I)]	$R_1 = 0.0544$ $wR_2 = 0.1284$	$R_1 = 0.0684$ $wR_2 = 0.1545$	$R_1 = 0.0464$ $wR_2 = 0.1156$	$R_1 = 0.0570$ $wR_2 = 0.1550$
R indices (all data)	$R_1 = 0.1309$ $wR_2 = 0.1437$	$R_1 = 0.1250$ $wR_2 = 0.1695$	$R_1 = 0.0686$ $wR_2 = 0.1224$	$R_1 = 0.0687$ $wR_2 = 0.1652$
largest diff. peak and hole [e Å^{-3}]	0.452 and −0.288	0.858 and −0.722	0.796 and −0.857	0.260 and −0.281

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Keywords: C–H activation · metallacycles · nitrogen heterocycles · ring-opening · yttrium

Table 2. Crystal and data collection parameters of complexes **5**–**8**.

	5	**6**·1/2C_7H_8	**7**	**8**
formula	$C_{72}H_{96}B_3N_{24}Y_3$	$C_{79}H_{90}B_2N_{20}Y_2$	$C_{34}H_{47}B_2N_{14}Y$	$C_{19}H_{21}N_2Y$
molecular weight	1596.88	1519.15	762.39	366.29
crystal color	colorless	colorless	colorless	colorless
crystal dimension [mm]	0.12×0.10×0.08	0.20×0.15×0.10	0.15×0.10×0.06	0.20×0.10×0.06
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	*P*21/*m*	*P*21/*c*	*P*1	*C*2/*c*
unit cell dimensions				
a [Å]	10.876(4)	16.607(5)	10.144(5)	30.738(6)
b [Å]	32.669(12)	21.350(7)	10.737(5)	8.3801(16)
c [Å]	14.435(5)	27.416(9)	18.917(9)	14.612(3)
α [°]	90	90.00	101.989(6)	90
β [°]	104.008(5)	95.907(5)	110.768(5)	118.276(4)
γ [°]	90	90.00	68.371(4)	87.697(6)
V [Å^3]	4976(3)	9669(5)	1851.6(15)	90
Z	2	8	2	8
ρ_{calcd} [g cm^{-3}]	1.006	1.004	1.367	1.468
μ [mm^{-1}]	1.779	1.204	1.621	3.517
F (000)	1656	3168	796	1504
radiation (λ=0.710730 Å)	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
T [K]	293(2)	293(2)	293(2)	293(2)
scan type	ω-2θ	ω-2θ	ω-2θ	ω-2θ
θ range [°]	1.454 to 25.00	1.56 to 26.01	1.12 to 25.00	1.50 to 26.00
h,*k*,*l* range	$-12\le h\le 12$	$-19\le h\le 19$	$-12\le h\le 12$	$-37\le h\le 37$
	$-31\le k\le 38$	$-25\le k\le 22$	$-11\le k\le 12$	$-10\le k\le 5$
	$-14\le l\le 17$	$-32\le l\le 28$	$-16\le l\le 22$	$-17\le l\le 18$
no. of reflections measured	20697	39651	7428	7069
no. of unique reflections	8907 [*R*(int) = 0.0783]	17017 [*R*(int) = 0.0753]	6229 [*R*(int) = 0.0495]	3261 [*R*(int) = 0.1041]
completeness to θ	97.2% (θ=25.242)	99.8% (θ=26.01)	95.6% (θ=25.00)	99.8% (θ=26.00)
max. and min. transmission		0.8860 and 0.7896	0.9090 and 0.7930	0.8167 and 0.5398
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	8907/20/510	17017/0/910	6229/2/479	3261/0/200
goodness-of-fit on F^2	0.915	0.824	1.001	1.013
final *R* indices [$I>2\sigma$ (*I*)]	R_1 = 0.0822	R_1 = 0.0509	R_1 = 0.0795	R_1 = 0.0567
	wR_2 = 0.2362	wR_2 = 0.1109	wR_2 = 0.2123	wR_2 = 0.1589
R indices (all data)	R_1 = 0.1428	R_1 = 0.1097	R_1 = 0.1164	R_1 = 0.0729
	wR_2 = 0.2615	wR_2 = 0.1271	wR_2 = 0.2451	wR_2 = 0.1693
largest diff. peak and hole [e Å^{-3}]	1.239 and −0.588	0.480 and −0.427	1.355 and −0.846	0.975 and −1.816

[1] a) E. Furimsky, F. E. Massoth, *Catal. Rev. Sci. Eng.* **2005**, *47*, 297–489; b) T. Kabe, A. Ishikawa, W. Qian, *Hydrodesulfurization and Hydrodenitrogenation*; Wiley-VCH, Chichester, UK, **1999**; c) R. Prins, In *A Handbook of Heterogeneous Catalysis* (Eds.: G. Ertl, H. Knozinger, J. Weitkamp), VCH, Weinheim (Germany), **1997**; d) G. Perot, *Catal. Today* **1991**, *10*, 447–472; e) T. C. Ho, *Catal. Rev. Sci. Eng.* **1988**, *30*, 117–160; f) J. R. Katzer, R. Sivasubramanian, *Catal. Rev. Sci. Eng.* **1979**, *20*, 155–208.

[2] V. L. Blair, W. Clegg, A. R. Kennedy, Z. Livingstone, L. Russo, E. Hevia, *Angew. Chem.* **2011**, *123*, 10031–10034; *Angew. Chem. Int. Ed.* **2011**, *50*, 9857–9860.

[3] a) A. R. Fout, B. C. Bailey, J. Tomaszewski, D. J. Mindiola, *J. Am. Chem. Soc.* **2007**, *129*, 12640–12641; b) B. C. Bailey, H. Fan, J. C. Huffman, M.-H. Baik, D. J. Mindiola, *J. Am. Chem. Soc.* **2006**, *128*, 6798–6799; c) J. A. Pool, B. L. Scott, J. L. Kiplinger, *Chem. Commun.* **2005**, 2591–2593; d) J. B. Bonanno, A. S. Veige, P. T. Wolczanski, E. B. Lobkowski, *Inorg. Chim. Acta* **2003**, *345*, 173–184; e) T. S. Kleckley, J. L. Bennet, P. T. Wolczanski, E. B. Lobkowski, *J. Am. Chem. Soc.* **1997**, *119*, 247–248; f) S. D. Gray, K. J. Weller, M. A. Bruck, P. M. Briggs, D. E. Wigley, *J. Am. Chem. Soc.* **1995**, *117*, 10678–10693; g) S. D. Gray, P. D. Smith, M. A. Bruck, D. E. Wigley, *J. Am. Chem. Soc.* **1992**, *114*, 5462–5463; h) J. R. Strickler, M. A. Bruck, D. A. Wigley, *J. Am. Chem. Soc.* **1990**, *112*, 2814–2816.

[4] a) M. A. Huertos, J. Perez, L. Riera, *J. Am. Chem. Soc.* **2008**, *130*, 5662–5663; b) M. A. Huertos, J. Perez, L. Riera, A. Menendez-Velazquez, *J. Am. Chem. Soc.* **2008**, *130*, 13530–13531.

[5] a) C. T. Carver, P. L. Diaconescu, *J. Am. Chem. Soc.* **2008**, *130*, 7558–7559; b) M. J. Monreal, S. Khan, P. L. Diaconescu, *Angew. Chem.* **2009**, *121*, 8502–8505; *Angew. Chem. Int. Ed.* **2009**, *48*, 8352–8355; c) C. T. Carver, D. Benitez, K. L. Miller, B. N. Williams, E. Tkatchouk, W. A. Goddard, P. L. Diaconescu, *J. Am. Chem. Soc.* **2009**, *131*, 10269–10278; d) K. L. Miller, B. N. Williams, D. Benitez, C. T. Carver, K. R. Ogilby, E. Tkatchouk, W. A. Goddard, P. L. Diaconescu, *J. Am. Chem. Soc.* **2010**, *132*, 342–355.

[6] For an example of C–H activation of pyridine by lanthanide dialkyl complex, see: a) K. C. Jantunen, B. L. Scott, J. C. Gordon, J. L. Kiplinger, *Organometallics* **2007**, *26*, 2777–2781; for other examples of C–H activation of N-heterocycles by organolanthanide derivatives, see: b) S. Arndt, B. R. Elvidge, P. M. Zeimentz, T. P. Spaniol, J. Okuda, *Organometallics* **2006**, *25*, 793–795; c) S. Arndt, T. P. Spaniol, J. Okuda, *Organometallics* **2003**, *22*, 775–781; d) K. H. den Haan, Y. Wlelstra, J. H. Tuben, *Organometallics* **1987**, *6*, 2053–2060; e) M. E. Thompson, S. M. Baxter, A. Ray Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer, J. E. Bercaw, *J. Am. Chem. Soc.* **1987**, *109*, 203–219; f) P. L. Watson, *J. Chem. Soc. Chem. Commun.* **1983**, 276–277.

[7] For some recent reviews on C–H activation, see: a) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879–5981; b) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 10236–10254; c) C. L. Sun, B. J. Li, Z. J. Shi, *Chem. Rev.* **2011**, *111*, 1293–1314; d) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215–1292.

[8] a) E.-i. Negishi, *Angew. Chem.* **2011**, *123*, 6870–6897; *Angew. Chem. Int. Ed.* **2011**, *50*, 6738–6764; b) A. Suzuki, *Angew. Chem.* **2011**, *123*, 6854–6869; *Angew. Chem. Int. Ed.* **2011**, *50*, 6722–6737; c) A. Suzuki, *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**.

[9] For some recent examples of dual C–H activations in transition-metal complexes, see: a) K. Morimoto, M. Itoh, K. Hirano, T. Satoh, Y. Shibata,

K. Tanaka, M. Miura, *Angew. Chem.* **2012**, *124*, 5455 – 5458; *Angew. Chem. Int. Ed.* **2012**, *51*, 5359 – 5362; b) J. Wencel-Delord, C. Nimphius, F. W. Patureau, F. Glorius, *Angew. Chem.* **2012**, *124*, 2290 – 2294; *Angew. Chem. Int. Ed.* **2012**, *51*, 2247 – 2251; c) J. Wencel-Delord, C. Nimphius, H.-G. Wang, F. Glorius, *Angew. Chem.* **2012**, *124*, 13175 – 13180; *Angew. Chem. Int. Ed.* **2012**, *51*, 13001 – 13005.

[10] For an example of the formation of two C–C bonds by multiple C–H activations, in which an intermediate with a C=C bond was presumed, see: H. Li, Z. He, X. Guo, W. Li, X. Zhao, Z. Li, *Org. Lett.* **2009**, *11*, 4176 – 4179.

[11] For some recent examples of rare-earth complexes with pyrazolyborate ligands, see: a) N. Marques, A. Sella, J. Takats, *Chem. Rev.* **2002**, *102*, 2137 – 2159; b) J. Cheng, K. Saliu, G. Y. Kiel, M. J. Ferguson, R. McDonald, J. Takats, *Angew. Chem.* **2008**, *120*, 4988 – 4991; *Angew. Chem. Int. Ed.* **2008**, *47*, 4910 – 4913; c) J. Cheng, M. J. Ferguson, J. Takats, *J. Am. Chem. Soc.* **2010**, *132*, 2 – 3.

[12] a) W. Yi, J. Zhang, Z. Chen, X. Zhou, *Organometallics* **2012**, *31*, 7213 – 7221; b) W. Yi, J. Zhang, Z. Chen, X. Zhou, *Inorg. Chem.* **2012**, *51*, 10631 – 10638; c) W. Yi, J. Zhang, F. Zhang, Z. Chen, X. Zhou, *Chem. Eur. J.* **2013**, *19*, 11975 – 11983; d) W. Yi, J. Zhang, L. Hong, Z. Chen, X. Zhou, *Organometallics* **2011**, *30*, 5809 – 5814; e) F. Han, J. Zhang, W. Yi, Z. Zhang, J. Yu, L. Weng, X. Zhou, *Inorg. Chem.* **2010**, *49*, 2793 – 2798.

[13] An example of silyl transfer, C – C coupling, rearrangement and formation of C=C double bonds in the reaction of scandium silyl complex with CO and isocyanide, see: B. K. Campion, R. H. Heyn, T. D. Tilley, *J. Am. Chem. Soc.* **1990**, *112*, 2011 – 2013.

[14] W. Yi, J. Zhang, M. Li, Z. Chen, X. Zhou, *Inorg. Chem.* **2011**, *50*, 11813 – 11824.

[15] For examples of the construction of M=C bonds by dual C–H bond activation of the CH_3 or CH_2R group, see a review: a) H. Werner, *Angew. Chem.* **2010**, *122*, 4822 – 4837; *Angew. Chem. Int. Ed.* **2010**, *49*, 4714 – 4728; or the following primary literature: b) C. Slugovc, K. Mereiter, S. Trofimenko, E. Carmona, *Angew. Chem.* **2000**, *112*, 2242 – 2244; *Angew. Chem. Int. Ed.* **2000**, *39*, 2158 – 2160; c) M. Paneque, M. L. Poveda, L. L. Santos, V. Salazar, E. Carmona, *Chem. Commun.* **2004**, 1838 – 1839; d) A. Prades, M. Poyatos, J. A. Mata, E. Peris, *Angew. Chem.* **2011**, *123*, 7808 – 7811; *Angew. Chem. Int. Ed.* **2011**, *50*, 7666 – 7669.

[16] For examples of the construction of rare-earth metal bridging carbenes by single or dual C–H bond activation of the CH_3 group, see: a) W. Zhang, Z. Wang, M. Nishiura, Z. Xi, Z. Hou, *J. Am. Chem. Soc.* **2011**, *133*, 5712 – 5715; b) J. Hong, L. Zhang, X. Yu, M. Li, Z. Zhang, P. Zheng, M. Nishiura, Z. Hou, X. Zhou, *Chem. Eur. J.* **2011**, *17*, 2130 – 2137; c) M. Zimmermann, D. Rauschmaier, K. Eichele, K. W. Törnroos, R. Anwander, *Chem. Commun.* **2010**, *46*, 5346 – 5348; d) R. Litlabø, M. Zimmermann, K. Saliu, J. Takats, K. W. Törnroos, R. Anwander, *Angew. Chem.* **2008**, *120*, 9702 – 9706; *Angew. Chem. Int. Ed.* **2008**, *47*, 9560 – 9663.

[17] Only three organic products such as 1-methylimidazole, 3,5-dimethylpyrazole, and cyclopentadiene were isolated from the hydrolytic products of the unidentified materials, and identified by GC/MS spectroscopy. This result is not very useful for understanding the mechanism for the formation of **7**.

[18] For some examples of rare-earth metallo-macrocycles or MOFs, see: a) D. Xue, A. J. Cairns, Y. Belmabkhout, L. Wojtas, Y. Liu, M. H. Alkordi, M. Eddaoudi, *J. Am. Chem. Soc.* **2013**, *135*, 7660 – 7667; b) G. Hou, H. Li, W. Li, P. Yan, X. Su, G. Li, *Cryst. Growth Des.* **2013**, *13*, 3374 – 3380; c) R. Decadt, K. Van Hecke, D. Depla, K. Leus, D. Weinberger, I. Van Driessche, P. Van Der Voort, R. Van Deun, *Inorg. Chem.* **2012**, *51*, 11623 – 11634; d) J. Luo, H. Xu, Y. Liu, Y. Zhao, L. L. Daemen, C. Brown, T. V. Timofeeva, S. Ma, H. Zhou, *J. Am. Chem. Soc.* **2008**, *130*, 9626 – 9627; e) J. Zhang, R. Cai, Z. Chen, X. Zhou, *Inorg. Chem.* **2007**, *46*, 321 – 327; f) B. Zhao, H. Li, Q. Shen, Y. Zhang, Y. Yao, C. Lu, *Organometallics* **2006**, *25*, 1824; g) Y. Obora, T. Ohta, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1997**, *119*, 3745 – 3755; h) D. M. Barnhart, D. L. Clark, J. C. Gordon, J. C. Huffman, J. G. Watkin, B. D. Zwick, *J. Am. Chem. Soc.* **1993**, *115*, 8461 – 8462.

[19] G. M. Sheldrick, SADABS, *A Program for Empirical Absorption Correction*; Göttingen (Germany), **1998**.

[20] G. M. Sheldrick, SHELXL-97, *Program for the Refinement of the Crystal Structure*; University of Göttingen (Germany), **1997**.

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