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Versatile Reactivity of Scorpionate-Anchored Yttrium–Dialkyl Complexes towards Unsaturated Substrates

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Abstract: A series of unusual chemicalbond transformations were observed in the reactions of high active yttrium–dialkyl complexes with unsaturated small molecules. The reaction of scorpionateanchored yttrium–dibenzyl complex $[Tp^{Me2}Y(CH_2Ph)_2(thf)]$ (1, $Tp^{Me2}=$ tri(3,5-dimethylpyrazolyl)borate) with phenyl isothiocyanate led to C=S bond cleavage to give a cubane-type yttrium–sulfur cluster, $\{Tp^{Me2}Y(\mu_3-S)\}_4$ (2), accompanied by the elimination of **Keywords:** C-H activation • cleavage reactions • heterocycles • insertion • yttrium to produce γ -deprotonation product $[(Tp^{Me2})_2Y]^+[Tp^{Me2}Y(N=C=CHPh)_3]^-$ (6), in which the newly formed N=C= CHPh ligands bound to the metal through the terminal nitrogen atoms. When this reaction was carried out in toluene at 120 °C, it gave a tandem γ deprotonation/insertion/partial-Tp^{Me2}degradation product, $[(Tp^{Me2}Y)_2(\mu$ -Pz)_2[μ - η^1 : η^3 -NC(CH₂Ph)CHPh]] (7, Pz=3,5-dimethylpyrazolyl).

Introduction

Rare-earth-metal-dialkyl complexes that contain monoanionic ancillary ligands (LLnR₂) have occupied a central place in the organometallic chemistry of these elements over the last decade, because the presence of two highly reactive σ-bonded hydrocarbon ligands may impart a marked reactivity onto their rare-earth-metal complexes that is difficult or impossible to achieve from their corresponding monoalkyl compounds.^[1] These complexes not only react facilely with the appropriate borate compounds, such as [Ph₃C][B- $(C_6F_5)_4$] or [PhNMe₂H][B(C_6F_5)_4], to generate cationic monoalkyl species that serve as excellent catalysts for the polymerization and copolymerization of a variety of olefins,^[2] but they are also useful precursors for the synthesis of a wide range of rare-earth-metal derivatives, such as rareearth-metal polyhydrides,^[3] rare-earth-metal-terminal-imido complexes,^[4] and rare-earth-metal-carbene complexes.^[5] However, the reactivity of rare-earth-metal-dialkyl complexes towards unsaturated substrates has remained almost unexplored so far.^[6] Encouraged by the results that rare-

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State Key Laboratory of Organometallic Chemistry Shanghai 200032 (P. R. China) E-mail: xgzhou@fudan.edu.cn earth-metal–dihydrides "LLnH₂" exhibit remarkable reactivity toward some unsaturated substrates, such as PhCN, CO, and CO₂, which is exquisitely different from those of rare-earth-metal monohydrides,^[7] we decided to investigate what new unique properties might be derived from cooperative interactions between two alkyl ligands.

Herein, we report the synthesis of scorpionate-anchored yttrium–dibenzyl complex $[Tp^{Me2}Y(CH_2Ph)_2(thf)]$ (1) and its reaction behavior towards a series of unsaturated substrates, which show interesting reactivity and lead to new products. The reaction products have been identified by X-ray diffraction analysis, thus demonstrating that the two benzyl ligands can undergo various tandem reactions with one unsaturated molecule in an unprecedented manner.

Results and Discussion

Tris(pyrazolyl)borates (Tp^{R,R'}) are among the most-versatile and most widely used supporting ligands in inorganic and organometallic chemistry,^[8] owing to the facile manipulation of their steric profile by variation of the substituents at the 3-positions of the pyrazolyl rings. Mono-Tp^{R,R'} yttrium–dialkyl complexes [(Tp^{Me,R})Y(CH₂SiMe₃)₂(thf)_x] (R=Me, x=1; R=tBu, x=0) have been synthesized by salt metathesis and alkane elimination, respectively.^[3e,9] Recently, we tried to prepare mono-Tp^{Me2} yttrium–di-silylamide complex [Tp^{Me2}Y(N(SiMe₃)₂)₂] by using salt metathesis between [Tp^{Me2}YCl₂(thf)₂] and KN(SiMe₃)₂; however, we only isolated the γ -methyl-deprotonation or Si–Me bond-cleavage products.^[10] However, the mono-Tp^{Me2} yttrium–dibenzyl complex [Tp^{Me2}Y(CH₂Ph)₂(thf)] (**1**) was facilely prepared by the reaction of $[Tp^{Me2}YCl_2(thf)_2]$ with two equivalents of KCH₂Ph in THF at room temperature and was isolated in 91% yield as colorless air- and moisture-sensitive crystals (Scheme 1). The constitution of compound **1** was unequivo-



Scheme 1. Synthesis of compounds 2 and 3 from compound 1.

cally established by single-crystal X-ray diffraction analysis (Figure 1), which indicated that compound **1** was a solvate monomer, in which the yttrium atom was bonded to a κ_3 -Tp^{Me2} ligand, two η^1 -benzyl groups, and one coordinated thf molecule to form a distorted octahedral geometry. No multi-hapto interactions were observed between the yttrium atom and the two benzyl groups in the solid state.^[11] The two almost-equivalent Y–C bond lengths (Y1–C1 2.457(8) Å, Y1–C8 2.418(8) Å) indicate that they are standard yttrium–carbon σ bonds and these values are comparable to the corresponding values in other lanthanide–benzyl complexes, such as $[Y(CH_2Ph)_3(thf)_3]$ (Y–C 2.452(3)–2.463(3) Å).^[12]



This equivalence of the two benzyl groups was also confirmed by the ¹H and ¹³C NMR spectra of compound 1 in solution. In the ¹H NMR (C₆D₆, RT) spectrum of compound 1, the three single peaks at $\delta = 5.55$, 2.38, and 2.10 ppm are attributed to the 4-H-Tp^{Me2} and Me-Tp^{Me2} groups, respectively, and the three multiple peaks at $\delta = 7.21 - 6.80$ ppm are attributed to the phenyl-ring protons of the two benzyl groups. However, the CH_2 peak of the benzyl group is buried in the peak of 5-Me-Tp^{Me2} at $\delta = 2.10$ ppm. Thus, we studied the variable-temperature ¹H NMR spectra of compound 1 (-40 to 60 °C, $[D_8]$ THF) and found that the original signal at $\delta = 2.10 \text{ ppm}$ (C₆D₆, RT) split into two signals at $\delta = 2.26$ and 2.20 ppm ([D₈]THF, -40 °C) in a 4:6 ratio, which were assignable to the resonances of the CH_2Ph and Me-Tp^{Me2} groups, respectively. Moreover, the resonances at $\delta = 2.38$ and 2.20 ppm are assignable to the *Me*-Tp^{Me2} groups in a 12:6 ratio. Notably, the integral ratio for the peaks of Me-Tp^{Me2} at $\delta = 2.38$ and 1.0 ppm in C₆D₆ at room temperature is 6:12, but it changes into 12:6 in [D₈]THF at -40 °C $(\delta = 2.37 \text{ and } 2.23 \text{ ppm})$. This result might be attributable to the solution effects of C_6D_6 and $[D_8]THF$.

The reaction of compound **1** with one equivalent of phenyl isothiocyanate smoothly took place at room temperature in THF. After workup, the structurally characterized metal complex $\{Tp^{Me2}Y(\mu_3-S)\}_4$ (**2**) was isolated in 68% yield, accompanied by the elimination of PhN=C(CH₂Ph)₂. The PhN=C(CH₂Ph)₂ byproduct was also confirmed by GCMS and ¹H NMR spectroscopy. X-ray analysis revealed that compound **2** adopted a tetranuclear cubane-like Y₄S₄ core structure that was formed from four "Tp^{Me2}Y(μ_3 -S)" units (Figure 2).^[13] Each yttrium atom was ligated by a κ^3 -scorpionate-Tp^{Me2} ligand (Y1–N1 2.519(3) Å, Y1–N1A 2.519(3) Å, Y1–N1B 2.519(3) Å) and three μ_3 -bridging S atoms (Y1–S2 2.6704(9) Å, Y1–S2A 2.6704(9) Å, Y1–S2C



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Figure 1. Molecular structure of compound 1; thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–C1 2.457(8), Y1–C8 2.418(8), Y1–O1 2.335(5), Y1–N2 2.502(6), Y1–N4 2.378(6), Y1–N6 2.485(6); Y1-C1-C2 116.4(6), Y1-C8-C9 130.1(6).

Figure 2. Molecular structure of compound **2**; thermal ellipsoids are set at 30% probability. Carbon atoms on the Tp^{Me2} moiety and all hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–S2 2.6704(9), Y1–S2A 2.6704(9), Y1–S2C 2.6704(9), Y1–N1 2.519(3), Y1–N1A 2.519(3), Y1–N1B 2.519(3); S2-Y1-S2A 85.59(4), S2A-Y1-S2C 85.59(4), Y1-S2-Y1A 94.25(3), Y1-S2-Y1C 94.25(3), Y1A-S2-Y1C 94.25(3).

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2.6704(9) Å). Cubane cluster **2** is similar to the known tetraoxo complex $Cp'_4Y_4O_4$ ($Cp' = C_5Me_4SiMe_3$).^[7e]

The formation of compound **2** indicated that a new C=S double-bond cleavage occurred during the isothiocyanate-insertion process. It is known that the insertion of isothiocyanate into metal–ligand bonds usually leads to the formation of insertion products,^[14] whilst the C=S double-bond cleavage of the isothiocyanate unit has only rarely been observed.^[15] The behavior of phenyl isothiocyanate in the reaction between compound **1** and PhNCS is similar to that of phenyl isocyanate in the reaction of yttrium polyhydride with PhNCO, which results in the cleavage of the C=O double bond.^[7g] Thus, we speculate that the formation of compound **2** might undergo a continuous Y–C σ -bond-insertion process, as shown in Scheme 2.

 $1 \xrightarrow{PhN=C=S} \left[\begin{array}{c} CH_2Ph \\ Ph-N \\ Ph-N \\ PhH_2C \\ Tp^{Me2} \\ CH_2Ph \\ \end{array} \right] \xrightarrow{Tp^{Me2}} insertion \left[\begin{array}{c} PhH_2C \\ Ph-N \\ Tp^{Me2} \\ Tp^{Me2} \\ PhH_2C \\ CH_2Ph \\ \end{array} \right] \xrightarrow{PhH_2C \\ CH_2Ph \\ PhH_2C \\ CH_2Ph \\ \end{array} \right] \xrightarrow{PhN=C(CH_2Ph)_2} 2$

Scheme 2. Plausible reaction process for the formation of compound 2.

The significant difference between the reactivities of yttrium-monobenzyl and yttrium-dibenzyl complexes^[14a] towards phenyl isothiocyanate led us to explore other heteroallenes, such as phenyl isocyanate. An equimolar reaction of compound 1 with phenyl isocyanate in THF at room temperature afforded an insertion and benzyl-deprotonation product, 3. THF, in 72% yield (Scheme 1). The solid-state structure of compound 3.THF was also determined by singlecrystal X-ray diffraction. Figure 3 shows that the two newly formed OC(CHPh)NPh ligands are bonded to two Y³⁺ ions in a bridged and side-on bonding mode and that there is an agostic Y…H interaction between the Y1 ion and the CHPh moiety (Y1...H 2.478(5) Å). The C1-C2 and C15-C16 (1.374(10) and 1.398(10) Å) bond lengths are significant shorter than that of a C-C single bond (1.50 Å), thus indicating partially delocalized double-bond character. Consistent with this observation, the C1-N1 (1.393(9) Å) and C1-O1 bonds (1.388(8) Å) are slightly shorter than those of C- (sp^2) -N and C (sp^2) -O single bonds, respectively. The newly formed amido ligands OC(CHPh)NPh are dianionic, bonded to an Y³⁺ center with a monoanionic Tp^{Me2} ligand, and the observed distances in the OC(CHPh)NPh ligand indicate charge delocalization. In the ¹H NMR spectrum of compound 3. THF at room temperature in C_6D_6 , the single peak at $\delta = 5.57$ ppm is assigned to the resonance of the 4*H*- Tp^{Me2} group and the two overlapping single peaks at $\delta =$ 2.02-2.16 ppm are assigned to the resonances of the Me-



Figure 3. Molecular structure of compound **3**; thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–N1 2.296(6), Y1–O1 2.353(5), Y1– O2 2.276(5), Y2–N2 2.312(7), Y2–O1 2.209(5), Y2–O2 2.383(5), Y1…H16 2.478(5), C1–N1 1.393(9), C1–O1 1.388(8), C1–C2 1.374(10), C15–N2 1.333(9), C15–O2 1.365(8), C15–C16 1.398(10); N1-C1-O1 105.2(8), N1-C1-C2 136.5(8), O1-C1-C2 118.1(9), N2-C15-O2 112.6(9), N2-C15-C16 133.4(9), O2-C15-C16 115.2(7).

Tp^{Me2} group. The CHPh fragment that is bound to the PhNCO unit is observed as a singlet at $\delta = 4.73$ ppm and the ¹³C NMR spectrum of compound **3** shows one resonance at $\delta = 68.07$ ppm, which is assignable to the CHPh proton. In an attempt to obtain more details about the agostic Y...H interaction in solution, we also studied the variable-temperature ¹H NMR spectra of compound **3**·THF (from -40 to 60 °C in [D₈]THF). The single peak at $\delta = 4.83$ ppm, which is assignable to the two CHPh groups, does not split into two single peaks in [D₈]THF at -40 °C. However, the two overlapping peaks that are assignable to 3-Me-Tp^{Me2} and 5-Me-Tp^{Me2} at $\delta = 2.16-2.02$ ppm split into four single peaks at $\delta =$ 2.42, 2.38, 2.24, and 1.94 ppm in a 6:12:6:12 ratios and the single peak at $\delta = 5.57$ ppm (C₆D₆, RT), which is assignable to the 4H-Tp^{Me2} group, also splits into two single peaks at $\delta = 5.85$ and 5.65 ppm in a 2:4 ratio in [D₈]THF at -40 °C. Thus, we speculate that compound 3. THF adopts a $C_{2\nu}$ -symmetric structure in solution, owing to the fast dissociation/ re-addition of THF (the THF molecule in the crystal lattice in C_6D_6 or the $[D_8]THF$ molecule in $[D_8]THF$). Indeed, we also cannot exclude the possibility that the agostic Y--H solid-state structure is maintained in solution, but undergoes rapid fluxional behavior, thus giving a time-averaged solution structure that has higher symmetry than the C_1 -symmetric solid-state structure.

The C=C double-bond character of the C1-C2 and C15-C16 bonds in compound **3** were also confirmed by the following reaction: Complex **3** can further react with Me₃SiCl under mild conditions to give a nucleophilic-addition product (**4**) in 87% yield, as shown in Scheme 3. Its solid-state structure (Figure 4) reveals that the Si-Cl bond of the Me₃SiCl group added across the Y-N bond and that the Me₃Si group is bonded with the CHPh moiety through a 1,3-migration process. Compound **4** contains a monoanionic

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Scheme 3. Synthesis of compound 4 from compound 3.



Figure 4. Molecular structure of compound **4**; thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–O1 2.305(2), Y1–N1 2.420(3), Y1–Cl1 2.568(1), C1–O1 1.283(4), C1–N1 1.326(5), C1–C2 1.511(5); O1-C1-N1 115.7(3), O1-C1-C2 118.0(3), N1-C1-C2 126.3(4).

amido ligand, OC(CH(SiMe₃)Ph)NPh, and has incorporated a chloride ligand into the coordination sphere of the metal. The C1–C2 bond length (1.511(5) Å) corresponds to a standard single bond. A singlet peak at δ =3.16 ppm is assigned to the C(sp³)–H resonance of the CH(SiMe₃)Ph group in the ¹H NMR spectrum of compound **4**. These results also indicate that a new C(sp³)–H functionalization of the CH₂Ph ligand has been realized by the reactions from compound **1** to compound **4**.

We speculate that the formation of compound **3** might proceed through two different pathways, as outlined in Scheme 4. In path a, compound **1** undergoes a PhCH₃-elimination step to yield a metal–carbene intermediate;^[5] then, the cycloaddition of isocyanate to the ytterbium–alkylidene intermediate forms compound **3**. In path b, compound **1** un-



Scheme 4. Plausible reaction processes for the formation of compound 3.

dergoes an insertion of phenyl isocyanate into one Y– CH₂Ph bond, followed by γ -deprotonation and PhCH₃-eleimation processes. Considering the fact that no ytterbium–alkylidene intermediate was determined in the ¹H NMR spectrum of compound **1**, we suggest that path b is more likely. Moreover, the result of the reaction of compound **1** with carbodiimide can also be used to exclude path a (see below).

The treatment of compound **1** with one equivalent of ArN=C=NAr in THF at room temperature produced a monoinsertion product, $[Tp^{Me2}Y(CH_2Ph)\{(RN)_2C(CH_2Ph)\}]$ (5, Ar = C₆H₃-*i*Pr-2,6), in almost-quantitative yield (Scheme 5).



Scheme 5. Synthesis of compound 5 from compound 1.

Complex 5 does not undergo further transformations, such as proton abstraction from the CH_2Ph group of the amidinate ligand or the elimination of $PhCH_3$, similar to compound 3, even at elevated temperatures (80 °C) for 24 h. These results might suggest that the ytterbium-alkylidene intermediate is not formed during the process for the formation of compound 3 (Scheme 4, path a).

Single-crystal analysis (Figure 5) and ¹H and ¹³C NMR spectroscopy confirmed that compound **5** was a mixed Tp^{Me2}/amidinate-yttrium-monobenzyl complex. In the ¹H NMR spectrum of compound **5**, the two single peaks at δ =5.63 and 5.30 ppm were assigned to the resonances of the 4*H*-Tp^{Me2} group in a 1:2 ratio, whilst the four single peaks at δ =2.50, 2.07, 1.94, and 1.87 ppm were assigned to the resonances of the *Me*-Tp^{Me2} protons in a 3:6:3:6 ratio.



Figure 5. Molecular structure of compound 5; thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–N1 2.390(2), Y1–N2 2.379(2), Y1–C33 2.451(3), C1–N1 1.331(3), C1–N2 1.336(3), C1–C2 1.520(4); N1-C1-N2 115.5(2), N1-C1-C2 122.7(3), N2-C1-C2 121.8(3).

Two multiple peaks at $\delta = 3.95$ and 3.45 ppm are assigned to the resonances of the $HC(CH_3)_2$ groups and the four double peaks (J=6.4) at $\delta = 1.62$, 1.50, 0.93, and 0.84 ppm are assigned to the resonances of the $HC(CH_3)_2$ groups in a 6:6:6:6 ratio. These results indicate that compound 5 is a C_s symmetrical solution. Two characteristic single peaks at $\delta =$ 3.84 and 2.11 ppm are assigned to the resonances of the NC- $(CH_2Ph)N$ and Y-CH₂Ph groups, respectively. Consistent with this observation, two resonances at $\delta = 56.42$ and 35.24 ppm, which were assignable to the Y-CH₂Ph and NC- $(CH_2Ph)N$ groups, were observed in the ¹³C NMR spectrum of compound 5. The molecular structure and important bond lengths and angles are listed in Figure 5. The central metal ion, Y^{3+} , is bonded to one κ^3 -Tp^{Me2} group, one η^1 benzyl group, and one chelating amidinate ligand to form a distorted octahedral geometry. The two C-N bond lengths of the amidinate group (C1-N1 and C1-N2, 1.331(3) and 1.336(3) Å, respectively) are approximately equivalent and significantly shorter than the lengths of the $C(sp^2)-N(sp^3)$ single bonds (1.47–1.50 Å), thus indicating that the π electrons of the C=N double bond in these structures are delocalized over the NCN unit. The Y-N1 and Y-N2 distances (2.390(2) and 2.379(2) Å) are intermediate between the values for a Y-N single bond and a Y-N coordinate bond and are longer than the corresponding values in [Cp₂Y- $\{(tBuN)_2CnBu\}$ (Y–N1 and Y–N2, 2.301(3) and 2.302(3), respectively).^[16] This result may be attributed to the larger steric hindrance of the Tp^{Me2} group compared with the Cp group, which decreases the interaction between the Y and N atoms. The Y1-C33 (2.451 Å) bond is a normal Y-C σ bond. The C1–C2 bond (1.520(4) Å) is consistent with a carbon-carbon single bond.

Investigations of the reactivity of rare-earth-metal-alkyl complexes toward organic nitriles provide many important organometallic reactions and interesting structures and they have found that they usually react with nitriles to give the insertion or C-H activation products.[17] However, no examples of reaction of rare-earth-metal-dialkyl complexes with nitriles have been reported so far. To further explore the reactivity of the yttrium-dialkyl complex, we also investigated the reaction of compound 1 with phenylacetonitrile and found that compound 1 could react with one equivalent of phenylacetonitrile in THF at room temperature to afford a structurally characterized complex, [(Tp^{Me2})₂Y]+[Tp^{Me2}Y(N= $C=CHPh_3^{-}(6)$, in 70% yield (based on the reaction stoichiometry), thus indicating that PhCH₂CN underwent a γ-deprotonation step to form an anionic ketenimino ligand that adopted an unusual bonding mode. When the reaction was carried out in toluene at 120°C, a tandem y-deprotonation/ insertion/partial-Tp^{Me2}-degradation product, [(Tp^{Me2}Y)₂(µ- $Pz_{2}[\mu-\eta^{1}:\eta^{3}-NC(CH_{2}Ph)CHPh]]$ (7, Pz=3,5-dimethylpyrazolyl), was isolated in 34% yield (based on the Y metal), as shown in Scheme 6. The ¹H NMR spectrum of compound 6 showed a single resonance at $\delta = 5.94$ ppm, which was assignable to the N=C=CHPh unit. Consistent with this observation, the bond parameters, such as N1-C1-C2 178.5(8)°, N1-C1 1.177(9) Å, and C1-C2 1.382(10) Å, also suggested



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Scheme 6. Two routes for the synthesis of compound 7 from compound 1.

that the PhCHCN ligand contained a ketenimine skeleton (Figure 6). Moreover, the newly formed N=C=CHPh anionic ligands bound to the central metal through a terminal nitrogen atom (Y1-N1 2.252(5) Å). To the best of our knowledge, this bond mode of the ketenimino ligand to lanthanide ions has not previously been reported.^[17]



Figure 6. Anionic structure of compound **6**; thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Y1–N1 2.252(5), Y1–N2 2.313(6), Y1–N3 2.290(5), N1–C1 1.177(9), C1–C2 1.382(10), N2–C9 1.127(8), C9–C10 1.357(10), N3–C17 1.133(8), C17–C18 1.381(10); N1-C1-C2 178.5(8), N2-C9-C10 176.6(10), N3-C17-C18 178.0(8).

The crystal structure of compound **7** is shown in Figure 7 and shows that the dianionic 1-azaallyl ligand [PhCH=C-(CH₂Ph)N]²⁻ has been formed through the insertion of the anionic PhCH=C=N⁻ group into the Y–C(benzyl) σ bond. The C1–C2 and C2–N1 bond lengths, 1.373(12) and1.335(12) Å, adopt intermediate values between the corresponding C–C and C–N single- and double-bond lengths, thus indicating that the π electrons of the C=C double bond in this structure are partially delocalized over the C-C-N unit.^[18] The Y1–N1 distance (2.147(7) Å) is significantly

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Figure 7. Molecular structure of compound 7; thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1-N1 2.147(7), Y2-N1 2.315(8), Y2-C1 2.678(11), Y2-C2 2.675(11), N1-C2 1.335(12), C2-C1 1.373(12), C2-C3 1.563(13); N1-C2-C1 120.9(9), N1-C2-C3 119.1(9), C1-C2-C3 119.8(9).

shorter than that of the Y2–N1 bond (2.315(8) Å) and is comparable to the values in rare-earth-metal-bridged imido complexes.^[7 h] Moreover, the almost-equivalent lengths of the Y2–C1 (2.678(11) Å) and Y2–C2 bonds (2.675(11) Å) shows that the C1–C2 double bond is coordinated to the Y2 ion in a side-on bonding mode. The source of the 3,5-dimethylpyrazolyl group might be the degradation of the Tp^{Me2} ligand at high temperatures.^[19]

Conclusion

In summary, we have investigated the equimolar reactions of rare-earth-metal-dialkyl complexes with some unsaturated substrates and revealed some unusual chemical-bond transformations, such as C=S cleavage and $C(sp^3)$ -H activation or functionalization. These results indicate that the presence of two highly active metal-carbon σ bonds in the dialkyl complexes offers a greater variety of reactivity beyond insertion compared to its monoalkyl analogue.

Experimental Section

General methods: All of the reactions were carried out under a dry and inert atmosphere by using either standard Schlenk techniques or under a nitrogen atmosphere in an MBRAUN glove box. The nitrogen gas in the glove box was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glove box were monitored by an O₂/H₂O Combi-Analyzer (MBRAUN) to ensure that both concentrations stayed below 1 ppm. The THF, toluene, and *n*-hexane solvents were heated at reflux and distilled over sodium benzophenone ketyl under a nitrogen atmosphere immediately prior to use. [TpMe₂YCl₂(thf)₂]^[2ha] and KCH₂Ph^[20b] were prepared according to literature methods. Phenyl isothiocyanate (PhNCS), phenyl isocyanate (PhNCO), and phenyacetonitrile (PhCH₂CN) were purchased from Aldrich and used without further purification. Elemental analysis was carried out on a Rapid CHN-O analyzer. ¹H and ¹³C NMR data were ob-

tained on a Bruker DMX-400 NMR spectrometer (¹H: 400 MHz, ¹³C: 100 MHz).

Synthesis of [Tp^{Me2}Y(CH₂Ph)₂(thf)] (1): In a glove box, benzyl potassium (KCH₂Ph, 0.260 g, 2.00 mmol) was added to a solution of [Tp^{Me2}YCl₂-(thf)] (0.529 g, 1.00 mmol) in THF (20 mL) at RT. After stirring overnight, the thick, pale-red solution was evaporated to dryness under vacuum and toluene (30 mL) was added to the residue. After stirring for 30 min, the mixture was filtered through Celite and the filtrate was concentrated to about 10 mL and then layered with n-hexane to afford compound 1 as colorless crystals. Yield: 0.583 g (91%); ¹H NMR (100 MHz, C_6D_6 , RT): $\delta = 7.17 - 7.21$ (m, 8H; C_6H_5), 6.80 (m, 2H; C_6H_5), 5.55 (s, 3H; 4H-Tp^{Me2}), 3.47 (m, 4H; O(CH₂CH₂)₂), 2.38 (s, 6H; CH₃ of Tp^{Me2}), 2.10 (two overlapping peaks, 16H; CH_3 of Tp^{Me2} and CH_2Ph), 1.11 ppm (m, 4H; O(CH₂CH₂)₂); variable-temperature ¹H NMR ([D₈]THF, from -40 to 60°C): at -40°C: $\delta = 6.80$ (m, 4H; C₆H₅), 6.67 (m, 4H; C₆H₅), 6.36 (m, 2H; C₆H₅), 5.77 (s, 3H; 4H-Tp^{Me2}), 2.37 (s, 12H; CH₃ of Tp^{Me2}), 2.28 (s, 4H; CH₂Ph), 2.23 (s, 6H; CH₃ of Tp^{Me2}); variable-temperature ¹H NMR ([D₈]THF, from -40 to 60 °C): at 60 °C: $\delta = 6.77$ (m, 4H; C₆H₅), 6.66 (m, 4H; C_6H_5), 6.34 (m, 2H; C_6H_5), 5.77 (s, 3H; 4H-Tp^{Me2}), 2.35 (s, 12H; CH₃ of Tp^{Me2}), 2.26 (s, 4H; CH₂Ph), 2.20 ppm (s, 6H, CH₃ of Tp^{Me2}); ¹³C NMR (100 MHz, C₆D₆, RT): $\delta = 154.70$ (s; 3-C-Pz), 145.66 (s; 5-C-Pz), 128.49 (s; CH₂C₆H₅), 124.45 (s; CH₂C₆H₅), 117.08 (s; CH₂C₆H₅), 106.30 (s; 4-C-Pz), 71.11 (s; thf), 56.26 (d, J(Y,C)=34 Hz; Y-CH₂C₆H₅), 25.07 (s; thf), 14.30 (s; 3-Me-Pz), 13.07 ppm (s; 5-Me-Pz). elemental analysis calcd (%) for C33H44BN6OY: C 61.89, H 6.92, N 13.12; found: C 62.12, H 7.01, N 12.89.

Synthesis of {Tp^{Me2}Y(μ_3 -S)}₄ (2): In a glove box, phenyl isothiocyanate (0.068 g, 0.50 mmol) was slowly added to a solution of compound 1 (0.320 g, 0.50 mmol) in THF (15 mL). After stirring overnight at RT, the solution was concentrated to dry under reduced pressure. To the residue was added toluene (5 mL) and then *n*-hexane was diffused into the concentrated toluene solution to give colorless crystals of compound 2. Yield: 0.569 g (68%); ¹H NMR (100 MHz, C₆D₆, RT): δ =5.56 (s, 3H; 4*H*-Tp^{Me2}), 2.75 (s, 9H; CH₃ of Tp^{Me2}), 2.06 ppm (s, 9H; CH₃ of Tp^{Me2}); ¹³C NMR (100 MHz, C₆D₆, RT): δ =150.91 (s; 3-*C*-Pz), 148.79 (s; 5-*C*-Pz), 107.12 (s; 4-*C*-Pz), 14.36 (s; 3-*Me*-Pz), 12.94 ppm (s; 5-*Me*-Pz); elemental analysis calcd (%) for C₆₀H₈₈B₄N₂₄S₄Y₄: C 43.08, H 5.30, N 20.10; found: C 42.85, H 5.24, N 20.29.

The mother solution was concentrated to dryness under reduced pressure to give an oily mixture. Then, the oily mixture was abstracted twice with *n*-hexane (10 mL). After removing the volatile compounds, the impure organic byproduct PhN=C(CH₂Ph)₂ was obtained and purified by fast column chromatography on silica gel. Yield: 0.091 g (64%); ¹H NMR (100 MHz, CDCl₃, RT): $\delta = 3.94$ (s, 4H; CH₂Ph), 7.01–7.48 ppm (m, 15H; C₆H₃).^[21]

 $[Tp^{Me^2}Y(thf)\{\mu\cdot\eta^1\!:\!\eta^3\!\cdot\!OC(CHPh)NPh\}\{\mu\cdot\eta^3\!:\!\eta^2\!\cdot\!OC\!\cdot$ Synthesis of (CHPh)NPh}YTp^{Me2}] (3): In a glove box, PhNCO (0.083 g, 0.70 mmol) was added to a solution of compound 1 (0.448 g, 0.70 mmol) in THF (15 mL) at RT. After stirring overnight, the reaction mixture was worked up by using the method described for the synthesis of compound 2. Colorless crystals of compound 3. THF were obtained in 72% yield (0.673 g). ¹H NMR (400 MHz, C_6D_6 , RT): $\delta = 6.24-8.04$ (m, 20 H; C_6H_5), 5.57 (s, 6H; 4H-Tp^{Me2}), 4.73 (s, 2H; CHPh), 3.52 (m, 8H; O(CH₂CH₂)₂), 2.02-2.16 (two overlapping peaks, 36H; CH₃-Tp^{Me2}), 1.44 ppm (m, 8H; O-(CH₂CH₂)₂); variable-temperature ¹H NMR ([D₈]THF, from -40 to 60°C): at -40°C: $\delta = 7.48$ (m, 4H; C₆H₅), 6.78 (m, 4H; C₆H₅), 6.64 (m, 4H; C_6H_5), 6.53 (m, 4H; C_6H_5), 6.25 (m, 4H; C_6H_5), 5.85 (s, 2H; 4H-Tp^{Me2}), 5.65 (s, 4H; 4H-Tp^{Me2}), 4.83 (s, 2H; CHPh), 2.42 (s, 6H; CH₃ of Tp^{Me2}), 2.38 (s, 12H; CH_3 of Tp^{Me2}), 2.24 (s, 6H; CH_3 of Tp^{Me2}), 1.94 ppm (s, 12H; CH₃ of Tp^{Me2}); variable-temperature ¹H NMR ([D₈]THF, from -40 to 60 °C): at 60 °C: $\delta = 7.48$ (m, 4H; C₆H₅), 6.79 (m, 4H; C₆H₅), 6.52 (m, 4H; C_6H_5), 6.22 (m, 8H; C_6H_5), 5.67 (s, 6H; 4H-Tp^{Me2}), 4.83 (s, 2H; CHPh), 2.38 (s, 24H; CH₃ of Tp^{Me2}), 2.05 ppm (s, 12H; CH₃ of Tp^{Me2}); ¹³C NMR (100 MHz, C_6D_6 , RT): $\delta = 167.81$ (s; OCN), 154.68 (s; 3-C-Pz), 152.38 (s; 3-C-Pz), 150.41 (s; 3-C-Pz), 149.77 (s; 5-C-Pz), 146.50 (s; 5-C-Pz), 145.23 (s; 5-C-Pz), 124.32 (s; CH₂C₆H₅), 121.19 (s; CHC₆H₅), 116.53 (s; CHC₆H₅), 115.94 (s; CHC₆H₅), 105.82 (s; 4-C-Pz), 75.67 (s; thf), 68.07 (s; CHC₆H₅), 25.82 (s; thf), 14.23 (s; 3-Me-Pz), 13.00 (s; 5-Me-Pz),

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12;73 ppm (s, 5-*Me*-Pz); IR (KBr): $\tilde{\nu}\!=\!2525$ cm $^{-1}$ (B–H); elemental analysis calcd (%) for $C_{66}H_{82}N_{14}B_2O_4Y_2$: C 59.38, H 6.19, N 14.69; found: C 59.67, H 6.22, N 14.45.

Synthesis of $[Tp^{Me2}YCl(\eta^2-N(Ph)C{CHPh(SiMe_3)}O)(thf)]$ (4): In a glove box, Me₃SiCl (0.054 g, 0.50 mmol) was slowly added to a solution of compound 3 (0.667 g, 0.50 mmol) in THF (10 mL) at RT. After stirring overnight, the reaction mixture was concentrated to dryness under reduced pressure. The residue was dissolved in toluene (6 mL). Colorless crystals of compound 4 were achieved in 74% yield (0.574 g) by the diffusion of n-hexane into a solution of compound 4 in toluene. ¹H NMR (400 MHz, C_6D_6 , RT): $\delta = 7.03-7.45$ (m, 10H; C_6H_5), 5.64 (s, 1H; 4H-Tp^{Me2}), 5.51 (s, 2H; 4H-Tp^{Me2}), 3.59 (m, 4H; O(CH₂CH₂)₂), 3.16 (s, 1H; CHPh), 2.19 (s, 6H; CH₃-Tp^{Me2}), 2.06 (s, 12H; CH₃-Tp^{Me2}), 1.18 (m, 4H; O(CH₂CH₂)₂), 0.35 (s, 3H; Si(CH₃)₃), 0.30 ppm (s, 6H; Si(CH₃)₃); ¹³C NMR (100 MHz, C_6D_6 , RT): $\delta = 183.35$ (s; OCN), 150.79 (s; 3-C-Pz), 144.15 (s; 3-C-Pz), 139.14 (s; 5-C-Pz), 137.89 (s; 5-C-Pz), 129.34 (s; C₆H₅), 129.18 (s; C₆H₅), 128.57 (s; C_6H_5), 128.06 (s; C_6H_5), 125.70 (s; C_6H_5), 125.35 (s; C_6H_5), 105.99 (s; 4-C-Pz), 70.77 (s; thf), 25.01 (s; thf), 21.46 (s; CHSiMe₃C₆H₅), 14.26 (s; 3-Me-Pz), 13.04 (s; 5-Me-Pz), 1.43 (s; SiMe₃), -1.46 ppm (s; SiMe₃); elemental analysis calcd (%) for C₃₆H₅₀BClN₇O₂SiY: C 55.71, H 6.49, N 12.63; found: C 55.96, H 6.63, N 12.41.

Synthesis of $[Tp^{Me^2}Y(CH_2Ph){(ArN)_2C(CH_2Ph)}]$ (5, $Ar = C_6H_3iPr_2$ -2,6): In a glove box, *N*,*N*'-2,6-diisopropylphenylcarbodiimide (BPC, 0.182 g, 0.50 mmol) was added to a solution of compound 1 (0.320 g, 0.50 mmol)

in THF (15 mL) at RT. The pale-yellow solution was stirred for 12 h. After removing the solvent under reduced pressure, the residue was dissolved in toluene (8 mL). The solution was layered with n-hexane to afford colorless crystals of compound 5·C₇H₈. Yield: 0.460 g (90%); ¹H NMR (400 MHz, C_6D_6 , RT): $\delta = 5.96-7.28$ (m, 16H; C_6H_5 or C_6H_3), 5.63 (s, 1H; 4H-Tp^{Me2}), 5.30 (s, 2H; 4H-Tp^{Me2}), 3.95 (m, 2H; CH-(CH₃)₂), 3.84 (s, 2H; (ArN)₂CCH₂Ph), 3.45 (m, 2H; CH-(CH₃)₂), 2.50 (s, 3H; CH₃ of Tp^{Me2}), 2.11 (s, 2H; CH₂Ph), 2.07 (s, 6H; CH₃ of Tp^{Me2}), 1.94 (s, 3H; CH₃ of Tp^{Me2}), 1.87 (s, 6H; CH₃ of Tp^{Me2}), 1.62 (d, J(H,H) = 6.4 Hz, 6H; CH(CH₃)₂), 1.50 (d, J(H,H) = 6.4 Hz, 6H; CH(CH₃)₂), 0.93 (d, J(H,H) =6.4 Hz, 6H; CH(CH₃)₂), 0.84 ppm (d, J(H,H)=6.4 Hz, 6H; CH(CH₃)₂); ¹³C NMR (100 MHz, C₆D₆, RT): $\delta = 179.42$ (s; NCN), 154.63 (s; 3-C-Pz), 149.78 (s; 3-C-Pz), 145.80 (s; 5-C-Pz), 145.58 (s; 5-C-Pz), 143.64 (s; 5-C-Pz), 142.89(s; 5-C-Pz), 129.87 (s; C_6H_5 or C_6H_3), 128.54 (s; C_6H_5 or C_6H_3), 126.79 (s; C₆H₅ or C₆H₃), 125.24 (s; C₆H₅ or C₆H₃), 125.15 (s; C₆H₅ or C_6H_3), 124.51 (s; C_6H_5 or C_6H_3), 124.00 (s; C_6H_5 or C_6H_3), 117.21 (s; C₆H₅ or C₆H₃), 106.64 (s; 4-C-Pz), 56.42 (d, J-(Y,C)=34 Hz; Y-CH₂C₆H₅), 35.24 (s; (ArN)₂CCH₂Ph), 28.21 (s; CHMe2), 25.40 (s; CHMe2), 25.30 (s; CHMe2), 14.38 (s; 3-Me-Pz), 13.06 ppm (s; 5-Me-Pz); elemental analysis calcd (%) for C₆₁H₇₈BN₈Y: C 71.62, H 7.68, N 10.95; found: C 71.35, H 7.56, N 11.14.

Synthesis of $[(Tp^{Me2})_2Y]^+[Tp^{Me2}Y(N=C=CHPh)_3]^-(6)$: In a glove box, to a solution of compound 1 (0.320 g, 0.50 mmol) in THF (15 mL) was dropwise added $PhCH_2CN$ (0.059 g, 0.5 mmol). After stirring for 24 h at ambient temperature, the solution was concentrated to dryness under reduced pressure. To the residue was added toluene (7 mL) and then *n*-hexane was diffused into the concentrated toluene solution gave colorless crystals of compound 6. Yield: 0.167 g (70%, based on the reaction stoichiometry); ¹H NMR (400 MHz, [D₈]THF, RT): $\delta = 7.00-7.31$ (m, 15H; C₆H₅), 5.94 (s, 3H; NCCHPh), 5.75 (s, 6H; 4H-Tp^{Me2}), 5.60 (s, 3H; 4H-Tp^{Me2}), 2.37 (br, 36H; CH₃ of Tp^{Me2}), 1.78 ppm (br, 18H; CH₃ of Tp^{Me2}); ¹³C NMR (100 MHz, [D₈]THF, RT): δ=206.02 (s; NCCHPh), 151.76 (s; 3-C-Pz), 145.93 (s; 5-C-Pz), 129.48 (s; C₆H₅), 128.72 (s; C₆H₅), 127.73 (s; C₆H₅), 120.42 (s; C₆H₅), 107.23 (s; 4-C-Pz), 91.95 (s; NCCHPh), 13.70 (s; 3-Me-Pz), 13.24 ppm (s; 5-Me-Pz); elemental analysis calcd (%) for C69H84B3N21Y2: C 58.45, H 5.97, N 20.75; found: C 58.71, H 6.02, N 20.48.

Synthesis of $[(Tp^{Me2}Y)_2(\mu-Pz)_3[\mu-\eta^1:\eta^3-NC(CH_2Ph)CHPh]]$ (7, Pz = 3.5dimethylpyrazolyl): In a glove box, a mixture of compound 1 (0.320 g, 0.50 mmol) and PhCH₂CN (0.059 g, 0.5 mmol) in toluene (15 mL) was heated in 120 °C for 24 h. The solution was concentrated to dryness under vacuum, the residue was washed with *n*-hexane $(2 \times 10 \text{ mL})$, and the solution in n-hexane was slowly vaporized in the glove box to afford colorless crystals of compound 7. Yield: 0.100 g (34% based on the Y metal); ¹H NMR (400 MHz, C₆D₆, RT): $\delta = 6.79-7.13$ (m, 10H, C₆H₅), 5.60 (two overlapping peaks, 8H; 4H-Tp^{Me2} and 4H-pyrazolyl), 4.02 (s, 1H; CHPh), 3.59 (s, 2H; CH₂Ph), 1.99–2.39 (m, 36H; CH₃ of Tp^{Me2}), 1.64 (s, 3H; 3-CH₃-pyrazolyl), 1.40 (s, 3H; 3-CH₃-pyrazolyl), 1.24 ppm (s, 6H; 5-CH₃-pyrazolyl); ¹³C NMR (100 MHz, C₆D₆, RT): δ = 208.64 (s; NCC), 150.92 (s; 3-C-Pz), 150.15 (s; 3-C-Pz), 144.99 (s; 5-C-Pz), 142.97 (s; 5-C-Pz), 137.89 (s; 3-C-pyrazolyl), 131.46 (s; 5-C-pyrazolyl), 129.33 (s; C₆H₅), 128.58 (s; C₆H₅), 128.19 (s; C₆H₅), 128.17 (s; C₆H₅), 127.62 (s; C₆H₅), 125.71 (s; C₆H₅), 105.98 (s; 4-C-Pz), 105.25 (s; 4-C-pyrazolyl), 43.77 (s; NCCHC₆H₅), 31.99 (s; CH₂C₆H₅), 14.38 (s; 3-Me-Pz), 13.13 (s; 3-Me-pyrazolyl), 13.05 (s; 5-Me-Pz), 12.63 ppm (s; 5-Me-pyrazolyl); elemental analysis calcd (%) for C55H71B2N17Y2: C 56.48, H 6.12, N 20.36; found: C 56.21, H 6.05, N 20.63.

X-ray data collection, structure determination, and refinement: Single crystals of complexes 1–7 suitable for X-ray diffraction were sealed under a nitrogen atmosphere in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART

Table 1. Crystal and data-collection parameters of complexes 1, 2, and 3.

	1	2	3.THF			
formula	C33H44BN6OY	$C_{60}H_{88}B4N_{24}S_4Y_4$	$C_{66}H_{82}B_2N_{14}O_4Y_2$			
$M_{ m w}$	640.46	1672.66	1334.90			
crystal color	colorless	colorless	colorless			
crystal dimensions [mm]	$0.15 \times 0.10 \times 0.06$	$0.20 \times 0.12 \times 0.10$	$0.20 \times 0.15 \times 0.08$			
crystal system	triclinic	cubic	monoclinic			
space group	$P\bar{1}$	Fd-3	P21/c			
a [Å]	10.771(4)	24.966(6)	22.118(7)			
b [Å]	11.285(4)	24.966(6)	15.085(4)			
c [Å]	16.001(6)	24.966(6)	21.202(6)			
α [Å]	80.193(5)	90.00	90.00			
B [°]	81.410(4)	90.00	98.694(5)			
γ [°]	63.949(4)	90.00	90.00			
V [Å ³]	1715.8(11)	15562(6)	1874.2(10)			
Ζ	2	8	4			
$ ho_{ m calcd} [m g cm^{-3}]$	1.240	1.428	1.268			
$\mu \ [\mathrm{mm}^{-1}]$	1.733	3.144	1.706			
F (000)	672	6848	2784			
radiation	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$			
(λ=0.710730 Å)						
T [K]	293(2)	293(2)	293(2)			
scan type	ω -2 θ	ω -2 θ	ω -2 θ			
θ range [°]	2.02-25.10	1.41-25.58	1.64-25.01			
h,k,l range	-11 < h < 12	-29 < h < 30	-23 < h < 26			
	-13 < k < 12	-30 < k < 30	-17 < k < 9			
	-19 < l < 16	-30 < l < 22	-24 < l < 25			
total reflns	7107	16425	28471			
unique reflns	5953	1237	12297			
	[R(int)=0.0471]	[R(int) = 0.0567]	[R(int)=0.1474]			
completeness to θ [%]	97.4 ($\theta = 25.10$)	$100 \ (\theta = 25.58)$	99.9 ($\theta = 25.01$)			
max transmission	0.9032,	0.7459,	0.8756,			
min transmission	0.7811	0.5748	0.7266			
refinement method	full-matrix least-squares on F^2					
data/restraints/parameters	5953/1/382	1237/0/75	12297/19/786			
GOF on F^2	0.977	1.078	1.002			
final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0689$	$R_1 = 0.0323$	$R_1 = 0.0640$			
	$wR_2 = 0.1711$	$wR_2 = 0.0848$	$wR_2 = 0.0933$			
R indices (all data)	$R_1 = 0.1438$	$R_1 = 0.0484$	$R_1 = 0.2150$			
	$wR_2 = 0.2144$	$wR_2 = 0.0945$	$wR_2 = 0.1138$			
largest diff. peak	0.896,	0.296,	0.764,			
and hole $[e A^{-3}]$	-0.993	-0.244	-0.439			

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Apex CCD diffractometer by using graphite-monochromated MoKa radiation ($\lambda = 0.71073$ Å). During the collection of the intensity data, no significant decay was observed. The intensities were corrected for Lorentzpolarization effects and empirical absorption by using the SADABS program.^[22] The structures were solved by using direct methods with the SHELXL-97 program.^[23] All non-hydrogen atoms were located from the difference Fourier syntheses. The H atoms were included at calculated positions with isotropic thermal parameters related to those of the supporting C atoms, but were not included in the refinement. All of the calculations were performed by using the Bruker Smart program. The atomic coordinates and equivalent isotropic displacement parameters, including all of the bond lengths and angles, as well as the anisotropic displacement parameters, are provided in the cif files. The crystal data of compounds ${\bf 6}$ and 7 show some high R values, owing to the poor crystal qualities. A summary of the crystallographic data and selected experimental information are listed in Table 1 and Table 2. CCDC-923866 (1), CCDC-923868 (2), CCDC-923869 (3), CCDC-923871 (4), CCDC-923867 (5), CCDC-923865 (6), and CCDC-923870 (7) 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.

Table 2	Crystal and	data-collection	parameters o	f comp	lexes 4 5	6 a	nd 7
1able 2.	Crystar and	uata-concerton	parameters	n comp	$\mathbf{I} \subset \mathbf{A} \subset \mathbf{S} = \mathbf{A}, \mathbf{S}$, u , a	nu /.

	4	$5 \cdot 1/2 C_7 H_8$	6	7
formula	C36H50BCIN7O2SiY	C61H78BN8Y	$C_{69}H_{84}B_3N_{21}Y_2$	$C_{55}H_{71}B_2N_{17}Y_2$
$M_{ m w}$	776.09	1023.03	1417.82	1169.73
crystal color	colorless	colorless	colorless	colorless
crystal dimensions [mm]	$0.15 \times 0.10 \times 0.08$	$0.15 \times 0.10 \times 0.06$	$0.20 \times 0.15 \times 0.12$	$0.18 \times 0.12 \times 0.08$
crystal system	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	C2/c	$P\bar{1}$	$P\bar{1}$
a [Å]	9.238(2)	41.320(11)	13.235(4)	12.740(5)
b [Å]	11.125(3)	11.088(3)	16.875(5)	13.349(5)
<i>c</i> [Å]	22.057(6)	25.297(7)	22.788(7)	21.247(8)
a [°]	95.400(3)	90.00	77.708(5)	83.124(5)
β[°]	96.336(3)	91.689(4)	87.210(5)	75.276(6)
γ [°]	113.859(3)	90.00	68.371(4)	87.697(6)
$V[Å^3]$	2036.3(9)	11585(5)	4620(3)	3469(2)
Z	2	8	2	2
$\rho_{\rm calcd} [\rm g \rm cm^{-3}]$	1.266	1.173	1.019	1.120
$\mu [\mathrm{mm}^{-1}]$	1.566	1.051	1.293	1.708
F (000)	812	4352	1476	1216
radiation ($\lambda = 0.710730$ Å)	Mo _{Kα}	Mo _{Kα}	$Mo_{K\alpha}$	Mo _{Kα}
<i>T</i> [K]	293(2)	293(2)	293(2)	293(2)
scan type	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ
θ range [°]	1.88-25.05	1.61-26.01	1.33-25.01	1.54-25.00
h,k,l range	-10 < h < 10	-50 < h < 45	-15 < h < 14	-12 < h < 15
	-8 < k < 13	-13 < k < 13	-20 < k < 17	-15 < k < 15
	-24 < l < 26	-31 < l < 27	-27 < l < 24	-25 < l < 22
total reflns	8517	25737	19270	14486
unique reflns	7066	11346	15951	12006
	[R(int) = 0.0859]	[R(int) = 0.0721]	[R(int) = 0.0647]	[R(int) = 0.0682]
completeness to θ [%]	98.0 $(\theta = 25.05)$	99.4 ($\theta = 26.01$)	97.9 ($\theta = 25.01$)	98.2 $(\theta = 25.00)$
max. and min.	0.8850,	0.9396,	0.8603,	0.8755,
transmission	0.7991	0.8583	0.7820	0.7486
refinement method		full-matrix least-	squares on F^2	
data/restraints/parameters	7066/0/455	11346/0/647	15951/3/880	12006/0/688
GOF on F^2	1.008	0.871	0.906	0.948
final R indices	$R_1 = 0.0510$	$R_1 = 0.0481$	$R_1 = 0.0941$	$R_1 = 0.0995$
$[I>2\sigma(I)]$	$wR_2 = 0.1054$	$wR_2 = 0.0834$	$wR_2 = 0.2065$	$wR_2 = 0.2744$
R indices (all data)	$R_1 = 0.0813$	$R_1 = 0.1168$	$R_1 = 0.2013$	$R_1 = 0.1752$
	$wR_2 = 0.1125$	$wR_2 = 0.0978$	$wR_2 = 0.3014$	$wR_2 = 0.3119$
largest diff. peak	0.549,	0.489,	1.291,	1.573,
and hole $[e\bar{\mathbf{A}}^{-3}]$	-0.692	-0.433	-0.641	-1.207

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