Synthesis, Structure, and Reactivity of $[\sigma:\eta^1:\eta^5\text{-}(OCH_2)(Me_2NCH_2)C_2B_9H_9]Ti(NR_2)$ (R = Me, Et)

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Interaction of $[Me_3NH][7,8\text{-}CH_2OCH_2\text{-}7,8\text{-}C_2B_9H_{10}]$ with $M(NR_2)_4$ gave the simple amine elimination products $[\eta^5\text{-}(CH_2OCH_2)C_2B_9H_9]M(NMe_2)_2(NHMe_2)$ (M = Zr (**2a**), Hf (**2b**)) or the unexpected C−O bond cleavage products $[\sigma:\eta^1:\eta^5\text{-}(OCH_2)(Me_2NCH_2)C_2B_9H_9]Ti(NR_2)$ (R = Me (**3a**), Et (**3b**)). The higher oxophilicity of the Ti center provides the driving force for the latter reactions. It is suggested that the C−O bond cleavage is prior to the amine elimination in the formation of **3a**,**b**. This serves as a convenient and practical method for the preparation of constrained-geometry half-sandwich metallacarboranes with two different functional sidearms. Complex **3a** can undergo a clean amine exchange reaction to produce new constrained-geometry titanacarborane amides. Reactions of **3a** with unsaturated molecules CyN═C═NCy, S═C═S, Xyl−N═C, PhC≡N, Bu^nN═C═S, Ph_2C═C═O, and PhN═C═O gave monoinsertion products. They, except for $[\sigma:\eta^1:\eta^5\text{-}(OCH_2)(Me_2NCH_2)C_2B_9H_9]Ti[\eta^3\text{-}CyNC(NMe_2)NCy]$ (**7**), do not react with amines. In sharp contrast, **7** can react readily with Me_2NH to regenerate **3a** and release guanidine, which leads to the discovery of new catalytic guanylation of amines. All new complexes were fully characterized by various spectroscopic techniques and elemental analyses. Most of them were further confirmed by single-crystal X-ray analyses.

Introduction

Constrained-geometry ligands (Cp-D) containing both monocyclopentadienyl (Cp) and σ-heteroatom (D) components have attracted considerable attention.[1] Group 3 and 4 metal complexes derived from these ligands are very active catalysts for polymerization/copolymerization of α-olefins[1,2] and catalytic addition of amines and alkynes to carbodiimides.[3] As an extension of the structural variations in Cp-D constrained-geometry ligands, the dicarbollide ion ($C_2B_9H_{11}^{2-}$) is rationally employed as an η^5 π-ligand instead of the Cp unit in the hope that incorporation of the dicarbollide fragment into the above constrained-geometry ligand framework would provide the opportunities for studying the effects of metal/charge combinations and metal unsaturation on the reactivity of group 4 metal complexes.[4] Several examples of group 4 metallacarboranes bearing tethered Lewis base functionalities have been prepared.[5−7] Their neutral alkyl derivatives can undergo C−H/C−O bond activation,[5c] and the chloride/amide species are active catalysts for ethylene polymerization in the presence of cocatalyst MAO (methyl aluminaoxane).[5d,6a,7c]

We have very recently found an unexpected reaction of $[Me_3NH][7,8\text{-}CH_2OCH_2\text{-}7,8\text{-}C_2B_9H_{10}]$ with $Ti(NMe_2)_4$, which leads to the isolation of a new constrained-geometry half-sandwich titanacarborane amide $[\sigma:\eta^1:\eta^5\text{-}(OCH_2)(Me_2NCH_2)C_2B_9H_9]Ti(NMe_2)$ incorporating two different sidearms; one is strongly bonded to the Ti center by taking the advantage of its high oxophilicity, whereas the other is hemilabile in nature. Preliminary results show that this complex is a very efficient catalyst

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for the guanylation of amines.[8] To understand the reaction pathways and the formation of $[\sigma:\eta^1:\eta^5\text{-}(OCH_2)(Me_2NCH_2)\text{-}C_2B_9H_9]Ti(NMe_2)$ and to study the reactivity pattern of this type of complexes toward unsaturated molecules, we have investigated in detail the reaction of $[Me_3NH][7,8\text{-}CH_2OCH_2\text{-}7,8\text{-}C_2B_9H_{10}]$ with $M(NR_2)_4$ (M = Ti, Zr, Hf; R = Me, Et) and the reactivity of the resultant constrained-geometry titanacarborane amides toward amines, RN=C=NR, S=C=S, Xyl−N=C, PhC≡N, Bu^nN=C=S, Ph_2C=C=O, PhN=C=O, and esters. The full account of this work is reported in this article.

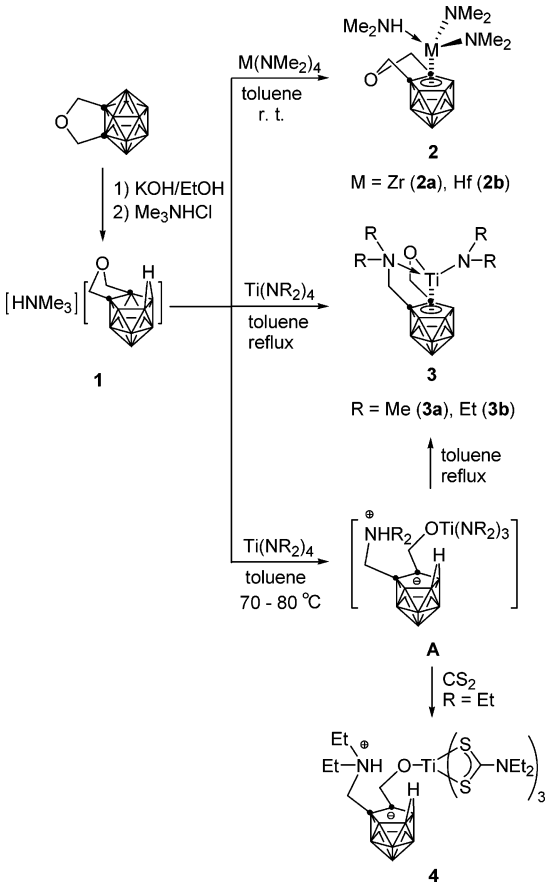
Results and Discussion

Reaction of 1 with $M(NR_2)_4$. μ-1,2-CH_2OCH_2-1,2-$C_2B_{10}H_{10}$ was prepared according to a literature method[9] and was converted to $[Me_3NH][\mu\text{-}7,8\text{-}CH_2OCH_2\text{-}7,8\text{-}C_2B_9H_{10}]$ (**1**) in 95% yield in KOH/EtOH solution followed by treatment with Me_3NHCl. Compound **1** reacted readily with 1 equiv of $M(NMe_2)_4$ (M = Zr, Hf) in toluene at room temperature to give the amine elimination[10] products $[\eta^5\text{-}(CH_2OCH_2)C_2B_9H_9]M(NMe_2)_2(NHMe_2)$ (M = Zr (**2a**), Hf (**2b**)) in almost quantitive yields (Scheme 1). They are stable in refluxing toluene and do not react further with another equivalent of **1**.

The ^{1}H NMR spectra of **2a**,**b** are very similar. They showed in pyridine-d_5 two doublets at ∼4.1 and ∼3.6 ppm with ^2J = 7.5 Hz assignable to the axial and equatorial protons of the methylene units, a singlet at ∼3.1 ppm corresponding to the two dimethylamido groups, and a singlet at ∼2.3 ppm attributable to the coordinated dimethylamine. Their ^{13}C NMR spectra were consistent with the ^{1}H NMR results. The ^{11}B NMR spectra of both **2a** and **2b** in pyridine-d_5 exhibited a 1:1:2:2:2:1 pattern. The compositions of **2a**,**b** were further confirmed by elemental analyses.

Under the same reaction conditions, however, treatment of **1** with $Ti(NR_2)_4$ (R = Me or Et) afforded a mixture of products, which were slowly converted to a major species upon heating at 80 °C and finally to another major product as the temperature was increased to 110 °C according to the NMR experiments. A suspension of **1** and $Ti(NR_2)_4$ (R = Me or Et) in toluene was then heated to reflux for 6 h to generate unexpected C−O bond cleavage complexes $[\sigma:\eta^1:\eta^5\text{-}(OCH_2)(R_2NCH_2)C_2B_9H_9]Ti(NR_2)$ (R = Me (**3a**), Et (**3b**)) in very good isolated yields. This is a convenient and practical method for the preparation of constrained-geometry half-sandwich metallacarboranes with two different functional sidearms, which are introduced in a single reaction. Many attempts to isolate the intermediate formed at 80 °C as indicated in NMR experiments failed due to its instability. We then employed an unsaturated molecule to trap this intermediate. Treatment of **1** with 1 equiv of $Ti(NEt_2)_4$ at 80 °C for 6 h (monitored by ^{11}B NMR), followed by addition of excess CS_2, gave, after recrystallization from THF, the insertion product $[\sigma\text{-}(OCH_2)(Et_2NHCH_2)C_2B_9H_{10}]Ti(\eta^3\text{-}S_2CNEt_2)_3$ (**4**) in 36% yield (Scheme 1).

Scheme 1



In the ^{1}H NMR spectrum (pyridine-d_5) of **3a**, four doublets at 5.50, 5.47 ppm with ^2J = 11.1 Hz and 3.61, 3.10 ppm with ^2J = 14.4 Hz assignable to the two sidearm CH_2 units, one singlet at 3.17 ppm corresponding to the dimethylamido protons, and two singlets at 2.31 and 2.28 ppm attributable to the sidearm N(CH_3)$_2$ group were observed. Its ^{13}C NMR spectrum showed two CH_2 signals at 77.2 and 65.5 ppm and three N(CH_3)$_2$ resonances at 50.8, 50.3, and 44.1 ppm, respectively. Inequivalent methyls of the sidearm amido group in the NMR spectra clearly indicate that the tethered amine is coordinated to the Ti metal center even in pyridine solution. The ^{11}B NMR of **3a** exhibited a 1:1:1:1:1:1:1:1:1 pattern in the range 13 to −18 ppm. Similar characteristics were also observed in the NMR spectra of **3b**. The ^{1}H NMR spectrum of **4** exhibited, in addition to the resonances of ethyl protons, a broad singlet at −2.05 ppm corresponding to the bridging B*H*B proton and four doublets at 5.46, 4.86 ppm with ^2J = 12.0 Hz and 3.78, 3.52 ppm with ^2J = 14.1 Hz assignable to the two sidearm CH_2 groups. A characteristic S_2CN carbon resonance at 202.8 ppm was observed in the ^{13}C NMR spectrum.[11] Its ^{11}B NMR displayed a 4:3:1:1 pattern, which is significantly different from that of **3b**.

Single-crystal X-ray diffraction studies confirmed that both **3a**,**b** adopt a three-legged piano stool structure containing an η^5-dicarbollyl ligand, one amido unit, and tethered amine and alkoxide ligands in the basal positions, as shown in Figures 1 and 2, respectively. It is very clear that a C−O bond is broken and a new C−N bond is formed during the reaction. For easy comparison, key structural parameters are compiled in Table 1. The average Ti−cage atom, Ti−N(sidearm), and Ti−

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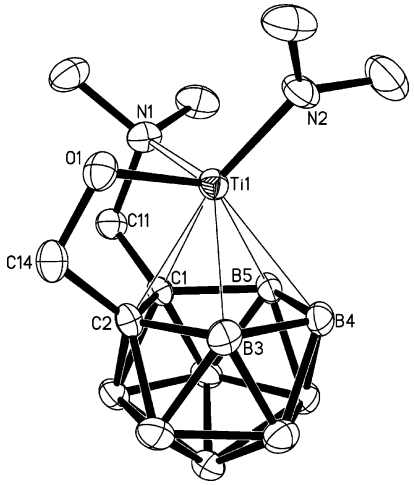

Figure 1. Molecular structure of $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)(Me_2NCH_2)\text{-}C_2B_9H_9]Ti(NMe_2)$ (**3a**).

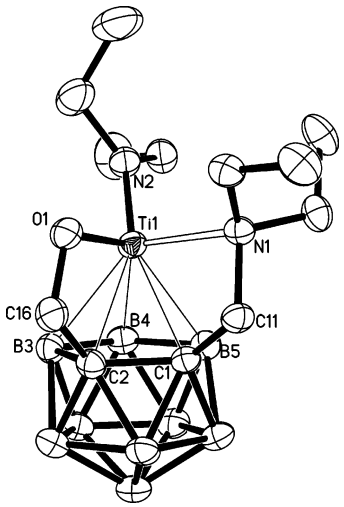

Figure 2. Molecular structure of $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)(Et_2NCH_2)\text{-}C_2B_9H_9]Ti(NEt_2)$ (**3b**).

N(amide) distances of 2.365(4), 2.205(3), and 1.862(3) Å in **3a** and 2.376(4), 2.246(3), and 1.868(3) Å in **3b** are comparable to the corresponding values of 2.432(5), 2.240(3), and 1.895(4) Å in $[\eta^1{:}\eta^5\text{-}(Me_2NCH_2)_2C_2B_9H_9]Ti(NMe_2)_2$,[6b] 2.395(3), 2.196(2), and 1.886(3) Å in $[\eta^1{:}\eta^5\text{-}(Pr^i_2C_6H_3N{=}CH)C_2B_9H_{10}]\text{-}Ti(NMe_2)_2$,[5d] 2.389(10), 2.128(4), and 1.911(4) Å in $[\eta^1{:}\eta^5\text{-}(Me_2C_6H_3N{=}CH)C_2B_9H_{10}]Ti(NMe_2)_2$,[5d] 2.396(5), 2.202(3), and 1.895(4) Å in $[\eta^1{:}\eta^5\text{-}(Me_2N)CH(NMe_2)C_2B_9H_{10}]Ti(NMe_2)_2$,[5d] and 2.413(5), 2.315(3), and 1.900(4) Å in $[\eta^1{:}\eta^5\text{-}(Bz_2NCH_2\text{-}CH_2)C_2B_9H_{10}]Ti(NMe_2)_2$.[6c] The Ti−O distances of 1.833(2) Å in **3a** and 1.845(2) Å in **3b** are shorter than that of 1.879(7) Å in $(\eta^5\text{-}C_5Me_5)Ti[\sigma{:}\eta^5\text{-}(OCHMe)C_2B_9H_{10}]$[12] and 1.869(2) Å in $(\eta^5\text{-}C_5Me_5)[\sigma{:}\eta^5\text{-}(OCHMe)C_2B_9H_{10}]Ti(CH_3CN)$.[12]

The molecular structure of **4** was also confirmed by single-crystal X-ray analyses. It is a zwitterionic salt, in which the Ti atom is η^3-bound to each $S_2C{-}NEt_2$ group and σ-bound to the O atom of the sidearm (Figure 3). As shown in Table 1, the Ti−O distance of 1.833(2) Å in **4** is very close to the corresponding values in **3a**,**b**. The average Ti−S distance of 2.532(1) Å is much shorter than that of 2.642(1) Å in $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)C_2B_{10}H_{10}]Zr(\eta^3\text{-}S_2C{-}NMe_2)_2$,[11] probably owing to steric reasons.

Full characterization of **4** helps us to understand the possible reaction pathway for the formation of **3b**, as shown in Scheme 1. Coordination of the oxygen atom in **1** to the Ti atom followed by nucleophilic attack of the amide leads to the cleavage of the C−O bond and the formation of a new N−C bond. Proton exchange between Me_3NH^+ and the newly formed amine results in the formation of an intermediate **A**. Insertion of CS_2 into the Ti−N bonds in **A** generates the product **4**. On the other hand, intramolecular amine elimination of **A** affords **3b**, which is promoted by heat. The higher oxophilicity of the Ti atom over the Zr and Hf resulted from the size effect,[13] facilitates the breaking of the C−O bond, and leads to different pathways in the reactions of $M(NMe_2)_4$ with **1**.

Reaction of 3a with Amines. Amine exchange reaction is a useful method for the preparation of metal amides. Complex **3a** reacted readily with 1 equiv of 4-methoxyaniline or 2 equiv of 2-amino-3-picoline in toluene at room temperature to give $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)(Me_2NCH_2)C_2B_9H_9]Ti[NH(C_6H_4\text{-}4\text{-}OMe)]$ (**5**) or $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)(Me_2NCH_2)C_2B_9H_9]Ti[\sigma{:}\eta^1\text{-}(2\text{-}NH\text{-}3\text{-}CH_3{-}C_5H_3N)][\eta^1\text{-}C_5H_3N\text{-}2\text{-}NH_2\text{-}3\text{-}CH_3]$ (**6**) in 61% and 46% yields, respectively (Scheme 2). The ^{1}H NMR spectra indicated the absence of the Me_2N amido groups in both **5** and **6** and supported a molar ratio of one aniline moiety per cage in **5** and two picoline units per cage in **6**. The ^{11}B NMR spectrum of **5** exhibited a 1:1:1:1:1:1:1:1:1 pattern, whereas a 1:1:1:2:1:1:2 pattern was observed for **6**.

An X-ray analysis revealed that **6** adopts a distorted-octahedral geometry by an η^5-dicarbollyl ligand, one oxygen and one nitrogen from the sidearms, and three nitrogens from the two picoline units, and showed one and a half toluene of solvation in the unit cell (Figure 4). The $Ti{-}N_{arm}$ and $Ti{-}O_{arm}$ distances of 2.398(3) and 1.931(2) Å in **6** are significantly longer than those observed in its parent complex **3a** (Table 1), probably due to very crowded environments around the Ti atom in **6**. The Ti−N(4) distance of 2.026(3) Å is much shorter than the Ti−N(5) distance of 2.212(3) Å, suggesting there is no charge delocalization over the N(4)−C(31)−N(5) unit.

Reaction of 3a with Unsaturated Molecules. Reaction of **3a** with 1 equiv of DCC (dicyclohexylcarbodiimide) in toluene gave, after simple workup, the monoinsertion product $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)(Me_2NCH_2)C_2B_9H_9]Ti[\eta^3\text{-}CyNC(NMe_2)NCy]$ (**7**) in 82% isolated yield (quantitative NMR yield). A characteristic CN_3 resonance at 174.9 ppm was observed in the ^{13}C NMR spectrum of **7**. The proton chemical shift of the Me_2N amido group was shifted from 3.17 ppm in **3a** to 2.80 ppm in **7**. Its ^{11}B NMR displayed a 1:5:2:1 pattern, which is very different from that of **3a**.

Single-crystal X-ray analyses confirmed that DCC inserted exclusively into the Ti−N σ-bond to form a guanidine unit, as shown in Figure 5. The C(15)−N(2)/N(3)/N(4) distances of 1.341(3)/1.373(3)/1.362(3) Å are similar, indicating the partial delocalization of electrons over N(2), N(3), N(4), and C(15) atoms. This argument is supported by the planarity of N(3), with the sum of angles of 359.9(2)°.

Treatment of **7** with Me_2NH regenerated **3a** with the formation of $CyN{=}C(NMe_2)NHCy$ as indicated by NMR analyses. This result suggests that **3a** can catalyze hydroamination of carbodiimides. This finding leads to a successful development of a new atom-economical catalytic process for the guanylation of amines with a very broad substrate scope of primary, secondary, heterocyclic, aliphatic, and aromatic amines.[8] The proposed catalytic cycle involves the insertion of carbo-

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Table 1. Selected Bond Lengths (Å) and Angles (deg)

	3a	3b	4	6	7	11b[a]	12	13	14	15
av Ti−cage atom	2.365(4)	2.376(4)		2.422(4)	2.418(3)	2.393(4)	2.377(4)	2.409(4)	2.402(4)	2.383(3)
Ti−O_{arm}	1.833(2)	1.845(2)	1.833(2)	1.931(2)	1.901(2)	1.882(2)	1.850(2)	1.873(2)	1.860(2)	2.059(1)
Ti−N_{arm}	2.205(3)	2.246(3)		2.398(3)	2.322(2)	2.353(3)	2.259(3)	2.311(3)	2.327(2)	2.358(2)
Ti−N	1.862(3)	1.868(3)		2.315(3)	2.179(2)	2.062(3)	2.288(2)	2.089(3)		
				2.026(3)	2.028(2)					
				2.212(3)						
Ti−O							1.896(2)	2.041(2)	2.056(2)	2.040(2)
									1.852(2)	1.775(2)
Ti−S			2.532(1)[b]			2.492(1)				
C_{cage}−C−N_{arm}	106.6(2)	107.0(2)		106.9(3)	107.1(2)	107.6(3)	105.9(2)	105.8(2)	106.1(2)	107.0(2)
C_{cage}−C−O_{arm}	103.1(2)	102.6(3)		103.2(3)	103.1(2)	103.4(3)	102.7(2)	101.7(2)	103.3(2)	103.2(2)
Ti−O_{arm}−C	105.6(2)	106.9(2)		107.0(2)	107.3(1)	106.1(2)	107.8(2)	108.3(2)	108.2(2)	103.9(1)
Ti−N_{arm}−C	94.3(2)	92.9(2)		93.7(2)	96.0(1)	93.1(2)	94.9(2)	94.2(2)	94.9(2)	94.8(1)

[a] Average values of two independent molecules in the unit cell. [b] Average value of six Ti−S bonds.

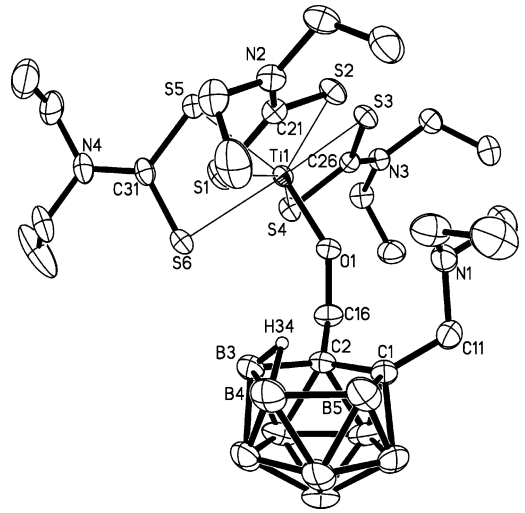


Figure 3. Molecular structure of [σ-(OCH_2)(Et_2NHCH_2)$C_2B_9H_{10}$]-Ti(η^3-S_2CNEt_2)$_3$ (**4**).

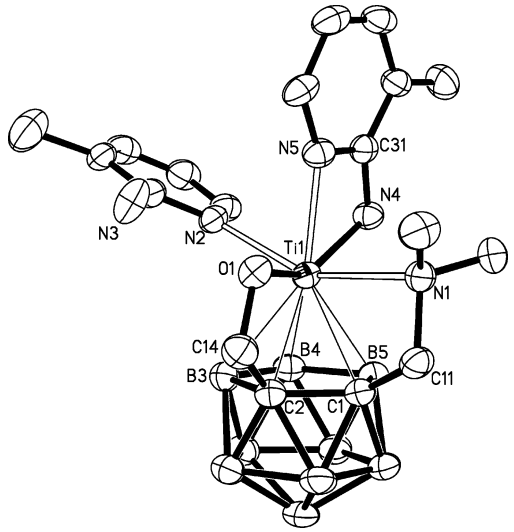
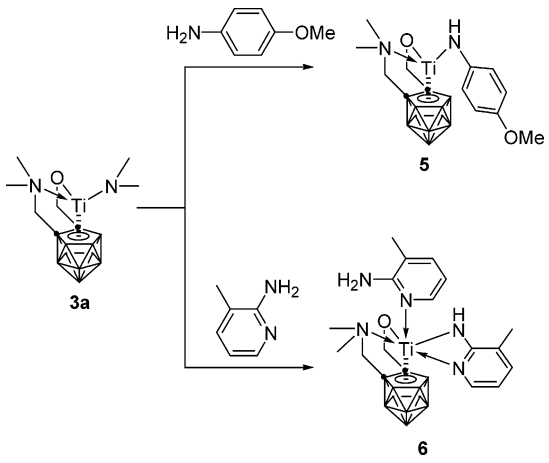


Figure 4. Molecular structure of [σ:η^1:η^5-(OCH_2)(Me_2NCH_2)-$C_2B_9H_9$]Ti[σ:η^1-(2-NH-3-CH_3−C_5H_3N)][η^1-C_5H_3N-2-NH_2-3-CH_3] (**6**) (the solvated toluene molecules are not shown).

Scheme 2



diimide into the Ti−amide bond followed by the protonation of the resultant intermediate with amines. These interesting results prompt us to explore the reactivity pattern of **3a** (as shown in Scheme 3) in search of new catalytic hydroaminations of unsaturated organic molecules.

Interaction of **3a** with 1.5 equiv of CS_2 in toluene at room temperature afforded [σ:η^1:η^5-(OCH_2)(Me_2NCH_2)$C_2B_9H_9$]Ti(η^3-S_2CNMe_2) (**8**) in 94% isolated yield. Complex **8** is insoluble in toluene, in which **3a** is soluble, which facilitates the separation. The ^{1}H NMR spectrum in pyridine-d_5 showed an upfield shift for $S_2CN(CH_3)_2$ protons and significant downfield shifts for all sidearm protons in comparison with its parent complex **3a**. A

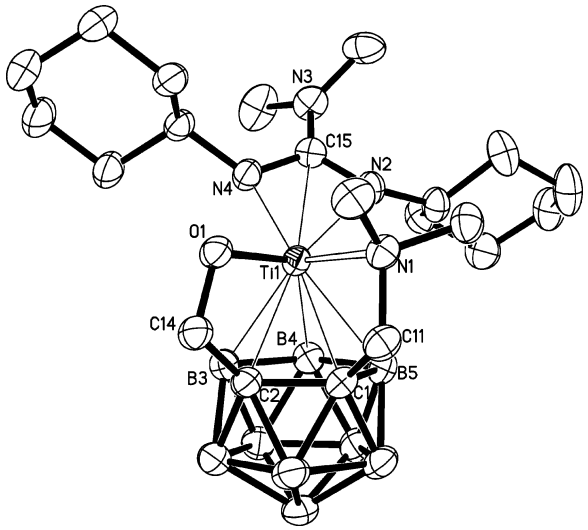
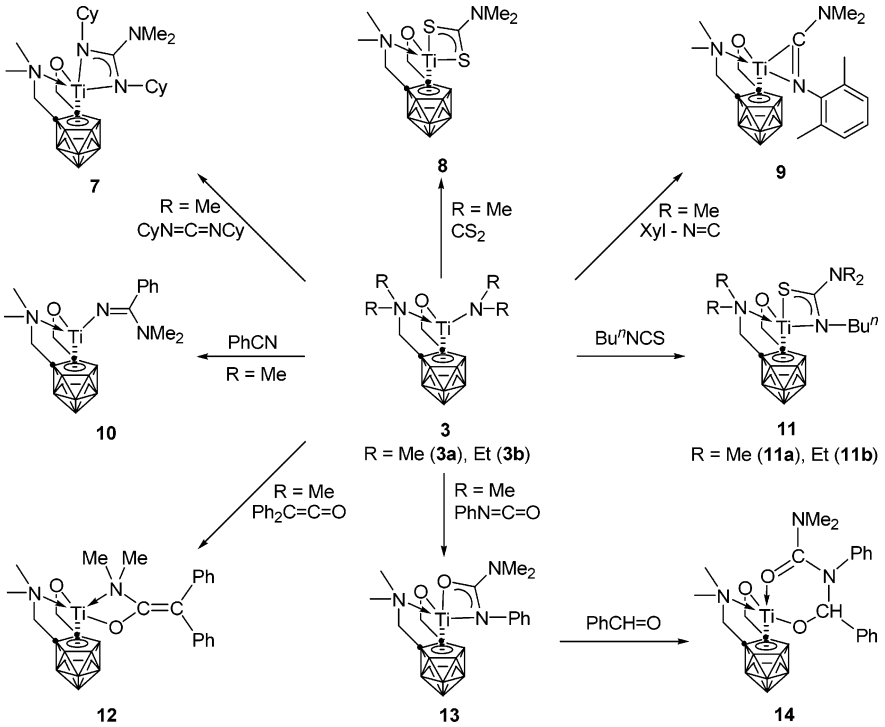


Figure 5. Molecular structure of [σ:η^1:η^5-(OCH_2)(Me_2NCH_2)-$C_2B_9H_9$]Ti[η^3-CyNC(NMe_2)NCy] (**7**).

unique ^{13}C resonance of the S_2CN unit at 201.3 ppm, which is very close to that of 202.8 ppm in **4**, 201.6 and 199.2 ppm in [η^5:σ-$Me_2C(C_9H_6)C_2B_{10}H_{10}$]Zr($\eta^3$-$S_2CNMe_2$)$_2$,[11] was also observed. The ^{11}B NMR displayed a 1:1:1:1:1:2:1:1 pattern. The composition of **8** was further confirmed by elemental anlyses.

Reaction of **3a** with 1 equiv of 2,6-xylylisonitrile in refluxing toluene generated [σ:η^1:η^5-(OCH_2)(Me_2NCH_2)$C_2B_9H_9$]Ti[η^2-

Scheme 3



$C(NMe_2)$═$N(C_6H_3$-2,6-$Me_2)$] (**9**) in 72% isolated yield. In addition to the sidearm and xylyl protons, two singlets at 3.38 and 2.64 ppm assignable to the N═$CN(CH_3)_2$ methyl protons (versus one singlet of amido protons at 3.17 ppm in **3a**) were observed in the ^{1}H NMR spectrum of **9**, indicating the restricted rotation around the C−NMe_2 single bond on the NMR time scale. This phenomenon is also observed in other metal−η^2-iminocarbamoyl complexes.[14] A characteristic signal of N*C*═N at 197.6 ppm was found in the ^{13}C NMR spectrum of **9**. Its ^{11}B NMR exhibited a 1:2:2:2:2 pattern. The composition was further confirmed by elemental analyses.

Treatment of **3a** with 1 equiv of benzonitrile in refluxing toluene afforded [σ:η^1:η^5-$(OCH_2)(Me_2NCH_2)C_2B_9H_9$]Ti[N═$C(NMe_2)$Ph] (**10**) in 92% isolated yield. In the ^{1}H NMR spectrum, the insertion of PhCN into the Ti−NMe_2 bond was found to result in a downfield shift of all sidearm protons and an upfield shift of amido protons compared to those of **3a**. The ^{13}C chemical shift of the CN_2 unique carbon was observed at 156.3 ppm, which is very close to that of 157.5 and 156.1 ppm observed in [η^5:σ-$Me_2C(C_9H_6)C_2B_{10}H_{10}$]Zr[N═$C(Ph)NMe_2]_2$.[11] The ^{11}B NMR showed a 1:1:1:1:1:1:1:1:1 pattern. Many attempts to grow single crystals failed.

An equimolar reaction of **3** with *n*-butyl isothiocyanate in refluxing toluene gave [σ:η^1:η^5-$(OCH_2)(R_2NCH_2)C_2B_9H_9$]Ti-[$\eta^3$-$SC(NR_2)NBu^n$] (R = Me (**11a**), R = Et (**11b**)) in 76−82% isolated yields. The ^{1}H NMR spectra of **11a**,**b** showed an upfield shift for the amido protons of the $NC(NR_2)S$ unit and a downfield shift for sidearm protons in comparison with those of **3a**,**b**. Unique ^{13}C resonances at 174.7 ppm in **11a** and 171.2 ppm in **11b** were observed. The ^{11}B NMR spectra exhibited a 1:1:1:1:1:1:1:2 pattern for both **11a** and **11b**.

The molecular structure of **11b** was further confirmed by single-crystal X-ray analyses, revealing there are two independent molecules in the unit cell. The representative one is shown in Figure 6. The C(21)−N(2)/N(3) distances of 1.329(5)/1.349(4) Å and planarity of N(3) with a sum of angles of 359.5(3)° suggest the electron delocalization over the $NC(NEt_2)S$ fragment.

Insertion of the C═C or C═O bond of a ketene into the Ti−O or M−N bond has been documented.[15] It is interesting to know how a ketene reacts with **3a**, as it contains both Ti−O and Ti−N bonds. Reaction of **3a** with 1 equiv of diphenylketene in refluxing toluene produced [σ:η^1:η^5-$(OCH_2)(Me_2NCH_2)C_2B_9H_9$]-Ti[$\sigma$:$\eta^1$-$OC(NMe_2)$═$CPh_2$] (**12**) in 84% isolated yield. Complex **12** showed no reactivity toward ketene. It was fully characterized by various spectroscopic techniques and elemental analyses.

Single-crystal X-ray analyses revealed that the Ti center in **12** is coordinated by two N and two O atoms and an η^5-dicarbollyl ligand in a four-legged piano stool geometry, as shown in Figure 7. This result confirms the insertion of the C═O bond into the Ti−N bond and inertness of the Ti−O bond toward the C═C bond of the ketene, probably due to steric reasons. Steric factors may also dominate the migration of the NMe_2 unit, leading to the *trans* arrangement of two amido groups. The C(15)−C(18) distance of 1.338(4) Å suggests a double bond. The Ti−O(2) distance of 1.896(2) Å is comparable to the Ti−O(1) distance of 1.850(2) Å. The Ti−N(1) distance of 2.259(3) Å is close to the Ti−N(2) distance of 2.288(2) Å.

It has been reported that PhNCO can insert into either a Ti−N or Ti−O bond.[16] Reaction of **3a** with PhNCO afforded exclusively [σ:η^1:η^5-$(OCH_2)(Me_2NCH_2)C_2B_9H_9$]Ti[$\eta^3$-$OC(NMe_2)$-NPh] (**13**) in 84% isolated yield. The Ti−O bond in **3a** remains intact. As shown in Figure 8, the arrangment of the two N and

(14) (a) Amor, F.; Sánchez-Nieves, J.; Royo, P.; Jacobsen, H.; Blacque, O.; Berke, H.; Lanfranchi, M.; Pellinghelli, M. A.; Tiripicchio, A. *Eur. J. Inorg. Chem.* **2002**, *11*, 2810. (b) Martins, A. M.; Ascenso, J. R.; de Azevedo, C. G.; Dias, A. R.; Duarte, M. T.; da Silva, J. F.; Veiros, L. F.; Rodrigues, S. S. *Organometallics* **2003**, *22*, 4218. (c) Wang, H.; Wang, Y.; Chan, H.-S.; Xie, Z. *Inorg. Chem.* **2006**, *45*, 5675.

(15) For examples, see: (a) Vuitel, L.; Jacot-Guillarmod, A. *Synthesis* **1972**, *11*, 608. (b) Blandy, C.; Gervais, D. *Inorg. Chim. Acta* **1981**, *47*, 197. (c) Ando, F.; Kohmura, Y.; Koketsu, J. *Bull. Chem. Soc. Jpn.* **1987**, *69*, 1564. (d) Liu, R.; Zhang, C.; Zhu, Z.; Luo, J.; Zhou, X.; Weng, L. *Chem.*−*Eur. J.* **2006**, *12*, 6940.

(16) For examples, see: (a) Wang, H.; Chan, H.-S.; Okuda, J.; Xie, Z. *Organometallics* **2005**, *24*, 3118. (b) Patten, T. E.; Novak, B. M. *Macromolecules* **1993**, *26*, 436. (c) Ghosh, R.; Nethaji, M.; Samuelson, A. G. *J. Organomet. Chem.* **2005**, *690*, 1282.

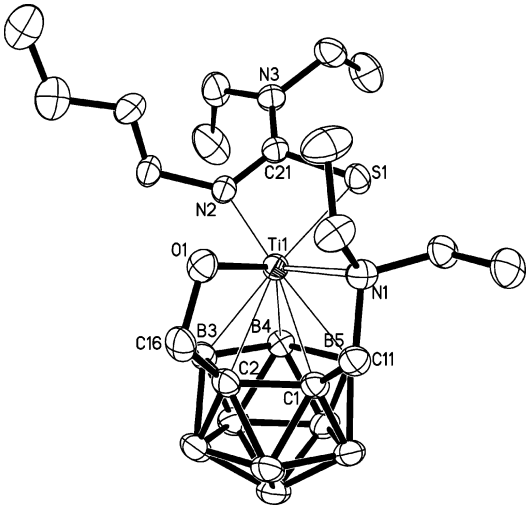


Figure 6. Molecular structure of $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)(Et_2NCH_2)\text{-}C_2B_9H_9]Ti[\eta^3\text{-}SC(NEt_2)NBu^n]$ (**11b**).

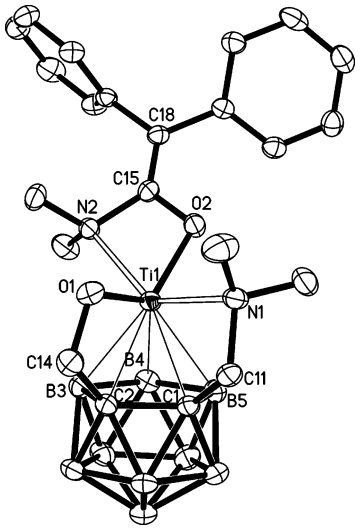


Figure 7. Molecular structure of $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)(Me_2NCH_2)\text{-}C_2B_9H_9]Ti[\sigma{:}\eta^1\text{-}OC(NMe_2){=}CPh_2]$ (**12**).

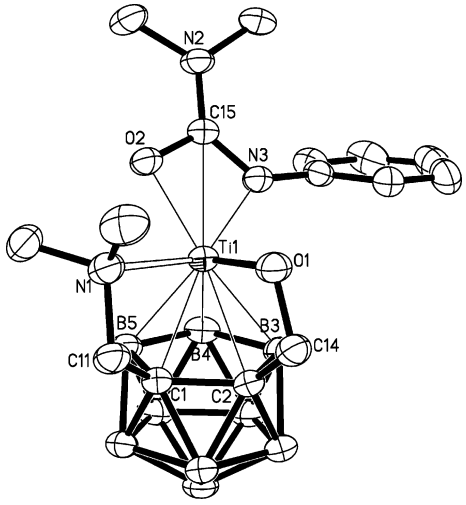


Figure 8. Molecular structure of $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)(Me_2NCH_2)\text{-}C_2B_9H_9]Ti[\eta^3\text{-}OC(NMe_2)NPh]$ (**13**).

two O atoms is similar to that observed in **12**. Two amido fragments are in *trans* positions to avoid steric repulsion. Different from other group 4 metal amide complexes,[11,16] **13** showed no reactivity toward PhNCO. On the other hand, **13**

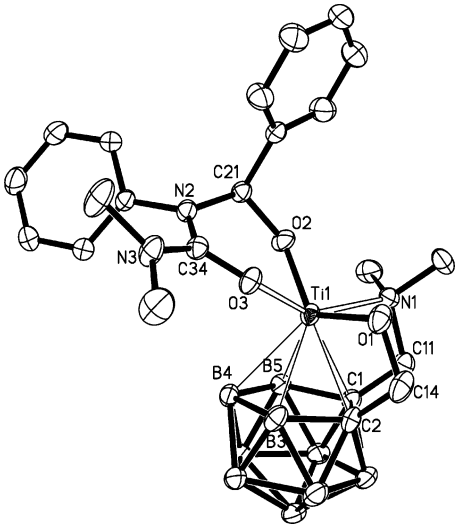
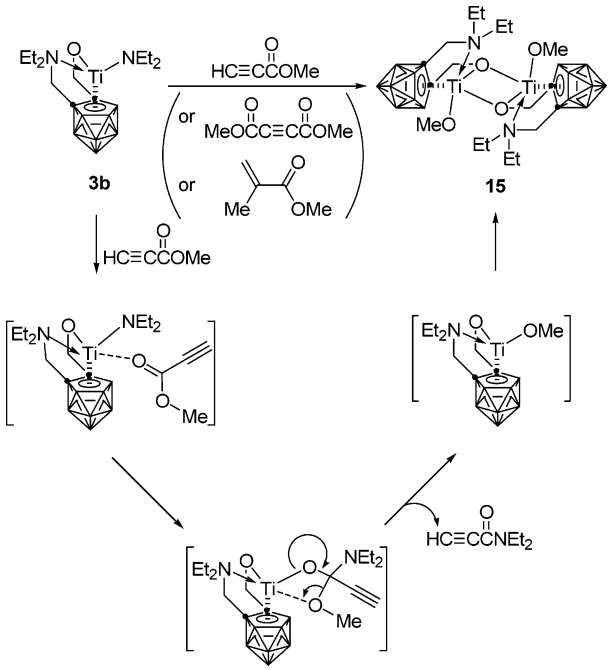


Figure 9. Molecular structure of $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)(Me_2NCH_2)\text{-}C_2B_9H_9]Ti[\sigma{:}\eta^1\text{-}OCH(Ph)N(Ph)C(NMe_2){=}O]$ (**14**).

Scheme 4



reacted readily with benzaldehyde, leading to the isolation of $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)(Me_2NCH_2)C_2B_9H_9]Ti[\sigma{:}\eta^1\text{-}OCH(Ph)N(Ph)C(NMe_2){=}O]$ (**14**) in 72% yield. Complex **14** was fully characterized by various spectroscopic techniques and elemental analyses. Single-crystal X-ray analyses confirmed that PhCH=O inserted into the Ti−N bond in **13** to form a six-membered metallacycle as shown in Figure 9. The significant differences in the Ti−O(2)/O(3) and C−O distances suggest that O(2) is an oxide and O(3) is an oxo.

Stoichoimetric reactions of **3b** with methyl esters such as methyl methacrylate (MMA), methyl propiolate, or dimethyl acetylenedicarboxylate afforded the same dimeric complex $[\{\sigma{:}\eta^1{:}\eta^5\text{-}(\mu\text{-}OCH_2)(Et_2NCH_2)C_2B_9H_9\}Ti(OMe)]_2$ (**15**) in ca. 80% isolated yield. It is suggested that high oxophilicity of the Ti atom is the driving force of these reactions. The formation of $HC{\equiv}CCONEt_2$ was confirmed by NMR and GC-MS analyses. Accordingly, a possible reaction pathway is proposed and shown in Scheme 4.

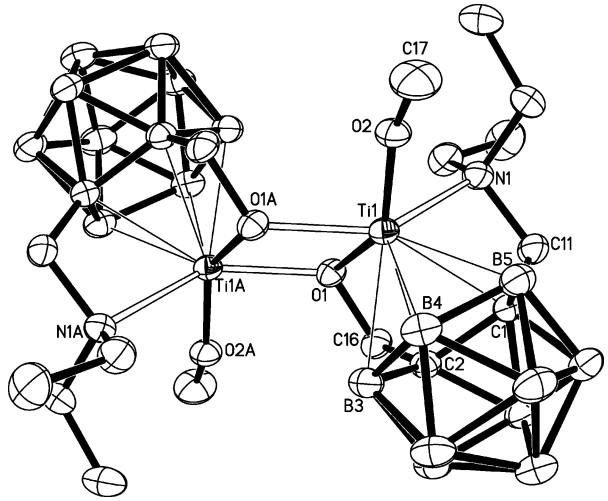


Figure 10. Molecular structure of [{σ:η^1:η^5-(μ-OCH_2)(Et_2NCH_2)-$C_2B_9H_9$}Ti(OMe)]$_2$ (**15**) (the solvated toluene molecule is not shown).

A unique singlet at 4.39 ppm of OCH_3 protons was observed in the ^{1}H NMR spectrum of **15**, in addition to the sidearm protons. The ^{11}B NMR spectrum exhibited nine peaks. An X-ray analysis revealed that **15** is a centrosymmetric dimer and showed one toluene of solvation. Each Ti atom is σ-bound to a terminal methoxyl group and two doubly bridging sidearm O atoms, η^5-bound to a dicarbollyl ligand and η^1-bound to the N atom of the sidearm in a typical four-legged piano stool geometry (Figure 10). The significantly short Ti−O(2) distance of 1.775(2) Å and a large C(17)−O(2)−Ti angle of 152.6(2)° indicate the presence of O(p_π)→Ti(d_π) interactions.[11,17]

The above results clearly show that a range of unsaturated molecules can insert exclusively into the Ti−N bond in **3** to form the corresponding insertion products (Scheme 3). Unfortunately, all these products (**8**−**13**) with the exception of **7** do not show any reactivity toward amines under various reaction conditions, even refluxing toluene.

Conclusion

Reaction of $M(NMe_2)_4$ with [Me_3NH][7,8-CH_2OCH_2-7,8-$C_2B_9H_{10}$] generated simple amine elimination products [η^5-(CH_2OCH_2)$C_2B_9H_9$]$M(NMe_2)_2(NHMe_2)$ (**2**) for M = Zr and Hf or unexpected C−O bond cleavage complexes [σ:η^1:η^5-(OCH_2)(R_2NCH_2)$C_2B_9H_9$]$Ti(NR_2)$ (R = Me (**3a**), Et (**3b**)). The latter is a convenient and practical method for the preparation of constrained-geometry half-sandwich metallacarboranes with two different functional sidearms. It is believed that the C−O bond is broken prior to the formation of the Ti−η^5-dicarbollyl bond after the full characterization of [σ-(OCH_2)(Et_2NHCH_2)-$C_2B_9H_{10}$]Ti(η^3-S_2CNEt_2)$_3$ (**4**). The higher oxophilicity of the Ti center provides the driving force for this reaction.

Amine exchange reaction of **3a** with amines (R′R″NH) afforded new constrained-geometry titanacarborane amides [σ:η^1:η^5-(OCH_2)(R_2NCH_2)$C_2B_9H_9$]Ti(NR′R″). A variety of unsaturated molecules such as carbodiimides, carbon disulfide, isonitrile, nitrile, isothiocyanate, ketene, and isocyanate can insert exclusively into the Ti−amide bond in **3** to give monoinsertion products. The Ti−O bond remains intact. These insertion products, except for [σ:η^1:η^5-(OCH_2)(Me_2NCH_2)-$C_2B_9H_9$]Ti[η^3-CyNC(NMe_2)NCy] (**7**), show no reactivities toward various amines. In sharp contrast, **7** can react readily with Me_2NH to regenerate **3a** and release guanidine, which leads to the discovery of a new catalytic guanylation of amines.[8]

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. μ-1,2-CH_2OCH_2-1,2-$C_2B_{10}H_{10}$[9] and diphenylketene[18] were prepared according to literature methods. All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.0 and 75.5 MHz, respectively. ^{11}B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.0 MHz. All chemical shifts were reported in δ units with reference to the residual protons and carbons of the deuterated solvents for proton and carbon chemical shifts and to external BF_3·OEt_2 (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd., U.K., or Shanghai Institute of Organic Chemistry, CAS, China.

Preparation of [Me_3NH][μ-7,8-CH_2OCH_2-7,8-$C_2B_9H_{10}$] (1). Compound μ-1,2-CH_2OCH_2-1,2-$C_2B_{10}H_{10}$ (1.86 g, 10.0 mmol) was dissolved in ethanol (50 mL), to which was added KOH (2.80 g, 50.0 mmol). The mixture was heated to reflux overnight. After removal of the solvent, the residue was dissolved in water (20 mL). Addition of Me_3NHCl (5.70 g, 60.0 mmol) afforded a white precipitate. Compound **1** was collected by suction filtration, washed with water, and dried under vacuum (2.23 g, 95%). ^{1}H NMR (acetone-d_6): δ 3.89 (d, J = 7.8 Hz, 2H) (CH*H*), 3.61 (d, J = 7.8 Hz, 2H) (C*H*H), 3.22 (s, 9H) (CH_3), −2.65 (brs, 1H) (B*H*B). ^{13}C-{^{1}H} NMR (acetone-d_6): δ 73.9 (CH_2), 46.4 (CH_3), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (acetone-d_6): δ −11.4 (2B), −14.1 (2B), −18.4 (3B), −30.6 (1B), −35.1 (1B). IR (KBr, cm^{-1}): ν 2527 (vs) (B−H). Anal. Calcd for $C_7H_{24}B_9NO$ (**1**): C, 35.69; H, 10.27; N, 5.95. Found: C, 35.27; H, 10.09; N, 5.70.

Preparation of [η^5-(CH_2OCH_2)$C_2B_9H_9$]Zr(NMe_2)$_2$($NHMe_2$) (2a). To a toluene (10 mL) solution of $Zr(NMe_2)_4$ (133 mg, 0.5 mmol) was added **1** (118 mg, 0.5 mmol), and the mixture was stirred at room temperature for 12 h. Removal of the solvent afforded **2a** as a pale yellow pure solid (195 mg, 98%). ^{1}H NMR (pyridine-d_5): δ 4.09 (d, J = 7.5 Hz, 2H) (C*H*H), 3.62 (d, J = 7.5 Hz, 2H) (CH*H*), 3.06 (s, 12H) ($N(CH_3)_2$); 2.34 (s, 6H) ($HN(CH_3)_2$). ^{1}H NMR (benzene-d_6): δ 3.95 (d, J = 8.4 Hz, 2H) (C*H*H), 3.51 (d, J = 8.4 Hz, 2H) (CH*H*), 2.71 (s, 12H) ($N(CH_3)_2$); 2.00 (d, J = 6.0 Hz, 6H) ($HN(CH_3)_2$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 74.3 (CH_2), 44.3 ($N(CH_3)_2$), 38.6 ($HN(CH_3)_2$), the cage carbon atoms were not observed. ^{13}C{^{1}H} NMR (benzene-d_6): δ 77.4 (CH_2), 44.2 ($N(CH_3)_2$), 40.6 ($HN(CH_3)_2$), the cage carbon atoms were not observed. ^{11}B-{^{1}H} NMR (pyridine-d_5): δ 1.2 (1B), −8.9 (1B), −11.9 (2B), −14.3 (2B), −16.2 (2B), −33.4 (1B). ^{11}B{^{1}H} NMR (benzene-d_6): δ 0.9 (1B), −5.5 (5B), −18.3 (2B), −20.1 (1B). IR (KBr, cm^{-1}): ν 2535 (vs) (B−H). Anal. Calcd for $C_8H_{25}B_9N_2OZr$ (**2a** − $HNMe_2$): C, 27.16; H, 7.12; N, 7.92. Found: C, 26.93; H, 6.98; N, 7.56.

Preparation of [η^5-(CH_2OCH_2)$C_2B_9H_9$]Hf(NMe_2)$_2$($NHMe_2$) (2b). This complex was prepared as a pale yellow solid from Hf-(NMe_2)$_4$ (177 mg, 0.5 mmol) and **1** (118 mg, 0.5 mmol) in toluene (10 mL) using the identical procedures reported for **2a** (235 mg, 97%). ^{1}H NMR (pyridine-d_5): δ 4.10 (d, J = 7.8 Hz, 2H) (C*H*H), 3.57 (d, J = 7.8 Hz, 2H) (CH*H*), 3.08 (s, 12H) ($N(CH_3)_2$); 2.36 (s,

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6H) (HN(CH_3)$_2$). ^{1}H NMR (benzene-d_6): δ 3.97 (d, J = 8.4 Hz, 2H) (CHH), 3.56 (d, J = 8.4 Hz, 2H) (CHH), 2.76 (s, 12H) (N(CH_3)$_2$); 2.03 (d, J = 6.0 Hz, 6H) (HN(CH_3)$_2$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 74.1 (*C*H$_2$), 43.9 (N(*C*H$_3$)$_2$), 38.1 (HN(*C*H$_3$)$_2$), the cage carbon atoms were not observed. ^{13}C{^{1}H} NMR (benzene-d_6): δ 77.2 (*C*H$_2$), 44.0 (N(*C*H$_3$)$_2$), 40.6 (HN(*C*H$_3$)$_2$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 1.5 (1B), −11.4 (1B), −13.1 (2B), −14.4 (2B), −16.7 (2B), −35.3 (1B). ^{11}B{^{1}H} NMR (benzene-d_6): δ 0.5 (1B), −4.0 (1B), −5.8 (4B), −18.3 (2B), −20.7 (1B). IR (KBr, cm^{-1}): ν 2547 (vs) (B−H). Anal. Calcd for $C_8H_{25}B_9HfN_2O$ (**2b** − HNMe$_2$): C, 21.78; H, 5.71; N, 6.35. Found: C, 22.14; H, 6.02; N, 6.27.

Preparation of [σ:η^1:η^5-(OCH$_2$)(Me$_2$NCH$_2$)C$_2$B$_9$H$_9$]Ti(NMe$_2$) (3a). To a toluene (40 mL) solution of Ti(NMe$_2$)$_4$ (1.12 g, 5.0 mmol) was added **1** (1.18 g, 5.0 mmol), and the suspension was heated to reflux for 6 h until a clear red solution was obtained. After filtration, the clear filtrate was concentrated to ca. 5 mL. Complex **3a** was isolated as orange crystals after this solution stood at room temperature for 12 h (1.42 g, 91%). ^{1}H NMR (pyridine-d_5): δ 5.50 (d, J = 11.1 Hz, 1H) (OCHH), 5.47 (d, J = 11.1 Hz, 1H) (OCHH), 3.61 (d, J = 14.4 Hz, 1H) (NCHH), 3.17 (s, 6H) (N(CH_3)$_2$), 3.10 (d, J = 14.4 Hz, 1H) (NCHH), 2.31 (s, 3H) (N(CH_3)$_2$), 2.28 (s, 3H) (N(CH_3)$_2$). ^{1}H NMR (benzene-d_6): δ 5.32 (d, J = 12.0 Hz, 1H) (OCHH), 5.02 (d, J = 12.0 Hz, 1H) (OCHH), 3.23 (s, 6H) (N(CH_3)$_2$), 2.95 (d, J = 14.4 Hz, 1H) (NCHH), 2.71 (d, J = 14.4 Hz, 1H) (NCHH), 1.70 (s, 3H) (N(CH_3)$_2$), 1.53 (s, 3H) (N(CH_3)$_2$). ^{1}H NMR (CDCl$_3$): δ 5.66 (d, J = 11.4 Hz, 1H) (OCHH), 5.45 (d, J = 11.4 Hz, 1H) (OCHH), 3.97 (d, J = 14.4 Hz, 1H) (NCHH), 3.76 (s, 6H) (N(CH_3)$_2$), 3.61 (d, J = 14.4 Hz, 1H) (NCHH), 2.77 (s, 3H) (N(CH_3)$_2$), 2.62 (s, 3H) (N(CH_3)$_2$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 77.2 (O*C*H$_2$), 65.5 (N*C*H$_2$), 50.8 (N(*C*H$_3$)$_2$), 50.3 (N(*C*H$_3$)$_2$), 44.1 (N(*C*H$_3$)$_2$), the cage carbon atoms were not observed. ^{13}C-{^{1}H} NMR (benzene-d_6): δ 77.9 (O*C*H$_2$), 66.4 (N*C*H$_2$), 54.0 (N(*C*H$_3$)$_2$), 51.0 (N(*C*H$_3$)$_2$), 44.2 (N(*C*H$_3$)$_2$), the cage carbon atoms were not observed. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 77.9 (O*C*H$_2$), 67.1 (N*C*H$_2$), 55.2 (N(*C*H$_3$)$_2$), 52.2 (N(*C*H$_3$)$_2$), 44.9 (N(*C*H$_3$)$_2$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 12.9 (1B), 1.0 (1B), −0.8 (1B), −3.4 (1B), −4.9 (1B), −9.7 (1B), −11.5 (1B), −13.9 (1B), −17.8 (1B). ^{11}B{^{1}H} NMR (benzene-d_6): δ 11.1 (1B), 2.4 (1B), 0.6 (1B), −1.9 (1B), −3.9 (1B), −10.2 (2B), −15.3 (1B), −17.6 (1B). ^{11}B{^{1}H} NMR (CDCl$_3$): δ 9.8 (1B), 1.5 (1B), 0.1 (1B), −3.1 (1B), −5.2 (1B), −10.7 (2B), −15.6 (1B), −18.7 (1B). IR (KBr, cm^{-1}): ν 2571 (vs) (B−H). Anal. Calcd for $C_8H_{25}B_9N_2OTi$ (**3a**): C, 30.95; H, 8.12; N, 9.02. Found: C, 30.75; H, 8.10; N, 8.80.

Preparation of [σ:η^1:η^5-(OCH$_2$)(Et$_2$NCH$_2$)C$_2$B$_9$H$_9$]Ti(NEt$_2$) (3b). This complex was prepared as orange crystals from Ti(NEt$_2$)$_4$ (1.68 g, 5.0 mmol) and **1** (1.18 g, 5.0 mmol) in toluene (40 mL) using the identical procedures reported for **3a** (1.39 g, 76%). ^{1}H NMR (pyridine-d_5): δ 5.89 (d, J = 11.7 Hz, 1H) (OCHH), 5.53 (d, J = 11.7 Hz, 1H) (OCHH), 4.32 (m, 2H) (CH_2CH$_3$), 4.04 (m, 2H) (CH_2CH$_3$), 3.96 (d, J = 14.7 Hz, 1H) (NCHH), 3.72 (d, J = 14.4 Hz, 1H) (NCHH), 2.92 (m, 4H) (CH_2CH$_3$), 1.14 (t, J = 7.2 Hz, 6H) (CH$_2$CH_3), 0.89 (m, 6H) (CH$_2$CH_3). ^{1}H NMR (benzene-d_6): δ 5.34 (d, J = 11.7 Hz, 1H) (OCHH), 5.12 (d, J = 11.7 Hz, 1H) (OCHH), 4.10 (m, 2H) (CH_2CH$_3$), 3.82 (m, 2H) (CH_2CH$_3$), 3.09 (d, J = 15.0 Hz, 1H) (NCHH), 3.03 (d, J = 15.0 Hz, 1H) (NCHH), 2.54 (m, 2H) (CH_2CH$_3$), 2.05 (m, 2H) (CH_2CH$_3$), 1.01 (t, J = 7.2 Hz, 6H) (CH$_2$CH_3), 0.39 (t, J = 7.2 Hz, 3H) (CH$_2$CH_3), 0.26 (t, J = 7.2 Hz, 3H) (CH$_2$CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 77.7 (O*C*H$_2$), 61.8 (N*C*H$_2$), 53.1 (*C*H$_2$CH$_3$), 49.0 (*C*H$_2$CH$_3$), 45.5 (*C*H$_2$CH$_3$), 13.6 (CH$_2$*C*H$_3$), 9.6 (CH$_2$*C*H$_3$), 7.7 (CH$_2$*C*H$_3$), the cage carbon atoms were not observed. ^{13}C{^{1}H} NMR (benzene-d_6): δ 78.1 (O*C*H$_2$), 62.7 (N*C*H$_2$), 53.7 (*C*H$_2$CH$_3$), 49.3 (*C*H$_2$CH$_3$), 45.8 (*C*H$_2$CH$_3$), 15.5 (CH$_2$*C*H$_3$), 9.9 (CH$_2$*C*H$_3$), 7.8 (CH$_2$*C*H$_3$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 9.9 (1B), 0.9 (1B), 0.0 (1B), −3.4 (1B), −5.1 (1B), −11.0 (2B), −15.2 (1B), −18.6 (1B). ^{11}B{^{1}H} NMR (benzene-d_6): δ 11.0 (1B), 2.4 (1B), 1.0 (1B), −2.2 (1B), −3.5 (1B), −9.9 (2B), −15.2 (1B), −17.3 (1B). IR (KBr, cm^{-1}): ν 2531 (vs) (B−H). Anal. Calcd for $C_{12}H_{33}B_9N_2OTi$ (**3b**): C, 39.32; H, 9.07; N, 7.64. Found: C, 39.80; H, 9.12; N, 7.50.

Preparation of [σ-(OCH$_2$)(Et$_2$NHCH$_2$)C$_2$B$_9$H$_{10}$]Ti(η^3-S$_2$CNEt$_2$)$_3$ (4). To a toluene (10 mL) solution of Ti(NEt$_2$)$_4$ (168 mg, 0.5 mmol) was added **1** (118 mg, 0.5 mmol), and the suspension was heated to 70−80 °C for 6 h. After the reaction mixture was cooled to ambient temperature, CS_2 (152 mg, 2.0 mmol) was added. The mixture was then stirred at room temperature for 12 h. The yellow precipitate was collected by filtration. Recrystallization from THF afforded **4** as yellow crystals (133 mg, 36%). ^{1}H NMR (pyridine-d_5): δ 5.46 (d, J = 12.0 Hz, 1H) (OCHH), 4.86 (d, J = 12.0 Hz, 1H) (OCHH), 4.36 (q, J = 6.9 Hz, 2H) (CH_2CH$_3$), 3.78 (d, J = 14.1 Hz, 1H) (NCHH), 3.69 (m, 12H) (CH_2CH$_3$), 3.52 (d, J = 14.1 Hz, 1H) (NCHH), 3.33 (q, J = 6.9 Hz, 2H) (CH_2CH$_3$), 1.35 (m, 6H) (CH$_2$CH_3), 1.10 (m, 18H) (CH$_2$CH_3), −2.05 (brs, 1H) (BHB). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 202.8 (S$_2$*C*N), 81.0 (O*C*H$_2$), 66.5 (N*C*H$_2$), 58.5 (*C*H$_2$CH$_3$), 56.1 (*C*H$_2$CH$_3$), 44.4 (*C*H$_2$CH$_3$), 11.8 (CH$_2$*C*H$_3$), 10.9 (CH$_2$*C*H$_3$), 8.2 (CH$_2$*C*H$_3$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ −9.6 (4B), −21.1 (3B), −32.3 (1B), −35.7 (1B). IR (KBr, cm^{-1}): ν 2521 (vs) (B−H). Anal. Calcd for $C_{23}H_{55}B_9N_4OS_6Ti$ (**4**): C, 37.27; H, 7.48; N, 7.56. Found: C, 37.68; H, 7.47; N, 7.28.

Preparation of [σ:η^1:η^5-(OCH$_2$)(Me$_2$NCH$_2$)C$_2$B$_9$H$_9$]Ti[NH-(C$_6$H$_4$-4-OMe)] (5). To a toluene (10 mL) solution of **3a** (311 mg, 1.0 mmol) was added 4-methoxyaniline (123 mg, 1.0 mmol) at −30 °C, and the mixture was then stirred at room temperature for 12 h. The solution was concentrated to ca. 3 mL. Complex **5** was isolated as a deep brown solid after this solution stood at room temperature for 24 h (237 mg, 61%). ^{1}H NMR (pyridine-d_5): δ 12.23 (brs, 1H) (NH), 6.76 (d, J = 9.0 Hz, 2H), 6.71 (d, J = 9.0 Hz, 2H) (aromatic CH), 5.80 (d, J = 11.1 Hz, 1H) (OCHH), 5.70 (d, J = 11.1 Hz, 1H) (OCHH), 3.89 (d, J = 14.7 Hz, 1H) (NCHH), 3.54 (s, 3H) (OCH_3), 3.39 (d, J = 14.7 Hz, 1H) (NCHH), 2.49 (s, 3H) (NCH_3), 2.38 (s, 3H) (NCH_3). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 153.4, 147.2, 116.5, 114.2 (aromatic *C*), 78.4 (O*C*H$_2$), 65.9 (N*C*H$_2$), 54.6 (O*C*H$_3$), 52.4 (N*C*H$_3$), 52.2 (N*C*H$_3$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 13.5 (1B), 2.0 (1B), 0.2 (1B), −2.9 (1B), −4.6 (1B), −8.9 (1B), −11.2 (1B), −13.9 (1B), −17.1 (1B). IR (KBr, cm^{-1}): ν 2541 (vs) (B−H). Anal. Calcd for $C_{13}H_{27}B_9N_2O_2Ti$ (**5**): C, 40.19; H, 7.00; N, 7.21. Found: C, 40.24; H, 6.60; N, 7.25.

Preparation of [σ:η^1:η^5-(OCH$_2$)(Me$_2$NCH$_2$)C$_2$B$_9$H$_9$]Ti[σ:η^1-(2-NH-3-CH$_3$−C$_5$H$_3$N)][η^1-C$_5$H$_3$N-2-NH$_2$-3-CH$_3$]·1.5C$_7$H$_8$ (6·1.5C$_7$H$_8$). This complex was prepared as red crystals from **3a** (311 mg, 1.0 mmol) and 2-amino-3-picoline (216 mg, 2.0 mmol) in toluene (10 mL) using the identical procedures reported for **5**, followed by recrystallization from toluene/THF (285 mg, 46%). ^{1}H NMR (pyridine-d_5): δ 9.74 (brs, 1H) (NH), 8.19 (d, J = 5.1 Hz, 1H), 7.81 (d, J = 5.1 Hz, 1H), 7.23 (d, J = 7.2 Hz, 1H) (aromatic CH), 7.3 − 7.1 (m, 7.5H) (aromatic CH), 7.02 (d, J = 7.2 Hz, 1H), 6.59 (dd, $^3J_1$ = 5.1 Hz, $^3J_2$ = 7.2 Hz, 1H) (aromatic CH), 6.42 (brs, 2H) (NH_2), 6.22 (dd, $^3J_1$ = 5.1 Hz, $^3J_2$ = 7.2 Hz, 1H) (aromatic CH), 5.71 (d, J = 11.4 Hz, 1H) (OCHH), 5.63 (d, J = 11.4 Hz, 1H) (OCHH), 3.92 (d, J = 14.7 Hz, 1H) (NCHH), 3.45 (d, J = 14.7 Hz, 1H) (NCHH), 2.39 (s, 3H) (NCH_3), 2.20 (s, 4.5H) (toluene), 2.15 (s, 3H) (NCH_3), 2.13 (s, 3H) (ArCH_3) , 1.98 (s, 3H) (ArCH_3). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 167.3, 158.4, 145.4, 138.7, 138.6, 136.9, 116.0, 114.3, 112.8, 110.5 (aromatic *C*), 137.6, 128.7, 128.0, 125.1 (toluene), 77.4 (O*C*H$_2$), 65.8 (N*C*H$_2$), 53.1 (N*C*H$_3$), 51.2 (N*C*H$_3$), 20.6 (toluene), 16.7 (Ar*C*H$_3$), 14.4 (Ar*C*H$_3$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 16.2 (1B), 3.9 (1B), 0.8 (1B), −3.8 (2B), −7.5 (1B), −11.1 (1B), −16.0 (2B). IR (KBr, cm^{-1}): ν 2542 (vs) (B−

Table 2. Crystal Data and Summary of Data Collection and Refinement for 3a, 3b, 4, 6·1.5C_7H_8, and 7

	3a	3b	4	6·1.5C_7H_8	7
formula	$C_8H_{25}B_9N_2OTi$	$C_{12}H_{33}B_9N_2OTi$	$C_{23}H_{55}B_9N_4OS_6Ti$	$C_{28.5}H_{46}B_9N_5OTi$	$C_{21}H_{47}B_9N_4OTi$
cryst size, mm	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.20	0.50 × 0.40 × 0.30	0.50 × 0.40 × 0.20	0.50 × 0.40 × 0.20
fw	310.49	366.59	741.26	619.89	516.82
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	*Cc*	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	13.647(3)	14.926(3)	16.458(3)	9.062(2)	9.799(2)
b, Å	7.167(2)	8.031(2)	14.762(3)	12.408(3)	11.521(2)
c, Å	18.496(4)	17.685(4)	17.517(3)	16.109(3)	14.453(3)
α, deg	90	90	90	80.89(3)	100.07(3)
β, deg	110.72(1)	105.44(3)	111.77(1)	86.30(3)	105.59(3)
γ, deg	90	90	90	70.29(3)	104.93(3)
V, Å^3	1692.0(6)	2043.4(7)	3952.2(13)	1683.5(6)	1465.4(5)
Z	4	4	4	2	2
D_{calcd}, Mg/m^3	1.219	1.192	1.246	1.223	1.171
radiation (*γ*), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2*θ* range, deg	4.7 to 56.7	4.8 to 50.0	2.9 to 56.7	4.0 to 50.0	3.0 to 50.8
μ, mm^{-1}	0.496	0.421	0.559	0.286	0.314
F(000)	648	776	1568	654	552
no. of obsd reflns	3414	3604	9819	5931	4727
no. of params refnd	190	226	405	406	325
goodness of fit	0.934	1.050	1.008	1.017	1.067
R1	0.042	0.053	0.045	0.061	0.047
wR2	0.106	0.145	0.113	0.160	0.144

Table 3. Crystal Data and Summary of Data Collection and Refinement for 11b, 12−14, and 15·C_7H_8

	11b	12	13	14	15·C_7H_8
formula	$C_{17}H_{42}B_9N_3OSTi$	$C_{22}H_{35}B_9N_2O_2Ti$	$C_{15}H_{30}B_9N_3O_2Ti$	$C_{22}H_{36}B_9N_3O_3Ti$	$C_{25}H_{60}B_{18}N_2O_4Ti_2$
cryst size, mm	0.40 × 0.30 × 0.20	0.30 × 0.20 × 0.10	0.30 × 0.20 × 0.10	0.30 × 0.20 × 0.10	0.30 × 0.20 × 0.10
fw	481.79	504.71	429.61	535.73	743.13
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	10.108(2)	13.986(1)	11.325(2)	11.920(1)	10.431(1)
b, Å	16.169(3)	12.447(1)	11.754(2)	15.011(2)	15.730(2)
c, Å	17.220(3)	16.066(2)	18.389(4)	15.748(2)	12.825(1)
α, deg	99.89(3)	90	90	90	90
β, deg	95.60(3)	110.29(1)	104.76(3)	100.65(1)	105.79(1)
γ, deg	92.94(3)	90	90	90	90
V, Å^3	2752.7(9)	2623.2(5)	2367.1(8)	2769.2(5)	2025.0(3)
Z	4	4	4	4	2
D_{calcd}, Mg/m^3	1.163	1.278	1.206	1.285	1.219
radiation (*γ*), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2*θ* range, deg	2.4 to 50.0	3.3 to 50.0	4.2 to 50.0	3.5 to 56.6	4.2 to 56.7
μ, mm^{-1}	0.402	0.350	0.378	0.340	0.428
F(000)	1024	1056	896	1120	780
no. of obsd reflns	7923	4622	3555	6873	5021
no. of params refnd	577	325	271	343	244
goodness of fit	1.178	1.012	1.117	0.991	1.059
R1	0.060	0.050	0.053	0.057	0.044
wR2	0.164	0.112	0.153	0.141	0.118

H). Anal. Calcd for $C_{25}H_{42}B_9N_5OTi$ (**6** + toluene): C, 52.33; H, 7.38; N, 12.20. Found: C, 51.96; H, 7.37; N, 12.01.

Preparation of [σ:η^1:η^5-(OCH$_2$)(Me$_2$NCH$_2$)C$_2$B$_9$H$_9$]Ti[η^3-CyNC(NMe$_2$)NCy] (7). To a toluene (10 mL) solution of **3a** (311 mg, 1.0 mmol) was added dicyclohexylcarbodiimide (206 mg, 1.0 mmol); the mixture was stirred at room temperature for 12 h and then heated to reflux for 30 min. The hot solution was filtered, and the clear filtrate was concentrated to ca. 3 mL. Complex **7** was isolated as orange crystals after this solution stood at room temperature for 12 h (424 mg, 82%). ^{1}H NMR (pyridine-d_5): δ 5.86 (d, J = 12.0 Hz, 1H) (OC*H*H), 5.71 (d, J = 12.0 Hz, 1H) (OCH*H*), 4.03 (d, J = 14.4 Hz, 1H) (NC*H*H), 3.44 (d, J = 14.4 Hz, 1H) (NCH*H*), 3.32 (m, 2H) (NC*H*), 2.80 (s, 6H) (N(CH_3)$_2$), 2.61 (s, 3H) (CH_3), 2.35 (s, 3H) (CH_3), 1.1−1.9 (m, 20H) (Cy). ^{1}H NMR ($CDCl_3$): δ 5.59 (d, J = 12.0 Hz, 1H) (OC*H*H), 5.54 (d, J = 12.0 Hz, 1H) (OCH*H*), 3.80 (d, J = 14.4 Hz, 1H) (NC*H*H), 3.40 (d, J = 14.4 Hz, 1H) (NCH*H*), 3.47 (m, 2H) (NC*H*), 2.92 (s, 6H) (N(CH_3)$_2$), 2.67 (s, 3H) (N(CH_3)$_2$), 2.40 (s, 3H) (N(CH_3)$_2$), 1.0−2.0 (m, 20H) (Cy). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 174.9 (N$_3$*C*), 78.1 (O*C*H$_2$), 65.2 (N*C*H$_2$), 54.0 (*C*H$_3$), 52.0 (*C*H$_3$), 40.3 (*C*H$_3$), 39.2, 34.6, 32.0, 26.8, 24.9, 14.8 (Cy), the cage carbon atoms were not observed. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 175.4 (N$_3$*C*), 78.5 (O*C*H$_2$), 66.0 (N*C*H$_2$), 54.7 (*C*H$_3$), 52.6 (*C*H$_3$), 41.2 (*C*H$_3$), 34.9, 33.7, 32.4, 27.2, 26.2, 25.5, 24.7 (Cy), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 12.3 (1B), −2.1 (5B), −9.6 (2B), −16.8 (1B). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 12.0 (1B), 1.8 (1B), −0.5 (1B), −3.7 (2B), −9.2 (1B), −11.9 (1B), −14.7 (1B), −17.6 (1B). IR (KBr, cm^{-1}): ν 2549 (vs) (B−H). Anal. Calcd for $C_{21}H_{47}B_9N_4OTi$ (**7**): C, 48.81; H, 9.17; N, 10.84. Found: C, 48.99; H, 9.09; N, 10.96.

Preparation of [σ:η^1:η^5-(OCH$_2$)(Me$_2$NCH$_2$)C$_2$B$_9$H$_9$]Ti(η^3-S$_2$CNMe$_2$) (8). To a toluene (10 mL) solution of **3a** (311 mg, 1.0 mmol) was added carbon disulfide (114 mg, 1.5 mmol), and the mixture was stirred at room temperature for 12 h. Complex **8** was collected as a yellow solid by filtration (363 mg, 94%). ^{1}H NMR (pyridine-d_5): δ 5.95 (d, J = 12.0 Hz, 1H) (OC*H*H), 5.77 (d, J = 12.0 Hz, 1H) (OCH*H*), 4.10 (d, J = 14.7 Hz, 1H) (NC*H*H), 3.55 (d, J = 14.7 Hz, 1H) (NCH*H*), 3.10 (s, 6H) (N(CH_3)$_2$), 2.63 (s, 3H) (CH_3), 2.50 (s, 3H) (CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 201.3 (S$_2$*C*N), 80.0 (O*C*H$_2$), 66.6 (N*C*H$_2$), 54.6 (*C*H$_3$), 52.2 (*C*H$_3$), 39.5 (*C*H$_3$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 17.9 (1B), 4.9 (1B), 2.0 (1B), −1.9 (1B), −2.8 (1B), −5.8 (2B), −10.4 (1B), −14.7 (1B). IR (KBr, cm^{-1}):

ν 2527 (vs) (B−H). Anal. Calcd for $C_9H_{25}B_9N_2OS_2Ti$ (**8**): C, 27.96; H, 6.52; N, 7.25. Found: C, 27.62; H, 6.59; N, 7.24.

Preparation of [σ:η^1:η^5-(OCH$_2$)(Me$_2$NCH$_2$)C$_2$B$_9$H$_9$]Ti[η^2-C(NMe$_2$)N(C$_6$H$_3$-2,6-Me$_2$)] (9). This complex was prepared as a yellow solid from **3a** (311 mg, 1.0 mmol) and 2,6-xylyl isonitrile (131 mg, 1.0 mmol) in toluene (10 mL) using the identical procedures reported for **7** (318 mg, 72%). ^{1}H NMR (pyridine-d_5): δ 7.25 (t, J = 7.2 Hz, 1H), 7.15 (d, J = 7.2 Hz, 2H) (C$_6H_3$), 5.97 (d, J = 11.7 Hz, 1H) (OC*H*H), 5.47 (d, J = 11.7 Hz, 1H) (OCH*H*), 4.36 (d, J = 14.7 Hz, 1H) (NC*H*H), 3.57 (d, J = 14.7 Hz, 1H) (NCH*H*), 3.38 (s, 3H) (NCH_3), 2.64 (s, 3H) (NCH_3), 2.38 (s, 3H) (NCH_3), 2.24 (s, 3H) (NCH_3), 2.23 (s, 3H) (ArCH_3), 2.20 (s, 3H) (ArCH_3). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 197.6 (N*C*N), 145.4, 130.7, 128.7, 128.0, 125.8, 125.0 (aromatic *C*), 77.4 (O*C*H$_2$), 66.3 (N*C*H$_2$), 53.7 (N*C*H$_3$), 49.7 (N*C*H$_3$), 43.6 (N*C*H$_3$), 36.3 (N*C*H$_3$), 17.8 (Ar*C*H$_3$), 14.8 (Ar*C*H$_3$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 7.3 (1B), −0.56 (2B), −3.5 (2B), −10.0 (2B), −17.6 (2B). IR (KBr, cm^{-1}): ν 2553 (vs) (B−H), 1636 (s) (C═N). Anal. Calcd for $C_{17}H_{34}B_9N_3OTi$ (**9**): C, 46.23; H, 7.76; N, 9.51. Found: C, 46.00; H, 7.70; N, 9.79.

Preparation of [σ:η^1:η^5-(OCH$_2$)(Me$_2$NCH$_2$)C$_2$B$_9$H$_9$]Ti[N═C(NMe$_2$)Ph] (10). This complex was prepared as an orange solid from **3a** (311 mg, 1.0 mmol) and benzonitrile (103 mg, 1.0 mmol) in toluene (10 mL) using the identical procedures reported for **7** (380 mg, 92%). ^{1}H NMR (pyridine-d_5): δ 7.27 (m, 3H), 7.05 (m, 2H) (aromatic *H*), 5.72 (d, J = 11.4 Hz, 1H) (OC*H*H), 5.62 (d, J = 11.4 Hz, 1H) (OCH*H*), 3.91 (d, J = 14.4 Hz, 1H) (NC*H*H), 3.37 (d, J = 14.4 Hz, 1H) (NCH*H*), 2.98 (s, 6H) (NCH_3), 2.58 (s, 3H) (NCH_3), 2.23 (s, 3H) (NCH_3). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 156.3 (N$_2$*C*), 136.7, 128.5, 127.9, 126.6 (aromatic *C*), 77.9 (O*C*H$_2$), 65.1 (N*C*H$_2$), 52.0 (N*C*H$_3$), 51.8 (N*C*H$_3$), 38.1 (N*C*H$_3$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 9.2 (1B), −0.7 (1B), −3.0 (1B), −4.2 (1B), −5.5 (1B), −9.2 (1B), −12.7 (1B), −14.7(1B), −19.8 (1B). IR (KBr, cm^{-1}): ν 2548 (vs) (B−H), 1550 (s) (C═N). Anal. Calcd for $C_{15}H_{30}B_9N_3OTi$ (**10**): C, 43.56; H, 7.31; N, 10.16. Found: C, 44.05; H, 7.46; N, 9.70.

Preparation of [σ:η^1:η^5-(OCH$_2$)(Me$_2$NCH$_2$)C$_2$B$_9$H$_9$]Ti[η^3-SC(NMe$_2$)NBu^n] (11a). This complex was prepared as a yellow solid from **3a** (311 mg, 1.0 mmol) and *n*-butyl isothiocyanate (115 mg, 1.0 mmol) in toluene (10 mL) using the identical procedures reported for **7** (324 mg, 76%). ^{1}H NMR (pyridine-d_5): δ 5.86 (d, J = 12.0 Hz, 1H) (OC*H*H), 5.73 (d, J = 12.0 Hz, 1H) (OCH*H*), 4.10 (m, 1H) (NC*H*HPr^n), 3.99 (d, J = 14.7 Hz, 1H) (NC*H*H), 3.86 (m, 1H) (NCH*H*Pr^n), 3.47 (d, J = 14.7 Hz, 1H) (NCH*H*), 2.96 (s, 6H) (NCH_3), 2.58 (s, 3H) (NCH_3), 2.40 (s, 3H) (NCH_3), 1.41 (m, 2H) (NCH$_2$CH_2Et), 1.13 (m, 2H) (CH_2CH$_3$), 0.75 (t, J = 7.5 Hz, 3H) (CH$_2$CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 174.7 (N$_2$*C*S), 79.3 (O*C*H$_2$), 65.1 (N*C*H$_2$), 53.5 (N*C*H$_3$), 53.1 (N*C*H$_3$), 45.4 (N*C*H$_2$Pr^n), 39.5 (N*C*H$_3$), 30.4 (NCH$_2$*C*H$_2$Et), 20.0 (*C*H$_2$CH$_3$), 13.3 (CH$_2$*C*H$_3$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 15.0 (1B), 3.6 (1B), 0.7 (1B), −2.4 (1B), −4.0 (1B), −6.9 (1B), −11.3 (1B), −16.2 (2B). IR (KBr, cm^{-1}): ν 2548 (vs) (B−H). Anal. Calcd for $C_{13}H_{34}B_9N_3OSTi$ (**11a**): C, 36.68; H, 8.05; N, 9.87. Found: C, 36.59; H, 8.12; N, 9.99.

Preparation of [σ:η^1:η^5-(OCH$_2$)(Et$_2$NCH$_2$)C$_2$B$_9$H$_9$]Ti[η^3-SC(NEt$_2$)NBu^n] (11b). This complex was prepared as yellow crystals from **3b** (367 mg, 1.0 mmol) and *n*-butyl isothiocyanate (115 mg, 1.0 mmol) in toluene (10 mL) using the identical procedures reported for **7**, followed by recrystallization from DME (395 mg, 82%). ^{1}H NMR (pyridine-d_5): δ 5.94 (d, J = 12.0 Hz, 1H) (OC*H*H), 5.79 (d, J = 12.0 Hz, 1H) (OCH*H*), 4.03 (m, 1H) (NC*H*HPr^n), 3.89 (d, J = 14.7 Hz, 1H) (NC*H*H), 3.74 (m, 1H) (NCH*H*Pr^n), 3.70 (d, J = 14.7 Hz, 1H) (NCH*H*), 3.48 (m, 4H) (NCH_2CH$_3$), 2.76 (m, 2H) (NCH_2CH$_3$), 2.53 (m, 2H) (NCH_2CH$_3$), 1.36 (m, 2H) (NCH$_2$CH_2Et), 1.19 (t, J = 7.2 Hz, 6H) (NCH$_2$CH_3), 1.12 (m, 2H) (CH$_2$CH_2CH$_3$), 1.04 (t, J = 7.2 Hz, 3H) (NCH$_2$CH_3), 0.87 (t, J = 7.2 Hz, 3H) (NCH$_2$CH_3), 0.78 (t, J = 7.2 Hz, 3H) ((CH$_2$)$_3$CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 171.2 (N$_2$*C*S), 79.5 (O*C*H$_2$), 60.9 (N*C*H$_2$), 53.7 (N*C*H$_2$CH$_3$), 48.8 (N*C*H$_2$CH$_3$), 45.6 (*C*H$_2$Pr^n), 31.4 (NCH$_2$*C*H$_2$Et), 19.7 (CH$_2$*C*H$_2$CH$_3$), 13.7 (NCH$_2$*C*H$_3$), 13.4 (NCH$_2$*C*H$_3$), 12.3 ((CH$_2$)$_3$*C*H$_3$), 10.9 (NCH$_2$*C*H$_3$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 13.7 (1B), 4.2 (1B), 1.0 (1B), −2.8 (2B), −8.2 (1B), −10.1 (1B), −16.0 (2B). IR (KBr, cm^{-1}): ν 2544 (vs) (B−H). Anal. Calcd for $C_{17}H_{42}B_9N_3OSTi$ (**11b**): C, 42.38; H, 8.79; N, 8.72. Found: C, 42.46; H, 8.78; N, 8.79.

Preparation of [σ:η^1:η^5-(OCH$_2$)(Me$_2$NCH$_2$)C$_2$B$_9$H$_9$]Ti[σ:η^1-OC(NMe$_2$)═CPh$_2$] (12). This complex was prepared as orange crystals from **3a** (311 mg, 1.0 mmol) and diphenylketene (194 mg, 1.0 mmol) in toluene (10 mL) using the identical procedures reported for **7**, followed by recrystallization from DME (424 mg, 84%). ^{1}H NMR (pyridine-d_5): δ 7.52 (m, 2H), 7.30 (m, 4H), 7.22 (m, 2H), 7.07 (m, 2H) (aromatic *H*), 6.01 (d, J = 11.7 Hz, 1H) (OC*H*H), 5.92 (d, J = 11.7 Hz, 1H) (OCH*H*), 3.97 (d, J = 14.4 Hz, 1H) (NC*H*H), 3.47 (d, J = 14.4 Hz, 1H) (NCH*H*), 2.90 (s, 3H) (NCH_3), 2.83 (s, 3H) (NCH_3), 2.63 (s, 6H) (NCH_3). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 163.3 (N*C*O), 142.9, 142.5, 140.2, 130.2, 129.9, 129.0, 128.7, 128.1, 128.0, 127.8, 126.4, 124.5, 124.1 (aromatic and olefinic *C*), 80.2 (O*C*H$_2$), 63.7 (N*C*H$_2$), 54.0 (N*C*H$_3$), 50.8 (N*C*H$_3$), 40.2 (N*C*H$_3$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 16.3 (1B), 3.6 (1B), 1.3 (1B), −1.3 (1B), −3.0 (1B), −7.2 (1B), −10.3 (1B), −13.5(1B), −15.9 (1B). IR (KBr, cm^{-1}): ν 2552 (vs) (B−H). Anal. Calcd for $C_{22}H_{35}B_9N_2O_2Ti$ (**12**): C, 52.36; H, 6.99; N, 5.55. Found: C, 52.49; H, 6.77; N, 5.37.

Preparation of [σ:η^1:η^5-(OCH$_2$)(Me$_2$NCH$_2$)C$_2$B$_9$H$_9$]Ti[η^3-OC(NMe$_2$)NPh] (13). This complex was prepared as orange crystals from **3a** (311 mg, 1.0 mmol) and phenyl isocyanate (119 mg, 1.0 mmol) in toluene (10 mL) using the identical procedures reported for **7** (361 mg, 84%). ^{1}H NMR (pyridine-d_5): δ 7.89 (d, J = 7.8 Hz, 1H), 7.31 (m, 2H), 7.01 (t, J = 7.8 Hz, 1H), 6.94 (t, J = 7.8 Hz, 1H) (aromatic *H*), 5.96 (d, J = 12.0 Hz, 1H) (OC*H*H), 5.74 (d, J = 12.0 Hz, 1H) (OCH*H*), 4.12 (d, J = 14.4 Hz, 1H) (NC*H*H), 3.60 (d, J = 14.4 Hz, 1H) (NCH*H*), 2.92 (s, 6H) (NCH_3), 2.62 (s, 3H) (NCH_3), 2.52 (s, 3H) (NCH_3). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 197.6 (O*C*N$_2$), 145.4, 130.7, 128.7, 128.0, 125.8, 125.0 (aromatic *C*), 77.4 (O*C*H$_2$), 66.3 (N*C*H$_2$), 53.7 (N*C*H$_3$), 49.7 (N*C*H$_3$), 43.6 (N*C*H$_3$), 36.3 (N*C*H$_3$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 18.0 (1B), 5.4 (1B), 3.1 (1B), −2.7 (3B), −6.8 (1B), −10.2 (1B), −15.6 (1B). IR (KBr, cm^{-1}): ν 2538 (vs) (B−H). Anal. Calcd for $C_{15}H_{30}B_9N_3O_2Ti$ (**13**): C, 41.94; H, 7.04; N, 9.78. Found: C, 42.01; H, 7.33; N, 9.68.

Preparation of [σ:η^1:η^5-(OCH$_2$)(Me$_2$NCH$_2$)C$_2$B$_9$H$_9$]Ti[σ:η^1-OCH(Ph)N(Ph)C(NMe$_2$)═O] (14). This complex was prepared as yellow crystals from **13** (215 mg, 0.5 mmol) and benzaldehyde (53 mg, 0.5 mmol) in toluene (10 mL) using the identical procedures reported for **7** (193 mg, 72%). ^{1}H NMR (pyridine-d_5): δ 8.79 (s, 1H) (NC*H*(Ph)O), 7.89 (m, 2H), 7.53 (m, 2H), 7.43 (m, 2H), 7.31 (m, 2H), 7.01 (t, J = 7.5 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H) (aromatic *H*), 5.96 (d, J = 12.3 Hz, 1H) (OC*H*H), 5.74 (d, J = 12.3 Hz, 1H) (OCH*H*), 4.12 (d, J = 14.7 Hz, 1H) (NC*H*H), 3.59 (d, J = 14.7 Hz, 1H) (NCH*H*), 2.92 (s, 6H) (NCH_3), 2.62 (s, 3H) (NCH_3), 2.53 (s, 3H) (NCH_3). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 191.8 (O═*C*N$_2$), 136.4, 133.9, 129.1, 128.7, 128.3, 128.0, 127.8, 125.1, 122.2, 121.7, 120.0, 119.9 (aromatic *C*), 80.6 (N*C*H(Ph)O), 79.0 (O*C*H$_2$), 65.1 (N*C*H$_2$), 54.9 (N*C*H$_3$), 50.6 (N*C*H$_3$), 35.8 (N*C*H$_3$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 17.5 (1B), 5.0 (1B), 2.7 (1B), −3.0 (3B), −7.1 (1B), −10.4 (1B), −16.0 (1B). IR (KBr, cm^{-1}): ν 2539 (vs) (B−H), 1573 (s) (C═O). Anal. Calcd for $C_{22}H_{36}B_9N_3O_3Ti$ (**14**): C, 49.33; H, 6.77; N, 7.84. Found: C, 49.62; H, 6.82; N, 7.38.

Preparation of [{σ:η^1:η^5-(μ-OCH_2)(Et_2NCH_2)$C_2B_9H_9$}Ti(OMe)]$_2$·C_7H_8 (15·C_7H_8). This complex was prepared as pale yellow crystals from **3b** (367 mg, 1.0 mmol) and methyl propiolate (84 mg, 1.0 mmol) in toluene (10 mL) using the identical procedures reported for **7**, followed by recrystallization from THF/toluene (308 mg, 83%). ^{1}H NMR (pyridine-d_5): δ 7.26 (t, J = 7.2 Hz, 2H) (toluene *H*), 7.16 (m, 3H) (toluene *H*), 5.87 (d, J = 11.7 Hz, 2H) (OC*H*H), 5.80 (d, J = 11.7 Hz, 2H) (OCH*H*), 4.39 (s, 6H) (O*C*H$_3$), 3.71 (d, J = 15.0 Hz, 2H) (NC*H*H), 3.63 (d, J = 15.0 Hz, 2H) (NCH*H*), 3.43 (m, 2H) (N*C*H$_2$CH$_3$), 3.08 (m, 2H) (N*C*H$_2$CH$_3$), 2.56 (m, 4H) (N*C*H$_2$CH$_3$), 2.20 (s, 3H) (toluene C*H*$_3$), 0.84 (t, J = 7.2 Hz, 6H) (NCH$_2$C*H*$_3$), 0.77 (t, J = 7.2 Hz, 6H) (NCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 137.7, 128.7, 128.0, 125.1 (toluene *C*), 79.3 (O*C*H$_2$), 65.3 (N*C*H$_2$), 60.8 (O*C*H$_3$), 50.5 (N*C*H$_2$CH$_3$), 47.6 (N*C*H$_2$CH$_3$), 20.6 (toluene *C*H$_3$), 10.7 (NCH$_2$*C*H$_3$), 5.1 (NCH$_2$*C*H$_3$), the cage carbon atoms were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 14.3 (1B), 2.1 (1B), 0.3 (1B), −2.0 (1B), −3.8 (1B), −8.1 (1B), −10.6 (1B), −13.4 (1B), −16.8 (1B). IR (KBr, cm^{-1}): ν 2549 (vs) (B−H). Anal. Calcd for $C_{25}H_{60}B_{18}N_2O_4Ti_2$ (**15** + C_7H_8): C, 40.41; H, 8.14; N, 3.77. Found: C, 40.57; H, 8.62; N, 3.51.

Alternate Method. Complex **15** was also prepared in 79% yield from the reaction of **3b** (367 mg, 1.0 mmol) with MMA (100 mg, 1.0 mmol) in toluene (10 mL), or 73% yield from the reaction of **3b** (367 mg, 1.0 mmol) with dimethyl acetylenedicarboxylate (142 mg, 1.0 mmol) in toluene (10 mL) using the identical procedures described above.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under nitrogen in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[19] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on F^2 using the SHELXTL program package.[20] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Tables 2 and 3, respectively. Further details are included in the Supporting Information.

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Supporting Information Available: Crystallographic data in CIF format for **3a**, **3b**, **4**, **6**·1.5C_7H_8, **7**, **11b**, **12**, **13**, **14**, and **15**·C_7H_8. This material is available free of charge via the Internet at http://pubs.acs.org.

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