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2010년 2월

석사학위 논문

**Multi-Functionalized dicarbollide  
Ligand Systems for Group 4 and 13  
Metal complexes**

2010년 2월 25일

조선대학교 대학원

화학과

김하연

Multi-Functionalized dicarbollide  
Ligand Systems for Group 4 and 13  
Metal complexes

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이 논문을 이학 석사학위신청 논문으로 제출함

2009년 10월

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# 김하연의 석사학위논문을 인준함

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## 1. ABSTRACT

### Multi-Functionalized dicarbollide Ligand Systems for Group 4 and 13 Metal complexes

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A series of group 4 metal complexes with  $\pi,\sigma$ -type bonding interaction of the formula  $[\{R(\eta^5-C_2B_9H_9)(CH_2)(\eta^1-NMe_2)\}M(NMe_2)_2]$  ( $R = CH_2NMe_2$ ,  $M = Ti$  **7**,  $Zr$  **8**;  $R = PPh_2$ ,  $M = Ti$  **9**,  $Zr$  **10**), was produced by the reaction of group 4 metal amides ( $M(NMe_2)_4$ ;  $M = Ti$ ,  $Zr$ ) with the multi-functionalized dicarbollyl ligands,  $nido\text{-}7,8\text{-}C_2B_9H_{10}\text{-}7,8\text{-}[(\mu\text{-}H)NMe_2(CH_2)]_2$  (3) and  $nido\text{-}7,8\text{-}C_2B_9H_{10}\text{-}[(\mu\text{-}H)PPh_2NMe_2CH_2]$  (6), respectively. The structures of the multi-functionalized dicarbollyl group 4 metal complexes were established by X-ray diffraction studies of **7**, **9**, and **10**, which verified an  $\eta^5;\eta^1$ -bonding mode derived from the multi-functionalized dicarbollyl ligand. NMR spectrum data suggested that an intramolecular M–N coordination was intact in solution, resulting in a stable piano-stool structure with two dimethylamido ligands residing

in two of the leg positions. The reaction of **3** and **6** with  $\text{MMe}_3$  ( $\text{M} = \text{Al, Ga}$ ) in toluene led to the formation of unusual  $\sigma,\sigma$ -type  $\text{R}\rightarrow\text{M}\leftarrow\text{N}$  coordinated complexes  $(\text{Dcab}^{RN})\text{MMe}_2$  ( $\text{R} = \text{CH}_2\text{NMe}_2$ ,  $\text{M} = \text{Al } \mathbf{11}$ ,  $\text{Ga } \mathbf{12}$ ;  $\text{R} = \text{PPh}_2$ ,  $\text{M} = \text{Al } \mathbf{13}$ ,  $\text{Ga } \mathbf{14}$ ). The molecular structures of **11**, **13**, and **14** have been confirmed by single crystal X-ray diffraction and NMR spectral studies.

## 2. 국문초록

4족 금속 화합물과  $\left[\{R(\eta^5-C_2B_9H_9)(CH_2)(\eta^1-NMe_2)\}M(NMe_2)_2\right]$  ( $R = CH_2NMe_2$ ,  $M = Ti$  **7**,  $Zr$  **8**  $R = PPh_2$ ,  $M = Ti$  **9**,  $Zr$  **10**)의  $\pi, \sigma$ -형태의 결합은 4족 금속 아마이드 ( $M(NMe_2)_4$   $M = Ti$ ,  $Zr$ )와 다기능성 dicarbollyl ligands, *nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>-7,8-[ $(\mu\text{-}H)NMe_2(CH_2)$ ]<sub>2</sub> (3) 그리고 *nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>-[ $(\mu\text{-}H)PPh_2NMe_2CH_2$ ] (6) 각각의 반응에 의해 생성된다. Dicarbollyl-4족 금속 화합물의 다기능 구조들인 **7**번, **9**번, 그리고 **10**번 화합물은 X-ray 회절분광법에 의해 설명되어진다. 다기능성 dicarbollyl 리간드로부터  $\eta^5:\eta^1$ -결합 형태를 하고 있다는 것이 확인되었다. 분자내 M-N 배위는 NMR 데이터로 확인하였다. 안정한 피아노 스타일 구조로 두 개의 dimethylamido 리간드가 두 개의 다리 위치에 존재한다는 결론을 얻었다. 톨루엔 용액에서 **3**번과 **6**번 화합물은  $MMe_3$  ( $M = Al$ ,  $Ga$ )와  $\sigma, \sigma$ -형태의  $R \rightarrow M \leftarrow N$  배위화합물 ( $R = CH_2NMe_2$ ,  $M = Al$  **11**,  $Ga$  **12**;  $R = PPh_2$ ,  $M = Al$  **13**,  $Ga$  **14**)을 형성한다. **11**번, **13**번, 그리고 **14**번 금속화합물의 분자 구조들은 단결정 X-ray 회절법과 NMR에 의해 확인되어졌다.

### 3. Introduction

The preparation of new types of constrained-geometry complexes is currently of interest because of remarkable activity for copolymerization of ethylene with  $\alpha$ -olefins.<sup>1</sup> One of the reference catalysts is the titanium complex  $[(\eta^5\text{-Me}_4\text{C}_5)\text{Me}_2\text{Si}(\eta^1\text{-BuN}')]\text{TiCl}_2$ ,<sup>2</sup> which represents a characteristic  $\pi,\sigma$ -bonding interaction at the titanium metal centre. The term ‘constrained geometry’ is derived from the half-sandwich structure of these complexes, in which one ancillary ligand tethered to the cyclopentadienide ( $\text{Cp}^-$ ) ring functions as a  $\sigma$ -donor.<sup>3</sup>

In the search for new types of ligand systems for which  $\pi,\sigma$ -coordination may be plausible, the dicarbollyl moiety has been employed as a  $\pi$ -bonding group instead of the cyclopentadienyl ligand ( $\text{Cp}$ ). The dicarbollide dianion is a versatile ligand that is an isolobal inorganic analogue of the  $\text{Cp}^-$  ion.<sup>4</sup> To prepare constrained-geometry complexes with this dicarbollyl functionality is a challenging project since incorporation of a dicarbollyl fragment into the ligand frame work will create new metal/charge combinations. The formal replacement of the monoanionic  $\text{Cp}^-$  ligand in  $[\text{CpM(III)}]^{+2}$  with the isolobal, dianionic dicarbollyl ligand  $(\text{C}_2\text{B}_9\text{H}_{11})^{-2}$  to give  $[(\text{C}_2\text{B}_9\text{H}_{11})\text{M(III)}]^{+1}$  fragment reduces the overall charge by one unit, but leaves the gross structural and metal frontier orbital properties unchanged. Consequently, complex design of this type can potentially be used to control secondary metal/ligand interactions; the weaker ionic character of the pendent neutral amino group enhances the metal’s  $\pi$ -bonding capability with the dicarbollyl ligand through an  $\eta^5$ -coordination.

As part of our efforts to search for the incorporation of the versatile dicarbollide ancillary ligand into a donor chelate array through the functionalization of the  $\text{C}_2\text{B}_3$  unit with various pendant donors is an effective means of altering the coordination environment of the parent non-functionalized dicarbollyl compounds. Recently, achelating dicarbollide ligand with an aminoalkyl

donor was investigated in the context of ligand design for homogeneous olefin polymerization catalysts.<sup>5</sup> In such aligand system, the amine coordinates only weakly to group 4 metals and forms relatively labile complexes due to the lack of a  $\pi$ -donor capability. Moreover, we have previously described the preparation of titanium complexes containing bis(dimethylamino)dicarbollide ligand.<sup>6</sup> As an extension of this work we report here the synthesis and crystal structural characterization of the hetero-multi-functionalized dicarbollyl ligands *nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>-7,8-[ $(\mu$ -H)NMe<sub>2</sub>CH<sub>2</sub>]<sub>2</sub> (3) and *nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>-[Ph<sub>2</sub>P( $\mu$ -H)NMe<sub>2</sub>CH<sub>2</sub>] (6) and its use in the preparation of the group 4 and 13 dicarbollyl derivatives [<{R( $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)( $\eta^1$ -NMe<sub>2</sub>CH<sub>2</sub>)}M(NMe<sub>2</sub>)<sub>2</sub>] (R = CH<sub>2</sub>NMe<sub>2</sub>, M = Ti 7, Zr 8; R = PPh<sub>2</sub>, M = Ti 9, Zr 10) and [<{( $\eta^1$ -R)( $\eta^1$ -NMe<sub>2</sub>)(CH<sub>2</sub>)(C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)}MMe<sub>2</sub>] (R = CH<sub>2</sub>NMe<sub>2</sub>, M = Al 11, Ga 12; R = PPh<sub>2</sub>, M = Al 13, Ga 14), obtained by reacting the ligands with M(NMe<sub>2</sub>)<sub>4</sub> (M = Ti, Zr) or MM<sub>3</sub> (M = Al, Ga), respectively.

#### 4. Results and Discussion

The new diamino-*o*-carboranyl ligand with contains two pendar tamine donors was synthesized in excellent yield from commercially available starting materials. Thus, the one pot generation of 1,2-*o*-carboranyl *bis*(*N,N*-dimethylmethanamine) was accomplished by insitide protonation of *o*-carborane with 2 equiv of *n*-BuLi and treatment with Eschenmoser's salt ( $\text{CH}_2\text{NMe}_2^+\text{I}^-$ ).<sup>7</sup> The straight for ward and complete conversion of 1,2-*o*-carboranyl *bis*(*N,N*-dimethylmethanamine) in to *nido*-(*N,N*- $\mu$ -H)-*bis*(dimethylaminomethyl)dicarbollyl ligand, abbreviated as Dcab<sup>NN</sup>H, **3**, was then achieved by heating in neat methanol (Scheme1). An X-ray structural determinationon crystals formed from there action revealed the formula of the salt to be the zwitterionic form of **3** with a dimethylamino unit linked to the dimethylammonium cation by a N–H $\cdots$ N hydrogen bond. Spectroscopic characterization of zwitterionic dicarbollyl ligand **3** showed that the bis(dimethylamino) group was linked to the *nido* cage carborane. The characteristic asymmetric pattern in the  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum in the range –12 to –38 ppm and the presence of an absorption at ca. –3.0 ppm in the  $^1\text{H}$  NMR spectrum imply a B–H–B interaction on the C<sub>2</sub>B<sub>3</sub> open face. Most importantly, the  $^1\text{H}$  NMR spectra of these complexes displayed a singlet pattern for the four methyl protons of the dimethylamino group at 2.69 ppm. The methylene protons of the NCH<sub>2</sub> group are, however, diastereotopic, each giving rise to an AB spin pattern (3.07, 3.53 ppm). The dicarbollyl*bis*(dimethylamino) derivative (Dcab<sup>NN</sup>)M(NMe<sub>2</sub>)<sub>2</sub> (M = Ti **7**, Zr **8**) were prepared by treatment of **3** with M(NMe<sub>2</sub>)<sub>4</sub> (M = Ti, Zr; Scheme1).

**Scheme 1.** Synthesis of  $\text{Dcab}^{NN}\text{H}$  **3**, and those group 4 metal complexes **7** and **8**.

The homologous series of bis(dimethylaminomethyl)dicarbollyl group 4 metal complexes ( $\text{Dcab}^{NN}\text{M}(\text{NMe}_2)_2$  ( $\text{M} = \text{Ti}$  **7**,  $\text{Zr}$  **8**) was prepared by reaction of 1:1 mixtures of  $\text{Dcab}^{NN}\text{H}$  **3** and  $\text{M}(\text{NMe}_2)_4$  in toluene at room temperature (Scheme 1). The overall yields obtained from these reactions typically ranged from 84% to 78%. Several structural features were deduced from the spectral data of complexes **7–8**. The deprotonation of the ligand **3** was evident from the disappearance of the bridge hydrogens of  $\text{B}=\text{H}=\text{B}$  and  $\text{N}=\text{H}=\text{N}$  ( $^1\text{H}$  NMR:  $\delta$  -2.05 and 3.49). The  $^1\text{H}$  NMR spectra of **7–8** exhibited two singlets at 3.48, 3.66 (**7**), 3.21, 3.59 (**8**) ppm corresponding to the each methyl protons of the dimethylamido ligands, respectively, due to the asymmetric group 4 metal center. The coordination of one of the nitrogen atoms of the  $\text{NMe}_2$  unit to the Ti and Zr was evident from the downfield shift of  $\text{NMe}_2$  protons in the  $^1\text{H}$  NMR spectrum. The methylene protons of the  $\text{NCH}_2$  groups in **7–8** were diastereotopic, each giving rise to an AB spin pattern and a broad singlet for the non-coordinated aminomethyl unit. The most significant difference between the  $^1\text{H}$  NMR spectra of **7–8** and those of the parent ligand system **3** was a downfield shift of signals for the one of the methylene proton of  $\text{NCH}_2$ , from about 3.3 ppm for **3** to 3.53–4.07 ppm for **7–8**. The signals for the one of the methyl protons on the  $\text{NMe}_2$  group were also shifted downfield (from 2.69 to 2.86 (**7**) and 2.87 ppm (**8**), respectively). These shifts are consistent with similar findings for other intramolecularly coordinated group 4 metal complexes containing

methylene spacers such as  $(Dcab^N)M(NMe_2)_2$ , ( $M = Ti, Zr$ ). In addition, the  $^{11}B$  chemical shifts were similar to those observed for other dicarbollyl metal complexes and support the proposed  $\eta^5$ -coordination.<sup>4,11</sup> The spectroscopic data for complexes **7–8** indicated that the one of the dimethylamino group of the side chain was coordinated to the metal center in all cases. Compounds **7–8** are among the first examples of dicarbollyl group 4 metal complexes with intramolecular coordination of a bis(dimethylaminomethyl) donor function in the side chain.

As part of ongoing our research into the utility of the hetero multi-functionalized dicarbollyl ligand in group 4 metal complexes, new types of  $[(diphenylphosphino)(dimethylaminomethyl)]$ dicarbollide, abbreviated as  $Dcab^{PN}H$  **6**, were prepared by applying a standard deboronation procedure<sup>8</sup> to  $[(diphenylphosphino)(dimethylaminomethyl)]$ -*o*-carborane ( $Cab^{PN},closo-1-PPh_2-2-Me_2NCH_2-1,2-C_2B_{10}H_{10}$ ) (Scheme 2).

**Scheme 2.** Synthesis of  $Dcab^{PN}H$  ligand **6**, and those group 4 metal complexes **9** and **10**.

In this procedure, reaction of **5** with KOH in ethanol at 78 °C and subsequent protonation with phosphoric acid lead to the formation of deboronated zwitterionic compound **6**. An X-ray structural determination carried out on the crystals produced by this reaction revealed the formula of the salts to be the zwitterionic form *nido*-7-PPh<sub>2</sub>-( $\mu$ -H)-8-Me<sub>2</sub>NCH<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>. Figure 2 shows the conformation of the PPh<sub>2</sub> and NMe<sub>2</sub> tethered open dicarbollide structures of **6**; the availability of potential multidentate  $\eta^5:\eta^1$ -dicarbollyl ligand functionalities can clearly be discerned in these structures.

Spectroscopic characterization of compound **6** shows at the aminomethyl and diphenylphosphino groups are linked to the *nido* cage carborane. The characteristic asymmetric pattern in the  $^{11}\text{B}$  NMR spectrum in the range -6.7 to -35.4 ppm and the present of an absorption at -3.02 ppm in the  $^1\text{H}$  NMR spectrum imply a B-H-B interaction on the  $\text{C}_2\text{B}_3$  open face. Most importantly, the  $^1\text{H}$  NMR spectrum of **6** display a singlet pattern for the methylene unit to the amino nitrogen atom at around 3.2 ppm for  $\text{CH}_2\text{NMe}_2$  group.

Reaction of the zwitterionic compound of **6** with  $\text{M}(\text{NMe}_2)_4$  in toluene gave new types of CGC complexes, formulated as the amino-phosphino dicarbollyl species ( $\text{Dcab}^{PN}$ ) $\text{M}(\text{NMe}_2)_2$  ( $\text{M} = \text{Ti}$  **9**,  $\text{Zr}$  **10**, Scheme 2). The precise structures of these compounds are unknown due to our inability to obtain single crystals for X-ray analysis. Complexes **9–10** decomposed slowly in solution or during crystallization. Several structural features were established from the spectral data yielded by **9–10**. The deprotonation of **6** was evident from the disappearance of the bridge hydrogens of B-H-B and N-H-P ( $^1\text{H}$  NMR:  $\delta$  -3.01, 8.67 (**6**)). The  $^1\text{H}$  NMR spectrum of **9–10** revealed two signals for the methyl groups at the dimethylamino group of the side chain due to the asymmetric group 4 metal center. The methylene protons of the  $\text{NCH}_2$  groups in **9–10** were diastereotopic, each giving rise to an AB spin pattern. The most significant difference between the  $^1\text{H}$  NMR spectrum of **6** and **9–10** were the downfield shift of signals for the methylene proton of  $\text{NCH}_2$ . For complexes **7–8** these signals were observed at about 2.3 ppm while **9–10** showed values of 2.72–3.31 ppm. The signals for the methyl protons at the dimethylamino group were also shifted downfield (from 1.68 to 2.11 ppm). Corresponding downfield shifts for the  $\text{NCH}_2$  adjacent to the nitrogen atom were also observed in the  $^{13}\text{C}$  NMR spectra. This observation is consistent with similar findings for other intramolecularly coordinated metal complexes that contain methylene spacers. In addition, the  $^{11}\text{B}$  chemical shifts were similar to those observed for other dicarbollyl metal complexes and support the proposed  $\eta^5$ -coordination. The spectroscopic data for complexes **9–10**

indicated that the dimethylamino group of the side chain was coordinated to the metal center in all cases.

As part of our efforts to search for new types of multi-functionalized dicarbollyl group 13 metal complexes, we wish to report here the synthesis and characterization of alkylaluminum and gallium complexes. Previously, we have described the synthesis of  $\pi,\sigma$ -coordinated dicarbollylamino group 13 metal complexes.<sup>9</sup> A similar protocol was applied to the preparation of zwitterionic dicarbollyl group 13 metal complexes with intramolecular coordination of a *N,N*- or *P,N*-donor unit as shown in Scheme 3.

**Scheme 3.** Synthesis of  $(Dcab^{DN})MMe_2$  ( $D = CH_2NMe_2$ ,  $M = Al$  **11**,  $Ga$  **12**;  $D = PPh_2$ ,  $M = Al$  **13**,  $Ga$  **14**).

Treatment of **3** or **6**<sup>10</sup> with 1 equiv of trimethylaluminum (TMA) in toluene at reflux for 10 h gave aluminum  $\sigma,\sigma$ -bonded complexes of the general formula  $[(\eta^1\text{-}D)RC_2B_9H_9(\eta^1\text{-}NMe_2CH_2)]AlMe_2$  ( $D = CH_2NMe_2$  **3**,  $PPh_2$  **6**) in moderate yields, respectively. While monitoring the reaction progress by <sup>1</sup>H NMR, we observed the exclusive formation of *N,N*'- or *N,P*-coordinated complexes in an early stage and this condition was maintained for the reaction time. <sup>1</sup>H NMR spectra of **11** and **13** contain two distinctive Al-*Me* peaks at around  $\delta$  -0.21 ~ -0.42 and a bridging hydrogen peak at around  $\delta$  -3.01 ~ -3.03, indicating only one methyl group on TMA was removed. Disappearance of a  $N\cdots H\cdots P$  proton and an up-field shift of methyl groups of  $NMe_2$  and aromatic proton of  $PPh_2$  indicate presence of two dative  $\sigma$ -bonding of  $Me_2N\rightarrow Al\leftarrow PPh_2$ . Thus,  $\sigma,\sigma$ -bonded

structures were proposed based on the observation of diastereotopic splitting pattern of the methylene unit and two separate methyl resonances for the coordinated amino functionality ( $CH_2NMe_2$ ). The  $^{27}Al$  NMR chemical shift of these derivatives (**11**, +125; **13**, +121) confirms that the central aluminum atoms are tetracoordinated.<sup>10</sup> Single-crystal X-ray structural studies authenticated  $\sigma,\sigma$ -interactions at the group 13 metal centers (see Figure 6 for **11** and 7 for **13**).

Gallium  $\sigma,\sigma$ -bonded complexes were also produced from the same synthetic protocol (Scheme 3). Similar to the reaction of aluminum,  $\sigma,\sigma$ -bonded complexes were identified for the reaction time, based on  $^1H$  NMR characterization. As shown in Table 1, gallium  $\sigma,\sigma$ -bonded complexes (**12** and **14**) exhibit characteristic shifts and splitting patterns of Ga-Me, CH<sub>2</sub>, PPh<sub>2</sub>, and NMe<sub>2</sub> groups.

**X-ray structural studies on  $\sigma,\sigma$ - and  $\pi,\sigma$ -CGCs.** X-ray structural studies confirmed the geometries characteristic for  $\eta^1;\eta^1$ -type complexes and  $\eta^5;\eta^1$ -type CGCs. These included  $\eta^1;\eta^1$ -type (**11**, **13**, and **14**) and  $\eta^5;\eta^1$ -type CGCs complexes (**4**, **7**, **9**, and **10**). Some general structural features are compared in Table 3-6, where selected bond distances and angles on each ligand system, methylene- and ethylene-tethers, are separately presented in Table 5 and 6, respectively. Detailed information on structural determinations and the structural features of all eight compounds discussed here are provided in the Supporting Information.

An X-ray analysis of **3** indicates  $\sigma,\sigma$ -bonding interactions, where there is an attachment of the aluminum atom to the boron atom on dicarbollyl ring and the nitrogen atom of tethered methylamine. Such a  $\sigma,\sigma$ -bonding permits the formation of a five-membered Al-B-C-C-N ring (Figure 2). Moreover, one B-H terminal hydrogen is located between the aluminum and the B11 atoms hence indicating agostic-interaction<sup>12</sup> with electron-deficient aluminum centre. The geometry at

aluminum is distorted tetrahedral with constrained angles of  $85.3(2)^\circ$  and the nitrogen geometry is regular tetrahedral within small range of variation [ $108.3(4) \sim 110.7(3)^\circ$ ]. Also, the endo-cyclic C7-C12-N bond angle is  $110.9(4)^\circ$ , which is small range of variation from the tetrahedral  $sp^3$ -C value. Structure of **3** resembles to the complex  $[(\eta^1\text{-Cp}^*)(\text{CH}_2)_2(\eta^1\text{-NMe}_2)]\text{Al}(\text{Me})_2$  **B**<sup>2b</sup> in a sense that it has the  $\sigma, \sigma$ -bonding mode. This species is believed to be a kinetically stabilized complex intermediate in which initial  $\sigma$ -electronic interaction of the aluminum atom with the amine side arm and the concomitant  $\eta^1$ -type bonding with neighboring dicarbollyl unit.

A comparison of general structural features of  $\pi, \sigma$ -CGCs with the methylene-spaced ligand system, is given in Table 5. Complex **5** may serve as an example for outlining the general characteristics of this class of compounds. As shown in Figure 3, the asymmetric unit contains two molecules related by local twofold symmetry and the structure of the two independent molecules is essentially identical. The central aluminum atom in **5** is coordinated to a methyl ligand and an amine nitrogen in a  $\sigma$ -bonding manner, while a dicarbollyl unit in a  $\pi$ -bonding interaction. The Al-C(Me) and Al-N bond are in a normal range, having values of and  $2.037 \text{ \AA}$  (av), respectively.<sup>13</sup> The aluminum metal is centered approximately over the ring, giving rise to a Al-C<sub>2</sub>B<sub>3</sub> face (centroid) [w (av C<sub>2</sub>B<sub>3</sub> (centroid) is the centroid of the dicarbollyl ring] distance of  $1.713 \text{ \AA}$  (av). The dicarbollyl unit is symmetrically  $\eta^5$ -coordinated to the aluminum atom. Thus, the Al-C7 linkage [ $2.302 \text{ \AA}$  (av)] is similar to the Al-C8 bonds [ $2.253 \text{ \AA}$  (av)], which in turn are themselves similar to the Al-B9/in0/in1 bonding (for values, see Table 2) [in range of  $2.216s$ ,  $2.200 \text{ \AA}$  (av)]. The connec  $\text{\AA}$  (a $2.200$  veclin centroid of dicarbollyl ring and the C7 bridge is bent out of the dicarbollyl ligand plane toward the metal center. The corresponding C<sub>2</sub>B<sub>3</sub>(centroid)-2.200 The camountand p $137.71^\circ/137.96^\circ$ . The of  $2.216s$ ,  $2.200 \text{ \AA}$  (av)]. The conne $03.6^\circ$  (av), 0 veclinfar away riom the tetrahedral  $sp^3$ -C value. The “constrained geometry” character in a series of related

compounds is probably best characterized by the C<sub>2</sub>B<sub>3</sub>(centroid)-metal-nitrogen angle ( $\alpha$ -angle in Table 5), which responds sensitively to steric and electronic changes at the metal centre. In **5**, it amounts to 103.43° (av). The coordination geometry of the ligand nitrogen atom is distorted tetrahedral within range of 100.4° ~ 112.7°. The Al-bound methyl group is directed over the boron atoms of the dicarbollide cage face due to the aluminum-coordinated NMe<sub>2</sub> sidearm. It is clear that the interactions between the apical aluminum and the boron with the C<sub>2</sub>B<sub>3</sub> pentagonal face are weakened upon complexation with NMe<sub>2</sub> sidearm. The tilt angles of the Al-bound methyl group from the Al-B10 and Al-C<sub>2</sub>B<sub>3</sub> centroid axes are 113.56 and 152.41° (av), respectively.

As shown in Figure 4, the structure of aluminum complex **6** reveals that it is isomorphous and isostructural to **5**. The central aluminum atom is  $\pi$ -bound to the dicarbollyl fragment and  $\sigma$ -bound to the methylamine side arm in a constrained manner. The centroid distance from the aluminum atom (1.703 Å) is smaller than that found in **5**, indicating that there are strong  $\pi$ -bonding interactions between Al<sup>3+</sup> and dicarbollide.<sup>14</sup> Methyl substituent on the carbon atom of the C<sub>2</sub>B<sub>3</sub> pentagonal face renders stronger interaction with central aluminum. All other bond distances and angles around the aluminum and the nitrogen atoms are similar to those found in **5**. The structures of **5** and **6** reported here represent the first solid-state structural information on constrained-geometry aluminum complexes with  $\eta^5;\eta^1$ -mode coordination. This results were communicated recently.<sup>15</sup>

As shown in Figure 5, complex **7** serves as an example to outline the general characteristics of  $\pi,\sigma$ -bonded gallium CGCs. The central gallium atom is pseudo-tetrahedrally coordinated to the methyl ligand [Ga-C(Me), 1.949(8) Å], the NMe<sub>2</sub> sidearm [Ga-N, 2.100(5) Å], and the C<sub>2</sub>B<sub>3</sub> plane of the dicarbollyl ligand [Ga-C<sub>2</sub>B<sub>3</sub> (centroid), 1.862 Å]. The Ga-N distance is consistent with a regular Ga-N ( $sp^3$ ) single bond,<sup>16</sup> and confirms that the N-donor atom is coordinated to the metal in a strain-free manner. The C<sub>2</sub>B<sub>3</sub> ligand is an  $\eta^5$ -coordinated to the gallium metal centre, but rather unsymmetrically with short Ga-B and long Ga-C

distances.<sup>12b,17</sup> It is well-known that metallacarborane compounds containing the  $[nido\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]^{2-}$  and  $[nido\text{-}2,3\text{-C}_2\text{B}_4\text{H}_6]^{2-}$  ligands and their C-substituted derivatives may exhibit varying degrees of distortion from idealized closo geometry by undergoing a “slipping” of the capping metal across the  $\text{C}_2\text{B}_3$  cage face in the direction of the apical boron atom.<sup>14f</sup> Thus, the Ga-B9/B10/B11 [2.236(8)/ 2.213(7)/ 2.313(6) Å] linkage is markedly shorter than the Ga-C7/C8 [2.546 (5)/ 2.515(6) Å] linkage. The corresponding  $\text{C}_2\text{B}_3$  (centroid)-C7-C12 angle is 133.40°. The endo-cyclic C7-C12-N bond angle is 104.4(4)°, which is departed from the tetrahedral  $sp^3\text{-C}$  value. In **7**,  $\alpha$ -angle is 92.55°, which is markedly shorter than that found in **5**. In compound **7**, the direction of the Ga-bound methyl group is pointing toward the B10 atom of the  $\text{C}_2\text{B}_3$  open face.

Another template systems designed to stabilize  $\pi,\sigma$ -CGCs was the ethylene-bridged dicarbollyl/amine ligand system. However, an evidence supporting the  $\eta^1;\eta^1$ -coordination of the dicarbollyl/ethylamino group to the aluminum atom in complex **14** is provided by X-ray crystal structure analy an. As shown in Figure 6, complex **14** is structurally related to **3** in a sense that it adopts  $\eta^1;\eta^1$ -type aluminum CGC with ethylene spacene Complex **14** ure titutescommilin geometry found in  $\sigma,\sigma$ -type bonding fa s $[(\eta^1\text{-Cp}^*)(\text{CH}_2)_2(\eta^1\text{-NBn}_2)]\text{Alth}_e$  **B**.<sup>2b</sup> The central aluminum atom ihat it adopts h1;h1-tB11 atom and tw1;methyl ligands in a  $\sigma$ -bonding fashion. The dibenzylamino fragmey at it adopts to the aluminum in the rem in a sbasal site of the overall pseudo-tetrahedral uraloy ation gcompl a six-memberts B-AdoN-C-C-C ripl. Selected bo.2b eplths to tangles fa s**14** are lanald in Table 6 lex 1n Supporting Ialoy ation. The AdoN bo.2b eplth iha 2.066(2) Å, which laes within the usual range fa sa d a sb bo.2bbetwsen aluminum a.2bnitrogen atomnu<sup>m3</sup> Smmilin to **3**, H11 atom at;h1-tB11 ite of s tgptlic interaction <sup>in</sup>with h1- aluminum metal. In general, metric parameters around the aluminum center are similar to those found in **3**.

## 5. Experimental Section

**5.1. General Procedures.** All manipulations were performed under a dry, oxygen-free, nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmosphere HE-493 dry box. THF was freshly distilled over potassium benzophenone. Toluene, n-hexane, n-pentane was dried and distilled from sodium benzophenone. Dichloromethane and hexane were dried and distilled over CaH<sub>2</sub>. <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1, 96.3, 75.4, and 121.4 MHz respectively. All boron-11 chemical shifts were referenced to BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (0.00 ppm) with a negative sign indicating an upfield shift. All proton and carbon chemical shifts were measured relative to internal residual peaks from the lock solvent (99.5% C<sub>6</sub>D<sub>6</sub>, 99.5% CDCl<sub>3</sub>) and then referenced to Me<sub>4</sub>Si (0.00 ppm). IR spectra were recorded on a Biorad FTS-165 spectrophotometer spectrometer. High-resolution mass spectra were measured at the Korea Basic Science Institute. Elemental analyses were performed with a Carlo Erba Instruments CHNS-OEA 1108 analyzer. All melting points were uncorrected. *o*-Carborane was purchased from the Katchem and used without purification. All other reagents were obtained from commercial suppliers (Aldrich and TCI) and used as received.

**5.2. Preparation of [closo-1,2-(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] 2.** To a stirred solution of *o*-carborane **1** (0.72 g, 5 mmol) in toluene (100 mL) was added 2.5 M *n*-BuLi (4.4 mL) via a syringe through a serum cap at 0°C. The resulting white suspension was stirred at 25 °C for 10 min and then placed in an ice bath. When the toluene solution was cold, the Eschenmoser's salt, CH<sub>2</sub>=NMe<sub>2</sub><sup>+</sup>I<sup>-</sup> (2.03 g, 11.1 mmol) was added to the lithio-*o*-carborane. The reaction temperature was maintained at 0 °C for 1 h. The reaction mixture was then slowly warmed to room temperature. After stirring for an additional 12 h at refluxing temperature, the reaction mixture was filtered and then dried *in vacuo* to give a white crystalline powder. The resulting residue was taken up in a minimum of

*n*-pentane and then recrystallized from this solution by cooling it to -5 °C to afford **2** as colorless crystals. Yield: 86% (1.1 g, 4.3 mmol). Mp: 87 °C. Anal. Calcd for C<sub>8</sub>H<sub>26</sub>B<sub>10</sub>N<sub>2</sub>: C, 37.18; H, 10.14; N, 10.84. Found: C, 37.30; H, 10.12; N, 10.80. IR spectrum (KBr pellet, cm<sup>-1</sup>) ν(B–H) 2640, 2580, ν(C–H) 3001, 2829, 2781. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.32 (s, 12H, N(CH<sub>3</sub>)<sub>2</sub>), 3.11(s, 4H, NCH<sub>2</sub>). <sup>13</sup>C NMR(CDCl<sub>3</sub>) δ 46.7 (N(CH<sub>3</sub>)<sub>2</sub>), 62.6 (NCH<sub>2</sub>). <sup>11</sup>B NMR (CDCl<sub>3</sub>) δ -3.9 (4B), -10.8 (6B).

**5.3. Preparation of [nido-7,8-(NMe<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]** **3.** Compound **2** (0.78 g, 3.0 mmol) was dissolved in degassed MeOH (20 mL) and then refluxed under N<sub>2</sub> for 12 h. MeOH was removed under reduced pressure, and the residue was washed with Et<sub>2</sub>O (10 mL × 3). The volatiles were removed under vacuum provided the final crude product. The product was purified by recrystallization from ethanol to 95 % yield (0.95 g, 3.8 mmol). Mp: 294 °C (dec.). Anal. Calcd for C<sub>8</sub>H<sub>27</sub>B<sub>9</sub>N<sub>2</sub>: C, 38.65; H, 10.95; N, 11.25. Found: C, 38.52; H, 10.98; N, 11.30. IR spectrum (KBr pellet, cm<sup>-1</sup>) ν(B–H) 2593, 2509, ν(C–H) 3025, 2989, 2963. <sup>11</sup>B NMR ((CD<sub>3</sub>)<sub>2</sub>SO)) δ -7.5 (3B), -15.5 (2B), -19.5 (2B), -34.1 (1B), -36.8 (1B).

**5.4. Preparation of [closo-1-PPh<sub>2</sub>-2-CH<sub>2</sub>NMe<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]** **5.** To a stirred solution of 1-PPh<sub>2</sub>-*o*-carborane **4** (1.64 g, 5.0 mmol) in toluene (100 mL) was added 2.5 M *n*-BuLi (1.3 mL, 3.3 mmol) via a syringe through a serum cap at 0 °C. The resulting white suspension was stirred at 25 °C for 10 min and then placed in an ice bath. When the toluene solution was cold, the Eschenmoser's salt, CH<sub>2</sub>=NMe<sub>2</sub><sup>+</sup>I<sup>-</sup> (1.02 g, 5.5 mmol) was added to the 1-PPh<sub>2</sub>-2-lithio-*o*-carborane. The reaction temperature was maintained at 0 °C for 1 h. The reaction mixture was then slowly warmed to room temperature. After stirring for an additional 12 h at refluxing temperature, the reaction mixture was filtered and then dried *in vacuo* to give a white crystalline powder. The resulting

residue was taken up in a minimum of *n*-pentane and then recrystallized from this solution by cooling it to -5 °C to afford **5** as colorless crystalline solids. Yield: 81 % (1.56 g, 4.05 mmol). Mp: 86 °C. Anal. Calcd for C<sub>17</sub>H<sub>28</sub>B<sub>10</sub>NP: C, 52.97; H, 7.32; N, 3.63. Found: C, 5nd:1; H, 7.28; N, 3.60. IR spectrum (KBr pellet, cm<sup>-1</sup>) v(B-H) 2638, 2584, v(C-H) 2988, 2nd: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.32 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 3.13 (s, 2H, NCH<sub>2</sub>), 7.28–7.34 (m, 10H, P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 47.2 (N(CH<sub>3</sub>)<sub>2</sub>), 63.1 (NCH<sub>2</sub>), 125.7 (P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>), 134.6 (P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>). <sup>11</sup>B NMR (CDCl<sub>3</sub>) δ -4.5 (2B), -6.2 (1B), -9.7 (2B), -11.2 (3B), -12.5 (2B). <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 18.4

**5.5. Preparation of [*nido*-7-PPh<sub>2</sub>-8-CH<sub>2</sub>NMe<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] 6.** Compound **5** (1.16 g, 3.0 mmol) and KOH (0.22 g, 4.0 mmol) were dissolved in degassed EtOH (20 mL) and then refluxed under N<sub>2</sub> for 12 h. EtOH was removed under reduced pressure, and the residue was suspended in benzene (60mL). Azeotropic distillation was then performed to remove H<sub>2</sub>O and EtOH, and the remaining white solid was dried under vacuum overnight. The solid was mixed with benzene (30mL) under N<sub>2</sub> to form a slurry, and then H<sub>3</sub>PO<sub>4</sub> was added; the resulting two-phase mixture was stirred vigorously for 15 h. The volatiles were removed by rotary evaporation under reduced pressure and the residue was washed with H<sub>2</sub>O to yield an off-white solid. The product was purified by recrystallization from acetone to yield **6** as colorless crystals. Yield: 94% (1.06 g, 2.8 mmol). Mp: 268°C (dec.). Anal. Calcd for C<sub>17</sub>H<sub>29</sub>B<sub>9</sub>NP: C, 54.35; H, 7.78; N, 3.73. Found: C, 54.31; H, 7.73; N, 3.70. IR spectrum (KBr pellet, cm<sup>-1</sup>) v(B-H) 2590, 2511, v(C-H) 3020, 2982, 2887. <sup>11</sup>B NMR ((CD<sub>3</sub>)<sub>2</sub>SO)) δ -6.7 (1B), -14.8 (2B), -18.6 (3B), -31.6(1B), -35.7 (2B). <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -1.35

**5.6. Preparation of [ $\eta^5:\eta^1$ -(NMe<sub>2</sub>CH<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>CH<sub>2</sub>NMe<sub>2</sub>)]Ti(NMe<sub>2</sub>)<sub>2</sub> 7.** Over a period of 30 min, a 20 mL toluene solution of Ti(NMe<sub>2</sub>)<sub>4</sub> (0.45 g, 2.0 mmol) was added to a stirred solution of **3** (0.50 g, 2.0 mmol) in toluene (20mL) at 0

°C. After addition was complete, the cold bath was removed and the solution was stirred at room temperature for 36 h. Solvent was removed in vacuo and the residue purified by recrystallization with CH<sub>2</sub>Cl<sub>2</sub>/toluene mixture at -30 °C. Yield 84% (0.64 g, 1.68 mmol); mp 131 °C (dec.). HRMS *m/z* Calcd 384.3335, Obsd 384.3322. Anal. Calcd for C<sub>12</sub>H<sub>37</sub>B<sub>9</sub>N<sub>4</sub>Ti: C, 37.67; H, 9.75; N, 14.64. Found: C, 37.74; H, 9.77; N, 14.69. IR (KBr, pellet, cm<sup>-1</sup>) v(B-H) 2593, 2520, 2510, v(C-H) 2989, 2964, 2855. <sup>11</sup>B NMR (CDCl<sub>3</sub>) δ -3.9 (1B), -11.5 (2B), -18.6 (2B), -24.7 (1B), -9.2 (1B), -43.1 (1B), -46.1 (1B).

**5.7. Synthesis of 8:** A procedure analogous to that used to prepare 7 was used, but starting from the zwitterions **3** (0.50 g, 2.0 mmol) with Zr(NMe<sub>2</sub>)<sub>4</sub> (0.54 g, 2.0 mmol). Yield 78% (0.66 g, 1.56 mmol). mp 138 °C (dec.). HRMS *m/z* Calcd 426.2903, Obsd 426.2897. Anal. Calcd for C<sub>12</sub>H<sub>37</sub>B<sub>9</sub>N<sub>4</sub>Zr: C, 33.84; H, 8.75; N, 13.15. Found: C, 33.86; H, 8.80; N, 13.26. IR spectrum (KBr pellet, cm<sup>-1</sup>) v(B-H) 2587, 2518, 2508, v(C-H) 2994, 2950, 2880. <sup>11</sup>B NMR (96.3 MHz, CDCl<sub>3</sub>) δ -4.5 (1B), -12.7 (2B), -17.6 (2B), -30.5 (2B), -36.7 (2B).

**5.8. Synthesis of 9:** A procedure analogous to that used to prepare 7 was used, but starting from the zwitterions **6** (0.75 g, 2.0 mmol) with Ti(NMe<sub>2</sub>)<sub>4</sub> (0.45 g, 2.0 mmol). Yield 87% (0.88 g, 1.74 mmol). mp: 133 °C (dec.). HRMS *m/z* Calcd 511.3199, Obsd 511.3191. Anal. Calcd for C<sub>21</sub>B<sub>9</sub>H<sub>39</sub>N<sub>3</sub>PTi: C, 49.49; H, 7.71; N, 8.24. Found: C, 49.53; H, 7.9.; N, 8.29. IR spectrum (KBr pellet, cm<sup>-1</sup>) v(B-H) 2588, 2520, 250m-1v(C-H) 3002, 2978, 2951. <sup>11</sup>B NMR (96.3 MHz, CDCl<sub>3</sub>) δ -5.6 (1B), -9.7 (1B), -17.4 (1B), -31.4 (2B), -35.2 (3B), -37.8 (1B), -41.3 (1B). <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -11.5

**5.9. Synthesis of 10:** A procedure analogous to that used to prepare 7 was used, but starting from the zwitterions **6** (0.75 g, 2.0 mmol) with Zr(NMe<sub>2</sub>)<sub>4</sub> (0.72 g, 2.0 mmol). Yield 65% (0.72 g, 1.3 mmol). mp: 128 °C (dec.). HRMS

*m/z* Calcd 553.2766, Obsd 553.2758. Anal. Calcd for C<sub>21</sub>B<sub>9</sub>H<sub>39</sub>N<sub>3</sub>PZr: C, 45.61; H, 7.11; N, 7.60. Found: C, 45.58; H, 7.14; N, 7.63. IR spectrum (KBr pellet, cm<sup>-1</sup>)  $\nu$ (B-H) 2567, 2528, 2508,  $\nu$ (C-H) 2984, 2955, 2948. <sup>11</sup>B NMR (96.3 MHz, CDCl<sub>3</sub>)  $\delta$  -7.4 (1B), -12.8 (1B), -19.4 (2B), -30.4 (3B), -34.6 (1B), -42.5 (1B). <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  -11.6

**5.10. Preparation of  $[(\eta^1\text{-NMe}_2\text{CH}_2\text{C}_2\text{B}_9\text{H}_{10})\text{CH}_2(\eta^1\text{-NMe}_2)]\text{AlMe}_2$  11.** To a stirred 20 mL of toluene solution containing **3** (0.50 g, 2.0 mmol) was added a 5 mL of toluene solution of AlMe<sub>3</sub>(0.14 g, 2.0 mmol) by cannula at -78 °C. After addition was complete, the dry-ice/acetone bath was removed and the solution was refluxed under N<sub>2</sub> for 12 h. The formation of **3** was demonstrated by <sup>1</sup>H NMR spectroscopy. Removal of the volatiles under vacuum and the residue purified by recrystallization with a toluene at -15 °C. Yield: 91% (0.55 g, 1.82 mmol). mp: 135 °C (dec.). HRMS *m/z* Calcd 306.3218, Obsd 306.3212. Anal. Calcd for C<sub>10</sub>B<sub>9</sub>H<sub>32</sub>AlN<sub>2</sub>: C, 39.42; H, 10.59; N, 9.20. Found: C, 39.18; H, 10.54; N, 9.27. IR spectrum (KBr pellet, cm<sup>-1</sup>)  $\nu$ (B-H) 2568, 2525,  $\nu$ (C-H) 3105, 2993, 2951. <sup>11</sup>B NMR (96.3MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -6.7 (1B), -10.4 (1B), -16.9 (2B), -26.7 (2B), -34.7 (2B), -39.1 (1B).

**5.11. Synthesis of 12.** A procedure analogous to that used to prepare **11** was used, but starting from the zwitterions **3** (0.50 g, 2.0 mmol) with GaMe<sub>3</sub> (0.23 g, 2.0 mmol). Yield: 71% (0.49 g, 1.42 mmol). mp: 130 °C (dec.). HRMS *m/z* Calcd 348.2659, Obsd 348.2648. Anal. Calcd for C<sub>10</sub>B<sub>9</sub>H<sub>32</sub>GaN<sub>2</sub>: C, 34.57; H, 9.28; N, 8.06. Found: C, 34.60; H, 9.33; N, 8.00. IR spectrum (KBr pellet, cm<sup>-1</sup>)  $\nu$ (B-H) 2570, 2531, 2518,  $\nu$ (C-H) 2994, 2972. <sup>11</sup>B NMR (96.3MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -7.1 (2B), -13.4 (1B), -21.6 (1B), -28.4 (2B), -31.3 (1B), -32.8 (1B), -38.5 (1B).

**5.12. Synthesis of 13.** A procedure analogous to that used to prepare **11** was used, but starting from the zwitterions **6** (0.75 g, 2.0 mmol) with AlMe<sub>3</sub> (0.14 g, 2.0 mmol). Yield: 80% (0.69 g, 1.6 mmol). mp: 125 °C (dec.). HRMS *m/z* Calcd

433.3082, Obsd 433.3071. Anal. Calcd for  $C_{19}B_9H_{34}AlNP$ : C, 52.86; H, 7.94; N, 3.24. Found: C, 52.81; H, 8.00; N, 3.21. IR spectrum (KBr pellet,  $\text{cm}^{-1}$ )  $\nu(\text{B}-\text{H})$  2574, 2555, 2512,  $\nu(\text{C}-\text{H})$  3100, 2986, 2980.  $^{11}\text{B}$  NMR (96.3 MHz,  $C_6D_6$ )  $\delta$  -11.3 (2B), -18.4 (1B), -20.1 (1B), -26.7 (2B), -28.4 (1B), -31.5 (1B), -38.3 (1B).  $^{31}\text{P}$  NMR ( $CDCl_3$ )  $\delta$  -42.8

**5.13. Synthesis of 14.** A procedure analogous to that used to prepare **11** was used, but starting from the zwitterions **6** (0.75 g, 2.0 mmol) with  $GaMe_3$  (0.23 g, 2.0 mmol). Yield: 74% (0.70 g, 1.48 mmol). mp: 122 °C (dec.). HRMS  $m/z$  Calcd 475.2522, Obsd 475.2513. Anal. Calcd for  $C_{19}B_9H_{34}GaNP$ : C, 48.10; H, 7.22; N, 2.95. Found: C, 48.06; H, 7.17; N, 2.98. IR spectrum (KBr pellet,  $\text{cm}^{-1}$ )  $\nu(\text{B}-\text{H})$  2581, 2564,  $\nu(\text{C}-\text{H})$  3104, 2988, 2961.  $^{11}\text{B}$  NMR (96.3 MHz,  $C_6D_6$ )  $\delta$  -10.5 (1B), -19.7 (2B), -21.5 (1B), -28.6 (1B), -30.4 (3B), -36.7 (1B).  $^{31}\text{P}$  NMR ( $CDCl_3$ )  $\delta$  -41.9

**5.14. Crystal Structure Determination** Crystals of **3**, **6**, **7**, **9**, **10**, **11**, **13**, and **14** were obtained from toluene at -15 °C, sealed in glass capillaries under argon, and mounted on the diffractometer. Preliminary examination and data collection were performed using a Brucker SMART CCD detector system single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source (40 kV × 50 mA) using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). Preliminary unit cell constants were determined with a set of 45 narrowframe ( $0.3^\circ$  in  $\omega$ ) scans. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package was used for data collection, and SAINT was used for frame integration.<sup>18</sup> Final cell constants were determined by a global refinement of  $xyz$  centroids of reflections harvested from the entire data set. Structure solution and refinement were carried out using the SHELXTL-PLUS software package.<sup>18</sup>

## 6. References

1. (a) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587. (b) Siemeling, U. *Chem. Rev.* **2000**, *100*, 1495. (c) Braunschweig, H.; Breitling, F. M. *Coordi. Chem. Rev.* **2006**, *250*, 2691.
2. (a) Jutzi, P.; Dahlhaus, J.; Bangel, M. *J. Organomet. Chem.* **1993**, *460*, C13. (b) Jutzi, P.; Dahlhaus, J.; Neumann, B.; Stammler, H. -G. *Organometallics* **1996**, *15*, 747. (c) Pietryga, J. M.; Gorden, J. D.; Macdonald, C. L. B.; Voigt, A.; Wiacek, R. J.; Cowley, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 7713. (d) Wiacek, R. J.; Macdonald, C. L. B.; Jones, J. N.; Pietryga, J. M.; Cowley, A. H. *Chem. Commun.* **2003**, 430. (e) Pietryga, J. M.; Jones, J. N.; Mullins, L. A.; Wiacek, R. J.; Cowley, A. H. *Chem. Commun.* **2003**, 2072.
3. (a) Sapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (b) Okuda, J. *Chem. Ber.* **1990**, *123*, 1649. (c) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (d) Chen, Y. X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451. (e) Alt, H. G.; Reb, A.; Milins, W.; Weis, A. *J. Organomet. Chem.* **2001**, *628*, 169.
4. (a) Lanza, G.; Fragalà, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 8257. (b) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274. (c) Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, Jr., V. G.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 8291.
5. Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem.* **1993**, *105*, 1714.
6. Drew, D. A.; Haaland, A. *Chem. Commun.* **1972**, 1300.
7. Fisher, J. D.; Shapiro, P. J.; Budzelaar, P. H. M.; Staples, R. J. *Inorg. Chem.* **1998**, *37*, 1295.
8. (a) Teclé, B.; Corfield, P. W. R.; Oliver, J. P. *Inorg. Chem.* **1982**, *21*, 458. (b) Schulz, S.; Häming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G.

M. *Angew. Chem.* **1994**, *106*, 1052. (c) Fisher, J. D.; Shapiro, P. J.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 271.

9. see also: Budzelaar, P. H. M.; Engelberts, J. J.; Lenthe, J. H. v. *Organometallics* **2003**, *22*, 1562.

10. (a) Kim, D. -H.; Won, J. H.; Kim, S. -J.; Ko, J.; Kim, S. -H.; Cho, S.; Kang, S. O. *Organometallics* **2001**, *20*, 4298. (b) Lee, J. -D.; Lee, Y. -J.; Son, K. -C.; Cheong, M.; Ko, J.; Kang, S. O. *Organometallics* **2007**, *26*, 3374.

11. Lee, Y. -J.; Lee, J. -D.; Jeong, H. -J.; Son, K. -C.; Ko, J.; Cheong, M.; Kang, S. O. *Organometallics* **2005**, *24*, 3008.

12. (a) Young, D. A. T.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 5687. (b) Schubert, D. M.; Bandman, M. A.; Rees, W. S., Jr.; Knobler, C. B.; Lu, P.; Nam, W.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2046. (c) Demachy, I.; Volatron, F. *Eur. J. Inorg. Chem.* **1998**, 1015. (d) Cowley, A. R.; Downs, A. J.; Marchant, S.; Macrae, V. A.; Taylor, R. A. *Organometallics* **2005**, *24*, 5702.

13. (a) Bradley, D. C.; Coumbarides, G.; Harding, I. S.; Hawkes, G. E.; Maia, I. A.; Mottevalli, M. *J. Chem. Soc., Dalton Trans.* **1999**, 3553. (b) Doyle, D.; Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **2000**, 4093. (c) Fooken, U.; Khan, M. A.; Wehmschulte, R. J. *Inorg. Chem.* **2001**, *40*, 1316. (d) Su, W.; Kim, Y.; Ellern, A.; Guzei, I. A.; Verkade, J. G. *J. Am. Chem. Soc.* **2006**, *128*, 13727. (e) Andrews, P. C.; Calleja, S.; Maguire, M. *Polyhedron* **2006**, *25*, 1625. (f) Su, W.; Kobayashi, J.; Ellern, A.; Kawashima, T.; Verkade, J. G. *Inorg. Chem.* **2007**, *46*, 7953.

14. (a) Young, D. A. T.; Willey, G. R.; Hawthorne, M. F.; Churchill, M. R.; Reis, A. H., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 6663. (b) Churchill, M. R.; Reis, A. H., Jr.; Young, D. A.; Wiley, G. R.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1971**, 298. (c) Churchill, M. R.; Reis, A. H., Jr. *J. Chem. Soc., Dalton Trans.* **1972**, 1317. (d) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.;

Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5367. (e) Getman, T. D.; Shore, S. G. *Inorg. Chem.* **1988**, *27*, 3439. (f) Schubert, D. M.; Bandman, M. A.; Rees, W. S., Jr.; Knobler, C. B.; Lu, P.; Nam, W.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2046.

15. Son, K. -C.; Lee, Y. -J.; Cheong, M.; Ko, J.; Kang, S. O. *J. Am. Chem. Soc.* **2006**, *128*, 12086.

16. (a) Andrews, P. C.; Gardiner, M. G.; Raston, C. L.; Tolhurst, V. -A. *Inorg. Chim. Acta* **1997**, *259*, 249. (b) Hosmane, N. S.; Lu, K. -J.; Zhang, H.; Maguire, J. A. *Organometallics* **1997**, *16*, 5163. (c) Lee, J. -D.; Baek, C. -K.; Ko, J.; Park, K.; Cho, S.; Min, S. -K.; Kang, S. O. *Organometallics* **1999**, *18*, 2189. (d) Bensiek, S.; Bangel, M.; Neumann, B.; Stammier, H. -G.; Jutzi, P. *Organometallics* **2000**, *19*, 1292. (e) Tian, X.; Fröhlich, R.; Pape, T.; Mitzel, N. W. *Organometallics* **2005**, *24*, 5294.

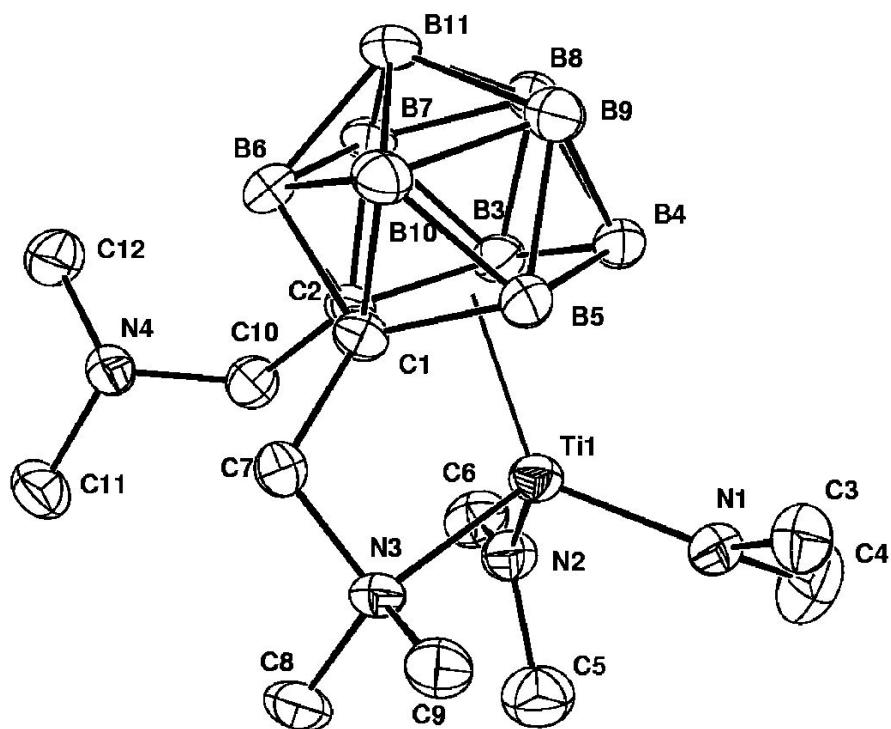
17. (a) Grimes, R. N.; Rademaker, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 6498. (b) Grimes, R. N.; Rademaker, W. J.; Denniston, M. L.; Bryan, R. F.; Greene, P. T. *J. Am. Chem. Soc.* **1972**, *94*, 1865. (c) Hosmane, N. S.; Lu, K. -J.; Zhang, H.; Jia, L. *Organometallics* **1991**, *10*, 963. (d) Saxena, A. K.; Maguire, J. A.; Hosmane, N. S. *Chem. Rev.* **1997**, *97*, 2421. (e) Hosmane, N. S. *J. Organomet. Chem.* **1999**, *581*, 13.

18. (a) SMART and SAINT; Bruker Analytical X-ray Division, Madison, WI, 2002. (b) Sheldrick, G. M. SHELXTL-PLUS Software Package; Bruker Analytical X-ray Division, Madison, WI, 2002.

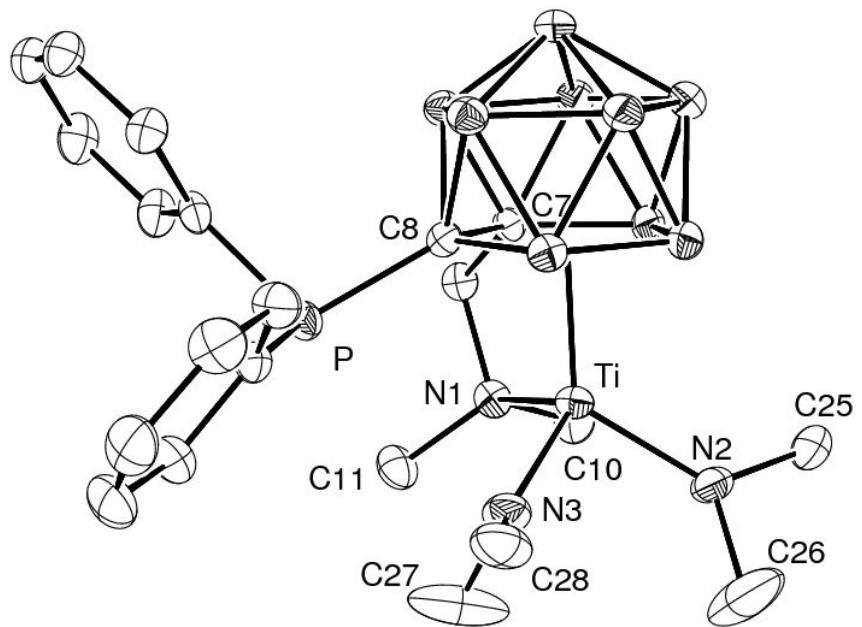
Table 1. Comparison of the NMR Spectroscopic Data for Compounds **3**, **6**, and **7–14**

Comp	<sup>1</sup> H NMR ( <i>d</i> )				<sup>13</sup> C NMR ( <i>d</i> )			
	CH <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	M–N(CH <sub>3</sub> ) <sub>2</sub>	M–CH <sub>3</sub>	CH <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	M–N(CH <sub>3</sub> ) <sub>2</sub>	M–CH <sub>3</sub>
<b>3<sup>a</sup></b>	3.07, 3.53	2.69			65.0	43.4		
<b>6<sup>a</sup></b>	2.99, 3.42	2.66			64.2	42.6		
<b>7<sup>b</sup></b>	2.93, 4.12	2.54, 2.86	3.48, 3.66		69.6	52.3	47.2, 52.6	
	3.56 (free)	2.33 (free)			64.4 (free)	47.8 (free)		
<b>8<sup>b</sup></b>	2.94, 4.12	2.55, 2.87	3.50, 3.67		70.1	52.8	48.1, 53.0	
	3.55 (free)	2.34 (free)			64.1 (free)	47.5 (free)		
<b>9<sup>b</sup></b>	2.93, 4.13	2.52, 2.85	3.46, 3.63		69.5	52.1	47.2, 52.3	
<b>10<sup>b</sup></b>	2.95, 4.12	2.55, 2.88	3.49, 3.67		70.0	52.6	48.0, 52.8	
<b>11<sup>c</sup></b>	2.34, 2.51	1.54		-0.21	71.5	56.8		-8.72
<b>12<sup>c</sup></b>	2.40, 2.54	1.62		0.61	71.8	57.1		1.45
<b>13<sup>c</sup></b>	2.38, 2.55	1.61		-0.27, -0.49	71.8	57.2		-7.47, -9.51
<b>14<sup>c</sup></b>	2.41, 2.62	1.66		0.56, 0.84	72.2	57.6		1.51, 2.97

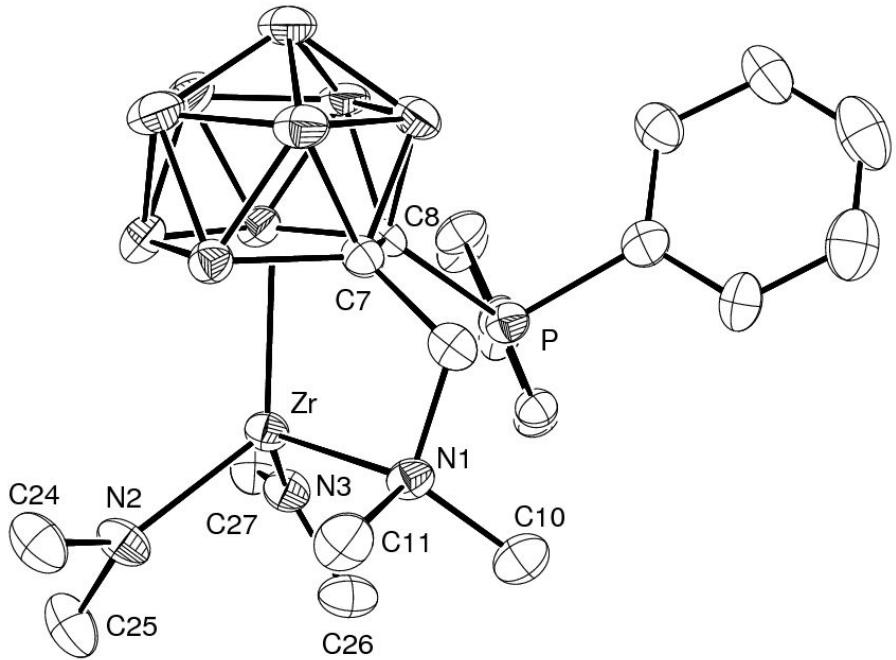
<sup>a</sup>(CD<sub>3</sub>)<sub>2</sub>SO was used as the solvent and the chemical shifts are reported relative to the residual H of the solvent. <sup>b</sup>CDCl<sub>3</sub> was used as the solvent and the chemical shifts are reported relative to the residual H of the solvent. <sup>c</sup>C<sub>6</sub>D<sub>6</sub> was used as the solvent and the chemical shifts are reported relative to the residual H of the solvent.



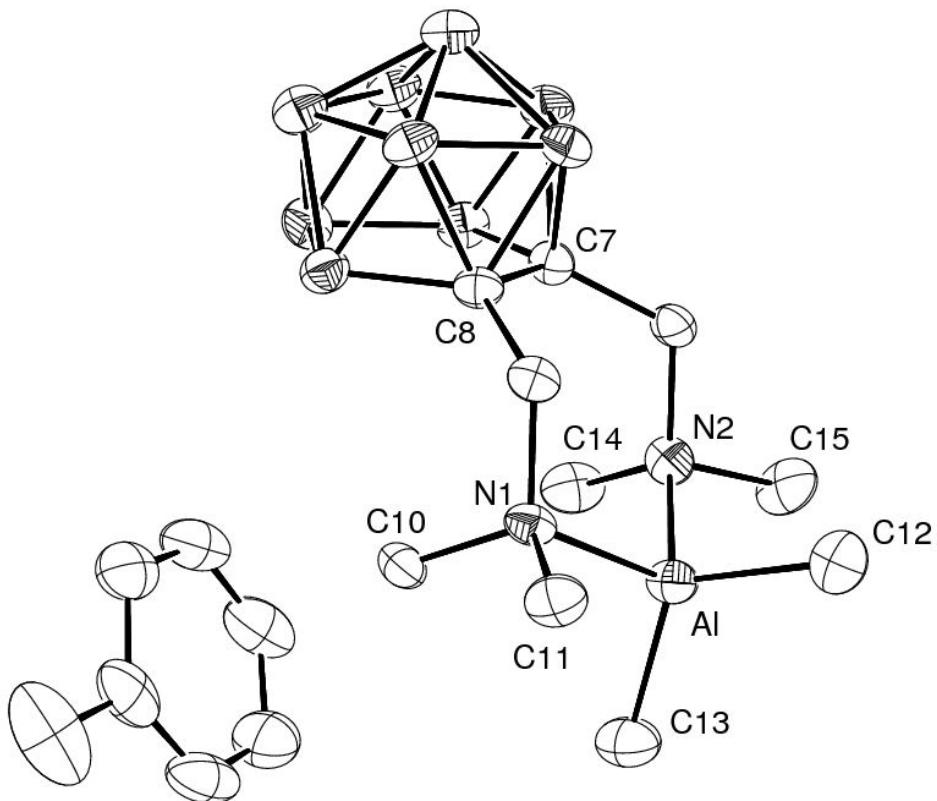
**Figure 1.** Molecular structure of **7** with thermal ellipsoids drawn at the 30% level.



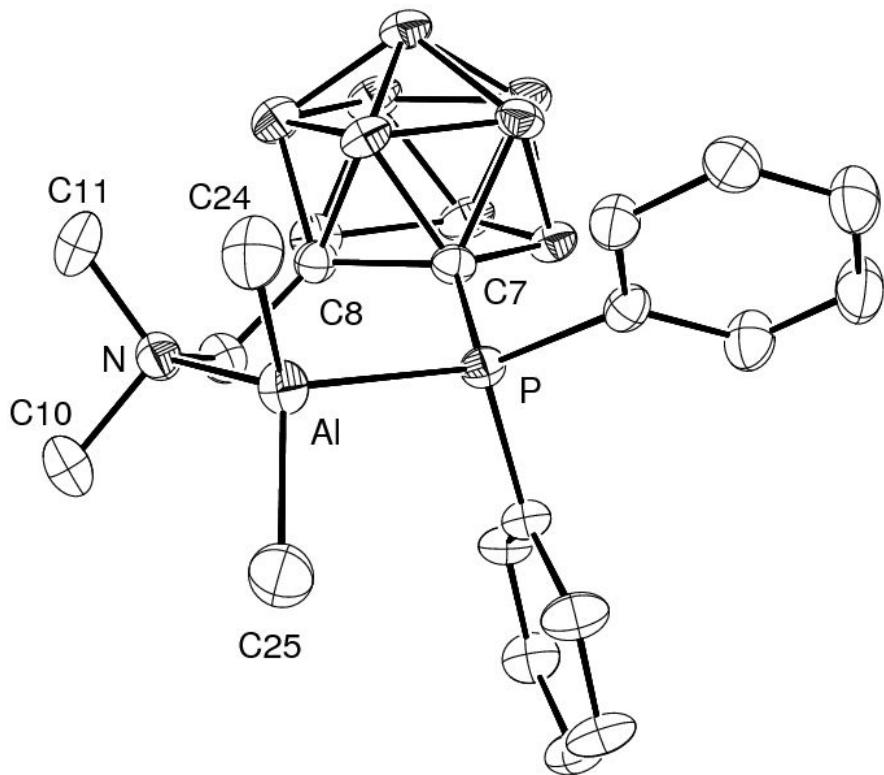
**Figure 2.** Molecular structure of **9** with thermal ellipsoids drawn at the 30% level.



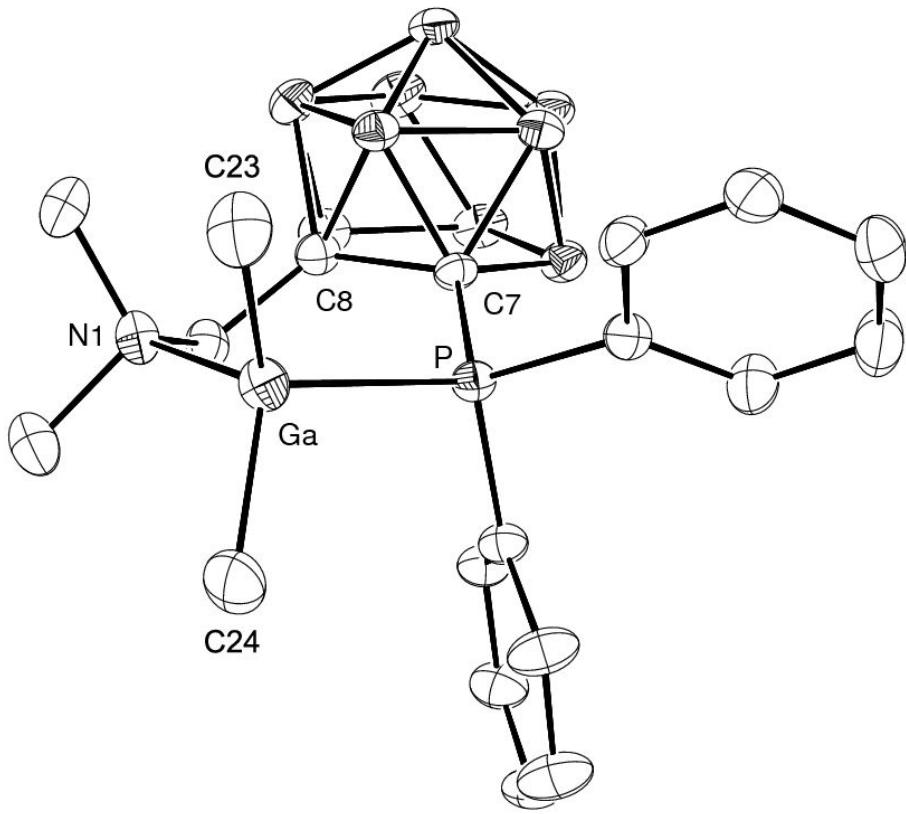
**Figure 3.** Molecular structure of **10** with thermal ellipsoids drawn at the 30% level.



**Figure 4.** Molecular structure of **11** with thermal ellipsoids drawn at the 30% level.



**Figure 5.** Molecular structure of **13** with thermal ellipsoids drawn at the 30% level.



**Figure 6.** Molecular structure of **14** with thermal ellipsoids drawn at the 30% level.

Table 1. Crystal data and structure refinement for **3**.

Identification code	kor055
Empirical formula	C <sub>9</sub> H <sub>31</sub> B <sub>9</sub> N <sub>2</sub>
Formula weight	264.65
Temperature	293(2) K
Wavelength	0.71070 Å
Crystal system, space group	Orthorhombic, P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Unit cell dimensions	<i>a</i> = 10.5791(7) Å <i>b</i> = 11.3215(2) Å <i>c</i> = 14.9539(9) Å
Volume	1791.0(3) Å <sup>3</sup>
Z, D <sub>calc</sub>	4, 0.981 g/cm <sup>3</sup>
<i>m</i>	0.049 mm <sup>-1</sup>
<i>F</i> (000)	576
Crystal size	0.5 x 0.5 x 0.4 mm
q range for data collection	2.26 to 25.96 °
Limiting indices	0 ≤ h ≤ 13, 0 ≤ k ≤ 13, 0 ≤ l ≤ 18
Reflections collected / unique	2006 / 2006 [R(int) = 0.0000]
Completeness to q = 25.96	100.0 %
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	2006 / 0 / 201
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.059
Final R indices [I>2s (I)]	<sup>a</sup> R <sub>1</sub> = 0.1164, <sup>b</sup> wR <sub>2</sub> = 0.2728
R indices (all data)	<sup>a</sup> R <sub>1</sub> = 0.2925, <sup>b</sup> wR <sub>2</sub> = 0.3492
Absolute structure parameter	9(10)
Largest diff. peak and hole	0.211 and -0.206 e.Å <sup>-3</sup>

<sup>a</sup> $R_1 = \frac{1}{\sum} |F_o| - |F_c|$  (based on reflections with  $F_o^2 > 2sF^2$ ),

<sup>b</sup> $wR_2 = [\frac{w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}]^{1/2}$ ;  $w = 1/[s^2(F_o^2) + (0.095P)^2]$ ;  $P = [\max(F_o^2, 0) + 2F_c^2]/3$  (also with  $F_o^2 > 2sF^2$ )

Table 2. Bond lengths [Å] for **3**.

N(1)-C(5)	1.442(2)	C(1)-B(3)	1.740(2)
N(1)-C(4)	1.445(1)	B(1)-B(4)	1.73(3)
N(1)-C(3)	1.498(1)	B(1)-B(2)	1.73(3)
N(2)-C(7)	1.452(1)	B(1)-B(3)	1.75(2)
N(2)-C(8)	1.493(1)	B(1)-B(6)	1.76(2)
N(2)-C(9)	1.503(2)	B(1)-B(5)	1.77(2)
N(2)-C(6)	1.507(1)	B(2)-B(3)	1.70(2)
C(2)-C(1)	1.539(1)	B(2)-B(9)	1.71(3)
C(2)-B(3)	1.64(2)	B(2)-B(6)	1.73(2)
C(2)-B(9)	1.65(2)	B(3)-B(4)	1.73(2)
C(2)-B(2)	1.697(2)	B(4)-B(5)	1.75(2)
C(1)-C(3)	1.484(1)	B(4)-B(11)	1.75(2)
C(1)-B(11)	1.606(2)	B(5)-B(11)	1.69(2)
B(6)-B(10)	1.76(2)	B(5)-B(10)	1.74(2)
B(11)-B(10)	1.79(2)	B(5)-B(6)	1.79(2)
B(10)-B(9)	1.85(3)	B(6)-B(9)	1.73(2)
C(1)-B(4)	1.701(2)		

Table 3. Angles [deg] for **3**.

C(5)-N(1)-C(4)	110.2(1)	B(2)-B(1)-B(6)	59.5(1)
C(5)-N(1)-C(3)	111.5(1)	B(3)-B(1)-B(6)	106.4(1)

C(4)-N(1)-C(3)	109.5(1)	B(4)-B(1)-B(5)	59.9(1)
C(7)-N(2)-C(8)	109.1(9)	B(2)-B(1)-B(5)	107.5(1)
C(7)-N(2)-C(9)	111.2(1)	B(3)-B(1)-B(5)	106.7(1)
C(8)-N(2)-C(9)	109.2(9)	B(6)-B(1)-B(5)	60.9(9)
C(7)-N(2)-C(6)	108.5(1)	B(4)-C(1)-B(3)	60.2(9)
C(8)-N(2)-C(6)	109.1(1)	C(1)-C(3)-N(1)	114.4(9)
C(9)-N(2)-C(6)	109.7(1)	C(2)-B(2)-B(3)	57.7(8)
C(1)-C(2)-B(3)	66.3(9)	C(2)-B(2)-B(9)	58.0(9)
C(1)-C(2)-B(9)	112.9(1)	B(3)-B(2)-B(9)	108.3(1)
B(3)-C(2)-B(9)	114.3(1)	C(2)-B(2)-B(1)	103.8(1)
C(1)-C(2)-B(2)	113.7(1)	B(3)-B(2)-B(1)	61.2(1)
B(3)-C(2)-B(2)	61.3(1)	B(9)-B(2)-B(1)	109.2(1)
B(9)-C(2)-B(2)	61.4(9)	C(2)-B(2)-B(6)	103.3(1)
C(3)-C(1)-C(2)	115.2(9)	B(3)-B(2)-B(6)	109.8(1)
C(3)-C(1)-B(11)	124.9(1)	B(9)-B(2)-B(6)	60.1(1)
C(2)-C(1)-B(11)	112.8(9)	B(1)-B(2)-B(6)	61.1(9)
C(3)-C(1)-B(4)	120.4(9)	C(2)-B(3)-B(2)	61.0(1)
C(2)-C(1)-B(4)	109.1(9)	C(2)-B(3)-B(4)	103.3(1)
B(11)-C(1)-B(4)	64.0(9)	B(2)-B(3)-B(4)	108.3(1)
C(3)-C(1)-B(3)	113.2(9)	C(2)-B(3)-C(1)	54.1(7)
C(2)-C(1)-B(3)	59.6(8)	B(2)-B(3)-C(1)	103.9(1)
B(11)-C(1)-B(3)	113.5(1)	B(4)-B(3)-C(1)	58.8(8)
B(4)-B(1)-B(2)	106.9(1)	C(2)-B(3)-B(1)	105.5(1)
B(4)-B(1)-B(3)	59.5(9)	B(2)-B(3)-B(1)	60.3(1)
B(2)-B(1)-B(3)	58.5(1)	B(4)-B(3)-B(1)	59.6(1)
B(4)-B(1)-B(6)	108.5(1)	C(1)-B(3)-B(1)	103.5(1)
C(1)-B(4)-B(3)	61.0(8)	B(2)-B(6)-B(1)	59.4(1)

C(1)-B(4)-B(1)	106.2(1)	B(10)-B(6)-B(1)	109.7(1)
B(3)-B(4)-B(1)	60.9(1)	B(9)-B(6)-B(5)	107.3(1)
C(1)-B(4)-B(5)	101.3(9)	B(2)-B(6)-B(5)	106.6(1)
B(3)-B(4)-B(5)	108.8(1)	B(10)-B(6)-B(5)	58.8(9)
B(1)-B(4)-B(5)	61.3(9)	B(1)-B(6)-B(5)	59.7(1)
C(1)-B(4)-B(11)	55.4(7)	C(1)-B(11)-B(5)	108.0(1)
B(3)-B(4)-B(11)	107.0(1)	C(1)-B(11)-B(4)	60.6(8)
B(1)-B(4)-B(11)	107.1(1)	B(5)-B(11)-B(4)	60.9(9)
B(5)-B(4)-B(11)	57.7(9)	C(1)-B(11)-B(10)	108.4(1)
B(11)-B(5)-B(10)	63.1(9)	B(5)-B(11)-B(10)	59.9(9)
B(11)-B(5)-B(4)	61.4(9)	B(4)-B(11)-B(10)	110.0(1)
B(10)-B(5)-B(4)	113.0(1)	B(5)-B(10)-B(6)	61.6(8)
B(11)-B(5)-B(1)	108.1(1)	B(5)-B(10)-B(11)	57.0(8)
B(10)-B(5)-B(1)	110.1(1)	B(6)-B(10)-B(11)	104.2(9)
B(4)-B(5)-B(1)	58.8(1)	B(5)-B(10)-B(9)	104.0(1)
B(11)-B(5)-B(6)	107.3(1)	B(6)-B(10)-B(9)	57.1(9)
B(10)-B(5)-B(6)	59.6(9)	B(11)-B(10)-B(9)	100.6(1)
B(4)-B(5)-B(6)	106.4(1)	C(2)-B(9)-B(2)	60.6(9)
B(1)-B(5)-B(6)	59.3(9)	C(2)-B(9)-B(6)	105.6(1)
B(9)-B(6)-B(2)	59.3(1)	B(2)-B(9)-B(6)	60.6(9)
B(9)-B(6)-B(10)	64.2(1)	C(2)-B(9)-B(10)	105.1(1)
B(2)-B(6)-B(10)	112.0(1)	B(2)-B(9)-B(10)	108.7(1)
B(9)-B(6)-B(1)	107.2(1)	B(6)-B(9)-B(10)	58.7(9)

Table 1. Crystal data and structure refinement for 6.

Identification code	kor113
Empirical formula	C <sub>9</sub> H <sub>30</sub> B <sub>9</sub> N <sub>3</sub> Ti
Formula weight	325.55
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Unit cell dimensions	$a = 17.510(2)$ Å $b = 13.151(2)$ Å $c = 8.044(1)$ Å
Volume	1852.3(4) Å <sup>3</sup>
Z, D <sub>calc</sub>	4, 1.167 g/cm <sup>3</sup>
<i>m</i>	0.454 mm <sup>-1</sup>
F(000)	688
Crystal size	0.25 x 0.15 x 0.10 mm
q range for data collection	2.33 to 28.29 °
Limiting indices	-22 ≤ h ≤ 23, -11 ≤ k ≤ 17, -10 ≤ l ≤ 10
Reflections collected / unique	12979 / 2400 [R(int) = 0.1718]
Completeness to q = 28.29	99.9 %
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	2400 / 0 / 116
Goodness-of-fit on $F^2$	1.000
Final R indices [I>2s(I)]	<sup>a</sup> R <sub>1</sub> = 0.0841, <sup>b</sup> wR <sub>2</sub> =0.2149
R indices (all data)	<sup>a</sup> R <sub>1</sub> = 0.2187, <sup>b</sup> wR <sub>2</sub> =0.3043
Extinction coefficient	0.0025(17)
Largest diff. peak and hole	0.808 and -0.828 e. Å <sup>-3</sup>

<sup>a</sup> $R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$  (based on reflections with  $F_o^2 > 2sF^2$ ),

<sup>b</sup> $wR_2 = [\sum w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}; w = 1/[s^2(F_o^2) + (0.095P)^2]; P = [\max(F_o^2, 0) + 2F_c^2]/3$   
(also with  $F_o^2 > 2sF^2$ )

Table 2. Bond lengths [ $\text{\AA}$ ] for **6**.

Ti(1)-N(2)	1.891(5)	C(1)-B(2)*	1.717(9)
Ti(1)-N(2)*	1.891(5)	C(1)-B(2)	1.717(9)
Ti(1)-N(1)	2.220(7)	C(2)-B(5)	1.699(1)
Ti(1)-C(1)	2.351(7)	C(2)-B(2)	1.736(9)
Ti(1)-B(6)*	2.384(7)	C(2)-B(3)	1.739(1)
Ti(1)-C(2)*	2.384(7)	B(1)-B(3)	1.762(1)
Ti(1)-C(2)	2.384(7)	B(1)-B(3)*	1.762(1)
Ti(1)-B(5)	2.433(8)	B(1)-B(2)*	1.778(1)
Ti(1)-B(5)*	2.433(8)	B(1)-B(2)	1.778(1)
N(1)-C(4)	1.487(7)	B(1)-B(4)	1.781(2)
N(1)-C(4)*	1.487(7)	B(2)-B(2)*	1.776(2)
N(1)-C(3)	1.490(1)	B(2)-B(3)	1.777(1)
N(2)-C(6)	1.276(1)	B(3)-B(4)	1.758(1)
N(2)-C(5)	1.423(1)	B(3)-B(5)	1.796(1)
C(1)-C(3)	1.504(1)	B(4)-B(3)*	1.758(1)
C(1)-C(2)	1.602(8)	B(4)-B(5)	1.774(1)
C(1)-B(6)*	1.602(8)	B(4)-B(5)*	1.774(1)
C(1)-C(2)*	1.602(8)	B(5)-B(5)*	1.75(2)

Table 3. Angles [deg] for **6**.

N(2)-Ti(1)-N(2)*	102.7(3)	N(2)-Ti(1)-B(5)*	123.6(3)
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N(2)-Ti(1)-N(1)	103.4(2)	N(2)*-Ti(1)-B(5)*	89.6(3)
N(2)*-Ti(1)-N(1)	103.4(2)	N(1)-Ti(1)-B(5)*	127.1(3)
N(2)-Ti(1)-C(1)	128.5(2)	C(1)-Ti(1)-B(5)*	68.5(3)
N(2)*-Ti(1)-C(1)	128.5(2)	B(6)*-Ti(1)-B(5)*	41.3(3)
N(1)-Ti(1)-C(1)	63.4(3)	C(2)*-Ti(1)-B(5)*	41.3(3)
N(2)-Ti(1)-B(6)*	158.3(2)	C(2)-Ti(1)-B(5)*	69.3(3)
N(2)*-Ti(1)-B(6)*	93.7(2)	B(5)-Ti(1)-B(5)*	42.1(5)
N(1)-Ti(1)-B(6)*	86.3(2)	C(4)-N(1)-C(4)*	107.8(8)
C(1)-Ti(1)-B(6)*	39.6(2)	C(4)-N(1)-C(3)	110.7(5)
N(2)-Ti(1)-C(2)*	158.3(2)	C(4)*-N(1)-C(3)	110.7(5)
N(2)*-Ti(1)-C(2)*	93.7(2)	C(4)-N(1)-Ti(1)	114.8(4)
N(1)-Ti(1)-C(2)*	86.3(2)	C(4)*-N(1)-Ti(1)	114.8(4)
C(1)-Ti(1)-C(2)*	39.6(2)	C(3)-N(1)-Ti(1)	97.7(5)
N(2)-Ti(1)-C(2)	93.7(2)	C(6)-N(2)-C(5)	102.3(8)
N(2)*-Ti(1)-C(2)	158.3(2)	C(6)-N(2)-Ti(1)	123.5(7)
N(1)-Ti(1)-C(2)	86.3(2)	C(5)-N(2)-Ti(1)	134.2(5)
C(1)-Ti(1)-C(2)	39.6(2)	C(3)-C(1)-C(2)	118.6(4)
B(6)*-Ti(1)-C(2)	67.2(3)	C(3)-C(1)-B(6)*	118.6(4)
C(2)*-Ti(1)-C(2)	67.2(3)	C(2)-C(1)-B(6)*	110.9(7)
N(2)-Ti(1)-B(5)	89.6(3)	C(3)-C(1)-C(2)*	118.6(4)
N(2)*-Ti(1)-B(5)	123.6(3)	C(2)-C(1)-C(2)*	110.9(7)
N(1)-Ti(1)-B(5)	127.1(3)	C(3)-C(1)-B(2)*	119.9(6)
C(1)-Ti(1)-B(5)	68.5(3)	C(2)-C(1)-B(2)*	113.4(6)
B(6)*-Ti(1)-B(5)	69.3(3)	B(6)*-C(1)-B(2)*	63.0(4)
C(2)*-Ti(1)-B(5)	69.3(3)	C(2)*-C(1)-B(2)*	63.0(4)
C(2)-Ti(1)-B(5)	41.3(3)	C(3)-C(1)-B(2)	119.9(6)
C(2)-C(1)-B(2)	63.0(4)	B(3)-B(1)-B(3)*	107.6(8)

B(6)*-C(1)-B(2)	113.4(6)	B(3)-B(1)-B(2)*	108.0(6)
C(2)*-C(1)-B(2)	113.4(6)	B(3)*-B(1)-B(2)*	60.3(5)
B(2)*-C(1)-B(2)	62.3(6)	B(3)-B(1)-B(2)	60.3(5)
C(3)-C(1)-Ti(1)	92.0(5)	B(3)*-B(1)-B(2)	108.0(6)
C(2)-C(1)-Ti(1)	71.4(3)	B(2)*-B(1)-B(2)	59.9(6)
B(6)*-C(1)-Ti(1)	71.4(3)	B(3)-B(1)-B(4)	59.5(4)
C(2)*-C(1)-Ti(1)	71.4(3)	B(3)*-B(1)-B(4)	59.5(4)
B(2)*-C(1)-Ti(1)	132.6(4)	B(2)*-B(1)-B(4)	107.5(6)
B(2)-C(1)-Ti(1)	132.6(4)	B(2)-B(3)-B(5)	107.4(5)
C(1)-C(2)-B(5)	109.3(6)	B(3)*-B(4)-B(3)	107.9(8)
C(1)-C(2)-B(2)	61.8(4)	B(3)*-B(4)-B(5)	108.3(7)
B(5)-C(2)-B(2)	113.9(5)	B(3)-B(4)-B(5)	61.1(5)
C(1)-C(2)-B(3)	109.4(5)	B(3)*-B(4)-B(5)*	61.1(5)
B(5)-C(2)-B(3)	62.9(5)	B(3)-B(4)-B(5)*	108.3(7)
B(2)-C(2)-B(3)	61.5(4)	B(5)-B(4)-B(5)*	59.0(7)
C(1)-C(2)-Ti(1)	69.1(3)	B(3)*-B(4)-B(1)	59.7(4)
B(5)-C(2)-Ti(1)	70.9(3)	B(3)-B(4)-B(1)	59.7(4)
B(2)-C(2)-Ti(1)	129.3(4)	B(5)-B(4)-B(1)	108.6(7)
B(3)-C(2)-Ti(1)	130.3(5)	B(5)*-B(4)-B(1)	108.6(7)
N(1)-C(3)-C(1)	106.8(6)	C(2)-B(5)-B(5)*	105.2(4)
C(1)-B(2)-C(2)	55.3(3)	C(2)-B(5)-B(4)	105.1(6)
C(1)-B(2)-B(2)*	58.9(3)	B(5)*-B(5)-B(4)	60.5(3)
C(2)-B(2)-B(2)*	104.4(3)	C(2)-B(5)-B(3)	59.6(4)
C(1)-B(2)-B(3)	102.7(5)	B(5)*-B(5)-B(3)	107.8(4)
C(2)-B(2)-B(3)	59.3(4)	B(4)-B(5)-B(3)	59.0(5)
B(2)*-B(2)-B(3)	107.5(4)	C(2)-B(5)-Ti(1)	67.8(3)
C(1)-B(2)-B(1)	103.6(5)	B(5)*-B(5)-Ti(1)	69.0(2)

C(2)-B(2)-B(1)	104.8(6)	B(2)*-B(2)-B(1)	60.0(3)
B(3)-B(2)-B(1)	59.4(5)	B(1)-B(3)-B(2)	60.3(5)
C(2)-B(3)-B(4)	104.1(6)	C(2)-B(3)-B(5)	57.4(4)
C(2)-B(3)-B(1)	105.4(6)	B(4)-B(3)-B(5)	59.9(5)
B(4)-B(3)-B(1)	60.8(6)	B(1)-B(3)-B(5)	108.4(6)
C(2)-B(3)-B(2)	59.2(4)	B(4)-B(5)-Ti(1)	125.0(5)
B(4)-B(3)-B(2)	108.6(6)	B(3)-B(5)-Ti(1)	124.4(5)

Table 1. Crystal data and structure refinement for 7.

Identification code	kor074m
Empirical formula	C <sub>10</sub> H <sub>32</sub> B <sub>9</sub> N <sub>3</sub> Ti
Formula weight	339.58
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 <sub>1</sub> /n
Unit cell dimensions	a = 9.429(1) Å. b = 14.827(1) Å β = 91.795(2) ° c = 13.606(1) Å
Volume	1901.2(3) Å <sup>3</sup>
Z, D <sub>calc</sub>	4, 1.186 g/cm <sup>3</sup>
m	0.445 mm <sup>-1</sup>
F(000)	720
Crystal size	0.25 x 0.15 x 0.10 mm
q range for data collection	2.03 to 28.32 °
Limiting indices	-12 ≤ h ≤ 7, -19 ≤ k ≤ 17, -18 ≤ l ≤ 18
Reflections collected / unique	13684 / 4727 [R(int) = 0.0643]
Completeness to q = 28.32	99.7 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4727 / 0 / 224
Goodness-of-fit on F <sup>2</sup>	0.997
Final R indices [I>2s(I)]	<sup>a</sup> R <sub>1</sub> = 0.0495, <sup>b</sup> wR <sub>2</sub> =0.1065
R indices (all data)	<sup>a</sup> R <sub>1</sub> = 0.1013, <sup>b</sup> wR <sub>2</sub> =0.1248
Largest diff. peak and hole	0.402 and -0.327 e.Å <sup>-3</sup>

<sup>a</sup>R<sub>1</sub> = å||F<sub>o</sub>|-|F<sub>c</sub>|| (based on reflections with F<sub>o</sub><sup>2</sup>>2sF<sup>2</sup>),

<sup>b</sup> $wR_2 = [\sqrt{w(F_o^2 - F_c^2)^2} / \sqrt{w(F_o^2)^2}]^{1/2}$ ;  $w = 1/[s^2(F_o^2) + (0.095P)^2]$ ;  $P = [\max(F_o^2, 0) + 2F_c^2]/3$  (also with  $F_o^2 > 2sF^2$ )

Table 2. Bond lengths [Å] for 7.

Ti(1)-N(2)	1.900(2)	C(2)-B(9)	1.682(4)
Ti(1)-N(3)	1.901(2)	C(2)-B(4)	1.702(4)
Ti(1)-N(1)	2.255(2)	C(2)-B(3)	1.732(4)
Ti(1)-B(11)	2.359(3)	B(1)-B(3)	1.757(4)
Ti(1)-C(1)	2.385(2)	B(1)-B(4)	1.767(4)
Ti(1)-B(10)	2.426(3)	B(1)-B(2)	1.772(5)
Ti(1)-B(9)	2.456(3)	B(1)-B(6)	1.782(5)
Ti(1)-C(2)	2.484(2)	B(1)-B(5)	1.797(5)
N(1)-C(4)	1.485(3)	B(2)-B(11)	1.763(4)
N(1)-C(5)	1.494(3)	B(2)-B(3)	1.768(4)
N(1)-C(3)	1.503(3)	B(2)-B(6)	1.773(5)
N(2)-C(7)	1.461(3)	B(3)-B(4)	1.756(4)
N(2)-C(8)	1.483(3)	B(4)-B(5)	1.764(4)
N(3)-C(10)	1.462(4)	B(4)-B(9)	1.780(4)
N(3)-C(9)	1.473(3)	B(5)-B(6)	1.770(4)
C(1)-C(3)	1.514(3)	B(5)-B(10)	1.776(4)
C(1)-C(2)	1.593(3)	B(5)-B(9)	1.780(4)
C(1)-B(11)	1.663(4)	B(6)-B(11)	1.764(4)
C(1)-B(3)	1.725(4)	B(6)-B(10)	1.797(4)
C(1)-B(2)	1.726(4)	B(9)-B(10)	1.760(4)
C(2)-C(6)	1.531(3)	B(10)-B(11)	1.752(4)

Table 3. Angles [deg] for 7.

N(2)-Ti(1)-N(3)	99.8(9)	C(4)-N(1)-C(5)	106.6(2)
N(2)-Ti(1)-N(1)	104.4(9)	C(4)-N(1)-C(3)	110.4(2)
N(3)-Ti(1)-N(1)	108.7(9)	C(5)-N(1)-C(3)	110.3(2)
N(2)-Ti(1)-B(11)	157.5(1)	C(4)-N(1)-Ti(1)	114.0(2)
N(3)-Ti(1)-B(11)	97.2(1)	C(5)-N(1)-Ti(1)	117.4(2)
N(1)-Ti(1)-B(11)	83.9(9)	C(3)-N(1)-Ti(1)	97.8(1)
N(2)-Ti(1)-C(1)	124.4(9)	C(7)-N(2)-C(8)	107.7(2)
N(3)-Ti(1)-C(1)	135.8(9)	C(7)-N(2)-Ti(1)	141.8(2)
N(1)-Ti(1)-C(1)	62.8(8)	C(8)-N(2)-Ti(1)	110.5(2)
B(11)-Ti(1)-C(1)	41.1(9)	C(10)-N(3)-C(9)	108.2(2)
N(2)-Ti(1)-B(10)	122.6(1)	C(10)-N(3)-Ti(1)	122.8(2)
N(3)-Ti(1)-B(10)	88.8(1)	C(9)-N(3)-Ti(1)	126.9(2)
N(1)-Ti(1)-B(10)	126.3(9)	C(3)-C(1)-C(2)	117.8(2)
B(11)-Ti(1)-B(10)	42.9(1)	C(3)-C(1)-B(11)	118.2(2)
C(1)-Ti(1)-B(10)	69.5(9)	C(2)-C(1)-B(11)	112.3(2)
N(2)-Ti(1)-B(9)	88.3(9)	C(3)-C(1)-B(3)	120.0(2)
N(3)-Ti(1)-B(9)	120.8(9)	C(2)-C(1)-B(3)	62.8(2)
N(1)-Ti(1)-B(9)	125.9(9)	B(11)-C(1)-B(3)	113.7(2)
B(11)-Ti(1)-B(9)	70.2(1)	C(3)-C(1)-B(2)	121.5(2)
C(1)-Ti(1)-B(9)	66.8(9)	C(2)-C(1)-B(2)	112.6(2)
B(10)-Ti(1)-B(9)	42.3(9)	B(11)-C(1)-B(2)	62.6(2)
N(2)-Ti(1)-C(2)	91.4(8)	B(3)-C(1)-B(2)	61.7(2)
N(3)-Ti(1)-C(2)	157.8(9)	C(3)-C(1)-Ti(1)	92.2(2)
N(1)-Ti(1)-C(2)	86.8(8)	C(2)-C(1)-Ti(1)	74.3(1)
B(11)-Ti(1)-C(2)	67.9(9)	B(11)-C(1)-Ti(1)	68.6(1)
C(1)-Ti(1)-C(2)	38.1(8)	B(3)-C(1)-Ti(1)	134.6(2)

B(10)-Ti(1)-C(2)	69.0(9)	B(2)-C(1)-Ti(1)	129.5(2)
B(9)-Ti(1)-C(2)	39.8(9)	C(6)-C(2)-C(1)	120.3(2)
C(6)-C(2)-B(9)	125.0(2)	C(1)-B(3)-C(2)	54.9(1)
C(1)-C(2)-B(9)	108.9(2)	C(1)-B(3)-B(4)	101.9(2)
C(6)-C(2)-B(4)	115.3(2)	C(2)-B(3)-B(4)	58.4(2)
C(1)-C(2)-B(4)	110.2(2)	C(1)-B(3)-B(1)	104.6(2)
B(9)-C(2)-B(4)	63.5(2)	C(2)-B(3)-B(1)	105.4(2)
C(6)-C(2)-B(3)	109.9(2)	B(4)-B(3)-B(1)	60.4(2)
C(1)-C(2)-B(3)	62.3(2)	C(1)-B(3)-B(2)	59.2(2)
B(9)-C(2)-B(3)	113.9(2)	C(2)-B(3)-B(2)	104.2(2)
B(4)-C(2)-B(3)	61.5(2)	B(4)-B(3)-B(2)	107.6(2)
C(6)-C(2)-Ti(1)	107.3(2)	B(1)-B(3)-B(2)	60.3(2)
C(1)-C(2)-Ti(1)	67.6(1)	C(2)-B(4)-B(3)	60.1(2)
B(9)-C(2)-Ti(1)	69.2(1)	C(2)-B(4)-B(5)	105.4(2)
B(4)-C(2)-Ti(1)	128.6(2)	B(3)-B(4)-B(5)	109.0(2)
B(3)-C(2)-Ti(1)	127.7(2)	C(2)-B(4)-B(1)	106.3(2)
N(1)-C(3)-C(1)	106.6(2)	B(3)-B(4)-B(1)	59.8(2)
B(3)-B(1)-B(4)	59.8(2)	B(5)-B(4)-B(1)	61.2(2)
B(3)-B(1)-B(2)	60.1(2)	C(2)-B(4)-B(9)	57.7(2)
B(4)-B(1)-B(2)	107.0(2)	B(3)-B(4)-B(9)	108.1(2)
B(3)-B(1)-B(6)	108.1(2)	B(5)-B(4)-B(9)	60.3(2)
B(4)-B(1)-B(6)	106.7(2)	B(1)-B(4)-B(9)	108.9(2)
B(2)-B(1)-B(6)	59.9(2)	B(4)-B(5)-B(6)	107.4(2)
B(3)-B(1)-B(5)	107.5(2)	B(4)-B(5)-B(10)	108.5(2)
B(4)-B(1)-B(5)	59.3(2)	B(6)-B(5)-B(10)	60.9(2)
B(2)-B(1)-B(5)	106.8(2)	B(4)-B(5)-B(9)	60.3(2)
B(6)-B(1)-B(5)	59.3(2)	B(6)-B(5)-B(9)	107.2(2)

C(1)-B(2)-B(11)	56.9(2)	B(10)-B(5)-B(9)	59.3(2)
C(1)-B(2)-B(3)	59.1(2)	B(4)-B(5)-B(1)	59.5(2)
B(11)-B(2)-B(3)	106.9(2)	B(6)-B(5)-B(1)	59.9(2)
C(1)-B(2)-B(1)	103.9(2)	B(10)-B(5)-B(1)	109.2(2)
B(11)-B(2)-B(1)	107.3(2)	B(10)-B(9)-Ti(1)	68.0(1)
B(3)-B(2)-B(1)	59.5(2)	B(4)-B(9)-Ti(1)	126.1(2)
C(1)-B(2)-B(6)	103.5(2)	B(5)-B(9)-Ti(1)	124.2(2)
B(11)-B(2)-B(6)	59.9(2)	B(11)-B(10)-B(9)	104.2(2)
B(3)-B(2)-B(6)	108.0(2)	B(11)-B(10)-B(5)	105.9(2)
B(1)-B(2)-B(6)	60.4(2)	B(9)-B(10)-B(5)	60.4(2)
B(9)-B(5)-B(1)	107.6(2)	B(11)-B(10)-B(6)	59.6(2)
B(11)-B(6)-B(5)	105.6(2)	B(9)-B(10)-B(6)	106.9(2)
B(11)-B(6)-B(2)	59.8(2)	B(5)-B(10)-B(6)	59.4(2)
B(5)-B(6)-B(2)	107.9(2)	B(11)-B(10)-Ti(1)	66.5(1)
B(11)-B(6)-B(1)	106.8(2)	B(9)-B(10)-Ti(1)	69.8(1)
B(5)-B(6)-B(1)	60.8(2)	B(5)-B(10)-Ti(1)	126.0(2)
B(2)-B(6)-B(1)	59.8(2)	B(6)-B(10)-Ti(1)	123.2(2)
B(11)-B(6)-B(10)	58.9(2)	C(1)-B(11)-B(10)	106.7(2)
B(5)-B(6)-B(10)	59.7(2)	C(1)-B(11)-B(2)	60.4(2)
B(2)-B(6)-B(10)	108.3(2)	B(10)-B(11)-B(2)	110.8(2)
B(1)-B(6)-B(10)	108.9(2)	C(1)-B(11)-B(6)	106.6(2)
C(2)-B(9)-B(10)	107.8(2)	B(10)-B(11)-B(6)	61.5(2)
C(2)-B(9)-B(4)	58.8(2)	B(2)-B(11)-B(6)	60.4(2)
B(10)-B(9)-B(4)	108.5(2)	C(1)-B(11)-Ti(1)	70.3(1)
C(2)-B(9)-B(5)	105.6(2)	B(10)-B(11)-Ti(1)	70.6(1)
B(10)-B(9)-B(5)	60.2(2)	B(2)-B(11)-Ti(1)	129.0(2)
B(4)-B(9)-B(5)	59.4(2)	B(6)-B(11)-Ti(1)	128.9(3)

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C(2)-B(9)-Ti(1)

71.0(1)

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Table 1. Crystal data and structure refinement for **9**.

Identification code	kor017m		
Empirical formula	$C_{11}H_{37}B_9N_4Zr$		
Formula weight	413.96		
Temperature	293(2) K		
Wavelength	0.71073 Å		
Crystal system, space group	Triclinic, <i>P</i>		
Unit cell dimensions	<i>a</i> = 9.2199(8) Å	$\alpha$ = 90.037(2) °	
	<i>b</i> = 9.2777(8) Å	$\beta$ = 96.908(2) °	
	<i>c</i> = 13.842(1) Å	$\gamma$ = 113.269(2) °	
Volume	1078.3(2) Å <sup>3</sup>		
Z, D <sub>calc</sub>	2, 1.275 g/cm <sup>3</sup>		
<i>m</i>	0.511 mm <sup>-1</sup>		
<i>F</i> (000)	432		
Crystal size	0.30 x 0.15 x 0.15 mm		
q range for data collection	2.39 to 28.35 °		
Limiting indices	$-12 \leq h \leq 11, -12 \leq k \leq 12, -18 \leq l \leq 13$		
Reflections collected / unique	8012 / 5315 [R(int) = 0.0800]		
Completeness to q = 28.35	98.4 %		
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>		
Data / restraints / parameters	5315 / 0 / 244		
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.923		
Final R indices [I>2s(I)]	<sup>a</sup> <i>R</i> <sub>1</sub> = 0.0388, <sup>b</sup> <i>wR</i> <sub>2</sub> = 0.0855		
R indices (all data)	<sup>a</sup> <i>R</i> <sub>1</sub> = 0.0556, <sup>b</sup> <i>wR</i> <sub>2</sub> = 0.0894		
Largest diff. peak and hole	0.963 and -0.760 e.Å <sup>-3</sup>		

<sup>a</sup> $R_1 = \frac{\sum |F_o - F_c|}{\sum |F_o|}$  (based on reflections with  $F_o^2 > 2sF^2$ ),

<sup>b</sup> $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ;  $w = 1/[s^2(F_o^2) + (0.095P)^2]$ ;  $P = [\max(F_o^2, 0) + 2F_c^2]/3$  (also with  $F_o^2 > 2sF^2$ )

Table 2. Bond lengths [Å] for **9**.

Zr(1)-N(3)	2.033(2)	C(1)-B(3)	1.721(4)
Zr(1)-N(2)	2.054(2)	C(2)-B(9)	1.642(4)
Zr(1)-N(4)	2.450(2)	C(2)-B(3)	1.723(4)
Zr(1)-B(11)	2.567(3)	C(2)-B(4)	1.725(4)
Zr(1)-B(10)	2.577(3)	B(1)-B(2)	1.761(5)
Zr(1)-N(1)	2.579(2)	B(1)-B(3)	1.762(5)
Zr(1)-B(9)	2.609(3)	B(1)-B(4)	1.774(5)
Zr(1)-C(1)	2.617(2)	B(1)-B(6)	1.776(5)
Zr(1)-C(2)	2.655(3)	B(1)-B(5)	1.792(5)
N(1)-C(4)	1.461(4)	B(2)-B(3)	1.757(5)
N(1)-C(5)	1.476(4)	B(2)-B(6)	1.764(5)
N(1)-C(3)	1.486(4)	B(2)-B(11)	1.769(4)
N(2)-C(6)	1.458(4)	B(3)-B(4)	1.780(5)
N(2)-C(7)	1.462(4)	B(4)-B(5)	1.764(5)
N(3)-C(8)	1.454(4)	B(4)-B(9)	1.786(4)
N(3)-C(9)	1.467(4)	B(5)-B(6)	1.773(5)
N(4)-C(10)	1.465(4)	B(5)-B(10)	1.781(5)
N(4)-C(11)	1.484(3)	B(5)-B(9)	1.784(4)
C(1)-C(3)	1.502(4)	B(6)-B(11)	1.773(4)
C(1)-C(2)	1.573(4)	B(6)-B(10)	1.777(4)
C(1)-B(11)	1.656(4)	B(9)-B(10)	1.763(4)
C(1)-B(2)	1.714(4)	B(10)-B(11)	1.754(4)

Table 3. Angles [deg] for **9**.

N(3)-Zr(1)-N(2)	116.4(9)	N(3)-Zr(1)-C(2)	83.5(9)
N(3)-Zr(1)-N(4)	89.0(9)	N(2)-Zr(1)-C(2)	153.9(9)
N(2)-Zr(1)-N(4)	80.6(8)	N(4)-Zr(1)-C(2)	118.5(8)
N(3)-Zr(1)-B(11)	144.0(1)	B(11)-Zr(1)-C(2)	61.5(9)
N(2)-Zr(1)-B(11)	95.3(1)	B(10)-Zr(1)-C(2)	62.6(9)
N(4)-Zr(1)-B(11)	114.0(9)	N(1)-Zr(1)-C(2)	78.3(8)
N(3)-Zr(1)-B(10)	130.9(1)	B(9)-Zr(1)-C(2)	36.3(9)
N(2)-Zr(1)-B(10)	108.2(1)	C(1)-Zr(1)-C(2)	34.7(8)
N(4)-Zr(1)-B(10)	78.8(8)	C(4)-N(1)-C(5)	108.6(3)
B(11)-Zr(1)-B(10)	39.9(9)	C(4)-N(1)-C(3)	109.5(3)
N(3)-Zr(1)-N(1)	88.4(9)	C(5)-N(1)-C(3)	107.9(3)
N(2)-Zr(1)-N(1)	85.2(8)	C(4)-N(1)-Zr(1)	117.9(2)
N(4)-Zr(1)-N(1)	162.6(8)	C(5)-N(1)-Zr(1)	114.7(2)
B(11)-Zr(1)-N(1)	77.2(9)	C(3)-N(1)-Zr(1)	97.2(2)
B(10)-Zr(1)-N(1)	115.5(8)	C(6)-N(2)-C(7)	109.2(3)
N(3)-Zr(1)-B(9)	92.0(1)	C(6)-N(2)-Zr(1)	119.4(2)
N(2)-Zr(1)-B(9)	146.9(1)	C(7)-N(2)-Zr(1)	131.0(2)
N(4)-Zr(1)-B(9)	83.5(9)	C(8)-N(3)-C(9)	108.4(2)
B(11)-Zr(1)-B(9)	65.3(1)	C(8)-N(3)-Zr(1)	135.4(2)
B(10)-Zr(1)-B(9)	39.8(1)	C(9)-N(3)-Zr(1)	116.3(2)
N(1)-Zr(1)-B(9)	113.8(9)	C(10)-N(4)-C(11)	109.1(2)
N(3)-Zr(1)-C(1)	108.0(9)	C(10)-N(4)-Zr(1)	123.9(2)
N(2)-Zr(1)-C(1)	119.3(9)	C(11)-N(4)-Zr(1)	110.6(2)
N(4)-Zr(1)-C(1)	140.6(8)	C(3)-C(1)-C(2)	115.7(2)

B(11)-Zr(1)-C(1)	37.2(9)	C(3)-C(1)-B(11)	123.4(2)
B(10)-Zr(1)-C(1)	63.1(9)	C(2)-C(1)-B(11)	111.7(2)
N(1)-Zr(1)-C(1)	56.1(8)	C(3)-C(1)-B(2)	120.8(2)
B(9)-Zr(1)-C(1)	61.2(9)	C(2)-C(1)-B(2)	111.6(2)
B(11)-C(1)-B(2)	63.3(2)	B(4)-B(1)-B(5)	59.3(2)
C(3)-C(1)-B(3)	113.4(2)	B(6)-B(1)-B(5)	59.6(2)
C(2)-C(1)-B(3)	62.9(2)	C(1)-B(2)-B(3)	59.4(2)
B(11)-C(1)-B(3)	114.8(2)	C(1)-B(2)-B(1)	104.7(2)
B(2)-C(1)-B(3)	61.5(2)	B(3)-B(2)-B(1)	60.1(2)
C(3)-C(1)-Zr(1)	95.2(2)	C(1)-B(2)-B(6)	103.4(2)
C(2)-C(1)-Zr(1)	74.0(1)	B(3)-B(2)-B(6)	108.5(3)
B(11)-C(1)-Zr(1)	69.7(1)	B(1)-B(2)-B(6)	60.5(2)
B(2)-C(1)-Zr(1)	131.3(2)	C(1)-B(2)-B(11)	56.8(2)
B(3)-C(1)-Zr(1)	135.2(2)	B(3)-B(2)-B(11)	107.6(2)
C(1)-C(2)-B(9)	111.7(2)	B(1)-B(2)-B(11)	108.3(2)
C(1)-C(2)-B(3)	62.8(2)	B(6)-B(2)-B(11)	60.2(2)
B(9)-C(2)-B(3)	115.6(2)	C(1)-B(3)-C(2)	54.3(2)
C(1)-C(2)-B(4)	112.3(2)	C(1)-B(3)-B(2)	59.0(2)
B(9)-C(2)-B(4)	64.0(2)	C(2)-B(3)-B(2)	102.8(2)
B(3)-C(2)-B(4)	62.2(2)	C(1)-B(3)-B(1)	104.3(2)
C(1)-C(2)-Zr(1)	71.4(1)	C(2)-B(3)-B(1)	104.1(2)
B(9)-C(2)-Zr(1)	70.3(1)	B(2)-B(3)-B(1)	60.1(2)
B(3)-C(2)-Zr(1)	132.5(2)	C(1)-B(3)-B(4)	103.0(2)
B(4)-C(2)-Zr(1)	131.9(2)	C(2)-B(3)-B(4)	59.0(2)
N(1)-C(3)-C(1)	109.9(2)	B(2)-B(3)-B(4)	107.8(2)
B(2)-B(1)-B(3)	59.8(2)	B(1)-B(3)-B(4)	60.1(2)
B(2)-B(1)-B(4)	107.9(2)	C(2)-B(4)-B(5)	102.7(2)

B(3)-B(1)-B(4)	60.5(2)	C(2)-B(4)-B(1)	103.6(2)
B(2)-B(1)-B(6)	59.8(2)	B(5)-B(4)-B(1)	60.8(2)
B(3)-B(1)-B(6)	107.7(2)	C(2)-B(4)-B(3)	58.9(2)
B(4)-B(1)-B(6)	107.3(2)	B(5)-B(4)-B(3)	107.9(3)
B(2)-B(1)-B(5)	107.2(2)	B(1)-B(4)-B(3)	59.4(2)
B(3)-B(1)-B(5)	107.5(2)	C(2)-B(4)-B(9)	55.7(2)
B(5)-B(4)-B(9)	60.3(2)	B(10)-B(9)-B(4)	108.6(2)
B(1)-B(4)-B(9)	107.8(2)	B(5)-B(9)-B(4)	59.2(2)
B(3)-B(4)-B(9)	106.0(2)	C(2)-B(9)-Zr(1)	73.4(1)
B(4)-B(5)-B(6)	107.9(2)	B(10)-B(9)-Zr(1)	69.2(1)
B(4)-B(5)-B(10)	108.9(2)	B(5)-B(9)-Zr(1)	127.0(2)
B(6)-B(5)-B(10)	60.0(2)	B(4)-B(9)-Zr(1)	131.3(2)
B(4)-B(5)-B(9)	60.5(2)	B(11)-B(10)-B(9)	105.0(2)
B(6)-B(5)-B(9)	106.5(2)	B(11)-B(10)-B(6)	60.3(2)
B(10)-B(5)-B(9)	59.3(2)	B(9)-B(10)-B(6)	107.1(2)
B(4)-B(5)-B(1)	59.9(2)	B(11)-B(10)-B(5)	107.3(2)
B(6)-B(5)-B(1)	59.8(2)	B(9)-B(10)-B(5)	60.4(2)
B(10)-B(5)-B(1)	108.2(2)	B(6)-B(10)-B(5)	59.8(2)
B(9)-B(5)-B(1)	107.2(2)	B(11)-B(10)-Zr(1)	69.8(1)
B(2)-B(6)-B(5)	107.9(3)	B(9)-B(10)-Zr(1)	71.1(1)
B(2)-B(6)-B(11)	60.0(2)	B(6)-B(10)-Zr(1)	127.8(2)
B(5)-B(6)-B(11)	106.8(2)	B(5)-B(10)-Zr(1)	129.0(2)
B(2)-B(6)-B(1)	59.7(2)	C(1)-B(11)-B(10)	105.6(2)
B(5)-B(6)-B(1)	60.7(2)	C(1)-B(11)-B(2)	59.9(2)
B(11)-B(6)-B(1)	107.5(2)	B(10)-B(11)-B(2)	109.0(2)
B(2)-B(6)-B(10)	108.2(2)	C(1)-B(11)-B(6)	105.4(2)
B(5)-B(6)-B(10)	60.2(2)	B(10)-B(11)-B(6)	60.5(2)

B(11)-B(6)-B(10)	59.2(2)	B(2)-B(11)-B(6)	59.7(2)
B(1)-B(6)-B(10)	109.1(2)	C(1)-B(11)-Zr(1)	73.0(1)
C(2)-B(9)-B(10)	105.9(2)	B(10)-B(11)-Zr(1)	70.4(1)
C(2)-B(9)-B(5)	105.3(2)	B(2)-B(11)-Zr(1)	131.2(2)
B(10)-B(9)-B(5)	60.3(2)	B(6)-B(11)-Zr(1)	128.6(2)
C(2)-B(9)-B(4)	60.2(2)		

Table 1. Crystal data and structure refinement for **10**.

Identification code	kor173
Empirical formula	C <sub>17</sub> B <sub>18</sub> H <sub>44</sub> N <sub>2</sub> Zr
Formula weight	562.34
Temperature	293(2) K
Wavelength	0.71070 Å
Crystal system, space group	Monoclinic, P2 <sub>1</sub> /c
Unit cell dimensions	$a = 18.0299(1)$ Å $b = 10.4035(6)$ Å $\beta = 96.555(9)$ ° $c = 16.090(2)$ Å
Volume	2998.3(5) Å <sup>3</sup>
Z, D <sub>calc</sub>	4, 1.246 g/cm <sup>3</sup>
$m$	0.380 mm <sup>-1</sup>
$F(000)$	1160
Crystal size	0.50 x 0.40 x 0.4 mm
q range for data collection	1.14 to 25.97 °
Limiting indices	-22 ≤ h ≤ 22, 0 ≤ k ≤ 12, 0 ≤ l ≤ 19
Reflections collected / unique	6093 / 5868 [R(int) = 0.0336]
Completeness to q = 25.97	
Refinement method	100.0 %
Data / restraints / parameters	Full-matrix least-squares on $F^2$
Goodness-of-fit on $F^2$	5868 / 0 / 368
Final R indices [I>2s (I)]	0.589
R indices (all data)	<sup>a</sup> R <sub>1</sub> = 0.0356, <sup>b</sup> wR <sub>2</sub> = 0.0913
Largest diff. peak and hole	<sup>a</sup> R <sub>1</sub> = 0.0699, <sup>b</sup> wR <sub>2</sub> = 0.1180
	0.941 and -0.577 e.Å <sup>-3</sup>

<sup>a</sup>R<sub>1</sub> =  $\frac{1}{\sum} \frac{\|F_o\| - \|F_c\|}{\|F_o\|}$  (based on reflections with  $|F_o|^2 > 2sF^2$ ),

<sup>b</sup> $R_2 = [\sqrt{w(F_o^2 - F_c^2)^2} / \sqrt{w(F_o^2)^2}]^{1/2}$ ;  $w = 1/[s^2(F_o^2) + (0.095P)^2]$ ;  $P = [\max(F_o^2, 0) + 2F_c^2]/3$  (also with  $F_o^2 > 2sF_c^2$ )

Table 2. Bond lengths [Å] for **10**.

Zr(1)-N(2)	2.461(3)	B(1)-B(2)	1.752(6)
Zr(1)-C(1)	2.466(3)	B(1)-B(3)	1.765(6)
Zr(1)-C(6)	2.470(3)	B(1)-B(6)	1.781(6)
Zr(1)-B(11)	2.474(4)	B(1)-B(4)	1.783(6)
Zr(1)-N(1)	2.486(3)	B(1)-B(5)	1.786(6)
Zr(1)-C(7)	2.488(3)	B(2)-B(6)	1.762(6)
Zr(1)-B(22)	2.496(4)	B(2)-B(3)	1.770(6)
Zr(1)-C(2)	2.507(3)	B(3)-B(11)	1.771(5)
Zr(1)-B(20)	2.577(4)	B(3)-B(4)	1.773(6)
Zr(1)-B(10)	2.577(4)	B(4)-B(11)	1.764(6)
Zr(1)-B(21)	2.591(4)	B(4)-B(5)	1.766(6)
Zr(1)-B(9)	2.595(4)	B(4)-B(10)	1.784(6)
N(1)-C(5)	1.485(5)	B(5)-B(6)	1.764(6)
N(1)-C(3)	1.487(5)	B(5)-B(10)	1.769(5)
N(1)-C(4)	1.489(5)	B(5)-B(9)	1.769(6)
N(2)-C(10)	1.484(4)	B(6)-B(9)	1.772(6)
N(2)-C(9)	1.487(4)	B(13)-B(22)	1.766(6)
N(2)-C(8)	1.499(4)	B(13)-B(14)	1.768(6)
C(1)-C(3)	1.511(5)	B(13)-B(17)	1.771(7)
C(1)-C(2)	1.597(4)	B(14)-B(15)	1.768(7)
C(1)-B(11)	1.662(5)	B(15)-B(16)	1.763(7)
C(1)-B(3)	1.708(5)	B(15)-B(20)	1.772(6)

C(1)-B(2)	1.714(5)	B(16)-B(17)	1.756(7)
C(2)-B(9)	1.679(5)	B(16)-B(21)	1.763(6)
C(2)-B(6)	1.709(6)	B(16)-B(20)	1.769(7)
C(2)-B(2)	1.731(5)	B(17)-B(22)	1.762(6)
B(9)-B(10)	1.730(6)	B(17)-B(21)	1.775(7)
B(10)-B(11)	1.758(5)	B(20)-B(21)	1.747(7)
C(6)-C(8)	1.494(5)	B(12)-B(16)	1.784(7)
C(6)-C(7)	1.592(5)	B(12)-B(17)	1.784(7)
C(6)-B(22)	1.665(5)	B(21)-B(22)	1.740(6)
C(6)-B(14)	1.706(5)	C(100)-C(105)	1.357(8)
C(6)-B(13)	1.708(5)	C(100)-C(101)	1.412(9)
C(7)-B(20)	1.675(6)	C(100)-C(106)	1.492(9)
C(7)-B(15)	1.711(5)	C(101)-C(102)	1.415(10)
C(7)-B(14)	1.733(5)	C(102)-C(103)	1.288(9)
B(12)-B(14)	1.750(6)	C(103)-C(104)	1.331(8)
B(12)-B(13)	1.760(7)	C(104)-C(105)	1.366(8)
<u>B(12)-B(15)</u>	<u>1.773(7)</u>		

Table 3. Angles [deg] for **10**.

N(2)-Zr(1)-C(1)	119.8(9)	B(5)-B(6)-B(9)	60.0(2)
N(2)-Zr(1)-C(6)	59.0(1)	C(2)-B(6)-B(1)	104.6(3)
C(1)-Zr(1)-C(6)	178.8(1)	B(2)-B(6)-B(1)	59.3(2)
N(2)-Zr(1)-B(11)	83.4(1)	B(5)-B(6)-B(1)	60.5(3)
C(1)-Zr(1)-B(11)	39.3(1)	B(9)-B(6)-B(1)	108.2(3)
C(6)-Zr(1)-B(11)	139.5(1)	C(2)-B(9)-B(10)	105.5(3)
N(2)-Zr(1)-N(1)	103.4(1)	C(2)-B(9)-B(5)	105.1(3)

C(1)-Zr(1)-N(1)	58.8(1)	B(10)-B(9)-B(5)	60.7(2)
C(6)-Zr(1)-N(1)	121.2(1)	C(2)-B(9)-B(6)	59.3(2)
B(11)-Zr(1)-N(1)	78.9(1)	B(10)-B(9)-B(6)	108.9(3)
N(2)-Zr(1)-C(7)	84.4(1)	B(5)-B(9)-B(6)	59.7(2)
C(1)-Zr(1)-C(7)	143.2(1)	C(2)-B(9)-Zr(1)	68.0(2)
C(6)-Zr(1)-C(7)	37.5(1)	B(10)-B(9)-Zr(1)	70.0(2)
B(11)-Zr(1)-C(7)	133.7(1)	B(5)-B(9)-Zr(1)	126.2(2)
N(1)-Zr(1)-C(7)	147.4(1)	B(6)-B(9)-Zr(1)	124.9(2)
N(2)-Zr(1)-B(22)	79.6(1)	B(9)-B(10)-B(11)	106.3(3)
C(1)-Zr(1)-B(22)	141.4(1)	B(9)-B(10)-B(5)	60.7(2)
C(6)-Zr(1)-B(22)	39.2(1)	B(11)-B(10)-B(5)	106.7(3)
B(11)-Zr(1)-B(22)	153.4(1)	B(9)-B(10)-B(4)	108.0(3)
N(1)-Zr(1)-B(22)	85.4(1)	B(11)-B(10)-B(4)	59.7(2)
C(7)-Zr(1)-B(22)	64.7(1)	B(5)-B(10)-B(4)	59.6(2)
N(2)-Zr(1)-C(2)	145.3(1)	B(9)-B(10)-Zr(1)	71.0(2)
C(1)-Zr(1)-C(2)	37.5(1)	B(11)-B(10)-Zr(1)	66.5(2)
C(6)-Zr(1)-C(2)	143.5(1)	B(5)-B(10)-Zr(1)	127.2(3)
B(11)-Zr(1)-C(2)	64.9(1)	B(4)-B(10)-Zr(1)	123.5(2)
N(1)-Zr(1)-C(2)	84.8(1)	C(1)-B(11)-B(10)	106.3(3)
C(7)-Zr(1)-C(2)	106.9(1)	C(1)-B(11)-B(4)	106.0(3)
B(22)-Zr(1)-C(2)	135.1(1)	B(10)-B(11)-B(4)	60.9(2)
N(2)-Zr(1)-B(20)	121.5(1)	C(1)-B(11)-B(3)	59.6(2)
C(1)-Zr(1)-B(20)	116.4(1)	B(10)-B(11)-B(3)	109.6(3)
C(6)-Zr(1)-B(20)	64.8(1)	B(4)-B(11)-B(3)	60.2(2)
B(11)-Zr(1)-B(20)	140.1(1)	C(1)-B(11)-Zr(1)	70.1(2)
N(1)-Zr(1)-B(20)	118.8(1)	B(10)-B(11)-Zr(1)	72.8(2)
C(7)-Zr(1)-B(20)	38.6(1)	B(4)-B(11)-Zr(1)	130.5(2)

B(22)-Zr(1)-B(20)	66.5(2)	B(3)-B(11)-Zr(1)	128.3(2)
C(2)-Zr(1)-B(20)	80.6(1)	C(8)-C(6)-C(7)	116.6(3)
N(2)-Zr(1)-B(10)	82.4(1)	C(8)-C(6)-B(22)	123.9(3)
C(1)-Zr(1)-B(10)	65.7(1)	C(7)-C(6)-B(22)	110.0(3)
C(6)-Zr(1)-B(10)	113.7(1)	C(8)-C(6)-B(14)	113.6(3)
B(11)-Zr(1)-B(10)	40.7(1)	C(7)-C(6)-B(14)	63.3(2)
N(1)-Zr(1)-B(10)	118.7(1)	B(22)-C(6)-B(14)	114.3(3)
C(7)-Zr(1)-B(10)	93.5(1)	C(8)-C(6)-B(13)	119.9(3)
B(22)-Zr(1)-B(10)	152.8(1)	C(7)-C(6)-B(13)	112.4(3)
C(2)-Zr(1)-B(10)	64.5(1)	B(22)-C(6)-B(13)	63.1(2)
B(20)-Zr(1)-B(10)	107.2(1)	B(14)-C(6)-B(13)	62.3(2)
N(2)-Zr(1)-B(21)	118.7(1)	C(8)-C(6)-Zr(1)	94.8(2)
C(1)-Zr(1)-B(21)	115.7(1)	C(7)-C(6)-Zr(1)	71.9(2)
C(6)-Zr(1)-B(21)	65.4(1)	B(22)-C(6)-Zr(1)	71.3(2)
B(11)-Zr(1)-B(21)	155.0(1)	B(14)-C(6)-Zr(1)	134.0(2)
N(1)-Zr(1)-B(21)	84.2(1)	B(13)-C(6)-Zr(1)	132.8(2)
C(7)-Zr(1)-B(21)	64.8(1)	C(6)-C(7)-B(20)	111.8(3)
B(22)-Zr(1)-B(21)	40.0(1)	C(6)-C(7)-B(15)	110.9(3)
C(2)-Zr(1)-B(21)	95.5(1)	B(20)-C(7)-B(15)	63.1(2)
B(20)-Zr(1)-B(21)	39.5(2)	C(6)-C(7)-B(14)	61.6(2)
B(10)-Zr(1)-B(21)	145.8(1)	B(20)-C(7)-B(14)	114.4(3)
N(2)-Zr(1)-B(9)	117.1(1)	B(15)-C(7)-B(14)	61.8(2)
C(1)-Zr(1)-B(9)	64.7(1)	C(6)-C(7)-Zr(1)	70.7(2)
C(6)-Zr(1)-B(9)	115.6(1)	B(20)-C(7)-Zr(1)	73.6(2)
B(11)-Zr(1)-B(9)	66.8(1)	B(15)-C(7)-Zr(1)	134.0(2)
N(1)-Zr(1)-B(9)	121.5(1)	B(14)-C(7)-Zr(1)	131.1(2)
C(7)-Zr(1)-B(9)	79.9(1)	C(6)-C(8)-N(2)	108.3(3)

B(22)-Zr(1)-B(9)	139.7(1)	B(14)-B(12)-B(13)	60.5(3)
C(2)-Zr(1)-B(9)	38.4(1)	B(14)-B(12)-B(15)	60.3(3)
B(20)-Zr(1)-B(9)	73.9(1)	B(13)-B(12)-B(15)	107.9(3)
B(10)-Zr(1)-B(9)	39.1(1)	B(14)-B(12)-B(16)	107.8(3)
B(21)-Zr(1)-B(9)	108.2(2)	B(13)-B(12)-B(16)	107.0(3)
C(5)-N(1)-C(3)	109.3(3)	B(15)-B(12)-B(16)	59.4(3)
C(5)-N(1)-C(4)	105.4(3)	B(14)-B(12)-B(17)	108.3(3)
C(3)-N(1)-C(4)	107.7(3)	B(13)-B(12)-B(17)	60.0(3)
C(5)-N(1)-Zr(1)	122.6(2)	B(15)-B(12)-B(17)	106.9(3)
C(3)-N(1)-Zr(1)	94.4(2)	B(16)-B(12)-B(17)	59.0(3)
C(4)-N(1)-Zr(1)	116.1(2)	C(6)-B(13)-B(12)	104.1(3)
C(10)-N(2)-C(9)	105.3(3)	C(6)-B(13)-B(22)	57.2(2)
C(10)-N(2)-C(8)	109.0(3)	B(12)-B(13)-B(22)	107.4(3)
C(9)-N(2)-C(8)	109.8(3)	C(6)-B(13)-B(14)	58.8(2)
C(10)-N(2)-Zr(1)	125.6(2)	B(12)-B(13)-B(14)	59.5(3)
C(9)-N(2)-Zr(1)	111.3(2)	B(22)-B(13)-B(14)	106.6(3)
C(8)-N(2)-Zr(1)	95.1(2)	C(6)-B(13)-B(17)	104.0(3)
C(3)-C(1)-C(2)	116.0(3)	B(12)-B(13)-B(17)	60.7(3)
C(3)-C(1)-B(11)	124.1(3)	B(22)-B(13)-B(17)	59.8(2)
C(2)-C(1)-B(11)	110.2(3)	B(14)-B(13)-B(17)	108.1(3)
C(3)-C(1)-B(3)	120.4(3)	C(6)-B(14)-C(7)	55.1(2)
C(2)-C(1)-B(3)	112.3(3)	C(6)-B(14)-B(12)	104.6(3)
B(11)-C(1)-B(3)	63.4(2)	C(7)-B(14)-B(12)	104.6(3)
C(3)-C(1)-B(2)	113.7(3)	C(6)-B(14)-B(13)	58.9(2)
C(2)-C(1)-B(2)	62.9(2)	C(7)-B(14)-B(13)	103.2(3)
B(11)-C(1)-B(2)	114.3(3)	B(12)-B(14)-B(13)	60.0(3)
B(3)-C(1)-B(2)	62.3(2)	C(6)-B(14)-B(15)	103.1(3)

C(3)-C(1)-Zr(1)	94.5(2)	C(7)-B(14)-B(15)	58.5(2)
C(2)-C(1)-Zr(1)	72.7(2)	B(12)-B(14)-B(15)	60.5(3)
B(11)-C(1)-Zr(1)	70.6(2)	B(13)-B(14)-B(15)	107.8(3)
B(3)-C(1)-Zr(1)	132.5(2)	C(7)-B(15)-B(16)	103.7(3)
B(2)-C(1)-Zr(1)	134.2(2)	C(7)-B(15)-B(14)	59.7(2)
C(1)-C(2)-B(9)	111.7(3)	B(16)-B(15)-B(14)	107.9(3)
C(1)-C(2)-B(6)	111.1(3)	C(7)-B(15)-B(20)	57.4(2)
B(9)-C(2)-B(6)	63.1(2)	B(16)-B(15)-B(20)	60.1(3)
C(1)-C(2)-B(2)	61.9(2)	B(14)-B(15)-B(20)	108.0(3)
B(9)-C(2)-B(2)	114.2(3)	C(7)-B(15)-B(12)	104.5(3)
B(6)-C(2)-B(2)	61.6(2)	B(16)-B(15)-B(12)	60.6(3)
C(1)-C(2)-Zr(1)	69.9(2)	B(14)-B(15)-B(12)	59.2(3)
B(9)-C(2)-Zr(1)	73.6(2)	B(20)-B(15)-B(12)	108.3(3)
B(6)-C(2)-Zr(1)	133.8(2)	B(17)-B(16)-B(15)	108.5(3)
B(2)-C(2)-Zr(1)	130.5(2)	B(17)-B(16)-B(21)	60.6(3)
N(1)-C(3)-C(1)	108.3(3)	B(15)-B(16)-B(21)	108.2(3)
B(2)-B(1)-B(3)	60.4(2)	B(17)-B(16)-B(20)	107.8(3)
B(2)-B(1)-B(6)	59.8(2)	B(15)-B(16)-B(20)	60.2(3)
B(3)-B(1)-B(6)	107.6(3)	B(21)-B(16)-B(20)	59.3(3)
B(2)-B(1)-B(4)	108.0(3)	B(17)-B(16)-B(12)	60.5(3)
B(3)-B(1)-B(4)	60.0(2)	B(15)-B(16)-B(12)	60.0(3)
B(6)-B(1)-B(4)	106.6(3)	B(21)-B(16)-B(12)	108.9(3)
B(2)-B(1)-B(5)	107.5(3)	B(20)-B(16)-B(12)	108.0(3)
B(3)-B(1)-B(5)	107.4(3)	B(16)-B(17)-B(22)	106.0(3)
B(6)-B(1)-B(5)	59.3(3)	B(16)-B(17)-B(13)	107.8(3)
B(4)-B(1)-B(5)	59.3(2)	B(22)-B(17)-B(13)	60.0(2)
C(1)-B(2)-C(2)	55.3(2)	B(16)-B(17)-B(21)	59.9(3)

C(1)-B(2)-B(1)	104.7(3)	B(22)-B(17)-B(21)	58.9(2)
C(2)-B(2)-B(1)	104.9(3)	B(13)-B(17)-B(21)	108.1(3)
C(1)-B(2)-B(6)	103.4(3)	B(16)-B(17)-B(12)	60.5(3)
C(2)-B(2)-B(6)	58.6(2)	B(22)-B(17)-B(12)	106.5(3)
B(1)-B(2)-B(6)	60.9(3)	B(13)-B(17)-B(12)	59.3(3)
C(1)-B(2)-B(3)	58.7(2)	B(21)-B(17)-B(12)	108.3(4)
C(2)-B(2)-B(3)	103.3(2)	C(7)-B(20)-B(21)	105.4(3)
B(1)-B(2)-B(3)	60.1(3)	C(7)-B(20)-B(16)	105.0(3)
B(6)-B(2)-B(3)	108.2(3)	B(21)-B(20)-B(16)	60.2(3)
C(1)-B(3)-B(1)	104.4(3)	C(7)-B(20)-B(15)	59.5(2)
C(1)-B(3)-B(2)	59.0(2)	B(21)-B(20)-B(15)	108.6(3)
B(1)-B(3)-B(2)	59.4(2)	B(16)-B(20)-B(15)	59.7(3)
C(1)-B(3)-B(11)	57.0(2)	C(7)-B(20)-Zr(1)	67.8(2)
B(1)-B(3)-B(11)	107.4(3)	B(21)-B(20)-Zr(1)	70.7(2)
B(2)-B(3)-B(11)	106.5(3)	B(16)-B(20)-Zr(1)	126.5(3)
C(1)-B(3)-B(4)	103.6(3)	B(15)-B(20)-Zr(1)	125.1(3)
B(1)-B(3)-B(4)	60.5(2)	B(22)-B(21)-B(20)	105.9(3)
B(2)-B(3)-B(4)	107.6(3)	B(22)-B(21)-B(16)	106.7(3)
B(11)-B(3)-B(4)	59.7(2)	B(20)-B(21)-B(16)	60.5(3)
B(11)-B(4)-B(5)	106.6(3)	B(22)-B(21)-B(17)	60.2(3)
B(11)-B(4)-B(3)	60.1(2)	B(20)-B(21)-B(17)	107.9(3)
B(5)-B(4)-B(3)	107.9(3)	B(16)-B(21)-B(17)	59.5(3)
B(11)-B(4)-B(1)	106.9(3)	B(22)-B(21)-Zr(1)	67.1(2)
B(5)-B(4)-B(1)	60.4(2)	B(20)-B(21)-Zr(1)	69.8(2)
B(3)-B(4)-B(1)	59.5(2)	B(16)-B(21)-Zr(1)	126.0(3)
B(11)-B(4)-B(10)	59.4(2)	B(17)-B(21)-Zr(1)	124.2(3)
B(5)-B(4)-B(10)	59.8(2)	C(6)-B(22)-B(21)	106.9(3)

B(3)-B(4)-B(10)	108.4(3)	C(6)-B(22)-B(17)	106.2(3)
B(1)-B(4)-B(10)	108.2(3)	B(21)-B(22)-B(17)	60.9(3)
B(6)-B(5)-B(4)	108.1(3)	C(6)-B(22)-B(13)	59.7(2)
B(6)-B(5)-B(10)	107.6(3)	B(21)-B(22)-B(13)	109.9(3)
B(4)-B(5)-B(10)	60.6(2)	B(17)-B(22)-B(13)	60.3(3)
B(6)-B(5)-B(9)	60.2(2)	C(6)-B(22)-Zr(1)	69.6(2)
B(4)-B(5)-B(9)	107.1(3)	B(21)-B(22)-Zr(1)	73.0(2)
B(10)-B(5)-B(9)	58.5(2)	B(17)-B(22)-Zr(1)	130.4(3)
B(6)-B(5)-B(1)	60.2(2)	B(13)-B(22)-Zr(1)	127.8(2)
B(4)-B(5)-B(1)	60.2(3)	C(105)-C(100)-C(101)	117.1(6)
B(10)-B(5)-B(1)	108.8(3)	C(105)-C(100)-C(106)	120.6(8)
B(9)-B(5)-B(1)	108.1(3)	C(101)-C(100)-C(106)	122.3(8)
C(2)-B(6)-B(2)	59.8(2)	C(100)-C(101)-C(102)	118.2(6)
C(2)-B(6)-B(5)	104.0(3)	C(103)-C(102)-C(101)	121.8(7)
B(2)-B(6)-B(5)	108.1(3)	C(102)-C(103)-C(104)	120.1(7)
C(2)-B(6)-B(9)	57.6(2)	C(103)-C(104)-C(105)	121.9(7)
B(2)-B(6)-B(9)	108.2(3)	C(100)-C(105)-C(104)	120.9(6)

Table 1. Crystal data and structure refinement for **11**.

Identification code	kor520
Empirical formula	C <sub>23</sub> H <sub>34</sub> B <sub>9</sub> NO <sub>2</sub> Ti
Formula weight	501.70
Temperature	233(2)K
Wavelength	0.71073Å
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>m</i>
Unit cell dimensions	<i>a</i> = 7.6576(3) Å

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	$b = 20.2081(9)$	Å	$\beta = 111.729(1)$ °
	$c = 9.4735(4)$	Å	
Volume	1361.8(1)	Å <sup>3</sup>	
Z, D <sub>calc</sub>	2,	1.224	g/cm <sup>3</sup>
$m$		0.336	mm <sup>-1</sup>
$F(000)$	524		
Crystal size	0.18	x 0.16	x 0.14 mm
q range for data collection	2.02	to	28.34 °
Limiting indices	-10	≤ h ≤ 10, -26	≤ k ≤ 26, -12
Reflections collected / unique	12		
Completeness to q = 25.96	18785	/ 3476	[R(int) = 0.0573]
Refinement method	99.8	%	
Data / restraints / parameters	Full-matrix least-squares on $F^2$		
Goodness-of-fit on $F^2$	3476	/ 0	/ 185
Final R indices [I>2s (I)]	1.027		
R indices (all data)	<sup>a</sup> $R_1 = 0.0459$ ,	<sup>b</sup> $wR_2=0.0964$	
Largest diff. peak and hole	<sup>a</sup> $R_1 = 0.0996$ ,	<sup>b</sup> $wR_2=0.1247$	
	0.321	and -0.316	e.Å <sup>-3</sup>

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<sup>a</sup> $R_1 = \frac{|\sum F_o - |F_c|}{\sum |F_c|}$  (based on reflections with  $F_o^2 > 2sF^2$ ),  
<sup>b</sup> $wR_2 = [\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}]^{1/2}$ ;  $w = 1/[s^2(F_o^2) + (0.095P)^2]$ ;  $P = [\max(F_o^2, 0) + 2F_c^2]/3$  (also with  $F_o^2 > 2sF^2$ )

Table 2. Bond lengths [Å] for **11**.

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Ti(1)-O(1)	1.7789(2)	B(3)-C(2)	1.734(4)
Ti(1)-O(1)*	1.7789(2)	B(3)-B(3)*	1.770(8)
Ti(1)-N(1)	2.177(3)	B(4)-B(2)*	1.755(4)

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Ti(1)-C(1)	2.332(3)	B(4)-B(5)*	1.776(4)
Ti(1)-C(2)	2.352(2)	B(4)-B(5)	1.776(4)
Ti(1)-B(6)*	2.352(2)	B(5)-C(2)	1.704(4)
Ti(1)-C(2)*	2.352(2)	B(5)-B(5)*	1.757(6)
Ti(1)-B(5)	2.387(3)	C(2)-C(1)	1.619(3)
Ti(1)-B(5)*	2.387(3)	C(1)-C(3)	1.508(5)
O(1)-C(5)	1.353(3)	C(1)-B(6)*	1.619(3)
N(1)-C(4)	1.489(3)	C(1)-C(2)*	1.619(3)
N(1)-C(4)*	1.489(3)	C(1)-B(3)*	1.707(4)
N(1)-C(3)	1.491(4)	C(5)-C(6)	1.372(3)
B(1)-B(3)*	1.757(5)	C(5)-C(10)	1.379(3)
B(1)-B(3)	1.757(5)	C(6)-C(7)	1.364(4)
B(1)-B(4)	1.763(7)	C(7)-C(8)	1.357(4)
B(1)-B(2)*	1.771(5)	C(8)-C(9)	1.382(4)
B(1)-B(2)	1.771(5)	C(9)-C(10)	1.386(4)
B(2)-C(2)	1.722(4)	C(101)-C(103)	1.360(4)
B(2)-B(4)	1.755(4)	C(101)-C(102)	1.365(4)
B(2)-B(3)	1.766(5)	C(102)-C(103)*	1.358(4)
B(2)-B(5)	1.775(4)	C(103)-C(102)*	1.358(4)
B(3)-C(1)	1.707(4)		

Table 3. Angles [deg] for **11**.

O(1)-Ti(1)-O(1)*	102.3(1)	O(1)-Ti(1)-B(5)*	92.7(9)
O(1)-Ti(1)-N(1)	98.3(7)	O(1)*-Ti(1)-B(5)*	128.3(9)
O(1)*-Ti(1)-N(1)	98.3(7)	N(1)-Ti(1)-B(5)*	128.3(1)
O(1)-Ti(1)-C(1)	127.6(6)	C(1)-Ti(1)-B(5)*	69.9(1)

O(1)*-Ti(1)-C(1)	127.6(6)	C(2)-Ti(1)-B(5)*	71.1(1)
N(1)-Ti(1)-C(1)	63.5(1)	B(6)*-Ti(1)-B(5)*	42.1(1)
O(1)-Ti(1)-C(2)	162.1(9)	C(2)*-Ti(1)-B(5)*	42.1(1)
O(1)*-Ti(1)-C(2)	93.9(9)	B(5)-Ti(1)-B(5)*	43.2(1)
N(1)-Ti(1)-C(2)	86.7(9)	C(5)-O(1)-Ti(1)	172.4(2)
C(1)-Ti(1)-C(2)	40.5(8)	C(4)-N(1)-C(4)*	108.5(3)
O(1)-Ti(1)-B(6)*	93.9(9)	C(4)-N(1)-C(3)	111.8(2)
O(1)*-Ti(1)-B(6)*	162.1(9)	C(4)*-N(1)-C(3)	111.8(2)
N(1)-Ti(1)-B(6)*	86.7(9)	C(4)-N(1)-Ti(1)	112.7(2)
C(1)-Ti(1)-B(6)*	40.5(8)	C(4)*-N(1)-Ti(1)	112.7(2)
C(2)-Ti(1)-B(6)*	69.2(1)	C(3)-N(1)-Ti(1)	99.3(2)
O(1)-Ti(1)-C(2)*	93.9(9)	B(3)*-B(1)-B(3)	60.5(3)
O(1)*-Ti(1)-C(2)*	162.1(9)	B(3)*-B(1)-B(4)	107.8(3)
N(1)-Ti(1)-C(2)*	86.7(9)	B(3)-B(1)-B(4)	107.8(3)
C(1)-Ti(1)-C(2)*	40.5(8)	B(3)*-B(1)-B(2)*	60.1(2)
C(2)-Ti(1)-C(2)*	69.2(1)	B(3)-B(1)-B(2)*	108.2(3)
O(1)-Ti(1)-B(5)	128.3(9)	B(4)-B(1)-B(2)*	59.6(2)
O(1)*-Ti(1)-B(5)	92.7(9)	B(3)*-B(1)-B(2)	108.2(3)
N(1)-Ti(1)-B(5)	128.3(1)	B(3)-B(1)-B(2)	60.1(2)
C(1)-Ti(1)-B(5)	69.9(1)	B(4)-B(1)-B(2)	59.6(2)
C(2)-Ti(1)-B(5)	42.1(1)	B(2)*-B(1)-B(2)	107.4(3)
B(6)*-Ti(1)-B(5)	71.1(1)	B(2)*-B(4)-B(2)	108.8(3)
C(2)*-Ti(1)-B(5)	71.1(1)	B(2)*-B(4)-B(1)	60.5(2)
C(2)-B(2)-B(4)	105.1(2)	B(2)-B(4)-B(1)	60.5(2)
C(2)-B(2)-B(3)	59.6(2)	B(2)*-B(4)-B(5)*	60.4(2)
B(4)-B(2)-B(3)	107.7(3)	B(2)-B(4)-B(5)*	108.0(2)
C(2)-B(2)-B(1)	105.5(2)	B(1)-B(4)-B(5)*	108.6(3)

B(4)-B(2)-B(1)	60.0(2)	B(2)*-B(4)-B(5)	108.0(2)
B(3)-B(2)-B(1)	59.6(2)	B(2)-B(4)-B(5)	60.4(2)
C(2)-B(2)-B(5)	58.3(2)	B(1)-B(4)-B(5)	108.6(3)
B(4)-B(2)-B(5)	60.4(2)	B(5)*-B(4)-B(5)	59.3(2)
B(3)-B(2)-B(5)	108.1(2)	C(2)-B(5)-B(5)*	105.6(1)
B(1)-B(2)-B(5)	108.3(2)	C(2)-B(5)-B(2)	59.3(2)
C(1)-B(3)-C(2)	56.1(2)	B(5)*-B(5)-B(2)	108.0(2)
C(1)-B(3)-B(1)	103.8(2)	C(2)-B(5)-B(4)	105.0(2)
C(2)-B(3)-B(1)	105.6(3)	B(5)*-B(5)-B(4)	60.4(1)
C(1)-B(3)-B(2)	103.1(2)	B(2)-B(5)-B(4)	59.3(2)
C(2)-B(3)-B(2)	58.9(2)	C(2)-B(5)-Ti(1)	67.8(1)
B(1)-B(3)-B(2)	60.4(2)	B(5)*-B(5)-Ti(1)	68.4(7)
C(1)-B(3)-B(3)*	58.8(1)	B(2)-B(5)-Ti(1)	123.9(2)
C(2)-B(3)-B(3)*	105.0(2)	B(4)-B(5)-Ti(1)	124.0(2)
B(1)-B(3)-B(3)*	59.8(2)	C(3)-C(1)-B(3)*	121.3(2)
B(2)-B(3)-B(3)*	107.9(2)	B(6)*-C(1)-B(3)*	62.8(2)
C(1)-C(2)-B(5)	108.9(2)	C(2)*-C(1)-B(3)*	62.8(2)
C(1)-C(2)-B(2)	109.0(2)	C(2)-C(1)-B(3)*	113.4(2)
B(5)-C(2)-B(2)	62.4(2)	B(3)-C(1)-B(3)*	62.4(3)
C(1)-C(2)-B(3)	61.1(2)	C(3)-C(1)-Ti(1)	92.4(2)
B(5)-C(2)-B(3)	112.9(2)	B(6)*-C(1)-Ti(1)	70.4(1)
B(2)-C(2)-B(3)	61.4(2)	C(2)*-C(1)-Ti(1)	70.4(1)
C(1)-C(2)-Ti(1)	69.1(1)	C(2)-C(1)-Ti(1)	70.4(1)
B(5)-C(2)-Ti(1)	70.0(1)	B(3)-C(1)-Ti(1)	131.1(2)
B(2)-C(2)-Ti(1)	128.8(2)	B(3)*-C(1)-Ti(1)	131.1(2)
B(3)-C(2)-Ti(1)	128.2(2)	N(1)-C(3)-C(1)	104.8(3)
C(3)-C(1)-B(6)*	118.1(2)	O(1)-C(5)-C(10)	118.7(2)

C(3)-C(1)-C(2)*	118.1(2)	C(6)-C(5)-C(10)	120.5(2)
C(3)-C(1)-C(2)	118.1(2)	C(7)-C(6)-C(5)	120.3(3)
B(6)*-C(1)-C(2)	111.0(3)	C(8)-C(7)-C(6)	120.3(3)
C(2)*-C(1)-C(2)	111.0(3)	C(7)-C(8)-C(9)	120.1(3)
C(3)-C(1)-B(3)	121.3(2)	C(8)-C(9)-C(10)	120.2(3)
B(6)*-C(1)-B(3)	113.4(2)	C(5)-C(10)-C(9)	118.6(3)
C(2)*-C(1)-B(3)	113.4(2)	C(103)-C(101)-C(102)	120.1(3)
C(2)-C(1)-B(3)	62.8(2)	C(103)*-C(102)-C(101)	120.2(3)
O(1)-C(5)-C(6)	120.8(2)	C(102)*-C(103)-C(101)	119.7(3)

Table 1. Crystal data and structure refinement for **13**.

Identification code	kor506	
Empirical formula	$C_{25}H_{38}B_9NO_2Ti$	
Formula weight	529.75	
Temperature	233(2)K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, $P2_1/c$	
Unit cell dimensions	$a = 11.7288(7)$ Å	$\beta = 91.940(2)^\circ$
	$b = 11.7786(7)$ Å	
	$c = 22.3691(1)$ Å	
Volume	3088.5(3) Å <sup>3</sup>	
Z, D <sub>calc</sub>	4, 1.139	g/cm <sup>3</sup>
$m$	0.300 mm <sup>-1</sup>	
$F(000)$	1112	
Crystal size	0.2 x 0.17 x 0.09 mm	
q range for data collection	1.74 to 28.31 °	
Limiting indices	$-15 \leq h \leq 15, -15 \leq k \leq 15, -28 \leq l \leq 29$	
Reflections collected / unique	31249 / 7664 [R(int) = 0.1214]	
Completeness to q = 25.96	99.7 %	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	7664 / 9 / 356	
Goodness-of-fit on $F^2$	0.995	
Final R indices [I>2s (I)]	<sup>a</sup> $R_1 = 0.0811, {}^b wR_2 = 0.2134$	
R indices (all data)	<sup>a</sup> $R_1 = 0.2357, {}^b wR_2 = 0.3167$	
Largest diff. peak and hole	0.559 and -0.339 e.Å <sup>-3</sup>	

<sup>a</sup> $R_1 = \frac{1}{\sum |F_o|} \sum |F_o - F_c|$  (based on reflections with  $F_o^2 > 2sF^2$ ),

<sup>b</sup> $wR_2 = [\frac{1}{\sum w(F_o^2 - F_c^2)^2}]^{1/2}; w = 1/[s^2(F_o^2) + (0.095P)^2]; P = [\max(F_o^2, 0) + 2F_c^2]/3$  (also

with  $F_o^2 > 2sF^2$ )

Table 2. Bond lengths [Å] for **13**.

Ti(1)-O(1)	1.782(3)	B(8)-B(9)	1.800(1)
Ti(1)-O(2)	1.783(4)	B(9)-C(2)	1.695(9)
Ti(1)-N(1)	2.190(4)	B(9)-B(10)	1.759(9)
Ti(1)-C(1)	2.327(5)	B(10)-B(11)	1.718(8)
Ti(1)-C(2)	2.343(6)	B(11)-C(1)	1.640(8)
Ti(1)-B(11)	2.344(6)	C(1)-C(3)	1.503(7)
Ti(1)-B(9)	2.362(6)	C(1)-C(2)	1.594(8)
Ti(1)-B(10)	2.395(6)	C(13)-C(18)	1.378(7)
O(2)-C(13)	1.360(6)	C(13)-C(14)	1.387(7)
O(1)-C(6)	1.353(6)	C(14)-C(15)	1.409(8)
N(1)-C(5)	1.475(7)	C(14)-C(19)	1.505(8)
N(1)-C(3)	1.476(7)	C(15)-C(16)	1.368(8)
N(1)-C(4)	1.484(7)	C(16)-C(17)	1.356(9)
B(3)-B(5)	1.745(1)	C(17)-C(18)	1.386(8)
B(3)-B(4)	1.754(1)	C(6)-C(11')	1.288(1)
B(3)-B(8)	1.772(1)	C(6)-C(7)	1.431(9)
B(3)-B(6)	1.773(9)	C(6)-C(11)	1.720(3)
B(3)-B(7)	1.780(1)	C(7)-C(8')	1.355(1)
B(4)-C(2)	1.713(1)	C(7)-C(12)	1.486(1)
B(4)-C(1)	1.717(9)	C(7)-C(8)	1.660(4)
B(4)-B(8)	1.748(1)	C(8)-C(9)	1.370(5)
B(4)-B(5)	1.782(1)	C(9)-C(10)	1.380(5)
B(5)-C(1)	1.709(8)	C(10)-C(11)	1.400(4)

B(5)-B(11)	1.751(8)	C(8')-C(9')	1.398(2)
B(5)-B(6)	1.753(1)	C(9')-C(10')	1.342(2)
B(6)-B(11)	1.740(9)	C(10')-C(11')	1.422(2)
B(6)-B(7)	1.758(9)	C(105)-C(104)	1.330(2)
B(6)-B(10)	1.780(8)	C(105)-C(106)	1.394(2)
B(7)-B(10)	1.767(9)	C(104)-C(103)	1.407(2)
B(7)-B(8)	1.772(1)	C(103)-C(102)	1.422(1)
B(7)-B(9)	1.782(9)	C(102)-C(101)	1.500(2)
B(8)-C(2)	1.719(9)	C(101)-C(106)	1.374(2)

Table 34. Angles [deg] for 13.

O(1)-Ti(1)-O(2)	103.3(2)	B(3)-B(8)-B(9)	107.8(5)
O(1)-Ti(1)-N(1)	98.3(2)	B(7)-B(8)-B(9)	59.8(4)
O(2)-Ti(1)-N(1)	102.0(2)	C(2)-B(9)-B(10)	105.7(4)
O(1)-Ti(1)-C(1)	126.7(2)	C(2)-B(9)-B(7)	104.4(5)
O(2)-Ti(1)-C(1)	128.5(2)	B(10)-B(9)-B(7)	59.9(4)
N(1)-Ti(1)-C(1)	63.1(2)	C(2)-B(9)-B(8)	58.9(4)
O(1)-Ti(1)-C(2)	93.6(2)	B(10)-B(9)-B(8)	108.0(4)
O(2)-Ti(1)-C(2)	159.7(2)	B(7)-B(9)-B(8)	59.3(4)
N(1)-Ti(1)-C(2)	86.3(2)	C(2)-B(9)-Ti(1)	68.3(3)
C(1)-Ti(1)-C(2)	39.9(2)	B(10)-B(9)-Ti(1)	69.3(3)
O(1)-Ti(1)-B(11)	162.1(2)	B(7)-B(9)-Ti(1)	124.4(4)
O(2)-Ti(1)-B(11)	92.5(2)	B(8)-B(9)-Ti(1)	124.2(4)
N(1)-Ti(1)-B(11)	86.4(2)	B(11)-B(10)-B(9)	105.0(4)

C(1)-Ti(1)-B(11)	41.1(2)	B(11)-B(10)-B(7)	105.7(4)
C(2)-Ti(1)-B(11)	69.3(2)	B(9)-B(10)-B(7)	60.7(4)
O(1)-Ti(1)-B(9)	92.0(2)	B(11)-B(10)-B(6)	59.6(3)
O(2)-Ti(1)-B(9)	124.7(2)	B(9)-B(10)-B(6)	107.9(4)
N(1)-Ti(1)-B(9)	128.2(2)	B(7)-B(10)-B(6)	59.4(4)
C(1)-Ti(1)-B(9)	70.1(2)	B(11)-B(10)-Ti(1)	67.2(3)
C(2)-Ti(1)-B(9)	42.2(2)	B(9)-B(10)-Ti(1)	67.3(3)
B(11)-Ti(1)-B(9)	71.8(2)	B(7)-B(10)-Ti(1)	123.3(4)
O(1)-Ti(1)-B(10)	128.0(2)	B(6)-B(10)-Ti(1)	123.1(4)
O(2)-Ti(1)-B(10)	89.5(2)	C(1)-B(11)-B(10)	108.3(4)
N(1)-Ti(1)-B(10)	128.4(2)	C(1)-B(11)-B(6)	107.4(4)
C(1)-Ti(1)-B(10)	70.4(2)	B(10)-B(11)-B(6)	62.0(4)
C(2)-Ti(1)-B(10)	71.1(2)	C(1)-B(11)-B(5)	60.4(3)
B(11)-Ti(1)-B(10)	42.5(2)	B(10)-B(11)-B(5)	111.3(5)
B(9)-Ti(1)-B(10)	43.4(2)	B(6)-B(11)-B(5)	60.3(4)
C(13)-O(2)-Ti(1)	158.5(3)	C(1)-B(11)-Ti(1)	68.9(3)
C(6)-O(1)-Ti(1)	172.2(4)	B(10)-B(11)-Ti(1)	70.3(3)
C(5)-N(1)-C(3)	113.0(5)	B(6)-B(11)-Ti(1)	128.2(4)
C(5)-N(1)-C(4)	106.8(5)	B(5)-B(11)-Ti(1)	127.1(4)
C(3)-N(1)-C(4)	111.7(5)	C(3)-C(1)-C(2)	116.7(5)
C(5)-N(1)-Ti(1)	112.7(3)	C(3)-C(1)-B(11)	119.3(5)
C(3)-N(1)-Ti(1)	99.0(3)	C(2)-C(1)-B(11)	111.0(4)
C(4)-N(1)-Ti(1)	113.8(4)	C(3)-C(1)-B(5)	123.0(5)
B(5)-B(3)-B(4)	61.2(4)	C(2)-C(1)-B(5)	112.6(5)
B(5)-B(3)-B(8)	108.2(5)	B(11)-C(1)-B(5)	63.0(3)
B(4)-B(3)-B(8)	59.4(4)	C(3)-C(1)-B(4)	120.1(5)
B(5)-B(3)-B(6)	59.8(4)	C(2)-C(1)-B(4)	62.2(4)

B(4)-B(3)-B(6)	108.7(5)	B(11)-C(1)-B(4)	114.2(5)
B(8)-B(3)-B(6)	107.7(5)	B(5)-C(1)-B(4)	62.7(4)
B(5)-B(3)-B(7)	107.1(5)	C(3)-C(1)-Ti(1)	92.5(3)
B(4)-B(3)-B(7)	107.4(5)	C(2)-C(1)-Ti(1)	70.6(3)
B(8)-B(3)-B(7)	59.9(4)	B(11)-C(1)-Ti(1)	70.0(3)
B(6)-B(3)-B(7)	59.3(4)	B(5)-C(1)-Ti(1)	130.5(4)
C(2)-B(4)-C(1)	55.4(3)	B(4)-C(1)-Ti(1)	130.7(4)
C(2)-B(4)-B(8)	59.6(4)	C(1)-C(2)-B(9)	109.9(4)
C(1)-B(4)-B(8)	103.5(5)	C(1)-C(2)-B(4)	62.4(4)
C(2)-B(4)-B(3)	105.5(5)	B(9)-C(2)-B(4)	114.2(5)
C(1)-B(4)-B(3)	103.6(5)	C(1)-C(2)-B(8)	110.4(5)
B(8)-B(4)-B(3)	60.8(4)	B(9)-C(2)-B(8)	63.6(4)
C(2)-B(4)-B(5)	103.7(5)	B(4)-C(2)-B(8)	61.2(4)
C(1)-B(4)-B(5)	58.4(4)	C(1)-C(2)-Ti(1)	69.5(3)
B(8)-B(4)-B(5)	107.6(5)	B(9)-C(2)-Ti(1)	69.5(3)
B(3)-B(4)-B(5)	59.1(4)	B(4)-C(2)-Ti(1)	129.9(4)
C(1)-B(5)-B(3)	104.3(5)	B(8)-C(2)-Ti(1)	129.7(4)
C(1)-B(5)-B(11)	56.6(3)	N(1)-C(3)-C(1)	105.2(4)
B(3)-B(5)-B(11)	106.9(5)	O(2)-C(13)-C(18)	119.0(5)
C(1)-B(5)-B(6)	103.8(4)	O(2)-C(13)-C(14)	119.5(5)
B(3)-B(5)-B(6)	60.9(4)	C(18)-C(13)-C(14)	121.5(5)
B(11)-B(5)-B(6)	59.6(3)	C(13)-C(14)-C(15)	117.1(5)
C(1)-B(5)-B(4)	58.9(4)	C(13)-C(14)-C(19)	121.0(5)
B(3)-B(5)-B(4)	59.6(4)	C(15)-C(14)-C(19)	121.8(6)
B(11)-B(5)-B(4)	105.9(5)	C(16)-C(15)-C(14)	120.9(6)
B(6)-B(5)-B(4)	108.3(5)	C(17)-C(16)-C(15)	120.8(6)
B(11)-B(6)-B(5)	60.2(4)	C(16)-C(17)-C(18)	120.1(6)

B(11)-B(6)-B(7)	105.2(4)	C(13)-C(18)-C(17)	119.5(6)
B(5)-B(6)-B(7)	107.7(5)	C(11')-C(6)-O(1)	122.8(7)
B(11)-B(6)-B(3)	106.2(5)	C(11')-C(6)-C(7)	120.0(8)
B(5)-B(6)-B(3)	59.3(4)	O(1)-C(6)-C(7)	117.2(6)
B(7)-B(6)-B(3)	60.5(4)	C(11')-C(6)-C(11)	24.4(9)
B(11)-B(6)-B(10)	58.4(3)	O(1)-C(6)-C(11)	104.3(1)
B(5)-B(6)-B(10)	108.3(4)	C(7)-C(6)-C(11)	136.2(1)
B(7)-B(6)-B(10)	59.9(4)	C(8')-C(7)-C(6)	121.5(9)
B(3)-B(6)-B(10)	108.6(5)	C(8')-C(7)-C(12)	117.2(9)
B(6)-B(7)-B(10)	60.7(4)	C(6)-C(7)-C(12)	121.2(6)
B(6)-B(7)-B(8)	108.4(5)	C(8')-C(7)-C(8)	28.4(1)
B(10)-B(7)-B(8)	108.9(5)	C(6)-C(7)-C(8)	93.2(1)
B(6)-B(7)-B(3)	60.2(4)	C(12)-C(7)-C(8)	145.2(2)
B(10)-B(7)-B(3)	108.9(5)	C(9)-C(8)-C(7)	136.0(3)
B(8)-B(7)-B(3)	59.9(4)	C(8)-C(9)-C(10)	120.0(4)
B(6)-B(7)-B(9)	107.9(5)	C(9)-C(10)-C(11)	124.0(3)
B(10)-B(7)-B(9)	59.4(4)	C(10)-C(11)-C(6)	109.0(2)
B(8)-B(7)-B(9)	60.8(4)	C(7)-C(8')-C(9')	116.0(1)
B(3)-B(7)-B(9)	108.2(5)	C(10')-C(9')-C(8')	123.4(1)
C(2)-B(8)-B(4)	59.2(4)	C(9')-C(10')-C(11')	118.1(1)
C(2)-B(8)-B(3)	104.5(5)	C(6)-C(11')-C(10')	120.9(1)
B(4)-B(8)-B(3)	59.8(4)	C(104)-C(105)-C(106)	113.0(3)
C(2)-B(8)-B(7)	103.8(5)	C(105)-C(104)-C(103)	120.0(2)
B(4)-B(8)-B(7)	108.0(5)	C(104)-C(103)-C(102)	124.8(2)
B(3)-B(8)-B(7)	60.3(4)	C(103)-C(102)-C(101)	118.7(2)
C(2)-B(8)-B(9)	57.5(3)	C(106)-C(101)-C(102)	106.0(2)
B(4)-B(8)-B(9)	107.5(5)	C(101)-C(106)-C(105)	138.0(3)

Table 1. Crystal data and structure refinement for **14**.

Identification code	kor506	
Empirical formula	$C_{25}H_{38}B_9NO_2Ti$	
Formula weight	529.75	
Temperature	233(2)K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, $P2_1/c$	
Unit cell dimensions	$a = 11.7288(7)$ Å	$\beta = 91.940(2)^\circ$
	$b = 11.7786(7)$ Å	
	$c = 22.3691(1)$ Å	
Volume	3088.5(3) Å <sup>3</sup>	
Z, D <sub>calc</sub>	4, 1.139	g/cm <sup>3</sup>
$m$	0.300 mm <sup>-1</sup>	
$F(000)$	1112	
Crystal size	0.2 x 0.17 x 0.09 mm	
q range for data collection	1.74 to 28.31 °	
Limiting indices	$-15 \leq h \leq 15, -15 \leq k \leq 15, -28 \leq l \leq 29$	
Reflections collected / unique	31249 / 7664 [R(int) = 0.1214]	
Completeness to q = 25.96	99.7 %	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	7664 / 9 / 356	
Goodness-of-fit on $F^2$	0.995	
Final R indices [I>2s (I)]	<sup>a</sup> $R_1 = 0.0811, {}^b wR_2 = 0.2134$	
R indices (all data)	<sup>a</sup> $R_1 = 0.2357, {}^b wR_2 = 0.3167$	
Largest diff. peak and hole	0.559 and -0.339 e.Å <sup>-3</sup>	

<sup>a</sup> $R_1 = \frac{1}{\sum |F_o|} \sum |F_o - F_c|$  (based on reflections with  $F_o^2 > 2sF^2$ ),

<sup>b</sup> $wR_2 = [\frac{1}{\sum w(F_o^2 - F_c^2)^2}]^{1/2}; w = 1/[s^2(F_o^2) + (0.095P)^2]; P = [\max(F_o^2, 0) + 2F_c^2]/3$  (also

with  $F_o^2 > 2sF^2$ )

Table 2. Bond lengths [Å] for **14**.

Ti(1)-O(1)	1.782(3)	B(8)-B(9)	1.800(1)
Ti(1)-O(2)	1.783(4)	B(9)-C(2)	1.695(9)
Ti(1)-N(1)	2.190(4)	B(9)-B(10)	1.759(9)
Ti(1)-C(1)	2.327(5)	B(10)-B(11)	1.718(8)
Ti(1)-C(2)	2.343(6)	B(11)-C(1)	1.640(8)
Ti(1)-B(11)	2.344(6)	C(1)-C(3)	1.503(7)
Ti(1)-B(9)	2.362(6)	C(1)-C(2)	1.594(8)
Ti(1)-B(10)	2.395(6)	C(13)-C(18)	1.378(7)
O(2)-C(13)	1.360(6)	C(13)-C(14)	1.387(7)
O(1)-C(6)	1.353(6)	C(14)-C(15)	1.409(8)
N(1)-C(5)	1.475(7)	C(14)-C(19)	1.505(8)
N(1)-C(3)	1.476(7)	C(15)-C(16)	1.368(8)
N(1)-C(4)	1.484(7)	C(16)-C(17)	1.356(9)
B(3)-B(5)	1.745(1)	C(17)-C(18)	1.386(8)
B(3)-B(4)	1.754(1)	C(6)-C(11')	1.288(1)
B(3)-B(8)	1.772(1)	C(6)-C(7)	1.431(9)
B(3)-B(6)	1.773(9)	C(6)-C(11)	1.720(3)
B(3)-B(7)	1.780(1)	C(7)-C(8')	1.355(1)
B(4)-C(2)	1.713(1)	C(7)-C(12)	1.486(1)
B(4)-C(1)	1.717(9)	C(7)-C(8)	1.660(4)
B(4)-B(8)	1.748(1)	C(8)-C(9)	1.370(5)
B(4)-B(5)	1.782(1)	C(9)-C(10)	1.380(5)
B(5)-C(1)	1.709(8)	C(10)-C(11)	1.400(4)

B(5)-B(11)	1.751(8)	C(8')-C(9')	1.398(2)
B(5)-B(6)	1.753(1)	C(9')-C(10')	1.342(2)
B(6)-B(11)	1.740(9)	C(10')-C(11')	1.422(2)
B(6)-B(7)	1.758(9)	C(105)-C(104)	1.330(2)
B(6)-B(10)	1.780(8)	C(105)-C(106)	1.394(2)
B(7)-B(10)	1.767(9)	C(104)-C(103)	1.407(2)
B(7)-B(8)	1.772(1)	C(103)-C(102)	1.422(1)
B(7)-B(9)	1.782(9)	C(102)-C(101)	1.500(2)
B(8)-C(2)	1.719(9)	C(101)-C(106)	1.374(2)

Table 34. Angles [deg] for **14**.

O(1)-Ti(1)-O(2)	103.3(2)	B(3)-B(8)-B(9)	107.8(5)
O(1)-Ti(1)-N(1)	98.3(2)	B(7)-B(8)-B(9)	59.8(4)
O(2)-Ti(1)-N(1)	102.0(2)	C(2)-B(9)-B(10)	105.7(4)
O(1)-Ti(1)-C(1)	126.7(2)	C(2)-B(9)-B(7)	104.4(5)
O(2)-Ti(1)-C(1)	128.5(2)	B(10)-B(9)-B(7)	59.9(4)
N(1)-Ti(1)-C(1)	63.1(2)	C(2)-B(9)-B(8)	58.9(4)
O(1)-Ti(1)-C(2)	93.6(2)	B(10)-B(9)-B(8)	108.0(4)
O(2)-Ti(1)-C(2)	159.7(2)	B(7)-B(9)-B(8)	59.3(4)
N(1)-Ti(1)-C(2)	86.3(2)	C(2)-B(9)-Ti(1)	68.3(3)
C(1)-Ti(1)-C(2)	39.9(2)	B(10)-B(9)-Ti(1)	69.3(3)
O(1)-Ti(1)-B(11)	162.1(2)	B(7)-B(9)-Ti(1)	124.4(4)
O(2)-Ti(1)-B(11)	92.5(2)	B(8)-B(9)-Ti(1)	124.2(4)
N(1)-Ti(1)-B(11)	86.4(2)	B(11)-B(10)-B(9)	105.0(4)

C(1)-Ti(1)-B(11)	41.1(2)	B(11)-B(10)-B(7)	105.7(4)
C(2)-Ti(1)-B(11)	69.3(2)	B(9)-B(10)-B(7)	60.7(4)
O(1)-Ti(1)-B(9)	92.0(2)	B(11)-B(10)-B(6)	59.6(3)
O(2)-Ti(1)-B(9)	124.7(2)	B(9)-B(10)-B(6)	107.9(4)
N(1)-Ti(1)-B(9)	128.2(2)	B(7)-B(10)-B(6)	59.4(4)
C(1)-Ti(1)-B(9)	70.1(2)	B(11)-B(10)-Ti(1)	67.2(3)
C(2)-Ti(1)-B(9)	42.2(2)	B(9)-B(10)-Ti(1)	67.3(3)
B(11)-Ti(1)-B(9)	71.8(2)	B(7)-B(10)-Ti(1)	123.3(4)
O(1)-Ti(1)-B(10)	128.0(2)	B(6)-B(10)-Ti(1)	123.1(4)
O(2)-Ti(1)-B(10)	89.5(2)	C(1)-B(11)-B(10)	108.3(4)
N(1)-Ti(1)-B(10)	128.4(2)	C(1)-B(11)-B(6)	107.4(4)
C(1)-Ti(1)-B(10)	70.4(2)	B(10)-B(11)-B(6)	62.0(4)
C(2)-Ti(1)-B(10)	71.1(2)	C(1)-B(11)-B(5)	60.4(3)
B(11)-Ti(1)-B(10)	42.5(2)	B(10)-B(11)-B(5)	111.3(5)
B(9)-Ti(1)-B(10)	43.4(2)	B(6)-B(11)-B(5)	60.3(4)
C(13)-O(2)-Ti(1)	158.5(3)	C(1)-B(11)-Ti(1)	68.9(3)
C(6)-O(1)-Ti(1)	172.2(4)	B(10)-B(11)-Ti(1)	70.3(3)
C(5)-N(1)-C(3)	113.0(5)	B(6)-B(11)-Ti(1)	128.2(4)
C(5)-N(1)-C(4)	106.8(5)	B(5)-B(11)-Ti(1)	127.1(4)
C(3)-N(1)-C(4)	111.7(5)	C(3)-C(1)-C(2)	116.7(5)
C(5)-N(1)-Ti(1)	112.7(3)	C(3)-C(1)-B(11)	119.3(5)
C(3)-N(1)-Ti(1)	99.0(3)	C(2)-C(1)-B(11)	111.0(4)
C(4)-N(1)-Ti(1)	113.8(4)	C(3)-C(1)-B(5)	123.0(5)
B(5)-B(3)-B(4)	61.2(4)	C(2)-C(1)-B(5)	112.6(5)
B(5)-B(3)-B(8)	108.2(5)	B(11)-C(1)-B(5)	63.0(3)
B(4)-B(3)-B(8)	59.4(4)	C(3)-C(1)-B(4)	120.1(5)
B(5)-B(3)-B(6)	59.8(4)	C(2)-C(1)-B(4)	62.2(4)

B(4)-B(3)-B(6)	108.7(5)	B(11)-C(1)-B(4)	114.2(5)
B(8)-B(3)-B(6)	107.7(5)	B(5)-C(1)-B(4)	62.7(4)
B(5)-B(3)-B(7)	107.1(5)	C(3)-C(1)-Ti(1)	92.5(3)
B(4)-B(3)-B(7)	107.4(5)	C(2)-C(1)-Ti(1)	70.6(3)
B(8)-B(3)-B(7)	59.9(4)	B(11)-C(1)-Ti(1)	70.0(3)
B(6)-B(3)-B(7)	59.3(4)	B(5)-C(1)-Ti(1)	130.5(4)
C(2)-B(4)-C(1)	55.4(3)	B(4)-C(1)-Ti(1)	130.7(4)
C(2)-B(4)-B(8)	59.6(4)	C(1)-C(2)-B(9)	109.9(4)
C(1)-B(4)-B(8)	103.5(5)	C(1)-C(2)-B(4)	62.4(4)
C(2)-B(4)-B(3)	105.5(5)	B(9)-C(2)-B(4)	114.2(5)
C(1)-B(4)-B(3)	103.6(5)	C(1)-C(2)-B(8)	110.4(5)
B(8)-B(4)-B(3)	60.8(4)	B(9)-C(2)-B(8)	63.6(4)
C(2)-B(4)-B(5)	103.7(5)	B(4)-C(2)-B(8)	61.2(4)
C(1)-B(4)-B(5)	58.4(4)	C(1)-C(2)-Ti(1)	69.5(3)
B(8)-B(4)-B(5)	107.6(5)	B(9)-C(2)-Ti(1)	69.5(3)
B(3)-B(4)-B(5)	59.1(4)	B(4)-C(2)-Ti(1)	129.9(4)
C(1)-B(5)-B(3)	104.3(5)	B(8)-C(2)-Ti(1)	129.7(4)
C(1)-B(5)-B(11)	56.6(3)	N(1)-C(3)-C(1)	105.2(4)
B(3)-B(5)-B(11)	106.9(5)	O(2)-C(13)-C(18)	119.0(5)
C(1)-B(5)-B(6)	103.8(4)	O(2)-C(13)-C(14)	119.5(5)
B(3)-B(5)-B(6)	60.9(4)	C(18)-C(13)-C(14)	121.5(5)
B(11)-B(5)-B(6)	59.6(3)	C(13)-C(14)-C(15)	117.1(5)
C(1)-B(5)-B(4)	58.9(4)	C(13)-C(14)-C(19)	121.0(5)
B(3)-B(5)-B(4)	59.6(4)	C(15)-C(14)-C(19)	121.8(6)
B(11)-B(5)-B(4)	105.9(5)	C(16)-C(15)-C(14)	120.9(6)
B(6)-B(5)-B(4)	108.3(5)	C(17)-C(16)-C(15)	120.8(6)
B(11)-B(6)-B(5)	60.2(4)	C(16)-C(17)-C(18)	120.1(6)

B(11)-B(6)-B(7)	105.2(4)	C(13)-C(18)-C(17)	119.5(6)
B(5)-B(6)-B(7)	107.7(5)	C(11')-C(6)-O(1)	122.8(7)
B(11)-B(6)-B(3)	106.2(5)	C(11')-C(6)-C(7)	120.0(8)
B(5)-B(6)-B(3)	59.3(4)	O(1)-C(6)-C(7)	117.2(6)
B(7)-B(6)-B(3)	60.5(4)	C(11')-C(6)-C(11)	24.4(9)
B(11)-B(6)-B(10)	58.4(3)	O(1)-C(6)-C(11)	104.3(1)
B(5)-B(6)-B(10)	108.3(4)	C(7)-C(6)-C(11)	136.2(1)
B(7)-B(6)-B(10)	59.9(4)	C(8')-C(7)-C(6)	121.5(9)
B(3)-B(6)-B(10)	108.6(5)	C(8')-C(7)-C(12)	117.2(9)
B(6)-B(7)-B(10)	60.7(4)	C(6)-C(7)-C(12)	121.2(6)
B(6)-B(7)-B(8)	108.4(5)	C(8')-C(7)-C(8)	28.4(1)
B(10)-B(7)-B(8)	108.9(5)	C(6)-C(7)-C(8)	93.2(1)
B(6)-B(7)-B(3)	60.2(4)	C(12)-C(7)-C(8)	145.2(2)
B(10)-B(7)-B(3)	108.9(5)	C(9)-C(8)-C(7)	136.0(3)
B(8)-B(7)-B(3)	59.9(4)	C(8)-C(9)-C(10)	120.0(4)
B(6)-B(7)-B(9)	107.9(5)	C(9)-C(10)-C(11)	124.0(3)
B(10)-B(7)-B(9)	59.4(4)	C(10)-C(11)-C(6)	109.0(2)
B(8)-B(7)-B(9)	60.8(4)	C(7)-C(8')-C(9')	116.0(1)
B(3)-B(7)-B(9)	108.2(5)	C(10')-C(9')-C(8')	123.4(1)
C(2)-B(8)-B(4)	59.2(4)	C(9')-C(10')-C(11')	118.1(1)
C(2)-B(8)-B(3)	104.5(5)	C(6)-C(11')-C(10')	120.9(1)
B(4)-B(8)-B(3)	59.8(4)	C(104)-C(105)-C(106)	113.0(3)
C(2)-B(8)-B(7)	103.8(5)	C(105)-C(104)-C(103)	120.0(2)
B(4)-B(8)-B(7)	108.0(5)	C(104)-C(103)-C(102)	124.8(2)
B(3)-B(8)-B(7)	60.3(4)	C(103)-C(102)-C(101)	118.7(2)
C(2)-B(8)-B(9)	57.5(3)	C(106)-C(101)-C(102)	106.0(2)
B(4)-B(8)-B(9)	107.5(5)	C(101)-C(106)-C(105)	138.0(3)

## 저작물 이용 허락서

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논문제목	한글 : 4족과 13족 금속 화합물을 위한 다기능성 Dicarballide Ligand계의 합성 영문 : Multi-Functionalized dicarballide Ligand Systems for Group 4 and 13 Metal complexes				

본인이 저작한 위의 저작물에 대하여 다음과 같은 조건아래 조선대학교가 저작물을 이용할 수 있도록 허락하고 동의합니다.

### - 다음을 -

- 저작물의 DB구축 및 인터넷을 포함한 정보통신망에의 공개를 위한 저작물의 복제, 기억장치에의 저장, 전송 등을 허락함.
- 위의 목적을 위하여 필요한 범위 내에서의 편집·형식상의 변경을 허락함. 다만, 저작물의 내용변경은 금지함.
- 배포·전송된 저작물의 영리적 목적을 위한 복제, 저장, 전송 등은 금지함.
- 저작물에 대한 이용기간은 5년으로 하고, 기간종료 3개월 이내에 별도의 의사표시가 없을 경우에는 저작물의 이용기간을 계속 연장함.
- 해당 저작물의 저작권을 타인에게 양도하거나 또는 출판을 허락을 하였을 경우에는 1개월 이내에 대학에 이를 통보함.
- 조선대학교는 저작물의 이용허락 이후 해당 저작물로 인하여 발생하는 타인에 의한 권리 침해에 대하여 일체의 법적 책임을 지지 않음
- 소속대학의 협정기관에 저작물의 제공 및 인터넷 등 정보통신망을 이용한 저작물의 전송·출력을 허락함.

2009년 11월 27일

저작자: 김 하연 (서명 또는 인)

조선대학교 총장 귀하

## 감사의 글

길고도 짧은 대학원 생활을 마무리 하며 지난 시간들을 돌이켜 보니 많은 아쉬움과 후회가 남습니다. 학문적 성취 뿐 아니라 고마운 많은 분들께 감사의 인사를 전하기 못했기에 아쉬움이 더 큰 것 같습니다. 제가 이렇게 성장하기까지 직·간접적으로 힘이 되고 방향을 잡아주셨던 많은 분들께 감사의 말씀을 전하고자 합니다.

본 논문이 완성되기까지 학문의 길로 이끌어 주시고 첫 제자라서 많은 관심과 애정을 갖고 좋은 결실을 맺을 수 있도록 지도하여 주시고 학문적인 부분 이외에도 많은 가르침을 주셔서 성장할 수 있게 도와주신 이 종대 교수님께 진심으로 감사드립니다.

바쁘신 중에도 논문 심사를 맡아 주시고 격려해 주신 조 성동 교수님 그리고 이 범규 교수님께 깊은 감사드립니다.

대학원 과정 중 좋은 가르침을 주신 송 기동 교수님, 고 문주 교수님, 손홍래 교수님, 류 설 교수님께 감사드리며 실험적인 면과 심리적인 면에서 많은 도움을 주신 조 대원 교수님께도 감사드립니다. 한 명, 한 명 이름을 다 열거하지는 못하지만 많은 선배, 후배, 동기들에게 고맙다는 말을 전하고 늘 응원해주고 격려해 주는 나의 친구들, 석사과정 동안 함께 의지하며 지내온 하나님뿐인 동기 효숙이에게 또한 고마움을 전합니다.

좋은 조건에서 실험을 할 수 있도록 배려해 주시고 논문 작성 과정에서 세심하게 검토해 주신 고려대학교 강 상우 교수님과 실험 과정 중에 많은 도움을 준 고려대학교 대학원생들에게 깊은 감사를 드립니다.

석사과정동안 아낌없는 관심과 배려를 해 주신 모든 분들께 감사드리며 때로는 당근으로, 때로는 채찍으로 지도해 주시고, 늘 제가 새롭게 다짐하고 도전할 수 있는 자극과 가르침을 주셨던 부분들 잊지 않고 앞으로 큰 밑거름으로 사용하도록 하겠습니다.

끝으로 부족함이 많음에도 불구하고 한결같은 마음으로 오늘의 제가 있기까지 지켜봐 주시고 보살펴 주시며 뒷바라지해주신 부모님께 감사드리고 사랑한다는 말씀을 전합니다.

모든 분들이 건강하시고 행복하시기를 진심으로 기원합니다.

2009년이 저물어가는 12월 어느 날에...

