

Unusual and unprecedented rings and cages derived from main group elements

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This research account presents our significant recent findings in the area of small cage main group metallocarboranes during the past several years. The highlights of these findings are as following: (1) The reactivity study on the *carbons apart* C_4B_8 -carborane led to the introduction of an unusual carborane species that acts as a restricted electron-acceptor by removing only the valence electrons of a group 1 or group 2 metal, thus forming the corresponding alkali and alkaline earth metal compounds. Further reactivity study of these species in solvent extraction of radioactive cesium metal ion ($^{137}Cs^+$) from nuclear wastes has rekindled our interest to explore new avenues in this area of main group metallocarborane research. (2) The syntheses and structures of main group metallocarboranes have exemplified their rich structural and coordination chemistry beyond their existence as versatile synthons for the production of other metallocarboranes of *d*- and *f*-block elements. (3) Synthesis and reactivity study on half- and full-sandwich gallacarboranes opened up the possibility of using such compounds as precursors in the formation of conducting materials. (4) Even though two germanium atoms are present formally in +2 and +4 oxidation states, the reactivity study on the mixed-valence digermacarboranes with Lewis bases shows no indication of *exo*-polyhedral Ge(IV) atom being the Lewis acid site. And finally, (5) our research has demonstrated that the 'electron-deficient' cages can be quantitatively transformed into the corresponding 'electron-precise' heterocyclic rings.

THERE has been extensive research reported on the chemical and structural properties of the metallocarboranes in the pentagonal bipyramidal (MC_2B_4) and the icosahedral (MC_2B_9) cage systems¹. These complexes are generally synthesized by the reaction of the mono- or dianions of the *nido*- C_2B_4 or C_2B_9 carboranes with suitable metal reagents. Much of the emphasis for these studies comes from the fact that the two *nido*-carboranes have 6 π electrons delocalized on a C_2B_3 open pentagonal face that are very similar to the primary metal-bonding orbitals of the cyclopentadienide ligand, $[C_5H_5]^-$. Our research in this area has involved syn-

thetic, structural, reactivity and theoretical studies on the full- and half-sandwich metallocarboranes derived from the interactions of $[nido-2-(SiMe_3)-n-(R)-2,n-C_2B_4H_4]^{2-}$ [$n = 3, 4$; $R = SiMe_3, Me, H$] with main group², *d*-group³, and *f*-group metals⁴. Here we report some of our latest results in this fascinating area of carborane research.

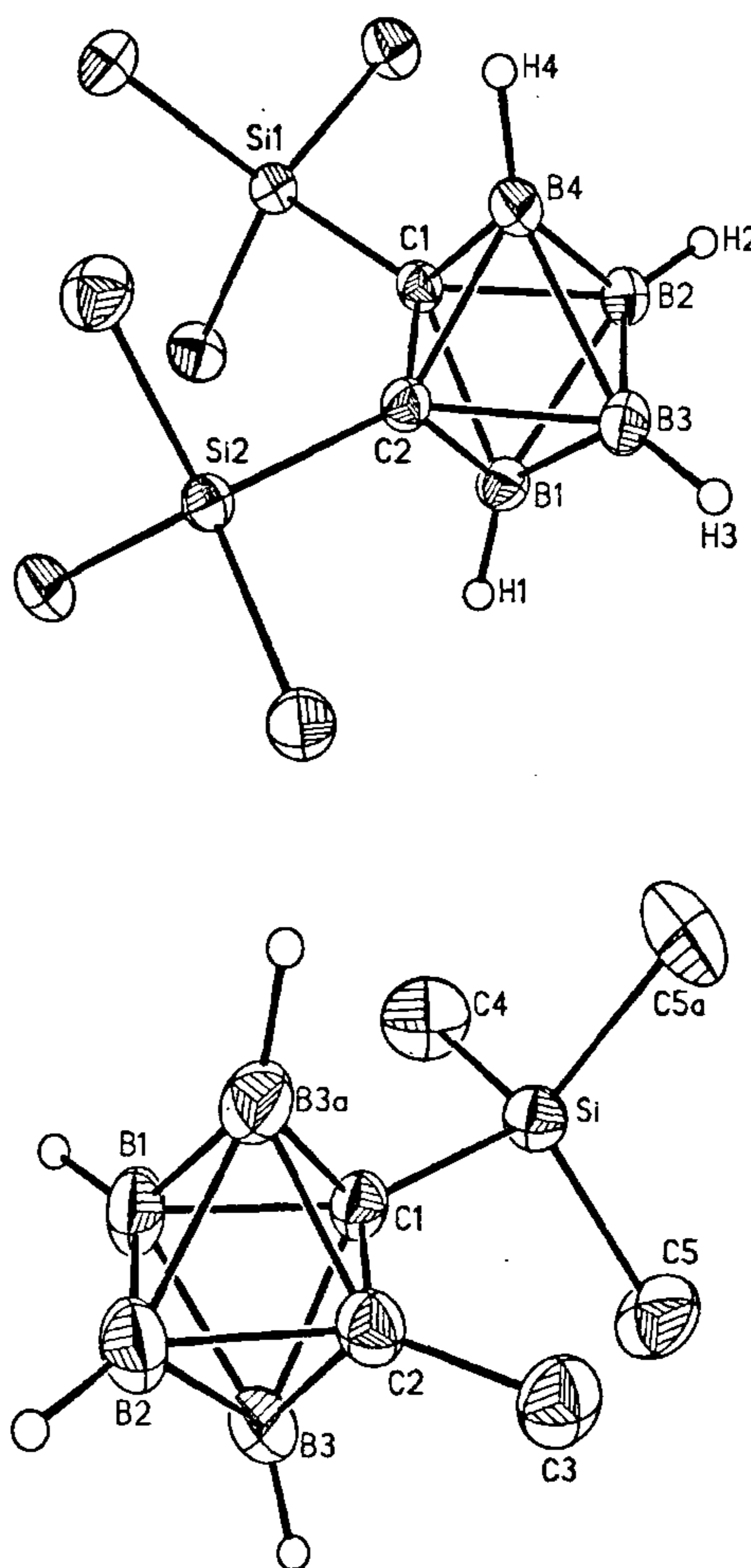


Figure 1. Crystal structures of *closo*-1-($SiMe_3$)-2-(R)-1,2- $C_2B_4H_4$ ($R = SiMe_3, Me$).

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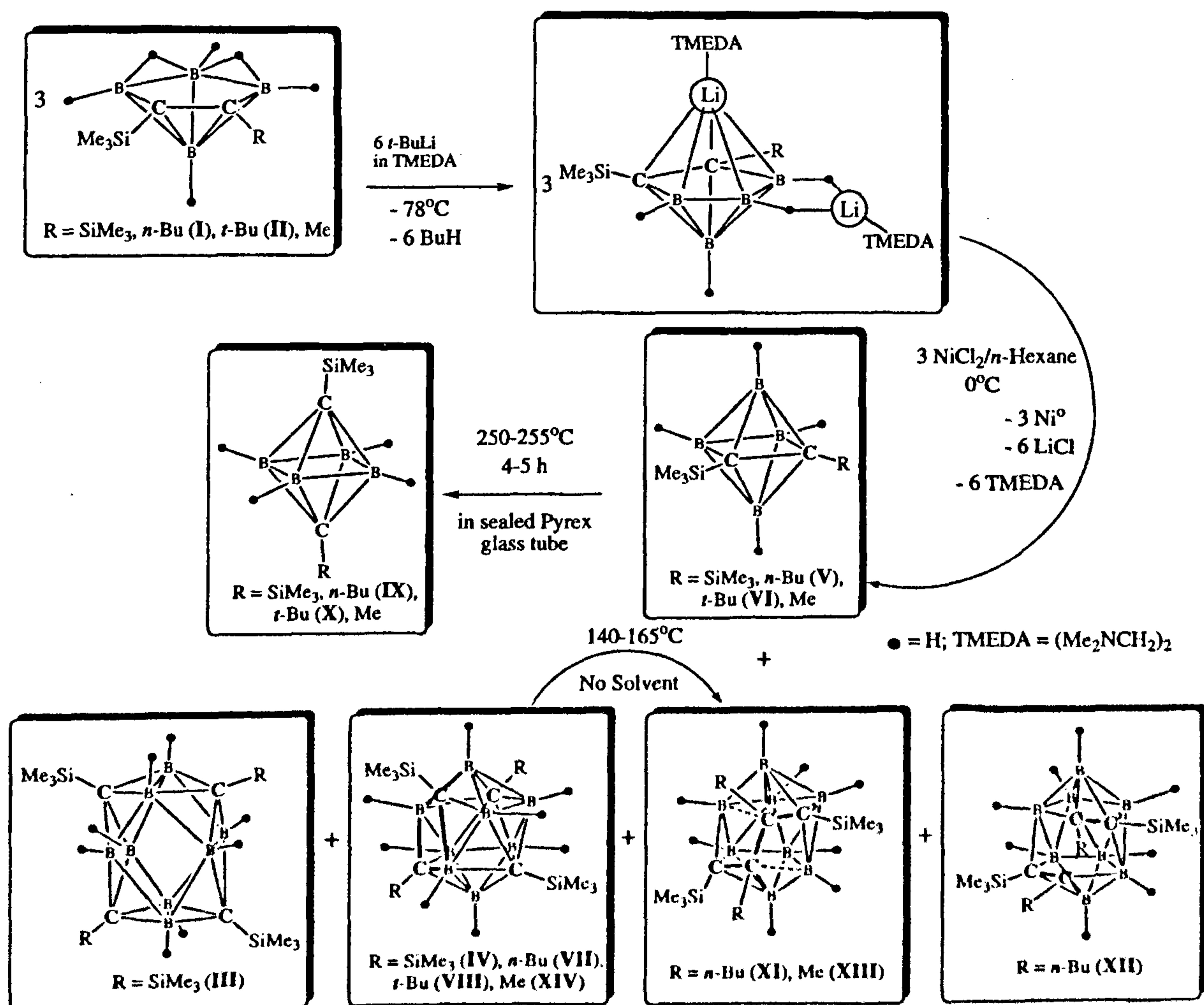
This paper is dedicated to Prof. S. S. Krishnamurthy on the occasion of his 60th birthday.

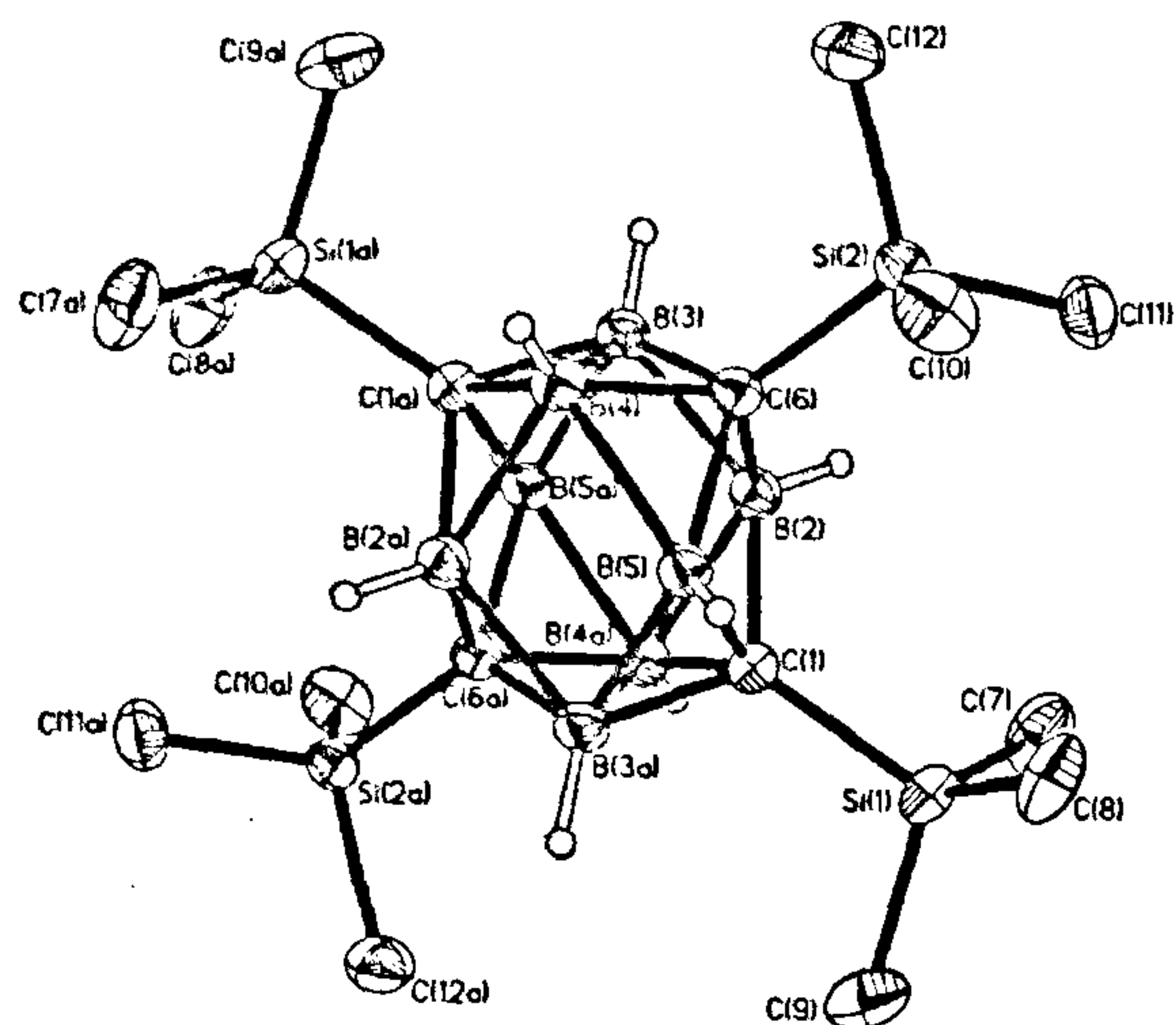
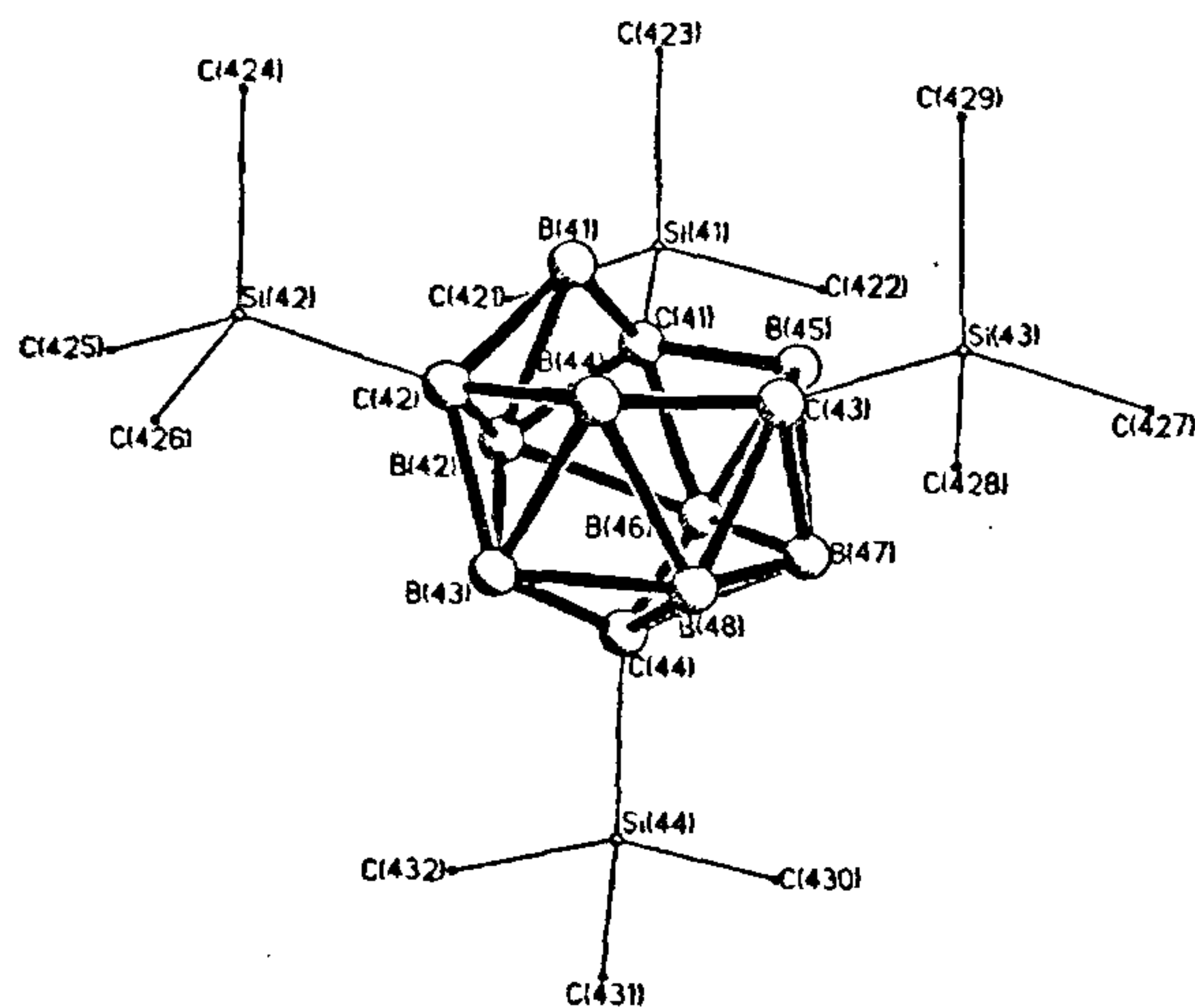
Syntheses of C_2B_4 and C_4B_8 -carboranes

The reaction of the 2,3- C_2B_4 -carborane dianion with $NiCl_2$ in hexane did not give the nickelacarborane but instead underwent oxidative cage closure reactions to produce the corresponding *closo*-1-($SiMe_3$)-2-(R)-1,2- $C_2B_4H_4$ (see Figure 1) and nickel metal⁵. In addition, we observed an accompanying oxidative cage fusion process that led to the formation of the novel tetracarbon carboranes, *nido*-2,4, x,y -($SiMe_3$)₄-2,4, x,y - $C_4B_8H_8$ ($x = 7$, $y = 9$, (III in Scheme 1); $x = 6$, $y = 12$, (IV in Scheme 1)) (refs 6, 7). Since all cage carbon atoms are separated by at least one boron atom, they will subsequently be referred to as the 'carbons apart' isomers. Grimes and co-workers first reported on the syntheses, structures and reactivities of several tetracarbon carboranes, all of which possessed the common structural feature. The cage carbons were localized on one side of very distorted icosahedral cages⁸⁻¹². In one of these 'carbons adjacent' isomers the carbon atoms were

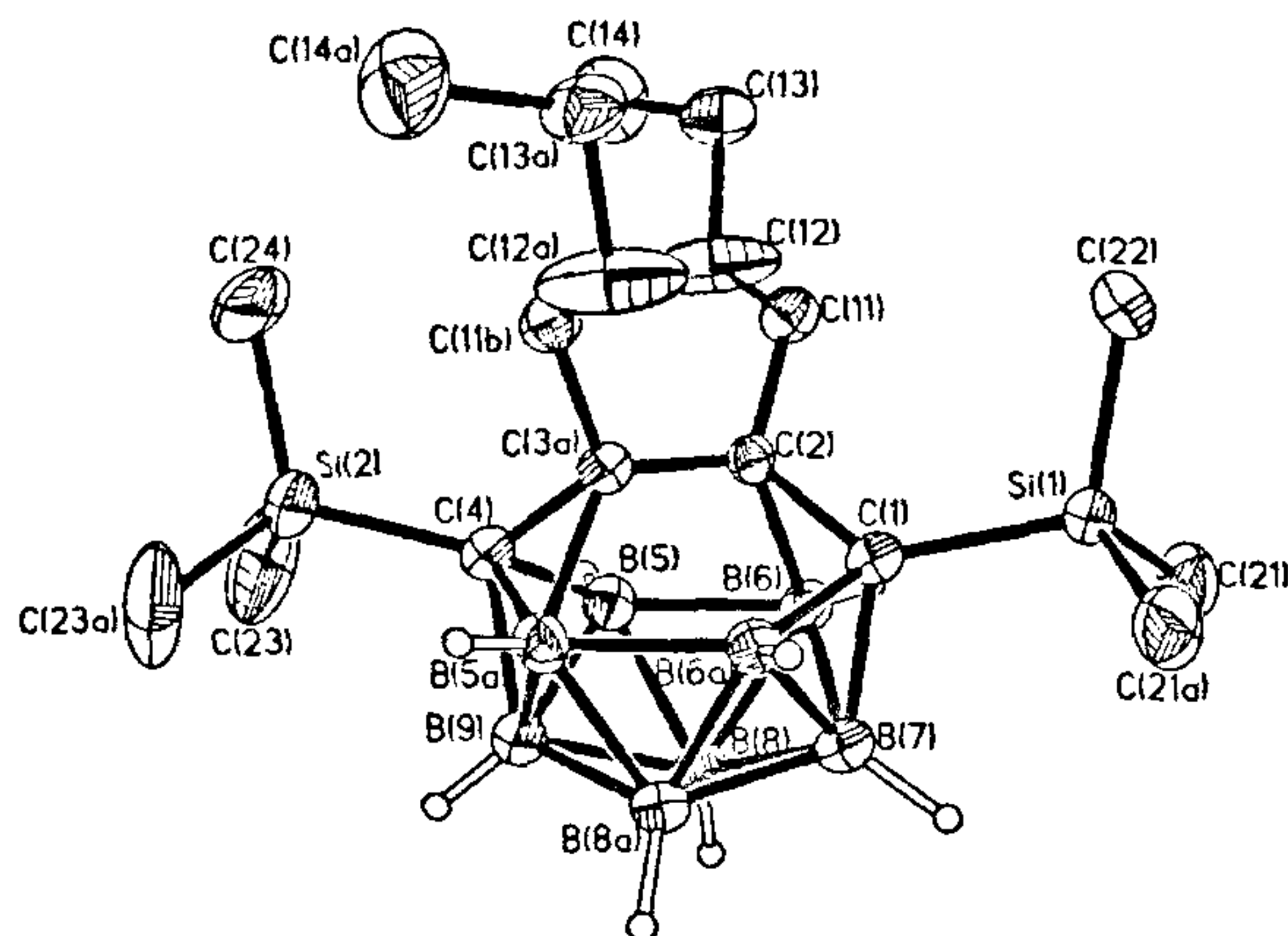
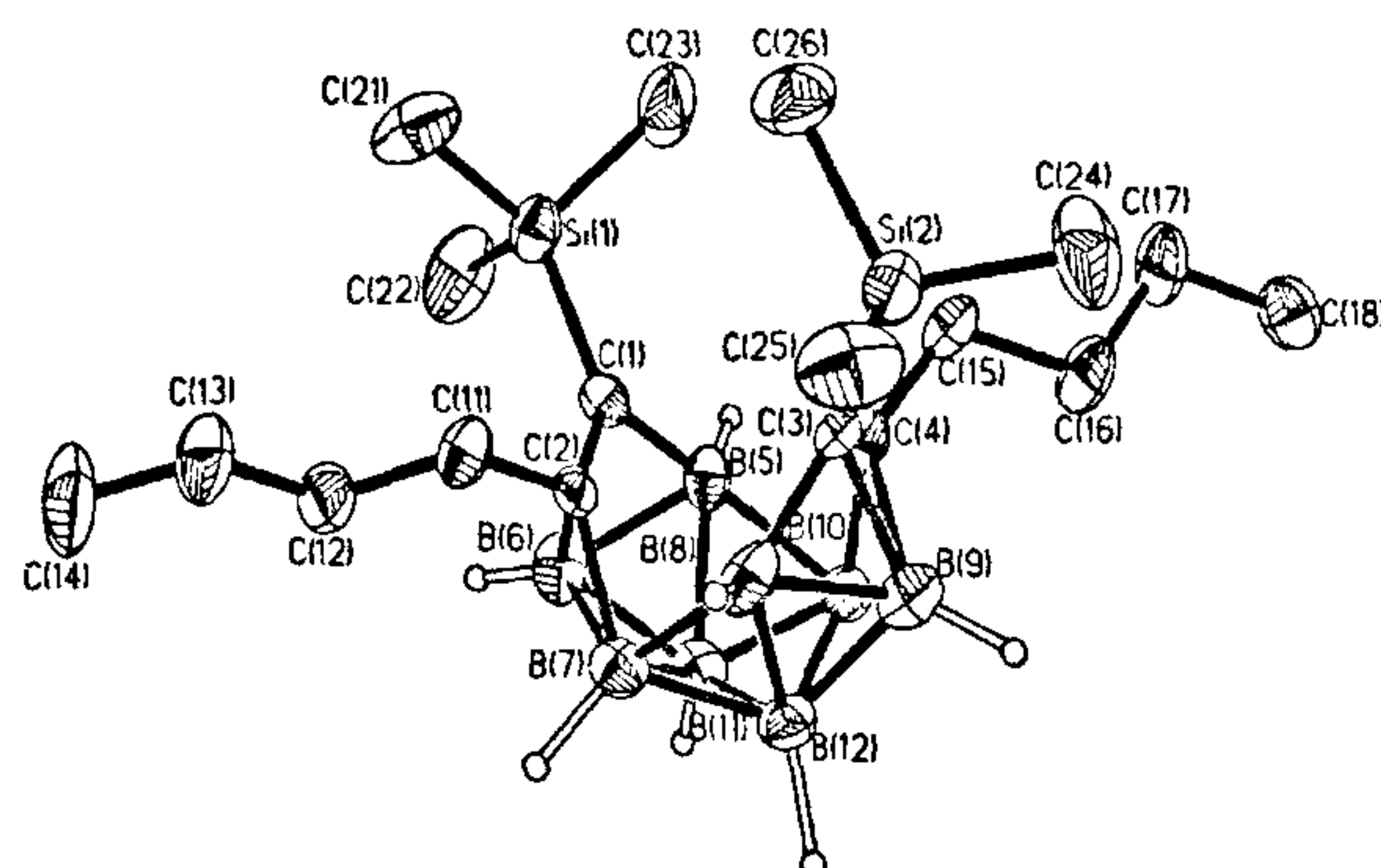
bonded contiguously in a Z-shaped pattern¹⁰, while in the other, the middle C-C bond was ruptured leading to a more open structure¹¹. However, the proximate locations of the cage carbons were maintained in all isomers. These 'carbons adjacent' compounds were obtained as the products from the mild air oxidation of the metal-hydride complexes ($R_2C_2B_4H_4$)₂MH_x (M = Fe ($x = 2$), Co ($x = 1$); R = CH₃, C₂H₅, *n*-C₃H₇ and CH₂C₆H₅) (refs 8, 9, 12). On the other hand, when the dianions, [*nido*-2-($SiMe_3$)-3-(R)-2,3- $C_2B_4H_4$]²⁻ (R = $SiMe_3$, *n*-Bu or *t*-Bu) were oxidized by $NiCl_2$ a completely different set of tetracarbon carboranes were produced^{6,7}.

In these trimethylsilyl-substituted compounds, the cage carbons were more evenly dispersed throughout the cage, being separated by at least one boron to give, the so-called 'carbon apart' compounds. One of these, the *nido*-2,4,7,9-($SiMe_3$)₄-2,4,7,9- $C_4B_8H_8$, is of particular interest in that it is a 12-vertex cage whose structure is based more on a cuboctahedron than an icosahedron (Figure 2) (refs 6, 7). This geometry is of interest in that

Scheme 1. Syntheses of *closo*- C_2B_4 - and *nido*- C_4B_8 -carboranes.

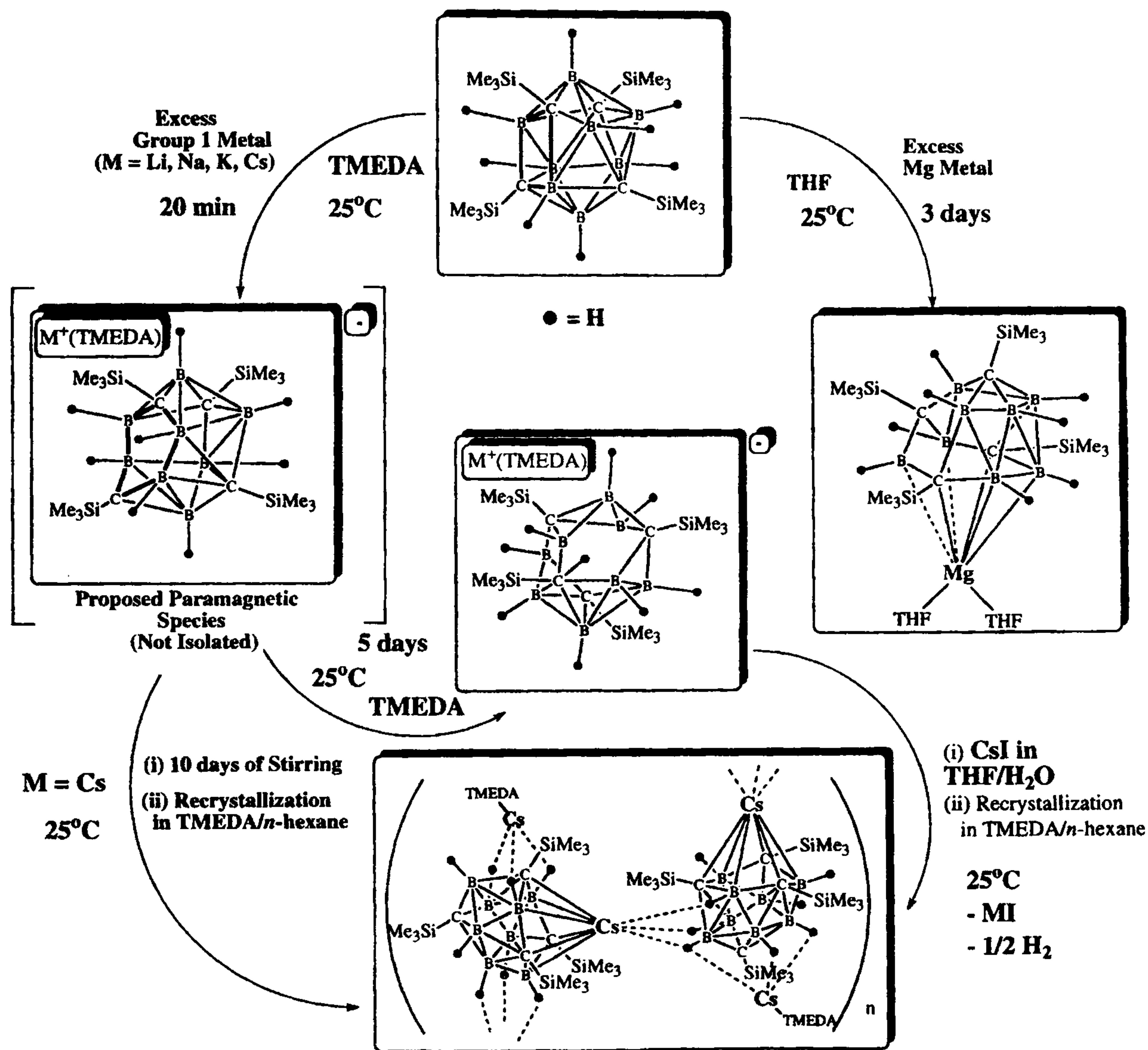
Figure 2. *nido*-2,4,7,9-(SiMe₃)₄C₄B₈H₈.Figure 3. *nido*-2,4,6,12-(SiMe₃)₄C₄B₈H₈.

a cuboctahedral structure was proposed by Lipscomb for the key intermediate in the diamond-square-diamond (DSD) mechanism for the rearrangement of *closo*-1,2-C₂B₁₀H₁₂ to *closo*-1,7-C₂B₁₀H₁₂ (ref. 13). The other isomer, exemplified by *nido*-2,4,6,12-(SiMe₃)₄-2,4,6,12-C₄B₈H₈, had a more traditional *nido*-cage structure with an open C₃B₃ face surmounting a B₅ ring and an apical cage carbon (Figure 3) (ref. 7). Most of the C₄B₈ carboranes exhibit nonrigid stereochemistry, showing multiple isomerization or fluxional behaviour in solution^{7,8,11}. When two of the SiMe₃ moieties were substituted by less bulkier *n*-butyl groups, both 'carbons adjacent' and 'carbons apart' isomers of C₄B₈-carborane were isolated. Moreover, the geometries of these 'carbons adjacent' isomers are identical to those observed by Grimes (Figures 4 and 5) (ref. 7).

Figure 4. 1,4-(SiMe₃)₂-2,3-(*n*-Bu)₂C₄B₈H₈.Figure 5. 2,8-(SiMe₃)₂-3,9-(*n*-Bu)₂C₄B₈H₈.

Reactivities of 'carbons apart' C₄B₈-carboranes

Both 'carbons adjacent' and 'carbons apart' C₄B₈-carboranes can be reduced to give dianionic cages, which on metallation produced, at least formally, 13-vertex metallacarboranes. Grimes and co-workers have reported the syntheses of a large number of d-block metallacarboranes in the 'carbons adjacent' system^{1(a),14,15}. Multiple structures were found for a particular carborane and metal group. These were thought to arise from the metal coordination of the numerous isomers of the C₄B₈ dianions that were present in reaction solutions. While the reports on the metallacarboranes derived from the 'carbons adjacent' carboranes are fairly extensive, the only metallacarboranes in the 'carbons apart' system that have been published are those contained in our preliminary reports on [(THF)₄Li][(SiMe₃)₄C₄B₈H₉], [*exo*-Cs(TMEDA)-1-Cs-2,4,7,9-(SiMe₃)₄-2,4,7,9-C₄B₈H₈] and (THF)₂Mg(SiMe₃)₄C₄B₈H₈ whose synthetic pathways are shown in Scheme 2 (refs 16, 17). According to this scheme the room temperature reaction between a TMEDA solution of 2,4,7,9-tetracarba-*nido*-dodecaborane (12),



Scheme 2. Syntheses of tetracarbon-carborane compounds of group 1 and group 2 metals.

(SiMe₃)₄C₄B₈H₈, and excess cesium metal, in the absence of naphthalene and aromatic solvents, produced the novel EPR-silent species, [*exo*-[(μ-H)₂Cs(TMEDA)]-1-Cs-2,4,7,9-(SiMe₃)₄-2,4,7,9-C₄B₈H₈]_n, the first example of a cesium compound in which the metal interacts with the carborane cage sequentially to form repeating metal-carborane units¹⁷. The X-ray diffraction study on the cesium complex confirmed its polymeric structure in which each C₄B₈-carborane fragment serves as a ligand to two Cs atoms, bonded to one through an open six-membered face and to the other via upper- and lower-belt M-H-E (where E = B or C) interactions (Figure 6) (ref. 17). This structural feature is somewhat similar to that of the Sr complex of the [C₂B₁₀H₁₂]²⁻ ligand, reported by Hawthorne and coworkers¹⁸. However, the interatomic distances of Cs to the carborane cages are such that it could be regarded as a cesium-carborane complex in which some degree of interaction

exists between the metal and the π-electron density on the carborane cage. Since this cesium compound can also be prepared by an ion-exchange reaction directly from lithium, sodium or potassium salts of the C₄B₈-cage (see Figure 6b), further study of this and related compounds in solvent extraction of radioactive cesium metal (¹³⁷Cs) from nuclear waste is envisioned.

Under similar reaction conditions, the 'carbons apart' tetracarbon carborane, *nido*-2,6-(R)₂-4,12-(SiMe₃)₂-2,4,6,12-C₄B₈H₈ (R = SiMe₃, *n*-butyl), and several of its B-alkylated derivatives, react with Mg metal in THF to produce magnesacarboranes in yields ranging from 57% to 74% (Scheme 2) (refs 16, 19). Two types of cages were found, one in (THF)₂Mg(SiMe₃)₄(B-Me)C₄B₇H₇ and the other in (L)₂Mg(SiMe₃)₂(R)₂(B-Y)C₄B₇H₇ (L = THF, R = SiMe₃, Y = *t*-Bu; L = THF, R = SiMe₃, Y = H; (L)₂ = TMEDA, R = *n*-Bu, Y = H). Both cages showed the presence of electron precise carbon and bo-

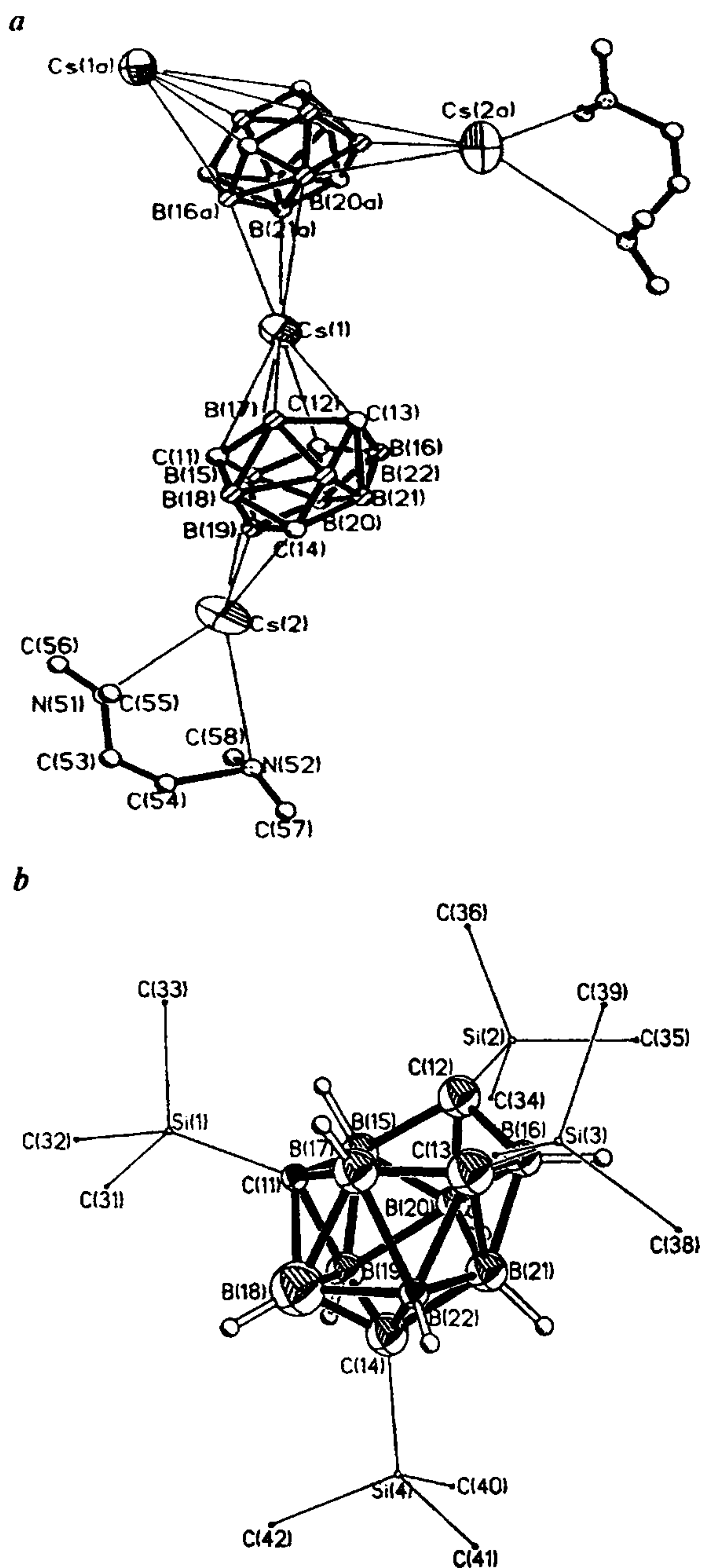


Figure 6. Crystal structure of the dicesiacarborane complex; *a*, a cesiacarborane unit in a polymeric chain; *b*, C_4B_8 carborane cage without the cesium metals.

ron atoms, as well as electron deficient fragments (see Figure 7). On the other hand, the reactions of *nido*-2,4,6,12- $(SiMe_3)_4$ -2,4,6,12- $C_4B_8H_8$ with the group 1 metals followed a different course in which two distinct steps occurred (Scheme 2). The first step formed the

paramagnetic, $[(SiMe_3)_4C_4B_8H_8]^-$ intermediate, which, in a slower step, reacted with a second equivalent of the metal to give the diamagnetic $[(SiMe_3)_4C_4B_8H_8]^{2-}$. For the lighter metals, this dianion picked up a proton to give the products, $[(THF)_4M][(SiMe_3)_4C_4B_8H_9]$ ($M = Li, Na$ or K), in 35–54% yield¹⁹. In the case of Cs, no protonation occurred and the final product was a polymeric dicesiacarborane, $[exo-Cs(TMEDA)-1-Cs(SiMe_3)_4C_4B_8H_8]_n$, isolated in 41% yield. In group 1 metallacarboranes, the lighter metal was solvated by four THF molecules and was not involved in the cage, while in cesium compound one Cs occupied an apical position above a C_3B_3 open face of one carborane and bonded to a B_3 face of a neighbouring carborane. The second Cs, solvated by a TMEDA molecule, occupies an *exo*-polyhedral position and was not part of the polymeric chain (see Figure 6).

Reactivity of 'carbons adjacent' C_4B_8 -carborane

A 'carbons adjacent' magnesacarborane, *exo*- $(\mu-H)_3Mg(THF)_3(SiMe_3)_2(Me)_2C_4B_8H_8$ was synthesized, in 81% yield, by the reaction of the metal with the $(SiMe_3)_2(Me)_2C_4B_8H_8$ precursor. Single crystal X-ray diffraction studies showed the compound to be composed of an *exo*-polyhedral $[Mg(THF)_3]^{2+}$ cation that is loosely bound to a $[(SiMe_3)_2(Me)_2C_4B_8H_8]^{2-}$ cage. This carborane polyhedron is best described as ten-vertex *arachno*- $(SiMe_3)_2C_2B_8H_8$ cage that subtends an electron precise MeC=CMe fragment (Figure 8) (ref 19).

Conversion of carborane cage into electron-precise heterocyclic ring

The dominant structural patterns found in alkyl and aromatic hydrocarbons are reflections of the structures of elemental carbon (diamond or graphite) where added hydrogen atom across the C–C bonds gives 'electron precise-carbon hydrides'. In a similar way the structures of boron hydrides are reflections of the icosahedral units found in elemental boron. The replacement of a $(BH)^-$ unit by a CH or CR unit gives the corresponding 'electron-deficient' carborane derivatives²⁰. Although the magnesacarboranes in Figure 7 consisted of both electron-precise atoms and an electron-deficient carborane unit in a single cage framework, there have been no reports on the conversion of an electron-deficient carborane cage essentially into an electron-precise heterocyclic ring. As part of our exploration of new methodologies in this area, a neat sample of *nido*-2,3- $(SiMe_3)_2$ -2,3- $C_2B_4H_6$ was reacted with a large excess of wet *N,N,N,N*-tetramethylethylenediamine (TMEDA) *in vacuo* with constant stirring at room temperature for 7 days that transformed the 'electron-deficient' carborane cage into a seven-membered 'electron-precise' heterocyclic ring, 1-trimethylsilyl-3,6-dimethyl-3,6-diaza-

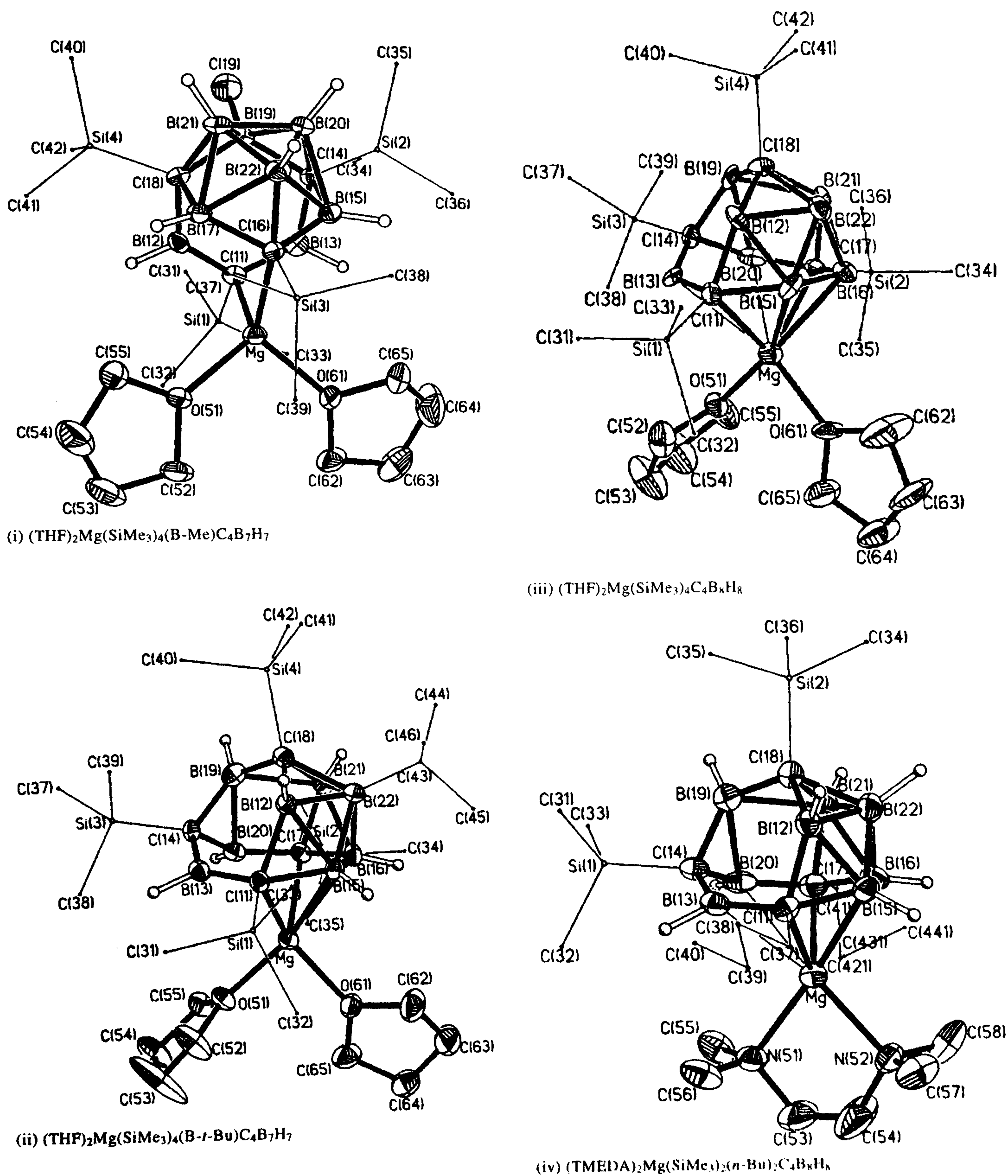
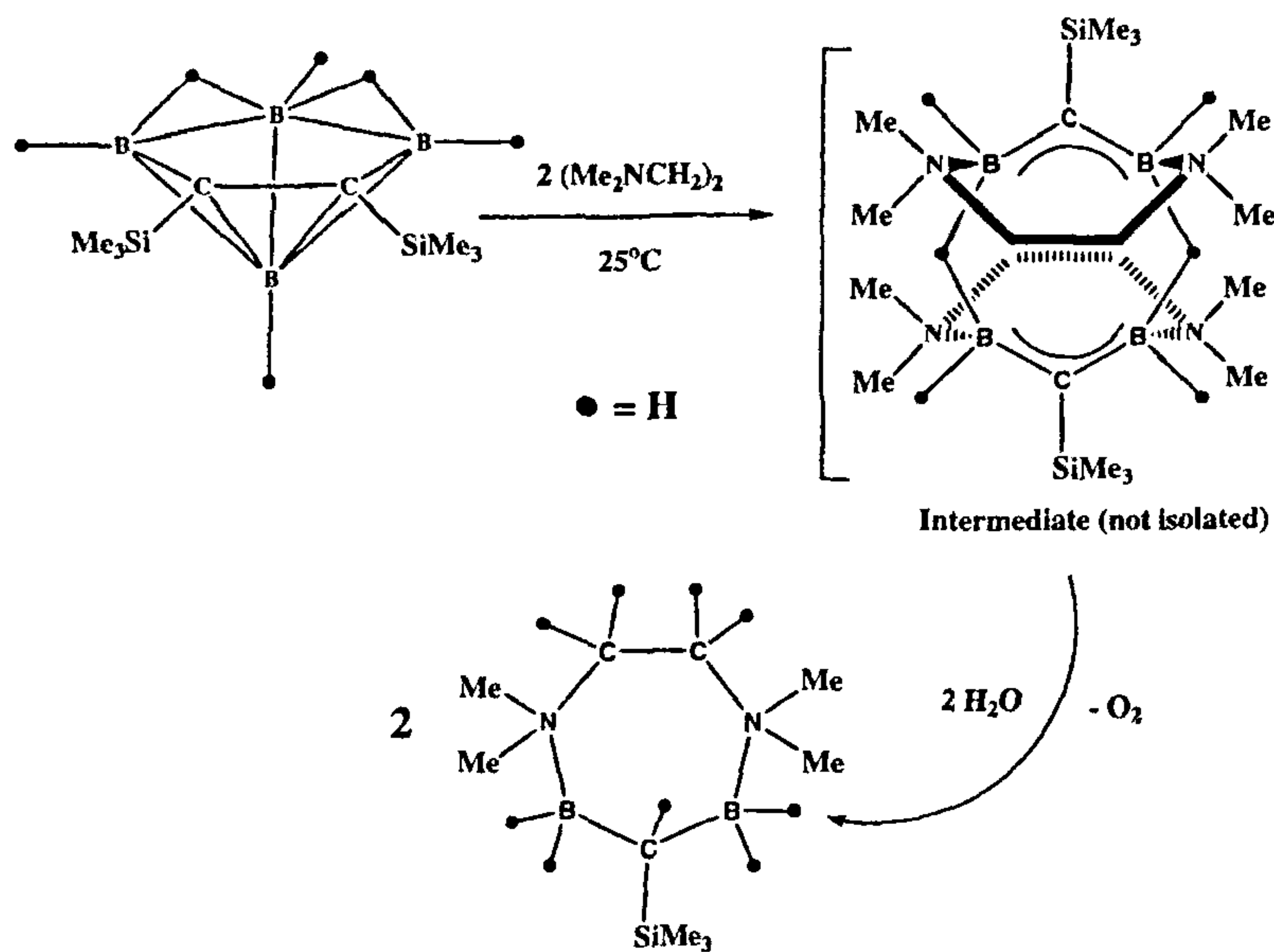


Figure 7. Crystal structures of magnesacarboranes, (i)-(iv), of the C_4B_x -cage systems.



Scheme 3. Conversion of electron-deficient cage to electron-precise ring.

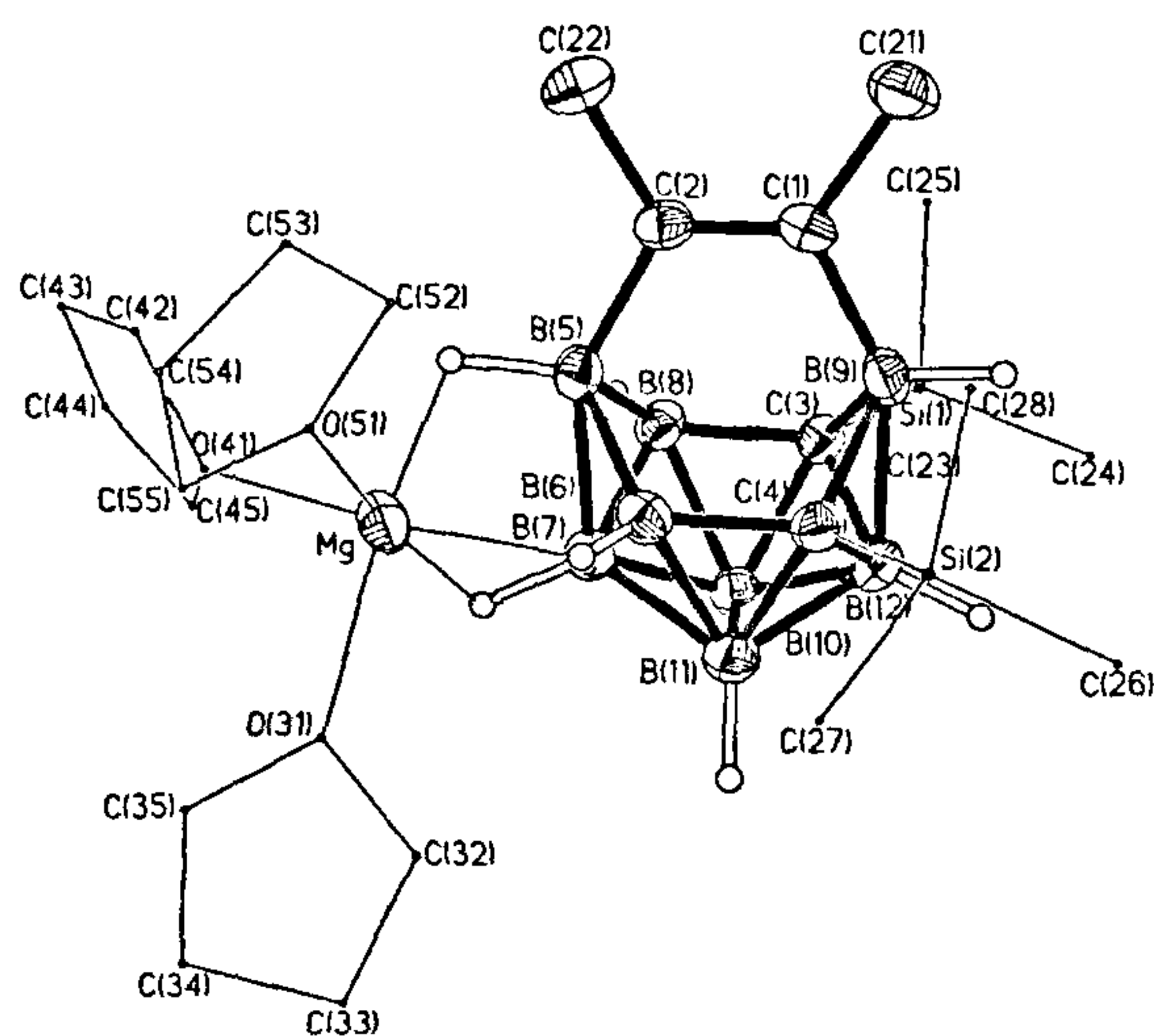


Figure 8. Crystal structure of *exo*-(μ -H)₃Mg(THF)₃(SiMe₃)₂(Me)₂C₄B₈H₈.

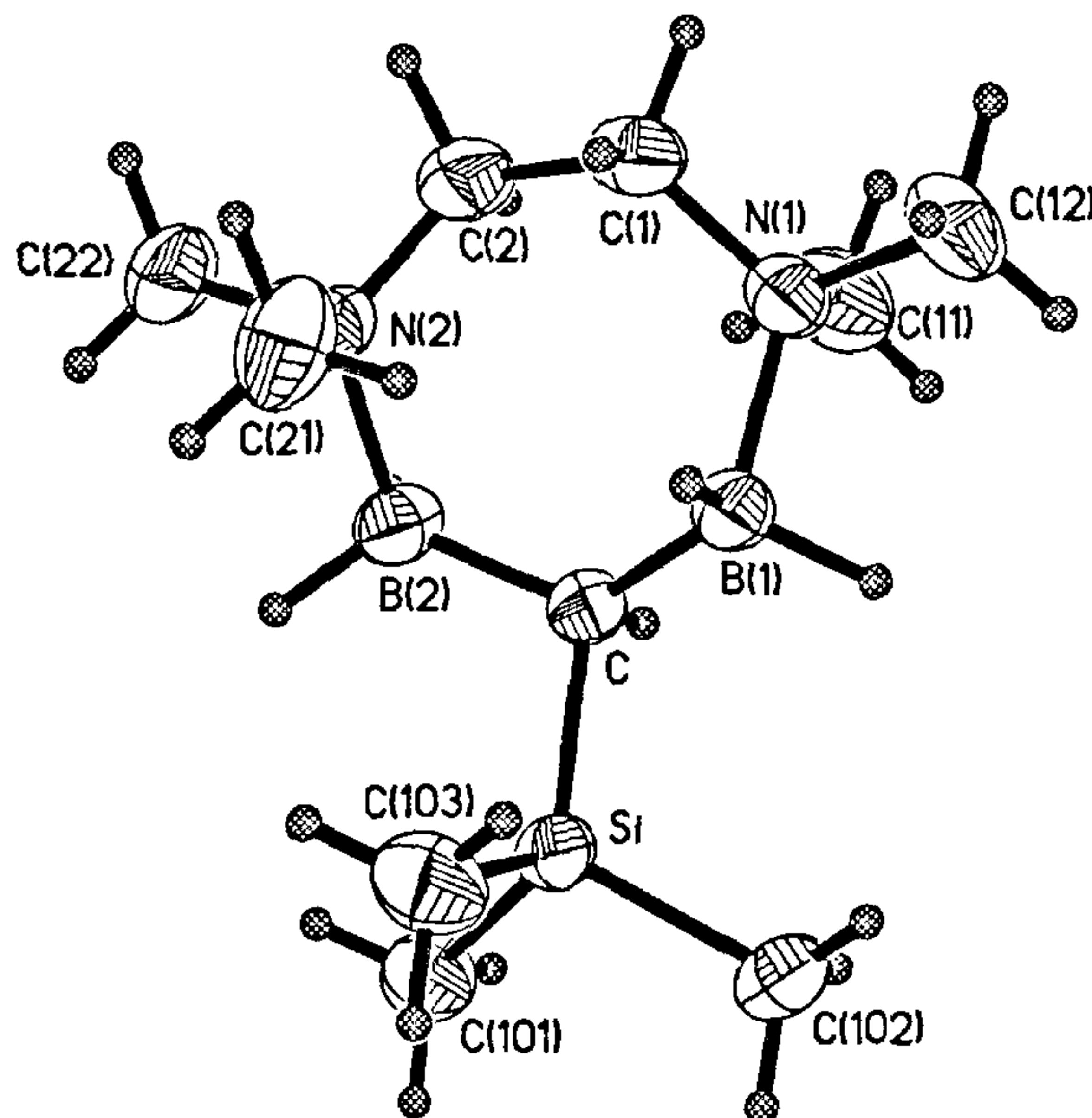


Figure 9. Electron-precise heterocyclic ring.

1,4,5-tricarbaheptaborane (Scheme 3) whose solid state geometry was confirmed by X-ray crystallography (see Figure 9) (ref. 21).

Reactivity of C₂B₄-carboranes with group 13 elements

There have been a number of reports on the syntheses, structures and reactivities of half-sandwich alkylgal-lacarboranes of both the 'carbons adjacent' and 'carbons

apart' C₂B₄-carborane systems^{2(a)}. These reports collectively demonstrated that the reactive part of the molecule is the apical gallium metal that acts as a Lewis acid site by making donor-acceptor complexes with 2,2'-bipyridine, 2,2'-bipyrimidine, and 2,2':6',2''-terpyridine. In each complex, the apical gallium is slip-distorted away from the cage carbons and, in the case of the 1,2,4-Ga(CR)₂B₄H₄, the metal is away from the unique boron above the C₂B₃ bonding face. Nonetheless,

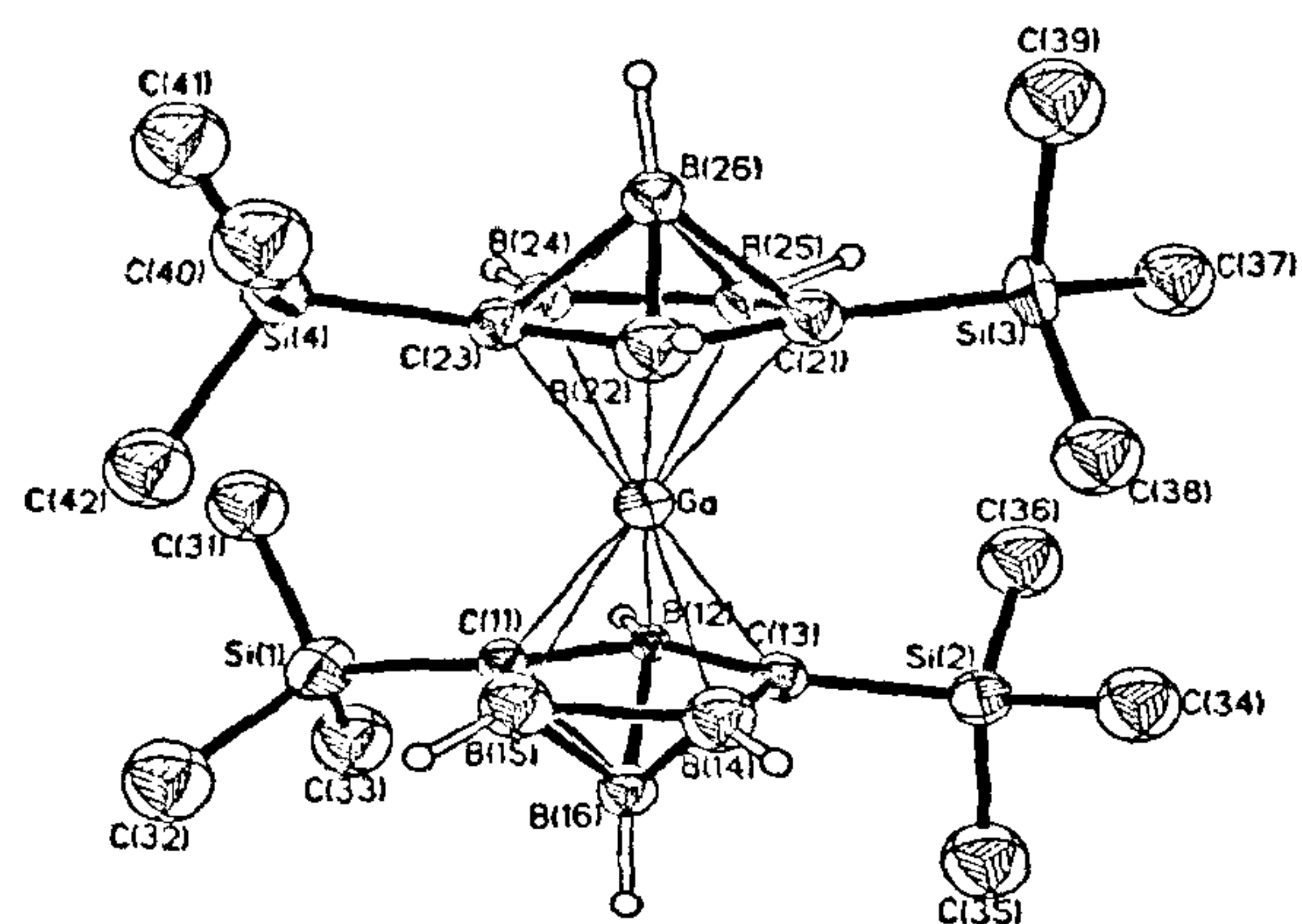


Figure 11. Crystal structure of the 'c-apart' anionic *commo*-gallacarborane.

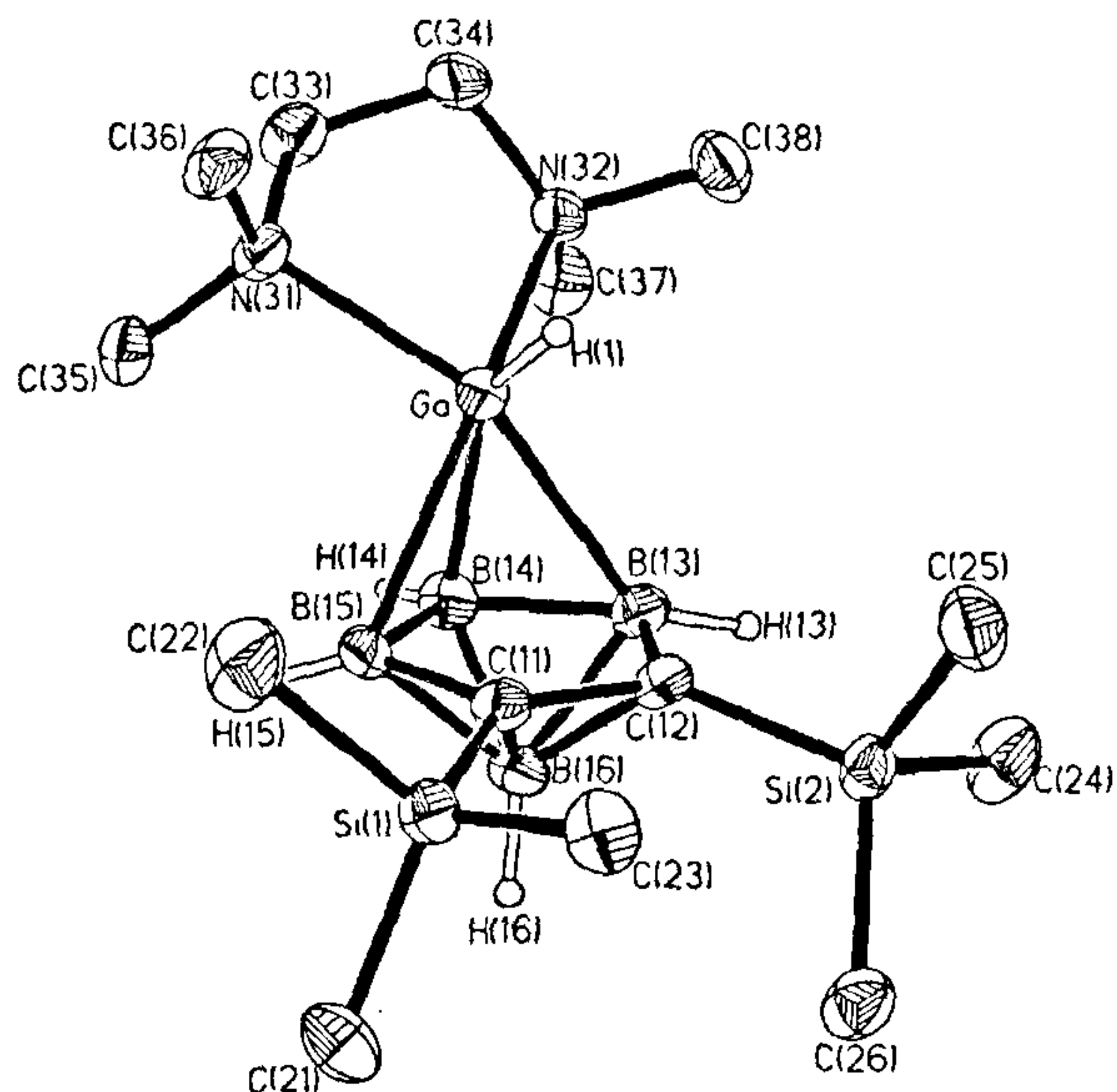


Figure 13. Crystal structure of the 'c-adjacent' *closo*-gallacarborane hydride.

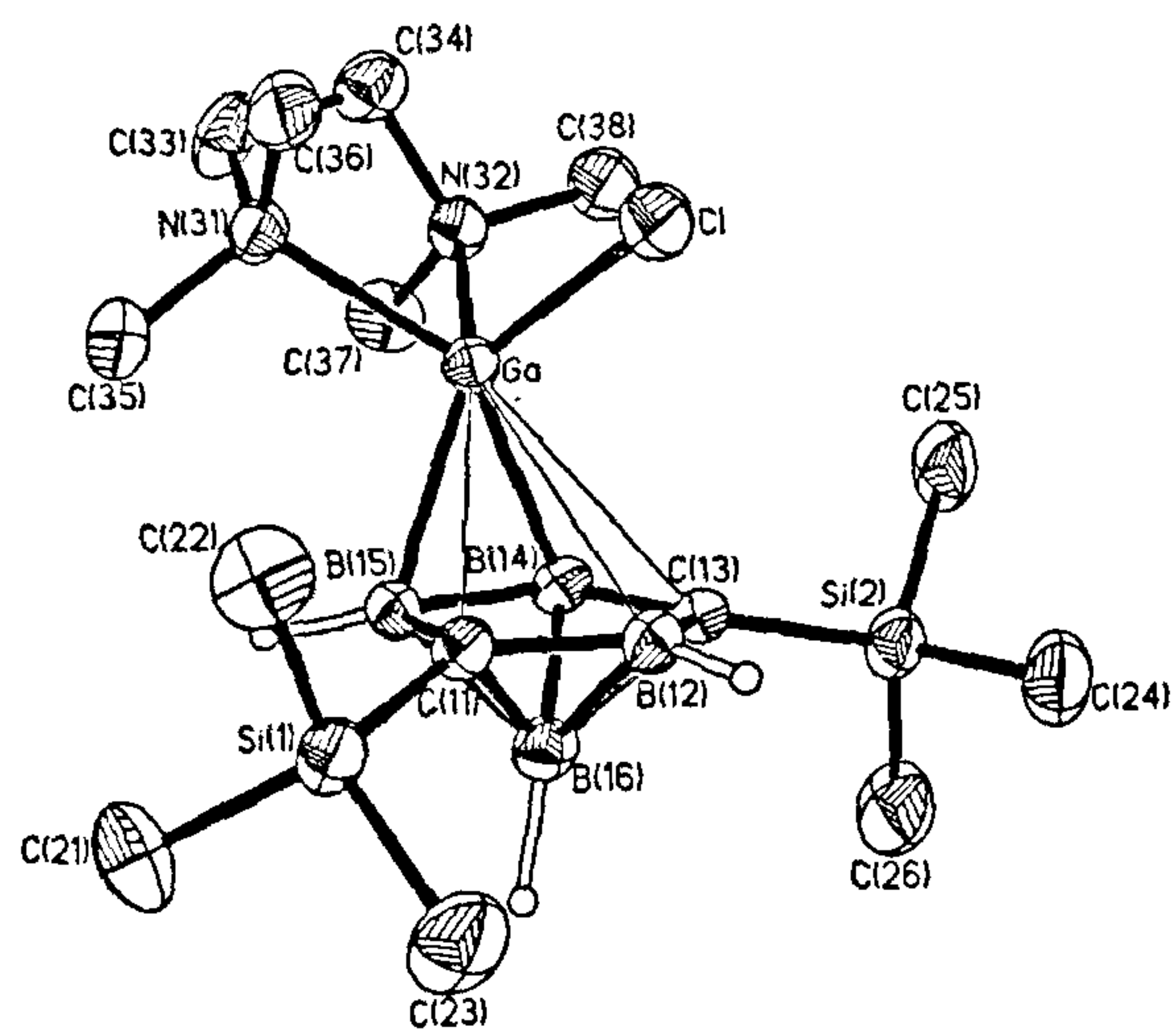


Figure 12. Crystal structure of the 'c-apart' *closo*-chlorogallacarborane.

A surprising formation of Ga(II)-Ga(II)-linked digallacarborane was observed in the reaction of $[\text{Ga}(t\text{-Bu})\text{Cl}_2]_2$ with the disodium compound of the 'C-apart' carborane dianion, in 1:2 stoichiometry²⁵. The two major products were half-sandwich gallacarborane and a novel digallacarborane, which could be separated by fractional distillation and sublimation. The crystal structure of the digallacarborane (Figure 14) exhibits the shortest Ga-Ga bond distances known to date. All evidence shows that there is no multiple metal-metal bonding. While the mechanism for the formation of this species is not known, the dependence on the nature of the group 1 metal in the precursor indicates that this compound is probably not the result of a simple elimination of *t*-Bu groups during the isolation of the half-sandwich gallacarborane via vacuum distillation²⁵.

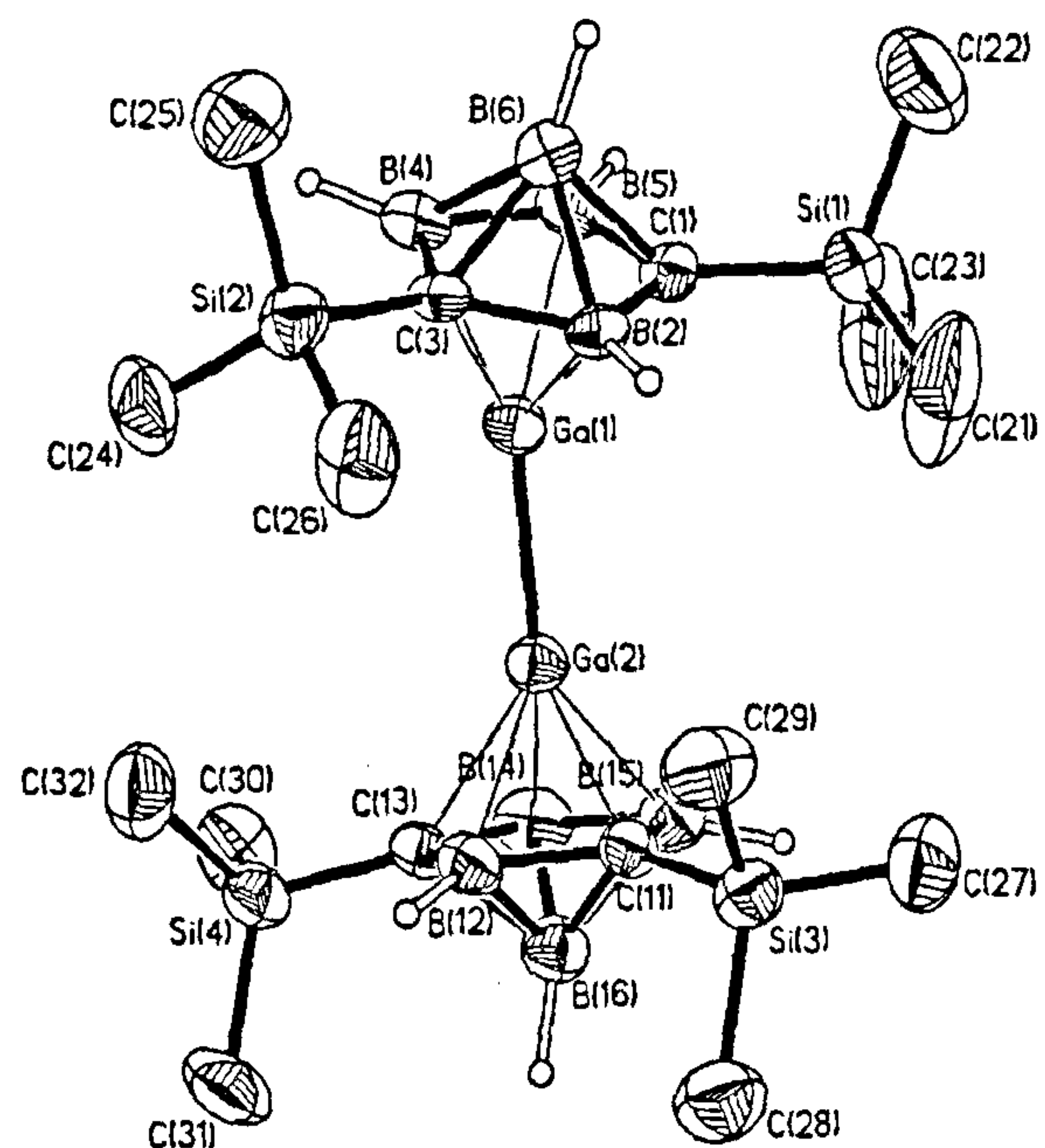
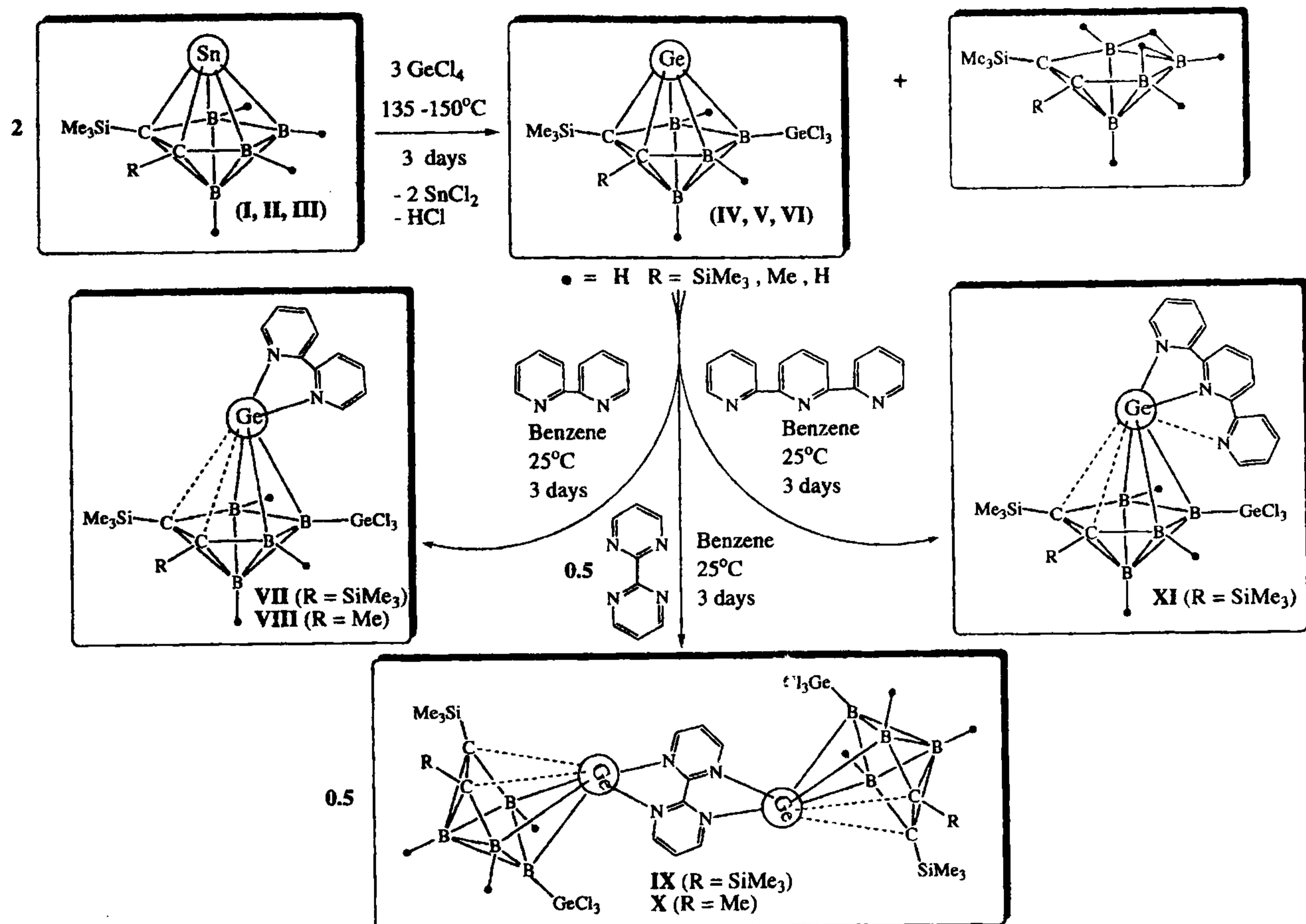


Figure 14. Crystal structure of the neutral Ga(II)-Ga(II)-linked digallacarborane.

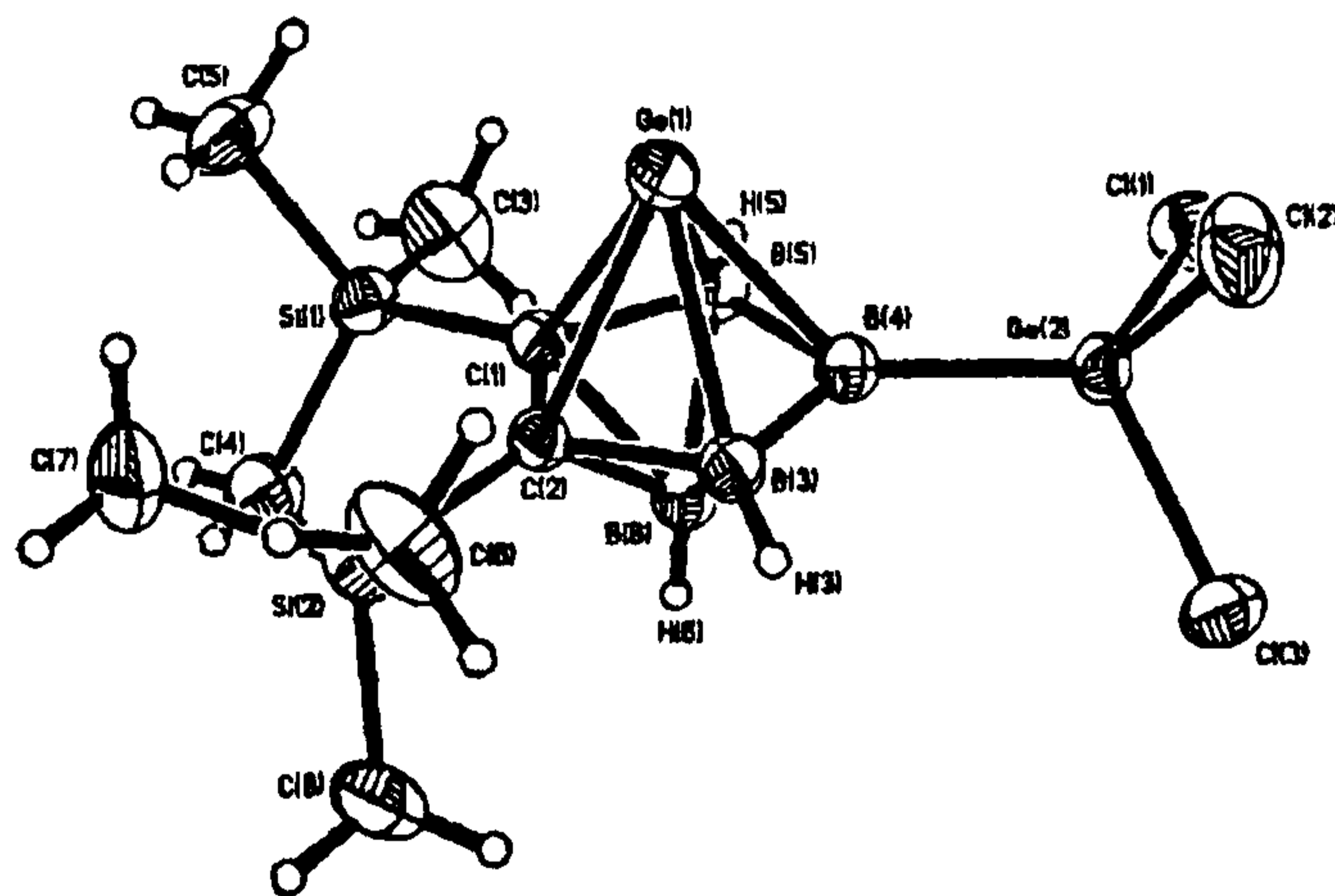
Reactivity of C_2B_4 -carboranes with group 14 elements

Research in the area of group 14 metallacarboranes has been quite active in recent years^{1(b,c),2(a)}. All elements in



Scheme 5. Syntheses of mixed valence germacarboranes and their adducts.

that group have been inserted into carborane cages and a wealth of structural information is available on a number of half-sandwich, *closo*-carboranes of germanium, tin and lead as well as the full-sandwich, *commo*-complexes of silicon, germanium and tin^{2(a)}. These studies show that a definite structure-oxidation state relationship exists in these systems; in the *closo*-complexes the capping group 14 elements are in formal +2 oxidation states, while the *commo*-complexes contain the elements in their +4 states. The coordination chemistry of *closo*-M^{II}C₂B₄ metallacarboranes has also been investigated and the structures of the resulting donor-acceptor complexes involving Lewis bases such as 2,2'-bipyridine (C₁₀H₈N₂), 2,2'-bipyrimidine (C₈H₆N₄), (ferrocenylmethyl)-*N,N*-dimethylamine, [(η⁵-C₅H₅)-Fe(η⁵-C₅H₄CH₂(Me)₂N)], and 2,2':6',2''-terpyridine (C₁₅H₁₁N₃) have been reported^{1(c),2(a)}. The structures of these adducts show that, despite having a 'lone pair' of electrons, the group 14 element acts as a Lewis acid and bonds to the base. Coordination by the base leads to a distortion of the MC₂B₄ cage in that the metal atom is dislocated, or slipped toward the boron side of the C₂B₃ face of the carborane ligand; in all cases the base molecules are oriented opposite the cage carbons. These results raised the general question as to what would be the outcome of

Figure 15. Structure of the mixed valence *closo*-germacarborane.

the reactions between Lewis bases and metallacarboranes possessing two potential acid sites, an M^{II} and an M^{IV} metals. In an effort to ascertain which metal atom would be the preferred acid site and to obtain more information regarding the structure, bonding and reactivity pattern of the new class of mixed-valence metallacarboranes, we have synthesized several B-GeCl₃-

substituted *closo*-germacarboranes, [1-Ge-2-(SiMe₃)-3-(R)-5-(GeCl₃)-2,3-C₂B₄H₃] (R = SiMe₃, Me and H), as outlined in Scheme 5. A representative structure, when R = SiMe₃, is shown in Figure 15 (ref. 26). This scheme summarizes the reactions leading to the formation of the mixed valence germacarboranes. No neutral GeCl₃ substituted carborane was found in the reaction products, indicating that the initial step in the reaction sequence is the reductive insertion of germanium to form a *closo*-germacarborane, which then reacts with a second GeCl₄ molecule to give the mixed valence complex and HCl. Such a substitution is not unreasonable from an energy standpoint. For example, *ab initio* molecular orbital calculations at the B3LYP/6-31G* level showed that ΔE for eq. (1) would be -20.83 kJ/mol^{26(b)}.

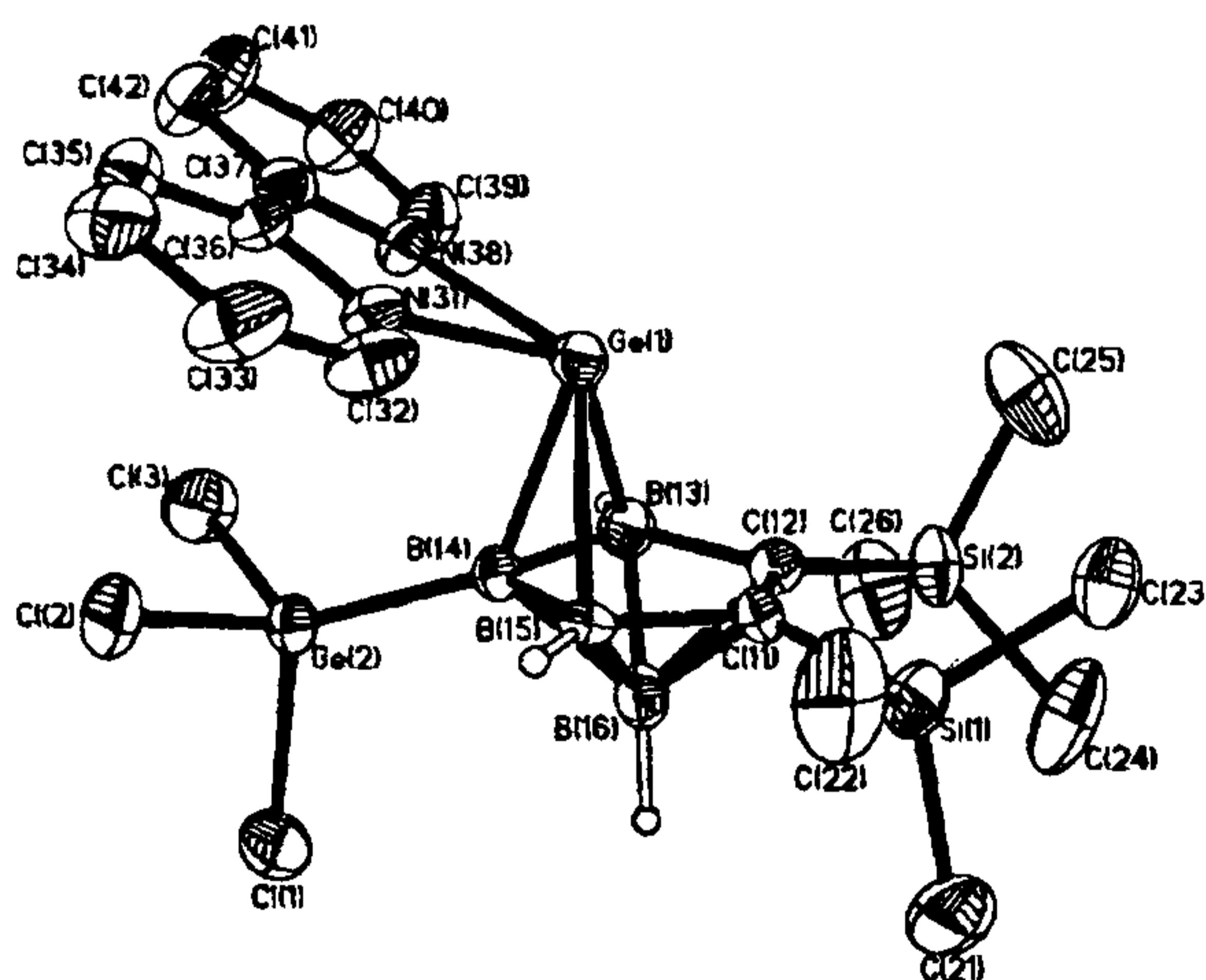
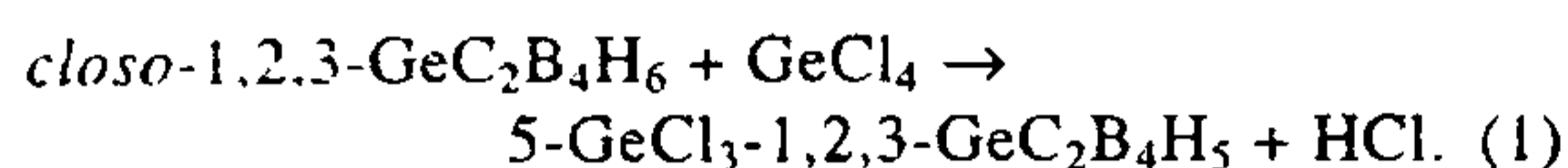


Figure 16. Structure of the 2,2'-bipyridine-adduct of the mixed valence germacarborane.

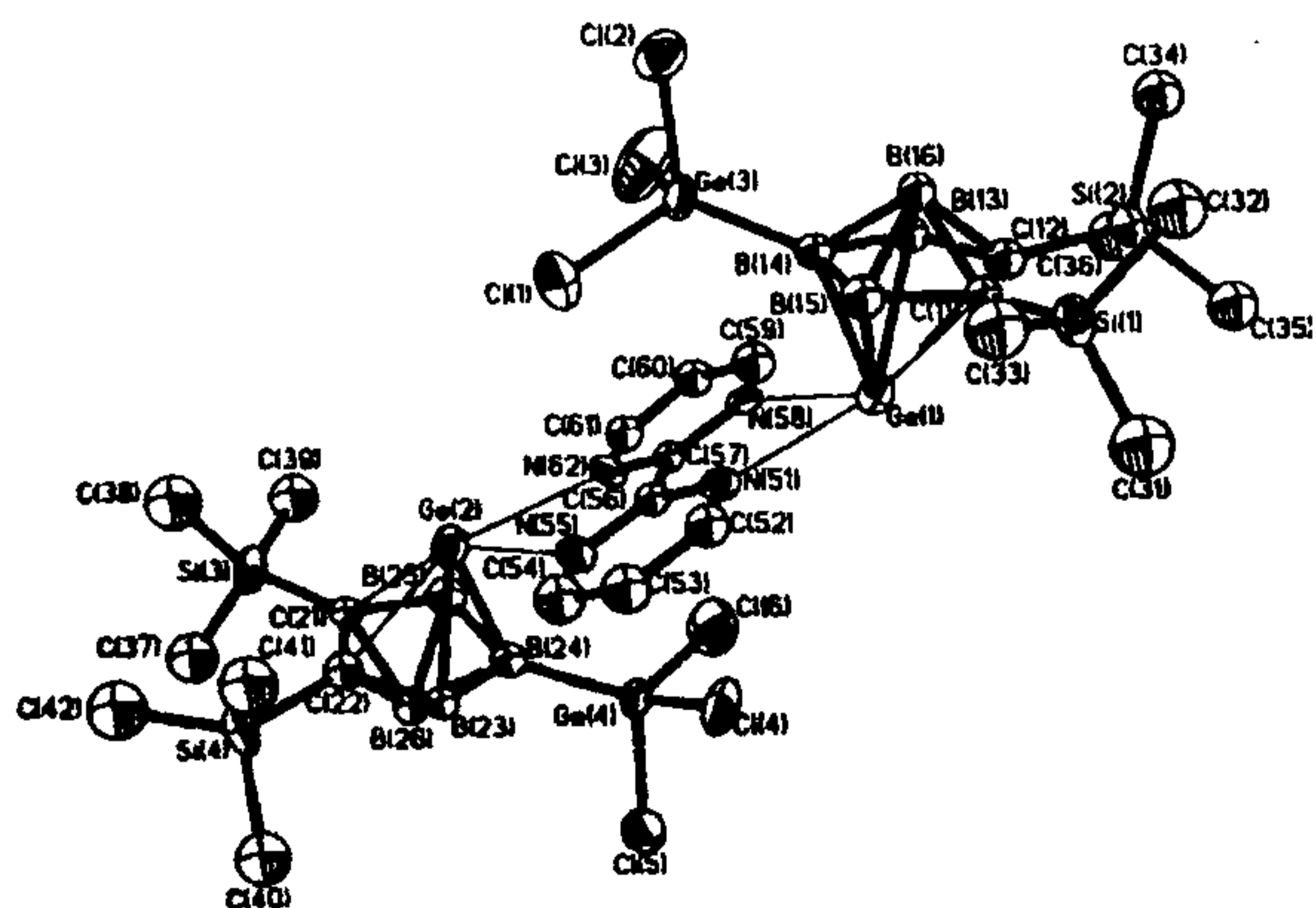


Figure 17. Crystal structure of the 2,2'-bipyrimidine adduct of a mixed valence *closo*-germacarborane complex.

Although this value is only approximate and is for the gas phase, it does indicate that the substitution of a GeCl₃ unit for a terminal H would be an energetically favourable reaction.

There are two Lewis acid sites in *closo*-germacarboranes (see Figure 15), the apical Ge(II) and the exopolyhedral Ge(IV). While one would qualitatively expect the higher oxidation state Ge to be the site for base coordination, just the opposite was found with all Lewis bases studied (2,2'-bipyridine, 2,2'-bipyrimidine and 2,2':6':2''-terpyridine) in which the donor N atoms bond exclusively with the apical Ge(II) (see Figures 16 and 17, for example)^{26(b)}. It is of interest to note that the reaction of the underivatized germacarboranes with the *bis*(bidentate) ligand C₈H₆N₄ resulted in 1:1 donor-acceptor complexes^{1(c),2(a)}, rather than the bridged compound shown in Figure 17 (ref. 26(b)). In this regard, the mixed valence *closo*-germacarboranes are more analogous to the stannacarboranes which react with C₈H₆N₄ to give bridged 2:1 complexes^{1(c),2(a)}. Thus, even though two germanium atoms are present, no evidence has been found to indicate that the Ge(IV) atoms in these compounds act as Lewis acid sites. An inspection of the LUMO and LUMO + 1 molecular orbitals obtained from *ab initio* calculations at the HF/3-21G* level of theory shows localization only on the apical Ge(II) and carborane cage. Therefore, from frontier orbital considerations one would predict that the lower valence apical germanium would be the preferred reaction site for a nucleophile. It seems that the Ge(IV) atoms in the mixed valence *closo*-germacarboranes have their valences well-satisfied through bonding to the three chlorine atoms and the unique borons; even strong nucleophiles displace, rather than disrupt, the GeCl₃ moiety^{26(b)}.

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