Supraicosahedral (metalla)carboranes*

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Abstract: Although supraicosahedral (hetero)boranes have long been of interest to theoreticians, the area is under-developed from a synthetic viewpoint. The synthesis of supraicosahedral carboranes by reduction then capitation (*RedCap*) of C_2B_{10} species is attractive, but unsuccessful as long as the cage carbon atoms are free to separate in the reduction step. Studies on 4,1,6-MC_2B_{10} 13-vertex metallacarboranes have shown that the partial degradation of such species can be a facile process, in spite of the fact that the binding energy of the metal atom to the carborane framework can be at least as high as that of a {BH} fragment. These findings support the general concept of the kinetic instability of 1,6-C_2B_{11} species, explaining why a supraicosahedral carborane could not be made from 1,2-$C_2B_{10}H_{12}$. However, tethering together the two cage C atoms with a $C_6H_4(CH_2)_2$ strap ultimately allowed the synthesis of the first supraicosahedral carborane. This species has a henicosahedral geometry, and there is evidence that a facile rearrangement from kinetic to thermodynamic isomer has occurred. The *RedCap* synthesis of this unprecedented cluster has the potential to be applied successively, yielding 14-, 15-, 16-, etc. vertex carboranes, the larger of which may be sufficiently kinetically stable to exist without a C,C tether.

INTRODUCTION

The chemistry of boranes and heteroboranes is dominated by the 12-vertex icosahedron, and there are many hundreds of examples of such species known [1]. Although subicosahedral chemistry is less developed, it is still extensive [2]. In contrast, the field of supraicosahedral (hetero)borane chemistry is relatively poorly developed—there are only tens of examples of such species, mainly 13-vertex compounds of docosahedral geometry [3], and a handful of 14-vertex species, of bicapped hexagonal antiprismatic shape [4].

However, the area of supraicosahedral (hetero)boranes has long been of interest to computational chemists. In 1992, Lipscomb and Massa computed the geometries of species $B_nH_n^{2-}$ for $n = 13$–24 [5], work that was followed up by Schleyer and coworkers ($n = 13$–17) at a higher level of theory in 1998 [6]. The area was further stimulated by the discovery of fullerenes, since it was recognized that each of these carbon clusters had a BH "dual" (e.g., $B_{32}H_{32}$ is the dual of C_{60}, $B_{37}H_{37}$ is the dual of C_{70}) achieved by simple geometrical mapping [7]. Boustani et al. later showed [8] that the stability per BH vertex of several of these duals was comparable with that of the ubiquitous $B_{12}H_{12}$.

Possible syntheses

Continuing the fullerene analogy, it has been pointed out [7] that an attractive synthetic route to supraicosahedral boranes might be the laser ablation of appropriate metal borides in an atmosphere of H_2. We are not aware that this approach has yet yielded supraicosahedral boron-based clusters. Supraicosahedral carboranes could, in principle, be prepared by a template approach involving elimination of a metal atom linking two appropriate units, e.g., elimination of Co from the well-known species $[Co(C_2B_9H_{11})_2]^-$. Although a similar technique has been used successfully to prepare C_4B_8 carboranes from two C_2B_4 units [9], there are no current reports of supraicosahedral carboranes being synthesized in this way.

An alternative approach to supraicosahedral carboranes, that of polyhedral expansion, is based on the successful synthesis of icosahedral and supraicosahedral metallacarboranes. As is well known (Fig. 1) $C_2B_{10}H_{12}$ can be readily <u>dec</u>apitated to $nido$-$C_2B_9H_{11}{}^{2-}$, which in turn can either be <u>met</u>allated to afford an icosahedral metallacarborane or (re)<u>cap</u>itated by reaction with BRX_2 to regenerate an icosahedral carborane. We conveniently describe these overall reactions as *DecMet* and *DecCap*, respectively. In addition, $C_2B_{10}H_{12}$ can be <u>red</u>uced to the 12-vertex $nido$-$C_2B_{10}H_{12}{}^{2-}$, <u>met</u>allation of which affords supraicosahedral metallacarboranes by an overall *RedMet* sequence [3]. We wondered if B atom capitation of $nido$-$C_2B_{10}H_{12}{}^{2-}$ would yield 13-vertex carboranes by the hitherto unreported *RedCap* approach. In principle, *RedCap* is to *DecCap* as *RedMet* is to *DecMet*. The last three are all proven synthetic routes, so why not the first?
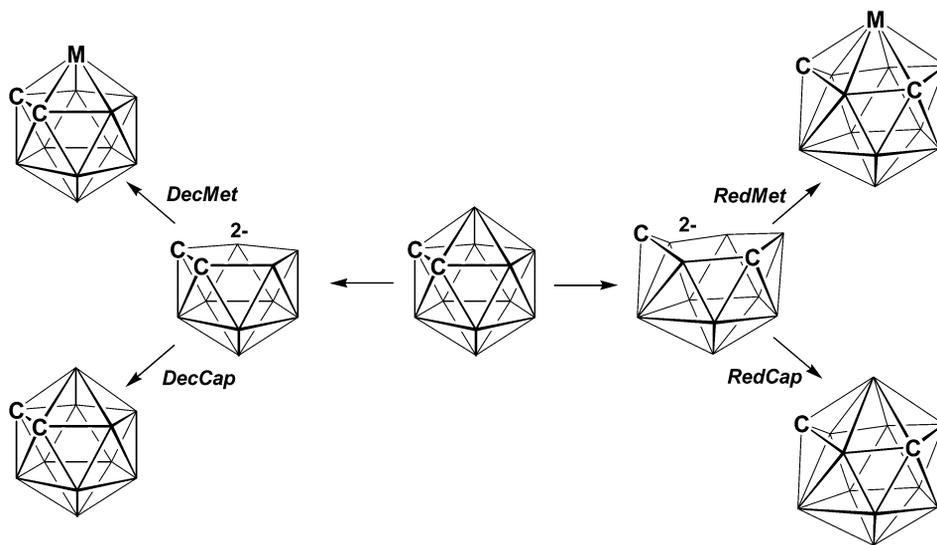
Fig. 1 *DecMet*, *DecCap*, *RedMet*, and *RedCap* strategies starting from 1,2-$C_2B_{10}H_{12}$.

The *RedCap* approach to supraicosahedral carboranes looks attractive, but there was already a warning in the literature that it might not be successful. Schleyer and coworkers have shown (Fig. 2) that the cumulative BH addition energies of the series $B_nH_n{}^{2-}$ (n = 5–17) do not decrease smoothly [6], but rather that the 12-vertex member is particularly stable, and the 13-vertex member particularly unstable.

In fact, the clusters with 13, 14, and 15 vertices are all less stable than $B_{12}H_{12}{}^{2-}$. Although clusters with 16 and 17 vertices are more stable than $B_{12}H_{12}{}^{2-}$ and, indeed, rejoin the overall downward curve, the 12-vertex to 13-vertex step is a clear synthetic bottleneck. The fact that in boron chemistry the icosahedron is something of a thermodynamic sink is already well known. In the context of the current work, we are reminded of this fact by the tendency of the kinetic form of $C_2B_{10}H_{12}{}^{2-}$ (having a
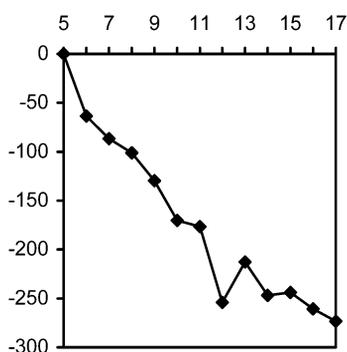
Fig. 2 Energy (kcal mol^{-1}, y axis) vs. n (x axis) for $B_nH_n^{2-}$ (from ref. [6]).

supraicosahedral electronic and geometric structure) to collapse to its thermodynamic form (having an icosahedral electronic and geometric structure), shown in Fig. 3.
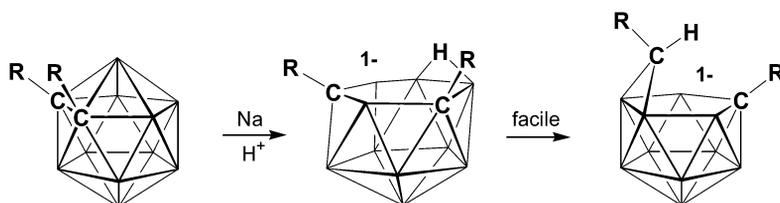
Fig. 3 Transformation of kinetic isomer of $C_2B_{10}^-$ to thermodynamic isomer.

RESULTS

Undaunted, we attempted the *RedCap* synthesis of *closo*-C_2B_{11} carboranes following Fig. 4. We were confident of the basic shape of the *nido*-C_2B_{10} intermediate from the theoretical work of McKee et al. [10] and Hermansson et al. [11], and from the experimental work of Hawthorne et al. [12]. However, in spite of trying a number of variations of R and R′, and performing the reactions in a wide variety of solvents under a range of conditions, we were never able successfully to isolate a supraicosahedral product from *RedCap* chemistry starting with 1,2-$C_2B_{10}H_{12}$.
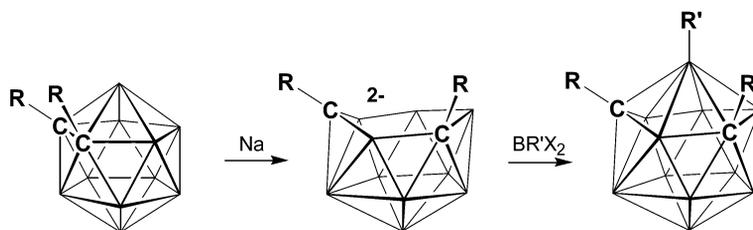
Fig. 4 Proposed (but unsuccessful) *RedCap* synthesis of C_2B_{11} from 1,2-R_2-1,2-$C_2B_{10}H_{10}$.

Supraicosahedral metallacarboranes

As already noted, the synthesis of supraicosahedral metallacarboranes by the *RedMet* approach is well established [3]. Previously, 4,1,6-MC_2B_{10} species have been reported for transition metals [3], group 1 metals [13], group 2 metals [14], lanthanides [15], and actinides [16]. There have been no reports of supraicosahedral metallacarboranes of the *p*-block metals.

In seeking to extend the range of supraicosahedral metallacarboranes available we have prepared several new compounds by *RedMet* of both $1,2-C_2B_{10}H_{12}$ and $1,2-Ph_2-1,2-C_2B_{10}H_{10}$. Our interests have primarily been to understand more about the isomerization processes of supraicosahedral metalla-carboranes, more about fluxional processes in $4,1,6-MC_2B_{10}$ species, and to extend the range of supraicosahedral metallacarboranes known.

Isomerization

All structurally characterized MC_2B_{10} metallacarboranes have the metal atom in the high-connected vertex 4 and one carbon atom in the low-connected vertex 1, consistent with their relative electro-negativities (see Fig. 5 for docosahedral numbering scheme). There are no fewer than seven possible positions for the second carbon atom, but $4,1,5-MC_2B_{10}$ is an unlikely isomer since this would involve a high-connected C. The thermolysis of $4-Cp-4,1,6-CoC_2B_{10}H_{12}$ has been reported [3,17] to afford, successively, 4,1,8- and 4,1,12-isomers based on NMR spectroscopy, but these products have not been crystallographically characterized.
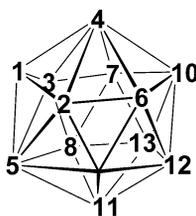
Fig. 5 Docosahedral numbering scheme.

We resynthesized $4-Cp-4,1,8-CoC_2B_{10}H_{12}$ and $4-Cp-4,1,12-CoC_2B_{10}H_{12}$, but found they are im-possibly disordered in the crystalline state. More fortunately, the Cp* analogs were either completely ordered or only partially disordered, and we were thus able to report structures of the homologous se-ries of 4,1,6-, 4,1,8- and 4,1,12-isomers of $Cp*CoC_2B_{10}H_{12}$ [18]. There is no evidence for the 4,1,2-iso-mer (this would involve formerly nonadjacent C atoms becoming adjacent), 4,1,10- or 4,1,11-isomers (these would be immediately apparent in the ^{11}B NMR spectrum due to their C_s symmetry), the absence of the last two implying that the mechanism of isomerization of $4,1,6-MC_2B_{10}$ species follows a spe-cific, restricted, pathway. However, this mechanism is barely explored and substantially more research in this area is clearly warranted.

Fluxionality

$4,1,6-MC_2B_{10}H_{12}$ species are fluxional in solution at room temperature, displaying only one resonance for the cage-CH protons in NMR spectra. For transition-metal species, this fluxionality can usually be arrested at low temperature allowing [19] estimation of the activation energy (E_{act}) for the fluxional process.

We have studied the fluxionality in a number of new $4,1,6-MC_2B_{10}H_{12}$ species and consistently find activation energies between 40 and 50 kJ mol^{-1} (Table 1). We have also studied the fluxionality of the species $4-(C_6H_6)-4,1,6-RuC_2B_{10}H_{12}$ theoretically [20]. We find (i) that the fluxional process oper-ating is the double diamond-square-diamond (d-s-d) one (via a C_s symmetric transition state) originally suggested by Hawthorne [17] (Fig. 6) and (ii) excellent agreement between E_{act} calculated for the ben-zene species and that estimated (^1H NMR) for the analogous *p*-cymene species.

p-*Block metallacarboranes*

As previously noted, there have been no previous reports of supraicosahedral metallacarboranes of the *p*-block metals. Since we had been unsuccessful in our attempted synthesis of $4,1,6-C_2B_{11}$ species start-ing from $1,2-C_2B_{10}$ carboranes, a *p*-block $4,1,6-MC_2B_{10}$ compound became an important target.

Table 1 Activation energies (kJ mol^{-1}) for the double d-s-d process in 4,1,6-MC$_2$B$_{10}$H$_{12}$.

M	E_{act} (calcd.)	E_{act} (exptl.)		Ref.
		^{1}H NMR	^{31}P NMR	
Ru(C$_6$H$_6$)	40.4			20
Ru(*p*-cymene)		43.1		20
Ni(dppe)		43.4	49.8	21
Mo(C$_3$H$_5$)(CO)$_2^-$		40.3		21
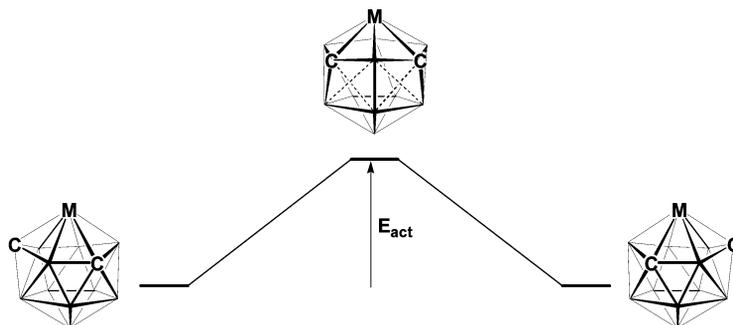
Fig. 6 The double d-s-d process involved in the fluxionality of 4,1,6-MC$_2$B$_{10}$ species.

Reduction of 1,2-C$_2$B$_{10}$H$_{12}$ and its C-dimethyl analogue followed by reaction with SnCl$_2$ was found to afford 4,1,6-SnC$_2$B$_{10}$H$_{12}$ and 1,6-Me$_2$-4,1,6-SnC$_2$B$_{10}$H$_{10}$, respectively, in reasonable yields. Both new compounds were characterized by a range of spectroscopic techniques and by XRD [22]. The structure of the dimethyl compound (Fig. 7) was unambiguous.
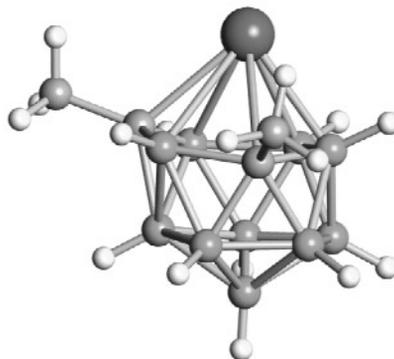
Fig. 7 1,6-Me$_2$-4,1,6-SnC$_2$B$_{10}$H$_{10}$.

Both species, the first supraicosahedral p-block metallacarboranes, are fluxional in solution, but the fluxionality cannot be arrested by cooling to –90 °C, and DFT calculation shows that E_{act} for 4,1,6-SnC$_2$B$_{10}$H$_{12}$ is only 25.4 kJ mol^{-1} [22].

13-Vertex to 12-vertex degradations

Calculations further reveal that in SnC$_2$B$_{10}$H$_{12}$ the binding energy of the Sn atom to the C$_2$B$_{10}$H$_{12}$ fragment is only 6.0 eV, c.f., a binding energy of 8.5 eV for {BH} to the same fragment [23]. This is an important result in that it suggests that our failure to prepare 1,6-C$_2$B$_{11}$ species may be due more to their

kinetic instability than any inherent thermodynamic instability. At about the same time, we recognized that 12-vertex products were occasionally formed in the intended syntheses of supraicosahedral species. Thus, Hawthorne has previously reported [3] a small amount of $3\text{-Cp-}3,1,2\text{-CoC}_2\text{B}_9\text{H}_{11}$ from *RedMet* (CpCo) of $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$, and we found that the analogous thing happens in the Cp* system [18]. We also noted the minor production of $3\text{-I-}1,2\text{-C}_2\text{B}_{10}\text{H}_{11}$ from *RedCap* (BI$_3$) of $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ [24].

These findings suggest degradation of a 13-vertex system to a 12-vertex system by {BH} loss—reaffirmation that the icosahedron is a thermodynamic sink. The degradation could occur either before or following the metallation/capitation step, and we have recently seen evidence for both these possibilities. Thus, ca. 10 % of the reduced carborane $[7,8\text{-}\mu\text{-}\{C_6H_4(CH_2)_2\}\text{-}7,8\text{-C}_2\text{B}_{10}\text{H}_{11}]^-$ degrades to $[7,8\text{-}\mu\text{-}\{C_6H_4(CH_2)_2\}\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$ after 1 week at room temperature in CDCl$_3$ solution [24], while the red 13-vertex molybdacarborane $4\text{-}(C_7H_7)\text{-}1,6\text{-Ph}_2\text{-}4,1,6\text{-MoC}_2\text{B}_{10}\text{H}_{10}$ slowly gives way to the green $2\text{-}(C_7H_7)\text{-}1,8\text{-Ph}_2\text{-}2,1,8\text{-MoC}_2\text{B}_9\text{H}_9$ on chromatographic purification [25]. In the latter case, we reasonably assume that the initial (transient) decomposition product is $3\text{-}(C_7H_7)\text{-}1,2\text{-Ph}_2\text{-}3,1,2\text{-}$ $\text{MoC}_2\text{B}_9\text{H}_9$, which spontaneously transforms to its C-atom isomerized analog to relieve untenable steric crowding [26].

Overall, the isolation of the supraicosahedral stannacarborane and the degradation of 13-vertex products to 12-vertex analogs gave us renewed hope that 13-vertex carboranes were realistic synthetic targets. If $1,6\text{-C}_2\text{B}_{11}$ could not be isolated because of its kinetic instability, our attention naturally turned to other isomers of the C_2B_{11} system.

Isomers of C_2B_{11} carboranes

There are five isomers of $1\text{-C}_2\text{B}_{11}\text{H}_{13}$—it is not unreasonable to restrict ourselves to only those isomers that have a cage C atom at the low-connected vertex 1. In order of decreasing thermodynamic stability [23] these isomers are those with the second cage C atom at position 12, 6, 10, 2, and 4 (see Fig. 5 for numbering scheme). However, of these five isomers there exist realistic synthetic routes to only $1,6\text{-C}_2\text{B}_{11}$, $1,10\text{-C}_2\text{B}_{11}$, and $1,2\text{-C}_2\text{B}_{11}$ carboranes.

The $1,6\text{-C}_2\text{B}_{11}$ carboranes would be afforded by *RedCap* applied to either $1,2\text{-C}_2\text{B}_{10}$ or $1,7\text{-C}_2\text{B}_{10}$ precursors, since these have a common reduced form. But we have tried and failed to isolate $1,6\text{-C}_2\text{B}_{11}$ carboranes in our initial *RedCap* experiments. $1,10\text{-C}_2\text{B}_{11}$ carboranes might be expected by *RedCap* applied to $1,12\text{-C}_2\text{B}_{10}$ species (Fig. 8) although the precise nature of the product of reduction of $1,12\text{-C}_2\text{B}_{10}$ has yet to be described.
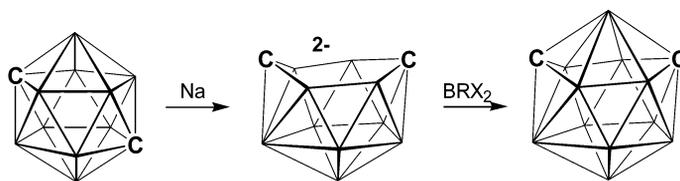
Fig. 8 Presumed *RedCap* synthesis of $1,10\text{-C}_2\text{B}_{11}$ carboranes from $1,12\text{-C}_2\text{B}_{10}$ species.

In contrast, it is established that *tethering* the C atoms of $1,2\text{-C}_2\text{B}_{10}$ leads to $[7,8\text{-C}_2\text{B}_9]^{2-}$ on reduction [27], capitation of which should lead to $1,2\text{-C}_2\text{B}_{11}$ carboranes. Although $1,2\text{-C}_2\text{B}_{11}$ is predicted to be thermodynamically the least favorable of the accessible isomers of $1,2\text{-C}_2\text{B}_{11}$ it could be kinetically trapped (and therefore isolatable) since the mechanism of decomposition of $1,6\text{-C}_2\text{B}_{11}$ carboranes to $1,2\text{-C}_2\text{B}_{10}$ icosahedra involves relative movement of the cage C atoms.

First supraicosahedral carborane

This approach was subsequently borne out, as reduction of 1,2-μ-{$C_6H_4(CH_2)_2$}-1,2-*closo*-$C_2B_{10}H_{10}$ in THF followed by treatment with $BPhCl_2$ yielded the first example of a closed, 13-vertex C_2B_{11} carborane (Fig. 9). The new compound was characterized by ^{1}H, ^{11}B, and ^{13}C NMR spectroscopies, mass spectrometry, and by single-crystal XRD [28]. Note that the structural study reveals that the compound is not docosahedral in shape—the polyhedron formed has 21 rather than 22 faces (one face is a CCBB trapezium) and is therefore a *henicosahedron*. Topologically, the docosahedron and henicosahedron are related by a single diamond-"square" transformation. Moreover, the {BPh} unit is found to be 5-connected.
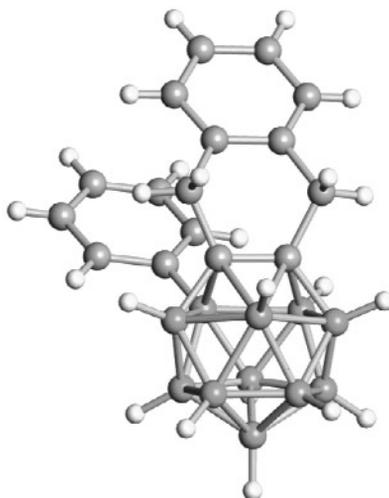
Fig. 9 A supraicosahedral carborane.

By DFT calculation, we find the docosahedron is preferred over the henicosahedron for $B_{13}H_{13}^{2-}$, but by only 3.8 kJ mol^{-1}. For 1,2-$C_2B_{11}H_{13}$, the reverse is the case, by only 7.4 kJ mol^{-1}. The near equienergetic nature of these two polyhedra allows us to rationalize the stereochemistry of the supraicosahedral carborane. We believe that the initial product of the *RedCap* reaction is a henicosahedron in
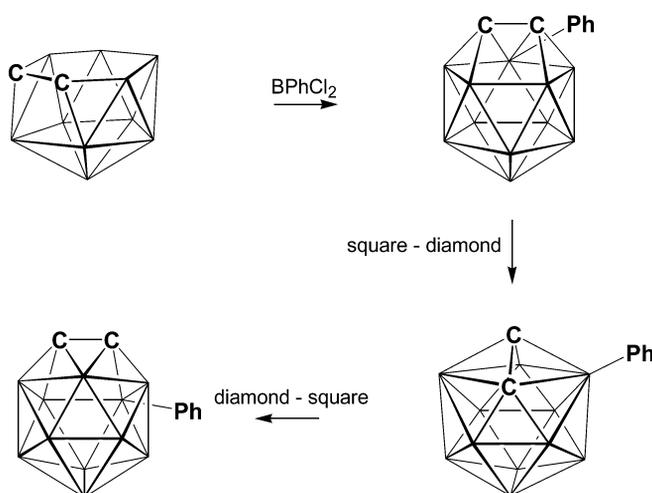
Fig. 10 Suggested sequence for the synthesis and rearrangement of the C_2B_{11} carborane.

which, as would be expected, the capping {BPh} unit is 6-connected. This kinetic isomer then converts, by a square → diamond transformation to a 4-Ph-1,2-C_2B_{11} docosahedron, which subsequently undergoes a (different) diamond → square rearrangement to yield the final, thermodynamic product characterized crystallographically. This proposed sequence is shown in Fig. 10.

SUMMARY AND FUTURE STUDIES

We have utilized the *RedCap* technique to synthesize the first example of a closed, 13-vertex carborane. A feature of the synthetic method is that it can, in principal, be applied successively. Consequently, we are actively pursuing the sequential synthesis of 14-, 15-, 16-, etc. vertex carboranes by this approach. For the moment, we are limited to tethering the cage C atoms since not to do so does not allow the isolation of surpaicosahedral carboranes (we believe for reasons of kinetic instability). However, we would clearly wish future studies not to be restricted by tethering. Calculations suggest that the higher supraicosahedral species (with perhaps 16, 17, or 18 vertices, see Fig. 2) may be sufficiently stable not to require strapping, so we are also investigating systems with removable tethers which would be cleaved off at this point. This would then allow a full investigation of the chemistry of these new supraicosahedral carboranes and their derivatives, including study of C atom isomerization.

ACKNOWLEDGMENTS

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