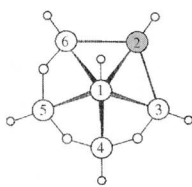
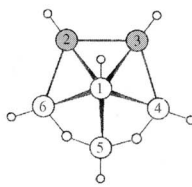


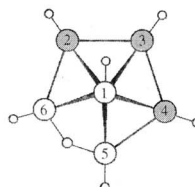
(50) B_6H_{10}
nido-hexaborane(10)



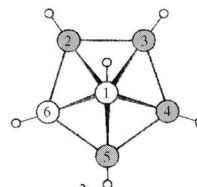
(51) CB_5H_9
2-carba-*nido*-
hexaborane(9)



(52) $C_2B_4H_8$
2,3-dicarba-*nido*-
hexaborane(8)



(53) $C_3B_3H_7$
2,3,4-tricarba-*nido*-
hexaborane(7)



(54) $C_4B_2H_6$
2,3,4,5-tetracarba-*nido*-
hexaborane(6)

6.5 Carboranes^(1,17,68-71)

Carboranes burst onto the chemical scene in 1962–3 when classified work that had been done in the USA during the late 1950s was cleared for publication. The succeeding 30 y has seen a tremendous burgeoning of activity, as a result of which the carboranes and the related metallocarboranes (p. 189) now occupy a strategic position in the chemistry of the elements, since they overlap and give coherence to several other large areas including the chemistry of polyhedral boranes, transition-metal complexes, metal-cluster compounds and organometallic chemistry. The field has become so vast that it is only possible to give a few illustrative examples of the many thousands of known compounds, and to indicate the general structural features and reactivity. The vast majority of carboranes (>95%) have two C atoms in the cluster, reflecting their ready formation from alkynes (see below). A few have one C atom and there are a growing number incorporating three or even four C atoms as cluster vertices.

Carboranes (or more correctly carbaboranes) are compounds having as the basic structural unit a number of C and B atoms arranged on

the vertices of a triangulated polyhedron. Their structures are closely related to those of the isoelectronic boranes (p. 161) [$BH \equiv B^- \equiv C$; $BH_2 \equiv BH^- \equiv B.L \equiv CH$]. For example, *nido*- B_6H_{10} (structures 10, 50) provides the basic cluster structure for the 4 carboranes CB_5H_9 (51), $C_2B_4H_8$ (52), $C_3B_3H_7$ (53) and $C_4B_2H_6$ (54), each successive replacement of a basal B atom by C being compensated by the removal of one H_μ . Carboranes have the general formula $[(CH)_a(BH)_mH_b]^{c-}$ with a CH units and m BH units at the polyhedral vertices, plus b “extra” H atoms which are either bridging (H_μ) or *endo* (i.e. tangential to the surface of the polyhedron as distinct from the axial H_t atoms specified in the CH and BH groups; H_{endo} occur in BH_2 groups which are thus more precisely specified as BH_2H_{endo}). It follows that the number of electrons available for skeletal bonding is $3e$ from each CH unit, $2e$ from each BH unit, $1e$ from each H_μ or H_{endo} , and ce from the anionic charge. Hence:

total number of skeletal bonding electron pairs = $\frac{1}{2}(3a + 2m + b + c) = n + \frac{1}{2}(a + b + c)$, where $n (= a + m)$ is the number of occupied vertices of the polyhedron.

closo-structures have $(n + 1)$ pairs of skeletal bonding electrons (i.e. $a + b + c = 2$).

nido-structures have $(n + 2)$ pairs of skeletal bonding electrons (i.e. $a + b + c = 4$).

arachno-structures have $(n + 3)$ pairs of skeletal bonding electrons (i.e. $a + b + c = 6$).

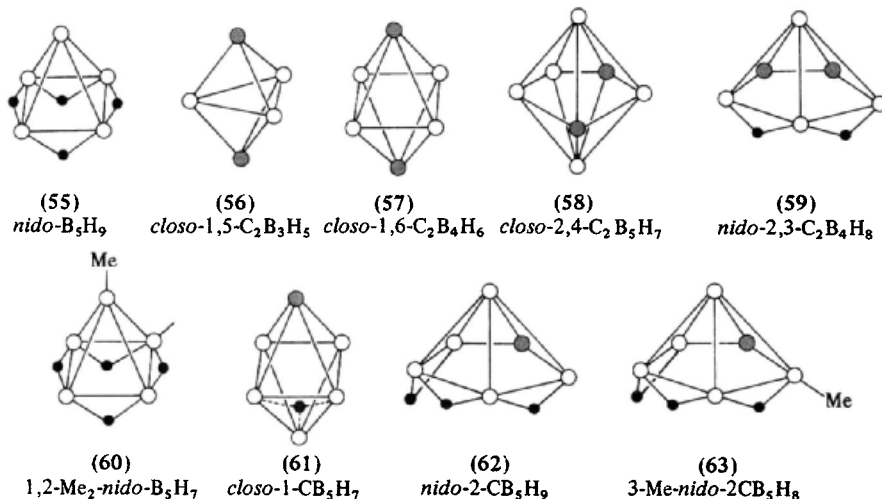
If $a = 0$ the compound is a borane or borane anion rather than a carborane. If $b = 0$ there are no H_μ or H_{endo} ; this is the case for all *closo*-carboranes except for the unique octahedral

⁶⁸ R. N. GRIMES, *Carboranes*, Academic Press, New York, 1970, 272 pp.

⁶⁹ H. BEALL, Chap. 9 in ref. 9, pp. 302–47. T. ONAK, Chap. 10 in ref. 9, pp. 349–82.

⁷⁰ R. E. WILLIAMS, Coordination number–pattern recognition theory of carborane structures, *Adv. Inorg. Chem. Radiochem.* **18**, 67–142 (1976). R. E. WILLIAMS, Chap. 2 in G. A. OLAH, K. WADE and R. E. WILLIAMS (eds.), *Electron Deficient Boron and Carbon Clusters*, Wiley, New York, 1991, pp. 11–93.

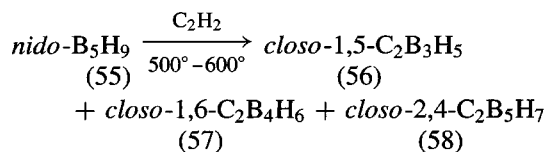
⁷¹ R. N. GRIMES, *Adv. Inorg. Chem. Radiochem.* **26**, 55–117 (1983).



monocarbaborane, 1-CB₅H₇, which has a triply bridging H_μ over one B₃ face of the octahedron. If *c* = 0 the compound is a neutral carborane molecule rather than an anion.

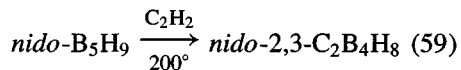
Nomenclature⁽¹²⁾ follows the well-established oxa-aza convention of organic chemistry. Numbering begins with the apex atom of lowest coordination and successive rings or belts of polyhedral vertex atoms are numbered in a clockwise direction with C atoms being given the lowest possible numbers within these rules.†

Closo-carboranes are the most numerous and the most stable of the carboranes. They are colourless volatile liquids or solids (depending on mol wt.) and can be prepared from an alkyne and a borane by pyrolysis, or by reaction in a silent electric discharge. This route, which generally gives mixtures, is particularly useful for small *closo*-carboranes (*n* = 5–7) and for some intermediate *closo*-carboranes (*n* = 8–11), e.g.

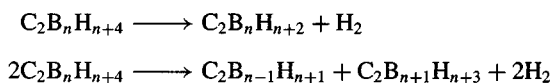


† As frequently happens in a rapidly developing field, nomenclature and numbering for the carboranes gradually evolved to cope with increasing complexity. Consequently, many systems have been used, often by the same author in successive years, and the only safe procedure is to draw a labelled diagram and convert to the preferred numbering system.

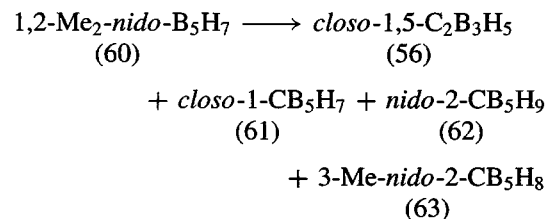
Milder conditions provide a route to *nido*-carboranes, e.g.:

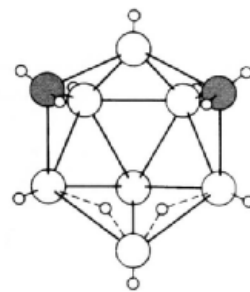
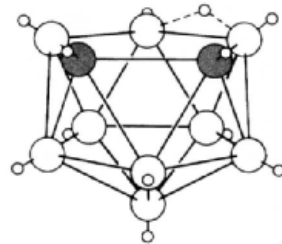
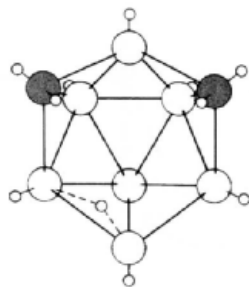
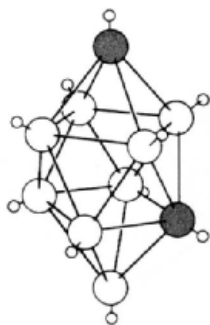


Pyrolysis of *nido*- or *arachno*-carboranes or their reaction in a silent electric discharge also leads to *closo*-species either by loss of H₂ or disproportionation:

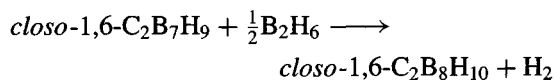
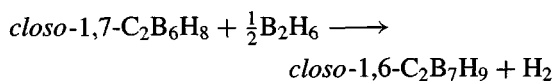


For example, pyrolysis of the previously mentioned *nido*-2,3-C₂B₄H₈ gives the 3 *closo*-species shown above, whereas under the milder conditions of photolytic closure the less-stable isomer *closo*-1,2-C₂B₄H₆ is obtained. Pyrolysis of alkyl boranes at 500–600° is a related route which is particularly useful to monocarbaboranes though the yields are often low, e.g.:

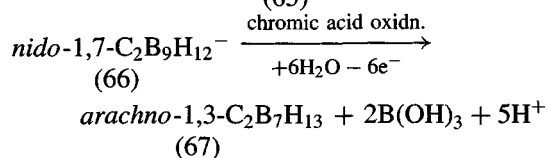
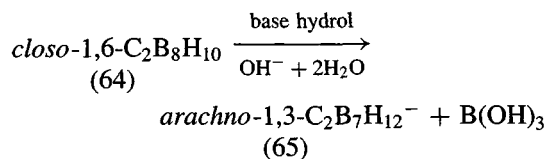


(64) *closo*-1,6-C₂B₈H₁₀ (65) *arachno*-1,3-C₂B₇H₁₂⁻(66) *nido*-1,7-C₂B₉H₁₂⁻ (67) *arachno*-1,3-C₂B₇H₁₃

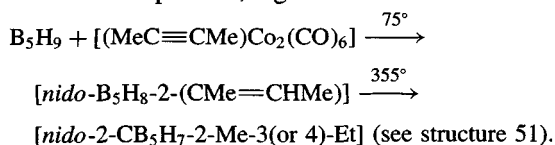
Cluster expansion reactions with diborane provide an alternative route to intermediate *closo*-carboranes, e.g.:



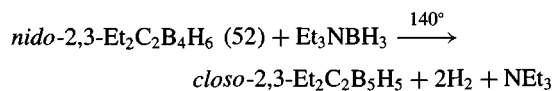
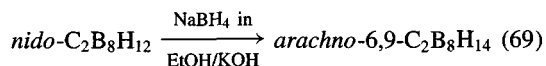
Conversely, cluster degradation reactions lead to more open structures, e.g.:



Other convenient routes to carboranes, selected from the growing number of recently reported syntheses, are as follows. Monocarbon carboranes can be prepared in good yield by the transition-metal catalysed hydroboration of alkenes followed by thermal rearrangement of the intermediate product, e.g.⁽⁷²⁾



The two isomers are each obtained in about 30% yield. Again, the Me₂S-promoted reaction of *nido*-B₁₀H₁₄ with bis(trimethylsilyl) ethyne, Me₃SiC≡CSiMe₃, results in monocarbon insertion by internal hydroboration and SiMe₃ group migration to give [*nido*-7-CB₁₀H₁₁-7-((Me₃Si)₂CH)-9-(Me₂S)] structure (68) in 28% yield.⁽⁷³⁾ New dicarbaboranes can be obtained from preformed *nido*-dicarbaboranes either by reducing them to give the corresponding *arachno* species⁽⁷⁴⁾ or by a capping reaction to give a *closo*-dicarbaborane,⁽⁷⁵⁾ e.g.



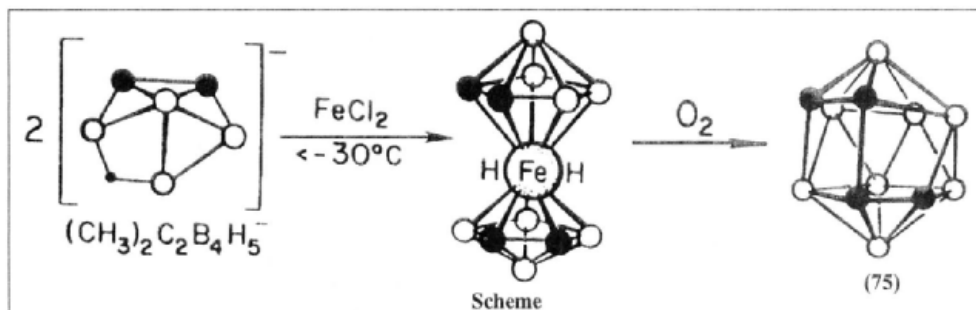
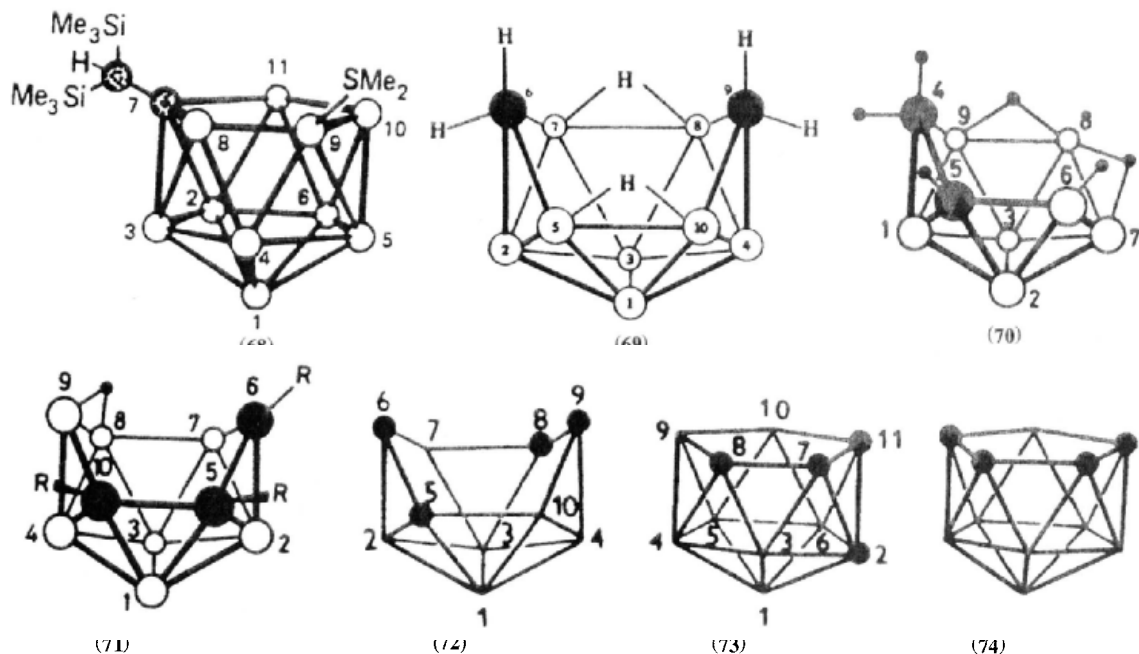
A convenient route to three-carbon carboranes is the hydroboration of an alkyne with a preformed dicarbaborane. For example,⁽⁷⁶⁾ reaction of ethyne (or propyne) with *arachno*-4,5-C₂B₇H₁₃ (70) in hexane at 120°C gives a mixture of tri- and tetra-carbaboranes, e.g. (71), (72), (73), (74) in modest yield. Access to other

⁷² R. L. ERNEST, W. QUINTANA, R. ROSEN, P. J. CARROLL and L. G. SNEDDON, *Organometallics* **6**, 80–8 (1987).

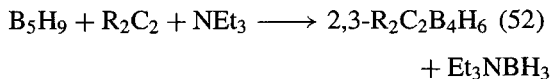
⁷⁴ Z. JANOUŠEK, J. PLEŠEK, S. HEŘMÁNEK and B. ŠTÍBR, *Polyhedron* **4**, 1797–8 (1985).

⁷⁵ J. S. BECK, A. P. KAHN and L. G. SNEDDON, *Organometallics* **5**, 2552–3 (1986).

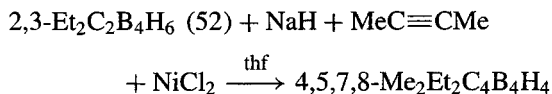
⁷⁶ B. ŠTÍBR, T. JELINEK, Z. JANOUŠEK, S. HEŘMÁNEK, E. DRDÁKOVÁ, Z. PLZÁK and J. PLEŠEK, *J. Chem. Soc., Chem. Commun.*, 1106–7 (1987). B. ŠTÍBR, T. JELINEK, E. DRDÁKOVÁ, S. HEŘMÁNEK and J. PLEŠEK, *Polyhedron*, **7**, 669–70 (1988).



tetracarboranes was greatly facilitated by the discovery of oxidative fusion reactions in 1974; these involve the construction of large clusters by metal-promoted face-to-face fusion of smaller clusters.⁽⁷¹⁾ For example, bridge-deprotonation of 2,3- $R_2C_2B_4H_6$ (see structure 52) with alkali metal hydride, followed by treatment with $FeCl_2$ and exposure to O_2 yields the desired product $R_4C_4B_8H_8$ (75) (see Scheme above). The starting material is available in multigram amounts via the room-temperature reaction of B_5H_9 with alkynes in the presence of NEt_3 :



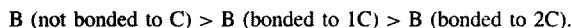
Metal-promoted alkyne-insertion reactions afford another good method (see structure 12 for cluster geometry and numbering).⁽⁷⁷⁾



⁷⁷ M. G. L. MIRABELLI and L. G. SNEDDON, *Organometallics* **5**, 1510-11 (1986).

Some Further Generalizations Concerning Carboranes

1. Carbon tends to adopt the position of lowest coordination number on the polyhedron and to keep as far from other C atoms as possible (i.e. the most stable isomer has the greatest number of B-C connections).
2. Boron-boron distances in the cluster increase with increasing coordination number (as expected). Average B-B distances are: 5-coordinate B 170 pm, 6-coordinate B 177 pm, 7-coordinate B 186 pm.
3. Carbon is somewhat smaller than B and interatomic distances involving C are correspondingly shorter. Thus B-C and C-C distances are about 165 pm and 145 pm, respectively, for 5-coordinate C; the corresponding values for 6-coordinate C are 172 pm and 165 pm.
4. Negative electronic charge on B is computed to decrease in the sequence:



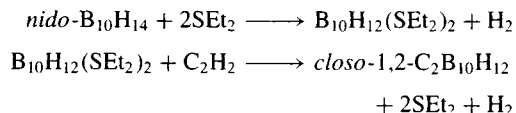
Within each group the B with lower coordination number has a greater negative charge than those with higher coordination.

5. CH groups tend to be more positive than BH groups with the same coordination number (despite the higher electronegativity of C). This presumably arises because each C contributes 3e for bonding within the cluster whereas each B contributes only 2e.
6. In *nido*- and *arachno*-carboranes H_μ is more acidic than H_i and is the one removed on deprotonation with NaH.

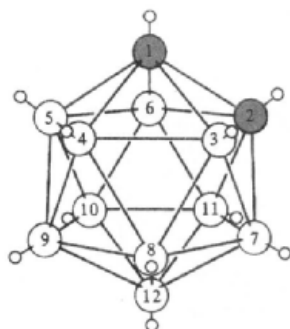
In general *nido*- (and *arachno*-) carboranes are less stable thermally than are the corresponding *closo*-compounds and they are less stable to aerial oxidation and other reactions, due to their more open structure and the presence of labile H atoms in the open face. Most *closo*-carboranes are stable to at least 400° though they may undergo rearrangement to more stable isomers in which the distance between the C atoms is increased. Some other structural and bonding generalizations are summarized in the Panel. Note, however, that kinetic control during synthesis may result in the isolation of a thermodynamically less favoured structure, with contiguous C atoms, while electronic factors in carboranes with as many as four C atoms may result in distortions or other deviations from the structures predicted on the basis

of the simple application of electron counting rules.⁽⁷¹⁾

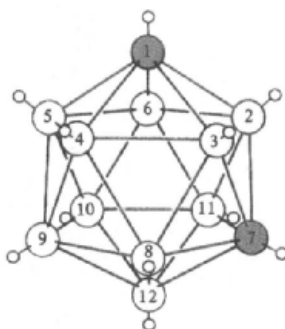
The three isomeric icosahedral carboranes (76–78) are unique both in their ease of preparation and their great stability in air, and consequently their chemistry has been the most fully studied. The 1,2-isomer in particular is available on the multikilogram scale. It is best prepared in bulk by the direct reaction of ethyne with decaborane in the presence of a Lewis base, preferably Et_2S :



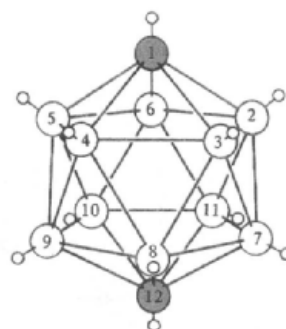
The 1,7-isomer is obtained in 90% yield by heating the 1,2-isomer in the gas phase at 470°C



(76) *ortho*-carborane,
1,2-C₂B₁₀H₁₂ (mp 320°C)



(77) *meta*-carborane,
1,7-C₂B₁₀H₁₂ (mp 265°C)



(78) *para*-carborane,
1,12-C₂B₁₀H₁₂ (mp 261°C)

for several hours (or in quantitative yield by flash pyrolysis at 600° for 30 s). The 1,12-isomer is most efficiently prepared (20% yield) by heating the 1,7-isomer for a few seconds at 700°C. The mechanism of these isomerizations has been the subject of considerable speculation but definitive experiments are hard to devise. The “diamond-square-diamond” mechanism has been proposed (Fig. 6.19) for the $1,2 \rightleftharpoons 1,7$ isomerization, but the 1,12 isomer cannot be generated by this mechanism. Moreover, the activation energy required to pass through the cubo-octahedral transition state is likely to be rather high. An alternative proposal, which could, in principle, lead to both the 1,7 and the 1,12 isomers, is the successive concerted rotation of the 3 atoms on a triangular face, and a third possible mechanism involves the concerted basal twisting of two parallel pentagonal pyramids comprising the icosahedron. Vertex extrusion to a capping position, followed by reinsertion at an adjacent site in the cluster has also been suggested. It is extremely difficult to devise experiments to test these mechanisms, but where this has been achieved (as in the case of the disubstituted derivative of (58), *closo*-5-Me-6-Cl-2,4-C₂B₅H₆, for example) the results rule out triangular face rotation and are consistent with a “diamond-square-diamond” mechanisms.⁽⁷⁸⁾ It is conceivable that for other clusters the various mechanisms operate in different temperature ranges or that two (or more) mechanisms are

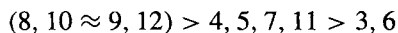
⁷⁸ Z. J. ABDU, G. ABDU, T. ONAK and S. LEE, *Inorg. Chem.* **25**, 2678–83 (1986).

active simultaneously. For recent definitive work on *closo*-C₂B₁₀H₁₂ see refs. 79 and 80.

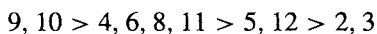
An entirely different form of isomerism, which is attracting increasing attention, is described in the Panel opposite.

An extensive derivative chemistry of the icosahedral carboranes has been developed, especially for 1,2-C₂B₁₀H₁₂. Terminal H atoms attached to B undergo facile electrophilic substitution and the sequence of reactivity follows the sequence of negative charge density on the BH_t group:⁽⁸¹⁾

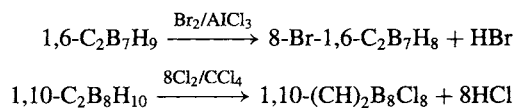
closo-1,2-C₂B₁₀H₁₂ :



closo-1,7-C₂B₁₀H₁₂ :



Similar reactions occur for other *closo*-carboranes, e.g.:



It is noteworthy that, despite the greater electronegativity of C, the CH group tends to be more

⁷⁹ S.-H. WU and M. JONES *J. Amer. Chem. Soc.* **111**, 5373–84 (1989).

⁸⁰ G. M. EDVENSON and D. F. GAINES *Inorg. Chem.* **29**, 1210–16 (1990).

⁸¹ D. A. DIXON, D. A. KLEIR, T. A. HALGREN, J. H. HALL and W. N. LIPSCOMB, *J. Am. Chem. Soc.* **99**, 6226–37 (1977).

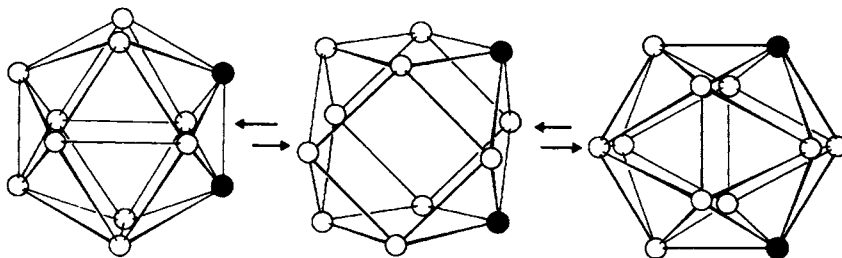
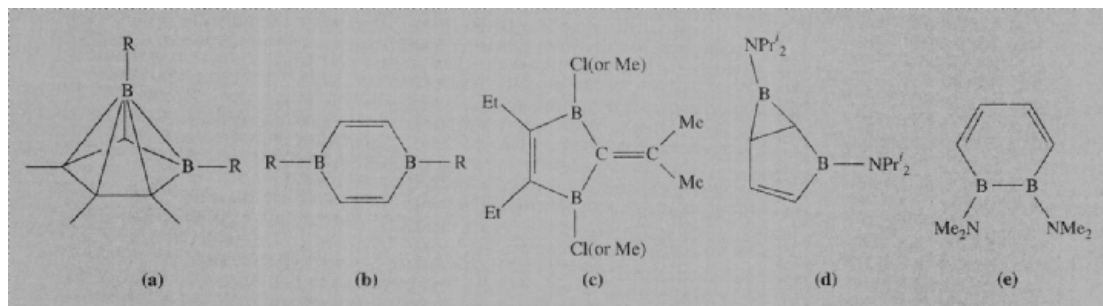


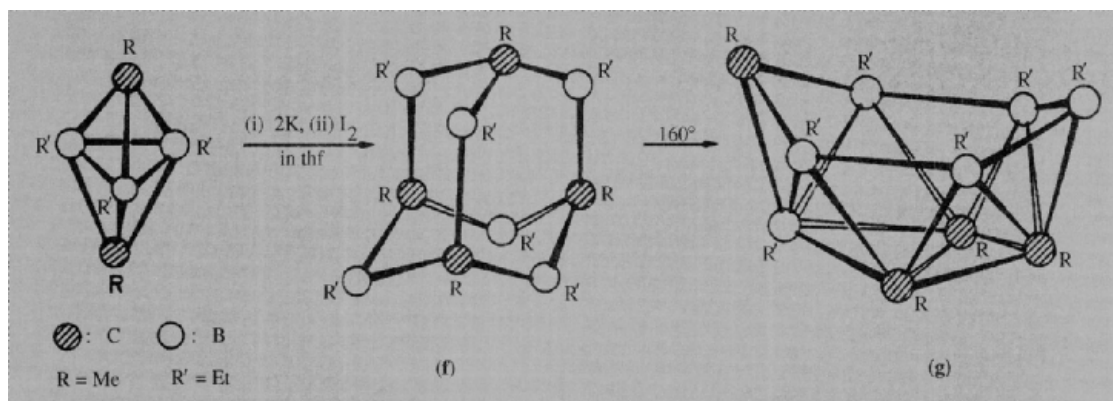
Figure 6.19 The interconversion of 1,2- and 1,7-disubstituted icosahedral species via a proposed cubo-octahedral intermediate formed during four “diamond-square-diamond” rearrangements.

“Classical-Nonclassical” Valence Isomerism

A novel and far-reaching type of isomerism concerns the possibility of valence isomerism between “nonclassical” (electron-deficient) clusters and “classical” organoboron structures. Thus, n -vertexed *nido*-boranes, B_nH_{n+4} , have cluster structures with $4H_\mu$ — cf. (9), (10), (11) — whereas the precisely isoelectronic n -vertexed *nido*-tetracarboranes, $C_4B_{n-4}H_n$, have no bridging H atoms and can, in principle, adopt either a cluster borane structure or one of several classical organic structures. For example, derivatives of $C_4B_2H_6$ could adopt either the *nido*-2,3,4,5-tetracarbahexaborane structure (a) — i.e. (54) — or the 1,4-dibora-2,5-cyclohexadiene structure (b). As might be expected, the 3-coordinate B atoms in (b) are stabilized by π -donor substituents (e.g. R = F, OMe) whereas when R = alkyl, rearrangement to the *nido*-carbaborane (a) occurs.⁽⁸²⁾ The novel diborafulvene isomer (c) has also been synthesized in good yield^(82,83) and two other isomers, (d) and (e) have been stabilized as ligands in Ru- and Rh-complexes.



Similar possibilities arise for 10-atom clusters. Thus, dimerization of the *closo*- C_2B_3 cluster 1,5- $Me_2C_2B_3Et_3$ (56) by means of K metal then I_2 in thf yields the “classical” adamantane derivative $Me_4C_4B_6Et_6$ (f); when this is heated to 160° the *nido*-tetracarbadecaborane cluster (g) is obtained rapidly and quantitatively.⁽⁸⁴⁾ It will be noted that in (f) all four C atoms are 4-coordinate and all six B atoms are 3-coordinate, whereas in (g) the three C atoms in the C_3 triangular face are 5-coordinate while the boron atoms are variously 4, 5 or 6 coordinate.



⁸²V. SCHÄFER, H. PRITZKOW and W. SIEBERT, *Angew. Chem. Int. Edn. Engl.* **27**, 299–300 (1988) and references cited therein. See also B. WRACKMEYER and G. KEHR, *Polyhedron* **10**, 1497–506 (1991).

⁸³G. E. HERBERICH, H. OHST and H. MAYER, *Angew. Chem. Int. Edn. Engl.* **23**, 969–70 (1984).

⁸⁴R. KÖSTER, G. SEIDEL and B. WRACKMEYER, *Angew. Chem. Int. Edn. Engl.* **24**, 326–7 (1985).

positive than the BH groups and does not normally react under these conditions.

The weakly acidic CH_i group can be deprotonated by strong nucleophiles such as LiBu or RMgX ; the resulting metalated carboranes $\text{LiCCHB}_{10}\text{H}_{10}$ and $(\text{LiC})_2\text{B}_{10}\text{H}_{10}$ can then be used to prepare a full range of *C*-substituted derivatives $-\text{R}$, $-\text{X}$, $-\text{SiMe}_3$, $-\text{COOH}$, $-\text{COCl}$, $-\text{CONHR}$, etc. The possibility of synthesizing extensive covalent C-C or siloxane networks with pendant carborane clusters is obvious and the excellent thermal stability of such polymers has already been exploited in several industrial applications.

Although *closo*-carboranes are stable to high temperatures and to most common reagents, M. F. Hawthorne showed (1964) that they can

be specifically degraded to *nido*-carborane anions by the reaction of strong bases in the presence of protonic solvents, e.g.:

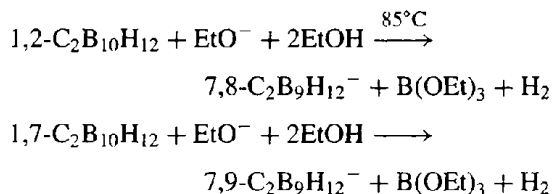


Figure 6.20 indicates that, in both cases, the BH vertex removed is the one adjacent to the two CH vertices: since the C atoms tend to remove electronic charge preferentially from contiguous B atoms, the reaction can be described as a nucleophilic attack by EtO^- on the most positive (most electron deficient) B atom in the

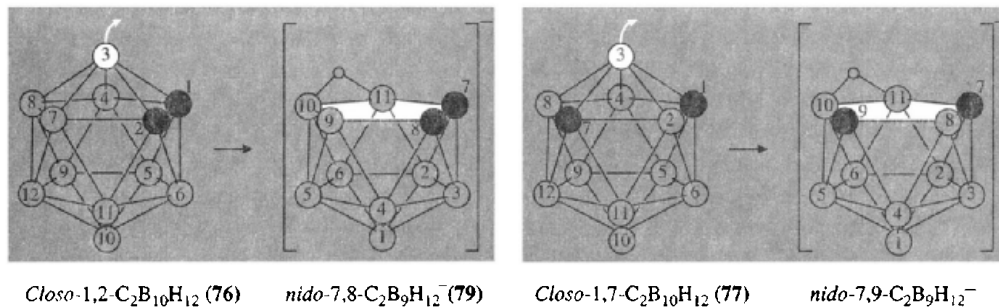


Figure 6.20 Degradation of *closo*-carboranes to the corresponding debor-*nido*-carborane anions.

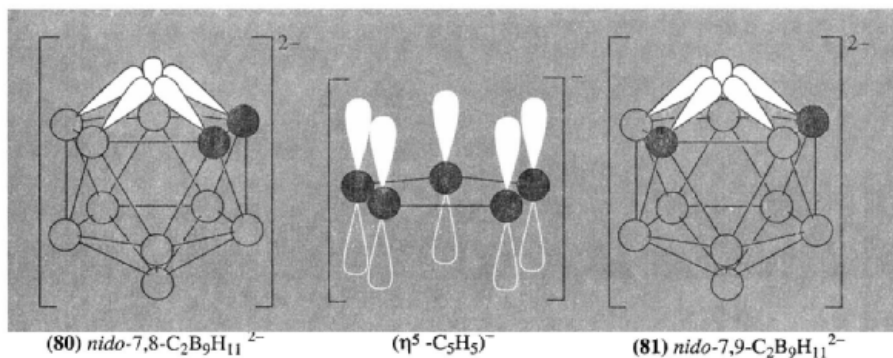


Figure 6.21 Relation between $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ and C_5H_5^- . In this formalism the *closo*-carboranes $\text{C}_2\text{B}_{10}\text{H}_{12}$ are considered as a coordination complex between the pentahapto 6-electron donor $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ and the acceptor BH^{2+} (which has 3 vacant orbitals). The *closo*-structure can be regained by capping the open pentagonal face with an equivalent metal acceptor that has 3 vacant orbitals.

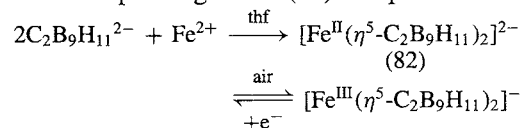
cluster. Deprotonation of the monoanions by NaH removes the bridge proton to give the *nido*-dianions 7,8-C₂B₉H₁₁²⁻ (80) and 7,9-C₂B₉H₁₁²⁻ (81). It was the perceptive recognition that the open pentagonal faces of these dianions were structurally and electronically equivalent to the pentahapto cyclopentadienide anion ($\eta^5\text{-C}_5\text{H}_5^-$) (Fig. 6.21) that led to the discovery of the metallocarboranes and the development of some of the most intriguing and far-reaching reactions of the carboranes. These are considered in the next section.

6.6 Metallocarboranes^(1,17,85-90)

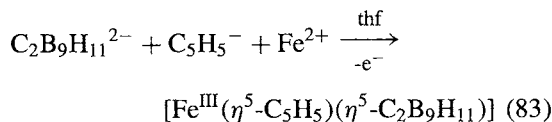
There are now at least a dozen synthetic routes to metallocarboranes including (i) coordination using *nido*-carborane anions as ligands, (ii) polyhedral expansion reactions, (iii) polyhedral contraction reactions, (iv) polyhedral subrogation and (v) thermal metal transfer reactions. These first five routes were all devised by M. F. Hawthorne and his group in the period 1965-74 and have since been extensively exploited and extended by several groups. Examples of each will be given before mentioning some of the more recent routes that have been developed. It is worth noting that the carborane dianions (80) and (81) are both more effective as ligands than is $\eta^5\text{-C}_5\text{H}_5^-$, perhaps because of the more favourable angles of the orbitals, the lower electronegativity of boron and the higher formal anionic charge. Thus, the carboranes form stable sandwich complexes with Cu^{II}, Al^{III} and

Si^{IV}, for example, whereas cyclopentadienyl does not.^(90,91)

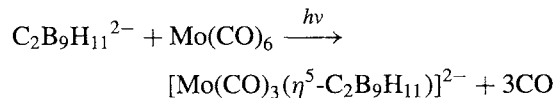
(i) *Coordination using nido-carborane anions as ligands* (1965). Reaction of C₂B₉H₁₁²⁻ with FeCl₂ in tetrahydrofuran (thf) with rigorous exclusion of moisture and air gives the pink, diamagnetic bis-sandwich-type complex of Fe(II) (structure 82) which can be reversibly oxidized to the corresponding red Fe(III) complex:



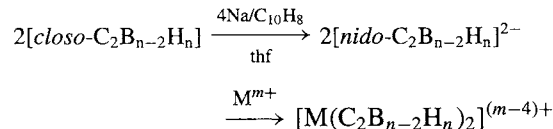
When the reaction is carried out in the presence of NaC₅H₅ the purple mixed sandwich complex (83) is obtained:



The reaction is general and has been applied to many transition metals as well as lanthanides and actinides.⁽⁹²⁾ Variants use metal carbonyls and other complexes to supply the capping unit, e.g.



(ii) *Polyhedral expansion* (1970). This entails the 2-electron reduction of a *closo*-carborane with a strong reducing agent such as sodium naphthalide in thf followed by reaction with a transition-metal reagent:



The reaction, which is quite general for *closo*-carboranes, involves the reductive opening of an *n*-vertex *closo*-cluster followed by metal

⁸⁵ R. N. GRIMES, *Pure Appl. Chem.* **39**, 455-74 (1974).

⁸⁶ K. P. CALLAHAN and M. F. HAWTHORNE, *Pure Appl. Chem.* **39**, 475-95 (1974).

⁸⁷ G. B. DUNKS and M. F. HAWTHORNE, Chap. 11 in ref. 9, pp. 383-430.

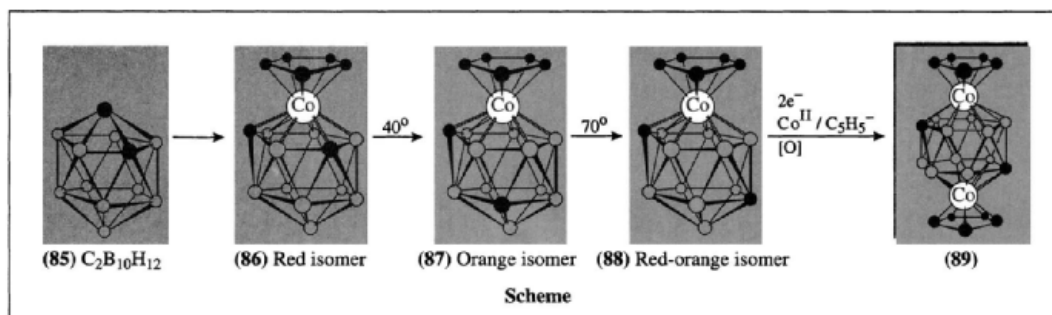
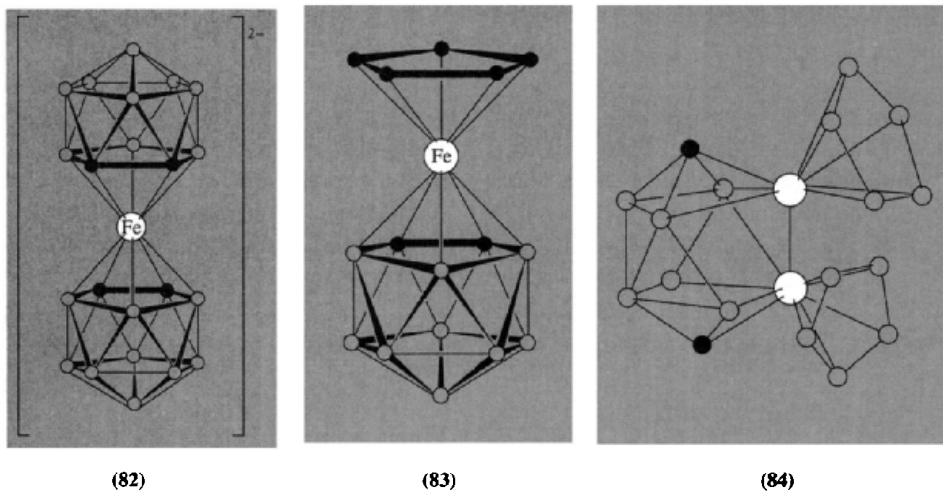
⁸⁸ K. P. CALLAHAN and M. F. HAWTHORNE, *Adv. Organometallic Chem.* **14**, 145-86 (1976).

⁸⁹ R. N. GRIMES, Chap. 2 in E. BECHER and M. TSUTSUI (eds.), *Organometallic Reactions and Syntheses* **6**, 63-221 (1977).

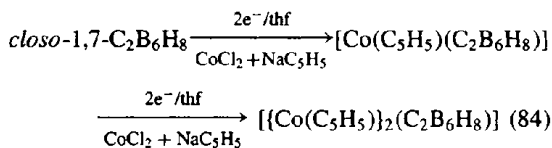
⁹⁰ D. M. SCHUBERT, M. A. BANDMAN, W. S. REES, C. B. KNOBLER, P. LU, W. NAM and M. F. HAWTHORNE, *Organometallics* **9**, 2046-61 (1990), and refs. cited therein.

⁹¹ D. M. SCHUBERT, W. S. REES, C. B. KNOBLER and M. F. HAWTHORNE, *Organometallics* **9**, 2938-44 (1990), and refs. cited therein.

⁹² M. J. MANNING, C. B. KNOBLER and M. F. HAWTHORNE, *J. Am. Chem. Soc.* **110**, 4458-9 (1988).



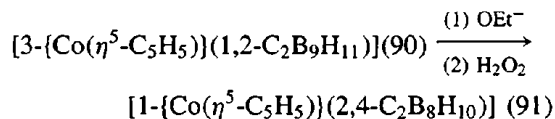
insertion to give an $(n + 1)$ -vertex *closo*-cluster. Numerous variants are possible including the insertion of a second metal centre into an existing metalloborane, e.g.:



The structure of the bimetallic 10-vertex cluster was shown by X-ray diffraction to be (84). When the icosahedral carborane 1,2-C₂B₁₀H₁₂ was used, the reaction led to the first supraicosahedral metalloboranes with 13- and 14-vertex polyhedral structures (85)–(89). Facile isomerism of the 13-vertex monometalloboranes was observed as indicated in the scheme above (in which ● = CH and ○ = BH).

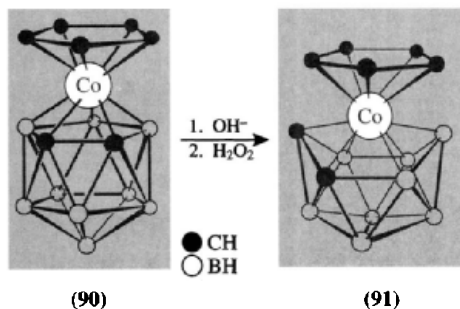
(iii) *Polyhedral contraction* (1972). This involves the clean removal of one BH group from

a *closo*-metalloborane by nucleophilic base degradation, followed by oxidative closure of the resulting *nido*-metalloborane complex to a *closo*-species with one vertex less than the original, e.g.:

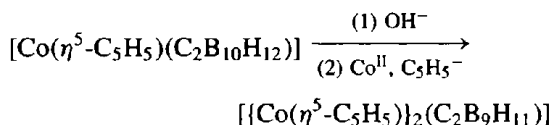


Polyhedral contraction is not so general a method of preparing metalloboranes as is polyhedral expansion since some metalloboranes degrade completely under these conditions.

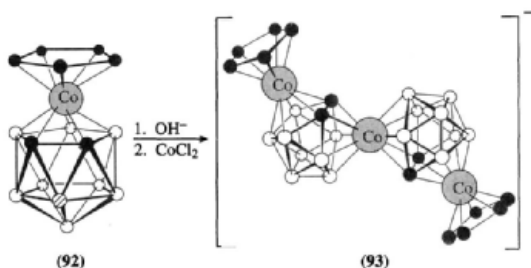
(iv) *Polyhedral subrogation* (1973). Replacement of a BH vertex by a metal vertex without changing the number of vertices in the cluster is termed polyhedral subrogation. It is an offshoot of the polyhedral contraction route in that degradative removal of the BH unit is followed by reaction with a transition metal ion rather than



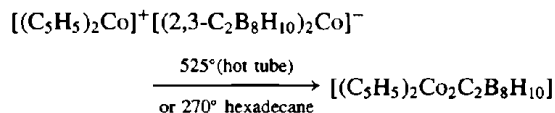
with an oxidizing agent, e.g.:



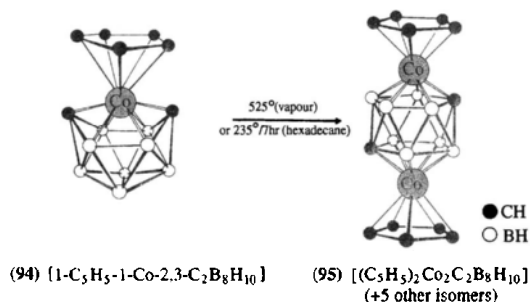
The method is clearly of potential use in preparing mixed metal clusters, e.g. (Co + Ni) or (Co + Fe), and can be extended to prepare more complicated cluster arrays as depicted below, the subrogated B atom being indicated as a shaded circle in (92).



(v) *Thermal metal transfer* (1974). This method is less general and often less specific than the coordination of *nido*-anions or polyhedral expansion; it involves the pyrolysis of pre-existing metallocarboranes and consequent cluster expansion or disproportionation similar to that of the *closo*-carboranes themselves (p. 182). Mixtures of products are usually obtained, e.g.:

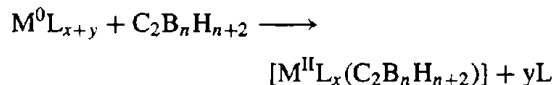


Similarly:

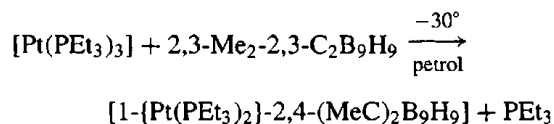


A related technique (R. N. Grimes, 1973) is direct metal insertion by gas-phase reactions at elevated temperatures; typical reactions are shown in the scheme (p. 192). The reaction with $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ also gave the 7-vertex *closo*-bimetallocarborane (101) which can be considered as a rare example of a triple-decker sandwich compound; another isomer (102) can be made by base degradation of $[(\text{Co}(\eta^5\text{-C}_5\text{H}_5))(\text{C}_2\text{B}_4\text{H}_6)]$ followed by deprotonation and subrogation with a second $\{\text{Co}(\eta^5\text{-C}_5\text{H}_5)\}$ unit.⁽⁸⁵⁾ It will be noted that the central planar formal $\text{C}_2\text{B}_3\text{H}_5^{4-}$ unit is isoelectronic with C_5H_5^- .

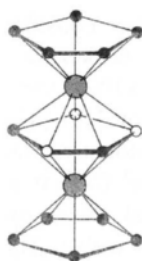
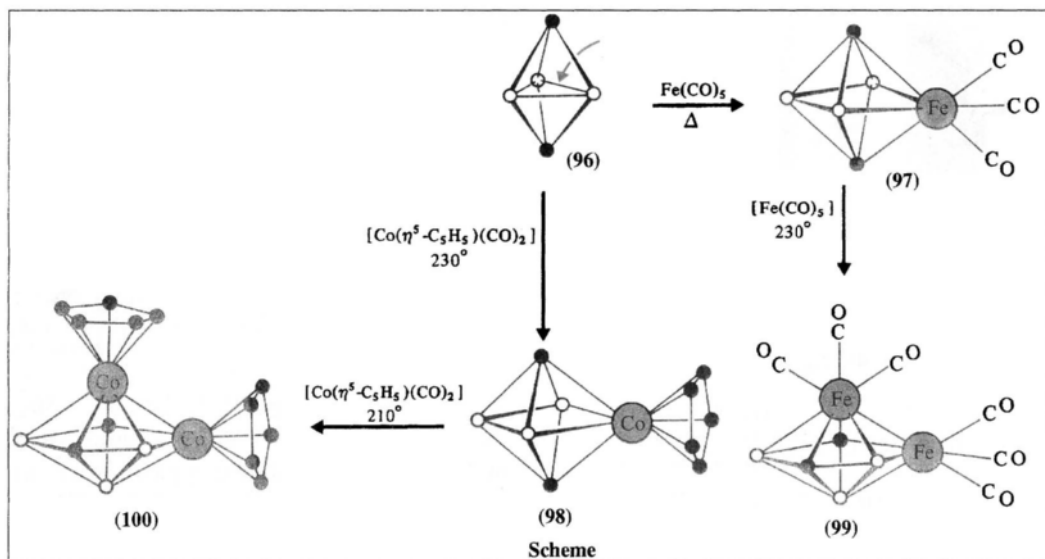
A particularly elegant route to metallocarboranes is the *direct oxidative insertion of a metal centre* into a *closo*-carborane cluster: the reaction uses zero-valent derivatives of Ni, Pd and Pt in a concerted process which involves a net transfer of electrons from the nucleophilic metal centre to the cage.⁽⁹³⁾



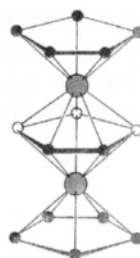
where L = PR_3 , C_8H_{12} , RNC, etc. A typical reaction is



⁹³ F. G. A. STONE, *J. Organometallic Chem.* **100**, 257–71 (1975).

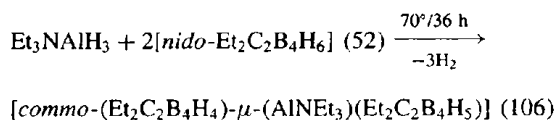
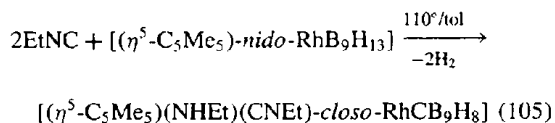
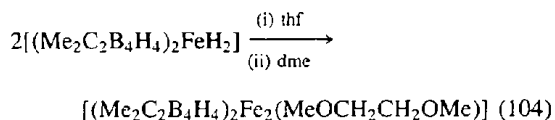
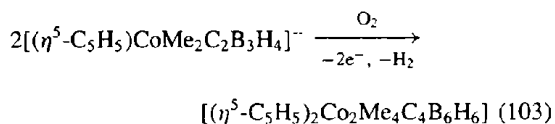


(101)



(102)

Many novel cluster compounds have now been prepared in this way, including mixed metal clusters. Further routes involve the *oxidative fusion of dicarbon metallacarborane anions* to give dimetal tetracarborane clusters such as (103) and (104);⁽⁷¹⁾ the *insertion of isonitriles into metallaborane clusters* to give monocarbon metallacarboranes such as (105);⁽⁹⁴⁾ and the reaction of small *nido*-carboranes with alane adducts such as Et_3NAlH_3 to give the *commo* species (106);⁽⁹⁵⁾

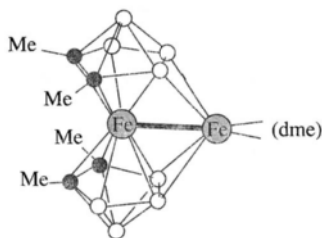


⁹⁴ E. J. DITZEL, X. L. R. FONTAINE, N. N. GREENWOOD, J. D. KENNEDY, Z. SISAN, B. ŠTÍBR and M. THORNTON-PETT, *J. Chem. Soc., Chem. Commun.*, 1741–3 (1990). See also N. N. GREENWOOD and J. D. KENNEDY, *Pure Appl. Chem.* **63**, 317–26 (1991) and refs. therein.

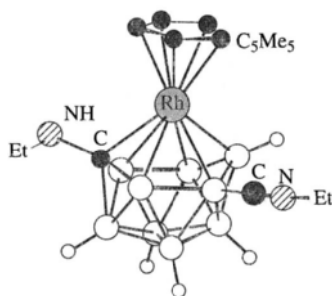
⁹⁵ J. S. BECK and L. G. SNEDDON, *J. Am. Chem. Soc.* **110**, 3467–72 (1988).



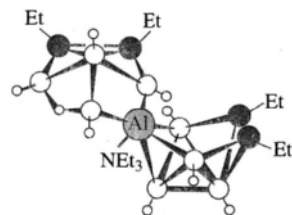
(103)



(104)



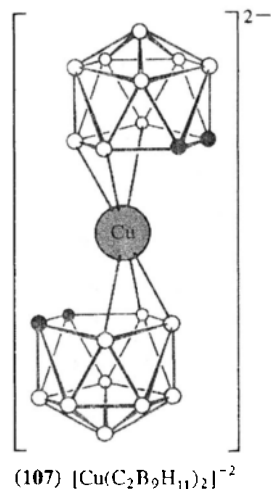
(105)



(106)

Numerous other aluminacarborane structural types have also recently been synthesized by a variety of routes⁽⁹¹⁾ and, indeed, the burgeoning field of metallocarborane chemistry now encompasses the whole Periodic Table with an almost bewildering display of exotic and unprecedented structural types.

The electron-counting rules outlined for boranes (p. 161) and carboranes (p. 181) can readily be extended to the metallocarboranes (see Panel on next page). For bis-complexes of 1,2-C₂B₁₀H₁₁²⁻ which can be regarded as a 6-electron penta-hapto ligand, it has been found that "electron-sufficient" (18-electron) systems such as those involving d⁶ metal centres (e.g. Fe^{II}, Co^{III} or Ni^{IV}) have symmetrical structures with the metal atom equidistant from the 2 C and 3 B atoms in the pentagonal face. The same is true for "electron-deficient" systems such as those involving d² Ti^{II} (14-electron), d³ Cr^{III} (15-electron), etc., though here the metal-cluster bonds are somewhat longer. With "electron excess" complexes such as [Ni^{II}(C₂B₁₀H₁₁)₂]²⁻ and the corresponding complexes of Pd^{II}, Cu^{III} and Au^{III} (20 electrons), so-called "slipped-sandwich" structures (107) are observed in which the metal atom is significantly closer to the 3 B atoms than to the 2 C atoms. This has been thought by some to indicate π-allylic bonding to the 3 B but is more likely to arise from an occupation of orbitals that are antibonding with respect to both the metal and the cluster thereby leading to an opening of the 12-vertex

(107) [Cu(C₂B₉H₁₁)₂]²⁻

closo-structure to a pseudo-*nido* structure in which the 12 atoms of the cluster occupy 12 vertices of a 13-vertex polyhedron.⁽⁹⁶⁾ A similar type of distortion accompanies the use of metal centres with increasing numbers of electron-pairs on the metal and it seems that these electrons may also, at least in part, contribute to the framework electron count with consequent cluster opening.⁽⁹⁷⁾ Thus, progressive opening of the

⁹⁶ D. M. P. MINGOS, M. I. FORSYTH and A. J. WELCH, *J. Chem. Soc., Chem. Commun.*, 605-7 (1977). See also G. K. BARKER, M. GREEN, F. G. A. STONE and A. J. WELCH, *J. Chem. Soc., Dalton Trans.*, 1186-99 (1980); D. M. P. MINGOS and A. J. WELCH, *ibid.* 1674-81.

⁹⁷ H. M. COLQUHOUN, T. J. GREENHOUGH and M. G. H. WALLBRIDGE, *J. Chem. Soc., Chem. Commun.*, 737-8 (1977); see also H. M. COLQUHOUN, T. J. GREENHOUGH

Electron-counting Rules for Metallocarboranes and Other Heteroboranes

As indicated on pp. 161 and 174 each framework atom (except H) uses 3 atomic orbitals (AOs) in cluster bonding. For B, C, and other first-row elements this leaves one remaining AO to bond exopolyhedrally to $-H_t$, $-X$, $-R$, etc. In contrast, transition elements have a total of 9 valence AOs (five d, one s, three p). Hence, after contributing 3 AOs to the cluster, they have 6 remaining AOs which can be used for bonding to external ligands and for storage of nonbonding electrons. In *closo*-clusters the $(n + 1)$ MOs require $(2n + 2)$ electrons from the B, C and M vertex atoms. In its simplest form the electron counting scheme invokes only the total number of framework MOs and electrons, and requires no assumptions as to orbital hybridization or formal oxidation state. For example, the neutral moiety $\{Fe(CO)_3\}$ has 8 Fe electrons and 9 Fe AOs: since 3 AOs are involved in bonding to 3 CO and 3 AOs are used in cluster bonding, there remain 3 AOs which can accommodate 6 (nonbonding) Fe electrons, leaving 2 Fe electrons to be used in cluster bonding. Neutral $\{Fe(CO)_3\}$ is thus precisely equivalent to $\{BH\}$, as distinct from $\{CH\}$, which provides 3 electrons for the cluster. Other groups such as $\{Co(\eta^5-C_5H_5)\}$ and $\{Ni(CO)_2\}$ are clearly equivalent to $\{Fe(CO)_3\}$.

An alternative scheme that is qualitatively equivalent is to assign formal oxidation states to the metal moiety and to consider the bonding as coordination from a carborane ligand, e.g. $\{Fe(CO)_3\}^{2+} \eta^5$ -bonded to a cyclocarborane ring as in $\{C_2B_9H_{11}\}^{2-}$. This is acceptable when the anionic ligand is well characterized as an independent entity, as in the case just cited, but for many metallocarboranes the "ligands" are not known as free species and the presumed anionic charge and metal oxidation state become somewhat arbitrary. It is therefore recommended that the metalborane cluster be treated as a single covalently bonded structure with no artificial separation between the metal and the rest of the cluster; electron counting can then be done unambiguously on the basis of neutral atoms and attached groups.

To the structural generalizations on carboranes (p. 185) can be added the rule that, in metallocarboranes, the M atom tends to adopt a vertex with high coordination number: M occupancy of a low CN vertex is not precluded, particularly in kinetically controlled syntheses, but isomerization to more stable configurations usually results in the migration of M to high CN vertices.

Other main-group atoms besides C can occur in heteroborane clusters and the electron-counting rules can readily be extended to them.⁽¹⁷⁾ Thus, whereas each $\{BH\}$ contributes 2 e and $\{CH\}$ contributes 3 e to the cluster, so $\{NH\}$ or $\{PH\}$ contributes 4 e, $\{SH\}$ contributes 5 e, $\{S\}$ contributes 4 e, etc. For example, the following 10-vertex thiaboranes (and their isoelectronic equivalents) are known: *closo*-1-SB₉H₉ ($B_{10}H_{10}^{2-}$), *nido*-6-SB₉H₁₁ ($B_{10}H_{13}^-$) and *arachno*-6-SB₉H₁₂ ($B_{10}H_{14}^{2-}$). Similarly, the structures of 12-, 11- and 9-vertex thiaboranes parallel those of boranes and carbaboranes with the same skeletal electron count, the S atom in each case contributing 4 electrons to the framework plus an *exo*-polyhedral lone-pair.

cluster is noted for complexes of 1,2-C₂B₉H₁₁²⁻ with Re^I (d⁶), Au^{III} (d⁸), Hg^{II} (d¹⁰) and Tl^I (d¹⁰s²) as shown in structures (108)–(111). Thus the Re^I (d⁶) complex (108) is a symmetrically bonded 12-vertex cluster with Re–B 234 pm and Re–C 231 pm. The Au^{III} (d⁸) complex (109) has the metal appreciably closer to the 3 B atoms (221 pm) than to the 2 C atoms (278 pm). With the Hg^{II} (d¹⁰) complex (110) this distortion is even more pronounced and the metal is pseudo-σ-bonded to 1 B atom at 220 pm; there is

some additional though weak interaction with the other 2 B (252 pm) but the two Hg...C distances (290 pm) are essentially nonbonding. Finally, the Tl^I (d¹⁰s²) complex (111), whilst having the Tl atom more symmetrically located above the open face, has Tl–cluster distances that exceed considerably the expected covalent Tl^I–B distance of ~236 pm; the shortest Tl–B distance is 266 pm and there are two other Tl–B at 274 pm and two Tl–C at 292 pm: the species can thus be regarded formally as being closer to an ion pair $[Tl^+(C_2B_9H_{11})^{2-}]$.

In general, metallocarboranes are much less reactive (more stable) than the corresponding metallocenes and they tend to stabilize higher oxidation states of the later transition metals, e.g. $[Cu^{II}(1,2-C_2B_9H_{11})_2]^{2-}$ and $[Cu^{III}(1,2-C_2B_9H_{11})_2]^-$ are known whereas cuprocene

and M. G. H. WALLBRIDGE, *J. Chem. Soc., Chem. Commun.*, 1019–20 (1976); 737–8 (1977); *J. Chem. Soc., Dalton Trans.*, 619–28 (1979); *J. Chem. Soc., Chem. Commun.*, 192–4 (1980); G. K. BARKER, M. GREEN, F. G. A. STONE, A. J. WELCH and W. C. WOLSEY, *J. Chem. Soc., Chem. Commun.*, 627–9 (1980), K. NESTOR, B. ŠTIBR, T. JELÍNEK and J. D. KENNEDY, *J. Chem. Soc., Dalton Trans.*, 1661–3 (1993).