Dicarbadodecaborane Rearrangements: An Appraisal of Rotational Mechanisms*

Yvonne V. Roberts and Brian F. G. Johnson
Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

The advantages and limitations of a number of mechanisms proposed for dicarbadodecaborane rearrangement have been considered and a direct comparison of two; triangular face rotation and rotation *via* an anticubeoctahedron, undertaken for a range of 12-vertex species.

The definitive mechanism for the rearrangements of icosahedral *closo* carboranes has proved elusive for 30 years.[1] The general feeling is that there should exist a single set of vertex motions, from which *all* the observed experimental rearrangements may be choreographed. However, the conditions under which these rearrangements are known to occur have precluded the isolation of any intermediates if, indeed, any exist. This lack of mechanistic signposting greatly increases the burden of proof for any postulated rearrangement route.

Lipscomb and his co-workers[2] were the first to propose a mechanism for the isomerisation of 1,2- to 1,7-dicarbadodecaborane.[2] Their mechanism [Fig. 1(*a*)] involves a cubeoctahedral complementary geometry; the midpoint polyhedron of their postulated, six-fold, diamond-square-diamond (d.s.d.) process. However, this mechanism could not explain the corresponding 1,7 to 1,12 rearrangement, observed at much higher temperatures,[3,4] because it maintains the antipodal relationships of all vertices. Consequently, a modified proposal was offered,[5] involving weighted rotation of triangular faces in the cubeoctahedron.

Other mechanisms have also been proposed. These include: relative rotation of fused pentagonal pyramids (five-fold d.s.d.);[1,6] isolated triangular face rotation (t.f.r.) in the ground-state icosahedron (two, three-fold d.s.d.s),[5,6] and stepwise combinations of opposite pairs of faces (six-fold d.s.d.);[7] and the *nido* 12-vertex mechanism[8,9] (see Fig. 1). Indeed, Gaines and Edvenson[9] suggest that all previous mechanisms may simply be facets of their own proposal, arising from varying numbers of d.s.d. processes within the *nido* intermediate.

The feasibility of d.s.d. transformations appears not to be in doubt. Indeed, single d.s.d. transformations have been electronically induced in icosahedral wolfracarborane complexes and the molecular structures of both the *closo*- and *hyper*- (or *iso*-) *closo* species have been determined by X-ray crystallography.[10,11]

If the rearrangements of icosahedral carboranes are based *solely* on combinations of d.s.d. transformations, then it is apparent that a minimum of five d.s.d.s are required to effect icosahedral rearrangement. However, most of the postulated mechanisms require six, for which there must be good reason.

We wish to propose a six-fold d.s.d. mechanism, based on an anticubeoctahedral geometry, as a preferential route for carborane rearrangements. Several years ago[12] we suggested that the anticubeoctahedron, which is closely related to the cubeoctahedron, would provide a satisfactory complementary geometry for the fluxional behaviour exhibited by the icosahedral ligand shell of $[Fe_3(CO)_{12}]$ and many of its derivatives. Whilst we fully appreciate the bonding differences between metal clusters and carborane compounds, we believe that mechanistic and geometric similarities should exist.

Discussion

The relationship between the cubeoctahedron and the anticubeoctahedron is clear. The former has a 3:6:3′ arrangement of vertices (related to cubic close packed, c.c.p.) and the latter a 3:6:3 relationship (related to hexagonal close packed, h.c.p.). However, icosahedral rearrangement through an anticubeoctahedron (see Fig. 2) has the significant advantage of removing the antipodal relationship of some of the vertices. The mechanism has a similar effect to face rotation in the cubeoctahedron, but in one, concerted motion.

The same combinations of d.s.d.s, albeit in two, three-fold steps, have been investigated by Wales and Stone,[13] who found it not unreasonable according to their tensor surface harmonic (TSH) calculations. Relative-energy calculations have been carried out by several groups on a variety of 12-vertex shapes.[14–16] Most agree[15,16] that the anticubeoctahedron is of a higher energy than the cubeoctahedron and, as such, rule it out as an intermediate or transition state. However, the cubeoctahedron itself must undergo a second rearrangement, in order to destroy antipodal relationships, and so direct comparison of the two geometries may not be valid in this context.

The D_{3h} icosahedron is considered to be the preferred complementary geometry for icosahedral rearrangement. We wish to raise three objections. First, if models of the D_{3h} icosahedron are prepared (see Fig. 3), retaining the B–B and B–C distances as before, additional close contacts between B atoms and B or C atoms are formed and three, very strained, 'six-co-ordinate' vertices are generated. As the shapes of the vertex atomic orbitals are not expected to change, it is difficult to see how effective orbital overlaps can be maintained, in this *non-spherical* polyhedron, from a purely geometric viewpoint. Secondly, C atoms in carboranes prefer polyhedral positions of low co-ordination number.[17] In t.f.r. the D_{3h} intermediate has (for 1,2 $\longrightarrow$ 1,7) a 'seven-co-ordinate' C and a 'six-co-ordinate' C, which is not in keeping with the previous observation. In the anticubeoctahedron all vertices are 'five-co-ordinate'. Thirdly, the D_{3h} icosahedron is, supposedly, a much lower-energy intermediate shape than the others.[14–16] However, it is a fully triangulated polyhedron and yet is only halfway towards full icosahedral interchange, *i.e.* another triangular face rotation is *still* required. The I_h icosahedral shape will only be achieved if the same face, or the one directly opposite, rotates. No other face will do. Experimentally, therefore, one would expect to be able to isolate the D_{3h} icosahedral intermediates for some substituted carboranes, especially metallacarboranes which have accessible rearrangements under mild conditions.[17,18] As far as we are aware, none has been reported.

---

* *Supplementary data available* (No. SUP 56987, 15 pp.): raw data and algorithms. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

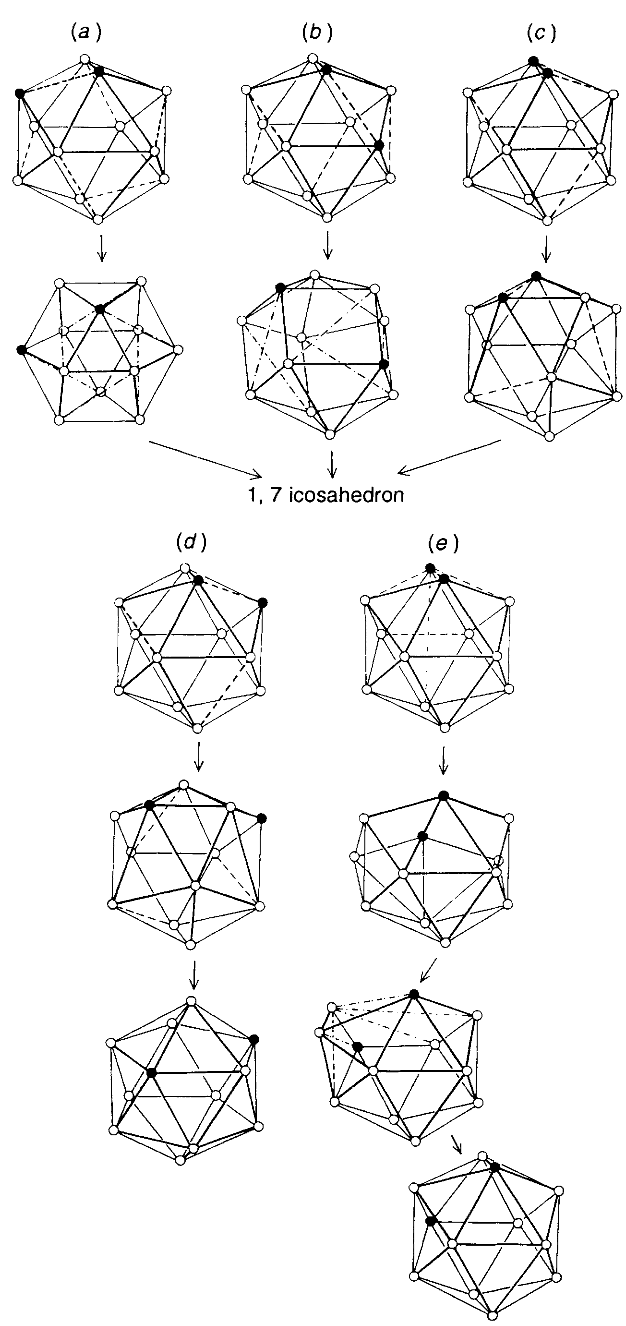


Fig. 1 Postulated mechanisms for carborane rearrangement: (*a*) cubeoctahedral intermediate, (*b*) rotation of pentagonal pyramids, (*c*) isolated triangular face rotation, (*d*) combinations of face rotations and (*e*) *nido* 12-vertex intermediate. – – –, Edges broken; — · — edges formed

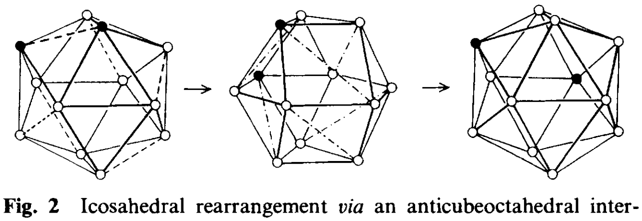


Fig. 2 Icosahedral rearrangement *via* an anticubeoctahedral intermediate

Icosahedral interconversion *via* cubeoctahedra, anticubeoctahedra and D_{3h} icosahedra are all 'symmetry allowed' processes (in the Woodward–Hoffmann sense) based on the criteria proposed by Wales and Mingos.[19] All involve six d.s.d.s (and in the case of the modified cubeoctahedral route, probably more). The six d.s.d.s cannot be carried out stepwise, as this would involve three, symmetry-forbidden processes.[20] The question then arises as to the relative energies of two three-fold d.s.d.s and a single six-fold d.s.d. process. Wales and Stone[13] comment that 'the smaller the number of simultaneous d.s.d. processes occurring in a symmetry-allowed rearrrangement, the more favourable it will be', but add that their results 'also show that a linear dependence upon the number of open faces should not be expected'. Whether two three-fold $\geqslant$ single six-fold (in energy terms) or *vice versa* will also depend upon the type and position of the substituents on the carborane, *i.e.* one would not expect precisely the same results for 1,2- and 1,7-dicarbadodecaborane. The splitting between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO) may be increased (and a process, therefore, favoured) by having substituent atoms at the edges of a face which opens during rearrangement.[13] For an anticubeoctahedron every vertex forms a corner of a square face; such is not the case for an isolated t.f.r. mechanism. Heteroatoms, of course, lower the overall symmetry of the icosahedron and the substitution of CR for BH vertices increases rates of rearrangements, particularly if R is a π donor.[13] It is also believed[14] that CR vertices preferentially labilise faces *trans* to themselves. This makes it ever more likely that the second face rotation of a t.f.r. mechanism will be *trans* to the first. The only remaining variable is whether the second face is con- or dis-rotatory with respect to the first. Wu and Jones[7] favour a mixture of both, whereas Wales and Stone[13] only considered disrotation. We do not feel that conrotating faces would be possible in a concerted six-fold d.s.d. motion and do not favour the two-step D_{3h} icosahedral approach for the reasons stated earlier.

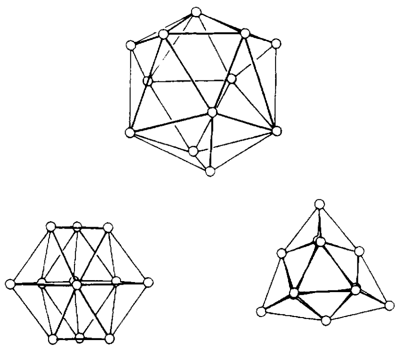


Fig. 3 The D_{3h} icosahedron

As yet, we have made no further mention of the *nido* intermediate pathway. This is not a purely d.s.d. mechanism and so cannot be directly compared with t.f.r. or the anticubeoctahedral route, but we feel that it cannot be entirely ignored. There are several problems with this mechanism. First, it seems unlikely from Wade's rules, that $C_2B_{10}H_{12}$ or its neutral derivatives would be capable of achieving a *nido* 12-vertex configuration. In contrast, $[C_2B_{10}H_{12}]^{2-}$ would be expected to be *nido* and, given its near-instantaneous reactions with metal complex fragments to form *closo* 13-vertex species, would appear to be so.[21,22] Secondly, the dianion exhibits fluxional behaviour not seen in the neutral carboranes, *i.e.* the 1,7 to 1,2 rearrangement. If the *nido* configuration were truly the transition-state geometry for *closo* carboranes, then one would expect no differences. Thirdly, if the *nido* configuration of $C_2B_{10}H_{12}$ is possible, one might expect to be able to trap out 13-vertex species with appropriate metal complex fragments, although the relative position of the carbon atoms would be largely irrelevant, since 13-vertex species are fluxional in their own right. As far as we are aware, all the known 13-vertex *closo*-metallacarboranes containing *nido* 12-vertex carborane fragments have been synthesised from $[C_2B_{10}H_{12}]^{2-}$ dianions, rather than neutral carborane species.

Table 1 Vertex permutation matrices for t.f.r.; I = identity

(*a*) Face type α

I	A	A′	B	B′	C	C′	D	D′	E	E′
1	3	2	4	3	5	4	6	5	2	6
2	1	3	2	2	2	2	2	2	6	1
3	2	1	1	4	3	3	3	3	3	3
4	4	4	3	1	1	5	4	4	4	4
5	5	5	5	5	4	1	1	6	5	5
6	6	6	6	6	6	6	5	1	1	2
7	7	7	7	7	7	7	7	7	7	7
8	8	8	8	8	8	8	8	8	8	8
9	9	9	9	10	9	9	9	9	9	9
10	10	10	10	10	10	10	10	10	10	10
11	11	11	11	11	11	11	11	11	11	11
12	12	12	12	12	12	12	12	12	12	12

(*b*) Face type β

I	A	A′	B	B′	C	C′	D	D′	E	E′
1	1	1	1	1	1	1	1	1	1	1
2	7	11	2	2	2	2	2	2	2	2
3	3	3	8	7	3	3	3	3	3	3
4	4	4	4	4	9	8	4	4	4	4
5	5	5	5	5	5	5	10	9	5	5
6	6	6	6	6	6	6	6	6	11	10
7	11	2	3	8	7	7	7	7	7	7
8	8	8	7	3	4	9	8	8	8	8
9	9	9	9	9	8	4	5	10	9	9
10	10	10	10	10	10	10	9	5	6	11
11	2	7	11	11	11	11	11	11	10	6
12	12	12	12	12	12	12	12	12	12	12

(*c*) Face type γ

I	A	A′	B	B′	C	C′	D	D′	E	E′
1	1	1	1	1	1	1	1	1	1	1
2	3	7	2	2	2	2	2	2	11	6
3	7	2	4	8	3	3	3	3	3	3
4	4	4	8	3	5	9	4	4	4	4
5	5	5	5	5	9	4	6	10	5	5
6	6	6	6	6	6	6	10	5	2	11
7	2	3	7	7	7	7	7	7	7	7
8	8	8	3	4	8	8	8	8	8	8
9	9	9	9	9	4	5	9	9	9	9
10	10	10	10	10	10	10	5	6	10	10
11	11	11	11	11	11	11	11	11	6	2
12	12	12	12	12	12	12	12	12	12	12

(*d*) Face type δ

I	A	A′	B	B′	C	C′	D	D′	E	E′
1	1	1	1	1	1	1	1	1	1	1
2	2	2	2	2	2	2	2	2	2	2
3	3	3	3	3	3	3	3	3	3	3
4	4	4	4	4	4	4	4	4	4	4
5	5	5	5	5	5	5	5	5	5	5
6	6	6	6	6	6	6	6	6	6	6
7	8	12	7	7	7	7	7	7	12	11
8	12	7	9	12	8	8	8	8	8	8
9	9	9	12	8	10	12	9	9	9	9
10	10	10	10	10	12	9	11	12	10	10
11	11	11	11	11	11	11	12	10	7	12
12	7	8	8	9	9	10	10	11	11	7

Table 2 Vertex permutation matrices for the anticubeoctahedral pathway: I = identity

I	A	A′	B	B′	C	C′	D	D′	E	E′
1	1	1	1	1	1	1	1	1	1	1
2	5	4	3	2	4	3	6	5	2	6
3	10	5	8	3	9	4	11	6	7	2
4	6	2	4	5	5	6	2	3	3	4
5	2	3	5	6	6	2	3	4	4	5
6	4	8	2	11	3	7	5	9	6	10
7	9	10	7	8	8	9	10	11	11	7
8	12	6	12	4	12	5	12	2	12	3
9	11	7	9	10	10	11	7	8	8	9
10	3	12	6	12	2	12	4	12	5	12
11	8	9	11	7	7	8	9	10	10	11
12	7	11	10	9	11	10	8	7	9	8

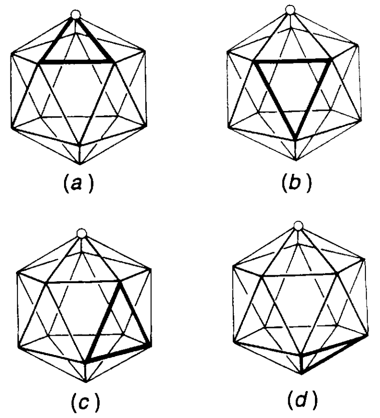

(*a*) (*b*) (*c*) (*d*)

Fig. 4 Face types in t.f.r. mechanisms: (*a*) α, (*b*) β, (*c*) γ, and (*d*) δ

Of course, mechanistic speculation is pointless unless it can explain experimental observations. The first of these is that 1,2- $\longrightarrow$ 1,7- and 1,7- $\rightleftharpoons$ 1,12-dicarbadodecaborane at higher temperatures. If we consider single t.f.r. mechanisms (see Fig. 4), then there are 40 possible operations [20 faces × 2 possible directions of rotation, see Table 1 (*a*)–(*d*)]. In order to make use of Tables 1 and 2, choose a vertex from I (identity), say 2, and follow it around the matrix. For example, in Table 2, mode A, vertex 2 ends up at position 5. Hence $x,2,y \longrightarrow x',5,y'$ and so on.

For a 1,2-substituted dicarbadodecaborane, 5/8 (25/40) of all operations retain 1,2 substitution and 3/8 convert 1,2 to 1,7. For a 1,7-substituted icosahedron, 7/20 of all operations retain a 1,7 configuration, 7/40 convert 1,7 to 1,12 and, most importantly, the majority (19/40) change 1,7 back to 1,2. For a 1,12-substituted icosahedron, 1/2 stay as 1,12 and 1/2 revert back to 1,7 substitution.

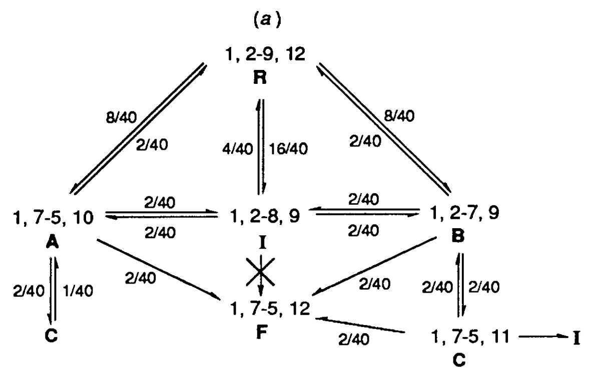
If we now consider the anticubeoctahedral route, there are 10 modes of operation (5 sets of d.s.d.s × 2 possible directions of rotation). For a 1,2 configuration, 1/5 of operations change 1,2 to 1,7; the rest retain 1,2 substitution (see Table 2). For a 1,7 configuration, 3/5 of operations retain 1,7 substitution, 1/5 convert 1,7 to 1,12 and only 1/5 revert back to 1,2. All operations convert 1,12- to 1,7-dicarbadodecaborane, which might explain why it is so difficult to generate the former by thermolysis of the latter and why decomposition is so extensive. The forcing conditions needed to favour 1,7 $\longrightarrow$ 1,12 over 1,12 $\longrightarrow$ 1,7 may be perilously close to the breakdown temperature of the carborane.

Isomerisation information is available for a number of icosahedral carborane species. We shall apply single t.f.r. and anticubeoctahedral operations to these species and compare our results with those observed.

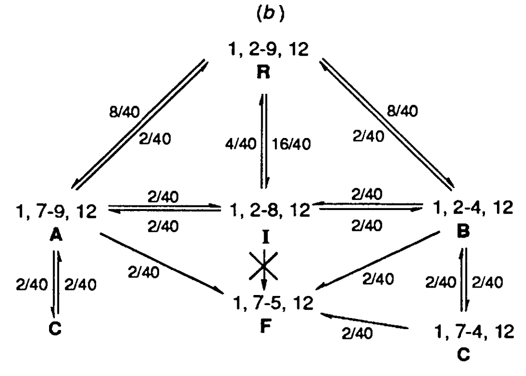
(1) *2,7-(μ-2-oxopropane-1,3-diyl)-1,2-dicarbadodecaborane*.—Wu and Jones' bridged species 2,7-(μ-2-oxopropane-1,3-diyl)-**1**[7] can be thought of as a 1,2,7-substituted carborane, where the short bridge spanning C^2 and B^7 forces them to remain adjacent. This automatically renders some rearrangement modes inoperable. Additionally, modes which place the two carbon atoms in a 1,12 configuration, or revert from a 1,7 configuration of C atoms to a 1,2 arrangement, are disallowed. Hence, the parent carborane **1** has 32 available t.f.r. modes and eight anticubeoctahedral modes, leading to differing proportions of species **1**–**5**.* Exact calculations of these proportions

---

* Compounds **2**–**5** are the 2,3-, 7,12-, 7,8- and 7,2-isomers of **1**.



Plus others (see below)



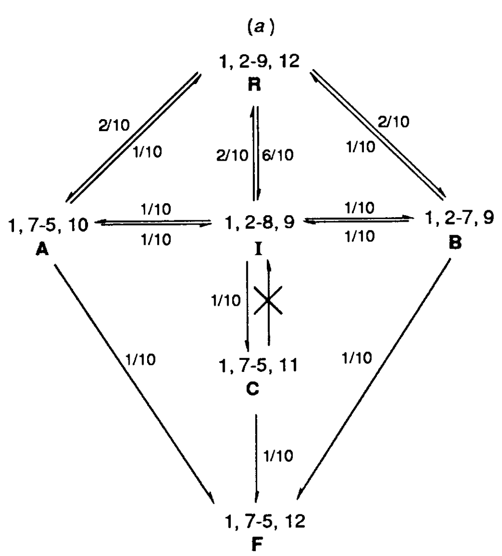
Plus intermediates which do not directly lead to F:
1,2–7,12 1,7–2,12 1,7–8,12 1,2–3,12

1,2–8,12 ≡ 1,2–8,9
1,2–4,12 ≡ 1,2–7,9
1,2–3,12 ≡ 1,2–3,9
1,7–2,12 ≡ 1,7–2,5
1,7–9,12 ≡ 1,7–5,10
1,2–7,12 ≡ 1,2–5,9
1,7–8,12 ≡ 1,7–5,6
1,7–4,12 ≡ 1,7–5,11

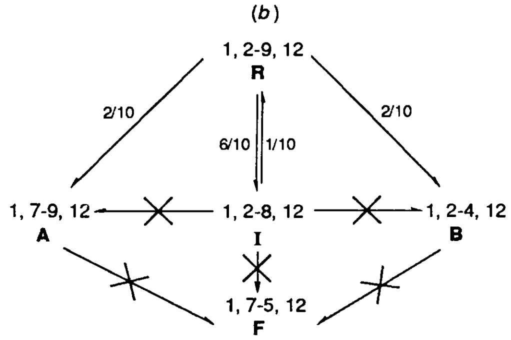
Scheme 1 Products of rearrangement of 9,12-dichloro-1,2-dimethyl-1,2-dicarbadodecaborane *via* t.f.r.

are available as SUP 56987 or may be derived from Tables 1 and 2. Similar arguments apply to the further rearrangements of **2**–**5**.

The relative yields for the rearrangement of species **5** *via* t.f.r. or anticubeoctahedral mechanisms are given in Tables 3 and 4 respectively. The same starting number of units of **1** were used for each method. A similarity in distributions is immediately apparent and not unexpected. For simplicity, weighting of individual modes has not been employed, so neither distribution fits the observed data perfectly, in that they both produce more species **4** than observed experimentally. The anticubeoctahedral mechanism might be deemed the more favourable because it depletes **1** and **2** more rapidly than does the t.f.r., in line with experiment. Both mechanisms account for the increased turnover of mixtures of **1** and **2** but, again, the anticubeoctahedral mechanism is more efficient; 2/8 of its modes convert **2** into **5** compared with 1/8 of t.f.r. modes. Additionally, the anticubeoctahedral mechanism produces no species **4** from **2**, whereas the t.f.r. does (1/16 of available modes).



Plus other intermediates which do not lead directly to F:
1,2–9,5 1,2–3,9 1,7–5,6 1,7–2,5



Plus other 1,2-*y*,12 and 1,7-*y*,12 species;
1,*x*-*y*,12 cannot sustain the 1,12 relationship through the anticubeoctahedral route if vertex 1 is the point of reference

1,2–8,12 ≡ 1,2–8,9
1,2–4,12 ≡ 1,2–7,9
1,2–3,12 ≡ 1,2–3,9
1,7–4,12 ≡ 1,7–5,11
1,2–7,12 ≡ 1,2–5,9
1,7–9,12 ≡ 1,7–5,10

Scheme 2 Products of rearrangement of 9,12-dichloro-1,2-dimethyl-1,2-dicarbadodecaborane *via* anticubeoctahedral pathways

(2) 9,12-*Dichloro*-1,2-*dimethyl*-1,2-*dicarbadodecaborane*.—The rearrangement of this tetrasubstituted species, investigated by Hart and Lipscomb,[23] is not straightforward. Part of the problem lies in the distribution of the substituents on the original carborane, each Cl^- being *ortho* to the other Cl, *meta* to one CMe group and *para* (*i.e.* antipodal) to the other. With the possible exception of pure d.s.d., any rearrangement process will initially destroy at least one of these relationships leading to a large number of products. Equally, the proposed final product 5,12-dichloro-1,7-dimethyl-1,7-dicarbadodecaborane, has a very symmetric pattern of substitution which retains a $\mathrm{Cl}^- \cdots \mathrm{CMe}$ antipodal relationship.

There is also a slight complication with regard to the numbering of the vertices in the intermediate stages. For example, one of the initial products of the rearrangement has been labelled 8,9-dichloro-1,2-dimethyl-1,2-dicarbadodecaborane, but it could equally be labelled 8,12-dichloro-1,2-dimethyl. The difference may appear to be semantic, but it has an effect on the distribution of products for both t.f.r. and anticubeoctahedral processes. The results of these conversions appear in Schemes 1 and 2. It is interesting that exactly the same intermediates are responsible for converting the 1,2-9,12 species **R** into the 1,7-5,12 species **F** for both processes. The conversion rate is again higher for the anticubeoctahedral route, though it

Table 3 Product distribution for the rearrangement of the 2,7-bridged 1,2-dicarbadodecaborane **1** by t.f.r.

1	**2**	**3**	**4**	**5**
5.25	1	0.5	1	0.25
3.57	1.34	0.75	1.56	0.77
2.51	1.37	0.86	1.90	1.35
1.82	1.26	0.90	2.12	1.89
1.35	1.09	0.91	2.27	2.37
1.02	0.92	0.90	2.38	2.77

Table 4 Product distribution for the rearrangement of the compound **1** by the anticubeoctahedral mechanism

1	**2**	**3**	**4**	**5**
4	2	1	1	0
2.5	2	0.9	1.9	1.7
1.75	1.63	1.07	2.11	1.44
1.28	1.25	1.06	2.42	1.98
0.95	0.95	1.13	2.58	2.38
0.71	0.71	1.15	2.76	2.66

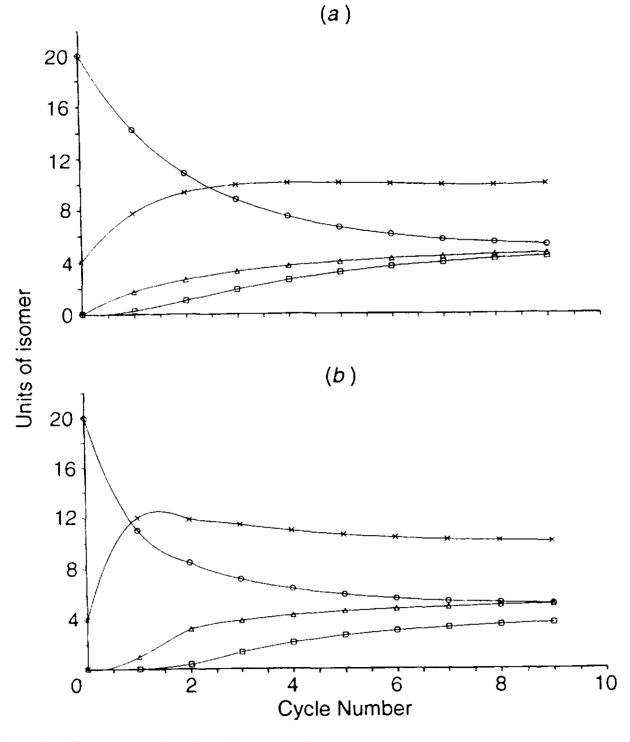


Fig. 5 Product distribution profiles for the rearrangement of 1,2-dicarba[3-^{10}B]dodecaborane *via* (*a*) t.f.r. and (*b*) anticubeoctahedral pathways. Vertices: 3* (○), 4* (×), 8* (△) and **12*** (□)

must again be stressed that no weighting scheme has been applied.

(3) 1,2-*Dicarba-*[3-^{10}B]*dodecaborane*.—Thermolysis of this carborane at 350 °C results in scrambling of the ^{10}B isotopic distribution, without isomerisation of the *ortho*-carborane.[9] Four vertex types exist, due to the symmetry of the parent carborane. Vertices 4,5,7 and 11 (4*) are equivalent, as are 3 and 6 (3*), 8 and 10 (8*), 9 and 12 (12*). The distribution of ^{10}B between these four vertex types was monitored by Edvenson and Gaines[9] over time and the reaction profile obtained was compared with calculated reaction profiles for a *nido* intermediate pathway and a cubeoctahedral intermediate with triangular face rotation. Neither mechanism fitted the observed data particularly well.

Similar distribution calculations, carried out for t.f.r. and anticubeoctahedral intermediate routes, produce the reaction profiles shown in Fig. 5. Differences in calculation procedure account for the different figures associated with the profiles. The shapes are the important bits of information. The distributions generated by t.f.r. appear unsatisfactory on a number of points. The rate of growth of vertices 4* and the decline of 3* are too slow and too much 8* is produced in the early stages. The anticubeoctahedral profile appears to fit much better: the rise of 4* and decline of 3* are much more marked. However, the amount of 8* produced is, again, too high in comparison with 3*, with a noticeable 'surge' in the early stages. In both cases, the proportions of 3*:4*:8*:12* settle out to the expected 2:4:2:2.

(4) 9-*Bromo-*1,2-*dicarbadodecaborane*.—We have deliberately left aside the rearrangement of this compound until now, even though it should chronologically have appeared much earlier, because it represents one of the few species to have been investigated through the full range of isomerisations, from *ortho* (1,2) to *para* (1,12) moieties. Initially, in 1967, Lipscomb and co-workers[24] described its isomerisation to a range of *ortho* (1,2) and *meta* (1,7) products. Mechanisms based on rotations of pentagonal prisms were rejected in favour of cubeoctahedral routes, with and without face rotations. The authors found that the observed distribution of products could only be approached by theory if specific weighting schemes were applied to some modes of the cubeoctahedral/face rotation mechanism, dependent upon the *ortho* isomer in question. We have also put constraints onto our system of t.f.r. or anticubeoctahedral mechanisms, assuming that the starting species is pure 9-bromo-1,2-dicarbadodecaborane. As far as we are aware, no mechanism yet postulated can convert a single *ortho* isomer into the full range of *meta* isomers in one step, so we have allowed *ortho–ortho* isomerisation to take place before conversion into *meta* isomers. No *meta–meta* conversion was observed in the original study and is precluded here.

For the *ortho* isomers the same system of vertex labelling has been employed as for the previous section. Hence, the products 9-*o*, 8-*o*, 4-*o* and 3-*o* are formed (see SUP 56987). For the *meta* isomers, vertex 5 is equivalent to 12 (antipodal to 7 and 1 respectively), hence 5-*m*, vertices 9 and 10 are equivalent (9-*m*), 2 and 3 are equivalent (2-*m*) and 4, 6, 8 and 11 are equivalent (4-*m*).

For both t.f.r. and anticubeoctahedral mechanisms, at least half of 9-*o* stays as 9-*o* upon *ortho–ortho* conversions (20/32 and 4/8 respectively). In the anticubeoctahedral mechanism there is a slight complication in that 1,2,9 species have different isomerisation patterns to 1,2,12, so the average of the two distributions was used (see SUP 56987). Neither mechanism produces 3-*o* directly from 9-*o*, but the anticubeoctahedral route produces more 8-*o* (3/8 of 9-*o*, *cf.* 8/32 for t.f.r.). Hence the t.f.r. mechanism relies more heavily on the presence of 9-*o* for the distribution of *meta* isomers, whereas the anticubeoctahedral distribution of *meta* isomers is also reliant on the amount of 8-*o*.

The distributions of *ortho* and *meta* isomers created by both t.f.r. and anticubeoctahedral mechanisms are given in Table 5. We have assumed that the production of *meta* isomers is the driving force, as it should theoretically be, and that all *ortho* isomers will rearrange at the same rate. In reality this may not be the case. However, the agreement between our unweighted, calculated figures and those derived experimentally by Lipscomb after 210 min at 425 °C is reasonable, except that both are significantly high in 4-*o* and low in 4-*m*. This would appear to indicate that 4-*o* converts more rapidly than the other isomers and, indeed, it and its products significantly contribute to the formation of 4-*m* (see SUP 56987).

Hart and Lipscomb[25] went on, in 1969, to describe the rearrangement of 9-bromo-1,7-dicarbadodecaborane, 9-*m*. All possible *meta* isomers were found to be formed, along with the *para* isomer (*p*). We have modelled the *meta* isomer system, following similar rules to those employed above. Again, *meta–meta* isomerisation was allowed prior to *meta–para*. In this case

Table 5 Rearrangement product distributions of 9-bromo-1,2-dicarbadodecaborane

	9-*o*	8-*o*	4-*o*	3-*o*	9-*m*	5-*m*	4-*m*	2-*m*
(*a*) t.f.r.								
	100	0	0	0	0	0	0	0
	50	20	10	0	10	10	0	0
	29.50	18	14.50	2	17	15.50	3	0.50
	19.08	13.75	14.93	3.45	21.75	19.18	6.45	1.43
(*b*) Anticubeoctahedral								
	100	0	0	0	0	0	0	0
	40	30	10	0	10	10	0	0
	25	20	17	2	16	14	5	0
	16	14.90	16.10	4.20	21.50	16.50	10.40	0.40
(*c*) Experimental								
t/h								
	100	0	0	0	0	0	0	0
0.5	68	21	3	0	3	4	1	0
1.0	21	23	8	1	6	7	3	0
3.5	20	14	8	4	15	18	17	4

Table 6 Rearrangements of *meta*- and *para*-bromocarboranes by t.f.r.

	p	2-*m*	4-*m*	5-*m*	9-*m*
(*a*) 9-*m*					
	0	0	0	0	100
1st cycle	12.50	0	25	12.50	50
5th cycle	19.86	12.87	32.03	17.27	18.01
(*b*) 5-*m*					
	0	0	0	100	0
1st	12.50	0	25	50	12.50
5th	19.86	12.87	32.03	18.01	17.27
(*c*) 4-*m*					
	0	0	100	0	0
1st	12.50	12.50	50	12.50	12.50
5th	19.86	16.01	32.13	16.01	16.01
(*d*) 2-*m*					
	0	100	0	0	0
1st	12.50	62.50	25	0	0
5th	19.86	22.41	32.03	12.87	12.87
(*e*) *p*					
	100	0	0	0	0
1st	50	10	20	10	10
5th	20.60	15.89	31.77	15.89	15.89

Table 7 Rearrangements of *meta*- and *para*-bromocarboranes by the anticubeoctahedral route

	p	2-*m*	4-*m*	5-*m*	9-*m*
(*a*) 9-*m*					
	0	0	0	0	100
1st cycle	25	0	12.50	12.50	50
5th cycle	33.30	11.18	24.28	16.92	14.31
(*b*) 5-*m*					
	0	0	0	100	0
1st	25	0	25	50	0
5th	33.31	12.10	25.13	17.38	12.10
(*c*) 4-*m*					
	0	0	100	0	0
1st	25	12.50	37.50	12.50	12.50
5th	33.31	12.94	24.82	16.01	12.94
(*d*) 2-*m*					
	0	100	0	0	0
1st	25	50	25	0	0
5th	33.31	15.22	25.13	14.26	12.10
(*e*) *p*					
	100	0	0	0	0
1st	50	10	20	10	10
5th	33.41	12.95	24.79	15.93	12.95

Table 8 Experimental distributions of *meta*- and *para*-bromocarboranes

t/h	*p*	2-*m*	4-*m*	5-*m*	9-*m*
(*a*) 9-*m*					
1	2	3	16	0	79
5	8	15	40	5	31
36	48	9	19	16	8
(*b*) 5-*m*					
5	24	6	14	52	5
55	48	8	19	18	8
(*c*) 4-*m*					
1	4	23	58	4	12
5	16	16	42	10	18
48	46	8	21	17	8
(*d*) 2-*m*					
1	4	40	51	2	3
5	16	16	42	8	17
55	48	9	19	16	8
(*e*) *p* Chloro-					
5	79	4	6	9	2
36	48	4	18	17	9
(*f*) *p* Fluoro-					
49	47	13	20	16	4

there is only one *para* isomer, which was also allowed to revert back to *meta*, in line with experiment.

This time a complication arises in the anticubeoctahedral mechanism for 1,12,*n para* species. These rearrange differently from *para* species with alternative antipodal pairs, *e.g.* 2,9,*n*. Therefore, the average distribution of 1,12,*n* and the five alternative settings was used (see SUP 56987). We have assumed that all conversions will occur at the same rate when, in reality, *meta–para* should be the driving force and the reverse direction disfavoured.

The results of our unweighted calculations, along with the experimental results published by Lipscomb, appear in Tables 6–8. There is a noticeable difference between the theoretical isomer distributions, with the anticubeoctahedral mechanism producing superior results. As with the experimental results, the final isomer distributions are remarkably self-consistent and virtually independent of the identity of the initial isomer used. This is the first time there has been a clear difference in product distributions between the t.f.r. and anticubeoctahedral calculations. Both produce a shortfall in the *para* isomer, but even if the *para–meta* conversion rate were slowed, the pattern of *meta* isomers would not alter significantly in either case. It would certainly not be enough, in itself, to bring the t.f.r. results in line with the anticubeoctahedral.

The calculations we have made have not taken account of electronic effects or symmetry effects arising from the use of more than one heteroatom type. For example, we have treated all 1,12,*n*-substituted icosahedra as identical, regardless of the identity of each of the three substituents/heteroatoms involved. Owing to this, we have no immediate response to the variation in isomer distributions on going from chloro- to fluoro-1,12-dicarbadodecaborane.

Table 9 Distribution of *meta* and *para* products from the rearrangement of 9-chloro-1-carba-7-phosphadodecaborane

	*m*9	*m*12	*m*8	*m*5	*m*4	*m*2	*p*7	*p*2
(*a*) t.f.r.								
	100	0	0	0	0	0	0	0
1st cycle	50	6.25	12.50	6.25	12.50	0	6.25	6.25
5th cycle	16.28	7.55	15.55	9.68	17.91	13.16	9.63	10.22
10th cycle	14.23	6.62	15.16	9.44	18.36	16.18	9.48	10.51
(*b*) Anticubeoctahedral								
	100	0	0	0	0	0	0	0
1st	50	12.50	0	0	12.50	0	12.50	12.50
5th	18.10	14.08	9.93	5.33	9.72	11.50	16.05	15.28
10th	16.90	13.83	10.40	5.37	9.36	12.73	16.39	15.02
(*c*) Experimental								
t/h								
4	78	2	6	2	2	3	3	5
8	60	2	8	3	5	7	5	10
Final	9	5	8	10	12	8	19	30

(5) *Chlorophosphacarborane.*—n-*Chloro*-1,2(7/12)-*carbaphosphadodecaborane*. This carborane species, studied by Wong and Lipsomb,[26] contains two different heterovertices in the cage, as well as a chloride substituent on one of the boron vertices. The effect of the lowered symmetry is to increase the number of distinct *ortho*, *meta* and *para* isomers. For example, two forms of *para* isomers exist; one with the chloro substituent adjacent to the CH vertex and one with Cl adjacent to the P vertex. Hence the rearrangement distributions of isomers become more finely divided and the calculations more complex. In our calculations on the chlorophosphacarboranes the CH vertex is always given the lower vertex number, usually (but not always) 1, with the P vertex *ortho*, *meta* or *para* to it. Hence 3-chloro-1-carba-2-phosphadodecaborane would be denoted as *o*3 and 3-chloro-2-carba-6-phosphadodecaborane would transcribe to *m*4.

The rearrangements of both *ortho*- and *meta*-phosphacarboranes were reported. Starting with the *ortho* species, there are six possible isomers, vertices 8 and 10 are equivalent (*o*8), 7 and 11 are equivalent (*o*7), 4 and 5 are equivalent (*o*4), 3 and 6 are equivalent (*o*3), but 9 and 12 are not (*o*9 and *o*12). These isomers have six *meta* counterparts, *m*9, *m*12, *m*5, *m*8, *m*4, *m*2, and two *para* (*p*7 and *p*12).

When the rearrangement of *o*9 was examined, the product mixture was found to consist largely (77%) of *m*9 with 13% *m*12 and 10% of other *meta* isomers.[26] No discernible *ortho* residues remained, although *o*8 had been detected during the course of the experiment. Therefore, *ortho–meta* conversion is the overriding reaction.

If we consider the product distributions formed from *o*12 by t.f.r. and anticubeoctahedral rearrangements, quite different outcomes are found. As before, *o*12 anticubeoctahedral rearrangements were treated as the average of 1(C), 2(P), 12(Cl) and five alternative settings, *e.g.* 2(C), 3(P), 9(Cl). The t.f.r. mechanism converts *o*12 into *m*9 and *m*12 in 1 : 1 ratio, whereas the anticubeoctahedral ratio is 7:5. These *ortho–meta* conversions are the major reaction path. The small amount of *ortho–ortho* conversions accounts for the appearance of *o*8 and then the trace amounts of other *meta* isomers. The amount of *o*8 produced (4%) during the course of the reaction should not significantly alter the *m*9 : *m*12 product ratios, slightly favouring the anticubeoctahedral route.

The rearrangement of *m*9 is altogether more complicated, as it incorporates *meta–meta*, *meta–para*, *para–para* and *para–meta* conversions (see SUP 56987). The theoretical product distributions for t.f.r. and anticubeoctahedral rearrangements are given, along with the experimental figures, in Table 9. Both sets of theoretical figure are disappointing, but mainly due to the fact that *para* rearrangements play a much smaller role than we had assumed. In that respect the anticubeoctahedral route would be favoured, since it produces more *para* products than does t.f.r. from the unweighted scheme (31 compared with 20%). We do not consider weighting schemes, as it should be possible to contrive a near 'fit' of most product distributions eventually. Instead, we prefer to let the unweighted calculations stand or fall on their own (de)merits.

Conclusion

The last example clearly highlights the pitfalls of theoretically modelling experimental data. Oversimplification of the problem is always something to beware, but there are also problems with the data itself. In order to obtain more detailed data, under reasonable conditions, the symmetry of the icosahedral moiety must be progressively lowered by use of labels, substituents and heterovertices which may be 'tracked' by a standard physical technique. However, in doing so, the steric and electronic composition of the species is also changed. Thus, in the above case a BH vertex is replaced by a bare P atom with accessible d orbitals.

Eventually, it would have to be argued that the complex under examination is so far removed from the original dicarborane species that any rearrangement mechanism derived from the hybrid should not simply be applied to the parent. It is for that very reason we have not included the rearrangements of any metallacarboranes in this paper.

What we have done is to stand back and appraise the t.f.r. and anticubeoctahedral mechanisms in terms of what must happen to the icosahedron as it follows each rearrangement pathway. The calculated vertex permutation patterns were then applied to recorded experimental data. The overall results for *ortho–meta* transformations are quite similar between the two mechanisms. This is not surprising: as we pointed out earlier, the anticubeoctahedral mechanism may be seen as two concerted t.f.r.-type rotations, therefore yielding similar results. However, the differences between the two mechanisms show much more clearly in *meta*/*para* transformations, where the advantage clearly lies with the anticubeoctahedral mechanism.

It has been mooted that different mechanisms may be employed in going from *ortho–meta* to *meta–para* transformations. This may be true, but we can see no good reason why. Chemistry is not by nature capricious, merely ingenious.

References

1 D. Grafstein and J. Dvorak, *J. Inorg. Chem.*, 1963, **2**, 1123.

2 A. Kaczmarcyzk, R. D. Dobrott and W. N. Lipscomb, *Proc. Natl. Acad. Sci. USA*, 1962, **48**, 729.

3 S. Papetti and T. L. Heying, *J. Am. Chem. Soc.*, 1964, **86**, 2295.

4 V. I. Stanko, V. A. Brattsev and Yu. V. Gol'tyapin, *Zn. Obshch. Khim.*, 1969, **39**, 2686.

5 E. L. Muetterties and W. N. Knoth, *Polyhedral Boranes*, Marcel Dekker, New York, 1968, p. 70.

6 L. I. Zakharkin and V. N. Kalinin, *Dokl. Akad. Nauk. SSSR*, 1966, **169**, 590.

7 S.-H. Wu and M. Jones, *J. Am. Chem. Soc.*, 1989, **111**, 5373.

8 H. S. Wong and W. N. Lipscomb, *Inorg. Chem.*, 1975, **14**, 1350.

9 G. M. Edvenson and D. F. Gaines, *Inorg. Chem.*, 1990, **29**, 1210.

10 M. J. Altfield, J. A. K. Howard, A. N. de H. Jeffs, C. H. Nunn and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 2219.

11 N. Carr, D. F. Mullica, E. L. Sappenfield and F. G. A. Stone, *Organometallics*, 1992, **11**, 3697.

12 B. F. G. Johnson, *J. Chem. Soc., Chem. Commun.*, 1976, 703; B. F. G. Johnson, C. E. Anson, D. Braga, A. W. Bott, R. E. Benfield and E. A. Marseglia, *J. Chem. Soc., Chem. Commun.*, 1988, 889; B. F. G. Johnson and A. W. Bott, *J. Chem. Soc., Dalton Trans.*, 1990, 2437.

13 D. J. Wales and A. J. Stone, *Inorg. Chem.*, 1987, **26**, 3845.

14 D. J. Fuller and D. L. Kepert, *Inorg. Chem.*, 1982, **21**, 163.

15 M. J. Dewar and M. L. McKee, *Inorg. Chem.*, 1978, **17**, 1569.

16 B. M. Gimarc, D. S. Warren, J. J. Ott and C. Brown, *Inorg. Chem.*, 1991, **30**, 1598.

17 M. F. Hawthorne, K. P. Callahan and R. J. Wiesema, *Tetrahedron*, 1974, **30**, 1795.

18 D. R. Baghurst, R. C. B. Copley, H. Fleischer, D. M. P. Mingos, G. O. Kyd, L. J. Yellowlees, A. J. Welch, T. R. Spalding and D. J. O'Connell, *J. Organomet. Chem.*, 1993, **447**, C64.

19 D. J. Wales and D. M. P. Mingos, *Polyhedron*, 1989, **8**, 1933.

20 D. J. Wales, D. M. P. Mingos and L. Zhenyang, *Inorg. Chem.*, 1989, **28**, 2754.

21 C. G. Salentine and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1975, **97**, 426, 428.

22 D. F. Dustin, G. B. Dunks and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1973, **95**, 1109.

23 H. V. Hart and W. N. Lipscomb, *Inorg. Chem.*, 1973, **12**, 2644.

24 H. D. Kaesz, R. Baur, H. A. Beall and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1967, **89**, 4218.

25 H. V. Hart and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1969, **91**, 771.

26 H. S. Wong and W. N. Lipscomb, *Inorg. Chem.*, 1975, **14**, 1350.

Received 20*th September* 1993; *Paper* 3/05643K