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An assessment of the intercarbon stretching phenomenon in C-substituted “*pseudocloso*” $\{3,1,2\text{-}RuC_2B_9\}$ metalladicarbaboranes

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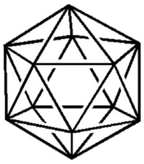
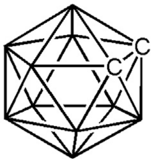
DFT calculation of cluster shapes and their related boron-vertex ^{11}B nuclear shieldings for a range of substituted 12-vertex metalladicarbaborane cluster compounds $[3,1,2\text{-}R_2\text{-}3\text{-}(\eta^6\text{-}C_6H_6)\text{-}3,1,2\text{-}RuC_2H_9H_9]$ confirms that the array of experimentally observed C—C distances in the group of progressively more open *closo*, ‘*semipseudocloso*’ and ‘*pseudocloso*’ clusters results from the inherent propensity of the $[(\eta^6\text{-}C_6H_6)RuC_2H_9H_9R_2]$ cluster to occupy, *in the absence of steric drivers*, either *closo*-structured *or* so-called ‘*pseudocloso*’-structured fundamental local minima on the overall potential energy surface. The shallow profiles of the potential wells, together with the electronic and steric influences of substituents on the cluster carbon vertices, alter the relative energies of the *closo* and ‘*pseudocloso*’ minima, and alter the energy profile between them, thereby accounting for the observed variations in the distances in the crystallographically measured C—C separations. We propose that these differ fundamentally due to either the *closo* or ‘*pseudocloso*’ configuration being electronically preferred, with some instances of the ‘*pseudocloso*’ configuration being compressed towards *closo* by packing forces, or stretched further beyond ‘*pseudocloso*’ by steric effects of bulky substituents on carbon. This contrasts with one view postulated in the literature which holds that steric repulsion between the C-bound substituents is the sole driver that forces an inherently fundamental *closo* cluster to open into an anomalous ‘*pseudocloso*’ configuration. In two reported cases, the cluster flexibility is evident in solution and, in these cases, GIAO calculation of the ^{11}B chemical shieldings explains the measured ^{11}B chemical shifts, which can be interpreted in terms of the dynamic interchange of the *closo* and ‘*pseudocloso*’ species. A currently held view is that the ‘weighted average’ of ^{11}B chemical shifts reflects the inherent degree of electronic ‘*pseudocloso*’ character in a particular cluster can therefore often equally be rationalised in terms of lability between similarly stable fundamentally *closo* and ‘*pseudocloso*’ forms.

1. Introduction

In the early 1970s Wade and others developed rules that correlated the relationships between the shapes and sizes of clusters of atoms in molecules and the numbers of electrons associated with the intracluster bonding [1–4]. A key cluster shape was the twelve-vertex icosahedron — as represented by the regular icosahedral framework of the $[closo\text{-}B_{12}H_{12}]^{2-}$ anion (schematic **I**) and by the shapes of its closely related congeners, such as neutral $[closo\text{-}1,2\text{-}C_2B_{10}H_{12}]$ (schematic **II**) of which the structure deviates from regular icosahedral symmetry principally because of the smaller sizes of the carbon *versus* the boron atoms.



I



II

Transition-element centres that can be regarded as making contributions to cluster bonding mimicking that of a {BH(*exo*)} cluster vertex, such as $\{Co(\eta^5\text{-}C_5H_5)\}$ and $\{Ru(\eta^6\text{-}C_6H_6)\}$, can also figure as cluster components, and so species such as $[(\eta^5\text{-}C_5H_5)CoC_2B_9H_{11}]$ and $[(\eta^6\text{-}(C_6H_6)RuC_2B_9H_{11})]$ also exhibit icosahedral cluster geometries (schematic cluster structure **III**) [5,6]. These deviate from the regular icosahedral symmetry of $[B_{12}H_{12}]^{2-}$ because of the larger sizes of the metal atoms as well as the smaller sizes of the carbon atoms. In the mid-1970s it was found

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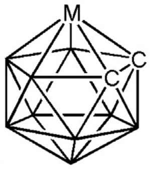
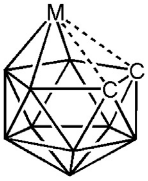
that the incorporation of transition-element centres such as $\{Pt(PMe_2Ph)_2\}$ produce structures that are more open than that of a triangular-faced icosahedron. These deviate from icosahedral in that the metal-to-carbon distances now are much longer, and can be regarded as being beyond a range associated with strong intracluster bonding interaction (Schematic **IV**). Such 'slipped' species have received detailed analysis from Mingos and co-workers [7,8] and elegant experimental further elucidation from Wallbridge and co-workers [9–13]. In simplistic terms the 'slippage' of cluster opening arises because these types of metal centre have a tendency to bind to the remainder of the cluster principally by the use of two orbitals rather than the three utilized by {CH}, $\{Co(\eta^5\text{-}C_5H_5)\}$ and $\{Ru(\eta^6\text{-}C_6H_6)\}$, and the metal-to-cluster bonding connectivity is correspondingly diminished [14].

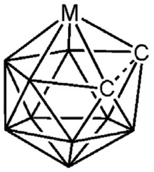


III

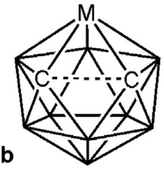


IV

More recently, a different type of distortion of the basic icosahedral $\{closo\text{-}3,1,2\text{-}MC_2B_9\}$ geometry **III** has become increasingly exemplified, largely as a result of work by Welch and co-workers [15,16] and by Chizhevsky and coworkers [17–20] This is shown, for example, by certain C-substituted derivatives of $[3\text{-}(\eta^6\text{-}MeC_6H_4^{iso}Pr)\text{-}closo\text{-}3,1,2\text{-}RuC_2B_9H_{11}]$, in which the intercarbon distance is observed to be 'stretched' in crystallographically-determined solid-state structures to distances beyond those normal for intracluster intercarbon separations (Schematics **Va** and **Vb**). In this context, such 'normal' cluster intercarbon separations are exemplified by values of around 1.63 Å, as exhibited by $[3\text{-}(\eta^6\text{-}C_6H_6)\text{-}closo\text{-}3,1,2\text{-}RuC_2H_9H_{11}]$ (Schematic **III**) [5], and around 1.62 Å as exhibited by $[closo\text{-}1,2\text{-}C_2B_{10}H_{12}]$ itself (Schematic **II**) [21].

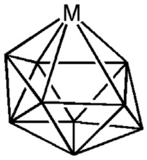


Va

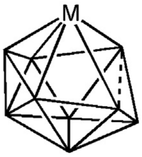


Vb

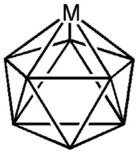
We have long been interested in this type of cluster-connectivity, for example in the stretching of the closed ten-vertex geometry **VI** of certain ostensibly *closo* $\{IrB_9\}$ species to give so-called '*isonido*' ten-vertex geometries **VII** [22,23] and in the similar stretchings of ostensibly *closo* nine-vertex geometries **VIII** to give nine-vertex '*isonido*' geometries **IX** [24–26]. A comprehensive investigation of these ten-vertex and nine-vertex systems is, however, severely inhibited by the dearth of suitable sets of examples and the current experimental difficulty of generating such suitable examples. However, the nice experimental delineations by Welch and Chizhevky of the **III** *versus* **V** phenomenon in the much better represented twelve-vertex *closo*-type system, and the consequently greater library of compounds available, together with the contemporary availability of faster computing for reliable DFT calculations of structure, energetics, and magnetic shielding of nuclei, now permit a usefully more meaningful investigation of this stretching phenomenon in formally *closo* twelve-vertex, $\{closo\text{-}3,1,2\text{-}MC_2B_9\}$ system.



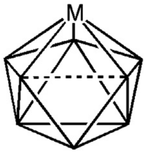
VI



VII



VIII



IX

The cluster opening observed in such species can be regarded as an example of 'skeletal disobediency' [27], in that the twelve-vertex geometric structures in question do not conform with the straightforward *closo*/*nido*/*arachno* Williams–Wade geometrical and electron-counting paradigm [1–4], but in that they exhibit a cluster opening from pure deltahedral *closo*, which may be regarded as anomalous. In this last regard, two related distinct extremes of concept may be invoked, which may be described as cluster flexibility on one hand and cluster fragility on the other. In the first of these, arbitrarily dubbed 'flexibility', a change in cluster constituent or substituent may induce a distortion of the cluster geometry – a shift in a single thermodynamic, structural, and electronic minimum, as represented schematically in **Xa** → **Xb** (Fig. 1, uppermost diagram). In these schematics (and in schematics **XI** → **XII** mentioned shortly below) the horizontal dimension is a structural coordinate, and the vertical an energy coordinate. If the energy minima are shallow, then an additional aspect of cluster flexibility about the minima can be induced by perturbations such as intermolecular and intramoleclar packing forces in the solid state (hatched arrows in Fig. 1 upper). In the second concept, a cluster structure may be geometrically and electronically 'fragile' in that a change in cluster constituents or substituent or, in the solid state, packing forces, will induce a catastrophic change to another geometrical and electronic type – a shift in the relative energies of two geometrical and electronic minima, as represented in schematics **XI** → **XII** in Fig. 1 (lower). In this latter case, with approximately equal energies for **XI** and **XII**, and a low activation barrier **A**, fluxionality may result in solution, making the 'flexibility' and 'fragility' categories of behaviour difficult to distinguish. As the barrier decreases, the two concepts will merge. In both cases, intermolecular and intramolecular packing forces in the solid state may influence the relative energies and relative geometric positions of the minima, again rendering differentiation difficult if assessment is based on crystallographic results; further, again in both cases, if the minima are broad and shallow then the solid-state or solvation forces may significantly flex structures from their free-molecule dimensions (e.g. hatched arrows in Fig. 1).

In this present work we address these ideas by consideration of the twelve-vertex ruthenadicarbaboranes of general, formally '*closo*', constitution $[3\text{-}(\eta^6\text{-}Ar)\text{-}1\text{-}R\text{-}2\text{-}R'\text{-}closo\text{-}3,1,2\text{-}RuC_2B_9H_{10}]$. We compare both new and reported structural and ^{11}B NMR chemical shift data with the results from new DFT