# Synthetic, structural and computational studies on adducts of the 4,1,2-SnC<sub>2</sub>B<sub>10</sub> supraicosahedral stannacarborane<sup>†</sup>

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Received 29th October 2009, Accepted 2nd December 2009 First published as an Advance Article on the web 27th January 2010 DOI: 10.1039/b922644c

The stannacarborane  $1,2-\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4,1,2-closo-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (1) and its adducts with 2,2'-bipyridine (bipy), 1,10-phenanthroline (o-phen) and 4,4'-diphenyl-2,2'-bipyridine (Ph<sub>2</sub>bipy), 1,2-µ-(CH<sub>2</sub>)<sub>3</sub>-4-(bipy)-4,1,2-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**2**), 1,2-µ-(CH<sub>2</sub>)<sub>3</sub>-4-(*o*-phen)-4,1,2-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**3**) and  $1,2-\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4-(Ph<sub>2</sub>bipy)-4,1,2-closo-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (4), respectively, together with the analogous compound 1,2- $\mu$ -{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>}-4-(bipy)-4,1,2-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (5) have been prepared and characterised. In solution at ambient temperature, compounds 1–5 all display NMR spectra which are interpreted in terms of (time-averaged)  $C_s$  molecular symmetry, but whilst (effectively)  $C_s$  symmetry is retained in the structures of 2-5 in the crystal (*i.e.* henicosahedral cage structures are observed), 1 has a  $(C_1$ -symmetric) docosahedral structure. A method for quantifying the "percentage docosahedral character" of 13-vertex  $1,2-C_2$  heteroboranes is described, based on the angles around the C1C2B9B5 quadrilateral. The structures of "carbons adjacent" 1-5 all reveal less slipping of the Sn atom (or  $\{SnL_2\}$  fragment) across the C<sub>2</sub>B<sub>4</sub> carborane face than has previously been observed in analogous "carbons apart" 4,1,6-closo-SnC<sub>2</sub>B<sub>10</sub> species, a surprising result in the context of previous studies of slipping in icosahedral platinacarboranes. A computational study of "carbons adjacent" and "carbons apart" icosahedral and supraicosahedral platinacarboranes has revealed that the origin of this observation is steric control of the slipping distortion in both "carbons apart" species and in the "carbons adjacent" 13-vertex species, with orbital interactions proving dominant only in the case of the "carbons adjacent" icosahedral compound.

## Introduction

In 2002 we reported the first supraicosahedral p-block metallacarboranes 4,1,6-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>12</sub> and 1,6-Me<sub>2</sub>-4,1,6-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, arising from reduction of 1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> or its C,C'-dimethyl analogue, followed by treatment with SnCl<sub>2</sub>.<sup>1</sup> Very recently we described a number of adducts of the dimethyl species with chelating Lewis bases L<sub>2</sub>.<sup>2</sup> The structures of these adducts, studied both crystallographically and computationally, confirmed that the supraicosahedral stannacarboranes resemble their icosahedral<sup>3</sup> and sub-icosahedral<sup>4</sup> analogues in their Lewis acid behaviour, giving rise to adducts in which (i) there is an enhanced slip of the Sn atom relative to the uncomplexed precursor and (ii) the stereochemical influence of the Sn lone pair of electrons is clearly evident.

The slip of metal atoms across a carborane ligand face was thoroughly studied with respect to icosahedral  $\{L_2M\}C_2B_9$  species more than 30 years ago (M = Pt or Pd, L = typically phosphine).<sup>5</sup> A key finding of this work was that the slip distortion,  $\Delta$ , was

greater in 3,1,2-MC<sub>2</sub>B<sub>9</sub> species (cage C atoms adjacent)<sup>5</sup> than in 2,1,7-MC<sub>2</sub>B<sub>9</sub> species (cage C atoms separated),<sup>6</sup> a result that was rationalised by the results of molecular orbital (MO) calculations at the extended Hückel level.

In 4,1,6-MC<sub>2</sub>B<sub>10</sub> supraicosahedral compounds the cage C atoms are separated by a single B atom, as they are in 2,1,7-MC<sub>2</sub>B<sub>9</sub> icosahedral species. A known 13-vertex C-adjacent isomer is 4,1,2-MC<sub>2</sub>B<sub>10</sub>, but to prepare this it is usually necessary to first tether the cage C atoms of 1,2-*closo*-C<sub>2</sub>B<sub>10</sub> icosahedra with a short exopolyhedral tether, to prevent their separation in the initial reduction step, the same strategy used to prepare the first supraicosahedral carborane.<sup>7</sup> Following our report of 4,1,6-SnC<sub>2</sub>B<sub>10</sub> species, Xie prepared such a 4,1,2-SnC<sub>2</sub>B<sub>10</sub> compound and determined the structures of its adducts with MeCN, THF and dme (dme = dimethoxyethane).<sup>8</sup>

In view of the superficial similarity in the relationship between 4,1,6-SnC<sub>2</sub>B<sub>10</sub> and 4,1,2-SnC<sub>2</sub>B<sub>10</sub> and that between 2,1,7-MC<sub>2</sub>B<sub>9</sub> and 3,1,2-MC<sub>2</sub>B<sub>9</sub>, we wondered if adducts of 4,1,2-SnC<sub>2</sub>B<sub>10</sub> compounds would also show increased slip distortions relative to their 4,1,6-SnC<sub>2</sub>B<sub>10</sub> cousins. Hence we report here the results of synthetic and structural studies on a number of adducts of 4,1,2-SnC<sub>2</sub>B<sub>10</sub> stannacarboranes using exclusively bidentate L<sub>2</sub> bases similar to those we used in our earlier work. Surprisingly, the 4,1,2-SnC<sub>2</sub>B<sub>10</sub> species are *less* slipped than their 4,1,6-SnC<sub>2</sub>B<sub>10</sub> analogues. We trace the origin of this unexpected result by computational studies of model compounds.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Computational models and additional plots referred to in the text. CCDC reference numbers 751644–751648 (compounds 1–5 respectively). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b922644c

## **Results and discussion**

### Synthesis and spectroscopy

Reduction of  $1,2-\mu$ -(CH<sub>2</sub>)<sub>3</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> by sodium in THF in the presence of naphthalene, followed by treatment with SnCl<sub>2</sub>, affords a modest yield of the pale yellow stannacarborane 1,2- $\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4,1,2-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (1) after work-up. Compound 1 was initially characterised by mass spectrometry and NMR spectroscopy. The highest mass signal in the mass spectrum appears as a characteristic heteroborane envelope from 298 to 308 with the most intense peak at m/z 302. In the <sup>1</sup>H NMR spectrum are multiplets of equal intensity between  $\delta$  3.20 and 1.90 due to the tether protons, whilst the  ${}^{11}B{}^{1}H{}$  spectrum consists of five signals between  $\delta$  +8.0 and -0.5, of relative ratio 2:4:1:1:2 from high frequency to low frequency, all of which become doublets on retention of proton coupling. The molecular structure of 1, subsequently determined crystallographically (vide infra), is that of an asymmetric docosahedral cage, and the presence of a mirror plane implied by the  ${}^{11}B{}^{1}H{}$  spectrum is readily rationalised by a diamond-trapeziumdiamond fluctional process in solution, similar to that proposed for the transition-metal metallacarboranes  $1,2-\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4,4-(PMe<sub>2</sub>Ph)<sub>2</sub>-4,1,2-closo-PtC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> and 1,2-µ-(CH<sub>2</sub>)<sub>3</sub>-4-dppe-4,1,2-closo-NiC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>),<sup>9</sup> which is rapid on the NMR timescale.

Room temperature reaction of a toluene solution of 1 and toluene solutions of 2,2'-bipyridine (bipy), 1,10-phenanthroline (o-phen) and 4,4'-diphenyl-2,2'-bipyridine (Ph<sub>2</sub>bipy) result in immediate precipitation of the yellow adducts 1,2-µ-(CH<sub>2</sub>)<sub>3</sub>-4-(bipy)-4,1,2-closo-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (2), 1,2- $\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4-(o-phen)-4,1,2closo-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (3) and 1,2-µ-(CH<sub>2</sub>)<sub>3</sub>-4-(Ph<sub>2</sub>bipy)-4,1,2-closo- $SnC_2B_{10}H_{10}$  (4), respectively, in good yields. The <sup>1</sup>H NMR spectra of 2-4 all show, in addition to resonances due to the bipy, o-phen or Ph<sub>2</sub>bipy ligands, four multiplets in the ratio 2:2:1:1 at  $\delta$  3.15– 2.95, 2.85-2.65, 2.05-1.90 and 1.80-1.65, respectively, assigned to the protons of the  $(CH_2)_3$  tether. Peaks in the  ${}^{11}B{}^{1}H{}$  NMR spectra of 2-4 are shifted to low frequency compared to those in 1, appearing as a 3:2:2:2:1 pattern for 2 and 3 and a 3:2:4:1 for 4, between  $\delta$  +4.0 and -11.0. The <sup>1</sup>H and <sup>11</sup>B spectra imply (at least time-averaged)  $C_{\rm s}$  molecular symmetry in solution (assuming, in the latter, that the integral-3 resonances are 2+1 co-incidences and the integral-4 resonance is a 2+2 co-incidence). As will be discussed subsequently, the structures of 2-4 in the solid state are effectively henicosahedral (Fig. 1, right) and  $C_s$ -symmetric for a 4,1,2-SnC<sub>2</sub>B<sub>10</sub> heteroatom pattern.

To provide a link between these adducts of the  $(CH_2)_3$ -tethered stannacarborane **1** and the MeCN, THF and dme adducts of 1,2- $\mu$ -{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>}-4,1,2-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> previously reported by Xie,<sup>8</sup> we have further treated a toluene solution of 1,2- $\mu$ -{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>}-4,1,2-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> with bipy to afford the bright yellow bipyridyl adduct 1,2- $\mu$ -{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>}-4-(bipy)-4,1,2-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> the <sup>1</sup>H NMR spectrum is unremarkable, with appropriate resonances in terms of multiplicity, integral and chemical shift, for the protons of the bipy ligand and  $\alpha,\alpha$ -*o*-xylylene tether. Peaks in the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum are considerably broader than those of **2**-4, but nevertheless a clear 2:2:2:1:1:2 pattern, from  $\delta$  +7.5 to -10.5, is evident. Again, the NMR spectra of **5** 



Fig. 1 The docosahedron (left) and henicosahedron (right) and numbering schemes.

imply a  $C_{\rm s}$ -symmetric molecule, at least in solution at room temperature.

#### Molecular structures

The molecular structures of compounds 1–5 have all been determined by single-crystal diffraction studies.

We have previously shown<sup>9</sup> that 4,1,2-MC<sub>2</sub>B<sub>10</sub> compounds can exist in the solid-state with either docosahedral or henicosahedral structures, the topological difference between which is the formal absence of a C2-B5 connectivity in the latter. Thus, in the docosahedron the C1C2B9B5 unit is a diamond, with a measureable difference in C1-C2-B9 and C2-C1-B5 angles and a measureable difference in C2-B9-B5 and B9-B5-C1 angles, whereas in the henicosahedron the C1C2B9B5 unit is trapezoidal and the C1-C2-B9 and C2-C1-B5 angles are equal, as are the C2-B9-B5 and B9–B5–C1 angles (Fig. 1). For the series of metallacarboranes 1,2- $\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4-L-4,1,2-*closo*-MC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> we found a continuum of structure type from henicosahedral (ML = CoCp, Ru{pcym} {p-cym = C<sub>6</sub>H<sub>4</sub>Me<sup>i</sup>Pr-1,4}), through intermediate (ML =  $Pt\{PMe_2Ph\}_2$ ) to essentially docosahedral (ML = Ni{dppe}, although both the platinum and nickel species were clearly fluctional in solution via a henicosahedral intermediate as noted above.

In the present study it is immediately apparent that the cage of the ligand-free stannacarborane 1 (Fig. 2) appears to be best described as docosahedral, whilst those of the adducts 2–5 (Fig. 3–6) are best described as henicosahedral. To place these and other 1,2-C<sub>2</sub> carboranes and heterocarboranes quantitatively on the continuum of structure type from docosahedral to henicosahedral we define the angle  $\phi$  as the average of the differences between angles C1–C2–B9 and C2–C1–B5 and angles C2–B9–B5 and B9–B5–C1, *i.e.* 

$$\phi = (|C1-C2-B9-C2-C1-B5| + |C2-B9-B5-B9-B5-C1|)/2$$

For a  $C_s$ -symmetric henicosahedron  $\phi = 0$ , and  $\phi$  increases as the C2–B5 distance shortens and the structure becomes docosahedral. Table 1 lists  $\phi$  values for all structurally characterised 13-vertex 1,2-C<sub>2</sub> carboranes and heterocarboranes of which we are aware. The "most docosahedral" species, 1,2- $\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4dppe-4,1,2-*closo*-NiC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, has  $\phi = 41.55^{\circ}$ . We now define *x*,



**Fig. 2** Perspective view of compound **1**. Thermal ellipsoids are drawn at the 50% probability level except for H atoms.



Fig. 3 Perspective view of compound 2 (molecule  $\alpha$ ). Thermal ellipsoids are drawn at the 40% probability level except for H atoms.



Fig. 4 Perspective view of compound 3. Thermal ellipsoids as for Fig. 2.

the "percentage docosahedral character", as  $x = (\phi/41.55) \times 100\%$ .<sup>‡</sup> For a perfect henicosahedron x = 0% and for the docosahedral nickelacarborane x = 100%. By this approach the percentage docosahedral character of all 13-vertex 1,2-C<sub>2</sub> carboranes and heterocarboranes can be assessed on a common scale. The 1,2-C<sub>2</sub>B<sub>11</sub> carboranes are all essentially henicosahedral. The 4,1,2-MC<sub>2</sub>B<sub>10</sub> metallacarboranes appear to be predominantly henicosahedral, § but are somewhat more spread, displaying henicosahedral, docosahedral and effectively intermediate, *e.g.* 1,2- $\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4,4-(PMe<sub>2</sub>Ph)<sub>2</sub>-4,1,2-*closo*-PtC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (III), structures.



Fig. 5 Perspective view of compound 4 (molecule  $\beta$ ). Thermal ellipsoids as for Fig. 2.



Fig. 6 Perspective view of compound 5. Thermal ellipsoids as for Fig. 2.

The ligand-free stannacarborane 1 has x = 80.3% and is confirmed as essentially docosahedral, whilst the adducts 2–5, with x between 0.0 and 21.6, are essentially henicosahedral.

This report constitutes the first time a ligand-free 4,1,2-SnC<sub>2</sub>B<sub>10</sub> species has been structurally characterised. Table 2 hosts selected molecular parameters for compounds 1–5 studied, where  $\Delta$  is the slip distortion of the Sn atom measured relative to the centroid of the B5B9B12B13B8 least-squares plane,  $\Delta_{\Delta}$  is the additional slip accompanying adduct formation, z is the perpendicular distance of the Sn atom from that least-squares plane and  $\theta$  is the inclination of the  $L_2$  ligand, the dihedral angle between B5B9B12B13B8 and Sn4N41CCN42 planes. In 1 the Sn-cage atom distances vary somewhat from the corresponding distances in 1,6-Me<sub>2</sub>-4,1,6*closo*-SnC<sub>2</sub>B<sub>10</sub>,<sup>1</sup> connectivities to vertex atoms 1, 2, 3 and 7 being longer (by 0.04–0.13 Å) whilst those to 6 and 10 are shorter (by 0.09 and 0.05 Å respectively). Moreover, there is greater internal variation in these distances, 0.35 Å in 1 compared to 0.26 Å in the 4,1,6-SnC<sub>2</sub>B<sub>10</sub> species, in spite of which the Sn atom in 1 is less slipped ( $\Delta = 0.14$  Å) than that in the 4,1,6-isomer ( $\Delta =$ 0.27 Å).<sup>2</sup> As noted in the introduction, in studies of isomeric icosahedral platinacarboranes in which the two cage C atoms were both adjacent<sup>5</sup> and non-adjacent,<sup>6</sup> it was found that the greater slip distortion occurred in the former case. Thus the measurement of a smaller slip in 1 (C atoms adjacent) compared to that in 1,6-Me<sub>2</sub>-4,1,6-closo-SnC<sub>2</sub>B<sub>10</sub> (C atoms non-adjacent) is significant. We return to this point later.

The molecular structures of the bipy, *o*-phen and  $Ph_2bipy$  adducts of 1, compounds 2–4, respectively, are shown in Fig. 3–5 (compounds 2 and 4 crystallise with two independent molecules in the asymmetric fraction of the unit cell; only molecule A is

<sup>‡</sup> Since our docosahedral model compound is chosen arbitrarily it may be that future species will be "more docosahedral" and have *x* values >100%. § However this has not always been recognised, *e.g.* in ref. 8 the line diagrams of the adducts are drawn as docosahedral whilst the crystallographically-determined structures are clearly henicosahedral.

Compound	Туре	CCDC refcode	Reference	$\phi/^{\circ}$	x
I	$4,1,2-CoC_2B_{10}$	GAQHIQ	9	0.20	0.5
II	$4,1,2-RuC_2B_{10}$	GAQHOW	9	0.33	0.8
III	$4,1,2-PtC_2B_{10}$	GAQHUC	9	28.44	68.4
IV	$4,1,2-NiC_2B_{10}$	GAQJAK	9	41.55	100
V	$4,1,2-CoC_2B_{10}$	BOKZAC	10	32.53, 41.32 <sup>b</sup>	78.3, 99.4
VI	$4,1,2-SnC_2B_{10}$	GUZSOJ	8	0.93	2.2
VII	$4,1,2-SnC_2B_{10}$	GUZSUP	8	4.23	10.2
VIII	$4,1,2-SnC_2B_{10}$	GUZTAW	8	4.98	12.0
IX	$4,1,2-CoC_2B_{10}$	POYHEQ	11	6.17	14.8
Х	4,1,2-NaC <sub>2</sub> B <sub>10</sub>	BIYVOU	12	3.32	8.0
XI	$4,1,2-ZrC_2B_{10}$	IYUVED	13	9.41	22.6
XII	$4,1,2-ZrC_2B_{10}$	IYUVIH	13	0.66	1.6
XIII	$1,2-C_2B_{11}$	TUSGAP	7	11.61	27.9
XIV	$1,2-C_2B_{11}$	JEWZER	14	0.00 <sup>c</sup>	0
XV	$1,2-C_2B_{11}$	JEWZAN	14	6.70	16.1
XVI	$1,2-C_2B_{11}$	NEGSUO	15 <sup>d</sup>	2.99, 6.09 <sup>e</sup>	7.2, 14.7
1	$4,1,2-SnC_2B_{10}$		this work	33.37	80.3
2	$4,1,2-SnC_2B_{10}$		this work	$7.46, 0.97^{e}$	18.0, 0.02
3	$4,1,2-SnC_2B_{10}$		this work	4.68	11.3
4	$4,1,2-SnC_2B_{10}$		this work	$6.76, 8.98^{c}$	16.3, 21.6
5	$4,1,2-SnC_2B_{10}$		this work	5.80	14.0

 Table 1
 Structural analysis of the cages of 13-vertex 1,2-C2 heteroboranes<sup>a</sup>

I, 1,2- $\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4-Cp-4,1,2-*closo*-CoC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>; **II**, 1,2- $\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4-(*p*-cym)-4,1,2-*closo*-RuC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>; **III**, 1,2- $\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4-(PMe<sub>2</sub>Ph)<sub>2</sub>-4,1,2-*closo*-PtC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>; **IV**, 1,2- $\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4-dppe-4,1,2-*closo*-NiC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>; **VI**, 1-Me-4-(PEt<sub>3</sub>)-4,6/7- $\mu$ -{Co(PEt<sub>3</sub>)<sub>2</sub>- $\mu$ -(H)<sub>2</sub>}-4,1,2-*closo*-CoC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>; **VI**, 1,2- $\mu$ -{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>}-4-thf-4,1,2-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>; **VII**, 1,2- $\mu$ -{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>}-4-thf-4,1,2-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>; **VII**, 1,2- $\mu$ -{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>}-4-thf-4,1,2-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>; **VIII**, 1,2- $\mu$ -{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>}-4-thf-4,1,2-*closo*-NaC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>; **VII**, 1,2- $\mu$ -{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>}-4-thf-4,1,2-*closo*-CaB<sub>10</sub>H<sub>10</sub>; **XII**, 1,2- $\mu$ -{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>+4-thf-4,1,2

Table 2 Selected molecular parameters  $(\text{\AA}, \circ)$  in experimental compounds 1–5 and model compounds A and B<sup>a</sup>

	1	Α	2α	2β	В	3	4α	4β	5
Sn4–C1	2.545(2)	2.549	2.813(17)	2.879(18)	2.832	2.803(2)	2.821(4)	2.782(4)	2.849(4)
Sn4–C2	2.727(3)	2.762	2.92(2)	2.824(17)	2.787	2.820(2)	2.797(4)	2.864(5)	2.852(4)
Sn4–B6	2.582(3)	2.560	2.95(2)	2.82(2)	2.742	2.899(3)	2.732(5)	2.988(6)	2.872(4)
Sn4–B10	2.375(3)	2.365	2.50(2)	2.43(2)	2.458	2.521(2)	2.469(5)	2.604(6)	2.550(5)
Sn4–B7	2.492(3)	2.514	2.46(2)	2.47(2)	2.535	2.448(2)	2.585(5)	2.441(5)	2.485(5)
Sn4–B3	2.692(3)	2.675	2.786(19)	2.897(19)	2.903	2.755(2)	2.949(5)	2.671(5)	2.775(5)
C1–C2	1.445(3)	1.463	1.40(3)	1.44(3)	1.437	1.433(3)	1.431(6)	1.420(6)	1.430(5)
C2–B5 <sup>b</sup>	2.056(4)	1.954	2.33(3)	2.45(3)	2.434	2.410(3)	2.359(7)	2.378(7)	2.399(6)
Sn4–N41			2.419(16)	2.399(15)	2.623	2.4481(17)	2.433(4)	2.462(4)	2.382(3)
Sn4–N42			2.396(15)	2.396(14)	2.608	2.4460(18)	2.419(4)	2.415(4)	2.418(3)
$\Delta^{c}$	0.144	0.117	0.392	0.410	0.330	0.341	0.331	0.400	0.320
$\Delta_{\Lambda}{}^{d}$			0.248	0.266	0.212	0.197	0.187	0.256	0.176
$Z^{e}$	3.455	3.432	3.644	3.644	3.612	3.631	3.648	3.635	3.661
$\theta^{f}$			24.26	25.68	31.23	30.16	27.13	16.04	29.51
$\phi^{g}$	33.37	28.8	7.46	0.97	3.3	4.68	8.98	6.76	5.80
$x^h$	80.3	69.2	18.0	0.02	7.8	11.3	21.6	16.3	14.0

<sup>*a*</sup> A is the optimised model of compound 1 and B the optimised model of compound 2. In both model compounds the exopolyhedral –(CH<sub>2</sub>)<sub>3</sub>– tethers were replaced by two H substituents. Optimisation was performed using Gaussian 03. Optimised parameters shown italicised for emphasis. <sup>*b*</sup> For the henicosahedral species 2–5 the smaller of the C2–B5 and C1–B9 distances is quoted, since these molecules could be numbered in one of two enantiomorphic ways. <sup>*c*</sup> A is the slipping parameter of the Sn4 atom, defined as its displacement, parallel to the best (least-squares) plane through B5B9B12B13B8, from the point directly above the centroid of that plane. <sup>*d*</sup>  $\Delta_{\Delta}$  is the increase in slipping for compounds 2–5 relative to 1. <sup>*c*</sup> *z* is the perpendicular displacement of the Sn4 atom from the B5B9B12B13B8 plane. <sup>*f*</sup>  $\theta$  is the inclination of the bipyridyl ligand, the dihedral angle between Sn4N41CCN42 and B5B9B12B13B8 planes. <sup>*f*</sup>  $\theta$  is defined in the text as (|C1-C2-B9 - C2-C1-B5| + |C2-B9-B5 - B9-B5-C1|)/2. <sup>*h*</sup> *x* is the "percentage docosahedral character", defined as ( $\phi/41.55$ ) × 100%.

shown in Fig. 3 and only B is shown in Fig. 5). Structurally, adduct formation is accompanied by (i) a change in cage structure from essentially docosahedral (x = 80.3% in 1) to essentially henicosahedral (x = 0-21.6% in 2-4), (ii) increased slipping of the Sn atom, from  $\Delta = 0.14$  Å to  $\Delta = 0.33-0.41$  Å and (iii) a slight reduction (ca. 0.01–0.04 Å) in the length of the C1– C2 connectivity. The slipping is predominantly away from cage C atoms, as evidenced by significantly increased Sn-C1/C2 and Sn-B3/B6 distances (averages¶ of 2.64 Å in 1 to 2.81–2.86 Å in 2-4 for Sn-C1/C2, and 2.64 Å in 1 to 2.83-2.86 Å in 2-4 for Sn-B3/B6) although the fact that Sn-B7/B10 also increases (average 2.43 Å in 1 to 2.47–2.52 Å in 2–4) means that the overall structural change is more complicated and, indeed, we note that the Sn atom in 2–4 is displaced further from the  $B_5$  reference plane (3.63–3.65 Å) than it is in 1 (3.45 Å). A similar phenomenon accompanied adduct formation of 1,6-Me<sub>2</sub>-4,1,6-closo-SnC<sub>2</sub>B<sub>10</sub>.<sup>2</sup> The increase in slipping that accompanies adduct formation,  $\Delta_{\Delta}$ , is 0.19–0.27 Å in 2–4, less than in the isomeric 4,1,6-SnC<sub>2</sub> $B_{10}$  species (0.28–0.39 Å).<sup>2</sup> Since they both start from a smaller base and change by less, overall, therefore, the slipping parameters in the carbons adjacent compounds 2-4, 0.33-0.41 Å, are ca. 0.2-0.25 Å smaller than in the 4,1,6 species. The origins of this unexpected result are discussed subsequently. The slight shortening of C1-C2 as a consequence of increasing slip is reminiscent of the situation in slipped icosahedral 3,1,2-MC<sub>2</sub>B<sub>9</sub> species in which case the origin has been traced to reduced depopulation of a carborane ligand orbital which is C/C bonding in nature.

The bipy, o-phen and Ph<sub>2</sub>bipy ligands in 2-4 are oriented such that their N atoms are opposite the cage C atoms. This reflects the greater trans influence of the facial boron atoms, B3, B7, B10 and B6, over the (facial) carbon atoms, C1 and C2. Thus Sn-C bonding is somewhat weaker than Sn-B bonding (further evidence for this is the direction of slip of the Sn atom) and, to compensate, the bipy, o-phen and Ph<sub>2</sub>bipy ligands position themselves trans to cage C with the Sn lone pair of electrons trans to B. In the related 4,1,6-SnC<sub>2</sub>B<sub>10</sub> adducts a broadly similar orientation of the exopolyhedral ligands was observed, with one N atom trans to the degree-5 C atom C6 and the other trans to the connectivity between the degree-4 C atom C1 and the degree-5 B atom B2.<sup>2</sup> In bipyridyl adducts of 4,1,10-SnC<sub>2</sub> $B_{10}$  the exopolyhedral ligand lies *trans* to the degree-5 C atom C10, whilst in 4,1,12-SnC<sub>2</sub>B<sub>10</sub> it lies trans to the degree-4 C atom C1,16 these results affording the ranking of trans influence as  $B_{degree-5} > C_{degree-4} > C_{degree-5}$ . The origin of the general result that the carbon atoms in heterocarboranes have a relatively weak trans influence lies in the fact that the frontier molecular orbitals of carborane ligands are predominantly localised on the facial boron atoms.5

The stereochemical influence of the Sn lone pair of electrons is reflected not only in the orientation of the bipy, *o*-phen and Ph<sub>2</sub>bipy ligands in **2–4** but also in their inclination, at an angle  $\theta$  of *ca*. 30° to the B5B9B12B13B8 reference plane. A slight difference in inclination angle ( $\theta = 16^\circ$ ) exists for **4B** although we note that in **4** there is clear evidence of intermolecular  $\pi$ - $\pi$  interactions in the crystal. Sn–N distances in **2–4** are 2.42–2.46 Å, somewhat longer than those (2.35–2.43 Å) in the related 4,1,6-SnC<sub>2</sub>B<sub>10</sub> adducts,<sup>2</sup> which may be related to the smaller slipping distortions in the present compounds.

We determined the structure of **5** (Fig. 6) for comparison with that of **2**, to see if the two different tethers,  $\mu$ -(CH<sub>2</sub>)<sub>3</sub>and  $\mu$ -{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>}-, had any effect on structure. Although the comparison is somewhat compromised by the relatively poor precision of the structural determination of **2** (a consequence of poor crystal size and quality) it is evident from the data in Table 2 that any differences are minor. One interesting feature of the structure of **5** is that the C<sub>6</sub> ring of the tether and the Sn4N41CCN42 sequence are nearly co-planar (dihedral angle 8.14°). In the crystal both the  $\alpha, \alpha$ -o-xylylene tether and the bipy ligand are involved in quasi-graphitic interactions with equivalent units across inversion centres.

The overall similarity between the molecular structures of 2 and 5 provides a link between the structures of our supraicosahedral 4,1,2-SnC<sub>2</sub>B<sub>10</sub> adducts and those of Xie, who used the  $\mu$ - $\{C_6H_4(CH_2)_2\}$ -tethered carborane and MeCN, THF and dme as external ligands (compounds VI, VII and VIII, respectively, of Table 1). Even though he used a mixture of mono- and bidentate Lewis bases in his study Xie concluded "a stronger base leads to an increased slip distortion of the tin from the centre of the  $C_2B_4$  bonding face".<sup>8</sup> However, Xie based this conclusion on measured Sn-cage atom distances, and did not actually calculate the slip distortions. In view of our interest in this general family of compounds we have calculated  $\Delta$  for Xie's compounds (0.205, 0.253 and 0.223 Å, respectively, measuring slip with respect to the lower B<sub>5</sub> pentagon, or 0.320, 0.377 and 0.365 Å, respectively, measuring slip with respect to the centroid of the upper C<sub>2</sub>B<sub>4</sub> ring) and find no such correlation.

#### **Computational studies**

A significant conclusion from the structural studies above is that the slipping distortion in the "carbons adjacent" 4,1,2-SnC<sub>2</sub>B<sub>10</sub> stannacarborane 1 is less than in its "carbons apart" 4,1,6- analogue 1,6-Me<sub>2</sub>-4,1,6-closo-SnC<sub>2</sub> $B_{10}H_{10}$ ,<sup>1</sup> and that this difference is maintained in the adducts of 1 reported here compared to adducts of 1,6-Me<sub>2</sub>-4,1,6-closo-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>.<sup>2</sup> This is in contrast to established work on the slipping distortions in icosahedral platina- or palladacarboranes5,6 where the reverse is true. To check whether this difference is due to the change from icosahedral to supraicosahedral or from group 10 element to Sn, we have calculated  $\Delta$  for the supraicosahedral platinacarboranes 1,2- $\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4,4-(PMe<sub>2</sub>Ph)<sub>2</sub>-4,1,2-closo-PtC<sub>2</sub>B<sub>10</sub>H<sub>10</sub><sup>9</sup> and 4,4-(PMe<sub>2</sub>Ph)<sub>2</sub>-4,1,6closo-PtC<sub>2</sub>B<sub>10</sub>H<sub>12</sub>.<sup>17</sup> These are 0.08 and 0.52 Å, respectively, clearly revealing a fundamental difference between icosahedral and supraicosahedral metallacarboranes in terms of the magnitude of metal slipping as a function of C atom position.

To probe the origins of this difference, we have extended our previous density functional theory (DFT) calculations<sup>18</sup> on 13-vertex stannacarboranes<sup>2</sup> to include the "carbons-adjacent" species **1** and **2** reported here. In addition, we have revisited the structural trends in icosahedral and supraicosahedral platinacarboranes noted above.<sup>5,17</sup> Calculations on **1** and **2** employed the model systems **A** and **B** respectively, where the exopolyhedral–(CH<sub>2</sub>)<sub>3</sub>– tethers were replaced by two H substituents. Table 2 shows that key computed and derived distances in **A** and **B** compare well with those determined experimentally for **1** and **2** although, as noted

<sup>¶</sup> Since compounds **2–4** are essentially henicosahedral with local mirror symmetry passing through the cage it is necessary to average Sn–C1 and Sn–C2, Sn–B3 and Sn–B6, and Sn–B7 and Sn–B10.

in our previous studies,<sup>2</sup> there is a tendency to overestimate the Sn–cage interactions in the bipy adduct  $\mathbf{B}$ .

In order to assess the factors controlling the degree of slipping in 12- and 13-vertex metallacarboranes we turned to the family of platinacarboranes, specifically icosahedral 3,3-(PEt<sub>3</sub>)<sub>2</sub>-3,1,2-closo-PtC<sub>2</sub>B<sub>9</sub>H<sub>11</sub> (XVII)<sup>5</sup> and 1,7-Me<sub>2</sub>-2,2-(PMe<sub>2</sub>Ph)<sub>2</sub>-2,1,7closo-PtC<sub>2</sub>B<sub>9</sub>H<sub>9</sub> (XVIII)<sup>6</sup> and supraicosahedral 1,2-µ-(CH<sub>2</sub>)<sub>3</sub>-4,4- $(PMe_2Ph)_2-4,1,2-closo-PtC_2B_{10}H_{10}$  (III)<sup>9</sup> and 4,4- $(PMe_2Ph)_2-4,1,6$ closo-PtC<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (XIX).<sup>17</sup> Focussing on these platinum systems has the benefit of benchmarking the approach adopted here against earlier studies of slipping in the icosahedral species.5 In the calculations, species XVII, XVIII, III and XIX were represented by simplified models C, D, E and F respectively, in which all phosphine ligands were replaced by PH<sub>3</sub> and all exopolyhedral C-substituents were replaced by H (see Fig. 7 for line diagrams of all the model compounds A-F). As found previously<sup>17</sup> the calculations reproduce the experimental structures well, both in terms of the orientations of the  $\{Pt(PH_3)_2\}$  fragments relative to the open face of the carborane cage and the slipping parameters (see Table 3 for the latter; full computed geometries are supplied in the ESI<sup>†</sup>).



Fig. 7 Line diagrams and numbering of computational models A-F.

The origins of the slipping distortions in C-F were investigated by considering the interaction of the  $\{Pt(PH_3)_2\}^{2+}$  fragment with the appropriate *nido*- $\{C_2B_n\}^{2-}$  cage (n = 9, 10). In the analysis we have made use of the energy decomposition scheme available within the Amsterdam Density Functional (ADF) code.<sup>19</sup> In this approach the interaction between two fragments can be broken up into "steric" and "orbital interaction" energy terms. The steric interaction is overall destabilising and is composed of the electrostatic interaction derived from the different charge distributions associated with each fragment, as well as a Pauli repulsion term due to interaction of occupied orbitals in each fragment. The orbital interaction arises from the overlap of occupied orbitals on one fragment with unoccupied orbitals of the other and is therefore stabilising. Where appropriate, this term can be further factored into contributions arising within different orbital symmetries. Symmetry therefore greatly facilitates

**Table 3** Comparison of experimentally- (X-ray diffraction) and computationally- (DFT) determined connectivities and slip distances (Å) and conformations  $(\chi, ^{\circ})$  in platinacarboranes

(i) 12-vertex compounds						
	XVII <sup>5</sup>	$\mathbf{C}^{a}$		XVIII <sup>6</sup>	$\mathbf{D}^{a}$	
CCDC	EPTBOR10		CCDC	CMPBPT10		
Pt3–C1	2.530(7)	2.794	Pt2–C1 <sup>c</sup>	2.442(7)	2.465	
Pt3-C2	2.613(7)	b	Pt2–C7	2.452(8)	Ь	
Pt3–B4	2.283(8)	2.240	Pt2–B6	2.261(8)	2.283	
Pt3–B7	2.277(8)	b	Pt2-B11	2.255(9)	Ь	
Pt3–B8	2.264(8)	2.212	Pt2–B3	2.270(9)	2.253	
Pt3–P1	2.2759(18)	2.379	Pt2–P1 <sup>d</sup>	2.303(2)	2.381	
Pt3–P2	2.2843(18)	b	Pt2–P2	2.249(2)	2.342	
Δ	0.411	0.699	$\Delta$	0.141	0.081	
$\chi^{e}$	75.9	90	$\chi^{e}$	10.1	0	
(ii) 13-vert	ex compounds					
	III <sup>9</sup>	Ef		XIX <sup>17</sup>	$\mathbf{F}^{f}$	
CCDC	GAQHUC		CCDC	HEYZOB		
Pt4–C1	2.381(8)	2.396	Pt2–C1	2.1652(12)	2.153	
Pt4–C2	2.626(8)	2.855	Pt2–B2	2.4438(15)	2.439	
Pt4–B3	2.322(8)	2.299	Pt2–B3	2.3961(14)	2.442	
Pt4–B6	2.301(7)	2.292	Pt2–C6	2.8131(13)	2.894	
Pt4–B7	2.305(7)	2.279	Pt2–B7	2.2631(14)	2.230	
Pt4–B10	2.265(7)	2.236	Pt4–B10	2.3692(14)	2.412	
Pt4–P1 <sup>g</sup>	2.3046(18)	2.383	Pt2–P1 <sup>h</sup>	2.2710(3)	2.346	
Pt4–P2	2.3001(17)	2.398	Pt2–P2	2.3129(4)	2.420	
Δ	0.080	0.195	$\Delta$	0.518	0.583	
$\chi^{i}$	61.1	68.2	$\chi^i$	148.7	141.3	

<sup>*a*</sup> Structure optimised in *C*<sub>s</sub> symmetry. <sup>*b*</sup> Equivalent to previous distance by symmetry. <sup>*c*</sup> Molecule renumbered relative to that in reference 6. <sup>*d*</sup> P1 lies over B3. <sup>*c*</sup> Conformation defined as dihedral angle between PtP<sub>2</sub> and PtB<sub>3</sub> planes, where the three B atoms in the latter are those that lie in the cage mirror plane. <sup>*f*</sup> Structure optimised in *C*<sub>1</sub> symmetry. <sup>*s*</sup> P1 lies over B6. <sup>*h*</sup> P1 lies over B7–B10. <sup>*i*</sup> Conformation defined as dihedral angle between PtP<sub>2</sub> and C1B10B11 planes, where  $0 < \chi < 90$  represents, in projection, one phosphine ligand lying in the B3 quadrant and  $90 < \chi < 180$  represents one phosphine ligand lying in the B7 quadrant.

the analysis and so for this reason the geometries of **C** and **D** (and **E**, see below) were recomputed in  $C_s$  symmetry with the ADF code. Importantly, this did not significantly affect the extent of slipping compared to the data in Table 3 where no symmetry constraint was applied.

In the following we will consider how the steric and orbital interaction energy terms vary as the  $\{Pt(PH_3)_2\}^{2+}$  fragment is moved across the open face of the  $\{C_2B_n\}^{2-}$  fragment. The approach adopted is shown in Fig. 8 for the "carbons adjacent" icosahedral model **C**. Initially, the Pt atom of the  $\{Pt(PH_3)_2\}^{2+}$  fragment is placed directly above the centroid of the lower  $\{B_5\}$  belt ( $\Delta = 0$ ) and then displaced, either toward ( $-\Delta$ ) or away



Fig. 8 Definition of slipping in the model compound C.



Fig. 9 Frontier orbital interactions in C and D

 $(+\Delta)$  from the carbon atoms, along the vector perpendicular to this Pt-centroid axis which passes through the position of the metal atom in the {Pt(PH<sub>3</sub>)<sub>2</sub>}<sup>2+</sup> fragment in the fully-optimised geometry. In all cases except **F** (see below) this analysis could be performed such that  $C_s$  symmetry was maintained throughout. At each point thus generated the steric and orbital interaction terms were calculated without any relaxation of either the {Pt(PH<sub>3</sub>)<sub>2</sub>}<sup>2+</sup> or {C<sub>2</sub>B<sub>n</sub>}<sup>2-</sup> fragments. Although this approach will tend therefore to exaggerate the various contributions to the interaction energy, the trends within these terms should be secure.

Previously, the orientation and slipping of the  ${Pt(PR_3)_2}^{2+}$ fragment in XVII/C have been rationalised in terms of preferential frontier molecular orbital interactions (see Fig. 9||). Thus strong overlap of the  ${Pt(PR_3)_2}^{2+}$  a" LUMO with the HOMO of the  $C_2 B_9 H_{11}^{2-}$  cage dictates a perpendicular orientation of the  ${Pt(PR_3)_2}^{2+}$  moiety with respect to the mirror plane of the cage. Positive slipping towards a position above B8 arises via maximising bonding overlap between the  ${Pt(PR_3)_2}^{2+}$  LUMO+1 and the a' HOMO-1 of the  $\{C_2B_9H_{11}\}^{2-}$  fragment which is strongly localised on the B atoms of the open face (especially B8). For the carbons apart isomer, XVIII/D, the a" HOMO-LUMO interaction again controls  $\{Pt(PH_3)_2\}^{2+}$  fragment orientation which in this case lies in the cage mirror plane. The a' HOMO-1 of the  $\{C_2B_9H_{11}\}^{2-1}$ fragment now displays little localisation and this, coupled to the relatively even distribution of the  $\{C_2B_9H_{11}\}^{2-}$  HOMO means that only a minor slipping is seen.

The results of the energy decomposition analyses for these 12vertex systems are shown in Fig. 10, with **C** on the left hand side and **D** on the right. For **C** the total interaction energy shown in plot (a) finds a minimum value at  $\Delta \approx +0.7$  Å and appears to be a compromise between the orbital interaction term [plot (b), in purple] which is most stabilising at  $\Delta ca. +1.0$  Å and steric interactions [plot (b), in green] which minimise at  $\Delta$  *ca.* +0.2 Å. Plot (c) shows that the stabilising a" orbital interaction (in blue) is the more significant orbital interaction, it being more stabilising at higher  $\Delta$ ; the a' interaction (in red) does, however, also contribute to the positive slip. Thus, although the a" orbital interaction is the most important single contribution to the positive slipping (as revealed by the earlier EHMO analysis<sup>5</sup>) the present approach highlights the role played by other factors, especially the steric interaction, in controlling the detailed extent of slipping.

For model species **D** the total energy is dominated by the steric interaction term with the relevant two plots being nearly superimposable. In contrast, the orbital interaction is only weakly dependent on  $\Delta$  and this arises from counteracting trends in the a' and a'' contributions. This weak dependence of the orbital interaction on  $\Delta$  is again consistent with the EHMO study.<sup>5</sup> What emerges in the present study is the far greater importance of the steric interaction term in determining the extent of slipping in the "carbons apart" 12-vertex system, a feature that will also be prominent in rationalising the structures of the 13-vertex systems.

Results of the energy decomposition analysis for the 13-vertex model systems **E** and **F** are shown in Fig. 11 and some further comment is required on the models used in these cases. Both **E** and **F** exhibit  $C_1$  structures in their fully optimised forms. For **E**, in order to facilitate the analysis, a henicosahedral  $C_s$  structure was adopted which corresponds to a transition state that interconverts two equivalent docosahedral minima. This  $C_s$  structure is only 7.3 kcal mol<sup>-1</sup> above the  $C_1$  minimum and allows  $C_s$  symmetry to be maintained upon displacement of {Pt(PH<sub>3</sub>)<sub>2</sub>}<sup>2+</sup> to  $\pm \Delta$ . Test calculations on the  $C_1$  form indicate that the outcomes of the analysis are not significantly affected by this simplification (see ESI<sup>†</sup>). For **F** no convenient close-lying  $C_s$  structure exists and so the analysis was performed on the fully optimised  $C_1$  form.

As shown in Fig. 11, for **E** (left hand side) the destabilising steric interaction is minimised around  $\Delta = 0.0$  while the orbital interaction terms are actually least stabilising at that point. Displacement in either direction therefore enhances the overall orbital

<sup>||</sup> The fragmentation of C employed here, into doubly charged  $\{C_2B_9H_{11}\}^{2^-}$ and  $\{Pt(PH_3)_2\}^{2^+}$  fragments, differs from that used previously,<sup>5</sup> where neutral  $\{C_2B_9H_{11}\}$  and  $\{Pt(PH_3)_2\}$  fragments were used.



Fig. 10 Energy decomposition analyses for C (left) and D (right). Plots are (a) total interaction energy, (b) steric (green) and orbital (purple) interaction energy terms and (c) a' (red) and a'' (blue) orbital interaction terms vs.  $\Delta$ .

interaction, however, this does not outweigh the destabilisation arising from the steric interaction. The net result is that only a small negative slipping occurs. Orbital interactions are therefore less important in determining  $\Delta$  in this case and for this reason the contributions from a' and a" symmetry are relegated to the ESI.<sup>†</sup> For **F** the somewhat larger positive slipping is again seen to result primarily from the steric interaction term that minimises around  $\Delta$  *ca.* +0.5 Å. This is only slightly perturbed by the orbital interaction term, resulting in an overall slip of  $\Delta$  *ca.* +0.6 Å.

## Conclusions

The ligand-free 4,1,2-SnC<sub>2</sub>B<sub>10</sub> compound 1 and its bipy, *o*-phen and Ph<sub>2</sub>bipy adducts **2–4** have been prepared and fully characterised, together with the bipy adduct **5** of the known

species  $1,2-\mu$ -{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>}-4,1,2-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>. In the solid state compound **1** has a docosahedral structure, whilst **2–5** are essentially henicosahedral. A method of quantifying the "percentage docosahedral character" of a *closo*-13-vertex cluster is described. The "carbons adjacent" compounds **1–5** are all significantly less slipped than analogous "carbons apart" 4,1,6-SnC<sub>2</sub>B<sub>10</sub> species, an apparently surprising result in the context of earlier work on "carbons adjacent" and "carbons apart" icosahedral platinacarboranes. However, a computational study of "carbons adjacent" and "carbons apart" 12- and 13-vertex platinacarboranes reveals that only in one case, that of the "carbons adjacent" 12-vertex metallacarborane, is the degree of slipping determined by orbital effects. For all the other systems studied (12-vertex "carbons apart" and both "carbons apart" and both "carbons apart" and "carbons apart" apart.





Fig. 11 Energy decomposition analyses for E (left) and F (right). Plots are (a) total interaction energy, (b) steric (green) and orbital (purple) interaction energy terms vs.  $\Delta$ .

significant and the degree of slipping reflects the dominant role played by steric interactions.

variations thereof. All other reagents and solvents were supplied commercially.

## Experimental

#### Synthesis

Experiments were performed under dry, oxygen-free N<sub>2</sub>, using standard Schlenk techniques, although subsequent manipulations were sometimes performed in the open laboratory. All solvents were freshly distilled from the appropriate drying agents under nitrogen immediately before use [CH2Cl2; CaH2: THF, toluene and 40-60 petroleum ether; sodium wire] or were stored over 4 Å molecular sieves and were degassed (3×freeze-pump-thaw cycles) before use. IR spectra were recorded from CH<sub>2</sub>Cl<sub>2</sub> solutions on a Perkin-Elmer Spectrum RX FT spectrophotometer. NMR spectra at 400.1 MHz (<sup>1</sup>H) or 128.4 MHz (<sup>11</sup>B) were recorded on a Bruker DPX-400 spectrometer from CD<sub>2</sub>Cl<sub>2</sub> solutions at room temperature. EI mass spectrometry was carried out using a Kratos Concept mass spectrometer. Elemental analyses were determined by the departmental service (compound 1 only; for 2-5 only sufficient material was obtained for NMR and crystallographic studies).  $1,2-\mu-(CH_2)_3-1,2-closo-C_2B_{10}H_{10}^{20}$  and  $1,2-\mu-\{C_6H_4(CH_2)_2\}-4,1,2 \mathit{closo}\text{-}SnC_2B_{10}H_{10}{}^8$  were prepared by literature methods or slight

1,2-µ-(CH<sub>2</sub>)<sub>3</sub>-4,1,2-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (1). A solution of 1,2-µ- $(CH_2)_3$ -1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (150 mg, 0.81 mmol) in dry, degassed, THF (20 mL) was stirred with sodium pieces (130 mg, 5.7 mmol) and naphthalene (ca. 10 mg) at room temperature for 48 h. The resulting dark-green solution was transferred via cannula to a dry, degassed, frozen (-196 °C) solution of SnCl<sub>2</sub> (153 mg, 0.81 mmol) in THF (10 mL), and the reagents then allowed to warm to 0 °C with stirring. The crude, dark brown reaction mixture was evaporated to dryness and then suspended in CH<sub>2</sub>Cl<sub>2</sub> (40 mL). The mixture was filtered and all volatiles were removed in vacuo, yielding a white solid (60 mg, 25%). C<sub>5</sub>H<sub>16</sub>B<sub>10</sub>Sn requires C 19.8, H 5.82. Found C 19.9, H 5.44%. IR,  $v_{\text{max}}$  2547 cm<sup>-1</sup> (B–H). <sup>11</sup>B{<sup>1</sup>H} NMR, δ 7.73 (2B), 6.45 (4B), 4.12 (1B), 1.06 (1B), -0.27 (2B). <sup>1</sup>H NMR, δ 3.20–3.10 (m, 2H, (CH<sub>2</sub>)<sub>3</sub>), 2.85-2.75 (m, 2H, (CH<sub>2</sub>)<sub>3</sub>),  $2.05-1.90 (m, 2H, (CH_2)_3)$ . MS:  $m/z 302 (M^+)$ , 119 (M-C<sub>5</sub>H<sub>16</sub>B<sub>10</sub>). Recrystallisation by diffusion of a CH<sub>2</sub>Cl<sub>2</sub> solution and 40-60 petroleum ether at -30 °C afforded pale-yellow diffraction-quality block crystals of 1.

1,2- $\mu$ -(CH<sub>2</sub>)<sub>3</sub>-4-(bipy)-4,1,2-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (2). A solution of 1 (10 mg, 0.03 mmol) in dry, degassed toluene (5 mL) was added

to a dry, degassed toluene solution (3 mL) of 2,2'-bipyridine (6 mg, 0.04 mmol), and the resulting yellow suspension stirred for 24 h. On settling, the toluene was removed using a gas-tight syringe, leaving a yellow solid which was washed with petroleum ether (2 × 10 mL) and dried *in vacuo* to afford **2** as a yellow solid (10 mg, 73%). IR,  $v_{\text{max}}$  2518 cm<sup>-1</sup> (B–H). <sup>11</sup>B{<sup>1</sup>H} NMR,  $\delta$  3.55 (3B), 2.30 (2B), -4.05 (2B), -5.16 (2B), -10.78 (1B). <sup>1</sup>H NMR,  $\delta$  8.99 (d, 2H, bipy), 8.22 (d, 2H, bipy), 8.13 (d of d, 2H, bipy), 7.69 (d of d, 2H, bipy), 3.05–2.95 (m, 2H, (CH<sub>2</sub>)<sub>3</sub>), 2.77–2.68 (m, 2H, (CH<sub>2</sub>)<sub>3</sub>), 1.99–1.90 (m, 1H, (CH<sub>2</sub>)<sub>3</sub>), 1.78–1.66 (m, 1H, (CH<sub>2</sub>)<sub>3</sub>). Small crystals were grown by vapour diffusion of 40–60 petroleum ether and a CH<sub>2</sub>Cl<sub>2</sub> solution of **2** at 5 °C.

**1,2-\mu-(CH<sub>2</sub>)<sub>3</sub>-<b>4-**(*o*-phen)-**4,1,2**-*closo*-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (3). Likewise, a solution of **1** (30 mg, 0.10 mmol) in dry, degassed toluene (10 mL) was stirred with a dry, degassed toluene solution (10 mL) of 1,10-phenanthroline (20 mg, 0.11 mmol) to afford 31 mg (64%) of **3**. IR,  $v_{\text{max}}$  2540 cm<sup>-1</sup> (B–H). <sup>11</sup>B{<sup>1</sup>H} NMR,  $\delta$  3.73 (3B), 2.36 (2B), -4.25 (2B), -5.07 (2B), -10.69 (1B). <sup>1</sup>H NMR,  $\delta$  9.34 (d, 2H, phen), 8.59 (d, 2H, phen), 8.05 (s, 2H, phen), 8.00 (d of d, 2H, phen), 3.15–3.05 (m, 2H, (CH<sub>2</sub>)<sub>3</sub>), 2.82–2.72 (m, 2H, (CH<sub>2</sub>)<sub>3</sub>), 2.05–1.95 (m, 1H, (CH<sub>2</sub>)<sub>3</sub>), 1.80–1.70 (m, 1H, (CH<sub>2</sub>)<sub>3</sub>). Crystals by solvent diffusion of 40–60 petroleum ether and a CH<sub>2</sub>Cl<sub>2</sub> solution of **3** at 5 °C.

**1,2-µ-(CH<sub>2</sub>)<sub>3</sub>-4-(Ph<sub>2</sub>bipy)-4,1,2-***closo***-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (4). In the same way, a solution of <b>1** (10 mg, 0.03 mmol) in dry, degassed toluene (10 mL) was allowed to react with a dry, degassed toluene solution (10 mL) of 4,4'-diphenyl-2,2'-bipyridine (12 mg, 0.04 mmol), yielding 15 mg (82%) of **4**. IR,  $v_{max}$  2522 cm<sup>-1</sup> (B–H). <sup>11</sup>B{<sup>1</sup>H} NMR,  $\delta$  3.70 (3B), 2.41 (2B), -4.13 (4B), -10.79 (1B). <sup>1</sup>H NMR,  $\delta$  9.03 (d, 2H, Ph<sub>2</sub>bipy), 8.45 (2, 2H, Ph<sub>2</sub>bipy), 7.91 (d, 2H, Ph<sub>2</sub>bipy), 7.82–7.73 (m, 4H, Ph<sub>2</sub>bipy), 7.64–7.55 (m, 6H, Ph<sub>2</sub>bipy), 3.05–2.99 (m, 2H, (CH<sub>2</sub>)<sub>3</sub>), 2.80–2.70 (m, 2H, (CH<sub>2</sub>)<sub>3</sub>), 2.01–1.920 (m, 1H, (CH<sub>2</sub>)<sub>3</sub>), 1.78–1.69 (m, 1H, (CH<sub>2</sub>)<sub>3</sub>). The product was crystallised by solvent diffusion of 40–60 petroleum ether and a CH<sub>2</sub>Cl<sub>2</sub> solution of **4** at 5 °C.

Table 4 Crystallographic data for compounds 1–5

**1,2-μ-{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>}-4-(bipy)-4,1,2-***closo***-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (5). A solution of 1,2-μ-{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>}-4,1,2-***closo***-SnC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (70 mg, 0.192 mmol) in dry, degassed toluene (10 mL) was added to a dry, degassed toluene solution (10 mL) of 2,2'-bipyridine (90 mg, 0.575 mmol), and the resulting yellow suspension stirred for 24 h. After settling, the toluene was removed using a gas-tight syringe, leaving a yellow solid, subsequently washed with petroleum ether (2 × 10 mL) and dried** *in vacuo* **to afford <b>5** as a yellow solid (61 mg, 61%). IR, CH<sub>2</sub>Cl<sub>2</sub>,  $v_{max}$  2521 cm<sup>-1</sup> (B–H). <sup>11</sup>B{<sup>1</sup>H} NMR,  $\delta$  7.19 (br, 2B), 4,16 (br, 2B). 2.92 (br, 2B), -3.65 (br, 1B), -5.62 (br, 1B), -10.48 (br, 2B). <sup>1</sup>H NMR,  $\delta$  8.87 (d, 2H, bipy), 8.24 (d, 2H, bipy), 8.04 (d of d, 2H, bipy), 7.60 (d of d, 2H, bipy), 7.27–7.10 (m, 4H, C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 3.98 (d, 2H, C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>). Diffraction-quality crystals were grown by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution of **5** at room temperature.

### Crystallography

Intensity data from 1 and 3-5 were collected from single crystals on a Bruker X8 APEX2 diffractometer using Mo-Ka X-radiation, with crystals mounted in inert oil on a cryoloop and cooled to 100 K by an Oxford Cryosystems Cryostream. Data from compound 2, which affords only very small crystals were collected by the EPSRC National Crystallographic Service at Southampton using a Bruker-Nonius APEX II diffractometer equipped with a Bruker-Nonius FR591 rotating anode and confocal mirror monochromator with Mo-Ka X-radiation at 120 K. The structures were solved by direct methods and refined by full-matrix least-squares. All non-H atoms were refined with anisotropic displacement parameters, although it was necessary to restrain the anisotropy, in 2, of four B atoms and four C atoms (two methylene, one solvent and one bipy) and, in 4, of three B atoms, one cage C and one bipy C atom, using the ISOR command.<sup>21</sup> In compound 2 there is  $\frac{1}{4}$  molecule of  $CH_2Cl_2$  per molecule of stannacarborane, and in 5 the solvent was modelled as  $\frac{1}{2}$  molecule of hexane per molecule of stannacarborane. The crystal of 1 was treated as a two-component twin, indexed using CELL\_NOW,<sup>22</sup>

	1	2	3	4	5
Formula	$C_5H_{16}B_{10}Sn$	$C_{15}H_{24}B_{10}N_2Sn \cdot \frac{1}{4}CH_2Cl_2$	$C_{17}H_{24}B_{10}N_2Sn$	$C_{27}H_{32}B_{10}N_2Sn$	$C_{20}H_{26}B_{10}N_2Sn \cdot \frac{1}{3}C_6H_{14}$
M	302.97	480.38	483.17	611.34	549.94
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/Å	11.520(3)	10.1522(8)	8.2556(14)	7.58370(10)	11.8737(7)
b/Å	7.4934(17)	18.4533(17)	23.479(4)	37.9500(8)	14.0561(8)
c/Å	14.040(3)	22.9010(19)	10.8500(15)	19.5831(4)	15.2938
β (°)	92.078(10)	93.834(5)	98.566(9)	96.6860(10)	109.310(3)
$U/Å^3$	1211.2(5)	4280.7(6)	2079.6(6)	5597.71(18)	2408.9(2)
Ζ	4	8	4	8	4
<i>F</i> (000)/e	584	1908	960	2464	1107
$D_{\rm c}/{\rm Mg}~{\rm m}^{-3}$	1.661	1.491	1.543	1.451	1.516
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	2.062	1.261	1.236	0.935	1.077
$\theta_{\rm max}$ (°)	27.53	27.59	34.33	23.61	28.62
Data measured	31929	26476	67393	77776	54270
Unique data, n	3577	9313	8582	8186	6141
$R_{\rm int}$	0.0643	0.1057	0.1006	0.0712	0.0690
$R$ , w $R_2$ (obs. data)	0.0251, 0.0792	0.1885, 0.3476	0.0392, 0.0788	0.0376, 0.0695	0.0396, 0.0889
S	1.150	2.375	0.967	1.076	0.932
Variables	164	533	301	721	346
$E_{\rm max}, E_{\rm min}/{ m e}~{ m \AA}^{-3}$	0.733, -0.637	1.931, -1.824	1.307, -1.411	0.986, -0.771	1.175, -1.100

using HKLF5 which includes both components. Data from 2 were also treated as a two-component twin but refined using the twin law -1000-1.001.6501 and HKLF4 data. This proved to be the best model and data set for these crystals arising from many attempts including the use of synchrotron data. Data from 3–5 was corrected for absorption using SADABS.<sup>24</sup> For 3, 5 and some H atoms in 1, cage-bound H atoms were located in difference Fourier maps and freely refined. Cage H atoms of 4 and the remaining cage H atoms in 1 were constrained to B–H 1.10 Å. In all cases, H atom thermal parameters were set to  $1.2 \times U_{eq}$  of the attached B or C atom. Table 4 contains further experimental details. **Calculations** 

All geometries were optimised without constraints using Gaussian 03, Revision C.02<sup>18</sup> employing the BP86 functional.<sup>25</sup> 6-31G\*\* basis sets were used for B, C, H and N atoms<sup>26</sup> whilst for P, Pt and Sn the Stuttgart relativistic ECP<sup>27</sup> was employed with additional d-polarization functions for P and Sn. Local minima were confirmed as such through analytical frequency calculations. Energy decomposition analyses were performed with ADF2009.01,<sup>19</sup> applying symmetry constraints, if appropriate, as described in the text. The BP86 function was employed and ZORA/TZ2P basis sets were used for all atoms. Geometry measurements were made using Mercury.<sup>28</sup>

scaled and absorption corrected using TWINABS<sup>23</sup> and refined

## Acknowledgements

We thank the EPSRC for funding (PDA supported by DTA studentship; DE and DMcK supported by project EP/E02971X/1) and the EPSRC National Crystallographic Service at the University of Southampton for data from compound 2.

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