Bonding Studies of Derivatives of Pentaborane(9) Through Self-consistent Charge Calculations

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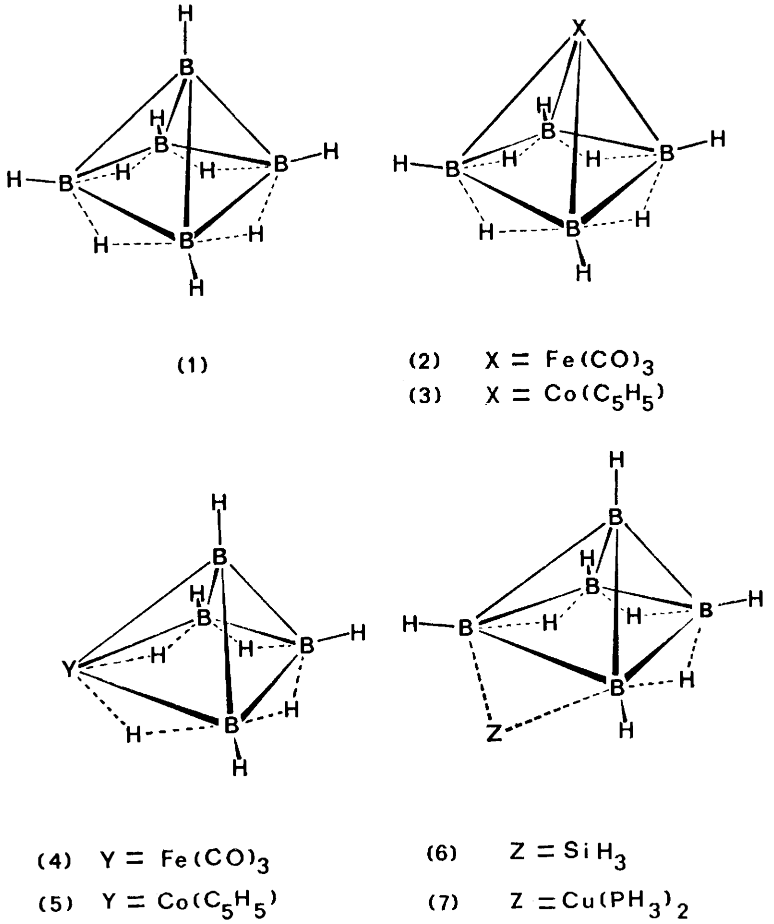
Derivatives of pentaborane(9) have been studied by self-consistent charge calculations to examine multicentre bonding and the application of the ' isolobal, pseudo-isoelectronic ' principles. The results reproduce previously reported photoelectron spectra reasonably well. Interpretation of the results suggests that the differences encountered in bonding apical and basal units are similar for BH, $Fe(CO)_3$, and $Co(\eta^5-C_5H_5)$ groups. The highest occupied molecular orbitals of B_5H_9 involve apical boron 2*p* orbitals and correlate well with cluster orbitals in 1-[$B_4H_8Fe(CO)_3$] and 1-[$B_4H_8Co(\eta^5-C_5H_5)$] which largely involve metal 3*d* orbitals. However the next cluster orbital in B_5H_9 has no direct counterpart in the metal derivatives. The metallo-units appear to be bonded into the cluster by a one-electron, two-orbital combination rather than the two-electron, three-orbital method used by BH. Similarly for the 2-isomers. Replacement of a bridging hydrogen by a μ-(SiH_3) unit leaves the cluster substantially unaltered. However with a μ-[$Cu(PH_3)_2$] bridging unit the major bonding contribution combines boron *s* and *p* and a copper 4*p* orbital in an ' open ' three-centre bond.

THE quite recent realisation of the ability of boranes to form numerous derivatives with metallo-containing groups has produced a rapid development in the investigation of these compounds. Derivatives based on boranes with two to eleven boron atoms have been prepared, characterised, and had their chemistry investigated. However, whereas borane clusters have been subject to extensive theoretical investigations of the most sophisticated type,[1] theoretical studies of small metalloboranes have been virtually non-existent to date except for an X_α-SW calculation on 1-[$B_4H_8Fe(CO)_3$].[2] By far the most important use of theory in the discussion of patterns in structure and bonding in these compounds has been in the application of the ' isolobal, pseudo-isoelectronic ' principles, which designate fragments such as $Fe(CO)_3$, $Co(\eta^5-C_5H_5)$, and BH as pseudo-isoelectronic



(1)

(2) X = $Fe(CO)_3$
(3) X = $Co(C_5H_5)$

(4) Y = $Fe(CO)_3$
(5) Y = $Co(C_5H_5)$

(6) Z = SiH_3
(7) Z = $Cu(PH_3)_2$

FIGURE 1 Pentaborane(9) and derivatives studied and structurally interchangeable.[3] Although this model has met with considerable success in correlating the structures of boranes, metalloboranes and metal clusters, and corresponding carboranes and derivatives, it provides little information on the details of the bonding.

We decided to initiate an investigation in detail of the bonding of metalloboranes by making self-consistent charge calculations on B_5H_9 and a number of its metallo-derivatives (Figure 1). Both the system and computational technique were chosen by the following considerations. The metallo-derivatives of B_5H_9 are small enough to be computationally tractable, yet the borane contains three distinct multicentre bonding sites, namely the apical boron, basal boron, and bridging-hydrogen positions. Derivatives of B_5H_9 with metallo-groups occupying each of these three sites are known and have been characterised structurally, a situation at present unique among the derivatives of small borane clusters. Self-consistent charge calculations are very much more accurate than the extended Hückel calculation used to discuss isolated units, providing results reasonably comparable with those from *ab-initio* calculations for the valence molecular orbitals (m.o.s). They do suffer from certain problems, which however are identifiable and are discussed where relevant and allowance made for them. Obviously the calculations are not particularly sophisticated, but we are of the opinion that properties determined by summation over the occupied set of molecular orbitals are well represented. Thus we make no claim that the energies or ordering of molecular orbitals are particularly accurate, although in most cases where experimental data (photoelectron spectroscopy, p.e.s.) are available one or both of these are well supported, but that quantities such as localised charges and overlap populations can be sensibly used for discussion of bonding. This should be particularly true of these molecules which have a large energy gap between occupied and unoccupied m.o.s. Further, in cases where the contributions to the bonding of the metallo-unit to the borane cluster can be located in one or two m.o.s then it is reasonable to assume that these provide a good representation of the orbital structure of the bonding.

COMPUTATIONAL

The method used was the FORTICON 8 program of Hoffmann and co-workers.[4] This calculation is an all-valence electron calculation [3*d*, 4*s*, and 4*p* a.o.s (atomic orbitals) on transition-metal atoms, 2*s*, and 2*p* on second-row atoms] and was used in its charge iteration mode. Iterations were continued until successive ones produced $<10^{-4}$ e^- change in the charge on any atom. The well known problem of obtaining convergence with such self-consistent charge calculations (SCC) was eased by an improved damping scheme and use of a Madelung correction.

In some cases SCC calculations and in fact *ab-initio* calculations are subject to aberations which have been referred to as ' counter-intuitive orbital mixing,' COM.[5] It occurs when a.o.s on different centres have a large overlap, but are very different in energies. This results in some high-energy occupied m.o.s with small antibonding contributions from these a.o.s. The mixing is small enough to have no effect on the energetics of the m.o. energy scheme but when combined with the large overlap it causes considerable problems with orbital occupations and overlap population analyses. COM has only been found in systems π bonded to metal atoms (*e.g.* ferrocene) and is typified by significant negative occupation of metal 4*s* and 4*p* a.o.s (those a.o.s with large overlap with the 2*p* a.o.s of the donating system) and negative overlap populations between the π-donating system and the metal.

Hoffmann has proposed an improvement to the Wolfsberg–Helmholtz formula for the H_{ij} elements of the secular determinant designed to minimise COM effects and this is also built into the program used in the calculations. We only observe the effects of COM in the $Co(\eta^5\text{-}C_5H_5)$ containing compounds, and then only involving the $Co\text{-}(\eta^5\text{-}C_5H_5)$ bonding. This of course is exactly where they would be expected. However in the following discussion the $Co(\eta^5\text{-}C_5H_5)$ unit is considered as a complete replacement for BH units and its internal bonding is not really relevant. Thus although, as expected, the calculation gets the electron distribution inside the $Co(\eta^5\text{-}C_5H_5)$ unit wrong, this does not significantly affect the information on the bonding of this unit to the rest of the molecule. This important point is further supported by the fact that the description of the cluster bonding in these compounds is very similar to that for compounds containing $Fe(CO)_3$ units which are not subject to COM effects.

The geometries used were taken from either electron-diffraction data for B_5H_9 [6] and $[Fe(CO)_3(\eta^4\text{-}C_4H_4)]$ [7] or *X*-ray diffraction data for $2\text{-}[B_4H_8Co(\eta^5\text{-}C_5H_5)]$ [8] and data from related $Fe(CO)_3$ and $Co(\eta^5\text{-}C_5H_5)$ containing compounds.[9] For compound (6) the structure was based on electron-diffraction data for 1- and $2\text{-}B_5H_8(SiH_3)$ [10] and *X*-ray diffraction data on $B_5H_7Br(\mu\text{-}SiMe_3)$.[11] The structure of (7) was based on *X*-ray diffraction data on $B_5H_8[\mu\text{-}Cu(PPh_3)_2]$.[12] Bond lengths of Si–H (150 pm) and P–H (144 pm) were used.[13] Calculations involving slight variations on the chosen geometries of (2) and (4) were made. Changing the position of the metallo-unit by ±10% with respect to the B_4H_8 group produced no significant changes in the results.

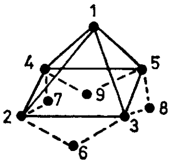
RESULTS AND DISCUSSION

B_5H_9.—As a preliminary to the discussion of the metalloboranes we review the bonding in B_5H_9 as described by the SCC calculation. Our interest centres on the bonding of the three types of multicentre bonding site so we ignore the m.o.s providing bonding to the terminal hydrogen atoms. This is consistent with the general tactic of this paper, by which we consider replacement of complete BH units by metallo-units. The details of the multicentre bonding can be considered from a number of different pieces of information provided by the calculation, namely: the gross atomic charges (Table 1), the overlap populations (Table 2), and the m.o. energy levels and their LCAO expansion (Figure 2).

The presence of two distinct types of BH unit in the molecule is shown by the localised charges, the apical position being significantly negatively charged. The overlap populations bonding these units into the molecule are slightly different, the apical unit being more strongly bonded into the cluster, further reflecting the excess of charge available for bonding associated with

TABLE 1

Charges localised on BH, $Fe(CO)_3$, and $Co(\eta^5\text{-}C_5H_5)$ units in molecules (1)—(5) of Figure 1



Molecule	Sites as shown in diagram 1	2	3	5	6	8	Charge on metal atom
(1)	−0.210	0.094			−0.041		
(2)	0.209	−0.065			0.011		0.920
(3)	0.319	−0.056			−0.024		0.786
(4)	−0.257	0.480	−0.050	0.150	−0.092	0.035	0.948
(5)	−0.263	0.491	−0.069	0.088	−0.142	0.015	0.863

this unit. More important is that the two units derive their overlap populations from very different types of interaction. The basal BH unit obtains nearly half its bonding through interaction with bridging-hydrogen atoms, whereas the apical unit is purely bonded to the other boron atoms. These comments typify the distinction of bonding environments mentioned above.

The m.o. diagram obtained from the SCC calculation agrees well with two previous *ab-initio* calculations [14,15] and with a photoelectron spectrum,[15] assuming Koopmann's theorem applies, both as to the energy and the order of the m.o.s. The m.o.s involved in multicentre bonding are depicted in Figure 2. The 'isolobal' orbital description of a BH unit is most easily identified for the apical BH. Isolation of contributions on this centre to the three highest occupied molecular orbitals (h.o.m.o.s) [$e(\alpha, \beta)$ and $a_1(\gamma)$] and the lowest energy m.o. (a_1) in the molecule would give the usual hybridised picture of the 'isolobal' description. The same picture is a reasonable representation of an isolated basal BH unit, although, as stated above, bonding inside the cluster is very different. Thus for B_5H_9 the concept of two electrons and three orbitals available for cluster bonding is fairly well supported by the SCC calculation.

The bond lengths in B_5H_9 are $(BH)_{apical}\text{–}(BH)_{basal}$ 173 pm and $(BH)_{basal}\text{–}(BH)_{basal}$ 180 pm and these are obviously in agreement with the overlap populations of Table 2, both the total and site-to-site populations. This

TABLE 2

Overlap populations in molecules (1)—(7) of Figure 1 and $[Fe(CO)_3(\eta^4\text{-}C_4H_4)]$ (8) [a]

Molecule	Unit [b]	Sites 1	2	3	4	5	6	7	8	9	Total
(1)	(BH)-1		0.528	2	2	2	−0.054	6	6	6	1.896
	(BH)-2	0.528		0.293	3	−0.139	0.409	6	−0.033	8	1.737
	(H)-6	−0.054	0.409	2	−0.033	4		−0.012	7	−0.004	0.670
(2)	$[Fe(CO)_3]$-1		0.296	2	2	2	−0.058	6	6	6	0.952
	(BH)-2	0.296		0.443	3	−0.070	0.425	6	−0.033	8	1.879
	(H)-6	−0.058	0.425	2	−0.034	4		−0.008	7	−0.003	0.705
(3)	$[Co(\eta^5\text{-}C_5H_5)]$-1		0.215	2	2	2	−0.066	6	6	6	0.596
	(BH)-2	0.215		0.443	3	−0.089	0.417	6	−0.034	8	1.563
	(H)-6	−0.066	0.417	2	−0.034	4		−0.008	6	−0.003	0.717
(4)	(BH)-1		0.254	0.634	3	0.490	−0.032	6	−0.070	8	1.808
	$[Fe(CO)_3]$-2	0.254		0.121	3	−0.218	0.298	6	−0.079	8	0.716
	(BH)-3	0.634	0.121		−0.124	0.355	0.423	−0.039	0.384	−0.089	1.665
	(BH)-5	0.490	−0.218	0.355	3		−0.056	6	0.417	8	1.754
	(H)-6	−0.032	0.298	0.423	−0.042	−0.056		0.060	0.008	−0.033	0.618
	(H)-8	−0.070	−0.079	0.384	−0.090	0.417	0.008	−0.032		0.118	0.656
(5)	(BH)-1		0.135	0.691	3	0.502	−0.027	6	−0.073	8	1.819
	$[Co(\eta^5\text{-}C_5H_5)]$-2	0.135		0.035	3	−0.201	0.231	6	−0.087	8	0.423
	(BH)-3	0.691	0.035		−0.142	0.367	0.462	−0.035	0.385	−0.093	1.670
	(BH)-5	0.502	−0.201	0.367	3		−0.055	6	0.422	8	1.769
	(H)-6	−0.027	0.231	0.462	−0.035	−0.055		0.075	0.070	−0.030	0.691
	(H)-8	−0.073	−0.083	0.385	−0.093	0.422	0.017	−0.030		0.110	0.556
(6)	(BH)-1		0.525	2	0.505	4	−0.065	−0.070	7	−0.078	1.777
	(BH)-2	0.525		0.424	0.267	−0.176	0.292	0.453	−0.056	−0.037	1.692
	(SiH_3)-6	−0.065	0.292	2	−0.038	4		−0.015	7	−0.066	0.467
	[Totals for other sites: (BH)-4 1.595, (H)-7 0.633, (H)-9 0.756]										
(7)	(BH)-1		0.419	2	0.535	4	−0.056	−0.068	7	−0.063	1.653
	(BH)-2	0.419		0.478	0.173	−0.142	0.350	0.429	−0.026	−0.035	1.646
	$[Cu(PH_3)_2]$-6	−0.056	0.350	2	−0.069	4		−0.035	7	−0.007	0.429
	[Totals for other sites: (BH)-4 1.452, (H)-7 0.659, (H)-9 0.640]										
(8)	$[Fe(CO)_3]$-1		0.185	2	2	2					0.740
	(CH)-2	0.185		0.845	3	−0.143					1.732
	(No bridging hydrogens)										

[a] Symmetry equivalent entries in a single row are referred to the first occurrence of that entry [b] Labels on units of a particular molecule refer to the site labels of Table 1

is not simply a case of the geometry used determining the overlap population analysis which is used to interpret the geometry. The site-to-site $(\mathrm{BH})_{\mathrm{apical}}$–$(\mathrm{BH})_{\mathrm{basal}}$ population is twice that of $(\mathrm{BH})_{\mathrm{basal}}$–$(\mathrm{BH})_{\mathrm{basal}}$ and would suggest a much greater disparity in bond lengths. The observed situation is due to the contribution of bridging-hydrogen atoms to the $(\mathrm{BH})_{\mathrm{basal}}$–$(\mathrm{BH})_{\mathrm{basal}}$ bonding.

1-[$B_4H_8Fe(CO)_3$] *and* 1-[$B_4H_8Co(\eta^5$-$C_5H_5)$]. *Apical* BH *Replacement.*—Replacement of the apical BH by a metallo-group maintains the C_{4v} symmetry of the cluster (if metal ligands are ignored) and comparison with the borane is relatively straightforward. Table 2 shows the overlap population bonding the metallo-unit to the B_4H_8 base is *ca.* 50% of that bonding the apical BH in B_5H_9. This result has been discussed previously [16] and interpreted as showing these compounds to be even more 'electron-deficient' cluster compounds than B_5H_9. In (2) and (3) this deficiency is associated with charge separation inside the metallo-unit. The Fe atom of (2) carries nearly a +1 charge, the electron being largely delocalised over the carbonyl ligands. This 'missing' electron is therefore not available for cluster bonding and the overlap population between metallo-unit and borane base is correspondingly reduced. The same comments apply equally to the $Co(\eta^5$-$C_5H_5)$ unit of (3). The complete metallo-unit is overall positively charged, Table 1, a marked difference to the apical BH unit of B_5H_9.

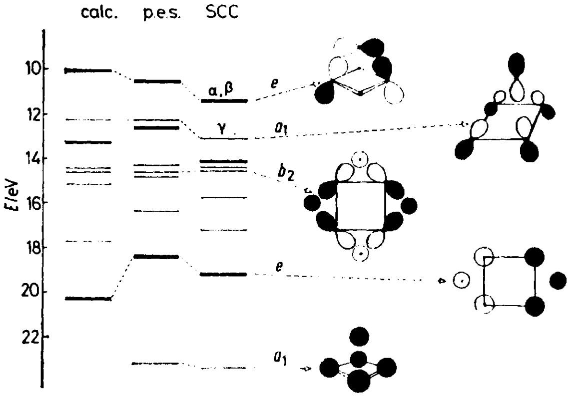


FIGURE 2 Energy level diagram and cluster orbitals for B_5H_9 (Heavy lines indicate pairs of degenerate orbitals, light lines indicate single orbitals)

The comparison of the cluster bonding m.o.s is obtained from Figures 2, 3, and 4. The three cluster h.o.m.o.s are labelled α, β, and ε in Figure 3, and their composition depicted in Figure 4. The roles of the apical boron $2p_x$ and $2p_y$ a.o.s in B_5H_9 are taken up by the iron $3d_{xz}$ and $3d_{yz}$ with some admixture of $4p_x$ and $4p_y$. However no m.o. corresponding to the a_1 h.o.m.o. of B_5H_9 (γ) is found in the metalloboranes. According to the 'isolobal' principle the $3d_{z^2}$, $4s$, and $4p_z$ metal a.o.s should combine to form a hybrid orbital which takes on the role of the boron $2s$ and $2p_z$ orbitals. In fact the $3d_{z^2}$ a.o. is only involved in iron-carbonyl, or Co–(η^5-C_5H_5), bonding and plays no part in cluster bonding. The basal part from the a_1 cluster m.o. of B_5H_9 is identified at lower energy, the ε_1 m.o. of Figure 4. This m.o. plays a very significant part in basal cluster bonding. The B–B bond length used was the same as that in B_5H_9, 180 pm, yet despite a large reduction in the basal-apical overlap populations, the total overlap population bonding basal BH units into the molecule is actually increased compared to B_5H_9 (Table 2). The basal BH units have enhanced B–B bonding through the ε cluster m.o. The net positive charge in the metallo-units implies more electron density localised on the borane base compared to B_5H_9 and is a further reflection of the enhanced B–B bonding.

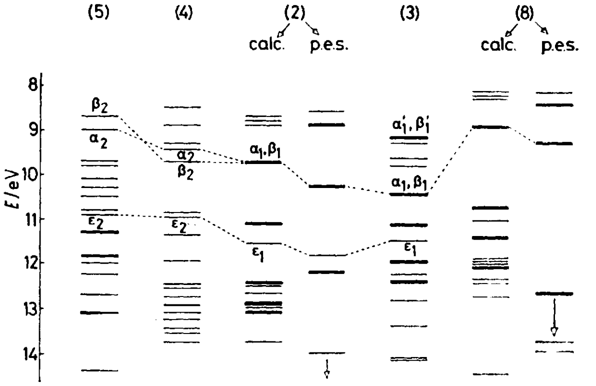


FIGURE 3 Energy level diagram for compounds (2)—(5) and (8) (Vertical arrows indicate several, possibly up to nine, orbitals involved in p.e.s. in this region)

In Figure 3 the m.o. energy levels obtained from the SCC calculation are compared with those from p.e.s.[17] To achieve the correspondence of these energy levels we have had to apply an energy shift to our m.o. energies. Such linear shifts of m.o. energies are common features of these calculations and are presumably related to the fact that inner shells are ignored. This 'frozen core' approach is known to produce a general shift of energies without any particular effect on the structure of valence m.o.s. The m.o. energy levels after applying this shift compare well with the p.e.s. and an X_α-SW calculation. The three h.o.m.o.s of (2) are involved in iron–carbonyl bonding, and the subsequent order of m.o.s agrees with

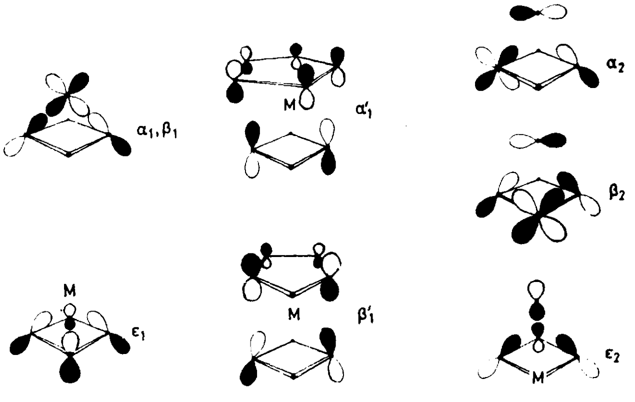


FIGURE 4 Representation of highest occupied cluster m.o.s in (2)—(5) and (8)

experimental assignments for this molecule. The two h.o.m.o.s of (3) (α'_1, β'_1) are of particular interest and are shown in Figure 4. Although the metal contribution is small (*ca.* 9% and therefore not shown in Figure 4) it accounts for most of the $4p_x$, $4p_y$ contributions to the metallo-unit–borane bonding. Some $3d$ metal a.o. contribution is found in these m.o.s and is an antibonding arrangement corresponding to the α_1 and β_1 m.o.s. This is not a COM effect but is due to the shift in energy of the $3d$ a.o.s on going from Fe to Co. The next three orbitals are Co–(η^5-C_5H_5) bonding although they have large contributions of cobalt *d* a.o.s, and are hence labelled '*d* lone pairs'. These three m.o.s correspond with the three h.o.m.o.s of (2). It is notable that the m.o. diagram of (3) has many formal similarities to that of ferrocene. Below 10 eV m.o.s are not susceptible to COM effects and the m.o.s correspond sensibly with those of (2). As stated above, and as is clear from Table 2, COM effects do not significantly interfere with the overall description of metallo-unit–borane bonding already discussed.

In relation to these molecules we include in this section some comments concerning [Fe(CO)$_3$(η^4-C_4H_4)], compound (8). The bonding in this molecule as described by the SCC calculation is remarkably similar to that in (2). The details are easily extracted from Tables 1 and 2 and Figures 3 and 4. However, the important point is that this molecule should be one in which COM effects operate, and hence by implication so should (2). But as shown by Figure 3, the first five h.o.m.o.s are in good agreement with p.e.s. [18] as were those of (2), and the details of the m.o.s, orbital occupations, and overlap populations show no evidence of COM effects. It appears that SCC calculations on Fe(CO)$_3$ containing molecules are relatively free of COM effects, and comparison of Co(η^5-C_5H_5) containing molecules with these allows some identification of these effects.

2-[B_4H_8Fe(CO)$_3$] *and* 2-[B_4H_8Co(η^5-C_5H_5)]. *Basal* BH *Replacement.*—Replacement of basal BH unit by a metallo-group reduces the symmetry of the cluster to C_s and the convenience of representing bonding in terms of individual m.o.s is lost to a large extent. However, the properties obtained by summation over the set of occupied m.o.s still allow interpretation of the bonding and some comments about individual m.o.s are possible. The total overlap population associated with the metallo-groups in these compounds is markedly less than that in the 1-isomer and much smaller than that of the BH replaced. In effect the replacement units are very weakly bonded into the cluster. Antibonding overlap with the opposite B atom is greater than in B_5H_9, whilst bonding overlap with apical and adjacent B atoms is reduced. The metallo–(BH)$_4$ overlaps contribute *ca.* 0.2 to the total population in (4) and *ca.* 0 in (5), and the metallo-units are held into the complex largely by interactions with the adjacent bridging-hydrogen atoms.

These results correlate with some of the known chemistry of the [B_4H_8Co(η^5-C_5H_5)] compounds. In the preparation of the 1- and 2-isomers it is found that the 2-isomer is formed initially as the kinetically stable product, but on heating the 1-isomer is obtained as the final and thermodynamically stable compound. The basal BH unit of B_5H_9 is less efficiently bonded into the cluster than the apical BH although the difference is not large. More important is that a large percentage of the basal BH overlap population arises from interaction with bridging hydrogens, and these bonds are probably more easily broken than the boron–boron bonds involved in a direct apical replacement. Once the 2-isomer is formed it is clear that it is a far less stable compound and rearrangement to the 1-isomer is preferred.

A number of similarities exist between the 1- and 2-isomers. Charge separation is found inside the metallo-units (Table 1) causing reduced cluster bonding of the metallo-unit. The highest-energy cluster-bonding m.o.s α_2 and β_2, shown in Figure 4, are as expected, one involving metal *d* orbital subrogating the basal boron *p* orbitals, α_2, and one largely a B_5H_9 orbital with some non-bonding metal contribution, β_2. The in-plane metal *d* orbital, similar to α_2, provides bonding to the bridging-hydrogen atoms but cannot be represented by a single m.o. due to the low symmetry. As in the 1-isomer the ε_2 m.o. of Figure 4 is a residual of the γ orbital of Figure 2 without metal contribution and is consistent with the enhancement of B–B bonding in those molecules. For example, in the Fe(CO)$_3$ compound, overlap populations B_{apical}–B_{basal} and B_{basal}–B_{basal} are 0.591 and 0.423 compared with 0.576 and 0.349 in B_5H_9, and the corresponding bond lengths are 167 and 176 pm compared with 169 and 180 pm.

A Critique of the Isolobal Principle.—As stated above, the a.o. contributions on B atoms in cluster m.o.s in B_5H_9 agree well with the isolobal description of the isolated BH. We are now in a position to consider whether the extension of this principle to metallo-units in clusters is supported by the calculations. In Table 3 we list the overlap populations of metal a.o.s and the four B atoms in compounds (2)—(5) and in Table 4 the orbital occupations of these a.o.s. (For the 2-isomer the *z* axis is through the metal atom and the opposite B atom, and the apical B atom is in the positive *yz* plane, so the a.o.s are directly comparable.)

For the Fe(CO)$_3$ containing compounds Table 4 shows that the $3d_{xz}$, $3d_{yz}$, $4p_x$, and $4p_y$ orbitals account for *ca.* 90% of the cluster-bonding overlap. The 2-isomer metallo-unit is more weakly bonded than the 1-isomer as previously discussed and this is due to a reduction of both *d* and *p* overlaps. The associated m.o.s have been discussed and are in general agreement with the isolobal principle. However, the absence of any cluster-bonding contribution from the $3d_{z^2}$, $4s$, and $4p_z$ orbitals is obvious from Table 3 and is a major divergence from the isolobal principle. From Table 4 we see that the Fe atoms have approximately $3d^64p^1$ configuration, giving a +1 charge on these atoms. Such a configuration is unusual, $3d^7$ being common for predominently ionic or organometallic complexes, but may be expected from the isolobal principle.

For the Co(η^5-C_5H_5) containing compounds, (3) and

(5), much the same is true, but COM effects are evident from the Tables. The large negative overlap population associated with the $4p_z$ orbital is a case in point. Some negative overlap is expected in the 2-isomer due to interaction with the opposite B atom [*cf.* B_5H_9 and (4)] but not as much as is found. This is only associated with the $4p$ a.o.s due to their large overlaps with boron a.o.s. The $3d_{z^2}$ orbital, which does not show COM effects, is not involved in cluster bonding. The negative occupation of the $4p_z$ orbital is a further reflection of this problem, compounded with the COM effects associated with Co–(η^5-C_5H_5) bonding. Table 3 gives an approximate $3d^8$ configuration for Co, but COM effects have reduced the $4p$ occupation by *ca.* 0.4 and it is reasonable to assume that if COM effects were not operative $3d^7 4p^1$ would be more accurate.

TABLE 3

Overlap populations between metal a.o.s and B atoms in molecules (2)—(5)

	Metal a.o.								
Molecule	$3d_{x^2-y^2}$	$3d_{z^2}$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	$4s$	$4p_x$	$4p_y$	$4p_z$
(2)	0.078	0.047	0.002	0.296	0.295	0.045	0.184	0.170	0.061
(3)	0.093	0.004	0.004	0.277	0.277	0.198	0.126	0.126	−0.222
(4)	0.031	0.009	−0.039	0.127	0.106	0.030	0.034	0.028	−0.044
(5)	0.033	0.013	−0.027	0.152	0.123	0.015	0.096	0.053	−0.302

In summary, we would propose that so far as the highly directional m.o.s are concerned (the α and β m.o.s of Figures 2 and 3 and those providing metallo-group–bridging-hydrogen bonding in the 2-isomer), the isolobal principle provides a good description of the isolated units ability to form cluster bonds, namely through a combination of $3d$ and $4p$ a.o.s. However the ' hybrid a_1 '[3c] orbital is not found to be involved in cluster bonding, and charge separation inside the metallo-unit leads to fewer electrons being available for cluster bonding than expected. We would suggest that for metallo-units in metalloboranes a ' one-electron, two-orbital ' description of their involvement in cluster bonds is more apposite than the ' two-electron, three-orbital ' description obtained from comparison with boranes.

TABLE 4

Occupations of metal a.o.s in molecules (2)—(5)

	Metal a.o.								
Molecule	$3d_{x^2-y^2}$	$3d_{z^2}$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	$4s$	$4p_x$	$4p_y$	$4p_z$
(2)	1.22	1.22	1.24	1.02	1.02	0.32	0.42	0.42	0.20
(3)	1.83	1.93	1.90	1.23	1.23	0.21	0.09	0.09	−0.29
(4)	1.26	1.36	1.26	0.92	1.04	0.30	0.35	0.38	0.18
(5)	1.89	1.93	1.83	1.17	1.37	0.14	0.06	0.08	−0.36

$B_5H_8(\mu\text{-}SiH_3)$ *and* $B_5H_8[\mu\text{-}Cu(PH_3)_2]$. *Bridging Hydrogen Replacement.*—The bonding of bridging hydrogens in (1) is achieved through three of the m.o.s of Figure 2. These m.o.s are easily localised to give the orbital structure of the bonding of any one bridging-hydrogen atom and this is shown in Figure 5. On replacing the hydrogen atom by SiH_3 it can be seen from Table 2 that the associated overlap population is reduced by 30% from the B_5H_9 value. With the reduction of symmetry from C_{4v} to C_s, the m.o.s providing this overlap are strongly localised and are shown in Figure 5. It can be seen that an sp^3 hybrid on the Si atom forms the bridging lobe of the closed three-centre bond.

The m.o. energy levels show very good agreement with the p.e.s.[19] without any correction to the energies. The m.o. at −11.62 eV of Figure 5 is the third h.o.m.o., the top two being directly derived from the two h.o.m.o.s of B_5H_9. The reduction of bonding overlap is directly attributable to the more diffuse nature of the silicon $3s$ and $3p$ orbitals compared with the $1s$ of hydrogen. However this does not obscure the fact that the bridging bonding in (2) and (6) is basically the same.

A quite different result is found for compound (7). The Cu atom is coplanar with the adjacent boron and apical boron atoms, and the B–Cu–B angle is *ca.* 45°. Given this geometry it is impossible for a Cu d orbital to complete a closed three-centre bond involving orbitals on the adjacent boron atoms similar to those used in (1). The bonding of the $Cu(PH_3)_2$ unit is achieved by stabilisation of one of the $4p$ orbitals by interaction with a completely different set of orbitals on the adjacent boron atoms. This stabilisation of a $4p$ orbital effectively displaces one of the $3d$ orbitals which becomes a virtual orbital. The m.o.s providing the bonding of the $Cu(PH_3)_2$ unit are shown in Figure 5 together with the localised bonding structure arising from them. The overlap population of 0.429 is largely due to the $4p$ orbital which is involved in an open three-centre bond. As it is impossible, even on intuitive grounds, to suggest an alternative bonding scheme for this site given the geometry of the molecule, we believe this to be the first clear case of an open three-centre bond characterised in metalloboranes.

From Table 1 it can be seen that replacement of H by SiH_3 has little effect on the rest of the bonding of the borane cluster. The total overlap population for any one site is reduced for all sites from their B_5H_9 values but not by a great amount. The most notable change is that the loss of overlap between the adjacent borons to the silicon atom is balanced by a marked increase in overlap population between the adjacent boron atoms themselves.

This is due to the shorting of this boron–boron distance (169 pm *cf.* 180 pm in B_5H_9) in an attempt to maximise overlap with the silicon atoms. This effect is even more marked in (7). The adjacent boron–boron bond is of similar length (170 pm), and other boron–boron bond lengths are not much changed from B_5H_9 (177, 181 pm).

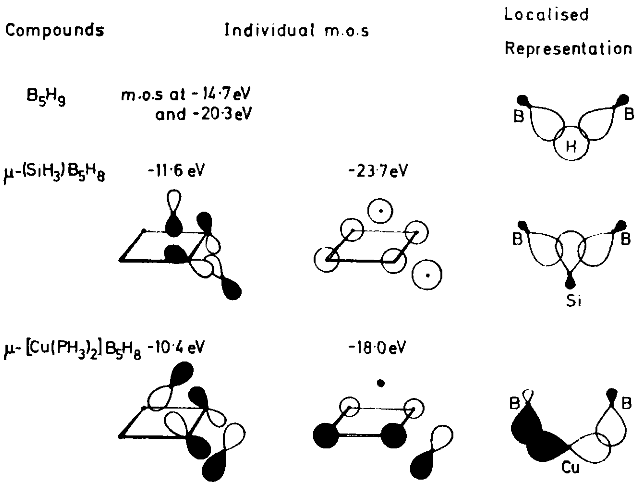


FIGURE 5 Representation of orbitals involved in bridge bonding

The completely different bonding in this molecule however produces weaker bonding between the 2, 4 positions (Table 2) than would be expected [0.173, *cf.* 0.267 in $B_5H_8(SiH_3)$ and 0.293 in B_5H_9]. This is further shown in the reduced total overlap population associated with the 4, 5 sites.

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