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SELF-CONSISTENT CHARGE AND CONFIGURATION (SCCC) CALCULATIONS ON 1,6-DICARBA-CLOSO-HEXABORANE (6), 2,4-DICARBA-CLOSO-HEPTABORANE (7) AND THEIR METALLO-DERIVATIVES

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Abstract : The bonding in 1, 6-dicarba-closo-hexaborane [6] [1], [$C_2B_3H_5${$Fe(CO)_3$}] [II]. 2,4-dicarba-closo-heptaborane[7] [III], [$C_2B_4H_6${$Fe(CO)_3$}] [IV], and [$C_2B_3H_5${$Fe(CO)_3$}$_2$] [V] was investigated by carrying out self consistent and configuration [SCCC] calculations. These investigations show that an apical boron atom uses $2p_x$, $2p_y$ atomic orbitals and a [2s, $2p_z$] hybrid orbital for bonding with rest of the cluster. In cluster compounds containing $Fe(CO)_3$ units, the iron atom uses predominantly [$3d_{xz}$, $4p_x$] and [$3d_{yz}$, $4p_y$] combinations for bonding with the rest of the cluster and there is no evidence for the involvement of a [4s, $4p_z$, $3d_z2$] hybrid orbital similar to the [2s, $2p_z$] hybrid observed in the boron analogue. Analysis of the total overlap population associated with metallo-group and the rest of the cluster shows that the $Fe(CO)_3$ group is weakly bonded into the cluster when compared with BH group of compounds in which $Fe(CO)_3$ is replaced by BH. This analysis also indicates that $Fe(CO)_3$ group uses less than two electrons for cluster bonding.

1. Introduction

Understanding of the electronic structure and bonding of metal carbonyl clusters is of present interest. The number of orbitals involved in bonding [> 100 atomic orbitals] makes it difficult to perform detailed molecular orbital calculations on metal carbonyl clusters. But it is believed that certain metallo groups such as $Fe(CO)_3$ and $Co(CO)_3$ are isolobal and isoelectronic with the BH and CH groups respectively. In terms of Wade's approach[19] a BH or a $Fe(CO)_3$ group formally supplies two electrons for cluster bonding whereas CH and $Co(CO)_3$ groups supply three each. In addition, many boranes, carboranes, metalloboranes, metallocarboranes, and metal carbonyl clusters have similar geometries.[13,19] Thus the study of the electronic structure and bonding of boranes, carboranes, metallo-boranes and metallo-carboranes could be used to compare the bonding capabilities of transition metal carbonyl fragments, $M(CO)_3$ with those of the BH or CH Units in cluster compounds. In our study, self-consistent charge and configuration (SCCC) calculations were used to investigate the bonding in 1,6-dicarba-closo-hexaborane[6] [I], [$C_2B_3H_5$ {$Fe(CO)_3$}] [II], 2,4-dicarba-closo-heptaborane [7] [III], [$C_2B_4H_6$ {$Fe(CO)_3$}] [IV] and [$C_2B_3H_5$ {$Fe(CO)_3$}$_2$] [V].

2. Computational Method

The method used was the FORTICON[8] programme of Hoffman and co-workers[15] This calculation is an all valence electron, extended Huckel calculation [3d, 4s and 4p atomic orbitals on transition metal atoms, 2s and 2p on second row atoms and on hydrogen atom are used] and was used in its charge iteration mode according to H_{ii} = VSIE[Q] where H_{ii} is the diagonal Hamiltonian matrix element and VSIE[Q] is the valence state ionisation energy of orbital i when the atom has total charge Q. The off diagonal Hamiltonian matrix elements are calculated in the normal manner[9] using the expression,

$$H_{ii} = k \frac{S_{ii}}{2} [H_{ii} + H_{jj}]$$

where ki is a constant.

The VSIE[Q] functions are assumed to be of the form,

$$\mathrm{VSIE}[Q] = AQ^2 + BQ + C$$

where A,B and C are parameters,[16,20] which depend on the atom and the orbital. Iterations are continued until successive ones produced $< 10^{-4}$e change in the charge on any atom [e = electronic charge]. The well known problem of obtaining convergence with such self-consistent charge calculations was eased by an improved damping scheme and by the use of a Madelung correction. The orbital occupations are summed separately over the p and d orbitals on each atom. The resulting p and d occupations, along with s occupations, are damped according to the equation

$$\rho_r^{\text{input } k+1} = \rho_r^{\text{input } k} + (\rho_r^{\text{output } k} - \rho^{\text{input } k})$$

where ρ is the summed orbital occupation of a given type, s,p or d, indexed by r on the k^{th} cycle and λ is a damping parameter.

The geometries of carboranes used were taken from reported,[17,18] electron diffraction data. The same geometries were used for metallocarboranes. The geometry of the $Fe(CO)_3$ unit was taken from that of [$Fe(CO)_3$ η^4-C_4H_4][10]. Fe – C and C–O bond lengths of 0.182 nm and 0.115 nm respectively were used. Changing the position of the metallo-units by ± 10% with respect to the carborane base produced no significant change in the results.

Table 1. Gross atomic charges in molecules [I] – [V]

Molecules	Atom sites as shown in diagrams [I] to [V]										
	1	2	3	4	5	6	7	Carbonyl group			
								Carbon		Oxygen	
								d	e	d	e
[I]	–0.014	0.094	0.094	0.094	0.094	–0.014	–	–	–	–	–
[II]	–0.055	0.057	0.074	0.057	0.733	–0.055	–	0.041	–	–0.200	–
[III]	0.124	–0.022	0.105	–0.022	0.070	0.070	0.124	–	–	–	–
[IVa]	0.824	–0.062	0.066	–0.062	0.043	0.043	0.095	0.043	–	–0.202	–
[IVb]	0.078	–0.037	0.077	–0.044	0.780	0.057	0.078	–	0.028	–	–0.216
[Va]	0.723	–0.074	0.038	–0.074	0.026	0.026	0.723	0.040	–	–0.200	–
[Vb]	–0.848	0.010	0.096	–0.065	2.615	0.054	0.054	0.102	–0.080	–0.220	–0.312.

d – Charge on the carbon/oxygen atom of carbonyl group when the Fe(CO)$_3$ unit is apical.

e – Charge on the carbon/oxygen atom of carbonyl group when the Fe(CO)$_3$ unit is basal.

Note: 1,2,3 etc. corresponds to the atom positions labelled 1,2,3 etc. in the diagrams [I] to [V].

Table 2. Charges localised on BH_2 Ch and $Fe(CO)_3$ units in molecules [I] – [V]

	Atom sites as shown in diagrams [I] – [IV]						
Molecule	1	2	3	4	5	6	7
[I]	−0.045	0.022	0.022	0.022	0.022	−0.045	–
[II]	−0.013	−0.034	0.002	−0.034	0.271	−0.103	–
[III]	0.055	−0.051	0.034	−0.051	−0.021	−0.021	0.055
[IVa]	0.344	−0.111	−0.026	−0.111	−0.063	−0.063	0.027
[IVb]	−0.001	−0.069	−0.003	−0.081	0.217	−0.042	−0.021
[Va]	0.250	−0.127	−0.069	−0.127	−0.086	−0.086	0.250
[Vb]	−1.204	−0.033	0.007	−0.118	1.447	−0.060	−0.038

Table 3. Overlap population in molecules [I] and [II]

Bond	I	II
$C^{1[6]}-B2$	0.579	0.740
$C^{1[6]}-B^3$	0.579	0.672
$C^{1[6]}-B^5$	0.579	–
$C^{1[6]}-Fe^5$	-	0.340
B^2-B^3	0.519	0.570
B^2-Fe^5	–	0.285
$C^{1[2]}-H$	0.841	0.877
$B^{2[4]}-H$	0.816	0.839
B^3-H	0.816	0.806

3. Results and Discussion

The details of the cluster bonding in carboranes and metallocarboranes can be considered from three pieces of information provided by the SCCC calculation. They are [i] the gross atomic charges [ii] the overlap populations and [iii] the molecular orbital energy levels and their LCAO expansions.

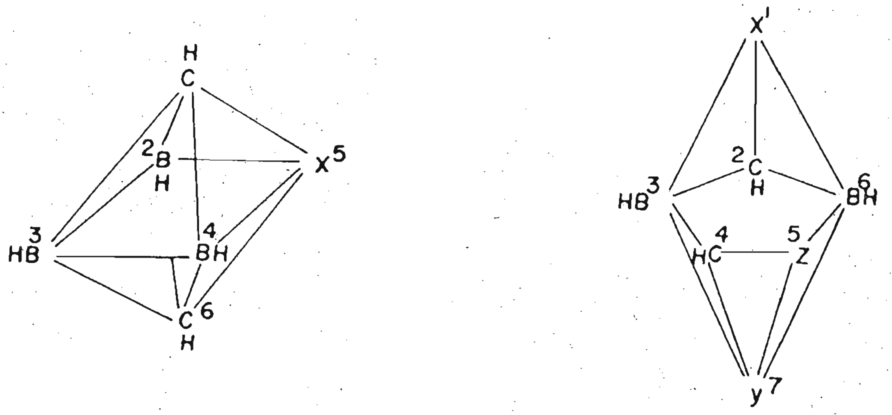
3.1 1,6-$C_2B_4H_6$ [I] and 2,4-$C_2B_5H_7$ [III]

The gross atomic charges (Table 1) and the overlap populations (Table 3) indicate that the four BH units in 1,6-$C_2B_4H_6$ are equivalent and so are the two CH units. This is in agreement with the predicted[17] D_{4h} symmetry of the molecule. The presence of three distinct type of BH units in 2,4-

$C_2B_5H_7$ is shown by the localised charges [Tables 1 and 2], the boron atom in apical position being more positively charged. The overlap populations [Table 4] bonding these BH units into the cluster [in 2,4-$C_2B_5H_7$] are slightly different and reflect the positive charges on boron atoms. Thus the two apical BH units are less strongly bonded into the cluster when compared with the three basal BH units. The gross atomic charges on carbons and borons agree with the more electronegative character of carbon compared with boron. Our values for located charges on C–H and B–H moieties [–0.045 and 0.022 respectively] of 1,6-$C_2B_4H_6$ are comparable with the values [–0.05 and 0.03 respectively] reported[12] earlier by a different SCF calculation. Three cluster bonding molecular orbitals are found in 1,6-$C_2B_4H_6$. The HOMO[$2b_{2g}$] is a B_4 combination [E = –11.75eV] followed by a degenerate pair [$3e_u$] [E = –12.38eV] which has C_2B_4 combination. In 2,4-$C_2B_5H_7$, two cluster bonding molecular orbitals [E = – 25.95 and –12.81eV] of C_2B_5 combination have been found in addition to the HOMO [E = –11.2eV] which is a combination of mainly the planar carbon and boron atoms. Our results [Table 4] also show that in 2,4-$C_2B_5H_7$, the site to site $[BH]_{basal}$ – $[BH]_{basal}$ overlap population is

Table 4. Overlap populations in Molecules [III] – [V]

Bond	[III]	[IVa]	[IVb]	[Va]	[Vb]
$B^{1[7]}$ – H	0.836	0.828	0.862	–	0.856
C^2 – H	0.827	0.861	0.830	0.881	0.852
B^3 – H	0.836	0.858	0.838	0.871	0.848
C^4 – H	0.827	0.861	0.856	0.881	0.891
$B^{6[5]}$ – H	0.839	0.860	9.860	0.871	0.881
B^7 – H	0.836	0.828	0.860	–	0.856
$B^{7[1]}$ – C^2	0.469	0.536	0.518	–	0.558
B^3 – C^2	0.776	0.865	0.823	0.985	0.879
B^3 – $B^{7[1]}$	0.355	0.414	0.394	–	0.427
$B^{6[5]}$ – $B^{7[1]}$	0.447	0.538	0.584	–	0.657
B^6 – C^2	0.726	0.878	0.785	0.994	0.908
[B^5 – C^4]					
B^6 – B^5	0.693	0.751	–	0.842	
B^7 – C^4	0.469	0.536	0.651	–	0.712
Fe^1 – C^2	–	0.359	–	0.245	0.183
Fe^1 – B^3	–	0.294	–	0.235	0.147
Fe^1 – C^4	–	0.359	–	0.245	0.141
Fe^1 – $B^{6[5]}$	–	0.290	–	0.212	0.115
Fe^5 – $B^{7[1]}$	–	–	0.315	–	0.293
Fe^5 – C^2	–	–	0.340	–	0.299
Fe^5 – B^6	–	–	0.285	–	0.217
Fe^1 – Fe^5	–	–	–	–	0.777



(I) X = BH

(II) X = $Fe(CO)_3$

(III) X = Y = Z = BH

(IVa) X = $Fe(CO)_3$; Y = Z = BH

(IVb) X = Y = BH; Z = $Fe(CO)_3$

(Va) X = Y = $Fe(CO)_3$; Z = BH

(Vb) X = Z = $Fe(CO)_3$; Y = BH

SCHEME – [I]

greater than that of $[BH]_{basal} - [BH]_{apical}$ population and this is in agreement with the difference in observed[18] bond lengths [BH] basal – $[BH]_{basal}$ = 0.1659nm, $[B^1H] - [B^5H]$ = 0.1772nm and $[B^1H] - [B^3H]$ = 0.1852mm].

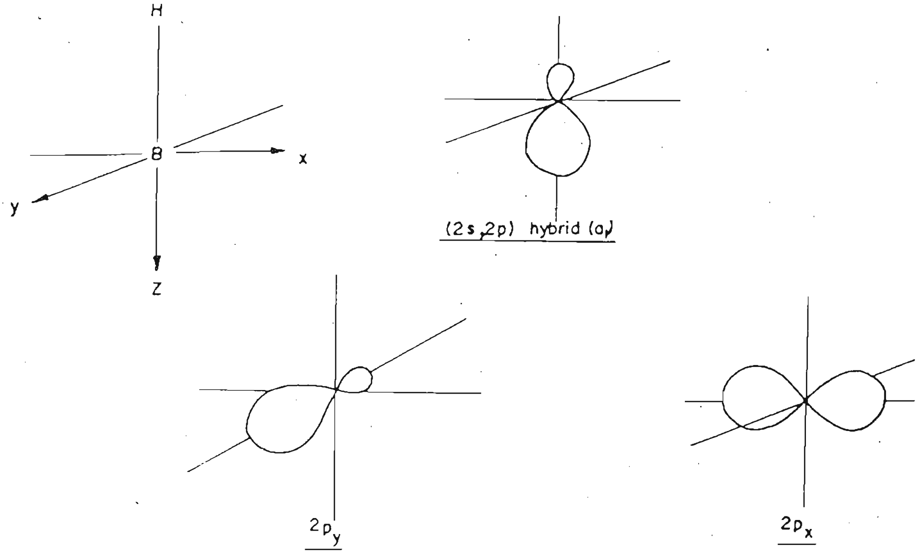
Let us commence the discussion of metallocarboranes by comparing the orbitals available on BH and $Fe(CO)_3$ units for cluster bonding. In terms of Wade's approach[19] both the BH and the $Fe(CO)_3$ units use two electrons and three orbitals for cluster bonding. Iron in the $Fe(CO)_3$ unit has nine valence shell orbitals [c.f. boron which has four valence shell orbitals], three of these are used to form M–C δ-bonds, three more as well as three electron pairs are used to form π-bonds to the carbonyl groups. This leaves the Fe atom with three valence shell orbitals and two electrons.

SCCC calculations show that in BH the HOMO is a δ-level composed of 2s and 2p while LUMOs[e] [$2p_x$ and $2p_y$] are the π-levels. In the case of $Fe(CO)_3$, the HOMO is a hybrid [a_1] orbital having 4s, $4p_z$ and $3d_z2$ components and the LUMOs[e] orbitals are formed from [$4p_x$, $3d_{xz}$] and [$4p_y$, $3d_{yz}$] combination as has been reported.[11] This is in agreement with Wade's skeletal electron counting technique. Thus the orbitals* available for cluster bonding on BH and $Fe(CO)_3$ units, as shown in Figure 1, are similar in symmetry as reported[11] earlier. [*The 2D projections of the HOMO and LUMO orbitals of BH and $Fe(CO)_3$ units obtained by z plot programme[1-4,9,16,20] also had similar shapes].

3.2 $[C_2B_3H_5\{Fe(CO)_3\}]$ [II]

Replacement of the BH unit is 1,6-$C_2B_4H_6$ by the $Fe(CO)_3$ unit, as in [II], increases [Table 1] the net negative charge on carbons by 0.041 and decreases the positive charge on boron by values in the range 0.020–0.037. Table 3 shows that the overlap population bonding the metallo-unit to the $C_2B_2H_4$ base is about 57% of that bonding the BH in 1,6-$C_2B_4H_6$. In other words the replacement of a BH unit by a $Fe(CO)_3$ group makes the resulting compound even more electron-deficient than the parent carborane. A similar result has been observed in borane clusters.[7] Table [I] shows that the iron atom of ferracarborane [II] carries a positive charge [0.733] and this may be the reason for the reduction in overlap population betwen the metallo-unit and carborane base. The positive charge on iron atom may be due to the valence electrons in iron atom being largely delocalised over the carbonyl ligands. Replacement of a BH unit in 1,6-$C_2B_4H_6$ by a $Fe(CO)_3$ unit did not change the energy of the cluster orbitals appreciably. The comparison of the cluster bonding molecular orbitals shows that the roles of the boron $2p_x$ and $2p_y$ atomic orbitals in carboranes are taken up by the iron $3d_{xz}$ and $3d_{yz}$ with some admixture of $4p_x$ and $4p_y$. According to the isolobal principle the $3d_z2$, 4s and $4p_z$ metal atomic orbitals should combine to form a hybrid orbital which takes on the role of the boron 2s and $2p_z$ orbitals. In $Fe(CO)_3$, the $3d_z2$ atomic orbital is involved in bonding but plays no

(a) BH cluster orbitals



(b) Fe(CO)3 cluster orbitals

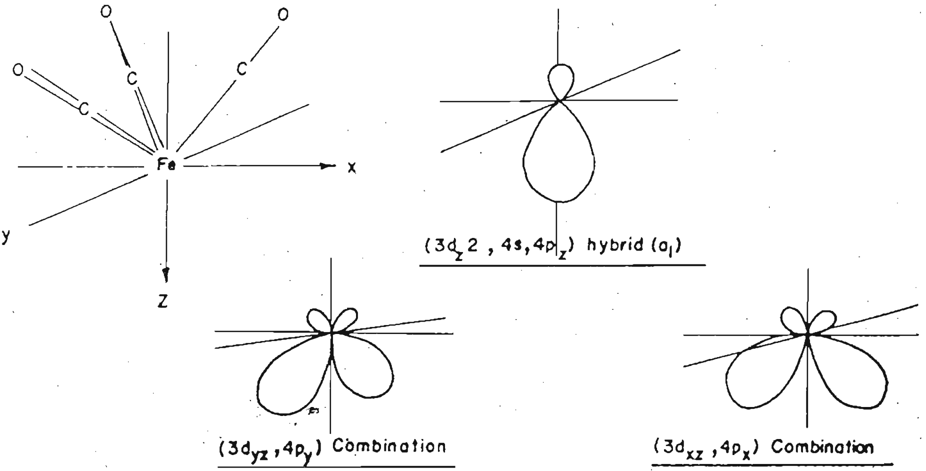


Figure 1. The orbitals available for cluster bonding on BH and $Fe(CO)_3$ units.

significant part in cluster bonding, whereas, the a_1 cluster molecular orbital of BH unit [which is equivalent to 2s, $2p_z$ hybrid of boron atom] plays a significant part in cluster bonding. A similar result has been reported[8] in metalloboranes. LCAO expansion of HOMO of [II] shows that it has a small contribution from the $3d_{x^2-y^2}$ of Fe and carbonyl carbon and oxygen atomic orbitals.

Table 5. Total energy of Valence Electrons

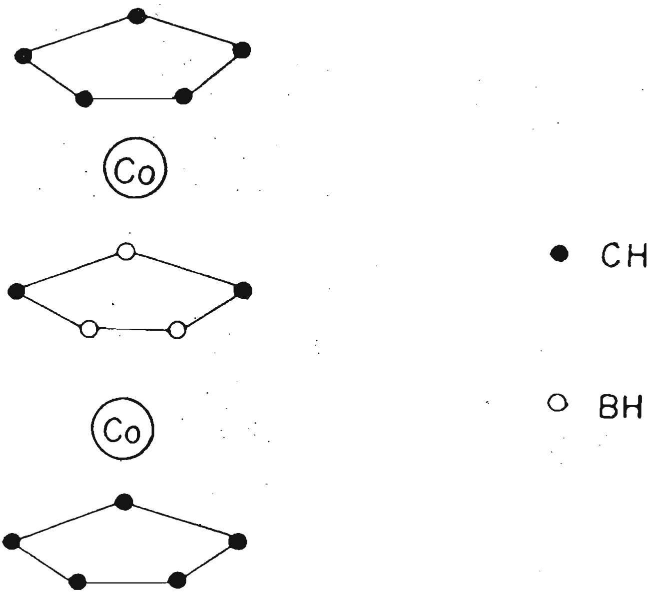
Molecule	Energy/eV
[I]	−403.8
[II]	−940.0
[III]	−462.3
[IVa]	−992.4
[IVb]	−987.9
[Va]	−1538.1
[Vb]	−1521.5

3.3 $[C_2B_4H_6\{Fe(CO)_3\}]$ [IV]

The replacement of an apical BH unit in 2,4-$C_2B_5H_7$ as in [IVa], [i] increases the net negative charge on carbon atoms by 0.040 [ii] decreases the positive charges on boron atoms [Table 1] and [iii] decreases the overlap population bonding the replaced site $Fe(CO)_3$, c.f.BH, to the $C_2B_3H_5$ base by about 27%. The replacement of a basal BH unit by a $Fe(CO)_3$ unit in 2,4-$C_2B_5H_7$ as in [IVb], also increases the net negative charges on carbon atoms but the increase is low [0.015 on C^2 and 0.022 on C^4] and decrease the positive charges on boron atoms [again the decrease is low, Table 1]. The total overlap population associated with the metallo-group in [IVb] is markedly less than that in [IVa] and is much smaller than that of the BH replaced [Ca 54%]. There is a corresponding increase in overlap population between adjacent boron and carbon atoms in [IVa] and [IVb] [Table 4] compared with those in 2,4 $C_2B_5H_7$. The total overlap population associated with the metallo-group and the total energy of valence electrons [Table 5] indicate that the 1-isomer [IVa] is more stable than the 5-isomer [IVb]. As mentioned earlier, the 2,4-$C_2B_5H_7$ has three cluster bonding molecular orbitals. two of C_2B_5 combinations and the third [HOMO] of basal carbon and boron atoms combination. The replacement of either the apical B^1H or basal B^5H by a $Fe(CO)_3$ unit did not change the energy of any of these orbitals appreciably. The comparison of the LCAO expansion of these orbitals shows that there is no significant contribution from the metal $3d_z2$, 4s and $4p_z$ atomic orbitals to these cluster bonding molecular orbitals and the roles of $2p_x$ and $2p_y$ atomic orbitals of boron are taken up by iron $3d_{xz}$ and $3d_{yz}$ atomic orbitals with small contributions from $4p_x$ and $4p_y$. LCAO expansion of HOMOs of both the ferracarboranes [IVa] and [IVb] show that they have a small contribution from the $3d_{x^2-y^2}$ atomic orbital of iron and carbonyl carbon and oxygen atomic orbitals.

3.4 $[C_2B_3H_5\{Fe(CO)_3\}_2]$ [V]

The replacement of the second apical BH unit by a $Fe(CO)_3$ unit as in [Va], increases the negative charge on carbon atoms further but the increase is low [0.012 compared with 0.040 in IVa] and decreases the positive charge on basal boron atoms by similar ratios [Table 1]. The total overlap population associated with bonding of $Fe(CO)_3$ unit with $C_2B_3H_5$ base had also been decreased further by about the same ratio [Ca 27%]. The replacement of the basal B^5H unit by the $Fe(CO)_3$ unit, as in [Vb], changes the charge on C^2 from −0.062 to +0.010 [but the charge on C^4 has changed only slightly from −0.062 to 0.065] and increases the positive charges on boron atoms [Table 1]. Also, it should be noted in [Vb], Fe^1 atom has a negative net charge whereas Fe^5 atom has a high positive net charge [Table 1]. The total overlap populations associated with the bonding of metallo-groups with the rest of the cluster units in [Vb] are markedly less than those in [Va] and shows that the basal $Fe^5(CO)_3$ unit is weakly bonded into the cluster unit when compared with the apical $Fe(CO)_3$ unit. The total overlap population associated with the bonding of metallo-groups with the rest of the cluster unit and the total energy of valence electrons [Table 5] suggest that the compound [Va] is more stable than compound [Vb].



SCHEME [2]

It is interesting to note that the compound 1,7,2,4-$[(\eta 5\text{-}C_5H_5)_2 Co_2C_2B_3H_5]$ [VI] which is analogous to [Va] had been synthesised[6] and is stable. Our calculations also show that the replacement of either B^1H or B^7H or B^1H and B^5H by $Fe(CO)_3$ units did not change the energy of cluster bonding molecular orbitals appreciably. Analysis of LCAO expansion of molecular orbitals for [Va] and [Vb] is too complex because of the two $Fe(CO)_3$ units present in these molecules. But LCAO expansion of HOMOs of [Va] and [Vb] show that there are contributions from $3d_{x^2-y^2}$ atomic orbitals of iron atoms and atomic orbitals of the carbonyl carbon and oxygen.

3.5 Comparison of bonding by BH and $Fe(CO)_3$ units

As mentioned earlier in terms of Wade's approach the BH and the $Fe(CO)_3$ units use two electrons each and the CH unit uses 3 electrons for cluster bonding. The overlap population and the atomic orbital contributions in cluster molecular orbitals in carboranes and metallocarboranes studied show that the BH and the CH units use approximately two electrons each and that the $Fe(CO)_3$ unit uses less than two electrons [varies with the position and the number of BH units replaced by $Fe(CO)_3$ units] for cluster bonding. Our results [Tables 3 and 4] also show that the CH unit uses only one electron from carbon for the C—H bond. Hence the fourth electron from carbon must have become delocalised into the cluster bonding. The total overlap populations associated with the bonding of $Fe(CO)_3$ groups into the cluster in all ferracarboranes studied are much smaller than those of the BH replaced. Table 1 shows that in ferracarboranes [except the Fe^1 of (Vb)] the iron atoms carry net gross positive atomic charges and these positive charges on iron atoms may be the reason for the reduction in total overlap population between the $Fe(CO)_3$ unit and the rest of the cluster unit. The analysis of localised charges on the $Fe(CO)_3$ units [Table 2] and the gross atomic charges on the carbonyl carbon and the oxygen atoms [Table 1] suggest that the high positive charges on iron atoms may be due to the valence electrons in iron atom being largely delocalised over the carbonyl ligands and this may be the reason for weak bonding between the $Fe(CO)_3$ unit and the rest of the cluster unit.

As discussed earlier, the analysis of LCAO of the cluster bonding molecular orbitals shows that only $3d_{xz}$, $3d_{yz}$, $4p_x$ and $4p_y$ atomic orbitals of iron atom are used in cluster bonding but all 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals of both boron and carbon atoms are used.

4. Conclusion

SCCC calculations on carbones [I] and [III] and ferracarboranes [II] [IVa], [IVb], [V] and [Vb] show that even though in terms of Wade's approach, the BH and the $Fe(CO)_3$ units are considered to be isolobal and isoelectronic, the $Fe(CO)_3$ unit is weakly bonded into the cluster when compared with the BH unit replaced and this may be due to the valence electrons in iron atom being largely delocalised over the carbonyl ligands in ferracarboranes. Our calculations also show that even though the CH unit appears to use only two electrons for cluster bonding the third electron may be delocalised into the cluster. The comparison of the LCAO of the cluster bonding molecular orbitals shows that even though the roles of $2p_x$ and $2p_y$ atomic orbitals of boron are taken up by the iron $3d_{xz}$ and $3d_{yz}$ orbitals with some admixture of $4p_x$ and $4p_y$ atomic orbitals there is no evidence for the involvement of [4s, $4p_z$, $3d_{z^2}$] hybrid orbital which is analogous to boron [2s, $2p_z$] hybrid.

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