Bonding in Clusters. Part 2.[1] Hexaborane(10) and Related Metalloboranes

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Investigation of the bonding in $Fe(CO)_3$ derivatives of hexaborane(10) by self-consistent charge calculations provides a rationalisation for the formation of the only observed isomer 4-$[B_5H_9Fe(CO)_3]$. The highest occupied molecular orbital (h.o.m.o.) of this isomer is directly comparable to that in B_6H_{10}. Calculations on $[C_2B_3H_7Fe(CO)_3]$ and observations on Co(η-C_5H_5) derivatives of B_6H_{10} are used to suggest possible reasons for the stability of the known compounds. These results are used to predict that the most favourable structure of $[C_4BH_5Fe(CO)_3]$ should contain adjacent $Fe(CO)_3$ and BH units in the basal plane. Previously reported photoelectron spectra are reasonably well reproduced by the calculations. Metalloborane derivatives of unknown isomers of B_6H_{10} with B subrogated by $Mn(CO)_3$ or Fe(η-C_5H_5) units are similarly treated. Analysis of the bonding leads to an understanding of why the reported isomers are formed. Finally, the μ-bonded complex μ-$[Fe(CO)_4]B_6H_{10}$ has been analysed. Consideration of the frontier orbitals of B_6H_{10} and $Fe(CO)_4$ leads to the construction of a unique bridged bond between the previously non-bonding electron density in the h.o.m.o. of B_6H_{10} and an Fe 3*d* orbital.

IN a previous publication we investigated the bonding in metallo-derivatives of pentaborane(9) through self-consistent charge calculations (SCC).[1] A major intention of that paper was to investigate the 'pseudo-isoelectronic, isolobal' description of metallo-units in clusters. The high symmetry of B_5H_9 allowed only a relatively small number of structurally distinct metallo-derivatives to be considered. Here we extend the series of calculations to *nido*-hexaborane(10) and its metallo-derivatives. Since B_6H_{10} contains four distinct BH sites and an unbridged B–B bond, Figure 1, twice as many metalloboranes are possible. Despite this, only a small number of compounds are actually known. These have BH subrogated by $Fe(CO)_3$ or Co(η-C_5H_5), or B subrogated by $Mn(CO)_3$ or Fe(η-C_5H_5) and the previously terminal H occupying a bridging position. This paper contains the results of our calculations on some of these compounds and their possible isomers, also the μ-bonded complex between B_6H_{10} and $Fe(CO)_4$, and some unknown B_6H_{10} isomers. We have tried to relate our calculations with the experimentally observed trends in stabilities and photoelectron spectra where available. The computational details have been discussed previously.[1]

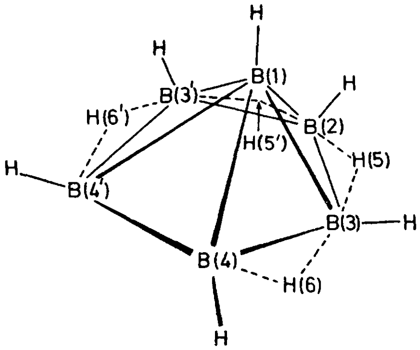


FIGURE 1 Hexaborane(10) structure

RESULTS AND DISCUSSION

B_6H_{10} *and* 4-$[B_5H_9Fe(CO)_3]$.—Following the previous approach,[1] we first discuss the bonding of B_6H_{10} as

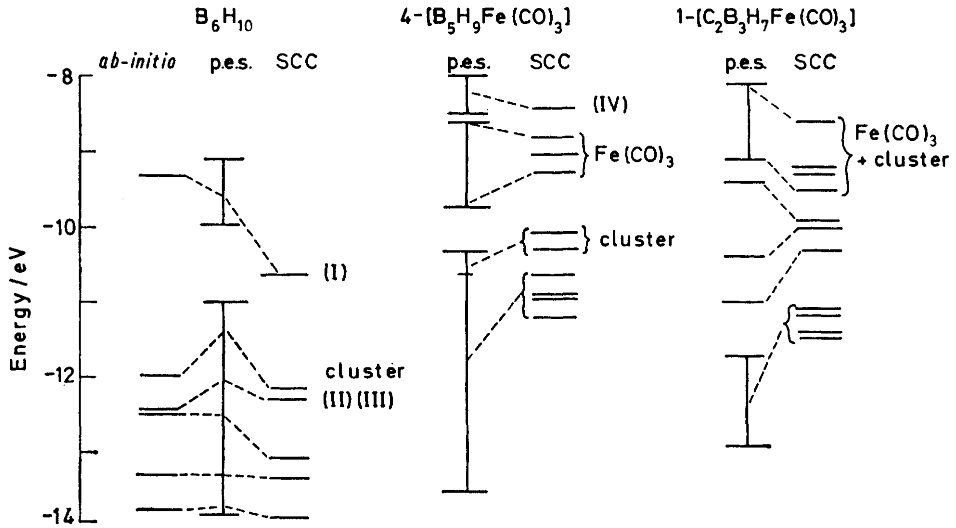
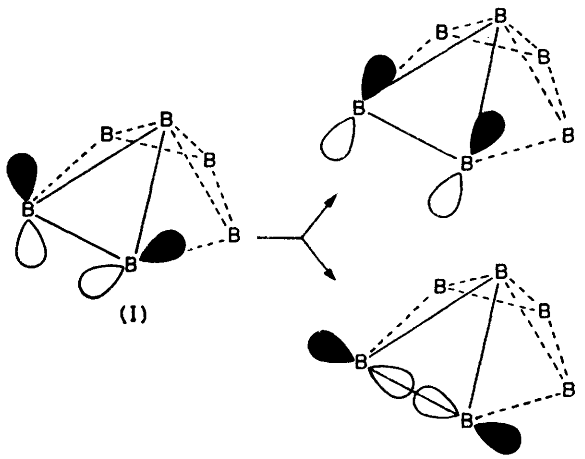


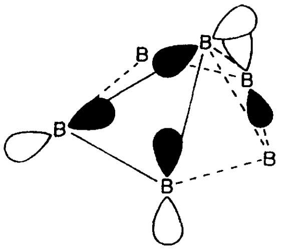
FIGURE 2 Energy-level diagram for B_6H_{10}, 4-$[B_5H_9Fe(CO)_3]$, and 1-$[C_2B_3H_7Fe(CO)_3]$

described by SCC calculations and then compare calculations on the possible $[B_5H_9Fe(CO)_3]$ isomers in an attempt to account for the fact that only the 4-isomer has been isolated.[2] For B_6H_{10}, freezing the hydrogen atoms which are fluxional in solution at room temperature produces the C_s symmetry found in the solid state.[3] This lower symmetry compared to C_{4v} for B_5H_9 makes detailed discussion of the bonding in B_6H_{10} more complex. However, concentrating on summed properties such as overlap populations, charges, *etc.*, allows an adequate description without the need to discuss individual molecular orbitals (m.o.s) in detail. The C_s symmetry provides four unique BH units [and hence four possible $Fe(CO)_3$ isomers] and two unique bridging H sites (Figure 1).

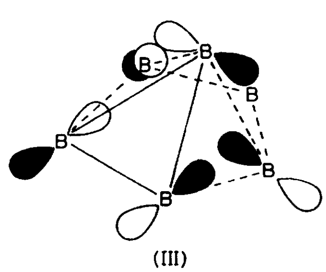
The m.o. energy levels from the SCC calculation of B_6H_{10} are compared with experiment[4] in Figure 2 and with a previous *ab-initio* calculation.[5] The agreement is reasonably good and some m.o.s can be described in localised bonding terms [(I)—(III)]. The highest occupied molecular orbital (h.o.m.o.) is of particular interest being completely localised on the unbridged boron–boron bond (I). This assignment is supported by a MNDO calculation[6] but appears to be somewhat different to that derived from a simpler ring-polar model.[4] The electron density provided by this m.o. is equivalent to that involving any boron in 2- or 3-positions, but, without the stabilisation from the proton bridge it is left high in energy, higher even than the cluster bonding m.o.s (II) and (III). The electron density in (I) may be resolved into a B–B σ-bonding component and a non-bonding component truly perpendicular to the bond. The σ component represents only a very small part of the total bonding density between the boron atoms and the density described by the h.o.m.o. is best considered as 'bridging non-bonding' density. The importance of this will become obvious in the discussion of μ-bonded species such as μ-$[Fe(CO)_4]B_6H_{10}$ below. The orbitals (II) and (III) are cluster bonding orbitals and directly correlate with the degenerate h.o.m.o. of B_5H_9.[1]



(I)



(II)



(III)

The number of unique sites in B_6H_{10} makes detailed tabulation of site-to-site overlap populations (o.p.) very extensive and not particularly valuable in this case. The overlap populations between unique BH, H-bridging, and $Fe(CO)_3$ sites in the possible ferraborane isomers are given in the Table.

For B_6H_{10}, the total overlap populations between apical and basal BH units, and between adjacent hydrogen-bridged BH units, are in the range 0.35—0.50 electrons. The unique unbridged BH–BH system has an o.p. of 0.81 electrons *i.e.* approximately twice as large as any other BH • • • BH system. The C_s symmetry of this molecule makes extraction of evidence for the isolobal description of BH units difficult. Even so it is quite clear. The $2p$ orbitals of the apical B atom (the most symmetric site) are all equivalently occupied ($2s$ 0.91; $2p_x$, $2p_y$, and $2p_z$ 0.68 each), but the overlap populations to the other B atoms are $2s$ 0.69, $2p_x$ 0.74, $2p_y$ 0.79, and $2p_z$ 0.11 which clearly agrees with the isolobal description of an s and two p a.o.s involved in cluster bonding.[7] The corresponding results for the other B atom on the σ_v plane (*i.e.* the 2-position in Figure 1) are $2s$ 0.58, $2p_x$ 0.17, $2p_y$ 0.58, and $2p_z$ 0.57, and again the evidence is clear. The 3- and 4-positions are complicated by the low symmetry but the isolobal description is seen to apply even in these cases and has been discussed elsewhere.[8] The evidence for the isolobal–isoelectronic description of BH and $Fe(CO)_3$ units in isomers of $[B_5H_9Fe(CO)_3]$ has been discussed similarly.[8]

The only well characterised $Fe(CO)_3$ derivative of B_6H_{10} is the 4-isomer.[2] However, SCC calculations were performed on all four possible isomers using geometries based on the known isomer and related ferraboranes.[2,9] The total overlap populations bonding the $Fe(CO)_3$ unit to the rest of the molecule are shown in the Table. It is clear that the known isomer is predicted on this basis to be the most stable of the base-subrogated isomers. The reason for this is found from the Table and lies in the geometry of the metallo-unit sites. It can be best explained by comparison with the base-subrogated derivative of B_5H_9. In $2\text{-}[B_4H_8Fe(CO)_3]$[6] the metallo-unit is held in the cluster by two bonds to bridging hydrogens of o.p. 0.298, two bonds to adjacent BH units of o.p. 0.121, and one to the apical BH of o.p. 0.254; negative o.p. with other centres reduces the total o.p. to 0.716. All the isomers of $[B_5H_9Fe(CO)_3]$ have total o.p.s greater than this. An inspection of the Table shows that the 2-isomer has almost identical bonding o.p.s to the B_5H_9 derivative but its higher total is due to reduced negative o.p.s with other centres. The geometries used were based on those observed for $[B_5H_8Fe(CO)_3]^-$ and μ-$[Cu(PPh_3)_2][B_5H_8Fe(CO)_3]$,[9] and 2-$[B_4H_8Co(\eta$-$C_5H_5)]$,[10] noting that the subrogation of BH by a metallo-unit leaves the borane part of the molecular geometry basically unchanged and simply introduces the longer boron-metal bond lengths. This results in a reduction of bond angle at the subrogated site from 90° to 74° in 2-$[B_4H_8$-$Co(\eta$-$C_5H_5)]$ and from 107° to 88°, 105° to 79°, and 110° to 84° in the 2-, 3-, and 4-isomers of $[B_5H_9Fe(CO)_3]$ respectively, whilst maintaining the B–Fe bond lengths at *ca.* 205 ± 1 pm. From the Table it can be seen that the effect of reducing this bond angle is to reduce o.p. with the apical B atom, and with adjacent bridge-bonded basal B atoms. So potentially the 2-isomer should be the most stable, and the 4-isomer the least. However the existence of the unique bond adjacent to the metallo-site in the 4-isomer completely overrides these considerations. A very strong bond is formed between the Fe(4) and B(4′) atoms making the 4-isomer by far the most stable of the base-subrogated isomers. The effect of the bond-angle change on the o.p. of metallo-unit to bridging hydrogen is erratic, but the 2-, 3-, and 4-$[B_5H_9Fe(CO)_3]$ isomers all have values of *ca.* 0.30. Previously we stated that the metallo-unit of 2-$[B_4H_8Fe(CO)_3]$ was held in the cluster predominantly by this bonding, and the same would be true of 2- and 3-$[B_5H_9Fe(CO)_3]$ if formed. The 4-$[B_5H_9$-$Fe(CO)_3]$ isomer is different in that half of its total o.p. is located in a single strong two-centre bond and this is undoubtedly the reason for it being the only observed basal isomer. The Table would suggest that the 1-isomer is equally viable having a total o.p. almost identical to that of the 4-isomer. The observed thermally induced (180°) rearrangement of 2-$[B_4H_8Co(\eta$-$C_5H_5)]$ [11,12] to the thermodynamically more stable 1-isomer was in complete agreement with our previously discussed results.[1] However in the preparation of 4-$[B_5H_9Fe(CO)_3]$, using a hot–cold reactor operating at (230—260) °C–25 °C, no other isomers were reported; in fact continued heating at 200 °C produced 1-$[B_4H_8Fe(CO)_3]$.[13] The production of 1-$[B_5H_9Fe(CO)_3]$ is clearly unfavourable in this case, and we would suggest that this is associated with the need for an apical metallo-unit to form five weak bonds to the basal borons compared with three stronger bonds, including the unbridged Fe–B bond, found in the basal site.

Overlap populations in metalloboranes containing either $Fe(CO)_3$ or $Mn(CO)_3$ units

Unit site		Other sites 1	2	3	3′	4	4′	5	5′	6	6′	Total
$Fe(CO)_3$	1		0.239	0.226	0.226	0.173	0.173	−0.059	−0.059	−0.060	−0.060	0.807
	2	0.243		0.125	0.125	−0.117	−0.117	0.300	0.300	−0.050	−0.050	0.760
	3	0.193	0.144		−0.125	0.170	−0.133	0.277	−0.012	0.276	−0.057	0.734
	4	0.147	−0.108	0.159	−0.120		0.479	−0.043	−0.013	0.313	−0.025	0.794
$Mn(CO)_3$	1		0.133	0.130	0.130	0.125	0.125	← *a* →				0.316
	2	0.061		0.024	0.024	−0.136	−0.136	0.279	0.279	← *b* →		0.287

[a] Total of bridging hydrogens −0.065. [b] Total of other bridging hydrogens −0.110.

As far as the cluster bonding of the $Fe(CO)_3$ unit is concerned, the same comments apply as those made previously.[1,8] Important points are that there is no significant contribution from one of the available a.o.s (*e.g.* the Fe $3d_{z^2}$ in the 1-isomer) and less electron density is involved in cluster bonding than would have been expected if delocalisation of charge onto the carbonyls had not occurred.

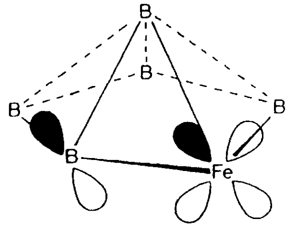
A related compound is the carborane derivative $[C_2B_3$-$H_7Fe(CO)_3]$ which has the $Fe(CO)_3$ group in the apical position. An *ab-initio* calculation on this compound has been reported.[14] The SCC calculation shows that the overlap population holding the $Fe(CO)_3$ unit in the molecule is significantly less than that in the ferraboranes with the metallo-unit in the basal plane. However it can be clearly seen that other isomers are unfavourable for $[C_2B_3H_7Fe(CO)_3]$.

The structural equivalent to the 4-$[B_5H_9Fe(CO)_3]$ isomer is not viable as the carbon atoms occupying the 4,4′ sites do not provide the necessary unbridged bonding electron density and there are no 5,5′ bridging hydrogens, which also eliminates the 3-isomer as a possibility. The bond angle at the 2-position in the carborane is *ca.* 100°, and introduction of a metallo-unit will reduce this to *ca.* 76°, clearly an unfavourable angle from the discussion above. Thus the apically substituted isomer is the most probable.

An overlap population analysis of the known $[C_2B_3$-$H_7Fe(CO)_3]$ isomer shows that the $Fe(CO)_3$ to BH unit bonds provide the majority of the bonding, 0.57, compared with 0.13 from $Fe(CO)_3$ to CH units.

The above discussion has a bearing on the proposed structure of $[C_4BH_5Fe(CO)_3]$, another metallocarborane related to B_6H_{10}.[15] Since the metallo-unit is more effectively bonded to BH rather than CH units, the $Fe(CO)_3$ apical or a basal structure with the metallo-unit adjacent to BH should be preferred. More important however is that a basal structure allows the $Fe(CO)_3$ and BH units to bond in a unique unbridged bond of the type which we have seen in ferraboranes is particularly strong. Hence an adjacent basal $Fe(CO)_3$–BH structure as proposed by Fehlner [15] is the most likely.

The calculated m.o. energies in 4-[$B_5H_9Fe(CO)_3$] and [$C_2B_3H_7Fe(CO)_3$] are compared with their photoelectron spectra (p.e.s.) in Figure 2. The SCC results for both show reasonable agreement and our assignments, while broadly similar to those of Fehlner and co-workers,[16] vary in details of the composition of some m.o.s. The h.o.m.o. of 4-[$B_5H_9Fe(CO)_3$], (IV), is directly comparable with that of B_6H_{10} with very little of Fehlner's 'ring-polar' interaction. The unbridged non-bonding density contained in the 4-isomer is different to that of the h.o.m.o. of B_6H_{10} in that it is located directly below the B–Fe bond and not directed to the position which would be taken by a bridging hydrogen atom. This electron density is still high in energy, higher than the $Fe(CO)_3$ bonding m.o.s, the next three ionisations, which were the h.o.m.o. of all $Fe(CO)_3$ derivatives of B_5H_9, and again higher than the cluster bonding m.o.s which are the following two ionisations. In the metallocarborane the three lowest energy ionisations are due to $Fe(CO)_3$ as there is no unique bond density.

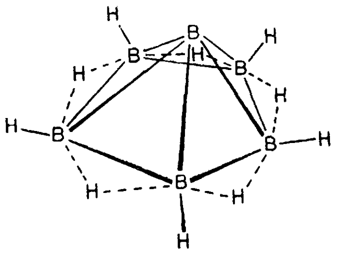


(IV)

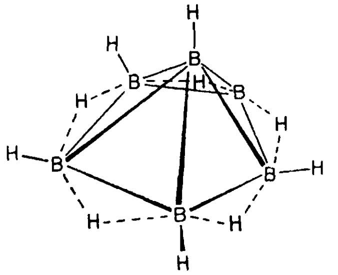
Finally a comment on the preparation of 1-[$B_5H_9Co(\eta\text{-}C_5H_5)$] is worthwhile.[17] This compound was prepared by the hot–cold reactor technique at 225–75 °C. No other isomers were reported. The bridging hydrogen atoms were fluxional down to —45 °C. While SCC calculations on η-C_5H_5 containing compounds are suspect due to COM (counter-intuitive orbital mixing) effects,[18] we find that results from $Fe(CO)_3$ containing compounds can generally be applied to analogous $Co(\eta\text{-}C_5H_5)$ derivatives; this is clearly not such a case. As discussed above the 1-isomer is potentially as viable as the 4-isomer, and some feature is distinguishing between the two types of BH subrogation. The isomer 1-[$B_5H_9Co(\eta\text{-}C_5H_5)$] is isoelectronic with, and a structural analogue of, ferrocene, and we feel that this is the source of its particular stability. It may be due either to some ring–ring stabilising interaction, or the η-C_5H_5 ligand polarising the Co to B_5 cluster bonding m.o.s of the metallo-unit such that five bonds can be favourably formed. The thermal isomerisation of 2-[$B_4H_8Co(\eta\text{-}C_5H_5)$] to the 1-isomer is possibly a manifestation of these effects, and a further example is discussed below. It should be noted that we did find evidence for ring–ring interaction in our calculations of B_5H_9 derivatives, however due to COM effects we are unable to claim this as a definite cause of stability.

Metallo-derivatives of Unknown B_6H_{10} *Isomers* (V) *and* (VI).—Removing the proton from the apical BH or a basal BH unit in B_6H_{10} and placing it in the unbridged position produces isomers (V) and (VI) which are unknown in borane chemistry but for which metallo-derivatives are known. Compounds $B_5H_{10}X$ reported are for (V), X = $Fe(\eta\text{-}C_5H_5)$,[12] and for (VI), X = BeY (Y = Cl, Br, Me, or BH_4),[19] $Fe(\eta\text{-}C_5H_5)$,[12] and $Mn(CO)_3$.[20] In each case the metallo-unit is equivalent to B according to Wades' rules and no case has been reported in which a BH unit in (V) or (VI) has been replaced.

The $Fe(\eta\text{-}C_5H_5)$ derivative of (V) was prepared by thermal isomerisation of the (VI) derivative at 175—180 °C. This reaction is similar to the previously discussed isomerisation of 2-[$B_4H_8Co(\eta\text{-}C_5H_5)$]. The manganese compound was prepared by thermolysing a mixture of B_5H_9, [$Mn_2(CO)_{10}$], and H_2 at 140 °C. It appeared to show no tendency to isomerise even at 220 °C.



(V)



(VI)

Because of COM effects we decided to investigate isomers (V) and (VI) with B replaced by $Mn(CO)_3$. The purpose of our calculations was to find out why the metalloboranes are known in the absence of the boranes, and what effect the removal of the unique unbridged bond would have on the cluster bonding. We had previously performed MNDO calculations on the known B_6H_{10} and isomers (V) and (VI) to determine the sequence of thermochemical stability.[6] The heats of formation clearly showed the known isomer (Figure 1) as the most stable with (VI) then (V), the values being 18.8, 45.0, 75.5 kcal mol^{-1} respectively.* The differences, whilst not particularly large, were attributable to the fact that the B atom did not have the necessary directional properties in its a.o.s for strong cluster bonding in (V), and an excessive charge separation occurs in (VI). These are effectively the reasons for the non-appearance of isomers (V) and (VI). However, metallo-units exist which although pseudo-isoelectronic with B, have a.o. combin-

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* Throughout this paper: 1 cal = 4.148 J; 1 eV ≈ 1.60×10^{-19} J.

ations which are isolobal with BH, and are capable of delocalising charge over other ligands. Hence the metallo-derivatives are stable where the borane precursors are not. SCC calculations were performed using geometries based on data from $[B_3H_8Mn(CO)_3]$,[21] the related $[B_3H_8Cr(CO)_4]^-$,[22] and the relevant B_6H_{10}-based ferraboranes. These geometries were in very good agreement with those generated by taking the MNDO optimised geometries for (V) and (VI) and introducing the B–Mn bonds, as described above for the base-subrogated ferraboranes. The B–Mn–B bond angle obtained from either method for the (VI) derivative was 85°. Analysis shows that the total overlap populations bonding the metallo-unit to the cluster are similar, being 0.317 [isomer (V)] and 0.290 [isomer (VI)]. As in the case of the $Fe(CO)_3$ derivatives, the calculations can be correlated with the fact that only isomer (VI) is observed by considering the strengths of the individual bonds. The $Mn(CO)_3$-containing isomer of (V) has five bonds to the metallo-unit of approximately 0.13 overlap population each and the total is reduced by antibonding interactions with the bridging hydrogens (−0.07 each). The (VI) isomer has two strong bonds to the adjacent bridging hydrogens of o.p. 0.28 each and significant antibonding occurs only with the distant boron atoms across the basal plane. However, of more importance than the overlap populations in this case is the intrinsic higher stability of (VI) compared with (V) for the borane precursors. Unlike the $[B_5H_9Fe(CO)_3]$ isomers which were all derivatives of the known borane, these two $Mn(CO)_3$-containing compounds are derivatives of different B_6H_{10} isomers. Although no detailed statement can be made about the relative stabilities of the manganaborane from the borane results, it is reasonable to assume that B subrogation would not reverse the stability trend. It is probable that the stabilities are quite close. Thus when an extra effect is introduced, for example the possibility of a ferrocene type structure with its concomitant stabilising effect, the compound related to (V) is thermodynamically favoured as in the case of $[B_5H_{10}Fe(\eta\text{-}C_5H_5)]$.[12]

As the geometries used in these calculations are estimated we have tried varying the most significant quantity, the B–Mn–B bond angle, to test the validity of the assumptions. Calculations were performed on the $Mn(CO)_3$ derivative of (VI) with bond angles of 95° and 75°. The total o.p.s between borane and metallo-unit in these calculations were 0.23 and 0.27 respectively suggesting that the 85° angle assumed in our initial calculation, taking B_{apical}–B_{basal} and bridged B_{basal}–B_{basal} bonds to be those found in B_6H_{10} and introducing $Mn(CO)_3$ with a Mn–B bond of 210 pm, was reasonable.

A corollary of our previous discussions [1] of the 'isoelectronic, isolobal' description of $Fe(CO)_3$ can be applied to $Mn(CO)_3$, which is considered to be equivalent to B.[7] The boron atom would provide one electron for cluster bonding spread over four available a.o.s (2*s*,2*p*'s). The $Mn(CO)_3$ unit provides less than half this number of electrons (see Table) and hence shows the same effect of delocalisation onto carbonyl ligands as $Fe(CO)_3$ does when compared to BH. As Hoffmann and co-workers [23] have pointed out, $Mn(CO)_3$ is isolobal with $Fe(CO)_3$.

The calculated m.o. energy levels suggest that the photoelectron spectra of $Mn(CO)_3$ derivatives of (V) and (VI) would show distinctly different features. The first band from (V) containing three ionisations which are mainly metal '*d*' in character would be separated by *ca.* 1 eV from the second band derived from two cluster bonding m.o.s. The (VI) isomer would show a first ionisation band due to two cluster bonding m.o.s and one metal-based m.o. followed by a mainly metal-based ionisation then another cluster bonding m.o. The separations would be *ca.* 0.7 and 0.4 eV respectively.

μ-$[Fe(CO)_4]B_6H_{10}$, *A Metalloborane Molecular Complex.* —The 'bridging non-bonding' electron density between B(4) and B(4′) (Figure 1) which has been discussed above provides B_6H_{10} with the ability to act as a Lewis base. Suitable Lewis acids are various metal centres. Only a few complexes are known including μ-$[Fe(CO)_4]B_6H_{10}$, *trans*-$[Pt(B_6H_{10})_2Cl_2]$ and related rhodium and iridium complexes,[24] and the μ-$[Fe(CO)_4]B_7H_{12}^-$ derivative.[9b] The molecular structure of the anion has been determined and was used with data from B_6H_{10} to construct a geometry for μ-$[Fe(CO)_4]B_6H_{10}$. This compound can be considered as a complex between $Fe(CO)_4$ and B_6H_{10} molecules held together by a weak two-electron donation from the borane to iron. In such complexes it is expected that the molecular bonding is predominantly that of the components with complex formation affecting only the frontier orbitals. To test this we performed SCC calculations on $Fe(CO)_4$, μ-$[Fe(CO)_4]B_6H_{10}$, and for comparison, $[Fe(CO)_5]$.

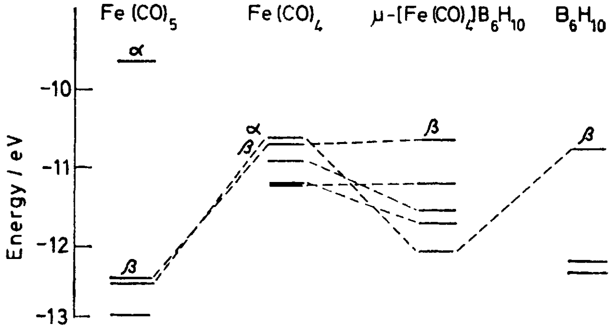
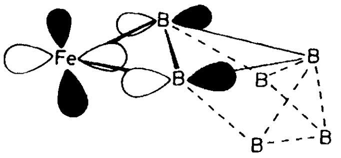


FIGURE 3 Energy-level diagram for frontier orbitals of B_6H_{10}, $Fe(CO)_4$, μ-$[Fe(CO)_4]B_6H_{10}$, and $[Fe(CO)_5]$ (α indicates l.u.m.o., β indicates h.o.m.o.)

Starting from the basic $[Fe(CO)_5]$ structure with axial CO groups along the *z* axis and removing an equatorial ligand along the *x* axis produced $Fe(CO)_4$ in a C_{2v} geometry. The calculation of $Fe(CO)_4$ gave m.o. energy levels as shown in Figure 3. The h.o.m.o. and l.u.m.o. (lowest unoccupied molecular orbital) are very close in energy (separated by 0.08 eV) and are both composed of pure metal a.o.s, being d_{xy}, and a combination of $d_{x^2-y^2}$ and d_{z^2} respectively. The l.u.m.o. is opposite in phase to a lower energy m.o. which provides bonding to all four carbonyls. In fact the calculation shows that the metal a.o.s which one might expect to be involved with bonding, for example the d_{xy} orbital of the h.o.m.o. and the $d_{x^2-y^2}$ orbital of the l.u.m.o., are not fully effective because of a lack of stabilisation duly provided by the missing carbonyl group. On forming the [Fe(CO)$_5$] molecule the l.u.m.o. and lower energy m.o. mentioned become mixed and the $d_{x^2-y^2}$ and d_{z^2} a.o.s appear in separate m.o.s both providing bonding to carbonyls, the former to the added carbonyl group. The d_{xy} orbital of the h.o.m.o. is now also strongly involved in carbonyl bonding, but to carbonyl groups that were already present. The additional carbonyl has simply had the effect of stabilising the d_{xy} orbital so that it can contribute to molecular bonding.

On forming the μ-bonded borane complex the bonding pattern is somewhat different. The four h.o.m.o.s are iron–carbonyl bonding m.o.s and correlate with the four h.o.m.o.s of Fe(CO)$_4$ as shown in Figure 3. The major change to these m.o.s is that the pure metal m.o.s of Fe(CO)$_4$ are now stabilised suffcently to be fully involved in carbonyl bonding. The $d_{x^2-y^2}$ component of the Fe(CO)$_4$ l.u.m.o. interacts with the non-bonding electron density of the h.o.m.o. of B_6H_{10} to form the m.o. (VII)



(VII)

and this accounts for nearly all the molecular complex bonding. The h.o.m.o. of B_6H_{10} has separated into the non-bonding part and the σ-bonding part discussed above, with the latter now found at lower energy typical of boron–boron bonding m.o.s. This has become stabilised by the removal of the excess of electron density. The angle of 120° found between the borane basal plane and the plane containing the Fe and two adjacent boron atoms is a direct result of the bonding shown in (VII) since the angle the non-bonding electron density in (I) makes with the borane basal plane is 60°.

The possibility of 4-[B_5H_9Fe(CO)$_3$] forming a μ-bonded complex could be considered. This is highly unlikely since although the metalloborane has large electron density in the region of the unbridged bond, it is not directed to the ' vacant ' bridging position, but rather to below the basal plane of the molecule. Any attempt to donate this density to *e.g.* Fe(CO)$_4$ would certainly involve large steric interactions between Fe(CO)$_4$ and the basal B_4Fe plane.

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