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The Electronic Structure of Dicarbacyclopentaboranyliron Tricarbonyl, $B_3C_2H_7Fe(CO)_3$

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The electronic structure of dicarbacyclopentaboranyliron tricarbonyl, $B_3C_2H_7Fe(CO)_3$, has been obtained by an ab initio technique. It was found that the carborane portion attracted 2.03 electrons from the iron tricarbonyl. The mode of bonding between these two components is mainly ionic due to attraction between the charged species. The donated electrons which originate from the 4s and 4p orbitals of iron, occupy the pseudo π orbitals of the carborane and the σ orbitals of the boron–boron framework bonds.

Introduction

The gas-phase reaction between dicarba-*nido*-hexaborane(8) and iron pentacarbonyl produces a metallocarborane, dicarbacyclopentaboranyliron tricarbonyl ($B_3C_2H_7Fe(CO)_3$) [1]. A recent crystal structure determination [2] revealed that this species contains a planar B_3C_2 ring symmetrically π bonded to the iron atom. This seems to imply that the π orbitals of the carborane are involved in cementing together the structure of the metallocarborane. It has been suggested [2] that the carborane moiety possesses a dinegative charge so as to be analogous to the related species, π-$C_5H_5Fe(CO)_3^+$. Strict analogy with the metallocene would also mean the existence of a six π-electron system in the carborane portion although the presence of two B–H–B bridges directed away from the metal is expected to modify this parallelism (Fig. 1).

There have been a plethora of theoretical investigations into the electronic structure of boron compounds [3–8]. Currently, however, there is a paucity of information pertaining to the electronic structure of the metallocarboranes which occupy an important position in the chemistry of boron. Therefore, in order to attain knowledge about the electronic framework of a metallocarborane and, furthermore, to examine quantitatively the aforementioned bonding scheme, it was decided to acquire by an *ab initio* calculational technique the electronic structure of $B_3C_2H_7Fe(CO)_3$.

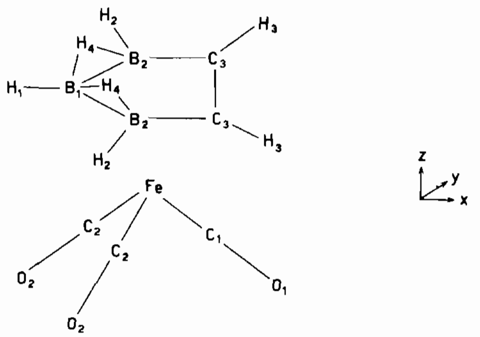

Fig. 1. The molecular structure and numbering system of $B_3C_2H_7Fe(CO)_3$.

Method

The calculational framework was based on the LCAO–MO–SCF method [9] in which the atomic orbitals were represented by a minimal basis set of Slater-type orbitals augmented by the inclusion of Fe 4*p* orbitals of exponent 0.85 [10]. The Slater-type orbitals, whose exponents were extracted from the work of Clementi and Raimondi [11], were simulated by a linear combination of five gaussian type orbitals in a manner perfected by Stewart [12]. The geometry of the metallocarborane was constructed from the X-ray structural data [2].

Results and Discussion

The orbital populations of $B_3C_2H_7Fe(CO)_3$ are presented in Table I. It can be seen that there has been an electronic movement towards the carborane portion leaving the iron tricarbonyl moiety with a +2.03 charge. As the carbonyl groups carry excess electrons (~0.2e), it is the iron orbitals which have been stripped of electrons. The main source of these donated electrons is the 4*s* orbital with a substantial contribution emanating from 3*d* orbitals. The Fe 4*p* orbitals contribute only marginally to the bonding situation. The electronic distribution in the carborane

TABLE I. The Electronic Distribution of $B_3C_2H_7Fe(CO)_3$

Electron Densities

B_1	*s*	3.091	Fe	*s*	5.897
	pσ	1.818		*p*	11.928
	pπ	0.952		*d*	5.363
	total	5.861		*total*	23.188
B_2	*s*	3.028	C_1	*s*	3.514
	pσ	1.650		*p*	2.586
	pπ	0.981		*total*	6.100
	total	5.659			
			C_2	*s*	3.536
C_3	*s*	3.212		*p*	2.639
	pσ	2.292		*total*	6.175
	pπ	1.047			
	total	6.551	O_1	*s*	3.859
				p	4.261
H_1		0.843		*total*	8.120
H_2		0.840			
H_3		0.800	O_2	*s*	3.862
H_4		0.814		*p*	4.243
				total	8.105

Overlap Populations

B_1-B_2	0.630	$Fe-C_1$	0.067
B_1-H_1	0.946	$Fe-C_2$	−0.069
B_1-H_4	0.440	$Fe-B_1$	−0.538
B_2-C_3	1.016	$Fe-B_2$	−0.242
B_2-H_2	0.886	$Fe-C_3$	−0.040
B_2-H_4	0.376	C_1-O_1	1.152
C_3-C_3	1.070	C_2-O_2	1.124
C_3-H_3	0.936		

section is polarised towards the framework atoms with the boron and carbon atoms bearing a negative charge while the hydrogen atoms possess a positive charge. Analysis of the π-electron character of the boron and carbon atoms reveals that a total of 5.01 electrons are present. If it is borne in mind that the bridging hydrogens will most certainly contribute to this "π" system, then these results verify the earlier qualitative suggestions which were made about the bonding in the molecule [2].

It is perhaps more instructive, to compare the electronic structure of the metallocarborane with those of the component iron tricarbonyl and carborane species. The results of the calculations on the neutral and dinegative anion of the carborane are presented in Table II. The anion has a similar electronic distribution to that of the metallocarborane except that there is a greater electronic drift from the hydrogen atoms in the latter. Comparison of the electronic structures of the neutral and coordinated carborane reveals that the extra electronic charge can be apportioned to the hydrogens (0.09) and the main group atoms (1.94). For the boron atom, B_1, and the carbon atoms, C_3, the majority of the excess charge resides in the π-orbital whereas for the boron atoms, B_2, only a small percentage of the excess charge is located in the π-orbital and a large proportion of this extra charge is present in the *s* and the *pσ* orbitals. Formation of the metallocarborane generally induces an increase in the overlap population of the bonds. The only bonds which suffer a decrease are the B_2-C_3 and B_1-H_4 bonds while notable increases occur for the B_1-B_2 and C_3-C_3 bonds. The extra electrons residing on B_2 are involved in enlarging the populations of the $B_1-B_2\sigma$ bonds.

From the overlap population data we conclude that the neutral carborane must possess a low-lying vacant orbital which is bonding in nature. Examination of the eigenvalues of the neutral and the dinegative ionic form of $B_3C_2H_7$ confirms this assertion. The energy of the highest filled orbital lies at −0.288au while the lowest empty orbital is located at −0.112au. The gap between the occupied and vacant orbitals in the dianionic species is calculated to be 0.425au indicating that further electronic addition is highly unlikely. It is interesting to note that the lowest unoccupied orbital of the neutral carborane is indeed occupied in the dianionic species and, moreover in the process becomes more stable than the highest occupied orbital. Analysis of the eigenvectors and the orbital bond populations of this molecular orbital confirms that the majority of the orbital–orbital interactions are bonding and the framework bonds have large positive overlap populations. Comparison of the total energies of the neutral and dianionic forms of the carborane reveals that the addition of two electrons destabilises the system by 159 $kJmol^{-1}$. This is an unusually low value, the corresponding amount for B_2H_4 is 678 $kJmol^{-1}$, [13] and gives some indication of the electron affinity of the carborane.

The electronic structures of the dipositive cation and the neutral form of $Fe(CO)_3$ were calculated. For both species the inter-bond angle was varied in order to procure a calculated energy minimum. The acquired angles were 100° and 113° for the neutral and the cationic species respectively. The removal of two electrons, not unexpectedly, allows the inter-bond angle to expand. The Mulliken population analysis of the two species is presented in Table III. Comparison of the electronic structures of the dipositive cation of $Fe(CO)_3$ and the coordinated $Fe(CO)_3$ reveals a gross similarity. Differences do exist, however, and for the metallocarborane we find that there is a much smaller electronic population on the iron atom due to a greater polarisation of charge towards the carbonyl groups while for the dipositive cation the oxygen atoms possess a positive charge.

In the neutral $Fe(CO)_3$ there is a drift of electronic charge towards the carbonyl groups of 0.3 electrons/group. Coordination to the carborane reduces this polarisation only slightly, leaving a negative charge on the carbon and oxygen atoms. Formation of the

TABLE II. The Electron Structure of $B_3C_2H_7^{2-}$, $B_3C_2H_7$, $B_3C_2H_5^{4-}$ and $C_5H_5^-$.

		$B_3C_2H_7^{2-}$	$B_3C_2H_7$	$B_3C_2H_5^{4-}$	$C_5H_5^-$
Electron Densities					
B_1	*s*	2.942	2.997	2.985	
	pσ	1.674	1.874	1.835	
	pπ	1.064	0.322	1.125	
	total	5.680	5.193	5.945	
B_2	*s*	2.875	2.882	2.941	
	pσ	1.619	1.467	1.771	
	pπ	0.976	0.934	1.073	
	total	5.470	5.283	5.785	
C_3	*s*	3.115	3.175	3.094	3.152
	pσ	2.219	2.322	2.160	1.980
	pπ	1.141	0.793	1.364	1.200
	total	6.475	6.290	6.618	6.332
H_1		0.948	0.836	1.082	
H_2		0.953	0.830	1.089	
H_3		0.893	0.783	0.994	0.868
H_4		0.895	0.799	–	
Overlap Populations					
B_1–B_2		0.571	0.343	1.098	–
B_2–C_3		1.088	1.121	1.074	–
C_3–C_3		1.081	0.824	1.044	0.814
H_1–B_1		0.913	0.892	0.845	–
H_2–B_2		0.892	0.881	0.839	–
H_4–B_1		0.462	0.454	–	–
H_4–B_2		0.384	0.364	–	–
H_3–C_3		0.912	0.906	0.874	1.007

TABLE III. The Electronic Distribution of $Fe(CO)_3$ and $Fe(CO)_3^{2+}$.

		$Fe(CO)_3^{2+}$	$Fe(CO)_3$
Overlap Populations			
Fe	*s*	6.310	6.654
	p	11.999	12.941
	d	5.558	5.500
	total	23.867	25.095
C	*s*	3.527	3.546
	p	2.586	2.642
	total	6.113	6.188
O	*s*	3.880	3.862
	p	4.050	4.251
	total	7.930	8.113
Electronic densities			
Fe–C		–0.114	–0.042
C–O		1.180	1.098

metallocarborane however, drastically alters the *s* and *p* orbital populations of Fe. Of the 1.91 electrons displaced from Fe, 1.01 electrons emanates from the 4*p* orbitals, 0.76 electrons are removed from the 4*s* level while the 3*d* population is reduced by 0.14 electrons. The orbital character of the highest filled level of $Fe(CO)_3$ mirrors this electron loss as it is a non-bonding orbital composed largely of Fe 4*p* and 4*s* orbitals. The calculated energy of this orbital is –0.164au, and as the energy gap between this orbital and the next highest filled orbital is 0.204au, the labile nature of the electronic content of the highest filled orbital is readily understood. The energy of the highest orbital of $Fe(CO)_3^{2+}$ is –0.778au and is considered too stable for further electronic migration. Inspection of the relevant total energies discloses that removal of two electrons from $Fe(CO)_3$ and relaxation of the geometry requires 1353 $kJmol^{-1}$. The energy of ionisation of the electrons totals 1381 $kJmol^{-1}$ and therefore the geometrical reorganisation stabilises the system by 28 $kJmol^{-1}$.

During the optimisation of the inter-bond angles of $Fe(CO)_3$ and $Fe(CO)_3^{2+}$, the C–Fe–C angle was varied to include 120°, the planar form of these species. This enabled the calculation of the inversion barrier to be carried out, resulting in a value of 288 $kJmol^{-1}$ and 128 $kJmol^{-1}$ for the neutral and the dipositive cation respectively. The neutral species adopts a more pyramidal structure and a larger inversion barrier is to be expected. Removal of two electrons from $Fe(CO)_3$ widens the inter-bond angle by 13° with a concomitant reduction in the energy of the inversion barrier.

As the electronic structures of the two components of the metallocarborane have been discussed, it is now pertinent to examine the changes which occur when the two species combine to form $B_3C_2H_7Fe(CO)_3$. The eigenvalues of the higher filled orbitals of the three molecules are presented in Figure 2. Formation of the anion and cation from the appropriate neutral species results in the eigenvalues of the compound undergoing a destabilisation and stabilisation respectively. On combination, the eigenvalues are restored to values consistent with a neutral moiety due to the presence of an adjacent counterion. Examination of the corresponding eigenfunctions enables the construction of a simple correlation diagram for the higher filled orbitals to be performed (Figure 2). It can be seen that, in general, the orbitals of the carborane are destabilised upon combination while the orbitals corresponding to the iron tricarbonyl have become more stable. Most of the orbitals can be correlated directly with the corresponding orbital of the component as there is only a minimum amount of mixing of the two systems. Only two orbitals of the metallocarborane exhibit considerable interlacing of the two orbital networks. Further analysis reveals that this interaction is between the Fe d_{z^2} orbital and the P_z orbitals of the carbon and boron atoms of the carborane moiety. The general lack of interaction is further manifested in the small positive or negative bond populations between iron and the atoms of the carborane species. Hence covalent bonding between the two components is unimportant and the mode of combination is therefore mainly ionic in character, whereby, two electrons are transferred to and from the appropriate neutral species with a stabilisation arising from the interaction of the two charged species.

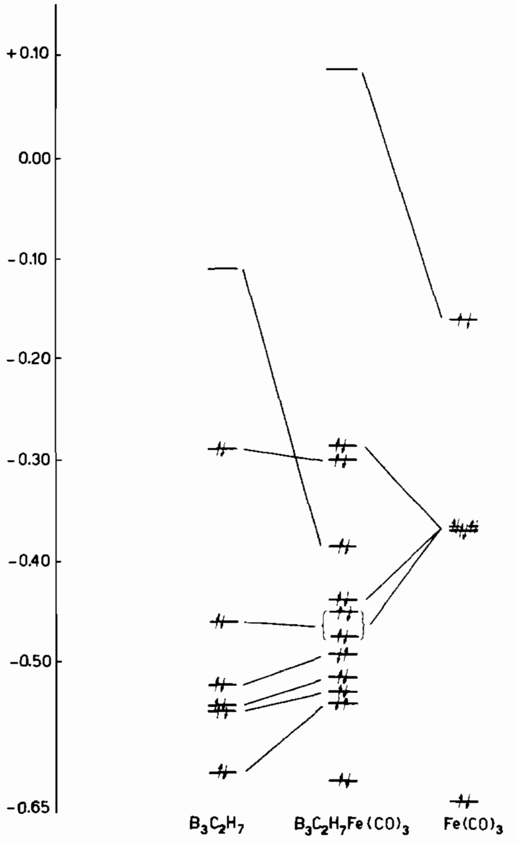

Fig. 2. The energies (in au) of the higher-filled molecular oribals of $B_3C_2H_7$, $B_3C_2H_7Fe(CO)_3$ and $Fe(CO)_3$.

The energetics of combination can be represented by

$$B_3C_2H_7Fe(CO)_3 \xleftarrow{-899\ \mathrm{kJmol^{-1}}}$$

$$\left\{\begin{array}{l} Fe(CO)_3 \xrightarrow{1353\ \mathrm{kJmol^{-1}}} Fe(CO)_3^{2+} \\ B_3C_2H_7 \xrightarrow{159\ \mathrm{kJmol^{-1}}} B_3C_2H_7^{2-} \end{array}\right\}$$

$$\xrightarrow{-2411\ \mathrm{kJmol^{-1}}} B_3C_2H_7Fe(CO)_3$$

It can be seen that the metallocarborane possesses a large energy of stabilisation with respect to the ionic and the neutral components. Hence, the electron transfer processes, although requiring energy for the formation of both ionic moieties, produces a very stable situation when the two species are bonded together.

Finally, it is of interest to compare the electronic structure of the isoelectronic species $B_3C_2H_7^{2-}$, $B_3C_2H_5^{4-}$ and $C_5H_5^-$ and these are outlined in Table II. The main difference between these compounds arises from the electronic distribution. For $B_3C_2H_5^{4-}$ the four anionic electrons are smeared over the framework atoms producing large negative charges on the boron and carbon atoms. In the case of $C_5H_5^-$ we have, of course, a symmetrical distribution of charge which, together with a charge polarisation across the C–H bond, results in a −0.332 charge on the carbon atoms. The π-system of $C_5H_5^-$ and $B_3C_2H_5^{4-}$ contain 6.0 electrons and four of these are present in the two highest filled orbitals. The π-electronic distribution of the tetraanionic species bears a strong resemblance to that found in the pseudo π-electronic system of $B_3C_2H_7^{2-}$. The highest filled–lowest empty orbital–orbital energy gap for these species is of the same order having a value 0.425au, 0.466au and 0.575au for $B_3C_2H_7^{2-}$, $B_3C_2H_5^{4-}$ and $C_5H_5^-$ respectively. The highest filled eigenvalues are all high in energy and are found at +0.226au, +0.788au and −0.01au for $B_3C_2H_7^{2-}$, $B_3C_2H_5^{4-}$, and $C_5H_5^-$ respectively. The value for $B_3C_2H_5^{4-}$ indicates that a metallic complex incorporating this species would have to bear a large positive charge in order to normalise the energy levels.

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