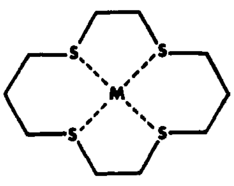


5

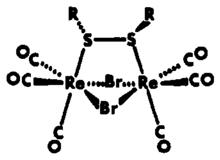
the metal M form a nearly perfect square plane. The macrocyclic thioether ligand is uncharged. M might be Cu^{2+} or Ni^{2+}. Note that the M-S distance in the Cu^{2+} complex is 2.303 Å,[18] very close to half the 4.667-Å S---S hole diameter in B_8S_{16}. The Ni-S distance in **5** is a little smaller at 2.176 Å.[19]

It is possible, though less likely, that B_8S_{16} might form complexes through bonds from one of the bridging sulfurs to a metal. Ru(II) complexes with the analogues thiophene (**6**) and tetrahydrothiophene (**7**) have been prepared.[20]

6

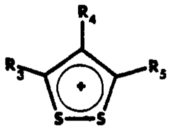
7

The least likely binding sites of B_8S_{16} would be the adjacent or peripheral sulfurs of the five-membered rings. Neutral molecules of the type R-S-S-R rarely form complexes in which both sulfurs participate in bonding. A few examples have been documented such as the binuclear rhenium complex **8** with bridging bromines and a disulfide.[21]



8

Another analogue is the 1,2-dithiolium cation **9**, which forms unidentate complexes.[22]



9

The closest analogue of B_8S_{16} would be the trithiadiborolanes, $S_3B_2R_2$, which have long been known. Apparently, there have been no reports of complex formation involving these small rings as ligands.

Studies are in progress on the σ electronic structure of B_8S_{16} to gain insight into the complex-forming potential of this interesting new macrocycle. As part of this work we find that the results of extended Hückel calculations show that B_8S_{16} has 16 occupied π molecular orbitals arranged in sets of four, supporting our simple electron-counting procedure and the results of the Hückel molecular orbitals analysis reported above.

Registry No. B_8S_{16}, 73825-17-9.

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Incorporation of Unsaturated Hydrocarbons into a Borane Cage. A Model for the Irreversible Adsorption of Alkynes

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It is demonstrated that a series of boranes and carboranes may be used to model the way in which the carbon-carbon multiple bonds of unsaturated hydrocarbons are progressively weakened, and ultimately cleaved, on interaction with an array of electropositive atoms. Specifically, molecular orbital and bond energy calculations are used to probe the changes that occur when tetraborane(10) reacts with ethylene or acetylene to form hydrogen and the *closo*-carboranes 1,2- and 1,6-$C_2B_4H_6$ via arachno and nido precursors. The driving force for the stepwise cluster oxidation is provided by a progressive increase in the boron-carbon bonding, which is accompanied by transfer of electronic charge to the carbon atoms. The results provide a rationale for the behavior of unsaturated hydrocarbons on surfaces and argue strongly against a carbonium ion like model for the adsorbed state.

The discovery that alkynes could be incorporated into borane cages to yield carboranes led to the production of a class of compounds whose unique properties have been exploited by numerous research groups.[2,3] Carboranes are generally prepared by the reaction of unsaturated hydrocarbons with boranes, and although a variety of intermediate products are known, ultimately the reaction yields carbyne units (≡CR) in a borane framework. One of the advantageous features of the carboranes (and boranes) is the existence of series of well-characterized compounds. These have provided insight into the systematics of cluster structure and provide the primary experimental evidence for the cluster-electron counting rules.[4] We now point out that the series of compounds illustrated in Figure 1 provides a vehicle for studying the in-

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(1) (a) University of Notre Dame. (b) University of Durham.

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(5) Although the series in Figure 1 is not necessarily a real synthetic route to 1,6-$C_2B_4H_6$, it is known that **2** yields some **5**, **5** yields **6**, and **6** yields **7**.[2,6]

(6) Franz, D. A.; Grimes, R. N. *J. Am. Chem. Soc.* **1970**, *92*, 1438. Franz, D. A.; Miller, V. R.; Grimes, R. N. *Ibid.* **1972**, *94*, 412.

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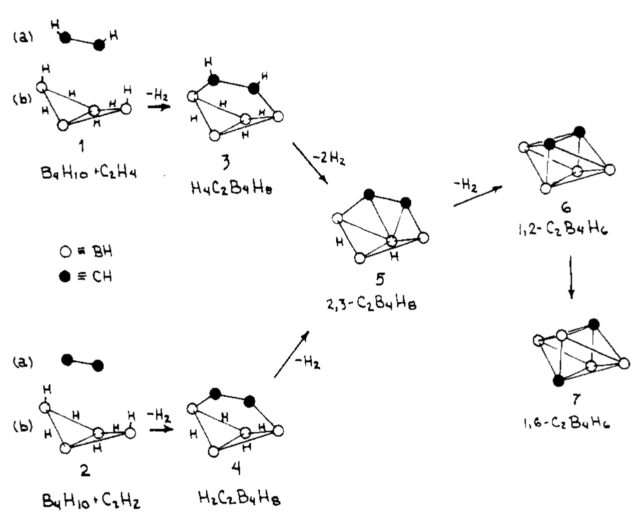

Figure 1. Model compounds for the cleavage of unsaturated hydrocarbons by a borane.

Table I. Total Energies and Lowest Ionization Potentials

	total energy (au)		ionization potential			
			this work			
compd[a]	this work	lit.	G-70	MNDO[e]	lit.	exptl
1a	−77.0718		8.77	10.13		10.51[f]
1b	−103.1255	−104.2559[b]	10.58	11.84	11.73[b]	11.5[g]
2a	−75.8533		9.52	10.97		11.40[f]
2b	−103.1255	−104.2559[b]	10.58	11.84	11.73[b]	11.5[g]
3	−179.1261		10.39	11.66		
4	−177.8954		7.98	10.04		
5	−176.8789	−178.744[c]	8.76	10.88	9.44[c]	9.6[h]
6	−175.7651	−177.601[d]	9.71	11.81	9.90[d]	
7	−175.7657	−177.625[d]	8.52	11.00	9.31[d]	9.9[h]

[a] See Figure 1. [b] Reference 9. [c] Reference 10. [d] Reference 11. [e] Reference 15. [f] Reference 12. [g] Reference 13. [h] Reference 14.

corporation of an unsaturated hydrocarbon into an array of electropositive atoms. The series is firmly based experimentally as all except two of the model compounds (**3** and **4**) have been structurally characterized[2] and all except one (**4**) are known compounds.[7] The known thermal stability order, **7** > **6** > **5** > **2**,[5] establishes the tendency for net overall *oxidation* (loss of H_2) proceeding from **1** to **7** and resulting in the formal *reduction* of the unsaturated hydrocarbon. We demonstrate below that real reduction, in the sense of net electronic charge flow to the C_2 moiety, takes place in going from **1** to **7**. In addition, a partitioning of the atom–atom interactions identifies the driving force for the C_2 cleavage and suggests fundamental similarities with the same process occurring on metal surfaces.

Calculations

Molecular Orbital. To probe the distribution of electron density in this series of molecules, we have carried out GAUSSIAN 70[8] (STO-3G basis set) calculations on molecules **1**–**7**. Experimental geometries[2] were used for all species except **3** and **4** for which hypothetical, but reasonable, geometries were used. Selected representative results are given in Table I where they are compared with similar quantities from earlier calculations[9-11] as well as with experimental information derived from photoelectron spectroscopy.[12-14] Total energies are all somewhat higher than those from the SCF calculations of Lipscomb et al.[9-11] Lowest Koopmans ionization potentials are lower than both the previous SCF values and the MNDO values calculated for the geometries used here.[15] However, trends in these quantities through the series are independent of method. In addition, trends in ionization potentials correlate well with available experimental values. The useful properties of interest, Mulliken overlap populations and charges, are tabulated in Tables II and III. The overlap populations were summed for each type of nearest neighbor interaction in the molecules, and the percent π contribution to the total CC overlap population is also given in Table II. As far as charges are concerned, once again absolute differences compared to literature values exist but trends through the series are the same.

Table II. Total Mulliken Overlap Populations for Various Interactions

compd[a]	BHB	BB	BH_{endo}	BH_{exo}	CH	BC	CC	CC (% π)
1a,b	1.57	0.81	0.85	1.66	1.56	0.0	0.60	32
2a,b	1.57	0.81	0.85	1.66	0.81	0.0	0.90	52
3	1.58	0.80		1.67	1.52	0.79	0.38	0
4	1.58	0.80		1.67	0.78	0.81	0.61	32
5	0.78	0.97		1.67	0.80	1.10	0.44	17
6	0.0	1.21		1.62	0.78	1.33	0.29	8
7	0.0	0.79		1.56	0.77	2.05	0.0	0

[a] See Figure 1.

Table III. Mulliken Charges

	this work		lit.
compd[a]	q_C	$q_C + q_H$	q_C
1a	−0.123	0.0	
2a	−0.109	0.0	
3	−0.198	−0.151	
4	−0.159	−0.107	
5	−0.148	−0.053	−0.016[b]
6	−0.178	−0.064	−0.08[c]
7	−0.232	−0.128	−0.10[c]

[a] See Figure 1. [b] Reference 10. [c] Reference 11.

Energetics. As MO methods do not include correlation effects, the calculated total energies (Table I) cannot be used to obtain bond energies. Thus, the energetics of the series in Figure 1 have been approached from a semiempirical viewpoint. Each member of the sequence of model compounds shown in Figure 1 has an enthalpy of atomization that may be represented as the sum of a set of individual energy term values $E(\text{C–C})$, $E(\text{B–C})$, $E(\text{B–B})$, etc. (eq 1). These enthalpy

$$\Delta H_{\text{atom}}(C_2B_4H_x) = E(\text{C–C}) + \sum E(\text{B–C}) + \sum E(\text{B–B}) + \sum E(\text{B–H})_{\text{term.}} + \sum E(\text{B–H})_{\text{bridge}} \quad (x = 6, 8, 10, 12) \quad (1)$$

contributions can be estimated from the respective bond lengths

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(7) Even compound **4**, which is isoelectronic with benzvalene, is known in the sense that it has been shown to be an intermediate in a kinetic study of the reaction of B_4H_{10} with C_2H_2. See ref 6 as well as: Franz, D. A.; Grimes, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 387. The last reference presents a discussion of the insertion of C_2H_2 into the borane framework.

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Table IV. Bond Enthalpies and Standard Enthalpies of Atomization for Addition Products of Acetylene and Ethylene to Tetraborane(10) (kJ mol^{-1})

species	E-(C–C)	ΣE(C–H) + E(C–C)	ΣE-(B–C)	ΣE(B–B) + E(B–H)$_{term}$ + E(B–H)$_{bridge}$	ΔH_{atom}
B_4H_{10}				4400[a]	4400[a]
C_2H_2	960	1640			1640[b]
C_2H_4	520	2250			2250[b]
$C_2B_4H_{12}$	340	1980	700	3740	6420
$C_2B_4H_{10}$	520	1340	700	3740	5780
$C_2B_4H_8$	420	1240	1340	3020	5600
1,2-$C_2B_4H_6$	340	1160	1840	2310	5310
1,6-$C_2B_4H_6$		820	2340	2130	5290

[a] ΔH_{atom}(exptl) = 4354 kJ mol^{-1}; ΔH_{atom}(calcd) = 4403 kJ mol^{-1}.[16] [b] Reference 29.

with use of empirical bond energy–bond length correlations of the type previously shown to be appropriate for boron–boron and boron–hydrogen bonds in *nido*- and *arachno*-boranes, B_nH_{n+4} and B_nH_{n+6}.[16] The energy of a bond is allowed to vary with its length according to eq 2 and 3. Terminal B–H bonds

$$E(\mathrm{B{-}B}) = 1.766 \times 10^{11}[d(\mathrm{B{-}B})]^{-4.0} \qquad (2)$$

$$E(\mathrm{B{-}H}) = 4.476 \times 10^{11}[d(\mathrm{B{-}H})]^{-4.4} \qquad (3)$$

in boranes and borane anions, $B_nH_n^{2-}$, generally are of length 119 pm,[9,17,18] giving a corresponding bond enthalpy, E(B–H)$_{term}$, of 330 kJ mol^{-1}. Bridging hydrogen atoms are attached more weakly, an average E(B–H)$_{bridge}$ in B_4H_{10} being 202 kJ mol^{-1}.

Few thermochemical data are available for carboranes, but standard enthalpies of formation of 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$ are known.[19] From these, a boron–carbon bond of length 171 pm[20] is estimated to have an energy contribution of 227 kJ mol^{-1}. In trialkylboranes, R_3B (R = Me, Et, *n*-Pr, *i*-Pr, or *n*-Bu), a boron–carbon single bond of length 158 pm[21] has an energy of 350 kJ mol^{-1}.[22] Assuming a relationship of the type $E(\mathrm{X{-}Y}) = A[d(\mathrm{X{-}Y})]^{-k}$ leads to eq 4. Structural

$$E(\mathrm{B{-}C}) = 4.340 \times 10^{14}[d(\mathrm{B{-}C})]^{-5.5} \qquad (4)$$

data are available for the carboranes $C_2B_4H_8$,[23] 1,2-$C_2B_4H_6$,[24,25] and 1,6-$C_2B_4H_6$.[26] By use of eq 2–4, and with the assumption that all E(C–H) = 410 kJ mol^{-1},[27] individual bond enthalpies and standard enthalpies of atomization can be calculated. These are summarized in Table IV.

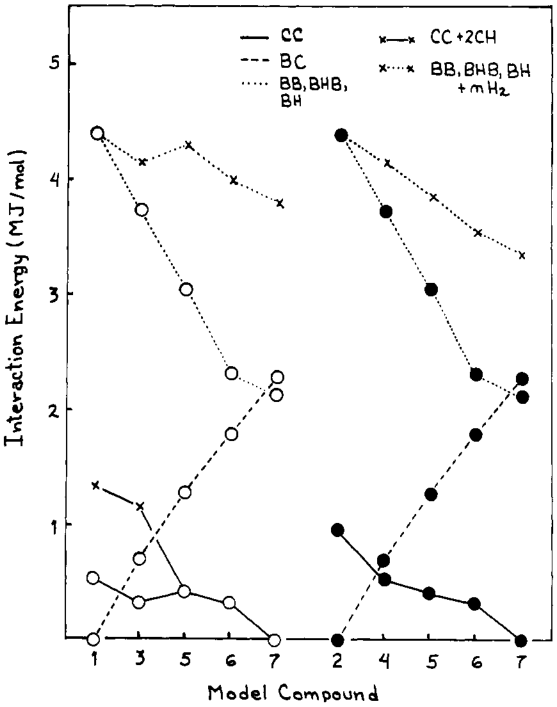

Figure 2. Selected energy term values from Table IV for the two series of model compounds. The open circles refer to the series involving C_2H_4 and the closed circles to that involving C_2H_2.

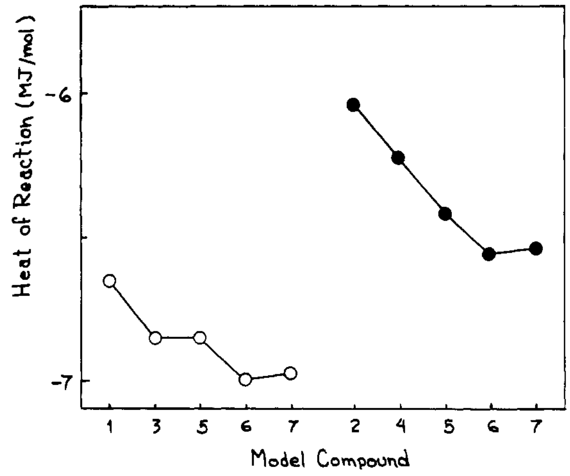

Figure 3. Heat of reaction for 2C + 4B + xH → $C_2B_4H_{x-2n}$ + $n$$H_2$ for x = 14 or 12. The open circles refer to x = 14 and the closed circles to x = 12.

The carboranes $C_2B_4H_{12}$ and $C_2B_4H_{10}$ (Figure 1) are both structurally and thermochemically uncharacterized. Localized bonding about each carbon atom gives a carbon–carbon double bond in $C_2B_4H_{10}$ (E(C=C) = 520 kJ mol^{-1}) and a corresponding single bond in $C_2B_4H_{12}$ (E(C—C) = 340 kJ mol^{-1}).[27-29] In both structures, single boron–carbon bonds are invoked with E(B–C) = 350 kJ mol^{-1}. It is assumed that the B_4H_8 unit in these carboranes will closely resemble that in the parent B_4H_{10}, the skeletal bond lengths not being significantly changed by any decrease in the dihedral angle, which may occur when the unit is bridged by the hydrocarbon. The sum of the boron–boron and boron–hydrogen bond enthalpy contributions in $C_2B_4H_{10}$ and $C_2B_4H_{12}$ is thus given by $\Delta H_{atom}(B_4H_{10}) - 2E(\mathrm{B{-}H})_{term}$. All the contributing bond energies and the standard enthalpies of atomization are summarized in Table IV.

Correlations

Inspection of Table II shows that some of the overlap populations remain constant, i.e., the exopolyhedral interactions. This is in line with the energy term values, which are taken to be constant through the series: E(B–H)$_{term}$ = 330

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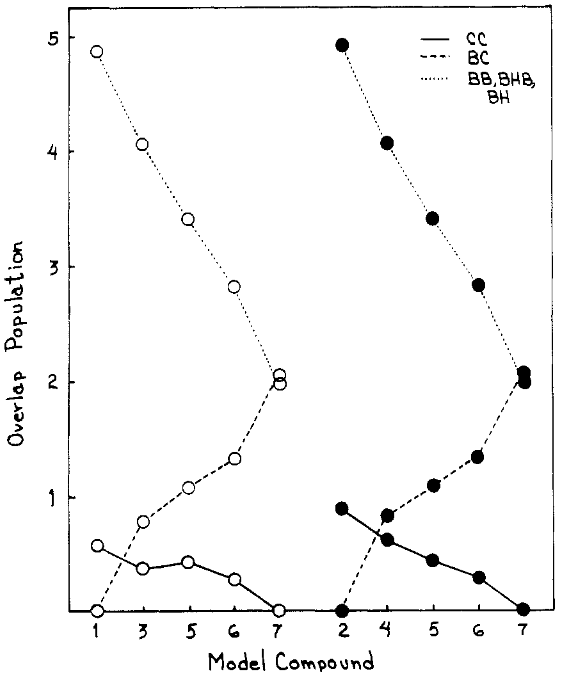

Figure 4. Selected Mulliken overlap populations for the two series of model compounds. The open circles refer to the series involving C_2H_4 and the closed circles to that involving C_2H_2.

kJ mol^{-1} and E(C–H) = 410 kJ mol^{-1}. However, other empirical energy terms shown in Table IV vary significantly and these are plotted in Figure 2. The total heats of reactions 5 and 6 are plotted in Figure 3, demonstrating an increase in

$$2C + 4B + 14H \rightarrow C_2B_4H_{14-2n} + nH_2 \qquad (5)$$

$$2C + 4B + 12H \rightarrow C_2B_4H_{12-2n} + nH_2 \qquad (6)$$

stability as the carbon atoms are incorporated into the cage (E(H–H) = 432 kJ mol^{-1}). The trends agree with qualitative information from observed reactions except that 1,2- and 1,6-$C_2B_4H_6$ (**6** and **7**) are predicted to have the same heat of atomization within experimental error.[30] On the other hand, a value for the heat of reaction of 2,3-$C_2B_4H_8$ → 1,6-$C_2B_4H_6$ + H_2 of −90 kJ mol^{-1} obtained from appearance potential measurements[31] is consistent with the value of −120 kJ mol^{-1} obtained here. It is clear from the changes in the heats of reaction (eq 5 and 6, Figure 3) that the increasing stability across the series is due to the increasing B–C interaction (Table IV and Figure 2). In fact, the B–C increase across the series more than compensates for the decrease in the C–C and borane cage energy terms. Figure 2 shows that the latter terms decrease even when adjusted for the H_2 produced.

The variation in Mulliken overlap populations across the series is shown in Figure 4; the same trends prevail as for the energy term values just discussed. Although the various types of overlap populations should not be quantitatively compared, clearly it is the increase in the BC interaction that leads to increasing stability across the series. The striking similarity between Figures 2 and 4 is emphasized in Figure 5, where the BC energy term values and the BC overlap populations are compared. Such a correlation is reasonable as both the overlap populations and the energy term values reflect the attractive interaction of the pairs of atoms. The former depends on distance by definition while the analysis of the energetics as carried out here includes a dependence on distance. The congruence of the two approaches permits the correlation of other calculated properties with the energy term values.

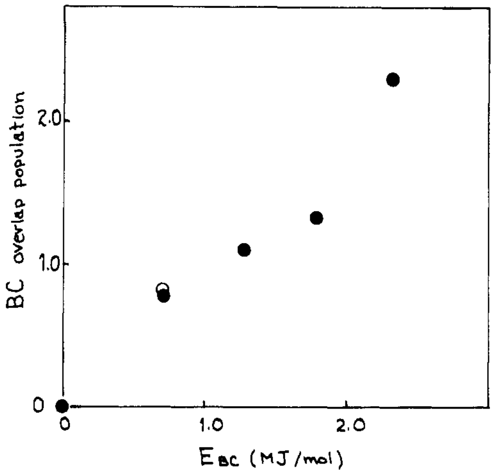

Figure 5. Mulliken overlap population for the BC interactions vs. total BC interaction energy. Open circles refer to the series involving C_2H_4 and the closed circles to that involving C_2H_2.

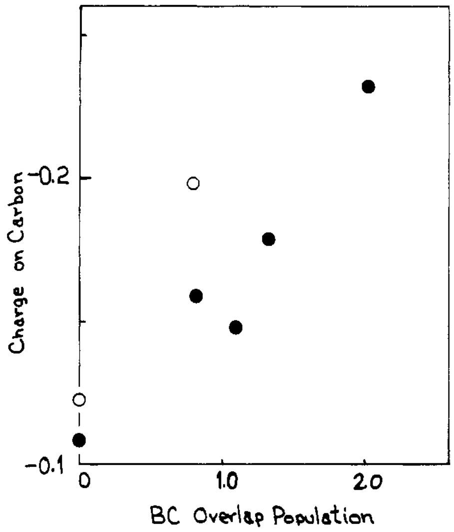

Figure 6. Mulliken charge on carbon vs. Mulliken overlap population for the BC interaction. Open circles refer to the series involving C_2H_4 and the closed circles to that involving C_2H_2.

A prominent feature of the calculations is the net transfer of negative charge from the boron cage to the CH moiety as one proceeds through the series (Table III). As shown in Figure 6 this increasing charge correlates well with the increasing BC overlap population; i.e., as the BC interaction increases, electron density is transferred to carbon. In a simple yet pleasing sense, the driving force for the cleavage of the alkyne by the borane cage is the net difference in electronegativities of boron in the cage and carbon in the alkyne. This picture supports the concept of electronegativity equilization[32] as an important method by which to understand the changes occurring in Figure 1. Thus, even though the entire cluster is oxidized in going from **1** to **7**, it is the reduction of the carbon fragment that provides the principal driving force for the reaction.

As shown in Figure 7 the net transfer of charge to the carbon atoms also correlates with the decrease in the percent π contribution to the total CC overlap population. The incorporation of the alkyne into the cage results in the smooth reduction of the triple bond (Table II). In the case of the alkenes the reduction of the double bond is complicated by

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(30) Lipscomb et al. have suggested 7 to be 60 kJ mol^{-1} more stable than 6.[11]

(31) Beltram, G.; Fehlner, T. P., unpublished data.

(32) Sanderson, R. T. *Science (Washington, D.C.)* **1951**, *114*, 670. Ray, N. K.; Samuels, L.; Parr, R. G. *J. Chem. Phys.* **1979**, *70*, 3680.

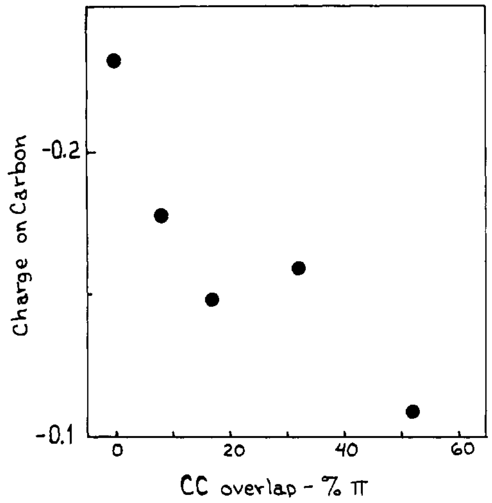

Figure 7. Charge on carbon vs. percent π contribution to the CC overlap population for the C_2H_2 series.

the dehydrogenation of the carbon moiety, and a simple connection between π character and charge transferred is not possible. Finally, there is no correlation of charge on the alkyne carbon with the lowest ionization potential of the system (Tables I and III). The energies of the highest occupied molecular orbitals (negative of ionization potentials) result from rather detailed orbital interactions and have no simple relationship with either the energetics or charge distribution.

Relevance

Prerequisite to understanding the role of transition-metal surfaces in heterogeneous catalytic processes is a knowledge of the mechanism and energetics of chemical bond formation and destruction on such surfaces. The spontaneous, irreversible adsorption of alkynes and alkenes on transition-metal surfaces has been known for some time,[33] and the products of the cleavage, surface carbynes, have now been implicated in a number of important reactions.[34-36] The spontaneous cleavage of alkynes (at elevated temperatures) under homogeneous conditions also occurs with transition metals to form bis(carbyne) clusters[37] and with boranes to form carboranes.[2] The latter observations suggest that the surface-homogeneous cluster analogy[38] might provide one way to obtain further insight into the difficult question of surface energetics. Although clusters have been used as structural models for ligand–metal surface interactions,[39] no one has as yet considered the mechanistic and energetic implications of such a model in terms of the known fragmentation of admolecules on or in both clusters and surfaces.

The first question to be considered is to what extent the B_4 cage in Figure 1 represents an M_4 metal cluster. It has already been established that boranes serve as structural and bonding models for a significant number of metal clusters.[40] This is not surprising as boron, like a transition metal, has an available empty valence orbital, readily forming adducts with Lewis bases. The major difference between them is that the metal can form more than one such donor–acceptor bond. However, if some of the metal's free orbitals are saturated with ligands, the metal fragment behaves very much like a borane fragment, e.g., $Fe(CO)_3$ and BH. This is most evident in the ferraboranes where not only similar geometrical structures[41] but similar electronic structures are found.[42] It is very clear from photoelectron spectroscopic and theoretical studies that B 2p orbitals are a good match energywise for Fe 3d orbitals.[43] Perhaps it is not surprising then that metal analogues of two of the model compounds in Figure 1 have been characterized, i.e., $Co_4(CO)_{10}C_2R_2$[44] and $Ru_4(CO)_{12}C_2R_2$[45] $\approx$ 1,2-$C_2B_4H_6$ and $(Cp)_2Ni_2Fe_2(CO)_6C_2R_2$[46] $\approx$ 2,3-$C_2B_4H_8$ as well as closely related compounds, e.g., $(Cp)_3Co_3C_2R_2$[6] $\approx$ 1,5-$C_2B_3H_5$. Thus, even though boron is not a transition metal, the B_4 cage serves to mimic the basic covalent interactions between an unsaturated hydrocarbon and an array of four metal atoms.

Consequently, the model described above can provide insight into the questions of metal cluster energetics. For example, consider the conversion of $Co_4(CO)_{10}C_2R_2$, which is analogous to 1,2-$C_2B_4H_6$ (**6**), to a structure analogous to 1,6-$C_2B_4H_6$ (**7**). The net enthalpy change for **6** → **7** results from the gain in two BC interactions and the loss of a CC and a BB interaction. The CoC interaction energy in $Co_3(CO)_9CH$ has been estimated to be 146 kJ mol^{-1}, which is about half the BC single-bond energy.[47] Thus, any change analogous to **6** → **7** for the cobalt cluster would almost certainly be endothermic as the CC interaction lost would be roughly equivalent to the two CoC interactions gained and it is unlikely that the breakup of the Co_4 "butterfly" would be exothermic.

The second question is the extent to which an M_4 cage can be taken to represent an excised fragment of a metal surface. Chemisorption can be a spatially localized phenomenon if the adsorbate only significantly perturbs a few metal atoms near the adsorbate.[48] This forms the rationale for using small metal fragments to theoretically model the essential aspects of the ligand–surface bond.[49] In Figure 1, B_4H_{10} represents the "metal" surface. It is possible that B_4H_{10} is a better representation of a metal surface than a bare B_4 cage having the same geometry simply because the hydrogen atoms both represent the rest of the metal and serve to terminate the bonding network. However, this particular arrangement of boron atoms only models one of many possible surface sites. Finally, the net process depicted in Figure 1 differs from the surface process in one essential feature. The B_4 part of the cluster is oxidized by two "reactions": one leading to formation of H_2 and the other to reduction of the unsaturated hydrocarbon. For adsorption of C_2H_2 but not C_2H_4, no hydrogen production is required in the metal system. It is clear from Figure 2 that the generation of H_2 from the B_4H_x fragment is an endothermic process and, thus, the chemisorption and cleavage of hydrocarbons on a metal surface should be even

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more favorable energetically. These considerations suggest that for the metal surface–alkyne reaction the basic driving force should be the same, i.e., negative charge transfer to the hydrocarbon. As the transition metals commonly used have lower electronegativities than carbon, this seems quite reasonable.

If the correlation with increasing charge does carry over to metal systems, then there should be a correlation between the ease of carbyne formation and the ease of charge transfer, i.e., the difference in electronegativities of the metal and carbon. For a given metal, C_2H_2 reacts more readily than C_2H_4 to form surface CH species.[50] This is consistent with our thesis as sp-hybridized carbon is more electronegative than sp^2-hybridized carbon. The irreversible chemisorption of hydrocarbons on various supported metals leads to residues with H/C ratios close to 1. The percent retention of a hydrocarbon as well as the fraction of surface covered by irreversible adsorbed species decreases as one moves from the iron group to the nickel group,[51] again correlating well with the change in electronegativity of the metal.

Although the description of carbyne formation driven by charge transfer is consistent with chemical intuition, charge flow in exactly the opposite direction of adsorption has been postulated previously.[52] On the basis of the negative change in metal work function following chemisorption of alkenes and alkynes, the suggestion has been made that the coordinated hydrocarbon has more positive ion character than negative character. There is no simple and pictorial MO theory for metals, and it is unlikely that a change in work function is simply connected to adsorbate charge. Even in our simple B_4C_2 model with well-defined MO's the lowest ionization potential varies unpredictably across the series and does not correlate with charge.[53]

There have been many approaches to the calculation of adsorption energies of which bond energy partitioning methods are one, e.g., the crystal field–surface orbital–bond energy bond order method.[55] The energetics of the series in Figure 1 tests the appropriateness of such an approach for a surface species. Figure 5 demonstrates a fairly linear correlation between the Mulliken overlap and the total BC interaction energy. The largest deviation from the curve is for **7** where the BC energy is underestimated. Note that in going from **6** to **7**, the B_4 "butterfly" structure is lost. We suggest, then, that as long as there are no large disruptions of the metal surface structure caused by the admolecule, the various energy partitioning methods are valid even if crude. Thus, the structures of the metal analogues of the compounds in Figure 1 may be used to gain insight into surface reaction energies for unsaturated hydrocarbons. The potential usefulness of such an approach depends on the characterization of more metal analogues of heteroboranes as well as the generation of suitable metal–carbon interaction energies.

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Vibrational Investigations of Polyoxometalates. 1. Valence Force Field of $Mo_6O_{19}^{2-}$ Based on Total Isotopic Substitution (^{18}O, ^{92}Mo, ^{100}Mo)

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A normal-coordinate treatment of the hexamolybdate anion $Mo_6O_{19}^{2-}$ was performed by using an internal valence force field. Total isotopic substitution (^{18}O, ^{92}Mo, ^{100}Mo) allowed previous erroneous assignments to be corrected. A reasonable force field accounting for the experimental data of the four isotopic derivatives is proposed. The principal force constants are discussed in relation with the geometry of the anion. In particular, the stretching force constants k_t (7.46 mdyn Å^{-1}), k_b (2.35 mdyn Å^{-1}), and k_c (0.47 mdyn Å^{-1}), respectively, agree with double bonds Mo–O_t, single bonds Mo–O_b, and very loose Mo–O_c bonds.

Introduction

Polyoxometalates are of great interest to workers in various fields of chemistry (e.g., ionic conductivity, photoconductivity, electronic hopping, catalysis, etc.). Their reactivity with other compounds, in particular with organometallic subunits, is widely studied. Moreover they can be considered as simplified models of three-dimensional frameworks. A good knowledge of their structural properties is required for a better understanding of the observed phenomena: the vibrational techniques can be suitable for this purpose. However, the assignments of IR and Raman spectra of such large polynuclear complexes are difficult and should be followed by a normal-coordinate analysis. Only a few attempts have been made up to now, probably because of the complexity of the theoretical treatment.

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