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Evidence for the Adsorption of Oriented *nido*-$R_2C_2B_4H_6$ Carborane Cluster Molecules on Si(111) Surfaces

Sunwoo Lee,[†] Dongqi Li,[†] P. A. Dowben,*,[†] F. Keith Perkins,[‡] M. Onellion,[‡] and James T. Spencer*,[§]

Contribution from the Department of Physics, Syracuse University, Syracuse, New York 13244-1130, the Department of Chemistry, Center for Science and Technology, Syracuse University, Syracuse, New York 13244-4100, and the Department of Physics and the Materials Science Program, University of Wisconsin, Madison, Wisconsin 53706. Received May 29, 1991

Abstract: Angle-resolved photoemission has provided clear evidence that the initial adsorption of the small heteroborane cluster molecule *nido*-2,3-diethyl-2,3-dicarbahexaborane(8), $(C_2H_5)_2C_2B_4H_6$, on Si(111) surfaces at 90 K occurs with partial dissociation of the cluster and results in the loss of ethyl groups (C_2H_5) from the molecule. The $C_2B_4H_6$ carborane fragment adsorbs molecularly on the Si(111) surface with the basal C_2B_3 plane of the cage parallel with the Si(111) surface normal. The complete assignment of the photoemission features and the molecular orientation of the cage is possible from a comparison of the experimental photoemission results with MNDO semiempirical theoretical calculations on *nido*-$(C_2H_5)_2C_2B_4H_6$ and *nido*-$C_2B_4H_8$.

Introduction

Angle-resolved photoemission has been successfully used to determine the orientation of molecularly adsorbed surface species. Typically, such studies have been applied to small diatomic molecules such as nitrogen,[1] carbon monoxide,[2] bromine,[3] iodine,[4] and only rarely to "large" molecules such as benzene.[5] With the increasing importance of molecular precursors, especially the boron-containing compounds,[6b–d] to selective area processing,[6] the characterization of weakly chemisorbed species such as carboranes and boranes is increasingly important.[7,8] Such weakly bound states are potential precursor states to dissociative adsorption[7] and are essential to selective area deposition chemical pathways. This paper represents the first study of the bonding orientation of a very large (polyatomic, multielemental) molecule of low (C_{1s}) symmetry, *nido*-2,3-diethyl-2,3-dicarbahexaborane(8) [$(C_2H_5)_2C_2B_4H_6$], with angle-resolved photoemission. This report also is the first surface science study of any carborane or heteroborane cluster species, although a study of decaborane (14) has been recently undertaken.[7]

Experimental Section

The *nido*-2,3-diethyl-2,3-dicarbahexaborane(8) (diethylcarborane) cluster, shown schematically in Figure 1, was prepared and purified with use of literature methods.[9] The identity and purity of the compound were determined by NMR, FT-IR, and mass spectral measurements. The diethylcarborane was admitted to the vacuum system through a standard leak valve and adsorbed on a polished n-type Si(111) single-crystal surface that had been precooled to 90 K via a liquid nitrogen cooled sample manipulator. Exposures reported in this work were uncorrected for the ionization gauge cross sections. The experimental sample was prepared and cleaned as described in detail elsewhere.[8a] The photoemission experiments were carried out at the Synchrotron Radiation Center[10] with an angle-resolved photoemission system equipped with a hemispherical electron energy analyzer as described in the literature.[11] All the photoemission spectra for this study were taken with the electrons collected normal to the surface. The light source used was the 1 GeV ring which was dispersed by a 3-m toroidal grating monochromator. The combined resolution of the monochromator and the electron energy analyzer was 0.19 eV. Two light incidence angles were employed to vary the orientation of the light vector potential with respect to the surface normal. A 70° light incidence angle with respect to the surface normal represented an orientation in which the light vector potential was oriented largely along the surface normal (p-polarized light). A 37° light incidence angle provided an incident light vector potential which was oriented with a large component along the surface (s + p polarized light). All binding energies reported in this work are with respect to the valence band edge of the clean silicon surface.

Results

Photoemission spectra for both s- and p-polarized light with increasing exposure of the diethylcarborane to the Si(111) surface are shown in Figure 2. For the clean Si(111) substrate, bands are observed at binding energies of 1.9 ± 0.1, 3.5 ± 0.1, and 6.5 ± 0.1 eV as well as the clean Si(111) surface state at 1.0 eV seen in p-polarized light. With the adsorption of diethylcarborane, the silicon photoemission features are suppressed. This suppression is particularly dramatic in p-polarized light and is less pronounced in s-polarized light. The differences observed in the spectra between the s- and p-polarized light is particularly dramatic for the smaller exposures (1–2 langmuirs, where 1 langmuir = 1×10^{-6} Torr s).

After the completion of four langmuirs of diethylcarborane exposure to Si(111) at 90 K, seven features attributable to the

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[†] Department of Physics and the Solid State Science & Technology Program, Syracuse University.

[‡] Department of Physics and the Materials Science Program, University of Wisconsin.

[§] Department of Chemistry and the Center for Molecular Electronics, Syracuse University.

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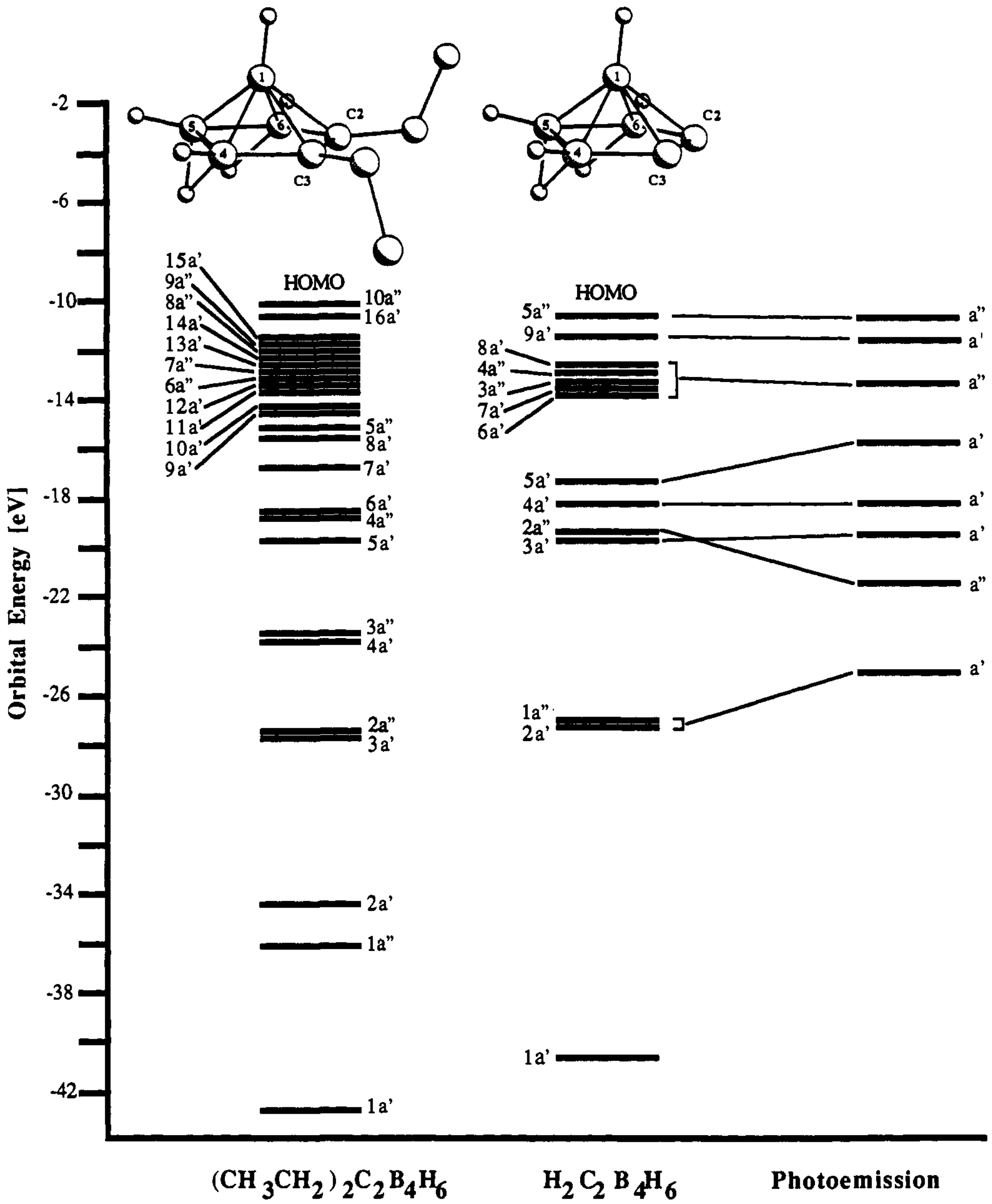

Figure 1. MNDO calculated minimum energy geometries for *nido*-2,3-$(CH_3CH_2)_2$-2,3-$C_2B_4H_6$ and *nido*-2,3-$H_2C_2B_4H_6$. The protons on the borane cages and ethyl groups have been omitted for clarity. The cage numbering scheme is indicated. The energy levels of *nido*-2,3-$(CH_3CH_2)_2$-2,3-$C_2B_4H_6$ and *nido*-2,3-$C_2B_4H_8$ are compared to the photoemission data applying a constant voltage offset. The constant voltage shift of 7.3 eV, to account for work function and screening effects, has been added to the photoemission binding energies.

molecular orbitals of cluster are evident with p-polarized light. The strong diethylcarborane-induced p-polarized photoemission features appear at binding energies of 4.6 ± 0.1, 6.6 ± 0.1, 8.6 ± 0.1, 10.6 ± 0.1, and 12.3 ± 0.1 eV with weaker features appearing at 14.6 ± 0.2 and 17.2 ± 0.2 eV. In s-polarized light, the features at about 10.6, 14.6, and 17.2 eV were not readily apparent until an exposure of 16 langmuirs was achieved.

With increasing diethylcarborane exposure beyond 4 langmuirs, the diethylcarborane-induced photoemission feature at 6.5 eV becomes the dominant feature relative to the features at 12.6 ± 0.2 and 13.3 ± 0.2 eV, as evident in the p-polarized light. A new feature is also observed at very large diethylcarborane exposures, at 3.2 eV, which is not observed at smaller exposures due to the large silicon density of states at the same binding energy. At the very large exposures, there is essentially no difference in the photoemission spectra in s- and p-polarized light.

Discussion

The pronounced differences between the photoemission spectra for the smaller diethylcarborane exposures in s- and p-polarized light is indicative of molecular adsorption on Si(111) with a preferential orientation. Randomly oriented molecules would result in photoemission spectra that differ little for s- versus p-polarized light. With increasing exposure to diethylcarborane, the photoemission results in s- and p-polarizations become virtually identical, indicating the adsorption of molecular species with increasing random orientations with respect to the surface normal (the symmetry axis of this experiment).

Auger electron spectroscopy (AES) for the boron–carbon films deposited from the decomposition of diethylcarborane following 2–6 langmuirs of exposure show a boron-to-carbon ratio ranging from about 2:1 to 1:1 but certainly not as low as 2:3. This suggests that the initial molecular adsorption of diethylcarborane occurs with an accompanying loss of exopolyhedral ethyl groups during the adsorption process.

The abundance of sharp (narrow half width) photoemission features, as opposed to the broad features (1–2 eV half width) at about 5–7 eV binding energy, provides strong evidence that the exposure of diethylcarborane to the Si(111) surface results in the adsorption of some associative or molecular carborane species. In order to understand the photoemission result, a complete study of the bonding of selected boranes and carboranes with

Table I. Calculated Orbital Energies and Observed Photoemission Binding Energies for *nido*-2,3-Diethyl-2,3-dicarbahexaborane(8) and *nido*-2,3-Dicarbahexaborane(8)

orbital assignment[a]	MNDO energy levels for $(C_2H_5)_2C_2B_4H_6$[b,c]	MNDO energy levels for $H_2C_2B_4H_6$[b-d]	photoemission binding energies[b,c,e]	energy difference[g]
10a″	10.33	10.56 (5a″)	3.2	7.4
16a′	10.93	11.60 (9a′)	4.6	7.0
15a′	12.23			
9a″	12.57			
8a″	12.91			
14a′	13.00	12.89 (8a′)		
13a′	13.16			
7a″	13.27	13.39 (4a″)		
6a″	13.61	13.67 (3a″)	6.5	7.2
12a′	13.77	13.74 (7a′)		
11a′	13.87	13.96 (6a′)		
10a′	14.45			
9a′	14.62			
5a″	15.15			
8a′	15.54			
7a′	16.45	17.23 (5a′)	8.6	8.8
6a′	18.29			
4a″	18.32	18.13 (4a′)	10.6[f]	7.5
5a′	19.57	19.55 (2a″)	14.6[f]	5.0
3a″	23.24	19.75 (3a′)	12.3	7.4
4a′	23.71			
2a″	27.46	26.87 (1a″)	17.2[f]	9.7
3a′	27.59	26.99 (2a′)		
2a′	34.23			
1a″	36.08			
1a′	42.26			

[a] Assignment for $(C_2H_5)_2C_2B_4H_6$. [b] In eV. [c] Higher values shown indicate lower energy orbitals. [d] Orbital assignments for $H_2C_2B_4H_6$ are given in parentheses. [e] Low coverage molecular photoemission features. [f] Observed with p-polarized light only. [g] Energy difference (in eV) = [MNDO ($H_2C_2B_4H_6$) − ARUPS binding energies].

MNDO theoretical calculations was undertaken.[12-15] The results are displayed in Figure 1. The MNDO structural optimization procedures similar to those reported for other heteroborane clusters were used in this work.[12,16] Orbital assignments and connectivities were made by inspection of the atomic orbital coefficients of the LCAO set for each molecular orbital. Interactions between filled and virtual orbitals were neglected.

From the data presented in Figure 2, it is difficult to reconcile the photoemission spectra for 1–6 langmuir exposures with the MNDO calculated molecular orbitals for diethylcarborane. If diethylcarborane, however, loses ethyl groups with the initial adsorption on clean Si(111), then the photoemission results should be more consistent with the molecular orbital structure for the parent *nido*-2,3-$C_2B_4H_8$ compound, shown schematically in Figure 1. The agreement observed between the photoemission data and the MNDO calculations for the parent *nido*-2,3-$C_2B_4H_8$ cage is very good. This observed correlation together with the Auger electron spectroscopic results permits the conclusion that the initial adsorption of diethylcarborane results in the loss of ethyl groups. Hydrogen may also be lost from the bridging hydrogen atoms of carborane cage on adsorption which, however, cannot be detected in the experiment.

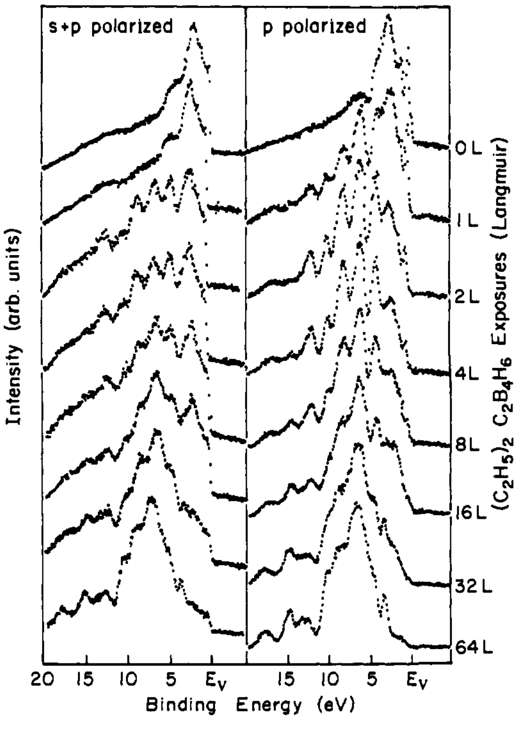

Figure 2. The photoemission spectra of Si(111) at 90 K with increasing exposure to *nido*-2,3-$(CH_3CH_2)_2$-2,3-$C_2B_4H_6$. All photoelectrons were collected normal to the surface. The incident photon energy was 55 eV.

By assigning the photoemission spectral features from the calculations, it is apparent that the low coverage photoemission bands at 10.6, 14.6, and 17.2 eV result from the boron and carbon 2s and $2p_z$ orbital contributions, where z is roughly along the B(6)–C(2) or B(4)–C(3) axes. These features are only seen with the p-polarized light. It is thus possible to conclude that the *nido*-2,3-$C_2B_4H_6$ molecular fragment bonds with either C(2) and/or C(3) bonded to the surface or the B(5) atom bonded to the surface with the basal C_2B_3 plane of the carborane molecule roughly along the surface normal. From photoemission alone we cannot distinguish among these two possibilities. Given that this fragment is a result of ethyl group loss, however, it is apparent that the molecular fragment is bonded via C(2) and C(3) to the Si(111) surface. This is schematically shown in Figure 3.

This molecular orientation relative to the surface and the bonding assignment are based upon a comparison of the pho-

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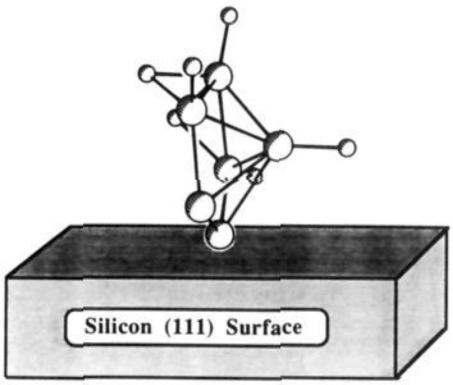

Figure 3. Schematic representation showing the orientation of the adsorbed carborane molecule on the Si(111) surface.

toemission binding energies with the MNDO derived bonding energies. The differences between the calculated energies for the parent *nido*-2,3-$C_2B_4H_8$ cage and the binding energies observed for the adsorbed molecular species at low coverage is about 7.3 ± 0.2 eV except for the photoemission bands at 8.6, 14.6, and 17.2 eV. By applying the assignments shown in Figure 1 and Table I, the photoemission features which have binding energies smaller than expected (the 8.6 eV band) can be assigned to molecular orbitals with substantial C(2) or C(3) atomic contributions. If the carbons are bound to the Si(111) surface via lone pair p-electrons, then these carborane molecular orbitals would be either nonbonding or only very weakly bonding. The photoemission feature at 14.6 eV has a binding energy much greater than expected based on a comparison of the MNDO calculated molecular orbital energies and the photoemission features. This feature can be assigned to a molecular orbital with large C(2) and C(3) 2s components and would strongly bond with the silicon surface with the orientation of carbon atoms toward the silicon surface.

With increasing exposure, further carborane molecular species are adsorbed. The increase in the intensity and width of the 6.5 eV feature relative to the other photoemission features, as seen in Figure 2, is indicative of the adsorption of molecular species *with* ethyl groups intact. This is confirmed by the existence of two molecular orbital features at 12.6 and 13.3 eV which cannot be reconciled with the calculated *nido*-2,3-$C_2B_4H_8$ molecular orbitals (Figure 1). Thus, with increasing molecular coverage, molecular adsorption results in no loss (or at least a smaller loss) of ethyl groups and a decreasing amount of molecular fragmentation. Similar results have been observed for highly reactive molecular diatomic species.[3,4]

On the basis of the photoemission results, it is apparent that with increasing molecular coverage the molecular species adsorb with increasingly random orientations. This may be a consequence of the presence of the relatively bulky exopolyhedral ethyl groups in the adsorbed molecular species. These ethyl species would effectively provide a significant steric blocking of the C(2) and C(3) atoms with respect to the surface. In addition, the ethyl groups are not as rigidly oriented as the *nido*-2,3-$C_2B_4H_6$ cage framework and would therefore make adsorption in one specific orientation difficult.

Conclusion

In summary, on the basis of angle-resolved photoemission results and MNDO theoretical calculations, it appears that the initial adsorption of diethylcarborane on Si(111) at 90 K results in the loss of ethyl units. The adsorption of the parent *nido*-2,3-$C_2B_4H_8$ fragment is otherwise molecular. This molecular fragment bonds to the surface with the basal plane of the carborane molecule essentially parallel with the surface normal. Subsequent molecular adsorption results in little or no fragmentation, but the molecules adsorb with increasingly random orientations with respect to the surface normal.

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From Stoichiometry to Catalysis: Electroreductive Coupling of Alkynes and Carbon Dioxide with Nickel–Bipyridine Complexes. Magnesium Ions as the Key for Catalysis

Sylvie Dérien, Elisabet Duñach,* and Jacques Périchon

Contribution from the Laboratoire d'Electrochimie, Catalyse et Synthèse Organique, CNRS, UMR 28, 2 rue Henri-Dunant, 94320 Thiais, France. *Received January 23, 1991*

Abstract: The incorporation of carbon dioxide into nonactivated alkynes catalyzed by electrogenerated nickel–bipyridine complexes affords α,β-unsaturated acids in moderate to good yields. The electrocarboxylation reaction was undertaken on a preparative scale in the presence of a sacrificial magnesium anode: the formation of acids from alkynes is stoichiometric with respect to the nickel complex if performed in a two-compartment cell but can be made catalytic in a single-compartment cell. An intermediate nickelacycle was isolated from the reaction with 4-octyne. The cleavage of this metallacycle by magnesium ions is the key step to explain catalysis.

Introduction

The vast natural abundance of carbon dioxide in the world makes it an attractive raw material for the synthesis of organic compounds. The development of catalytic reactions that form C–C bonds from CO_2 has the potential to provide short, economical routes to functionalized products.

The coordination chemistry of carbon dioxide and its biological, chemical, photochemical, and electrochemical activity have been recently reviewed.[1-3] Although CO_2 binding to metal complexes

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