

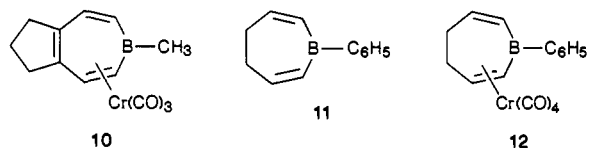
**Table I.** Comparison of the  $^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{13}\text{C}$  NMR Chemical Shift Values of 1-Methyl-4,5-cyclopentoborepin (**5**) with Similar Compounds

	<b>5</b> <sup>a</sup>	<b>10</b> <sup>a</sup>	<b>11</b> <sup>b</sup>	<b>12</b> <sup>b</sup>
$^1\text{H}$ NMR				
H <sub>2(7)</sub>	7.49 (d, $J = 12.8$ Hz)	4.66 (d, $J = 11.8$ Hz)	6.80	3.88
H <sub>3(6)</sub>	7.76 (d, $J = 12.8$ Hz)	6.09 (d, $J = 11.8$ Hz)	7.20	4.58
H <sub>8(10)</sub>	3.09 (t, $J = 7.6$ Hz)	2.94, 3.32 m		
H <sub>9</sub>	2.03 (quin, $J = 7.6$ Hz)	2.05 m		
BCH <sub>3</sub>	0.98	0.94		
$^{11}\text{B}$ NMR				
	53.6	49.2	54.6	29.7
$^{13}\text{C}$ NMR				
C <sub>2(7)</sub>	148.5 (br)	100.7 (br)	135.9	91.3
C <sub>3(6)</sub>	145.3	112.0	156.7	112.8
C <sub>4(5)</sub>	147.6	117.2		
C <sub>8(10)</sub>	39.7	38.5		
C <sub>9</sub>	23.5	23.8		
BCH <sub>3</sub>	11.0 (br)	6.4 (br)		

<sup>a</sup>The NMR spectra were obtained by using a Bruker AM-300 or WH-360 spectrometer. The spectra were measured from dilute  $\text{CDCl}_3$  solutions with  $\text{Me}_4\text{Si}$  as an internal reference for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra while external  $\text{BF}_3\text{-OEt}_2$  was used to calibrate the  $^{11}\text{B}$  NMR spectra. <sup>b</sup>Reference 20.

wavelength band has prominent vibrational fine structure ( $\lambda_{\text{max}}$  327, 320, 314, 309, 305, 298 nm) as is commonly observed for aromatic rings. These bands are red-shifted from those of cycloheptatriene ( $\lambda_{\text{max}}$  199, 261 nm) but closely match those of tropone ( $\lambda_{\text{max}}$  225, 312 nm).<sup>14</sup> Thus the UV spectrum suggests that the boron atom of **5** is extensively conjugated to the hexatriene moiety.

The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{11}\text{B}$  NMR chemical shift values of **5** are compared with similar compounds in Table I. Certainly the most striking feature of the  $^1\text{H}$  NMR spectrum is the diatropic shift shown by the borepin ring protons. Both the  $\alpha$ - and  $\beta$ -hydrogen signals are shifted downfield from those of the model compound 1-phenylboracyclohepta-2,6-diene (**11**).<sup>15</sup> This effect is consistent with substantial ring current and/or electron donation from the carbon to boron atoms.<sup>16</sup>



The  $^{13}\text{C}$  NMR spectra of vinyl boranes such as **11** usually show that the  $\beta$ -carbons are highly deshielded, while the  $\alpha$ -carbons are not.<sup>17,18</sup> It is assumed that there is substantial electron donation from the  $\beta$ -carbon to boron. The  $^{13}\text{C}$  NMR spectrum of borepin **5** is unusual in that both the  $\alpha$ - and  $\beta$ -positions are almost equivalently deshielded, which suggests electron donation from both positions. On the other hand, the  $^{11}\text{B}$  chemical shift of **5** is only slightly upfield from that of **11**. Apparently only little more net transfer of electron density to B occurs in **5** than in **11**.<sup>17,19</sup>

Many aromatic rings can serve as  $6\pi$  ligands toward transition metals. Thus we find that borepin **5** reacts with tris(acetonitrile)chromium tricarbonyl in refluxing THF to afford 50% of tricarbonyl(1-methyl-4,5-cyclopentoborepin) chromium (**10**) as yellow crystals, mp 56–60 °C. The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{11}\text{B}$  NMR chemical shifts are summarized in Table I. The signals for C<sub>2(7)</sub>, C<sub>3(6)</sub>, and C<sub>4(5)</sub> show substantial upfield shifts in comparison to

the corresponding signals for **5**, indicating that the six ring carbon atoms are  $\pi$ -coordinated to Cr. A similar shift is shown in the  $^1\text{H}$  NMR spectra for the H<sub>2(7)</sub> and H<sub>3(6)</sub> signals. However, the  $^{11}\text{B}$  signal for **10** is shifted only slightly upfield from that of **5**. This is in marked contrast to various boradienes such as **11** which experience more substantial upfield  $^{11}\text{B}$  shifts on complexation.<sup>20,21</sup> Thus the NMR data suggest that borepin serves as a  $\eta^7$  rather than a  $\eta^7$  ligand.

**Acknowledgment.** We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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### Bonding of Noble Metals to Semiconductor Surfaces: First-Principles Calculations of Cu and Ag on Si(111)

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Received August 11, 1986

Understanding the bonding between noble metals and semiconductor surfaces is of fundamental importance in a wide range of technological applications including electronic devices and catalytic processes. Although it has been known for more than 40 years that the synthesis of methylchlorosilanes (direct process)<sup>1</sup> is catalyzed by Cu atoms,<sup>2</sup> a complete understanding of the role of the metal atoms in this process is still lacking.<sup>3</sup> Cu has unique

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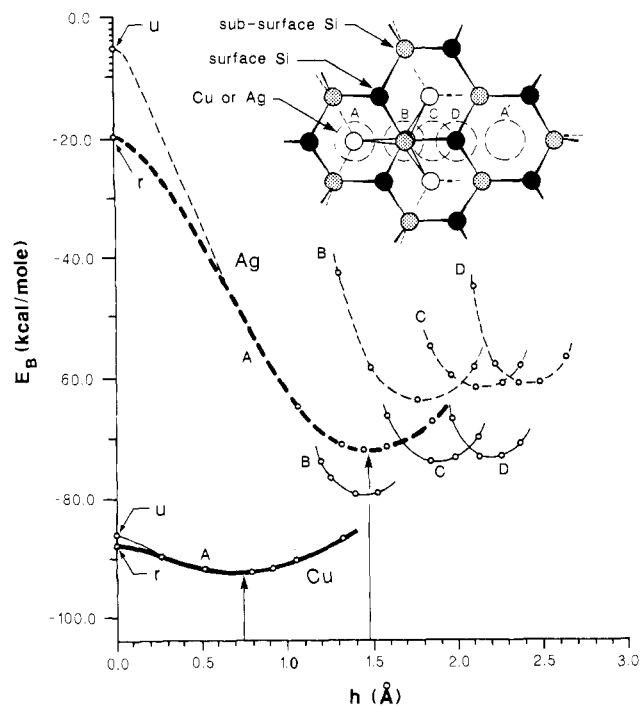
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**Figure 1.** Binding energies,  $E_B$ , of single Cu (solid lines) and Ag atoms (broken lines) on a 20-atom Si(111) cluster. The height,  $h$ , refers to the normal distance between the adsorbate atoms and the plane of the surface Si atoms. The four different adsorption sites are labeled as A (3-fold hollow), B (on top of 4-fold-coordinated subsurface Si), C (bridge), D (on top of 3-fold-coordinated surface Si), and A' (3-fold hollow with missing third layer Si). For the in-plane geometries ( $h = 0$ ), binding energies for unrelaxed (u) and relaxed (r) surface Si atoms are shown.

properties in contrast with its congener Ag, which exhibits significantly lower catalytic activity.

Our first-principles quantum-mechanical approach to the electronic structure and energetics of Cu and Ag atoms on a Si(111) surface shows that both Cu and Ag atoms are chemisorbed in 3-fold hollow sites at equilibrium heights of 0.74 and 1.48 Å above the Si(111) surface with binding energies of 92 and 72 kcal/mol, respectively. Cu has a much lower penetration barrier than Ag (4 kcal/mol vs. 53 kcal/mol). Therefore, at elevated temperatures, Cu is expected to diffuse into the Si lattice whereas Ag should desorb into the gas phase. New Auger and thermal desorption spectroscopy measurements<sup>4</sup> confirm this picture.

The clean Si(111) surface is known to reconstruct,<sup>5</sup> gaining 8 kcal/mol per surface Si atom;<sup>6</sup> this energy is substantially smaller than the Cu and Ag chemisorption energies. Hence, reconstruction is energetically secondary and the unreconstructed surface is used as the starting point. In this study, the Si(111) surface is represented by a cluster consisting of 20 Si atoms. The bonds toward the bulk are saturated with 26 H atoms. Bonding of single Cu and Ag atoms in hollow, bridge, and on-top adsorption geometries is explored as shown in Figure 1.

The many-body problem is treated by solving the local spin density equations<sup>7,8</sup> self-consistently with the DMOL/86 program.<sup>9</sup> The single-particle cluster orbitals are expanded variationally in 485 numerically generated atomic basis functions. In these spin-unrestricted calculations, overlap and Hamiltonian matrix elements are evaluated by a numerical integration technique using

a grid of about 24 000 points. Self-consistent total-energy calculations are carried out for about 50 different geometries.

The calculations reveal that at equilibrium both Cu and Ag atoms are adsorbed in 3-fold hollow sites with binding energies of 92 and 72 kcal/mol and adsorption heights of 0.74 and 1.48 Å, respectively.<sup>10</sup> This shows that, even at low coverages, Cu and Ag interact with the dangling bonds of three neighboring surface Si atoms, making the 3-fold hollow site energetically more favorable. From recent surface extended X-ray absorption fine structure (SEXAFS) measurements<sup>11</sup> it has been concluded that the Ag-Si bond distance is  $2.45 \pm 0.05$  Å. Our theoretical value for a rigid substrate is 2.67 Å, which is surprisingly close to the sum of the Bragg-Slater atomic radii<sup>12</sup> ( $1.60 + 1.10 = 2.70$  Å). Isothermal desorption spectroscopy measurements<sup>13</sup> reported for the Ag/Si system for increasing Ag coverage yield binding energies of 68 and 65 kcal/mol and vibrational frequencies of 77 and 60  $\text{cm}^{-1}$ , respectively. Our model represents the low-coverage limit where binding energies and vibrational frequencies should be larger than these experimental values: we obtain 72 kcal/mol for the Ag/Si(111) binding energy and 90  $\text{cm}^{-1}$  for the vibrational frequency (assuming a rigid substrate).

The calculated Cu-Si equilibrium distance is 2.34 Å (the sum of the Bragg-Slater radii would give 2.45 Å). Most significantly, the frequency of the vibration perpendicular to the surface is surprisingly low (58  $\text{cm}^{-1}$ ). Consequently, as Cu is moved from its equilibrium height ( $h = 0.74$  Å) into the plane of the silicon surface ( $h = 0$  in Figure 1), the total energy increases by only 6 kcal/mol. Geometry optimization of the three nearest-neighbor silicon atoms results in a gain of 2 kcal/mol, due to a displacement of the Si atoms by 0.04 Å away from the Cu atom and 0.03 Å away from the surface. Thus, the penetration barrier for Cu is only 4 kcal/mol. In contrast, the corresponding value for Ag is 53 kcal/mol with the nearest-neighbor Si atoms displaced by 0.12 Å away from Ag and 0.01 Å away from the surface. Auger electron spectroscopy (AES) measurements for Cu/Si(111) reveal<sup>14</sup> that at room temperature, Cu atoms do not diffuse into the Si lattice. However, high-energy core-level Auger electron experiments<sup>15</sup> indicate that Cu/Si(111) (1.1 monolayers) annealed at 600 °C results in a silicon surface with 6-fold coplanar geometry and with the Cu atoms in hollow sites  $0.1 \pm 0.1$  Å underneath the surface plane.

In conclusion, first-principles calculations reveal striking differences in the bonding of Cu and Ag on a Si(111) surface: (i) Cu has a higher chemisorption energy and a significantly lower penetration barrier than Ag. This theoretical result is substantiated by previous<sup>11,15</sup> and new<sup>4</sup> experimental evidence showing that at elevated temperatures Cu diffuses into the Si lattice whereas Ag remains above the surface until it desorbs into the gas phase. (ii) Cu is found to weaken the bonding between adjacent surface and subsurface Si atoms markedly more than Ag. These structural and electronic differences, obtained by first-principles local spin density total-energy calculations, shed new light on the bonding between noble metals and semiconductor surfaces and may well account for the fact that Cu, in contrast to Ag, has a high catalytic activity in the direct process.

**Acknowledgment.** Work at Northwestern University was supported by the Office of Naval Research (Grant 00014-81-K-0438). S.-H. Chou is grateful to J. H. Weaver for his hospitality and encouragement during her stay in his laboratory at the University of Minnesota.

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