NCCN dissociation on this surface. Initial dosing of CN onto Cu(111) at 300 K followed by water adsorption at around 150 K yielded a band around 2050 cm^{-1} as before, suggesting that any tendency toward CN reorientation is kinetically hindered under these conditions.

An explanation for the oxygen-induced reorientation of adsorbed cyanogen is that the electronegative oxygen atoms generate relatively electron-deficient surface sites at which σ coordination via the carbon should be favored relative to side-on bonding. Another factor may be steric hindrance to the flat CN orientation caused by coadsorbed oxygen. Although this is unlikely to be dominant at the moderate oxygen coverages encountered here, the presence of this electronic effect suggests a close proximity between the oxygen and cyanogen adsorbate. Methyl isocyanide, CH_3NC, (but not acetonitrile, CH_3CN) can also bind to Pt(111) in an end-on configuration under some conditions.[6b] It would therefore appear that the usual preference for side-on CN surface coordination in uhv can be altered by relatively subtle changes in the system state, at least when the carbon atom is available for surface coordination.

An apparent difference between the surface-uhv and electrochemical systems is that CN adsorbs formally as a cyanogen radical and cyanide anion, respectively, in these two experiments. This distinction, however, is blurred and perhaps removed entirely by the adsorbate–surface charge sharing that will necessarily occur upon chemisorption.

From the present evidence, the structural differences observed for adsorbed CN in these environments may arise from differences in the excess metal charge thus induced as well as from the effect of the diffuse-layer cations and solvent dipoles upon the charge distribution in the electrochemical case. The present results suggest that the first as well as the last factor may account for the interestingly disparate behavior of adsorbed CN in the metal-uhv and electrochemical systems.

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1-Methyl-4,5-cyclopentenoborepin:[1] A Neutral Boron Analogue of Tropylium

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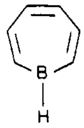
The seven-membered unsaturated heterocycle borepin (**1**) is of substantial theoretical interest. To the extent that its sp^2-hybridized boron atom is able to accept π-electron density from carbon, borepin is the neutral boron analogue of tropylium **2**.[2,3]



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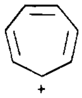

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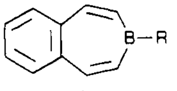

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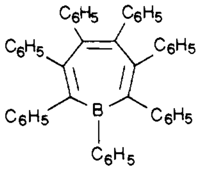
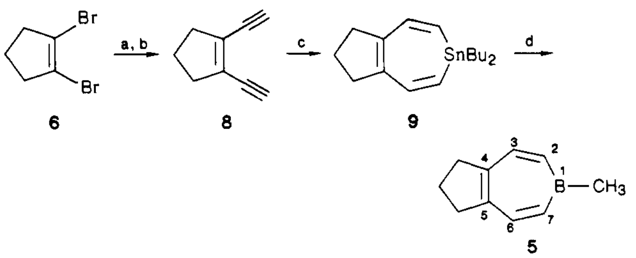


4

Ab initio molecular orbital calculations indicate that borepin should be a planar although weakly conjugated system.[4] Heavily substituted borepins[5–8] such as **3**[5] and **4**[6] have been prepared.[7,8] The spectral properties of **3** and **4** suggest that they are aromatic.[5,6] Since it can be argued that heavy substitution may mask the intrinsic properties of the borepin ring system, an examination of less substituted derivatives would be desirable.[9] We now wish to report on a synthesis of borepin **5** which bears only alkyl substituents (Scheme I).

Scheme I[a]



[a] (a) $HC\equiv CSiMe_3$, $Pd(PPh_3)_2Cl_2$, piperidine; (b) K_2CO_3, CH_3OH; (c) Bu_2SnH_2, KOH/18-crown-6 ether/benzene; (d) $MeBBr_2$, pentane.

Our synthesis involves an extension of the van der Kerk method for the preparation of boron heterocycles from diacetylenes via organotin intermediates.[5,10] The required starting diacetylene **8** was prepared from the readily available 1,2-dibromocyclopentene (**6**).[11] Thus Pd^{II}-catalyzed coupling of **6** with (trimethylsilyl)acetylene in piperidine gave 97% of 1,2-bis[(trimethylsilyl)ethynyl]cyclopentene[12] (**7**) which on treatment with K_2CO_3 in methanol afforded 35% of the labile 1,2-diethynylcyclopentene (**8**) as a colorless oil that quickly darkened on standing at 25 °C. Hydrostannation of **8** by dibutyltin dihydride catalyzed by powdered KOH/18-crown-6 ether in benzene at 25 °C[13] gave 46% of 1,1-dibutyl-4,5-cyclopentenostannepin (**9**) as a yellow oil. Fortunately, **9** can be obtained in high purity by washing with water, followed by filtration and solvent removal since attempted distillation at 110 °C resulted in decomposition to indane through the formal loss of dibutylstannylene. The reaction of the stannepin with methylboron dibromide in pentane at 25 °C gave 35% of the desired 1-methyl-4,5-cyclopentenoborepin[1] which was isolated by Kugelrohr distillation at 86 °C (0.002 torr) as a colorless, air-sensitive oil, mp 10–12 °C. High-resolution mass spectroscopy showed a molecular ion at m/z 144.1114 (calcd for $^{12}C_{10}{}^{1}H_{13}{}^{11}B$: 144.1110).

The UV spectrum (cyclohexane) of **5** consists of bands centered at 223 nm (log ϵ, 4.37) and 315 nm (log ϵ, 3.94). The higher

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(1) By IUPAC rules, **5** is named 3,6,7,8-tetrahydro-3-methylcyclopenta[*d*]borepin. The name 1-methyl-4,5-cyclopentenoborepin with numbering shown was chosen for consistency with **11** and **12** in Table I.

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(12) All new compounds gave satisfactory analytical and/or spectral data. **7**: ^{1}H NMR ($CDCl_3$) δ –0.32 (s, 18 H), 1.96 (quin, J = 7 Hz, 2 H), 2.58 (t, J = 7 Hz, 4 H); *MS*, m/z 260 (M^+). **8**: ^{1}H NMR ($CDCl_3$) δ 1.91 (quin, J = 7 Hz, 2 H), 2.51 (t, J = 7 Hz, 4 H), 3.38 (s, 2 H); *MS*, m/z 116 (M^+). **9**: ^{1}H NMR ($CDCl_3$) δ 0.88 t, 0.95 t, 1.34 m, 1.49 m (2 C_4H_9), 1.76 (quin, J = 7.5 Hz, CH_2), 2.62 (t, J = 7.5 Hz, 2 CH_2), 5.95 (d, J = 13 Hz, J_{SnH} = 85 Hz, 2 $C_\alpha H$), 6.98 (d, J = 13 Hz, SnH = 132 Hz, 2 $C_\beta H$); ^{13}C NMR ($CDCl_3$) 10.1, 13.6, 27.1, 29.0 (C_4H_9), 22.3 (CH_2), 40.0 (CH_2), 130.2 ($C_\alpha H$), 141.4 (C), 142.4 ($C_\beta H$); *MS*, m/z 295 ($M^+ - C_4H_9$). **10**: *IR* ($CDCl_3$) cm^{-1} 1986 s, 1935 m, 1901 m; *MS* m/z 280 (M^+).

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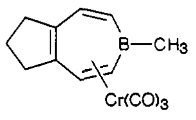
Table I. Comparison of the ^{1}H, ^{11}B, and ^{13}C NMR Chemical Shift Values of 1-Methyl-4,5-cyclopentoborepin (**5**) with Similar Compounds

	5[a]	**10**[a]	**11**[b]	**12**[b]
		^{1}H NMR		
$H_{2(7)}$	7.49 (d, J = 12.8 Hz)	4.66 (d, J = 11.8 Hz)	6.80	3.88
$H_{3(6)}$	7.76 (d, J = 12.8 Hz)	6.09 (d, J = 11.8 Hz)	7.20	4.58
$H_{8(10)}$	3.09 (t, J = 7.6 Hz)	2.94, 3.32 m		
H_9	2.03 (quin, J = 7.6 Hz)	2.05 m		
BCH_3	0.98	0.94		
		^{11}B NMR		
	53.6	49.2	54.6	29.7
		^{13}C NMR		
$C_{2(7)}$	148.5 (br)	100.7 (br)	135.9	91.3
$C_{3(6)}$	145.3	112.0	156.7	112.8
$C_{4(5)}$	147.6	117.2		
$C_{8(10)}$	39.7	38.5		
C_9	23.5	23.8		
BCH_3	11.0 (br)	6.4 (br)		

[a] The NMR spectra were obtained by using a Bruker AM-300 or WH-360 spectrometer. The spectra were measured from dilute $CDCl_3$ solutions with Me_4Si as an internal reference for ^{1}H and ^{13}C NMR spectra while external BF_3–OEt_2 was used to calibrate the ^{11}B NMR spectra. [b] Reference 20.

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

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



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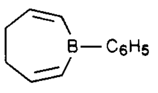
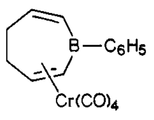


11



12

The ^{13}C NMR spectra of vinyl boranes such as **11** usually show that the β-carbons are highly deshielded, while the α-carbons are not.[17,18] It is assumed that there is substantial electron donation from the β-carbon to boron. The ^{13}C NMR spectrum of borepin **5** is unusual in that both the α- and β-positions are almost equivalently deshielded, which suggests electron donation from both positions. On the other hand, the ^{11}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**.[17,19]

Many aromatic rings can serve as 6π 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-cyclopentenoborepin) chromium (**10**) as yellow crystals, mp 56–60 °C. The ^{1}H, ^{13}C, and ^{11}B NMR chemical shifts are summarized in Table I. The signals for $C_{2(7)}$, $C_{3(6)}$, and $C_{4(5)}$ show substantial upfield shifts in comparison to the corresponding signals for **5**, indicating that the six ring carbon atoms are π-coordinated to Cr. A similar shift is shown in the ^{1}H NMR spectra for the $H_{2(7)}$ and $H_{3(6)}$ signals. However, the ^{11}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}B shifts on complexation.[20,21] Thus the NMR data suggest that borepin serves as a η^6 rather than a η^7 ligand.

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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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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)[1] is catalyzed by Cu atoms,[2] a complete understanding of the role of the metal atoms in this process is still lacking.[3] Cu has unique

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