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Reorientation of Adsorbed Cyanogen on Cu(111) by Oxygen Preadsorption, As Probed by Using High-Resolution EELS: Comparison with Electrosorbed Cyanide

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We report results that indicate that monocyanogen (CN), adsorbed on Cu(111) in an ultrahigh vacuum (uhv) environment with the molecular axis parallel to the surface, is reoriented to terminally bonded CN, characteristic of CN$^-$ binding in electrochemical and bulk-phase systems, in the presence of preadsorbed atomic oxygen.

Detailed information on adsorbate orientation as well as molecular structure can be furnished by high-resolution electron energy-loss spectroscopy (HREELS). We have shown that CN as well as HCN and a variety of nitriles adsorb on Pd(111), Pd(100), and Cu(111) with the CN group oriented "parallel" to the surface.[2] This intriguing behavior stands in sharp contrast to the vibrational spectra of cyanide and nitriles at metal-solution interfaces obtained by using infrared and/or surface-enhanced Raman methods.[3] Thus, several studies of CN$^-$ on gold, silver, and copper electrodes report intense C-N stretching bands with frequencies significantly higher than those for uncoordinated CN$^-$ (2080 cm^{-1}).[3] This is consistent with σ bonding via the carbon atom by analogy with similar observations for bulk-phase cyano coordination.[4] Similar behavior is also observed for benzonitrile adsorption at gold, silver, and copper electrodes, implying end-on nitrile coordination.[5] Consequently, it is of interest to delineate the physical and/or chemical modifications to the molecularly simple metal-uhv interface that can induce a transformation from the "side-on" bonding geometry to the more usual "end-on" orientation.

Figure 1a,b shows a typical HREELS spectrum of CN resulting from 100 langmuirs of NCC exposure (langmuir = 1 × 10^{-6} torr s), dissociatively adsorbed on Cu(111) at 300 K. Details of the HREELS instrument and the experimental arrangement are given elsewhere.[2,7] Only two vibrational bands are observed, an intense loss at 195 cm^{-1} and a much weaker feature at 2045 cm^{-1}. These are similar to corresponding peaks observed around 280 and 1980 cm^{-1} for CN on Pd(111) and Pd(100)[2a-c] and are assigned to metal-CN and C-N stretching (ν_{CN}) modes, respectively.

Markedly different cyano HREELS features are observed, however, if the Cu(111) surface is predosed with oxygen. Spectrum c results from a 60-langmuir dosage of O_2 on Cu(111) at 300 K. The oxygen coverage is around 0.1 under these conditions. The weak band at 238 cm^{-1} has been identified as a surface-oxygen vibration, involving a dissociated (atomic) oxygen layer.[8] Spectrum d (magnified further in e) results from dosing subsequently with 20 langmuirs of NCCN at 300 K. The ν_{CN} band now occurs at a substantially higher frequency, ca. 2140 cm^{-1}, and is considerably more intense than that obtained in the absence of adsorbed oxygen (compare b and e). The low-frequency peak is now much weaker and is obscured by the surface-oxygen mode. Exposing the surface to oxygen *after* preadsorbing cyanogen had essentially no effect on the HREEL spectra.

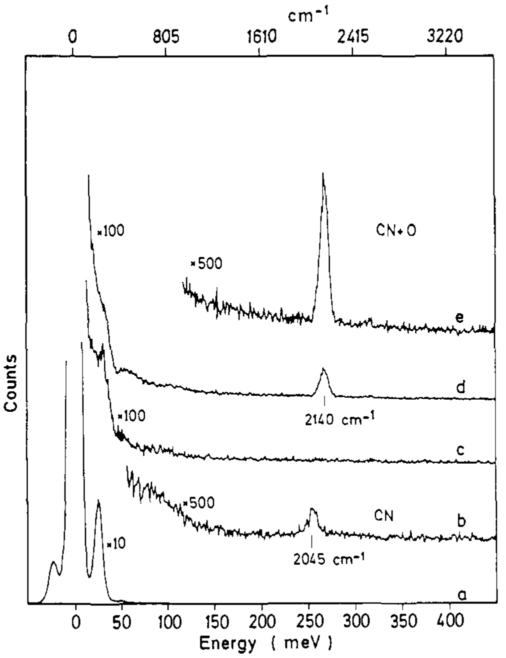

Figure 1. HREELS on CN on Cu(111); primary electron energy 1.5 eV, $\theta = 55°$. Scaling factors given for each spectrum are magnifications relative to the elastic peak intensity. Key to surface-dosing conditions: (a) and (b), 100 langmuirs of NCCN dosed at 300 K; (c), 60 langmuirs of oxygen at 300 K; (d) and (e), 20 langmuirs of NCCN, dosed after oxygen adsorption as in (c). Note that spectra b and e have the same magnification.

This substantial (ca. 100 cm^{-1}) upshift in the ν_{CN} frequency upon oxygen preadsorption is indicative of metal coordination via the carbon atom,[4] therefore involving a vertical (or at least tilted) surface orientation. Also consistent with this interpretation is the markedly greater ν_{CN} intensity, since such a configuration will involve a larger dynamic dipole moment normal to the surface than for the parallel orientation. Indeed, in contrast to the 2045-cm^{-1} feature, the 2140-cm^{-1} loss exhibits a marked intensity-angular dependence, verifying the occurrence of a surface dipole scattering mechanism consistent with a vertical or tilted adsorbate orientation.

It has been speculated that cyanate (NCO) is formed from coadsorbed O and CN on Cu(111) under conditions similar to those considered here.[9b] However, the HREELS data render this possibility very unlikely. Thus NCO should yield a C-O stretch around 1300-1350 cm^{-1},[10] which is entirely absent here (spectra d and e); also surface- as well as bulk-coordinated NCO$^-$ yields ν_{CN} frequencies, $\gtrsim$2190 cm^{-1}, that are higher than those observed here.[10,11] (Incidentally, contamination by carbon monoxide is absent in the experiments reported here; CO does not adsorb on copper at room temperature.)[12]

We also conducted experiments aimed at inducing the coadsorption of CN and water on Cu(111) in an attempt to provide a closer analogy to electrochemical systems. One difficulty, however, is that water adsorption on Cu(111) occurs only below 175 K,[13] which is close to the threshold temperature required for

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(2) (a) Kordesch, M. E.; Stenzel, W.; Conrad, H. *J. Electron Spectrosc. Relat. Phenom.* **1986**, *39*, 89. (b) Kordesch, M. E.; Stenzel, W.; Conrad, H. *Surf. Sci.* **1986**, *175*, L689. (c) Kordesch, M. E.; Stenzel, W.; Conrad, H. submitted for publication in *Surf. Sci.* (d) Kordesch, M. E.; Stenzel, W.; Conrad, H.; Weaver, M. J., manuscript in preparation.

(3) For example: (a) Kunimatsu, K.; Seki, H.; Golden, W. G.; Gordon, J. G., II; Philpott, M. R. *Surf. Sci.* **1985**, *158*, 596. (b) Benner, R. E.; von Raben, K. U.; Dornhaus, R.; Chang, R. K.; Laube, B. L.; Otto, F. A. *Surf. Sci.* **1981**, *102*, 7. (c) Corrigan, D. S.; Gao, P.; Leung, L.-W. H.; Weaver, M. J. *Langmuir* **1986**, *2*, 744.

(4) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978; p 259.

(5) (a) Gao, P.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 5040. (b) Leung, L.-W. H.; Gosztola, D.; Weaver, M. J. *Langmuir*, in press. (c) Bewick, A.; Pons, S. *Adv. Infrared Raman Spectrosc.* **1985**, *12*, Chapter 1.

(6) (a) Avery, N. R.; Matheson, T. W.; Sexton, B. A. *Appl. Surf. Sci.* **1985**, *22/23*, 384. (b) Avery, N. R.; Matheson, T. W. *Surf. Sci.* **1984**, *143*, 110. (c) Sexton, B. A.; Avery, N. R. *Surf. Sci.* **1983**, *129*, 21.

(7) Unwin, R.; Stenzel, W.; Garbout, A.; Conrad, H.; Hoffman, F. *Rev. Sci. Instrum.* **1984**, *55*, 1809.

(8) Dubois, L. H. *Surf. Sci.* **1982**, *119*, 399.

(9) (a) Habraken, F. H. P. M.; Kieffer, E. Ph.; Bootsma, G. A. *Surf. Sci.* **1979**, *83*, 45. (b) Solymosi, F.; Kiss, J. *Surf. Sci.* **1981**, *108*, 368.

(10) For example: Norbury, A. H.; Linha, A. I. P. *J. Chem. Soc. A* **1968**, 1598.

(11) Corrigan, D. S.; Weaver, M. J. *J. Phys. Chem.* **1986**, *90*, 5300.

(12) Kessler, J.; Thieme, F. *Surf. Sci.* **1977**, *67*, 405.

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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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(13) For example: Sass, J. K.; Bange, K.; Dohl, R.; Piltz, E.; Unwin, R. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 354.

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

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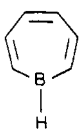
The seven-membered unsaturated heterocycle borepin (**1**) is of substantial theoretical interest. To the extent that its sp^2-hybridized boron atom is able to accept π-electron density from carbon, borepin is the neutral boron analogue of tropylium **2**.[2,3]



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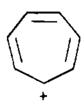

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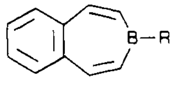

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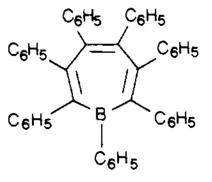
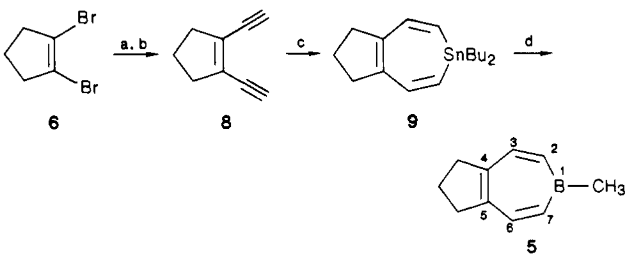


4

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.

(2) Vol'pin, M. E. *Russ. Chem. Rev.* (*Engl. Transl.*) **1960**, *29*, 129.

(3) van der Kerk, S. M. *J. Organomet. Chem.* **1981**, *215*, 315.

(4) Schulman, J. M.; Disch, R. L.; Sabio, M. L. *J. Am. Chem. Soc.* **1982**, *104*, 3785; **1984**, *106*, 7696; *Tetrahedron Lett.* **1983**, *24*, 1863. Allinger, N. L.; Siefert, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 752.

(5) (a) Leusink, A. J.; Drenth, W.; Noltes, J. G.; van der Kerk, G. J. M. *Tetrahedron Lett.* **1967**, 1263. (b) Axelrad, G.; Halpern, D. *J. Chem. Soc. D* **1971**, 291.

(6) Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 4436.

(7) van Tamelen, E. E.; Brieger, G.; Untch, K. G. *Tetrahedron Lett.* **1960**, *8*, 14.

(8) Jeffries, A. T., III; Gronowitz, S. *Chem. Scr.* **1973**, *4*, 183.

(9) (a) A preparation of 1-methylborepin has been claimed, although proper characterization is lacking. See: van der Kerk, S. M.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1981**, *215*, 303. (b) 1-Hydroxy-4,5-cyclohexenoborepin has been reported in a thesis. Limited data are available. See: Halpern, D. F. Ph.D. Thesis, CUNY 1971.

(10) Leusink, A. J.; Noltes, J. G.; Budding, H. A.; van der Kerk, G. J. M. *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 1036.

(11) Wittig, G.; Pohlke, R. *Chem. Ber.* **1961**, *94*, 3276. Favorsky, A.; Chestakowskij, M. F. *Bull. Soc. Chim. Fr.* **1936**, *3*, 1732.

(12) All new compounds gave satisfactory analytical and/or spectral data. **7**: ^1H 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**: ^1H 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**: ^1H 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^+).

(13) Märkl, G.; Baier, H.; Liebl, R. *Synthesis* **1977**, 842.

0002-7863/87/1509-1879$01.50/0 © 1987 American Chemical Society