In summary, these results provide the first direct observation in the reaction between a metallocene dialkyl and methylalumoxane of a "cation-like" $Cp_2ZrCH_3^+$ species, the entirety of which undergoes facile ethylene insertion. These results also argue that the Al:Zr stoichiometry required for complete **1** → **2** conversion is considerably lower than employed in typical catalytic reactions.[1-3]

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Registry No. 1, 115942-68-2; ethylene, 74-85-1.

The Electron Momentum Density in the Highest Energy Occupied Molecular Orbital of Borazine, $B_3N_3H_6$: Evidence for Localization

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Borazine, $B_3N_3H_6$, is often called an "inorganic benzene" implying it to be a highly conjugated molecule; however, the actual extent of borazine aromaticity remains an open issue.[1-4] Two of the outer occupied orbitals of borazine, $1a_2''$ and $1e''$, correlate with the two occupied π orbitals of benzene. Molecular orbital calculations indicate that the electron density associated with these orbitals is delocalized over the nitrogen and, to a lesser extent, the boron atoms.[3] On the other hand, calculations using spin-coupled valence bond theory to introduce electron correlation have indicated that correlated π-electrons are better described in terms of semilocalized orbitals. An experimental test to discriminate between the delocalized Hartree–Fock and a more localized correlated description would be desireable.

To analyze the $1e''$ HOMO of borazine we have used (e,2e) spectroscopy.[5-7] This technique involves the impulsive ejection of an electron from a molecule by electron impact with simultaneous determination of the energies and momenta of the ejected and scattered electrons. Energy and momentum conservation give the binding energy and momentum of the ejected electron at the instant of impact. When a sufficient number of (e,2e) events have been accumulated, the cross section for the ionization process as a function of the momentum of the ejected electron can be determined. Within the plane-wave impulse approximation, this cross section is proportional to the spherically averaged orbital electron momentum overlap density (OVD) between the neutral target and the residual cation. The OVD is in turn similar to, but not identical to, the momentum density (MD) of the canonical molecular orbital (CMO) from which the electron has been ejected.

Table I. Vertical Binding Energies (eV) of the Three Highest Valence MOs of Borazine

orbital	exptl BE,[a] eV	previous work[b] $-\epsilon_i$	previous work[b] ΔE_{UHF}[c]	present work $-\epsilon_i$	present work $\Delta E_{HF\text{-}CI}$[d]
$1e''(\pi)$	10.1	11.3	9.4	11.3	10.4
$6e'(\sigma)$	11.4	12.4	11.4	12.8	11.9
$1a_2''(\pi)$	12.8	14.1	13.0	14.2	13.2

[a] Reference 8. [b] Reference 9. [c] ΔE_{UHF} is the difference in total energy at the UHF level between neutral molecule and cation. [d] $\Delta E_{HF\text{-}CI}$ is the difference in total energy at the HF-CI level between neutral molecule and cation.

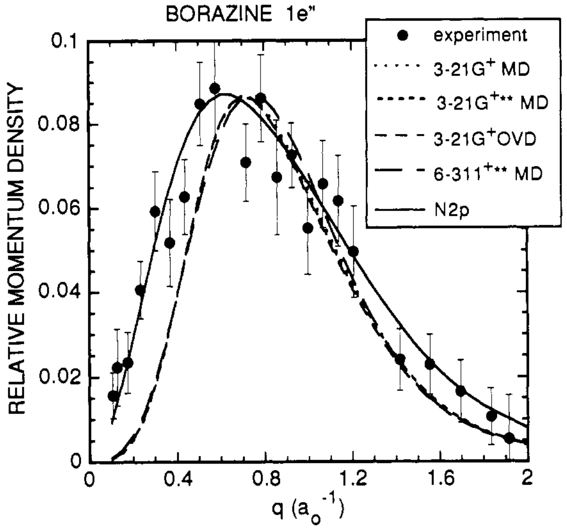

Figure 1. Experimental (e,2e) cross sections and calculated canonical molecular orbital momentum densities (MD) and neutral–cation overlap densities (OVD) for the HOMO of borazine.

We focus only on the outermost MO with a binding energy of 10.1 eV. Although first identified as a σ orbital,[8] later calculations showed conclusively that it is the $1e''$ π orbital.[9] Our calculations confirm this result. The (e,2e) apparatus, with a resolution of 1.4 eV, cannot resolve the features observed in the photoelectron spectrum at 10.1, 11.4, and 12.8 eV that are identified with the three highest orbitals of borazine: the $1e''$ π orbital, the $6e'$ of σ character, and the $1a_2''$ π orbital, respectively (see ref 9 and our Table I). The three features merge into one broad peak in the (e,2e) binding energy spectrum; however, setting the instrument at 9.8 eV can separate the intensity associated with the 10.1-eV feature from the others. The measured (e,2e) cross section is shown in Figure 1. The measurement was initially compared to a calculated MD for the $1e''$ CMO represented by a 3-21G^{+**} basis set. As shown in the Figure 1, the calculated density is significantly more narrow (smaller full width at half maximum) than the experimental measurement. To interpret this difference it is important to understand the relation between position space and momentum space representations. The momentum density is the square modulus of the momentum space wave function, which in turn is the Fourier transform of the position space wave function. The Fourier transformation of a function gives a function that bears an inverse relation to the original function. In other words, Fourier transformation of a compact function yields a diffuse function while transformation of a diffuse function gives a compact function. This leads to the initial conclusion that the $1e''$ electron density is significantly more compact in position space than predicted by the CMO calculation. To confirm this, a number of alternative explanations must be considered. These

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include: (1) inadequacy in the basis set, (2) a significant difference between the OVD and the MD, (3) instrumental broadening of the experimental density, (4) contamination of the 1e″ density by the 6e′, and (5) the effect of geometric distortion on the momentum density.

In order to test the importance of these possibilities, we have carried out calculations of the 1e″ MD using 3-21G$^+$, 3-21G^{+**}, and 6-311^{+**} bases. The OVD was then explicitly calculated from CI wave functions using a 3-21G$^+$ basis. In order to compare our calculations with observations, the effect of finite angular and energy resolution of the instrument has been simulated using the convolution procedure devised by Bawagan.[10] The momentum scale for the experimental results was adjusted accordingly, and the effects of resolution on the transmission function of the instrument was accounted for by a calibration against argon as explained previously.[11] Initially a geometry optimization was performed on borazine at the SCF 3-21G** level in D_{3h} symmetry using the program GAMESS,[12] obtaining B–N, B–H, and N–H bond distances of 1.429, 1.198, and 0.998 Å, respectively, and a B–N–B angle of 122.3°. These values are in good agreement with electron diffraction results[13] (R(B–N) = 1.435 Å, ∠B–N–B = 122.5°) and with previous calculations.[2] We then added diffuse s- and p-functions on B and N so as to better represent the low-momentum components[14] which are underestimated by split-valence bases.[15] As mentioned above, the momentum density obtained for the 1e″ HOMO of $B_3N_3H_6$ with this 3-21G^{+**} basis set is clearly more localized in momentum space than the experimental result, although its maximum is at about the same position.

We next calculated CI wave functions for neutral $B_3N_3H_6$ and its various cations and used them to evaluate binding energies and OVDs using the program MELD.[16] Due to computer limitations we were forced to employ for the CI calculations only a 3-21G$^+$ basis (e.g., diffuse s- and p-functions, but no polarization functions); however, the spin-coupled calculations,[4] going beyond the SCF model, have yielded similar descriptions of correlation effects using both double-ζ and polarized-triple-ζ bases, so our 3-21G$^+$ basis set should still recover an important fraction of the correlation effects. The 3-21G$^+$ canonical MO is almost indistinguishable from the 3-21G^{+**} result, indicating that polarization functions have little effect upon the momentum densities at the Hartree–Fock level. Freezing the six B1s and N1s core orbitals employing 29 virtual orbitals in the CI and using C_{2v} symmetry, we obtained the binding energies shown in Table I. These are comparable to experimental binding energies[8] as well as those from previous SCF calculations.[9] The calculated molecule–cation OVD for the lowest energy $(1e'')^{-1}$ cation is also shown in Figure 1. Although its amplitude at small momentum is increased somewhat compared to that of the 1e″ CMO, its overall agreement with the experimental result is only slightly improved.

Contributions from the 6e′ orbital, with an experimental binding energy of 11.4 eV, cannot explain the discrepancy between measurement and calculation since our energy resolution is sufficient to all but exclude the contributions from this orbital. In any event, the 6e′ orbital has too little amplitude at momentum values above 1.0 a_0^{-1} to explain the observed amplitude in the high-momentum region.

Calculations indicate that the $(1e'')^{-1}$ cation in $B_3N_3H_6$ shows an appreciable Jahn–Teller distortion.[17] We have previously seen Jahn–Teller effects in the momentum densities of cyclopropane and have analyzed them by considering distortions of the cations;[18] however, using equilibrium geometries for the borazine cations calculated at the SCF 3-21G level (which are almost identical to those previously reported[17]), we find a MD for either component of the 1e″ MO almost identical to that in the neutral molecule. Our CI calculations are certainly limited in scope because of our small basis set and our truncation of the virtual orbital space, but they do yield accurate binding energies (Table I) and give an energy lowering using K orbital virtuals[19] of 0.3175 hartrees compared to the SCF result (almost 10 times larger than that from a full-valence VB calculation[4]). Thus, at least on energetic grounds, the CI calculations are of reasonable accuracy.

Finally, it is worth noting that previous (e,2e) studies of benzene[20] and *p*-dichlorobenzene[21] also showed experimental cross sections systematically broader than those calculated at the double-ζ SCF level. Inclusion of diffuse functions would be expected to move momentum density to lower values of momentum rather than making the distribution of density broader.

We are led to the conclusion that the borazine 1e″ ionization is much more localized in character than theory predicts. To emphasize this conclusion we show in Figure 1 the momentum density calculated at the SCF 3-21G^{+**} level for the N2p electron in ^{4}S atomic nitrogen. The experimental cross-section for the 1e″ orbital resembles that of an isolated N2p orbital more than a (N2p,B2p)-π CMO. Such localization may be present in either the neutral molecule or the cation, or both. Broken-symmetry Hartree–Fock and CI calculations may be needed to describe it correctly.[22]

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2D ^{13}C-Coupled HMQC–ROESY: A Probe for NOEs between Equivalent Protons

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There have been an increased number of naturally occurring C_2 symmetric molecules showing biological activities.[3] In the structure determination of such symmetric molecules, some difficulties due to the presence of two equivalent units in a molecule may arise. We have demonstrated methods for the detection of the chemical connectivity between equivalent carbons of a C_2 molecule, hopeaphenol (**1**),[4] from an isotopomeric point of view.[5]

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