tained from **1** and $\{(\eta^5\text{-}C_5H_5)Ru(CO)_2\}_2$ and from $\{Cp_2{}^*HfN_2\}_2N_2$[35] and **2a**. We are presently further investigating the generality of this process and the chemistry of the diylidene moiety.

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Registry No. 1, 54387-50-7; **2a**, 12154-95-9; **2b**, 32028-30-1; **3a**, 82482-56-2; **3b**, 82482-57-3; *cis*-$Cp_2{}^*\overline{ZrOCHMeCHMeO}$, 82482-58-4; *trans*-$Cp_2{}^*\overline{ZrOCHMeCHMeO}$, 82534-93-8; Fe, 7439-89-6.

Supplementary Material Available: Listings of fractional coordinates and thermal parameters, bond distances and angles, and structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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[35] Prepared by reduction of $Cp_2{}^*HfI_2$ with Na–K alloy in DME at –40 °C under 1 atm of nitrogen: Seidler, P.; Hillhouse, G., to be submitted for publication.

Structure of the NO Dimer

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The structure of the NO dimer in the gas phase was determined from measurements of rotational transition frequencies for $^{14}NO–^{14}NO$, $^{15}NO–^{15}NO$, and $^{14}NO–^{15}NO$. Microwave transition frequencies were measured by using the Flygare–Balle spectrometer.[1,2] The measurement of rotational transition frequencies for different isotopic combinations allowed an unambiguous determination of the NNO angle (θ) of 99.6(4)°. The NN bond length is 2.237 (2) Å, and the NO bond length is 1.161 (6) Å. This is the structure for the $v = 0$ vibrational state.

The NO dimer is weakly bound in the gas phase with a binding energy of about 4 kcal. The structure of the dimer in a crystal lattice was studied some time ago.[3,4] The solid-phase data were interpreted[4] as due to a planar cis structure with an NNO angle of 101° and an NN bond of 2.18 Å. The existence of a cis structure as well as other conformations for $(NO)_2$ were indicated by matrix isolation studies.[5] The NO dimer was observed in the gas phase by molecular beam spectroscopy,[6,7] and rotational constants for one isotopic species were obtained. The cis planar structure was confirmed, but since only two independent moments of inertia were obtained, the structure could not be unambiguously determined. Their data were consistent with an NNO angle of 85 (5) or 95 (5)°.

In the present work the $2_{12} \rightarrow 3_{03}$ transitions were measured for $^{14}NO–^{14}NO$ and $^{15}NO–^{15}NO$, and the $1_{01} \rightarrow 1_{10}$ transitions were measured for $^{14}NO–^{15}NO$ and $^{15}NO–^{15}NO$. The measured frequencies are listed in Table I. The four available transition frequencies for the most common isotopic form, used to determine the rotational constants for $^{14}NO–^{14}NO$, are $A = 25829.71$, $B = 5614.542$, $C = 4605.671$, and the distortion constant $D_J = 0.029$ MHz. Of the three possible symmetric top basis distortion constants, the data set is most sensitive to D_J. Rather few rotational transitions for this complex are available in the normal microwave range since $(NO)_2$ has a *b*-axis dipole moment and the rotational constants are fairly large.

Table I. Transition Frequencies for the NO Dimer (MHz)

	$^{14}NO–^{14}NO$	$^{15}NO–^{15}NO$	$^{14}NO–^{15}NO$
$1_{01} \rightarrow 1_{10}$	21 224.041[a]	20 444.831 (10)	20 827.68 (3)
$1_{11} \rightarrow 2_{02}$	187.501[a]		
$2_{02} \rightarrow 2_{11}$	22 269.738[a]		
$2_{12} \rightarrow 3_{03}$	11 267.403 (10)	11 159.303 (3)	

[a] Calculated from data in ref 7.

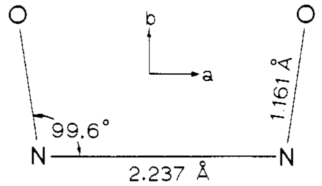

Figure 1. Structure of the NO dimer.

The inertial defect is $\Delta = 0.151$ amu Å^2, and this indicates a planar structure. Although the inertial defect is small, it complicates the structure determination somewhat so structures were determined by using each of the three possible pairs of rotational constants. In order to obtain rotation constants for $^{15}NO–^{15}NO$, it was assumed that D_J and Δ would be the same as observed for $^{14}NO–^{14}NO$. Using the observed transition frequencies, we obtained the rotational constants for $^{15}NO–^{15}NO$ of $A = 24919.63$, $B = 5463.130$, and $C = 4474.797$ MHz.

The dimers were formed by expanding a 5% mixture of NO in argon at 1 atm pressure through an 0.8-mm nozzle into the Fabry–Perot microwave cavity. The beam and microwave signal were pulsed and superheterodyne detection was used.

The N–N bond length was obtained directly from the difference in *B* rotational constants for $^{14}NO–^{14}NO$ and $^{15}NO–^{15}NO$ as with the Kraitchman method.[8] The value of the N–N bond length is 2.237 (2) Å and includes error estimates for rotational distortion and vibration effects. The *b*-axis component of the N–O separation was obtained from the *A* rotational constants. The *a*-axis component of the NO bond length was found by fixing the N–N bond length and adjusting the structure to fit the rotational constants. These components were used to obtain the N–O bond length and NNO angle. Using *A* and *B*, we find 1.1609 Å and 99.59°. Using *A* and *C* gives 1.1612 Å and 99.68°, and for *B* and *C* we have 1.1652 Å and 99.55°. The most consistent results were obtained by using the *A* and *B* or *A* and *C* rotational constants. Favoring the *A,B* and *A,C* results, we have an N–O bond length of 1.161 (6) Å and NNO angle $\theta = 99.6(4)$°. The structure is shown in Figure 1. Hyperfine structure was observed on all transitions, but this will be discussed in a later publication. So that the structure could be confirmed, rotational constants were calculated for the $^{15}NO–^{14}NO$ $1_{01} \rightarrow 1_{10}$ transition. The calculated frequency was 20824.5 MHz, in good agreement with the observed frequency of 20827.68 MHz.

The observed N–N bond length of 2.236 Å is much longer than calculated values[9,10] of 1.77 and 1.62 Å. The N–O bond length of 1.161 Å is only slightly longer than the NO free-molecule bond length of 1.154 Å. The measured NNO angle $\theta = 99.6$° is reasonably close to calculated values[9,10] of 106 and 112°. A

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somewhat larger SSO angle of 112.7° was observed[11] for the SO dimer.

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Registry No. Nitric oxide dimer, 16824-89-8.

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Atom Connectivities in Polyhedral Boranes Elucidated via Two-Dimensional *J*-Correlated ^{11}B–^{11}B FT NMR: A General Method

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The application of ^{11}B nuclear magnetic resonance spectroscopy to molecular structure determination in boron clusters is limited in practice by two inherent problems: signal broadness (10–100 Hz), which frequently causes peak overlap and masks coupling information, and the scarcity of general, reliable correlations between chemical shift and structure. The first of these difficulties is mitigated in strong magnetic fields, which resolve resonances sufficiently to eliminate much of the overlap. The advent of two-dimensional (2-D) NMR spectroscopy during the past 6 years has provided a powerful new approach for eliciting structural information from NMR spectra. Although a variety of 2-D techniques has been applied primarily to ^{1}H, ^{13}C, and ^{31}P nuclei,[1] our group has reported the use of heteronuclear 2-D NMR of spin-coupled ^{11}B–^{1}H systems[2] wherein resonances that are overlapped in the ordinary (1-D) ^{11}B or ^{1}H spectrum are effectively resolved in the 2-D experiment.

We now report the utilization of a *homonuclear* ^{11}B–^{11}B 2-D NMR procedure to reveal spin–spin coupling (and hence direct bonding) interactions in borane frameworks and its successful application to a wide variety of borane and heteroborane species. This extension of the Jeener 2-D NMR experiment[3] to ^{11}B systems is, to our knowledge, the first demonstration of homonuclear *J*-correlated 2-D FT NMR of a quadrupolar nucleus and holds promise of developing into a routine structural tool.

The theory underlying this procedure has been presented elsewhere,[4] and the experimental details *for spin-$^1/_2$ systems* have been described.[5] In our work, results are given via three-dimensional plots in which the x and y coordinates are ^{11}B chemical shift (at 115.8 MHz) in ppm relative to $BF_3{\cdot}O(C_2H_5)_2$ (positive shifts to low field) and the z direction, normal to the page, is peak intensity. Figure 1 presents two examples that are typical of the ~30 compounds studied thus far. In each spectrum, the peaks on the diagonal ($F_1 = F_2$) correspond to the normal one-dimensional ^{11}B FT NMR spectrum; these peaks represent resonances whose precession frequencies are unchanged by the mixing pulse. The off-diagonal or cross peaks, located at δ_A, δ_B (and equivalently at δ_B, δ_A, so that each spectrum exhibits mirror symmetry relative to the diagonal) are a consequence of spin–spin coupling between $^{11}B_A$ and $^{11}B_B$. Since such coupling is significant only for adjacent nuclei, this information relates directly to the boron–boron connectivity in the framework.

In the spectrum of the small carborane 2,3-$(C_2H_5)_2C_2B_4H_6$ (Figure 1a), the cross peaks P and Q indicate coupling between the apex boron, B(1), and the basal boron nuclei B(4, 6) and B(5), respectively. Peak R arises from an impurity in the sample; the absence of any cross peaks involving R illustrates the value of this technique in analyzing mixtures.[6,7]

A significant feature in Figure 1a is the *absence* of a cross peak between the basal boron resonances B(4, 6) and B(5). We have noted, in general, that *coupling is absent between boron atoms in B–H–B bridge bonds*; this observation is consistent with molecular orbital calculations on boranes such as B_2H_6, B_5H_9, and $B_{10}H_{14}$ which indicate that the electron density in B–H–B bridges is centered on hydrogen and is negligible along the B–B vector.[8] In contrast, the 2-D ^{11}B–^{11}B spectrum of the 2,3-$(C_2H_5)_2C_2B_4H_5^-$ anion, obtained by bridge deprotonation of the neutral carborane, *does* contain a B(4, 6)–B(5) cross peak, as expected since these nuclei are directly bonded when the bridging proton between them is removed.

Figure 1b presents the spectrum of the cobaltaborane 6-$[C_5(CH_3)_5]CoB_9H_{13}$, which contains six boron environments in a 2:2:2:1:1:1 ratio. The cross peaks establish B–B connectivities and permit the assignment of the six resonances to specific framework borons (again the absence of coupling between the hydrogen-bridged atoms B(9) and B(8, 10) is notable). The unique topology revealed by these data is entirely consistent with the structure established by X-ray crystallography.[9]

The success of this technique rests on the clear detection of scalar ^{11}B–^{11}B coupling, whose significance as a contributor to line width was demonstrated earlier in our laboratory.[10] Although $J_{^{11}B-^{11}B}$ is small relative to the resonance line width and is not normally resolved (usually, $2\pi JT_1 < 1$, and the nuclei are partially decoupled), it is nevertheless sufficient to generate significant cross peaks in the 2-D experiment. Such peaks result from a magnetization transfer process that is more efficient than the J modulation of the free induction decay by the scalar coupling. This phenomenon has been quantitatively analyzed for $I = {}^1/_2$ systems.[5a]

The power of 2-D ^{11}B–^{11}B *J*-correlated FT NMR spectroscopy in structure elucidation is twofold: in a relatively fast experiment, it can reveal the coordination of each boron nucleus with respect to its boron neighbors, and it provides unambiguous assignments of ^{11}B resonances without resort to isotopic labeling or extensive decoupling experiments. In addition the method can be utilized to study mixtures, as noted above, as well as reactive species. Moreover, extension of this approach to other quadrupolar nuclei may be feasible.

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(5) (a) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *44*, 542. (b) The pulse sequence $(\pi/2)_x$–t_1–$(\pi/2)_\phi$–t_2 (acquisition) where $\phi = +x, +y, -x, -y$ is used to generate the t_1, t_2 data matrix in which t_1 is incremented by the inverse of the sweep width of the F_1 dimension and t_2 has the same meaning as the acquisition time in a normal (1-D) experiment. The phase shifting of the second transmitter pulse relative to the receiver has the dual purpose of eliminating axial peaks and permitting the use of quadrature detection in both dimensions. Samples were run unlocked in a stable magnetic field (8.5 T) with a ^{11}B resonance frequency of 115.8 MHz. Uninterrupted, incoherent ^{1}H decoupling at low levels was employed. The carborane sample was neat, and the t_1, t_2 matrix of 128 × 256 data points required less than 5 min for accumulation. The cobaltaborane sample (0.29 mmol, 74 mM) involved a 1-h accumulation time in which 400 transients were collected for each of the 128 t_1 values. Spectra were obtained on a Nicolet Magnetics Corp. NT-360/Oxford spectrometer, and all data manipulation utilized standard Nicolet software with a 1280/293B data system. Workup of the data including contour plots required 20–30 min.

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