Correlation of Thallium–Boron Nuclear Spin States by Two-dimensional N.M.R. Spectroscopy: Magnitudes and Relative Signs of Couplings $^nJ(^{205}Tl–^{11}B)$† in the *nido*-Thallaundecaborane Anion $[Me_2TlB_{10}H_{12}]^-$

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2D COSY $^{11}B–^{11}B$ n.m.r. spectroscopy on *nido*-$[Me_2TlB_{10}H_{12}]^-$ correlates individual ^{11}B doublet components that are associated with particular ^{205}Tl spin-states; this permits the determination of the magnitudes and relative signs of various intracluster coupling constants $^nJ(^{205}Tl–^{11}B)$ and hence yields bonding information.

The determination of both short- and long-range *endo* internuclear spin–spin coupling constants in polyhedral borane species is important in establishing empirical correlations as structural diagnostics, and for the development and assessment of cluster bonding theories. Study is however inhibited because these couplings are often small and hence obscured by ^{11}B-relaxation-induced broadening in the n.m.r. spectra of both ^{11}B and any other coupled nuclei involved.

We now report that the presence of the high-γ high-$\psi^2_s(0)$ high-abundance spin-$\frac{1}{2}$ nucleus ^{205}Tl in a metallaborane permits the observation of a variety of intracluster *endo* couplings, and that the relative signs of these are readily determined by ^{11}B homonuclear 2D COSY n.m.r. spectroscopy.

The ^{11}B n.m.r. spectrum, with $\{^1H(\text{broad-band noise})\}$ decoupling, of the eleven-vertex *nido*-7-metallaundecaborane anion $[Me_2TlB_{10}H_{12}]^-$ is shown in Figure 1. Boron resonances occur with six distinct chemical shifts, of which four are seen to be doublets arising from couplings $^nJ(^{205}Tl–^{11}B)$. Ambiguity in the overlapping region at $\delta(^{11}B)$ *ca.* −2 to −6 p.p.m. is resolvable by 'partially relaxed' spectroscopy using the π-delay-$\pi/2$ pulse sequence.[1,2] The lines are readily assigned (Table 1) by relative intensity, by similarity of shifts and relative linewidths to the parent substrate $B_{10}H_{14}$, and on the assumption that the larger couplings arise from atoms closer to the metal centre.[3] The assignments and resolution of the crowded region are established independently by ^{11}B 2D COSY n.m.r. spectroscopy[4] in which moderate to strong correlations occur between the resonances of all the chemically distinct adjacent sites apart from between B(2,3) and B(4,6), where only a weak off-diagonal response occurs, and between B(8,11) and B(9,10), where no off-diagonal response occurs (Figure 2). This last is expected, because hydrogen-bridged boron pairs in ten-boron *nido*-decaboranyl derivatives typically have small or effectively zero couplings $^1J(^{11}B–^{11}B)$.[5]

Because each component of a particular ^{11}B doublet corresponds to a particular ^{205}Tl spin-state, only one component of a particular doublet arising from ^{205}Tl splitting correlates with a particular component of another such doublet, so that only two off-diagonal correlations link a given pair of doublets. The sense of these two pairwise correlations gives the relative signs of the two couplings $^nJ(^{205}Tl–^{11}B)$. Thus in $[Me_2TlB_{10}H_{12}]^-$ it happens that all the interdoublet off-diagonal correlations occur either between high-frequency doublet components or between low-frequency doublet components, and there is no high-frequency/low-frequency component correlation for any pair of doublets. The relative signs of all the observed $^nJ(^{205}Tl–^{11}B)$ in $[Me_2TlB_{10}H_{12}]^-$ are therefore all the same, presumably positive.

The magnitudes of these couplings are also of interest, for two reasons. First, the couplings $^1J(^{205}Tl–^{11}B)$ and $^2J(^{205}Tl–^{11}B)$ are some one to two orders of magnitude smaller than commonly observed for $^1J(^{205}Tl–^{13}C)$ in typical organothal-

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† Although ^{10}B and ^{203}Tl are present, the discussion is limited for brevity to ^{11}B and ^{205}Tl.

Table 1. Selected boron-11 n.m.r. parameters for a saturated solution of $[TlMe_2]^+[Me_2TlB_{10}H_{12}]^-$ in $(CD_3)_2CO$ at +21°C.

Assignment	$\delta(^{11}B)$/p.p.m.[a]	Relative intensity	$^nJ(^{205}Tl-^{11}B)$/Hz	n[b]	Approx. $T_1(^{11}B)$/ms
(8,11)	+8.2	2B	+173	1	2.9
(1)	+3.0	1B	+84	2	15.5
(2,3)	−3.1	2B	+258	1	9.7
(5)	−2.8	1B	<30	2	17.3
(9,10)	−4.7	2B	<30	2	9.0
(4,6)	−31.7	2B	+77	2	23.1

[a] Relative to Ξ 32 083 971 Hz (nominally $[BF_3(OEt_2)]$ in $CDCl_3$ solution). [b] Note that, in polyhedral chemistry, the superscript *n* in the descriptor ^nJ signifies the number of polyhedral edges on the shortest edge-path connecting the two nuclei in question, and in contrast to classical structures, does *not* generally imply a coupling pathway defined by *n* two-electron two-centre bonds.

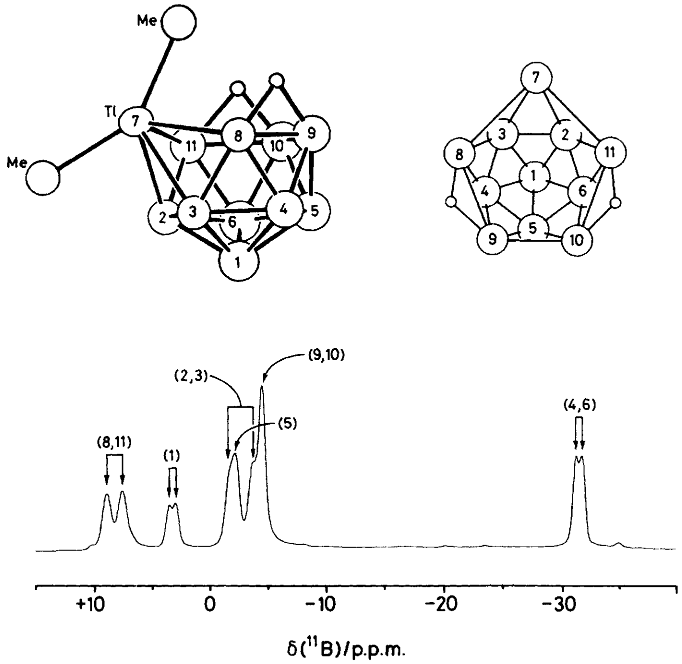

Figure 1. 128 MHz $^{11}B\{^1H$(broad-band noise)$\}$ n.m.r. spectrum of $[TlMe_2]^+[Me_2TlB_{10}H_{12}]^-$ in $(CD_3)_2CO$ solution at +21 °C, with (above left) a representation of the *nido*-thallaundecaborane cluster structure with *exo*-terminal H atoms omitted for clarity, and (above right) an alternative schematic view showing the mirror-plane symmetry of the anion.

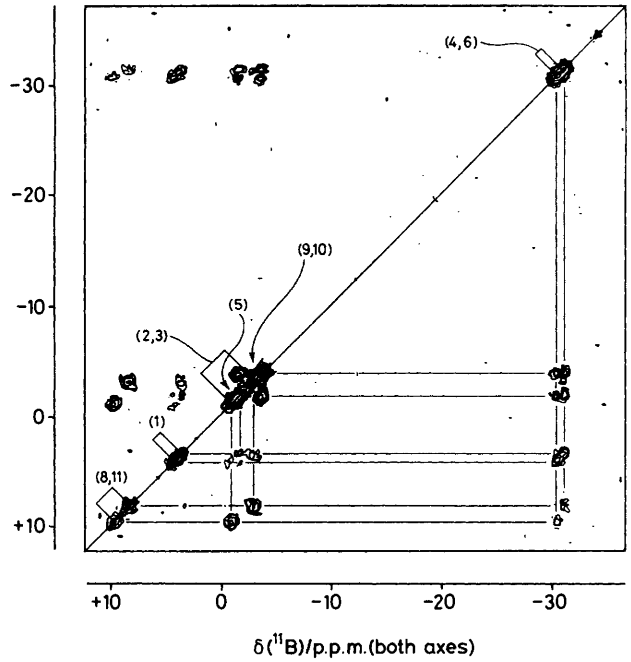

Figure 2. Symmetrized contour plot of a COSY-45 ^{11}B experiment performed on a $(CD_3)_2CO$ solution of $[TlMe_2]^+[Me_2TlB_{10}H_{12}]^-$ at 128 MHz with $\{^1H$(broad-band noise)$\}$ decoupling. The COSY-45 sequence was chosen to reduce intensity in the diagonal; a COSY-90 experiment will in this system exhibit the same selective correlations. 128 Time-domain points were used, and double sine-bell window functions. Total accumulation time was about 1 hour.

lium(III) species,[6] whereas the assumption of a Fermi-contact mechanism together with reasonable estimates of $\psi^2{}_s(0)$ for ^{13}C and ^{11}B would predict $^nJ(^{205}Tl-^{13}C)$ to be only one or two times as large for equivalent bonding. The low values in $[Me_2TlB_{10}H_{12}]^-$ presumably arise because bonding in the cluster σ-framework only has low boron 2s-character, the remainder being radially directed towards *exo*-bound atoms rather than tangentially to the *endo* cluster-bonding scheme. Second, all the observed *endo* couplings $^nJ(^{205}Tl-^{11}B)$ have a similar order of magnitude, whereas with classical non-cluster compounds ^1J(X–Y) are more typically at least an order of magnitude higher than ^2J(X–Y). The origins of this are also in the nature of the *endo*-polyhedral bonding. In an 'electron-deficient' cluster two adjacent atoms will generally be linked by delocalized multicentre σ-bonding rather than with a classical 2-electron 2-centre bond, and any coupling ^1J will therefore often be smaller than otherwise expected. Conversely, non-adjacent atoms may often be linked by 2-electron bonds *via* extended σ-type molecular orbitals, and longer range couplings ^nJ will be correspondingly larger.

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