

Tetrakis(t-butyl)tetraborane(4), Bu_t^4B_4 ; Synthesis of the First Peralkyl Derivative of a $2N$ Framework Electron Count Deltahedral Borane

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Summary The reaction of B_4Cl_4 with lithium alkyls results in the formation of alkylated and peralkylated derivatives of the tetraboron framework; the examples reported include EtB_4Cl_3 , $\text{Et}_2\text{B}_4\text{Cl}_2$, and Bu_t^4B_4 .

THE boron subhalides are a little-studied series of molecular cluster compounds that seem to violate the usual framework electron count–structural correlation, (Wade's Rules)¹. Where known, the structures are deltahedral rather than the capped deltahedra predicted for $2N$ framework electrons in a polyhedron of N vertices.² The subhalide structures are usually rationalized by assuming that backbonding from halogen to the boron cage is involved. One obvious chemical test of this hypothesis is to substitute the halide ligands in one of the subhalides to determine if the boron–boron linkages are stable in the absence of backbonding ligands; alkyl groups were selected as substituents unlikely to engage in backbonding.

As yet, the only subhalide for which detailed molecular

orbital calculations are available is the smallest, B_4Cl_4 . While the bonding in this compound may differ from that of the larger subhalides in that it is thought to occur by means of three-centred orbitals localized in the faces of the boron tetrahedron, both experimental and theoretical results have been interpreted to indicate that substantial amounts of ligand-to-cluster backbonding are present.³ The purpose of the present study was to determine whether halogen ligands are required to stabilize the tetraboron cage, or if species like $\text{R}_2\text{B}_4\text{Cl}_2$ or R_4B_4 , once formed, might have sufficient stability to allow their isolation and characterization.

Tetraboron tetrachloride, B_4Cl_4 ,⁴ was allowed to interact with substoichiometric amounts of ethyl-lithium. The reaction results in two new liquids, EtB_4Cl_3 and $\text{Et}_2\text{B}_4\text{Cl}_2$, which can be separated by low-temperature distillation. The properties of these new species, especially in comparison with B_4Cl_4 , see Table, are clearly consistent with their formulation.

TABLE. Properties of B_4Cl_4 and mono- and di-ethyl derivatives of B_4Cl_4 .

Compound	B_4Cl_4		EtB_4Cl_3		$\text{Et}_2\text{B}_4\text{Cl}_2$	
Colour, phase at 23 °C	yellow,	solid	yellow,	liquid	yellow,	liquid
Mass spectral fragmentation pattern high mass region ^a	B_4Cl_4 , B_3Cl_3 , B_2Cl_2 , B_3Cl_3 ,	100% 90% — 81%	RB_4Cl_3 , B_4Cl_3 , RB_4Cl_2 , RB_3Cl_2 ,	93% 48% 14% 100%	$\text{R}_2\text{B}_4\text{Cl}_2$, RB_3Cl_2 , $\text{R}_2\text{B}_3\text{Cl}$,	100% 95% 60%
Exact mass: ion	—	—	$\text{Et}^{11}\text{B}_4^{35}\text{Cl}_3$	—	$\text{Et}_2^{11}\text{B}_4^{35}\text{Cl}_2$	—
Observed mass; ($\Delta m/e$, p.p.m.)	—	—	177.9832; (1.6)	—	172.05378; (3.5)	—
¹¹ B n.m.r., δ /p.p.m. ^b	—85	—	—89.6 (3)	—120 (1)	—94.9 (1)	—125 (1)
¹ H n.m.r., δ^c	—	—	1.56 (2)	1.15 (3)	1.58 (2)	1.18 (3)

* R = Et. ^b Positive δ shielded relative to $\text{BF}_3\text{-OEt}_2$. ^c Relative to Me_4Si .

For each compound the isotopic intensities of the molecular ions are near those calculated, although the loss of small amounts of hydrogen is indicated. I.r. absorptions characteristic of ethyl groups and cage stretches (near 990 cm^{-1}) are observed. Both EtB_4Cl_3 and $\text{Et}_2\text{B}_4\text{Cl}_2$ are unchanged after two months at ambient temperature indicating at least fair thermal stability.

t-Butyl-lithium was utilized to prepare the fully alkylated derivative of B_4Cl_4 . Tetraboron tetrachloride was vacuum-distilled on to Bu^tLi , 2-fold excess, in pentane. After 15 min the mixture was filtered, the excess of alkyl-lithium reacted with MeI and, after refiltration, all volatile material was removed. Only a clear glassy solid, m.p. 45°C , remained. Mass spectrum (high mass ions only): 272, Bu^t_4B_4 , 100%; 257, $\text{Bu}^t_3\text{B}_4\text{CMe}_2$, 15%; 215, Bu^t_3B_4 , 90%; other ions, e.g., Bu^t_2B , were also present. Molecular ion intensities, *m/e*, measured (calculated): 273, 20.8% (16.5%); 272, 100% (100%); 271, 88.7% (89.0%); 270,

30.6% (31.8%); 269, 9.6% (5.1%). ^1H n.m.r.: δ 1.1; ^{11}B n.m.r. δ 135.1 (s) p.p.m. deshielded from $\text{BF}_3\text{-OEt}_2$. The vibrational spectra will be reported separately.

These results indicate that the tetraboron framework is stable in the absence of some or even all of the original halide substituents, demonstrating that backbonding, while it may well be present in B_4Cl_4 , is not required.⁵ Perhaps more importantly, there appears to be no *a priori* reason to expect that peralkyl derivatives of other boron subhalides cannot be synthesized. The geometry of the B_4 cluster in the peralkyl species is not known, at present, but the structural consequences of halide substitution are currently under investigation.

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⁵ The bonding of the tetraboron framework in the (then hypothetical) absence of chloride ligands has been discussed: D. A. Kleier, J. Bicerano, and W. N. Lipscomb, *Inorg. Chem.*, 1980, **19**, 216.