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### The Search for the Least-Coordinating Anion

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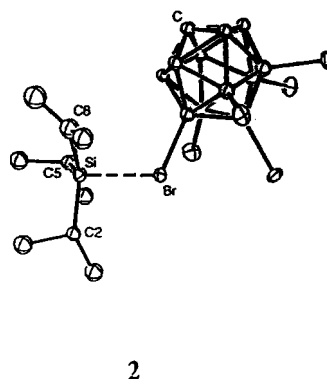
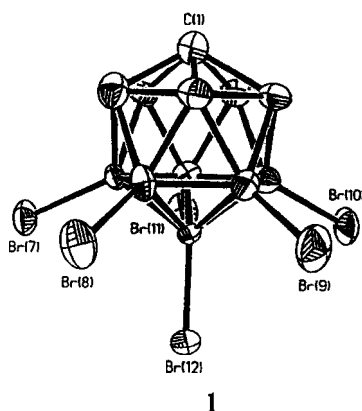
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## THE SEARCH FOR THE LEAST-COORDINATING ANION: DERIVATIZING THE ICOSAHERAL *CLOSO*-CARBORANE ANION $\text{CB}_{11}\text{H}_{12}^-$ .

Robert W. Reed, Zuowei Xie, Janet Manning, Rajeev Mathur, Robert Bau and Christopher A. Reed\*, Chemistry Department, University of Southern California, Los Angeles, California, U.S.A., 90089-0744.

The brominated carborane,  $\text{Br}_6\text{-CB}_{11}\text{H}_6^-$  (structure 1) is the most recent candidate for the least coordinating anion. It has wide application to the chemistry of reactive cations. The closest approach to date to the long sought silylium ion,  $\text{R}_3\text{Si}^+$ , utilized this anion in the structurally characterized compound  $(i\text{-Pr}_3\text{Si}^{\delta+})(\text{Br}_6\text{-CB}_{11}\text{H}_6^{\delta-})^1$  (structure 2).



The success of the 12-vertex carborane cage in producing anions of exceptionally low nucleophilicity and kinetic inertness arises from the strong  $\sigma$ -bonding in the icosahedral framework. Nevertheless, we have been able to develop substitution chemistry of  $\text{CB}_{11}\text{H}_{12}^-$  which enables us to manipulate nucleophilicity and solubility to considerable extent. For example lithiation at carbon and subsequent alkylation affords derivatives of greater solubility while systematic electrophilic halogenation at boron has been achieved to produce most of the mono, di, tri and hexa halogenated species for  $\text{X}=\text{Cl}, \text{Br}, \text{I}$ .

1. Christopher A. Reed\*, Zuowei Xie, Robert Bau, and Alan Benesi. *Science* 262, 402 (1993).