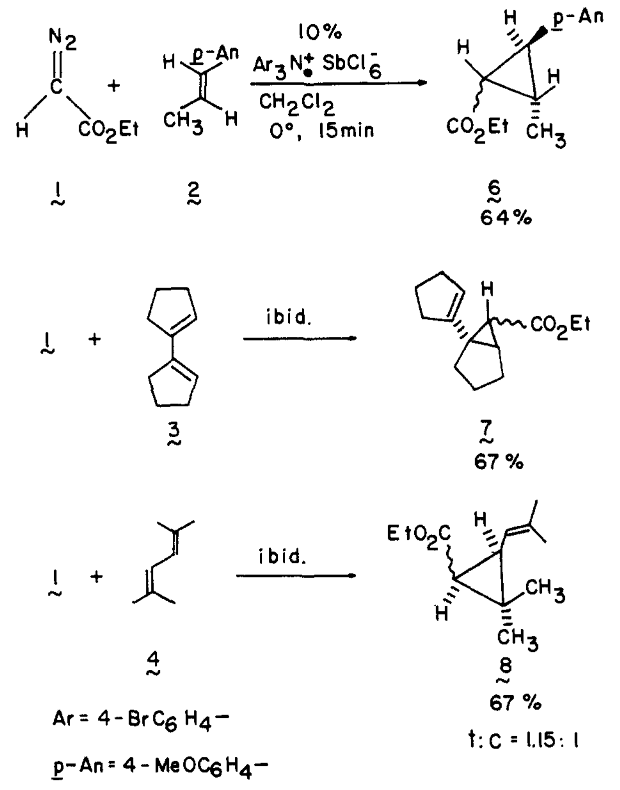
Scheme I

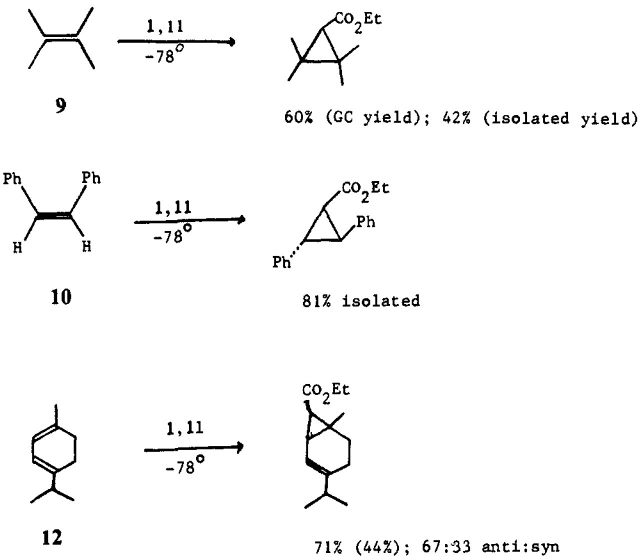


After a 15-min reaction time, excess sodium methoxide-methanol was added to quench cation radicals and the reaction mixture subjected to aqueous workup. The cyclopropane products (**6**-**8**; Scheme I) were purified by preparative TLC and preparative GC. Structure assignments are based upon GC/MS, IR, and ^{13}C and ^{1}H NMR (500 MHz, COSY).[13]

Less ionizable substrates, such as 2,3-dimethyl-2-butene (**9**) and *cis*- and *trans*-stilbene (**10**) could not be efficiently cyclopropanated with **5** as the initiator, but facile cyclopropanation of these substrates occurred (Scheme II), even at −78 °C, with the more potent single electron acceptor tris(2,4-dibromophenyl)aminium hexachloroantimonate (**11**).[14] The higher selectivities available at −78 °C make this procedure useful even for the relatively ionizable substrates, as illustrated by the selective cyclopropanation of α-terpinene (**12**; Scheme II).

That these triarylaminium salt initiated cyclopropanations are mechanistically cation radical chain processes is supported by application of the 2,6-di-*tert*-butylpyridine criterion[15] and by the fact that these same reactions occur using other hole-catalyst/initiator systems, including photosensitized electron transfer[16-18] and heterogeneous catalysis on 13X zeolite.[19] The premise that ionization of **1** is not competitive with ionization of **2**-**4**, and **10**-**12** is supported by the observation that **1** is stable in the presence of **5** (0 °C, 15 min, dichloromethane). The circumstance that hole-catalyzed/initiated cyclopropanation occurs via ionization of the π functionality to be cyclopropanated suggests that these reactions should be highly selective with respect to functional groups and especially so in view of the availability of initiators spanning a wide range of oxidation potentials.

Scheme II



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(13) The syn/anti isomers of **7** and **8** were separated by preparative GC. Decoupled 500-MHz ^{1}H NMR decisively reveal the stereochemistry of each isomer. Yields of **6**-**8** are corrected GC yields. Yields in Scheme II are isolated yields (silica gel chromatography).

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First Structural Characterization of a Boron-Centered Radical: X-ray Crystal Structure of $[Li(12\text{-crown-}4)_2]^+[BMes_3]^{\bullet-}$

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The reaction between triaryl boron compounds (BAr_3) and alkali metals (M = Li-Rb) in ether solvents to give the reduced salts $[M]^+[BAr_3]^-$ was first reported in 1924 by Krause.[2] The triarylboron anions, which are isoelectronic with the triarylmethyl radicals, may be paramagnetic provided they remain as unassociated species in solution.[3] It is apparent that the steric properties of the aryl substituent play a key role in determining the structure, as well as the magnetic and spectral characteristics, of these interesting compounds. For example, the sodium salts of the triphenylborane and related anions were found to be diamagnetic in ether or THF, presumably due to the association of ion pairs into ion clusters.[4] On the other hand, Chu and Weissmann[5] showed that the more crowded trimesitylboron ($BMes_3$ Mes = 2,4,6-$Me_3C_6H_2$−) reacts readily with sodium in THF to give an intense blue solution and inferred from magnetic susceptibility

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(1) A. P. Sloan Foundation Fellow, 1985-1989.

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(3) More recently the work of Berndt and co-workers has shown that other types of boron-centered radical species such as $[B_2R_4]^{\bullet-}$ (R = *t*-Bu, *n*-pentyl) or cyclo-$[(BRRCRT)_2]^{\bullet-}$ are possible although no structures have yet emerged. Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 482. Klusik, H.; Berndt, A. *J. Organomet. Chem.* **1982**, *232*, C21; *234*, C17. Wehrmann, R.; Pues, C.; Klusik, H., Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 372.

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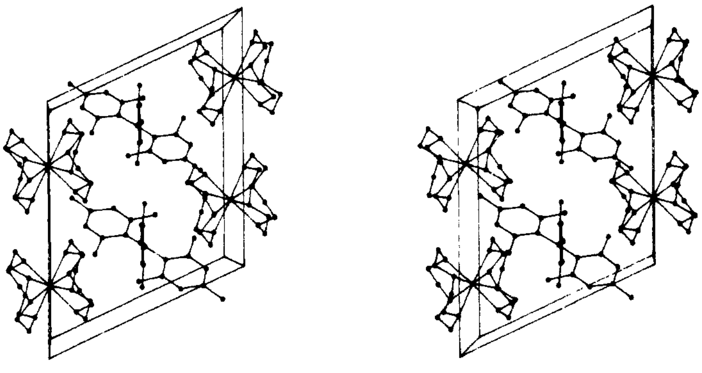

Figure 1. Stereoview of the unit cell of $[\mathrm{Li(12\text{-}crown\text{-}4)_2}]^+[\mathrm{BMes_3}]^{\bullet-}$ (**1**).

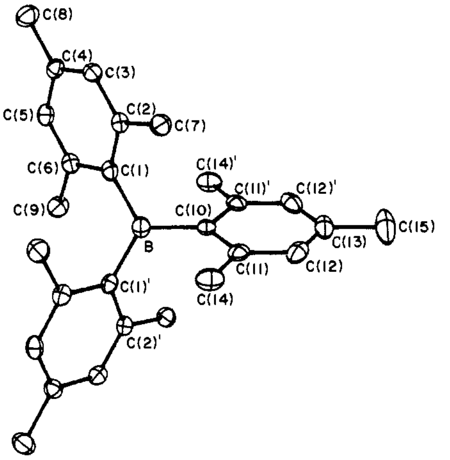

Figure 2. Computer-generated diagram of the anion of **1** showing numbering scheme (**2** is numbered similarly).

measurements that $[\mathrm{Na}]^+[\mathrm{BMes_3}]^{\bullet-}$ was monomeric in the concentration range 0.05–0.15 M. Almost simultaneously Brown and Dodson proposed that, on the basis of its chemistry, the unpaired electron in $[\mathrm{BMes_3}]^{\bullet-}$ was highly delocalized.[6] Further studies involving EPR[7] and electrochemical[8] measurements have since confirmed this view. More recently $\mathrm{BMes_3}$ itself has been studied from the point of view of conformational analysis[9] and its use in solution as an nonpolar aprotic medium for dissolving metal reductions.[10] Although the structures of both $\mathrm{BPh_3}$[11] and $\mathrm{BMes_3}$[9] are known, no X-ray structural data have appeared on the reduced radical species. In this paper we present the first structural determination of a free $[\mathrm{BAr_3}]^{\bullet-}$ radical anion which was crystallized as the crown ether salt $[\mathrm{Li(12\text{-}crown\text{-}4)_2}]^+[\mathrm{BMes_3}]^{\bullet-}$ (**1**).

Compound **1** was synthesized as follows. Under rigorously anaerobic and anhydrous conditions, $\mathrm{BMes_3}$ (1.1 g, 3 mmol) in THF (40 mL) was stirred for 1 h with lithium powder (30 mg, ca. 4 mmol). The solution became intensely blue. Filtration to remove the excess lithium followed by the addition of 12-crown-4 (1.05 g, 6 mmol) resulted in the precipitation of the product **1** as glittering blue crystals. These were redissolved by warming and cooled slowly to give crystals of suitable size for X-ray diffraction studies. Yield, 1.2 g, 55%. Compound **1** exhibits remarkable thermal stability. Facets of the crystals were still visible in the melting point apparatus at 230 °C with rapid decomposition occurring at ca. 240 °C.

Table I. Selected Bond Distances (Å) and Angles (deg) for **1** (anion only) and **2**

	compound	
	1 (anion)	**2**
B–C(1)	1.592 (2)	1.579 (2)
B–C(10)	1.608 (4)	1.580 (3)
C(1)–C(2)	1.429 (2)	1.414 (3)
C(1)–C(6)	1.425 (3)	1.417 (2)
C(10)–C(11)	1.422 (2)	1.419 (2)[a]
C(1)–B–C(1′)	121.8 (2)	117.4 (2)
C(1)–B–C(10)	119.1 (1)	121.3 (1)
C(2)–C(1)–C(6)	115.2 (1)	117.4 (1)
C(11)–C(10)–C(11′)	115.7 (2)	117.8 (2)
B–C(1)–C(2)	123.2 (1)	121.8 (1)
B–C(1)–C(6)	121.5 (1)	120.7 (2)
B–C(10)–C(11)	122.2 (1)	121.1 (1)[b]

[a] All other ring C–C distances the same are within experimental error. [b] All remaining angles are very similar in both molecules.

The crystal structure[12] of **1** was determined to establish the existence of $[\mathrm{BMes_3}]^{\bullet-}$ as a free noninteracting radical anion. Although the structure of the precursor, $\mathrm{BMes_3}$ (**2**), was already known and not in doubt[9] we redetermined its structure at 130 K to enable an isothermal comparison with **1**.

The structure of **1** is illustrated as a stereoview in Figure 1. The numbering scheme for **1** (**2** is numbered similarly) is given in Figure 2. A list of the important structural parameters for both **1** and **2** is given in Table I. There are no intermolecular contacts between cation and anion greater than Σ (covalent radii + 1.5 Å, including H's). Both compounds are planar at boron as required by the presence of a crystallographic 2-fold axis. The angles at boron deviate only slightly from 120°. It is immediately apparent that the structural differences between **1** and **2** are slight and mainly involve the bond distances and angles surrounding boron. For example the B–C bonds in **1** average 0.02 Å or 3% longer than in **2**. Apart from the C(1)–C(2) and C(1)–C(6) distances in **1** which are also slightly longer, the remaining ring C–C bonds are almost identical in length. In both **1** and **2** the rings and their substituent carbon atoms show little deviation from planarity. In addition, the C(1) rings have almost identical dihedral angles (48.6° vs. 49.9°) with respect to the central $\mathrm{BC_3}$ plane. However, in **1** the remaining C(10) ring has a greater dihedral angle (57.2°) than the C(10) ring in **2** (51.3°). Nevertheless the total dihedral angles of 154.4°, **1**, and 151.1°, **2**, are very similar.

The above data show that the addition of one electron to the $\mathrm{BMes_3}$ system has a small effect on its ground-state structure. Apart from the slight lengthening of the B–C bonds in **1**, the remaining structural parameters are virtually identical. In molecular orbital terms, the addition of one electron to the lowest available energy level involving a combination of the boron p-orbital and the ring π-orbitals results in a minor change in the number of electrons. This small difference is also in agreement with measured bond distances. The structure of **1** is also in agreement with the relative ease of addition of an electron to $\mathrm{BAr_3}$ compounds since this process does not seem to require any extensive reorganization of orbitals in these molecules. Further studies on reduced triarylboron species with various combinations of ligand types and sizes are under way.

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Summary of crystallographic data, tables of atom coordinates, thermal parameters, bond distances and angles, hydrogen coordinates, and structure factors (9 pages). Ordering information is given on any current masthead page.

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(12) Crystal data at 130 K with Mo Kα (λ = 0.71069 Å) radiation: **1**, monoclinic *P*2/*c*, *Z* = 2, *a* = 12.724 (5) Å, *b* = 11.596 (4) Å, *c* = 15.224 (7) Å, *β* = 115.25 (3)°, *R* = 0.039, 310 parameters, 2691 unique observed data; **2**, monoclinic *C*2/*c*, *Z* = 4, *a* = 11.743 (3) Å, *b* = 11.642 (3) Å, *c* = 16.899 (4), *β* = 106.04 (2)°, *R* = 0.044, 201 parameters, 2954 unique observed data.