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Notes

Generation and Characterization of the Tris(pentafluorophenyl)borane Radical Anion

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Summary: The anion derived from $B(C_6F_5)_3$ has been detected by EPR, and the boron and fluorine hyperfine splitting constants have been determined. Treatment of $B(C_6F_5)_3$ with the reductant $Cp^*{}_2Co$ in THF at −50 °C rapidly results in a dark blue (λ_{max} = 603 nm) paramagnetic solution containing the anion radical. The half-life for disappearance of λ_{max}, about 10 min at room temperature, is consistent with that of the EPR signal.

Introduction

The catalysis of α-olefin polymerization by organometallic compounds has often involved the use of $B(C_6F_5)_3$ as a cocatalyst.[1] Extensive studies have elucidated its role as a strong electrophile, capable of abstracting an alkyl ligand from a metal dialkyl to generate the active cationic form.[1,2] In addition, $B(C_6F_5)_3$ has attracted attention as a Lewis acid catalyst in organic transformations.[3]

However, little is known of the ability of $B(C_6F_5)_3$ to function as a one-electron oxidant, a mode of reactivity that may be relevant to its role in the activation of polymerization catalysts.[4] We have recently shown that an azazirconacyclobutene undergoes one-electron oxidation in the presence of $B(C_6F_5)_3$, but we did not detect the $B(C_6F_5)_3$ radical anion.[5] Green and co-workers have just reported that an η^2-vinyl Mo complex undergoes one-electron oxidation by $B(C_6F_5)_3$, but also were unable to detect $B(C_6F_5)_3{}^{\bullet-}$.[6] (The electron acceptor has also remained elusive in other cases where Lewis acid/solvent combinations ($AlCl_3/CH_2Cl_2$, $AlCl_3/CH_3NO_2$, BF_3/SO_2, $SbCl_5/PhNO_2$) oxidize neutral organic molecules by one electron.[7])

In an effort to generate $B(C_6F_5)_3{}^{\bullet-}$ independently, we earlier treated $B(C_6F_5)_3$ with alkali metals and with cobaltocene.[5] Nonfluorinated triarylboranes are readily reduced to radical anions with Na in ether solvents,[8,9] but $B(C_6F_5)_3$ gave no radical anion under the same conditions (even with Na/K). Treatment of $B(C_6F_5)_3$ with cobaltocene ($E_{1/2}(Cp_2Co) = -0.86$ V vs SCE in CH_2Cl_2)[10] led to attack by boron on a cyclopentadienyl ring, without evidence for radical anion formation.

It seemed plausible that decamethylcobaltocene $Cp^*{}_2Co$ would favor the one-electron reduction of $B(C_6F_5)_3$, since $Cp^*{}_2Co$ is a strong reducing agent ($E_{1/2}(Cp^*{}_2Co) = -1.48$ V vs SCE in CH_2Cl_2)[10] and its methyl groups should sterically preclude ring attack. We now report the generation of the $B(C_6F_5)_3$ radical anion in solution and its characterization by EPR spectroscopy.

Results and Discussion

The treatment of a THF solution of $B(C_6F_5)_3$ with an equimolar $Cp^*{}_2Co$ solution rapidly resulted in the generation of an unstable paramagnetic dark blue species (**1**) ($t_{1/2} \approx 2$ min at room temperature). Due to its transient nature, we prepared **1** at low temperature under inert atmosphere for EPR analysis. The deep blue solution ($\lambda_{max} \approx 600$ nm) decomposed to a diamagnetic pale yellow solution, with the principal identifiable components being $Cp^*{}_2Co^+$ and $B(C_6F_5)_4{}^-$.[11]

X-band EPR analysis of the reaction of $B(C_6F_5)_3$ (30 mM) with $Cp^*{}_2Co$ (30 mM) in THF at −50 °C led to the detection of a sharp, strong signal. The spectrum exhibited a well-resolved 14-line pattern centered at g_{iso} = 2.010 (Figure 1a). Hyperfine coupling with ^{10}B contributes additional fine structure at the wings of the spectrum. A computer simulation[12] (Figure 1b) of the EPR spectrum is consistent with $B(C_6F_5)_3{}^{\bullet-}$. The para-

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[11] The cation $Cp^*{}_2Co^+$ appears in the ^1H NMR spectrum (δ = 1.7),[10] and the anion $B(C_6F_5)_4{}^-$ is observed in the ^{11}B NMR spectrum (δ = −16) by a Bruker 300 MHz NMR spectrometer.

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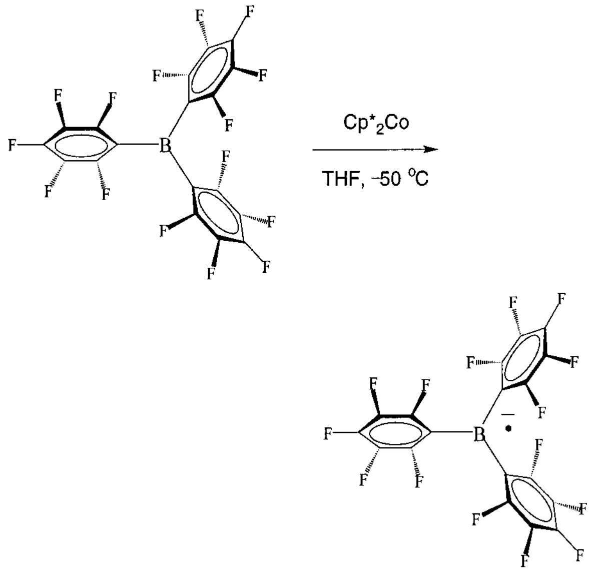

(1)

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magnetic Cp^*_2Co does not introduce ambiguity in the EPR detection of $B(C_6F_5)_3^{\bullet-}$ at experimental temperature; due to its fast spin−lattice relaxation, Cp^*_2Co can only be observed at very low temperature, ca. 15 K.[10]

The value of $a(^{11}B)$ for **1**, 10.5 G,[13] is similar to that reported for other triarylborane radical anions, $B(Mes)_3^{\bullet-}$ (10.32 G)[14] and $BPh_3^{\bullet-}$ (9.8 G).[9c] The $a(^{19}F)$ values for **1** are 4.60 G (6F), 1.30 G (6F), and 5.30 G (3F). We assume that the larger $a(^{19}F)$ (6F) arises from the ortho fluorines and therefore assign 4.60 G to them, 1.30 G to the meta fluorines, and 5.30 G to the para fluorines. These values are comparable to those ($a(o\text{-}^{19}F) = 2.76$ G, $a(m\text{-}^{19}F) = 1.61$ G, $a(p\text{-}^{19}F) = 6.80$ G) reported for the isoelectronic tris(pentafluorophenyl)methyl radical.[15]

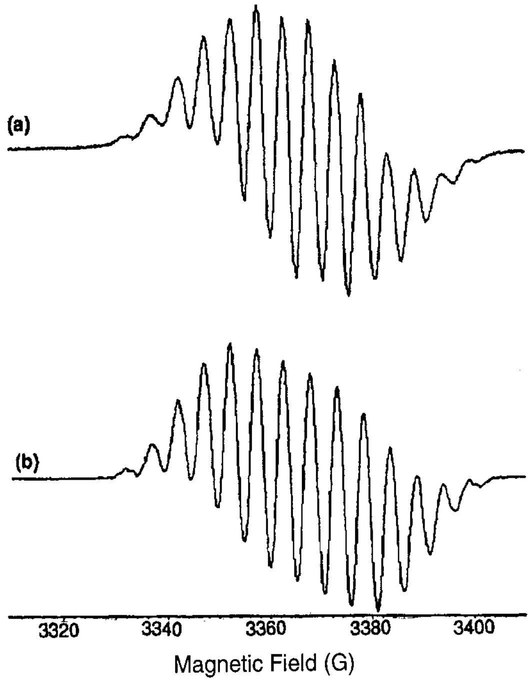

Figure 1. X-band EPR spectrum of **1** in THF at −50 °C, $v = 9.458$ GHz: (a) experimental spectrum; (b) simulated spectrum with a Lorentzian peak-to-peak line width of 1.30 G.

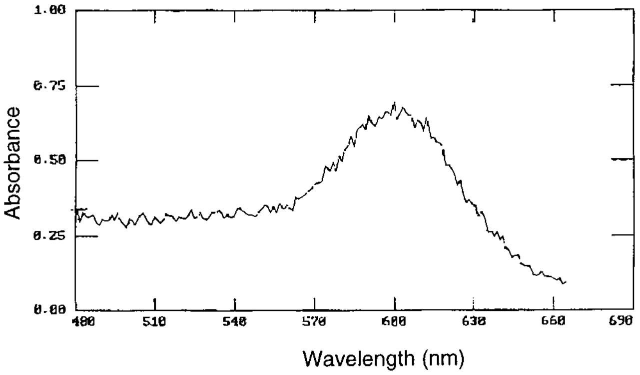

Figure 2. UV/vis absorption spectrum of **1** ($\lambda_{max} \approx 600$ nm) in THF at −50 °C.

The UV/vis spectrum (Figure 2) of **1** in THF at −50 °C showed a broad absorption near 600 nm, responsible for the deep blue color. Similar absorptions have been reported for previous triarylborane radical anions,[9c,16,17] although previous workers have not demonstrated that they arise from the species responsible for the EPR signal. We have therefore monitored the decay of the 600 nm absorbance and the EPR signal. Rate measurements obtained from a UV/vis spectrometer at 15 and 23 °C suggest a half-life of about 10 min at 0 °C for the absorbance, whereas observation at about 0 °C in our EPR spectrometer shows a half-life of about 5 min, close enough to be consistent with attributing the 600 nm absorbance to the radical anion. The absorption is likely due to an electronic transition from the boron p-orbital to an antibonding π-molecular orbital.[18]

Rapid electron self-exchange has been observed between $B(Mes)_3^{\bullet-}$ and $B(Mes)_3$ in THF ($k = 4 \times 10^9$ M^{-1} s^{-1}).[19] We have therefore examined the EPR line width of $B(C_6F_5)_3^{\bullet-}$ in the presence of free $B(C_6F_5)_3$ in THF and have observed no broadening due to electron self-exchange. The limited solubility of **1** has thus far precluded experiments in other solvents.

Some organodiborane radical anions, with a one-electron σ-bond, are known,[20,21] suggesting the possibility that the $B(C_6F_5)_3^{\bullet-}$ is associated with an additional molecule of $B(C_6F_5)_3$. However, the multiplicity of our EPR signal precludes such a dimeric structure, at least in THF.

In summary, we have provided evidence for the $B(C_6F_5)_3$ radical anion in solution and have demonstrated that $B(C_6F_5)_3$ can serve as a one-electron oxi-

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(12) The computer simulation was performed using WINEPR SimFonia software, Version 1.25; the simulated spectrum included an 18.2% ^{10}B contribution and an 81.8% ^{11}B contribution.

(13) The uncertainties for the calculated hfs constants (G) at the 99% confidence level are $^{11}B = \pm 0.20$, $^{10}B = \pm 0.07$, $o\text{-}^{19}F = \pm 0.08$, $m\text{-}^{19}F = \pm 0.09$, $p\text{-}^{19}F = \pm 0.07$.

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dant. We are attempting to determine the thermodynamics of $B(C_6F_5)_3$ reduction.

Experimental Section

General Procedure. All manipulations were performed under inert atmosphere in a glovebox or by conventional Schlenk techniques. Tetrahydrofuran was distilled under a nitrogen atmosphere from sodium benzophenone ketyl. Cp^*_2Co was prepared as in ref 10. $B(C_6F_5)_3$ was sublimed before use.

The EPR spectrum was recorded on a Bruker 200D X-band EPR spectrometer (9.458 GHz) with a field modulation amplitude of 2 G. Fourteen scans of 2024 points each (sweep width 200 G) were acquired. The temperature was maintained at −50 °C with the use of a Bruker ST 100/700 variable-temperature assembly.

The UV/vis spectrum was recorded at −50 °C from a HITECH SF-40 stopped-flow spectrophotometer (1000 scans/s). The instrument was equipped with a HITECH SF-3L support unit to control temperature.

Tris(pentafluorophenyl)borane Radical Anion (1). $B(C_6F_5)_3$ (0.008 g, 0.015 mmol) and Cp^*_2Co (0.005 g, 0.015 mmol) were separately dissolved in THF (0.5 mL) in NMR tubes, capped with rubber septa. In a dry ice/acetone bath at −78 °C, the $B(C_6F_5)_3$ solution was added to the orange Cp^*_2Co solution by cannula. For EPR analysis, the resulting dark blue solution was transferred into a capped glass pipet, sealed at the tip (1 mm i.d.).

Reaction Kinetics. The kinetic profile for the decomposition of **1** (4 mM) was collected at 15 and 23 °C from a Hewlett-Packard 8453 UV/vis spectrophotometer and at 0 °C from a Bruker 200D X-band EPR spectrometer. The kinetic trace at 23 °C was monitored ($\lambda_{max} = 603$ nm), with a first-order rate of $5.7(1) \times 10^{-3}$ s^{-1}. Kinetic measurements of $3.4(1) \times 10^{-3}$ s^{-1} at 15 °C (by UV/vis) and $2.6(1) \times 10^{-3}$ s^{-1} at 0 °C (by EPR) were also obtained.

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