Fluorinated 9-borafluorenes vs. conventional perfluoroaryl boranes — Comparative Lewis acidity

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Abstract: Perfluorinated 9-phenyl-9-borafluorene, 1, is an antiaromatic analog of the well-known tris(pentafluorophenyl)borane. Spectroscopic, structural, and electrochemical studies have been performed on 1 and its Lewis base adducts with MeCN, THF, and PMe₃ with a view to assessing its comparative Lewis acid strength relative to $B(C_6F_5)_3$. For the sterically undemanding Lewis base MeCN, 1 and $B(C_6F_5)_3$ have comparable LA strengths, while for more sterically prominent THF, 1 is clearly the stronger Lewis acid (LA) based on competition experiments. We conclude that steric factors, rather than antiaromaticity, are the most important determinants in the LA strength differences between 1 and $B(C_6F_5)_3$.

Key words: boranes, Lewis acids, fluorinated compounds, heterocycles.

Résumé : Le 9-phényl-9-borafluorène perfluoré (1) est un analogue antiaromatique du tris(pentafluorophényl)borane bien connu. Afin d'évaluer son acidité relative à celle du $B(C_6F_5)_3$, on a effectué des études spectroscopiques, structurales et électrochimiques sur le composé 1 et sur les adduits qui résultent de sa réaction avec les bases de Lewis MeCN, THF et PMe₃. Sur la base d'expériences de compétition, on a observé que dans le cas de la base de Lewis MeCN qui n'impose pas de demandes stériques spéciales, les forces des acides de Lewis du composé 1 et du $B(C_6F_5)_3$ sont comparables alors que, avec le THF qui impose des contraintes stériques plus grandes, l'acidité de Lewis du composé 1 est nettement plus grande. On en conclut que les facteurs stériques, plutôt que l'antiaromaticité, sont plus importants dans la détermination des différences des forces d'acidité de Lewis entre le composé 1 et le $B(C_6F_5)_3$.

Mots clés : boranes, acides de Lewis, composés fluorés, hétérocycles.

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Introduction

Highly fluorinated aryl boranes are an important class of Lewis acids because of their high thermal stability, resistance to hydrolysis, and Lewis acid strength (1). Although they have been known for many years (2), their application as activators for single-site olefin polymerization catalysts (3) has sparked interest in defining other applications in areas as diverse as organic synthesis (4), weakly coordinating anion development (5), and cationic polymerization initiation (6). Since Lewis acid strength is related to the effectiveness of the boranes in many of these applications (7), efforts to modulate the Lewis acid properties of the parent tris-(pentafluorophenyl)borane have utilized several strategies, including the use of larger, more fluorinated aryl groups (8) and the replacement of one C_6F_5 group with poorly π -donating but electronegative substitutents like $-NC_4H_4$ (9). In some instances, weakening the Lewis acid strength by substitution with nonfluorinated aryl groups is beneficial for a given ap-

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plication (10). It is thus clear that the ability to modulate Lewis acid strength is beneficial for the applications of this family of boranes.

One intriguing strategy for increasing the Lewis acid strength of $B(C_6F_5)_3$ without drastically elevating the steric imposition of the aryl groups about boron is to incorporate the boron center into an antiaromatic ring framework. Using this strategy, we and Marks and co-workers (11) independently prepared the perfluorinated 9,10-diboraanthracene Lewis acid shown in Chart 1. Marks found it to be an exceptionally strong Lewis acid (12), eclipsing $B(C_6F_5)_3$ in competition experiments with low-steric-demand Lewis bases like acetonitrile. In fact, the second boron center is also highly Lewis acidic in these compounds, often performing independently from the first. Taking a cue from early work on boroles by Eisch et al. (13), we developed a second family of antiaromatic perfluoroaryl boranes, the 9-borafluorene compounds 1 and 2 (14) (Chart 1), a closer structural analog of the parent $B(C_6F_5)_3$. A detailed study on the coordination chemistry of compounds 1 and 2 with the unusual Lewis base "Cp*AlI" showed that they exhibit chemical behavior that is more borane-like than borole-like (15); that is, compounds 1 and 2 coordinate the aluminum Lewis base in an η^1 fashion, rather than undergoing two-electron reduction to give higher hapticity π complexes. Here we show that these reactivity patterns can be extended to more conventional Lewis bases and discuss the relative LA strength of 1 relative to the parent borane $B(C_6F_5)_3$. Structural, competition,

Chart 1.



and electrochemical studies suggest that steric factors dominate in determining the relative Lewis acidity in these compounds and that the antiaromaticity of **1** is not a significant progenitor of its high Lewis acidity.

Results and discussion

The pentafluorophenyl (1) and methyl (2) 9-borafluorene derivatives were prepared as previously reported (14) and reacted with the sterically differentiated but comparably basic (16) Lewis bases acetonitrile (MeCN) and tetrahydrofuran (THF) and the stronger base trimethylphosphine (PMe₃) to form 1:1 Lewis acid - Lewis base adducts (eq. [1]). In the case of MeCN and THF, an excess of base was used, while for PMe₃ near stoichiometric amounts were employed. In all cases, the compounds 1·LB and 2·LB were isolated in good yields as solids simply by removal of the solvent in vacuo. Immediately upon introduction of the Lewis base (LB), orange solutions of 1 and lime green solutions of 2 decolorized, as coordination of the Lewis base disrupted the strong π - π transition involving the low-lying boron-based LUMO, which is responsible for the colors in 1 and 2. Lewis base coordination fills this orbital, and the LUMO is now a higher energy formally π^* orbital; the increase in the energy gap causes the absorption to shift out of the visible range. Similar behavior has been observed in unfluorinated 9borafluorenes, which have been employed as colourimetric sensors for fluoride ions (17). Although labile (vide infra), the equilibria strongly favor the adducts **1·LB** and **2·LB**; for the stronger Lewis acid **1**, adducts **1·LB** do not relinquish their Lewis bases even with gentle heating under vacuum. All were formed as analytically pure, colorless solids that could be fully characterized using standard methods.

Upon complexation, resonances in the ¹H NMR spectra for the coordinated bases in 1.LB shift downfield significantly; for example, the resonance for the methyl group of the MeCN base in 1. MeCN shifts to 2.66 ppm vs. 2.10 ppm for free MeCN (18) as electron density is removed by the Lewis acid. For 2. MeCN, the opposite trend is observed for the B-Me signal, which shifts upfield by 0.7 ppm upon complexation. In the ¹⁹F NMR spectra of 1·LB, similar effects to those observed in the adducts of $B(C_6F_5)_3$ are exhibited: namely, a contraction of the chemical shift difference between the *para-* and *meta-*fluorines ($\Delta \delta_{p,m}$) (19). In B(C₆F₅)₃, this value is approximately 18 ppm in noncoordinating solvents, but upon treatment with acetonitrile a value of 8.4 ppm is found (20). The changes observed in 1. MeCN vs. free 1 indicate that the $\Delta \delta_{p,m}$ value in the $-C_6F_5$ ring goes from 14.7 to 6.4 ppm upon complexation of MeCN. Upfield shifts of varying severity are also observed in the fluorines of the borafluorene framework and analogous patterns are revealed in the THF and PMe₃ adducts.

The ¹¹B NMR spectra also show a distinct difference between the tricoordinate, base-free Lewis acids and the tetracoordinated adducts (21). In the case of the free acids, the ¹¹B NMR chemical shift for the synthesized 9-borafluorene derivatives ranges from δ 56.0 to δ 67.3. In general, the range in ¹¹B chemical shift for tetrahedral boron occurs at much higher field than related tricoordinate systems. The ¹¹B NMR chemical shifts for the adducts of **1**·LB and **2**·LB occur between δ 8.6 and δ –15.2 ppm. Both **1**·PMe₃ and **2**·PMe₃ exhibit coupling in the ¹¹B NMR spectra (δ –14.2 and –11.4, ¹J_{B-P} = 87 and 66 Hz, respectively).

The IR spectra of both **1·MeCN** and **2·MeCN** were recorded, and a diagnostic band for the C=N stretching mode was observed at 2361 and 2364 cm⁻¹, respectively, similar to that observed for the B(C₆F₅)₃ adduct ($v_{C=N} = 2367 \text{ cm}^{-1}$). The frequency of the C=N stretching mode for the free base is found at significantly lower wavenumbers ($v_{C=N} = 2253 \text{ cm}^{-1}$), indicative of a weaker carbon–nitrogen bond compared with that in the adducts. As the donor orbital of MeCN has slight antibonding character with respect to the CN linkage, complexation will remove some of the electron density from this orbital, which will strengthen the CN bond and result in the observed shift in $v_{C=N}$ (20).

A crystal structure of 1·MeCN was obtained, and a view with selected metrical data is presented in Fig. 1 (see also Table 1).² Compared to the structure of **1**, there is elongation

²Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 4074. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 280874, **1·MeCN** and 280873, [Cp*₂Co]⁺[**1·C**I]⁻ contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Fig. 1. Crystalmaker model of the molecular structure of **1·MeCN** with atom labeling scheme. Selected bond lengths (Å): B(1)—N(1) 1.581(3), B(1)—C(1) 1.620(3), B(1)—C(12) 1.612, B(1)—C(13) 1.617(3), N(1)—C(19) 1.133(3), C(1)—C(2) 1.366(3), C(1)—C(6) 1.413(3), C(2)—C(3) 1.384(3), C(3)—C(4) 1.364(3), C(4)—C(5) 1.384(3), C(5)—C(6) 1.389(3), C(6)—C(7) 1.481(3). Selected bond angles (°): C(1)-B(1)-N(1) 106.5(2), C(1)-B(1)-C(12) 98.8(2), B(1)-N(1)-C(19) 171.0(2), C(1)-C(6)-C(7)-C(12) 1.6(2).



of the B-C bonds in both the C_6F_5 ring and the 9borafluorene fragment. In 1-MeCN, B(1)-C(1), B(1)-C(12), and B(1)—C(13) are 1.620(3), 1.612(3), and 1.617(3) Å, respectively (cf. 1.555(4) and 1.547(3) Å, respectively, for the analogous bonds in 1). This is the result of the rehybridization of the boron from sp^2 to sp^3 and the increase in coordination number. The N(1)-B(1)-C(1) and N(1)-B(1)-C(13) angles are 106.5(2)° and 110.2(2)°, respectively, indicative of a distorted tetrahedral environment about boron. The internal angle in the 9-borafluorene is even more compressed than in the free acid; the C(1)-B(1)-C(12) angle is 98.8(2)°, compared with 103.5(2)°. The MeCN base has remained linear $(N(1)-C(19)-C(20) = 179.1(2)^{\circ})$ and is bonded in an essentially linear orientation with the boron center. The B(1)-N(1)-C(19) angle is 171.0(2)°, and the acetonitrile methyl group is oriented slightly over the 9-borafluorene ring. The B(1)—N(1) distance (1.581(3) Å) and the C=N triple bond (N(1)—C(19) = 1.133(3) Å) are quite close to those observed in the MeCN adduct of B(C₆F₅)₃ reported by Erker and co-workers (20) (for the equivalent bonds, the B-N and C-N distances are 1.616(3) and 1.124(3) Å, respectively). The same group has performed an accurate determination of the crystal structure of free acetonitrile using a Laser zone melting apparatus (22). From this, the bond length of the C=N triple bond (α phase, T = 208 K) was found to be 1.141(2) Å. Thus, there is a measurable contraction of the C=N bond upon complexation in both cases. This correlates with the observed bond strengthening in the IR spectra of **1**·MeCN as the $v_{C=N}$ band shifts to considerably higher wavenumbers.

In the case of the structure of base free 1, Marks and coworkers (12) noted a small but statistically relevant elongation of one of the aryl C=C bonds in the 9-borafluorene

Table 1. Summary of data collection and structure refinement details for $1 \cdot MeCN$ and $[Cp*_2Co]^+[1 \cdot Cl]^-$.

	1·MeCN	[Cp* ₂ Co]+[1·Cl] ⁻
Formula	C ₂₆ H ₉ BF ₁₃ N	C ₃₈ H ₃₀ F ₁₃ BClCo
fw	593.15	838.83
Temperature (K)	198.2	170.15
Crystal size (mm ³)	0.006 3	0.028
λ (Å)	0.710 69	0.710 69
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}(#2)$	$P\overline{1}(#2)$
a (Å)	8.967 5(9)	13.597(3)
<i>b</i> (Å)	11.599 8(8)	13.678(3)
<i>c</i> (Å)	12.026 4(8)	9.927 5(11)
α (°)	108.632(3)	90.641(15)
β (°)	102.337(3)	90.757(13)
γ (°)	92.938(5)	103.348(16)
V (Å ³)	1148.2(2)	1796.0(6)
Ζ	2	2
Reflections	8855	6647
Unique reflections	3822	6357
No. of variables	370	487
R_1	0.035	0.050
wR_2	0.050	0.049
GoF	1.18	2.09

framework, namely the C=C bond of the five-membered core ring. This result was also noted in the structures of perfluorinated 9,10-diphenyl-9,10-diboranthracene (11) and 1,2-bis[bis(pentafluorophenyl)boryl] tetrafluorobenzene (11*b*, 23). This effect is also apparent in the adduct, **1·MeCN**. The bond lengths for C(1)—C(6) and C(7)—C(12) are 1.413(3) and 1.415(3) Å, respectively, while the average of the remaining bonds is 1.376(3) Å. The difference in the bond lengths is similar to those observed in the aforementioned cases.

In our original communication, we noted that 1 exhibits LA strength comparable with that of $B(C_6F_5)_3$ by both the Childs method (24) and that of Laszlo and Teston (25), which uses the relative energies of the π^* orbital of LAcomplexed crotonaldehyde to assess LA strength. Furthermore, in a competition experiment for the sterically undemanding MeCN, we found a slight preference for 1.MeCN over MeCN·B(C_6F_5)₃, the equilibrium constant being 1.3 at 25 °C. This preference is further emphasized when the sterically more bulky base THF is used in this experiment. Thus, when a 1:1:1 mixture of 1, $B(C_6F_5)_3$, and THF in d_8 toluene was analyzed by ¹H and ¹⁹F NMR spectroscopy, it was found that the equilibrium lies completely towards 1.THF within the detection limits of NMR spectroscopy. Remarkably, even though $B(C_6F_5)_3$ is known to form a stable, isolable complex with THF, in a competitive situation, 1 dominates the competition for this Lewis base. That this is a thermodynamic preference is illustrated by the fact that identical results are obtained when equilibrium is approached from either side of the equation and by EXSY NMR experiments in the MeCN system, which show that the acetonitriles coordinated to both Lewis acids are exchanging with each other on this timescale. Unfortunately, similar competition experiments using PMe3 were precluded by the

nearly total insolubility of the $Me_3P \cdot B(C_6F_5)_3$ adduct in common solvents (1).

The rather marked dependence of the relative LA strength on the steric properties of the Lewis base employed suggests that the differences in Lewis acidity observed between 1 and $B(C_6F_5)_3$ are grounded in steric factors, rather than the fact that 1 exhibits antiaromaticity. Indeed, a comparison between the bond lengths associated with the borafluorene moiety in 1 vs. 1. MeCN shows that little change in the C— C distances is observed upon complexation of the base. This suggests that the π character of the ring framework is not perturbed significantly, i.e., the system does not become more aromatic (or less antiaromatic) as the base coordinates the boron center. Accordingly, the Julg A values (26) (a measure of aromaticity based on metrical bond distances (27)) for both the five- and six-membered rings do not change significantly in 1. MeCN vs. 1. In fact, while the A values for the flanking six-membered rings remain essentially the same, at 0.96 and 0.97 in 1 and 1. MeCN, respectively,³ the A(5) value for **1·MeCN** is actually less (0.89) than that for uncomplexed 1 (0.92). The A(5) value in 1·MeCN is comparable to that of 0.88 observed by West and co-workers (27b)for the neutral 9-sila- and 9-germa-fluorenyl systems, which also contain pyramidal atoms in the 9 position.

Given this discussion, we conclude that the reason 9borafluorene **1** is a Lewis acid of competitive or superior strength to $B(C_6F_5)_3$ (despite being less fluorinated) stems from the greater steric accessibility of the boron center and the lowered back strain encountered upon the pyramidalization of the boron center, which occurs upon complexation of a Lewis base. The flatness of the borafluorene ring substitutent is the main reason for the relaxing of these steric factors; further, the pyramidalization of boron in going from **1** to **1**·L**B** likely relieves strain in the C-B-C moiety of the five-membered ring. Although long a matter of debate, it has been recently acknowledged that steric factors, particularly the onset of back strain, dominate in determining the relative Lewis acidity of the boron trihalides BX₃ (28, 29).

Although antiaromaticity is likely not playing a strong role in determining the relative Lewis acidity of **1**, given the propensity of boroles to undergo two-electron reduction to form aromatic borollides (30), it seemed reasonable to presume that **1** could be reduced more readily than $B(C_6F_5)_3$. Norton and co-workers (31) have reported on the difficulties associated with reduction of $B(C_6F_5)_3$, but estimate an E_{red} of -0.9 V vs. SCE based on measured E_{red} values for Mes₃B, Mes₂ $B(C_6F_5)$, and Mes $B(C_6F_5)_2$ (Mes = 2,4,6-Me₃ C_6H_2) (31*c*). While the electron-withdrawing pentafluorophenyl groups make the boranes easier to reduce from a thermodynamic perspective, the lack of steric protection afforded by the C_6F_5 groups (as opposed to the Mes substitutent, for example) renders the radical anion extremely reactive, even with the surfaces of electrodes.

Cyclic voltammetry (CV) studies were performed on **1** in a variety of solvents using tetrabutylammonium tetrakis-(pentafluorophenyl)borate (32) as the supporting electrolyte. Experiments in the noncoordinating solvents CH_2Cl_2 and α,α,α -trifluorotoluene were unsuccessful, so THF was employed. Model experiments on the unfluorinated analogue of 1, 9-phenyl-9-borafluorene, show that, at scan rates of 500 mV s⁻¹ (33), a reversible reduction and oxidation process occurs with a reduction potential of -2.16 V vs. ferrocene (Fc), a similar value to that found for BPh₃. From the available data, it is not possible to determine if the CV of 9-phenyl-9-borafluorene is indicative of a one- or a twoelectron process. Under the same conditions, the CV of 1 revealed an irreversible process with a reduction potential at -2.42 V vs. Fc. The very negative potential obtained for 1 in THF was puzzling since it implies that 1 is more difficult to reduce than the unfluorinated analog and runs counter to the expected trend evidenced in the $Mes_nB(C_6F_5)_{3-n}$ series. On the other hand, the value for the reduction potential of 1 in THF is similar to those reported by Campbell (34) on the electrochemistry of simple aromatic fluorinated compounds. Although not directly comparable, since they are determined in different solvents, pentafluorobenzene and decafluorobiphenyl showed a first reduction wave at -2.84 and -2.20 V, respectively. These observations suggest the possibility that the reduction process does not actually take place at the boron center, but at the fluorinated aromatic framework, i.e., we are observing the reduction of 1.THF rather than 1 under these conditions. Campbell also detected the presence of species arising from the rupture of aromatic C-F bonds, which suggests that a similar decomposition pathway might be operating in our case, i.e., via Ar-F scission. Alternatively, the high negative potential for the onset of reduction of 1 may be due to a large kinetic barrier to its reduction, as was observed for $B(C_6F_5)_3$ (31).

Since attempts to generate 1^{2-} via electrochemical means failed, chemical reduction of 1 was attempted. Given that an earlier study indicated that Al(I) reagents were not sufficiently reducing (15), harsher reducing agents (C_8K , Li, Na, or K) were employed in a variety of solvents (Et₂O, THF, toluene, benzene, bromobenzene, or α, α, α -trifluorotoluene). Unfortunately, these invariably produced ill-defined mixtures. Not surprisingly, reactions involving alkali metals in nondonor solvents proved extremely slow, and after work up, the main products recovered were unreacted 1 and decomposition by-products. Furthermore, attempts to stabilize the putative $1^{\hat{2}}$ by addition of crown ethers were also unsuccessful; only coordination of one of the ether oxygen atoms to the boron center was observed in the ¹⁹F NMR spectrum. Given the slow kinetics associated with heterogeneous reductants, we sought a reducing agent that would allow the process to be carried out under homogeneous conditions.

Norton and co-workers (31) have shown that Cp_2^Co is an effective reductant for $B(C_6F_5)_3$. Reaction between **1** and 2 equiv. of Cp_2^Co in benzene or toluene led to the precipitation of an oily phase with recovery of 2 equiv. of unreacted Cp_2^Co from the supernatant. Analysis of the oily material by ¹⁹F NMR spectroscopy showed an extremely complex pattern arising from decomposition. However, this oily material was diamagnetic in nature, as judged by its silent EPR spectrum, even at low temperatures (ca. –50 °C). The presence of one remaining equivalent of reducing agent suggests

³These values are slightly depressed from the expected values near 1.00 because of the observed lengthening of the C—C bond that the sixand five-membered rings share compared with the other C—C bonds in the flanking six-membered rings observed in these and other systems. Despite the slightly lower A value, these rings are essentially fully aromatic.

Fig. 2. Crystalmaker model of the molecular structure of $[Cp*_2Co]^+[1\cdotCl]^-$ with atom labeling scheme. Selected bond lengths (Å): B(1)—Cl(1) 1.910(9), B(1)—C(13) 1.618(11), B(1)—C(1) 1.617(10), C(1)—C(2) 1.381(10), C(2)—C(3) 1.373(10), C(3)—C(4) 1.350(11), C(4)—C(5) 1.397(11), C(5)—C(6) 1.368(9), C(6)—C(7) 1.491(10). Selected bond angles (°): C(1)-B(1)-C(12) 97.9(6), C(1)-B(1)-C(13) 113.1(7), C(12)-B(1)-C(13) 114.9(6), C(1)-B(1)-Cl(1) 109.8(5), C(12)-B(1)-Cl(1) 106.9(6), C(13)-B(1)-Cl(1) 113.1(6).



that the initially formed radical anion is highly reactive and that Cp*₂Co is not sufficiently reducing to produce 1^{2–}. In accord with this postulate, the reaction of Cp*₂Co and 1 in CH₂Cl₂ took place cleanly within seconds, as judged by NMR spectroscopy. The ¹H NMR spectrum showed only a singlet at δ 1.70, corresponding to the expected hydrogen resonances for the Cp* units of the diamagnetic Cp*₂Co⁺ cation. ¹⁹F NMR spectroscopy clearly revealed a pattern of seven different well-defined signals in the expected range. The difference in chemical shift between the *meta-* and *para*-fluorines of the C₆F₅ ring ($\Delta \delta_{m,p}$ 4.7 ppm) was indicative of borate formation and a significant degree of charge separation. The negative value obtained by ¹¹B{¹H} NMR spectroscopy of δ –14 is also consistent with formation of a borate center.

Single crystals of the product of this reaction were obtained by slow diffusion of hexanes into a CH_2Cl_2 solution of the compound, generated as described above. The molecular structure of the salt $[Cp^*_2Co]^+[1\cdot Cl]^-$ is shown in Fig. 2 and is in accord with all the spectral data. There are no unusual contacts in the structure, and the ions are well separated with a boron—cobalt distance of 7.556(59) Å. The B(1)—Cl(1) distance of 1.910(9) Å is in the expected range for chloroborates, and the boron center in $[Cp^*_2Co]^+[1\cdot Cl]^$ shows a distorted tetrahedral environment with a C(1)-B(1)-C(12) angle of 97.9(6)°, also within the expected range by comparison with related compounds.

The outcome can be rationalized in terms of chloride abstraction from the CH_2Cl_2 solvent, the sole possible source of chloride in the reaction (Scheme 1). A potential direct abstraction of Cl^- by 1 is negated, since 1 is an indefinitely stable species in CH_2Cl_2 , as well as in most chlorinated solvents. Thus, the first step may involve the direct reaction between 1 and Cp^*_2Co . Based on the previous observations for the reaction of 1 with Cp^*_2Co in less polar solvents, where only 1 equiv. of Cp^*_2Co was found to react with 1, a plausible mechanism might involve the intermediacy of a highly reactive, monoanionic radical species. The radical





anion rapidly abstracts Cl^{\cdot} from solvent to form $[Cp^*_{2}Co]^+[1\cdot Cl]^-$. Alternatively, the CH_2Cl_2 solvent may mediate this reaction by electron transfer from $Cp^*_{2}Co$ to the solvent, which then gives up a chloride ion to 1. Although this option is not depicted in the scheme, our data do not exclude this as a possibility.

Taken together, the observations garnered from the experiments aimed at two-electron chemical and electrochemical reduction of **1** suggest that this compound behaves more similarly to its perfluoroaryl borane brethren than its nonfluorinated 9-borafluorene analogs. While one-electron reduction is fairly facile, the resulting radical anion is extremely reactive, abstracting atoms from solvent and (or) undergoing dimerization processes.

In conclusion, we find the antiaromatic perfluorinated 9phenyl-9-borafluorene **1** to be of comparable or greater Lewis acid strength than the noncyclic parent borane $B(C_6F_5)_3$, mainly because of the lesser back strain engendered in adducts upon pyramidalization of the boron center, owing to the flat $C_{12}F_8B$ ring system. The antiaromaticity associated with this function does not appear to play a significant role in determining the Lewis acidity of the system. The high Lewis acidity of **1** contributes to the difficulty in carrying out two-electron reduction chemistry that is facile in unfluorinated analogs.

Experimental section

General procedures

An Innovative Technologies or Vacuum Atmospheres argon-filled glove box was employed for manipulation and storage of oxygen and moisture-sensitive compounds. Reactions were performed using a double manifold argon/vacuum line and modified Schlenk line techniques. Matheson Oxisorb-W gas purification cartridges were used to remove residual oxygen and moisture in the argon stream. Glassware was dried overnight (80–110 °C) and then assembled warm and evacuated on the vacuum line or placed in the glovebox antechamber while hot. Glassware consisted of swivel frit apparatus and line connectors equipped with Kontes valves and round-bottom flasks equipped with ground glass joints. Unless otherwise noted, the introduction of solvent in all

manipulations using the argon/vacuum line was via vacuum transfer with condensation at -80 °C (acetone - dry ice bath). Solvents were purchased from Aldrich and dried and deoxygenated before use in the following procedures. Hexanes, toluene, and THF were dried and deoxygenated via passage through a Grubbs/Dow purification system (35) and were stored in evacuated bombs over titanocene (36) (hexanes and toluene) or sodium - benzophenone ketyl (THF). Benzene was deoxygenated by bubbling argon through the solvent and was dried over sodium and stored over the sodium - benzophenone ketyl. Diethyl ether and methylene chloride were predried over LiAlH₄ and CaH₂, respectively, and subsequently stored over sodium - benzophenone ketyl and CaH₂, respectively. All deuterated solvents for NMR experiments were purchased from Cambridge Isotopes. Deuterated benzene, toluene, and THF were dried over 4 Å molecular sieves, stored over sodium - benzophenone ketyl, and distilled prior to use. Deuterated methylene chloride and bromobenzene were dried over 4 Å molecular sieves, stored over CaH₂, and distilled prior to use. After distillation, the deuterated solvents were stored in the glove box, in glass bombs equipped with Kontes valves. NMR spectra were obtained on Bruker AC 200 MHz (1H), AMX 300 MHz (1H, 19 F, 11 B{ 1 H}), DRX 400 MHz (1 H, 13 C{ 1 H}), or Varian 200 MHz (${}^{11}B$, ${}^{11}B{}^{1}H{}$, ${}^{31}P{}^{1}H{}$) spectrometers. All NMR spectral data are reported in ppm, and NMR spectra of ¹H and ¹³C were internally referenced to the residual solvent peak. The other nuclei were referenced externally with the following standards: ¹¹B (BF₃·OEt₂, δ 0), ¹⁹F (C₆F₆, δ -163.0), ³¹P $(H_3PO_4, \delta 0)$. For all air- and (or) moisture-sensitive compounds and reactions, NMR samples were prepared in the glove box and the NMR tubes were capped with rubber septa. Temperature calibration for the NMR spectra was achieved by monitoring the ¹H NMR spectrum of methanol or ethylene glycol (37).

Cyclic voltammetry studies were carried out in a threeelectrode cell using a PerkinElmer EG & G instrument (Princeton Applied Research) potentiostat, model 283, connected to a drybox and equipped with a PowerCVTM PowerSuite cyclic voltammetry software. A platinum disk electrode (1.6 mm diameter) and a platinum wire were used as the working electrode and the counter electrode, respectively. A silver wire was employed as a pseudoreference electrode. All the electrodes were purchased from BAS, Inc. All cyclic voltammetry experiments and handling of solids were performed in an argon-filled drybox at room temperature. THF (5 mL, previously dried and degassed) was syringed into an electrochemical cell containing $[n-Bu_4N][B(C_6F_5)_4]$, and the mixture was stirred until complete dissolution to give a solution of concentration 0.1 mol L^{-1} . A background test was run, and in cases where traces of oxygen were detected, the system was additionally degassed by blowing argon through the solution with the aid of a Pasteur pipette. The samples (0.01 mol L^{-1}) were then run at 50, 100, 200, 500, and 1000 mV s⁻¹ using Cp₂Fe (0.01 mol L⁻¹) as an internal standard. Electrochemical grade [n-Bu₄N][B(C₆F₅)₄] was synthesized according to literature procedures (32) and dried overnight at 130 °C.

Elemental analysis was performed by Dorothy Fox or Roxanna Smith within the department using a Control Equipment Corporation (CEC) 440 elemental analyzer. IR spectral samples were analyzed as KBr plates using a NEXUS 470 FT-IR ESP spectrometer. Electron paramagnetic spectra (EPR) were recorded on a Bruker EMX spectrometer at -50 °C, referencing externally against diphenylpicrylhydrazyl (DPPH, g = 2.0036) as a standard. $C_6F_5BC_{12}F_8$ (1), $CH_3BC_{12}F_8$ (2), $C_6H_5BC_{12}H_8$, and $B(C_6F_5)_3$ ·MeCN were synthesized via literature procedures. B(C₆F₅)₃ was purchased from Boulder Scientific and purified by reaction with Me₂SiH(Cl) in hexanes followed by vacuum sublimation (120 °C, dynamic vacuum). Reagent quantities of PMe₃ and MeCN were dried using 4 Å molecular sieves and CaH₂, respectively, then freshly distilled before use or vacuum transferred directly into reaction vessels. All other reagents were purchased from Aldrich Chemicals and used as received.

Preparation of C₁₂F₈BC₆F₅(CH₃CN) (1·MeCN)

C₁₂F₈BC₆F₅ (0.081 g, 0.17 mmol) was placed in a roundbottom flask, and the flask was evacuated and cooled to -78 °C. Methylene chloride (10 mL) was condensed onto the solid, and the solution was stirred. CH₃CN (excess) was then condensed onto the stirred solution. Immediately on exposure to the CH₃CN vapours, the green colour of the 9borafluorene discharged. The reaction was warmed to room temperature and stirred for 30 min. The solvent was removed in vacuo, and a white powder was obtained. Yield: 0.088 g, 99%. IR (KBr, cm⁻¹) v: 2361 (C=N stretch). ¹H NMR (CD₂Cl₂) δ : 2.66 (s, 3H, *Me*CN). ¹¹B{¹H} NMR $(C_6D_6) \delta$: -8.7 (br). ¹⁹F NMR (CD₂Cl₂) δ : -134.6 (m, 4F, overlapped 2F o-C₆F₅), -136.3 (m, 2F), -155.6 (m, 2F), -156.9 (m, 2F), -157.7 (m, 1F, p-C₆F₅), -164.1 (m, 2F, m-C₆F₅). Anal. calcd. for C₁₆H₃BF₁₃N: C 46.64, H 0.59, N 2.72; found: C 46.25, H 0.85, N 2.71.

Preparation of C₁₂F₈BC₆F₅(THF) (1·THF)

Synthesis was identical to the method employed for $C_{12}F_8BC_6F_5(CH_3CN)$ using $C_{12}F_8BC_6F_5$ (0.084 g, 0.18 mmol). Yield: 0.097 g, 100%. ¹H NMR (CD₂Cl₂) δ : 4.24 (m, 4H, THF), 2.15 (m, 4H, THF). ¹¹B{¹H} NMR (C₆D₆) δ : 4.1. ¹⁹F NMR (CD₂Cl₂) δ : -126.2 (m, 2F, *o*-C₆F₅), -132.6 (m, 2F), -133.7 (m, 2F), -134.5 (m, 2F), -154.6 (m, 2F), -157.1 (m, 1F, *p*-C₆F₅), -163.7 (m, 2F, *m*-C₆F₅). Anal. calcd. for $C_{18}H_8BF_{13}O$: C 48.39, H 1.48; found: C 48.19, H 1.27.

Preparation of C₁₂F₈BC₆F₅(PMe₃) (1·PMe₃)

Synthesis was identical to the method employed for $C_{12}F_8BC_6F_5(CH_3CN)$ using $C_{12}F_8BC_6F_5$ (0.082 g, 0.17 mmol). Yield: 0.094 g, 99%. ¹H NMR (CD_2Cl_2) δ : 1.31 (d, 9H, ²J_{H-P} = 11.0 Hz). ¹¹B{¹H} NMR (C_6D_6) δ : -15.2 (d, ¹J_{B-P} = 87 Hz). ¹⁹F NMR (CD_2Cl_2) δ : -130.4 (m, 2F, *o*- C_6F_5), -133.4 (m, 2F) -133.7 (m, 2F), -156.0 (m, 2F), -156.6 (m, 2F), -157.8 (m, 1F, *p*- C_6F_5), -163.7 (m, 2F, *m*- C_6F_5). ³¹P{¹H} NMR (C_6D_6) δ : -14.2 (m). Anal. calcd. for $C_{17}H_9BF_{13}P$: C 45.85, H 1.65; found: C 45.57, H 1.60.

Typical conditions for competition experiments

1·THF (0.008 g, 15 μ mol) and B(C₆F₅)₃ (0.008 g, 16 μ mol) were weighed into an NMR tube and d_8 -toluene (~0.5 mL) was added. The signals in the NMR spectra were identified by comparison to authentic samples. Equilibrium

constants were evaluated by integration of the ¹⁹F NMR spectra of all peaks that were baseline separated.

Preparation of [Cp*₂Co]⁺[1·Cl]⁻

Cp*₂Co (35 mg, 0.11 mmol) was dissolved in ca. 3 mL of CH₂Cl₂ in a vial and added dropwise to a solution of **1** (50 mg, 0.11 mmol), also dissolved in ca. 3 mL of CH₂Cl₂. The brown solution was stirred for 20 min and then layered with hexanes. After cooling overnight at -35 °C, brown crystals of [Cp*₂Co]⁺[**1**·Cl]⁻ were obtained. Yield: 45 mg, 53%. ¹H NMR (CD₂Cl₂) δ: 1.70 (s, 15H, C₅(CH₃)₅). ¹³C{¹H} NMR (C₆D₆) δ: 94.0 (s, C₅(CH₃)₅), 7.1 (s, C₅(CH₃)₅). ¹¹B{¹H} NMR (C₆D₆) δ: -14.0. ¹⁹F{¹H} NMR (CD₂Cl₂) δ: -130.2 (2F, *o*-F), -136.5 (2F), -137.2 (2F), -158.5 (2F), -159.9 (2F), -161.0 (1F, *m*-F), -165.7 (2F, *p*-F). Anal. calcd. for C₃₈H₃₀F₁₃BClCo: C 54.36, H 3.58; found: C 54.21, H 3.35.

Preparation of C₁₂F₈BMe(CH₃CN) (2·MeCN)

C₁₂F₈BMe (0.053 g, 0.16 mmol) was weighed into a round-bottom flask, which was evacuated and cooled to −78 °C. Methylene chloride (10 mL) was condensed onto the solid, and the solution was stirred. CH₃CN (~2 mL, excess) was then condensed onto the stirred solution. Immediately on exposure to the CH₃CN vapors, the green colour of the 9-borafluorene discharged. The reaction was warmed to room temperature and stirred for an additional 30 min. The solvent was removed in vacuo, and a white powder was obtained. Yield: 0.058 g, 97%. IR (KBr, cm⁻¹) v: 2364 (C≡N stretch). ¹H NMR (CD₂Cl₂) δ: 2.42 (s, 3H, *Me*CN), 0.38 (s, 3H, *BMe*). ¹¹B{¹H} NMR (C₆D₆) δ: −5.1. ¹⁹F NMR (CD₂Cl₂) δ: −135.5 (m, 2F), −138.4 (m, 2F), −157.6 (m, 2F), −158.1 (m, 2F). Anal. calcd. for C₁₅H₆BF₈N: C 49.87, H 1.67, N 3.86; found: C 49.54, H 1.37, N 3.57.

Preparation of C₁₂F₈BMe(THF) (2·THF)

Synthesis was identical to the method employed for $C_{12}F_8BMe(CH_3CN)$ using $C_{12}F_8BMe$ (0.057 g, 0.18 mmol). Yield: 0.069 g, 99%. ¹H NMR (CD₂Cl₂) δ : 4.04 (m, 4H, THF), 2.04 (m, 4H, THF), 0.40 (s, 3H, B*Me*). ¹¹B{¹H} NMR (C₆D₆) δ : 8.6. ¹⁹F NMR (CD₂Cl₂) δ : -135.0 (m, 2F), -136.2 (m, 2F), -156.9 (m, 2F), -157.5 (m, 2F). Anal. calcd. for $C_{17}H_{11}BF_8O$: C 51.81, H 2.81; found: C 51.65, H 2.65.

Preparation of C₁₂F₈BMe(PMe₃) (2·PMe₃)

Synthesis was identical to the method employed for $C_{12}F_8BMe(CH_3CN)$ using $C_{12}F_8BMe$ (0.053 g, 0.17 mmol). Yield: 0.060 g, 92%. ¹H NMR (CD₂Cl₂) δ : 1.20 (d, 9H, ²J_{H-P} = 11.0 Hz, PMe₃), 0.36 (d, 3H, ³J_{H-P} = 19.0 Hz, BMe). ¹¹B{¹H} NMR (C₆D₆) δ : -14.0 (d, ¹J_{B-P} = 66 Hz). ¹⁹F NMR (CD₂Cl₂) δ : -134.5 (m, 2F), -134.7 (m, 2F), -158.1 (m, 2F), -158.3 (m, 2F). ³¹P{¹H} NMR (C₆D₆) δ : -11.4 (m). Anal. calcd. for $C_{16}H_{12}BF_8P$: C 48.28, H 3.04; found: C 48.20, H 2.47.

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