

The One-Electron Oxidation of an Azirirconacyclobutene in the Presence of B(C₆F₅)₃

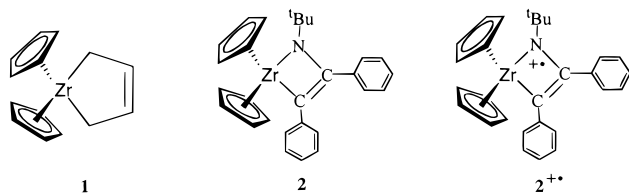
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Erker has used B(C₆F₅)₃ to generate active olefin polymerization catalysts by opening zirconacycles such as **1**.¹ In an effort to extend this work to heteroatom-substituted zirconacycles, we treated **2** with B(C₆F₅)₃. To our surprise, the result is a partial oxidation to a radical cation, **2**^{•+}.



A typical ¹H NMR spectrum of **2** after the addition of B(C₆F₅)₃ is shown in Figure 1. One set of phenyl resonances has broadened to the point of disappearance; the ^tBu signal has broadened substantially; the C₅H₅ resonance and the other phenyl resonances do not broaden significantly; the chemical shifts remain unchanged. Less broadening is observed when smaller amounts of B(C₆F₅)₃ are added. There is no immediate change in the ¹⁹F NMR spectrum of the B(C₆F₅)₃.

Such selective broadening has been seen in the ¹H NMR spectrum of partially oxidized chlorophyll a and explained by electron exchange with the corresponding radical cation.³ Indeed, the EPR spectrum of the radical cation **2**^{•+} is readily detectable at *g* = 2.0118 when solutions of **2** are treated with B(C₆F₅)₃ (Figure 2a). The observable hyperfine coupling constants (G) are *a*_N = 7.0, *a*_{H_a} = 3.2, *a*_{H_b} = 1.0, *a*_{H_c} = 3.7; those for the other protons are too small to be resolved.

While examining the ¹H NMR spectrum of partially reduced *p*-xylene, de Boer and MacLean derived the basic equations for the effect of electron exchange on NMR spectra.⁴ Equation 1 describes the line broadening due to exchange of an electron, Δ(*T*_{2ex}⁻¹), as a function of the mole fractions of the neutral and radical (f_N and f_R), the lifetime of the radical τ_R, the hyperfine coupling constant *a*, and the electron spin lattice relaxation time, *T*_{1e}.

$$\Delta(T_{2ex}^{-1}) = \frac{f_R \tau_R a^2 / 4}{1 + f_N \tau_R^2 a^2 / 4 + 2 \tau_R T_{1e}^{-1}} \quad (1)$$

Equation 1 has two limiting cases. In the large hyperfine limit,^{4–7} *a* is large enough that f_Nτ_R²*a*²/4 ≫ 1 + 2τ_R*T*_{1e}⁻¹; in the small hyperfine limit,^{4–7} *a* is small enough that f_Nτ_R²*a*²/4 + 2τ_R*T*_{1e}⁻¹ ≪ 1. Equations 2 and 3 show the consequences of these

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(1) Karl, J.; Erker, G.; Fröhlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 11165 and references therein.

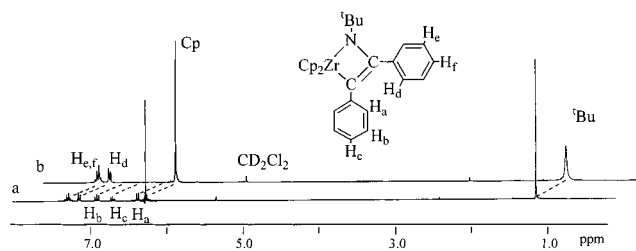


Figure 1. The 300 MHz ¹H NMR spectrum (CD₂Cl₂; 293 K) of **2** (a), and **2** (45 mM) with 16 mM B(C₆F₅)₃ (b). The taller peaks are truncated.

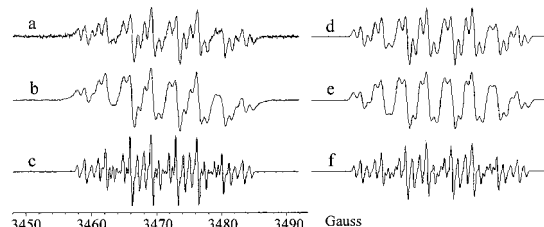


Figure 2. EPR spectra (9.775 GHz) of **2**^{•+} in CD₃C₆D₅. (a) **2** (49 mM) + B(C₆F₅)₃ (12 mM); (b) **2** (47 mM), **2**^{•+} (0.45 mM); (c) **2**^{•+} (0.45 mM). Complex **2**^{•+} in (b) and (c) was generated via oxidation of **2** with [(CpMe)₂Fe]⁺ (see text). Simulations used *a*_N = 7.0 G; *a*_{H_a} = 3.2 G; *a*_{H_b} = 1.0 G; *a*_{H_c} = 3.7 G; line broadening (G): (d) 0.65; (e) 0.85; (f) 0.40.

conditions. In eq 2, Δ(*T*_{2ex}⁻¹) is directly proportional to the rate constant for electron exchange *k*; in eq 3, Δ(*T*_{2ex}⁻¹) is inversely proportional to *k*. Thus, resonances in the large hyperfine limit will broaden as the temperature is raised, while those in the small hyperfine limit will sharpen.

$$\Delta(T_{2ex}^{-1}) = k[\text{Radical}] \quad (2)$$

$$\Delta(T_{2ex}^{-1}) = ([\text{Radical}]/[\text{Neutral}]^2)(1/4)(a^2)k^{-1} \quad (3)$$

In the present case the neutral species is **2**, the radical is **2**^{•+}, and *k* is the rate constant for electron exchange between them (eq 4). The phenyl resonances (H_a, H_b, and H_c) of solutions of **2** that contain **2**^{•+} show⁸ the increase in ¹H NMR line width with temperature expected in the large hyperfine limit (although f_Nτ_R²*a*²/4 ≈ 1).⁹



The ^tBu and C₅H₅ resonances of solutions of **2** that contain **2**^{•+} sharpen with temperature in the manner expected from eq 3, and are thus characteristic of the small hyperfine limit. The

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(5) These have been referred to as the slow exchange⁴ (or strong pulse⁶) limit and rapid exchange⁴ (or weak pulse⁷) limit cases, respectively. We prefer the terms large hyperfine and small hyperfine because there is only one *k* for exchange.

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(8) The solutions used for these experiments were prepared by oxidizing **2** with [(C₅H₅Me)₂Fe][B(C₆F₅)₄] (as mentioned later in the text). The amount of the radical cation **2**^{•+} in solutions prepared from the reaction of **2** and B(C₆F₅)₃ increases with time, along with slow formation of products that are diamagnetic but have not been identified.

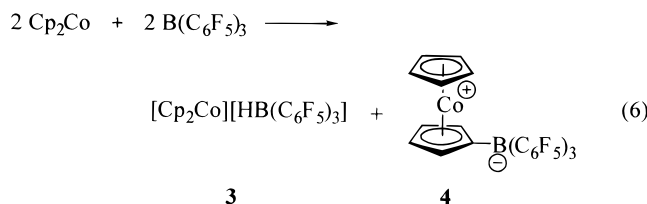
(9) If we use the *k* obtained from eq 5 at a typical [2] of 50 mM, τ_R is 1.33 × 10⁻⁷ s; f_N ≈ 1 and *a*(H_c) = 3.7 G (1 × 10⁷ Hz) make f_Nτ_R²*a*²/4 equal to 0.48—less than 1, and not in the large hyperfine limit. A quantitative test of eq 2 is difficult because the H_a, H_b, and H_c resonances in the ¹H NMR spectrum of **2** broaden significantly even at very small concentrations of **2**^{•+}.

temperature dependence of the width of the C₅H₅ resonance of **2** (Table S-1 in Supporting Information) implies an E_a of 4.1(1) kcal/mol for k .

Solutions of **2**⁺ that are free of **2** can be generated by oxidation. The CV of **2** shows a reversible one-electron oxidation at $E_{1/2}^o = -0.07$ V vs SCE in CH₂Cl₂ ([ⁿBu₄N][PF₆], 0.1 N; 50 mV/s), and the 1,1'-dimethylferricinium cation oxidizes **2** quantitatively to **2**⁺ (which can be reduced cleanly back to **2** by cobaltocene). The EPR of **2**⁺ generated with [(C₅H₄Me)₂Fe][B(C₆F₅)₄] (Figure 2c) is sharper in the absence of exchange with **2** and broadens upon addition of **2** (Figure 2b). From the excess line width in Figure 2b, ΔW , eq 5¹⁰ gives an exchange rate constant k of 1.5×10^8 M⁻¹ s⁻¹ at 293 K, implying from eq 3 and the width of the 'Bu ¹H NMR resonance at 293 K a hyperfine a_{Bu} of 0.071 G; the hyperfine of the C₅H₅ protons is similarly calculated to be 0.018 G. Oxidation of a solution of **2** with small amounts of ferricinium permits the determination of the ¹H NMR line broadening produced by a given amount of **2**⁺, and implies that less than 1% of the **2** is oxidized to **2**⁺ in a B(C₆F₅)₃ experiment.¹¹

$$k = 1.54 \times 10^7 \frac{\Delta W}{[\text{Neutral}]} \quad (5)$$

In an effort to generate a radical anion from B(C₆F₅)₃ we have treated it with cobaltocene. No radical anion is observed, but the products **3**¹² and **4** are formed cleanly in a one-to-one ratio (eq 6); the structure of **4** has been confirmed by X-ray diffraction.¹³ The oxidation of *two* cobalts to Co(III) has produced the hydride ligand in the anion of **3**, suggesting an electrophilic attack on a Cp ring of Cp₂Co.^{14,15}



Further experiments have shown that B(C₆F₅)₃ is remarkably difficult to reduce. In the presence of alkali metals a THF solution

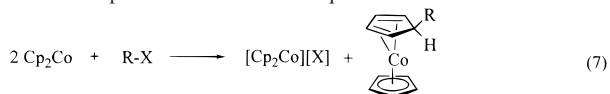
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(11) The broadening of the ¹H NMR 'Bu resonance produced by addition of B(C₆F₅)₃ solutions (~12 mM) to solutions of **2** (50 mM) varies between 5 and 25 Hz, whereas the broadening produced by 150 μM of ferricinium (enough to oxidize only 0.3% of the **2**) is 44 Hz.

(12) ¹H NMR (CD₂Cl₂) of **3**: δ 5.65 (s, 10 H); 3.65 (q, 1H, $J_{\text{B-H}} = 90$ Hz). [HB(C₆F₅)₃]⁻ is known: (a) Yang, X.; Stern, C. L.; Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1375. (b) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (c) Temme, B.; Erker, G. *J. Organomet. Chem.* **1995**, *488*, 177. (d) Röttger, D.; Schmuck, S.; Erker, G. *J. Organomet. Chem.* **1996**, *508*, 263.

(13) Crystal data for **4**: monoclinic space group $P2_1/n$ (No. 14), $a = 15.998(2)$ Å, $b = 10.116(1)$ Å, $c = 16.401(2)$ Å, $\beta = 110.918(2)^\circ$, $V = 2479.4(4)$ Å³, $Z = 4$, $T = 203$ K, R_1 ($I > 2\sigma(I)$) = 6.66%, GOF = 1.023. ¹H NMR (CD₂Cl₂) for **4**: δ 5.44 (br, 2H), 5.41 (br, 2H) 5.17 (s, 5H); ¹⁹F NMR: δ -128.1 (d, $J_{\text{F-F}} = 22.6$ Hz), -159.9 (t, $J_{\text{F-F}} = 21.2$ Hz), -164.8 (t, $J_{\text{F-F}} = 18.4$).

(14) The reaction of cobaltocene with Lewis acids has been examined in an effort to explain the mechanism of eq 7.¹⁵



The initial step in reaction 7 is generally thought¹⁵ to be an electron transfer, forming the RX^{-•} radical anion. The enhanced reactivity of BBr₃ (relative to CHBr₃ and Me₃N → BBr₃) toward Cp₂Co has been interpreted¹⁵ in terms of formation of BBr₃^{-•}. However, it is possible that the Cp₂Co/BBr₃ reaction begins with electrophilic attack by BBr₃ on cobaltocene (before formation of the charged intermediate), and it is possible that reaction 6 gives rise to a radical anion at some stage.

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of B(C₆H₅)₃ rapidly turns blue, reflecting the formation of the radical anion B(C₆H₅)₃^{-•}.¹⁶ In the presence of Na or Na/K alloy a THF solution of B(C₆F₅)₃ remains colorless, and we see no evidence of a radical anion via EPR or ¹⁹F NMR.¹⁷

The radical anion B(C₆F₅)₃^{-•} does appear in the negative ion mass spectrum of B(C₆F₅)₃, but CV experiments on B(C₆F₅)₃ have failed to provide evidence for the formation of the radical anion by reversible reduction in solution. (Electrochemistry on B(C₆F₅)₃ is complicated by the fact that it interacts with the anions—PF₆⁻, BF₄⁻, and ClO₄⁻—of common supporting electrolytes, as shown by ¹⁹F NMR.) Reversible reduction is also unobservable for B(C₆H₅)₃; the radical anion apparently becomes adsorbed on electrode surfaces.¹⁶

No radical other than **2**⁺ can be detected when the reaction of **2** with B(C₆F₅)₃ is examined by EPR. Because so little of the **2** is converted to **2**⁺, the possibility that impurities play a role cannot be excluded. Addition of (H₂O)B(C₆F₅)₃¹⁸ (traces of which remain even after sublimation of commercial B(C₆F₅)₃) or [PhNMe₂H][B(C₆F₅)₄] to solutions of **2** causes formation of **2**⁺, although less cleanly than does B(C₆F₅)₃ alone. We have always observed the formation of some **2**⁺ from the reaction of **2** and B(C₆F₅)₃ no matter how carefully the reagents are purified (recrystallization, sublimation, etc.).

“There is no definite knowledge of either the nature of the counterion or the fate of the electrons”¹⁹ in many reactions that generate radical cations. For example, various Lewis acid/solvent combinations (AlCl₃/CH₂Cl₂, AlCl₃/CH₃NO₂, BF₃/SO₂, SbCl₅/PhNO₂, etc.)^{19,20} oxidize neutral organic molecules by one electron, but [as Bard, Ledwith, and Shine have noted for aromatic substrates] “the final state of the electron acceptor is not too well-known”, and the “Lewis-acid anion radical has never been detected”.¹⁹ The formation of some **2**⁺ from **2** can also be effected by another Lewis acid, methyl alumoxane (Aldrich, 10% in toluene).

The above results raise the possibility that one-electron transfer is involved in other reactions of B(C₆F₅)₃.

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Supporting Information Available: Experimental details, ¹H NMR line widths, and X-ray structural information on **4** (PDF). An X-ray crystallographic file on **4**, in CIF format, is also available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) The reaction of B(C₆F₅)₃ with Na or Na/K alloy in a variety of solvents (diglyme, toluene, THF, Et₂O, and toluene/THF mixtures) resulted in slow decomposition of the B(C₆F₅)₃ (¹⁹F NMR). These reactions were not noticeably exothermic, but extreme caution should be exercised in the reaction of perfluorinated organics with alkali metals (see the Caution in Marsella, J. A.; Gilicinski, A. G.; Coughlin, A. M.; Pez, G. P. *J. Org. Chem.* **1992**, *57*, 2856–2860).

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