

Figure 2. Steady-state cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ at a gold electrode modified with 1.5- μm -thick porous Al_2O_3 film impregnated with PVP by contact with 0.5% (w/v) PVP solution in CH_3OH : (A) 1.0 mM $\text{K}_4\text{Fe}(\text{CN})_6$, 0.1 M CF_3COONa , pH 8.0, $v = 50$ mV/s; identical voltammograms are produced in this solution at a bare gold electrode of the same geometric surface area. (B) Medium transfer experiment: the electrode from (A) was first exposed to a 1mM $\text{K}_4\text{Fe}(\text{CN})_6$, pH 3.0 solution and then transferred to a 0.1 M $\text{CF}_3\text{COOH}/\text{CF}_3\text{COONa}$, pH 2.8 solution (continuous line);¹⁰ dashed line, blank voltammogram, 30 μM $\text{K}_4\text{Fe}(\text{CN})_6$, pH 8.0.¹⁰

ferrocyanide oxidation along the oxide pores by the solution ferricyanide ions inside the pores.

Concluding, the open and well-characterized microstructure of these rigid aluminum oxide films is the most attractive and advantageous feature of this material as an electrode matrix. We have shown an example of reagent immobilization along the oxide pores by impregnation of the oxide structure with a polymer. Electron transport in these types of systems consists of a lateral electron or charge propagation along the pores and constitutes for us a separate problem of considerable interest.

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Registry No. $\text{Fe}(\text{CN})_6^{3-}$, 13408-62-3; $\text{Fe}(\text{CN})_6^{4-}$, 13408-63-4; Al_2O_3 , 1344-28-1; Au, 7440-57-5; H_3PO_4 , 7664-38-2; PVP (homopolymer), 25232-41-1; aluminum, 7429-90-5.

Hydride Sponge: 1,8-Naphthalenediylbis(dimethylborane)

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The complexation of cations with rigid polydentate ligands has been studied in numerous research groups during the past 2 decades.¹ It is only very recently, however, that the converse problem of anion complexation by electron-deficient compounds has received widespread attention. Lehn et al.² and Schmidtchen³ have elegantly determined the complexing abilities of rigid polyaza cations with their counterions. The work of Shriver and Biallas⁴ on 1,2-diborylethanes and also that of Kuivila et al.⁵ on distannylmethanes has demonstrated chelate effects in nonrigid bidentate Lewis acids interacting with Lewis bases. Shore et al.⁶

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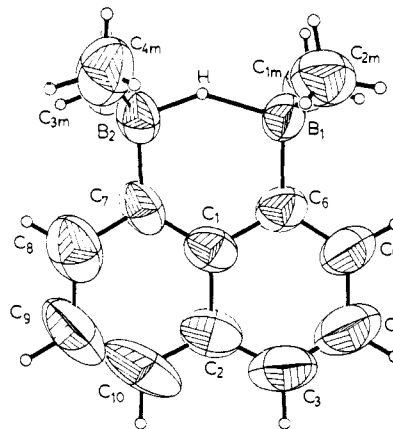
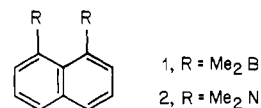


Figure 1. Perspective ORTEP drawing of 1-H^+ in crystalline $1\text{-KH}(\text{dioxane})_3$.

have prepared bridged hydrides from flexible 1,4-diborylbutanes. However, the synthesis and complexing properties of multidentate Lewis acids that are both rigid and uncharged have not been previously reported.

Conformationally defined oligoboranes are promising candidates for electron-deficient hosts that could engage in multidentate complexation with guest anions. As a prototypical example, we report the synthesis and hydride-abstracting ability of 1,8-naphthalenediylbis(dimethylborane) (**1**). This novel bis(borane) may be viewed as the electron-deficient counterpart of 1,8-bis(dimethylamino)naphthalene (**2**), "proton sponge".⁷ Just as **2**



possesses a surprisingly high proton affinity due to the enforced interaction of its lone pairs, compound **1** might be expected to complex strongly with small anions by virtue of its convergent vacant p orbitals on the boranyl groups, which are forced substantially out of conjugation with the naphthalene ring by steric repulsion of the methyls on boron. The only previous mention⁸ of an unbridged 1,8-diborylnaphthalene was an account of an unsuccessful attempt to prepare the bis(diiodoboryl) derivative.

A solution of 1,8-dilithionaphthalene⁹ was prepared¹⁰ by treating 3.43 g (9.0 mmol) of 1,8-diiodonaphthalene¹¹ dissolved in 100 mL of Et_2O with 7.1 mL (20 mmol) of 2.8 M *n*-BuLi at 0 °C for 10 min under Ar. The resulting dilithiate solution was cooled to -70 °C and transferred by cannula into a solution of Me_2BOEt ¹² (2.5 g, 29 mmol) in 20 mL of Et_2O , which also was held at -70 °C. The combined solution was stirred and allowed to warm to +10 °C, then recooled to -70 °C. Boron trifluoride etherate (2.46 mL, 2.84 g, 20 mmol) was added,¹³ the solution was again allowed to warm to +10 °C, and then the volatile components were removed in vacuo. The residue was extracted at ambient temper-

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(10) This dilithium reagent is usually generated from the 1,8-dibromide. We found the diiodide to be more conveniently obtained. The dilithiate did not react appreciably with the iodobutane side product under the conditions reported here. Interestingly, 1,8-dilithionaphthalene was unreactive toward MeI when prepared in hydrocarbon solvent.

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ature under Ar with 20 mL of dry hexane; the extract was cooled to -70°C and filtered under Ar. Concentration of the filtrate gave 1.27 g (68%) of **1** as an air-sensitive orange oil contaminated with small amounts of hydrocarbon impurities. Further purification was achieved by vacuum distillation, giving 0.81 g (43%) of a pale yellow oil: bp 130°C (0.01 kPa); ^1H NMR [(CD₂)₄O] (vs. Me₄Si) δ 7.85 (d of d, 1, $J_{2,3} = 7.9$, $J_{2,4} = 1.6$ Hz, C₂H), 7.62 (d of d, 1, $J_{4,3} = 6.9$, $J_{4,2} = 1.7$ Hz, C₄H), 7.44 (d of d, 1, $J_{3,2} \approx J_{3,4} \approx 7$ Hz, C₃H), 1.02 (s, 6, Me); ^{13}C NMR (vs. Me₄Si) δ 137.8, 134.3, 132.5, 130.8, 125.6, 14.5 (br); ^{11}B NMR (vs. BF₃·OEt₂) δ +79; mass spectrum, m/z (relative intensity) 208 (100, M⁺), 193 (26), 177 (44), 168 (60), 153 (75); high-resolution mass spectrum calcd for $^{12}\text{C}_{14}\text{H}_{18}\text{B}_2$ 208.1589, found 208.1600.

When a sample of **1** was treated with excess KH suspended in (CH₂)₄O or (CD₂)₄O, a borohydride was obtained as evidenced by upfield shifts of the ^1H and ^{11}B NMR signals. It was isolated by evaporating the solvent from the supernatant solution and crystallization of the residue in CH₂Cl₂. Anal. Calcd for C₁₄H₁₉B₂K: C, 67.80; H, 7.72; B, 8.72; K, 15.76. Found: C, 67.65; H, 7.78; B, 8.54; K, 15.58. The resulting solid adduct displayed a very broad IR band at 2065 cm⁻¹ and an ^{11}B NMR signal at +4 ppm, indicative of a bridged monohydride structure.¹⁵ (The ^1H NMR peaks were centered at 7.1 and 0.0 ppm vs. Me₄Si.) Recrystallization of the solid from dioxane gave single crystals whose structure was determined¹⁶ by X-ray diffraction (see Figure 1). The calculated structure verified that the adduct was in fact a bridged hydride. The two B-H bond lengths are 1.20 (5) and 1.49 (5) Å, while the B-H-B bond angle is 142 (4)°. These values are consistent with previously reported data for B₂(C₄H₈)₂H₃⁻ as well as with a theoretical calculation¹⁷ on B₂H₇⁻. The B-H bond lengths in **1**·KH are somewhat longer than the experimentally determined¹⁸ bridging bond lengths in B₂H₇⁻. Otherwise, the formation of **1**·KH appears to involve less strain and the loss of fewer degrees of freedom than does the formation of previously described bridged borohydrides.

Compounds **1** abstracted hydride from a variety of triorganoborohydrides, including triphenylborohydride,¹⁹ dimethyl-1-naphthylborohydride,²⁰ and the monohydride of the bis(borane)²¹ from the reaction of butadiene with 2 equiv of 9-borabicyclononane. Thus, hydride anion is strongly chelated by **1**, forming a complex of unusual thermodynamic stability. (This behavior is reminiscent of that of **2** with monoammonium salts, leading us to propose that **1** be trivially named "hydride sponge".) The complex is kinetically stable as well, failing to reduce benzaldehyde in (CH₂)₄O solution over 18 h at 60 °C. In an additional experiment, hydride was removed from bis(cyclopentadienyl)zirconium chloride hydride by **1**, which suggests **1** as a nondestructive reagent for detecting and sequestering hydride in organometallic systems.²²

The behavior of **1** in the presence of anhydrous fluoride donors indicates that **1** forms a bridged adduct with fluoride as well. This adduct is characterized by a ^1H NMR doublet at 0.06 ppm (J_{HF}

= 19 Hz) and a broad ^{19}F NMR signal at 195 ppm upfield from CFCl₃. On the other hand, **1** seems to interact weakly with chloride and bromide.

Further investigations of the physical organic chemistry of 1,8-diborylnaphthalenes are in progress. In addition, the 1,8-diborylnaphthyl unit may be useful as a building block in assembling anion binders containing several boranyl substituents, whose boron atoms are definitely spaced.

Supplementary Material Available: A listing of atomic positional and thermal parameters [K][C₁₄H₁₉B₂·3O₂C₄H₈ (7 pages). Ordering information is given on any current masthead page.

The Total Synthesis of Quinocarcinol Methyl Ester[†]

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Takahashi and Tomita recently reported the isolation of two new antitumor antibiotics, quinocarcinol (**1**) and quinocarcin (**2**), from *Streptomyces melanovineus*.¹ These structures² invite comparison with another compound of similar biological behavior, naphthyrindinomycin (**3**).^{3,4} Given the congruence of naphthyrindinomycin in its quinoidal segment with antibiotics such as the mitomycins,^{5a} saframycin,^{5b} and renieromycin,^{5c} it might well have been conjectured that this substructure is critical for biological capability. However, the apparently potent activity of the quinocarcins would tend to suggest that the hexahydroiminoazepinoisoquinoline ring system, bearing a hydroxymethyl group at the 5-position, may house much of the antibiotic function.

Our interest in the recently discovered quinocarcins evolved from a long-term pursuit directed to the total synthesis of naphthyrindinomycin. A strategy that resulted in a tetracyclic subunit, epimeric with that present in compound **3**, has recently been disclosed.⁶ With some rather considerable modification this blueprint provided the basis for a synthetic attack on the quinocarcins. An account of experiments that led to the first total synthesis of quinocarcinol (**1**) is provided herein.

The first subtarget was the vinylisoquinolinol **13**. A new sequence to reach this ring system was devised.⁷ Commercially available *m*-hydroxybenzaldehyde (**4**) was allylated (sodium hydride, allyl bromide, 93%) to afford **5**.^{8b} Claisen rearrangement (*N,N*-dimethylaniline, 230 °C) gave, not unexpectedly,^{9a} a pre-

[†] This paper is dedicated to Professor Peter Yates on the occasion of his 60th birthday.

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(8) (a) This compound was characterized by its NMR, infrared, and mass spectral properties. (b) This compound was characterized by its NMR, infrared, and mass spectral properties, as well as by combustion analysis.

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