(in the heterogeneous reaction mixtures) aggregates of lithium cyclopropylcarboxide are involved in the formation of XVIII, one unit of the aggregate serving to anchor it to the isopropyllithium hexamer, another one providing a trans C—H bond for lithiation.

Finally, we note that synthons containing nucleophilic carbon are important tools of organic synthesis. The lithiation of cyclopropylcarbinols—themselves valuable synthons owing to the large number of ways in which they can be prepared and subjected to further transformation[20]—holds promise of providing a new kind of such species.[21-23]

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(22) Part of this work has been carried out with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) via the Netherlands Foundation for Chemical Research (S.O.N.).
(23) NOTE ADDED IN PROOF. Referring to a recent paper (W. A. Beavers, S. E. Wilson, Bernard Gordon III, R. B. Bates, and A. R. Romano, *Tetrahedron Lett.*, 1675 (1979), J. Stapersma has suggested that cyclopropyllithiums, which on carboxylation yield X, may also undergo 1,2-hydrogen shift leading to XVIII.

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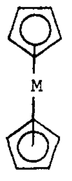
Bis(borabenzene)iron. Nucleophilic and Electrophilic Substitution in Borabenzene–Iron Complexes

Sir:

Metallocene (**1**) and bis(arene)-metal (**2**) systems are among the most familiar organometallic compounds. Bis(borabenzene)-transition metal derivatives (**3**) are formally



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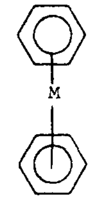

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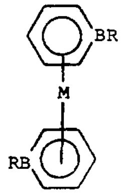

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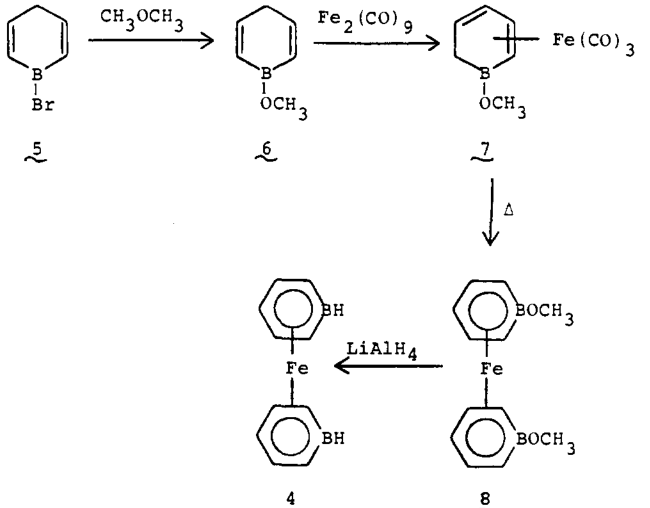
similar, since the borabenzene moiety behaves as a 6-π-electron ligand.[1] Bis(1-substituted borabenzene)cobalt compounds were first prepared by Herberich in 1970 via a ring expansion of cobaltocene with boron halides.[2] Subsequently, it was found that the reaction of alkali metal salts of 1-substituted borabenzene anions with appropriate metal halides gave 1-substituted borabenzene–metal derivatives.[3,4] Although substantial data are now available for 1-substituted complexes,[5] the parent system $M(C_5BH_6)_2$ has not previously been prepared.[6] We now report on bis(borabenzene)iron (**4**) prepared by a novel route.



Addition of 1-bromo-1,4-dihydroborabenzene[3] (**5**) to excess dimethyl ether gave a nearly quantitative conversion into the corresponding methoxyborane **6**: ^{1}H NMR[7] δ 2.49 (m, 2 H), 2.86 (s, 3 H), 5.95 (dt, J = 12, 1.5 Hz, 2 H), 6.90 (br d, J = 12 Hz, 2 H); ^{11}B NMR δ 38.1; mass spectra m/e 108. Heating **6** to 100 °C for 12 h with an excess of $Fe_2(CO)_9$ gave the conjugated diene–$Fe(CO)_3$ complex **7** as a very air-sensitive yellow oil: ^{1}H NMR δ 0.72 (d, J = 17 Hz, exo H_6),[8] 1.20 (dd, J = 17, 6 Hz, endo H_6),[8] 1.94 (d, J = 9.5 Hz, H_2), 2.81 (dd, J = 7, 6 Hz, H_5), 3.25 (s, OCH_3), 4.75 (dd, J = 7, 5.5 Hz, H_4), 5.45 (dd, J = 9.5, 5.5 Hz, H_3); ^{11}B NMR δ 38.8; mass spectra m/e 248. In contrast to previously reported boradiene–metal complexes, the lack of any change in the ^{11}B chemical shift between **6** and **7** indicates there is no metal–boron bonding.[8,9] Heating **7** to 165 °C for 12 h gave bis(1-methoxyborabenzene)iron (**8**). Alternatively, **8** was obtained in higher yield directly from heating **6** with $Fe_2(CO)_9$ at 165 °C. Bis(1-methoxyborabenzene)iron (**8**) was obtained as a red oil: ^{1}H NMR δ 3.77 (s, OCH_3), 3.91 (d, J = 11 Hz, $H_{2,6}$), 4.38 (t, J = 7 Hz, H_4), 4.89 (dd, J = 7, 11 Hz, $H_{3,5}$); ^{11}B NMR δ 23.6; mass spectra m/e 270 (base peak, M^+ for $C_{12}H_{16}{}^{11}B_2{}^{56}Fe$).

The B-OCH_3 group undergoes facile nucleophilic dis-

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placement when **8** is treated with strong bases. Thus, methyllithium and **8** gave bis(1-methylborabenzene)iron in 87% yield. Similarly, the reaction of **8** with $LiAlH_4$ gave 85% of the desired **4**. Bis(borabenzene)iron, obtained as red octahedral crystals which sublimed at 165 °C, is readily characterized by its mass spectra *m/e* 210 (base peak, M^+ for $C_{10}H_{12}{}^{11}B_2{}^{56}Fe$), ^{11}B NMR δ 13.6 (d, J_{BH} = 129.4 Hz), and Ir (KBr) 2510 cm^{-1} (BH). The ^1H NMR spectrum shows a very closely spaced pattern consisting of a six-proton multiplet centered at δ 4.87 ($H_{3,5}$, H_4) and a four-proton multiplet at δ 4.63 ($H_{2,6}$). The ^{11}B decoupled proton spectrum showed the B-H resonance also at δ 4.63.

Crystals of **4** grown from toluene-heptane were subjected to a preliminary X-ray diffraction study. They belonged to the cubic crystal class, with a cell constant a = 9.799 Å. The data were consistent with space group P_a3. Since the measured density of 1.47 g/cm^3 (calcd 1.48 g/cm^3) requires four molecules of $C_{10}H_{12}B_2Fe$ in the unit cell, the molecules must lie at special positions on threefold axes of the crystal. As the overall point symmetry of bis(borabenzene)iron can be no higher than C_{2h}, the boron and carbon atoms were not differentiated. Further refinement seemed unwarranted.[10] However, it is particularly interesting to note that bis(borabenzene)iron is isostructural with the isoelectronic bis(benzene)chromium.[11]

Attempts to metalate bis(borabenzene)iron with butyllithium (ferrocene metalation conditions) gave only hydride displacement to bis(1-butylborabenzene)iron. Although **4** is ultimately destroyed by treatment with trifluoroacetic acid-d, the reisolated bis(borabenzene)iron shows incorporation of up to four α-D atoms: mass spectral envelope *m/e* 214–210; ^1H NMR diminished intensity at δ 4.63. Exchange at BH was small since there was no strong B-D IR absorption.[12] Thus, bis(borabenzene)iron undergoes electrophilic aromatic substitution primarily at carbon (α) and nucleophilic substitution at boron.

Acknowledgment. This work was partially supported by grants from the National Science Foundation.

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(12) Bis(borabenzene-d_1)iron, prepared from lithium aluminum deuteride and **8**, showed strong IR bands at 1920–1860 cm^{-1}. From the IR spectra of mixtures of bis(borabenzene)iron and bis(borabenzene-d_1)iron, it was estimated that there had been no more than 5% B–H exchange.

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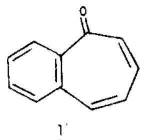
7-Phenoxy-3,4-benzotropone: Chemistry and Spectroscopy of an Isobenzotropone[1]

Sir:

Semiempirical molecular orbital calculations predict strong stabilization by π-electron delocalization in 2,3-benzotropone (**1**, 20.6 kcal/mol) and 4,5-benzotropone (**2**, 18.7 kcal/mol).[2] In sharp contrast, these calculations predict that 3,4-benzotropone (**3**) will be only weakly stabilized (3.4 kcal/mol) by π-electron delocalization.[2] These calculations also suggest that the tropone moiety has a bond-alternate structure and contributes little to the π-electron stabilization.[2] Examples of **1** and **2** have been known for some time.[3] Information on systems related to **3** is almost completely lacking. Bauld has provided chemical trapping evidence for ortho quinoidal dibenzotropones and has reported ν_{CO} values for these intriguing molecules,[4] and Yoshioka et al.[5] have suggested 2-hydroxy-3,4-benzotropone as an intermediate in a reaction. We report the generation and chemical and spectroscopic characterization of 7-phenoxy-3,4-benzotropone, an isobenzotropone.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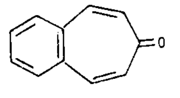
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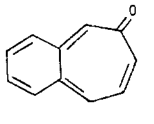
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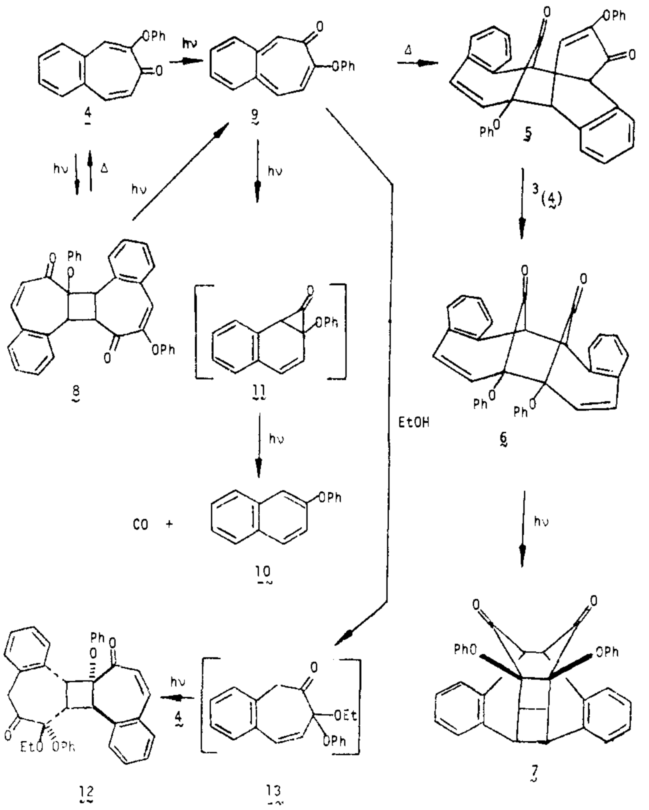
We have shown previously that irradiation of 2-phenoxy-4,5-benzotropone (**4**) gives three rearranged dimers (**5–7**).[6]



Labeling studies with ^{18}O labels in either the carbonyl group or the phenoxy group show that an oxygen to oxygen phenyl shift occurs in the formation of the dimers.[7] Irradiation of **4** in ethanol at −75 °C or at concentrations $>10^{-2}$ M in ethanol at room temperature gives a new dimer (**8**)[8] in addition to **5** and **6**.

Irradiation (<400 nm) of **4** in dilute ethanol solution at −78 °C produces a photostationary state involving **4** and a new product identified as 7-phenoxy-3,4-benzotropone (**9**), by the observations which follow. Irradiation (>400 nm) of the new product regenerates **4**. The ultraviolet spectrum of **9** shows

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