Borepins and group 15 element heteroles

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Abstract - The syntheses, spectroscopic and chemical properties of borepins, the group 15 element heteroles and their transition metal complexes are discussed.

INTRODUCTION

The study of the chemistry of heterobenzenes **1** involving boron (ref. 1) and the group 15 elements (ref. 2) has greatly enlarged our knowledge of aromaticity and heteroatom carbon multiple bonding. To extend this work we have sought to prepare analogous minimally substituted seven- and five-membered ring compounds **2**, **3**, and **4**.


E = BR, P, As, Sb, Bi

1   **2**

E = P, As, Sb, Bi

3   **4**
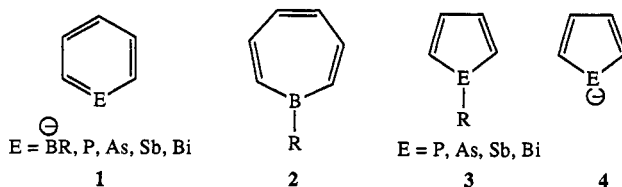
1-SUBSTITUTED BOREPINS

The heterocycle borepin **2** is of substantial theoretical interest, since it is the neutral boron analog of tropylium. However, M.O. calculations suggest that borepin is only weakly aromatic, since the electropositive boron may be unable to accept substantial π-electron density from the more electronegative carbon (ref. 3). Prior to our work only heavily substituted borepins such as **5** (ref. 4) and **6** (ref. 5) had been reported. Since it can be argued that this substitution may mask the intrinsic properties of the ring system, we have prepared minimally substituted borepin **10** (ref. 6).


5   **6**
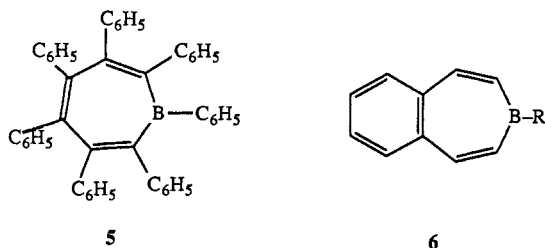
Scheme 1 Preparation of 1-methyl-4,5-cyclopentenoborepin, **10**

7   **8**   **9**   **10**
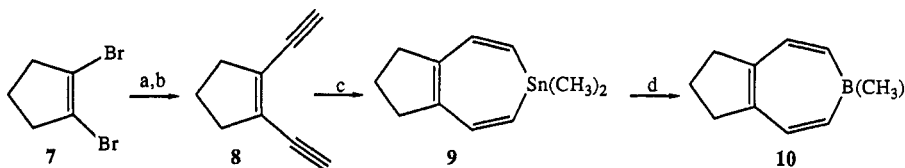
(a) HC≡CS · Me₃, Pd(PPh₃)₂Cl₂, CuI, piperidine; (b) AgNO₃ / C₂H₅OH; KCN / H₂O; (c) Me₂SnH₂, KOH, 18-Crown-6 ether, benzene; (d) CH₃BBr₂, pentane.

The above synthesis relies on the precedent of the van der Kerk conversion of 1,2-diethynylbenzene to **6** (ref. 5) with several important modifications. Enediyne **8** was selected as a starting material because the five-membered ring fixes the 1,2-diethynyl stereochemistry <u>cis</u> and 3,4-dialkyl-3-hexene-1,5-diynes are more robust than less substituted enediynes (ref. 7). Since thermal hydrostannation conditions (100° C, > 3h) polymerize 3-hexene-1,5-diyne, a mild base-catalyzed ring closure has been developed. The stannepin **9** is moderately thermally labile. Heating to 100° C gives indane and dimethyl stannylene, which can be trapped with CH₃I or (CH₃)₂S₂ (ref. 8). The exchange reaction of **9** with methylboron dibromide affords the desired borepin **10**.

Extension of this synthesis to the parent 1-methylborepin **14** is only moderately satisfactory. Since the major product of base catalyzed hydrostannation of <u>cis</u>-3-hexene-1,5-diyne is **12** rather than the desired stannepin **13**, only modest quantities of **14** are available. The conversion of **13a** to **14** has been reported by Nakadaira, Sato, and Sakurai (ref. 9).

a, R = n–C₄H₉
b, R = t–C₄H₉
c, R = CH₃
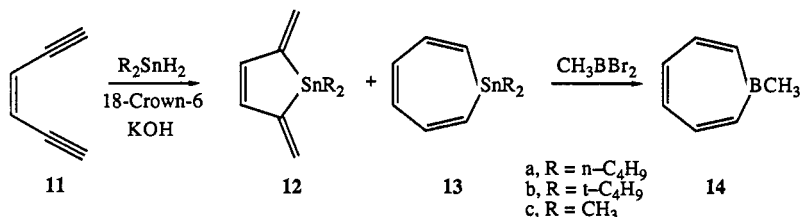
Unlike its stannepin precursor borepin **10** is thermally stable to 150° C in dilute solution. Its UV spectrum (λ_{max}223, 315 nm) closely matches that of tropone (λ_{max} 225, 312 nm) suggesting that the boron atom is strongly conjugated to the carbocyclic portion of the molecule. The ¹H NMR chemical shift values of borepin **10** show a substantial diatropic shift relative to 1-methyl-4,5-dihydroborepin **15**, which is consistent with a substantial ring current and/or electron donation from carbon to boron.
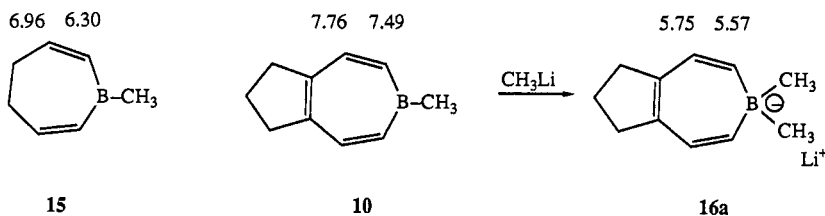

Fig. 1. Comparison of the ¹H NMR chemical shift values of 1-methyl-4,5-cyclopentenoborepin **10** with similar compounds.

Borepin **10** is attacked by nucleophiles at boron to produce the non-aromatic boratepin **16**. As expected there is a large paratropic shift for the olefin NMR signals of **16**. We have been unable to detect any of the boratanorcardiene valence **17**. These results contrast with those of Schuster who found that **19** was favored over **18** (ref. 10). Apparently this equilibrium is as sensitive to substitution effects as the better known cycloheptatriene/norcardiene equilibrium (ref. 11).
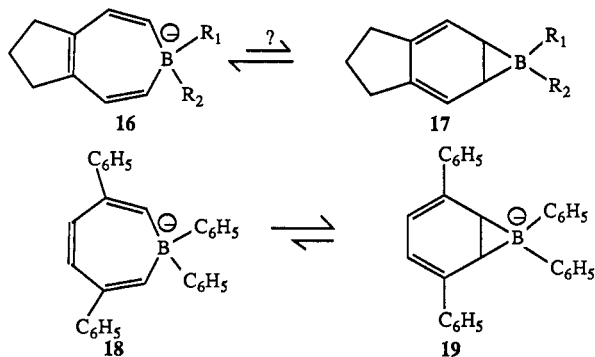
Borepins are good ligands towards transition metals. The reaction of **10** with Cr(CO)₃(CH₃CN)₃ in THF gives the Cr(CO)₃ adduct **20**. The upfield shifts observed for the boron and carbon signals in the NMR spectrum of **20** relative to **10** indicates that borepin is a heptahapto ligand. Benzoborepin **6** forms a similar adduct **21** in which the borepin rather than the benzo ring is coordinated to Cr. This adduct shows no tendency to undergo haptotropic migration to hypothetical benzo coordinated complex **22** (ref. 8).
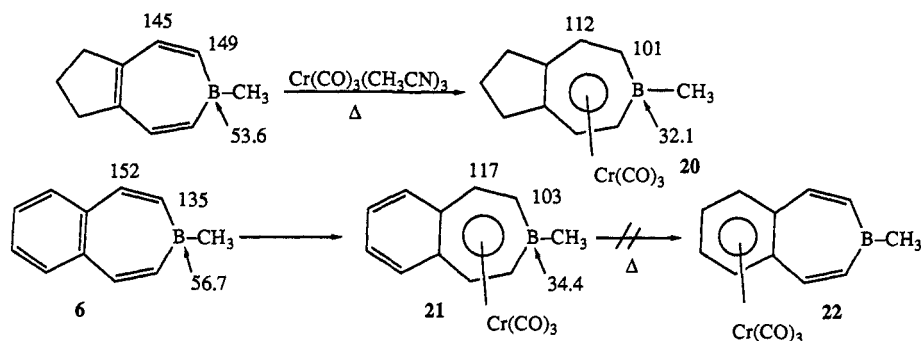
Fig. 2. Comparison of the ^{11}B and ^{13}C NMR chemical shift values of borepins with their Cr(CO)$_3$ complexes. The boron shifts are indicated with arrows.

GROUP 15 ELEMENT HETEROLES

The pyrrole analogs **3** and the corresponding anions **4** are of considerable interest for comparison to the better studied heterobenzenes **1**. Although phospholes are readily available (ref. 12), only more highly substituted derivatives of arsoles, stiboles, and bismoles had previously been reported (ref. 13-16). The well known preparation of perphenylheteroles from 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (**23** → **24**) (ref. 13) inspired the following synthesis of C-unsubstituted heteroles (ref. 17).
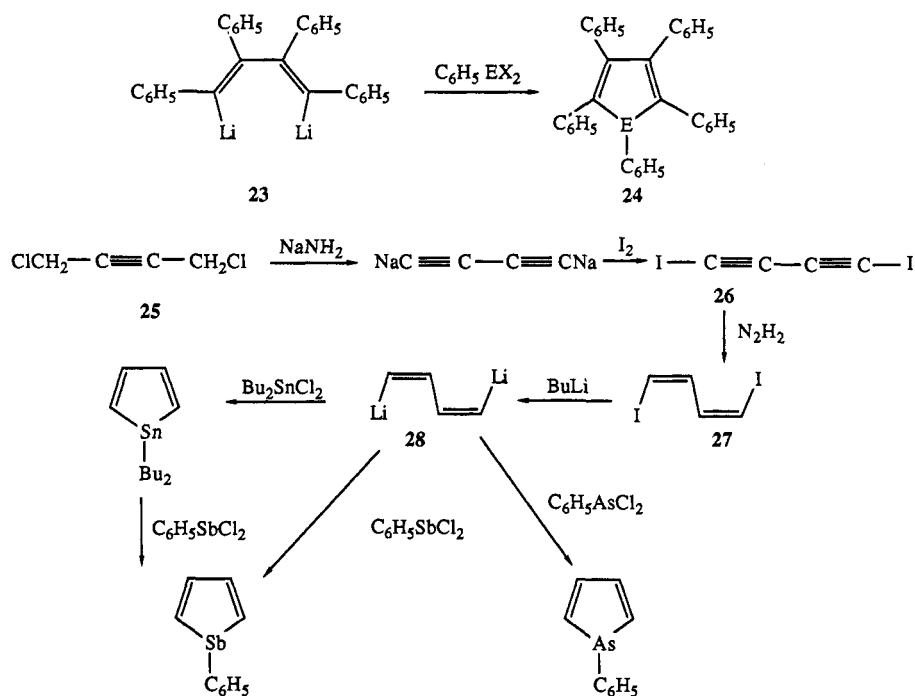
This synthesis suffers from two important limitations: (a) the explosive diiodide **26** is somewhat hazardous to handle in multigram quantities and (b) the lithiation of **27** is accompanied by extensive elimination which limits the yields of heteroles to 10-15%.

An alternative and more satisfactory preparation of **28** can be achieved using the Li/Sn exchange reaction (ref. 18). Thus treatment of 1,4-dichlorobutadiene with trimethylstannyllithium gives the stereoisomeric 1,4-bis(trimethyl-stannyl)-1,3-butadienes (**29, 30, 31**). Compounds **29** and **31** may be converted to the corresponding dilithio-butadienes (**32** and **28**) by treatment with excess methyllithium, while **29** and **30** can be converted to **28** by reaction with <1 equivalent of methyllithium. This conversion/isomerization is an apparent consequence of the greater stability of **28** over **32** which had been predicted on theoretical grounds (ref. 19).
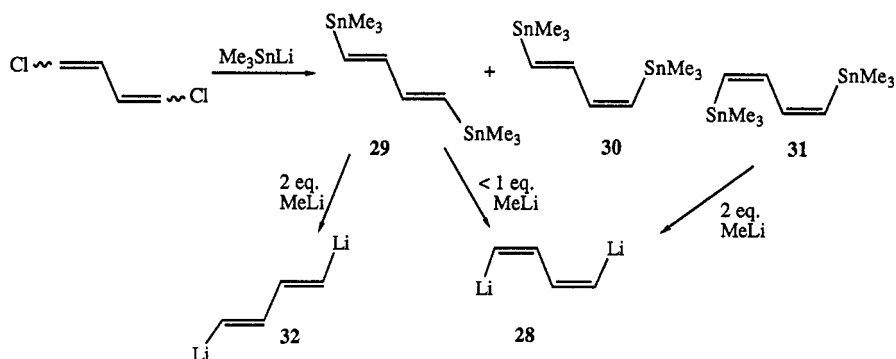
The availability of C-unsubstituted heteroles allows the preparation of the corresponding heteroferrocenes. The reaction of 1-phenylarsole with lithium in THF followed by treatment with $FeCl_2$ affords 1,1'-diarsaferrocene **33** as deep red air stable crystals (ref. 20). Electrochemical redox of **33** indicates that diarsaferrocene is harder to oxidize and easier to reduce than ferrocene. Like the corresponding diphosphaferrocene **34** the heterocyclopentadienyl rings withdraw more electron density from iron than do the cyclopentadienyl rings of ferrocene (Fig. 3).
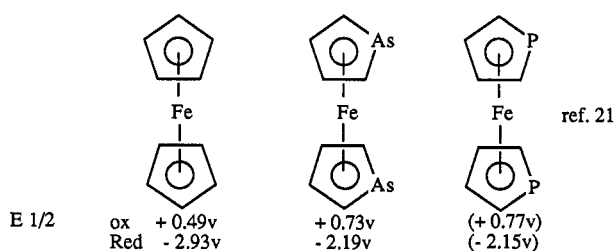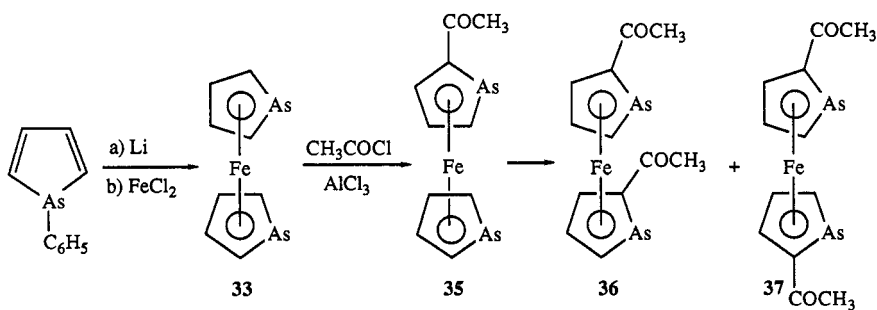

Fig. 3. Redox potentials by cyclic voltametry

1,1'-diarsaferrocene undergoes electrophilic aromatic substitution at the α-positions. Reaction with acetylchloride/$AlCl_3$ gives exclusively mono adduct **35**, and the two diastereomeric diacetyl diarsaferrocenes **36** and **37**.

Diarsaferrocene will undego rapid acid-catalyzed direction exchange. At -20° C in CF_3CO_2D/CH_2Cl_2 all four α-proton exchange, while heating for several hours at 70° C is necessary to effect exchange at the β-position. Competition experiments show that diarsaferrocene is more reactive than ferrocene or diphosphaferrocene. The relative reactivity of α/β positions is approximately 10^6. This large directive effect is much greater than that of substituted ferrocenes (ref. 22), but is reminiscent of that found for other metal-complexed heterocycles (ref. 23).
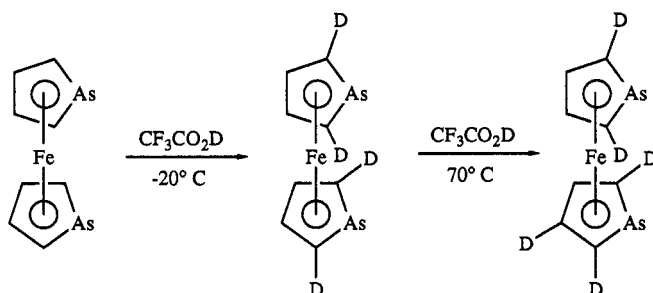
Acknowledgement

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