

Preliminary communication

INSERTION OF METHYLBORYLENE INTO C—H BONDS

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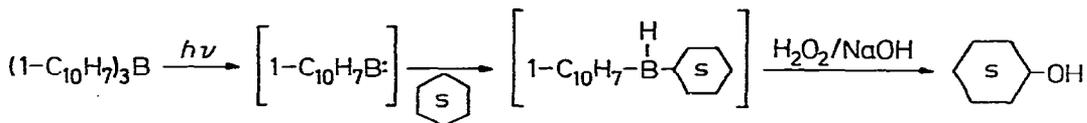
(Received January 2nd, 1980)

Summary

The insertion of methylborylene, MeB:, into C—H bonds in benzenechromium tricarbonyl and in ferrocene is described. Evidence is presented for the presence of B—H bonds in both insertion products. It is believed that in these and other reactions free methylborylene, MeB:, is involved.

We have previously shown that methylborylene can be generated by reducing methylboron dibromide with C₈K [1, 2].

The only (indirect) evidence for a borylene C—H insertion reaction reported previously was that obtained by Ramsey and Anjo [3], who found that cyclohexanol was obtained upon irradiation of tri-1-naphthylboron (I) in cyclohexane and treatment of the reaction mixture with basic aqueous dilute hydrogen peroxide. To explain this result the authors proposed the following sequence:

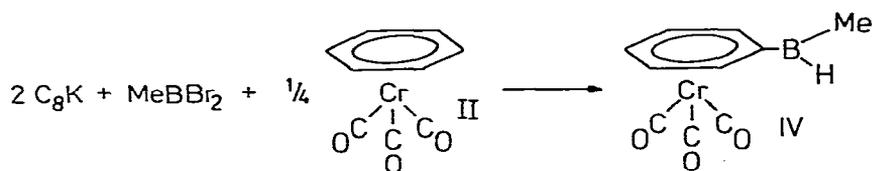


We now report the insertion of methylborylene into the C—H bonds of two transition metal sandwich complexes, viz. benzenechromium tricarbonyl (II) and ferrocene (III), and the direct identification of the primary insertion product in the first case.

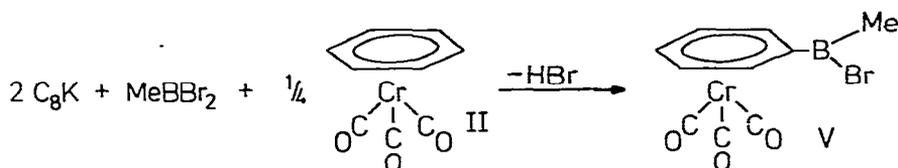
Benzenechromium tricarbonyl is quite unreactive towards electrophilic substitution and we observed that, in contrast to ferrocene, it does not react with methylboron dibromide. This observation is in agreement with that of Siebert and coworkers [4, 5] who obtained BX₂-substituted ferrocene upon treatment of this compound with BX₃ (X = Cl, Br, I).

Benzenechromium tricarbonyl was treated with excess C₈K and methylboron

dibromide (the latter two in a molar ratio 2/1) in boiling benzene. After filtering off the insoluble material, a clear, deep red solution was obtained. Removal of unchanged methylboron dibromide and the solvent (in vacuo) left a deep red paste, which upon sublimation ($130\text{--}170^\circ\text{C}/10^{-6}$ mmHg) yielded a lower zone of bright orange red crystals, and an upper zone of unreacted yellow II. The proton NMR spectra of the deep red solution and of the orange red sublimate (in benzene, reference TMS), apart from the presence of the methyl signal of MeBBr_2 at δ 0.90 ppm in the former, were completely identical. Both spectra exhibited the following signals: a doublet at δ 5.39 ppm, a triplet at δ 4.86 ppm, and a triplet at δ 4.18 ppm, with an intensity ratio of 2/1/2 and with J 6.6 Hz (these being the signals of the *ortho*-, *para*-, and *meta*-phenyl protons, respectively, in agreement with the data of Goetze and Nöth [6]). Both spectra showed a CH_3B resonance at δ 0.97 ppm (singlet). In addition, at δ 0.40 and 0.35 ppm two singlets were observed with an intensity ratio of 1/4, the intensity of both peaks taken together corresponding to one proton. These singlets, in our opinion, represent the BH resonance, which is split in two, because of the isotopic shift effect [7,8] caused by boron (the natural abundance ratio of ^{10}B and ^{11}B being 1/4). Evidently, the following reaction has occurred:



In principle, an electrophilic substitution reaction, brought about by the presence of C_8K could also have occurred:



The presence of only one set of phenyl signals (and of one methyl signal), strongly pointed to the occurrence of only one of these two reactions. In order to confirm the evidence for C—H insertion (the resonances at δ 0.40 and 0.35 ppm, ascribed to the hydride proton at boron), hexadeuterobenzenechromium tricarbonyl (VI) was synthesized and treated, as before, with an excess of C_8K and MeBBr_2 (in a molar ratio 2/1). The reaction went two to three times more slowly than with benzenechromium tricarbonyl. The product was sublimed ($130\text{--}170^\circ\text{C}/10^{-6}$ mmHg) to yield bright orange red crystals and yellow VI. The proton NMR spectrum of the orange red crystals showed only the CH_3B singlet at δ 0.97 ppm, while the phenyl signals and those assigned above to HB were absent.

Direct evidence for the presence of a B—H bond in compound IV was ob-

tained by treatment with water, hydrogen being evolved, as confirmed by GLC on molecular sieve 13X.

Upon reaction of ferrocene with excess C_8K and methylboron dibromide (in a molar ratio 2/1) in boiling benzene, in addition to electrophilic substitution, C—H insertion took place. The latter was again demonstrated by the evolution of hydrogen when water was added to the reaction product. From proton NMR evidence it was clear that substitution products had also been formed. Also in the spectra of this reaction mixture the isotopic shift effect for the boron hydride signal was observed. Because of the presence of both substitution and insertion products we were unable to isolate a discrete hydride in this case.

The insertion of methylborylene into C—H bonds via the reaction of an organic substrate with C_8K and $MeBBr_2$ does not proceed readily. When benzene or cyclohexane is used as a substrate, no phenol or cyclohexanol is found after work-up with basic aqueous dilute hydrogen peroxide (cf. Ramsey and Anjo [3]).

The insertion of carbenes into C—H bonds is more difficult than their addition to olefinic or acetylenic systems. Therefore, and in view of the fact that C—H insertions cannot be brought about via a carbenoid reaction like the Simmons—Smith reaction, we consider it likely that both the addition of methylborylene to olefinic or acetylenic systems and the insertion of methylborylene into C—H bonds takes place via a free borylene mechanism.

Acknowledgement

We wish to thank Mrs. H.J. Alberts-Jansen and Mr. A.L.M. van Eekeren for very helpful assistance in parts of this work.

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