NEW SYNTHESIS OF $B_9H_{13}L$ (L = WEAK LEWIS BASE) FROM $[B_{10}H_{10}]^{2-}$ BY CAGE OPENING AND DEGRADATION REACTIONS

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Abstract – The dianion *closo*- $[B_{10}H_{10}]^{2-}$ reacts in benzene suspension with strong acids and nitriles, acting as weak Lewis bases L , to produce LB_9H_{13} as major product along with smaller amounts of $6-(C_6H_5)B_{10}H_{13}$, $B_{10}H_{14}$ and other unidentified boranes. These products are separated on a silica gel column using a mixture of hexane and toluene as eluent. The reaction proceeds only incompletely when phosphanes are used as base.

A lot of attention has been paid in boron chemistry through past years on the development of suitable synthetic ways for LB_9H_{13} derivatives. These derivatives can be used to produce a wide variety of carbaboranes, heteroboranes and metallaboranes [1,2]. However, all synthetic ways to a wide variety of LB_9H_{13} , described until now in literature started from decaborane(14) or other open-cage boranes. The main preparative methods are based either on aqueous hydrolysis of the $[LB_{10}H_{13}]^-$ species [3], on alcoholysis of 6,9-*arachno*-(R_2S) $_2B_{10}H_{12}$ [3,4] derivatives or on direct reactions of the decaborane(14) with Lewis bases in alcohol [5]. A series of LB_9H_{13} derivatives was prepared by methathesis reactions of dialkylsulfide derivatives (R_2S) B_9H_{13} with stronger Lewis bases [3]. Other miscellaneous synthetic methods include: treatment of $i-B_9H_{15}$ in toluene with an excess of CH_3CN which gave $(CH_3CN)B_9H_{13}$ quantitatively, treatment of $M[B_9H_{14}]$ with HCl in diethylether which produced $[(C_2H_5)_2O]B_9H_{13}$ [6], pyrolysis of $[(CH_3)_3NH][B_9H_{14}]$ which yielded $[(CH_3)_3N]B_9H_{13}$ [7], and electrochemical oxidation of $[B_9H_{14}]^-$ in the presence of an appropriate ligand L which gave LB_9H_{13} [8]. The molecular structure of LB_9H_{13} shown in (fig.1) was determined by X-ray analysis [9,10].

Now we want to report the simple synthesis of the LB_9H_{13} species starting from the *closo*- $[B_{10}H_{10}]^{2-}$ anion. We found that the reactions of $(NH_4)_2[B_{10}H_{10}]$ with weak Lewis bases L in benzene under strongly acidic conditions produced directly LB_9H_{13} species. Similar reactions were already reported; however different reaction conditions led to other products. Thus, the reaction, known since a long time, of $[B_{10}H_{10}]^{2-}$ with HCl and excess of weak base $(CH_3)_2S$ produced $[B_{10}H_{11}]^-$ ion and 6,9- $[(CH_3)_2S]_2B_{10}H_{12}$ species as main products [11]. Recently, the reported [12] reaction of $[B_{10}H_{10}]^{2-}$ and triflic acid CF_3SO_3H performed in the absence of base gave $6-(C_6H_5)B_{10}H_{13}$ as the main product along with $6-(CF_3SO_3)B_{10}H_{13}$. As we found, the reaction of $[B_{10}H_{10}]^{2-}$ and CF_3SO_3H in the presence of CH_3CN produced only minor amount of the products from above reactions. The benzene phase contained $(CH_3CN)B_9H_{13}$ (60% yield) together with $6-(C_6H_5)B_{10}H_{13}$ (only 10% yield), traces of $B_{10}H_{14}$ and unidentified polymeric substances. These compounds were separated on silica gel column and characterized by ^{11}B NMR at 96.25 MHz $\{\delta(^{11}B)$ for $(CH_3CN)B_9H_{13}$: +16.8 (doublet, B_7 , J_{B-H} = 164 Hz), +3.9 (doublet, B_1 , J_{B-H} = 119 Hz), -15.32 (doublet, B_5 and B_9 , J_{B-H} = 143 Hz), -22.4 (broad, B_6 and B_8), -29.4 (doublet, B_4 , J_{B-H} = 121 Hz), -40.1 (doublet, B_2 and B_3 , J_{B-H} = 143 Hz); $\delta(^{11}B)$ for $6-(C_6H_5)B_{10}H_{13}$: +23.2 (singlet, 1B), +9.8 (doublet, 3B, J_{B-H} = 134 Hz), +1.1 (doublet, 2B, J_{B-H} = 148 Hz), -4.3 (doublet, 2B, J_{B-H} = 152 Hz), -32.6 (doublet, 1B, J_{B-H} = 153 Hz), -38.2 (doublet, 1B, J_{B-H} = 160 Hz); $\delta(^{11}B)$ for $B_{10}H_{14}$: +11.2 (doublet, 2B), +9.9 (doublet, 2B), -0.2 (doublet, 4B), -36.9 (doublet, 2B)} and by mass spectroscopy {for $(CH_3CN)B_9H_{13}$: m/z = 146.1, calculated 152.1, for $6-(C_6H_5)B_{10}H_{13}$: m/z = 192.3, calculated 198, for $B_{10}H_{14}$: m/z = 116.2, calculated 122}. Replacement of CF_3SO_3H for concentrated sulfuric acid provided the same products in the same yields. On contrary, no reaction was observed when H_3PO_4 was used as acid.

The reaction of $[B_{10}H_{10}]^{2-}$ with CF_3SO_3H and $(C_6H_5)_2CHCN$ in benzene gave $[(C_6H_5)_2CHCN]B_9H_{13}$ (20 % yield). This adduct was characterized by infrared spectroscopy {I.R data for $[(C_6H_5)_2CHCN]B_9H_{13}$: ν_{B-H} (terminal) = 2540 cm^{-1} , $\nu_{C\equiv N}$ = 2246 cm^{-1} , ν_{B-H} (bridge) = 1741 cm^{-1} , ν_{B-B} = 1100-1000 cm^{-1} }, by ^{11}B NMR $\{\delta(^{11}B)$ for $[(C_6H_5)_2CHCN]B_9H_{13}$: +16.0 (broad, 1B), +4.7 (doublet, 1B, J_{B-H} = 132 Hz), -17.8 (doublet, 2B, J_{B-H} = 144 Hz), -20.1 (broad, 3B), -39.3 (doublet, 2B, J_{B-H} = 148 Hz)} and by Electrospray(-) mass spectroscopy {this product was detected as $[C_6H_5CHCNB_9H_{13}]^-$, m/z = 227, calculated 226.2). In aqueous phase, the $[B_{10}H_{11}]^-$ anion has been found and characterized by ^{11}B NMR [14]. The reaction of $[B_{10}H_{10}]^{2-}$ with CF_3SO_3H and triphenylphosphane gave only about 10 % yield of the open-cage boranes found in the organic phase. To our knowledge the one step synthesis of LB_9H_{13} starting directly from *closo*- $[B_{10}H_{10}]^{2-}$ is unprecedented. Its advantage lies in easier availability and lower costs of $[B_{10}H_{10}]^{2-}$, which can be prepared by direct pyrolysis of $[(C_2H_5)_4N]BH_4$ [15]. Furthermore, this new method avoids handling of highly toxic and dangerous *nido*- $B_{10}H_{14}$. The *arachno*-6,9- $L_2B_{10}H_{12}$ in the reaction medium was not identified. However a possible mechanism (fig. 1) involves their formation and their degradation in acidic medium to LB_9H_{13} . 6- $(C_6H_5)B_{10}H_{13}$ is formed by electrophilic substitution of benzene by $[B_{10}H_{13}]^+$ [12]. The cage opening reaction of $[B_{10}H_{10}]^{2-}$ by acids in the presence of nitrile gave high yields of (nitrile) B_9H_{13} . With phosphanes only low yields of the respective derivatives were obtained. Apparently, phosphanes are readily protonated to phosphonium salts, and therefore, cannot act further as base.

Figure 1: Possible mechanism for the formation of $B_9H_{13}L$ from $B_{10}H_{10}^{2-}$

Experimental

^{11}B NMR spectra: Bruker AM300 spectrometer at 96.25 MHz (Et_2O-BF_3 as external reference; positive values down field) in C_6D_6 solutions. Infrared spectra: IR-FT Nicolet Magna 550 spectrometer using KBr pellets. Mass spectroscopy measurements: Fisons model 70E spectrometer (EI; 70 eV) or Electrospray(-) at the Mass Spectroscopy Laboratory, Central Analytical service of the CNRS, Solaise (France). Thin layer Chromatography was performed on Silufol [16] sheets using benzene as eluent. The spots were detected with I_2 vapor and $AgNO_3$ spraying.

Synthesis of $B_9H_{13}L$: in a typical reaction, 1.0 g of $(NH_4)_2[B_{10}H_{10}]$ (6.49 mmol) (Katchem, Prague) and 2 equivalents of the ligand L (nitrile or phosphane) were stirred in 50 ml of benzene at room temperature. 3 equivalents of concentrated acid (CF_3SO_3H or H_2SO_4) were added dropwise (~2 min). A yellow gummy material was formed which became dark yellow-green after a few minutes. After 1 h the reaction was stopped and the benzene solution was separated. TLC of one drop of the benzene solution showed at least 3 intense spots. The volume of benzene solution was reduced to 5 ml and then chromatographed on silica gel column (15 cm x 2 cm), eluting with hexane-toluene mixture (9V to 1V) gave pure 6- $B_{10}H_{13}(C_6H_5)$ and $B_{10}H_{14}$. Then, elution with pure toluene served to separate $B_9H_{13}L$. The purity of these products was monitored by TLC.

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