# A New Method for the Synthesis of Cyanohydroborates and Cyanoborane Complexes

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Mono- and di-cyanohydroborate and cyanoborane complexes can be conveniently prepared by treatment of tetrahydroborate and borane complexes with mercury(II) cyanide.

Only monocyano derivatives of the tetrahydroborate ion and of borane were known until now. The cyanotrihydroborates are widely used as selective reducing agents in organic and biochemical reactions.[1] Tumour inhibition and hypolipidemic activities have recently been described for amine–cyanoboranes and the amine–carboxyboranes[2] obtained therefrom. While the $BH_3CN^-$ ion is obtained in good yield in the reaction[3] of $BH_4^-$ with HCN, procedures for obtaining amine–cyanoboranes,[4–6] on the other hand, result in low yields,[4] are of limited scope,[5] or require very long reaction times.[6] In view of the actual and potential usefulness of the monocyano boron compounds more straightforward and convenient procedures for their preparations are desirable.

We have found that various types of cyanoboron compound can be more easily prepared *via* redox reactions using $Hg(CN)_2$ than by the reported methods.[3–6] In addition, this procedure permitted us to obtain the hitherto unknown dicyanodihydroborate ion.

Our results are summarized in the equations (1)—(5) [THF = tetrahydrofuran, diglyme = bis-(2-methoxyethyl) ether]. The HCN formed in reactions (2)—(5) was removed by continuously purging the reaction mixtures with $N_2$ and trapped in aqueous sodium hydroxide. The products of reactions (1)—(5), after separation from the mercury, were obtained by the following procedures.

$$2\,NaBH_4 + Hg(CN)_2 \xrightarrow[\text{reflux, 3 h}]{\text{THF}} 2\,NaBH_3CN + Hg + H_2 \quad (1)$$

$$2\,NaBH_4 + 3\,Hg(CN)_2 \xrightarrow[\text{reflux, 3 h}]{\text{diglyme}} 2\,NaBH_2(CN)_2 + 3\,Hg + 2\,HCN + H_2 \quad (2)$$

$$Me_2S{\cdot}BH_3 + Hg(CN)_2 \xrightarrow[\text{reflux, 0.5 h}]{\text{THF}} Me_2S{\cdot}BH_2CN + Hg + HCN \quad (3)$$

$$2\,Me_3N{\cdot}BH_3 + Hg(CN)_2 \xrightarrow[\text{reflux, 3 h}]{\text{diglyme}} Me_3N{\cdot}BH_2NCBH_3 + Hg + HCN + NMe_3 \quad (4)$$

$$4\text{-}XC_5H_4N{\cdot}BH_3 + Hg(CN)_2 \xrightarrow[\text{reflux, 3 h}]{\text{diglyme}} 4\text{-}XC_5H_4N{\cdot}BH_2CN + Hg + HCN \quad (X = CN, NMe_2) \quad (5)$$

$NaBH_3CN$ was isolated from the THF solution in 78% yield as described in the literature.[3] The diglyme solution from reaction (2) was evaporated to dryness and the residue recrystallized from dioxane to give a 92% yield of $NaBH_2(CN)_2{\cdot}2C_4H_8O_2$. Addition of amines ($4\text{-}NCC_5H_4N$, $4\text{-}Me_2NC_5H_4N$, $PhNH_2$) to $Me_2S{\cdot}BH_2CN$ [reaction (3)] in THF resulted in the formation of amine–cyanoborane complexes in good yields (72, 63, and 42%, respectively) using the following procedure. To the THF solution of these complexes water was added until the mixture became opalescent; it was then clarified with charcoal and most of the THF was eliminated in a stream of $N_2$. The crystalline products were purified further by thorough ether extraction. The products of reactions (4) and (5) were isolated through extraction with ether of the residues obtained after evaporation of the reaction mixtures under reduced pressure. Yields are: 81% for $Me_3N{\cdot}BH_2NCBH_3$, and 53% and 83% for $4\text{-}NCC_5H_4N{\cdot}BH_2CN$ and $4\text{-}Me_2NC_5H_4N{\cdot}BH_2CN$, respectively.

The redox reaction with $Hg(CN)_2$ takes place easily when the B–H bond of the compound in question has pronounced hydridic character [equations (1) and (3)]. On the other hand, the amine–cyanoboranes and the $BH_2(CN)_2^-$ ion, all of which contain B–H bonds which are very resistant to hydrolysis and oxidation, are not susceptible to reaction with $Hg(CN)_2$. It is remarkable that the dicyanoborate can be obtained in good yield in a one-step reaction with $Hg(CN)_2$. In view of the above results and those described[5,7] with $HgCl_2$ we suggest that similar redox reactions may well also take place with other $Hg^{II}$-compounds [*e.g.* $HgF_2$, $Hg(OAc)_2$, $Hg(SCN)_2$, *etc.*].

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