Nitrogen Base Donor–Cyanoborane Addition Compounds

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Summary Four amine–BH_2CN addition compounds have been prepared by the addition of the respective nitrogen base to acidified tetrahydrofuran solutions of the cyanotrihydroborate ion, and this reaction appears generally useful for the synthesis of donor–cyanoborane complexes.

THE cyanotrihydroborate ion, BH_3CN^-, was reported as early as 1951,[1,2] and a number of publications have appeared which describe new methods of synthesis,[3] spectral properties,[4] studies of hydrolysis and hydrogen exchange,[5] reducing properties,[6] complexation with transition metals,[7,8] and isomerization of the ion to the isocyano-derivative.[3] Further, on the basis of the ^{11}B n.m.r. spectrum of the respective solutions, Spielvogel and his co-workers have tentatively identified the product of the reaction of BH_3CN^- with anhydrous acids in tetrahydrofuran as the BH_2CN adduct of this solvent.[9] We offer supporting evidence for this conclusion; treatment of such tetrahydrofuran solutions with organic amines readily gives the corresponding amine–BH_2CN complexes. This reaction seems analogous to the formation of BH_3–amine complexes *via* nucleophilic substitution in the corresponding tetrahydrofuran-borane and seems generally useful for the preparation of donor–cyanoborane addition compounds. The preparation of the trimethylamine adduct is described below. The BH_2CN adducts of morpholine and 4-picoline as well as the bis(cyanoborane) complex of tetramethylethylenediamine were prepared by analogous routes (Table). Donor–BH_2CN complexes may prove useful precursors for new *B*-substituted four-co-ordinate boranes and boron ions.

Amine-cyanoboranes

Adduct	M.p.
Me_3NBH_2CN	63°
$4\text{-}MeC_5H_4NBH_2CN$	60—61°
$O(CH_2)_4NHBH_2CN$	104—106°
$(CH_2Me_2N)_2(BH_2CN)_2$	166—170°

A total of 8·6 g of $NaBH_3CN$ (0·14 mole) and 150 ml of tetrahydrofuran were treated at 0°, under nitrogen, with a solution of 1 M-HCl in tetrahydrofuran, prepared by dissolving the gas in this solvent at 20°. The acid was slowly added *via* a dropping funnel to the stirred $NaBH_3CN$ slurry until evolution of hydrogen ceased. A 2·1M-solution of Me_3N in tetrahydrofuran was then added to neutralize the excess of HCl following which additional Me_3N (8·9 g, 0·15 mole) was introduced into the resulting solution, and the mixture was stirred overnight at room temperature. Solid residue was separated from the bright yellow solution by filtration through a coarse sintered glass funnel under N_2. This solid was washed with fresh tetrahydrofuran, and traces of solvent were removed by evaporation *in vacuo*. The product was recrystallized from a mixture of ethanol, diethyl ether, and pentane. A total of 4·33 g (32·3% theory) of product was recovered by vacuum sublimation at 70°. The i.r. spectrum (solid solution in KBr) shows strong absorption in the B–H stretching region at 2410 cm^{-1} and less intense absorption in the $C\equiv N$ stretching region at 2185—2280 cm^{-1}. The ^1H n.m.r. spectrum (benzene solution) exhibits a singlet, attributed to methyl protons, at $-2·25$ p.p.m. relative to Me_4Si (external standard) and the ^{11}B n.m.r. spectrum consists of a well-resolved 1 : 2 : 1 triplet at 33·2 p.p.m. relative to $(MeO)_3B$ (external standard) with J_{B-H} 108 Hz.

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[1] G. Wittig, *Annalen*, 1951, **573**, 209.

[2] G. Wittig and P. Raff, *Z. Naturforsch.*, 1951, **6**b, 225.

[3] R. C. Wade, E. A. Sullivan, J. R. Berschied, jun., and K. F. Purcell, *Inorg. Chem.*, 1970, **9**, 2146.

[4] J. R. Berschied, jun., and K. F. Purcell, *Inorg. Chem.*, 1970, **9**, 624.

[5] M. M. Kreevoy and J. E. C. Hutchins, *J. Amer. Chem. Soc.*, 1969, **91**, 4329.

[6] R. F. Borch and H. D. Durst, *J. Amer. Chem. Soc.*, 1969, **91**, 3996.

[7] D. F. Shriver, *J. Amer. Chem. Soc.*, 1963, **85**, 1405.

[8] S. J. Lippard and P. S. Welcker, *Chem. Comm.*, 1970, 515.

[9] B. F. Spielvogel, J. M. Purser, and C. G. Moreland, Paper presented at Southeast Regional Meeting, American Chemical Society, Richmond, Va., Nov. 7, 1969. *Chem. and Engineering News*, Nov. 10, 1969, p. 38.