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Synthesis and Characterization of Some Pyridine *N*-Oxide−Cyanoborane Complexes[1]

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There has been considerable interest in the chemistry of cyanoborane complexes of *N*-bases,[2] partly due to their being considered as precursors of boron analogues of amino acids[3] and partly due to their potential therapeutic values.[4] However, no report on the cyanoborane complexes of the closely related bases, amine *N*-oxides, is found in the literature; even attempts to isolate the stable parent compounds, viz., the amine *N*-oxide−boranes[5,6] have met with either no[5] or little success.[6] We, therefore, report here the synthesis and characterization of some first examples of stable cyanoborane complexes of pyridine *N*-oxides.

Experimental Section

Pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 4-ethylpyridine, and 4-cyanopyridine were commercial products and were purified by usual methods. Sodium cyanotrihydroborate (Aldrich), a 30% H_2O_2 solution, and glacial acetic were used as received. Tetrahydrofuran (THF) was dried over $LiAlH_4$ and ethanol over CaO.

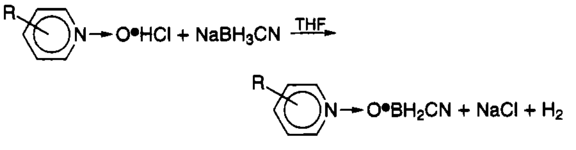
Pyridine *N*-oxides were prepared by peracetic acid oxidation of the corresponding pyridine,[7] and their hydrochlories were prepared by passing HCl gas through their solutions in dry ethanol, whereupon they were precipitated. They were washed with dry ethanol and finally dried in vacuum.

Infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer using NaCl cells. ^1H NMR spectra were recorded in DMSO-d_6 on a JEOL-JNM-FX-100 spectrometer using Me_4Si as interal reference. ^{11}B, ^{13}C, and ^{14}N NMR spectra were recorded on a Bruker AC-200 instrument at the University of Munich using respectively $Et_2O\cdot BF_3$ (external), Me_4Si (internal), and $NaNO_3$ (external) references. Boron was estimated volumetrically[8] and carbon, hydrogen, and nitrogen on a Perkin-Elmer 240C elemental analyzer. Conductances were measured on a Systronics 303 conductivity meter.

General Procedure for the Preparation of Pyridine *N*-Oxide−Cyanoborane Complexes. $NaBH_3CN$ (1.89 g, 30 mmol) and an appropriate pyridine *N*-oxide hydrochloride (30 mmol) were placed in a three-necked round-bottom flask, equipped with a reflux condenser, a nitrogen inlet, a gas bubbler, and a magnetic stirring bar, the whole setup having been previously flushed with dry nitrogen. THF (70 mL) was added to the mixture, which was first stirred at room temperature for ca. 30 min, during which time vigorous effervescence occurred. Then the mixture was refluxed overnight (ca. 18 h) by which time the gas evolution had ceased. After the mixture cooled to room temperature, the precipitated sodium chloride was removed by filtration, and the solvent was removed on a rotary evaporator to leave pale yellow thick masses as the product. These were washed with distilled water to remove the unreacted reactants, if any. The compounds were then redissolved in THF and precipitated with dry ether. After the ether was removed by decantation, the products were further washed with ether a few more times by decantation and finally dried in vacuum to leave the product as pale yellow thick liquid masses.

Results and Discussion

Although trifluoroborane adducts of pyridine *N*-oxides have been reported earlier,[8−10] $C_5H_5NO\cdot BH_3$ has been reported as too unstable to characterize,[5] and only evidence of the formation of $C_5H_5NO\cdot{\sim}0.45\ B_2H_6$ and $Me_3NO\cdot BH_3$ has been reported,[6] respectively, from tensimetric titration and ^{11}B NMR spectra; no stable borane adducts of amine *N*-oxides have so far been reported. Recently in an attempt to prepare dicyanoborane adducts of pyridine *N*-oxide $RC_5H_5NO\cdot BH(CN)_2$ from $NaBH_2(CN)_2$, only metathesis products $[RC_5H_5NOH][BH_2(CN)_2]$ could be isolated.[11] However, in the present study, reactions of pyridine *N*-oxide hydrochlorides with sodium cyanotrihydroborate have yielded pyridine *N*-oxide−cyanoborane complexes along with H_2 (eq 1). The products were obtained in 65−82% yields and are soluble in THF, DMF, and DMSO, moderately soluble in $CHCl_3$, and insoluble in benzene, ether, and light petroleum. The compounds prepared along with pertinent characterization data are given below.



(1)

$R = H, 2\text{-}CH_3, 3\text{-}CH_3, 4\text{-}CH_3, 4\text{-}C_2H_5, 4\text{-}CN$

$C_5H_5NO\cdot BH_2CN$ (1). Anal. Calcd for $C_6H_7N_2O$: C, 53.80; H, 5.27; N, 20.91; B, 8.07. Found: C, 53.14; H, 5.37; N, 20.52; B, 8.16. IR (cm^{-1}): 2390 vs, 2377 vs, sh (ν(BH)), 2280 w, 2195 s (ν(CN)), 1260 (ν(NO)), 1370 m, br (ν(BO)). $\delta(^1H)$: 7.68 d (3H) (Ar), 8.52 d (2H) (Ar). $\delta(^{11}B)$: −42.6 t. $\delta(^{14}N)$: −100 (ring N-atom). $\delta(^{13}C)$: 126.3, 126.7, 139.5, 141.3, 147.2.

$2\text{-}CH_3C_5H_4NO\cdot BH_2CN$ (2). Anal. Calcd for $C_7H_9BN_2O$: C, 56.82; H, 6.13; N, 18.93; B, 7.30. Found: C, 56.24; H, 6.20; N, 18.63; B, 7.28. IR (cm^{-1}): 2380 vs, 2370 vs, sh

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(ν(BH)), 2254 vs, 2199 ms (ν(CN)), 1221 m (ν(NO)), 1372 s (ν(BO)). $\delta(^1H)$: 2.44 s (3H) (CH_3), 7.56 m (3H) (Ar), 8.48 d (1H) (Ar). $\delta(^{11}B)$: −41.6 t.

$3\text{-}CH_3C_5H_4NO{\cdot}BH_2CN$ (3). Anal. Calcd for $C_7H_9BN_2O$: C, 56.82; H, 6.13; N, 18.93; B, 7.30. Found: C, 56.10; H, 6.29; N, 18.54; B, 6.88. IR (cm^{-1}): 2380 vs, 2370 vs, sh (ν(BH)), 2254 m, 2192 s (ν(CN)), 1280 m (ν(NO)), 1350 s (ν(BO)). $\delta(^1H)$: 2.32 s (3H) (CH_3), 7.84 d (2H) (Ar), 8.36 m (2H) (Ar). $\delta(^{11}B)$: −41.8 t. $\delta(^{14}N)$: −105 (ring N-atom). $\delta(^{13}C)$: 156.5, 165.5, 174.2, 175.9, 178.4 (ring C-atoms), 56.6 (CH_3).

$4\text{-}CH_3C_5H_4NO{\cdot}BH_2CN$ (4). Anal. Calcd for $C_7H_9BN_2O$: C, 56.82; H, 6.13; N, 18.93; B, 7.30. Found: C, 56.20; H, 6.23; N. 18.45; B, 6.86. IR (cm^{-1}): 2413 vs, 2396 vs, sh (ν(BH)), 2254 s, 2202 s (ν(CN)), 1232 ms (ν(NO)), 1368 s (ν(BO)). $\delta(^1H)$: 2.40 s (3H) (CH_3), 7.68 d (2H) (Ar), 8.32 d (2H) (Ar). $\delta(^{11}B)$: −42.6 t.

$4\text{-}C_2H_5C_5H_4NO{\cdot}BH_2CN$ (5). Anal. Calcd for $C_8H_{11}BN_2O$: C, 59.31; H. 6.84; N, 17.29; B, 6.67. Found: C, 58.92; H, 6.44; N, 16.10; B, 6.39. IR (cm^{-1}): 2410 s, 2370 vs, sh (ν(BH)), 2250 s, 2200 s (ν(CN)), 1200 m (ν(NO)), 1380 m (ν(BO)). $\delta(^1H)$: 1.08 t (3H) (CH_3), 2.64 q (2H) (CH_2), 7.50 d (2H) (Ar), 8.36 d (2H) (Ar). $\delta(^{11}B)$: −42.5 t.

$4\text{-}CNC_5H_4NO{\cdot}BH_2CN$ (6). Anal. Calcd for $C_7H_6BN_3O$: C, 52.89; H, 3.80; N, 26.43; B, 6.80. Found: C, 52.56; H, 3.97; N, 26.33; B, 6.64. IR (cm^{-1}): 2420 s, 2370 sh (ν(BH)), 2250 s, 2210 w (ν(CN)), 1250 s, br (ν(NO)), 1365 s (ν(BO)). $\delta(^1H)$: 7.88 d (2H) (Ar), 8.32 d (2H) (Ar). $\delta(^{11}B)$: −41.6 t.

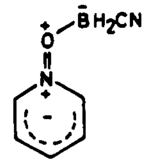
In the infrared region, the ν(BH) modes were found in the range 2370−2420 cm^{-1} as strong and broad bands with splittings observed as shoulders due to $\nu_s(BH_2)$ and $\nu_{as}(BH_2)$ modes, the isotope effect being possibly embedded in the broad envelopes. The ν(CN) modes were found as sharp bands in the range 2192−2254 cm^{-1}. No correlation of substituent effects to ν(CN) could, however, be made. The ν(BH) and ν(CN) data are in consonance with the previously reported values.[2a−e] The ν(NO) bands in the adducts appear at 1201−1280 cm^{-1} indicating a red shift from those in the free pyridine *N*-oxides. Appearance of the new bands in the range 1350−1380 cm^{-1} may be assigned to ν(BO) modes in consonance with the values in the literature.[12]

In the ^{1}H NMR spectra the aromatic proton resonances were found in two groups at δ 7.50−7.88 (d) and δ 8.32−8.52 (d), compared to those at δ 7.00−7.50 (d) and δ 8.24−8.47 in the free pyridine *N*-oxides. The methyl resonance occurs at δ 2.32−2.44 (s) and that for the ethyl group occurs at δ 1.08 (t) (CH_3) and δ 2.64 (q) (CH_2).

In the ^{11}B NMR spectra, $\delta(^{11}B)$ were found in the range −41.5 to −42.6 ppm as triplets with $^1J(B-H)$ = 88−94 Hz, indicating the tetracoordinate nature of boron.[13] The $\delta(^{11}B)$ values for $C_5H_5N{\cdot}BH_2CN$ and $RC_5H_4N{\cdot}BH_2CN$ have been reported as −15 ppm[13] and −15.4 to −20.7 ppm.[2e] Therefore, the triplets found at −41.5 to −42.6 ppm may be assigned to $RC_5H_4NO{\cdot}BH_2CN$. It may be noted that the substituents on the pyridine *N*-oxide ring have little effect on the $\delta(^{11}B)$ as the shielding of the boron nucleus is very little affected due to the absence of π-electron density. No such effect was also observed on the $\delta(^{11}B)$ for trifluoroborane−amine oxide adducts.[13]

^{14}N NMR spectra of two representative *N*-oxide−cyanoborane complexes have been recorded and $\delta(^{14}N)$ were found at −100 and −105 ppm for $C_5H_5NO{\cdot}BH_2CN$ and $3\text{-}CH_3C_5H_4NO{\cdot}BH_2CN$ respectively. However, no $\delta(^{14}N)$ signals for the CN group could be detected in either case. Since $\delta(^{14}N)$ values for C_5H_5N and C_5H_5NO are found at −62 and −85 ppm, respectively, and that for $C_5H_5N{\cdot}BH_3$ is found at −136 ppm, the $\delta(^{14}N)$ values of −100 and −105 ppm for the compounds under study should be due to the PyNO nitrogen atoms, as a result of the shielding effect.

^{13}C NMR spectra of the same representative compounds have been recorded. The spectrum of $C_5H_5NO{\cdot}BH_2CN$ showed five fairly strong resonances in the range δ 126.3−147.2 and that of $3\text{-}CH_3C_5H_4NO{\cdot}BH_2CN$ in the range of δ 156.5−178.4 due to the heteroaromatic ring carbon atoms in both cases. In the latter case a peak also at δ 56.6 may be assigned to the methyl carbon atom. In both cases, however, due to relaxation of the boron-bonded carbon, no peak owing to the cyano carbon atoms was found.[14] Pyridine *N*-oxide shows three $\delta(^{13}C)$ signals at 121.6 (γ-C), 125.7 (β-C), and 139.1 (α-C),[15] but on coordination of this with BH_2CN, the product gives five signals. One of the two canonical forms of pyridine *N*-oxide has the formal negative charge delocalized over the ring carbon atoms with a generation of positively charged nitrogen which is bonded to oxygen by a double bond. The oxygen is coordinated to BH_2CN, but there will be restricted rotation about N=O, whereby the symmetry will be lost (**I**). Consequently, the five carbon atoms will be inequivalent which is reflected in the appearance of five different ^{13}C signals. This is found to be true for unsymmetrically substituted pyridine[15] and should also be found for pyridine *N*-oxides.



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A conductance study of the compounds in chloroform has shown them to be nonelectrolytes, which suggests that the compounds were the desired adducts instead of metathesis products such as [RPyOH][BH_3CN], as was observed for the reactions of sodium dicyanodihydroborate with the pyridine *N*-oxides.[11]

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