

438. *The Preparation and Properties of Co-ordination Compounds of Boron Trichloride and Nitriles.*

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The preparation of twelve 1 : 1 complexes of nitriles with boron trichloride is reported; their hydrolysis, alcoholysis, base exchange, and pyrolysis are consistent with their formulation as co-ordination compounds. Comparisons are made with corresponding complexes of amines, ethers, sulphides, and nitro-compounds.

NITRILES have powerful donor properties and a large number of co-ordination compounds, particularly with Group II—IV halides are known. Thus the beryllium chloride (2 : 1),¹ magnesium bromide (3 : 1 and 4 : 1),² boron trihalide (1 : 1),^{1,3-11} and aluminium (1 : 1, 2 : 1, 3 : 2, and 1 : 2),¹² gallium(III) (1 : 1),¹³ titanium(IV) (1 : 1 and 2 : 1),^{6,8,14} and tin(IV) (2 : 1)^{6,8,14} chloride complexes have been prepared (molar ratios in parentheses refer to ligand : halide). Physical studies have been concerned with vapour-pressure^{5,10} and density,⁵ heats of formation⁵ and dissociation,^{5,10} cryoscopic determinations,^{5,8} dipole-moment,^{5,7,8} X-ray diffraction,⁴ and infrared spectroscopic measurements.^{6,11} On the other hand, chemical studies have been few and, apart from the pyrolysis of certain boron tribromide complexes (which were stated to give hydrogen bromide and alkyl bromide),⁹ have solely referred to their hydrolytic instability.

The range of 1 : 1 boron trichloride–nitrile complexes shown in the Table has been prepared in order: (1) to show that complex formation is general; (2) to study the structure of the complexes (it is shown¹¹ that they are co-ordination compounds, with nitrogen as the donor atom, and not products of addition across the multiple bond^{15,16}) which are

¹ Fricke and Ruschhaupt, *Z. anorg. Chem.*, 1925, **146**, 103; Fricke and Rode, *ibid.*, 1926, **152**, 347.

² Menschutkin, *Z. anorg. Chem.*, 1909, **61**, 111.

³ Gautier, *Compt. rend.*, 1866, **63**, 923; Patein, *ibid.*, 1891, **113**, 85; Bowlus and Nieuwland, *J. Amer. Chem. Soc.*, 1931, **53**, 3835.

⁴ Geller and Salmon, *Acta Cryst.*, 1951, **4**, 379; Hoard, Owen, Buzzell, and Salmon, *ibid.*, 1950, **3**, 130.

⁵ Laubengayer and Sears, *J. Amer. Chem. Soc.*, 1945, **67**, 164.

⁶ Coerver and Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.

⁷ Nespital, *Z. phys. Chem.*, 1932, **16**, B, 153.

⁸ Ulich, Hertel, and Nespital, *Z. phys. Chem.*, 1932, **17**, B, 21.

⁹ Johnson, *J. Phys. Chem.*, 1912, **16**, 1.

¹⁰ Brown and Johannesen, *J. Amer. Chem. Soc.*, 1950, **72**, 2934.

¹¹ Gerrard, Lappert, Pyszora, and Wallis, following paper.

¹² Perrier, *Compt. rend.*, 1895, **120**, 1423; Meerwein, Battenberg, Gold, Pfeil, and Willfang, *J. prakt. Chem.*, 1939, **154**, 83; Kablukow and Sachanow, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1762.

¹³ Heyne, Diss., Restock, 1955, pp. 10, 15, 22, 25.

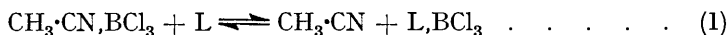
¹⁴ Henke, *Annalen*, 1858, **106**, 280; Pushin, Ristic, Parchomenko, and Ubovic, *ibid.*, 1942, **553**, 278.

¹⁵ Arnold, U.S.P. 2,402,589/1946.

¹⁶ Frazer, Gerrard, and Lappert, *J.*, 1957, 739.

shown to be unimolecular and undissociated in benzene; and (3) to investigate the influence of the hydrocarbon radical on the frequency and intensity of the CN infrared stretching vibration (see ref. 11).

It is noteworthy that *p*-methoxy- and *p*-nitro-benzonitriles formed complexes (with the nitrile group as donor¹¹), because both ethers and nitro-compounds¹⁷ are themselves highly reactive towards the trichloride; evidently the nitrile group is a better donor than either the ether or the nitro-group. On the other hand, the nitriles appear to be weaker donors than amines, because all the nitrile complexes are easily hydrolysed by cold water, unlike¹⁷ amine adducts. This was confirmed by showing that acetonitrile was displaced from its boron trichloride complex by pyridine, and supports earlier conclusions⁴ reached



from measurements of B-F bond lengths in boron trifluoride complexes of acetonitrile and methylamine. The replacement reaction (1) was also demonstrated with other bases (L = tetrahydrofuran or di-*n*-butyl sulphide; but no reaction with L = diethyl or bis-2-chloroethyl ether), whereas the reverse reaction was effected with the boron trichloride complex of bis-2-chloroethyl ether (but not with complexes of pyridine, tetrahydrofuran, or di-*n*-butyl sulphide). The overall conclusion (see also refs. 18—20) from displacement reactions appears to be that, with respect to boron trichloride as the reference Lewis acid, basic strengths fall off in the series: pyridine > tetrahydrofuran and di-*n*-butyl sulphide > acetonitrile > acyclic ethers.

Reaction of the acetonitrile complex with 2 or 3 mol. of *n*-butyl alcohol was straightforward and afforded di-*n*-butyl chloroboronate and tri-*n*-butyl borate, respectively, hydrogen chloride and acetonitrile being the other products. The reaction with 1 mol. of *n*-butyl alcohol, however, was more complicated and *t*-butyl alcohol (3 mol.) gave *t*-butyl chloride, boric acid, and acetonitrile. Equimolar interaction of the complex and *n*-butyl alcohol had been expected to yield *n*-butyl dichloroboronate and indeed this may have been formed as an intermediate because it disproportionated when treated with acetonitrile. Moreover, with *o*-nitrophenol, the complex did afford the dichloroboronate, which was unreactive towards the nitrile, presumably because of its chelate structure.²²

Thus, of the series (in decreasing acceptor strength) $\text{BCl}_3 > \text{RO}\cdot\text{BCl}_2 > (\text{RO})_2\text{BCl} > (\text{RO})_3\text{B}$, only the first forms adducts with nitriles. This may be compared with: (1) ethers,²³ which form unstable complexes (1 : 2) also with dichloroborinates (R = Et); (2) amines, which form complexes (2 : 1) also with chloroboronates (R = Buⁿ),²⁴ and even with borates (1 : 1) (if R = Me²⁵ or Aryl²⁶); and (3) sulphides,¹⁸ which form complexes only with the trichloride, but react with both dichloroboronate and chloroboronate (R = Buⁿ).

The complexes were very stable, but at high temperature slowly dissociated (evolution of boron trichloride) and decomposed (evolution of hydrogen chloride).

EXPERIMENTAL

General Procedures.—All the nitriles, except valero-²⁷ [b. p. 139°, n_D^{24} 1.3960 (Found: N, 16.7. Calc. for C₅H₉N: N, 16.85%)], *p*-methylbenzo-²⁸ [m. p. 29° (Found: N, 11.8. Calc.

¹⁷ Gerrard and Lappert, *Chem. Rev.*, 1958, **58**, 1081.

¹⁸ Lappert, *J.*, 1953, 2784.

¹⁹ Edwards, Gerrard, and Lappert, *J.*, 1957, 348.

²⁰ Edwards, Gerrard, and Lappert, *J.*, 1957, 377.

²¹ Gerrard and Lappert, *J.*, 1951, 1020; *Chem. and Ind.*, 1952, 53.

²² Colclough, Gerrard, and Lappert, *J.*, 1956, 3006.

²³ Wiberg and Sütterlin, *Z. anorg. Chem.*, 1931, **202**, 1.

²⁴ Lappert, *J.*, 1953, 667.

²⁵ Urs and Gould, *J. Amer. Chem. Soc.*, 1952, **74**, 2948.

²⁶ Colclough, Gerrard, and Lappert, *J.*, 1955, 907.

²⁷ Williamson, *J. prakt. Chem.*, 1854, **61**, 60.

²⁸ Clarke and Read, "Organic Syntheses," Wiley, New York, 1949, Coll. Vol. I, p. 514.

for C_8H_7N : N, 12.0%), *p*-methoxybenzo-²⁸ [m. p. 59° (Found: N, 10.0. Calc. for C_8H_7ON : N, 10.2%)], *p*-chlorobenzo-²⁸ [m. p. 92—93° (Found: N, 10.4. Calc. for C_7H_4NCl : N, 10.5%)], and *p*-nitrobenzo-nitrile²⁹ [m. p. 149—150° (Found: N, 18.7. Calc. for $C_7H_4O_2N_2$: N, 18.9%)], the boron trichloride and the solvents were commercial samples, dried and purified by standard methods. Complexes were analysed acidimetrically for chlorine and boron and nitrogen was estimated by the Kjeldahl procedure. M. p.s were taken in sealed capillary tubes, and molecular weights were determined cryoscopically in benzene.

Preparation of the Complexes.—These were obtained by dropwise addition of the nitrile (1 mol.) in an inert solvent to the cooled (0° to -78°) boron trichloride (1 mol.) in an inert solvent. The reactions were exothermal, and the solid complexes were isolated by filtration, washed with solvent, and dried at 20°/1 mm. The butyro-, valero-, and hexano-nitrile complexes were purified by distillation. The complexes were white, microcrystalline solids, or liquids (Table). The results are summarised in the Table.

R in R-CN, BCl ₃	M. p. ^a	Solvent	Yield (%)	Found (%)			Required (%)		
				N	Cl	B	N	Cl	B
CH ₃ ^b		C ₆ H ₆	93	8.8	66.0	6.9	8.85	67.1	6.8
C ₂ H ₅		n-C ₅ H ₁₂	89	8.05	61.2	6.4	8.1	61.8	6.3
n-C ₃ H ₇		n-C ₅ H ₁₂	98	7.5	57.0	5.8	7.5	57.1	5.8
n-C ₄ H ₉ ^c	34—38 ^h	n-C ₅ H ₁₂	98	6.9	52.7	5.5	7.0	53.1	5.4
n-C ₅ H ₁₁	^g	n-C ₅ H ₁₂	87	6.6	48.3	5.1	6.5	49.6	5.0
CH ₂ :CH	135—141	n-C ₅ H ₁₂	99	8.15	62.8	6.5	8.2	62.5	6.35
C ₆ H ₅ :CH ₂	131—134	CH ₂ Cl ₂ ^e	94	5.9	45.4	4.7	6.0	45.4	4.6
C ₆ H ₅ ^d		n-C ₅ H ₁₂	90	6.4	48.2	5.0	6.4	48.3	4.9
<i>p</i> -CH ₃ :C ₆ H ₄	136—142	n-C ₅ H ₁₂	94	5.9	45.0	4.7	6.0	45.4	4.6
<i>p</i> -Cl:C ₆ H ₄	127—133	n-C ₅ H ₁₂	92	5.5	41.0 ^f	4.3	5.5	41.8 ^f	4.25
<i>p</i> -CH ₃ O:C ₆ H ₄	107—113	CH ₂ Cl ₂ ^g	71	5.6	41.5	4.4	5.6	42.5	4.3
<i>p</i> -NO ₂ :C ₆ H ₄	121—127	CH ₂ Cl ₂	94	10.4	39.3	4.1	10.6	40.1	4.1

^a These data are given only for *new* compounds. Addition at 0°. ^c Found: *M*, 208. Calc. for C₅H₉NCl₃B: *M*, 200. ^d Found: *M*, 221. Calc. for C₇H₉NCl₃B: *M*, 220. ^e Precipitation completed by addition of n-pentane. ^f Easily-hydrolysed chlorine. ^g B. p. 52—55°/0.5 mm.; n_D^{20} 1.4795. ^h B. p. 61°/12 mm.

Pyrolysis of Complexes.—(a) *Hexanonitrile.* The complex (4.08 g.) was heated under reflux at 200° for 10 hr. Boron trichloride (0.78 g.) and hydrogen chloride (0.43 g.) were trapped by alkali. A residual black, viscous liquid, which solidified at 20° (2.79 g.) (Found: N, 10.9; B, 2.4%) and was involatile at 250°/0.1 mm., was obtained.

(b) *α-Toluenitrile.* This complex (4.22 g.), after 6 hr. at 150°, similarly afforded the trichloride (0.67 g.), hydrogen chloride (0.32 g.), and a solid (3.07 g.) (Found: N, 8.4; B, 2.6%).

Hydrolysis of Complexes.—All the complexes were easily hydrolysed to the nitrile, hydrogen chloride, and boric acid. For example, water (1.38 g., 3 mol.), suspended in methylene chloride (40 ml.), was added to the acetonitrile complex (4.04 g., 1 mol.) suspended in methylene chloride (5 ml.) at 20°. Boric acid (1.60 g., 100%) was immediately precipitated and filtered off. The filtrate was heated under reflux (0.5 hr.) to remove residual hydrogen chloride, and acetonitrile was determined as the complex (3.66 g., 91%) (Found: N, 8.6; Cl, 65.5; B, 7.0%) by addition of boron trichloride (3.3 g., 1.1 mol.). In a complementary experiment, hydrogen chloride (2.19 g., 95%) was evolved from the complex (3.34 g.) and water (1.15 g.).

Base Replacement.—Pyridine (3.04 g.) in methylene chloride (10 ml.) was added to the acetonitrile complex (6.08 g.) suspended in methylene chloride (10 ml.) at 20°, affording a residue of pyridine-boron trichloride²¹ (7.54 g., 100%) (Found: Cl, 54.2; B, 5.6; C₅H₅N, 40.7. Calc. for C₅H₅NCl₃B: Cl, 54.2; B, 5.5; C₅H₅N, 40.3%) and a material volatile at 20°/15 mm. and condensed at -78°. This contained acetonitrile, isolated as the boron trichloride complex (5.80 g., 96%) (Found: N, 8.7; Cl, 67.0; B, 6.9%) by addition of boron trichloride.

Similarly, tetrahydrofuran (2.77 g.) and the complex afforded acetonitrile [isolated as its boron trichloride complex (5.63 g., 93%) (Found: N, 8.7; Cl, 66.4; B, 7.0%)] and the tetrahydrofuran-boron trichloride adduct¹⁹ (7.25 g., 100%) (Found: Cl, 55.0; B, 5.8. Calc. for C₄H₈OCl₃B: Cl, 56.2; B, 5.7%).

Likewise, di-n-butyl sulphide (5.55 g.) and the complex afforded di-n-butyl sulphide-boron trichloride¹⁸ (9.88 g., 99%), b. p. 85°/0.5 mm., n_D^{20} 1.4951 (Found: Cl, 39.9; B, 4.1. Calc.

²⁹ Miller, "Organic Syntheses," Wiley, New York, 1955, Coll. Vol. III, p. 646.

for $C_8H_{18}SCl_3B$: Cl, 40.4; B, 4.1%), and acetonitrile, isolated as the complex (5.50 g., 92%) (Found: N, 8.7; Cl, 66.2; B, 6.9%).

Under similar conditions, bis-2-chloroethyl ether and the acetonitrile complex were quantitatively separated after being mixed and left for 1 hr. On the other hand, acetonitrile (1.24 g.) in methylene chloride (6 ml.) and the bis-2-chloroethyl ether-boron trichloride complex²⁰ (7.88 g.) in methylene chloride (10 ml.), under similar conditions at 20°, gave the acetonitrile complex (4.58 g., 95%) (Found: N, 8.64; Cl, 65.5; B, 6.9%) and bis-2-chloroethyl ether (4.38 g., 100%), b. p. 91–92°/40 mm., n_D^{20} 1.4573.

Diethyl ether did not react with the acetonitrile complex in methylene chloride during 1 hr., and the reverse order of replacement could not be tested owing to the instability of the diethyl ether-boron trichloride complex.²⁰ Under similar conditions, acetonitrile did not react with the boron trichloride complexes of tetrahydrofuran, pyridine, or di-n-butyl sulphide, as shown by quantitative analytical procedures described above.

Interaction of Butyl Alcohols and the Acetonitrile Complex.—n-Butyl alcohol (3.83 g., 1 mol.) was added to the complex (8.18 g., 1 mol.) suspended in methylene chloride (20 ml.) at 20°. There was a vigorous reaction. After 12 hr. the volatile matter, removed at 20°/15 mm. and collected at –80°, afforded acetonitrile, isolated as its complex (2.58 g., 94%) (Found: Cl, 66.0; B, 6.9%) on addition of boron trichloride. The residue was extracted with methylene chloride, affording a final residue of the acetonitrile complex (3.69 g., 90%) (Found: Cl, 66.4; B, 6.85%) and a filtrate which contained di-n-butyl chloroboronate (4.54 g., 91%), b. p. 45°/0.3 mm., n_D^{20} 1.4131 (Found: Cl, 18.7; B, 5.7. Calc. for $C_8H_{18}O_2ClB$: Cl, 18.4; B, 5.6%). In a complementary experiment, the complex (4.74 g.) gave hydrogen chloride (1.08 g., 98%).

Similarly, n-butyl alcohol (3.79 g., 2 mol.) in methylene chloride (10 ml.) and the complex (4.50 g., 1 mol.) in methylene chloride (5 ml.) gave hydrogen chloride (1.65 g., 88%), acetonitrile [isolated as the complex (3.48 g., 86%) (Found: N, 8.7; Cl, 66.8; B, 7.0%)], and di-n-butyl chloroboronate (4.05 g., 82%), b. p. 39–40°/0.3 mm., n_D^{20} 1.4125 (Found: Cl, 18.4; B, 5.7%); whilst n-butyl alcohol (5.32 g., 3 mol.) and the complex (3.79 g., 1 mol.) gave hydrogen chloride (2.43 g., 93%), acetonitrile [converted into the complex (3.79 g.)], and tri-n-butyl borate (5.06 g., 92%), b. p. 108–109°/10 mm., n_D^{20} 1.4101 (Found: B, 4.7. Calc. for $C_{12}H_{27}O_3B$: B, 4.7%).

s-Butyl alcohol (6.12 g., 3 mol.) and the complex (4.36 g., 1 mol.) gave hydrogen chloride (2.66 g., 89%), acetonitrile [as complex (3.86 g., 89%)], and tri-s-butyl borate (4.96 g., 78%), b. p. 78–79°/10 mm., n_D^{20} 1.3965 (Found: B, 4.6%).

In the absence of solvent (which confused analysis), t-butyl alcohol (5.90 g., 3 mol.) and the complex (4.00 g., 1 mol.) at 20° afforded material (7.30 g.) removed at 20°/15 mm. and collected at –78°, leaving boric acid (1.60 g. Calc.: 1.56 g.). The volatile matter showed two peaks on the vapour-phase chromatogram, corresponding to a synthetic mixture of acetonitrile (1 mol.) and t-butyl chloride (1 mol.). Determination of nitrogen and chlorine showed the presence of acetonitrile (0.95 g., 91%) and t-butyl chloride (5.65 g., 80%).

Interaction of n-Butyl Dichloroborinate and Acetonitrile.—The borinate (7.99 g., 1 mol.) in n-pentane (50 ml.) was added to the nitrile (2.12 g., 1 mol.) at 20°. Acetonitrile-boron trichloride (3.84 g., 94%) (Found: N, 8.8; Cl, 66.7; B, 6.9%) was precipitated and, after removal of solvent from the filtrate at 20°/15 mm., di-n-butyl chloroboronate (4.46 g., 90%), b. p. 39–40°/0.25 mm., n_D^{20} 1.4129 (Found: Cl, 18.3; B, 5.7%), was isolated.

Interaction of o-Nitrophenol with the Acetonitrile Complex.—The phenol (7.27 g., 1 mol.) in methylene chloride (10 ml.) was added to the complex (8.28 g., 1 mol.) suspended in methylene chloride (10 ml.). After 12 hr. the volatile matter, removed at 20°/15 mm. and condensed at –78°, afforded the acetonitrile complex (7.60 g., 92%) (Found: Cl, 66.0; B, 7.0%) when treated with boron trichloride, and from the residue o-nitrophenyl dichloroborinate (11.11 g., 97%) (Found: Cl, 31.8. Calc. for $C_6H_4O_3NCl_2B$: Cl, 32.3%) was obtained. In a complementary experiment, the complex (4.62 g.) gave hydrogen chloride (0.97 g., 92%).

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