sium nitrate solvent whereas the data reported above were obtained in an equimolar sodium nitrate–potassium nitrate solvent. The phase diagram for the K_2WO_4–WO_3 system[11] does not show the existence of a compound corresponding to $K_2W_2O_7$, whereas the phase diagram for the Na_2WO_4–WO_3 system[12] does show the formation of a compound corresponding to $Na_2W_2O_7$. It is not known whether this predilection against formation of the ditungstate species in the potassium tungstate system carries over to solutions of the tungstates. Further investigation of the cation effect in these nitrate solvents is presently underway.

Attempts to detect electrochemically species more condensed than the ditungstate have so far been unsuccessful. The primary difficulty lies in the slowness with which equilibrium is attained.

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[11] F. Hoermann, *Z. Anorg. Allgem. Chem.*, **177**, 170 (1928).

[12] F. Hoermann, *ibid.*, **177**, 167 (1928).

Notes

Contribution from the Department of Chemistry,
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A Novel Arylboron Dihalide and the Corresponding Boronic Acid

By C. A. Eggers and S. F. A. Kettle

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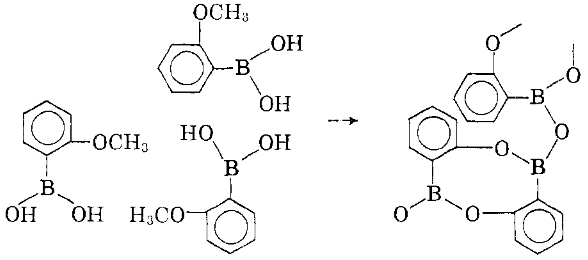
o-Anisylboron dichloride was first prepared by Michaelis and Behrens[1] by the action of boron trichloride on *o*-anisylmercuric chloride, a preparative technique which has recently been more fully studied.[2] In the course of an investigation into π bonding in the arylboron dihalides by variation of ring substituent we have repeated Michaelis and Behren's preparation. These authors did not, in fact, isolate *o*-anisylboron dichloride but identified it by the boronic acid formed when a solution of the halide was hydrolyzed. We have confirmed their work and find that when the solvent is removed from a solution of the halide a tar results. This is in contrast to the behavior of the corresponding *meta* and *para* anisyl derivatives which may be obtained in good yield. The tar formed in the *o*-anisyl case may be coordination polymer (it does not fume in moist air, for example, although the original solution did), but we have been unable to regenerate the original halide from it. It is far from clear why this behavior should be confined to the *ortho* derivative if only simple polymerization is involved and it appears that polymerization is a result of methyl group cleavage.

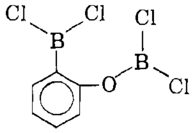
Since the *o*-anisylboronic acid may be readily prepared by the method of Bean and Johnson,[3] we attempted to prepare the dichloride from it. The most reliable method for this is by the action of boron trichloride on the boronic anhydride, although yields are not particularly good.[4]

Although *m*- and *p*-anisylboronic acids dehydrate readily at 40–50° under vacuum, the *ortho* acid sets to a hard resin (I) under these conditions. Comparison of the pmr spectra of the *ortho* acid with that of I showed that dehydration was accompanied by methanol elimination, possibly as shown below.

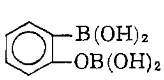


A somewhat similar reaction has been found to occur when *p*-anisylboron dichloride is heated, methyl chloride being eliminated and a resin left.[5]

When I was refluxed with boron trichloride in benzene the product was the novel compound *o*-(oxyboron dichloride)phenylboron dichloride (II). In accord with this the ^{11}B magnetic resonance spectrum of II showed two peaks. II, when hydrolyzed, gave the diboronic acid III. The dehydration of III did not proceed cleanly. It was not possible to isolate the corresponding anhydride; the infrared spectrum of the product suggested that I was among the products.



II



III

It is clear that when an alkoxide group is substituted *ortho* or *para*[5] to BCl_2 the O–alk bond is labilized, the effect of an *ortho* substituent being the greater. So,

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[1] A. Michaelis and M. Behrens, *Ber.*, **27**, 244 (1894).

[2] W. Gerrard, M. Howarth, E. F. Mooney, and D. E. Pratt, *J. Chem. Soc.*, 1582 (1963).

[3] F. R. Bean and J. R. Johnson, *J. Am. Chem. Soc.*, **54**, 4415 (1932).

[4] J. E. Burch, W. Gerrard, M. Howarth, and E. F. Mooney, *J. Chem. Soc.* 4916 (1960).

[5] S. H. Dandegaonker, W. Gerrard, and M. F. Lappert, *ibid.*, 2076 (1959).

o-anisylboron dichloride forms a resin at room temperature, but the *para* compound only after prolonged heating at 290–300°, and the *ortho* boronic acid eliminates methanol under mild conditions while this behavior has not been observed for the *para* acid. It is probable that there is a direct "through space" effect in the *ortho* case which is absent in the other. In accord with this suggestion it is found that the Slater 2p orbital overlap integrals between the *ortho* substituent atoms and the adjacent boron atom are small but not negligible ($S_{B_\sigma - O_\sigma} \simeq 0.04$; $S_{B_\sigma - C_\sigma} \simeq 0.17\text{–}0.01$).

Experimental Section

Attempted Preparation of *o*-Anisylboron Dichloride.—*o*-Anisylmercuric chloride was prepared by the action of mercuric chloride (85.0 g) on *o*-anisylmagnesium chloride, prepared from magnesium (7.1 g) and *o*-anisyl chloride (55.0 g) in tetrahydrofuran (200 ml) under nitrogen. The product of the reaction with mercuric chloride was poured into water and the solid extracted with and recrystallized from chloroform. A yield of 65 g of *o*-anisylmercuric chloride was obtained.

o-Anisylmercuric chloride (20.0 g) was shaken for 5 hr at room temperature in a large stoppered flask with a large excess of boron trichloride in dry benzene (100 ml). At the end of the reaction excess boron trichloride was removed *in vacuo*. The fact that mercuric chloride was precipitated, identified by qualitative tests, indicated that reaction had occurred. Removal of the benzene *in vacuo* gave a brown tar which did not fume in air and gave an nmr spectrum in which the methyl proton resonance was only about one-tenth of the expected intensity and was therefore not *o*-anisylboron dichloride. As its formation was not anticipated no attempt was made to collect the methyl chloride presumably evolved.

Preparation of I.—Reaction after the method of Bean and Johnson[8] of *o*-anisyl bromide (100.0 g) with magnesium (12.8 g) in tetrahydrofuran (250 ml) under nitrogen and subsequent reaction of this Grignard reagent at −78° with tri-*n*-butyl borate (123.0 g) and hydrolysis gave 41.89% *o*-anisylboronic acid, which was recrystallized from water. *Anal.* Calcd for $C_7H_9O_3B$: C, 55.3; H, 6.0. Found: C, 55.2; H, 6.1. Heated *in vacuo* at 40–50° *o*-anisylboronic acid (24.0 g) gave a hard brown resin, I (*ca.* 18 g). The starting material showed the expected methoxy proton resonance at 3.86 ppm, but this was absent in that of the resin, although in the aromatic proton region the two spectra were very similar.

Preparation of II.—The resin I (15.0 g) was refluxed with excess boron trichloride in benzene for 3 hr from water and Drikold condensers fitted in series, after allowing the initial reaction to subside. The solvent was removed *in vacuo* and the product sublimed at 88° (0.05 mm). The product, obtained in about 20% yield as a white powder which hydrolyzed rapidly on exposure to air, was *o*-(oxyboron dichloride)phenylboron dichloride. *Anal.* Calcd for $C_6H_4B_2OCl_4$: C, 28.1; H, 1.6. Found: C, 29.2; H, 2.2. The ^{11}B magnetic resonance spectrum of II recorded in CCl_4 at 20 Mcps showed two peaks of essentially equal intensity, a fairly sharp one at 7 ppm and a broad one at *ca.* 21 ppm downfield of an external trimethyl borate reference. The sharp peak is probably to be associated with the boron of the $OBCl_2$ group and the broad peak with that of the $CBCl_2$ group. This assignment is based on the fact that of 15 $ArBCl_2$ (Ar = substituted aryl) compounds we have studied, 14 have boron resonances between 36 and 38 ppm downfield of trimethyl borate (the exception is Ar = *p*-anisyl at 35.6 ppm), while $ArBF_2$ compounds have resonances in the range 6–7.5 ppm.[6] Our assignments then follow from simple electronegativity comparisons.

Preparation of *o*-(Oxydihydroxyboron)boronic Acid (III).—Addition of water to II resulted in immediate hydrolysis. The white product, recrystallized from water, was *o*-(oxydihydroxyboron)boronic acid. *Anal.* Calcd for $C_6H_8B_2O_5$: C, 39.5; H, 4.8. Found: C, 39.6; H, 4.4. An attempt was made to dehydrate this acid to give I. Dehydration *in vacuo* at 100° was accompanied by some darkening, and the infrared spectrum of the product indicated that although I, or some closely related material, was a major product, the dehydration had not proceeded cleanly.

Nmr Spectra.—Proton magnetic resonance spectra were recorded on a Varian A60 spectrometer, deuteriochloroform being used as solvent. Boron resonance spectra were recorded at 14,700 gauss on a modified AEI RS2 spectrometer.

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(6) C. A. Eggers and S. F. A. Kettle, to be published.

CONTRIBUTION FROM THE INORGANIC CHEMISTRY SECTION,
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A Broad-Line Proton Magnetic Resonance Study of Cobalt Tetracarbonyl Hydride

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A recent publication from these laboratories[3] reported the determination of the metal–hydrogen bond distance in manganese carbonyl hydride, $HMn(CO)_5$, the first such measurement in this class of compounds. In that investigation, the bond length was determined from the second moment of the broad-line proton magnetic resonance spectrum. The contribution of intermolecular dipole–dipole interactions was evaluated on the basis of a crystal structure determination by other workers[4] from which the heavy-atom positions were known. We have now measured the broad-line spectrum of polycrystalline cobalt tetracarbonyl hydride, $HCo(CO)_4$. Although no information is available on the crystal structure of this material, the fine structure observed in the nmr spectrum allows one to estimate the magnitude of intermolecular dipole–dipole interactions. Further, line separations provide an independent measure of the cobalt–hydrogen bond distance. In this note we report a semiquantitative determination of the Co–H distance (1.2 ± 0.1 A) and comment briefly on the use of the nmr method for structural investigation of polycrystalline samples of compounds providing examples of two-spin systems. Some sources of error in the broad-line technique are also discussed.

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(1) National Bureau of Standards.

(2) (a) Department of Chemistry, Massachusetts Institute of Technology; (b) National Science Foundation Graduate Fellow, 1953–1966.

(3) T. C. Farrar, W. Ryan, A. Davison, and J. W. Faller, *J. Am. Chem. Soc.*, **88**, 184 (1966).

(4) S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).