TABLE I

SPECTRAL MEASUREMENTS

Compound	Ir abs freq, cm^{-1} ν_3	Ir abs freq, cm^{-1} ν_4	Electronic spectral data, λ_{max}, cm^{-1}
$[CH_3NH_3]_3[FeCl_6]\cdot CH_3NH_3Cl$	257 ± 4	182	18,700
$[Co(NH_3)_6][FeCl_6]$	251 ± 4	181	22,400
	248 ± 5[a]	181[a]	. . .
$[Rh(pn)_3][FeCl]_6$	252 ± 4	182	18,730[b] 22,080

[a] From D. M. Adams and D. M. Morris, *J. Chem. Soc.*, 694 (1968). [b] From ref 1.

TABLE II

MAGNETIC AND MÖSSBAUER DATA

Compound	μ_{eff}, BM	Isomer shift,[a] mm/sec	Absorption width at half-max, mm/sec
$[CH_3NH_3]_3[FeCl_6]\cdot CH_3NH_3Cl$	6.00[b]	+0.746 ± 0.01	0.478 ± 0.03
$[Co(NH_3)_6][FeCl_6]$	5.96[b]	+0.744 + 0.01	0.471 ± 0.03
$[Rh(pn)_3]]FeCl_6]$	. . .	+0.777 ± 0.01	0.430 ± 0.03

[a] Relative to a sodium nitroprusside standard. [b] Calculated spin-only moment is 5.92 BM.

the established hexachloroferrate. Piper, *et al.*,[1] assigned this band to the $^6A_1 \rightarrow {}^4T_2$ (^4G) transition. Our band at 22,400 cm^{-1} does not agree very well with that of 22,080 cm^{-1} reported for the $[Rh(pn)_3][FeCl_6]$ compound. Piper assigned this band to the $^6A_1 \rightarrow {}^4E$, $^4A_1$ (^4G) transitions. However, it is possible that this is a charge-transfer band rather than a d → d transition. We feel that the evidence presented confirms the existence of the hexachloroferrate ion in the compound $(CH_3NH_3)_4FeCl_7$ and that the formula should be written as $[CH_3NH_3]_3[FeCl_6]\cdot CH_3NH_3Cl$. The double salt formation must increase the crystal lattice energy to the level required for stabilization of the hexachloroferrate(III) ion.

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Dichloroboronation of Aromatic Hydrocarbons. Mechanistic Aspects

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Dichloroboronation of aromatic hydrocarbons was first reported in 1959[1] and was later established as a relatively general synthesis of aryldichloroboranes[2]

$$3C_6H_6 + 3BCl_3 + Al \longrightarrow 3C_6H_5BCl_2 + AlCl_3 + {}^3/_2H_2$$

Synthesis conditions varied from 25 to 150°; minimal temperature for reaction was shown to be sensitive to the aluminum surface activity and to the nature of aromatic hydrocarbon. Aromatic hydrocarbons, *e.g.*, durene and mesitylene, with all hydrogen atoms vicinal to two C-methyl groups did not react—at least without isomerization of the arene. It was noted that the distribution of isomers obtained from toluene and the three xylenes "was typical of a classical Friedel–Crafts system run in the presence of aluminum trichloride."[2] A speculative reaction sequence was postulated as

$$ArH + BCl_3 \longrightarrow ArHBCl_3 \xrightarrow{AlCl_3} ArHBCl_2{}^+AlCl_4{}^-$$

$$ArHBCl_2{}^+ \longrightarrow ArBCl_2 + H^+$$

$$3H^+AlCl_4{}^- + Al \longrightarrow {}^3/_2H_2 + 4AlCl_3$$

Recently Eggers and Kettle[3] investigated the thermal stabilities of certain aryldichloroboranes and the sensitivity of the dichlorides to isomerization in the presence of trichloroborane. From the observation of no *apparent* isomerization in the presence of trichloroborane, they concluded that the arylboron dichlorides *do not isomerize* once formed and that in the synthesis there is an intermediate or transition state of "finite" independent existence wherein the rearrangements occur within the intermediate or transition-state lifetime. The experimental observations are incomplete and do not permit conclusions of this nature. None of the tests of isomerization was made under reaction conditions, *i.e.*, in the presence of all possible reactants or products.

Aryldichloroboranes do not thermally isomerize at 150° although there is very minor decomposition with the formation of aromatic hydrocarbons. (Studies were restricted to 1-(dichloroboryl)-2,5-dimethylbenzene and 1-(dichloroboryl)-3,5-dimethylbenzene for direct relevance to the Eggers and Kettle investigation.) The same behavior prevails in presence of (1) iodine, (2) aluminum, (3) aluminum(III) chloride, (4) methyl iodide, (5) trichloroborane, (6) mercury(II) chloride, and (7) mixtures of the preceding reagents. Hence there is no catalytic rearrangement.[4] There is however synthesis reversibility. Hydrogen chloride, a product of the dichloroboronation reaction, cleaves aryldichloroboranes to give arenes and trichloroborane. This is the reversible aspect of the synthesis.[5] Aromatic hydrocarbons rearrange in the presence of $HCl–AlCl_3$.[6] Consistently we find that at 150° excess hydrogen chloride in the presence of catalytic amounts of alu-

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(1) E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 2597 (1959).

(2) E. L. Muetterties, *ibid.*, **82**, 4163 (1960).

(3) C. A. Eggers and S. F. A. Kettle, *Inorg. Chem.*, **6**, 1975 (1967).

(4) Previous papers[1-3] have carried the connotation that dichlorohoronation is a clean reaction. There are however by-products including methylated arenes and viscous oils. Hence these specific studies do not emulate synthesis conditions. Nothing is as yet known about the nature of the oils but these are under current investigation. Yields of the oils increase with synthesis temperature.

(5) The aryldichloroborane synthesis proceeds to completion presumably by the irreversible reaction of hydrogen chloride and aluminum.

(6) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, pp 717, 718.

minum(III) chloride converts both 1-(dichloroboryl)-2,5- and 1-(dichloroboryl)-3,5-dimethylbenzene to trichloroborane and primarily *m*-xylene. Typical arene distributions were: *m*-xylene, 27–35%; *p*-xylene, 9–12%; *o*-xylene, ~10%; toluene, 15–23%; 1,2,4- and 1,3,5-trimethylbenzene, 22–36%; and small amounts of benzene and tetramethylbenzenes. The product distribution is similar to those reported for the $AlCl_3$–HCl isomerization of xylenes.[4] Hence, under these conditions, the presence of hydrogen chloride provides reversibility and the HCl–$AlCl_3$ couple is established as a catalyst for rearrangement of the hydrocarbon. Notably, in the context of the chloroboronation mechanism, *p*-xylene is rearranged primarily to the *meta* isomer *at 150°*.

These data do not disprove the Eggers and Kettle transition-state thesis but do establish an alternative pathway for the synthesis of 1-(dichloroboryl)-3,5-dimethylbenzene from *p*-xylene and trichloroborane at 150°. Reversibility and rearrangement is definitively established.

Under dichloroboronation synthesis conditions, the hydrogen chloride concentration is probably low. Hence, isomer distribution in the dichloroboronation reaction will be very sensitive to the synthesis rate and the cleavage rate both of which will vary significantly among the arenes and their BCl_2 derivatives. Fast synthesis rates are found for arenes in which a BCl_2 group can enter nonvicinal to a methyl or alkyl group. Synthesis rates for benzene and *p*-xylene differ by orders of magnitude. Extremely fast reactions have been observed[1,2] for benzene below room temperature.

Eggers and Kettle[3] reported that they could not reproduce the reported[2] synthesis of 1-(dichloroboryl)-2,5-dimethylbenzene from *p*-xylene and trichloroborane at ~30°. This was due to the presence of oxygen or insufficient activation of the aluminum surface. If the surface is adequately activated, exothermic and fast reactions between trichloroborane and arenes may occur and in fact have been observed.[2] We have successfully repeated the 1-(dichloroboryl)-2,5-dimethylbenzene synthesis at 30° many times. This isomer was the only one detected under these synthesis conditions. It should be noted that the most effective activation procedure is pretreatment of the aluminum metal with methyl iodide at 80–100° prior to introduction of the reagents (with rigorous exclusion of oxygen and moisture).

It was originally[2] reported that reaction of trichloroborane and *p*-xylene at 150° gave 1-(dichloroboryl)-2,5-dimethylbenzene. We have repeated this work and confirm the findings of Eggers and Kettle[2] that the product is 1-(dichloroboryl)-3,5-dimethylbenzene. This is the only isomer we found, but up to ~5% of another isomer could have been present and not detected by our analytical procedures.

Mechanistic studies of the dichloroboronation reaction are being continued. Alternative to the postulate first advanced[1,2] (*vide supra*) is dichloroboronation *via* an arylaluminum species. Model systems of arylalanes and -boranes will be examined for aryl group exchange and for arene rearrangements.

Experimental Section

Synthesis of Aryldichloroboranes.—The procedure described in ref 2 was explicitly followed. Yields obtained at 25–30° varied with the degree af aluminum activation. Failure to observe any reaction at 25–30° is due to gross oxygen contamination or to insufficient, *in situ*, activation of aluminum surface with methyl iodide or iodine. The former proved more effective; the required amount, depending upon the oxide coating of the aluminum, varied from 0.1 to 1.0 ml.

Identification of Isomers.—Two procedures were followed in the isolation and characterization of products after separation of aryldichloroboranes from arenes and other reactive products by distillation: (A) hydrolysis to the boronic acids, recrystallization of the acids, and vacuum drying at 150° (2 hr), and (B) a second vacuum distillation with essentially no fractionation of volatile material. Proton nmr spectral data (220 Mc) were employed to distinguish the isomers; spectral distinctions among possible isomers were unequivocal. It is estimated that specific isomers could have been present in the crude product at relative concentrations of 3–10% and would not be detected by this technique. Detection of small amounts of certain isomers was not critical to the arguments presented in the Discussion.

Isomerization Reactions.—Isomerizations were effected in sealed, evacuated glass tubes. The molar ratio of aryldichloroborane to catalyst or catalysts varied from 10:1 to 50:1. Procedures A and B above were followed by proton nmr characterization.

1-(Dichloroboryl)-2,5-dimethylbenzene Reaction with Hydrogen Chloride and Aluminum Chloride.—1-(Dichloroboryl)-2,5-dimethylbenzene, 3.04 g (0.0163 mol), was placed with 0.08 g of aluminum chloride in a 50-ml Hastelloy-C pressure vessel. The reactor was evacuated, charged with approximately 3 g (0.08 mol) of hydrogen chloride gas, and heated with agitation for 1 hr at 150°. The gases were vented and the remaining volatile products were distilled under vacuum (10^{-5} mm) through a trap cooled to 0°. Of the volatile products a trace af unidentified material (~2 mg) was retained at 0°; 1.34 g (77%) of a hydrocarbon mixture was collected at −80°. This fraction was separated on a 1,2,3-tris(2-cyanoethoxy)propane–NAW firebrick gas chromatographic column operating at 100°. Approximately 4% of the sample was made up of traces of unidentified compounds. The remaining portion was identified as benzene (0.5% of the identified materials, calculated from the area under the peak of the gc trace), determined from the mass spectrum, and toluene (23%), *m*- and *p*-xylene (44%), *o*-xylene (11%), 1,3,5-trimethylbenzene (8%), and 1,2,4-trimethylbenzene (14%) identified by infrared spectra. Estimates af the approximate relative concentrations of *m*- and *p*-xylenes were made by comparisons of the infrared spectrum of the mixture with spectra of known compositions. The ratio of *m*- to *p*-xylene was approximately 79:21. A small amount (<1%) of $C_{10}H_{14}$ assumed to be tetramethylbenzene was also present as determined by the mass spectrum of the mixture.

1-(Dichloroboryl)-3,5-dimethylbenzene Reaction with Hydrogen Chloride and Aluminum Chloride.—1-(Dichloroboryl)-3,5-dimethylbenzene, 2.99 g (0.0160 mol), was treated with 0.08 g of aluminum chloride and approximately 3 g (0.08 mol) of hydrogen chloride and analyzed, using procedures paralleling those employed for the 1,2,5 isomer. The recovery of volatile hydrocarbons was 1.48 g (87%), 95% of which was separated and identified. This and the product mixture from the 1,2,5 isomer contained the same components in different relative amounts. The 1,3,5 isomer yielded benzene (0.3%), toluene (15%), *m*- and *p*-xylene (39%), *o*-xylene (9%), 1,3,5-trimethylbenzene (13%), and 1,2,4-trimethylbenzene (23%). The approximate ratio of *m*- to *p*-xylene was 69:31. The product distribution may be clearly related to the interconversions encountered in reactions of xylenes with aluminum chloride and hydrogen chloride.[6]