Table I

Molar Conductivity, λ_M (25° and 1.00 mM), and the Observed Molecular Weights for Solutions of $[Pt(C_2H_4)Cl_2]_2$ (MW = 588.39) in Various Solvents

Solvent	Dielectric constant (25°)	Molar conductivity λ_M (25°), ohm^{-1} cm^2 mol^{-1}	Molar conductivity for uni-univalent salts,[a] ohm^{-1} cm^2 mol^{-1}	Mol wt
Dichloroethane	10.4	1.45	50–80	566.5
Methanol	7.4	8.88	100–120	292.3
Tetrahydrofuran	32.6	0.07	...	280.6
Acetone	20.5	7.4	120–180	264

[a] Landolt-Börnstein, "Physikalisch-Chemisch Tabellen," Vol. II, Springer-Verlag, Berlin, 1960, part 7, pp 359, 383, 432.

sociation of the dimeric molecules. Apparently, in the halogen solvents, in dichloroethane, and presumably in carbon tetrachloride, the dimers constitute the major component. The extensive dissociation in the oxygen-bearing solvent is believed to yield a square-planar molecular type as indicated in eq 1.

The spectra for the solution of $[Pt(C_2H_4)Cl_2]_2$ in the chlorinated hydrocarbons exhibit a well-developed peak at 360 mμ and a shoulder at 440 mμ which strongly resemble the features of the reflectance spectrum. In the oxygen-bearing solvents the peak is much less pronounced, and both it and the shoulder appear shifted to shorter wavelengths. The solubility in cyclohexane was too low to permit a molecular weight determination. Although it seems likely that the dimeric form is predominant in this solvent as well, the transition at about 360 mμ does not give nearly as well developed a peak. However, it has not been shifted to lower wavelengths as significantly as in the oxygen-bearing solvents.

The dissociation, indicated by reaction 1, is a consequence of the coordinating power of the oxygen atom in the solvent, functioning as a base. The dissociation in these solvents is essentially complete with no evident dependence upon the dielectric constant. Consequently, the chlorinated solvents, such as dichloroethane, which does not have the oxygen base function, do not effect the dissociation.

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The Preparation and Reactions of 1,2-Diphenyl-1,2-bis(dichloroboryl)ethylene

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Potentially reactive bis(dichloroboryl) sites produced by the addition of tetrachlorodiborane(4), B_2Cl_4, to acetylene and olefins[1] have prompted us to examine the reaction of B_2Cl_4 with diphenylacetylene and to study some reactions of the resulting product.

(1) G. Urry, J. Kerrigan, T. D. Parsons, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **76**, 5293 (1954); P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. D. Parsons, G. Urry, and H. I. Schlesinger, *ibid.*, **81**, 6368 (1959); C. Chambers, A. K. Holliday, and S. M. Walker, *Proc. Chem. Soc.*, 286 (1964).

Results and Discussion

Diphenylacetylene undergoes slow reaction at 0° with B_2Cl_4 in a 1:1 molar ratio in pentane and in methylene chloride to produce 1,2-diphenyl-1,2-bis-(dichloroboryl)ethylene, I.[2] Compared to acetylene,

$$B_2Cl_4 + C_6H_5C{\equiv}CC_6H_5 \longrightarrow \underset{\underset{\text{I}}{\overset{|}{BCl_2}\ \overset{|}{BCl_2}}}{C_6H_5C{=}CC_6H_5}$$
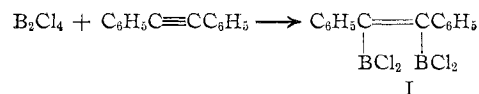
diphenylacetylene reacts relatively slowly with B_2Cl_4. Furthermore, the stoichiometry of the reaction is limited to a 1:1 molar ratio even at temperatures up to 30°, while acetylene reacts with B_2Cl_4 in 1:1 and 2:1 molar ratios.[1]

Compound I is a light yellow solid which is quite sensitive to moisture. It melts at about 60° under an atmosphere of dry nitrogen. Under vacuum it sublimes with some decomposition at or slightly above the fusion point.

Substitution Reactions.—The reaction of I with ethylene glycol in a 1:2 molar ratio in methylene chloride at 0° produced $C_2(C_6H_5)_2B_2(O_2C_2H_4)_2$, II, a white crystalline solid, which was shown to be monomeric by cryoscopic measurements. In the absence of a solvent no reaction occurred between I and ethylene glycol at 25°.

Treatment of I with 1,2-benzenediol (1:2 molar ratio), using pentane as a solvent, produced the monomeric product $C_2(C_6H_5)_2B_2(O_2C_6H_5)_2$, III. Identical conditions, except that methylene chloride was employed as the solvent, produced a dark greenish oil. Crystal formation from this oil could not be effected. Reactions for the formation of II and III are given as
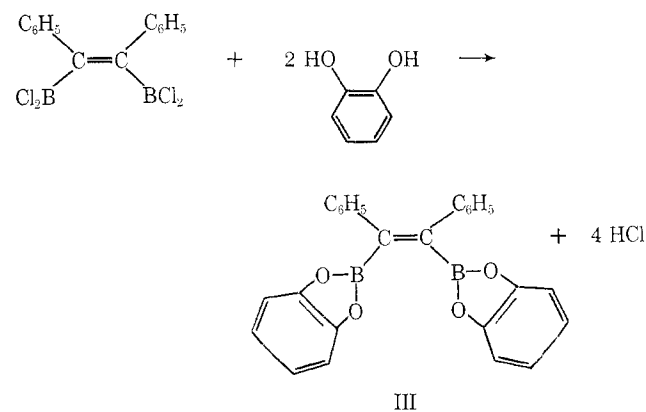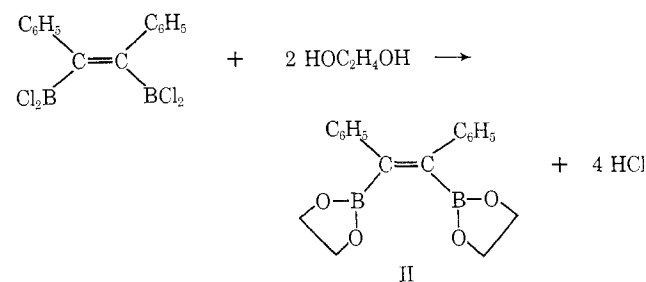
(2) A *cis* structure for I is assumed on the basis of recent studies of addition reactions of B_2Cl_4: R. W. Rudolph, *J. Am. Chem. Soc.*, **89**, 4216 (1967); M. Zeldin, A. R. Gatti, and T. Wartik, *ibid.*, **89**, 4217 (1967).

These compounds are stable under vacuum at temperatures above 100°. They are sensitive to moisture.

Alternative structures for II and III involving larger rings can be envisaged. An example is shown as
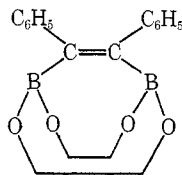
For the time being we tend to discount such structures. If such rings could form, we would expect a 1:1 molar ratio of reactants to favor their formation. However, when a 1:1 stoichiometry of reactants is employed, only polymeric materials are produced.

Attempts to form compounds containing nitrogen and sulfur in the ring by allowing ethylenediamine and ethanedithiol, respectively, to react with I in 2:1 and 1:1 molar ratios produced only polymeric materials. Experimental conditions similar to those used in the preparation of II and III were employed.

The reaction of I with methylamine and dimethylamine was studied both as a solid–gas phase reaction and as a solid–liquid phase reaction at 25°. In all cases, consumption of amine was less than the stoichiometric amount required for the reaction

$C_2(C_6H_5)_2B_2Cl_4 + 8NHRCH_3 \longrightarrow$

$\quad C_2(C_6H_5)_2B_2(NRCH_3)_4 + 4CH_3RH_2NCl \quad (R = H, CH_3)$
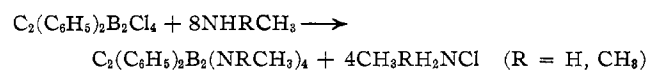
A mole ratio of 1:6.61 was determined when I was treated with methylamine while a 1:6.38 ratio was recorded for dimethylamine. Chambers and co-workers[3] reported that $Cl_2BC_2H_2BCl_2$ also reacted incompletely with dimethylamine (1:7.3 molar ratio).

Addition Reactions.—Trimethylamine, pyridine, and acetonitrile were found to form 2:1 adducts with I. The reactions took place in excess Lewis base. Temperatures of at least 45° were required for complete reaction. At 25°, nonstoichiometric adducts were formed.

Pyrolysis of I and Its Adducts.—Generally, it has been reported that thermal decomposition of B_2Cl_4–olefin addition compounds results in the evolution of BCl_3 and the formation of a polymeric residue. The ease with which I decomposes and the observation that the BCl_3 is a decomposition product suggested that controlled thermal decomposition of I might lead to the formation and isolation of the three-membered boron heterocyclic system, boracycloprop-2-ene or borirene
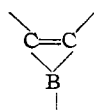
Compound I was pyrolyzed in individual experiments at 75, 105, 140, and 175°. Boron trichloride evolution increased with increasing temperature. A

white sublimate was isolated at all temperatures which by Cl and B analyses and ir spectra was identified as I. The residues from the pyrolyses were dark red viscous oils at the lower temperatures which became solids at higher temperatures. Pyrolysis at 90° for 1 hr yielded a solid residue with an apparent molecular weight of 355. Pyrolysis at 130° for 2 hr yielded a solid residue with an apparent molecular weight of 483. Examination of these solid residues by X-ray powder diffraction indicated only the presence of amorphous material. No evidence was obtained which would suggest that the monomeric three-membered ring
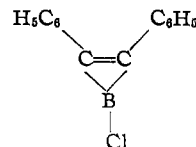
was formed.

The 2:1 adducts of trimethylamine, pyridine, and acetonitrile with I were pyrolyzed. It was anticipated that pyrolysis of these 2:1 adducts would intramolecularly displace the (Lewis base)·BCl_3 adduct and effect the formation of the coordinated three-membered heterocycle. Pyrolysis of the trimethylamine adduct at 100–110° afforded a white sublimate identified as $(CH_3)_3NHCl$, by its ir spectrum and analyses, and a volatile gas identified as $(CH_3)_3N$ by vapor pressure measurements. Continued heating at 140° for 6.5 hr produced additional $(CH_3)_3NHCl$, $N(CH_3)_3$, and a dark red residue which was amorphous (analyzed as 5.29% B vs. 4.70% for the 2:1 adduct).

Similarly, the pyrolysis of the pyridine 2:1 adduct with I at 120–130° effected the partial separation of a white solid and a liquid. The white solid was identified as pyridinium hydrochloride and the liquid as pyridine. The resulting reddish brown residue was amorphous and analyses at different stages of pyrolysis up to 250° showed increasing boron content. No evidence was obtained for the formation of the py·BCl_3 adduct. On the other hand, the pyrolysis of the acetonitrile 2:1 adduct at temperatures to 160° gave no sublimate but did liberate some acetonitrile. When I was placed in excess refluxing CH_3CN at 110°, a benzene-soluble material was recovered in addition to the benzene-insoluble 2:1 adduct of CH_3CN to I. Analysis of the soluble material gave a B:Cl ratio of 1.0. It is believed that dehydrohalogenation occurred to give $[C_2(C_6H_4)_2\text{-}B_2Cl_2·2CH_3CN]_x$, with the liberated hydrogen chloride reacting with CH_3CN to form acetimmonium chloride,[4] mp 6°.

Experimental Section

Materials.—B_2Cl_4 was prepared by the mercury-arc discharge method.[1] Matheson technical grade BCl_3 was used without further purification. Reagent grade NH_2CH_3, $NH(CH_3)_2$, and N-$(CH_3)_3$ were dried over Na under vacuum. The dried amines were recovered by vacuum distillation. Pyridine was dried by

(3) C. Chambers, A. K. Holliday, and S. M. Walker, *Proc. Chem. Soc.*, 286 (1964).

(4) A. E. Kulikova, *Zh. Obshch. Khim.*, **30**, 2180 (1960); *Chem. Abstr.*, **55**, 8345h (1961).

refluxing over Na. Diphenylacetylene (Matheson Coleman and Bell) and 1,2-benzenediol (Eastman) were used as received. Ethylene glycol was warmed to near its boiling point over a mixture of BaO and CaH₂ (slight excess above the anticipated moisture content of 5% by weight) and recovered by vacuum distillation. Acetonitrile was purified and dried initially by refluxing over $(P_2O_5)_2$ (5 g/l. of CH_3CN), followed by refluxing the distillate over CaH₂. The pure, dry CH_3CN was collected at 80°. Benzene, pentane, and CH_2Cl_2 were dried by refluxing over a mixture of CaCl₂ and CaH₂.

Apparatus.—Standard vacuum techniques were employed to handle volatile materials. Transfer of moisture- or air-sensitive nonvolatile materials took place in an inert-atmosphere box. Molecular weight determinations were achieved cryoscopically in C_6H_6 with the aid of a Beckman thermometer. X-Ray powder diffraction patterns of crystalline solids were obtained using Cu Kα radiation. Infrared spectra of solid samples were obtained from KBr disks.

All vacuum pyrolyses were carried out in a specially designed apparatus which allowed any sublimate to be isolated at −78°. The material being pyrolyzed was subjected to the reduced pressure of the vacuum pump at all times. A U trap cooled to −196° separated the pyrolysis equipment from the vacuum pump and condensed any other volatile material not collected at −78°.

Analyses.—Carbon and hydrogen analyses were commercially obtained. Boron analyses were performed by the Parr bomb fusion technique. Chlorine analyses were obtained by potentiometric titration with AgNO₃. Nitrogen determinations were performed by the micro Kjeldahl method.

Preparation of $C_2(C_6H_5)_2B_2Cl_4$.—Diphenylacetylene (19.6 g, 11 mmol) was introduced into a 200-ml vacuum reaction vessel which was connected to a vacuum line and evacuated. Dry pentane (60 ml) was distilled into the reaction vessel. B₂Cl₄ (13 mmol) was condensed into the reaction vessel in two equal increments 6 hr apart. The reaction was allowed to occur at 0° with stirring for a total of 15 hr. The product, a light yellow solid, was obtained by pumping away the solvent at room temperature. *Anal.* Calcd for $C_{14}H_{10}B_2Cl_4$: B, 6.33; Cl, 41.51; mol wt, 341.72. Found: B, 6.14; Cl, 38.9; mol wt, 335 (in C_6H_6).

Infrared spectrum (KBr, cm⁻¹): 3058 (vw), 3021 (vw), 1595 (w), 1570 (w), 1488 (m), 1437 (m), 1377 (s), 1295 (s, b), 1160 (m), 1072 (m), 1032 (w), 890 (w), 803 (w), 774 (m), 752 (s), 696 (s), 664 (m), 612 (vw), 530 (w).

Preparation of $C_2(C_6H_5)_2B_2(O_2C_2H_4)_2$.—$C_2(C_6H_5)_2B_2Cl_4$ (3.4 g, 10 mmol) and ethylene glycol (1.4 g, 22 mmol) were placed in a 100-ml reaction vessel which was connected to a vacuum line and evacuated. Methylene chloride (20 ml) was condensed onto the reactants. The mixture was stirred at −30° for 2 hr and then slowly warmed to 25° over a 5-hr period. The reaction appeared to go to completion at 0°. Removal of volatile materials at room temperature under vacuum afforded a white solid product. The reaction vessel was then warmed to 50° under vacuum to remove a slight excess of $C_2H_4(OH)_2$. *Anal.* Calcd for $C_{18}H_{18}$-B_2O_4: C, 67.56; H, 5.68; B, 6.76; mol wt, 320. Found: C, 65.69; H, 5.69; B, 6.44; mol wt, 325 (in C_6H_6).

X-Ray powder diffraction pattern data, d (relative intensity): 9.25 (vs), 7.25 (w), 6.81 (vw), 5.54 (m), 5.10 (s), 4.80 (vw), 4.49 (m), 4.33 (w), 4.13 (w), 3.80 (m), 3.72 (m), 3.49 (vs), 3.23 (w), 2.822 (s), 2.332 (m), 1.998 (m), 1.903 (vw), 1.631 (vw).

Infrared spectrum (KBr, cm⁻¹): 3058 (vw), 2976 (w), 2915 (m), 1592 (vw), 1585 (w), 1567 (w), 1490 (m), 1473 (m), 1441 (w), 1393 (s), 1366 (s), 1333 (s), 1323 (s), 1314 (s), 1234 (m), 1200 (s), 1171 (m), 1036 (m), 1007 (s), 948 (m), 934 (m), 859 (w), 781 (w), 776 (w), 757 (w), 712 (w), 705 (w), 554 (vw), 480 (vw).

Preparation of $C_2(C_6H_5)_2B_2(O_2C_6H_4)_2$.—A similar procedure was used here as described above. I was treated with 1,2-benzenediol in pentane in a 1:2 mole ratio. The product was a white crystalline solid. *Anal.* Calcd for $C_{26}H_{18}B_2O_4$: B, 5.20; mol wt, 416.08. Found: B, 5.39; mol wt, 391 (in C_6H_6).

X-Ray powder diffraction pattern data, d (relative intensity): 10.22 (vs), 6.97 (vw), 5.54 (s), 4.84 (w), 4.58 (w), 4.30 (vs),

3.83 (w), 3.67 (m), 3.55 (w), 3.43 (m), 3.19 (vw), 2.871 (vw), 2.536 (vw), 2.265 (vw).

Infrared spectrum (KBr, cm⁻¹): 3058 (vw), 3030 (vw), 1585 (w), 1570 (w), 1488 (m), 1468 (s), 1441 (w), 1399 (m), 1374 (s), 1330 (s), 1312 (s), 1250 (m, sh), 1224 (s), 1169 (m), 1124 (m), 1003 (w), 985 (w), 921 (w), 862 (w), 809 (m), 778 (m), 745 (s), 737 (s), 708 (s), 697 (m), 616 (w), 577 (w), 425 (w).

Preparation of $C_2(C_6H_5)_2B_2Cl_4 \cdot 2N(CH_3)_3$.—$C_2(C_6H_5)_2B_2Cl_4$ (0.39 g, 1.14 mmol) was introduced into a high-pressure vacuum vessel. $N(CH_3)_3$ (26.78 mmol) was condensed into the vessel. The mixture was stirred at 25° for 3 hr and then at 45° for 8 hr. The unreacted $N(CH_3)_3$ was removed and tensimetrically measured (24.51 mmol). A 2.27-mmol amount of $N(CH_3)_3$ was consumed in the reaction which gave a I to $N(CH_3)_3$ ratio of 1:1.99. The product was a white crystalline solid. Other experiments at 25° or lower, with or without the presence of solvent, gave incomplete reaction and generally a very light yellow solid. *Anal.* Calcd for $C_{20}H_{28}B_2Cl_4N_2$: C, 52.22; H, 6.15; B, 4.70; Cl, 30.84; N, 6.09. Found: C, 51.79; H, 6.19; B, 4.51; Cl, 29.65; N, 5.17.

X-Ray powder diffraction pattern data, d (relative intensity): 8.67 (s), 7.76 (w), 6.15 (vs), 5.04 (w), 4.62 (vw), 4.31 (s), 4.11 (m), 3.87 (m), 3.45 (w), 2.614 (vw).

Infrared spectrum (KBr, cm⁻¹): 3049 (vw), 3012 (w), 2950 (vw), 2688 (m), 2463 (w), 1595 (w), 1567 (w), 1484 (s), 1464 (s), 1453 (m), 1437 (w), 1412 (w), 1346 (w, b), 1256 (w), 1124 (m), 1095 (s), 1035 (s), 1011 (m), 968 (m), 944 (s), 830 (m), 794 (w), 780 (m), 767 (m), 751 (s), 742 (s), 708 (m), 695 (m), 670 (w), 562 (m), 504 (w), 440 (w), 410 (w, b).

Preparation of $C_2(C_6H_5)_2B_2Cl_4 \cdot 2CH_3CN$.—Compound I was heated with stirring in the presence of excess acetonitrile at 70° for 6 hr. Evaporation of the excess CH_3CN produced a light yellow solid and a small amount of a reddish viscous liquid. The solid was extracted with benzene. Two materials were isolated—one insoluble and the other soluble in C_6H_6. The C_6H_6-soluble material was dark yellow and was shown to be amorphous (analyzed 5.83% B and 18.64% Cl, B:Cl = 1.02). The desired product was a light tan solid insoluble in C_6H_6. The treatment of I with CH_3CN at 25° gave incomplete reaction. Prolonged refluxing of I in CH_3CN produced almost all polymeric material (C_6H_6 soluble). *Anal.* Calcd for $C_{18}H_{16}B_2Cl_4N_2$: B, 5.10; Cl, 33.46; N, 6.61. Found: B, 5.19; Cl, 32.50; N, 6.38.

X-Ray powder diffraction pattern data, d (relative intensity): 9.56 (vs), 8.51 (s), 7.66 (s), 5.85 (s), 5.11 (s), 4.70 (vs), 4.42 (w), 4.25 (m), 4.00 (m), 3.70 (m), 3.41 (s), 3.26 (w), 3.17 (m), 3.05 (s), 2.936 (w), 2.858 (m), 2.759 (vw), 2.702 (m), 2.501 (m), 2.222 (w).

Infrared spectra (KBr, cm⁻¹): 3049 (vw), 3021 (vw), 2967 (vw), 2907 (vw), 2331 (m), 1626 (s), 1595 (m), 1567 (vw), 1486 (s), 1437 (s), 1370 (s, b), 1258 (s, b), 1230 (s), 1166 (s), 1065 (m), 1028 (w), 931 (m), 779 (m), 749 (s), 726 (m), 701 (s), 573 (m), 568 (m), 539 (s), 524 (m).

Preparation of $C_2(C_6H_5)_2B_2Cl_4 \cdot 2C_5H_5N$.—Dry pyridine (10 ml) was condensed into a reaction vessel containing 0.60 g (1.76 mmol) of I. The solution was stirred at 25° for 12 hr and then at 45° for 6 hr. Evaporation of the excess pyridine afforded a light yellow solid. The resulting solid was extracted with C_6H_6. A small amount of yellow solid was recovered from the C_6H_6-soluble fraction which was shown to be amorphous by X-ray powder diffraction data and produced a broad, ill-defined ir spectrum. The desired white product was the C_6H_6-insoluble material. *Anal.* Calcd for $C_{24}H_{20}B_2Cl_4N_2$: B, 4.33. Found: B, 4.25.

Infrared spectra (KBr, cm⁻¹): 3096 (vw), 3030 (vw), 1623 (s), 1595 (w), 1570 (w), 1488 (m), 1451 (s), 1441 (m, sh), 1339 (w), 1118 (s), 1094 (s), 1028 (m), 950 (w), 869 (m), 816 (s), 773 (m), 748 (s), 711 (vw), 698 (vw), 560 (m).