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Behavior of *trans*-μ-Dichloro-dichlorobis(ethylene)-diplatinum(II) in Various Solvents[1]

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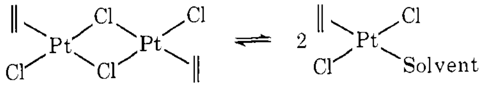
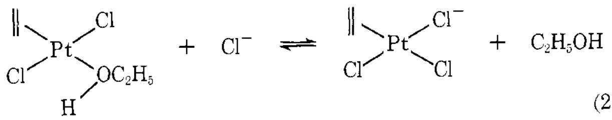
The dimeric nature of *trans*-μ-dichloro-dichlorobis(ethylene)diplatinum(II), $[Pt(C_2H_4)Cl_2]_2$, was demonstrated by the molecular weight determinations of Anderson,[2] who used the Barger–Rast method in benzene, and Chatt,[3] who measured the boiling point elevation for benzene where some slow decomposition occurs. However, McMane and Martin[4] reported that in ethanol the compound was largely present as monomeric units which were formed presumably by the reaction



(1)

In addition, they were able to measure the quotient for the rapidly established equilibrium (eq 2) in the presence of added HCl.



(2)

It is generally recognized that the reversible solvation reactions, of which reaction 2 is an example, deserve careful characterization since they provide a pathway for at least a portion of many ligand-substitution reactions of the complexes of platinum(II).[5] Consequently, the behavior of $[Pt(C_2H_4)Cl_2]_2$ in several different solvents has been characterized. $[Pt(C_2H_4)Cl_2]_2$ was prepared by the method of Chatt and Searle.[6] The infrared spectrum in a Nujol mull over the region from 250 to 4000 cm^{-1} was in substantial agreement with the bands reported in the literature.[7]

A reflectance spectrum of the solid compound recorded in the visible and near-uv region by a Beckman DU spectrophotometer is shown in Figure 1. This spectrum, which must be attributed to the undissociated dimer, clearly shows a maximum at about 360 mμ and a shoulder at *ca.* 440 mμ. In various solvents, however, there are considerable differences in the spectra exhibited by this material. Figure 2A shows spectra for solutions in methanol, acetone, tetrahydrofuran, and dichloroethane while Figure 2B shows spectra in ethanol, carbon tetrachloride, and cyclohexane.

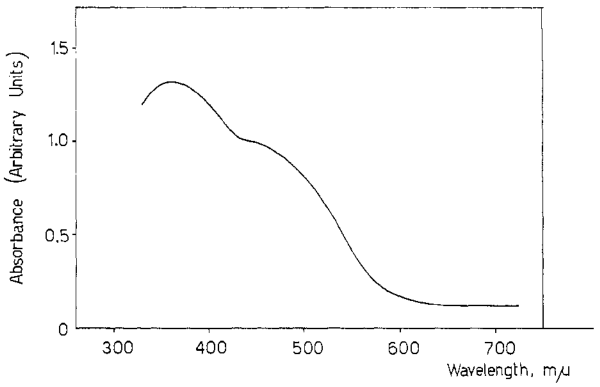


Figure 1.—Reflectance spectrum of *trans*-μ-dichloro-dichlorobis(ethylene)diplatinum(II).

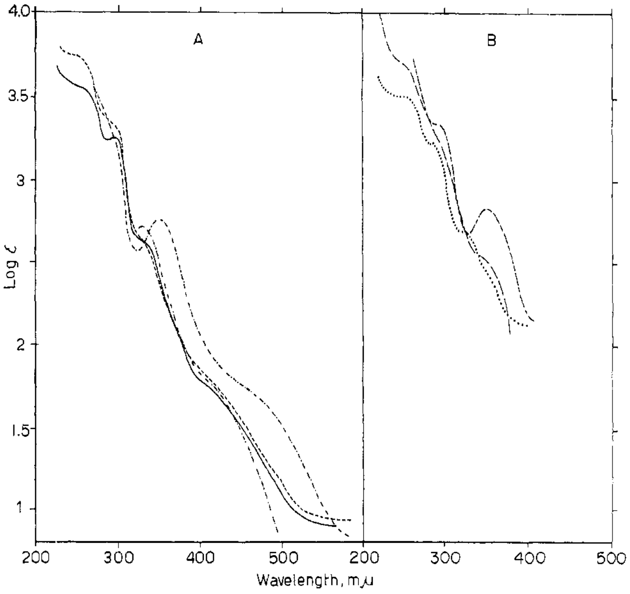


Figure 2.—Absorption spectrum of solutions of *trans*-μ-dichloro-dichlorobis(ethylene)diplatinum(II) in various solvents at 25°. (A) Spectra recorded with a Beckman Model DK2 spectrophotometer: —·—·, dichloroethane; —··—, acetone; ——, methanol; ------, tetrahydrofuran. (B) Spectra recorded with a Cary Model 14 spectrophotometer: -----, carbon tetrachloride; ······, ethanol; – – – –, cyclohexane.

The molar conductivity of solutions of $[Pt(C_2H_4)Cl_2]_2$ in several solvents has been evaluated by means of a conductivity bridge, LKB Type 3216B. The results are collected in Table I. Also in this table are the molecular weights obtained for this compound in the solutions as evaluated in a Mechrolab osmometer, Model 302, at 37°.

It appears from the data in Table I that in the oxygen-containing solvents the compound is largely present as monomeric units. The low conductances indicate that whereas there may be minor concentrations of ionic species, these are not a major factor in the dis-

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(1) Work was performed in part in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2529.

(2) J. S. Anderson, *J. Chem. Soc.*, 971 (1934).

(3) J. Chatt, *ibid.*, 3340 (1949).

(4) D. G. McMane and D. S. Martin, Jr., *Inorg. Chem.*, **7**, 1169 (1968).

(5) (a) A. F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 5; (b) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin & Co., New York, N. Y., 1965, Chapter 2.

(6) J. Chatt and M. L. Searle, *Inorg. Syn.*, **5**, 221 (1957).

(7) (a) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953); (b) J. P. Sorzano and J. P. Fackler, *J. Mol. Spectry.*, **22**, 80 (1967).

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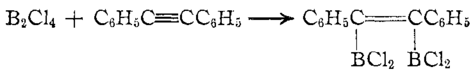
Potentially reactive bis(dichloroboryl) sites produced by the addition of tetrachlorodiborane(4), B_2Cl_4, to acetylene and olefins[1] have prompted us to examine the reaction of B_2Cl_4 with diphenylacetylene and to study some reactions of the resulting product.

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,



$$B_2Cl_4 + C_6H_5C{\equiv}CC_6H_5 \longrightarrow \underset{BCl_2}{C_6H_5C}{=}\underset{BCl_2}{CC_6H_5}$$

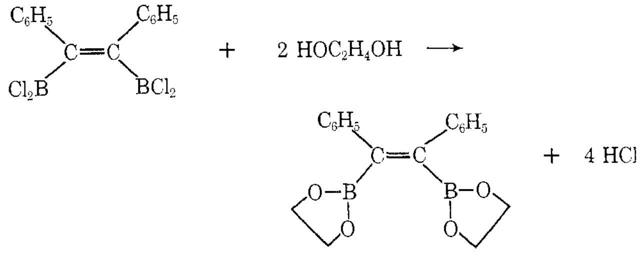
I

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]

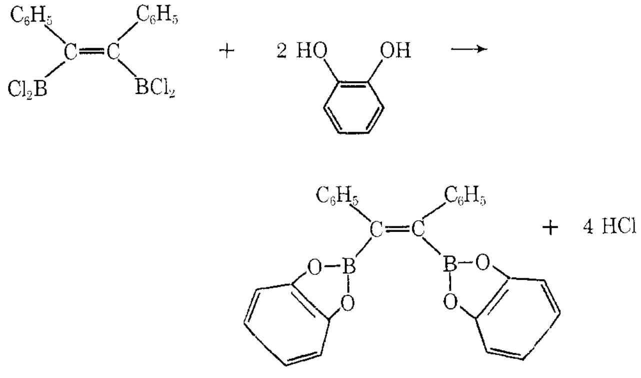
Compound I is a light yellow solid which is quite sensitive to moisture. It melts at about 60° under an atmosphere of dry nitrogen. Under vacuum it sublimes with some decomposition at or slightly above the fusion point.

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



II



III

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[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).

[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).