

The formation of the *cis*-[Pt(NH₃)₂Cl₂] by the reaction of NH₃ with [Pt(NH₃)Cl₃]⁻ may not be a direct substitution of ammonia for chloride. The high yield of the *cis*-isomer probably reflects the relative competition of chloride and ammonia to replace H₂O in the *cis*- and *trans*-[Pt(NH₃)Cl₂(H₂O)], both of which exist in the solutions in their equilibrium concentrations. However, the direct substitution of NH₃ in [Pt(NH₃)Cl₃]⁻ by a slow second-order process is not precluded.

The experimental work has indicated considerable differences in the ΔF^0 for the acid hydrolysis of chloride ligands in the Pt^{II} complexes. Because of these differences the concentrations of some hydrolysis products escape detection, despite the fact that all the hydrolysis reactions occur at nearly the same rates. No simple correlation of the stability

of the various complexes toward the acid hydrolysis with total ionic charge, the nominal charge distribution in the complex, or a geometrical arrangement of the groups to maximize the extent of π -bonding has appeared. Yet it appears that a satisfactory explanation for the stabilities of the various complexes must be presented before a satisfactory description of the substitution processes can be given.

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The Molecular Configuration of Dicobalt Hexacarbonyl Diphenylacetylene

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The configuration of dicobalt hexacarbonyl diphenylacetylene has been determined by X-ray crystal structure analysis and is reported at a preliminary stage of refinement. The crystals are monoclinic with $a = 16.01 \text{ \AA}$, $b = 15.94 \text{ \AA}$, $c = 8.015 \text{ \AA}$, and $\beta = 107.6^\circ$. There are four molecules in a unit cell of space group Cc-C_s⁴. The molecule has sixfold coordination about the cobalt atoms in a distorted octahedral configuration with the C-C bond of the acetylene approximately normal to the Co-Co bond in a distorted tetrahedral arrangement that gives approximate C_{2v} symmetry for the molecule, except for the benzene rings. The molecule can be related to the proposed structures of dicobalt octacarbonyl, which are based upon a trigonal bipyramidal system of bonds, by considering the bonds from the cobalt atoms to the acetylenic linkage as metal atom- π bonds similar to those found for the palladium chloride complexes with ethylene.

The compound dicobalt hexacarbonyl diphenylacetylene, (CO)₆Co₂[C₂(C₆H₅)₂], hereinafter referred to as DHDPA, is derived from dicobalt octacarbonyl through the replacement of two C≡O groups by the hydrocarbon ligand in a reaction that is quite general for alkynes.^{2,3} Dicobalt octacarbonyl, like most of the transition metal carbonyls, is active as a catalyst for introducing H₂ and/or C≡O into organic molecules and DHDPA can be regarded as simply a stable intermediate formed in a typical reaction of this type.⁴ The structure of DHDPA, determined through X-ray analysis and reported here at a preliminary stage of refinement, represents one of the first molecules to be studied which exhibit a multi-point attachment of a single organic molecule to more than one metal atom, possibly analogous to the postulated attachment of an organic substrate to a metal surface at more than one point during heterogeneous catalytic reactions.^{5,6} In the structure of DHDPA we have

definite structural evidence in support of such a theoretical model.

DHDPA forms dark purple crystals which are found to be monoclinic with the lattice parameters

$$\begin{aligned} a &= 16.01 \text{ \AA} \\ b &= 15.94 \text{ \AA} \\ c &= 8.015 \text{ \AA} \\ \beta &= 107.6^\circ \end{aligned}$$

These lattice parameters coupled with the measured density give an experimental value for the number of molecules per unit cell of $z = 3.82$ ($z = 4$). Systematic absences require the space group to be either C2/c or Cc, and, although the crystal morphology and the absence of any measurable piezoelectric effect favor the holohedry, the structure has been determined to occupy the space group Cc-C_s⁴, which has no positions of symmetry.

Complete X-ray intensity data were obtained for DHDPA with equi-inclination Weissenberg techniques using iron K α X-radiation. The structure has been solved and refined by straightforward methods of X-ray analysis, all in three dimensions *viz.*, a Patterson function, a Fourier synthesis based on the cobalt atoms alone, three cycles of least-squares refinement and a difference-Fourier synthesis in which the cobalt atoms were subtracted. All of the atoms of the structure are well resolved in the electron density maps and although the structure is not completely refined the configura-

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(2) H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, H. R. Markby and I. Wender, *THIS JOURNAL*, **76**, 1457 (1954).

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(5) B. M. W. Trapnell, "Chemisorption," Butterworths Scientific Publications, London, 1955, p. 218 *et seq.*

(6) I. Wender and H. W. Sternberg, "Advances in Catalysis and Related Subjects," Academic Press, Inc., New York, N. Y., 1957, p. 394 *et seq.*

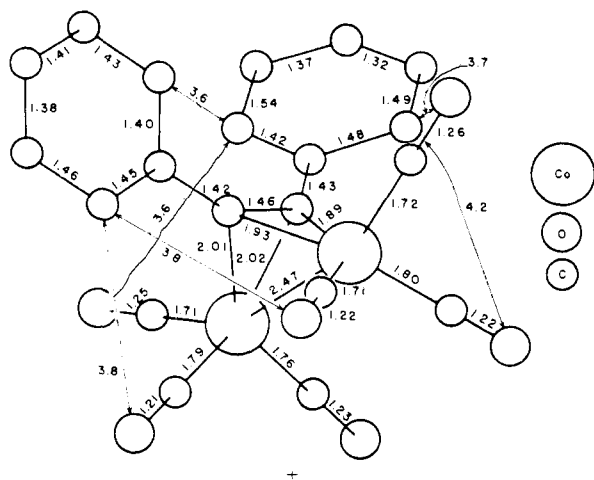


Fig. 1.—The bond lengths of dicobalt hexacarbonyl diphenylacetylene.

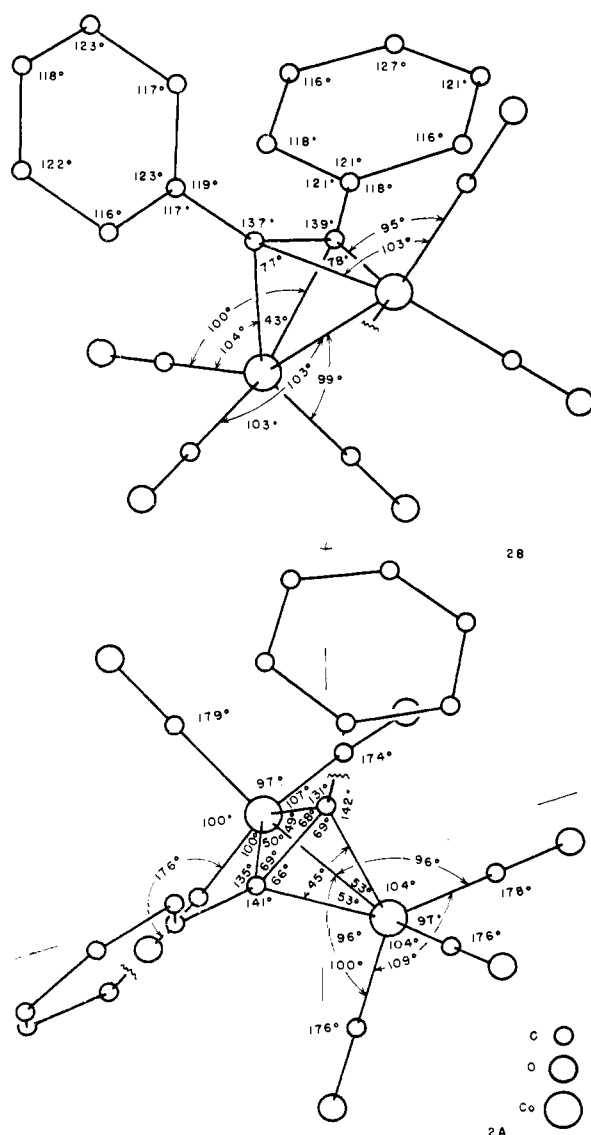


Fig. 2.—The bond angles of dicobalt hexacarbonyl diphenylacetylene.

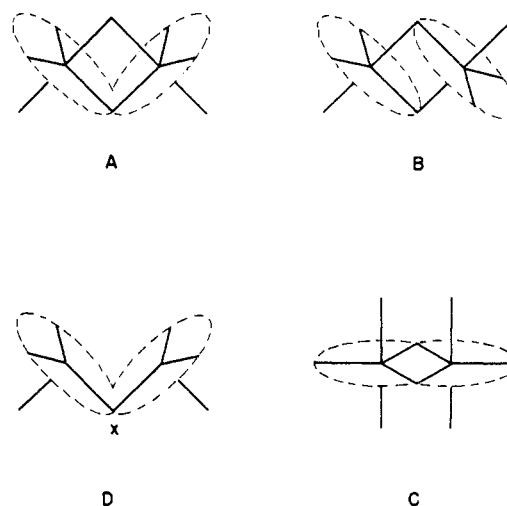


Fig. 3.—A, B and C are the three structures of dicobalt octacarbonyl which are based upon a trigonal bipyramidal configuration for the cobalt atoms.⁸ D is a simplified representation of the related structure found for dicobalt hexacarbonyl diphenylacetylene, where the x indicates the midpoint of the acetylenic linkage. The dp orbital which is not used for bonding is omitted from D.

tion of the molecule is definitely established. The reliability index "R" for the 986 observable reflections, of which only 16 were too weak to estimate, was 16% for the calculation of the structure factors used in the evaluation of the difference-Fourier synthesis. The details of the solution of the structure and a description of the results of further refinement will be reported elsewhere.

The dimensions and bond angles of the DHDPA molecule are shown in Figs. 1 and 2. Figures 1 and 2B are projections of the molecule along [001] onto (001), while Fig. 2A is a *b*-axis projection. The simplest description of the structure would be that the coordination about the cobalt atoms is sixfold, a distorted octahedral configuration presumably derived from d^2sp^3 hybridization, while the coordination about the acetylene carbon atoms is fourfold, a distorted tetrahedral configuration possibly derived from sp^3 hybridization. The Co-Co bond, 2.47 Å., is nearly normal (88°) to the C-C bond of the acetylene so that the molecule has very roughly the symmetry C_{2v} , except for the benzene rings, the planes of which make an angle of 62° with each other.

It is also possible to describe the configuration about the cobalt atoms of DHDPA in terms of a trigonal bipyramid, related to the generally accepted structure(s) of the parent compound dicobalt octacarbonyl,⁷⁻⁹ if a different type of bond is used from the metal atom to the acetylenic linkage; see Fig. 3. Three of the bonds are to the carbonyl groups and the fourth is directed toward the midpoint of the acetylenic bond, which places an orbital of each of the cobalt atoms in a position to overlap one of the two π -orbitals of the triple

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bond. This would then give two bonds which are similar to the metal atom-olefin bonds of the platinum (or palladium) chloride complexes with ethylene, as suggested by Chatt and Duncanson,¹⁰ and subsequently confirmed by the X-ray analysis of Dempsey and Baenziger¹¹ and that of Holden and Baenziger.¹²

The bond angles between the carbonyl groups and those from the acetylene to the benzene rings differ appreciably from the ideal values of either of the *approximate* models given above. Undoubtedly some of the distortion is due to steric interaction involving the benzene rings and also other molecules but on the other hand no attempt has been made to evaluate the contribution of the partial double bond character of the cobalt-carbonyl bonds to the configuration of the molecule. A knowledge of the molecular dimensions of the dimethylacetylene derivatives and of the acetylene derivative would be valuable for comparison since they would have considerable less structural hin-

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drance. A discussion of the relative merits of the two alternative systems of bonding for DHDPA, both of which lead to a closed krypton shell for the cobalt atoms, will be deferred until the structure is completely refined.

The structure which has been found for DHDPA is consistent with the absence of bridging carbonyl stretching frequencies in the infrared, the observed diamagnetism and the large observed dipole moment.^{2,3}

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[CONTRIBUTION FROM THE POLYMER RESEARCH INSTITUTE, POLYTECHNIC INSTITUTE OF BROOKLYN]

Reactions of Polymers with Reagents Carrying Two Interacting Groups. I. The Quaternization of Poly-(4-vinylpyridine) with Bromoacetic Acid^{1,2}

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Initial rates of quaternization of poly-(4-vinylpyridine) and 4-methylpyridine with bromoacetate ion and α -bromoacetamide were measured in water solution at 50°. The quaternizations of 4-methylpyridine are subject to a small positive salt effect. The reaction rate of the cationic polymer with bromoacetate increases sharply with an increase in the degree of ionization of the polymer and a decrease in the ionic strength of the solution due to the electrostatic attraction of the polycation with the anionic reagent. However, these variables have a smaller effect on the second-order rate constant for this reaction than on the apparent ionization constant of the pyridinium residues. It is concluded that in the transition state of the quaternization reaction the carboxylate group of the bromoacetate is at a lower electrostatic potential than the charges of the pyridinium residues.

Introduction

The generally accepted theories of enzyme action assume that a number of distinct sites of the enzyme cooperate in attaching themselves to different portions of the substrate molecule. A typical example of this principle is provided by the action of acetylcholine esterase, where an "esteratic site" of the enzyme is involved in the attack on the ester function, while an "anionic site" serves to stabilize the transition state by partly electrostatic interaction of a negatively charged site on the enzyme with the cationic end of the substrate molecule.³ In this and a following investigation, we shall explore the possibilities of producing similar cooperative effects in reactions of high polymers with bifunctional small molecules. In this study we selected the quaternization of partially ionized

poly-(4-vinylpyridine) with bromoacetate ions, since it might have been expected that the displacement of the bromine by an un-ionized pyridine residue would be aided by the interaction of the carboxylate with a neighboring cationic pyridinium group. The reaction of the anionic bromoacetate was compared with that of the uncharged bromoacetamide both in the quaternization of poly-(4-vinylpyridine) and its monofunctional analog 4-methylpyridine.

Experimental

Materials.—Bromoacetic acid of highest purity was melted, distilled under nitrogen, b.p. 118° (15 mm.) and kept frozen in a desiccator over sulfuric acid. The α -bromoacetamide was prepared by the procedure of Papendieck⁴ (m.p. 91°). Highest purity 4-methylpyridine was distilled under dry nitrogen from barium oxide, b.p. 64° (30 mm.), n_D^{25} 1.5034. Poly-(4-vinylpyridine) (PVPy) was prepared from freshly distilled 4-vinylpyridine by emulsion polymerization,⁵ with Tergitol P-28 (Carbide and Carbon Chem. Co.) as the emulsifier. The intrinsic viscosity of the polymer

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(2) Financial assistance of this study by the Office of Ordnance Research, U. S. Army, and by a grant of the Monsanto Chemical Company are gratefully acknowledged.

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