AN INVESTIGATION OF THE MICROWAVE ROTATIONAL SPECTRA OF METHYLSELENOCYANATE AND METHYLTHIOCYANATE

AND

THE PREPARATION OF SUBSTITUTED ACETYLENIC DICOBALTHEXACARBONYL COMPLEXES CONTAINING PHOSPHORUS AND ARSENIC DONOR LIGANDS

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ABSTRACT

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PART ONE: AN INVESTIGATION OF THE MICROWAVE ROTATIONAL SPECTRA OF METHYLSELENOCYANATE AND METHYLTHIOCYANATE

This part of the Thesis describes the results of a study of the rotational spectra of methylselenocyanate and methylthiocyanate in the region between 26.5 GHz and 40.2 GHz. In the case of the thiocyanate molecule, the spectrum was studied with the prime purpose of providing a model for the study of the previously unreported spectrum of methylselenocyanate. Particular attention was paid to the dependence of the barrier to internal rotation of the methyl group on the value of the rotational quantum number J.

For methylselenocyanate the rotational constants of five molecular species containing different isotopes of selenium were determined and an approximate structure is suggested which generates rotational constants which are in good agreement with the experimental values. The barrier to internal rotation of the methyl group was also calculated. The bonding in the XCN group and the origin of the barrier to internal rotation in molecules of this type are discussed.

PART TWO: THE PREPARATION OF SUBSTITUTED ACETYLENIC DICOBALTHEXACARBONYL DERIVATIVES CONTAINING PHOSPHORUS AND ARSENIC DONOR LIGANDS

This part of the Thesis reports the preparation and characterization of substituted acetylenic dicobalthexacarbonyl complexes in which up to four CO groups have been replaced by either monodentate or bidentate phosphorus and arsenic donor ligands.

With the monodentate ligands, complexes have been prepared having the general formula $(R_2C_2)Co_2(CO)_{6-n}(L)_n$, where R = Ph or CF_3 and L is a trialkyl phosphine or phosphite ligand. Some PF_3 derivatives have also been prepared. On the basis of a study of the infrared spectra of the disubstituted (n = 2) derivatives in the CO stretching region, structures for these complexes are suggested in which the axial CO groups are preferentially substituted. Possible reasons for this preference are discussed.

With bidentate ligands of the type $Ph_2M(CH_2)_nMPh_2$ where M = P or As and n = 1 or 2, di- and tetrasubstituted derivatives have been prepared in which the ligands are bridging the Co-Co bond. Trisubstituted complexes have also been prepared in which there is one bridging bidentate ligand and one ligand which is coordinated at one end only.

TABLE OF CONTENTS

PART ONE

PART TWO

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LIST OF TABLES

PART ONE

PART TWO

LIST OF ILLUSTRATIONS

PART ONE

PART TWO

PART ONE

AN INVESTIGATION OF THE MICROWAVE ROTATIONAL SPECTRA
OF
METHYLSELENOCYANATE AND METHYLTHIOCYANATE

CHAPTER I. INTRODUCTION.

The purpose of this part of the thesis is to present the results of an investigation of the rotational spectra of methylselenocyanate and methylthiocyanate in the frequency range of 26.5 GHz to 40.2 GHz. No previous reports of the rotational spectrum of methylselenocyanate have been published, and for methylthiocyanate it was desired to extend the frequency range studied beyond that of previous workers in order to make certain comparisons between the two molecules.

In the case of methylselenocyanate, the scope of the study was primarily to identify the spectral lines in the available frequency region and to measure their frequencies. This then permits calculation of the rotational constants and the determination of an approximate structure of the molecule. No attempt was made to determine a definitive structure of the molecule since this would have required separate isotopic substitution of each atom in the molecule. The scope of this work did not warrant the extensive problems associated with the isotopic enrichment of carbon and nitrogen in a system where there are already five major naturally occurring isotopes of selenium.

A further reason for studying the methylselenocyanate molecule was to determine the barrier to internal rotation of the methyl group about the carbon-selenium bond. Barrier determinations in other similar molecules containing the CH_3X- group (X = O, S, Se) have shown that the barrier height is always larger when X is sulphur than when X is oxygen. This has been observed in the CH_3XH, $CH_3XC{\equiv}N$ and $CH_3XC{\equiv}CH$ series. In the CH_3XH series the selenium species has also been studied and it has been found that the barrier is lower than that of the CH_3SH molecule and almost equal to the barrier in CH_3OH. It was of interest to measure the barrier height in CH_3SeCN in order to see whether a similar trend existed for the CH_3XCN series. This might then serve to further the understanding of the origin of these internal rotational barriers in molecules of this type.

In the case of methylthiocyanate the microwave rotational spectrum has previously been thoroughly investigated by several groups and much information about the molecule has been extracted. [1 - 7] One reason for the further investigation done here is that it was desirable to have a model for the study of the spectrum of CH_3SeCN. Since the two molecules are expected to have similar structures, their spectra should be subject to the same selection rules and hence should exhibit similar patterns. The spectrum of the methylselenocyanate molecule was expected to be considerably weaker and much more complex than that of methylthiocyanate due to the fact that selenium has five isotopes of significant natural abundance. The assignment of the spectral lines was therefore expected to be extremely difficult without the help of a model molecule.

The second reason for a further investigation of the thiocyanate spectrum was to extend the frequency region which had been studied. The only available transitions for the measurement of the barrier to internal rotation in the methylselenocyanate molecule were those which could lead to considerable error due to the non-ideal behaviour of the molecule at high rotational quantum numbers. From the error found in the barrier heights determined for methylthiocyanate from transitions between the same quantum levels, some information can be obtained on the accuracy of the barrier height calculated for CH_3SeCN.

It was considered necessary to first give an outline of the theory of rotational spectra. This is the subject of CHAPTER II, which commences with a brief discussion of molecular rotation in general, and then discusses certain areas which are specifically relevant to this work in detail. For a complete description of the principles and techniques of microwave rotational spectroscopy the reader is referred to several texts available.[8 - 11] CHAPTER III gives the experimental information including a description of the microwave spectrometer, and the results of the spectral investigations are presented in CHAPTER IV and CHAPTER V for methylthiocyanate and methylselenocyanate respectively. The thesis is concluded by a general discussion on two aspects of related molecules which contain the CH_3X- group. These two aspects are the origin of the barrier to internal rotation and the nature of the bonding in the XCN group.

CHAPTER II. THEORY OF ROTATIONAL SPECTROSCOPY.[8-11]

SECTION A. MOLECULAR ROTATION

When considering its rotational energy, a molecule is viewed as a rigid assembly of point masses. This "rigid body" posesses a unique center of mass (COM), and the positions of the individual atoms are described by a Cartesian coordinate system, the origin of which lies at the COM and the axes of which correspond to the principal moments of inertia of the molecule. No real system is entirely rigid but effects due to centrifugal distortion and internal motion can be treated by perturbation methods or can be ignored if they are small.

The principal moments of inertia of a molecule are best described using the classical concept of the "inertial ellipsoid". This ellipsoid has its center at the center of mass of the molecule and its shape corresponds to the envelope of lines constructed through the COM, the lengths of which are proportional to the moment of inertia of the molecule about that line as axis. An ellipsoid has three perpendicular principal axes, and if these axes are chosen as the Cartesian coordinate axes of the molecule and the moments of inertia along the direction of these principal axes are I_x, I_y and I_z, then the equation of the ellipsoid may be written

$$\frac{x^2}{I_x^2} + \frac{y^2}{I_y^2} + \frac{z^2}{I_z^2} = 1 \qquad \text{(II-A-1)}$$

where I_x, I_y and I_z are called the principal moments of inertia of the molecule.

These principal moments of inertia are calculated from the positions and masses of the atoms in the molecule. The method of calculation described here is that of Kraitchman,[12] and is as follows: If a molecule is made up of atoms of mass m_1, $m_2 \ldots m_i \ldots$, which are situated at distances (x_1, y_1, z_1), $(x_2, y_2, z_2) \ldots (x_i, y_i, z_i) \ldots$ from the origin of an arbitrary system of Cartesian coordinates, then the coordinates of the COM in this system, (x_o, y_o, z_o), are given by the following type of expression:

$$x_o = \frac{\sum_i m_i x_i}{\sum_i m_i} \qquad \text{(II-A-2)}$$

If a new Cartesian coordinate system is now set up with this COM as its origin, then the principal moments of inertia, I_x, I_y and I_z, can be determined from the roots, I, of the determinental equation

$$\begin{vmatrix} I_{xx} - I & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} - I & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} - I \end{vmatrix} = 0 \qquad \text{(II-A-3)}$$

The quantities I_{xx}, I_{yy}, and I_{zz} are defined by equations of the following type and are called moments of inertia:

$$I_{xx} = \sum_i m_i y_i^2 + \sum_i m_i z_i^2$$

$$- \frac{(\sum_i m_i y_i)^2 - (\sum_i m_i z_i)^2}{\sum_i m_i} \qquad \text{(II-A-4)}$$

The off-diagonal elements, I_{xy}, I_{xz}, etc., are called products of inertia and are defined by equations of the following type:

$$I_{xy} = - \sum_i m_i x_i y_i + \frac{(\sum_i m_i x_i)(\sum_i m_i y_i)}{\sum_i m_i} \qquad \text{(II-A-5)}$$

Solution of equation II-A-3 also gives the direction cosines of the principal axes of the molecule with respect to the original coordinate system chosen.

Molecular rotation is generally described in terms of these principal moments of inertia which are designated I_A, I_B and I_C so that $I_A < I_B < I_C$. A rotating molecule is classified based on the relative values of its three principal moments. An asymmetric rotor is one which has three non-equal moments of inertia, while a molecule which has its three moments equal is called a spherical rotor. Between these two extremes are symmetric rotors and linear molecules. A symmetric rotor has two moments which are equal in magnitude and therefore must have an axis of three- or more-fold symmetry. A prolate symmetric rotor has its two equal moments of inertia greater than the third ($I_A < I_B = I_C$). In an oblate symmetric rotor the two smaller principal moments of inertia are equal ($I_A = I_B < I_C$). A linear molecule is a special case of a symmetric rotor in which the moment of inertia about the internuclear axis is equal to zero.

The structure of a molecule can be determined from its rotational spectrum if several different isotopic species are examined. The position of a particular atom in a Cartesian coordinate system with its origin at the COM of the molecule can be calculated from the differences in the principal moments of inertia of two molecules containing different isotopes of that atom. These moments of inertia are determined directly from the line frequencies in the rotational spectrum of the molecule.

SECTION B. ROTATIONAL ENERGY LEVELS AND SPECTRA OF THE ASYMMETRIC ROTOR

In the case of the asymmetric rotor the energy levels are described by examining their behaviour as it begins to deviate from the two simple extremes of the prolate and oblate symmetric rotors. It is therefore necessary to first discuss the rotation of the symmetric rotor.

Figure II-B-1 illustrates the motion of a symmetric rotor molecule with three-fold symmetry. The symmetry axis of the molecule is designated as the z axis, and the molecule undergoes two types of motion. The symmetry axis precesses around the total angular momentum, P, and the molecule may spin about the symmetry axis at the same time. The rotational energy is given by

$$w = \frac{P_x^2}{2I_x} + \frac{P_y^2}{2I_y} + \frac{P_z^2}{2I_z} \qquad \text{(II-B-1)}$$

where x, y and z are the Cartesian coordinates along the principal axes, and I_x, I_y and I_z are the corresponding

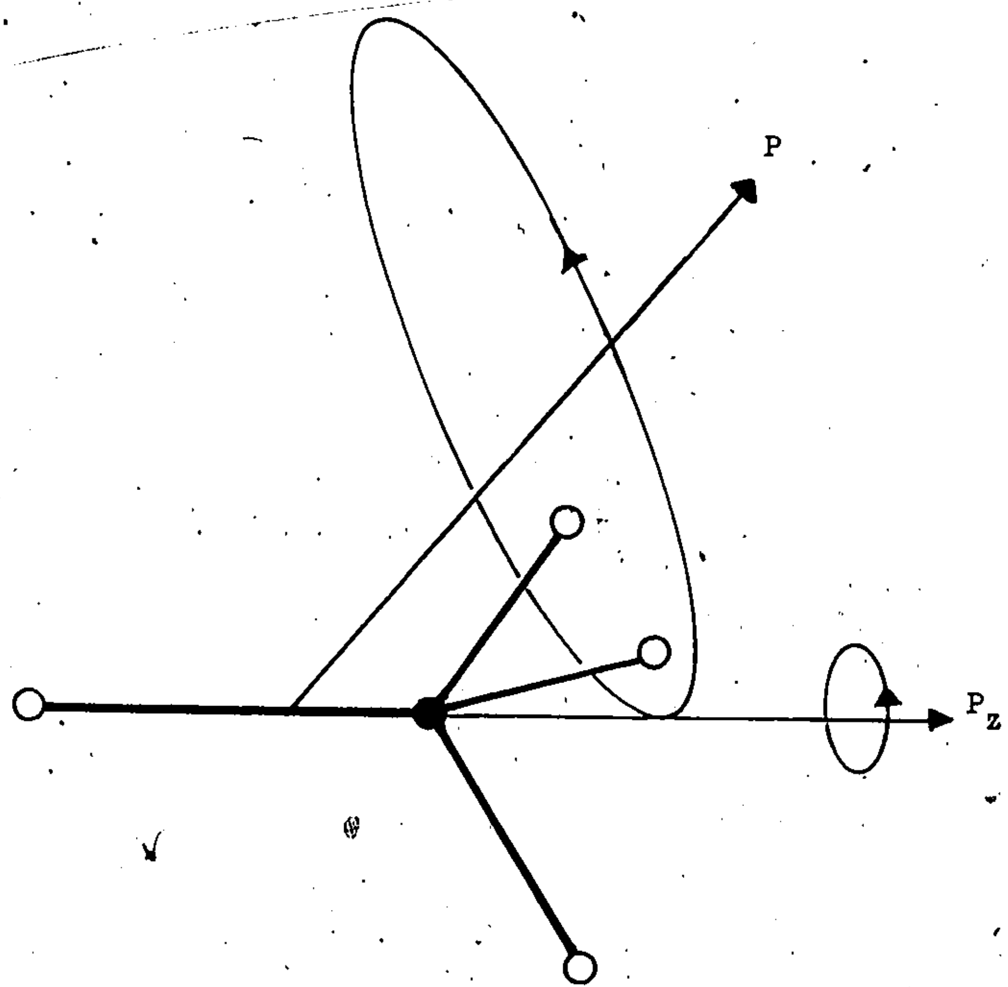

Figure II-B-1. The motion of a symmetric rotor as taken from ref. 8.

principal moments of inertia about these axes. P_x, P_y and P_z are the projections of the total angular momentum, P, on the x, y and z axes respectively, and

$$P^2 = P_x^2 + P_y^2 + P_z^2 \qquad \text{(II-B-2)}$$

In a symmetric rotor I_x is equal to I_y and is called I_B. The value of I_z is different from the other two and is designated I_A. These designations correspond to a prolate symmetric rotor where $I_A < I_B = I_C$. Equation (II-B-2) can then be rewritten

$$w = \frac{P^2}{2I_B} + P_z^2 \left(\frac{1}{2I_A} - \frac{1}{2I_B} \right) \qquad \text{(II-B-3)}$$

The square of the total angular momentum is quantized and is given by

$$P^2 = \frac{J(J+1)h^2}{4\pi^2} \qquad J = 0, \pm 1, \pm 2 \ldots$$

$$\text{(II-B-4)}$$

Similarly, the component of P along the z axis is quantized and is given by

$$P_z^2 = \frac{K^2h^2}{4\pi^2} \qquad K = J, J-1, \ldots -J \qquad \text{(II-B-5)}$$

Substitution of equations II-B-4 and II-B-5 into equation II-B-3 gives

$$w = \frac{J(J+1)h^2}{8\pi^2 I_B} + \left(\frac{h^2}{8\pi^2 I_A} - \frac{h^2}{8\pi^2 I_B}\right) K^2 \qquad \text{(II-B-6)}$$

In order to further simplify this expression, rotational constants A, B and C are defined by equations of the following type:

$$A = \frac{h}{8\pi^2 I_A} \qquad \text{(II-B-7)}$$

Equation II-B-6 then becomes

$$E = BJ(J+1) + (A - B)K^2 \qquad \text{(II-B-8)}$$

where E is the rotational energy in MHz if the rotational constants are expressed in MHz. For every value of J there are 2J + 1 values of K, but since the energy is independent of the sign of K, all levels of a given J are doubly degenerate when K is greater than zero.

The rotational constants of the asymmetric rotor are all different in that $A \neq B \neq C$. Any such molecule must lie between the extremes of an oblate symmetric rotor in which $A = B > C$, and the prolate symmetric rotor where $A > B = C$. If a molecule is only slightly asymmetric its energy levels can be described in terms of an asymmetry parameter, b. For a near-prolate asymmetric rotor b_p is defined by the following expression:

$$b_p = \frac{C - B}{2A - B - C} \qquad \text{(II-B-9)}$$

For the limiting case of the prolate symmetric rotor b_p reduces to a value of zero. It becomes increasingly negative as the molecule becomes more asymmetric. An analogous asymmetry parameter, b_o, is defined for the near oblate case:

$$b_o = \frac{A - B}{2C - B - A} \qquad \text{(II-B-10)}$$

A general asymmetry parameter is sometimes used called Ray's asymmetry parameter, κ, given by

$$\kappa = \frac{2B - A - C}{A - C} \qquad \text{(II-B-11)}$$

This parameter becomes -1 for the limiting case of the prolate symmetric rotor ($B = C$), and +1 for the oblate symmetric rotor ($A = B$).

The result of the existence of three non-equal rotational constants is that the quantum number K can no longer be used. In a symmetric rotor K is the projection of J on the symmetry axis of the molecule and therefore represents the component of the angular momentum along this axis. In the asymmetric rotor there is no single direction along which there is a constant component of the angular momentum and therefore K cannot describe the rotational state. The effect of only a slight asymmetry is to split the levels of a given K, which are degenerate in the symmetric rotor, into two distinct levels. These energy levels are then specified by the three numbers J, K_{-1} and K_{+1}, where K_{-1} and K_{+1} correspond to the value of K in the limiting cases of the prolate and oblate symmetric rotors respectively. Thus a specific level is designated $J_{K-1,\ K+1}$, for example, 4_{04}. The subscripts -1 and +1 refer to Ray's asymmetry parameter, κ, which is equal to -1 and +1 for the limiting cases of the prolate and oblate symmetric rotors respectively.

In addition to the convention of designating the energy levels of the asymmetric rotor just described, there are others which are widely used.[8] Since they have not been used in this work they will not be discussed.

Methylthiocyanate and methylselenocyanate are near-prolate asymmetric rotors and the expression used for the rotational energy is as follows:

$$E = \frac{B + C}{2}(J(J + 1)) + (A - \frac{B + C}{2})\omega \quad \text{(II-B-12)}$$

where ω is a function of K and b_p, and can be obtained from available tables[9] or can be evaluated by spectral analysis computer programs.

The rotational spectrum of a molecule arises from the presence of a permanent electric dipole moment. The rotation of a molecule at a certain frequency is then associated with an oscillating electric field which can come into resonance with radiation of the same frequency. The result may be emission or absorption of a photon, and thus such a molecule can undergo transitions between its rotational energy levels according to certain selection rules.

For the asymmetric rotor the selection rule for J is $\Delta J = 0, \pm 1$. Transitions of the type $\Delta J = 0$ are called Q-type transitions, and those with $\Delta J = \pm 1$ are called R-type transitions. The selection rules for K_{-1} and K_{+1} are given in Table II-B-1. They are dependent on the direction of the dipole moment in the molecule. In an asymmetric rotor the overall molecular dipole moment, μ, may lie along only one of the principal axes of the molecule, or it may have components along two, or all three, of these axes. These

TABLE II-B-1

ASYMMETRIC ROTOR SELECTION RULES FOR K_{-1} AND K_{+1}

Dipole Moment Component	K_{-1}	K_{+1}
μ_a	0, ±2, ±4..	±1, ±3, ±5..
μ_b	±1, ±3, ±5..	±1, ±3, ±5..
μ_c	±1, ±3, ±5..	0, ±2, ±4..

components of the dipole moment are designated μ_A, μ_B and μ_C corresponding to the axes of the principal moments of inertia I_A, I_B and I_C respectively.

From the table it can be seen that if the overall dipole moment lies completely along only one of the principal axes then the spectrum is simplified since only certain transitions can occur. Usually transitions with ΔK greater than ±1 are too weak to be observed. In most molecules the overall dipole moment has a larger component along one of the axes than along the other two, and therefore transitions associated with the one axis are much stronger than those associated with the other two. The designations a-type, b-type and c-type transitions are used depending on whether it is μ_A, μ_B, or μ_C respectively which allows the transition.

SECTION C. THE EFFECT OF THE INTERNAL ROTATION OF METHYL GROUPS ON ROTATIONAL SPECTRA

In molecules such as methylthiocyanate and methylselenocyanate the rotation of the methyl group relative to the rest of the molecule (often referred to as torsional motion) is hindered by a potential barrier. For theoretical reasons such barriers are divided into three classes depending on their magnitude. These are the low barrier, the intermediate barrier and the high barrier. Both molecules have barriers of intermediate height (0.5 kcal/mole to 4.0 kcal/mole), and therefore this will be the only case discussed in detail.

Figure II-C-1 illustrates the shape of such a potential barrier curve, V(α), for an internal rotor which has three-fold symmetry such as the methyl group. The function V(α) is given by the following expression:

$$V(\alpha) = \frac{V_3}{2}(1 - \cos 3\alpha) \qquad \text{(II-C-1)}$$

where V(α) is the potential energy associated with the internal rotation and α is the angle through which the rotation of the methyl group occurs relative to the rest of the molecule, or framework. The height of the barrier to internal rotation is V_3, thus designated because of its three-fold nature.

In order to develop the theory of internal rotation more clearly, a situation where the barrier height is much higher than this intermediate value will be discussed first. In such a case the internal rotation of the methyl group reduces to what is called a torsional vibration since the group is confined to a potential valley and never

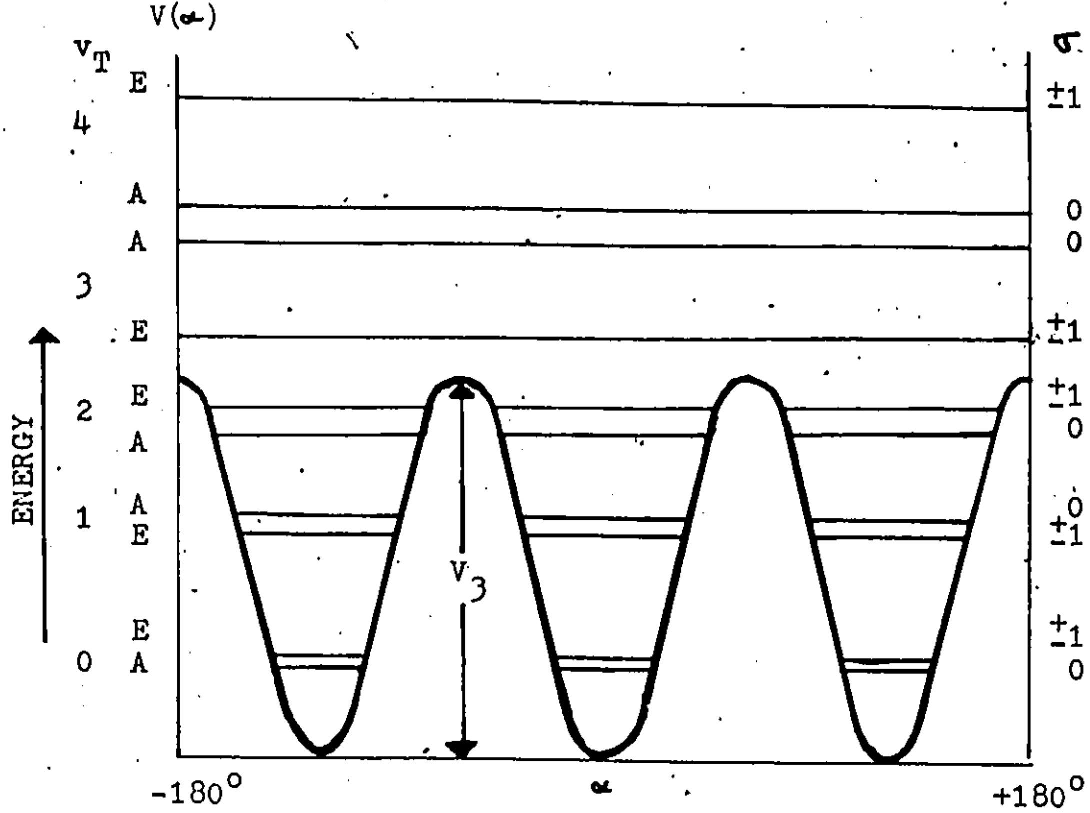

Figure 11-C-1. Torsional energy levels for a system with a three-fold barrier to internal rotation as taken from ref. 8.

escapes from it. This torsional vibration is merely an oscillation about the equilibrium position and is a conventional vibration characterized by the vibrational quantum number v_T, the allowed values of which are 0, 1, 2..., etc. The corresponding energy levels are triply degenerate because the three potential valleys are identical.

In the case of the intermediate barrier height the energy levels are examined as they deviate from this high barrier situation. This has been illustrated in Figure II-C-1 and it can be seen that the barrier is above only a few of the vibrational torsional levels. Here the ground torsional level is still well below the top of the barrier, but "tunneling" can occur through the barrier and rotation of the methyl group can take place.

The effect of this tunneling is to cause the torsional levels, which were triply degenerate in the high barrier case, to split into two levels specified by the quantum number σ. One of these is designated as the A level since it is non-degenerate. The other level is doubly degenerate and is therefore called the E level. The values of σ for the A and E levels are 0 and ± 1 respectively. The different v_T and σ levels are shown in the figure. It can be seen that the splitting of the torsional levels is small when $v_T = 0$, and becomes greater as the levels approach the top of the barrier.

The effects of internal rotation of a methyl group on the overall rotation of a molecule can now be considered. If no interaction occurred between the two types of rotation then the overall rotational energy levels could be obtained by simply adding the internal rotational energy levels given by equation II-C-1 to the rotational energy levels given previously in equation II-B-12. An interaction does occur, however, and when the torsional barrier is of intermediate height this interaction can be treated as a perturbation to the normal rotational energy levels. The complete mathematical treatment of this perturbation is given by Lin and Swalen. [13]

The resulting effect on the rotational spectrum of a molecule depends on its symmetry. In a symmetric rotor with an intermediate barrier height the rotation-torsion interaction causes a splitting of each energy level of a particular value of J and K into a doubly degenerate component associated with the $\sigma = \pm 1$ state, and a non-degenerate level associated with the $\sigma = 0$ state. The magnitude of the splitting is a function of K only and is not dependent on J. This splitting of the energy levels, however, does not affect the rotational spectrum of a symmetric rotor since the selection rules only allow changes in the value of J, and not in the value of K or in the torsional quantum numbers.

In an asymmetric rotor, transitions between levels differring in the value of K are allowed and the result is a splitting of the rotational lines into a doublet. The components of this doublet are called the A and E components of the line, corresponding to the transitions associated with $\sigma = 0$ and $\sigma = \pm 1$ respectively. Measurement of the frequency difference between these two components, $\Delta\nu_{AE}$, leads to a value for the barrier height. It should also be pointed out that the magnitude of this splitting depends on the torsional quantum level which the molecule is in when the rotational transition occurs. This is useful since often the splitting of the $v_T = 0$ lines is too small to be detected when the barrier value is small. If the population of the $v_T = 1$ and $v_T = 2$ torsional excited states is large enough to permit detection of rotational transitions associated with them, then the larger splitting of these lines can be used to calculate the barrier height.

Lin and Swalen [13] have described the calculation of the splitting of the rotational energy levels for a near-prolate asymmetric rotor using the Internal Axis Method (IAM). In this method the frame of reference is the axis of symmetry associated with the internal rotor itself. This is the method which has been used in the work reported here and a description of the calculation of the barrier height from the value of $\Delta\nu_{AE}$ is given below.

The splitting of a rotational energy level, ΔE_{JK}, associated with particular values of J and K, is given by

$$\Delta E_{JK} = \Delta_K + (\beta^2/4)((J + K)(J - K - 1)\Delta_{K-1} - 2(J(J + 1) - K^2)\Delta_K + (J - K)(J + K + 1)\Delta_{K+1}) \qquad \text{(II-C-2)}$$

where in the case of a near-prolate rotor K is K_{-1}. The term Δ_K in the above equation is a function of the value of K, the structure of the molecule, and the barrier height. It is given by the following expression:

$$\Delta_K = \frac{3}{2} Fa_1 (\cos \frac{2\pi\rho K}{3}) \qquad \text{(II-C-3)}$$

The terms F, ρ and ρ are functions of the structure of the molecule. F is given by the equation

$$F = \frac{h^2}{8\pi^2 r I_\alpha} \qquad \text{(II-C-4)}$$

where the value of r is given by

$$r = 1 - \frac{\lambda_y^2 I_\alpha}{I_y} - \frac{\lambda_z^2 I_\alpha}{I_z} \qquad \text{(II-C-5)}$$

Here, I_y and I_z are the principal moments of inertia of the molecule, and I_α is the moment of inertia of the internal rotor about the symmetry axis. The terms λ_y and λ_z are the direction cosines of the symmetry axis of the internal rotor with respect to the y and z principal axes of the molecule.

The term ρ is given by

$$\rho = (\rho_x^2 + \rho_y^2 + \rho_z^2)^{\frac{1}{2}} \qquad \text{(II-C-7)}$$

where

$$\rho_n = \frac{\lambda_n I_\alpha}{I_n} \qquad \text{(II-C-8)}$$

The following expression gives the value of β :

$$\sin\beta = \frac{\rho_y}{\rho} \qquad \text{(II-C-9)}$$

Returning to equation II-C-2, the following simplification can be made if transitions with $K_{-1} = 0$ are the only ones used in the barrier calculation:

$$\Delta E_{J0} = \Delta_0 + (\beta^2/2)(J(J+1)(\Delta_1 - \Delta_0)) \qquad \text{(II-C-10)}$$

The splitting of a spectral line, $\Delta\nu_{AE}$, due to a transition of the type $J \rightarrow J + 1$, $K_{-1} \rightarrow K_{-1}$ is then given by

$$\Delta\nu_{AE} = \Delta E_{(J+1)0} - \Delta E_{J0} \qquad \text{(II-C-11)}$$

which becomes

$$\Delta\nu_{AE} = \beta^2(\Delta_1 - \Delta_0)(J + 1) \qquad \text{(II-C-12)}$$

The terms Δ_0 and Δ_1 are obtained by substituting $K = 0$ and $K = 1$ respectively into equation II-C-3. The following expressions result:

$$\Delta_0 = \frac{3}{2} F a_1 \qquad \text{(II-C-13)}$$

$$\Delta_1 = \Delta_0 (\cos \frac{2\pi\rho}{3}) \qquad \text{(II-C-14)}$$

Substituting these two expressions into equation II-C-12 gives the following equation for $\Delta\nu_{AE}$:

$$\Delta\nu_{AE} = \frac{3\beta^2 a_1 F}{2}(\cos(\frac{2\pi\rho}{3}) - 1)(J + 1) \qquad \text{(II-C-15)}$$

The only unknown quantity in the above expression is the term a_1, and therefore it can be calculated from the splitting of the rotational line. This term is related to the term S which is in turn related to the barrier height, V_3, by the following equation:

$$V_3 = (9/4)FS \qquad \text{(II-C-16)}$$

The value of S is determined from the value of a_1 by graphical methods, formulas or tables which are available in the literature.[13]

CHAPTER III. EXPERIMENTAL.

SECTION A. SOURCE AND PREPARATION OF COMPOUNDS

1. Preparation of Methylselenocyanate

Methylselenocyanate was prepared by a modification of the method of Stolte.[14] Potassium selenocyanate (14 g, 0.1 moles) was dissolved in 10 ml of warm methanol and methyl iodide (14 g, 0.1 moles) was added. A white precipitate formed almost immediately on mixing. The resulting mixture was then heated to the boiling point of the solution and subsequently filtered using a sintered glass funnel to remove the precipitated potassium iodide.

Isolation and purification of the product was accomplished by trap-to-trap distillation at low temperatures. Removal of the methanol solvent and traces of methyl iodide by prolonged heating on a steam bath, as suggested by Stolte, was found to produce a yellow colouration of the product. This has been found to be due to the presence of trace amounts of $(CH_3Se)_2$ which is difficult to separate from CH_3SeCN.[15] Therefore the higher temperatures were avoided.

The trap-to-trap distillation was carried out by passing the filtered reaction mixture through a trap which was cooled to -30°. The product, which has a melting point of -7°, remained in this trap while the much more volatile components were removed. This procedure was then repeated in order to ensure removal of all traces of methanol and methyl iodide. The resulting colourless liquid was stored in a flask under vacuum at -15° until further use. Storage at room temperature under vacuum resulted in a yellow colouration after four of five days.

The product was identified by comparing its infrared spectrum with that reported in the literature.[16] The sample was tested for any trace amounts of methanol and methyl iodide by a careful examination of its microwave spectrum in regions where these two molecules have been reported to absorb. Strong, characteristic spectral lines have been reported between 29 and 30 GHz for methyl iodide, and between 26 and 31 GHz for methanol.[17] No trace of either substance was found.

2. Source of Methylthiocyanate

The sample of methylthiocyanate used was obtained from Fisher Scientific Inc. (Eastman #1139). No further purification was carried out.

3. Source of Methyl Iodide

The sample of methyl iodide which was used in the frequency calibration procedure was obtained from Fisher Scientific Inc. (#M-212). This same sample was used in the preparation of methylselenocyanate.

4. Source of Trimethylene Sulphide

Trimethylene sulphide, also used for frequency calibration purposes, was obtained from Fisher Scientifc Inc. (Eastman #7877).

5. Source of Potassium Selenocyanate

The sample of potassium selenocyanate, used in the preparation of methylselenocyanate, was obtained from Alfa Inorganics Inc. It was obtained in its highest purity and was used without further purification.

SECTION B. DESCRIPTION OF THE MICROWAVE SPECTROMETER

All microwave spectral measurements were made using an instrument constructed from the commercially available modular components of the Hewlett-Packard 8400 series of Molecular Rotational Resonance Spectrometers. The components used were the standard components available for the 8400 C model without the inclusion of the signal calibrator section. This is a device to measure signal intensities which were not of interest in this work. Figure II-B-1 is a simplified block diagram of the main components of this instrument. The important features of the various modular sections are discussed separately below.

1. Microwave Source and Frequency Stabilization System

Figure II-B-2 is a detailed illustration of the sweep oscillator and frequency stabilization system previously shown in block form in Figure II-B-1. The source of the microwave radiation is a backward wave oscillator (BWO) having the frequency range of 26.5 GHz to 40.2 GHz (R-band). This oscillator is contained as a plug-in unit within the H81-8690A Sweep Oscillator. The BWO oscillator frequency is stabilized by phase-locking it, via the 8709A Synchronizer, to harmonics generated by the low frequency (240 MHz to 400 MHz) 8466A Reference Oscillator.

Two sweep modes are available on the Sweep Oscillator, as well as a continuous wave (CW) function. The Start/Stop sweep mode is used for sweeps larger than 1 % of the frequency band of the BWO oscillator. The ΔF mode is

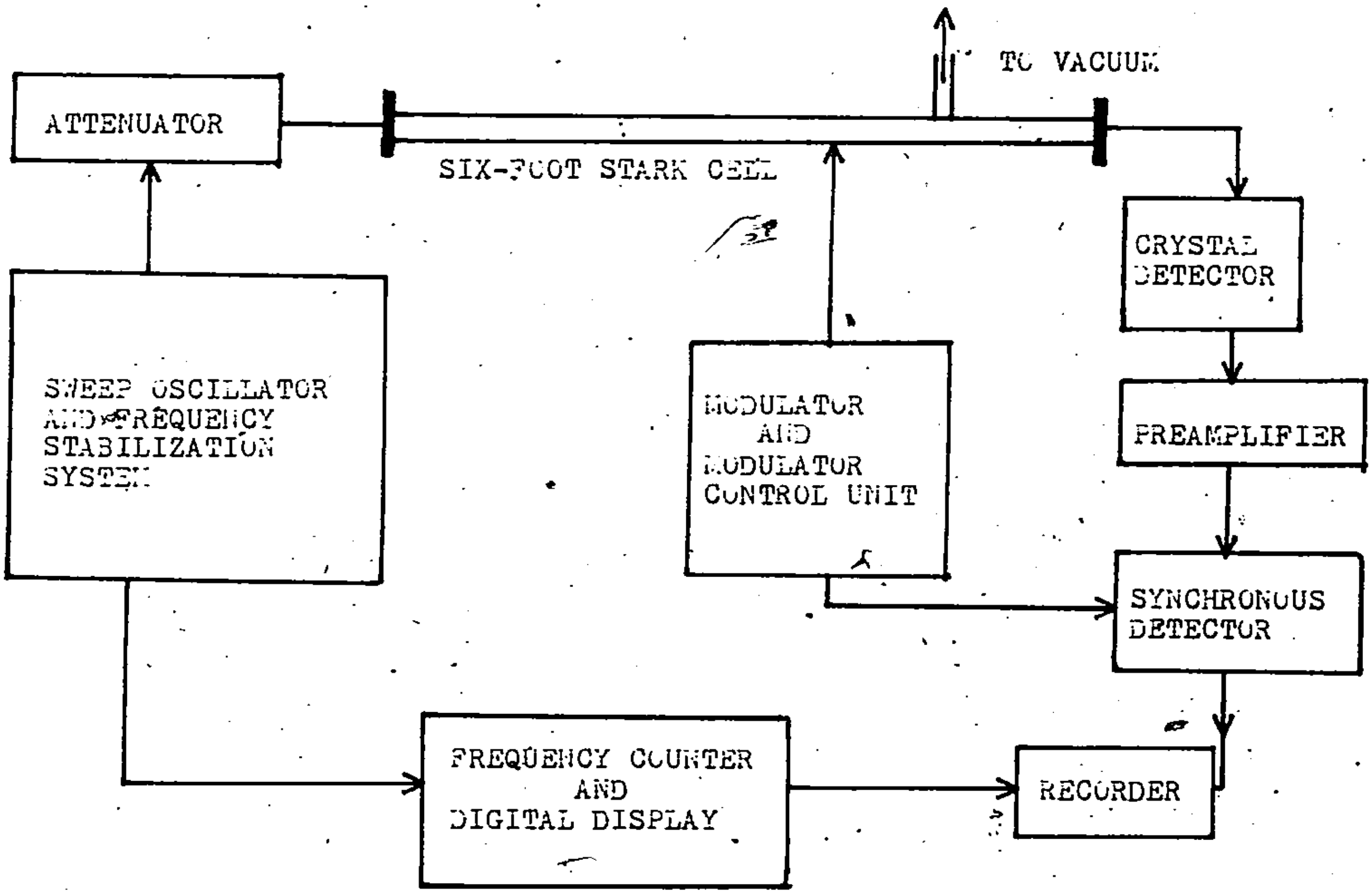

Figure III-B-1. Simplified block diagram of microwave spectrometer.

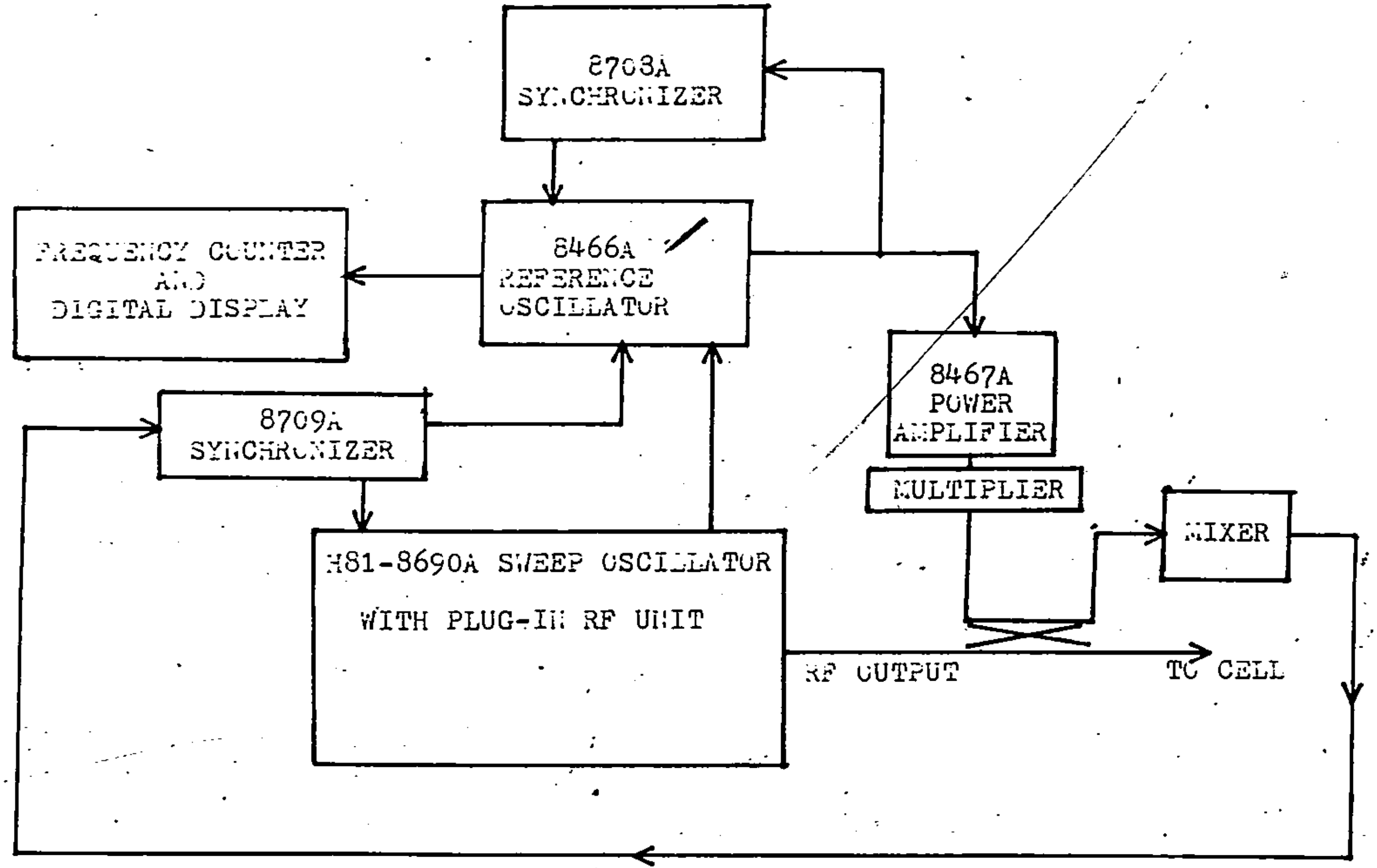

Figure III-B-2. Block diagram of spectrometer sweep oscillator and frequency stabilization system.

used for sweeping the very small ranges necessary when making precise line frequency measurements. When additional stability is required for making extremely precise line frequency measurements the 8708A Synchronizer is used. This stabilizes the frequency of the 8466A Reference Oscillator, and thereby results in a long-term stability of the BWO frequency. A digital frequency counter gives a direct frequency readout, and in the various sweep modes this frequency is recorded on the strip-chart recorder by a frequency marker.

2. Spectrometer Cell

The spectrometer cell is a Stark cell consisting of two three-foot lengths of waveguide of X-band dimensions which are gold-plated on the inside. The modulation voltage (See below) is applied by means of an electrode, or septum, which is a thin, gold-plated metal strip fitted into the cell along its length. This electrode is insulated from the sides of the cell by Teflon strips as illustrated in Figure III-B-3. The total volume of the cell is 500 cm^3. If low temperatures are required, the cell can be cooled with solid carbon dioxide.

The vacuum system connected to the cell consists of a roughing pump and an ion pump. A pressure of 10^{-9} torr can be obtained. Samples are introduced into

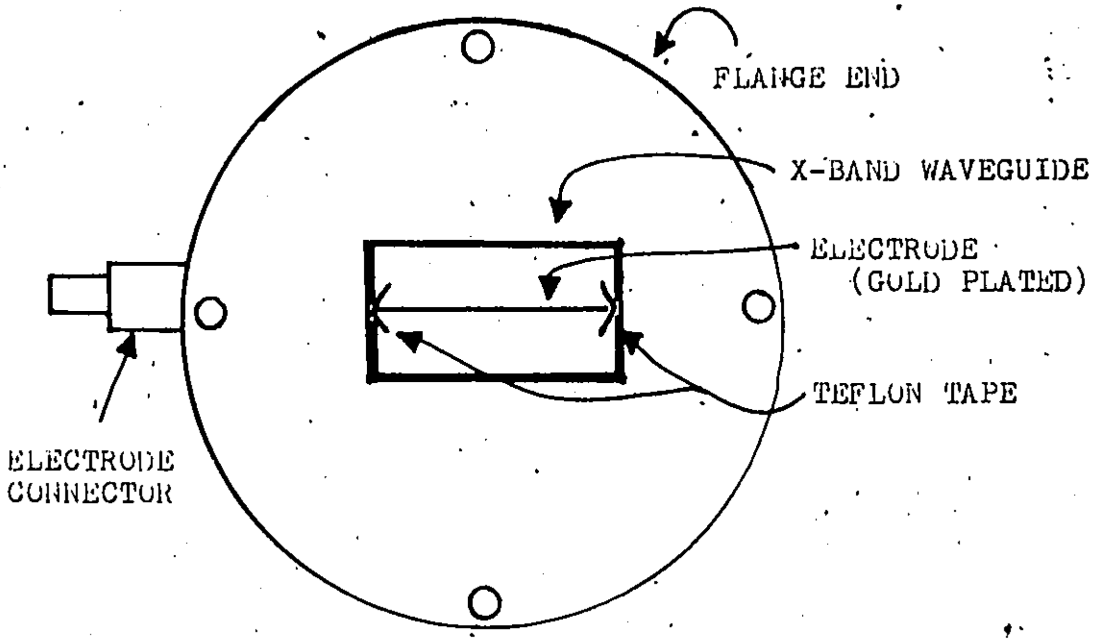

Figure III-B-3. Diagram of Stark cell viewed down its length.

the cell from a storage bulb and the sample pressure in the cell is read from a pressure gauge meter.

3. Modulation and Detection System

A simplified block diagram of the modulation and detection section of the spectrometer is included in Figure III-B-1. Stark modulation is employed using a square-wave modulation frequency of 33.333 kHz. The rise and fall times of the wave are 1.2 microseconds. The modulation voltages are generated and controlled by the 8421B Stark Modulator and the 8428B Modulator Control. The ground-to-base and base-to-peak voltages are continuously variable from 0-2000 volts and are displayed on a meter.

This modulation voltage is applied to the sample by means of the Stark electrode discussed above, and a reference signal is continuously applied to the 8420B Synchronous Detector. The Stark modulated microwave signal from the cell is then demodulated by the Crystal Detector and subsequently applied to the 8426D Preamplifier. This preamplified signal is fed to the Synchronous Detector which displays the absorption peak on a meter. The spectrum can also be recorded on a strip-chart recorder or an oscilloscope.

4. Techniques for Line Frequency Measurement

The spectrometer provides two techniques for the determination of precise spectral line frequencies. One is the Manual Sweep Method and the other is the Instrument Sweep Method. The choice of which technique is to be used is based on the desired precision, and on the width and strength of the spectral line involved.

The Manual Sweep Method is the most precise one and involves the use of the Frequency Tuning Vernier of the 8708A Synchronizer. The frequency is swept manually through the desired region in small increments, while the intensity of the absorption is read at each step from the meter of the 8420B Synchronous Detector. The corresponding frequency at each point is read from the digital frequency counter. These data are then plotted on a graph, and the points extrapolated to find the frequency at maximum absorption. This has been reported to give line frequencies to a precision of ±0.01 MHz, but it is only useful for very strong lines where the time constants can be kept small.[18] For weak lines where the time constants are large the method is too time consuming, and in the case of broad lines the precision obtained from this method is not warranted.

The Instrument Sweep Method is faster but less precise. It involves using the ΔF sweep mode of the instrument to scan a very small frequency range around the absorption line. The signal is recorded on the strip-chart recorder and the oscillator frequency is recorded at specified intervals on the chart by the frequency marker. The recorded peak is then triangulated to find the frequency at its maximum. The advantage of this method is that it can be easily used when the signal-to-noise ratio is not large. The precision obtained using this method is never better than ±0.03 MHz, and depends on the peak width and on the signal-to-noise ratio.

SECTION C. CALIBRATION OF OSCILLATOR FREQUENCY

The frequency readout of the spectrometer was calibrated with three lines in the spectrum of methyl iodide and four lines in the spectrum of trimethylene sulphide, both used as external standards. The observed and reported values of the spectral line frequencies are given in Table III-C-1. The frequencies of these seven lines were measured on the spectrometer using the Manual Sweep Method and are the average of two or more determinations which did not differ by greater than ±0.01 MHz. The measurements were carried out at room temperature using a sample pressure of 30 to 40 microns Hg and a modulation voltage of 1500.

TABLE III-C-1

FREQUENCY CALIBRATION DATA FOR METHYL IODIDE AND TRIMETHYLENE SULPHIDE USED AS EXTERNAL STANDARDS

Transition	Observed Frequency (MHz)	Reported Frequency (MHz)
A. METHYL IODIDE[19] ($J=1 \rightarrow J=2$, $K=0$)		
$F=5/2 \rightarrow F=7/2$	30179.69	30179.72 ±0.08
$F=9/2 \rightarrow F=7/2$	30046.95	30046.99 "
$F=3/2 \rightarrow F=3/2$	29872.45	29872.52 "
B. TRIMETHYLENE SULPHIDE[20]		
$2_{12} \rightarrow 3_{13}$ v=1	29559.11	29559.10 ±0.02
$2_{12} \rightarrow 3_{13}$ v=0	29564.94	29564.97 "
$2_{02} \rightarrow 3_{03}$ v=1	30779.29	30779.29 "
$2_{21} \rightarrow 3_{22}$ v=3	33274.09	33274.08 "

In the case of methyl iodide, it has been reported that the frequencies are accurate to ±0.08 MHz,[19] while those of trimethylene sulphide have been measured to ±0.02 MHz.[20] The tabulated data show that no observed frequency differs from a reported one by more than ±0.07 MHz. It is therefore concluded that the absolute accuracy of the spectrometer frequency readout is at least ±0.1 MHz. It should be pointed out, however, that this value for the accuracy is limited by the precision of the reported data for the two external standards. The precision of the instrument is greater than this and can be as good as ±0.01 MHz, and therefore all frequencies are reported to 0.01 MHz in this thesis. In some situations it is the frequency difference which is the important experimental information and therefore the precision of the measurement is important, and not the accuracy.

SECTION D. EXPERIMENTAL CONDITIONS USED IN LINE FREQUENCY MEASUREMENTS

1. Methylthiocyanate

In the case of the ^{32}S species of methylthiocyanate, the line frequencies were measured by the Instrument Sweep Method. Sample pressures of 5 to 15 microns were used and the spectrometer cell was cooled with solid carbon dioxide. For the ^{34}S species the Instrument Sweep Method was used. Sample pressures were 20 to 60 microns, and the cell was maintained at room temperature. A modulation voltage of 1500 volts was employed for both isotopic species. All reported line frequencies are the average of two separate determinations unless otherwise stated. These two values did not generally differ by more than ±0.05 MHz.

2. Methylselenocyanate

All spectral line frequencies reported for the five isotopic species of CH_3SeCN were measured using the Instrument Sweep Method. For the more abundant ^{78}Se and ^{80}Se species sample pressures of 10 to 50 microns were found to be suitable, depending on the strength of the line. In all other isotopic species a pressure of 55 to 60 microns was used. All measurements were made at room temperature and at a modulation voltage of 1400. Again the reported line frequencies are the average of two separate determinations unless otherwise stated.

SECTION E. DESCRIPTION OF COMPUTER PROGRAMS

1. PROGRAM CONSTNTS

PROGRAM CONSTNTS is a modified version of

PROGRAM CDCL obtained from J. J. Sloan at Queen's University in Kingston, Ontario. The modifications were in the format of the program only and the two programs are essentially identical. The program is primarily used to calculate a set of rotational constants, A, B and C, of a molecule from such information as the atomic masses, bond lengths and bond angles, according to Kraitchman's method discussed previously in CHAPTER 11.

The first part of the program calculates a set of Cartesian coordinates for the atoms in the molecule based on a molecule-fixed axis system specified by the input data. The center of mass (COM) of the molecule in this axis system is then evaluated by equation II-A-2. A new set of coordinates based on a COM origin are then evaluated, the new axis system being parallel to the original molecule-fixed system.

The second part of the program calculates the moments and products of inertia according to equations II-A-4 and II-A-5 respectively. From these it sets up and diagonalizes the determinental equation II-A-3, and solves it for the roots I_x, I_y and I_z, which are the principal moments of inertia of the molecule. The rotational constants A, B, and C are then evaluated. The program also gives the asymmetry parameters κ and b_p (or b_o), and the directions of the principal axes with respect to the positions of the atoms in the molecule. Using these principal axes, and the Pauling electronegativies specified in the input data, the program also calculates the principal components of the dipole moment.

2. PROGRAM LTSQ.

PROGRAM LTSQ is a modified version of the Rigid Asymmetric Rotor Fit Program (Version III) obtained from W. H. Kirchoff of the U. S. National Bureau of Standards. The main purpose of the program is to determine an experimental set of the rotational constants of a molecule from the observed rotational transition frequencies by a least squares procedure.

The program first calculates the rotational energy levels of the molecule from approximate rotational constants specified in the input data. This is done according to the method described in CHAPTER II, SECTION B. The transition frequencies are then calculated from the energy level differences. The least squares procedure then compares these calculated frequencies to the set of observed frequencies, and fits the difference, $\Delta\nu$, to an equation of the form

$$\Delta\nu = \frac{\partial\nu}{\partial A}\Delta A + \frac{\partial\nu}{\partial B}\Delta B + \frac{\partial\nu}{\partial C}\Delta C \qquad \text{(III-E-1)}$$

where ΔA, ΔB and ΔC are the corrections to the original approximate rotational constants specified in the input data. The least squares routine gives these coefficients and their standard deviations. The new values of the rotational constants are obtained by simply adding these correction coefficients to the approximate constants. The resulting uncertainties in the new rotational constants are then equal to the standard deviations of the coefficients. The program also provides for a second iteration, since $\Delta\nu$ is not a linear function of the rotational constants.

CHAPTER IV. METHYLTHIOCYANATE.

SECTION A. INTRODUCTION

The rotational spectrum of methylthiocyanate has been investigated by several different groups and these studies have led to a considerable amount of information about the molecule. [1 - 7] A complete structure has been determined by isotopic substitution of each atom in the molecule, and the barrier to internal rotation of the methyl group has been calculated. The quadrupole coupling constant of the ^{14}N nucleus and the three components of the molecular dipole moment have also been found.

The first reported study of the rotational spectrum of this molecule was that of Beard and Daily in 1949, [1] but they incorrectly assigned some of the spectral lines and therefore reported erroneous values for the rotational constants. The first accurate study was reported in 1965 by Nakagawa et al. [2, 3] They found the spectrum to be characteristic of a near-prolate asymmetric rotor, and measured the frequencies of about eighty lines in the spectrum of the ^{32}S species in the region between 8 and 34 GHz. All of these lines were found to be Q and R branch a-type transitions and no b or c-type transitions were detected. Many of the Q branch transitions were found to be split into their A and E components due to the hindered internal rotation of the methyl group. Several vibrational and torsional satellites were also found.

The various molecular parameters which were determined by Nakagawa et al. are listed in Table IV-A-1. Since a complete structure could not be determined from data on only one isotopic species, these authors suggested only an approximate structure which generated a set of rotational constants in good agreement with the experimental ones. This was accomplished by using assumed values for some of the more common bond distances and bond angles in the molecule, and adjusting the remaining unique ones until a good fit was obtained. They showed that, as expected, the C-S-C framework is bent with an angle of approximately 100°, and that the molecule has a plane of symmetry through the four heavy atoms.

From this structural data these authors determined the directions of the three principal axes in the molecule. These are illustrated in Figure IV-A-1. The a and b axes, associated with the A and B rotational constants respectively, were found to lie in the plane of symmetry, while the c axis is perpendicular to it. The component of the molecular dipole moment along the a axis, μ_a, was

TABLE IV-A-1

MOLECULAR PARAMETERS FROM THE SPECTRUM OF $CH_3{}^{32}SCN$

Parameter	Nakagawa [3]	Dreizler *et al.* [5-7]
A (MHz)	15796.2	15786.913
B (MHz)	4155.4	4155.535
C (MHz)	3354.2	3354.134
$I_A (=I_z)$ (amu $\AA^2$)	31.98	32.0222
$I_B (=I_y)$ (amu $\AA^2$)	121.60	121.6524
$I_C (=I_x)$ (amu $\AA^2$)	150.37	150.7188
I_α (amu $\AA^2$)	3.212	3.212
μ_a	4.03 D	4.11 D
μ_b	-	0.40 D
μ_c	0 D	0 D
F (MHz)	164.94	164.7
r	0.9541	-
$\lambda_a (=\lambda_z)$	-0.513	-0.4954
$\lambda_b (=\lambda_y)$	0.858	0.8689
V_3 (cal/mole)	1580	1569 ± 10
b_p	-0.0332872	-
κ	-0.87114	-0.87108

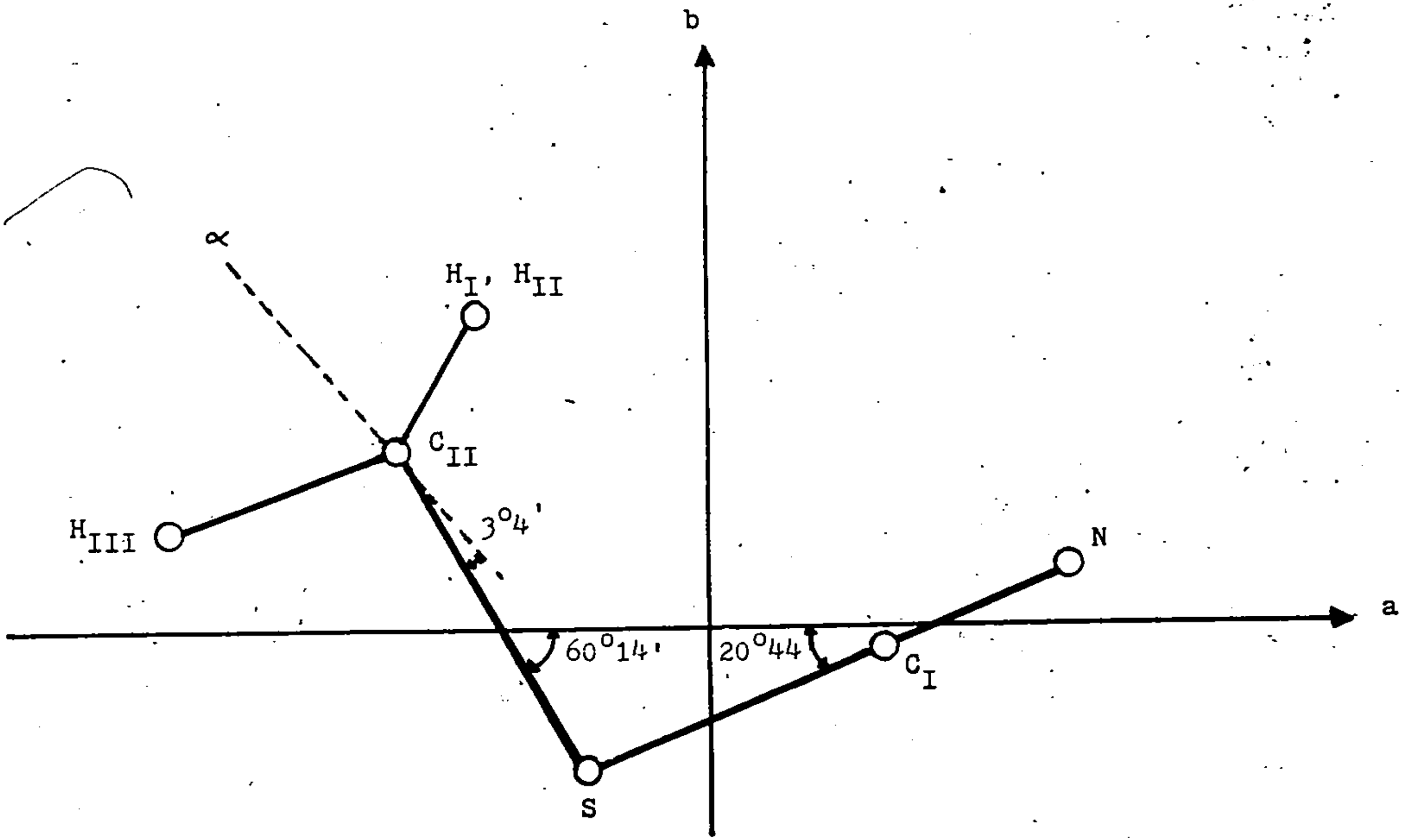

Figure IV-A-1. The orientation of the principal axes in CH_3SCN as taken from ref. 7. The α axis is the symmetry axis of the methyl group.

determined to be equal to 4.03 D, but the authors suggested that the b axis component of the dipole moment was zero since they were not able to detect any b-type transitions. A zero value for the c axis component is expected due the symmetry plane of the molecule.

The height of the barrier to internal rotation of the methyl group was calculated by Nakagawa et al. from the splitting between the A and E components of the Q branch lines with J = 5, 6, 7, 8. The transitions used were those originating from the ground torsional and vibrational states, and the resulting barrier height was found to be 1580 cal/mole. The A and E components of the R branch lines originating from the ground torsional state were unresolved, but those arising from the first torsional excited state were found to appear as a well-resolved doublet. The barrier height calculated from the splitting of the R branch J=1 → J=2 transitions originating from the v_T = 1 torsional satellites was found to be in good agreement with the value of 1580 cal/mole determined from the Q branch lines.

The vibrational satellites reported by these authors were observed as two weaker absorptions on the high frequency side of each main R branch line. They assigned these to rotational transitions originating from the first and second excited states of a normal vibrational bending mode, the frequency of which was estimated to be 160 cm^{-1}. The presence of a far infrared band at 190 cm^{-1} in the liquid state of the molecule,[21, 22] and at 171 cm^{-1} in the gaseous state [23] serve to further substantiate the existence of such a vibration. Later, a normal coordinate analysis of the molecule was carried out from which it was concluded that there should indeed be a low frequency bending vibrational mode and that it likely consists of a coupled C-S-C and S-C-N in-plane bend.[4]

A further study of the spectrum of the ^{32}S species of methylthiocyanate was reported in 1967 by Lett and Flygare.[4] Their values of the various molecular parameters are in good agreement with those of Nakagawa, but they obtained the higher resolution necessary for observing the splitting due to the nuclear quadrupole moment of the ^{14}N nucleus. This information was used by them to suggest that back-bonding by the sulphur atom according to the valence bond structure $H_3C-\overset{+}{\underset{..}{S}}=C=\underset{..}{N}\!:^{-}$ contributes approximately 10 % to the bonding in the SCN group.

In 1968 Dreizler and Mirri reported a study of the spectra of CH_3SCN and CD_3SCN at very high resolution.[5, 6] Although the main purpose of their work was to study the vibrational and torsional satellites, they also determined the various molecular parameters which had already been reported by Nakagawa. These are also listed in Table IV-A-1, and agreement is seen to be excellent.

With their higher resolution, Dreizler and Mirri were able to add to the information on the methylthiocyanate molecule by detecting the very weak b-type transitions which had not been previously observed. Inclusion of these b-type transitions for the Q branch in the calculation of the A rotational constant allowed them to determine a much more precise value for this parameter. The reason for this is that the value of A is much more dependent on the value of K than on J, and therefore depends more on these b-type transitions where $\Delta K = \pm 1$ than on the R branch, a-type transitions which have $\Delta K = 0$. In addition, they were able to determine the dipole moment component associated with the b axis, reported earlier by Nakagawa <u>et al</u>. to be equal to zero. The value of μ_b was found to be 0.4 ±0.1 D.

As mentioned above Dreizler and Mirri were primarily interested in the vibrational and torsional satellite peaks in the spectrum of this molecule. They estimated that, since the vibrational and torsional modes responsible for these satellites had frequencies which were very nearly equal, the coupling between them might be quite large. This would then lead to considerable error in any barrier height which was calculated from the A-E splitting of these lines.

They first measured the A-E splittings of both the vibrational and torsional satellites and then treated each case separately. From a complex perturbation treatment they first determined that the coupling of the bending mode with the the torsional motion would lead to large errors in calculating the barrier height from the A-E splittings of the vibrational satellite peaks. The same treatment could not be applied to the torsional satellites, but the authors have suggested that there is probably considerable interaction between the two types of motion in the first torsional excited state as well. They therefore concluded that only measurements on the ground vibrational and torsional states are likely to lead to accurate barrier values. Their reported value of V_3 as calculated from these ground state levels was in very good agreement with those previously reported (see Table IV-A-1) and was more precise.

In 1970 Dreizler, Rudolph and Schleser[7] published a report on the rotational spectra of five isotopic species of methylthiocyanate in the frequency range of 17 to 33 GHz. These five species were $CH_3SC^{15}N$, $CH_3S^{13}CN$, $CH_3{}^{34}SCN$, $^{13}CH_3SCN$ and CH_2DSCN. From the rotational constants of these five species and the data reported earlier on the ^{32}S and the fully deuterated species, they were able to calculate a complete structure of the molecule. This is illustrated in Figure IV-A-2. An interesting feature of the structure which was not mentioned in the earlier reports is that there is a "tilt angle" of 3° between the symmetry axis of the methyl group and the direction of the $(H_3)C-S$ bond.

SECTION B. RESULTS AND DISCUSSION

1. Rotational Spectrum

As discussed in CHAPTER I, the purpose of a further investigation into the spectrum of methylthiocyanate was to have a model for the study of the selenocyanate spectrum, and to extend the frequency region investigated in order to make comparisons between the two molecules. The results presented here are therefore discussed mainly in this respect.

The spectrum has been examined in the region between 27 and 40 GHz and several lines in the spectra of both the $CH_3{}^{32}SCN$ and the $CH_3{}^{34}SCN$ isotopic

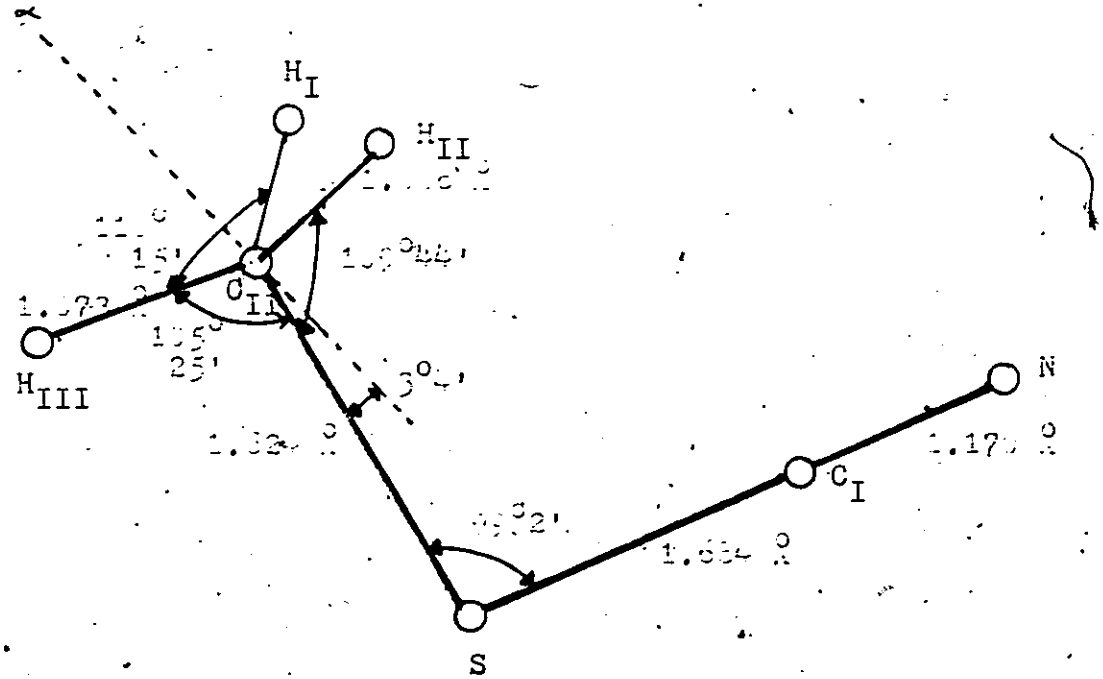

Figure IV-A-2. Structure of CH_3SCN as reported by Dreizler.[7] The α axis is the symmetry axis of the methyl group.

species have been identified and their frequencies have been measured. The ^{34}S species was detected in its natural abundance of 4.4 %. With two exceptions, these lines are all due to R branch transitions between the J=3 and J=4, and between the J=5 and J=6, rotational levels. They are all a-type transitions with $\Delta K_{-1} = 0$ and $\Delta K_{+1} = +1$. The two other lines are the A and E components of the torsional satellite of the $4_{04} \rightarrow 5_{05}$ transition originating from the first torsional excited state (v_T=1) of the ^{32}S species. Resolution of the ground torsional state lines into their A and E components was not possible with the available instrument. All of the transitions and their measured frequencies are listed in Tables IV-B-1 and IV-B-2 for the ^{32}S and ^{34}S species respectively.

The assignment of these spectral lines was accomplished by using information published by others to calculate the spectrum of the molecule in regions which had not previously been studied. The reliability of this method was first tested by examining several transitions reported by others in a frequency region which overlapped with the region available for the work reported here.

The transitions chosen for this test were J=3 → J=4 a-type transitions of the ^{32}S species as reported by Nakagawa <u>et al</u>.[3] Three were chosen which were well

TABLE IV-B-1

LINES MEASURED IN THE ROTATIONAL SPECTRUM OF $CH_3{}^{32}SCN$

Transition		Frequency (MHz)
A. $v_T = 0$, $\sigma = A,E$		
$3_{13} \rightarrow 4_{14}$		28359.28
$3_{03} \rightarrow 4_{04}$		29644.22
$3_{12} \rightarrow 4_{13}$		31557.25
$4_{14} \rightarrow 5_{15}$		35381.96
$4_{04} \rightarrow 5_{05}$		36776.06
$4_{23} \rightarrow 5_{24}$		37459.09
$4_{41} \rightarrow 5_{42}$		37638.04
$4_{40} \rightarrow 5_{41}$		
$4_{32} \rightarrow 5_{33}$		37673.44
$4_{22} \rightarrow 5_{23}$		38230.08
B. $v_T = 1$		
$4_{04} \rightarrow 5_{04}$	A	36714.11
$4_{04} \rightarrow 5_{05}$	E	36723.41

TABLE IV-B-2

LINES MEASURED IN THE ROTATIONAL SPECTRUM OF $CH_3{}^{34}SCN$

Transition	Frequency (MHz)
$v_T = 0,\ \sigma = A,E$	
$3_{13} \rightarrow 4_{14}$	28124.58
$3_{03} \rightarrow 4_{04}$	29411.44
$3_{22} \rightarrow 4_{23}$	29793.28
$3_{12} \rightarrow 4_{13}$	31358.14
$4_{14} \rightarrow 5_{15}$	35085.35
$4_{04} \rightarrow 5_{05}$	36472.06
$4_{23} \rightarrow 5_{24}$	37188.45
$4_{22} \rightarrow 5_{23}$	37997.75
$4_{13} \rightarrow 5_{14}$	39109.13

separated from other main absorptions, but which were reported to be surrounded by a characteristic pattern of vibrational and torsional satellites. The frequencies of these three transitions were then calculated by PROGRAM LTSQ using the rotational constants reported by Dreizler and Mirri,[6] and these calculated values were found to be within ±0.5 MHz of the values reported by Nakagawa. A search was then made for these lines at the predicted frequencies and in each case a very strong line was found which was surrounded by the expected satellite peaks. The transitions used and their calculated, reported and measured frequencies are listed [illegible] Table IV-B-3.

On the basis of this good agreement between the frequencies of the spectral lines as calculated by the program and those reported in the literature, it was felt that it was quite reliable to assign transitions which have not previously been reported by using the calculated frequencies. The observation of the characteristic pattern of satellite peaks wherever possible provided a further check. The spectrum of the ^{34}S species was assigned in a similar manner using the rotational constants and line frequencies published by Dreizler and co-workers.[7] These data are given in Table IV-B-4.

In addition to the spectral lines which were assigned in this way, a large number of weak lines

TABLE IV-B-3

TRANSITIONS USED IN THE SPECTRAL ASSIGNMENT FOR $CH_3{}^{32}SCN$

Transition	Reported Frequency (MHz)[a]	Calculated Frequency (MHz)[b]	Measured Frequency (MHz)
$3_{03} \rightarrow 4_{04}$	29644.36	29644.71	29644.22
$3_{13} \rightarrow 4_{14}$	28359.40	28359.65	28359.28
$3_{12} \rightarrow 4_{13}$	31557.42	31557.79	31557.25

[a] Ref. 3.

[b] Calculated using A = 15787.03 MHz, B = 4155.59 MHz and C = 3354.15 MHz.[3]

TABLE IV-B-5

TRANSITIONS USED IN THE SPECTRAL ASSIGNMENT FOR $CH_3{}^{34}SCN$

Transition	Reported Frequency (MHz) [a]	Calculated Frequency (MHz) [b]	Measured Frequency (MHz)
$3_{03} \rightarrow 4_{04}$	29411.44	29411.23	29411.44
$3_{13} \rightarrow 4_{14}$	28124.59	28124.46	28124.58
$3_{12} \rightarrow 4_{13}$	31358.37	31358.19	31358.14

---

[a] Ref. 7.

[b] Calculated using A = 15415.49 MHz, B = 4133.454 MHz and C = 3322.970 MHz.[7]

were detected in the spectral region studied, the frequencies of which were not measured. Others [3 - 7] have reported several Q branch transitions in the regions investigated by them, and therefore these unassigned lines are attributed to transitions of this type.

2. Rotational Constants

The rotational constants A, B and C were obtained for $CH_3{}^{32}SCN$ and $CH_3{}^{34}SCN$ from the spectral line data by the least squares fitting calculation of PROGRAM LTSQ. Table IV-B-5 lists the result of this calculation for the two species along with the values calculated by Dreizler and co-workers [6, 7] from their data. It can be seen that for both species the agreement is excellent between the previously reported values and the values obtained in the work done here.

The transitions used in the rotational constant calculation and their measured frequencies are given in Tables IV-B-6 and IV-B-7 for the ^{32}S and the ^{34}S species respectively. Also included in the tables are the transition frequencies calculated by PROGRAM LTSQ using the experimental set of rotational constants. The differences are seen to be no greater than ±0.22 MHz and are attributed mainly to [illegible]rifugal distortion effects within the

TABLE IV-B-5

CALCULATED ROTATIONAL CONSTANTS FOR $CH_3{}^{32}SCN$ and $CH_3{}^{34}SCN$

Constant	Value Determined in this Work (MHz)	Value Reported By Dreizler *et al.*[6,7] (MHz)
A. $CH_3{}^{32}SCN$		
A	15785 ± 3	15786.91 ± 0.06
B	4155.47 ± 0.03	4155.54 ± 0.01
C	3354.09 ± 0.02	3354.13 ± 0.01
B. $CH_3{}^{34}SCN$		
A	15419 ± 3	15421.4 ± 0.5
B	4133.43 ± 0.03	4133.45 ± 0.01
C	3322.96 ± 0.02	3322.89 ± 0.01

TABLE IV-B-6

OBSERVED AND CALCULATED FREQUENCIES OF TRANSITIONS USED IN THE DETERMINATION OF THE ROTATIONAL CONSTANTS OF $CH_3{}^{32}SCN$

Transition	Observed Frequency (MHz)	Calculated Frequency (MHz)[a]	Difference (MHz)
$3_{13} \rightarrow 4_{14}$	28359.28	28359.12	0.16
$3_{03} \rightarrow 4_{04}$	29644.22	29644.12	0.10
$3_{12} \rightarrow 4_{13}$	31557.25	31557.15	0.10
$4_{14} \rightarrow 5_{15}$	35381.96	35382.01	-0.05
$4_{04} \rightarrow 5_{05}$	36776.06	36776.28	-0.22
$4_{23} \rightarrow 5_{24}$	37459.09	37458.95	0.14
$4_{22} \rightarrow 5_{23}$	38230.08	38230.24	-0.16

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[a] Calculated using the observed rotational constants given in Table IV-B-5.

TABLE IV-B-7

OBSERVED AND CALCULATED FREQUENCIES OF TRANSITIONS USED IN THE DETERMINATION OF THE ROTATIONAL CONSTANTS OF $CH_3{}^{34}SCN$

Transition	Observed Frequency (MHz)	Calculated Frequency (MHz)[a]	Difference (MHz)
$3_{13} \rightarrow 4_{14}$	28124.58	28124.40	0.18
$3_{03} \rightarrow 4_{04}$	29411.44	29411.25	0.19
$3_{12} \rightarrow 4_{13}$	31358.14	31358.06	0.08
$4_{14} \rightarrow 5_{15}$	35085.35	35085.43	-0.08
$4_{04} \rightarrow 5_{05}$	36472.06	36472.26	-0.20
$4_{23} \rightarrow 5_{24}$	37188.45	37188.43	0.02
$4_{22} \rightarrow 5_{23}$	37997.75	37997.85	-0.10

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[a] Calculated using the observed rotational constants given in Table IV-B-5

molecule.

Not all of the observed transitions were included in the least squares calculation since it was found that inclusion of those with $K_{-1} > 2$ led to computed uncertainties in the rotational constants which were considerably larger than those obtained using only those transitions with $K_{-1} = 0$, 1 or 2. The actual values obtained for the rotational constants were not different when all of the observed transitions were used in the calculation.

3. Barrier to Internal Rotation

The barrier to internal rotation of the methyl group was calculated from the A-E splitting of the $4_{04} \rightarrow 5_{05}$ transition originating from the first torsional excited state ($v_T = 1$). The frequencies of these two lines were given in Table IV-B-1, and from these values, the splitting, $\Delta\nu_{AE}$, has been determined to be 9.3 ± 0.1 MHz. Using this value, and the structural parameters of Dreizler and Mirri as listed in Table IV-A-1, the barrier height was calculated to be 1770 ± 20 cal/mole.

Comparison of this value with the value of 1569 ± 10 cal/mole published by Dreizler et al.[5 - 7] shows that a considerable discrepancy exists. Two reasons are suggested for the somewhat higher value determined in the work reported here. The first reason has to do with the use of transitions of higher J for the barrier calculation. It is expected that the use of such transitions in the R branch would to lead to some error because of inaccuracies in the mathematical treatment of the perturbation, and also due to centrifugal distortion of the molecule at these higher rotational levels.[13]

The second possible reason for the error is related to the previously mentioned prediction of Dreizler and Mirri that measurements of barrier heights from lines originating from states other than the ground vibrational and torsional ones ~~could~~ lead to inaccurate values due to coupling between the two modes. The value reported in the literature was determined from Q branch ground torsional state lines, while the value reported here was calculated from the splitting of R branch lines associated with the first torsional excited state.

In order to obtain a more quantitative idea of the extent of the error incurred in the methods used in this work, the torsional barrier was calculated with the splitting of several different rotational lines of different values of J, all originating from the first torsional excited state. The line frequency data which were used were those reported by Nakagawa [3] and the results are given in

Table IV-B-8. It can be seen that the value of the calculated barrier height increases quite consistently as the value of J increases. It can also be seen that, even using the splitting of the transition of the lowest J values reported, a barrier height is obtained which is still higher than the literature value of 1569 ± 10.[6] This can be attributed to the error incurred by using the first torsional excited state for the calculation.

TABLE IV-B-8

BARRIER HEIGHTS CALCULATED FROM TRANSITIONS OF INCREASING VALUES OF J ORIGINATING FROM THE FIRST TORSIONAL EXCITED STATE ($v_T = 1$)

Transition	$\Delta\nu_{AE}$ (MHz)	Calculated Barrier Height (cal/mole)
$1_{01} \rightarrow 2_{02}$	5.11 [a]	1660 ± 10
$2_{02} \rightarrow 3_{03}$	7.02 [a]	1690 ± 10
$3_{03} \rightarrow 4_{04}$	8.31 [a]	1730 ± 10
$4_{04} \rightarrow 5_{05}$	9.3 [b]	1770 ± 20

[a] Ref. 3.

[b] This work.

CHAPTER V. METHYLSELENOCYANATE.

SECTION A. INTRODUCTION

No previous reports of the rotational spectrum of methylselenocyanate have been published, but some information about the molecule has been obtained from studies of its vibrational spectrum. Aynsley and co-workers [16] have studied the infrared and Raman spectra of the liquid and have stated that the expected C_s symmetry is confirmed. They have also reported a low frequency band at 168 cm^{-1} similar to that of methylthiocyanate, and have assigned it to a C-Se-C bending mode.

More recently Franklin et al., have studied the gas phase vibrational spectrum, and have confirmed the findings of Aynsley, including that of the presence of a low frequency band around 170 cm^{-1}. [24] They have reported that the spectra of CH_3SeCN and CH_3SCN are very similar in many respects and have suggested that the two molecules have the same structure based on similarities in band contours. They have also stated that, although it is not possible to draw firm conclusions from the vibrational spectrum as to the detailed bonding in CH_3SeCN, there is no reason to doubt that there is as much $\overset{+}{Se}=C=N^{-}$ character in methylselenocyanate as there is $\overset{+}{S}=C=N^{-}$ character in CH_3SCN. They have supported this suggestion using the measured frequencies of the Se-C(N) vibrational mode.

Finally, Millefiori and Fofani [25] have determined the dipole moment of CH_3SeCN in the liquid state, and have reported a value of 3.91 D. Comparison of this value with the value of 4.11 D available for methylthiocyanate (in the gas phase) [6] is indicative that the microwave spectrum of CH_3SeCN should have a comparable intensity to that of CH_3SCN.

SECTION B. RESULTS AND DISCUSSION

1. Rotational Spectrum

The rotational spectrum of methylselenocyanate has been examined in the region between 27 GHz and 40 GHz, and about seventy lines have been measured and assigned. These lines are due to molecules containing five different isotopes of selenium, all observed in their natural abundances. Table V-B-1 lists the atomic masses and natural abundances of the five isotopes concerned. The spectrum of the sixth naturally occurring isotope of

TABLE V-B-1

NATURALLY OCCURRING ISOTOPES OF SELENIUM DETECTED IN THE ROTATIONAL SPECTRUM OF METHYLSELENOCYANATE

Isotope	Natural Abundance (%)	Atomic mass (amu)[11]
^{76}Se	9.02	75.919207
^{77}Se	7.58	76.919911
^{78}Se	23.52	77.917314
^{80}Se	49.82	79.916527
^{82}Se	9.19	81.916707

selenium was too weak to be detected because of its low natural abundance.

The existence of these five isotopes of selenium renders the spectrum of the methylselenocyante molecule very complex since the overlapping spectra of five different species are observed. Therefore, in order to assign the observed spectral lines, the spectrum of the previously studied methylthiocyanate molecule was used as a model. It was expected that the two molecules should have the same basic structural shape and dipole moment orientation, and therefore should have similar rotational spectra since the relative values of the three rotational constants and the selection rules would be the same. Thus the spectrum of methylselenocyanate was expected to exhibit primarily a-type transitions of the type $J_{K_{-1},K_{+1}} \rightarrow J+1_{K_{-1},K_{+1}+1}$ in the same repeating pattern for each J level. A preliminary scan of the spectrum showed that such a pattern of transitions was indeed observed.

The identification of the spectral lines was accomplished by calculating their frequencies in a similar manner to that discussed above for the CH_3SCN spectrum. Using an assumed molecular structure for CH_3SeCN, based on structural information available for CH_3SCN and CH_3SeCH_3, [7, 21] the rotational constants of the five isotopic species of methylselenocyanate were calculated by PROGRAM CONSTNTS. These rotational constants were then used in PROGRAM LTSQ to calculate the rotational spectra of the two most abundant species, $CH_3{}^{80}SeCN$ and $CH_3{}^{78}SeCN$. It was thereby predicted that the J=4 → J=5, the J=5 → J=6 and the J=6 → J=7 transitions should be observed in the available region between 27 GHz and 40 GHz.

A search in the spectral regions around the calculated line frequencies showed the same characteristic pattern of peaks that was observed for CH_3SCN due to the various ground state transitions and their corresponding vibrational and torsional satellites. The frequencies of several of these lines were measured precisely and used in PROGRAM LTSQ to calculate more accurate rotational constants. This then permitted identification of the weaker and less well-resolved lines of the other isotopic species.

The assigned transitions and their measured frequencies are listed in Tables V-B-2 to V-B-8. All were a-type R branch transitions with $\Delta K_{-1} = 0$ and $\Delta K_{+1} = \pm 1$. Tables V-B-2 to V-B-6 give the frequencies of the five isotopic species originating from the ground vibrational and torsional levels. The splitting of these lines into their A and E components due to the internal rotation of the methyl group was not large enough to be resolved, but for the first torsional excited state of $CH_3{}^{80}SeCN$ the lines were found to be significantly split. The frequencies of five

TABLE V-B-2

LINES MEASURED IN THE ROTATIONAL SPECTRUM OF $CH_3{}^{82}SeCN$ IN THE GROUND VIBRATIONAL AND TORSIONAL STATES

Transition	Frequency (MHz) [a]
$4_{14} \rightarrow 5_{15}$	28068 ± 2
$4_{04} \rightarrow 5_{05}$	29109 ± 0.3
$4_{13} \rightarrow 5_{14}$	32254.45
$5_{15} \rightarrow 6_{16}$	33528.02
$5_{05} \rightarrow 6_{06}$	34391.22
$5_{24} \rightarrow 6_{25}$	36362.4 ± 0.1
$5_{14} \rightarrow 6_{15}$	38430.93
$5_{23} \rightarrow 6_{24}$	38468.05
$6_{16} \rightarrow 7_{17}$	38934.88
$6_{06} \rightarrow 7_{07}$	39707.33

[a] ± 0.08 MHz unless otherwise noted

TABLE V-B-3

LINES MEASURED IN THE ROTATIONAL SPECTRUM OF $CH_3{}^{80}SeCN$ IN THE GROUND VIBRATIONAL AND TORSIONAL STATES

Transition	Frequency (MHz) [a]
$4_{14} \rightarrow 5_{15}$	28153.19
$4_{04} \rightarrow 5_{05}$	29200.91
$4_{23} \rightarrow 5_{24}$	30405.21
$4_{32} \rightarrow 5_{33}$	30796.15
$4_{31} \rightarrow 5_{32}$	30884.70
$4_{22} \rightarrow 5_{23}$	31777.64
$4_{13} \rightarrow 5_{14}$	32322.30
$5_{15} \rightarrow 6_{16}$	33632.23
$5_{05} \rightarrow 6_{06}$	34501.79
$5_{24} \rightarrow 6_{25}$	36347.37
$5_{42} \rightarrow 6_{43}$	36948.95
$5_{41} \rightarrow 6_{42}$	36953.35
$5_{33} \rightarrow 6_{34}$	37000.66
$5_{32} \rightarrow 6_{33}$	37233.60
$5_{14} \rightarrow 6_{15}$	38508.92
$5_{23} \rightarrow 6_{24}$	38528.02
$6_{16} \rightarrow 7_{17}$	39056.92
$6_{06} \rightarrow 7_{07}$	39707.33

[a] ± 0.08 Mhz

TABLE V-B-4

LINES MEASURED IN THE ROTATIONAL SPECTRUM OF $CH_3{}^{78}SeCN$ IN THE GROUND VIBRATIONAL AND TORSIONAL STATES

Transition	Frequency (MHz) [a]
$4_{14} \rightarrow 5_{15}$	28243.01
$4_{04} \rightarrow 5_{05}$	29296.21
$4_{23} \rightarrow 5_{24}$	30494.99
$4_{22} \rightarrow 5_{23}$	31861.29
$4_{13} \rightarrow 5_{14}$	32407.09
$5_{15} \rightarrow 6_{16}$	33740.57
$5_{05} \rightarrow 6_{06}$	34616.89
$5_{24} \rightarrow 6_{25}$	36455.88
$5_{42} \rightarrow 6_{43}$	37053.98
$5_{33} \rightarrow 6_{34}$	37106.00
$5_{14} \rightarrow 6_{15}$	38621.14
$6_{16} \rightarrow 7_{17}$	39183.92
$6_{06} \rightarrow 7_{07}$	39841.08

[a] ± 0.08 MHz

TABLE V-B-5

LINES MEASURED IN THE ROTATIONAL SPECTRUM OF $CH_3{}^{77}SeCN$ IN THE GROUND VIBRATIONAL AND TORSIONAL STATES

Transition	Frequency (MHz) [a]
$4_{04} \rightarrow 5_{05}$	29332.3 ± 0.5
$4_{13} \rightarrow 5_{14}$	32461.7 ± 0.7
$5_{15} \rightarrow 6_{16}$	33795 ± 1
$5_{05} \rightarrow 6_{06}$	34676.3 ± 0.3
$5_{23} \rightarrow 6_{24}$	38679.30
$5_{14} \rightarrow 6_{15}$	
$6_{16} \rightarrow 7_{17}$	39249.08
$6_{06} \rightarrow 7_{07}$	39909.89

---

[a] ± 0.08 MHz unless otherwise noted

TABLE V-B-6

LINES MEASURED IN THE ROTATIONAL SPECTRUM OF $CH_3{}^{76}SeCN$ IN THE GROUND VIBRATIONAL AND TORSIONAL STATES

Transition	Frequency (MHz) [a]
$4_{14} \rightarrow 5_{15}$	28336.5 [illegible]
$4_{04} \rightarrow 5_{05}$	29395.3 ± 0.3
$5_{15} \rightarrow 6_{16}$	33853.11
$5_{05} \rightarrow 6_{06}$	34736.62
$6_{16} \rightarrow 7_{17}$	39315.91
$6_{06} \rightarrow 7_{07}$	39980.35

[a] ± 0.08 MHz unless otherwise noted

TABLE V-B-7

LINES MEASURED IN THE ROTATIONAL SPECTRUM OF CH$_3$^{80}SeCH IN THE FIRST TORSIONAL EXCITED STATE (v_T = 1)

Transition		Frequency (MHz) [a]
$4_{14} \rightarrow 5_{15}$	A	28120.81
	E	28133.31
$4_{04} \rightarrow 5_{05}$	A	29161.90
	E	29176.70
$5_{15} \rightarrow 6_{16}$	A	33595.03
	E	33607.70
$5_{05} \rightarrow 6_{06}$	A	34460.12
	E	34474.10
$6_{06} \rightarrow 7_{07}$	A	39663.31
	E	39675.80

[a] ±0.08 MHz

TABLE V-B-8

LINES MEASURED IN THE ROTATIONAL SPECTRUM OF $CH_3{}^{80}SeCN$ IN THE FIRST AND SECOND VIBRATIONAL EXCITED STATES

Transition	Frequency (MHz)[a] First Excited State	Second Excited State
$4_{14} \rightarrow 5_{15}$	28120.7	-
$4_{04} \rightarrow 5_{05}$	29242.7	-
$5_{15} \rightarrow 6_{16}$	33663.2	-
$5_{05} \rightarrow 6_{06}$	34544.5	-
$6_{16} \rightarrow 7_{17}$	39090.6	39123.5
$6_{06} \rightarrow 7_{07}$	39749.5	-

[a] ± 0.5 MHz

of these lines were measured precisely and are given in Table V-B-7.

The frequencies of several vibrational satellites observed in the spectrum of the ^{80}Se species are listed in Table V-B-8. These were assigned on the basis of a similar pattern of satellite peaks observed in the spectrum of CH_3SCN, 3 - 7 which have been attributed to the first and second excited states of a low frequency bending mode observed in the vibrational spectrum at 171 cm^{-1}. The existence of an equivalent vibrational mode in the methylselenocyanate molecule at 166 cm^{-1} has been mentioned above.

2. Rotational Constants

The rotational constants of the five isotopic species were determined from the measured spectral line frequencies by the least squares fitting calculation of PROGRAM LTSQ. The results are given in Table V-B-9. The rotational constants of the $CH_3{}^{80}SeCN$ molecule in the first vibrational excited state were also calculated and are included in the table. The values of the asymmetry parameters κ and b_p are also given.

The transitions used in the rotational constant calculation are listed in Tables V-B-10 to V-B-15

TABLE V-B-9

CALCULATED ROTATIONAL CONSTANTS AND ASYMMETRY PARAMETERS FOR METHYLSELENOCYANATE

Isotopic Species	A (MHz)	B (MHz)	C (MHz)	b_p	κ
A. Ground State					
^{82}Se	10107±9	3479.2±0.2	2622.3±0.1	-0.0607	-0.771
^{80}Se	10144.0±0.9	3483.34±0.02	2631.65±0.02	-0.0601	-0.773
^{78}Se	10196.9±0.9	3492.33±0.02	2640.45±0.02	-0.0597	-0.775
^{77}Se	10230±3	3497.00±0.06	2644.85±0.05	-0.0595	-0.775
^{76}Se	10255±1	3502.0±0.1	2649.50±0.03	-0.0594	-0.776
B. First Vibrational Excited State					
^{80}Se	10245±1	3495.80±0.09	2631.80±0.02	-0.0602	-0.773

TABLE V-B-10

OBSERVED AND CALCULATED FREQUENCIES OF TRANSITIONS USED IN THE DETERMINATION OF THE ROTATIONAL CONSTANTS OF $CH_3{}^{82}SeCN$

Transition	Observed Frequency (MHz)	Calculated Frequency[a] (MHz)	Difference (MHz)
$5_{15} \rightarrow 6_{16}$	33528.02	33528.70	-0.68
$5_{05} \rightarrow 6_{06}$	34391.22	34393.61	-1.39
$5_{14} \rightarrow 5_{15}$	38430.93	38430.78	0.15
$6_{16} \rightarrow 7_{17}$	38934.88	38934.40	0.48
$6_{06} \rightarrow 7_{07}$	39578.79	39577.63	1.16

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[a] Calculated using the rotational constants in Table V-B-9.

TABLE V-B-11

OBSERVED AND CALCULATED FREQUENCIES OF TRANSITIONS USED IN THE DETERMINATION OF THE ROTATIONAL CONSTANTS OF $CH_3{}^{80}SeCN$

Transition	Observed Frequency (MHz)	Calculated Frequency (MHz)[a]	Difference (MHz)
$4_{14} \rightarrow 5_{15}$	28153.19	28152.91	0.28
$4_{04} \rightarrow 5_{05}$	29200.91	29200.70	0.21
$4_{23} \rightarrow 5_{24}$	30405.21	30404.93	0.28
$4_{32} \rightarrow 5_{33}$	30796.15	30795.73	0.42
$4_{31} \rightarrow 5_{32}$	30884.70	30885.01	-0.31
$4_{22} \rightarrow 5_{23}$	31777.64	31777.57	0.07
$4_{13} \rightarrow 5_{14}$	32322.30	32322.10	0.20
$5_{15} \rightarrow 6_{16}$	33632.23	32632.10	0.13
$5_{05} \rightarrow 6_{06}$	34501.79	34501.81	-0.02
$5_{24} \rightarrow 6_{25}$	36347.37	36347.35	0.02
$5_{33} \rightarrow 6_{34}$	37000.66	37000.61	0.05
$5_{32} \rightarrow 6_{33}$	37233.60	37233.73	-0.13
$5_{14} \rightarrow 6_{15}$	38508.92	38509.07	-0.15
$5_{23} \rightarrow 6_{24}$	38528.02	38528.27	-0.25
$6_{16} \rightarrow 7_{17}$	39056.92	39057.11	-0.19
$6_{06} \rightarrow 7_{07}$	39707.33	39707.67	-0.34

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[a] Calculated using the rotational constants in Table V-B-9.

TABLE V-B-12

OBSERVED AND CALCULATED FREQUENCIES OF TRANSITIONS USED IN THE DETERMINATION OF THE ROTATIONAL CONSTANTS OF $CH_3{}^{78}SeCN$

Transition	Observed Frequency (MHz)	Calculated Frequency (MHz)[a]	Difference (MHz)
$4_{14} \rightarrow 5_{15}$	28243.01	28242.79	0.22
$4_{04} \rightarrow 5_{05}$	29296.21	29295.89	0.32
$4_{23} \rightarrow 5_{24}$	30494.99	30494.82	0.17
$4_{22} \rightarrow 5_{23}$	31861.29	31861.21	0.08
$5_{15} \rightarrow 6_{16}$	33740.57	33740.52	0.05
$5_{05} \rightarrow 6_{06}$	34616.89	34616.77	0.12
$5_{24} \rightarrow 6_{25}$	36455.88	36455.98	-0.10
$5_{33} \rightarrow 6_{34}$	37106.00	37106.13	-0.13
$5_{14} \rightarrow 6_{15}$	38621.14	38621.23	-0.09
$6_{16} \rightarrow 7_{17}$	39183.91	39184.13	-0.22
$6_{06} \rightarrow 7_{07}$	39841.08	39841.30	-0.22

---

[a] Calculated using the rotational constants in Table V-B-9.

TABLE V-B-13

OBSERVED AND CALCULATED FREQUENCIES OF TRANSITIONS USED IN THE DETERMINATION OF THE ROTATIONAL CONSTANTS OF $CH_3{}^{77}SeCN$

Transition	Observed Frequency (MHz)	Calculated Frequency[a] (MHz)	Difference (MHz)
$4_{13} \rightarrow 5_{14}$	32461.70	32461.50	0.20
$5_{15} \rightarrow 6_{16}$	33795.00	33795.54	-0.54
$5_{05} \rightarrow 6_{06}$	34676.30	34676.07	-0.23
$5_{14} \rightarrow 6_{15}$	38679.30	38679.48	-0.18
$6_{16} \rightarrow 7_{17}$	39249.08	39248.61	0.47
$6_{06} \rightarrow 7_{07}$	39909.89	39110.08	-0.19

---

[a] Calculated using the rotational constants in Table V-B-9.

TABLE V-B-14

OBSERVED AND CALCULATED FREQUENCIES OF TRANSITIONS USED IN THE DETERMINATION OF THE ROTATIONAL CONSTANTS OF $CH_3{}^{76}SeCN$

Transition	Observed Frequency (MHz)	Calculated Frequency (MHz)[a]	Difference (MHz)
$4_{14} \rightarrow 5_{15}$	28336.50	28336.28	0.22
$4_{04} \rightarrow 5_{05}$	29395.30	29395.38	-0.08
$5_{15} \rightarrow 6_{16}$	33853.11	33853.20	-0.09
$5_{05} \rightarrow 6_{06}$	34736.62	34736.59	0.03
$6_{16} \rightarrow 7_{17}$	39315.91	39160.01	-0.10
$6_{06} \rightarrow 7_{07}$	39980.35	39980.30	0.05

---

[a] Calculated using the rotational constants in Table V-B-9:

TABLE V-B-15

OBSERVED AND CALCULATED FREQUENCIES OF TRANSITIONS USED IN THE DETERMINATION OF THE ROTATIONAL CONSTANTS OF $CH_3{}^{80}SeCN$ IN THE FIRST VIBRATIONAL EXCITED STATE

Transition	Observed Frequency (MHz)	Calculated Frequency[a] (MHz)	Difference (MHz)
$4_{14} \rightarrow 5_{15}$	28120.77	28120.71	0.06
$4_{04} \rightarrow 5_{05}$	29242.70	29242.79	-0.09
$5_{15} \rightarrow 6_{16}$	33663.20	33663.17	0.03
$5_{05} \rightarrow 6_{06}$	34544.50	34544.39	0.11
$6_{16} \rightarrow 7_{17}$	39090.60	39090.07	-0.07
$6_{06} \rightarrow 7_{07}$	39749.50	39749.54	-0.04

---

[a] Calculated using the rotational constants in Table V-B-9.

along with their observed and calculated frequencies. As in the case of methylthiocyanate, not all of the assigned transitions were included in the least squares fitting procedure since some of the transitions of the higher values of K_{-1} led to large uncertainties. From the tables, it can be seen that the agreement between the observed and calculated line frequencies is better than ±0.55 MHz in all of the species except $CH_3{}^{82}SeCN$, where the differences are as high as 1.39 MHz. This is due to the partial overlap of these relatively weak lines with the intense, closely neighbouring ^{80}Se spectrum which prevented very precise determination of the transition frequencies.

3. Structure

Although it was not possible to determine a precise structure of the methylselenocyanate molecule from data on only the selenium isotopic species, an approximate structure has been determined which generates a set of rotational constants which are in good agreement with the experimental values. This approximate structure was determined by assuming some of the structural parameters from information obtained from the literature on related molecules, and then adjusting the remaining unique parameters until a close fit of the rotational constants was obtained.

The assumptions which were made concerned the structure of the methyl group, the length of the Se-C(H_3) bond, and the length of the C-N bond. These were based on data taken primarily from the microwave structural determinations of $(CH_3)_2Se$ [26] and CH_3SeH,[27] and from microwave structural information on the three related sulphur molecules: $(CH_3)_2S$,[28] CH_3SH [29] and CH_3SCN.[7] The structures of these five molecules are given in Table V-B-16, along with the suggested structure of methylselenocyanate.

Preliminary calculations showed that the rotational constants B and C were quite insensitive to the structure of the methyl group, and that only the constant A was affected significantly. The bond angles were therefore assumed to be tetrahedral in order to simplify calculations, although in the five molecules mentioned above H-C-H angles of slightly greater than 109° 28' have been reported. The C-H bond distance was assumed to be 1.091 Å, as reported by Pierce and Hayashi for $(CH_3)_2S$.[28] Other reported values in similar molecules range from 1.076 Å to 1.093 Å. It was also assumed that the symmetry axis of the methyl group coincides with the direction of the C-Se bond to that group.

A value of 1.955 Å was assumed for the length of the C-Se bond to the methyl group, based on values of 1.943(2) Å and 1.96(1) Å reported for the C-Se

TABLE V-B-16

STRUCTURES OF SOME RELATED MOLECULES CONTAINING THE CH_3X- GROUP (X = S, Se)

Parameter	CH_3SH [29]	$(CH_3)_2S$ [28]	CH_3SCN [7]	CH_3SeH [27]	$(CH_3)_2Se$ [26]	CH_3SeCN [a]
C-H (Å)	1.09(1)	1.091(5)	1.072(2)	1.088(6)	1.093(4)	1.091(ass.)
X-C(H_3) (Å)	1.819(5)	1.802(2)	1.824(2)	1.96(1)	1.943(2)	1.955(ass.)
X-C(N) (Å)	-	-	1.684(3)	-	-	1.836
C-N (Å)	-	-	1.170(2)	-	-	1.157(ass.)
H-C-H (°)	109.7(5)°	109.5°	109.7(2)°	110.2(2)°	110.3(3)°	109.5(ass.)
C-X-Y (°)	96.7(5)°	98.8(2)°	99.0(1)°	95.5(1.7)°	96.2(2)°	96.8°
Tilt Angle	2.2°	2.7°	3.1°	1.5°	2°	-

[a] This work.

bond lengths in $(CH_3)_2Se$ and CH_3SeH respectively. In methylthiocyanate the $S-C(H_3)$ bond length is reported to be 1.824(2) Å, a value which is somewhat larger than that in $(CH_3)_2S$ (1.802(2) Å) and closer to that of CH_3SH (1.819(5) Å). This value of 1.955 was therefore chosen to be larger than the C-Se bond length in $(CH_3)_2Se$ and almost equal to that in CH_3SeH.

The length of the C-N bond of the cyanide group was assumed to be 1.157 Å. Microwave spectral studies on HCN and CH_3CN have resulted in reported C-N bond lengths of 1.157 Å and 1.153 Å respectively,[11] and these have been confirmed by electron diffraction studies.[30] Dreizler et al.[7] have reported an exceptionally long value of 1.170(2) Å for the C-N distance in methylthiocyanate. This might be attributed to back-bonding by the sulphur atom as described in CHAPTER IV-A, but Pierce and Hayashi have reported a normal C-N distance of 1.157(2) Å from their study of the rotational spectrum of $S(CN)_2$.[31] Since the two molecules reportedly have similar amounts of back-bonding character,[31] it appears that a discrepancy exists. The value of 1.157 Å chosen for this work was therefore based on the more commonly reported value for the cyanide group.[11]

Using these assumed values, the remaining two structural parameters, the Se-C(N) bond length and the

C-Se-C bond angle, were determined by adjusting them until a close fit of the rotational constants was obtained. The values which were found were a S-C(N) distance of 1.836 Å and a C-Se-C angle of 96.8°. Figure V-B-1 illustrates the determined structure including the orientation of the principal axis system with respect to the positions of the atoms in the molecule. The observed and calculated values of the three rotational constants for the ^{80}Se species are compared in Table V-B-17.

A comparison of these two parameters, determined in this manner, with those from related molecules shows good agreement. For example, an electron diffraction study of CF_3SeCN has resulted in a reported Se-C(N) bond length of 1.854(16) Å, [32] and from the crystal structures of $Se(SeCN)_2$ [33] and 1,4-diselenocyanatobenzene [34] Se-C(N) bond lengths of 1.83 Å and 1.84(2) Å respectively have been reported. In addition, the value determined here is seen to be smaller than the Se-C bond length to the methyl group, in agreement with the methylthiocyanate structure in which the S-C(H_3) distance is 1.824(2) Å while the S-C(N) distance is 1.684(3) Å. [7]

The suggested value of 96.8° for the C-Se-C angle also compares well with related data in that a value of 96.2(2)° has been reported for $(CH_3)_2Se$ [26] which is only slightly smaller than the value given here. A similar trend

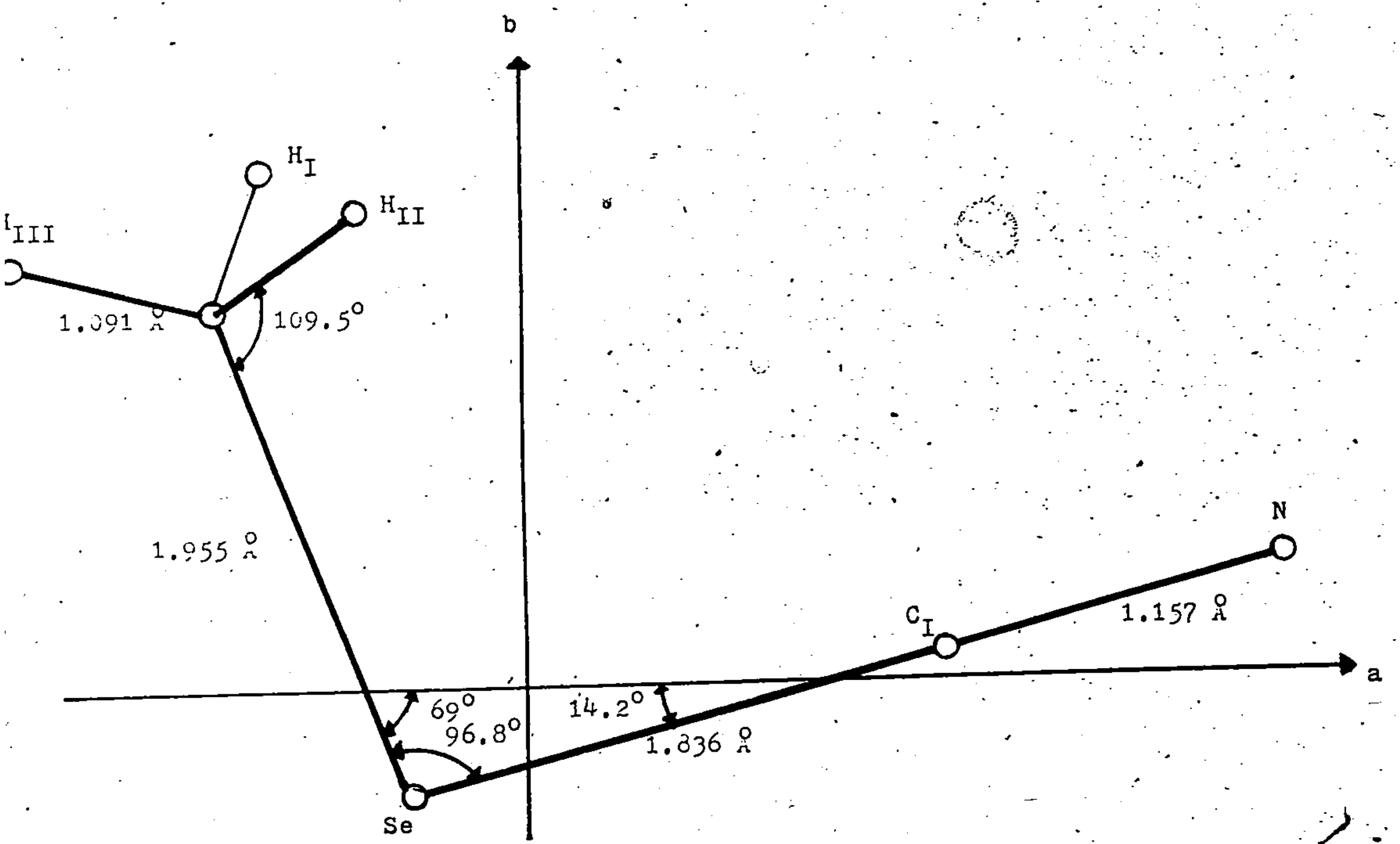


Figure V-B-I. Structure of CH_3SeCN illustrating the orientation of the principal axis system.

TABLE V-B-17

OBSERVED AND CALCULATED ROTATIONAL CONSTANTS OF $CH_3{}^{80}SeCN$

Constant	Observed Value (MHz)	Calculated Value [a] (MHz)
A	10144.0 ± 0.9	10147.02
B	3483.34 ±0.02	3478.78
C	2631.65 ± 0.02	2633.79

---

[a] Calculated using the structural parameters in Table V-B-16.

occurs in the analogous sulphur molecules where a value of 99.0(1)° has been reported for the C-S-C angle in CH_3SCN,[7] while in $(CH_3)_2S$ a slightly smaller value of 98.8(2)° has been given.[28]

Although it can be shown that several sets of structural parameters, within a small range of values, could have generated an equally good set of rotational constants, the set chosen, as listed in Table V-B-16, leads to the best overall comparisons with directly related molecules as argued above. The suggested structure is therefore not a definitive one, but is only meant to show that logical values for the structural parameters can generate rotational constants which are in good agreement with the observed ones. It can be definitely concluded, however, that the basic molecular shape of the molecule has been confirmed, in which the C-Se-C bond angle is less than 100° and the Se-C(N) bond length is significantly shorter than the Se-C bond to the methyl group. In order to obtain more precise information, a study of the rotational spectra of isotopically enriched species involving each atom in the molecule would be required.

4. Barrier to Internal Rotation

The barrier to internal rotation of the

methyl group was calculated from the A-E splitting of the spectral lines originating from the first torsional excited state ($v_T = 1$) of the ^{80}Se isotopic species. The transitions used were those with $K_{-1} = 0$. These are listed in Table V-B-18 with their frequencies and the corresponding value of the splitting, $\Delta\nu_{AE}$.

The method used to calculate the barrier height was the same as that used for methylthiocyanate and has been described in detail in CHAPTER II-C. The molecular parameters used in this calculation are listed in Table V-B-19. The values given there for λ_x and λ_y were calculated by PROGRAM CONSTANTS from the approximate structure determined above. The moment of inertia of the methyl rotor, I_α, was taken to be 3.212 amu Å^2. This is the value used by both Dreizler [6] and Nakagawa [3] in their work on methylthiocyanate and should not change significantly from molecule to molecule.

The results of the barrier calculation are given in Table V-B-20 for each of the three values of $\Delta\nu_{AE}$ from the three transitions used. First the value of a_1 is given as calculated from $\Delta\nu_{AE}$ according to equation II-C-15. Secondly the value of S is given as determined from the value of a_1 by graphical means, and finally the value of V_3 is given as calculated from S according to equation II-C-16.

TABLE V-B-18

TRANSITIONS USED IN THE CALCULATION OF THE BARRIER TO INTERNAL ROTATION FOR $CH_3{}^{80}SeCH$

Transition ($v_{\tau} = 1$)		Frequency (MHz) [a]	$\Delta\nu_{AE}$ (MHz) [b]
$4_{04} \rightarrow 5_{05}$	A	29161.90	14.80
	E	29176.70	
$5_{05} \rightarrow 6_{06}$	A	34460.12	13.98
	E	34474.10	
$6_{06} \rightarrow 7_{07}$	A	39663.31	12.49
	E	39675.80	

---

[a] ± 0.08 MHz

[b] ± 0.16 MHz

TABLE V-B-19

MOLECULAR PARAMETERS USED IN THE CALCULATION OF THE BARRIER TO INTERNAL ROTATION FOR CH$_3$^{80}SeH

Parameter	Value
I_A (= I_z)	49.82062 amu Å^2
I_B (= I_y)	145.318 amu Å^2
I_C (= I_x)	191.940 amu Å^2
I_α	3.312 amu Å^2
λ_y (= λ_b)	0.930
λ_x (= λ_a)	-0.359
F	161.818 GHz
r	0.973
β	0.269
ρ_x	0.0167
ρ_y	0.0206
ρ_z	0.0277
ρ	0.0767

TABLE V-B-20

RESULTS OF THE BARRIER CALCULATION FOR $CH_3{}^{80}SeCH$

Transition	$\Delta\nu_{AE}$[a] (MHz)	a_1 ($\times 10^3$)	S	V_3[b] (cal/mole)
$4_{04} \rightarrow 5_{05}$	14.80	12.36	44.6	1550
$5_{05} \rightarrow 6_{06}$	13.98	9.733	45.6	1590
$6_{06} \rightarrow 7_{07}$	12.49	7.453	48.2	1670

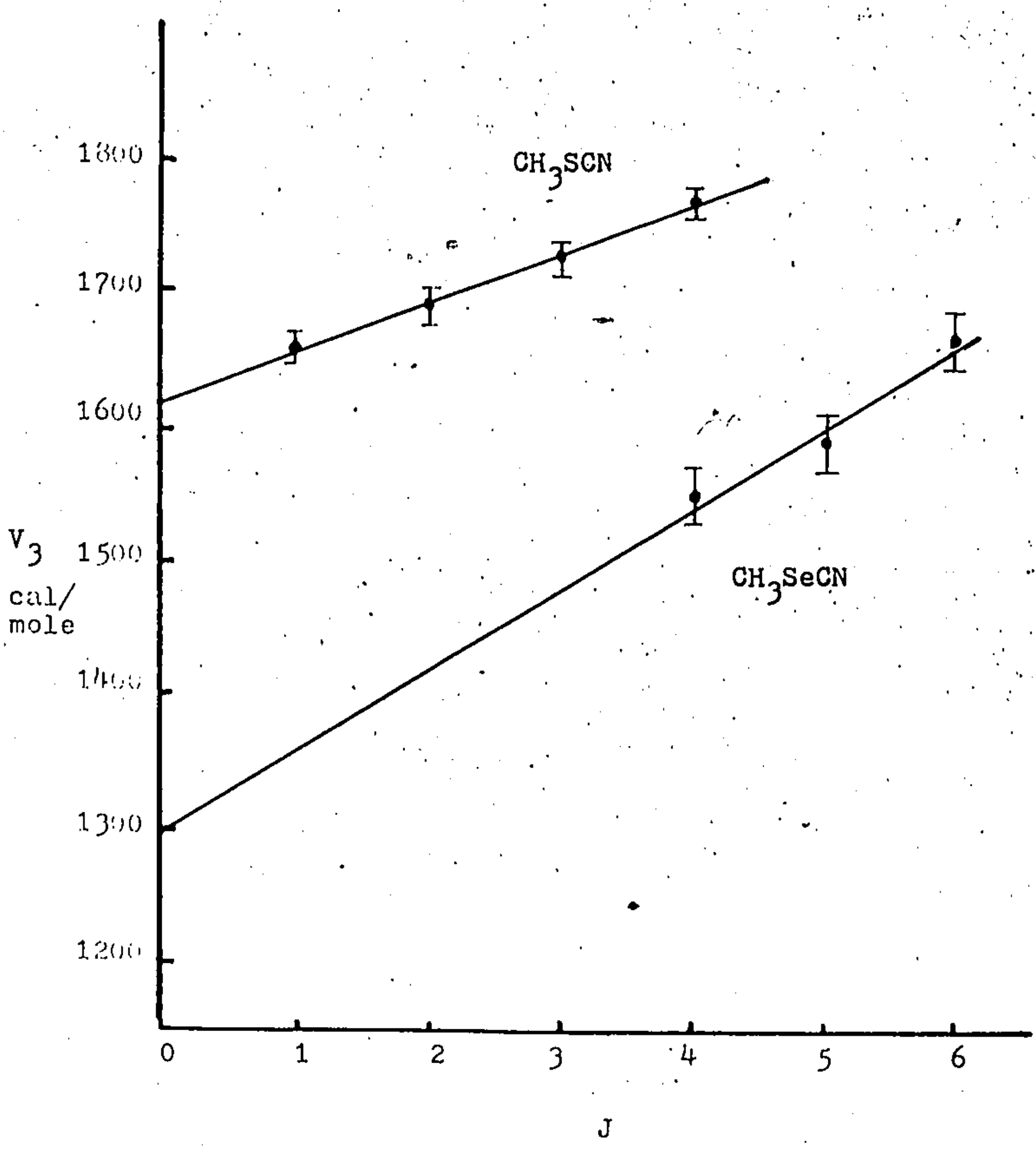
[a] ± 0.16 MHz

[b] ± 20 cal/mole

Examination of these barrier height results shows that the calculated value of V_3 increases with the value of J, and therefore a closer study of the results is needed before any conclusion can be made as to the true value of the barrier. A dependence of the barrier height on the nature of both the rotational and torsional level used in the calculation was observed for methylthiocyanate, and possible reasons for it were discussed in CHAPTER IV. Since CH_3SeCN and CH_3SCN are quite alike, as has been confirmed by the similarities in their spectra and structure, equivalent sources of error are expected to exist in the methylselenocyanate molecule.

In order to obtain a better value for the barrier height in CH_3SeCN, a comparison of the magnitude of the errors in the two molecules was carried out by plotting the calculated value of V_3 against J. These plots are given in Figure V-B-2. In both cases a linear dependence of V_3 on the value of J is observed, the slope being greater in the case of the selenocyanate. Extrapolation of the methylthiocyanate plot to J = 0 results in a barrier height of 1620 ± 10 cal/mole, still somewhat higher (3.2 %) than the literature value of 1569 ± 10.[6] As discussed in CHAPTER IV, this difference is presumably due to the use of the splitting of the first torsional excited rather than that of the ground state.

Figure V-B-2. The effect of the rotational level J on the calculated barrier height in CH_3SCN and CH_3SeCN.


CH$_3$SCN
CH$_3$SeCN
1800
1700
1600
1500
1400
1300
1200
V$_3$
cal/
mole
0
1
2
3
4
5
6
J

In the case of the methylselenocyanate plot, a similar extrapolation leads to a value of 1300 cal/mole for the barrier height. Application of the same 3.2 % correction factor to this value results in a value of 1260 cal/mole. Taking the uncertainties in the individual points into consideration, an uncertainty in the barrier height of ± 50 cal/mole is obtained, but a true estimate of the accuracy of this value is not easily arrived at since only three points were available for the plot and since only an approximate molecular structure was used in the calculation. It is therefore suggested that the true value of the barrier height is probably within ± 10 % of the value of 1260 cal/mole quoted above. It can be definitely concluded, however, that the barrier height in methylselenocyanate is significantly lower than in methylthiocyanate.

Table V-B-21 lists this value of 1260 cal/mole for methylselenocyanate along with the reported barrier heights for several other related molecules containing the CH_3X- group. As mentioned in CHAPTER 1, in the CH_3XH series the barrier height in the sulphur species is somewhat higher than in the molecules containing O or Se. With the addition of the value for CH_3SeCN it can be seen that the CH_3XCN molecules follow the same trend. Included in the table are the barrier heights for $CH_3OC\equiv CH$ and $CH_3SC\equiv CH$, and again the same trend is observed for the first two species of this series. No information of the selenium analogue has yet

TABLE V-B-21

BARRIERS TO INTERNAL ROTATION IN SOME RELATED MOLECULES CONTAINING THE CH_3X- GROUP (X = O, S, Se)

Molecule	V_3 (cal/mole)	Ref.
CH_3OH	1070	35
CH_3SH	1270 ± 10	29
CH_3SeH	1010 ± 50	27
CH_3OCN	1110	36
CH_3SCN	1569 ± 10	6
CH_3SeCN	1260 ± 125	this work
$CH_3OC{\equiv}CH$	1445	37
$CH_3SC{\equiv}CH$	1745	38

been published. A discussion of possible reasons for this trend and of the origin of the internal rotational barrier in molecules of this type is given in the next chapter.

CHAPTER VI. GENERAL DISCUSSION.

SECTION A. THE ORIGIN OF THE BARRIER TO INTERNAL ROTATION

Ever since it was discovered that the internal rotation of methyl groups in many molecules is not free, but hindered to a certain degree, a great deal of effort has been devoted to attempting to find a simple and useful theory to explain the origin of this barrier. The treatments have ranged from those which try to relate the barrier height to the chemical nature of the C-X bond or to some characteristic molecular distance (e.g., the length of the torsional axis in the series CH_3CH_3, CH_3SiH_3, CH_3GeH_3), to *ab initio* LCAO-MO calculations. A complete review of the subject has been published by Lowe.[36]

In the CH_3X- type molecules of interest here, no simple explanation for the observed barrier height trends is immediately evident. If the nature of the C-X bond was the important factor then a continuous trend would be expected, not one in which the highest barrier belonged to the sulphur species. The same thing would be expected if the barrier height was related to the length of the C-X bond, or, to the separation between the protons of the methyl rotor and the rest of the molecule in the eclipsed conformation. For example, a simple calculation using the available geometries for the CH_3XH series [27, 29, 35] shows that the separation between the methyl proton and the XH proton increases continuously with the size of the X atom. Thus the origin of the barrier cannot be accounted for by these simple correlations, or it must be a combination of several such factors.

Recently, Lowe and Parr [40] have developed an approach to barrier origins which has been quite useful in correlating the barrier heights in molecules of this type. This approach was first developed by Wyatt and Parr [43] and originally involved ab initio MO calculations on the ethane molecule to arrive at an origin for the barrier. Lowe has summarized the results of this treatment as follows: The barrier is essentially due to a large positive contribution from the change in nuclear-nuclear repulsion between the protons which occurs on going from the staggered to the eclipsed conformation of the ethane molecule, and a smaller negative contribution related to the change in the nuclear-electron attraction. The nuclear-nuclear repulsion term, given the symbol ΔV_{nn}, can be calculated from the geometry of the molecule, but the nuclear-electron term, ΔV_{ne}, can only be determined from the wave functions of the eclipsed and staggered forms.[36]

The approach of Lowe and Parr has centered around simplifying this explanation by showing that the ΔV_{ne} term can be likened to shielding of the nuclear charges due to the occupation of the hydrogen 1s orbitals. In this view, the barrier can be said to originate primarily from the nuclear-nuclear repulsion, but that this repulsion is moderated by shielding effects.

In order to extend this approach in a semi-empirical way to other similar molecules involving hydrogen-hydrogen interactions, Lowe and Parr have considered the three molecules CH_3OH, CH_3SH and CH_3SeH. They have suggested that in molecules of this type the following relationship might be used:

$$V_3 = f \cdot \Delta V_{nn} \qquad \text{(VI-A-1)}$$

Here f is related to the moderating effect of the ΔV_{ne} term, and therefore would always have a value less than one. It could be related to such questions as how the electron distribution in the O-H end of the CH_3OH molecule compares with that in the S-H end of CH_3SH. Such questions could be answered by considering electronegativity and other contributing effects such as induction and resonance.

Lowe and Parr have compared the experimental results on this series of molecules and have found them to fit this approach quite well. For example, the highest f value would be expected to occur in CH_3OH due to the high electronegativity of the oxygen molecule which causes the hydrogen nucleus to be less effectively screened than in the other molecules. The values of ΔV_{nn} were calculated for the three molecules from the available geometries, and the values of f were then determined using equation VI-A-1 and the published values of the barrier heights. These data are listed in Table VI-A-1. As expected, f decreases in the series in agreement with the relative electronegativities of the O, S, and Se atoms.

The observed trend in the barrier heights of these three molecules is therefore caused by a combination of the two factors, one causing the barrier heights to decrease in the series, the other causing them to increase. On the basis of f alone the barriers would be expected to decrease from CH_3OH through CH_3SeH, but the values of ΔV_{nn} are much greater for the S and Se species than for the O species. The product of these two factors then explains why CH_3SH has the highest barrier value.

One further question remains, and that is why the value of ΔV_{nn} is so much greater for CH_3SH and

TABLE VI-A-1

COMPARISON OF BARRIER ORIGIN PARAMETERS FOR CH_3XH MOLECULES

Molecule	$\Delta V_{nn.}$ (cal/mole)	f	V_3 (cal/mole)	Reference
CH_3OH	1190	0.88	1070	35
CH_3SH	1840	0.68	1270	29
CH_3SeH	1900	0.53	1010	27

CH_3SeH than for CH_3OH when the actual nuclear-nuclear separations are also greater in either the eclipsed or staggered forms. Thomas [27] has suggested that this is due to the value of the C-X-H angle which is considerably smaller for CH_3SH (96.5° [29]) and for CH_3SeH (95.5° [27]) than for CH_3OH (108.5° [35]). This causes the change in the proton-proton separation on going from the staggered to the eclipsed form to be greater in the S and Se species than in CH_3OH. Thus it is the change in repulsion energy accompanying the internal rotation which is the important factor, not the actual repulsion energy in the eclipsed form.

Lowe and Parr have suggested that their approach can be extended to molecules in which the interacting atoms are other than hydrogen, and the results have met considerable success. They explain the near constancy of the barrier on going from ethane to the fluorinated ethanes by saying that, although the nuclear-nuclear repulsions would be greater for fluorine than for hydrogen, there also exists a greater number of non-bonding electrons to shield the nuclear charge. Thus they are suggesting that the basic origin of the barrier is still the ΔV_{nn} term.

Using this idea, the observed trend in the barrier heights of the CH_3XCH series can be rationalized in a similar manner to that in the CH_3XH series. Here the variation in the barrier heights due to differences in a factor such as f is not expected to be as great as in the CH_3XH molecules since the difference in the electronegativities of the X atoms is not expected to have as large an effect on the shielding in the C≡N group as it does on the shielding in the X-H group. Thus the barrier heights should be more closely related to the differences in the nuclear-nuclear repulsions. Since the geometries of the CH_3XCN series, particularly the value of the C-X-C angle, should show the same trend as those of the CH_3XH molecules, then the relative magnitudes of the nuclear-nuclear repulsions should also be similar in the two series.

On the basis of these arguments, the difference in the barrier heights between the S and O species of the CH_3XCN series should be greater than observed in the CH_3XH series, and a smaller difference should be observed between the barriers of the S and Se species. This is what has been found (See Table V-B-21). The same approach can explain why the barrier in $CH_3SC{\equiv}CH$ is higher than that in $CH_3OC{\equiv}CH$.

One apparent weakness to this approach is that electron-electron repulsions have not been taken into consideration. Although these might be negligible when considering hydrogen-hydrogen interactions, they are likely to become more important when considering interactions between protons and other atoms or groups. Again, however, the difference between the electron-electron repulsions of the eclipsed and staggered forms should be subject to the same geometric influences as the ΔV_{nn} term, and therefore should show similar trends.

A further weakness of the Lowe-Parr theory is that it cannot explain why the barrier heights in the $CH_3XC{\equiv}CH$ series are so much higher than those of the CH_3XCN series when the geometry and electron distribution in the two types of molecules are expected to be very similar. Thomas has pointed out in his discussion of the CH_3XH series that, although the data indicate that much of the torsional barrier in these molecules can be accounted for by nuclear-nuclear repulsions, some contribution from other sources such as the nature of the C-X bond itself cannot be ruled out. In light of the comparison between the CH_3XCN and the $CH_3XC{\equiv}CH$ series it must be agreed that other factors are likely involved.

SECTION 8. BONDING IN THE XCN GROUP

With the publication of structural information on methylthiocyanate and related molecules, a certain amount of discussion has appeared in the literature concerning the bonding in the SCN group. Pauling [41] initiated this discussion by making some suggestions based on the microwave spectral investigation of CH_3SCN by Beard and Daily.[1] As mentioned in CHAPTER IV, their results were eventually shown to be in error, but at that time Pauling interpreted their abnormally short S-C(N) bond distance of 1.61 Å, and their C-S-C bond angle of 142°, to indicate that the principal resonance form of the molecule was $H_3C-\underset{..}{\overset{+}{S}}=C=\underset{..}{\overset{-}{N}}:$, which contributed about 70 per cent, and that the structure $H_3C-\underset{..}{\overset{..}{S}}-C\equiv N:$ only contributed about 30 per cent. He noted, however, that the reported angle of 142° was much larger than expected and suggested a smaller value of 113°.

Since "back-bonding" by sulphur to such a large extent seemed unlikely, other investigations were undertaken to determine a more exact structure. Dreizler and co-workers[7] found that, as expected, the bond angle was actually much smaller (about 100° and not 142°) and the S-C(N) bond distance larger (1.684 Å and not 1.61 Å) than the values suggested by Beard and Daily. However, this accurate value of the S-C(N) bond length is still smaller than the normal S-C single bond distance of 1.824 Å observed for the S-C bond to the methyl carbon, and is closer to the S=C double bond distance of 1.61 Å.[41]

The case of the related $S(CN)_2$ molecule provides further evidence that "back-bonding" by sulphur can occur in the SCN group. Pierce *et al.*[31] have studied the hyperfine structure in the rotational spectrum of this molecule and have determined the three components of the quadrupole coupling constant of the ^{14}N nucleus. These three components are directed along three axes of a Cartesian coordinate system, the origin of which lies at the nitrogen nucleus, and of which one of the axes coincides with the C-N bond. From these values two estimates of the amount of double bond character in the C-N bond were made.

The first estimate was based on the value of the coupling constant along the direction of the C-N bond. This was found by them to be considerably smaller than would be expected if the C-N bond was a pure triple bond, as in $H-C\equiv N$ or $CH_3C\equiv N$. This led to an estimate of 23 per cent for the amount of double bond character in the C-N bond, and thus an estimate of only 23 per cent for the contribution of the structure suggested by Pauling to be the principal resonance form.

The second estimate was based on a comparison of the two coupling constants which are perpendicular to the C-N axis. If the C-N bond was a pure triple bond, the electronic distribution about it should have cylindrical symmetry, and hence the coupling constants perpendicular to the C-N axis would be equal. Partial double bond character would lead to slightly different values, and this is what was found. On this basis, Pierce et al have estimated the amount of double bond character to be about 8 per cent.

Although these authors have admitted that these two estimates do not agree very well, they have concluded that the data indicate that "back-bonding" by sulphur is quite significant in $S(CN)_2$. The structure of the molecule has also been reported by them, and again the S-C bond distance (1.701 Å) has been found to be shorter than a normal S-C single bond distance. Pierce et al. have suggested that this bond length difference is all due to the "back-bonding" by sulphur, and not because of any differences in the hybridization of the two types of carbon atoms.

As discussed previously in CHAPTER IV, Lett and Flygare[4] have examined the quadrupole hyperfine splitting in the rotational spectrum of methylthiocyanate in a similar manner to that done for $S(CN)_2$. Their estimate of a 10 per cent contribution of the $H_3C-\overset{+}{\underset{..}{S}}=C=\overset{-}{\underset{..}{N}}:$ resonance form was based on the ^{14}N coupling constant along the C-N internuclear line. They also have reported that the coupling constants along the other two directions are non-equal, as has been reported for $S(CN)_2$. Ikeda et al.[42] have come to the same conclusion from their study of the pure quadrupole resonance in crystalline methylthiocyanate.

Although it is not generally condidered by these authors, one apparent weakness in using the values of the quadrupole coupling constants in this way must be pointed out. This is that some non-cylindrical symmetry of the electronic distribution in the C≡N group is expected on the basis of the asymmetry of the molecule alone. Estimates of the double bond character in the C-N bond based on the observation of a difference in coupling constants might therefore be misleading.

In the case of methylselenocyanate, it has been discussed in CHAPTER V that Franklin <u>et al</u>.[24] have suggested that there is no reason to doubt that there is as much "back-bonding" by Se in CH_3SeCN as there is by S in CH_3SCN. The structure of methylselenocyanate reported in this thesis shows that the Se-C(N) bond length of 1.836 Å is shorter than the Se-C(H_3) bond length of 1.955 Å by a value of 0.12 Å. The corresponding difference in CH_3SCN is 0.14 Å, but the suggested structure is not sufficiently precise to allow valid comparisons between the amounts of "back-bonding" in the two molecules to be made. There is, however, a significant difference in the two Se-C bond lengths in CH_3SeCN, and, as suggested by Pierce <u>et al</u>.,[31] this indicates a certain degree of "back-bonding".

Further information as to whether Se can take place in "back-bonding" in the XCN group to as great an extent as S, could be obtained from the quadrupole coupling constants of ^{14}N, but this is subject to the problems mentioned above. This was not possible with the resolution of the instrument available for this work, and, in fact, the complexity and lack of intensity of the spectrum might render it virtually impossible to observe the quadrupole hyperfine splitting at all.

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PART TWO

THE PREPARATION OF SUBSTITUTED ACETYLENIC DICOBALTHEXACARBONYL COMPLEXES CONTAINING PHOSPHORUS AND ARSENIC DONOR LIGANDS

CHAPTER I. INTRODUCTION.

SECTION A. GENERAL INTRODUCTION

The purpose of this part of the thesis is to describe the preparation of a series of acetylenic dicobalthexacarbonyl complexes in which the carbonyl groups have been substituted by phosphorus and arsenic donor ligands. This work is part of a more extensive project being undertaken in this laboratory in an attempt to provide further insight into the nature of the metal-alkyne bonding in such complexes, mainly through the use of X-ray crystallographic structure determinations.[1-3]

The metal-alkyne bond in transition metal complexes of acetylenes has long been the subject of much discussion. Of particular interest has been the possibility and extent of metal-to-ligand back-bonding involving the acetylene group. Various types of physical evidence have been presented supporting a bonding mechanism of this type, but there has been recent interest in correlations between the extent of the metal-alkyne back-bonding and the structure of the acetylenic molecule in the complex.[4-12] In general, the bonded acetylene is found to have a bent structure and the acetylenic C≡C bond length is observed to be considerably longer than in the uncoordinated molecule. These structural changes are considered to be a result of occupation of the π^* antibonding orbitals of the acetylene via the metal-alkyne back-bonding mechanism and theoretical calculations indicate that the degree of bending in the acetylene is a function of the extent of this back-bonding.[10, 11] Although some experimental evidence supports this,[4, 6] there has been no attempt to systematically vary the degree of back-bonding in a series of complexes and simultaneously observe the changes which take place in the ligand structure. X-ray crystallographic studies could provide this information.

One method of varying the degree of metal-alkyne back-bonding in complexes such as the acetylenic dicobalthexacarbonyls, is to substitute the carbonyl ligands by groups which are stronger donors and weaker acceptors than CO, such as those containing the heavy Group VA donor atoms. This causes the remaining ligands in the complex to participate in metal-ligand back-bonding to a greater extent in order to remove excess charge from the metal atoms. Thus it should be possible to prepare a series of complexes in which the metal-alkyne back-bonding progressively increases, by successively substituting the CO groups in such a system. The acetylenic dicobalthexacarbonyl complexes are particularly well suited to this type of study since there are six possible substitution products. Therefore a more extensive series is potentially available than with most other transition metal-alkyne systems.

One problem which arises in the preparation of such substituted complexes is that the increase in metal-CO back-bonding which occurs as substitution progresses, results in a complex in which the remaining carbonyl groups are more strongly bonded. This makes further substitution more difficult. Substituted derivatives of acetylenicdicobalthexacarbonyls have been reported in which one or two CO groups have been replaced,[13] but no reports of attempts to cause further substitution have been published. Work was therefore initiated in this laboratory to study these substitution reaction in greater depth, with the eventual aim of preparing the complete series of substituted complexes. This thesis reports the preparation of complexes in which up to four CO groups have been replaced.[a] Some initial attempts to prepare a fully substituted derivative are also described.

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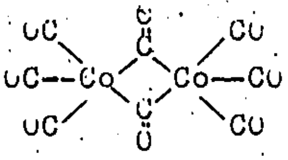
[a] The results of the work reported in this thesis were initially communicated at the 56th Annual Conference of the Chemical Institute of Canada, Montreal, 1973. Since that time, and during the final stages of the preparation of this thesis, a report has appeared (ref. 14) describing several tri- and tetrasubstituted complexes. The results given there are in good agreement with those described in this thesis and will not be discussed.

The remainder of this introductory chapter consists of three sections devoted to reviewing certain topics which are pertinent to this work. The first is a review of the acetylenic dicobalthexacarbonyls, presented primarily from an historical viewpoint. This has been included with the intention of providing the reader with some concept of the nature of this extensive series of complexes. The subject of alkyne-cobalt complexes in general has recently been comprehensively reviewed by Dickson and Fraser,[13] and several earlier reviews of transition metal alkynes have included sections on complexes of cobalt.[15-19] The reader is referred to these for more detailed information.

In the second section, the bonding between the metal atoms and the three types of ligands involved in the work reported in this thesis is discussed in detail. Further elaboration on the previously mentioned relationship between the structure of the alkyne ligand and the extent of π back-bonding is included there. Previous reports of substitution reactions of dicobalthexacarbonyl acetylenes with P, As and Sb ligands are then reviewed in the final section of this chapter.

SECTION B. INTRODUCTION TO ACETYLENIC DICOBALTHEXACARBONYL COMPLEXES

The first reports of the preparation of acetylenic dicobalthexacarbonyl complexes were published by Sternberg *et al.* in 1954 [20] and in 1956. [21] It was observed by them that dicobaltoctacarbonyl reacted quantitatively with alkynes at room temperature, resulting in the replacement of two carbonyl groups to form complexes of the general formula $(RC_2R')Co_2(CO)_6$. They found that the reaction, which can be represented by equation (1-B-1),



$$+ \quad RC{\equiv}CR' \longrightarrow (RC_2R')Co_2(CO)_6 + 2\ CO \qquad (1\text{-}B\text{-}1)$$

occurs with various types of alkynes, and that the resulting complexes are deeply coloured oils, or low-melting solids, and are diamagnetic. The complexes were also found to be quite soluble in all common organic solvents.

Examination of the infrared spectra of the complexes led these authors to conclude that the two moles of carbon monoxide displaced by the acetylene were the bridging carbonyl groups. In addition, the position of the C-H stretching frequency indicated that there was no carbon-carbon triple bond in the $(RC_2R')Co_2(CO)_6$ complexes. They therefore suggested that the alkyne group bridged the two cobalt atoms.

Two possible arrangements for this bridging structure were suggested. In one the C≡C bond of the alkyne is parallel to the Co-Co axis, and in the second it is perpendicular to the Co-Co axis, either in the same plane as this axis or above it. Sternberg _et al_. favoured the first arrangement from their studies of the infrared spectra and dipole moments of the complexes, but stated that a definite choice between the two postulated structures could not be made without X-ray structural evidence.

In 1959 Sly [22] provided this evidence in reporting the X-ray crystal structure determination of the diphenylacetylene dicobalthexacarbonyl complex. He showed that the basic structure of the complex is derived from substitution of the two bridging carbonyl groups in $Co_2(CO)_8$ as originally suggested, but that the C≡C bond of the acetylene is not parallel to the Co-Co axis. It was found to be perpendicular to the Co-Co axis and above it, as illustrated in Figure I-B-1. The phenyl groups are bent

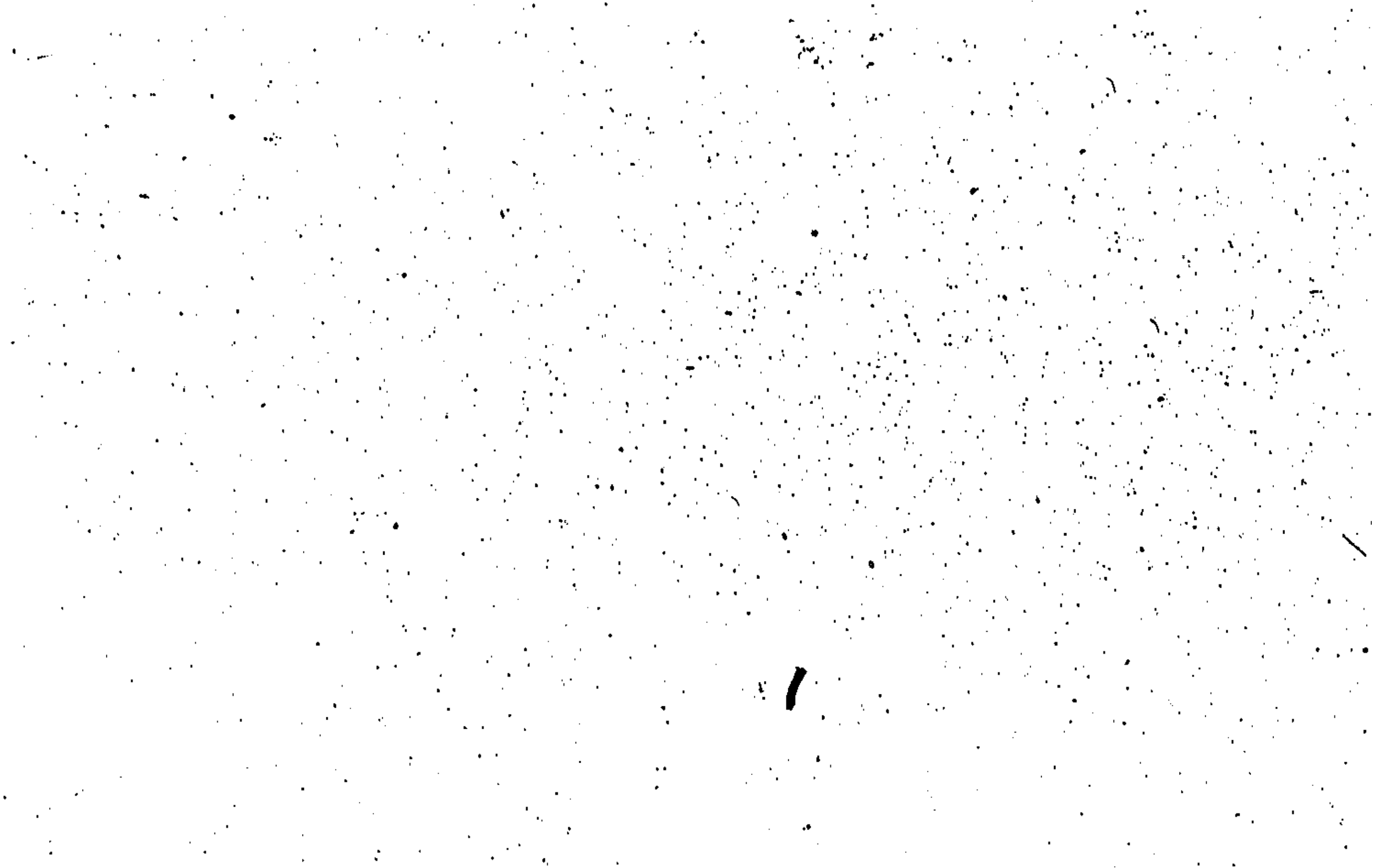
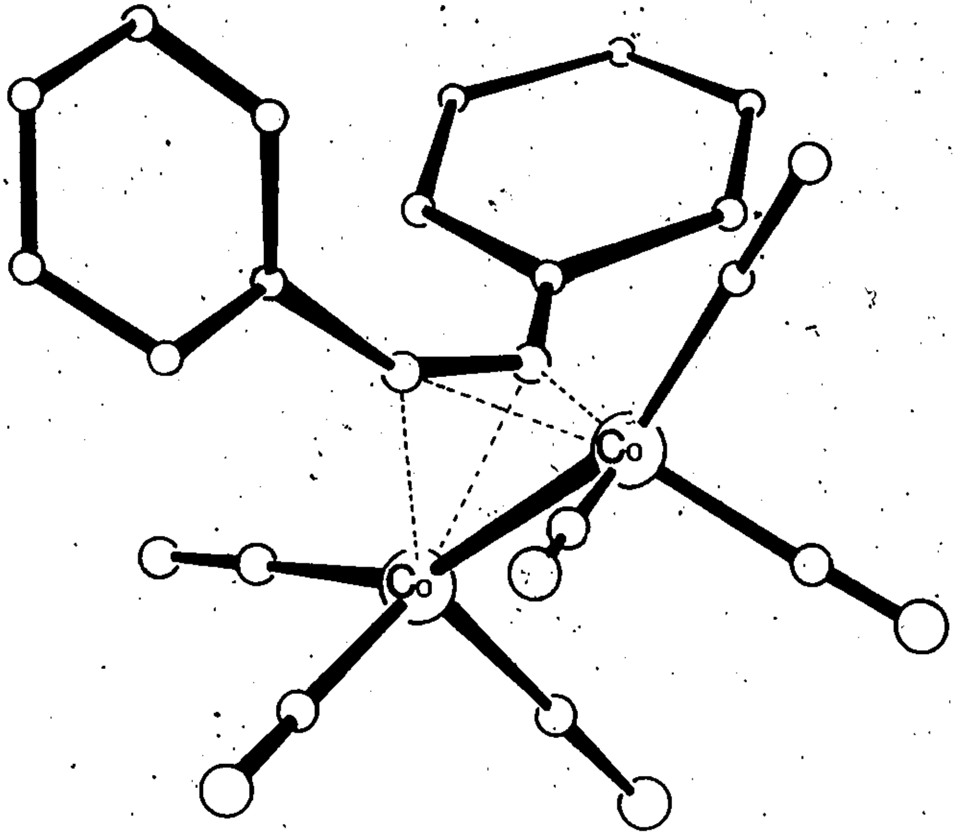


Figure I-B-1. The structure of diphenylacetylenehexacarbonyldicobalt as taken from ref. 22.


Co
Co

back away from the Co-Co axis, and form an angle of 140° with the $C\equiv C$ bond. The $C\equiv C$ bond length of 1.37 Å [22,23] is considerably longer than the $C\equiv C$ bond length of 1.20 Å [24] in the uncoordinated acetylene. The X-ray crystal structure determinations of other similar dicobalthexacarbonyl complexes have since provided confirmation of this basic structural arrangement.[3, 25-30]

With the publication of this crystal structure Sly suggested two possible schemes for the nature of the bonding in this type of complex. In one the geometry about each cobalt atom is trigonal bipyramid, and therefore the cobalt atoms are considered to be dsp^3 hybrids. One of these hybrid orbitals on each cobalt atom is directed towards the centre of the $C\equiv C$ bond of the alkyne. This scheme is illustrated in Figure I-B-2. In the second description the two cobalt atoms are d^2sp^3 hybrids and the carbon atoms have been rehybridized to sp^3. This second formulation requires the coordinated acetylenic bond to be essentially a C-C single bond, but this is not compatible with the observed C-C distance of 1.37 Å. Sly therefore favoured the first structure and also pointed out that it is equivalent to the metal-alkyne bonding scheme suggested by Chatt et al.[31] in which metal-to-ligand back-bonding occurs in addition to the ligand-to-metal forward donation. A further discussion of this is given in Section C of this Chapter.

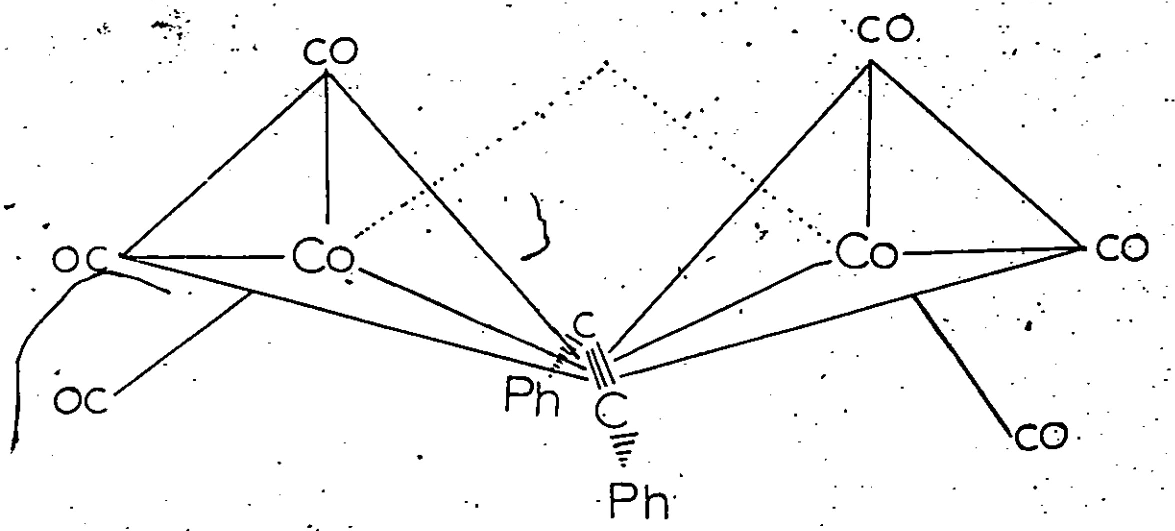


Figure I-B-2. Bonding scheme for $(Ph_2C_2)Co_2(CO)_6$ as suggested by Sly.[22]

Since the publication of these initial reports, further work in this area has shown that alkyne-dicobalthexacarbonyl complexes can be formed from almost any molecule containing the acetylene group. In addition, it has been found that they can be prepared in other ways besides the most general synthesis in which the alkyne is reacted with $Co_2(CO)_8$.[32-34]

A comprehensive list of the complexes which have been reported has been published by Dickson and Fraser.[13] The large majority are complexes of common organic acetylenes but an extensive series of fluorocarbon alkyne complexes has also been prepared,[33, 35-41] as well as a series of complexes containing silyl, germyl, stannyl and phosphino acetylenes.[30, 42-47] Some transition metal organometallic complexes containing uncomplexed acetylene groups, such as the methinylnonacarbonyl derivatives[25-26] and the ferrocenyl acetylenes,[48-49] also form dicobalthexacarbonyl complexes. Similar complexes have also been prepared from di- and triacetylenes for which it found that each triple bond reacts with one mole of dicobaltoctacarbonyl, even in conjugated acetylenes where steric effects might be expected to be a problem.[13]

Much of the interest in these acetylenic dicobalthexacarbonyl complexes has been concerned with the chemical reactions which they undergo. Of particular relevance to this thesis are CO substitution reactions involving P, As and Sb donor ligands but these are discussed in Section D of this chapter. A few reactions of more general interest will be described here. A wide variety of reactions occur but particularly noteworthy are those which involve chemical modification of the acetylene ligand. These are of considerable interest because of their possible applications to synthetic organic chemistry.

Several reports have been published of studies of both CO and alkyne exchange reactions in solution.[50-53] Cetini et al.[51] have reported that the rate constant for CO exchange decreases with increasing electronegativity of the R groups on the acetylene. This led them to suggest that exchange must first involve breaking of the metal-acetylene bond, since the increasing electronegativity of the R groups would be expected to strengthen this bond via back-bonding and weaken the metal-CO bonds. It has also been observed that the rate of exchange is considerably slower than that in $Co_2(CO)_8$ and its lactone derivatives,[52-53] and it has therefore been suggested that perhaps the presence of bridging CO groups is necessary in order for the dicobalt carbonyls to undergo rapid CO exchange.

For alkyne exchange it has been observed that an alkyne which has very electronegative R groups can displace a coordinated alkyne in which groups of lower electronegativity are present.[50] The implications of this in relation to the metal-alkyne bond are discussed in a later section. No kinetic or mechanistic information on these alkyne exchange reactions has been reported.

Nicholas and Pettit,[55, 120] and Seyferth and Wehman[121] have reported reactions in which modifications of the coordinated acetylene can be accomplished, even though the same treatment does not produce a parallel reaction in the uncoordinated alkyne. For example, Friedel-Crafts acylation on $(Ph_2C_2)Co_2(CO)_6$ produces $((CH_3C(O)C_6H_4)C_2Ph)Co_2(CO)_6$ whereas the free diphenylacetylene does not undergo acylation at all. The pure alkyne can then be retrieved by oxidation of the complex with Ce^{2+}.[121] A further example is that the olefinic part of an alkyne which contains double bonds can be selectively reduced when the alkyne is coordinated to a $Co_2(CO)_6$ fragment, the coordinated triple bond being inert to addition.[54] These observations have led to the suggestion of the general use of the $Co_2(CO)_6$ fragment as a blocking group for alkynes in organic molecules.[54]

Nicholas and Pettit[55] have also reported a series of acid-catalyzed hydrolysis and dehydration reactions which could not be accomplished unless the molecule was coordinated to a dicobalthexacarbonyl group. They have also discussed the possibility that α-acetylenic carbonium ions are stabilized by the $Co_2(CO)_6$ moiety, and that this is the reason for the observed reactions.

Lactone-heptacarbonyldicobalt complexes, in which the acetylene has been incorporated into a lactone moiety, are formed when the acetylenic dicobalthexacarbonyl complexes are reacted with excess CO under quite severe conditions (70°, 200 atm.).[56, 57] The two cobalt atoms in the lactone complex have been found to be no longer bridged by an acetylene molecule, but by both a CO group and a σ bonded carbon atom of the lactone group.[58] Hydrogenation of the butenolactone complex has been reported to result in the corresponding saturated lactone itself, and in butyric acid.[13, 56] On this basis it has been suggested that the formation of dimethylsuccinate from the reaction of C_2H_2, CO and $Co_2(CO)_8$ in methanol might proceed via the formation of $Co_3(CO)_9C-$ complexes which are reportedly formed from the lactone complexes.[13, 56]

The reaction of $(R_2C_2)Co_2(CO)_6$ derivatives with excess alkyne also results in complexes in which the acetylene has been incorporated into a completely different ligand.[36, 41, 59-63] These complexes have the general formula $Co_2(CO)_4(RC_2R')_3$, and structural studies have shown that the acetylene has been transformed into a species which is equivalent to two allyl groups joined by a C-C single bond.[58, 64] The ligand bridges the two cobalt atoms in the complex via cobalt-carbon σ bonds involving the carbon atoms at each end of the chain, and via π bonds to each of the allyl groups. This type of structure has become known as the "fly-over bridge".[64] Of particular interest is that degradation of such complexes has been reported to result in the formation of substituted benzenes. In this way many t-butyl, trifluoromethyl and phenyl benzenes of differing degrees of substitution have been prepared.[65]

Although the dicobalthexacarbonyl complexes provided the first example of a bridging alkyne type of complex, several other metal-metal systems have since been observed to form similar structures. However, none have been studied nearly as extensively as the dicobalt system. The most closely related system is a series of complexes which have been prepared from the reaction of acetylenes with $Rh_2(PF_3)_8$ by Bennett et al.[66, 67] An X-ray analysis of the structure of the PPh_3 disubstituted complex, $(Ph_2C_2)Rh_2(PF_3)_4(PPh_3)_2$, has shown the same structural features as the dicobalthexacarbonyl complexes.[66] These authors have suggested that the similarity between $Rh_2(PF_3)_8$ and $Co_2(CO)_8$ may be an indication that an equally extensive series of dirhodium-alkyne complexes might be prepared as has been observed for cobalt.[67]

Bennett et al[67] have also reported that these rhodium trifluorophosphine complexes are stereochemically non-rigid in that intramolecular exchange of the PF_3 groups occurs. They have explained this observation by suggesting a propellor-like rotation of the three PF_3 ligands about the Rh-Rh axis, with the acetylene remaining stationary. A preliminary investigation by these same authors showed that the same thing is occurring in the acetylenic dicobalthexacarbonyl complexes.

Other complexes which have shown the same bridging arrangement are the bis(cyclopentadienyl) complexes of nickel[68] and palladium.[69] In addition, diiron[70] and diniobium[71] complexes have been reported in which there are two such bridging alkyne groups, one situated on either side of the metal-metal axis. In all of these complexes, the acetylenic C≡C bond length has been found to be considerably lengthened from its value in the uncoordinated ligand, as has been found in the dicobalt complexes, and the R groups bonded to the acetylenic moiety have been found to be bent back away from the metal-metal axis forming an angle of about 140°.

SECTION C. BONDING IN ACETYLENIC DICOBALTHEXACARBONYL DERIVATIVES

In order to enter into any discussion on the acetylenic dicobalthexacarbonyl complexes and their substituted derivatives, it is necessary to describe the bonding between the cobalt atoms and the three types of ligands which are involved. Although there are differences between the metal-CO, the metal-phosphorus, and the metal-alkyne bonds, they all have the common feature that the three ligands are all π-acceptors. This means that they all possess vacant π orbitals which can accept electron density from filled metal orbitals. This results in a type of metal-to-ligand π back-bonding which supplements the σ-type of ligand-to-metal forward donation. The fact that stable complexes of these ligands can be prepared in which the metal is in a low oxidation state is a result of this property; since the high electron density on such metal atoms can be delocalized onto the ligands. Each of the three types of bonds will be discussed separately below.

1. The Metal-CO Bond

Much of the discussion in the field of

transition metal carbonyl complexes has been related to the metal-CO bond and to attempts to provide physical evidence for the existence of π back-bonding.[72-76] A detailed molecular orbital picture of the bonding in terminal CO groups has been formulated, and is summarized here as follows: There is first a σ-type of forward donation from the carbon atom to the metal via overlap of the filled carbon σ orbital (containing the lone-pair) and an empty metal orbital. Secondly, there is π back-bonding from the metal to the CO ligand via overlap of a filled dπ, or hybrid dpπ, metal orbital with an empty pπ* antibonding orbital of the carbonyl group.[77] Figure 1-C-1 illustrates this scheme.

Bonding of this type is termed "synergic". The drift of the electrons from the metal to the CO ligand will tend to make the CO as a whole more negative, and hence increase its donor capacity, while at the same time the forward donation to the metal will make the CO more positive, enhancing the acceptor strength of the π* orbitals. The two parts of the bond are therefore mutually reinforcing one another. Bridging CO groups are also observed in which the ligand is bonded to two metal atoms and a synergic bond mechanism is also thought to be operating there.[122]

A large amount of structural, spectral and

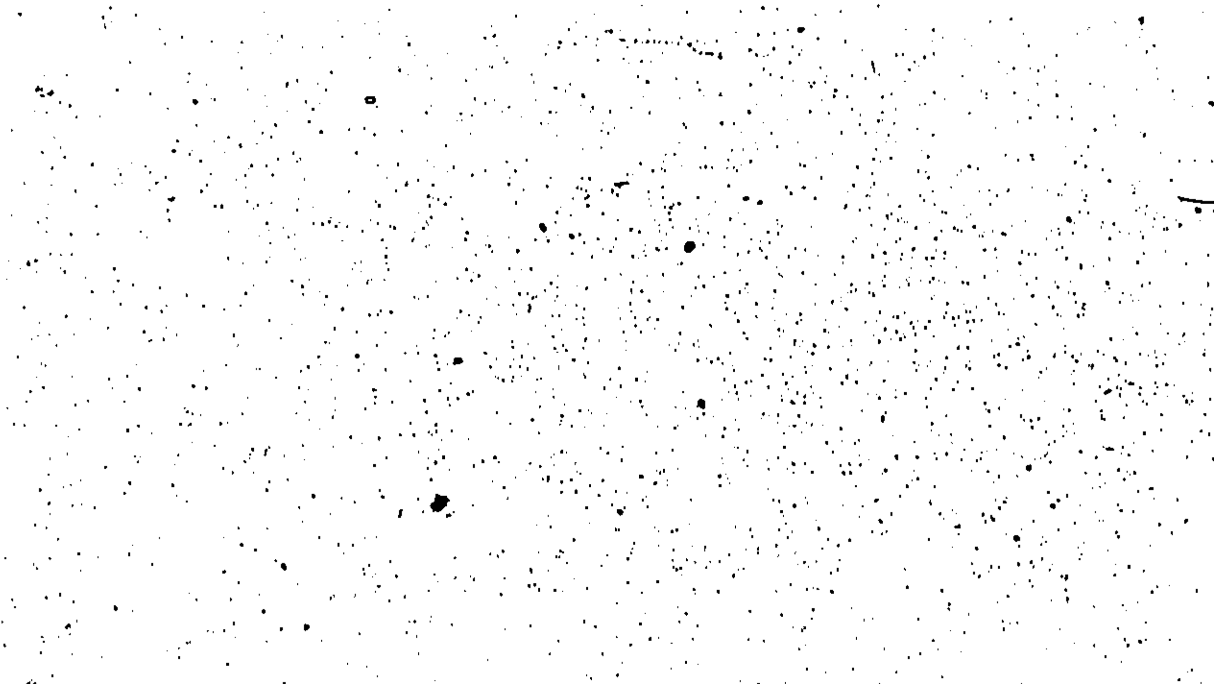
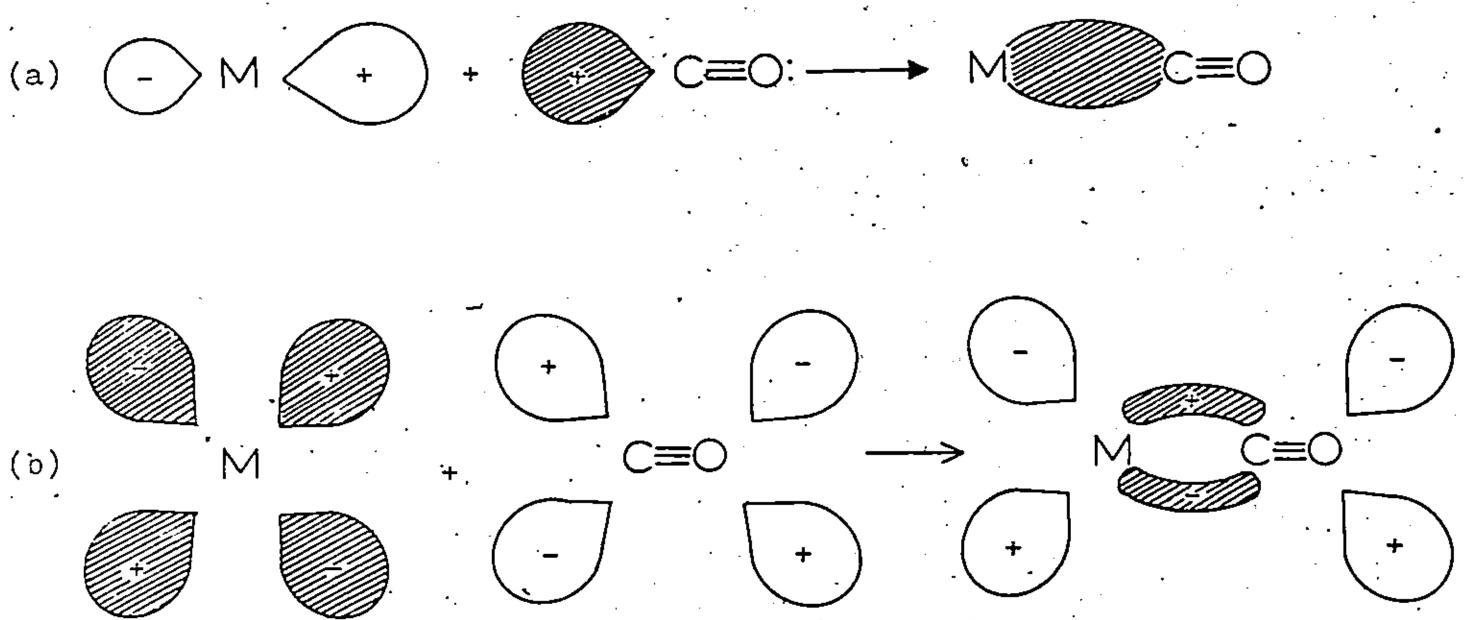


Figure I-C-1. Metal-CO bonding as taken from ref. 77.



(a) The formation of the ligand-to-metal sigma bond using an unshared pair of the carbon atom.

(b) The formation of the metal-to-carbon pi bond.

and kinetic evidence for this type of bonding has been presented, but the most direct physical evidence is provided by the vibrational spectra of the complexes in the CO stretching region.[78] The metal-CO back-donation results in occupation of π^* antibonding orbitals of the carbonyl group and therefore reduces the CO bond order. Thus a shift ~~of the CO~~ stretching frequency bands to lower frequencies should be observed on coordination of the CO ligand. The carbon monoxide molecule itself has a stretching frequency of 2143 cm^{-1}, and terminal CO groups are found to absorb in the region between 2125 cm^{-1} and 1850 cm^{-1}.[78] Thus the expected reduction of the bond order is observed.

This correlation has been extended in several ways by varying the degree of metal-carbon back-bonding in a given system. For example, substituting one of the CO ligands in a complex with a ligand of poorer back-bonding ability causes the remaining CO groups to accept $d\pi$ electrons to a greater extent. This occurs in order to prevent an excess of negative charge on the metal atom. Thus the metal-carbon bond order is increased and the CO bond order further reduced, and a further lowering of the CO stretching frequency is observed.[79] Other similar correlations have served to further substantiate this synergic bond mechanism.[79]

2. The Metal-Phosphorus Bond [a]

Ligands containing P, As or Sb donor atoms form a vast number of transition metal complexes, many of which are substituted metal carbonyl derivatives. The subject has recently been comprehensively reviewed by several authors,[80 - 84] and, as in the case of the CO complexes, much of the discussion has centered on the nature of the metal-ligand bond.

Such ligands are found to be quite strong Lewis bases,[92] and therefore it is conceivable that the ligand-to-metal σ donation might be a considerably more important part of the bond than is the case in metal-carbonyl bonding. However, these donor atoms have empty $d\pi$ orbitals which are suitable for $d\pi$-$d\pi$ metal-to-ligand back-bonding. Such a scheme is illustrated in Figure I-C-2. Much discussion has taken place on the relative importance of the σ and π contributions to the bond,[85-91] but it is now generally felt that a synergic bond mechanism similar to the metal-CO bond is operating, at least in complexes in which the metal is in low oxidation states.[85, 86, 93]

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[a] The metal-As and metal-Sb bonds are included in this description.

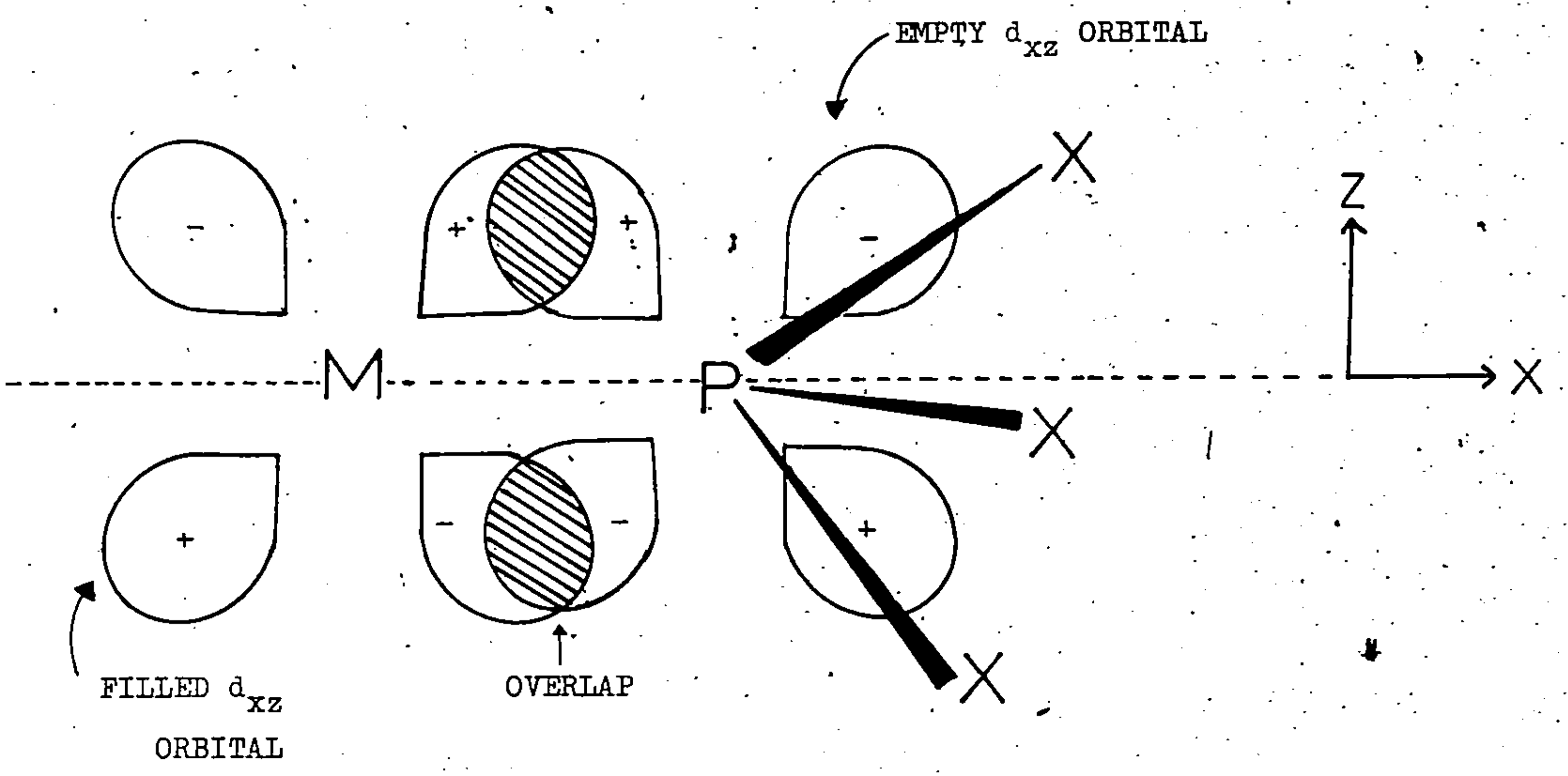


Figure I-C-2. Diagram showing the back-bonding from a filled metal d orbital to an empty phosphorus 3d orbital in the PX_3 ligand as taken from ref. 94. An exactly similar overlap occurs in the yz plane using the d_{yz} orbitals.

The most direct evidence for the existence of this dπ-dπ back-bonding comes from an investigation of the metal-phosphorus bond lengths in $(P(OPh)_3)Cr(CO)_5$ and $(PPh_3)Cr(CO)_5$. In the $P(OPh)_3$ complex the P-Cr bond length has been found to be 0.011 Å shorter than in the PPh_3 complex.[95, 96] The extent to which back-bonding occurs in these complexes should depend on the electronegativity of the groups attached to the donor atom in that, as the electronegativity is increased, a decrease in the σ-donor ability of the ligand, and an increase in its π-acceptor ability, should result. If only the σ bonding is important, then the P-Cr bond in the $P(OPh)_3$ complex should be weaker and longer than that in the PPh_3 complex, but exactly the opposite is observed. From this it is evident that back-donation does have a role in the metal-ligand bonding.

Infrared spectral studies have proven to be a useful tool for the classification of the relative donor-acceptor ability of ligands of this type. In general, it is observed that substitution of CO groups in metal carbonyl complexes by these groups causes a decrease in the CO stretching frequency. The CO stretching frequencies are also observed to decrease as the degree of substitution increases. These observations are explained by suggesting that the effect of substitution by a ligand which is a stronger donor and weaker acceptor than CO is to increase the overall charge donation to the metal. This in turn should increase the extent of metal-CO back-bonding to the remaining CO groups thereby reducing the CO bond order and causing the decrease in the CO stretching frequency.[85, 93]

As briefly mentioned in Section A of this chapter, this increase in metal-CO back-bonding which accompanies replacement of CO is expected to strengthen the metal-carbon bond to the CO group and thereby make further displacement of CO more difficult.[84] The best examples of this effect are provided by the series of $M(CO)_6$ complexes (M = Cr, Mo, W). For example, it has been reported that $Mo(CO)_6$ undergoes substitution by $P(n\text{-}C_4H_9)_3$ via a CO dissociative mechanism at measurable rates near 100°, but that further substitution of CO in the monosubstituted product requires temperatures above 100°.[87, 97] It has also been found that complete substitution of CO in these complexes is not generally possible except for PF_3, which is at least as good a π-acceptor as CO, and for multidentate ligands.[84]

3. The Metal-Alkyne Bond

The presently accepted description of the metal-alkyne bond in what are referred to as π complexes also involves a synergic bond mechanism similar to the metal-CO and metal-phosphorus bonds.[98] This model was originally proposed by Dewar[31] and by Chatt et al.[99] to explain the bonding in metal-olefin complexes, and was later extended to include acetylenes.[54, 100, 101] It involves a σ-type of forward donation from the ligand to the metal via overlap of the pπ bonding orbital of the ligand with empty metal orbitals. Metal-to-ligand back-bonding then occurs by overlap of the filled dπ, or hybrid dpπ, metal orbitals with the ligand $p\pi^*$ antibonding orbitals. Figure I-C-3 illustrates this scheme. In the case of acetylenes, there are two mutually perpendicular degenerate pπ orbitals, and therefore these ligands are capable of being bonded to two metal atoms in a bridging type of structure.

An important difference between this model and the metal-CO or metal-phosphorus bonding schemes described previously is that the ligand-to-metal σ-type component of the bond does not involve lone-pairs in σ orbitals of the donor atom, but involves π electrons in π bonding orbitals of the ligand. This is the reason for the classification of these complexes as π complexes. There has been considerable discussion in the literature, in reference to non-bridging alkyne complexes, as to whether carbon σ orbitals are involved in the bond to any great extent,[4-6, 10, 15, 102-106] but it is generally

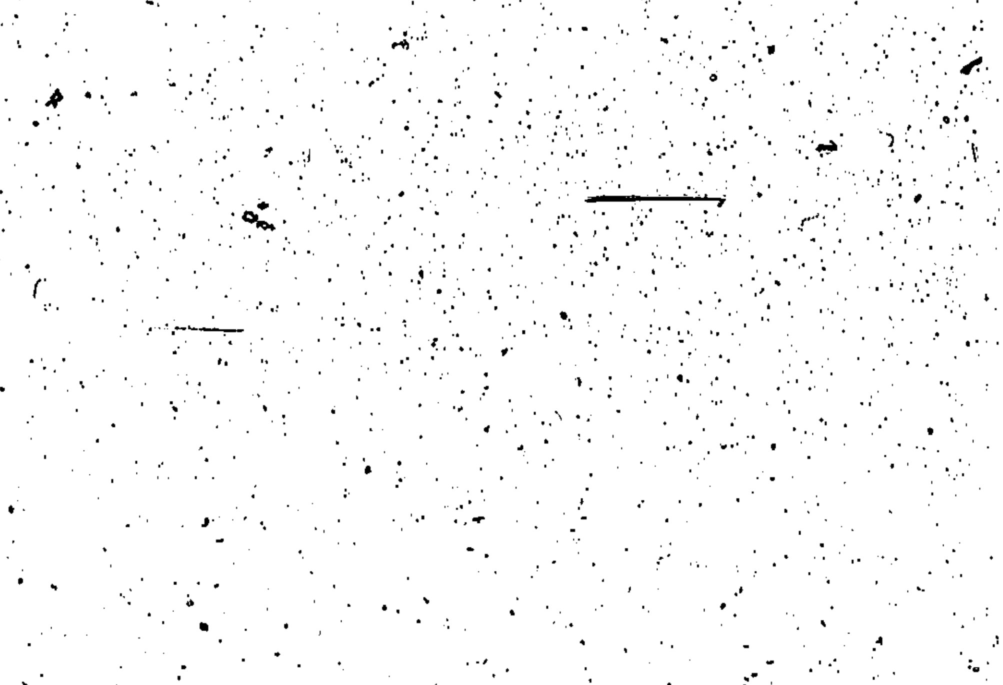
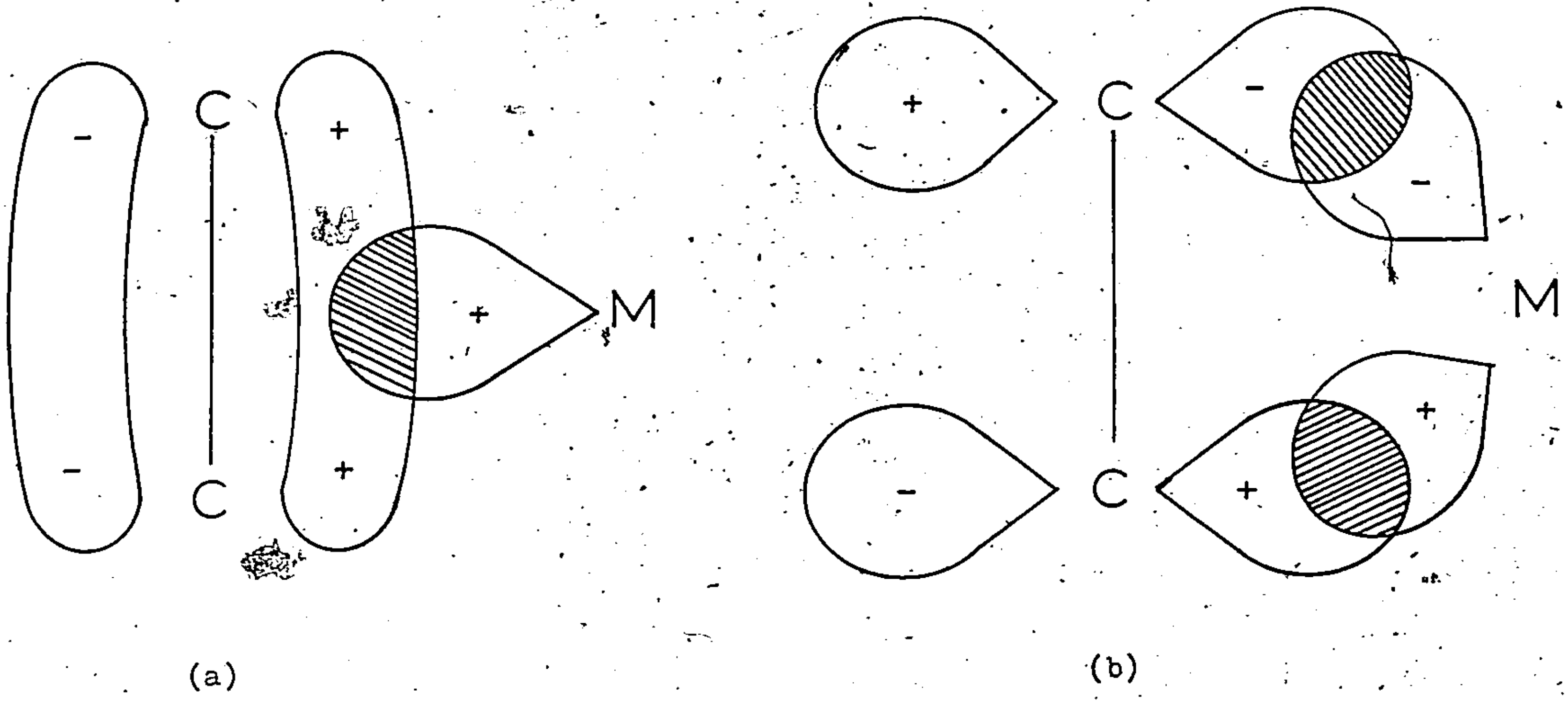


Figure I-C-3. Diagram of the molecular orbital version of metal-alkyne bonding as taken from ref. 98.



(a) Donation from filled π orbitals to vacant metal orbitals.

(b) Back-bonding from filled metal orbitals to acceptor π^* orbitals.

felt that it is mainly the π bonding orbitals which make up the forward part of the bond. [10]

As mentioned in Section B of this chapter, Sly [22] was the first to suggest that this type of bond existed in the dicobalthexacarbonyl acetylenes on the basis of his structure determination of the diphenylacetylene complex. Cetini _et al._ [50] have more recently suggested that perhaps the π back-bonding is the more important part of the bond based on their study of the relative stability of a series of complexes in which the electronegativity of the R and R' groups of the acetylene ligand is varied. The suggested explanation of the results was originally put forward by Chatt _et al._ [101] in a similar study on platinum-acetylene complexes, and is summarized here as follows: If the R groups are electron donors, this will render the acetylene π orbitals more easily available for the formation of the ligand-to-metal forward donation. On the other hand, a group with a very electronegative substituent should facilitate the back-donation of electrons by lowering the energy of the acetylene π^* antibonding orbitals.

Cetini _et al._ [50] observed the following order of stability in that each acetylene can replace in the complex, the derivatives which follow it, and can be replaced by those which precede it:

$(CF_3)_2C_2 > (COOCH_3)_2C_2 > (C_6H_5)_2C_2 > CH_3C_2C_6H_5 >$

$(CH_3)_2C_2 > HC_2C_6H_5 > HC_2CH_3 > H_2C_2 > (CH_2N(C_2H_5)_2)_2C_2$

Therefore it appears that the increased stability is linked to the higher electronegativity of the R groups, and therefore with a weak σ bond (forward donation) and a strong π bond (back-donation).

More conclusive evidence of a considerable degree of back-bonding in these complexes has been provided by infrared spectroscopic studies centered on the coordinated ligand itself.[8, 107, 108] The vibrational spectrum of $(HC\equiv CH)Co_2(CO)_6$ has been completely assigned and a band at 1402.3 cm^{-1} has been attributed to the C≡C stretching mode.[8, 9, 107] This band is 570 cm^{-1} lower than that in the free ligand and thus a considerable reduction in the C≡C bond order is confirmed. Similar shifts have been observed in the methylacetylene (590 cm^{-1}) and dimethylacetylene (680 cm^{-1}) complexes,[108] and in transition metal alkyne complexes in general.[112] In the dicyanoacetylene complex a reduction of both the C≡C and C≡N stretching frequencies has been observed.[109]

The observation of these changes in the

acetylene ligand on complexation has led to suggested bonding descriptions based on the similarity of the coordinated alkyne to electronic excited states which have been reported for the uncomplexed ligand. Mason [12] has recently considered the idea that π bonded ligands in general can resemble the spectroscopically observable excited states of the free molecules, and the observed cis-bent geometry of the coordinated acetylene in $(Ph_2C_2)Co_2(CO)_6$ led him to suggest that this relationship might apply to transition metal alkynes. He based this on the work of Ingold and King [110] who have reported that in the HC≡CH molecule, promotion of an electron from the highest π bonding orbital to the lowest energy π^* antibonding orbital leads to a trans-bent excited state which shows a complete change in σ bond hybridization from sp to trigonal planar sp^2. Mason has suggested that, since a similar cis-bent excited state is expected to exist which has almost the same energy, [10, 111] this would be preferred in the complexed state because of steric interactions with the $Co_2(CO)_6$ part of the molecule.

Iwashita <u>et al</u>. [9] have performed a normal coordinate analysis on the acetylene ligand in $(HC{\equiv}CH)Co_2(CO)_6$ which they suggest confirms the likeness of the coordinated and free excited state acetylene in vibrational frequency and structure. They have stated that this similarity must arise from occupation of the π^* antibonding orbitals of the ligand by electrons from the Co-alkyne bond through π back-bonding. They have further concluded that this similarity indicates that in the $HC\equiv CH$ complex one electron is completely subtracted from the bond π orbitals of the ligand (σ component), and that just one electron is added to the π^* antibonding orbitals (π component). This is equivalent to the effect of the electronic excitation in the free acetylene molecule.

Iwashita et al.[108] later reported nmr studies on acetylenes complexed in this way, and have found that the values of the ^{13}C-H coupling constants of the coordinated acetylene more closely resemble those of olefinic molecules rather than those of free acetylenes. They therefore have suggested this to be further evidence of the change in bond hybrizization from sp to sp^2 on coordination of the molecule.

More recently, interest has been shown in correlations between the degree of bending in the coordinated acetylene molecule and the extent of the π back-bonding. This has been discussed briefly in the introductory section of this chapter. Blizzard and Santry[10] have used MO calculations to investigate changes in the HCC angles of $HC\equiv CH$ as a function of the population of various orbitals. The results indicate that simple subtraction of electron density from the π bonding orbital (equivalent to σ forward donation) does not lead to any bending in the molecule, but that there is a direct relationship between the degree of bending and the amount of electron density added to the π^* antibonding orbital (equivalent to π back-bonding). Furthermore, the results also indicate that simultaneous removal and addition of equal amounts of electron density from and to the π and π^* orbitals respectively causes an even greater bending.

These authors have stated that quantitative predictions cannot be made since the two effects are operating together to bend the molecule, but have concluded [illegible], qualitatively, the results do indicate that any increase in π back-bonding to the acetylene should be accompanied by an increase in the bending in the molecule. They have also suggested that the mere presence of a cis-bent acetylene ligand in a transition metal complex is a strong indication that π back-bonding is occurring. More recent extensions of this type of calculation which include the metal atom [10] are in agreement with the predictions of Blizzard and Santry.

Experimental tests of this relationship are lacking. Blizzard and Santry have suggested that a reduction in the 2s character of the C≡C bond should accompany complexation of the acetylene ligands because of mixing of the carbon σ antibonding orbitals with the π antibonding orbitals used in the back-bonding. Therefore they have suggested that nmr studies might provide verification of their results, particularly studies of changes in the C≡C nuclear spin coupling constant. This experiment has not been carried out, but Cook et al.[4] have met with some success in using ^{13}C-H coupling constants in platinum-acetylene complexes to predict the bend-back angles from the percentage of s character in the carbon atom hybrid orbitals.

Davies and Payne[112] have recently reviewed the structural and infrared data on fourteen non-bridging transition metal alkyne complexes for which accurate structures are available. They have found that there appears to be a general trend such that as the C≡C bond is lengthened upon coordination, so the bend-back angle increases. However, this is only qualitative and exceptions were observed. These authors have also shown that there is a reasonably straight line relationship between the degree of bending and the magnitude of the shift in the C≡C stretching frequency, but have suggested the need for further precise X-ray structure determinations in order to provide verification of this. Part of the reason for the work presented in this thesis was to investigate the possibility of preparing a series of complexes for an eventual study of this type using X-ray crystallography.

Section D. SUBSTITUTION REACTIONS OF ACETYLENIC DICOBALT-HEXACARBONYLS WITH P, As AND Sb DONOR LIGANDS

Reaction of the acetylenic dicobalthexacarbonyl complexes with the heavy Group V donor ligands has been studied primarily with triphenylphosphine. It has been found that reacting the ligand and the complex together in refluxing hydrocarbon solvents for several hours, results in replacement of one or two carbonyl groups to form complexes of the formula $(RC_2R')Co_2(CO)_5PPh_3$ and $(RC_2R')Co_2(CO)_4(PPh_3)_2$.[8, 33, 35-37, 52, 59, 113] The same results can also be obtained using ultraviolet light. These substituted derivatives are generally air-stable, dark coloured, crystalline solids with melting points higher than the parent unsubstituted complex.[13] In relation to their stability, it has been reported that $(CF_3C_2CF_3)Co_2(CO)_4$-$(PPh_3)_2$ is considerably more stable to air oxidation than the parent hexacarbonyl.[36]

Other donor ligands such as $AsPh_3$, $SbPh_3$, PPh_2Cl, and $P(n\text{-}C_4H_9)_3$ have also been observed to form monosubstituted complexes,[114] and $P(OPh)_3$[46] and $P(n\text{-}C_4H_9)_3$[114-16] have been reported to form disubstituted complexes. A list of all of the substituted derivatives which have been reported [illegible] the literature is given in Table I-D-1.

TABLE I-D-1

KNOWN COMPLEXES OF FORMULA $(RC_2R')Co_2(CO)_{6-n}(L)_n$

$RC\equiv CR'$	L	n	References
HC_2H	PPh_3	1	8, 34, 113
HC_2H	PPh_3	2	8, 113
PhC_2Ph	PPh_3	1	59
PhC_2Ph	PPh_3	2	59
CF_3C_2H	PPh_3	2	37
$CF_3C_2CH_3$	PPh_3	2	36
$CF_3C_2CF_3$	PPh_3	2	13
$C_6F_5C_2H$	PPh_3	2	33
$C_6F_5C_2C_6F_5$	PPh_3	2	33, 35
HC_2H	$AsPh_3$	1	114
PhC_2Ph	$AsPh_3$	1	114
$CF_3C_2CF_3$	$AsPh_3$	1	114
$HO_2CC_2CO_2H$	$AsPh_3$	1	114
PhC_2Ph	$SbPh_3$	1	114
PhC_2Ph	$P(n\text{-}C_4H_9)_3$	1	114, 115, 116
PhC_2Ph	$P(n\text{-}C_4H_9)_3$	2	114, 115, 116
PhC_2Ph	PPh_2Cl	1	114
PhC_2Ph	$Ph_2PC_2CH_3$	2	46
$(C_6F_5)_2PC_2Ph$	$P(OPh)_3$	2	46

These substituted derivatives have also been prepared in other ways. Reactions (I-D-1) and (I-D-2) have resulted in the disubstituted complexes shown,[33, 115, 116] and both mono- and disubstituted complexes of PPh_3 have been prepared by reaction (I-D-3).[34]

$$Co_2(CO)_6(P(n\text{-}C_4H_9)_3)_2 + PhC_2Ph \longrightarrow (PhC_2Ph)Co_2(CO)_4(P(n\text{-}C_4H_9)_3)_2 \qquad \text{(I-D-1)}$$

$$((C_6F_5)_2C_2)Co_4(CO)_{10} + 4\ PPh_3 \longrightarrow 2\ ((C_6F_5)_2C_2)Co_2(CO)_4(PPh_3)_2 \qquad \text{(I-D-2)}$$

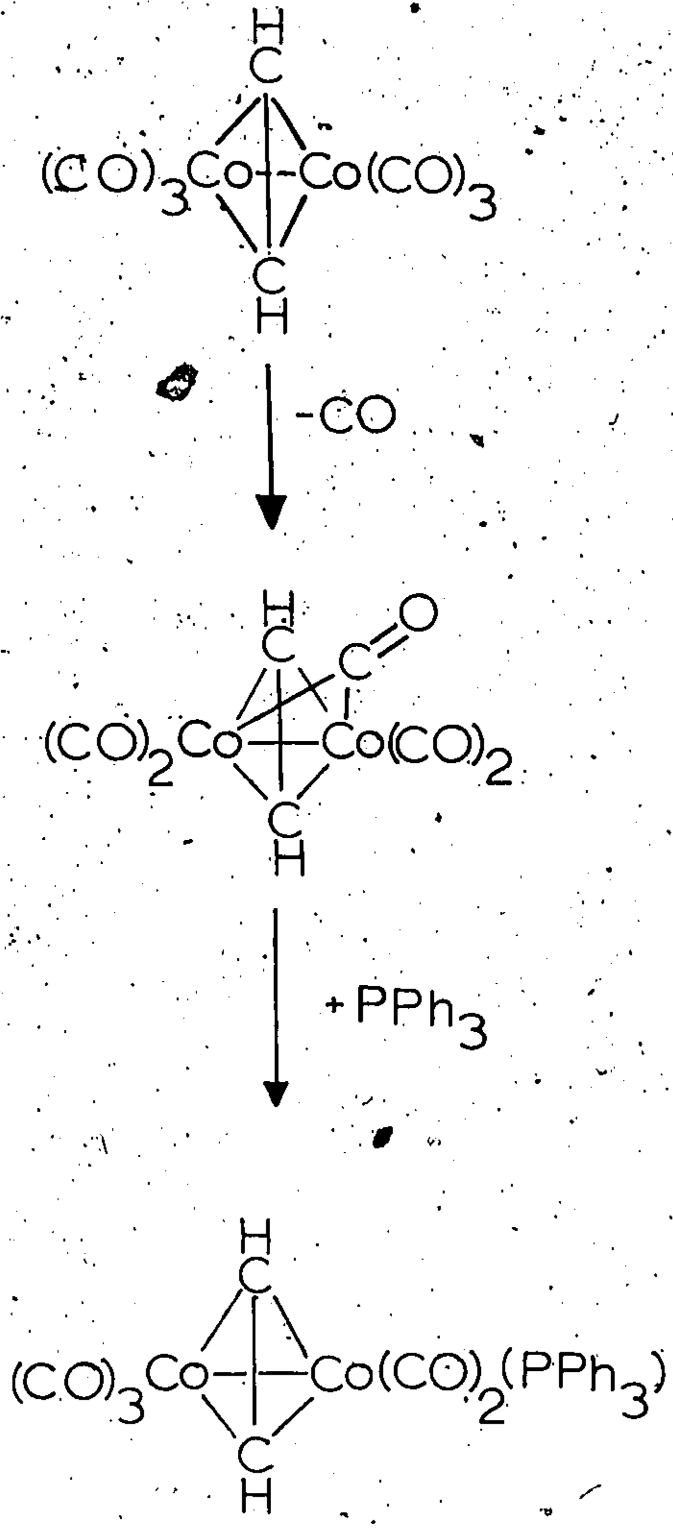
$$2\ HCo(CO)_4 + HC{\equiv}CH + n\ PPh_3 \longrightarrow (HC_2H)Co_2(CO)_{6-n}(PPh_3)_n \quad (n = 1, 2) \qquad \text{(I-D-3)}$$

Heck[113] has reported a study of the kinetics of the reaction of PPh_3 with the $HC{\equiv}CH$ and the $CH_3CH_2C{\equiv}CCH_2CH_3$ dicobalthexacarbonyl complexes, and has suggested that the substitution first involves dissociation of one carbonyl ligand to form a bridging carbonyl species as the rate determining step, and that attack by the phosphine then occurs in a fast reaction. This scheme is illustrated in Figure I-D-1. Heck has given no specific evidence for the existence of such a bridged intermediate but has made this suggestion in order to be consistent with the observation that at least one bridging carbonyl group is necessary for fast CO exchange in dicobalt carbonyl complexes. This has been mentioned previously in Section B of this chapter.

Cetini et al.[114] have studied the rates of these substitution reactions as a function of the acetylene group present in the molecule, and on the basis of these results have suggested a mechanism in which a partial dissociation, or loosening, of the Co-acetylene bond is the rate determining step. This suggestion was based on observations similar to those made earlier by them whereby the rate of CO exchange in these complexes was found to decrease with an increase in the metal-acetylene bond strength (see p. 130).[51]

Basato and Poe[115, 116] have more recently reported a study on the kinetics of the substitution of CO by $P(n\text{-}C_4H_9)_3$ in $(Ph_2C_2)Co_2(CO)_6$. They have found the reaction to proceed in two clearly separate stages corresponding to the formation of the mono- and disubstituted complexes respectively. The kinetic data have been interpreted to indicate that both stages proceed by

Figure I-D-1. Mechanism of substitution of CO by triphenylphosphine in $(H_2C_2)Co_2(CO)_6$ as suggested by Heck.[113]



H
C
(CO)3Co—Co(CO)3
C
H
-CO
H
C
C=O
(CO)2Co—Co(CO)2
C
H
+PPh3
H
C
(CO)3Co—Co(CO)2(PPh3)
C
H

concurrent associative and dissociative paths, in contrast to the results of Heck and of Cetini. Basato and Poe have also reported that the first stage of the reaction, which is the formation of the monosubstituted derivative, proceeds at a somewhat faster rate than the second stage.

Substituted acetylenic dicobalthexacarbonyl complexes have also been prepared with bidentate ligands of the Group V donor atoms. For example, the reaction of $(PhC_2H)Co_2(CO)_6$ with 1,2-bis(dimethylarsino)tetrafluorocyclobutene (ffars) has been reported to result in the substitution of two CO groups to form $(PhC_2H)Co_2(CO)_4$(ffars).[118] The same complex can be prepared by the reaction of PhC_2H with $Co_2(CO)_6$(ffars), and the phosphorus analogue has also been prepared in a similar reaction.[118] The ffars ligand has also been observed to exhibit monodentate behaviour in giving a monosubstituted complex of the formula $(PhC_2H)Co_2(CO)_5$(ffars). This can be subsequently converted to the disubstituted complex by heating it in solution.[118]

No structural studies of acetylenic derivatives of this type have been published but it has been suggested that the bidentate ligands are bridging the two cobalt atoms, rather than both donor atoms being bonded to the same cobalt atom. This is what has been

been reported for the $Co_2(CO)_6$(ffars) complex, from which the acetylenic derivatives can be prepared, based on the X-ray crystal structure.[117]

Carty et al.[30, 46] have reported a series of complexes of phosphinoacetylenes of the type Ph_2PC_2R where both the alkyne moiety and the phosphorus atom are coordinated to a cobalt atom. The complexes have the general formula $Co_4(CO)_{10}(Ph_2PC_2R)_2$, and the X-ray crystal structure has shown that they are essentialy dimers of two Co_2 units bridged by two phosphinoacetylene ligands. Each Ph_2PC_2R ligand is bonded to one $Co_2(CO)_5$ moiety via the acetylene part, and to the other via the phosphorus atom.[30] These complexes are therefore analogous to monosubstituted hexacarbonyl complexes. It has also been reported that further replacement of the CO groups can occur to give complexes which are analogous to disubstituted hexacarbonyl complexes.[46]

Not long after the work described in this thesis was carried out, Fukumoto et al.[119] reported a series of acetylenic dicobalt complexes containing bidentate ligands, some of which are equivalent to those prepared here. These complexes have the general formula $(Ph_2C_2)Co_2(CO)_4$-$(Ph_2MCH_2MPh_2)$ (M = P, As, Sb), and are therefore disubstituted. However, they were not prepared by the same route as the one used in this work but were formed by first reacting the ligand with $Co_2(CO)_8$ and subsequently treating the resulting $Co_2(CO)_6(Ph_2MCH_2MPh_2)$ complex with diphenylacetylene to give the bridging alkyne complex. These authors have suggested a structure for these complexes in which the bidentate donor ligand bridges the two cobalt atoms, but this had already been shown in a previously reported X-ray crystal structure determination of the phosphorus complex done by other workers in this laboratory.[1, 2]

No attempts aimed specifically at causing substitution beyond two carbonyl groups in these acetylenic complexes have been reported.[a] In the preparations of the various complexes mentioned above, ligand/complex mole ratios in excess of 2:1 were not generally used, and the reaction conditions were quite mild compared to those required for substitution of more than one CO group in other transition metal complexes.[84] This was an indication that there was a strong possibility of being able to cause further substitution if more severe conditions were used.

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[a] However, see footnote (a), p. 122.

CHAPTER II. RESULTS AND DISCUSSION: THE PREPARATION AND CHARACTERIZATION OF SUBSTITUTED DERIVATIVES.

SECTION A. DERIVATIVES OF MONODENTATE LIGANDS

1. Preparation of Mono- and Disubstituted Derivatives

Diphenylacetylenehexacarbonyldicobalt was found to react readily with one or two moles of several phosphorus donor ligands to form complexes of the general formulas $(Ph_2C_2)Co_2(CO)_5(L)$ and $(Ph_2C_2)Co_2(CO)_4(L)_2$ respectively. Table II-A-1 lists the complexes which have been prepared along with their characteristic colours and melting points. The compounds are found to be dark red, or brown, crystalline solids that are quite air stable, even in solution. Those involving the trialkyl phosphines and phosphites are very soluble in hydrocarbon solvents such as pentane and hexane, but are almost insoluble in very polar solvents such as methanol. The complexes of the triaryl derivatives are considerably less soluble in the hydrocarbons.

The syntheses were generally carried out by

TABLE II-A-1

MONO- AND DISUBSTITUTED DERIVATIVES OF $(Ph_2C_2)Co_2(CO)_6$

L	$(Ph_2C_2)Co_2(CO)_5(L)$	$(Ph_2C_2)Co_2(CO)_4(L)_2$
$P(OCH_3)_3$	Dark red crystals m.p. 103°-106°	Dark red crystals m.p. 152°-156°
$P(OC_2H_5)_3$	-	Dark red crystals m.p. 100°-102°
$P(O\text{-}i\text{-}C_3H_7)_3$	-	Dark red crystals m.p. 107°-109°
$P(OPh)_3$	Black crystals m.p. 110°-112°	Red crystals m.p. 185°-187°
PPh_3	Brown crystals m.p. 192°-194°	Red-brown crystals m.p. 220°-222°
$P(n\text{-}C_4H_9)_3$	Dark red crystals m.p. 85°-87°	Dark red crystals m.p. 99°-101°

refluxing a solution of ligand and complex in hexane in the desired mole ratio under an atmosphere of nitrogen gas. Rapid evolution of CO gas was usually observed for the first half-hour of the reaction but longer reaction times were always allowed to ensure complete formation of the desired product. This reduced the possibility of forming mixtures of the mono- and disubstituted products and thereby facilitated purification.

Isolation of the complexes was accomplished either by crystallization from the reaction mixture or by evaporation of the solvent in a stream of nitrogen gas or <u>in vacuo</u>. They were subsequently purified by chromatography and/or repeated crystallization from a suitable solvent mixtu[illegible]. Complete details of the synthesis of each compound are given in Section B of Chapter IV.

The complexes were identified by their elemental analyses and/or the characteristic pattern of CO stretching bands in their infrared spectra (see below). The analytical data are given in Table II-A-2.

With the exception of the tri-n-butylphosphine and triphenylphosphine derivatives, the compounds listed in Table II-A-1 have not previously been reported. However, substituted diphenylacetylenehexacarbonyldicobalt complexes of several other donor ligands have been reported,

TABLE II-A-2

ELEMENTAL ANALYSES OF MONO- AND DISUBSTITUTED DERIVATIVES OF $(Ph_2C_2)Co_2(CO)_6$ HAVING THE FORMULA $(Ph_2C_2)Co_2(CO)_{6-n}(L)_n$

L	n		Analysis (%)			
			C	H	Co	P
$P(OCH_3)_3$	1	Found	47.2	3.4	21.8	5.7
		Calc.	45.2	3.5	21.9	5.5
$P(OCH_3)_3$	2	Found	44.0	4.2	17.8	9.5
		Calc.	43.9	4.3	18.0	9.5
$P(OC_2H_5)_3$	2	Found	48.8	5.6	15.8	8.6
		Calc.	48.7	5.4	16.0	8.4
$P(O\text{-}i\text{-}C_3H_7)_3$	2	Found	52.3	6.4	14.2	7.7
		Calc.	52.4	6.3	14.3	7.5
$P(OPh)_3$	1	Found	59.0	3.4	16.2	4.1
		Calc.	59.5	3.4	15.8	4.2
$P(OPh)_3$	2	Found	63.2	3.9	11.3	6.2
		Calc.	63.0	3.9	11.5	6.0
PPh_3	2	Found	69.5	4.4	12.5	6.7
		Calc.	69.5	4.3	12.7	6.7
$P(n\text{-}C_4H_9)$	2	Found	62.1	7.6	14.5	7.9
		Calc.	62.1	7.9	14.5	7.6

as well as those containing acetylenes other than Ph_2C_2. The known complexes of this type have been reviewed in Section D of Chapter I. No simple mono- or disubstituted complexes of any of the trialkylphosphite ligands used here have previously been described.

Comparison of the tri-n-butylphosphine and triphenylphosphine complexes prepared here with those reported by others indicates that they are identical in all cases. Both $(Ph_2C_2)Co_2(CO)_5(P(n\text{-}C_4H_9)_3)$ and (Ph_2C_2)-$Co_2(CO)_4(P(n\text{-}C_4H_9)_3)_2$ have been described in connection with two kinetic studies on these substitution reactions, and their reported infrared spectra in the CO stretching region are in agreement with those recorded here.[114-116] In the case of the PPh_3 complexes, $(Ph_2C_2)Co_2(CO)_5(PPh_3)$ and $(Ph_2C_2)Co_2(CO)_4(PPh_3)_2$, the infrared spectra in the CO stretching region are identical to those reported by Kruerke et al.,[59] but the reported melting points of 143°-145° for the monosubstituted complex and 150°-153° for the disubstituted complex are not in agreement with the values found here of 192°-194° and 220°-222° respectively.

Two possible factors could account for this difference. In this work the compounds were recrystallized from dichloromethane/hexane mixtures, while Kruerke used diethylether/ligroin for the monosubstituted complex and benzene for the disubstituted complex. Thus different crystalline modifications may have been obtained. Associated solvent molecules are not expected to be a factor since the elemental analyses reported by Kruerke for both the mono- and disubstituted products and those reported here for the disubstituted product are all in good agreement with the calculated values. It is also possible that this discrepancy in the melting points is due to the fact that those of Kruerke were carried out in air and decomposition was observed while those reported here were carried out in an atmosphere of nitrogen gas and melting was observed.

2. Preparation of Tri- and Tetrasubstituted Derivatives

Although replacement of more than two carbonyl groups in any acetylenic dicobalthexacarbonyl complex has not previously been reported, it was found here that tri- and tetrasubstituted derivatives can be prepared by using higher temperatures than those required for mono- or disubstitution. Initial attempts to cause further substitution using large excesses of $P(n\text{-}C_4H_9)_3$, PPh_3 or $P(OPh)_3$ in refluxing benzene were unsuccessful, but the use of methylcyclohexane (b.p. 100°) and the smaller phosphite ligands led to the formation of $(Ph_2C_2)Co_2(CO)_2(P(OCH_3)_3)_4$ and $(Ph_2C_2)Co_2(CO)_2(P(OC_2H_5)_3)_4$. The analogous tetrasubstituted derivatives of $(CF_3C_2CF_3)Co_2(CO)_6$ were also prepared. Use of a ligand/complex mole ratio of exactly 3:1 resulted in the formation of the trisubstituted complex, $(Ph_2C_2)Co_2(CO)_3(P(OCH_3)_3)_3$.

Table II-A-3 lists the five complexes which have been prepared. Complete details of the preparation of each are given Section B of Chapter IV. The diphenylacetylene derivatives are dark red, crystalline solids, while those of hexafluoro-2-butyne have an orange-red appearance. They are considerably less stable in solution than the disubstituted derivatives and attempts to purify them by chromatography on silica gel resulted in a discolouration of the column material indicating that decomposition was taking place.

Identification of the complexes was accomplished by their elemental analyses and their infrared spectra in the CO stretching region. As in the case of the mono- and disubstituted complexes, characteristic patterns of peaks in this region allowed identification of those complexes for which elemental analyses were not carried out. The infrared spectra are discussed more fully in the next section. The elemental analyses are included in Table II-A-3.

Attempts to prepare tetrasubstituted

TABLE II-A-3

TRI- AND TETRASUBSTITUTED ACETYLENIC DICOBALTHEXACARBONYL DERIVATIVES

Complex		Analysis (%)				
		C	H	Co	F	P
$(Ph_2C_2)Co_2(CO)_3(P(OCH_3)_3)_3$	Found	41.5	5.0	14.6	-	12.2
Dark red crystals	Calc.	41.5	4.9	15.7	-	12.4
$(Ph_2C_2)Co_2(CO)_2(P(OCH_3)_3)_4$	Found	39.9	5.3	13.7	-	14.5
Dark red crystals	Calc.	39.6	5.4	13.9	-	14.6
$(Ph_2C_2)Co_2(CO)_2(P(OC_2H_5)_3)_4$	Found	47.5	7.0	11.7	-	12.3
Dark red crystals	Calc.	47.2	6.9	11.6	-	12.2
$(CF_3C_2CF_3)Co_2(CO)_2(P(OCH_3)_3)_4$	Found	-	-	-	-	-
Orange-red crystals	Calc.	-	-	-	-	-
$(CF_3C_2CF_3)Co_2(CO)_2$- $(P(OC_2H_5)_3)_4$	Found	36.0	5.9	11.6	11.5	12.5
Orange-red crystals	Calc.	36.0	6.0	11.8	11.4	12.4

derivatives with other phosphine and phosphite ligands were unsuccessful. Reaction of the diphenylacetylene complex with large excesses of $P(O\text{-}i\text{-}C_3H_7)_3$ or $P(O\text{-}n\text{-}C_4H_9)_3$ in refluxing methylcyclohexane for 48 and 80 hours respectively did not result in tetrasubstituted complexes, although examination of the infrared spectrum of the reaction mixture around 2000 cm^{-1} indicated that some substitution beyond two CO groups had taken place. A similar result was obtained with $P(OPh)_3$ after a reaction time of six hours, but longer reaction times (12-18 hours) resulted in decomposition to a pale violet insoluble solid. In contrast, reaction of the phosphine ligands, PPh_3 and $P(n\text{-}C_4H_9)_3$, with the diphenylacetylene complex in methylcyclohexane for 12-24 hours led only to the disubstituted complexes.

3. Infrared Spectra

The infrared spectra of the complexes were recorded in the region between 4000 cm^{-1} and 600 cm^{-1} and the observed band frequencies are listed in Chapter IV. Apart from the appearance of bands due to vibrations within the phosphorus ligand molecules themselves, the most significant differences between the spectra of the substituted complexes and those of the parent hexacarbonyls were found in the region of the CO stretching bands between 2100 cm^{-1}

and 1900 cm^{-1}. Tables II-A-4 and II-A-5 list the frequencies of the CO stretching bands for all the complexes prepared. In this region the spectra of similarly substituted complexes show a characteristc pattern of peak positions and intensities. A shift in the band positions towards lower frequencies occurs as the extent of substitution increases. As mentioned above, these factors have permitted identification of certain of the complexes for which elemental analyses were not carried out.

Figure II-A-1 illustrates the pattern of CO stretching bands for the four monosubstituted complexes prepared here. There are two well-separated groups of very strong absorptions and, with the exception of the $P(OPh)_3$ complex, a third band of medium intensity occurs at lower frequencies. In all cases the very strong absorptions consist of a single sharp peak above 2000 cm^{-1}, and two only partially resolved bands at a lower frequency. In some cases other shoulders are observed. In the $P(OPh)_3$ complex a shoulder on the low frequency side of the very strong bands might be attributed to the medium intensity absorption observed in the other complexes.

In the spectra of the disubstituted complexes illustrated in Figure II-A-2, the pattern is seen to be somewhat simpler. The bands are shifted to lower frequencies

TABLE-II-A-4

CO STRETCHING FREQUENCIES IN MONO- AND DISUBSTITUTED DERIVATIVES OF $(Ph_2C_2)Co_2(CO)_6$

Ligand	Band Frequencies (cm^{-1}) [a]
A. Monosubstituted Complexes	
$P(OPh)_3$	2078(vs), 2035(vs), 2020(vs), 2000(s, sh), 1987(m, sh)
$P(OCH_3)_3$	2072(vs), 2026(vs), 2008(vs), 1995(s, sh), 1972(m)
PPh_3	2068(vs), 2022(vs), 2004(~~vs)~~, 1995(s, sh), 1967(s)
$P(n\text{-}C_4H_9)_3$	2062(vs), 2010(vs), 2000(vs), 1985(s, sh), 1957(s)
B. Disubstituted Complexes	
$P(OPh)_3$	2052(vs), 2010(s, sh), 1991(vs)
$P(OCH_3)_3$	2038(vs), 1976(vs)
$P(OC_2H_5)_3$	2035(vs), 1972(vs)
$P(O\text{-}i\text{-}C_3H_7)_3$	2033(vs), 1968(vs), 1940(m, sh)
PPh_3	2028(vs), 1968(vs)
$P(n\text{-}C_4H_9)_3$	2020(vs), 1966(vs, sh), 1956(vs)

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[a] Recorded as solutions in C_2Cl_4. For complete details see Chapter IV-A.

TABLE II-A-5

CO STRETCHING FREQUENCIES IN TRI- AND TETRASUBSTITUTED DERIVATIVES OF ACETYLENIC DICOBALTHEXACARBONYL COMPLEXES

Complex	Band Frequencies[a] (cm^{-1})
$(Ph_2C_2)Co_2(CO)_3(P(OCH_3)_3)_3$	2000(s), 1945(s) 1943(m, sh)
$(Ph_2C_2)Co_2(CO)_2(P(OCH_3)_3)_4$	1950(s), 1928(s)
$(Ph_2C_2)Co_2(CO)_2(P(OC_2H_5)_3)_4$	1949(s), 1923(s)
$(CF_3C_2CF_3)Co_2(CO)_2(P(OCH_3)_3)_4$	1977(s), 1956(s)
$(CF_3C_2CF_3)Co_2(CO)_2(P(OC_2H_5)_3)_4$	1975(s), 1946(s)

[a] Recorded as solutions in C_2Cl_4 or CS_2. For complete details see Chapter IV.

Figure II-A-1. Infrared spectra of monosubstituted derivatives of $(Ph_2C_2)Co_2(CO)_6$ in the CO stretching region. Spectra were recorded as solutions in C_2Cl_4.

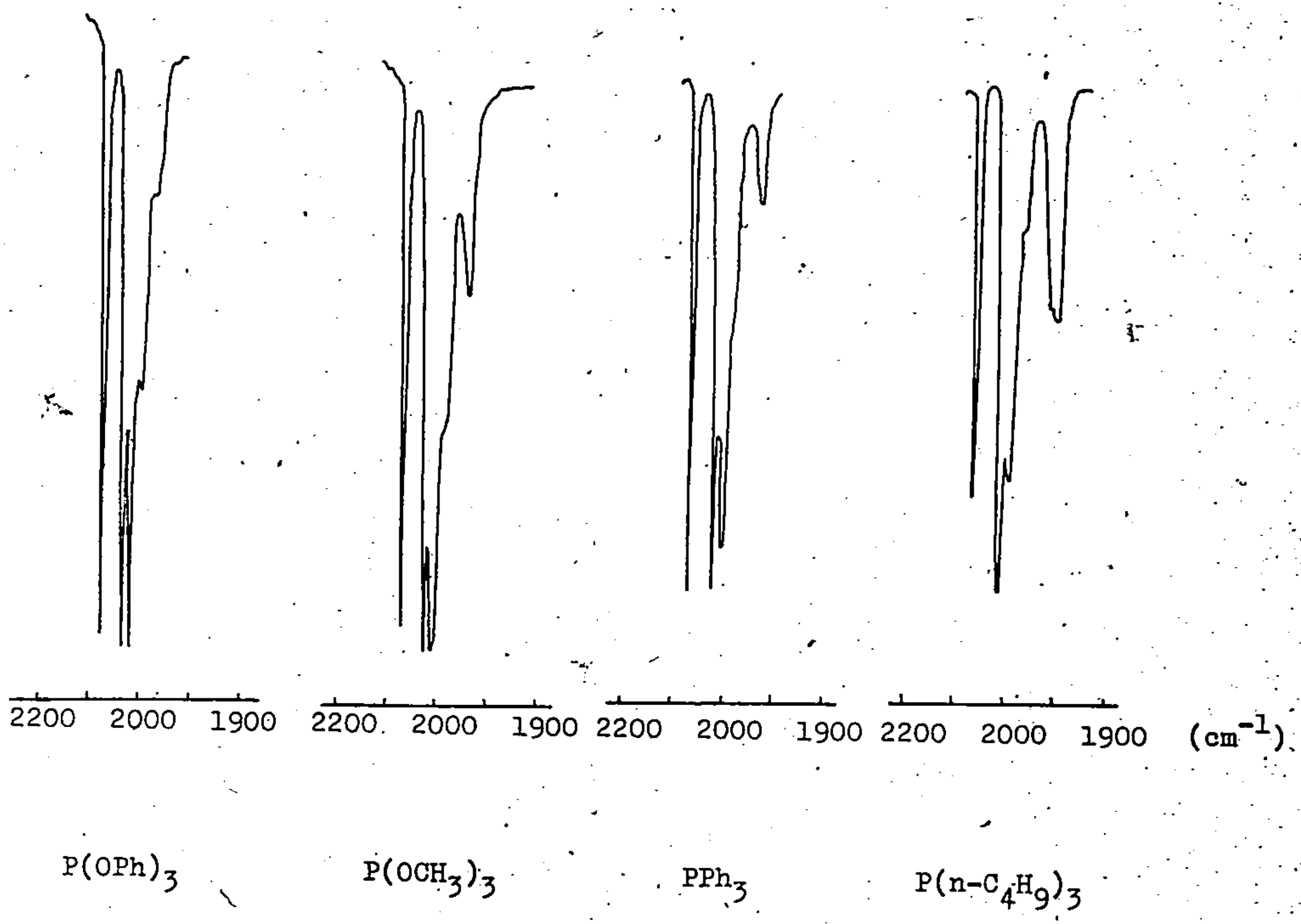
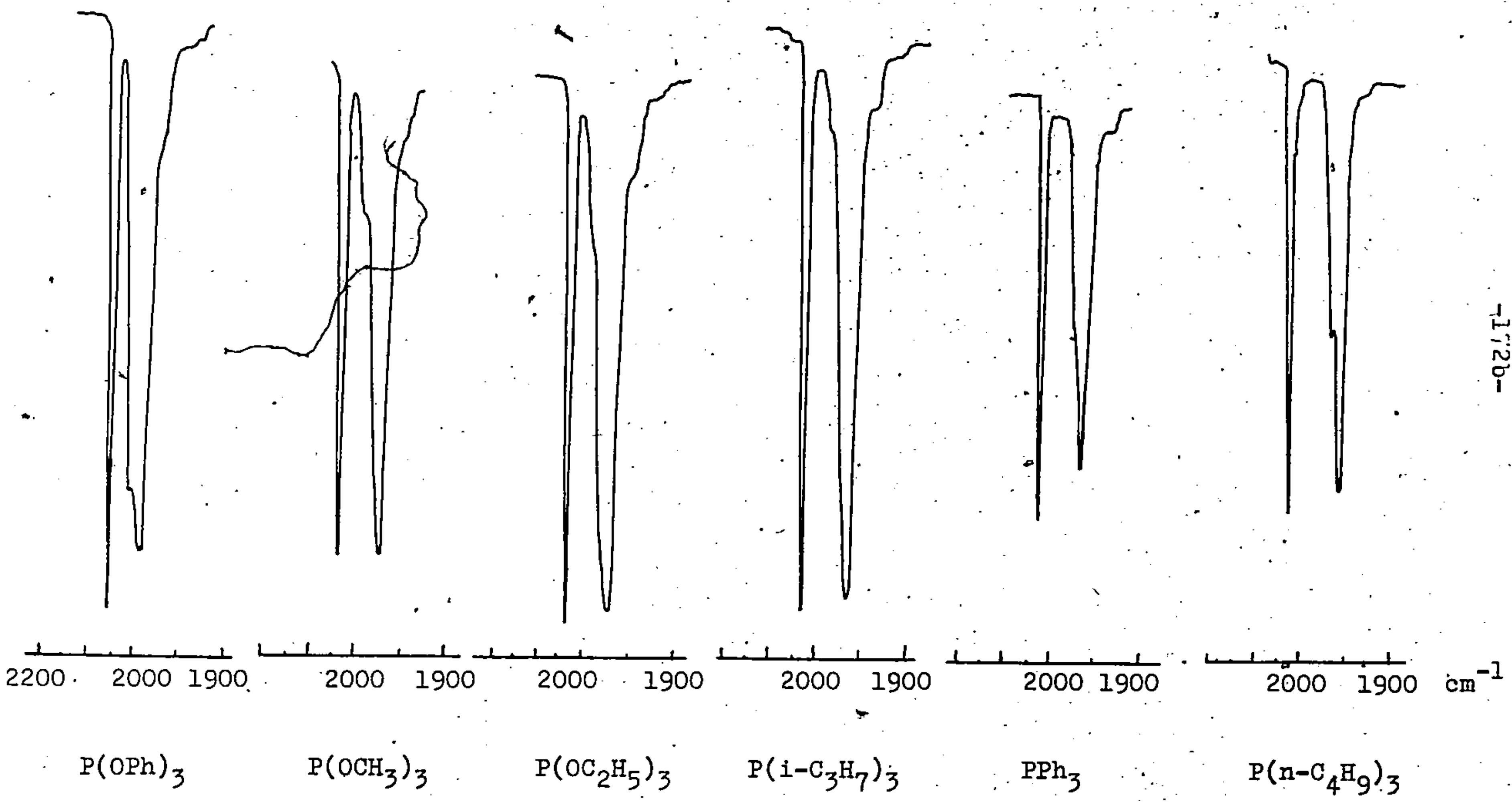

2200
2000
1900
2200
2000
1900
2200
2000
1900
2200
2000
1900
(cm^{-1})
P(OPh)$_3$
P(OCH$_3$)$_3$
PPh$_3$
P(n-C$_4$H$_9$)$_3$

Figure II-A-2. Infrared spectra of disubstituted derivatives of $(Ph_2C_2)Co_2(CO)_6$ in the CO stretching region. Spectra were recorded as solutions in C_2Cl_4.

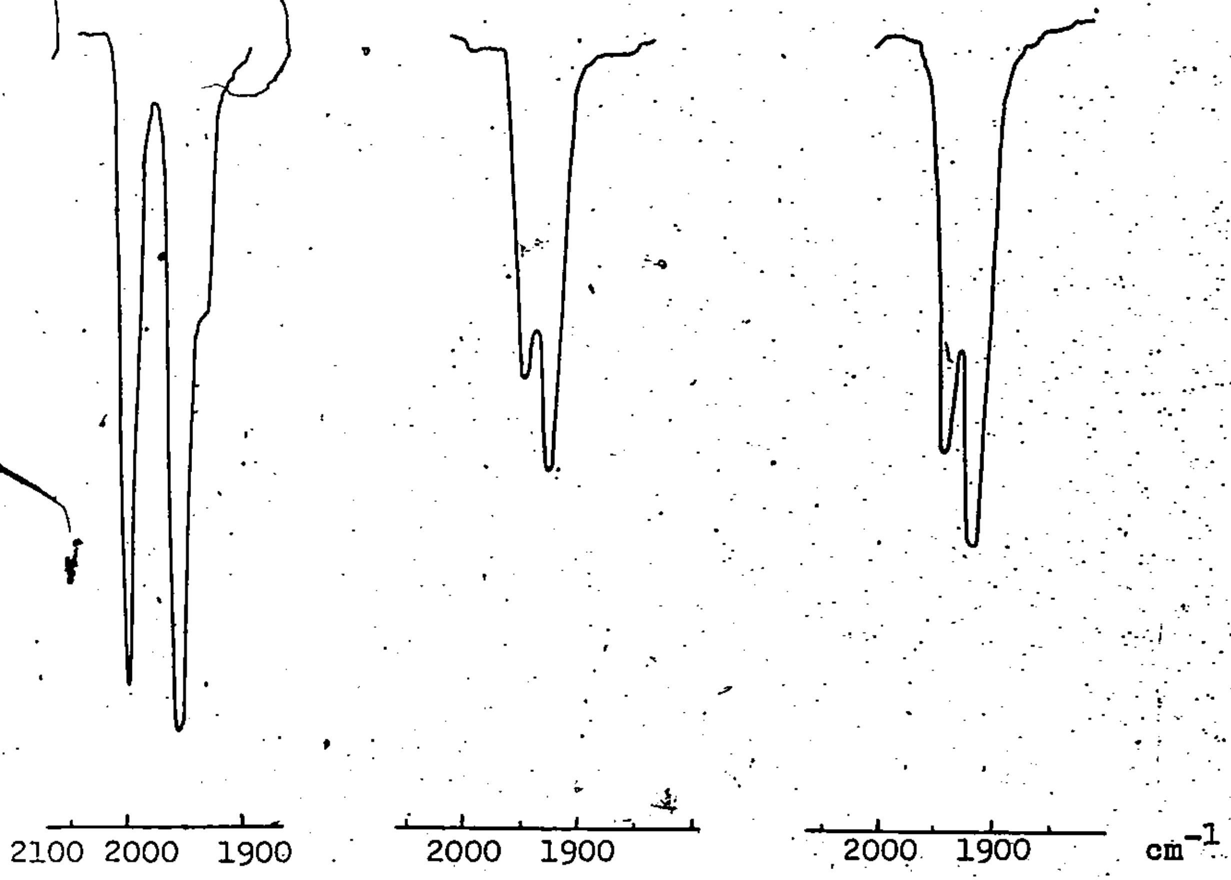

2200
2000
1900
2000
1900
2000
1900
2000
1900
2000
1900
2000
1900
cm^{-1}
P(OPh)$_3$
P(OCH$_3$)$_3$
P(OC$_2$H$_5$)$_3$
P(i-C$_3$H$_7$)$_3$
PPh$_3$
P(n-C$_4$H$_9$)$_3$

relative to the monosubstituted complexes, and only two very strong, well separated absorptions occur. The lower frequency absorption in some of the complexes consists of two distinct, but only partially resolved peaks. However, the asymmetry of this band in the other complexes indicates that it consists of two separate absorptions in all cases.

Further substitution continues to shift the CO stretching bands to lower frequencies as shown in Figure II-A-3 for the tri- and tetrasubstituted derivatives of the diphenylacetylene complex. The pattern of peaks in the trisubstituted complex is similar to that in the disubstituted derivative but the spectra are distinguishable by the frequency shift. The tetrasubstituted complexes show a broad absorption consisting of two only partially resolved bands of equal intensity. The spectra of the tetrasubstituted hexafluoro-2-butyne derivatives in this region are almost identical to those of the diphenylacetylene complexes except that the bands occur at a higher frequency.

The observed shift in the CO stretching bands to lower frequencies on substitution by the donor ligands has been observed in all acetylenic dicobalthexacarbonyl complexes for which infrared spectra have been reported.[13] Figure II-A-4 shows the CO stretching bands for the series of four $P(OCH_3)_3$ derivatives of the diphenylacetylene complex along with the parent

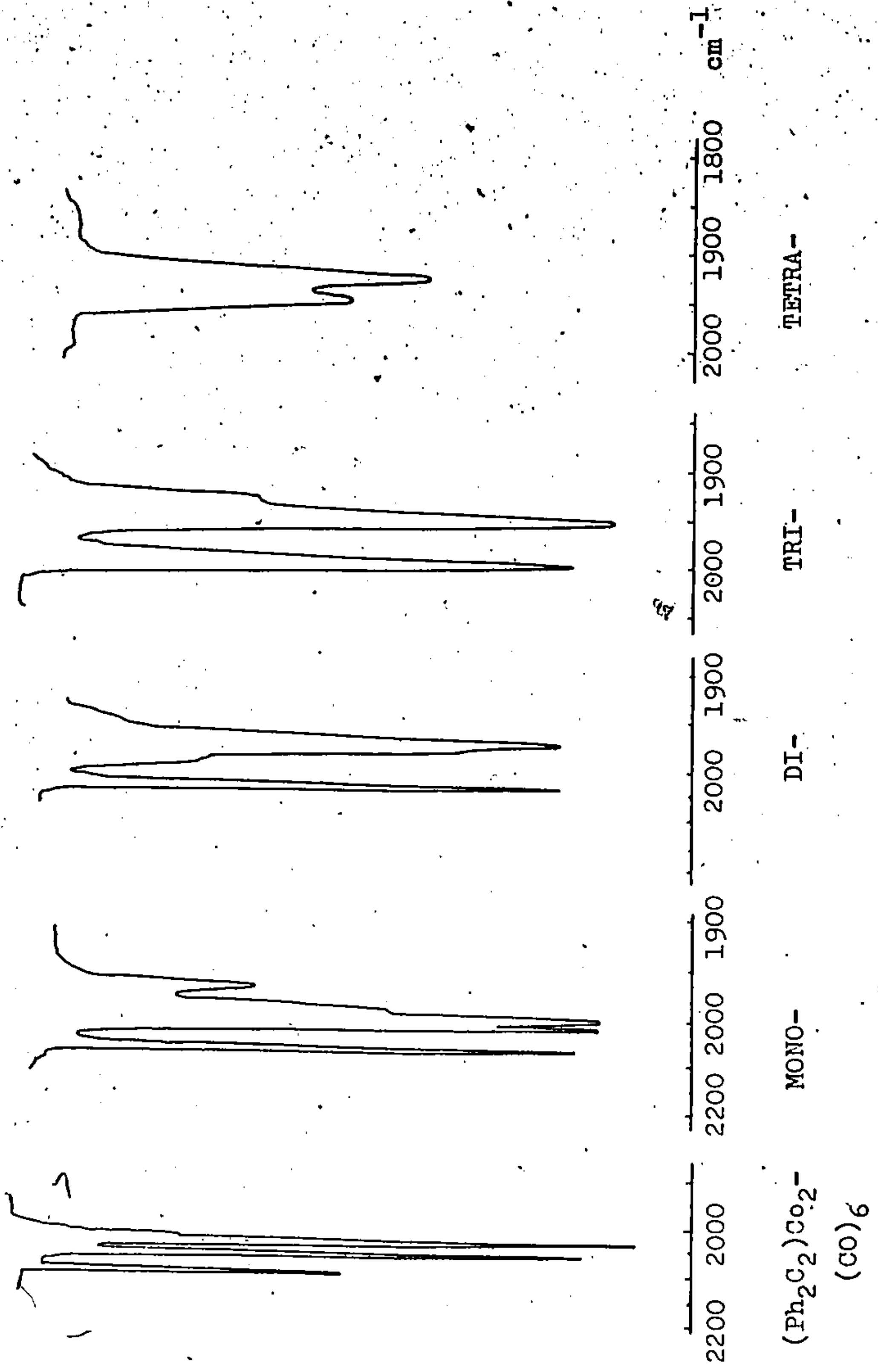
Figure II-A-3. Infrared spectra of tri- and tetra-substituted derivatives of $(Ph_2C_2)Co_2(CO)_6$ in the CO stretching region. Spectra were recorded as solutions in C_2Cl_4 or CS_2.



$P(OCH_3)_3$ $P(OCH_3)_3$ $P(OC_2H_5)_3$

TRISUBSTITUTED TETRASUBSTITUTED

Figure II-A-4. Infrared specrta of the series of substituted derivatives of $(Ph_2C_2)Co_2(CO)_6$ containing $P(OCH_3)_3$ in the CO stretching region. Spectra were recorded as solutions in C_2Cl_4.


cm^{-1}
1800
1900
2000
TETRA-
1900
2000
TRI-
1900
2000
DI-
1900
2000
2200
MONO-
2000
2200
$(Ph_2C_2)Co_2$-
$(CO)_6$

unsubstituted complex for comparison. From this illustration the trend towards lower frequencies as the extent of substitution increases is clearly seen.

These shifts in the frequencies of the CO stretching bands are observed in substituted metal-carbonyl complexes in general and can be explained in terms of the relative donor-acceptor properties of the phosphorus ligands compared to those of the carbonyl group.[93] As discussed in Chapter I, the CO group is a weak electron donor but is one of the strongest π-acceptor ligands known. Phosphorus is a stronger donor and weaker acceptor than carbon monoxide and therefore substitution of CO results in an increased electron density on the metal atom. This is then partly removed by an increase in the extent of the π back-bonding from the metal into the antibonding orbitals of the remaining CO groups. A decrease in the CO bond order results and thus the frequencies of the CO stretching vibrations are lowered.

A further observation in the spectra of these complexes is that the position of the CO stretching bands also depends on which phosphorus ligand is present in the complex (see Table II-A-4). The frequencies of the bands in the mono- and disubstituted complexes decrease in the following order:

$$P(OPh)_3 > P(OCH_3)_3 > P(OC_2H_5)_3 > P(O\text{-}i\text{-}C_3H_7)_3 >$$
$$PPh_3 > P(n\text{-}C_4H_9)_3$$

It can be seen that this order parallels the order of electronegativity, or electron withdrawing capacity, of the groups attached to the phosphorus atom.

Similar correlations have been observed in other metal carbonyl systems, and Tolman [123] has published an extensive study involving 70 different phosphorus ligands and their effects on the CO stretching frequencies in the $Ni(CO)_3L$ complexes. All of the ligands used in this work were included in Tolman's study and the same order of frequencies was observed.

Such correlations are most easily explained thus: As the electronegativity of the groups attached to the donor atom is increased, a decrease in the σ-donor ability of the ligand and an increase in its π-acceptor ability should result. [95] This should in turn decrease the back-bonding to the remaining CO groups and increase the CO bond order, thereby increasing the CO stretching frequency.

Some attempts have been made to interpret results of this type in terms of the relative importance of the σ and π contributions to the metal-ligand bond. Views on both extremes have been presented. On one extreme is the suggestion that the σ component in a series of PX_3 type ligands is small, but constant, and that the change in CO stretching frequencies reflects the differences in the π-acceptor abilty of the ligands only.[124-127] On the other hand, similar data have been interpreted by suggesting that there is little or no π component in any of these metal-ligand bonds, and that the increased electronegativity of the X groups merely results in a decreased σ-donor capacity of the ligand.[88, 89] This should also lead to a smaller degree of metal-CO back-bonding.

However, the danger of this type of argument has been pointed out[85, 93] in that the two effects cannot be separated because of the synergic nature of the bond. Some authors have therefore suggested that the differences in the CO stretching frequencies should only be interpreted in terms of the overall synergic donor-acceptor properties of the ligands, and not in terms of the result of variations in their σ or π bonding capacity alone.[85, 93, 110] Tolman[123] has suggested the use of the term "electron donor-acceptor property", while Haines and Stiddard have discussed such effects using the term "σ-π donor property".[93]

It now appears to be generally accepted

that there is not yet sufficient evidence to say to what extent the decreased electron density on the metal atom is due to the decreased donor ability or increased acceptor ability of the ligands.[128] Nevertheless, the demonstrated importance of π bonding in these complexes (see Section C of Chapter 1) has resulted in these molecules being generally classified on the basis of their relative π-acceptor strengths alone.

The position of the C≡C stretching band in these complexes is also of considerable interest. Complexation of an acetylene molecule usually results in a large shift in the frequency of this band,[112] and this has been discussed at some length in Chapter I in relation to the nature of the metal-alkyne bond. For example, Iwashita et al.[8, 9] have reported a shift of the C≡C stretching band in the HC≡CH molecule from 1972 cm^{-1} to 1402 cm^{-1} on its complexation to form $(HC{\equiv}CH)Co_2(CO)_6$. In the methylacetylene complex a shift from 2142 cm^{-1} to 1552 cm^{-1} has been observed, and in the dimethylacetylene complex the band has been reported to shift from 2313 cm^{-1} to 1633 cm^{-1}.[108] Shifts of a similar magnitude have also been observed in other acetylenic dicobalthexacarbonyl complexes.[37, 46]

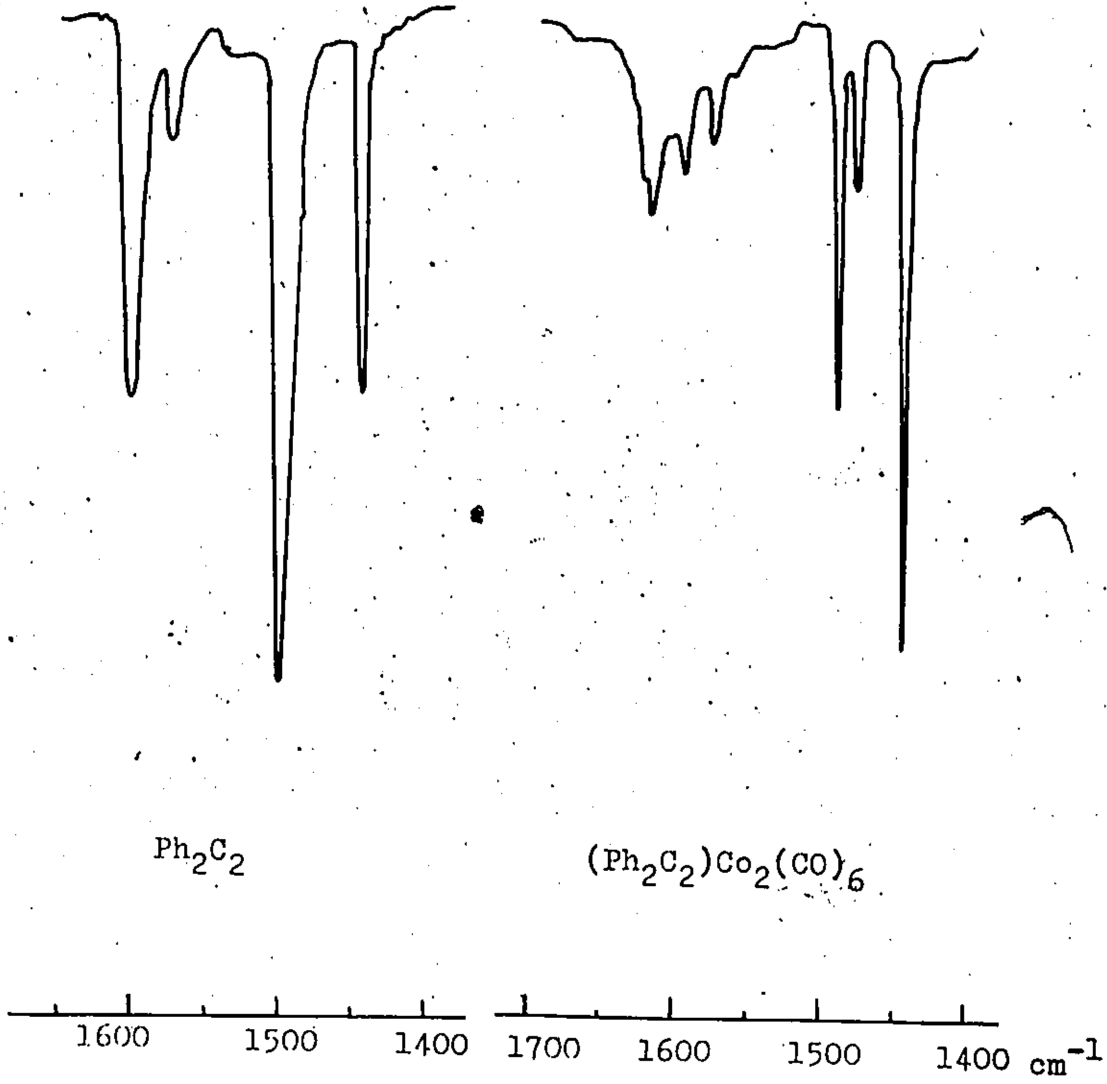
In Chatt's model of the metal-alkyne bond, these shifts are explained by suggesting that a reduction in the $C\equiv C$ bond order occurs, caused by π back-bonding from the metal atom into the π^* antibonding orbitals of the triple bond. As in the dicobalthexacarbonyl complexes, larger shifts are found to occur when the acetylene is bonded to two metal atoms since both sets of mutually perpendicular π^* orbitals are then involved.[101] On this basis then, the $C\equiv C$ stretching bands in the acetylenic dicobalthexacarbonyls might be expected to shift to lower frequencies when the CO groups are substituted by stronger donors in the same way that CO stretching frequencies are lowered on substitution of CO by phosphorus ligands. No reports of such correlations in any series of acetylenic metal carbonyl complexes have been published.

Reported studies on the infrared spectrum of the diphenylacetylenehexacarbonyldicobalt complex have centered only on the CO stretching bands, and the rest of the spectrum has not been assigned. In the Raman spectrum of the free diphenylacetylene molecule a strong band at 2220 cm^{-1} has been assigned to the $C\equiv C$ stretching mode.[129] On complexation of the ligand, its symmetry is reduced and this mode should be infrared active. It should therefore appear in the spectrum of the complex, but several strong bands in the spectrum of the ligand make this assignment difficult.

In the spectrum of the free ligand two bands which appear at 1605 cm^{-1} and 1575 cm^{-1} have been assigned to ring stretching modes, [130] but on complexation these two bands shift to lower frequencies, and a new weak band appears at 1618 cm^{-1}. Figure II-A-5 illustrates the spectra of the free ligand and the diphenylacetylene complex in this region. It is suggested that this new weak band is due to the C≡C stretching mode, and thus there is a shift of 600 cm^{-1} which is comparable to those reported for the other acetylene derivatives.

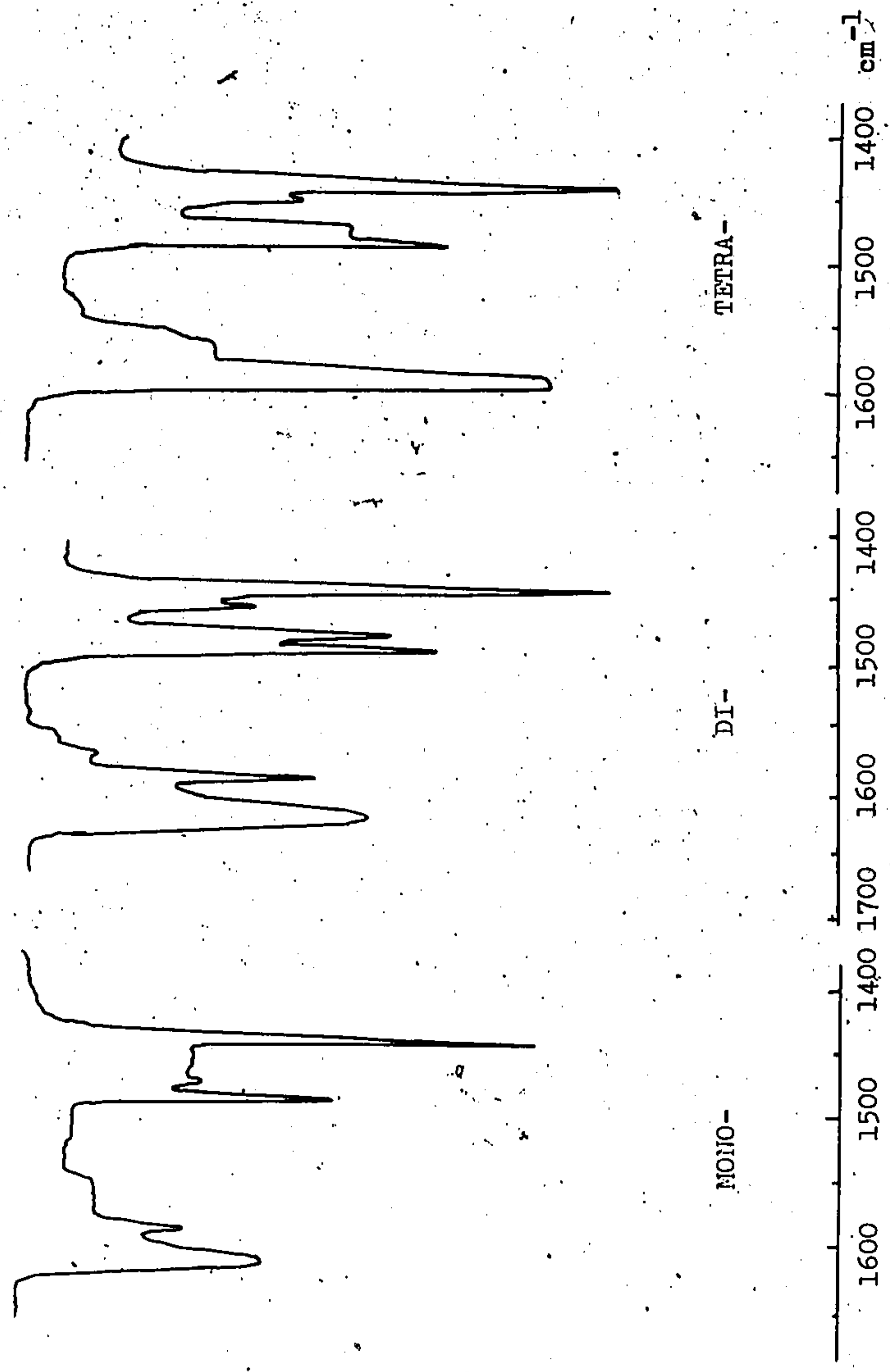
Part of the rationale for this assignment comes from an examination of the spectra of the substituted complexes in this region. These are illustrated in Figure II-A-6 for the mono-, di- and tetrasubstituted derivatives of $P(OCH_3)_3$. The free phosphite ligand has no absorption in the region under consideration, but this weak band which was observed at 1618 cm^{-1} in the unsubstituted complex becomes more prominent as substitution progresses. It is not significantly shifted in the mono- and disubstituted complexes, but in the tetrasubstituted derivative it appears at 1595 cm^{-1}. Since the frequencies of the ring stretching modes which occur in this region are not expected to be greatly affected by this substitution, this shift further confirms the assignment.

Figure II-A-5. Infrared spectra (1700-1400 cm^{-1}) of diphenylacetylene and diphenylacetylene-hexacarbonyldicobalt. Spectra were recorded as solutions in C_2Cl_4.



Ph_2C_2
$(Ph_2C_2)Co_2(CO)_6$
1600
1500
1400
1700
1600
1500
1400 cm^{-1}

Figure II-A-6. Infrared spectra (1700-1400 cm^{-1}) of substituted derivatives of diphenylacetylenehexacarbonyldicobalt containing trimethylphosphite. Spectra were recorded as solutions in C_2Cl_4.


cm^{-1}
1400
1500
1600
TETRA-
1400
1500
1600
1700
DI-
1400
1500
1600
MONO-

If this assignment is indeed correct, then this shift confirms the suggestion made above that substitution of CO by the phosphorus donors should increase the π back-bonding to the acetylene group and result in a decreased C≡C bond order. However, since the assignment is somewhat speculative, no definite conclusions can be made without further studies on other acetylenic dicobalthexacarbonyl complexes.

4. Structure

Although Birchall et al.[35] have made some suggestions as to the location of the phosphorus ligands in a disubstituted complex based on the infrared spectrum, no definite structural information has been reported on these substituted derivatives. The crystal structure of the diphenylacetylenehexacarbonyldicobalt complex has shown that there are two different positions for the carbonyl groups. Two CO groups on each cobalt atom point "down" away from the acetylene ligand, and one CO group on each of the metal atoms is directed "up" towards the same side of the molecule as the alkyne group (see Figure I-B-1). This basic arrangements of the ligands is not expected to change in the substituted derivatives.

Sly's suggestions as to the geometry and coordination around the cobalt atoms in these complexes have been discussed in Section B of Chapter I, but from a simple molecular orbital treatment of the bonding in the diphenylacetylene complex, Brown [23] has suggested that the coordination around the metal atoms most closely resembles a dsp^3 trigonal bipyramidal arrangement. This scheme is illustrated in Figure II-A-7. In this arrangement, one of the sp^2 hybrids in the trigonal plane of each cobalt atom is directed towards the mid-point of the C≡C bond of the acetylene group, while the remaining two sp^2 hybrids are involved in bonding with the two CO ligands which point "down". These two groups will therefore be referred to as the equatorial CO groups since, together with the acetylene, they are bonded via metal orbitals which are in the trigonal plane of the trigonal bipyramid. The remaining CO group, which points "up" will be referred to as the axial group. The second axial position is used for Co-Co bonding. [23]

In a disubstituted complex several arrangements are possible for the placement of the two phosphorus ligands. First, it can be safely assumed that both groups are not bonded to the same cobalt atom. The basis for this lies in the fact that the reaction of $Co_2(CO)_6(P(n\text{-}C_4H_9)_3)_2$ with diphenylacetylene has been found to give a complex of the formula $(Ph_2C_2)Co_2(CO)_4(P(n\text{-}C_4H_9)_3)_2$ which is identical to the one reported in this thesis. [115, 116] A crystal structure on the $Co_2(CO)_6(P(n\text{-}C_4H_9)_3)_2$ complex

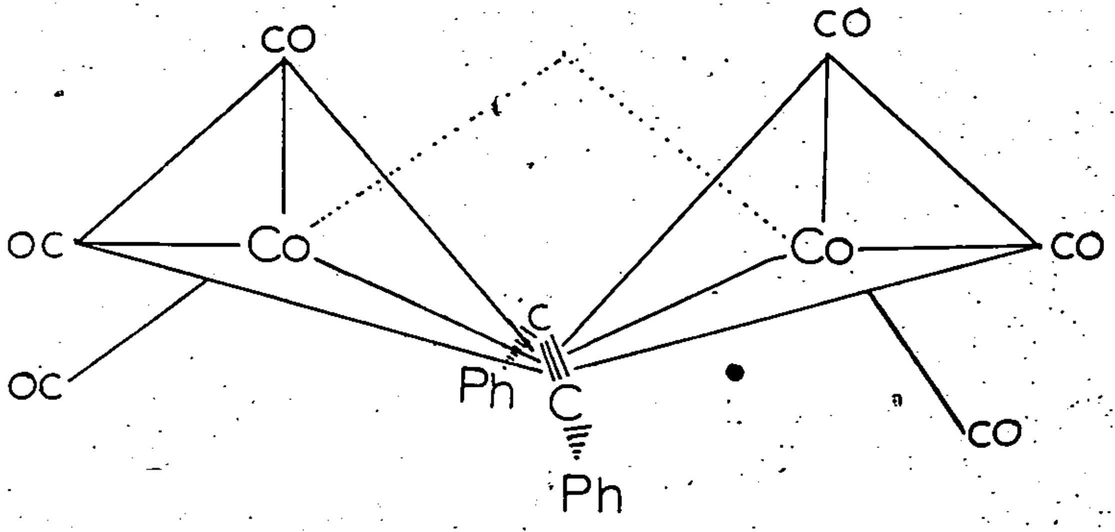


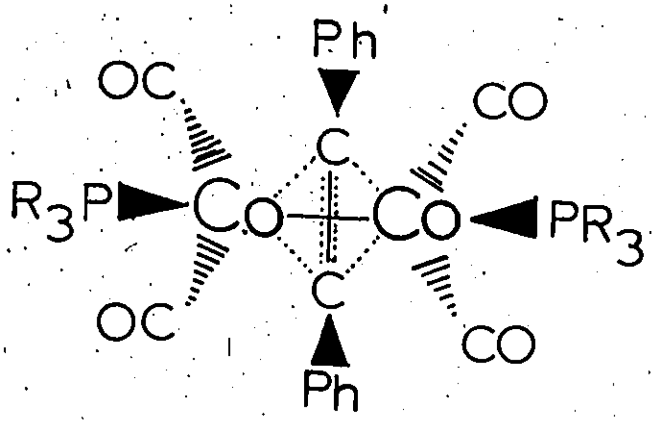
Figure II-A-7. Trigonal bipyramidal coordination around cobalt in $(Ph_2C_2)Co_2(CO)_6$ as taken from references 22 and 23.

has shown the two phosphine ligands to be symmetrically arranged in a linear P-Co-Co-P skeleton.[131] The four possible arrangements which remain are illustrated in Figure II-A-8.

Predictions as to the number of CO stretching bands in the infrared spectra of the disubstituted derivatives indicate that these molecules have a C_{2v} symmetry and correspond to structure (a) of Figure II-A-8. The two phosphorus ligands are therefore in the axial positions. Figure II-A-9 shows the four fundamental CO stretching modes for such an arrangement of carbonyl groups. Group theory predicts that only the A_1, B_1 and B_2 modes should be infrared-active, and thus only three CO stretching bands should be observed in the infrared spectrum if structure (a) is correct. Structures (b) through (d) all have lower symmetry for which four infrared-active CO stretching bands are predicted.

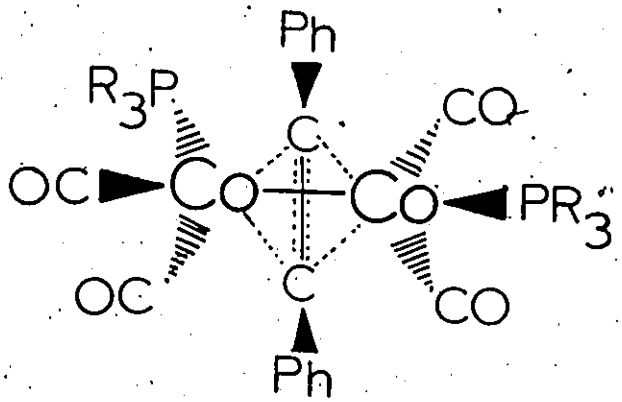
Birchall et al.[35] have used such arguments to conclude from the appearance of three strong, well-separated CO stretching bands in the spectrum of $(C_6F_5C_2C_6F_5)Co_2(CO)_4(PPh_3)_2$, that the molecule has a structure equivalent to (a). Several very weak shoulders were attributed to ^{13}CO vibrations. In the disubstituted complexes prepared here only two main absorptions occur in

Figure II-A-8. The possible arrangements of two phosphorus ligands in acetylenic dicobaltcarbonyl complexes.



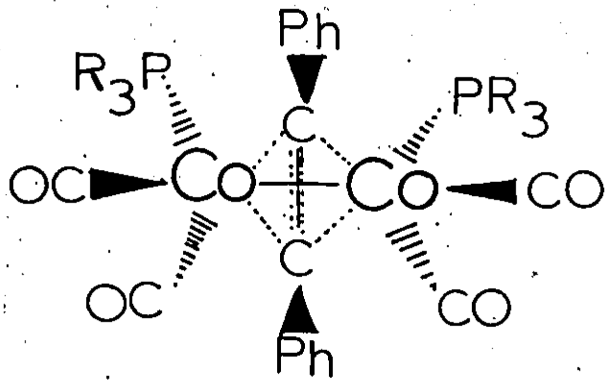
(a)

C_{2v}



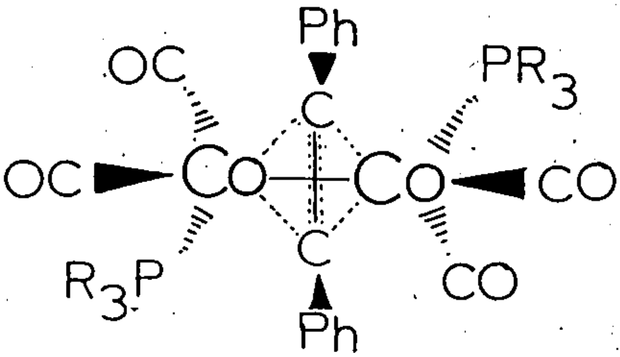
(b)

C_1



(c)

C_s



(d)

C_2

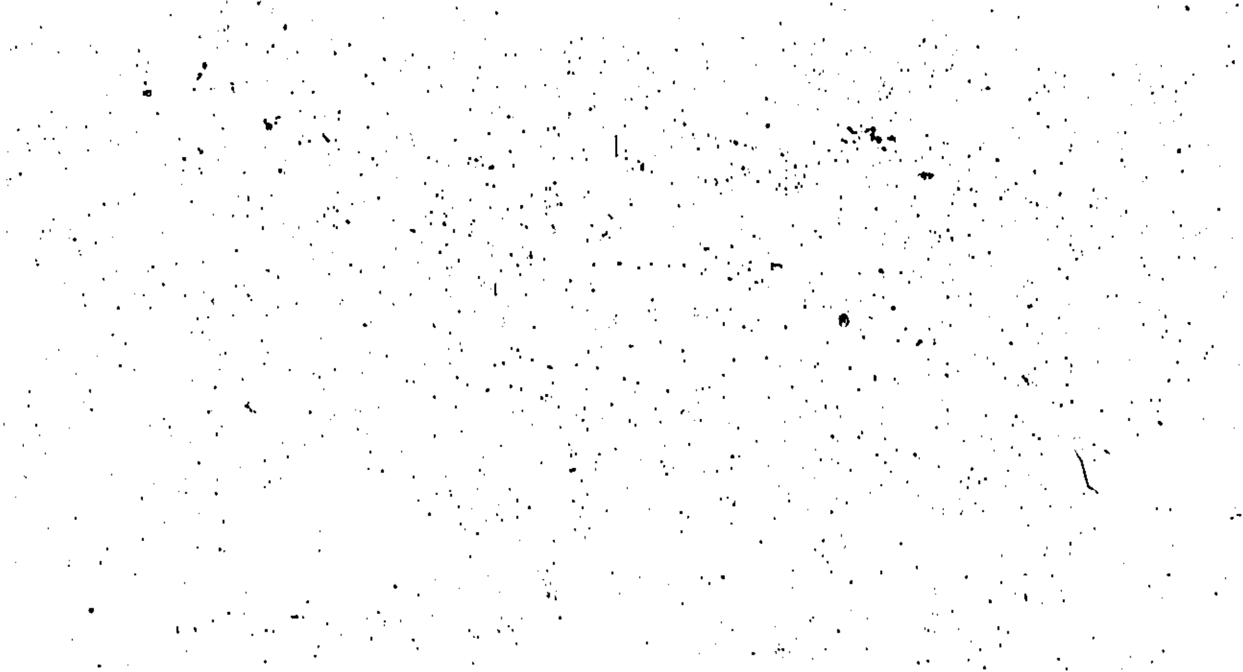
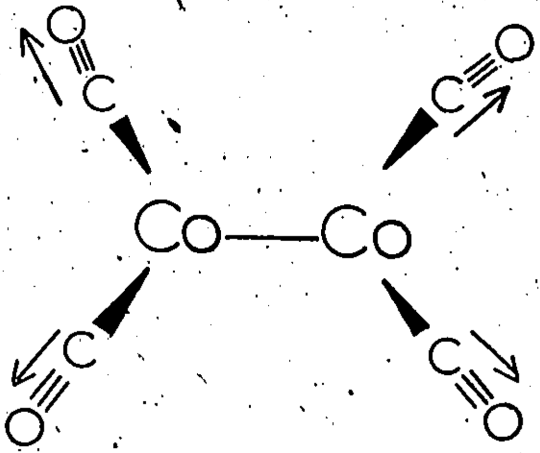
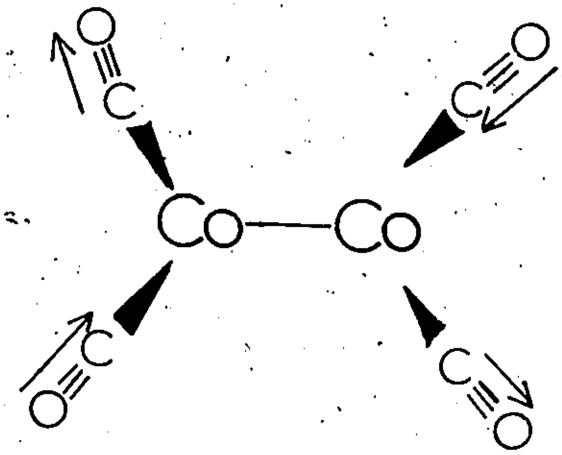


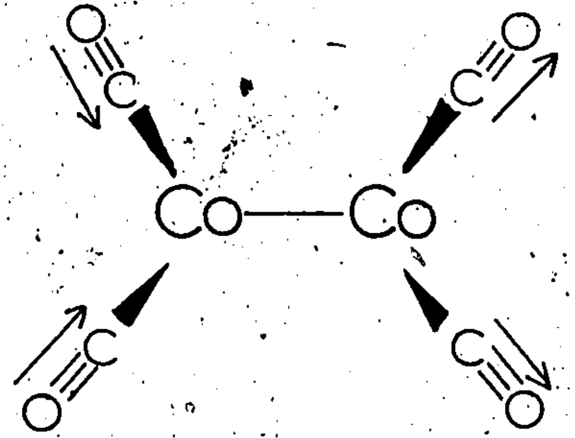
Figure II-A-9. The four CO stretching modes for a C_{2v} arrangement of carbonyl groups in $(Ph_2C_2)Co_2(CO)_4(PR_3)_2$.



A_1
active

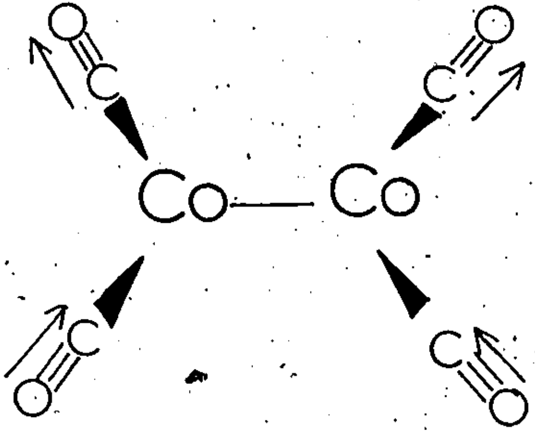


A_2
inactive



B_1

active



B_2

active

the CO stretching region, but in each case the lower frequency band is partially resolved into two distinct peaks, or has some asymmetry, as was shown in the preceding section. Thus it appears that a total of three bands is actually present in all complexes. It is therefore concluded that they all have structure (a) in which the two phosphorus ligands are in the axial positions.

The possibility that structure (a) is not correct, but that a fourth infrared band is simply too weak to be observed was considered, but was eliminated on the basis of studies done on a disubstituted complex containing a bidentate ligand to be discussed in the next section. An X-ray crystal structure on this complex done by other workers in this laboratory[1] has shown that the bis(diphenylphosphino)methane ligand, $Ph_2PCH_2PPh_2$, bridges the two cobalt atoms and has a structure equivalent to structure (c) of Figure II-A-8. In the infrared spectrum of this complex four distinct CO stretching bands are observed. Structures (b) and (d) should also exhibit four bands and therefore structure (a) is still the most likely one.

In other related complexes for which more definite structural information is available, this preference for the axial position by the ligand which is the stronger donor and weaker acceptor is also observed. Thus in the crystal structure of $(Ph_2C_2)Rh_2(PF_3)_4(PPh_3)_2$, which is found to be analogous to the acetylenic dicobalthexacarbonyl complexes, the triphenylphosphine groups are found to be directed towards the same side of the molecule as the acetylene.[66] The four PF_3 ligands, which are at least as good as CO in their π-acceptor ability,[132] are in the "down" positions.

In an attempt to prepare the tetrasubstituted $P(OCH_3)_3$ derivative of diphenylacetylenehexacarbonyldicobalt, other workers in this laboratory isolated a new tetrasubstituted complex having the formula $(Ph_2C_2)Co_2(CO)_2((CH_3O)_2POP(OCH_3)_2)(P(OCH_3)_3)_2$.[133] The crystal structure of this complex has been determined and is illustrated in Figure II-A-10. The bidentate phosphorus ligand bridges the Co-Co bond and occupies the equatorial positions along with the two CO groups. The two trimethylphosphite groups are in the axial positions. Again here the ligand which is the stronger donor and weaker acceptor prefers the "up" position. The fact that the bidentate ligand is not in the axial position, both in this complex and in the bis(diphenylphosphino)methane complex mentioned above, is easily explained by steric effects due to the presence of the acetylene on the "up" side of the molecule.

On the basis of this observed preference

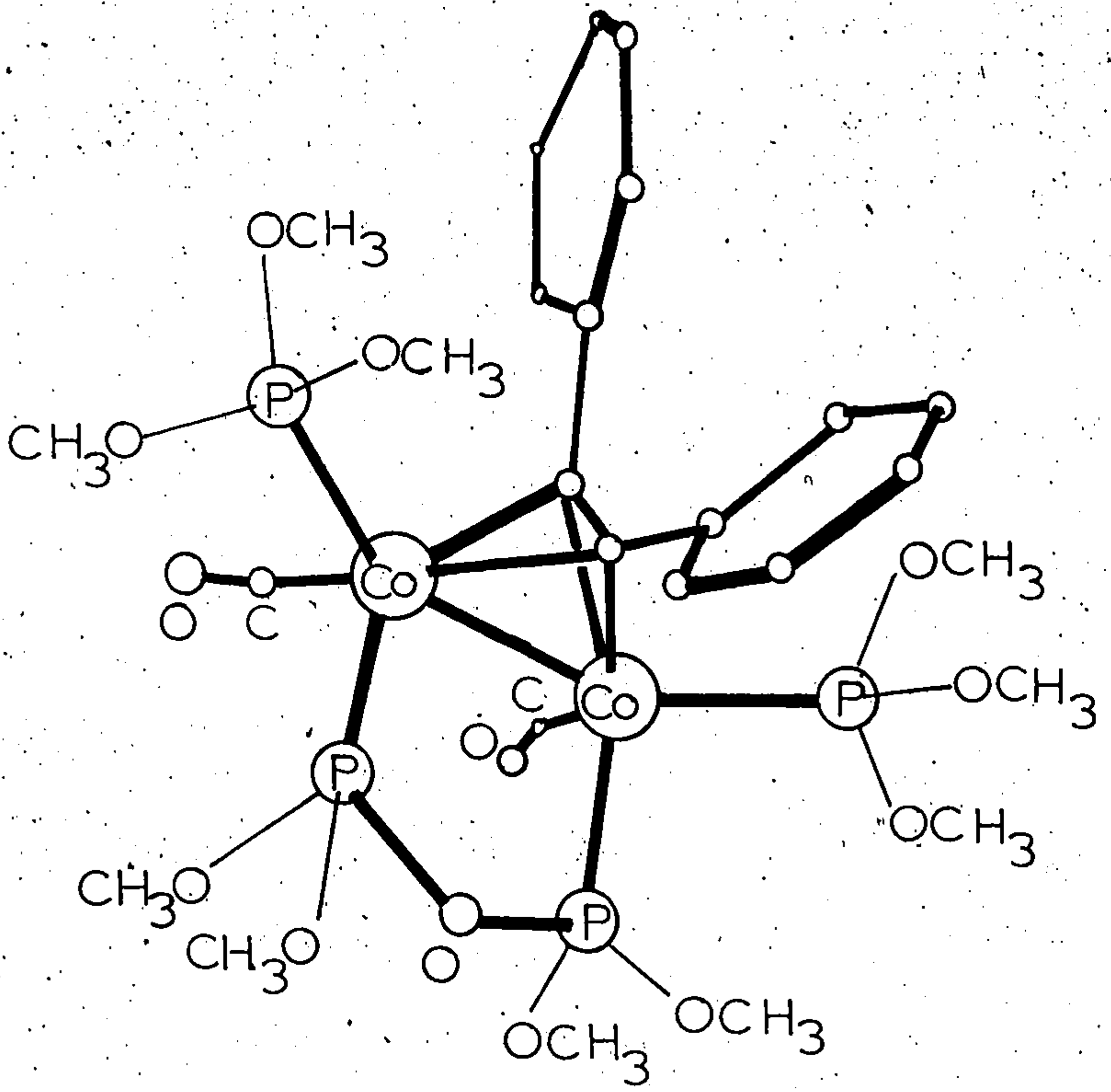


Figure II-A-10. The crystal structure of $(Ph_2C_2)Co_2(CO)_2$-$((CH_3O)_2POP(OCH_3)_2)(P(OCH_3)_3)_2$ as taken from ref. 133.

for the axial position, structures can be suggested for the mono-, tri- and tetrasubstituted derivatives in which axial substitution is favoured. The structures of these complexes are not discernible from their infrared spectra since all of the CO stretching bands are predicted to be infrared-active for any possible arrangement of ligands. The suggested structures are shown in Figure II-A-11.

Since there is more than one possible arrangement for the location of the phosphorus ligands in these complexes the existence of isomers might be expected, but none have been found. Very weak shoulders in the CO stretching region in the infrared spectra of some of the complexes were observed, but these are not pronounced or consistent enough to allow any definite conclusions to be drawn. Such shoulders have been assigned by others to ^{13}CO stretching vibrations.[35] No other evidence for the existence of more than one isomer was found for any of the complexes which were studied.

In light of the work of Bennett _et al_.[66] discussed in Chapter I, on the stereochemical non-rigidity of the rhodium-trifluorophosphine analogues of these complexes, the absence of isomers can be explained if there exists an energetic preference for the axial position. From ^{19}F nmr studies these authors have concluded that

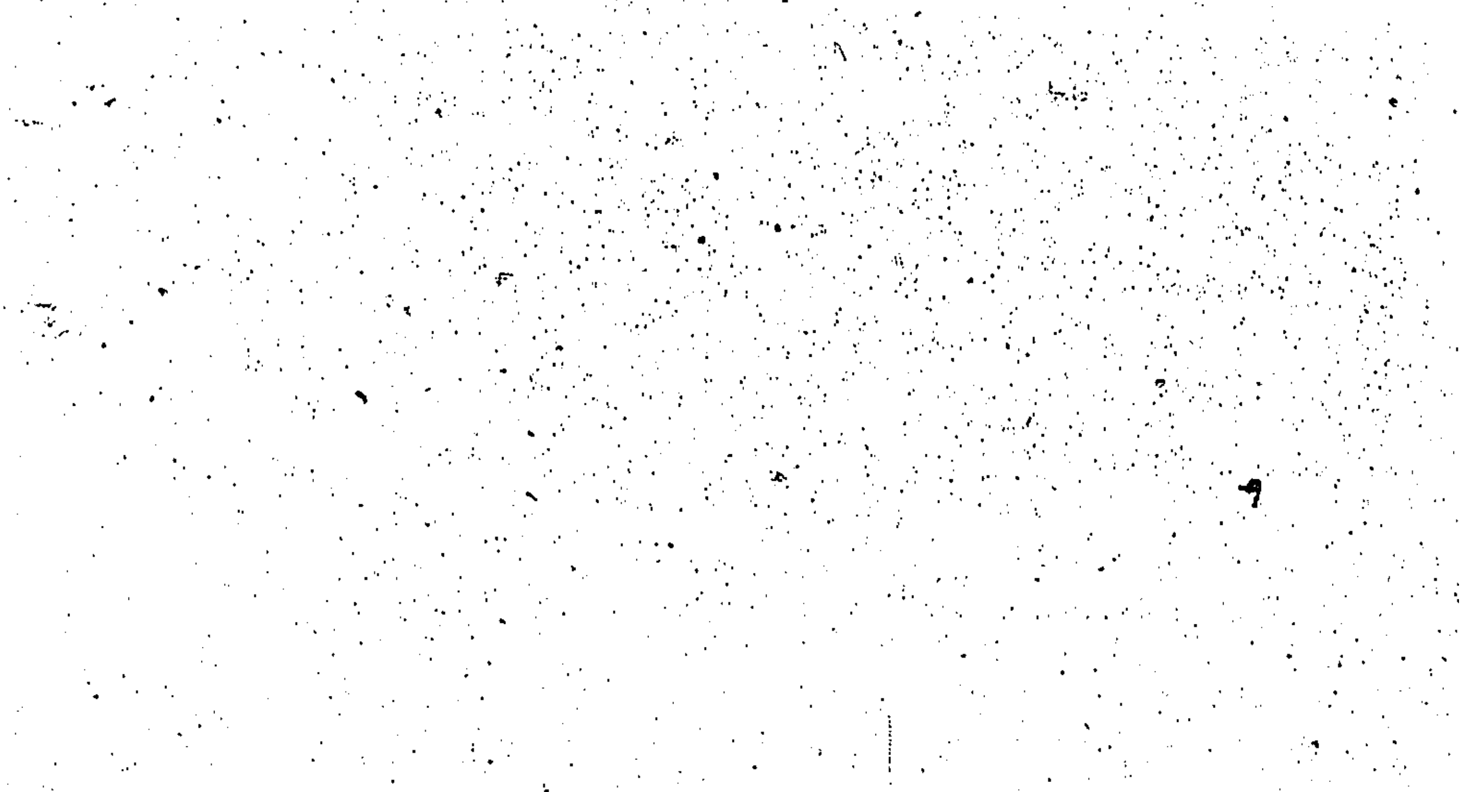
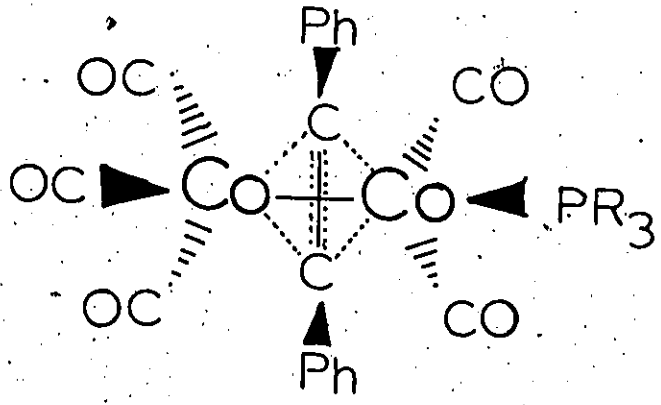
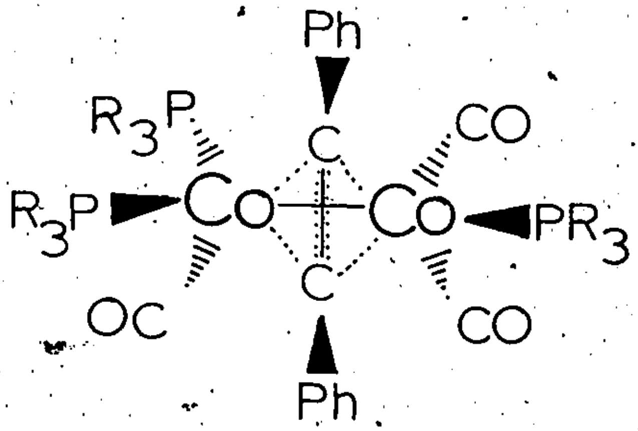


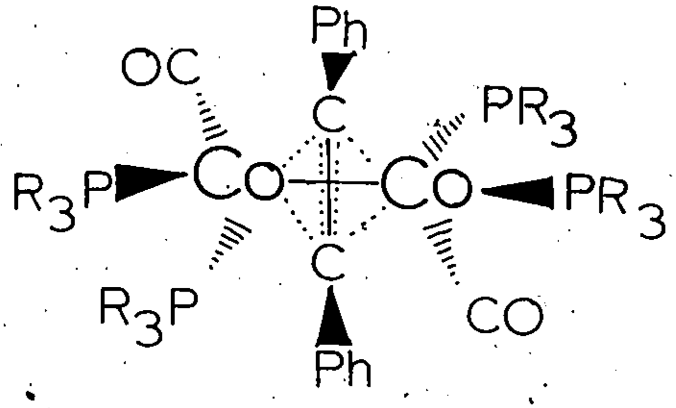
Figure II-A-11. Suggested structures for the mono-, tri- and tetrasubstituted derivatives of $(Ph_2C_2)Co_2(CO)_6$.



MONO-



TRI-



TETRArapid intramolecular exchange of the PF_3 groups occurs in the $(R_2C_2)Rh_2(PF_3)_6$ complexes. Intermolecular exchange was found to be relatively slow. This was explained by suggesting a propellor-like rotation of the PF_3 ligands about the Rh-Rh axis, the acetylene remaining stationary, or a concerted rotation of the $Rh_2(PF_3)_6$ unit with respect to the acetylene. A preliminary study of the ^{13}C nmr spectrum of the diphenylacetylenehexacarbonyldicobalt complex by the same authors indicated that intramolecular exchange of CO in this complex occurs at an even more rapid rate than in the $Rh-PF_3$ analogues.

If introduction of a phosphorus ligand in the axial position, is favoured energetically, then this intramolecular exchange should be hindered in the substituted complex. Thus it would not make any difference which CO group was substituted, by either an associative or dissociative mechanism, since the resulting complex would arrange itself into the most stable conformation. Only one isomer would then be observed, although others might be present to a small extent depending on the energy difference between the conformations.

The observed preference for the axial position would not appear to be caused by steric effects since interaction between an axial phosphorus ligand and the phenyl groups of the acetylene would likely favour the less crowded equatorial positions. It is therefore suggested that this preference is caused by electronic effects similar to the factors behind the trans-influence which has been discussed at length in the literature in reference to other metal systems.[128, 134-138] The main argument lies in the fact that there is a difference in the donor-acceptor properties of CO and phosphorus ligands, and that substitution of CO groups by these ligands could have different effects on the overall stability of the resulting molecule depending on whether it is an axial or equatorial group which is replaced.

The trans-influence in coordination complexes has recently been reviewed by Clark et al.,[128] and is defined as "the extent to which a ligand weakens the bond trans to it in the equilibrium state of the molecule". This distinguishes it from the trans-effect, which is defined as "the effect of a coordinated group on the rate of substitution reactions of the group trans to that group". The trans effect is a kinetic phenomonen and is therefore, in part, a description of the transition state of the substitution reaction.[128]

These authors have examined a large amount of theoretical and experimental data on the trans-influence in coordination complexes in an attempt to clarify the reasons behind it. They have concluded that this phenomenon depends primarily on σ bonding effects resulting from the demand of the ligands for s-character of the metal hybrid orbitals. Thus a ligand which forms a strong σ bond with the metal will take a larger share of the metal bonding orbitals, but in particular, a larger proportion of their s-character because of the lower energy of the s orbitals. This weakens the σ bonding to the other ligands which must share the same set of metal hybrid orbitals. Clark _et al_. have discussed this mainly in connection with square-planar Pt(II) complexes in which the directional properties of the metal hybrid orbitals results in only the _trans_ group being affected.

A similar situation is also expected to exist in complexes which have trigonal bipyramidal coordination since the metal hybrid orbitals used by the ligands in the equatorial plane are different from those used by the axial groups. From his MO study mentioned above on the $(Ph_2C_2)Co_2(CO)_6$ complex, Brown [23] has found that it is primarily the sp^2 hybrids which are used by the equatorial groups, and that the axial positions involve the d_{z^2} and p_z metal orbitals. In these complexes, the alkyne ligand and the two CO groups which are in the equatorial plane are all weak donors and do not form particularly strong σ bonds. Thus substitution of one of these groups by a stronger σ-donor such as phosphorus, would result in an increased s-character in this metal-ligand bond at the expense of the σ bonding to the other ligands in the equatorial plane. Substitution of an axial CO group would not have the same effect since only the one axial position is used in metal-ligand bonding.

Differences in the π bonding abilities of carbon monoxide and the phosphorus ligands might also be contributing to this preference of the poorer π-acceptor for the axial position. Orgel[137] has discussed how the presence of a strong π bonding ligand in the equatorial plane of a trigonal bipyramid should stabilize it by removing electron density from filled metal d orbitals which are directed along the metal-ligand axes of the other equatorial groups. Thus substitution of an equatorial CO group in the acetylenic dicobalthexacarbonyls by a poorer π-acceptor would weaken the metal-ligand σ bonds of the other equatorial groups. If an axial CO group is substituted, an increased electron density on the metal atom would also occur, but it would not occur specifically along the metal-ligand axes of the remaining groups. As far as changes in the π bonding to the remaining ligands is concerned, both equatorial and axial substitution of CO by phosphorus is expected to strengthen the π component of the bonds to an equal extent.

These arguments explaining the observed preference for the axial position by a ligand which is a stronger donor and weaker acceptor than CO can be summarized as follows: Equatorial substitution is expected to weaken the σ bonds to the remaining equatorial groups due to the increased demand for the s-character of the metal orbitals and due to the increased electron density along the equatorial metal-ligand axes specifically. Neither of these effects are expected to be nearly as great for axial substitution. Thus a more stable molecule results when the stronger donor-weaker acceptor is in the axial position.

SECTION B. DERIVATIVES OF BIDENTATE LIGANDS

In similar reactions to those used in the preparation of the derivatives of the monodentate ligands, di- and tetrasubstituted complexes were prepared containing one and two bidentate donor ligands respectively. Trisubstituted complexes were also prepared containing two ligand molecules in which one ligand is ~~not~~ acting as a bidentate ligand, but is "dangling". The ligands used were bis-(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)-ethane and their arsenic analogues. These ligands are listed in Table II-B-1 along with their corresponding formulas and abbreviations.

TABLE II-B-1

BIDENTATE PHOSPHINE AND ARSINE LIGANDS

Ligand	Abbreviation[a]
bis(diphenylphosphino)methane $Ph_2PCH_2PPh_2$	dpm
bis(diphenylarsino)methane $Ph_2AsCH_2AsPh_2$	dam
bis(diphenylphosphino)ethane $Ph_2PCH_2CH_2PPh_2$	dpe
bis(diphenylarsino)ethane $Ph_2AsCH_2CH_2AsPh_2$	dae

[a] Abbreviations used are those introduced by McAuliffe.[80]

As with the monodentate ligands, it was again found that disubstitution readily occurred in refluxing n-hexane, but that higher boiling solvents were necessary for the preparation of the tetrasubstituted complexes. Several disubstituted derivatives of both $(Ph_2C_2)Co_2(CO)_6$ and $((t\text{-}C_4H_9)_2C_2)Co_2(CO)_6$ were prepared. The reactions proceeded very rapidly and appeared to be complete in less than one hour, although longer reaction times were usually allowed. The complexes are all deeply coloured, red or green crystalline solids and are quite air stable, even in solution. They were found to be soluble in all common organic solvents, but in contrast to the monodentate derivatives, they are sufficiently insoluble in the saturated hydrocarbon solvents to permit recrystallization from hexane or pentane at room temperature.

Tetrasubstituted derivatives containing two ligand molecules were prepared in refluxing benzene or methylcyclohexane, although the higher boiling methylcyclohexane was used more often in order to decrease reaction times. Derivatives were prepared of three different acetylenic complexes. These are: $(Ph_2C_2)Co_2(CO)_6$, $((C_2H_5)_2C_2)Co_2(CO)_6$ and $((CF_3)_2C_2)Co_2(CO)_6$. Attempts to prepare tetrasubstituted derivatives of $((t\text{-}C_4H_9)_2C_2)Co_2(CO)_6$ were unsuccessful, as were attempts to prepare tetrasubstituted complexes of any of these four acetylenic derivatives with bis(diphenylarsino)ethane.

The tetrasubstituted complexes are all very air-stable and are almost completely insoluble in solvents such as hexane and pentane. However, they are soluble in the aromatic hydrocarbons such as benzene and toluene, and in dichloromethane. Mixtures of CH_2Cl_2 and hexane were generally used for crystallization, and in some cases the complexes have one associated CH_2Cl_2 molecule for each complex molecule in the crystalline state.

The di- and tetrasubstituted complexes which have been prepared are listed in Tables II-B-2 and II-B-3 respectively, along with their characteristic colours and melting points. Complete details of the synthesis of each compound are given in Section C of Chapter IV. The complexes were identified by their elemental analyses and/or by their characteristic patterns of CO stretching bands in the infrared spectra. The results of the elemental analyses are given in Tables II-B-4 and II-B-5. No tetrasubstituted derivatives have previously been reported, but the disubstituted complexes containing diphenylacetylene and the dpm and dam ligands were found to be identical to those reported by Fukumoto et al.[119] As discussed in Chapter I-D, Fukumoto used a different preparative route.

TABLE II-B-2

DISUBSTITUTED DERIVATIVES OF ACETYLENIC DICOBALT-HEXACARBONYL COMPLEXES CONTAINING BIDENTATE LIGANDS

Acetylene	Bidentate Ligand	Colour	Melting Point
Ph_2C_2	dpm	Dark red crystals	200°(dec.)
Ph_2C_2	dam	Dark red crystals	166°-168°
Ph_2C_2	dpe	Dark red crystals	178°-182°
Ph_2C_2	dae	Dark red crystals	179°-184°
$(t\text{-}C_4H_9)_2C_2$	dpm	Dark green crystals	-
$(t\text{-}C_4H_9)_2C_2$	dam	Dark red crystals	190°-193°

TABLE II-B-3

TETRASUBSTITUTED DERIVATIVES OF ACETYLENIC DICOBALTHEXACARBONYL COMPLEXES CONTAINING BIDENTATE LIGANDS

Acetylene	Bidentate Ligand	Colour	Melting Point
Ph_2C_2	dpm	Red-brown crystals	254°(dec.)
Ph_2C_2	dam	Red-brown crystals	192°-193°
Ph_2C_2	dpe	Black crystals	200°
$(C_2H_5)_2C_2$	dpm	Dark red crystals	270°
$(C_2H_5)_2C_2$	dam	Dark red crystals	210°-212°
$(CF_3)_2C_2$	dpm	Orange-red powder	200°
$(CF_3)_2C_2$	dam	Orange-red powder	290°-295°
$(CF_3)_2C_2$	dpe	Dark red crystals	-

TABLE II-B-4

ELEMENTAL ANALYSES OF DISUBSTITUTED DERIVATIVES

Complex		Analysis (%)			
		C	H	Co	P
$(Ph_2C_2)Co_2(CO)_4(dpm)$	Found	65.2	4.2	14.7	7.8
	Calc.	65.2	4.0	14.9	7.8
$(Ph_2C_2)Co_2(CO)_4(dpe)$	Found	65.3	4.3	14.4	7.5
	Calc.	65.5	4.2	14.6	7.7

TABLE II-B-5

ELEMENTAL ANALYSES OF TETRASUBSTITUTED DERIVATIVES

Complex		Analysis (%)				
		C	H	Co	F	P
$(Ph_2C_2)Co_2(CO)_2(dpm)_2 \cdot CH_2Cl_2$	Found	66.4	4.9	9.5	-	10.2
	Calc.	66.7	4.7	9.6	-	10.3
$(Ph_2C_2)Co_2(CO)_2(dam)_2 \cdot CH_2Cl_2$	Found	58.3	4.2	-	-	-
	Calc.	58.2	4.1	-	-	-
$(Ph_2C_2)Co_2(CO)_2(dpe)_2$	Found	70.1	5.1	10.2	-	10.6
	Calc.	71.1	5.1	10.3	-	10.8
$((CF_3)_2C_2)Co_2(CO)_2(dam)_2$	Found	52.6	3.3	-	8.4	-
	Calc.	52.5	3.4	-	8.9	-
$((C_2H_5)_2C_2)Co_2(CO)_2(dpm)_2$	Found	67.2	5.4	11.5	-	-
	Calc.	68.0	5.3	11.0	-	-

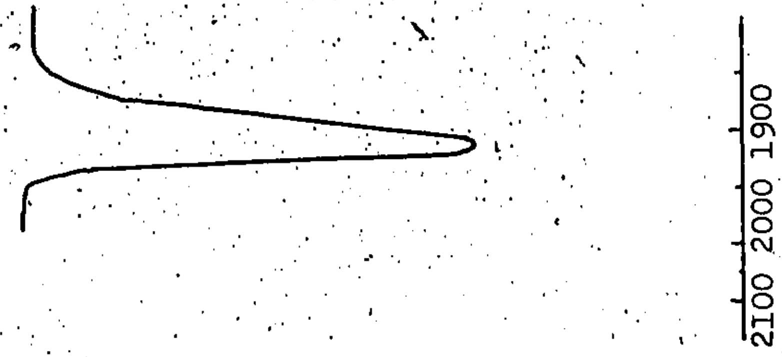
Typical infrared spectra in the CO stretching region are illustrated in Figure II-B-1. The spectra shown are those of $(Ph_2C_2)Co_2(CO)_4(dpm)$, $(Ph_2C_2)Co_2(CO)_2(dpm)_2$ and $(Ph_2C_2)Co_2(CO)_2(dpe)_2$, along with that of the parent unsubstituted complex for comparison. The CO stretching frequencies of all of the complexes studied are listed in Table II-B-6. The disubstituted derivatives have three well-separated, very strong bands, and then a weaker band at lower frequencies. The tetrasubstituted dpm and dam derivatives have a single strong absorption around 1920 cm^{-1} which is quite broad, but in the dpe derivatives this band is partially resolved into two peaks. The expected shift of the bands on increasing the degree of substitution is also observed.

Although almost identical intensity patterns of the CO stretching bands were found in all similarly substituted complexes, the frequencies of these bands were found to depend on which acetylene ligand was present in the molecule. In the disubstituted derivatives the frequencies were found to be lower in the ditertiarybutylacetylene complexes than in the diphenylacetylene complexes. In the tetrasubstituted complexes the frequencies were found to decrease in the following order:

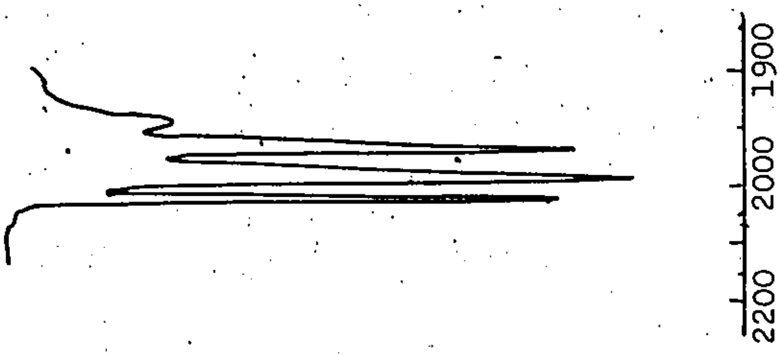
$$(CF_3)_2C_2 > Ph_2C_2 > (C_2H_5)_2C_2$$

Figure II-B-1. Infrared spectra in the CO stretching region of substituted derivatives of $(Ph_2C_2)Co_2(CO)_6$ containing bidentate ligands. Spectra were recorded as solutions in CH_2Cl_2 or C_2Cl_4.

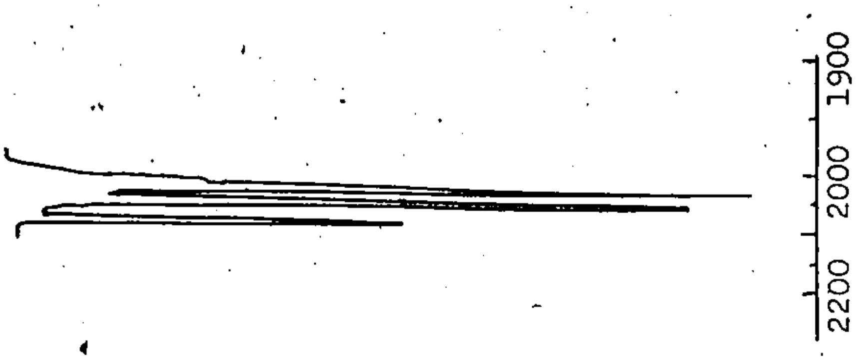
$-(CO)_2(dpe)_2$



$-(CO)_2(dpm)_2$



$-(CO)_4(dpm)$



$-(CO)_6$

TABLE II-B-6

CO STRETCHING FREQUENCIES IN COMPLEXES OF BIDENTATE LIGANDS

Acetylene	Bidentate Ligand	Band Frequencies (cm^{-1})
A. Disubstituted Complexes [a]		
Ph_2C_2	dpm	2033(s) 2000(s) 1975(s)
Ph_2C_2	dam	2028(s) 1998(s) 1971(s) 1950(w,sh)
Ph_2C_2	dpe	2035(s) 1997(s) 1977(s) 1955(m,sh)
Ph_2C_2	dae	2030(vs) 1994(vs) 1970(vs) 1945(s)
$(t\text{-}C_4H_9)_2C_2$	dpm	2010(vs) 1987(vs) 1956(vs) 1943(s)
$(t\text{-}C_4H_9)_2C_2$	dam	2012(vs) 1984(vs) 1955(vs) 1941(s)
B. Tetrasubstituted Complexes [b]		
Ph_2C_2	dpm	1918(s, br)
Ph_2C_2	dam	1920(s, br)
Ph_2C_2	dpe	1922(s) 1900(s)
$(CF_3)_2C_2$	dpm	1948(s)
$(CF_3)_2C_2$	dam	1945(s)
$(CF_3)_2C_2$	dpe	1952(s) 1930(s)
$(C_2H_5)_2C_2$	dpm	1895(s, br)
$(C_2H_5)_2C_2$	dam	1899(s, br)

---

[a] Spectra were recorded in solution in C_2Cl_4 or CS_2. For complete details see Chapter IV.

[b] Spectra were recorded in solution in CH_2Cl_2. For complete details see Chapter IV.

In both cases the order of frequencies parallels the decreasing electronegativity of the R groups on the acetylene.

Similar correlations between the electronegativity of the R group substituent on the acetylene and the CO stretching frequencies in the unsubstituted complexes have been reported by Cetini et al.,[50] and by Dickson and Yawney[109] for a large series of alkyne ligands. Carty[46] has also reported a related correlation between the CO stretching frequencies and the electronegativity of the substituents attached to the phosphorus atom in a series of acetylenic dicobalthexacarbonyl complexes of phosphinoacetylenes of the type $R_2PC{\equiv}CR'$.

These correlations are considered to be due to differences in the π-acceptor ability of the ligands.[46,50] Thus a very electronegative substituent attached to the acetylenic moiety facilitates the back-donation of electrons from the metal atom by lowering the energy of the acetylene π^* antibonding orbitals. This results in a reduced back-donation to the CO groups and thereby increases the CO bond order and the corresponding stretching frequency.

However, Dickson and Yawney[109] have pointed out that this type of argument ignores the changes in the donor ability of the alkyne ligands. A similar situation was discussed in Section A of this chapter in relation to the reported correlations between the CO stretching frequencies in phosphine substituted metal carbonyls and the electronegativity of the groups attached to the phosphorus atom. Increasing the electronegativity of the R groups on the acetylene should also decrease the σ-donor ability of the ligand. This should increase the CO stretching frequencies, thus paralleling the effect of the increased π-acceptor ability. It has therefore been suggested that the order established in these correlations can only reflect trends in the overall synergic donor-acceptor properties of the ligands.[85, 109]

Many transition metal complexes of these bidentate ligands have been reported in the literature and for recent comprehensive reviews the reader is referred to those by McAuliffe <u>et al</u>.[80, 81] The most common ligand in this group is $Ph_2PCH_2CH_2PPh_2$ and it has been observed that it can act both as a bidentate chelating ligand in which both ends are coordinated to the same metal atom, or as a bridging group between two metal atoms. Complexes containing the methane derivatives of these ligands are less common and prior to the studies in this laboratory, no example had been observed in which this type of ligand was involved in a bridge between two metal-metal bonded atoms. In addition, both the methane and ethane derivatives have been observed to exhibit monodentate behaviour. [138-143]

The structural nature of the complexes prepared here was of considerable interest since either chelating or bridged bonding is possible. The disubstituted derivative of dicobaltoctacarbonyl containing the ffars ligand, $Co_2(CO)_6$(ffars), was described in Chapter I, and it has been shown by X-ray crystallography to have a Co-Co bridged structure. [117, 118] Reaction of this type of complex with acetylenes gives complexes similar to those prepared here, but the tetrasubstituted derivatives of the type $Co_2(CO)_4(dpm)_2$ reportedly have both ends of the phosphine ligand bonded to the same cobalt atom. [144] However, reaction of these with acetylenes was attempted here without success, and therefore the bridging structure for both the di- and tetrasubstituted acetylenic complexes was expected.

The X-ray crystal structure determinations on both a disubstituted and a tetrasubstituted derivative have been carried out by other workers in this laboratory confirming the bridging structure. Figure II-B-2 illustrates the structure of the disubstituted complex, $(Ph_2C_2)Co_2(CO)_4$-(dpm), while the tetrasubstituted complex, $(Ph_2C_2)Co_2(CO)_2$- is shown in Figure II-B-3. Several features are noteworthy. In the disubstituted complex, the five-membered ring formed

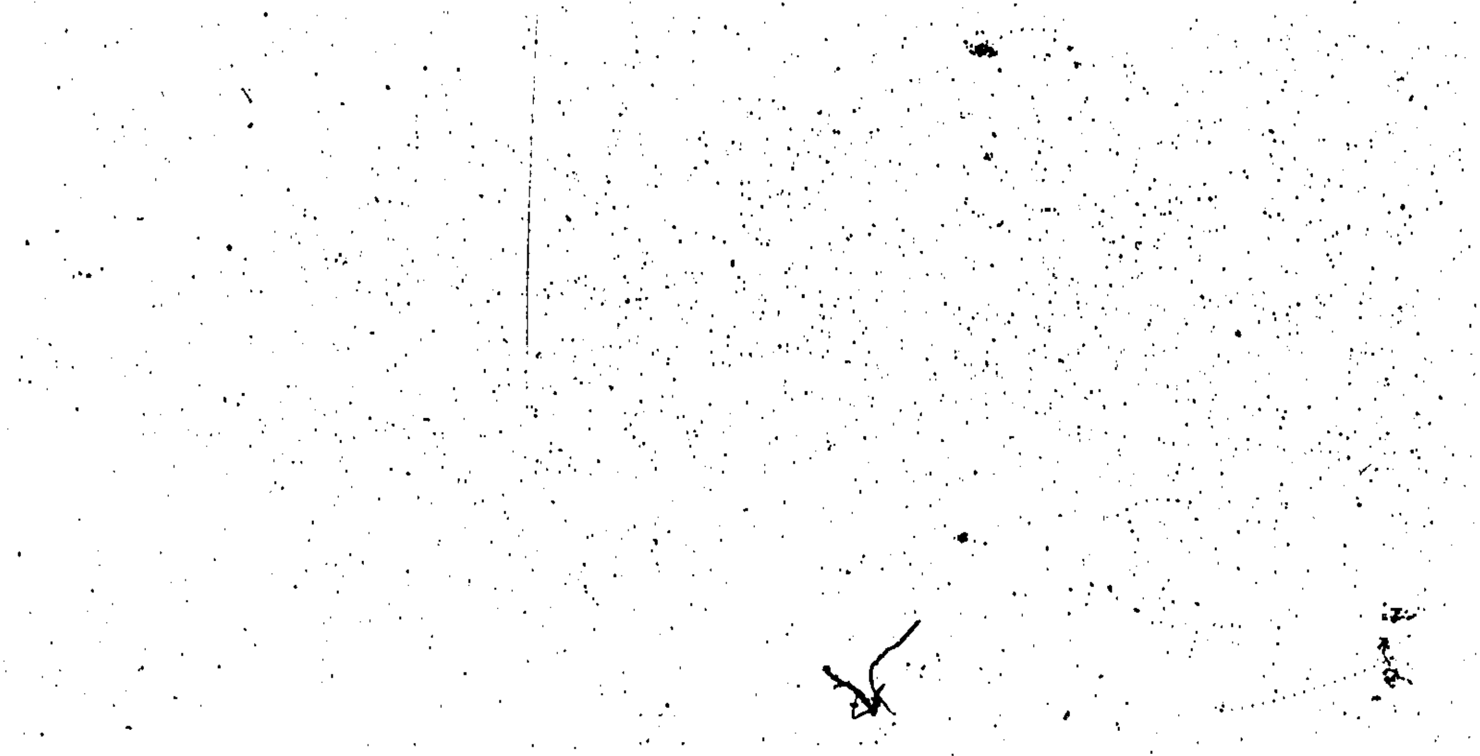


Figure II-B-2. Crystal structure of $(Ph_2C_2)Co_2(CO)_4(dpm)$ as taken from ref. 1.

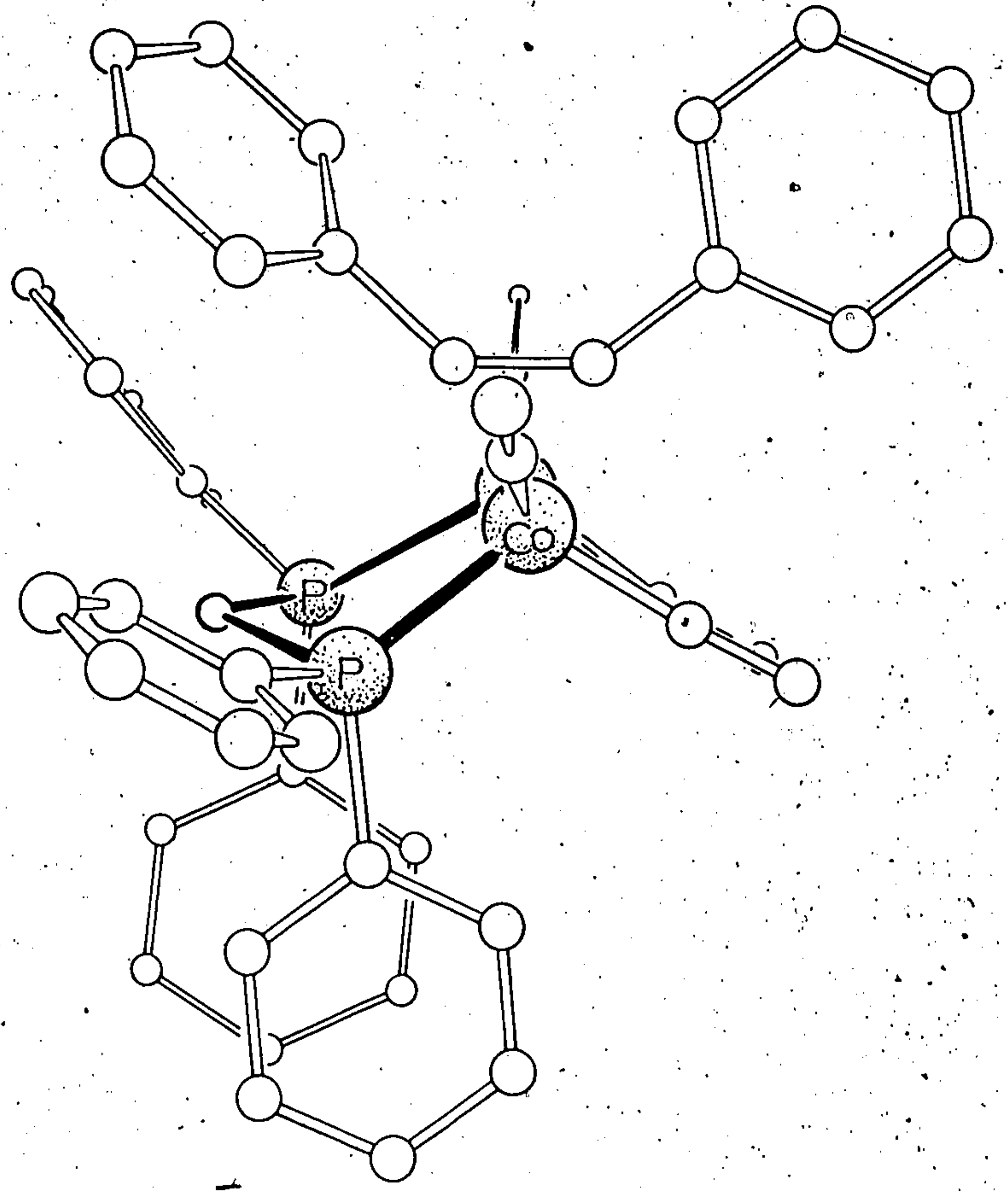
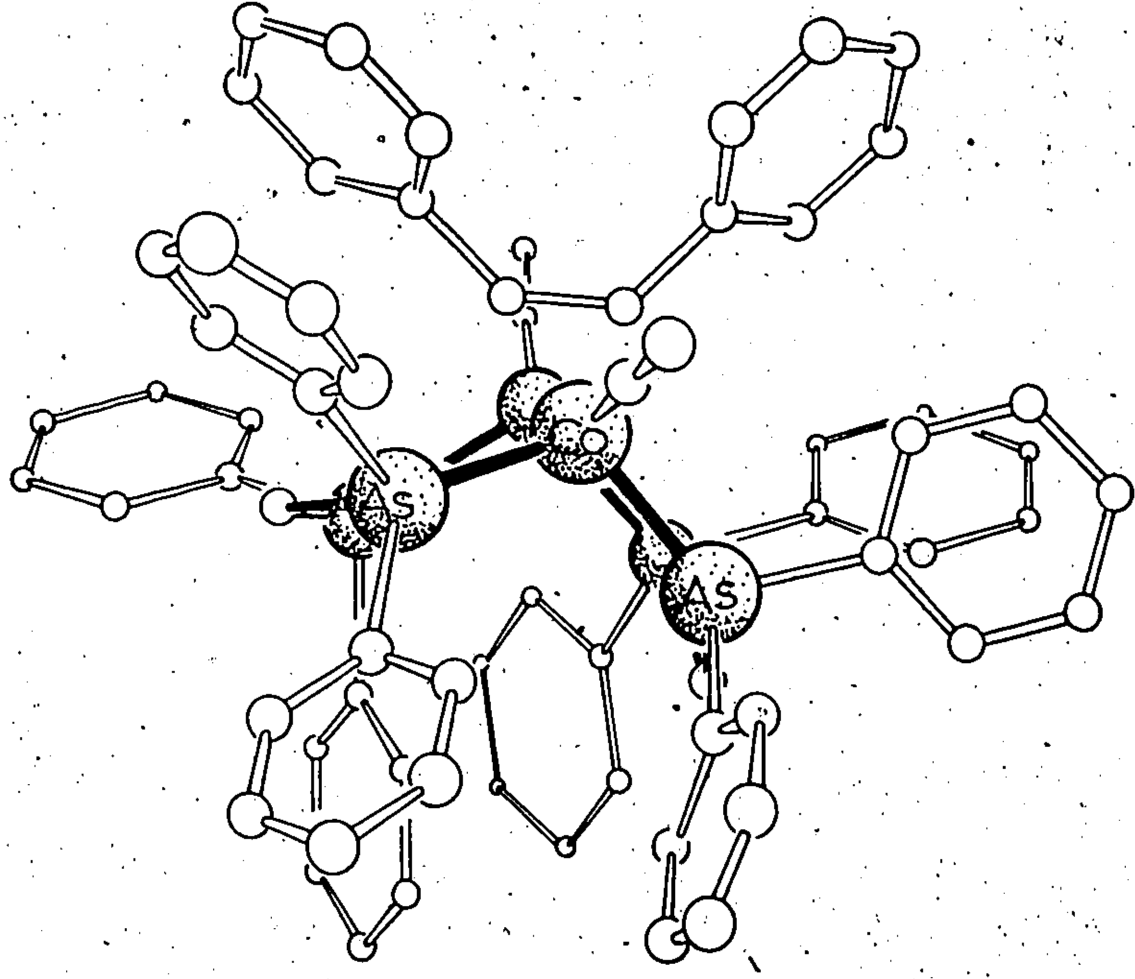

P
P
Co

Figure II-B-3. Crystal structure of $(Ph_2C_2)Co_2(CO)_2(dam)_2$ as taken from ref. 1.


As
As

by the ligand atoms and the two cobalt atoms is not planar, but is bent up towards the diphenylacetylene ligand. It has been suggested that this may be the result of possible interactions with the adjacent CO ligands, or as result of an artifact of the ligand itself. [1] Although it is not discernible in the view of the molecule shown here, it is also found that this five-membered ring is twisted in that a line joining the two phosphorus atoms is not parallel to the Co-Co axis.

In the tetrasubstituted complex containing the corresponding arsine ligand, it is found that one of the five-membered rings has the same configuration as that in the disubstituted phosphine complex, but that the second ring points down from the acetylenic moiety, and is not twisted. In both cases it can be seen that the ligands are in the equatorial positions, and that the axial positions are unsubstituted. In the complexes of the monodentate ligands a preference for the axial position was observed, but with the bidentate ligands a bridge between the two axial positions is impossible because of the presence of the acetylene ligand on this side of the molecule. The similarity in the properties of the other analogous complexes indicates that they all have the same bridged structure.

In addition to the di- and tetrasubstituted derivatives, a third type of complex has been isolated in which two ligand molecules are present but in which only three CO groups have been replaced. These were found to be trisubstituted complexes in which one of the ligands is acting as a bridging bidentate group and the other is acting as a monodentate ligand, or is "dangling".

The preparation of derivatives of this type was accomplished by reaction of the diphenylacetylene complex with two moles of ligand. When this reaction was carried out in hexane or cyclohexane, a wine-red colour rapidly appeared corresponding to the formation of the disubstituted form, and then further reaction occurred more slowly resulting in the precipitation of a grey-green powder. If the reaction was carried out in a solvent in which this grey-green powder was soluble such as benzene, only the tetrasubstituted complex resulted. With other acetylene ligands these trisubstituted derivatives could not be isolated, presumably due to a higher solubility in the solvents used.

The complexes which have been prepared are listed in Table II-B-7 along with pertinent physical and chemical data. It was difficult to obtain these derivatives in any high degree of purity because of disproportionation to form the disubstituted complexes, or further reaction

TABLE II-B-7

TRISUBSTITUTED DERIVATIVES OF DIPHENYLACETYLENE DICOBALT-HEXACARBONYL CONTAINING BIDENTATE LIGANDS

A. $(Ph_2C_2)Co_2(CO)_3(dpm)_2$

Melting Point: 245° (dec.)

CO Stretching Bands: 1990(s), 1943(s), 1902(w, sh) cm^{-1}

Analysis:	C	H	Co	P
% Found:	69.5	4.9	9.8	10.4
% Calc.:	69.4	4.6	10.0	10.5

B. $(Ph_2C_2)Co_2(CO)_3(dam)_2$

Melting Point: 177°-178°

CO Stretching Bands: 1991(s), 1943(s) cm^{-1}

Analysis:	C	H
% Found	60.3	4.1
% Calc.:	60.7	4.1

---

to form the tetrasubstituted variety. Elemental analyses indicated that two ligand molecules were present, but due to the difficulties in purification these data were not sufficiently precise to allow any conclusions to be drawn as to the number of CO groups which had been replaced.

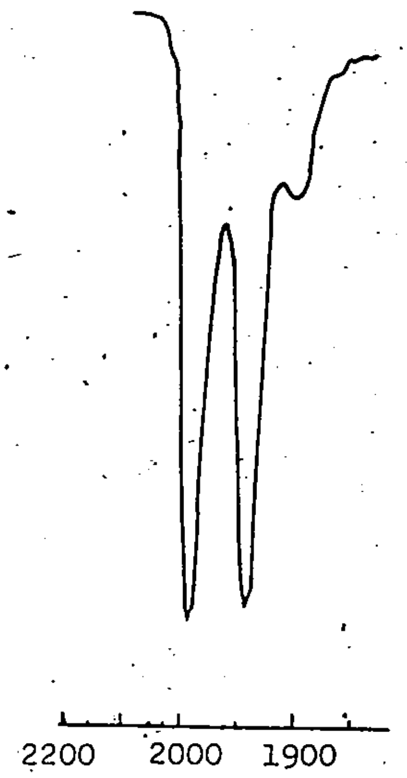
Further experiments indicated that these complexes were intermediates in the formation of the tetrasubstituted derivatives from the disubstituted derivatives. Reaction of the ligand with the hexacarbonyl complex in a 1:1 mole ratio was shown above to result in rapid formation of the disubstituted derivative. When a sample of this disubstituted product was dissolved in n-hexane and reacted with a further mole of the ligand the grey-green solid was formed, but if benzene was used only the tetrasubstituted derivative resulted. Furthermore, if the grey-green solid was dissolved in benzene and the solution refluxed for several hours, the tetrasubstituted derivative again resulted.

Two possibilities must be considered for the nature of such an intermediate. One is that the complexes have a structure which is analogous to a disubstituted complex and have two "dangling" ligands. However, it does not seem likely that such a complex would form from one in which both ends of a bidentate ligand were already coordinated. It is therefore concluded that these intermediate complexes are trisubstituted derivatives in which one ligand is coordinated at both ends and is bridging the two cobalt atoms, and the other ligand is coordinated at one end only, or is "dangling".

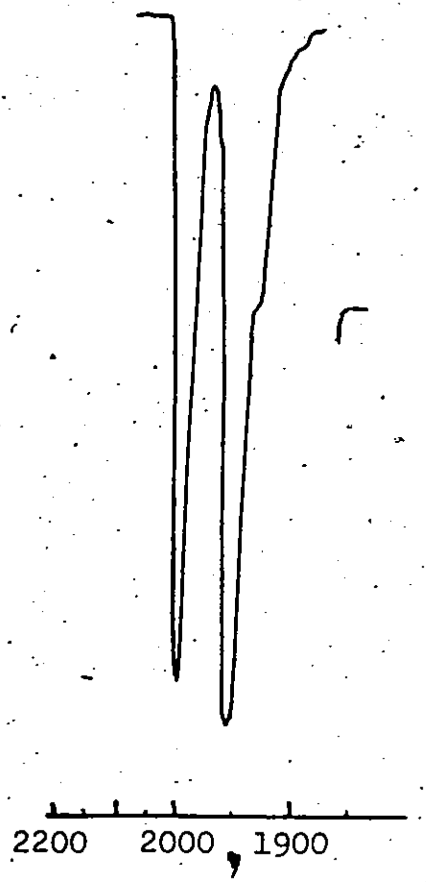
Figure II-B-4 illustrates a typical infrared spectrum in the CO stretching region along with those of the disubstituted PPh_3 complex and the trisubstituted $P(OCH_3)_3$ complex for comparison. As discussed in the previous section, a shift in the CO stretching frequencies is observed as the degree of CO substitution increases characteristic patterns occur. Therefore, if the complexes in question here are disubstituted with both ligands coordinated at one end only, their spectra in this region should closely resemble that of the disubstituted PPh_3 complex. The patterns are seen to be similar, but in the bidentate complexes the frequencies are much lower. The spectra much more closely resemble that of the trisubstituted $P(OCH_3)_3$ derivative and this is a further indication that these intermediate complexes are trisubstituted.

Several examples of such complexes containing "dangling" ligands have been reported in the literature. Basolo and co-workers [139-141] have found that the product of the reaction of dpe with $Fe(NO)_2(CO)_2$ is a complex of the formula $Fe(NO)_2(CO)(dpe)$ in which only one end of the bidentate ligand is coordinated. Closure of the ring

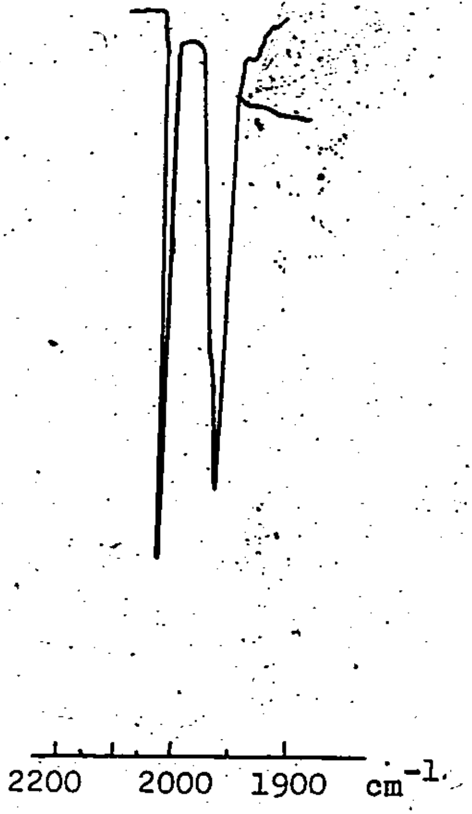
Figure II-B-4. Infrared spectra in the CO stretching region of $(Ph_2C_2)Co_2(CO)_3(dpm)_2$ and those of di- and trisubstituted monodentate derivatives for comparison.



$(Ph_2C_2)Co_2(CO)_3(dpm)_2$



$(Ph_2C_2)Co_2(CO)_3(P(OCH_3)_3)_3$



$(Ph_2C_2)Co_2(CO)_4(PPh_3)_2$

to form Fe(NO)$_2$(dpe) occurs on heating the complex in solution. Similar results have been found with the Co(NO)$_3$(CO) system.[141] X-ray crystallography has shown that in the seven-coordinate molybdenum complex, Mo(CO)$_2$-(dpm)$_2$Br$_2$, one of the dpm ligands is coordinated at both ends, but that the other is "dangling".[142, 143] In the analogous tungsten complex, W(CO)$_3$(dpm)$_2$Br$_2$, both dpm ligands are coordinated at one site only.[143] A further example which is more closely related to the complexes prepared here has been mentioned in Chapter I. This is the complex (Ph$_2$C$_2$)Co$_2$(CO)$_5$(ffars) in which only one end of the ffars ligand is bonded to a cobalt atom.[118] Heating this complex in solution causes further displacement of CO resulting in a Co-Co bridged species.

SECTION C. THE PREPARATION OF TRIFLUOROPHOSPHINE DERIVATIVES AND OTHER MISCELLANEOUS REACTIONS

This sections presents the results of several other reactions which were attempted but which were not successful in that the desired products were not obtained. These include a description of the preparation of some trifluorophosphine cobalt carbonyl derivatives and of some attempts to prepare a fully substituted acetylenic dicobalt derivative by direct substitution. Complete details of all the reactions described are given in Section 4 of Chapter IV.

Attempts to prepare a series of substituted acetylenic dicobalthexacarbonyl derivatives containing PF_3 were not successful, although some derivatives were isolated. In some metal-carbonyl systems it has been found that complete substitution of the CO groups by a phosphorus donor ligand can only be accomplished with PF_3, and that the PF_3 substituted derivatives are often much more stable than the corresponding unsubstituted metal complexes.[127] However, this was not found to be the case here. In those instances where substituted derivatives have been prepared, they are found to be somewhat less stable than the parent unsubstituted complexes.

Direct reaction of trifluorophosphine with the diphenylacetylene complex was attempted first. The reaction was carried out in n-pentane solution under a high pressure of PF_3 at room temperature. The reaction time was two weeks and a green solution resulted from which a dark green crystalline solid was isolated. The infrared spectrum of this product indicated the presence of CO, PF_3 and Ph_2C_2, and the elemental analysis corresponded to that of a disubstituted derivative, $(Ph_2C_2)Co_2(CO)_4(PF_3)_2$. The use of slightly higher temperatures appeared to result in decomposition of the product. Since a reaction time of two weeks resulted only in this disubstituted product, this direct route was abandoned as a method of preparing further substituted derivatives.

It has been reported in the literature that substituted acetylenic complexes of the type under investigation here can be prepared by first reacting dicobaltoctacarbonyl with the phosphine ligand, and subsequently replacing two further CO groups with the acetylene ligand. This route has been used to synthesize $(Ph_2C_2)Co_2(CO)_4(P(n-C_4H_9)_3)_2$ from $Co_2(CO)_6(P(n-C_4H_9)_3)_2$.[116] Attempts were therefore made to prepare PF_3 derivatives by this route.

Treatment of $Co_2(CO)_8$ with 400 psi of PF_3 at -20° for eight days resulted in a substance which was a dark brown, volatile liquid at room temperature but was a bright yellow solid at liquid nitrogen temperatures. This product was extremely air sensitive, and at room temperature, even under a vacuum, appeared to decompose resulting in a brown insoluble solid. Further characterization of this substance was therefore quite difficult, but its infrared spectrum indicated the presence of both terminal and bridging CO groups, and the presence of PF_3. It was therefore concluded that this product was probably a mixture of species of the type $Co_2(CO)_{8-n}(PF_3)_n$.

A 2-3 ml portion of this brown liquid was treated with ditertiarybutylacetylene in n-pentane solution at 0° for several days under a vacuum. A dark brown solution resulted from which crystals were obtained by slow evacuation of the solvent at -90°. Chromatography of this product showed only one dark red band. Characterization of the substance through its elemental analysis and its infrared spectrum indicated that it was a disubstituted derivative with the formula $((t\text{-}C_4H_9)_2C_2)Co_2(CO)_4(PF_3)_2$. It is therefore analogous to the diphenylacetylene complex discussed above which was prepared by direct substitution.

Reaction of dicobaltoctacarbonyl with PF_3 under slightly more vigorous conditions resulted in a mixture of this brown liquid with a second substance which was also a brown liquid at room temperature, but was somewhat less volatile than the first and was an orange solid at lower temperatures. It was suspected that this was a more fully substituted derivative with $n = 3$ or $n = 4$. However, attempts to obtain an amount sufficient to carry out further reactions were unsuccessful.

The use of higher temperatures and higher PF_3 pressures also resulted primarily in these yellow and orange solids, but in addition, a pale yellow, clear volatile liquid was formed which had a sharp, choking odour. This product was identified as $HCo(PF_3)_3(CO)$ from its infrared spectrum. Its formation is due to the presence of small amounts of HF in the trifluorophosphine, as has been reported by Kruck.[127]

Attempts were made to react this hydride with ditertiarybutylacetylene under ultraviolet radiation. The reaction was carried out under an atmosphere of nitrogen gas, and resulted in the formation of a dark red oil. The infrared spectrum of this product showed the presence of PF_3, terminal and bridging carbonyl groups, and ditertiarybutylacetylene. The oil appeared to be a mixture of a dark red substance and a deep blue substance; but an attempt to separate these two by trap-to-trap distillation resulted in complete decomposition of the red product to the blue product. Due to this decomposition and the observation that bridging CO groups were present, it was concluded that the desired acetylenic derivative had not been formed. For these reasons no further work was carried out. This inability of the acetylenic dicobalthexacarbonyl complexes to form stable PF_3 substituted derivatives is thought to be due to electronic factors and is discussed more fully in Chapter III.

Several attempts to prepare a fully

substituted derivative with the organophosphorus ligands by direct methods were also unsuccessful. Reaction of $(Ph_2C_2)Co_2(CO)_6$ with a large excess of trimethylphosphite in refluxing methylcyclohexane for several days gave only the tetrasubstituted derivative. Use of the slightly higher boiling solvent, toluene, led only to decomposition. Attempts were also made to substitute the two remaining CO groups in $(Ph_2C_2)Co_2(CO)_2(dpm)_2$ with monodentate ligands such as tri-n-butylphosphine and trimethylphosphite, but no significant results were obtained.

Another unsuccessful series of reactions resulted when attempts were made to prepare a substituted series of complexes of the ditertiarybutylacetylenehexacarbonyldicobalt complex. This complex was found to behave quite differently than the diphenylacetylene complex and other complexes which were investigated in that treatment with $P(n-C_4H_9)_3$ and PPh_3 led to decomposition of the metal-acetylene linkage. With tri-n-butylphosphine a monosubstituted derivative resulted, but one product of the reaction was identified as $Co_2(CO)_6(P(n-C_4H_9)_3)_2$ indicating that further substitution probably results in decomposition. With PPh_3 an insoluble solid was formed which could not be characterized. When the corresponding phosphite ligands were used, disubstituted derivatives were detected .

These observations suggest that perhaps

electronic factors are playing a part in this exceptional behaviour. It should also be mentioned that with other acetylenic derivatives tetrasubstituted complexes could readily be prepared with the bidentate ligands, but that only disubstituted complexes could be obtained with the ditertiarybutylacetylene complex. Possible reasons for this behaviour are discussed more fully in Chapter III.

CHAPTER III. GENERAL DISCUSSION.

On the basis of the results reported here several suggestions can be made to explain certain aspects of the behaviour of these acetylenic complexes. These center mainly on electronic factors, but it has been found that it is necessary to consider steric factors as well.

It was qualitatively observed that further displacement of CO became more difficult as the extent of substitution by a phosphorus-type ligand increased. For example, with the monodentate ligands mono- and disubstitution could be effected in refluxing n-hexane, but further substitution required the use of a higher boiling solvent. A similar observation occurred with the reactions of the bidentate ligands. It was also found that substitution beyond four CO groups could not be carried out.

Correlations of this type have been discussed in Chapter 1. In summary, it is expected that this effect is due to the increase in the electron density on the metal atom which accompanies the substitution of CO in a complex by a ligand which is a stronger donor and a weaker acceptor than the carbonyl group. This causes an increase in the metal-ligand back-bonding to the remaining CO groups, and presumably strengthens the metal-CO bond. Further substitution is therefore more difficult.[84, 87]

One system which has been studied quantitatively, and has been found to support this hypothesis, is the reaction of $Co(NO)(CO)_3$ with monodentate phosphine and phosphite ligands.[139-141] Kinetic studies on these reactions have shown that the rate of substitution by a ligand L,

$$Co(NO)(CO)_3 + L \longrightarrow Co(NO)(CO)_2L + CO \qquad \text{(III-1)}$$

proceeds at a much faster rate than further substitution by the same ligand,

$$Co(NO)(CO)_2L + L \longrightarrow Co(NO)(CO)L_2 + CO \qquad \text{(III-2)}$$

It has also been found that substitution of the second carbonyl group (equation III-2) proceeds at a faster rate when the ligand L present in the complex has a weak net charge-donating capacity and can therefore lessen the degree of metal-CO back-bonding. This occurs in spite of the fact that an associative mechanism is operating which should cause the rate to increase with increasing basicity of the incoming donor atom, as is observed in the first step.[139]

Although these observations indicate that electronic factors are important, these same studies have shown that the reaction rates also depend on the bulkiness of the L ligand. This indicates that steric factors are also playing a part and that the slower rate of the second substitution may not be due to electronic factors alone.

Basato and Poe have reported a similar observation from a study of the reaction of the diphenylacetylenehexacarbonyldicobalt complex with $P(n\text{-}C_4H_9)_3$.[116] Although this system is somewhat more complex kinetically than the one discussed above since simultaneous dissociative and associative mechanisms are operating, it was again found that the substitution of the second CO group occurs at a slower rate than formation of the monosubstituted complex. Since the CO groups involved are not both bonded to the same cobalt atom steric factors would not be expected to be important in this case. The difference in the rates must therefore be due mainly to electronic factors, namely the increase in metal-CO back-bonding.

For substitution beyond two carbonyl groups in these complexes, steric effects might be expected to be of greater importance since one phosphorus ligand is already present on each cobalt atom. The observation that tetrasubstituted derivatives could be prepared with $P(OCH_3)_3$ and $P(OC_2H_5)_3$, but not with the more bulky $P(O\text{-}i\text{-}C_3H_7)_3$ and $P(OPh)_3$, bears this out. However, electronic factors are evidently also important since it was observed that substitution beyond two CO groups could be obtained with the phosphite ligands, $P(O\text{-}n\text{-}C_4H_9)_3$ and $P(OPh)_3$, but not with the corresponding phosphines, $P(n\text{-}C_4H_9)_3$ and PPh_3, which are stronger donors and weaker acceptors.

Consideration of these electronic and steric factors allow certain suggestions to be made concerning methods which might lead to a fully substituted derivative by the direct methods used in this work. Since both the electron acceptor ability and the bulkiness of the ligand appear to be important, it is suggested that the use of the bicyclic ligand, $P(OCH_2)_3CCH_3$, might allow further substitution than has been observed. The reactions of this ligand have been studied extensively by Verkade et al.[145] and by Tolman.[146, 147] On the basis of its effects on the CO stretching frequencies in the complexes the ligand is considered to have a better acceptor ability than $P(OCH_3)_3$, and from cone angle calculations it is expected to be the most sterically favourable ligand available with the exception of PH_3.[145, 147] These factors have been substantiated by kinetic studies. It is therefore suggested that with such favourable conditions a fully substituted acetylenic dicobalthexacarbonyl complex might be prepared.

A further factor in the ability of these complexes to undergo CO substitution might be the electron acceptor ability of the acetylene ligand. As discussed in Chapter I, the electron withdrawing capacity of the R groups attached to the acetylene has an effect on the CO stretching frequencies in these complexes, and this should also affect the metal-CO bond strengths. Therefore the use of an acetylene in which the R groups have a greater electron withdrawing capacity than those used in this work might also facilitate the preparation of a fully substituted derivative, provided that steric factors are not dominant. On the basis of the reported CO stretching frequencies and relative stabilities of the acetylenic dicobalthexacarbonyls, two acetylenic derivatives which are better electron acceptors than those used in the work reported here are $N{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}N$ [50, 109] and $(C_6F_5)_2C_2$. [35]

It might also be possible to synthesize a fully substituted derivative by an indirect route involving mononuclear trialkylphosphite cobalt complexes of the type $XCo(P(OR)_3)_4$. Several reports have been published of the reactions of the CO analogues of these species with acetylenes and it has been found that acetylenic dicobalthexacarbonyls have resulted. For example, Peyronel and co-workers [107] have prepared $(HC{\equiv}CH)Co_2(CO)_6$ by passing $HC{\equiv}CH$ through a solution of $Hg(Co(CO)_4)_2$ while irradiating the solution with ultraviolet light. Several derivatives of more complex acetylenes have also been obtained in a similar manner.[148] A further example has been reported by Iwashita et al.[34] in which generation of $HCo(CO)_4$ from $Co(DMF)_6(Co(CO)_4)_2$ and HCl in the presence of HC≡CH and PPh_3 resulted in the formation of substituted acetylenic dicobalthexacarbonyls.

The preparation of $KCo(P(OR)_3)_4$, $HCo(P(OR)_3)_4$ and $Hg(Co(P(OR)_3)_4)_2$ derivatives has recently been reported[149-150] and it is suggested that the reaction of these with acetylenes might result in the desired fully substituted dicobalt complex. A further possibility would be to react acetylenes with the $Co_2(P(OR)_3)_8$ derivatives recently reported by Muetterties and Hirsehorn.[150]

The lack of success in obtaining substituted derivatives of the ditertiarybutylacetylene complex, and in preparing stable PF_3 substituted complexes, can also be attributed to electronic factors. It is expected that, due to the inductive effect of the t-butyl groups, ditertiarybutylacetylene would have a very poor acceptor ability and would therefore not be particularly effective in removing excess electron density from the metal atoms. This is borne out by the observed values of the CO stretching freque[illegible] in the dicobalthexacarbonyl complex. This would hinder the formation of phosphine substituted derivatives by both increasing the metal-CO bond strengths and reducing the stability of the resulting substituted complex, if formed. However, again steric factors cannot be completely ignored since it is possible that the bulky nature of the t-butyl groups combined with a small bend-back angle [112] may also be hindering the substitution reactions.

The peculiar behaviour of trifluorophosphine in its reactions with $Co_2(CO)_8$ and the acetylenic complexes can be explained on the basis of electronic factors since this ligand is atypical of the phosphorus donor ligands in that it is as good a π-acceptor as CO, or better. The chemistry of transition metal trifluorophosphine complexes has been reviewed by Kruck [127] and by Nixon [151] and it has been found that substitution of CO by PF_3 in a complex causes little or no change in the CO force constants of the remaining carbonyl groups. It is felt that this similarity of PF_3 to CO in its bonding capacity is due to the high electronegativity of the fluorine atoms which weakens the donor ability of the phosphorus atom and enhances the acceptor ability of its 3d orbitals by lowering their energy. [127, 151] This and the steric structure of the ligand account for its ability to form a wide variety of transition metal complexes for which corresponding CO complexes exist, some of which are even more stable than the parent unsubstituted complexes.

However, this strong acceptor ability of PF_3 has a negative effect on the binuclear cobalt carbonyls since it has been found that the presence of a stronger donor than CO is required to achieve increased stability. Thus $Co_2(CO)_8$ is an extremely air sensitive crystalline solid while the disubstituted complex, $Co_2(CO)_6(P(n\text{-}C_4H_9)_3)_2$, is quite air stable even in solution. [131] In the acetylenic dicobalthexacarbonyl complexes it has been reported that the organophosphine substituted derivatives are considerably more air stable than the parent hexacarbonyls . This has been used for the purification of acetylenic dicobaltcarbonyls when the unsubstituted complex was not sufficiently stable for an accurate microanalysis to be obtained. [33,36] In the work reported here it was observed that solutions of the diphenylacetylene complex deposited a white insoluble substance on standing in air, but that solutions of the disubstituted derivatives of the organophosphines and phosphites remained unchanged after several days in an open container.

It is possible that this increased stability is due to the presence of the stronger donor and weaker acceptor which increases the electron density on the metal atoms and thereby increases the back-bonding to the remaining π-acceptor groups in the complex. The resulting increase in the strength of the metal-CO bonds and the metal-acetylene bond would therefore be responsible for the increased stability of the complex. The PF_3 ligand would be unable to provide this increased stability due to its weak donor and strong acceptor properties and the PF_3 substituted complexes would therefore not be any more stable than the parent unsubstituted complex.

Finally, some comments must be made concerning the relationship proposed in Chapter I between the extent of CO substitution in these complexes and the degree of π back-bonding to the acetylene antibonding orbitals. In the work reported here it was observed that the band assigned to the C≡C stretching frequency shifted to lower frequencies on going from disubstitution to tetrasubstitution. This indicates that the phosphorus ligands are indeed increasing the back-bonding to the acetylene and causing a decrease in the C≡C bond order. Preparation of a fully substituted derivative is needed to provide further evidence of this correlation.

The effect of this increased back-bonding on the acetylene bend-back angle would have to be investigated by X-ray crystallography. Several crystal structures have been described briefly in this thesis, but the results of these concerning the bend-back angle are not conclusive since considerable distortions are present due to steric effects. A more systematic study is needed, and it is therefore suggested that the structures of the series of substituted derivatives of the monodentate ligands be determined, since the bidentate ligands might be complicating the factors which affect the bonding. Again, the structure of a fully substituted derivative would be necessary to provide solid evidence of the correlation.

CHAPTER IV. EXPERIMENTAL.

SECTION A. GENERAL EXPERIMENTAL DETAILS

All solution reactions involving non-gaseous reactants were carried out in an Erlenmeyer flask which had been modified with a sidearm and stopcock. A water-cooled reflux condenser was connected to the flask and an air-tight link was obtained by the use of a mercury bubbler. The reactants were generally weighed out into the flask directly and the solvent then added. The flask was then connected to the reflux condenser and the system was flushed with pre-dried nitrogen gas for two minutes via the sidearm. The reaction mixtures were stirred and heated by a magnetic stirrer/hotplate combination.

Reactions involving the gaseous reactants, PF_3 and $(CF_3)_2C_2$, were carried out in a Parr 71 ml stainless steel high pressure reaction vessel fitted with an appropriate pressure gauge. The vessel was lined with a removable glass liner and was connected to a vacuum line by adapters and rubber tubing. Solid reactants were weighed directly into the glass liner and the vessel was then sealed and evacuated. Where solvents were used, the vessel was first cooled to -196^{o} using liquid nitrogen, and then evacuated. This was subsequently repeated to ensure complete deaeration of the solvent. Gaseous reactants were condensed into the vessel from the vacuum line by cooling it to -196^{o}. Amounts were measured by weighing the gas supply cylinder.

Removal of carbon monoxide evolved during the course of a high pressure reaction was accomplished by cooling the reaction vessel with liquid nitrogen and then venting it to the vacuum line. Removal of excess gas at the end of a reaction was also accomplished via the vacuum line, passing the effluent through appropriate traps to collect any volatile products.

The chemicals and solvents used in all of the reactions reported here were obtained from the manufacturers listed in Table IV-A-1. They were used without further purification.

Column chromatography was carried out using silica gel powder (60-200 mesh) from the J.T. Baker Co. The chromatography columns used varied in diameter and length depending on the scale of the separation to be carried out. They were always packed wet.

TABLE IV-A-1

SOURCE OF CHEMICALS AND SOLVENTS

A. Chemicals

Bicyclo(2.2.1)-2,5-heptadiene	ChemSampCo
Bis(diphenylarsino)ethane	Alfa-Ventron
Bis(diphenylarsino)methane	Alfa-Ventron
Bis(diphenylphosphino)ethane	ROC/RIC
Bis(diphenylphosphino)methane	Alfa-Ventron
Cobalt(II) Iodide	Alfa-Ventron
Dicobaltoctacarbonyl (98%)	Alfa-Ventron
Diphenylacetylene	Eastman Kodak Co.
Di-t-butylacetylene	ChemSampCo
Diethylacetylene	ChemSampCo
Hexafluoro-2-butyne	TeroChem
Hydrogen Fluoride	Matheson
Tri-n-butylphosphine (pract.)	J.T. Baker
Tri-n-butylphosphite (pract.)	J.T. Baker
Triethylphosphine (pract.)	J.T. Baker
Triethylphosphite (pract.)	J.T. Baker
Trifluorophosphine	Strem Chemicals
Trimethylphosphite (pract.)	Eastman Kodak Co.
Triphenylphosphine	Alfa-Ventron
Triphenylphosphite	J.T. Baker
Tri-i-propylphosphite (pract.)	J.T. Baker

TABLE IV-A-1 (CONT'D)

B. Solvents

Benzene (reagent)	Fisher Scientific
Carbon Disulphide (spectranalyzed)	Fisher Scientific
Chloroform (N.F.)	Fisher Scientific
Cyclohexane (certified)	Fisher Scientific
Dichloromethane (certified)	Fisher Scientific
Diethylether (pract.)	Fisher Scientific
n-Hexane (certified)	Fisher Scientific
Methanol (absolute)	Fisher Scientific
Methylcyclohexane (pract.)	Eastman Kodak Co.
n-Pentane (pract)	Fisher Scientific
Tetrachloroethylene (reagent)	J.T. Baker
Toluene (reagent)	Fisher Scientific

Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee, USA.

Melting points were measured on a Gallenkamp melting point apparatus and were not corrected. A sample of the compound was crushed to a powder and packed in a capillary tube. The tube was subsequently flushed with nitrogen gas and sealed with putty.

Infrared spectra were recored on a Perkin-Elmer double beam grating infrared spectrometer (Model 457). Band frequencies are reported to ± 3 cm^{-1} unless otherwise specified. The spectra were calibrated using a polystyrene film at 2851.5 cm^{-1} and 1601.8 cm^{-1} [152] Abbreviations used in quoting band intensities are: vs: very strong; s: strong; m: medium; w: weak; vw: very weak; br: broad; sh: shoulder. All spectra were recorded in solution in 1.0 mm sodium chloride matched cells.

Reactions involving ultraviolet radiation were carried out using a Pen-Lite irradiation lamp. They were done in a tube about one inch in diameter to which the lamp was connected by a ground glass joint. The system could be flushed with nitrogen gas and vented with a mercury bubbler by its sidearm and stopcock. The reaction mixture was stirred with a magnetic stirrer.

The various acetylenic dicobalthexacarbonyl complexes which have been used have all been previously described in the literature. The syntheses used in the work reported here usually involved only slight modifications to the literature procedures, and, with the exception of the di-t-butylacetylene complex, the compounds were identified by comparing their infrared spectra with those which have been previously reported. The infrared spectrum of the di-t-butylacetylene derivative has not been published and therefore this complex was identified by its elemental analysis. Descriptions of the preparations of all four complexes are given below.

Diphenylacetylenehexacarbonyldicobalt was prepared by dissolving $Co_2(CO)_8$ (17.1 g, 0.050 moles) and Ph_2C_2 (8.9 g, 0.050 moles) in 100 ml of n-pentane and refluxing the solution under nitrogen gas for 24 hours with constant stirring. The resulting deep-red solution was filtered while still hot using a sintered glass funnel, and 150 ml of methanol was then added to the filtrate. This solution was concentrated <u>in vacuo</u> to a volume of 75 ml and cooled to -10° for 12 hours. Red crystals (8.2 g) were isolated by filtration and dried <u>in vacuo</u> for 12 hours. The product was identified by its infrared spectrum.[20,21]

Diethylacetylenehexacarbonyldicobalt was prepared by dissolving $Co_2(CO)_8$ (10.2 g, 0.030 moles) and diethylacetylene (2.5 g, 0.030 moles) in 50 ml of n-hexane and refluxing the solution under nitrogen gas for one hour with constant stirring. The reaction mixture was then cooled and filtered, and the solvent was evapourated from the filtrate in vacuo to yield a dark red oil. This product was dissolved in methanol and the solution cooled to -15° resulting in dark red crystals which were isolated by filtration. On warming to room temperature the product became a waxy solid. It was identified by its infrared spectrum.[20, 21]

The hexafluoro-2-butynehexacarbonyldicobalt complex was prepared in the Parr 71 ml high pressure reaction vessel. Dicobaltoctacarbonyl (3.5 g, 0.010 moles) was placed inside the glass liner in the reaction vessel and was dissolved in 20 ml of n-pentane. Hexafluoro-2-butyne (6 g, 0.040 moles) was then condensed into the vessel using liquid nitrogen and the reaction was left to proceed for 96 hours at room temperature. After every 24 hours the reaction vessel was cooled with liquid nitrogen and the evolved CO was pumped off.

At the end of the reaction period the vessel was opened and the contents of the glass liner were filtered. A bright red filtrate resulted. This was concentrated in a stream of nitrogen gas and then chromatographed on silica gel using n-pentane as the eluent. Two bands were eluted, the first being orange-red and the second being a dark brown colour and much smaller. The first band was collected and the solvent was evaporated vacuo. The residue was recrystallized by dissolving it in a small amount of n-pentane, adding methanol, and concentrating the solution in a stream of nitrogen gas. Cooling to -15° resulted in bright red crystals which were isolated by filtration, but the product became a waxy solid on warming to room temperature. It was identified by its infrared spectrum. [36, 153] The second dark brown band was identified as $Co_4(CO)_{12}$ from its infrared spectrum.

The ditertiarybutylacetylenehexacarbonyldicobalt complex was prepared by dissolving $Co_2(CO)_8$ (3.4 g, 0.010 moles) and $(t\text{-}C_4H_9)_2C_2$ (1.4 g, 0.010 moles) in 50 ml of n-hexane and refluxing the solution under nitrogen gas for 2 hours with constant stirring. The reaction mixture was then filtered and the solvent was evaporated <u>in vacuo</u>. The dark red residue was recrystallized from n-hexane to give a red crystalline solid, isolated by decanting the mother liquor. The product was dried <u>in vacuo</u> for 12 hours.

The product was identified by its elemental analysis. For di-t-butylacetylenehexacarbonyldicobalt,

$C_{16}H_{18}Co_2O_6$, the calculated elemental analysis gives % C = 45.28, % H = 4.25 and % Co = 27.83. The experimental analysis gave % C = 45.59, % H = 4.18 and % Co = 27.49. At temperatures above 100° the product decomposed without melting.

The infrared spectrum of the complex was recorded in tetrachloroethylene. The CO stretching bands were found to occur at 2090(m), 2048(s), 2024(s), 2015(s) 1993(m, sh) and 1966(vw) cm^{-1}. Other bands were observed at 2973(w), 2903(vw, sh), 2980(vw, sh), 1860(vw), 1586(vw), 1475(w), 1459(w), 1389(w), 1351(w), 1222(vw), 1207(vw), 974(vw), 840(vw), 694(w), 660(vvw) and 600(w) cm^{-1}.

SECTION B. DETAILS OF EXPERIMENTS IN II-A

1. Preparation of $(Ph_2C_2)Co_2(CO)_5(P(OCH_3)_3)$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmoles) and trimethylphosphite (0.13 g, 1.0 mmoles) were dissolved in 50 ml of n-hexane and the solution was heated to 50° under nitrogen gas for 12 hours with stirring. The solvent was then removed in a stream of nitrogen gas and the solid residue was redissolved in n-pentane. An equal volume of methanol was added and the solution was concentrated *in vacuo* and cooled to give a dark red crystalline solid which was isolated by filtration and dried *in vacuo* for 12 hours.

The theoretical elemental analysis for the product, $C_{22}H_{19}Co_2O_8P_2$, gives % C = 45.19, % H = 3.52, % Co = 21.85 and % P = 5.57. The experimental analysis gave % C= 47.16, % H = 3.44, % Co = 21.79 and % P = 5.74. The melting point of the product was found to be 103°-106°.

The infrared spectrum was examined in tetrachloroethylene and in carbon disulphide. In C_2Cl_4 the CO stretching bands were found to occur at 2072(vs), 2026(vs), 2008(vs), 1995(s, sh) and 1972(m) cm^{-1}. Other bands in tetrachloroethylene were observed to occur at 3070(vw), 3010(vw), 2955(w), 2848(vw), 1616(w), 1592(vw), 1488(w), 1442(w), 1180(w), 693(m), 630(vw), 621(vw) and 600(w) cm^{-1}. Several other bands were observed in CS_2 at 1058(w), 1028(m), 804(w), 785(w), 765(w) and 750(w) cm^{-1}. The CO stretching bands are illustrated on page 171.

2. Preparation of $(Ph_2C_2)Co_2(CO)_4(P(OCH_3)_3)_2$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmoles) and trimethylphosphite (0.25 g, 2.0 mmoles) were dissolved in 50 ml of n-hexane and the solution was refluxed under nitrogen gas for 10 hours with stirring. The solvent was then evaporated from the reaction mixture in a stream of nitrogen and the residue was redissolved in n-pentane. Methanol was added and the solution was concentrated *in vacuo* and cooled. Dark red crystals were isolated by decanting the mother liquor and were dried *in vacuo* for 12 hours.

The theoretical elemental analysis for the product, $C_{24}H_{28}Co_2O_{10}P_2$, gives % C = 43.90, % H = 4.27, % Co = 17.99 and % P = 9.45. The experimental analysis gave % C = 43.96, % H = 4.21, % Co = 17.75 and % P = 9.47. The melting point was found to be 152°-156°.

The infrared spectrum was examined in tetrachloroethylene and in carbon disulphide. In C_2Cl_4 the CO stretching bands were found to occur at 2038(vs) and 1976(vs) cm^{-1}. These are illustrated on page 172. Other bands in C_2Cl_4 were observed to occur at 3081(vw, sh), 3060(vw), 3000(w), 2950(m), 2904(vw), 2845(w), 1620(w), 1592(w), 1488(w), 1460(w), 1442(w), 1060(m, sh), 1032(s), 694(m), 631(vw) and 622(vw) cm^{-1}. In CS_2 several other bands were observed at 1180(m), 795(m), 780(m), 764(m) and 742(m) cm^{-1}.

3. Preparation of $(Ph_2C_2)Co_2(CO)_3(P(OCH_3)_3)_3$

Diphenylacetylenehexacarbonyldicobalt (0.94 g, 2.0 mmoles) and trimethylphosphite (0.75 g, 6.0 mmoles) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed under nitrogen gas for 72 hours with stirring. The solvent was then removed in a stream of nitrogen, and the red, oily residue was redissolved in n-hexane. This solution was chromatographed on silica gel using 1:1 $CHCl_3$-hexane as the eluent. Only the largest red band was eluted and the solvent was removed *in vacuo*. The solid residue was recrystallized by dissolving it in CH_2Cl_2, adding an equal amount of n-hexane, and concentrating and cooling the solution. A dark red crystalline solid was isolated by filtration and dried *in vacuo* for 12 hours.

The theoretical elemental analysis for the product, $C_{26}H_{37}Co_2O_{12}P_3$, gives % C = 41.49, % H = 4.92, % Co = 15.69 and % P = 12.37. The experimental analysis gave % C = 41.47, % H = 5.04, % Co = 14.61 and % P = 12.23.

The infrared spectrum was recorded in carbon disulphide and the CO stretching bands were observed to occur at 2000(s), 1945(s) and 1943(m, sh) cm^{-1}. These are illustrated on page 174. Other bands were observed at 3080(vw), 3055(vw), 3030(vw), 2990(w), 2948(w), 2897(vw), 2845(w), 1184(w), 1045(s), 770(m), 740(m), 697(w), 632(vw), 624(vw) and 603(w) cm^{-1}.

4. Preparation of $(Ph_2C_2)Co_2(CO)_2(P(OCH_3)_3)_4$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmoles) and trimethylphosphite (2.8 g, 22 mmoles) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed under nitrogen gas for 18 hours with stirring. The solvent was then removed in a stream of nitrogen gas and the residue was redissolved in CH_2Cl_2. An equal volume of n-hexane was added and the solution was concentrated *in vacuo* and cooled. Dark red crystals were obtained by decanting the mother liquor and were dried *in vacuo*. The product was recrystallized from CH_2Cl_2-hexane as above to give a dark red crystalline solid which was isolated by filtration and dried *in vacuo* for 12 hours.

The theoretical elemental analysis for the product, $C_{28}H_{46}Co_2O_{14}P_4$, gives % C = 39.62, % H = 5.42, % Co = 13.92 and % P = 14.62. The experimental analysis gave % C = 39.86, % H = 5.30, % Co = 13.71 and % P = 14.45. The melting point was found to be 186°-189°.

The infrared spectrum was recorded in tetrachloroethylene and in carbon disulphide. In C_2Cl_4

the CO stretching bands were observed to occur at 1950(s) and 1928(s) cm^{-1}. These are illustrated on page 174. Other bands were observed at 3050(w), 2990(w), 2900(w), 2840(w), 1595(w), 1488(w), 1547(w), 1442(w), 1345(vw), 1295(vw), 1275(vw), 1180(w), 1045(s), 736(m), 630(vw) and 622(vw) cm^{-1}. In CS_2 one further band was observed at 746(m) cm^{-1}.

5. Preparation of $((CF_3)_2C_2)Co_2(CO)_2(P(OCH_3)_3)_4$

Hexafluoro-2-butynehexacarbonyldicobalt (0.45 g, 1.0 mmole) and trimethylphosphite (1.6 g, 10 mmoles) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed under nitrogen gas for 48 hours with stirring. The reaction mixture was then cooled and the solvent was evaporated *in vacuo* resulting in a dark red oil due to the presence of excess $P(OCH_3)_3$. A small amount of n-pentane was added to this oil and the solution was cooled to -15°. A dark red crystalline solid was isolated by filtration and dried *in vacuo*.

The infrared spectrum of the product was recorded in tetrachloroethylene and the CO stretching bands were found to occur at 1977(s) and 1950(s) cm^{-1}. Other bands were observed in tetrachloroethylene solution at 2990(w), 2950(w), 2900(vw, sh), 2855(w), 1534(w), 1520(w), 1460(vw), 1260(m), 1139(s), 1114(s), 1040(s, br), 726(m) and 672(m) cm^{-1}.

6. Preparation of $(Ph_2C_2)Co_2(CO)_4(P(OC_2H_5)_3)_2$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and triethylphosphite (0.32 g, 2.0 mmoles) were dissolved in 50 ml of n-hexane and the solution was refluxed under nitrogen gas for one hour with stirring. The reaction mixture was then cooled and the solvent was evaporated *in vacuo*. The red residue was redissolved in n-pentane and an equal volume of methanol was added. The solution was concentrated and cooled to give a dark red crystalline solid which was isolated by filtration and dried *in vacuo* for 12 hours.

The theoretical elemental analysis for the product, $C_{30}H_{40}Co_2O_{10}P_2$, gives % C = 48.65, % H = 5.41, % Co = 15.95 and % P = 8.38. The experimental analysis gave % C =48.80, % H = 5.59, % Co = 15.77 and % P = 8.60. The melting point was found to be 100^{o}-102^{o}.

The infrared spectrum was recorded in tetrachloroethylene and in carbon disulphide. In C_2Cl_4 the CO stretching bands were found to occur at 2035(vs) and 1972(vs) cm^{-1}. These are illustrated on page 172. Other bands were observed in tetrachloroethylene at 1620(m), 1592(w), 1489(m), 1478(m), 1457(w), 1443(m), 1370(m), 1058(m, sh), 1035(s), 737(m), 694(m), 630(vw), 621(vw) and 600(m) cm^{-1}. In carbon disulphide additional bands were observed at 1160(w), 1100(w), 943(s), 780(m) and 765(m) cm^{-1}.

7. Preparation of $(Ph_2C_2)Co_2(CO)_2(P(OC_2H_5)_3)_4$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and triethylphosphite (0.8 g, 5.0 mmoles) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed under nitrogen gas for 48 hours with stirring. The solvent was then removed in a stream of nitrogen to leave an oily, red liquid. The remaining traces of solvent and excess triethylphosphite were removed <u>in vacuo</u> and the solid residue was redissolved in CH_2Cl_2. An equal volume of methanol was added and the solution was concentrated and cooled to give a dark red crystalline solid which was isolated by filtration and dried <u>in vacuo</u> for 24 hours.

The theoretical elemental analysis for the product, $C_{40}H_{70}Co_2O_{14}P_4$, gives % C = 47.24, % H = 6.89, % Co = 11.61 and % P = 12.20. The experimental analysis gave % C = 47.48, % H = 6.97, % Co = 11.71 and % P = 12.31.

The infrared spectrum was recorded in tetrachloroethylene and in carbon disulphide. In C_2Cl_4

the CO stretching bands were found to occur at 1949(s) and 1923(s) cm^{-1}. These are illustrated on page 174. Other bands were observed at 3052(vw), 2980(w), 2900(w), 2870(vw), 1595(w), 1490(w), 1480(vw, sh) 1457(vw), 1442(w), 1388(w), 1280(vw), 1270(vw, sh), 1100(w, sh), 1043(s), 725(w), 699(w), 632(vw) and 625(vw) cm^{-1}. One further band was observed in CS_2 at 938(s) cm^{-1}.

8. Preparation of $((CF_3)_2C_2)Co_2(CO)_2(P(OC_2H_5)_3)_4$

Hexafluoro-2-butynehexacarbonyldicobalt (0.45 g, 1.0 mmole) and triethylphosphite (2.0 g, 10 mmoles) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed under nitrogen gas for 30 hours with stirring. The reaction mixture was then cooled and the solvent removed *in vacuo*. The residue was dissolved in n-hexane and chromatographed on silica gel using 1:1 CH_2Cl_2-hexane as the eluent. Only a single wine-red band was observed and was eluted. Concentration of the eluent *in vacuo* and subsequent cooling to -15° resulted in a dark red crystalline solid which was isolated by filtration and dried *in vacuo* for 12 hours.

The theoretical elemental analysis for the product, $C_{30}H_{60}Co_2F_6O_{14}P_4$, gives % C = 36.0, % H = 6.0, % Co = 11.8, % F = 11.4 and % P = 12.4. The experimental analysis gave % C = 36.0, % H = 5.9, % Co = 11.6, % F = 11.5

and % P = 12.5.

The infrared spectrum of the product was recorded in tetrachloroethylene and CO stretching bands were observed at 1975(s) and 1946(s) cm^{-1}. Other bands were found to occur at 2984(w), 2937(w), 2900(w), 2870(vw), 1570(w), 1480(vw), 1389(w), 1358(m), 1192(s), 1110(s), 1040(s), 735(w) and 672(w) cm^{-1}.

9. Preparation of $(Ph_2C_2)Co_2(CO)_4(P(O\text{-}i\text{-}C_3H_7)_3)_2$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and triisopropylphosphite (0.39 g, 2.0 mmoles) were dissolved in 50 ml of n-hexane and the solution was refluxed under nitrogen gas for one hour with stirring. The reaction mixture was then cooled and the solvent evaporated <u>in vacuo</u>. The solid red residue was redissolved in n-pentane and an equal volume of methanol was added. The solution was concentrated <u>in vacuo</u> and cooled to give a dark red cyrstalline solid which was isolated by filtration and dried <u>in vacuo</u> for 12 hours.

The theoretical elemental analysis for the product, $C_{36}H_{52}Co_2O_{10}P_2$, gives % C = 52.43, % H = 6.31, % Co = 14.32 and % P = 7.52. The experimental analysis gave % C = 52.31, % H = 6.37, % Co = 14.15 and % P = 7.65. The melting point was found to be 107°-109°.

The infrared spectrum was recorded in tetrachloroethylene and the CO stretching bands were found to occur at 2033(vs), 1968(vs) and 1740(m, sh) cm^{-1}. These are illustrated on page 172. Other bands were observed at 3080(w), 3057(w), 2980(m), 2940(m), 2875(w), 1625(w), 1592(w), 1572(vw), 1490(w), 1480(w, sh), 1467(w), 1453(w), 1443(w), 1385(m), 1373(m), 1355(m, sh), 1282(vw), 1170(w), 1140(w), 1108(m), 1004(s), 976(s), 879(m), 722(m), 694(m), 630(vw), 622(vw) and 600(w) cm^{-1}.

10. Preparation of $(Ph_2C_2)Co_2(CO)_5(P(n-C_4H_9)_3)$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and tri-n-butylphosphine (0.20 g, 1.0 mmole) were dissolved in 50 ml of n-hexane and the solution was refluxed under nitrogen gas for 18 hours with stirring. The solvent was then evaporated in a stream of nitrogen gas and the residue was redissolved in n-pentane. Crystallization was accomplished by adding methanol and concentrating the solution *in vacuo* and cooling. Dark red crystals were isolated by filtration and dried *in vacuo* for 12 hours.

The infrared spectrum of the product was recorded in tetrachloroethylene and the CO stretching bands were observed at 2062(vs), 2010(vs), 2000(s, sh), 1985(m, sh), and 1957(s) cm^{-1}. These are illustrated on page 171. Other bands were observed at 3070(w, br), 2962(s), 2936(s), 2876(s), 1618(m), 1487(m), 1466(m), 1459(m), 1380(w), 1213(w), 696(s) and 600(w). The spectrum was also recorded in carbon disulphide and several other bands were observed at 1093(m), 1074(m), 1052(m), 1030(m), 1008(w), 972(w), 907(m), 775(m), 761(s), 724(m), 630(w) and 621(w) cm^{-1}. The melting point was found to be 85°-87°.

11. The Preparation of $(Ph_2C_2)Co_2(CO)_4(P(n-C_4H_9)_3)_2$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and tri-n-butylphosphine (0.4 g, 2 mmoles) were dissolved in 50 ml of n-hexane and the solution was refluxed under nitrogen gas for 3.5 hours with stirring. The resulting deep red solution was concentrated in a stream of nitrogen and cooled to -10°. After several hours dark red crystals had formed which were isolated by filtration. The product was recrystallized by dissolving it in n-pentane, adding an equal amount of methanol, and concentrating and cooling the solution. Filtration yielded dark-red crystals which were dried in vacuo for 12 hours.

The theoretical elemental analysis for the product, $C_{42}H_{64}Co_2O_4P_2$, gives % C = 62.07, % H = 7.88, % Co = 14.53 and % P = 7.64. The experimental analysis gave % C = 62.11, % H = 7.55, % Co = 14.46 and % P = 7.94. The melting point was found to be 99°-101°.

The infrared spectrum was recorded in tetrachloroethylene and in carbon disulphide. In C_2Cl_4 the CO stretching bands were found to occur at 2020(vs), 1966(vs, sh) and 1956(vs) cm^{-1}. These are illustrated on page 172. Other bands were observed at 3070(m, br), 2965(s), 2938(s), 2879(s), 1620(s), 1588(m), 1485(s), 1465(s), 1455(m, sh), 1441(s), 1415(m), 1378(m), 1305(w), 1280(w), 1211(m) and 698(s) cm^{-1}. In CS_2 further bands were found to occur at 1094(m), 1071(w), 1051(w), 1030(vw), 1007(vw), 972(vw), 908(m), 776(m), 761(s) and 724(m) cm^{-1}.

12. The Preparation of $(Ph_2C_2)Co_2(CO)_5(P(OPh)_3)$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and triphenylphosphite (0.31 g, 1.0 mmole) were dissolved in 50 ml of n-hexane and the solution was refluxed under nitrogen gas for 24 hours with stirring. The reaction mixture was then cooled to room temperature and filtered of a red solid which was identified as the disubstituted product, $(Ph_2C_2)Co_2(CO)_4(P(OPh)_3)_2$, from its infrared spectrum. The solvent was evaporated from the filtrate *in vacuo* and the resulting solid residue was chromatographed on silica gel using 1:3 $CHCl_3$-hexane as the eluent. Only the first larger, red band was eluted and the solvent was evaporated *in vacuo*. The residue was recrystallized by dissolving it in n-hexane and concentrating the solution in a stream of nitrogen gas and cooling. Black, needle-like crystals were isolated by decanting the mother liquor and were dried *in vacuo* for 12 hours.

The theoretical elemental analysis for the product, $C_{37}H_{25}Co_2O_8P$, gives % C = 59.5, % H = 3.4, % Co = 15.8 and % P = 4.2. The experimental analysis gave % C = 59.0, % H = 3.4, % Co = 16.2 and % P = 4.1. The melting point was found to be 110^0-112^0.

The infrared spectrum of the product was recorded in tetrachloroethylene and in carbon disulphide. In C_2Cl_4 the CO stretching bands were found to occur at 2078(vs), 2035(vs), 2020(vs), 2000(s, sh) and 1987(m, sh) cm^{-1}. Other bands were observed at 1617(m, sh), 1590(m), 1489(s), 1457(vw), 1443(vw), 1238(vw), 1219(m), 1196(s), 1164(m), 1074(w), 1028(w), 720(w), 693(s), 630(w) and 622(w) cm^{-1}. In CS_2 further bands were observed at 1009(w), 920(s), 900(s, sh), 775(s) and 765(m, sh) cm^{-1}. The CO stretching bands are illustrated on page 171.

13. The Preparation of $(Ph_2C_2)Co_2(CO)_4(P(OPh)_3)_2$

Diphenylacetylenehexacarbonyldicobalt

(0.40 g, 0.85 mmoles) and triphenylphosphite (0.40 g, 1.3 mmoles) were dissolved in 50 ml of n-hexane and the solution was refluxed under nitrogen gas for 12 hours with stirring. At that time a second portion of $P(OPh)_3$ (0.40 g, 1.3 mmoles) was added to the reaction mixture and refluxing was continued for a further 4 hours. The reaction mixture was then cooled to room temperature and filtered to yield a reddish-brown powder which was dried in air. This product was recrystallized twice by dissolving it in a minimum amount of CH_2Cl_2, adding an equal amount of n-hexane, and concentrating the solution in vacuo and cooling. The resulting bright red crystals were chromatographed on a silica gel column using 1:1 chloroform-hexane. Only one band was observed and this was eluted and the solvent was evaporated in vacuo. The residue was redissolved in CH_2Cl_2 and crystals were obtained by adding n-hexane and concentrating the solution in a stream of nitrogen gas and then cooling. Red crystals were isolated by filtration, washed with cold n-hexane and dried in vacuo for 12 hours.

The theoretical elemental analysis for the product, $C_{54}H_{40}Co_2O_{10}P_2$, gives % C = 63.04, % H = 3.89, % Co = 11.48 and % P = 6.03. The experimental analysis gave % C = 63.15, % H = 3.94, % Co = 11.29 and % P = 6.15. The melting point was found to be 185°-187°.

The infrared spectrum was recorded in tetrachloroethylene and in carbon disulphide. In C_2Cl_4 the CO stretching bands were found to occur at 2052(vs), 2010(s, sh) and 1991(vs) cm^{-1}. These are illustrated on page 172. Other bands were observed at 3070(w), 1618(m, sh), 1592(s), 1490(vs), 1458(w), 1444(w), 1289(vw), 1220(s), 1197(vs), 1164(s), 1075(w), 1029(m), 720(m), 693(s), 621(w) and 600(m) cm^{-1}. In CS_2 further bands were found to occur at 1009(m), 915(s), 895(m, sh), 860(m, sh), 774(s) and 768(m, sh) cm^{-1}.

14. The Preparation of $(Ph_2C_2)Co_2(CO)_5(PPh_3)$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and triphenylphosphine (2.9 g, 1.1 mmoles) were dissolved in 50 ml of cyclohexane and the solution was refluxed under nitrogen gas for 12 hours with stirring. The reaction mixture was then cooled to room temperature and a green-brown solid was isolated by filtration. This crude product was recrystallized by dissolving it in CH_2Cl_2, adding an equal amount of hexane, and concentrating the solution *in vacuo* and cooling. The resulting solid was chromatographed on silica gel using 1:3 $CHCl_3$-hexane. Only the first larger brown band was eluted and the solvent was evaporated *in vacuo.* The residue was finally recrystallized by dissolving it in

CH_2Cl_2, adding an equal amount of methanol, and concentrating the solution in vacuo and cooling. A green-brown solid was isolated by filtration and dried in vacuo for 12 hours.

The infrared spectrum of the product was recorded in tetrachloroethylene and in carbon disulphide. In C_2Cl_4 the CO stretching bands were found to occur at 2068(vs), 2022(vs), 2004(vs), 1995(s, sh) and 1967(s) cm^{-1}. Other bands were observed at 3060(m), 1615(m), 1590(w), 1482(m), 1435(s) and 696(s) cm^{-1}. In CS_2 other bands were found to occur at 1330(vw), 1308(vw), 1189(w), 1157(vw), 1095(m), 1074(w), 1032(w), 1003(w), 763(m), 747(m), 630(w), 621(w) and 600(m) cm^{-1}. The melting point was found to be 192°-194°.

15. The Preparation of $(Ph_2C_2)Co_2(CO)_4(PPh_3)_2$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and triphenylphosphine (0.60 g, 2.3 mmoles) were dissolved in 50 ml of n-hexane and the solution was stirred under nitrogen gas for 24 hours. At that time a green solid had precipitated and the reaction mixture was then refluxed for one-quarter of an hour. After cooling the mixture to room temperature, a green powder was isolated by filtration and was washed with hexane. This product was recrystallized by dissolving it in CH_2Cl_2, adding an equal amount of n-hexane, and concentrating the solution *in vacuo* and cooling. This procedure was repeated to give a dark green crystalline solid which was isolated by filtration and dried *in vacuo* for 12 hours.

The theoretical elemental analysis for the product, $C_{54}H_{40}Co_2O_4P_2$, gives % C = 69.53, % H = 4.29, % Co = 12.66 and % P = 6.65. The experimental analysis gave % C = 69.47, % H = 4.35, % Co = 12.48 and % P = 6.66. The melting point was found to be 220°-222°.

The infrared spectrum was recorded in tetrachloroethylene and in carbon disulphide. In C_2Cl_4 the CO stretching bands were found to occur at 2028(vs) and 1968(vs) cm^{-1}. These are illustrated on page 172. Other bands were observed at 3060(m), 1620(w), 1472(s), 1436(s) and 697(s) cm^{-1}. In CS_2 several other bands were found to occur at 1530(vw), 1509(w), 1480(vw), 1189(w), 1160(vw), 1093(s), 1074(w), 1031(w), 1002(w), 911(s), 804(w), 780(m), 760(m), 745(s), 629(vw) and 620(vw) cm^{-1}.

16. Treatment of $(Ph_2C_2)Co_2(CO)_6$ with Excess $P(O\text{-}i\text{-}C_3H_7)_3$

Diphenylacetylenehexacarbonyldicobalt

(0.47 g, 1.0 mmole) and triisopropylphosphite (2.0 g, 10 mmoles) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed under nitrogen gas for 48 hours with stirring. The solvent was then evaporated *in* a stream of nitrogen and the solid residue was redissolved in CH_2Cl_2. An equal volume of methanol was added and the solution was concentrated *in vacuo* and cooled. Dark red crystals were isolated by filtration.

The infrared spectrum of this product in the CO stretching region showed some traces of impurities but consisted predominantly of two strong bands at 1989 cm^{-1} and 1942 cm^{-1}. This pattern resembled that of a trisubstituted derivative most closely, while the weak impurity peaks at 2035 cm^{-1} and 1865 cm^{-1} were attributed to the disubstituted derivative. No trace of any absorption characteristic of a tetrasubstituted derivative was found in this region.

17. Treatment of $(Ph_2C_2)Co_2(CO)_6$ with Excess $P(O\text{-}n\text{-}C_4H_9)_3$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and tri-n-butylphosphite (2.0 g, 8 mmoles) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed under nitrogen gas for 80 hours with stirring. The solvent was then evaporated from the reaction mixture in a stream of nitrogen and a dark red oil resulted. Attempts to obtain the product in crystalline form were unsuccessful, presumably due to the difficulty in removing the excess $P(O\text{-}n\text{-}C_4H_9)_3$.

The infrared spectrum of this red oil in the CO stretching region showed strong bands at 1950 cm^{-1} and 1930 cm^{-1}, characteristic of a tetrasubstituted derivative, but a weaker band at 1985 cm^{-1} indicated that a considerable amount of the trisubstituted product was still present.

18. Treatment of $(Ph_2C_2)Co_2(CO)_6$ with Excess $P(OPh)_3$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and triphenylphosphite (2.1 g, 7 mmoles) were dissolved in 50 ml of methylcyclohexane and the solutiion was refluxed for 6 hours under nitrogen gas with stirring. At that point a small portion of the reaction mixture was removed and its infrared spectrum was recorded in the CO stretching region. Peaks at 2030 cm^{-1} and 1980 cm^{-1} indicated that a trisubstituted derivative had probably been formed. The reaction was allowed to continue for a further six hours, but the appearance of a violet solid in the reaction mixture indicated that the complex was decomposing.

19. Treatment of $(Ph_2C_2)Co_2(CO)_6$ with Excess PPh_3

Diphenylacetylenehexacarbonyldicobalt (0.23 g, 0.50 mmoles) and triphenylphosphine (0.6 g, 2.5 mmoles) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed under nitrogen gas for 12 hours with stirring. After cooling the reaction mixture to -15°, a green solid was isolated by filtration and was dried in vacuo. Its infrared spectrum was recorded in the CO stretching region and was found to be identical with that of an authentic sample of $(Ph_2C_2)Co_2(CO)_4(PPh_3)_2$.

20. Treatment of $(Ph_2C_2)Co_2(CO)_6$ with Excess $P(n\text{-}C_4H_9)_3$

Diphenylacetylenehexacarbonyldicobalt (0.23 g, 0.50 mmoles) and tri-n-butylphosphine (0.5 g, 2.5 mmoles) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed for 12 hours under nitrogen gas with stirring. At that point a further 2.5 mmoles of phosphine was added to the reaction mixture and the reaction continued for a further 12 hours. Evaporation of the solvent gave a red, oily residue from which a dark red crystalline solid was obtained by recrystallization from methanol. The infrared spectrum of this product in the CO stretching region was identical to that of the disubstituted derivative, $(Ph_2C_2)Co_2(CO)_4(P(n\text{-}C_4H_9)_3)_2$.

SECTION C. DETAILS OF EXPERIMENTS IN II-B

1. The Preparation of $(Ph_2C_2)Co_2(CO)_4(dpm)$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and bis(diphenylphosphino)methane (0.39 g, 1.0 mmole) were dissolved in 50 ml of n-hexane and the solution was refluxed under nitrogen gas for 1.5 hours with stirring. The reaction mixture was then concentrated in a stream of nitrogen and cooled to room temperature resulting in the crystallization of a deep red compound. The crystals were isolated by filtration, washed with three 50 ml portions of cold n-hexane, and dried *in vacuo* for 12 hours.

The theoretical elemental analysis for the product, $C_{43}H_{32}Co_2O_4P_2$, gives % C = 65.15, % H = 4.04, % Co = 14.90 and % P = 7.83. The experimental analysis gave % C = 65.23, % H = 4.16, % Co = 14.70 and % P = 7.83. The substance was found to melt with decomposition at 200°.

The infrared spectrum was recorded in tetrachloroethylene and in carbon disulphide. In C_2Cl_4 the CO stretching bands were found to occur at 2033(vs), 2000(vs) and 1975(vs) cm^{-1}. These are illustrated on page 209. Other bands were observed at 3070(w, sh), 3058(w) 3010(vw, sh), 1592(w), 1483(w) and 1435(w) cm^{-1}. In CS_2 other bands were found to occur at 1366(vw), 1328(vw), 1304(vw), 1276(vw), 1187(vw), 1175(vw), 1123(vw), 1095(w), 1072(vw), 1029(vw), 1002(vw), 968(vw), 922(vw), 840(vw), 785(w), 740(m), 720(w), 695(m), 632(vw) and 625(vw) cm^{-1}.

2. The Preparation of $(Ph_2C_2)Co_2(CO)_4(dam)$

Diphenylacetylenehexacarbonyldicobalt (0.24 g, 0.50 mmoles) and bis(diphenylarsino)methane (0.24 g, 0.50 mmoles) were dissolved in 50 ml of n-hexane and the solution was refluxed under nitrogen gas for 1.5 hours with stirring. The reaction mixture was then concentrated in a stream of nitrogen and cooled to room temperature resulting in the crystallization of a deep red product. The crystals were isolated by filtration, washed with three 50 ml portions of cold n-hexane, and dried *in vacuo* for 12 hours.

The infrared spectrum of the product was recorded in tetrachloroethylene and in carbon disulphide. In C_2Cl_4 the CO stretching bands were found to occur at 2028(vs), 1998(vs), 1971(vs) and 1950(m, sh) cm^{-1}. Other bands were observed at 3055(vw), 2980(vw), 2923(vw), 2860(vw), 1590(w, br), 1484(w), 1437(w), 1302(vw), 1079(vw), 1028(vw), 1003(vw), 740(w), 721(vw), 697(w), 670(vw, sh) and 625(vw, br) cm^{-1}. One further band was observed in CS_2 at 760(w) cm^{-1}. The melting point of the product was found to be 166°-168°.

3. The Preparation of $(Ph_2C_2)Co_2(CO)_4(dpe)$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and bis(diphenylphosphine)ethane (0.40 g, 1.0 mmole) were dissolved in 50 ml of cyclohexane and the solution was heated to about 50° under nitrogen gas for 18 hours with stirring. The reaction mixture was then filtered of a red solid and the solvent was evaporated from the filtrate *in vacuo*. The solid residue obtained on evaporation of the solvent was recrystallized by dissolving it in a minimum amount of CH_2Cl_2, adding an equal amount of n-hexane, and concentrating and cooling the solution. A red solid was isolated by filtration. The product was then chromatographed on silica gel using 1:2 chloroform-hexane and only one dark brown band was observed, although a brown colouration remained at the top of the column. The single band was eluted and the solvent was evaporated *in vacuo*. The residue was recrystallized from CH_2Cl_2 as described above to give a dark red crystalline solid which was dried *in vacuo* for 12 hours.

The theoretical elemental analysis for the product, $C_{44}H_{34}Co_2O_4P_2$, gives % C = 65.51, % H = 4.22, % Co = 14.64 and % P = 7.69. The experimental analysis gave % C = 65.32, % H = 4.34, % Co = 14.43 and % P = 7.45. The melting point was found to be 178°-182°.

The infrared spectrum was recorded in tetrachloroethylene and in carbon disulphide. In C_2Cl_4 the CO stretching bands were found to occur at 2035(vs), 1997(vs), 1977(vs) and 1955(s, sh) cm^{-1}. Other bands were observed at 3065(vw), 1591(vw), 1488(vw), 1438(w) and 698(m) cm^{-1}. In CS_2 other bands were observed at 1330(vw), 1305(vw), 1278(vw), 1085(vw), 1096(w), 1075(vw), 1031(vw), 1004(vw), 836(vw), 768(w), 744(w) and 624(vw) cm^{-1}.

4. The Preparation of $(Ph_2C_2)Co_2(CO)_4(dae)$

Diphenylacetylenehexacarbonyldicobalt (1.2 g, 2.4 mmoles) and bis(diphenylarsino)ethane (0.7 g, 1.4 mmoles) were dissolved in 50 ml of n-hexane and the solution was refluxed for 15 hours under nitrogen gas with stirring. The reaction mixture was then flitered while it was still hot and the resulting red powder was washed with several portions of hot n-hexane. This crude product was recrystallized by dissolving it in CH_2Cl_2, adding an equal amount of n-hexane, and concentrating the solution *in vacuo* and cooling. Dark red crystals were isolared by filtration and dried in vacuo for 12 hours.

The infrared spectrum of the product was recorded in carbon disulphide, and the Co stretching bands were found to occur at 2030(vs), 1994(vs), 1970(vs) and 1947(s) cm^{-1}. Other bands were observed at 3060(w), 2960(vw), 2915(vw), 1305(vw), 1187(vw), 1080(w), 1029(w), 1004(w), 768(w), 755(vw), 739(m), 697(vw), 674(vw) and 625(vw) cm^{-1}. The melting point was found to be 179°-184°.

5. The Preparation of $((t\text{-}C_4H_9)_2C_2)Co_2(CO)_4(dpm)$

Di-t-butylacetylenehexacarbonyldicobalt (0.21 g, 0.50 mmoles) and bis(diphenylphosphino)methane (0.19 g, 0.50 mmoles) were dissolved in 50 ml of n-hexane and the solution was refluxed under nitrogen gas for 1.5 hours with stirring. The reaction mixture was then concentrated in a stream of nitrogen to give a dark green solid which was isolated by filtration and dried in air.

The infrared spectrum of the product was recorded in carbon disulphide in the Co stretching region and the following bands were observed: 2010(vs); 1987(vs); 1956(vs) and 1943(s) cm^{-1} ± 10 cm^{-1}.

6. The Preparation of $((t\text{-}C_4H_9)_2C_2)Co_2(CO)_4(dam)$

Di-t-butylacetylenehexacarbonyldicobalt (0.21 g, 0.50 mmoles) and bis(diphenylarsino)methane (0.12 g, 0.25 mmoles) were dissolved in 50 ml of n-hexane and the solution was refluxed under nitrogen gas for 4 hours with stirring. The solution was then concentrated in a stream of nitrogen and cooled to -15°. After several hours dark red crystals had formed which were isolated by filtration and dried _in vacuo_ for 12 hours.

The infrared spectrum of the product was recorded in tetrachloroethylene and in carbon disulphide. In C_2Cl_4 the CO stretching bands were observed at 2012(vs), 1984(vs), 1955(vs) and 1941(vs) cm^{-1}. Other bands were found to occur at 3059(vw), 2970(vw), 2950(vw), 2930(vw), 2900(vw, sh), 2865(vw), 1484(w), 1475(vw, sh), 1457(vw), 1437(w), 1386(vw), 1078(vw), 1027(vw), 737(vw), 697(w), 648(vw) and 610(vw) cm^{-1}. In CS_2 several other bands were observed at 1357(vw), 1234(vw), 1207(vw), 1190(vw), 926(vw) and 840(vw) cm^{-1}. The melting point was found to be 190°-193°.

7. The Preparation of $(Ph_2C_2)Co_2(CO)_2(dpm)_2 \cdot CH_2Cl_2$

Diphenylacetylenehexacarbonyldicobalt

(0.47 g, 1.0 mmole) and bis(diphenylphosphino)methane (0.78 g, 2.0 mmoles) were dissolved in 50 ml of benzene and the solution was refluxed under nitrogen gas for 48 hours with stirring. A deep red solution resulted from which the solvent was evaporated in a stream of nitrogen. The oily residue was then dissolved in CH_2Cl_2 and filtered, and the solvent was evaporated to dryness in vacuo. The resulting red-brown product was recrystallized by dissolving it in a minimum amount of CH_2Cl_2, adding an equal amount of n-hexane, and concentrating the solution in vacuo and cooling. A red-brown crystalline solid was isolated by filtration and dried in vacuo for 12 hours.

The theoretical elemental analysis for the product, $C_{67}H_{56}Cl_2Co_2O_2P_4$, gives % C = 66.72, % H = 4.65, % Co = 9.49 and % P = 10.29. The experimental analysis gave % C = 66.36, % H = 4.86, % Co = 9.49 and % P = 10.18. The product was found to melt with decomposition at 254°.

The infrared spectrum was recorded in dichloromethane and in the CO stretching region a single, strong, broad band was observed at 1918 cm^{-1}. This is illustrated on page 209. Two other bands were found to occur at 1088(w) and 1027(vw) cm^{-1}. The product was not sufficiently soluble in any solvent which would have allowed the complete infrared spectrum to be recorded.

8. The Preparation of $(Ph_2C_2)Co_2(CO)_2(dam)_2\cdot CH_2Cl_2$

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and bis(diphenylarsino)methane (0.94 g, 2.0 mmoles) were dissolved in 50 ml of toluene and the solution was refluxed under nitrogen gas for 48 hours with stirring. The resulting deep red solution was filtered while it was still hot and the solvent was evaporated to dryness in a stream of nitrogen. The residue was dissolved in CH_2Cl_2 and filtered. Hexane was then added and the solution was concentrated *in vacuo* to give a red-brown crystalline solid which was isolated by filtration. This product was recrystallized by dissolving it in a minimum amount of CH_2Cl_2, adding an equal amount of n-hexane, and concentrating and cooling the solution. Filtration yielded red-brown crystals which were dried *in vacuo* for 12 hours.

The theoretical elemental analysis for the product, $C_{67}H_{56}As_4Cl_2Co_2O_2$, gives % C = 58.22 and % H = 4.06. The experimental analysis gave % C = 58.33 and % H = 4.12. The melting point was found to be 192°-193°.

The infrared spectrum was recorded in the CO stretching region in dichloromethane and a single strong band was observed at 1920 cm^{-1}. Other bands were also observed at 1590(w), 1078(w), 1028(w) and 1004(w) cm^{-1}.

9. The Preparation of $(Ph_2C_2)Co_2(CO)_2(dpe)_2$

Diphenylacetylenehexacarbonyldicobalt (0.94 g, 2.0 mmoles) and bis(diphenylphosphino) ethane (2.0 g, 5.0 mmoles) were dissolved in 75 ml of toluene and the solution was refluxed under nitrogen gas for 48 hours with stirring. The solvent was then evaporated from the reaction mixture *in vacuo* and the solid residue was redissolved in diethylether and filtered. The filtrate was concentrated *in vacuo* and cooled to yield a black, crystalline solid which was isolated by filtration. This product was recrystallized from diethylether and dried *in vacuo* for 12 hours.

The theoretical elemental analysis for the product, $C_{68}H_{58}Co_2O_2P_4$, gives % C = 71.08, % H = 5.05, % Co = 10,28 and % P =10.80. The experimental analysis gave % C = 70.82, % H = 5.13, % Co = 10.15 and % P = 10.60. The melting point was found to be 200°.

The infrared spectrum was recorded in carbon disulphide and in the CO stretching region two only partially resolved bands were observed at 1922(s) and 1900(s) cm^{-1}. These are illustrated on page 209. Other bands were found to occur at 3052(w), 1120(vw), 1095(vw), 1032(vw), 745(m), 700(s) and 670(vw) cm^{-1}.

10. The Preparation of $((C_2H_5)_2C_2)Co_2(CO)_2(dpm)_2$

Diethylacetylenehexacarbonyldicobalt (0.5 g, 1.25 mmoles) and bis(diphenylphosphino)methane (1.1 g, 6.0 mmoles) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed under nitrogen gas for 6 hours with stirring. The reaction mixture was then cooled to room temperature and filtered to yield a red solid which was dried *in vacuo*. This product was recrystallized by dissolving it in a minimum amount of CH_2Cl_2, adding an equal amount of *n*-hexane, and concentrating the solution *in vacuo* and cooling. Dark red crystals were isolated by filtration and were dried *in vacuo* for 12 hours.

The theoretical elemental analysis for the product, $C_{58}H_{54}Co_2O_2P_4$, gives % C = 68.0, % H = 5.3 and % Co = 11.5. The experimental analysis gave % C = 67.2, % H = 5.4 and % Co = 11.0. The melting point was found to be 270°.

The infrared spectrum was recorded in the CO stretching region in dichloromethane and a single, broad absorption was observed at 1895 cm^{-1}.

11. The Preparation of $((C_2H_5)_2C_2)Co_2(CO)_2(dam)_2$

Diethylacetylenehexacarbonyldicobalt (0.37 g, 1.0 mmole) and bis(diphenylarsino)methane (1.1 g, 2.3 mmoles) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed under nitrogen gas for 12 hours with stirring. The reaction mixture was then filtered while it was still hot to yield a red powder which was washed with several portions of n-hexane. This product was recrystallized by dissolving it in a minimum amount of CH_2Cl_2, adding an equal amount of n-hexane, and concentrating the solution *in vacuo* and cooling. Dark red crystals were isolated by filtration and were dried *in vacuo* for 12 hours.

The infrared spectrum of the product was recorded in carbon disulphide. In the CO stretching region a single broad absorption was observed at 1899 cm^{-1}. Other bands were found to occur at 3073(m, sh), 3056(m), 2998(w), 2963(m), 2928(m), 2868(w), 2836(w), 1305(w), 1270(vw), 1250(vw), 1186(w), 1160(vw), 1084(m, sh), 1078(m), 1045(w), 1029(m), 1004(m), 910(vw), 804(w), 736(s), 745(s), 699(s), 675(w, sh) and 663(w) cm^{-1}. The melting point of the product was found to be 210^0-212^0.

12. The Preparation of $((CF_3)_2C_2)Co_2(CO)_2(dpm)_2$

Hexafluoro-2-butynehexacarbonyldicobalt (0.47 g, 1.0 mmole) and bis(diphenylphosphino)methane (1.1 g, 1.0 mmole) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed under nitrogen gas for 4 hours with stirring. The reaction mixture was then filtered while it was still hot to yield an orange-red solid which was washed with several portions of hot hexane. This product was recrystallized from CH_2Cl_2 to give an orange-red powdery solid which was dried in vacuo for 12 hours.

The infrared spectrum of the product was recorded in the CO stretching region in dichloromethane and a single broad absorption was observed at 1948 cm^{-1}.

13. The Preparation of $((CF_3)_2C_2)Co_2(CO)_2(dam)_2$

Hexafluoro-2-butynehexacarbonyldicobalt (0.45 g, 1.0 mmole) and bis(diphenylarsino)methane (0.96 g, 2.0 mmoles) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed under nitrogen gas for 10 hours with stirring. A orange-red solid was obtained by filtering the reaction mixture while it was still hot.

This product was recrystallized by dissolving it in a minumum amount of CH_2Cl_2, adding an equal amount of n-hexane, and concentrating the solution <u>in vacuo</u> and cooling. An orange-red powdery solid was obtained by filtration and was dried <u>in vacuo</u> for 12 hours.

The theoretical elemental analysis of the product, $C_{56}H_{44}As_4Co_2F_6O_2$, gives % C = 52.5, % H = 3.44 and % F = 8.9. The experimental analysis gave % C = 52.6, % H = 3.30 and % F = 8.4. The melting point was found to be 290°-295°.

The infrared spectrum was recorded in the CO stretching region in CH_2Cl_2 and a single broad absorption was observed at 1945 cm^{-1}. In CS_2 several other bands were found to occur at 1262(w), 1194(w), 1120(w, br), 745(w) and 697(vw) cm^{-1}.

14. The Preparation of $((CF_3)_2C_2)Co_2(CO)_2(dpe)_2$

Hexafluoro-2-butynehexacarbonyldicobalt (0.45 g, 1.0 mmole) and bis(diphenylphosphino)ethane (1.1 g, 2.8 mmoles) were dissolved in 50 ml of methylcyclohexane and the solution was refluxed under nitrogen gas for 10 hours with stirring. A reddish-brown solid was obtained by filtering the reaction mixture while it was still hot. This product was recrystallized by dissolving it in a minimum amount of CH_2Cl_2, adding an equal amount of hexane, and concentrating and cooling the solution. The resulting dark red crystals were isolated by filtration and dried in vacuo for 12 hours.

The infrared spectrum of the product in the CO stretching region was recorded in dichloromethane and two only partially resolved bands were observed at 1952(s) and 1930(s) cm^{-1}. In CS_2 other bands were found to occur at 1245(w), 1184(m), 1095(m) 745(m), 700(m) and 600(w) cm^{-1}. The melting point was found to be 260°.

15. The Preparation of $(Ph_2C_2)Co_2(CO)_3(dpm)_2$

Diphenylacetylenehexacarbonyldicobalt (0.24 g, 0.50 mmoles) and bis(diphenylphosphino)methane (0.50 g, 1.3 mmoles) were dissolved in 50 ml of cyclohexane and the solution was refluxed under nitrogen gas for 20 hours with stirring. The reaction mixture was then filtered while it was still hot to yield a grey-green solid. This product was washed with 100 ml of cyclohexane and 100 ml of n-hexane and dried in air. It was then recrystallized by dissolving it in a minimum amount of CH_2Cl_2, adding an equal amount of n-hexane, and concentrating the solution in vacuo and cooling. A red-brown solid was isolated by filtration and dried in vacuo for 12 hours.

The theoretical elemental analysis of the product, $C_{67}H_{54}Co_2O_3P_4$, gives % C = 70.04, % H = 4.73, % Co = 10.25 and % P = 10.78. The experimental analysis gave % C = 69.50, % H = 4.87, % Co = 9.76 and % P = 10.39. The product was found to melt with decomposition at 245°.

The infrared spectrum of the product was recorded in dichloromethane in the CO stretching region and bands were found to occur at 1990(s), 1943(s) and 1902(w, sh) cm^{-1}.

16. The Preparation of $(Ph_2C_2)Co_2(CO)_3(dam)_2$

Diphenylacetylenehexacarbonyldicobalt (0.24 g, 0.50 mmoles) and bis(diphenylarsino)methane (0.47 g, 1.0 mmole) were dissolved in 50 ml of n-hexane and the solution was refluxed under nitrogen gas for 24 hours with stirring. The reaction mixture was then filtered while it was still hot and the resulting grey-green powdery solid was washed with several portions of n-hexane. The product was recrystallized by dissolving it in a minimum amount of CH_2Cl_2, adding an equal amount of n-hexane, and concentrating and cooling the solution. A red-brown crystalline soild was isolated by filtration and dried in vacuo for 12 hours.

The theoretical elemental analysis for the product, $C_{67}H_{54}As_4Co_2O_3$, gives % C = 60.74 and % H = 4.11. The experimental analysis gave % C = 60.34 and % H = 4.10.

The infrared spectrum in the CO stretching region was recorded in CH_2Cl_2 and two bands were observed at 1991(s) and 1943(s) cm^{-1} ± 5 cm^{-1}. Other weak bands were present in this region due to the rapid decomposition of the substance to $(Ph_2C_2)Co_2(CO)_4$(dam) in solution. The melting point was found to be 177°-178°.

17. The Preparation of $(Ph_2C_2)Co_2(CO)_2(dpm)_2$ from (Ph_2C_2)-$Co_2(CO)_3(dpm)_2$

A sample of $(Ph_2C_2)Co_2(CO)_3(dpm)_3$ was dissolved in 50 ml of toluene and the solution was refluxed under nitrogen gas for several hours with stirring. The solvent was then removed in a stream of nitrogen gas and the red-brown oily residue was dissolved CH_2Cl_2. An equal amount of n-hexane was added and the solution was concentrated in vacuo and cooled. Red-brown crystals were isolated by filtration and were dried in vacuo for 12 hours.

The infrared spectrum of this product in the CO stretching region was recorded in CH_2Cl_2 and showed only one quite broad absorption at 1920 cm^{-1}, identical to the spectrum of an authentic sample of $(Ph_2C_2)Co_2(CO)_2(dpm)_2$.

18. The Preparation of $(Ph_2C_2)Co_2(CO)_3(dpm)_2$ from $(Ph_2C_2)Co_2(CO)_4(dpm)$

Bis(diphenylphosphino)methane (0.1 g, 0.2 mmoles) and $(Ph_2C_2)Co_2(CO)_4(dpm)$ (0.5 g, 0.5 mmoles) were dissolved in 50 ml of cyclohexane and the solution was refluxed under nitrogen gas for 20 hours with stirring. The mixture was then filtered while it was still hot to yield a pale green solid which was washed with cyclohexane and dried in air. The filtrate was a deep red colour.

The infrared spectrum of the green solid was recorded in the CO stretching region in CS_2 and two strong absorptions were observed at 1990 cm^{-1} and 1943 cm^{-1}, identical to the spectrum of an authentic sample of the trisubstituted complex, $(Ph_2C_2)Co_2(CO)_3(dpm)_2$. The infrared spectrum of the filtrate in this region was identical to that of the tetrasubstituted complex, $(Ph_2C_2)Co_2(CO)_2(dpm)_2$.

19. Treatment of $((t\text{-}C_4H_9)_2C_2)Co_2(CO)_6$ with Excess Bis(diphenylphosphino)methane

Di-t-butylacetylenehexacarbonyldicobalt (0.42 g, 1.0 mmole) and bis(diphenylphosphino)methane (0.5 g, 1.4 mmoles) were dissolved in 50 ml of cyclohexane and the solution was refluxed under nitrogen gas for 20 hours with stirring. The reaction mixture was then concentrated in a stream of nitrogen and filtered to give a bright green solid which was washed with cyclohexane and dried in air. Solutions of this product were found to be very unstable in air and the solid itself completely decomposed to a light brown powder within three days in a closed container. The infrared spectrum of the product showed bands in the bridging-CO region and therefore no further work was done.

20. Attempts to Prepare Tetrasubstituted Derivatives of $(Ph_2C_2)Co_2(CO)_6$ and $((CF_3)_2C_2)Co_2(CO)_6$ with dae.

Diphenylacetylenehexacarbonyldicobalt (0.47 g, 1.0 mmole) and bis(diphenylarsino)ethane (1.0 g, 2 mmoles) were dissolved in 50 ml of cyclohexane and the solution was refluxed under nitrogen gas for 24 hours with stirring. Evaporation of the solvent _in vacuo_ yielded a brown powdery solid. Attempts to obtain a crystalline form of this product from CH_2Cl_2/hexane solutions were not successful. Attempts to chromatograph the substance on silica gel using dichloromethane were also unsuccessful in that it could not be eluted from the column.

The infrared spectrum of a CH_2Cl_2 solution of the product in the CO stretching region showed only a broad, flat band ranging between 2000 and 1900 cm^{-1}. An equivalent result was obtained when the same reaction was attepmted with the hexafluoro-2-butynehexacarbonyldicobalt complex.

21. Treatment of $Co_2(CO)_4(dam)_2$ with Diphenylacetylene

Bis(bis(diphenylarsino)methane)tetracarbonyldicobalt was prepared according to the method of Behrens and Aquila [144] and was identified by its infrared spectrum. A sample of this substance (0.08 g, 0.1 mmole) and diphenylacetylene (0.02 g, 0.1 mmole) were dissolved in 50 ml of benzene and the solution was refluxed under nitrogen gas for 80 hours with stirring. The solvent was then evaporated in a stream of nitrogen and a brown residue was obtained. Addition of n-pentane resulted in partial solution of this residue to give a light red solution, the infrared spectrum of which was identical to that of the disubstituted derivative, $(Ph_2C_2)Co_2(CO)_4(dam)$, in the CO stretching region. The pentane-insoluble portion was identified as starting material from its infrared spectrum.

A second reaction was attempted using ultraviolet radiation. A large excess of diphenylacetylene was used and the two substances were dissolved in benzene. The solution was exposed to ultraviolet radiation for 5 days under an atmosphere of nitrogen gas and the solvent was then evaporated to yield a brown residue. This product was chromatographed on silica gel using 1:3 $CHCl_3$-hexane and two separate bands were observed. These were eluted and were found to be identical to the two products in the above reaction.

SECTION D. DETAILS OF EXPERIMENTS IN II-C

1. The Preparation of $(Ph_2C_2)Co_2(CO)_4(PF_3)_2$

Diphenylacetylenehexacarbonyldicobalt (0.94 g, 2.0 mmoles) was dissolved in 10 ml of *n*-pentane and was placed in the glass liner inside the high pressure reaction vessel. The vessel was closed and cooled to -196° using liquid nitrogen. It was subsequently evacuated by using appropriate connections to the vacuum line. Trifluorophosphine (26 g, 300 mmoles) was condensed into the reaction vessel and the vessel was then warmed to room temperature resulting in a gauge pressure of 750 psi. The reaction was left to procced for two weeks at room temperature during which evolved CO gas was removed every three to five days.

At the end of this reaction period the excess PF_3 was removed via the vacuum line and the resulting dark green solution was filtered to remove any insoluble impurities. A dark green crystalline solid was obtained from the filtrate in the following manner: The solution was placed in a 50 ml round-bottom flask which was connected to the vacuum line. The solution was then cooled to -90° using an acetone-dry ice bath and the solvent was removed very slowly by opening the flask to the vacuum line by only a small amount. Over a period of two days dark green crystals were deposited on the sides of the flask. When all of the solvent had been removed the product was dried in vacuo for 24 hours. This product was then recrystallized by dissolving it in a minimum amount of n-pentane, adding an equal amount of methanol, and concentrating and cooling the solution. Dark green crystals were isolated by filtration and were dried in vacuo.

The theoretical elemental analysis for the product, $C_{18}H_{10}Co_2F_6O_4P_2$, gives % C = 37.0, % H = 1.71,

% Co = 20.2, % F = 19.5 and % P = 10.6. The experimental analysis gave % C = 37.0, % H = 1.66, % Co = 19.4, % F = 18.4 and % P = 10.6.

The infrared spectrum of the product was recorded in the CO and PF stretching regions in n-pentane. In the CO stretching region bands were observed at 2028(vs), 2041(vs), 2065(vs, sh) and 2075(vs) cm^{-1} and the PF stretching bands were observed at 870(vs) and 890(vs, sh) cm^{-1}. The remainder of the spectrum was recorded in carbon disulphide and in tetrachloroethylene. In CS_2 bands were found to occur at 3060(vw), 3030(vw), 2958(vw), 1255(vw), 1178(vw), 1075(vw), 1031(vw), 1002(vw), 765(s), 693(s), 675(w), 629(w) and 622(w) cm^{-1}. In C_2Cl_4 other bands were observed at 1489(vw), 1475(vw) and 1444(m) cm^{-1}.

2. Treatment of $Co_2(CO)_8$ with Trifluorophosphine

a) Treatment at -20° and 400 psi for Eight Days

Dicobaltoctacarbonyl (4.2 g, 10 mmoles) was placed inside the glass liner in the high pressure reaction vessel and the vessel was evacuated and cooled to -196°. Sufficient PF_3 was condensed into the vessel to result in a gauge pressure of 800 psi at room temperature. The reaction was left to proceed for eight days at -20°, the gauge pressure being 400 psi at this temperature. Every two days the evolved CO gas was removed. At the end of the reaction period the excess PF_3 was pumped out of the reaction vessel and the vessel was then opened and the glass liner and its contents were placed under a vacuum on the vacuum line at room temperature. The contents of the glass liner consisted mainly of a brown liquid which was found to be quite volatile and was therefore separated from the remaining components by condensing it into a trap at -196°. At this temperature this product is a yellow solid. The substance remaining in the glass liner was a dark brown, powdery solid, the nature of which was not further investigated.

On warming the yellow solid to room temperature it again became a dark brown liquid, but it appeared to be evolving a gas indicating that some decomposition was occurring at this temperature. This was substantiated by the observation that whenever the substance was transferred from one trap to another under vacuum, a non-volatile dark brown substance remained in the trap which was similar in appearance to the brown powdery solid described above. It was therefore concluded that the brown solid found in the glass liner was a result of the decomposition of the brown volatile liquid.

Further characterization of the volatile brown liquid was made very difficult due to its sensitivity to air and the fact that it decomposes even under vacuum at room temperature. An infrared spectrum of the product as a carbon disulphide solution indicated the presence of both terminal and bridging CO groups (peaks at 2060 and 1860 cm^{-1} respectively) and the presence of PF_3 (peaks at 890 and 877 cm^{-1}). It was therefore concluded that this product has a formula of the type $Co_2(CO)_{8-n}(PF_3)_n$.

A brown liquid of identical appearance and behaviour could be prepared in a similar manner using a variety of different pressures, temperatures, and reaction times from 300 psi and room temperature for 15 hours to pressures as high as 600 psi and reaction times as long as nine days.

This product will hereafter be referred to as (i).

b) Treatment at Room Temperature and 400 psi for Nine Days

The procedure described in (a) above was repeated using 1.0 g of $Co_2(CO)_8$ (2.5 mmoles) and sufficient PF_3 to result in a gauge pressure of 400 psi at room temperature. The total reaction time was nine days and the evolved CO gas was removed daily.

At the end of the reaction period the glass liner and its contents were placed under vacuum and the volatile components were trapped out at -196°. The major product was a volatile brown liquid - yellow solid identical to I, but a less volatile substance was also observed which was a bright orange solid at -196° and was a red-brown liquid at 0°. This also appeared to decompose at room temperature in a similar manner to I. The similarities in these two products indicate that they are both of the general formula $Co_2(CO)_{8-n}(PF_3)_n$, but n is expected to be larger in the orange product since more vigorous conditions were used in its preparation. This product will hereafter be referred to as (II).

c) Treatment at 20° and 1000 psi for Fifteen Days

The procedure described in (a) above was repeated using 4.2 g of $Co_2(CO)_8$ (10 mmoles) and sufficient PF_3 to result in a gauge pressure of 1000 psi at room temperature. The total reaction time was 15 days and the evolved CO gas was removed every 2-5 days.

At the end of the reaction period the glass liner and its contents were placed under vacuum and the volatile components were passed through traps at -25° and -96° into a trap at -196°. Products identical to I and II were collected in the trap at -25°, and a colourless solid was collected in the trap at -90°. This colourless solid was a clear, pale yellow liquid at room temperature and had a strong, choking odour. This product was expected to be $HCo(PF_3)_3(CO)$, formed due to the presence of HF in the trifluorophosphine as described by Kruck.[127]

3. Treatment of $Co_2(CO)_{8-n}(PF_3)_n$ with Di-t-butylacetylene

A 2-3 ml portion of the brown liquid (I) was condensed into a 50 ml round-bottom flask which was connected to the vacuum line. About 2-3 ml of di-t-butylacetylene and 15 ml of n-pentane were also condensed into the flask and the mixture was left to react at 0° for five days. The evolved CO gas was removed two or three times daily by venting the flask to the vacuum pump. Further amounts of n-pentane and di-t-butylacetylene were added once daily.

At the end of the reaction period the mixture was warmed to room temperature and all of the volatile components were pumped off leaving a dark reddish-brown solid residue. This was dissolved in n-pentane and filtered to remove some insoluble material, and red-brown crystals were obtained by evaporating the solvent very slowly *in vacuo* while maintaining its temperature at -90°. The product was dried *in vacuo*. Chromatography of a small portion of this substance on silica gel using n-pentane showed only one dark reddish-brown band.

The product was identified as a disubstituted derivative, $((t\text{-}C_4H_9)_2C_2)Co_2(CO)_4(PF_3)_2$, from its elemental analysis and its infrared spectrum. The theoretical elemental analysis for $C_{19}H_{19}Co_2F_6O_4P_2$ gives % C = 30.88, % H = 3.31, % Co = 21.69 % F = 20.96 and % P = 11.40. The experimental analysis gave % C = 30.85, % H = 3.18, % Co = 20.96, % F = 19.38 and % P = 10.60.

The infrared spectrum of the product was recorded in the CO and PF stretching regions in n-pentane. The CO stretching bands were found to occur at 2079(s), 2045(s) and 2020(vs) cm^{-1} and the PF stretching bands were found to occur at 887(s), 875(s, sh), 862(s) and 844(m) cm^{-1}. The remainder of the spectrum was recorded in tetrachloroethylene and bands were observed at 2972(w), 2950(vw, sh), 2930(vw, sh), 2905(vw, sh), 2885(vw, sh), 1474(w), 1469(w), 1389(w), 1369(w), 1320(vw), 1205(vw), 1022(vw), 966(vw), 690(vw), 655(vw) and 595(w) cm^{-1}.

4. The Preparation of $HCo(PF_3)_3(CO)$

The preparation of $HCo(PF_3)_3(CO)$ was carried out according to a modification of the method of Kruck. 127

Dicobaltoctacarbonyl (2.1 g, 5 mmoles) was placed in the glass liner inside the high pressure reaction vessel and the vessel was then evacuated and cooled to -196°. Sufficient PF_3 was condensed into the vessel to result in a gauge pressure of 1000 psi at room temperature, taking no precautions to remove HF from the PF_3 sample. The reaction was allowed to continue for 14 days at room temperature and the evolved CO gas was removed every 2-5 days.

The reaction vessel was opened and the glass liner and its contents were removed and were immediately placed under vacuum. The volatile components of the liner were condensed into a trap at -196° and appeared to consist mainly of a yellow solid identical to I above. A clear, pale yellow liquid which was much more volatile than I was also observed, and this was separated from the yellow solid by trap-to-trap distillation using a trap at -30° to remove I. The clear, yellow liquid was identified as $HCo(PF_3)_3(CO)$ from its infrared spectrum.[127]

5. Treatment of $HCo(PF_3)_3(CO)$ with Di-t-butylacetylene

Di-t-butylacetylene (0.5 ml) and $HCo(PF_3)_3(CO)$ (0.5 ml) were dissolved in n-hexane and the solution was irradiated with ultraviolet light for two hours under nitrogen gas with constant stirring. The reaction mixture became a wine-red colour at first but eventually became a much darker red. During the course of the reaction a small portion of the solution was removed and its infrared spectrum in the CO and PF stretching regions was recorded. Bands due to PF stretching and both terminal and bridging CO groups were observed.

At the end of the reaction period the solvent was removed *in vacuo* leaving a red oil. This was transferred to a vacuum line in order to purify it by trap-to-trap distillation, but on warming the substance to room temperature the sample slowly turned to a royal blue colour indicating that decomposition was occurring.

6. Treatment of $(Ph_2C_2)Co_2(CO)_6$ with Excess $P(OCH_3)_3$ in Toluene

Diphenylacetylenehexacarbonyldicobalt (0.23 g, 0.50 mmoles) and trimethylphosphite (1.2 g, 10 mmoles) were dissolved in 50 ml of toluene and the solution was refluxed under nitrogen gas for 80 hours with stirring. A deep red colour, characteristic of the tetra-substituted derivative, had formed at this point but visible signs of decomposition were present in the reaction mixture in the form of insoluble substances. The infrared spectrum of a portion of this reaction mixture showed only one broad band in the place of the two CO stretching bands of the tetrasubstituted derivative.

7. Treatment of $(Ph_2C_2)Co_2(CO)_2(dpm)_2$ with $P(OCH_3)_3$ and $P(n\text{-}C_4H_9)_3$

An excess of tri-n-butylphosphine and 0.1 g of $(Ph_2C_2)Co_2(CO)_2(dpm)_2$ (0.1 mmoles) were dissolved in 50 ml of toluene and the solution was refluxed under nitrogen gas for 4 days with stirring. The solvent was then evaporated *in vacuo* and the oily residue was chromatographed on silica gel using CH_2Cl_2. The first band was a red colour and was identified as the starting material from its infrared spectrum. Two other small bands were bright green and bright blue indicating that decomposition of the metal-acetylene linkage had likely occurred. A similar result was observed when the same reaction was carried out with trimethylphosphite.

8. Treatment of $((t\text{-}C_4H_9)_2C_2)Co_2(CO)_6$ with $P(OPh)_3$ and with $P(O\text{-}n\text{-}C_4H_9)_3$

Di-t-butylacetylenehexacarbonyldicobalt (0.21 g, 0.50 mmoles) and triphenylphosphite (0.31 g, 1.0 mmole) were dissolved in 40 ml of n-hexane and the solution was refluxed under nitrogen gas for one hour with stirring. A portion of the reaction mixture was then chromatographed on silica gel using n-hexane as the eluent and only one red-brown band was observed. This band was eluted and its infrared spectrum in the CO stretching region showed two bands at 2053 and 1995 cm^{-1}, characteristic of a disubstituted derivative. Analogous results were obtained when tri-n-butylphosphite was used.

8. Treatment of $((t\text{-}C_4H_9)_2C_2)Co_2(CO)_6$ with PPh_3 and with $P(n\text{-}C_4H_9)_3$

Di-t-butylacetylenehexacarbonyldicobalt (0.42 g, 1.0 mmole) and tri-n-butylphosphine (0.4 g, 2.0 mmoles) were dissolved in 40 ml of n-hexane and the solution was refluxed under nitrogen gas for 1 hour with stirring. A portion of the reaction mixture was then chromatographed on silica gel using n-hexane as the eluent. Two bands were observed. The first larger band was a dark brown colour and its infrared spectrum in the CO stretching region showed peaks characteristic of a monosubstituted derivative. The second band eluted was smaller than the first and was a bright red colour. Its infrared spectrum in the CO stretching region was identical to that of an authentic sample of $Co_2(CO)_6(P(n\text{-}C_4H_9)_3)_2$. When the same reaction was carried out with PPh_3, a light brown, insoluble solid resulted which was not further characterized.

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