ORGANOMETALLIC MOLECULES WITH NONRIGID STRUCTURES

by

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Submitted to the Department of Chemistry on August , 1970, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

CHAPTER I

Several new fluxional molecules containing substituted 1,2,7-trihaptobenzyl groups bound to the $(C_5H_5)Mo(CO)_2$ and $(C_5H_5)W(CO)_2$ residues have been prepared and their proton magnetic resonance spectra studied with the objective of elucidating the pathway and evaluating the activation parameters concerned in the fluxional behavior of this class of molecules. The molecules are less difficult to prepare and more stable than previously reported. The chief qualitative conclusion, derived from the study of the 3,5-diisopropylbenzyl compound, is that the $(C_5H_5)Mo(CO)_2$ residue has access to all four equivalent (including enantiomorphically related) positions of attachment to the benzyl group. A plausible pathway would be via a monohapto (i.e., σ-) benzyl$Mo(C_5H_5)(CO)_2$ intermediate, in which rotation about the C_1-C_7 bond of the benzyl group can occur.

CHAPTER II

An introduction is given to the problems of structure and dynamics in cyclopentadienyl metal compounds. The historical development of research in several systems is presented in terms of structural and mechanistic studies. The systems discussed are $(C_5H_5)_2Hg$, $(C_5H_5)_3PCuC_5H_5$, $(C_5H_5)_2Fe(CO)_2$, $(C_5H_5)_2Cr(NO)_2$, and $(C_5H_5)_nMR_{4-n}$ where M is Si, Ge, Sn or Pb. This chapter serves as a prelude for the following ones.

CHAPTER III

Several dynamic processes were found to occur in the molecules $(\underline{h}^5\text{-}C_5H_5)Ru(CO)_2(\underline{h}^1\text{-}C_5H_5)$ and $(\underline{h}^5\text{-}C_5H_5)Fe(CO)_2(\underline{h}^1\text{-}C_5H_5)$. Both molecules are fluxional, with the ruthenium compound undergoing 1,2 shifts at a

slightly lower rate than the iron compound. Rotational isomerism about the metal-$\underline{h}^1$-C_5H_5 bond axis occurs and the isomerization process is very rapid. At high temperatures, ($\underline{h}^5$-C_5H_5)$Fe(CO)_2$($\underline{h}^1$-C_5H_5) appears to undergo rapid dissociation and recombination via homolytic cleavage of the iron-C_5H_5 sigma bond.

CHAPTER IV

The compound bis-(indenyl)mercury has been prepared and its pmr spectrum studies as a function of temperature from -41 to 68°C. At the lowest temperatures a spectrum indicative of a bis-(1-monohapto-indenyl) mercury molecule is observed. As the temperature is raised this spectrum changes in a manner indicative of increasingly rapid occurrence of some process which exchanges the environments of the 1 and 3 protons of the indenyl groups. Concentration independence of the spectrum in the temperature range of intermediate exchange rate rules out a 2nd order intermolecular exchange. It is therefore suggested that the process is an intramolecular one with an activated state (or very short-lived intermediate) in which the mercury atom lies over the fact of the five-membered ring forming a kind of delocalized bond to three or more of the carbon atoms. Mercury is able to participate in such a transition state by utilizing additional 6p orbitals of its valence shell whereas the iron atom of ($\underline{h}^5$-C_5H_5)($\underline{h}^1$-C_9H_7)$Fe(CO)_2$ has no comparable orbitals available and, therefore, this latter molecule is not fluxional, as previously reported. Data reported here on chemical shifts for 1-indenyl compounds vitiate the argument used to assign the spectrum of $(C_2H_5)_3PCuC_5H_5$ and hence the question of whether 1,2 or 1,3 shifts predominate in that case is very much open. Similarly, the proposal that 1,2 shifts predominate in $(C_5H_5)_2Hg$ is also shown to lack proof.

CHAPTER V

The infrared spectra of the copper(I) compounds $(C_5H_5)CuPR_3$, R = C_2H_5, C_4H_9, and the mercury compounds $(C_5H_5)_2Hg$ and C_5H_5HgCl have been reinvestigated. Comparisons are made with the spectra of compounds which serve as models for pentahapto- and monohaptocyclopentadienylmetal systems. The following conclusions emerge unequivocally: (1) Contrary to the belief which has prevailed since 1956, the copper compounds contain pentahapto (i.e., "sandwich-bonded") rings, and (2) The mercury compounds contain monohapto (i.e., σ-bonded) rings. The significance of these results is discussed in relation to the physical, chemical and dynamical properties of the molecules.

CHAPTER VI

A convenient and general method for the preparation of ($\underline{h}^5$-C_5H_5)-(L)Cu compounds is described and illustrated for compounds with L = $(C_2H_5)_3P$, $(C_4H_9)_3P$, $(C_6H_5)_3P$, $(CH_3O)_3$ and CH_3NC. The method involves reaction of the appropriate $(LCuI)_4$ or $(LCuBr)_4$ compound with C_5H_5Tl. The compounds have all been characterized by analyses, pmr, infrared and mass spectra and for L = $(C_6H_5)_3P$ and $(C_2H_5)_3P$, by X-ray diffraction as pentahaptocyclopentadienyl compounds. The compound ($\underline{h}^5$-C_5H_5)-(CO)Cu has also been prepared by reaction of CuCl, C_5H_5Tl and CO in pentane at 0. It has a very high CO stretching frequency (2093 cm^{-1}) and decomposes rapidly at room temperature. Evidence is presented that some of these compounds interact strongly with sulfur dioxide.

CHAPTER VII

The infrared and proton magnetic resonance spectra of the gold(I) compounds $(C_5H_5)AuPR_3$, R = C_4H_9, C_6H_5, have been investigated. While it can be shown unequivocally that the molecules do not possess monohaptocyclopentadienyl structures, there is some uncertainty as to whether the molecules are rigorously pentahapto or whether there may be some slight distortion of the C_{5v} structure. The R = C_6H_5 compound, in solution, undergoes what appears to be rapid, intermolecular phosphine exchange at ambient temperature; the R = C_4H_9 molecule appears not to, but poor thermal stability precludes extensive investigation. The C_5H_5 proton resonance of $(C_5H_5)AuP(C_4H_9)_3$ undergoes a marked shift to lower field on going from aliphatic to aromatic solvents, a phenomenon which is reminiscent of the behavior of the ($\underline{h}^5$-C_5H_5)$CuPR_3$ molecules.

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FOREWORD

Chemists have been aware for some years that molecules are dynamic entities. That is , when circumstances permit, they are rapidly tumbling, flexing, twisting, bending, and vibrating. However, it has only been in the last few years that chemists have begun to discover and to appreciate[1] the extent to which certain molecules are dynamic. In particular, there exist certain molecules which have more than one thermally accessible structure and which can pass rapidly among these structures. When these structures are chemically identical the rearrangement is degenerate and the molecules are called fluxional[2,4] Other terms which will be used to encompass the larger class of molecules undergoing either degenerate or nondegenerate rapid rearrangements include "valence tautomers"[2], "stereochemically non-rigid"[2], and "stereochemically dynamic"[3] molecules.

The use of the adjective "rapid" to characterize these rearrangements is unfortunately not a rigorous means of classifying them. For nondegenerate tautomers one has some intuituve notion that the process is rapid if the rate of interconversion is fast enough to prevent separation by classical means at ambient temperatures. For fluxional molecules, even this working definition is meaningless since the molecule is passing among chemically identical configurations. However, since parts of the fluxional molecule are being permuted by the rearrangement process, the possibility exists of detecting the fluxionality by spectroscopic means. If the site interchange

process is fast (i.e. the lifetime in each configuration is sufficiently short) relative to the timescale[1] of the spectroscopic technique, then the permuted sites will become indistinguishable to this spectroscopic technique. Since most spectroscopic studies to date have been accomplished with nuclear magnetic resonance, it is generally accepted[2] that the term "rapid" implies a rate (ca. 10^{-1} - 10^{4} sec.$^{-1}$) which is rapid on the nmr timescale. This does not mean that other methods such as vibrational sepctroscopy, which has a much faster timescale, are not potentially useful. Indeed, the various physical techniques complement each other and frequently a combination of them is responsible for the discovery of a new nonrigid molecule, since the molecule may appear static to one form of spectroscopy (e.g. infrared) but dynamic to another (e.g. nmr).

Stereochemically nonrigid molecules constitute one area out of many in which chemists are becoming increasing aware of the necessity of viewing the geometry and dynamic behavior of molecules in terms of potential energy surfaces. The classical structures we know for molecules are no more than wells in these surfaces, and numerous properties of the molecule (e.g. how easily it is deformed) are reflected by the depth of the wells and the steepness of the sides. To rigorously describe a molecule, the entire potential energy surface containing all conceivable configurations of the molecule should be given; the more that is known about the shape of this surface, the more that is known about the molecule. Nonrigid molecules possess the characteristic that there are low energy pathways connecting some of the wells (the wells are identical if the molecule is fluxional). The activation energy for the rearrangement describes how high this pathway is, relative

to the ground state of the molecule. The mechanism of the rearrangement describes the exact pathway taken by the molecule. Figure F-1 illustrates some cross sections of parts of possible surfaces.

It can be seen from potential energy surfaces that there is a very subtle interplay of structural and dynamic properties. This is perhaps the most fascinating aspect of nonrigid molecules and the one that will reoccur throughout this thesis.

In the past few years, there has been a tremendous flurry of activity in the area of nonrigid organometallic molecules[2]. This has been due both to the availability of the sophisticated instrumentation (variable temperature high resolution and high sensitivity nmr) necessary to study these systems and also to the interest of many chemists in the structure, bonding, and reactions of organometallic molecules. The theoretical and computational means are presently available to calculate accurately nmr lineshapes as a function of exchange rate for complex systems and the possibility of obtaining reliable activation parameters for these processes makes studies even more attractive. The ultimate aim of these investigations is to learn something about the fundamental nature of structure and bonding in organometallic molecules and something about the fundamental nature of organometallic reactions. It follows that, especially for fluxional systems, the full understanding of the mechanism and energetics of the simplest possible types of organometallic reactions, i.e. those which are reversible, degenerate, and intramolecular, is potentially of great value.

This thesis reports in detail some studies which were carried out in attempts to elucidate the nature of stereochemical nonrigidity in several organometallic systems.

FIGURE F-1

Schematic cross sections of parts of potential energy surfaces for hypothetical nonrigid molecules. The ordinate is qualitative potential energy and the abscissa is the reaction coordinate.

a. The barrier is too high for fluxionality.

b. Fluxional process.

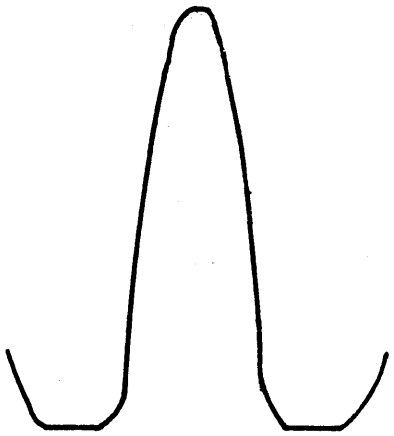
c. Rapid nondegenerate rearrangement.

d. Fluxional process proceeding through an intermediate.

e. System analogous to case d. but in which the intermediate configuration has become the ground state.

f. Rapid nondegenerate rearrangement proceeding through an intermediate.

a



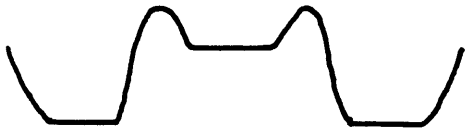
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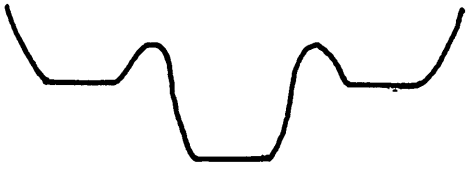
c



d



e



f



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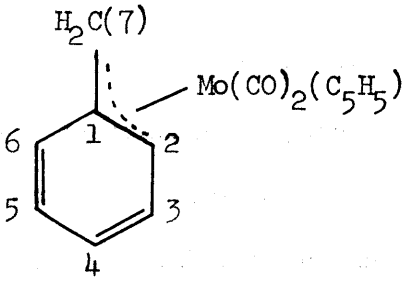
CHAPTER I

PROTON NMR STUDY OF THE FLUXIONAL BEHAVIOR OF SOME SUBSTITUTED (1,2,7-TRIHAPTOBENZYL)(PENTAHAPTOCYCLOPENTADIENYL)DICARBONYL COMPOUNDS OF MOLYBDENUM AND TUNGSTEN

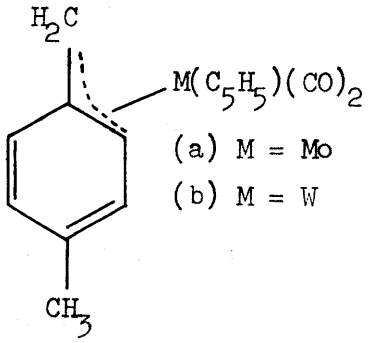
INTRODUCTION

The first example of a compound containing a benzyl group bonded to a metal atom in a manner which could be formally considered to involve the $C_6H_5CH_2$ group serving as a 3-electron donor to the metal atom (or the $C_6H_5CH_2^-$ anion serving as a 4-electron donor to a cation) was reported in 1966 by King and Fronzaglia.[1] The compound in question was $(C_6H_5CH_2)(C_5H_5)Mo(CO)_2$ and King and Fronzaglia proposed that the benzyl group is attached to the molybdenum atom through an allylic sequence of three carbon atoms, one of which is the exocyclic methylene carbon atom. In short, the suggested structure was that which would be designated in a recently proposed notation[2] as (1,2,7-trihapto-benzyl)(pentahaptocyclopentadienyl)dicarbonylmolybdenum, or ($\underline{h}^3$-$CH_2C_6H_5$)-($\underline{h}^5$-C_5H_5)$(CO)_2Mo$. A schematic representation is shown as I.

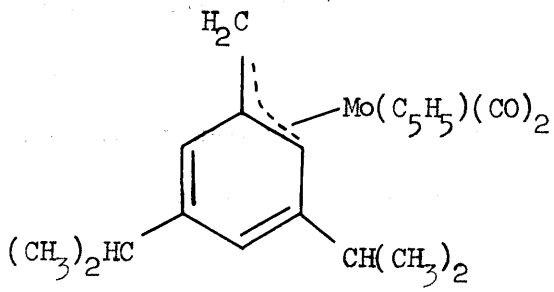
Of even greater interest, however, was the observation that the proton magnetic resonance (pmr) spectrum of the benzyl group showed a pronounced temperature dependence, changing from a pattern consistent with I at -30° to a simpler pattern at $+64^\circ$. The high temperature pattern, its relationship to the low temperature pattern, and the de-


H2C(7)
Mo(CO)2(C5H5)
1
2
3
4
5
6

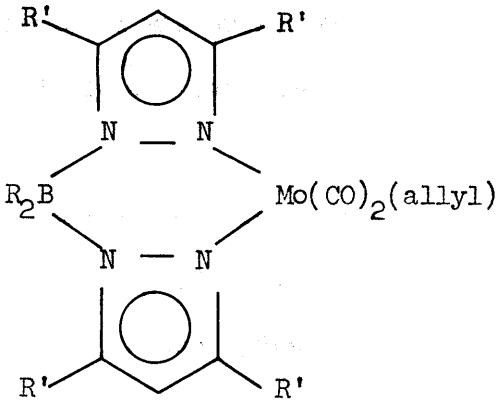
I


H2C
M(C5H5)(CO)2
(a) M = Mo
(b) M = W
CH3

II


H2C
Mo(C5H5)(CO)2
(CH3)2HC
CH(CH3)2

III


R'
R'
N
N
R2B
Mo(CO)2(allyl)
N
N
R'
R'

IV

tailed nature of the line shape changes at intermediate temperatures led to the conclusion that some process (or processes) of intermolecular rearrangement leading to time-average equivalence of the three pairs of protons on opposite edges of the benzyl group was accelerating markedly over the temperature range studied. Several hypotheses as to the rearrangement pathway were described, but no case was pressed for any particular one.

It is worth noting that the observations on this compound constitute one of the earliest reported descriptions of a fluxional organometallic molecule[3] in which the limiting low temperature spectrum, and the spectral changes leading thereto were observed. However, no detailed analysis leading to more thorough empirical description of the process or to closer definition of the mechanism was presented. The system seemed to us to merit this kind of study and the investigation reported here was therefore undertaken.

In conjunction with the chemical and pmr studies described here, an X-ray crystallographic study of the 4-methyl analog of I was carried out;[4] it showed that structures of type I do occur in the $C_5H_5Mo(CO)_2$-benzyl compounds and revealed structural details of importance in discussing rearrangement pathways. The detailed, three-dimensional structure is shown in Fig. I-1.

PREPARATION OF COMPOUNDS

The three compounds of main interest in this work are all new ones, having substituents on the benzyl ring. Using the numbering scheme shown in I they may be designated as the 1,2,7-trihapto-4-methylbenzyl derivatives of the $(C_5H_5)Mo(CO)_2$ and $(C_5H_5)W(CO)_2$ groups, IIa and IIb respectively, and the 1,2,7-trihapto-3,5-diisopropylbenzyl derivative of $(C_5H_5)Mo(CO)_2$, III. All were obtained by way of the appropriate monohaptobenzyl tricarbonyl intermediates following the general preparative route of King and Fronzaglia.[1]

For the molybdenum compounds, IIa and III, we found that conversion of the monohaptobenzyltricarbonyl compounds to the trihaptobenzyldicarbonyl compounds was conveniently accomplished by thermal decarbonylation. Only a few hours heating were required in any preparation, whereas King and Fronzaglia[1] indicated as the method of choice ultraviolet irradiation for five days to prepare I. For the tungsten compound, IIb, the photochemical method was found to be superior to simple heating.

Each of the dicarbonyl compounds we have prepared and studied shows only two sharp CO stretching bands in the infrared spectrum at 25°. Thus, unlike the simple allyl complex,[5,6] $C_3H_5Mo(CO)_2(C_5H_5)$, these compounds appear to be isomerically pure in solution at room temperature.

NUCLEAR RESONANCE STUDIES

Plan of Attack. - Before reporting the experimental results and considering their interpreation, it is necessary to explain the preliminary analysis upon which the design of the experiments were based.

A benzyl group, $C_6H_5CH_2$, possesses two planes of symmetry, one containing all of the atoms and the other, perpendicular to the first and passing through the atoms C_1, C_4 and C_7. As Fig. I-1 shows, the metal atom of the $(C_5H_5)Mo(CO)_2$ group does not lie in either of these planes. In order to discuss its location - and the locations of certain ring substituents - relative to the benzyl skeleton, we shall use the terms face and edge and avoid the equivocal term side. The two surfaces of the $C_6H_5CH_2$ group (i.e., the two sides of the first symmetry plane mentioned above) will be called the faces of the benzyl group. The sets of atoms (cf. I) C_7, C_1, C_2, C_3 and C_7, C_1, C_6, C_5 define what we shall call the edges of the benzyl group. In Fig. I-1 we see the Mo atom lying in a position defined (in part) by the specification of one of the two faces and one of the two edges. It is also important to note that the structure is further characterized by a particular rotational orientation of the $(C_5H_5)Mo(CO)_2$ group relative to the benzyl group, taking a line through the Mo atom and perpendicular to the mean plane of the benzyl group as the axis of rotation.

It is seen in Fig. I-2 that there are four equivalent positions for the $(C_5H_5)Mo(CO)_2$ group relative to the benzyl group. The two

positions in each of the pairs (α, δ) and (β, γ) are equivalent in the fullest sense, because the corresponding molecular configurations are interchangeable by rotations of the entire molecule as a rigid body; the α and δ configurations are enantiomorphous to the β and γ configurations, respectively. It should also be noted that in order to change one of the configurations to an enantiomorphous one, not only must the location of the metal atom be changed, e.g., from α to β, but an internal rotation of the $(C_5H_5)(CO)_2MO$ group relative to the benzyl group must also occur.

For brevity in the following discussion, the entire $(C_5H_5)(CO)_2MO$ or $(C_5H_5)(CO)_2W$ group will be denoted $\underset{\sim}{M}$, and the statement that $\underset{\sim}{M}$ occupies site α (or β, γ, δ) will imply that it has the rotational orientation as well as the positional coordinates appropriate to that site.

It was the objective of this investigation to determine how many of the four sites, α, β, γ, δ, are accessible to the $\underset{\sim}{M}$ group with sufficient frequency to produce observable effects in the pmr spectra. To put it another way, let us assume that a molecule starts with $\underset{\sim}{M}$ in site α. There are three distinct types of site exchange possible, viz., $\alpha \rightleftharpoons \beta$, $\alpha \rightleftharpoons \gamma$ and $\alpha \rightleftharpoons \delta$, and each will have detectably different effects in suitably designed pmr experiments. We wished to know the relative importance of these three types of shift and have therefore planned and carried out experiments intended to provide such information.

One particular distinction we wished to make among the several possible site exchange processes was between the $\alpha \longleftrightarrow \beta$ type, in which $\underset{\sim}{M}$ always remains over the same face, and any other type or combination of types in which $\underset{\sim}{M}$ would go from one face to the other. We shall designate these two classes of shift as suprafacial and antarafacial shifts, respectively. It would appear that the published results of King and Fronzaglia can be explained by the simple postulate of suprafacial ($\alpha \longleftrightarrow \beta$) shifts, but the observations are not inconsistent with certain antarafacial shift processes or with complex combinations of both suprafacial and antarafacial shifts.

It is clear that in order to determine by pmr studies whether antarafacial shifts occur frequently, the benzyl ring must be provided with one or more proton-bearing substituents capable of sensing differences between the environments over the two faces of the benzyl group. Two additional requirements are (1) that the substituent(s) be placed sufficiently far from the region of bonding of the benzyl group to $\underset{\sim}{M}$ that it will not seriously influence the nature of the fluxional processes and (2) that the equivalence of the two edges of the benzyl group be preserved. These restrictions leave as the only practical possibilities the introduction of one substituent in the 4 position or two identical substituents in the 3 and 5 positions. The use of the 3 and 5 positions was considered preferable since the effect of environmental differences on the two faces originating in the region of

C_7, C_1, C_2, C_6 might be too attenuated for a substituent at the 4 position.

Finally, there remained the question of what substituent to use. Several possibilities involving rigid bodies constrained to keep some hydrogen atoms permanently over each face of the benzyl group were considered but rejected. Such molecules were necessarily large and elaborate, thereby introducing serious synthesis problems and possibly solubility difficulties. Instead, isopropyl groups were used in the 3 and 5 positions. It is now well known that when a $-CXY_2$ group is bound to some disymmetric group the two Y groups cannot achieve equivalence in any rotational conformation or as a result of internal rotation, however rapid. The simplest alkyl CXY_2 system would be the ethyl group (X = CH_3, Y = H) but here the geminal H-H coupling superimposed on the quartet splitting due to the CH_3 group leads to a complex broad resonance,[7] which would be unsuited to our purposes. The isopropyl group, however, is well suited to our objectives since CH_3-CH_3' coupling will be negligible and the methyl resonances will be split only into doublets by the unique proton. There are several recent examples of this kind of use of isopropyl groups to detect inversion of disymmetric moieties to which they are attached; in particular, it was the elegant study[8] by Whitesides, supplemented by discussions with Professor Whitesides, which led to our adoption of the isopropyl substituents.

If only suprafacial shifts occur in the 3,5-diisopropyl compound then, in terms of the labelling scheme shown in Fig. I-3, there will be only g $\longleftrightarrow$ and g' $\longleftrightarrow$ h' exchanges. Thus, the four separate methyl (doublet) resonances which should be seen in the limiting low temperature spectrum will coalesce to two doublet resonances if only suprafacial shifts occur. If only antarafacial shifts of the $\alpha \longleftrightarrow \gamma$ type occur, only the site exchanges g $\longleftrightarrow$ g' and h $\longleftrightarrow$ h' will take place. Again, the resonances of the low temperature spectrum will coalesce to two doublet resonances. If antarafacial shifts of the type $\alpha \longleftrightarrow \delta$ occur then the only exchanges will ge g $\longleftrightarrow$ h' and g' $\longleftrightarrow$ h. These results are summarized in Fig. I-4. A combination of any two (or all three) of these types of shifts will lead to permutation of all sites and hence to coalescence of the spectrum to one doublet.

Data for the 4-Methylbenzyl Compounds. - The pmr spectra of the molybdenum and tungsten compounds were recorded at frequent temperature intervals from -30° to +60°. Three of these spectra for the molybdenum compound are presented in Fig. I-5. These spectra are entirely analogous to those reported by King and Fronzaglia[1] for the unsubstituted molybdenum compound. As may be seen from assignments shown in the figure, the observations at -30° are consistent with the molecular structure shown in Fig. I-1 while those at +60° can only be explained by assuming that at this temperature one or more processes of rearrangement are interchanging the environments of the two edges of the benzyl

ring fairly rapidly. Assuming that no rotation of the methylene group about the C_1-C_7 bond occurs, such an interchange could be accomplished by $\alpha \rightleftharpoons \beta$ shifts alone, or by $\alpha \rightleftharpoons \delta$ shifts alone. Of course, a random mixture of these two kinds of shifts or a random mixture of all three kinds of shifts (i.e., $\alpha \rightleftharpoons \gamma$ shifts as well) would also account for the observed coalescences. $\alpha \rightleftharpoons \gamma$ type shifts alone cannot account for the observations.

An approximate line shape analysis was performed on the spectra of compound IIa. Because of the overlapping of peaks, and the presence of spin-spin splittings showing second order effects, the procedures (described in the Experimental section) were necessarily less rigorous and less accurate than those used in simpler and more favorable cases. The resonances for the methylene protons and those for the ring protons ortho to the methylene group were each treated separately (see Fig. I-6) to give data on the rates of the two different site exchanges at various temperatures. It was found that each set of points gave a straight Arrhenius plot. From these plots the activation parameters given in Table I-1 were derived. It is clear that there is no significant difference between the two sets of parameters, and this is strikingly demonstrated by the upper part of Fig. I-7 which shows the two sets of points lying on the line defined by the mean values of log A and E_a for the two sets of protons.

Thus the rearrangement pathways responsible for the observed site exchanges, a $\longleftrightarrow$ b and c $\longleftrightarrow$ d, must either be one and the same, or they must be very similar. From the uncertainties in the data and in the derived parameters of activation we estimate, at about the 90% confidence level, that the rates of the two processes do not differ by more than a factor of ~ 4 anywhere in the temperature range studied.

A similar line shape analysis, using only one of the site exchanges, for the tungsten compound gave appreciably different activation parameters. The differences from the parameters for the molybdenum compound are certainly real, even if there are systematic errors in our procedure for evaluating these parameters, since the sets of spectra for the two compounds are qualitatively very similar so that systematic errors in the procedure should influence both sets of results about equally. The tungsten compound rearranges more slowly despite having an activation energy ~ 3 kcal/mole lower because it also has a much lower frequency factor. We are not at present disposed to offer any rationalization of these results.

Data for the Diisopropylbenzyl Compound. - Proton magnetic resonance spectra for this compound at three temperatures are shown in Fig. I-8. Because there are no protons at the 3 and 5 ring positions, the protons at the 2 and 6 positions (the c and d protons of Fig. I-3) now give rise to singlets in the low-temperature spectrum which collapse

and finally coalesce at higher temperatures. The unique ring proton (i) of course gives a sharp singlet at all temperatures. The behavior of all these resonances closely parallels that of the corresponding ones in the 4-methyl compounds. Moreover, using the c, d resonances (see Fig. I-9) a line shape analysis gave activation parameters (see Table I-1 and Fig. I-7) for $CDCl_3$ solution which are quite similar to those for (p-$CH_3C_6H_4CH_2$)(C_5H_5)$(CO)_2Mo$ in the same solvent. It seems clear that introduction of the isopropyl groups does not seriously alter the fluxional nature of the molecule.

The effect of solvents on the fluxional behavior was also studied using the diisopropyl compound. No significant difference in behavior was found using the three solvents $CDCl_3$, $CD_3C_6D_5$ and $(CD_3)_2CO$. This lack of significant solvent dependence, which is qualitatively apparent when spectra in the different solvents are compared, is shown quantitatively by the activation parameters listed in Table I-1. These parameters are the same within the experimental uncertainties for all three solvents. Thus, it would seem that solvent molecules play no intimate part in the transition state for rearrangement.

We turn now to the temperature dependence of the isopropyl methyl resonances. Figure I-10 shows these in the low- and high-temperature limits. At low temperature (-17°), the pattern is consistent with an instantaneous structure of the kind we have been assuming. Each of the four sets of methyl protons is coupled to the unique proton of its

own isopropyl group by ~ 6.8 Hz. The chemical shift difference between the g and g' protons is too small to resolve. Therefore, these give rise to a symmetrical doublet, each component of relative intensity 3. The h and h' sets differ in chemical shift by ~ 2.0 Hz; therefore, these protons give rise to a doublet (separation ~ 6.8 Hz) of doublets (separation ~ 2.0 Hz). The second highest component of this set is overlapped by the lower field component of the g, g' doublet.

In the high temperature spectrum (+75°) we find only a doublet with separation ~ 6.8 cps. Each component of this doublet is at least as narrow as were the individual components of the low-temperature multiplet. Thus, no resolvable chemical shift differences occur in the high temperature spectrum. This indicates that all four sets of methyl proton environments g, g', h and h' have become equivalent.

It is already known from the study of the 4-methyl compound that the fluxional pathway was such as to give time average equivalence to the two edges of the ring. It is now seen that the two faces also acquire time-average equivalence. If this were not the case, each peak in the high temperature spectrum would show a small splitting of about 1 cps (the average of the h, h' splitting (~ 2 Hz) and the g, g' splitting (~ 0 Hz)). Unless there is some curious and, so far as we know, unprecedented, decrease in the h, h' chemical shift difference as the temperature rises, the absence of any such secondary splitting

in the high-temperature spectrum is direct and unambiguous proof that the $(C_5H_5)(CO)_2Mo$ group has access to all four positions, α, β, γ, δ and passes among them rapidly, ≥ 10 jumps per second, at a temperature of $\sim 75^{\circ}C$.

The previous three paragraphs and Fig. I-10 pertain to results obtained for toluene-d_8 solutions. We have emphasized these results since the h, h' chemical shift difference was greater in that solvent than in any other one used. In fact, analogous studies were carried out in three other solvents, namely, $CDCl_3$, $(CD_3)_2CO$ and C_6H_5Cl (Fig. I-11). In these solvents the h, h' separations at low temperature were in the range 1.6 to 2.0 Hz. In all cases, however, the high temperature spectrum consisted of a doublet essentially identical to that shown in Fig. I-8 for the toluene solution at $+75^{\circ}$. Even granting that in <u>one</u> solvent there might be some remarkable temperature dependence of the h, h' chemical shift difference, such that it would decrease by a factor of ~ 0.2 on going from ~ -20 to $\sim +75^{\circ}$, it seems unlikely in the extreme that this would happen in all four of the solvents used.

DISCUSSION

As noted earlier, in the discussion underlying Fig. I-4, any <u>two</u> of the three kinds of shift (i.e., those shown vertically, horizontally and diagonally in the Figure) will suffice to give the $(C_5H_5)(CO)_2M$ moiety access to all four positions, α, β, γ and δ. While there is no

direct experimental evidence which requires any more detailed conclusion than this, we believe that it is reasonable to hypothesize a more specific pathway of rearrangement.

None of the experimental facts would seem to be at variance with the notion that these molecules pass randomly from one to another of the four equivalent (or enantiomorphous) configurations of the type shown in detail in Fig. I-1 by way of a 7-monohaptobenzyl intermediate. The latter must be assumed to be (a) short-lived and not directly observable, and (b) capable of undergoing fairly fast rotation about the C(1)-C(7) bond. Thus, starting from the α configuration of the trihaptobenzyl structure, the molecule would rearrange to the monohaptobenzyl intermediate, undergo simultaneously rotations about the C_1-C_7 and C_7-Mo bonds and revert to a trihaptobenzyl configuration with about equal probability of the new one being any one of the four.

It will be noted on examining this suggestion in detail that an $\alpha \longleftrightarrow \delta$ shift proceeding in this way would interchange the environments of the two edges of the phenyl ring but would not interchange the environments of the two benzyl protons (H_a and H_b). Thus, if the shifts of $(C_5H_5)(CO)_2M$ among the α, β, γ and δ positions were random, the rate of a, b exchange would be only two-thirds that of the rate of c, d exchanges. Although it was shown that the rates of these exchanges are the same within experimental error at all temperatures,

the errors are such that a ratio of two-thirds in these rates could not be distinguished from a ratio of unity. In fact, the ratio of rates would have to be less than ~ one-fourth before there would be any real chance of observing a statistically significant difference.

The trihapto-monohapto-trihapto pathway involves an intermediate which is cc rdinately unsaturated, having a so-called 16-electron configuration.[9] This is not unreasonable to postulate. It is simply an intramolecular type of dissociative ligand exchange. Coordinately unsaturated intermediates have previously been postulated for carbonyl insertion reactions of other complexes,[10] and for the rearrangement of certain π-allyl complexes involving rhodium.[11] Of direct relevance to the present case there was recently reported a class of π-allyl complexes of molybdenum, viz., the dipyrazolyl borate compounds, IV, containing bulky R' groups[12] which appear to be well-documented stable 16-electron complexes. The compound believed to be (1,2,3,9,10-pentahaptoindenyl)dicarbonyliodomolybdenum has also been put forward[13] as an example of a molybdenum complex with a 16-electron valence shell.

Finally, it may be noted that there is a feature peculiar to this type of "allyl" complex which may help significantly to lower the activation energy for rearrangement by the tri-, mono-, trihapto-pathway; this is a feature not present in simple allyl complexes of (C_5H_5)-$(CO)_2Mo$ and the latter have not, in fact, been observed to undergo any rearrangement leading to an A_4X spectrum.[6] The crystallographic

study[3] of ($\underline{h}^3$-$CH_3C_6H_4CH_2$)($\underline{h}^5$-C_5H_5)$(CO)_2Mo$ revealed a marked alternation of C-C bond lengths around the benzene ring, as may be seen in Fig. I-1. This indicates that the trihapto attachment of a benzyl group significantly lessens the benzenoid resonance.[14] If the molecule passes from the state with a trihapto ring to an intermediate or transition state configuration with a monohapto ring this resonance stabilization is recovered, thus making the monohapto configuration more energetically accessible.

Recently two bis(triethylphosphine)(trihaptobenzyl)palladium(II) complexes have been reported.[15] Since these appear to be fluxional, it is tempting to speculate that the trihaptobenzyl bonding system may facilitate nonrigidity in all organometallic systems.

EXPERIMENTAL

The preparation and all handling or organometallic compounds were carried out in an atmosphere of prepurified nitrogen, since the ($\underline{h}^3$-$CH_2C_6H_5$) compounds are somewhat air-sensitive as solids and extremely so when in solution. All solvents were dried in an appropriate manner, distilled and stored under nitrogen. The ($\underline{h}^1$-$CH_2C_6H_5$) compounds were also kept in the dark. Melting points of ($\underline{h}^3$-$CH_2C_6H_5$) compounds were determined in sealed, nitrogen-filled capillaries. Analyses were performed by Galbraith Microanalytical Laboratories.

(Monohapto-4-methylbenzyl)(pentahaptocyclopentadienyl)tricarbonylmolybdenum. - A procedure similar to that of King and Fronzaglia[1] for the monohaptobenzyl compound was employed, using 0.130 m of

$NaMo(CO)_3C_5H_5$ and 23.9 g (0.170 m) of p-$CH_3C_6H_4CH_2Cl$ in 500 ml of tetrahydrofuran. The crude product was recrystallized from methylene chloride/petroleum ether (35°-50°) at -78°C to yield 18.4 g (40%) of bright yellow solid, m.p. 94-96° (with slight decomposition).

Anal. Calcd. for $C_{16}H_{14}MoO_3$: C, 54.87; H, 4.03. Found: C, 54.7; H, 3.99.

The infrared spectrum (cyclohexane solution) showed strong bands at 2015 and 1935 cm^{-1} (± 5 cm^{-1}). The pmr spectrum consisted of a multiplet at τ2.96 (4H), and singlets at τ4.83 (5H), τ7.08 (2H), τ7.73 (3H).

Trihapto-4-methylbenzyl)(pentahaptocyclopentadienyl)dicarbonyl-molybdenum. - In a 50 ml 3-neck flask furnished with an inlet for nitrogen and a small air-cooled condenser which led to a vacuum pump was placed 1.00 g (2.0 mmol) of ($\underline{h}^1$-$CH_3C_6H_4CH_2$)(C_5H_5)$(CO)_3Mo$. The flask was maintained under vacuum (0.05 Torr) while immersed in an oil bath at 105° for 1.3 hr. Nitrogen was admitted, the flask was allowed to cool and the dark red pyrolysate was dissolved in benzene. This solution was chromatographed on silica gel (Merck silicic acid), eluting with 1:3 benzene/petroleum ether. Collection of the eluate was begun after infrared spectra showed all of the unreacted starting compound to have been eluted. The dark red zone was collected in the bottom of a sublimer and solvent concurrently removed in a stream of nitrogen. The residue was sublimed at 77°/0.04 Torr over a period of 7 hr yielding 0.105 g (11%) of a red-orange solid (m.p. 98-100°).

Anal. Calcd. for $C_{15}H_{14}MoO_2$: C, 55.91; H, 4.35. Found: C, 56.1; H, 4.10.

The infrared spectrum (cyclohexane) had strong bands at 1950 and 1875 cm^{-1} ($\pm$ 5 cm^{-1}). The compound is stable for several months when stored at $\sim 5^{\circ}$ under nitrogen.

3,5-Disopropylbenzyl Chloride. - Using the method of Wiley et al.[16] 45 g (0.25 m) of 3,5-diisopropyl phenol was pyrolyzed with 140 g (0.33 m) of triphenyldibromophosphorane at 300° for 18 hr. The crude 3,5-diisopropylphenyl bromide was distilled from the pyrolysis flask at aspirator pressure and was purified by vacuum fractionation, yielding 18.0 g (30%) of a colorless oil, b.p. 58-63°/0.1 Torr.

Anal. Calcd. for $C_{12}H_{17}Br$: C, 59.75; H, 7.12. Found: C, 60.5; H, 7.02.

The pmr spectrum of a $CDCl_3$ solution of the 3,5-diisopropylphenylbromide had the following resonances: doublet at τ2.80 (2H); multiplet at τ3.02 (1H); heptuplet at τ7.27 (2H); doublet at τ8.86 (12H).

3,5-Diisopropylphenyl bromide, 14.7 g (0.061 m) dissolved in 150 ml of anhydrous ether was treated with 0.070 m of commercial butyllithium in hexane at 0°, and after one hour with dry formaldehyde gas.[17] The mixture was then treated with water, the ether layer separated and the aqueous layer extracted twice with 150 ml portions of ether. The combined ether extracts were washed with 5% HCl solution,

followed by water and dried over anhydrous $MgSO_4$. The ether was then stripped from the filtered solution and the residue vacuum fractionated to yield 8.0 g (75%) of 3,5-diisopropylbenzyl alcohol as a colorless oil, b.p. 95-97°/0.35 Torr.

Anal. Calcd. for $C_{13}H_{20}O$: C, 81.18; H, 10.50. Found: C, 80.9; H, 10.8.

The pmr spectrum of a $CDCl_3$ solution had the following resonances: singlet at τ3.00 (3H); broad singlet at τ4.96 (1H); singlet at τ5.57 (2H); heptuplet at τ 7.22 (2H); doublet at τ8.82 (12H). The ir spectrum had a strong broad band at 3340 cm^{-1}.

The 3,5-diisopropylbenzyl alcohol, 6.32 g (0.033 m), was treated with 50 ml of thionyl chloride at 0° and the mixture was allowed to stand at room temperature for 12 hr. The excess thionyl chloride was then stripped off at aspirator pressure and the residue was fractionated in vacuum to afford 3.90 g (56%) of 3,5-diisopropylbenzyl chloride as a colorless oil, b.p. 76-77°/0.45 Torr.

Anal. Calcd. for $C_{13}H_{19}Cl$: C, 74.08; H, 9.10. Found: C, 73.2; H, 9.23.

The pmr spectrum of a $CDCl_3$ solution had the following resonances: singlet at τ2.97 (3H); singlet at τ5.68 (2H); septuplet at τ7.22 (2H); doublet at τ8.83 (12H).

(Monohapto-3,5-diisopropylbenzyl)(pentahaptocyclopentadienyl)-tricarbonylmolybdenum. - The method previously described for the p-methyl analog was employed with 0.020 m of $NaMo(CO)_3C_5H_5$ and 3.50 g

(0.0166 m) of diisopropylbenzyl chloride in 90 ml of tetrahydrofuran, to yield 4.5 g (64%) of a bright yellow solid, m.p. 91-92° (with slight decomposition).

Anal. Calcd. for $C_{21}H_{24}MoO_3$: C, 59.99; H, 5.77. Found: C, 60.1; H, 6.06.

The infrared spectrum of a cyclohexane solution had strong bands at 2010 and 1930 (doublet) cm^{-1} (± 5 cm^{-1}). The pmr spectrum of a solution in $CDCl_3$ had the following resonances: doublet at τ3.10 (2H); multiplet at τ3.28 (1H); singlet at τ4.85 (5H); singlet at τ7.07 (2H); heptuplet at τ7.19 (2H); doublet at τ8.79 (12H).

(Trihapto-3,5-diisopropylbenzyl)(pentahaptocyclopentadienyl)-molybdenum. - In the vessel described above for the p-methyl compound 1.0 g (2.4 mmol) of (h^1-$(C_3H_7)_2C_6H_3CH_2$)$(C_5H_5)Mo(CO)_3$ was pyrolyzed in high vacuum for 2.2 hr at 110°. The dark red pyrolysate was chromatographed as before and collection of eluate begun when the near absence of starting material was indicated by the ir spectrum. The dark red, viscous oil was pumped for 12 hrs in high vacuum and the solid then sublimed at 78°/0.04 Torr for 36 hr to yield 0.22 g (23%) of dark red crystals, m.p. 69-71°.

Anal. Calcd. for $C_{20}H_{24}MoO_2$: C, 61.22; H, 6.18. Found: C, 61.3; H, 5.79.

The infrared spectrum of a cyclohexane solution shows strong bands at 1955 and 1880 cm^{-1} (± 5 cm^{-1}).

(Monohapto-4-methylbenzyl)(pentahaptocyclopentadienyl)tricarbonyltungsten. - To a 50 ml tetrahydrofuran solution of 9.1 mmol of $NaW(CO)_3C_5H_5$, prepared by the method of Piper and Wilkinson[18] was added 2.11 g (15 mmol) of p-methylbenzyl chloride. The mixture was stirred for 24 hr and then worked up in the same way as were the corresponding molybdenum compounds to yield 1.74 g (55%) of pale yellow solid, m.p. 110-112°.

Anal. Calcd. for $C_{16}H_{14}WO_3$: C, 43.86; H, 3.23. Found: C, 44.1; H, 3.38.

The ir spectrum (cyclohexane) has strong bands at 2010 and 1920 cm^{-1} ($\pm$ 5 cm^{-1}). The pmr spectrum in $CDCl_3$: multiplet at τ2.93 (4H); singlet at τ4.40 (5H); singlet at τ7.01 (2H); singlet at τ7.73 (3H).

(Trihapto-4-methylbenzyl)(pentahaptocyclopentadienyl)dicarbonyltungsten. - The monohapto-4-methylbenzyl compound, 1.30 g (3.0 mmol), dissolved in 8 ml of benzene was placed in a Vycor tube which was attached by a ground glass joint to an additional joint that had been blown onto the bottom of a 50 ml 3-neck round-bottom flask. This flask was equipped through two of its regular necks with a gas inlet and a small condenser leading to a gas outlet. With a slow stream of nitrogen flowing through the system the apparatus was lowered into a large vessel of water in which there was also placed a 450 W, medium pressure Hanovia mercury lamp, close to the Vycor tube. The

monohaptobenzyl compound was irradiated for 24 hr. The volume of the dark-red solution was reduced to half by evaporation with a stream of nitrogen and the solution was chromatographed on silica gel, with a 1:2 mixture of benzene and petroleum ether serving as the eluent. As before infrared spectra were used to monitor the eluate and collection of an orange band was begun after it was seen that virtually all unchanged starting material had passed through. The residue from evaporation of the eluate was sublimed at 80°/0.05 Torr for 36 hr to yield 0.28 g (26%) of the orange solid product, m.p. 125-127°.

Anal. Calcd. for $C_{15}H_{14}WO_2$: C, 43.92; H, 3.45. Found: C, 44.1; H, 3.50.

The infrared spectrum (cyclohexane) had strong bands at 1945 and 1868 cm^{-1} (± 5 cm^{-1}). This compound is very similar to its molybdenum analog except that it reacts more readily with chlorinated solvents and is, in general, less soluble in organic media.

Diels-Alder Reactions. - In all experiments, the p-methyl molybdenum compound was stirred in benzene with the appropriate dienophile under nitrogen. The reactions were followed by infrared spectroscopy. In the case of dimethylacetylene dicarboxylate, no reaction was observed after stirring for one day at room temperature. Heating the mixture to ca. 60°, produced a brown, intractable solid whose infrared spectrum gave no evidence of metal carbonyl C-O stretches

or carboxylate C-O stretches. The supernatant also showed no trace of a metal carbonyl compound. Maleic anhydride produced a similar decomposition product after several hours of stirring at room temperature and tetracyanoethylene produced one almost immediately.

Spectroscopic Measurements. - Infrared spectra were recorded on Perkin-Elmer 237 and 337 spectrometers.

Nmr spectra were measured with a Varian Associates A-60 spectrometer. Temperature calibration was achieved by measuring the peak separation in methanol and ethylene glycol samples. The spectra were calibrated at the lowest temperature with a Krohn-Hite Model 450 oscillator and a Hewlett-Packard Model 524 electronic counter.

To assure rigorous exclusion of oxygen from nmr samples, solvents and tetramethylsilane were degassed and distilled under high vacuum directly onto the solids which had been previously placed in standard size nmr tubes using a nitrogen-filled glove box.

Treatment of Nmr Data. - The rate of rearrangement at a given temperature was estimated by comparison of experimental spectra with those calculated by the method of Kubo[19] and Sack[20] in a manner previously described[21,22] using a computer program written by Professor G. M. Whitesides of This Department for the IBM 360 computer. The computer output consisted of line shapes drawn by a Calcomp plotter and these were visually compared with experimental spectra.

To achieve maximum accuracy in kinetic measurements, spectra were recorded at minimum sweep width and maximum spectrum amplitude. In instances where spectral features were difficult to discern (e.g., near coalescence points) several scans were made of the spectrum. In cases where the separate resonances for each of two exchanging protons were discernable at all times during their collapse, computed spectra were fitted to give the best agreement with both signals. Where one resonance was obscured by other peaks in the spectrum during its collapse, computed spectra were fitted only to the completely visible resonance. In the case of the high field ring protons in $(\underline{h}^3\text{-}CH_3C_6H_4CH_2)(\underline{h}^5\text{-}C_5H_5)Mo(CO)_2$ each exchanging component was simulated as a doublet (due to ortho coupling) with the most intense component again split into a doublet (due to what was apparently long-range coupling). Furthermore, since the high field resonance was partially obscured by the cyclopentadienyl peak, the linewidth and intensity of the smaller component of the doublet was estimated from the spectrum in the fast exchange limit.

A computer program written by Mr. W.K. Bratton was used to fit Arrhenius plots by the method of least squares and to compute activation parameters.

Table I-1

Activation Parameters[a,c] for Site Exchanges

Compound	Solvent	Protons[b]	Log A	E_a kcal/mol	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ eu
IIa	$CDCl_3$	a,b	16.6 ± 0.2	19.2 ± 0.3	18.6 ± 0.3	15.6 ± 1.3
IIa	$CDCl_3$	c,d	16.2 ± 0.3	18.8 ± 0.4	18.2 ± 0.4	14.0 ± 1.3
IIb	$CD_3C_6D_5$	a,b	13.5 ± 0.2	15.9 ± 0.2	15.3 ± 0.2	1.3 ± 1.1
III	$CDCl_3$	c,d	14.9 ± 0.3	18.7 ± 0.4	18.1 ± 0.4	7.5 ± 1.3
III	$CD_3C_6D_5$	c,d	14.6 ± 0.3	18.3 ± 0.5	17.7 ± 0.5	6.2 ± 1.3
III	$(CD_3)_2CO$	c,d	14.9 ± 0.3	19.1 ± 0.4	18.4 ± 0.4	7.6 ± 1.3

(a) $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were evaluated at the temperature giving mean residence times of 0.01 sec.

(b) As identified by lower case letters in Figs. I-3 and I-5.

(c) Standard deviations are derived from the least-squares fitting of the Arrhenius plots.

FIGURE I-1

A quasiperspective view of the ($\underline{h}^3$-4-$CH_3C_6H_4CH_2$)($\underline{h}^5$-C_5H_5)-$(CO)_2Mo$ molecule, showing details of the stereochemistry and the more important interatomic distances (data from Ref. 4).

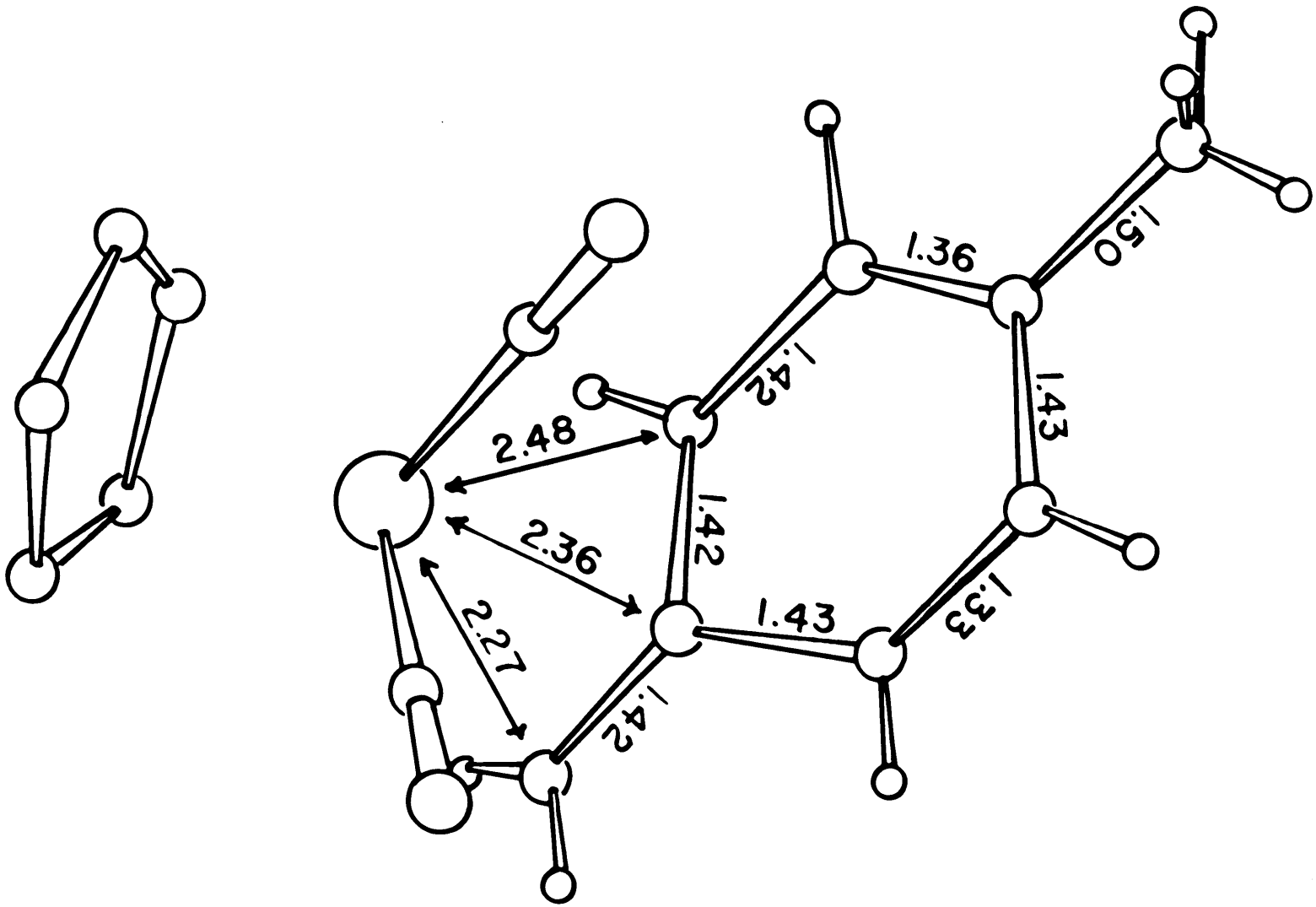

1.36
1.50
1.42
1.43
2.48
1.42
2.36
1.43
1.33
2.27
1.42

FIGURE I-2

A schematic drawing in which both the C_5H_5 ring and the benzyl group are seen edge-on, showing the four chemically equivalent locations of the $(C_5H_5)(CO)_2Mo$ group relative to the benzyl group. The initial position, α, is represented in heavy lines. Other positions, β, γ, δ are shown in lighter lines.

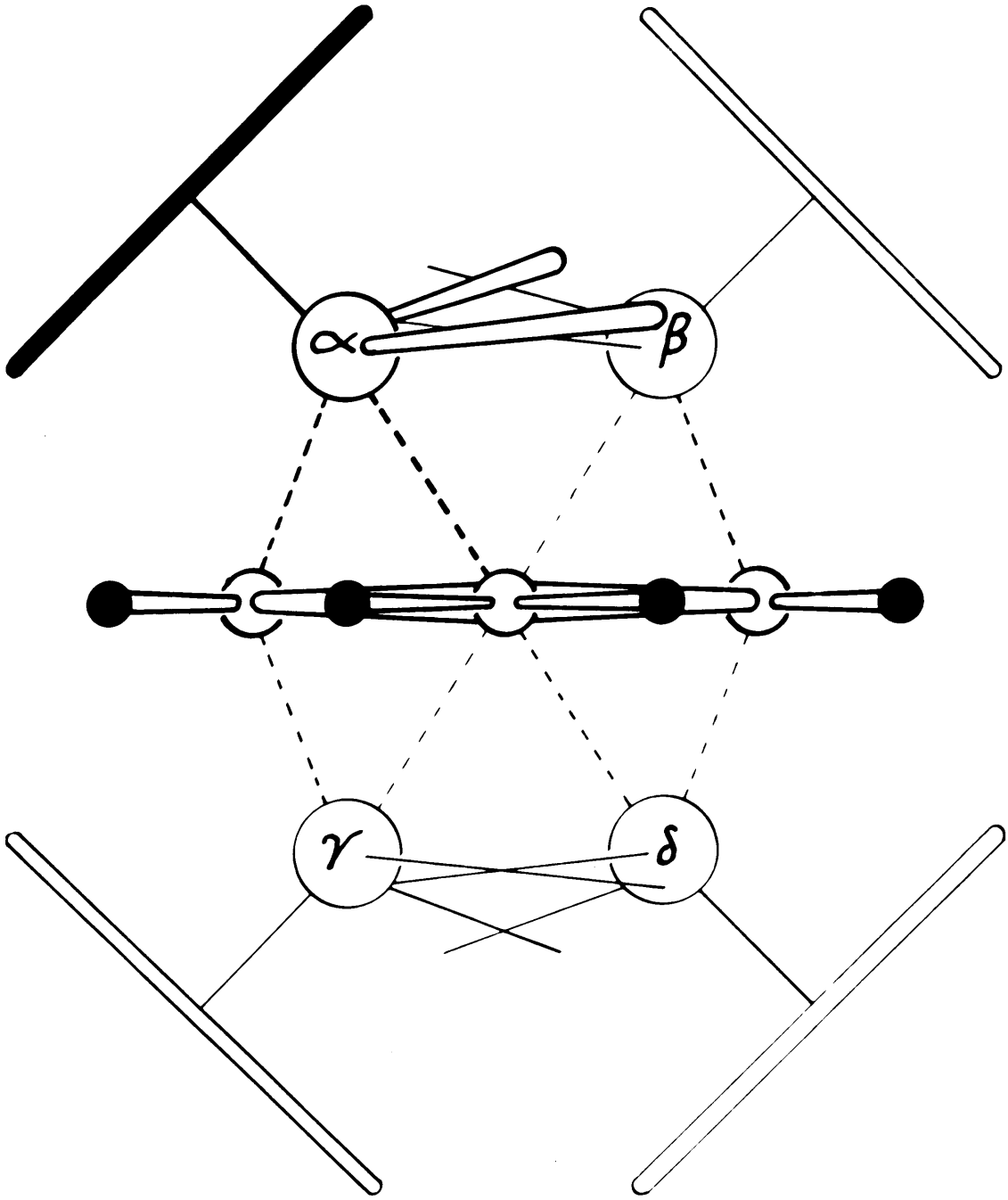

α
β
γ
δ

FIGURE I-3

A diagram showing how the various protons in the 3,5-diisopropylbenzyl compound are labelled.

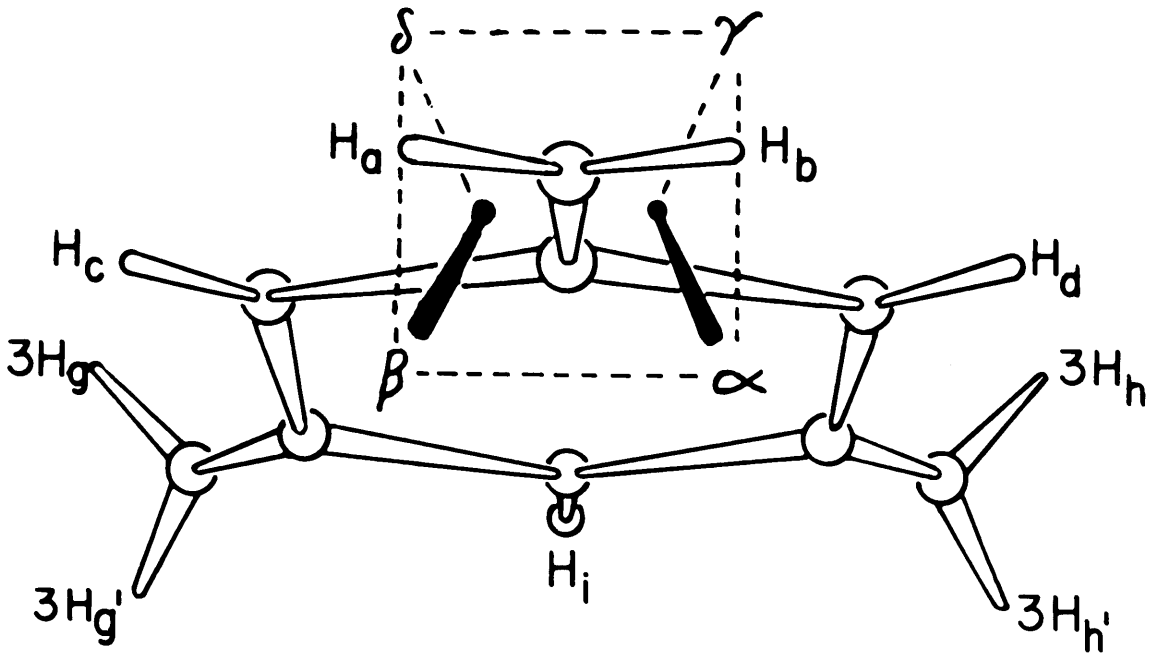

δ
γ
Ha
Hb
Hc
Hd
3Hg
β
α
3Hh
Hi
3Hg'
3Hh'

FIGURE I-4

A diagram summarizing the site exchanges of isopropyl methyl protons which will be effected by each of the three types of shift in the location of the $(C_5H_5)(CO)_2Mo$ group.

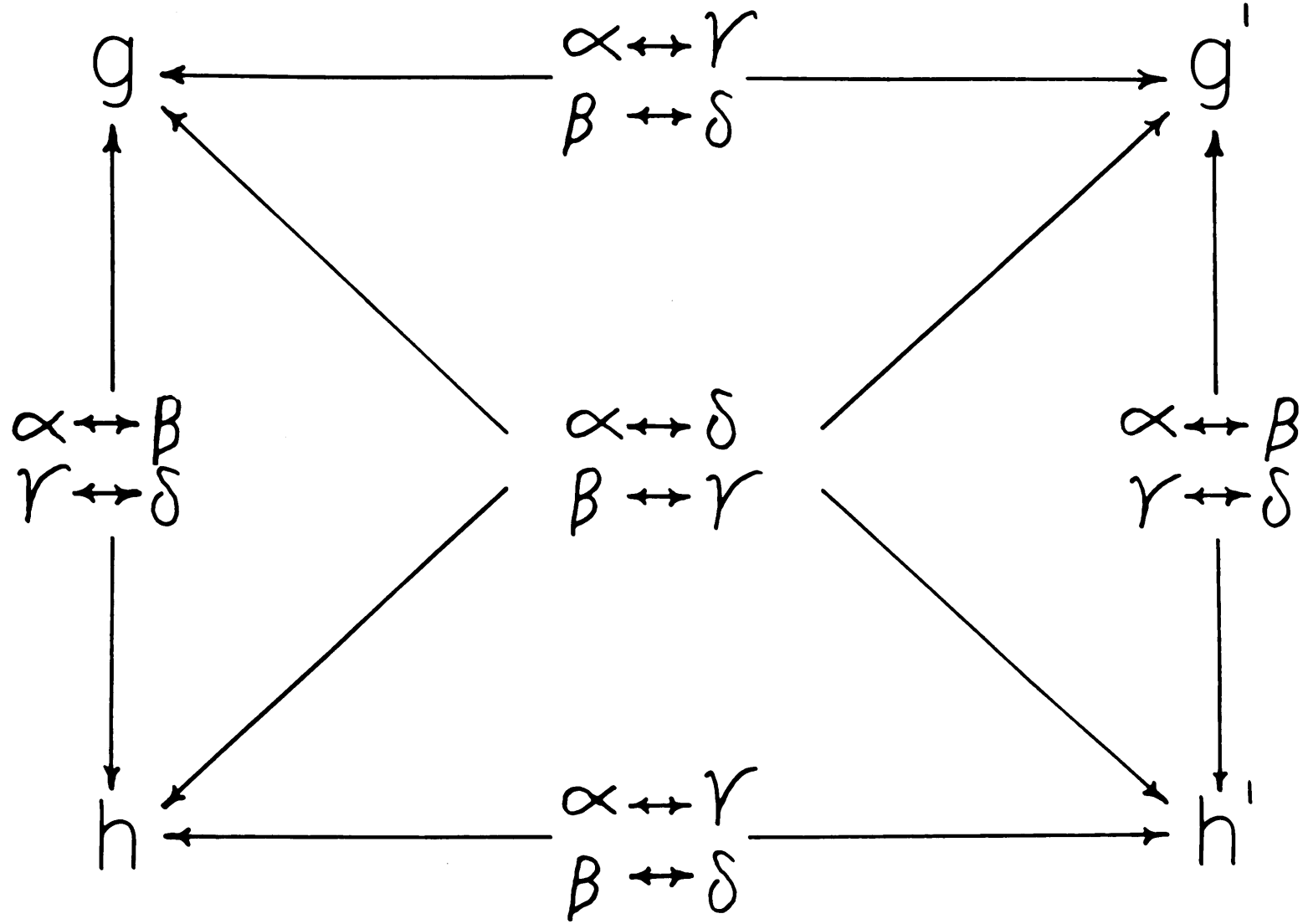
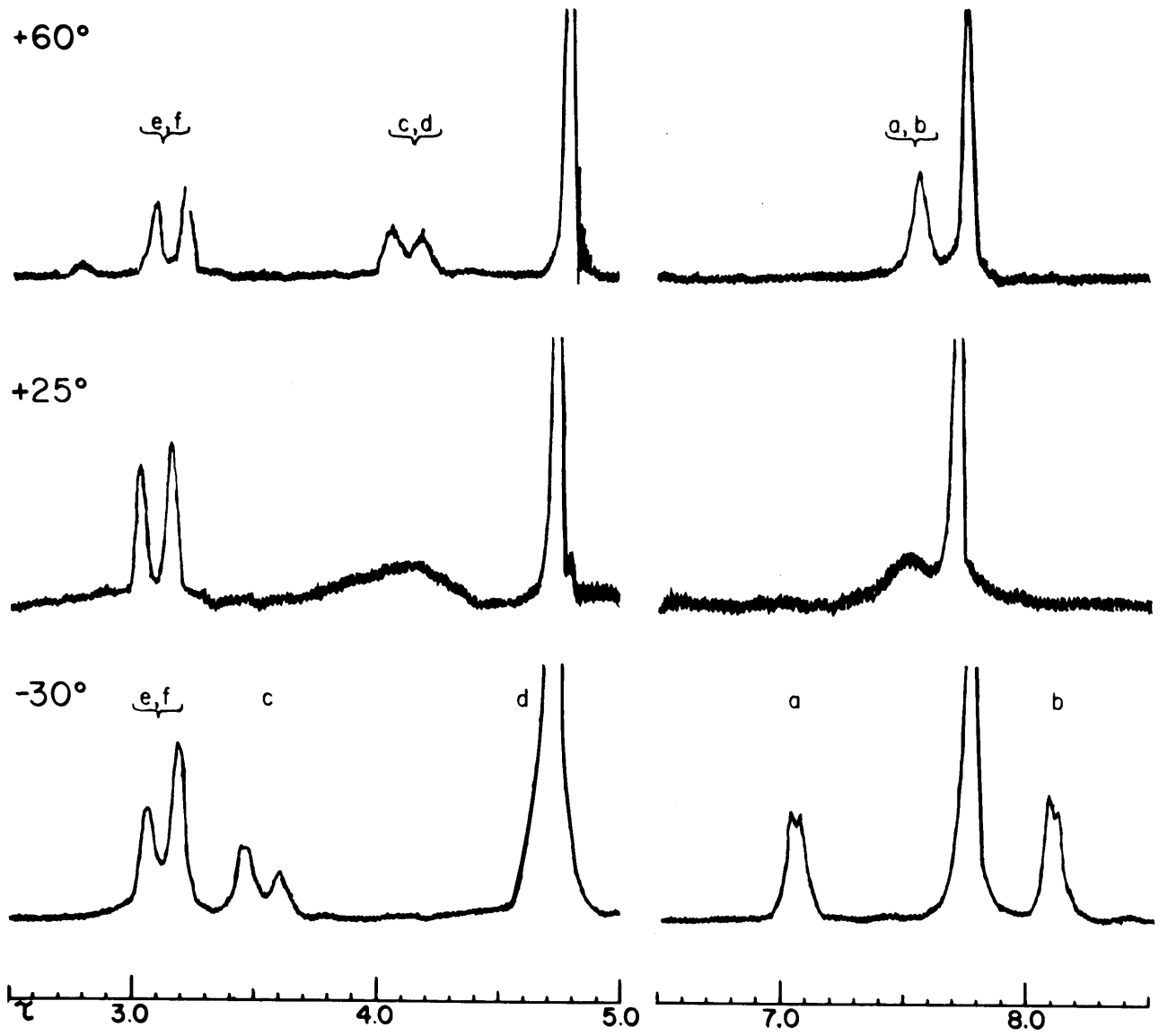

g
α ↔ γ
β ↔ δ
g'
α ↔ β
γ ↔ δ
α ↔ δ
β ↔ γ
α ↔ β
γ ↔ δ
h
α ↔ γ
β ↔ δ
h'

FIGURE I-5

Proton magnetic resonance spectra of (1,2,7-$\underline{h}^3$-4-methylbenzyl)($\underline{h}^5$-C_5H_5)$(CO)_2Mo$ at 60 mc. Approximately 0.1 M solutions in $CDCl_3$ were used. Small peaks are identified according to the diagram at the right. The large peaks at $\sim \tau 4.7$ and $\sim \tau 7.7$ are due to C_5H_5 and CH_3 respectively.


+60°
e,f
c,d
a,b
+25°
-30°
e,f
c
d
a
b
τ
3.0
4.0
5.0
7.0
8.0

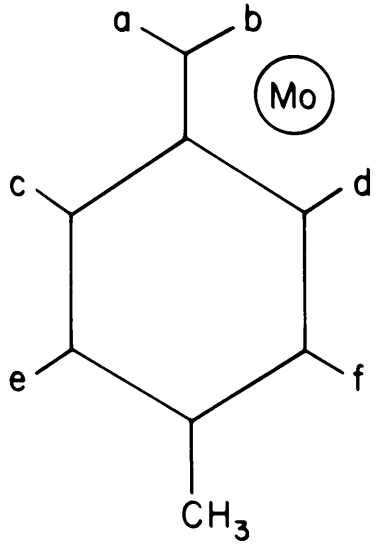

a
b
Mo
c
d
e
f
CH3

FIGURE I-6

Example of computer simulation of the exchange process in the methylene protons of $(CH_3C_6H_4CH_2)(C_5H_5)(CO)_2Mo$. At the right are the computer generated spectra for the mean lifetime indicated. At the left are the experimental spectra at expanded sweep width.

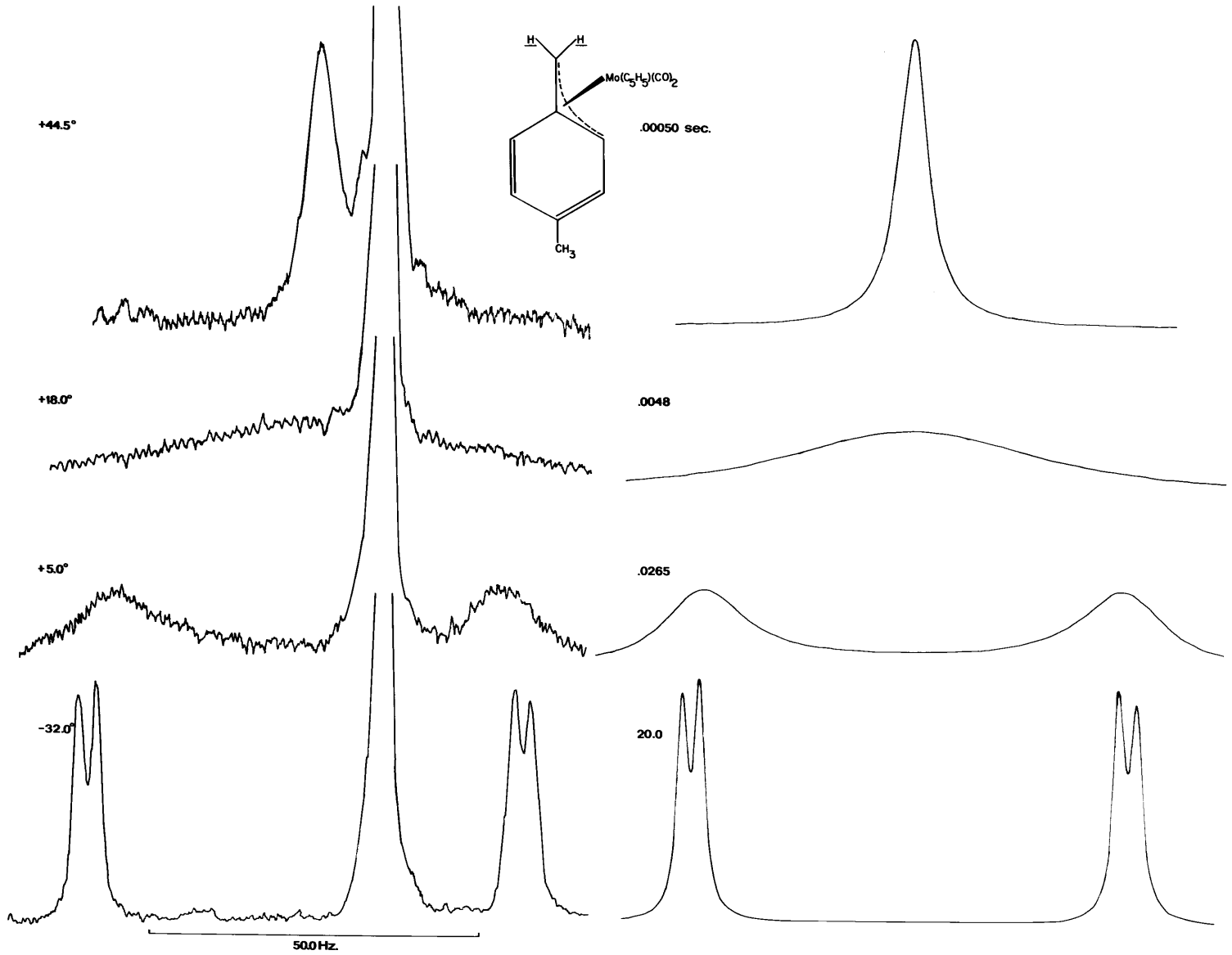

+44.5°
+18.0°
+5.0°
-32.0°
50.0 Hz.
H
H
Mo(C5H5)(CO)2
CH3
.00050 sec.
.0048
.0265
20.0

FIGURE I-7

Arrhenius plots for the site exchange processes observed in this study. Open circles and triangles are for the ring (c,d) and methylene (a,b) protons, respectively, of $(CH_3C_6H_4CH_2)(C_5H_5)(CO)_2Mo$. Filled triangles are for the methylene (a,b) protons of the tungsten analog. Filled circles are for the ring protons (c,d) of the 3,5-diisopropyl compound in acetone-d_6.

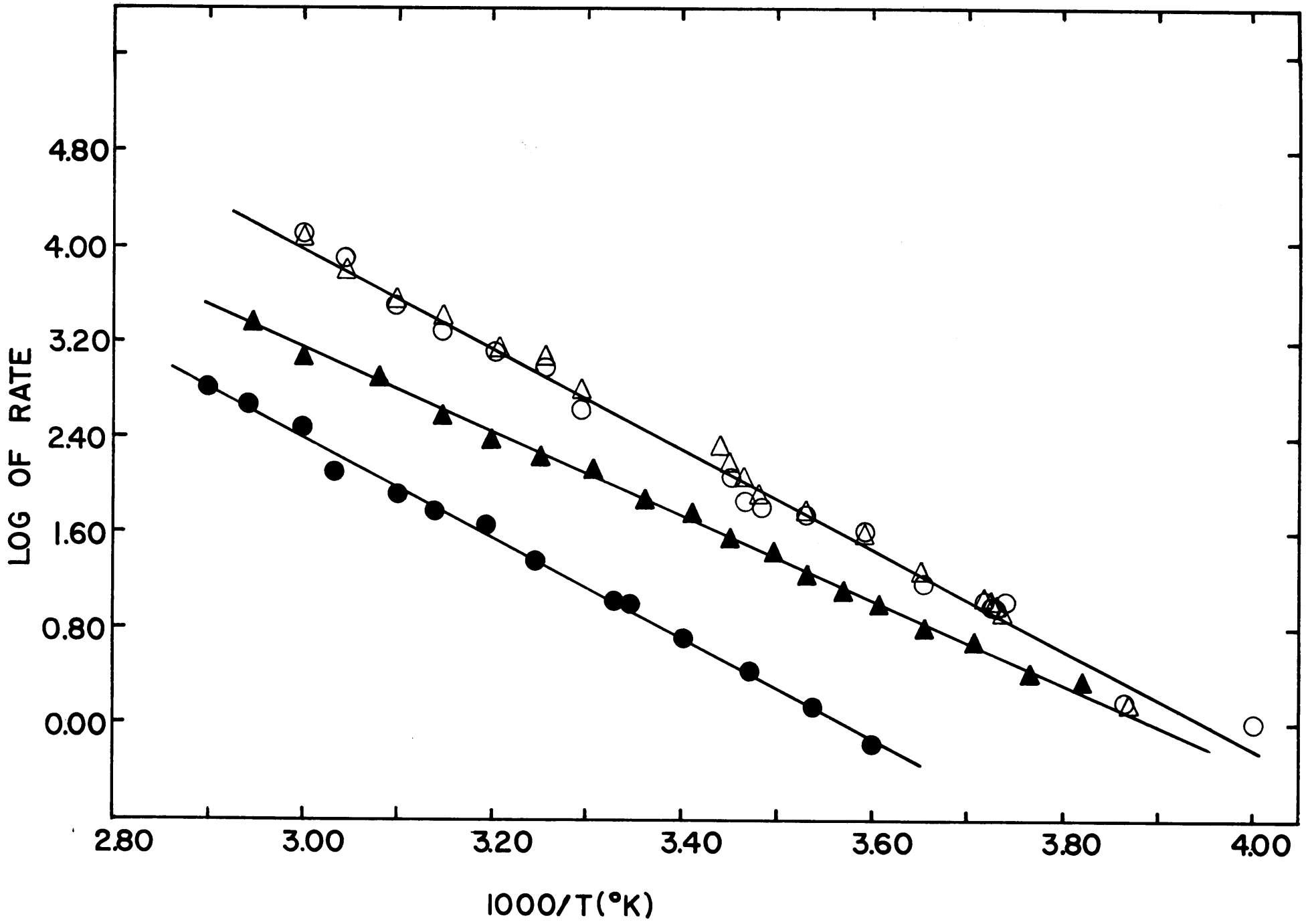

4.80
4.00
3.20
2.40
1.60
0.80
0.00
LOG OF RATE
2.80
3.00
3.20
3.40
3.60
3.80
4.00
1000/T(°K)

FIGURE I-8

Proton magnetic resonance spectra of (1,2,7-$\underline{h}^3$-3,5-diisopropylbenzyl)($\underline{h}^5$-C_5H_5)$(CO)_2Mo$ at 60 mc. Approximately 0.1 M solutions in toluene-d_8 were used. Peaks marked T are due to traces of toluene-d_7. Other small peaks are identified by letters corresponding to Fig. I-3. The strong lines at $\sim \tau 5.1$ and $\sim \tau 8.8$ are due to C_5H_5 and the isopropyl methyl groups, respectively. The broad multiplet at $\sim \tau 7.3$ is due to the single protons of the isopropyl groups.

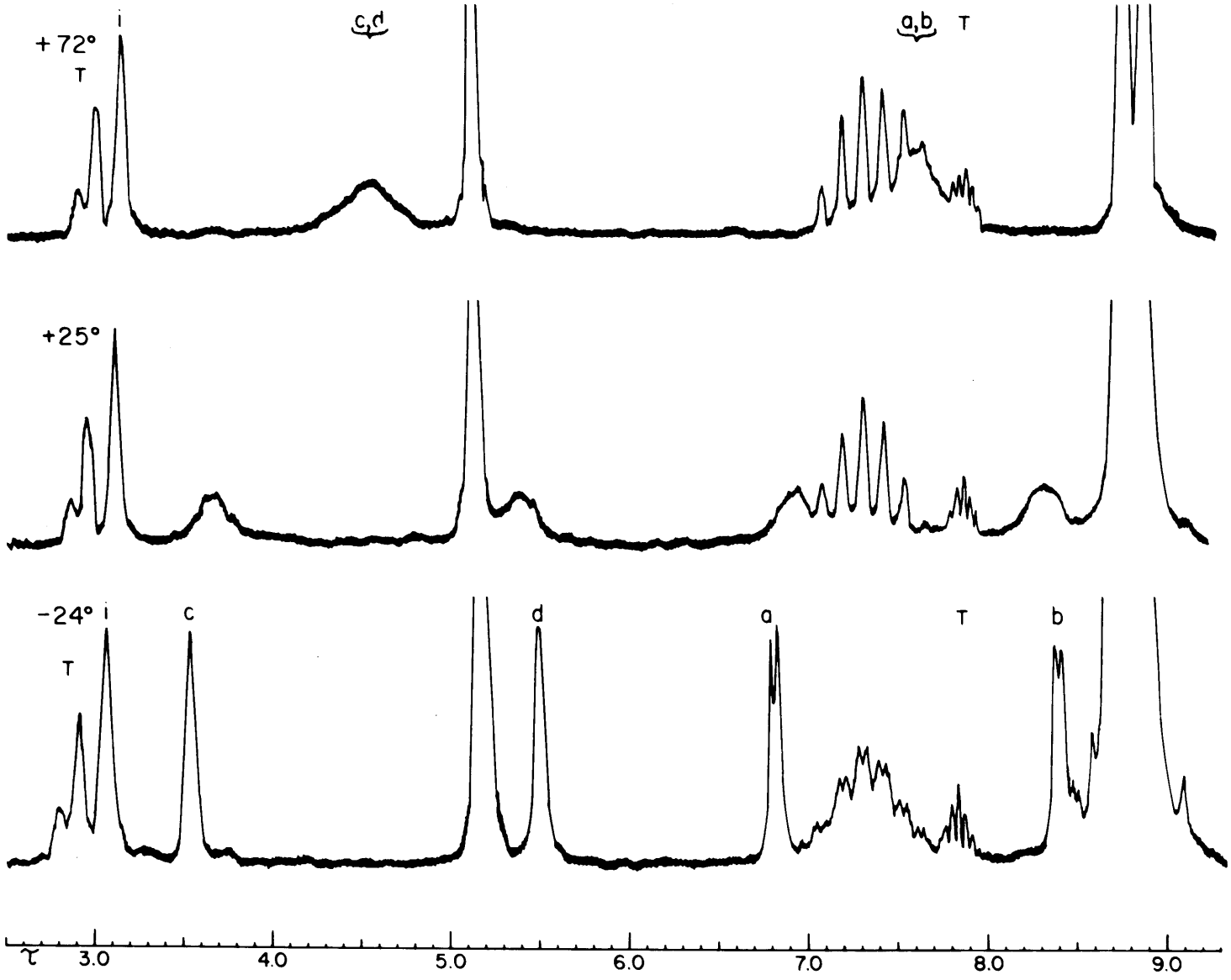

+72°
T
i
c,d
a,b
T
+25°
-24°
T
i
c
d
a
T
b
τ
3.0
4.0
5.0
6.0
7.0
8.0
9.0

FIGURE I-9

Example of the computer simulation of the exchange process in the ortho ring protons of (1,2,7-$\underline{h}^3$-3,5-diisopropylbenzyl)($\underline{h}^5$-C_5H_5)$(CO)_2Mo$. Computer generated spectra with the indicated mean lifetime are shown at the right and experimental spectra at the left.

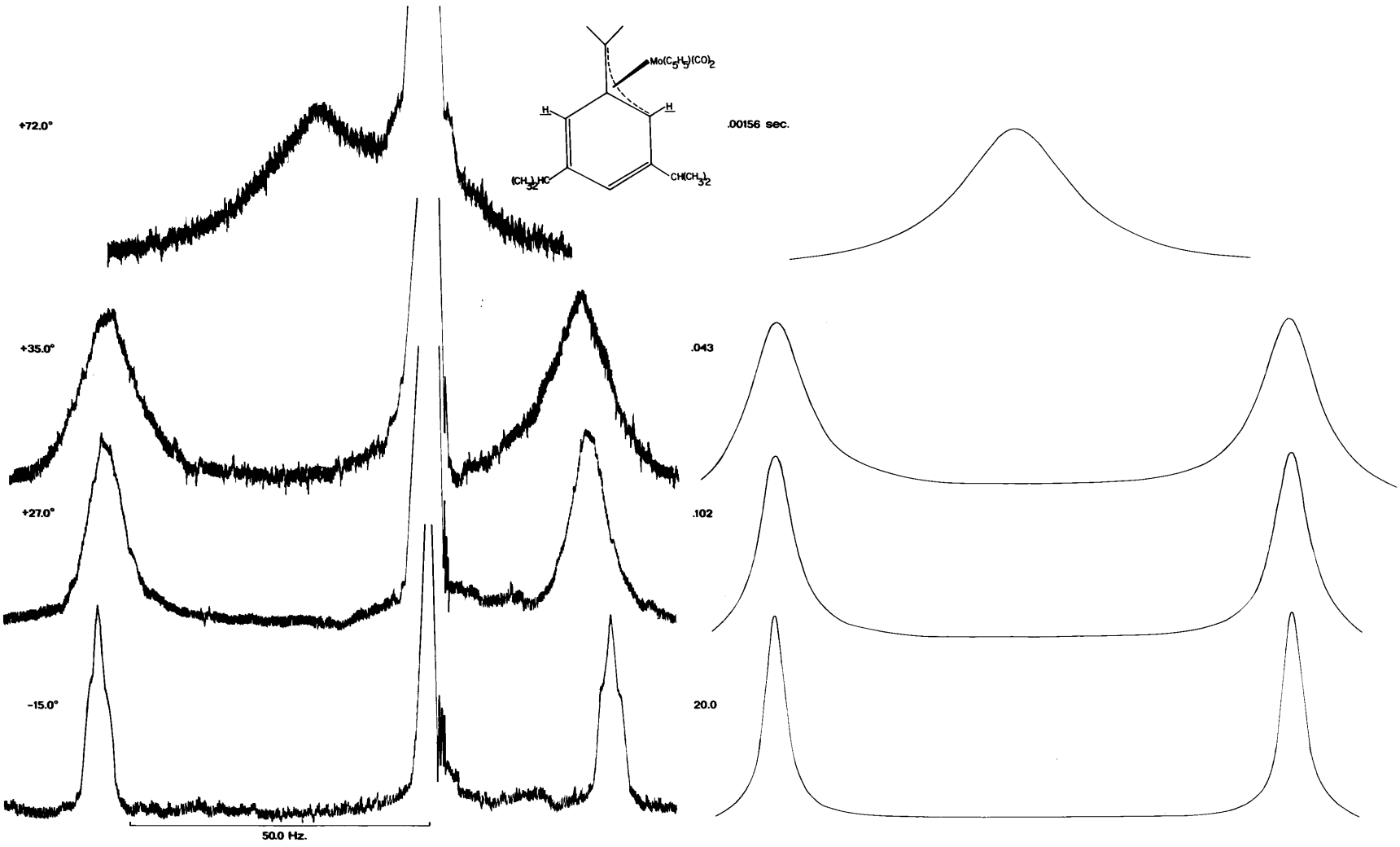

+72.0°
+35.0°
+27.0°
-15.0°
50.0 Hz.
Mo(C5H5)(CO)2
H
H
(CH3)2HC
CH(CH3)2
.00156 sec.
.043
.102
20.0

FIGURE I-10

Enlarged records of the isopropyl methyl resonances in the low temperature and high temperature limiting spectra in toluene-d_8.

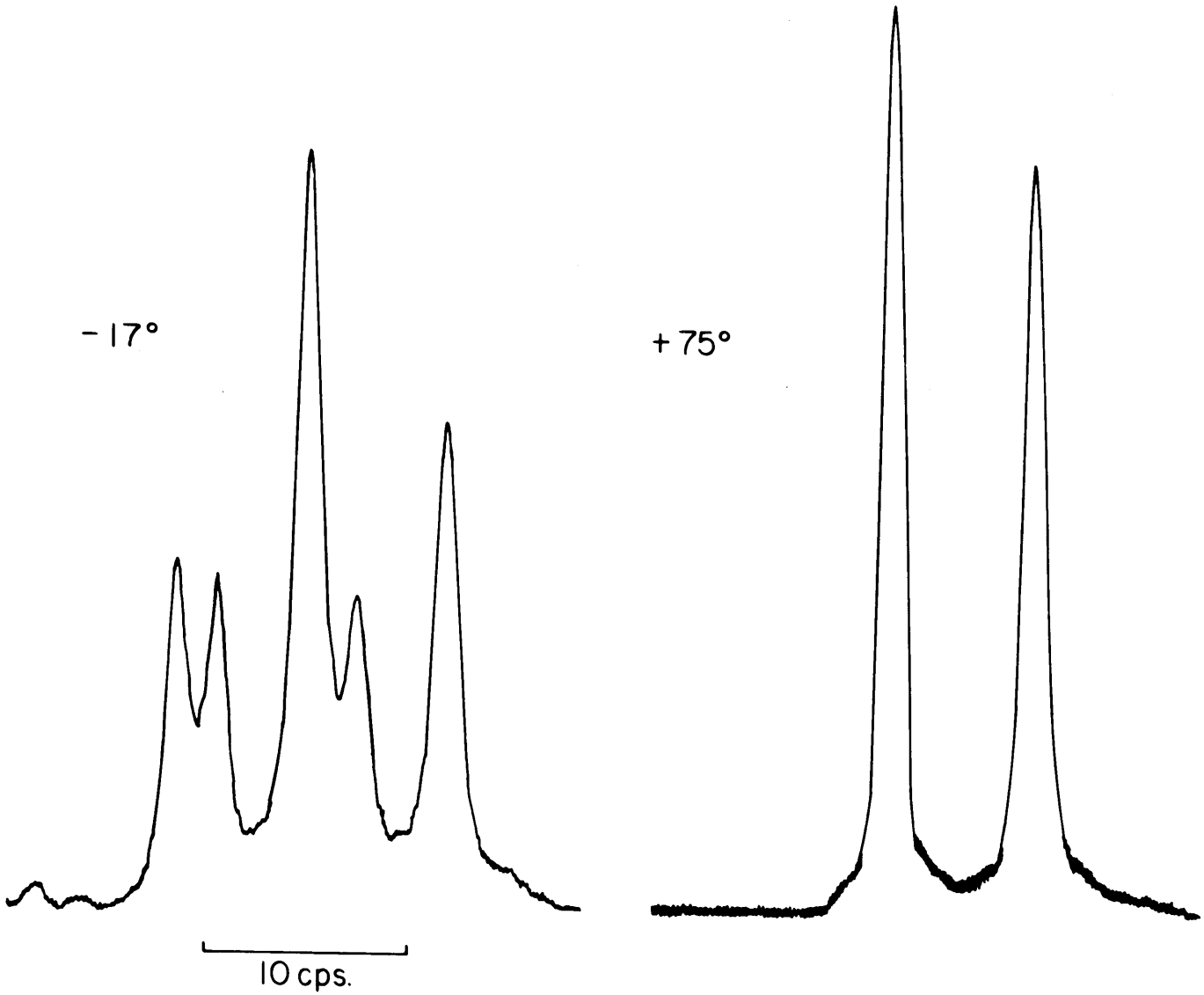
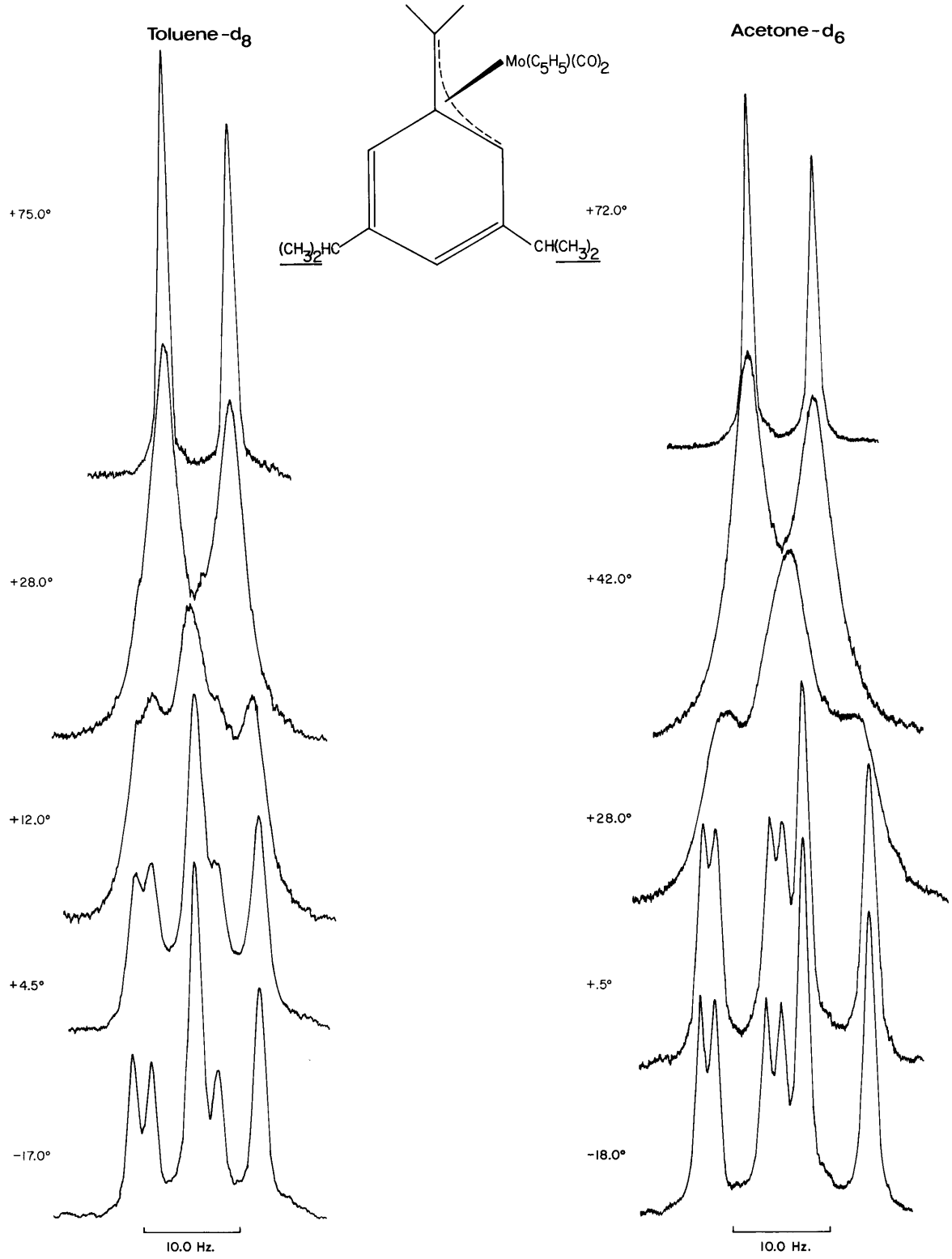

-17°
+75°
10 cps.

FIGURE I-11

Spectra of the isopropyl methyl resonances over a temperature range and in two different solvents.


Toluene-d_8
Acetone-d_6
$Mo(C_5H_5)(CO)_2$
$(CH_3)_2HC$
$CH(CH_3)_2$
+75.0°
+28.0°
+12.0°
+4.5°
-17.0°
+72.0°
+42.0°
+28.0°
+.5°
-18.0°
10.0 Hz.
10.0 Hz.

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CHAPTER II

INTRODUCTION TO PROBLEMS OF STRUCTURE AND DYNAMICS IN CYCLOPENTADIENYLMETAL COMPOUNDS

Beginning with the controversy concerning the structure of ferrocene,[1-4] it became apparent that there existed at least two possible geometrical configurations in which a metal could bond to a cyclopentadienyl ring. Using the recently proposed nomenclature rules[5] for organometallic compounds, these are the pentahapto (I) and monohapto (II) structures. In addition, there has been some discussion[6-8] of the possibility of a trihapto (III) structure existing, but at present, there is no evidence for it.[9] In 1956, Wilkinson and Piper[10]



I



II



III

reported the synthesis of bis(cyclopentadienyl)mercury(II) and triethylphosphinecyclopentadienylcopper(I), for which, on the basis of infrared, UV and chemical data, they proposed, with some reservations, structure II. Shortly thereafter, they reported[11] the synthesis of bis(cyclo-

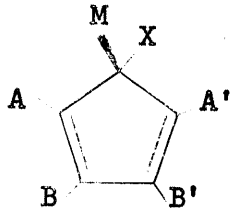
pentadienyl)dicarbonyliron and bis(cyclopentadienyl)dinitrosylchromium, suggesting that each molecule contained one $\underline{h}^1$ and one $\underline{h}^5$ ring. The pmr spectra of all the above compounds exhibited only a single resonance for all protons of the $\underline{h}^1$-C_5H_5 ring. With remarkable insight, they proposed that the presence of the single resonance could be caused by a migration of the metal atom about the ring at such a rate as to render the ring protons equivalent on the nmr time scale at room temperature.

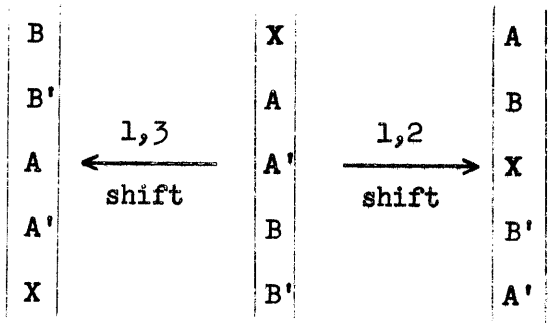
These molecules remained somewhat of a curiousity until nearly ten years later when the sophistication of X-ray crystallographic and nmr spectroscopic techniques facilitated the study of organometallic molecules to a much greater depth. At that time, the first evidence of fluxionality was brought forth and discussion of rearrangement mechanisms began. The following gives a brief discussion of the results which were obtained in the first studies and is intended to serve as a prelude to the following chapters by presenting the questions which were left unanswered and the possibilities for further studies which were generated.

$(\underline{h}^5\text{-}C_5H_5)Fe(CO)_2(\underline{h}^1\text{-}C_5H_5)$

In 1966, Bennett, et al.[12] reported X-ray and low temperature nmr studies on this compound. The structure in the solid state consisted of one $\underline{h}^5$-C_5H_5 ring and one $\underline{h}^1$-C_5H_5 ring as Wilkinson had predicted (and in accord with the noble gas formalism). The nmr spectrum was

temperature dependent and at ca. -80°, the h^1-C_5H_5 ring displayed the AA'BB'X pattern to be expected for a σ-cyclopentadienyl metal compound. The spectra were poorly resolved, but it was evident that on raising the temperature (and thus increasing the rate of rearrangement) the low field portion of the olefinic multiplet collapsed more rapidly than the high field olefinic portion. It could be shown that this was not consistent with a random exchange of sites in the h^1-C_5H_5 ring (which presumably would occur if a structure such as I were an intermediate) but was consistent with either 1,2 or 1,3 shift processes which do not permute all sites at the same rate,[13] as can be seen below. In both these cases, the olefinic protons are not

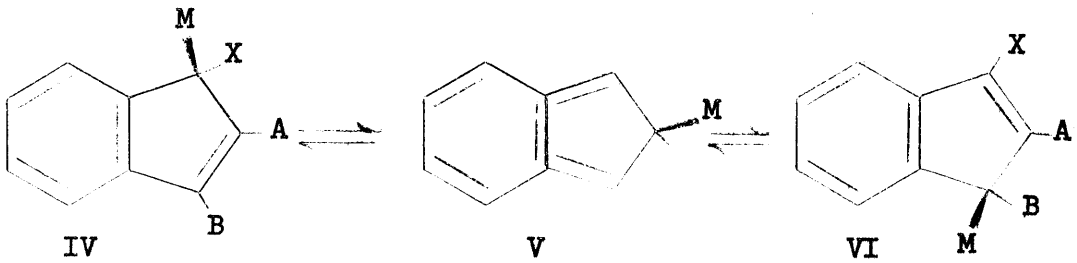




permuted at the same rate, and this would be expected to lead to an asymmetric collapse of the olefinic multiplet as the rearrangement rate increased. The problem, of course, is that unless the AA' and BB' multiplets can be assigned correctly, whether a 1,2 or 1,3 shift is occurring cannot be determined. On the basis of arguments about

the amount of fine structure in the olefinic multiplets and the reasonable assumption that $|J_{AX}| \geq |J_{BX}|$, the low field multiplet was assigned to AA', thus leading to the conclusion that 1,2 shifts were taking place in the rearrangement processes. This was intuitively satisfying since a 1,2 shift would be expected to have a lower activation energy than a 1,3 shift. Presumably, a bonding configuration such as III lies low enough in energy to provide an easily accessible pathway between the degenerate $\underline{h}^1$-C_5H_5 ground state configurations.

To further support the 1,2 shift hypothesis, Cotton, Musco and Yagupsky[14] reported studies on ($\underline{h}^5$-C_5H_5)Cr(NO)$_2$($\underline{h}^1$-C_5H_5) which was fluxional, rearranged more rapidly than ($\underline{h}^5$-C_5H_5)Fe(CO)$_2$($\underline{h}^1$-C_5H_5), and showed assymetric collapse of the olefinic multiplet (the low field portion collapsing more rapidly), and on a new indenyl compound, ($\underline{h}^5$-C_5H_5)Fe(CO)$_2$($\underline{h}^1$-C_9H_7) which was not fluxional. They argued that a 1,2 shift would cause the molecule to pass through a high energy isoindenoid intermediate (V) and thus the fact that no fluxionality was observed up to +70° mitigated against the 1,3 shift



IV V VI

mechanism. Also they were able to determine unambiguously (by deuteration and double resonance) the relative resonance positions of the A and B protons, and these assignments, when extrapolated to the $\underline{h}^1$-C_5H_5 system, yielded a 1,2 shift.

Still, it was desirable to obtain more direct and conclusive evidence for the 1,2 shift mechanism in $\underline{h}^1$-C_5H_5 molecules. Also, an understanding of the fluxional process required an understanding of the energetics of the rearrangement and also its dependence on the metal. The possibility of a fluxional indenyl molecule was intriguing as was the possibility of a $\sigma \rightleftharpoons \pi$ interchange of rings at high temperature, which would, by its activation energy, give some insight into the energy content of a $(C_5H_2)_2Fe(CO)_2$ molecule with two poly-hapto rings. These possibilities will be discussed in subsequent chapters.

Bis(cyclopentadienyl)mercury(II)

Numerous studies[14-16] by Russian workers interpreted infrared, ultraviolet and nmr data on $(C_5H_5)_2Hg$ as well as $(C_5H_5)HgX$, X = halogen, in terms of a pentahaptocyclopentadienyl-type of interaction. Since mercury normally forms dialkyls and diaryls by employing digonal, two electron sigma bonds, this conclusion was surprising; also the quality of the Russian experimental work was poor and some of their conclusions, though possibly correct, did not follow logically from their data. It cannot be overemphasized that predicting whether or

not a cyclopentadienyl-metal interaction will be pentahapto is not a trivial task. In the cases of $(C_5H_5)_2Sn$,[17] $(C_5H_5)_2Pb$,[18] $(C_5H_5)In$[19] and $(C_5H_5)Tl$[20], a nontransition metal is able to expand its coordination sphere to attain the h^5-C_5H_5 configuration (it should be noted, however, that the physical and chemical properties of these compounds are considerably different from those of their alkyl and aryl analogs).[21,22] The fact that some h^1-C_5H_5 molecules are fluxional also seems to indicate that polyhapto cyclopentadienyl metal configurations do not lie too high in energy above the ground state. In any case, the structure of $(C_5H_5)_2Hg$ was not at all clear and warranted further investigation. The extreme sensitivity of the crystalline samples to X-radiation precluded an X-ray structural determination.

Triethylphosphinecyclopentadienylcopper(I).

All available evidence since the original report of this compound indicated that it was a monohaptocyclopentadienyl[23] compound and that it was fluxional.[13] The pmr studies by Whitesides and Fleming[13] revealed that the collapse of the h^1-C_5H_5 olefinic multiplet was asymmetric with the high field side collapsing more rapidly. Invoking arguments about the constancy of chemical shifts in going from one h^1-C_5H_5 compound to another, these authors proposed that the rearrangement was proceeding via a 1,3 shift. Poor solubility prevented the recording of well-resolved spectra (the best spectra were

recorded in SO_2 solution, a solvent which is reactive toward many organometallics)[24] and it was apparent that this interesting molecule and its fluxional behavior merited further study.

Cyclopentadienyl Compounds of Group IV.

In 1965 Fritz and Kreiter[25] reported that several cyclopentadienyl compounds of silicon and germanium were fluxional. Since this discovery, substantial work done at M.I.T. on indenyl[26,27] and substituted cyclopentadienyl[28,29] derivatives of silicon, germanium and tin as well as the analysis of double resonance experiments,[30] has led to the conclusion that all compounds have monohapto structures and that 1,2 shifts dominate the rearrangement mechanisms whenever possible. Some evidence has been presented[31,32] that the cyclopentadienyl rings in $\underline{h}^1$-C_5H_5 Group IV molecules may be bent ("envelope—shaped"). The accuracy of these structural determinations leaves something to be desired and all other structural determinations on cyclopentadiene[33,34] and transition metal $\underline{h}^1$-cyclopentadienyls[8,12] supports a planar ring.

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CHAPTER III

FLUXIONAL BEHAVIOR AND OTHER DYNAMIC PROCESSES IN (PENTAHAPTOCYCLOPENTADIENYL)(MONOHAPTOCYCLOPENTADIENYL)-DICARBONYL COMPOUNDS OF IRON AND RUTHENIUM

INTRODUCTION

Initial studies[1] from This Laboratory established by X-ray diffraction that $(C_5H_5)_2Fe(CO)_2$ (1) contained one pentahapto and one monohapto cyclopentadienyl ring. Low temperature pmr studies showed this molecule to be fluxional and although the spectra were poorly resolved, it was evident that the low field portion of the olefinic multiplet collapsed more rapidly than the high field portion of the multiplet, thus indicating that a nonrandom shifting process of the metal about the ring was occurring. Arguments based on the amount of fine structure observed in the olefinic multiplets together with chemical shift and coupling constant arguments based on the h^1-indenyl analog[2] led to the postulation of the 1,2 shift mechanism.

It was felt that this system was important enough to the basic understanding of fluxional processes to merit further study. A rigorous, quantitative spectral analysis was necessary to make a secure argument based upon the magnitudes of coupling constants. Line shape analyses by computer simulation employing the Kubo-Sack[3,4] method would yield reasonably accurate activation parameters for the rearrange-

ment process and also, hopefully, yield information about the extent to which the 1,2 shift predominated. Also, it was of interest to examine how the rate of shifting depended on the particular transition metal sigma-bonded to the cyclopentadienyl ring.

RESULTS AND DISCUSSION

The compound ($\underline{h}^5$-C_5H_5)$Ru(CO)_2$($\underline{h}^1$-C_5H_5)[5, 14b] ($\underline{2}$) was synthesized by either of the following reactions:

$$(OC)_2RuCl_2 + NaC_5H_5 \xrightarrow{DME} (OC)_2Ru(C_5H_5)_2 \quad 1.1\%$$

$$(OC)_2RuI_2 + NaC_5H_5 \xrightarrow{DME} (OC)_2Ru(C_5H_5)_2 \quad 4.7\%$$

DME = 1,2-dimethoxyethane

The yields were poor by this method, but no more satisfactory procedure could be found; other solvents (diethyl ether and tetrahydrofuran) and other cyclopentadienylating reagents (TlC_5H_5) resulted in lower yields. The major product of all these reactions was invariably $[(C_5H_5)Ru(CO)_2]_2$. The 100 MHz pmr spectrum of($\underline{h}^5$-C_5H_5)$Ru(CO)_2$($\underline{h}^1$-C_5H_5) is nearly identical to that of ($\underline{h}^5$-C_5H_5)$Fe(CO)_2$($\underline{h}^1$-C_5H_5). It appears that the ruthenium compound is rearranging at a slightly slower rate, but the slow exchange limit spectrum is almost superimposable upon that of iron compound. The asymmetry of the collapse in the olefinic region is particularly dramatic, as can be seen in Fig. III-1.

The excellent quality of the 100 MHz spectra rendered them readily amenable to computer simulation for rate studies and spectral analysis. The activation parameters together with the standard deviations from the least squares fitting of the Arrhenius plots are given in Table III-1. Since the spectra of the two compounds are so similar, it is probable that any error introduced into the kinetic studies due to approximating spin multiplets as singlets, should be the same in both cases. It is evident that changing the metal from iron to ruthenium has only a small effect (ca.0.5 kcal/mole) on the activation energy for the fluxional process. This is in contrast to the cyclooctatetraene system where changing the metal from iron to ruthenium[6] has a considerable effect (ca. 4 kcal/mol) on the rate. The explanation for this observation is not obvious at the moment, but it is apparent that the two systems differ greatly and so must the demands on the metals as the molecules proceed along their respective reaction coordinates.

Starting with spin-spin coupling constants from analogous systems,[7-9] parameters were successively varied until computed[10] spectra best fit the experimental spectra recorded at the slow exchange limit (see Experimental section). An example of this procedure is shown in Fig. III-2. The coupling constants so obtained are given in Table III-2 along with standard deviations (for estimated errors see Experimental section). Since numerous combinations of coupling constants were tested, since iteration was begun from several widely different sets of par-

ameters, since the results for both the iron and ruthenium compounds agree, and since the ruthenium parameters were converted to 60 MHz data for an excellent match with 60 MHz spectra, reasonable confidence can be placed in these data. Within the AA'BB' system, the magnitudes and relative signs of all coupling constants can be found and these agree quite well with data from analogous systems[7-9] as can be seen in Table III-2. The computed spectrum was quite insensitive to variation of the signs of J_{12} and J_{13}; this is unfortunate since if one knew that H(1) were coupled to one olefinic multiplet with a negative coupling constant, the assignment of that multiplet as H(3)H(3') and thus the nature of the metal shift would follow unambiguously. Only $J_{13} < 0$ in this system would be consistent with numerous empirical and theoretical results.[11-13] However, the magnitudes of the coupling constants also allow an assignment,[14a] since one $\approx$ 1.2 Hz and the other $\approx$ 0 Hz (the H(1) resonance appears as a broadened triplet). From all empirical and theoretical data[11-13] available, only the assignment $J_{12} \approx 1.2$ Hz and $J_{13} \approx 0$ is tenable, i.e., the low field multiplet is due to H(2)H(2'). It appears the data in Table III-1 are consistent with the notion that in cyclopentadienyl and indenyl systems, the substitution of $(\underline{h}^5\text{-}C_5H_5)M(CO)_2$ for H only alters the allylic coupling constant, J_{13}, to any extent, and its magnitude is decreased almost to zero. The alternative assignment that the geminal coupling constant $J_{12} \approx 0$ does not seem at all reasonable in a system of this

geometry,[1,12,13] whereas, it is quite conceivable that $J_{13} \approx 0$.[11]

Subsequent to the completion of this study, similar though less refined data on $(C_5H_5)_2Ru(CO)_2$ was reported by a British group.[14b] They reached the same conclusion as put forward in this work.

Thus, using the assignment that the H(2)H(2') sites are exchanged more rapidly than the H(3)H(3') sites, one concludes that a 1,2 shift is occurring. The computer simulation also yields the fact that the 1,2 shift greatly predominates, though the match is not good enough to safely say 100%.

During the course of synthesizing compounds 1 and 2, it was observed that the high resolution infrared spectra in the region of the metal carbonyl C-O stretching bands revealed splitting of the two intense C-O stretches in this molecule by ca. 6-7 cm^{-1} (see Fig. III-3). Since an $M(CO)_2$ moiety can give rise to no more than two infrared-active ^{12}C-^{16}O stretches (a symmetric and an antisymmetric stretching vibration), the most reasonable explanation for this phenomenon is the presence of rotational isomers as portrayed in Fig. III-4. The X-ray structure of 1[1] shows that in the solid state, configuration (a) is preferred, but the fact that the two sets of bands are of approximately the same intensity* means that the free energy difference between the

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* It seems reasonable to assume that the extinction coefficients in the two isomers are about the same.

two forms is small. The fact that one $\underline{h}^5$-C_5H_5 resonance is observed in the pmr spectra of both compounds down to -100°C, indicates that the barrier to rotation is small. This is in contrast to $(C_5H_5)_3MoNO$ (3) where the configuration b is preferred in the solid state[18] and where the barrier to rotation is high[19] (see Fig. III-4). This is in accord with the observation that form a cannot be detected in the infrared spectrum[19] and presumably its high energy content contributes to the barrier to rotation about the molybdenum-$\underline{h}^1$-C_5H_5 bond axis.

It is evident from the studies on $(C_5H_5)_3MoNO$,[19] that the $\underline{h}^1$-C_5H_5 moiety would possess the magnetic anisotropy to impart a resolvable chemical shift difference to the $\underline{h}^5$-C_5H_5 resonances in the sets (1a, 1b) and (2a, 2b) had the slow exchange limit been reached by -100°. To investigate the thermodynamics of the rotational isomerism, the infrared spectra were examined over a range of temperatures and changes in relative intensities were analyzed by least squares methods. The details of this procedure are given in the Experimental Section. Small but reproducible changes in intensity were observed over a temperature range of 100°. Analysis of the log of the equilibrium constant versus reciprocal temperature plots (assuming equal extinction coefficients for both rotamers) by the method of least squares yielded the data of Table III-3 with the indicated standard deviations. The data for the analogous case of $ClCH_2CH_2Br$[21] are given for comparison. The noteworthy feature in the data for the organometallics is that the energy differences are very small.

Another feature of these molecules which is intriguing is the possibility of rapid interchange of the $\underline{h}^1$-C_5H_5 and $\underline{h}^5$-C_5H_5 rings at higher temperatures. There is only one well-documented example[24]



I

of a dynamic process such as this occurring, in $(\underline{h}^5\text{-}C_5H_5)_2Ti(\underline{h}^1\text{-}C_5H_5)_2$, and in this case the metal is part of a 16-electron valence system and thus coordinatively unsaturated. The polyhapto rings in $(C_5H_5)_3MoNO$[18] cannot be considered as truly pentahapto. Presumably a process such as I would proceed via a configuration in which the two cyclopentadienyl rings were equivalently bonded to the metal. It was of interest to explore what sort of activation energy was required to attain this configuration.

Samples of $(\underline{h}^5\text{-}C_5H_5)Fe(CO)_2(\underline{h}^1\text{-}C_5H_5)$ dissolved in $C_6D_5CD_3$ at temperatures as high as 120° exhibited two sharp lines in the nmr, with no indication of exchange. Decomposition occurred rapidly at these

temperatures to yield nearly equal quantities of ferrocene and $[(C_5H_5)Fe(CO)_2]_2$. Raising the temperature further for brief periods of time produced a rather remarkable effect in the ($\underline{h}^1$-C_5H_5) singlet resonance - either the intensity was greatly diminished relative to the ($\underline{h}^5$-C_5H_5) peak or in one case, emission spectra were recorded. No perturbation of other peaks in the spectrum was noted and the relative intensities of the $\underline{h}^1$-C_5H_5 and $\underline{h}^5$-C_5H_5 peaks returned to normal when the temperature was lowered. Essentially the same phenomenon was observed in methylcyclohexane solution.

This effect has been called chemically induced dynamic nuclear polarization (CIDNP)[25-32] and a brief discussion of its essential features will be given. It should be noted that all aspects of CIDNP are not completely understood at the present time; however, present theories[27-35] are able to explain most observations satisfactorily. When a transitory free radical pair is generated in an nmr sample solution, interaction of the electron spins within the radical pair combined with electron-nuclear hyperfine interaction can drastically change the population distribution in nuclear spin energy levels. Since this radical pair is usually very short-lived, it cannot be observed in the nmr spectrum. This radical pair can either collapse to form a diamagnetic product or the free radicals completely separate and undergo other reactions. When the diamagnetic species produced from the radical pair collapse is formed, the nuclear spin levels have not yet relaxed to the normal Boltzmann distribution populations. This

nonequilibrium spin distribution can give rise to spectral intensities which are vastly different in magnitude and, in the extreme, even in sign from those usually observed for the diamagnetic species (a type of Overhauser effect). This is called nuclear spin polarization and as Closs has pointed out,[33] it must occur in the product-forming steps of the reaction rather than in the formation of the paramagnetic species. That is, polarization is only observed in the nmr spectrum of the products of the radical reaction.

The magnitude of the polarization will depend on how far the nuclear spin level populations are perturbed from the Boltzmann distribution. It can be shown theoretically and demonstrated experimentally that the polarization can be very large.[33] The sign of the polarization (enhanced emission or absorption) will depend on how the spin populations are distributed. Excess population in the lower state will cause a normal absorption transition to be enhanced (the probability of absorption is increased) while excess population in the upper state will cause the transition to exhibit reduced intensity or emission, since the probability of downward transition is increased. If there is no net change of the total Zeeman energy in a spin system, then the net polarization will be zero. For example, spin multiplets frequently show enhanced parts and emitting parts, with the net integral through the mutliplet equal to zero (this has been called entropy polarization[29]). In a one-line system where either a single transition between two levels takes place or where all the transitions are degen-

erate (as in the present case), the observation of CIDNP means that there has been a net change in the total nuclear spin of the system, rather than just a redistribution in various directions such that the net change for the system is zero (this has been called energy polarization[29]).

That the high temperature pmr spectrum of ($\underline{h}^5$-C_5H_5)$Fe(CO)_2$($\underline{h}^1$-C_5H_5) shows slight polarization (emission) in the $\underline{h}^1$-C_5H_5 resonance is consistent with the following process,



in which radical recombination could presumably be either intra- or intermolecular. It could not be determined whether polarization was being observed in the $\underline{h}^5$-C_5H_5 ring attached to the iron. No polarization could be observed in any other peaks in the spectrum; it is not expected[28] for symmetrical recombination products such as $(C_5H_5)_2$[38] and $(C_5H_5)_2Fe_2(CO)_4$. The fact that CIDNP is observed in the present case does not prove that the radical reaction is the exclusive decomposition pathway; the CIDNP only means a radical pathway exists.[37]

EXPERIMENTAL

The organometallics prepared for this study ($(C_5H_5)_2Fe(CO)_2$ and $(C_5H_5)_2Ru(CO)_2$) were not particularly air-sensitive in the solid state. Consequently, all handling of the solids could be performed in the air, though the compounds were stored under nitrogen. Since solutions of these compounds are somewhat air sensitive, they were handled under an atmosphere of prepurified nitrogen. All solvents were dried in an appropriate manner, distilled, and stored under nitrogen.

Sodium cyclopentadienide was prepared in ether from sodium sand and freshly cracked cyclopentadiene. After removal of the ether by distillation at atmospheric pressure, the white powder was dried under high vacuum and was stored under nitrogen until used, at which time it was transferred by shaking through a glass-connecting tube under nitrogen.

Dicarbonyldichlororuthenium(II) and dicarbonyldiiodoruthenium(II) were prepared by methods in the literature.[38,39]

(Pentahaptocyclopentadienyl)(monohaptocyclopentadienyl)dicarbonyliron. - This compound was prepared by the general method of Bennett et al.,[1] except that sublimation was omitted and the product was recrystallized several times from pentane by slow cooling to -78°.

(Pentahaptocyclopentadienyl)(monohaptocyclopentadienyl)dicarbonylruthenium. From $(OC)_2RuI_2$. - To 1.64 g (4.0 mmole) of dicarbonyl-

diiodoruthenium(II) suspended in 100 ml dimethoxyethane at 0°, was added dropwise, 0.88 g (10.0 mmole) sodium cyclopentadienide dissolved in 100 ml dimethoxyethane. After stirring for 5 hr at 0°, the reaction mixture was stirred for 4 hr at room temperature. Next, the solvent was evaporated under high vacuum and the residue was extracted with 60 ml benzene in several portions. The benzene extracts were suction filtered under nitrogen and were then concentrated to ca. 15 ml under high vacuum. This solution was then chromatographed on deactivated alumina, eluting with 1/3 benzene/petroleum ether. Two yellow bands appeared on the column. The first to be collected was the desired product, and the second (which eluted with benzene) was $[(C_5H_5)Ru(CO)_2]_2$ (identified by its infrared and nmr spectrum[5]).

The first fraction was stripped of solvent at aspirator pressure and the resulting oily yellow solid was dissolved in a minimum amount of 1/4 benzene/petroleum ether and was rechromatographed on deactivated alumina, eluting with 1/4 benzene/petroleum ether. Again, the first yellow band was collected and the solvent stripped at aspirator pressure to yield a small amount of yellow solid. This was recrystallized from pentane at -78° and was then sublimed at 45°/0.01 mm to yield 54 mg (4.7%) of bright yellow solid, mp 53-54° (lit. 56°,[5] 52-53°[14b]).

Anal. Calcd. for $C_{12}H_{10}RuO_2$: C, 50.17; H, 3.52. Found: C, 50.2; H, 3.55.

(Pentahaptocyclopentadienyl)(monohaptocyclopentadienyl)dicarbonylruthenium. From $(OC)_2RuCl_2$. - The procedure described above was employed with 2.8 g (12.3 mmole) dicarbonyldichlororuthenium(II) and 2.8 g (32.0 mmole) sodium cyclopentadienide. The product obtained was 39 mg (1.1%) of yellow solid, mp 53-54°, which was identical to that obtained in the previous reaction.

Spectroscopic Measurements

Proton Magnetic Resonance. - For precision work, spectra were recorded at 100 MHz on a Varian Associates HA-100 spectrometer equipped with a variable temperature controller. Temperature measurements were made with a Digitec digital thermometer connected to a calibrated copper-constantan thermocouple inserted in the nitrogen stream just below the sample in the probe. The calibration of this system was frequently checked and measurements were also checked against those obtained by inserting a calibrated thermocouple into a serum stopper capped solvent sample while it was in the probe. A small heat exchanger was employed for sample cooling between room temperature and -30°, while a large heat exchanger was employed for temperatures below this. This system minimized temperature drift during the recording of spectra and allowed this drift to be constantly monitored. In most cases, after equilibration, the temperature of the nitrogen stream drifted no more than several tenths of a degree during the running of a spectrum. Spectra were calibrated by measuring the distance in Hz from the lock

signal with a Varian V-4315 electronic counter. Generally, several spectra at expanded sweep widths were recorded at each temperature.

Pmr samples were prepared by freeze-thaw degassing solvents and tetramethylsilane and distilling these directly onto the solid samples under high vacuum. The sample tubes were then sealed off under high vacuum. Spectra at 60 MHz were recorded on a Varian Associates A-60 nuclear magnetic resonance spectrometer equipped with a V-6040 variable temperature controller. Several spectra were recorded at each temperature. The spectra were calibrated with a Krohn-Hite model 450 oscillator and a Hewlett-Packard model 524 electronic counter.

Due to the rapid decomposition of ($\underline{h}^5$-C_5H_5)Fe(CO)$_2$($\underline{h}^1$-C_5H_5) at elevated temperatures, CIDNP experiments were performed by inserting the sealed sample tube after the probe of the A-60 had been equilibrated at high temperature (ca. 125°). Using cyclohexane as a resolution indicator, the machine was tuned as rapidly as possible and spectra recorded immediately. Usually the lifetime of the sample at these temperatures was no greater than three minutes.

Kinetic studies were carried out using a computer program[3,4] written by Professor G. M. Whitesides of This Department. In the case of the $\underline{h}^1$-cyclopentadienyl dicarbonylmetal compounds, it was necessary to simulate the multiplets in the olefinic region as two singlets, and the unique high field proton as a singlet. It was assumed that the exchange process involved 100% 1,2 shifts and it was not possible to ascertain

exactly how much random shifting could be mixed in before it could be detected. However, it could be determined that the 1,2 shift pathway predominates to a large degree.

Arrhenius plots were fitted by the method of least squares.

Spectral analysis was performed with the aid of the computer program NMRPLOT, written by Professor G.M. Whitesides of This Department. This program is a modified version of LAOCN3 and can be used to obtain Calcomp plots of theoretical spectra. Considerable variation of parameters was attempted before the iterative option in the program was employed. Initial parameters were obtained from analogous systems[7,8] and these were varied successively and in all directions. When a nearly satisfactory fit was obtained, the coupling constants and chemical shifts were refined iteratively. The standard deviations given by the program are probably too small even in optimum cases[20] and in low temperature studies where resolution was poorer, they should probably be multiplied by a factor of ca. five.

In the case of $(\underline{h}^5\text{-}C_5H_5)Ru(CO)_2(\underline{h}^1\text{-}C_5H_5)$, the 100 MHz spectral analysis was checked at 60 MHz and agreement was within the limits of the reproducibility of the 60 MHz spectra.

Infrared. - Room temperature spectra were recorded in hydrocarbon solvents on a Perkin-Elmer 521 spectrometer, which had been previously calibrated. The author thanks Miss Martine Debeau for assistance.

Variable temperature infrared spectra were recorded on a Perkin-Elmer 337 spectrometer equipped with a scale expansion apparatus similar to that supplied by the factory. The pen servomechanism was used to drive a Computer Control Industries infinite resolution potentiometer, and this was connected through an ordinate expansion control to a Leeds and Northrup Speedomax recorder. Temperature control for the sample was achieved in a variable temperature cell designed and kindly supplied to us by Professor G. M. Whitesides. The design was similar to the device described by Powling and Bernstein,[21] i.e., it used a nitrogen stream to heat or cool the sample. A Varian V-6040 temperature controller connected to the standard nmr probe thermistor/heater device was used to control the temperature of the nitrogen stream entering the cell. A calibrated copper-constantan thermocouple placed against the cell was employed to measure the sample temperature.

During low temperature runs, the sample area of the spectrometer containing the variable temperature cell was covered with plastic film and was kept under a blanket of dry nitrogen. The sample was given approximately one hour to equilibrate at each temperature and several spectra were recorded at each temperature.

Since in both $(\underline{h}^5\text{-}C_5H_5)(\underline{h}^1\text{-}C_5H_5)M(CO)_2$, where M = Fe and Ru, C-O stretching bands for the two different equilibrating rotomers were not well-resolved, the first step in data analysis was resolution of the component peaks in each doublet. This was accomplished by plotting ca. 30

points on each doublet and fitting these by a non-linear least squares method to an equation equal to the sum of two Lorenztian lines. It was assumed that the linewidths at one-half height of both components were equal and the parameters of intensities and peak separation were varied to obtain the best fit to the data. Computation was performed using a non-linear least squares program,[22] kindly supplied by Mrs. J. Bow of the M.I.T. Computation Center, on an IBM 360 computer. Assuming the ν_{CO} extinction coefficients in both rotomers were the same, equilibrium constant and temperature data were used to calculate ΔH and ΔS, employing a least squares computer program to fit the logK *vs.* 1/T plot. It should be mentioned that the accuracy of the values obtained for ΔH is not dependent on the assumption made about the extinction coefficients.[23]

TABLE III-1

Activation Parameters for Site Exchanges[a,b]

Compound	Solvent	Log A	E_a kcal/mole	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ eu
1	3:1 CS_2-$C_6D_5CD_3$	11.7 ± 0.1	9.8 ± 0.1	9.4 ± 0.1	-6.3 ± 0.6
2	3:1 CS_2-$C_6D_5CD_3$	11.2 ± 0.2	10.3 ± 0.3	9.7 ± 0.3	-9.1 ± 1.1

(a) $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were evaluated at the temperatures giving mean residence times of 0.01 sec.

(b) Standard deviations are derived from the least squares fitting of the Arrhenius plots.

TABLE III-2

Proton-Proton Coupling Constants (Hz)[a]

Compound	J_{12}	J_{13}	J_{23}	$J_{23'}$	$J_{22'}$	$J_{33'}$	Source
C_5H_6	+1.33 (0.004)	-1.51 (0.004)	5.05 (0.005)	1.09 (0.005)	1.98 (0.006)	1.91 (0.006)	Ref. 9
1	±1.17 (0.03)	±0.01 (0.03)	4.66 (0.05)	1.15 (0.04)	2.02 (0.07)	2.02 (0.06)	b
2	±1.22 (0.05)	±0.10 (0.06)	4.64 (0.06)	1.17 (0.05)	2.06 (0.09)	2.12 (0.08)	b
$C_5H_5Si(CH_3)Cl_2$	±0.9	-1.1	5.2	1.2	2.0	2.0	Ref. 16,17
Indene	+2.02 (0.02)	-1.98 (0.02)	5.58 (0.02)				Ref. 15
$(\underline{h}^5\text{-}C_5H_5)Fe(CO)_2(\underline{h}^1\text{-}C_5H_5)$	~ 2.3	~ 0	~ 5.5				Ref. 2

(a) The values given in parentheses for the first three entries are the standard deviations derived from the iterative fitting of the spectra. These are probably smaller than the true errors (see experimental section). The values given in parentheses for the indene data are the estimated errors.

(b) This work.

TABLE III-3

Thermodynamic Data for Rotational Isomerism

in ($\underline{h}^5$-C_5H_5)$M(CO)_2$($\underline{h}^1$-C_5H_5) Compounds

Process	ΔH kcal/mole	ΔS eu
1a ⇄ 1b	0.37 ± 0.04	0.55 ± 0.16
2a ⇄ 2b	0.25 ± 0.06	-0.62 ± 0.25
CH_2ClCH_2Br[a] trans ⇄ gauche	1.85 ± 0.15	

(a) Data of Ref. 21.

FIGURE III-1

Spectra of the olefinic multiplet of ($\underline{h}^5$-C_5H_5)Ru(CO)$_2$-($\underline{h}^1$-C_5H_5) recorded at several temperatures in 3:1 (v/v) CS_2-$C_6D_5CD_3$ at 100 MHz.

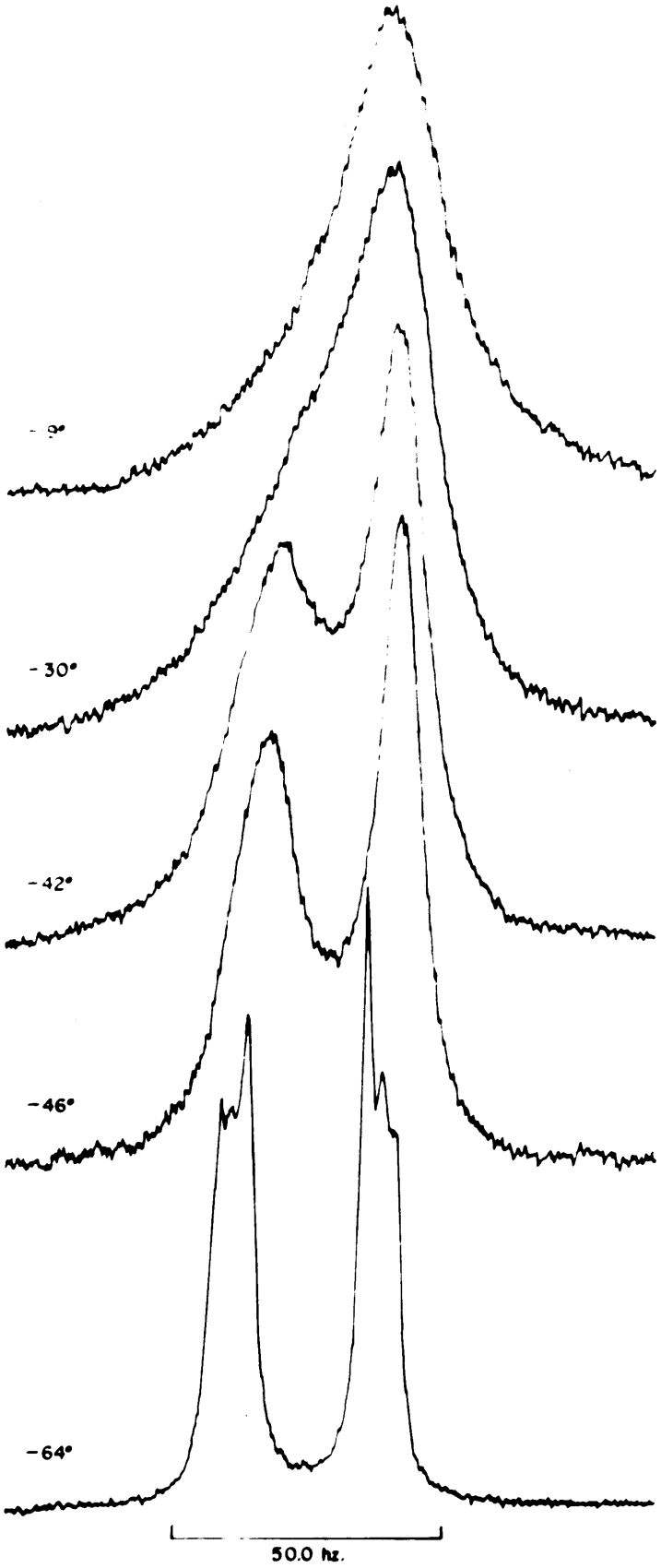

-9°
-30°
-42°
-46°
-64°
50.0 hz.

FIGURE III-2

Upper trace: Part of the limiting low temperature pmr spectrum of ($\underline{h}^5$-C_5H_5)$Ru(CO)_2$($\underline{h}^1$-C_5H_5) recorded at -82° in 3:1 (v/v) CS_2-$C_6H_5CD_3$ at 100 MHz. Abscissa Hz *vs.* TMS. Lower curve: computer simulated spectrum using J values given in Table III-2.

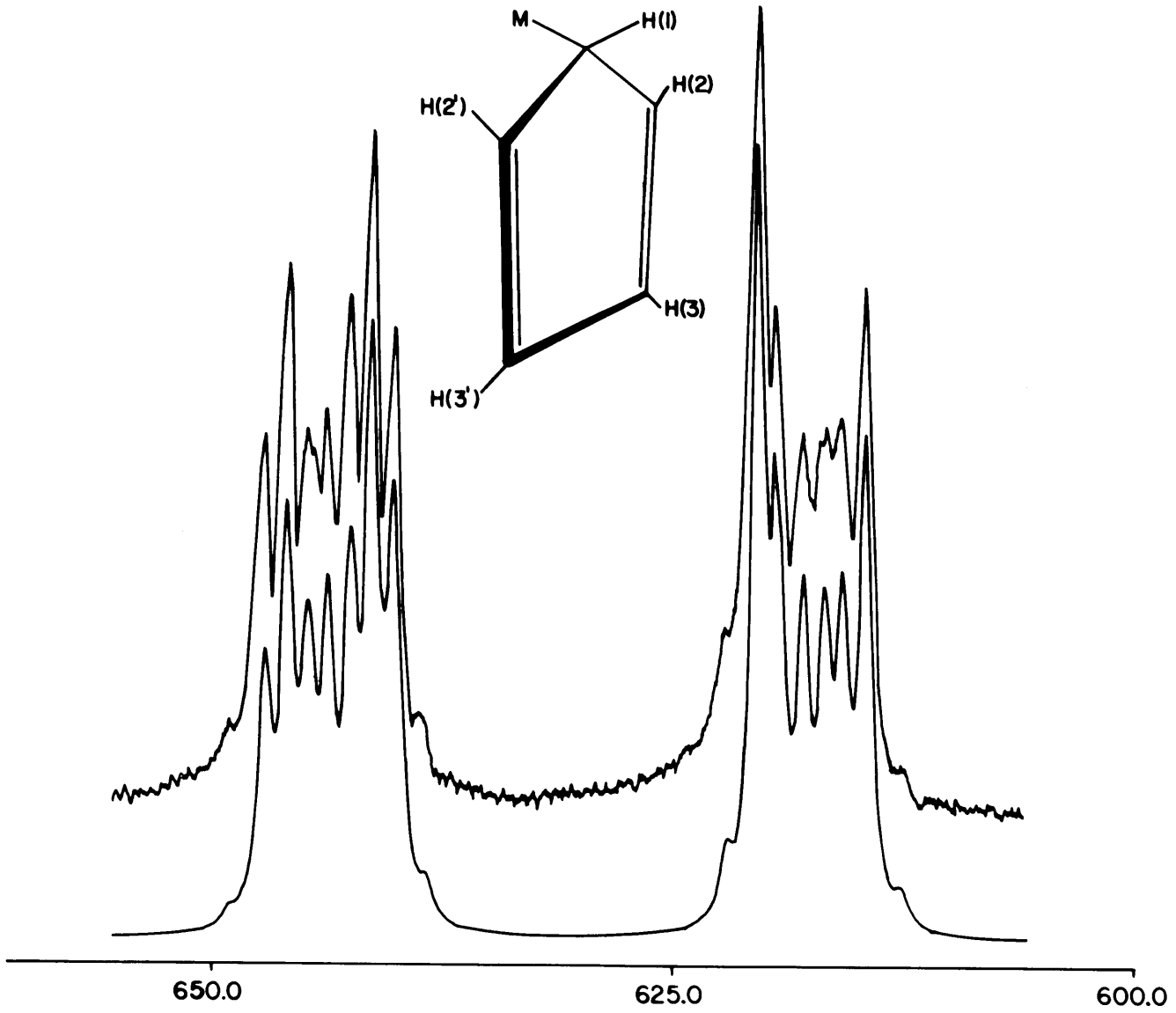

M
H(1)
H(2)
H(2')
H(3)
H(3')
650.0
625.0
600.0

FIGURE III-3

The infrared spectra in the C-O stretching region of ($\underline{h}^5$-C_5H_5)Ru(CO)$_2$($\underline{h}^1$-C_5H_5) and ($\underline{h}^5$-C_5H_5)Fe(CO)$_2$($\underline{h}^1$-C_5H_5) taken under conditions of high resolution. The ordinate is percent transmittance.

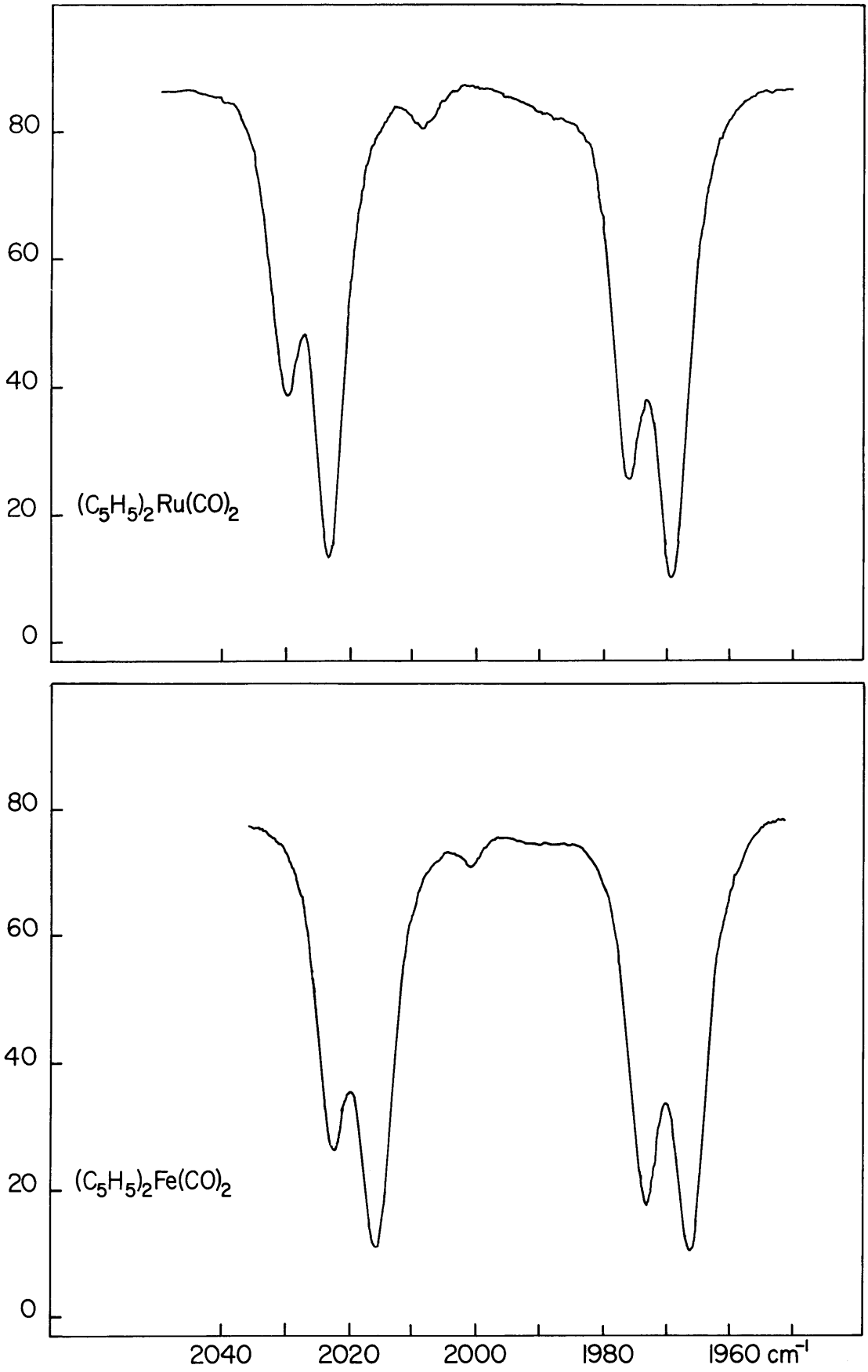
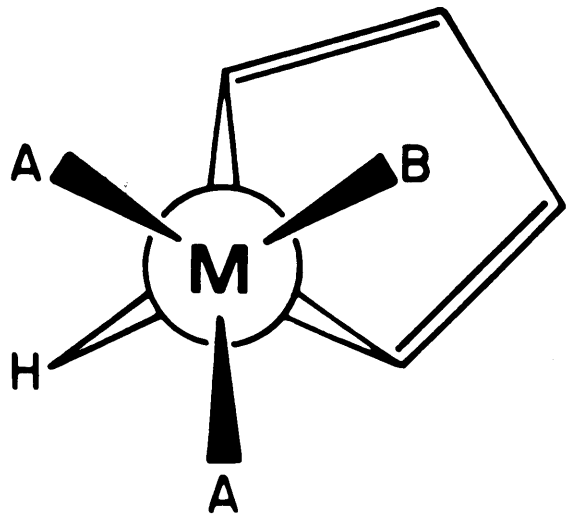

80
60
40
20
0
$(C_5H_5)_2Ru(CO)_2$
80
60
40
20
0
$(C_5H_5)_2Fe(CO)_2$
2040
2020
2000
1980
1960 cm^{-1}

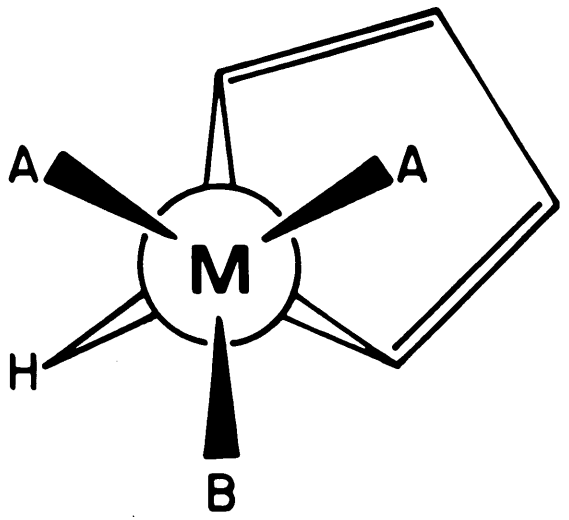
FIGURE III-4

Rotational isomerism about the metal-$\underline{h}^1$-C_5H_5 bond in complexes of the type $B_2AM(\underline{h}^1\text{-}C_5H_5)$. It should be noted that form b has an enantiomer which is not shown.

a



b



1 M=Fe; A=CO; B=$\underline{h}^5-C_5H_5$

2 M=Ru; A=CO; B=$\underline{h}^5-C_5H_5$

3 M=Mo; A=C_5H_5; B=NO

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CHAPTER IV

A FLUXIONAL INDENYLMERCURY COMPOUND

INTRODUCTION

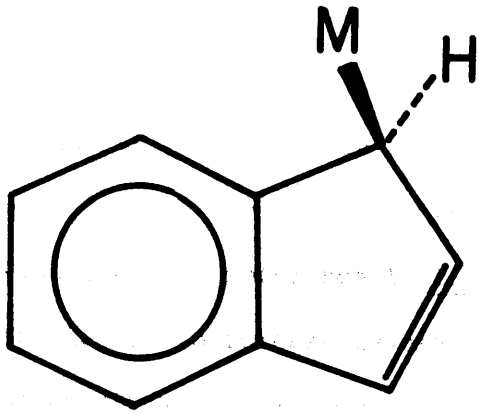
In a number of previous studies of fluxional organometallic molecules[1,2] containing conjugated cyclic olefinic molecules (e.g., C_8H_8) or radicals (e.g., C_5H_5, C_7H_7) bonded to a metal atom, it has been shown that, with the possible exception[3] of $C_5H_5CuP(C_2H_5)_3$, which shall be discussed later, the rearrangement pathways seem always to consist of a sequence of 1,2 shifts of the metal atom(s) relative to the ring, accompanied, of course, by concerted shifts of the π electrons of the ring.

In a previous study[4] from This Laboratory advantage was taken of the special properties of the indenyl group in order to confirm the assignment[5] of the limiting nmr spectrum and the rearrangement pathway in the case of $(\underline{h}^5\text{-}C_5H_5)(\underline{h}^1\text{-}C_5H_5)(CO)_2Fe$. Since the principles on which this work was based would be applicable in other cases as well, efforts to prepare and study indenyl derivatives of other metals have been made. We describe here the preparation and nmr study of bis-(1-monohaptoindenyl)mercury, which is a new compound.

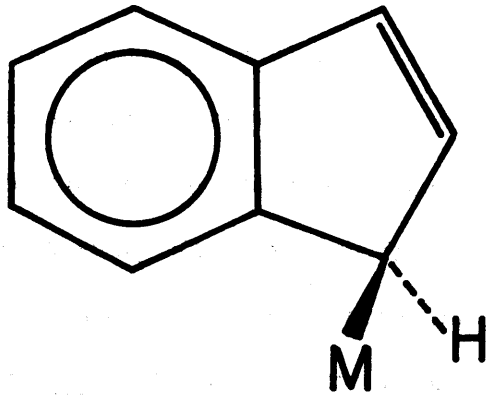
Before describing the results of the nmr study and their significance, the considerations essential to the design of the experiment will be presented.

The three structures involving a monohaptoindenyl-metal system are shown as I, II and III. Structures I and II are chemically equivalent (though enantiomorphous) and it is safe to assume that they are considerably more stable than III, since the delocalization energy of the σ-xylylene π-electron structure is about 9 kcal/mol less than that for the styrene-like π-system found in I and II.[6] In the case of ($\underline{h}^5$-C_5H_5)($\underline{h}^1$-C_9H_7)$(CO)_2Fe$[4] the 2-indenyl structure is so unfavorable that it does not serve as a suitable transition state or intermediate for the interconversion of I and II at a rate sufficient to cause broadening of the nmr spectrum even at +70°C (above which temperature the compound undergoes rapid decomposition).

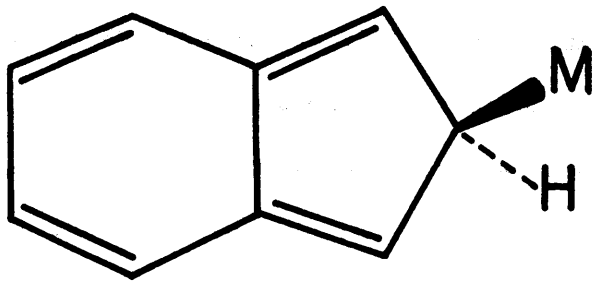
However, it is also possible for an indenyl group to function as a donor of several electrons (up to 5) thus forming some sort of π-complex, as represented schematically by IV provided the metal atom possesses the requisite number of vacant, low-lying orbitals. In the limit a (1,2,3,8,9-pentahaptoindenyl)metal-type of linkage is possible, as found, for example, in bisindenyliron[7] (also called dibenzoferrocene). It is reasonable to suppose that with an appropriate metal a structure of type IV in which the metal has its primary interaction with the C1, C2 and C3 carbon atoms thereby leaving the benzenoid resonance largely unperturbed might be fairly stable. Mercury could be an appropriate metal in this sense owing to its capability of expanding its coordination number from two (linear bonds using digonal,



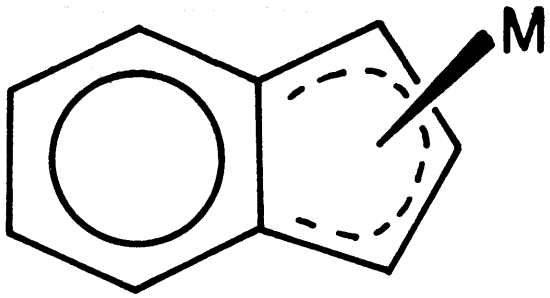
I



II



III



IV

sp hybrids) to three or four by including one or both of its remaining 6p orbitals in the set used for bonding.

With specific reference to bisindenylmercury, the above considerations led us to foresee several possible results in the study of the nmr spectrum of that compound over a range of temperatures:

Case 1: If the mercury atom, like the (h^5-C_5H_5)Fe(CO)$_2$ group, were limited to a two-electron, two-center (i.e., σ-interaction) with the indenyl group we would observe a sharp spectrum containing the HAB pattern due to the hydrogen atoms of C1, C2 and C3, respectively, as well as a sharp WXYZ pattern from the four aromatic protons, up to the highest temperatures of observation.

Case 2: If the mercury atom were to have a preferred coordination number of 2, so that a bis-(1-monohaptoindenyl)structure would be the most stable structure, but at the same time have the possibility of expanding that coordination number without too great a promotion energy, the molecule could be fluxional,under (1) but this would collapse at intermediate temperatures and eventually become an AA'B-XX'YY'-type of spectrum.

Case 3: If the mercury were to prefer using all four of its valence shell (6s and 6p) orbitals the compound would have two rings bonded in the manner IV permanently. Its nmr spectrum would then be of the AA'B-XX'YY' type at all temperatures.

Case 4: Finally, there is the possibility that a structure with one 1-monohapto and one 1,2,3-trihapto-(or other multihapto)indenyl ring might be preferred. Presumably at intermediate and/or higher temperatures the rings would interchange their roles rapidly giving rise to an AA'B-XX'YY' spectrum while at low temperatures a complex superposition of the spectra of the two types of ring would be observed.

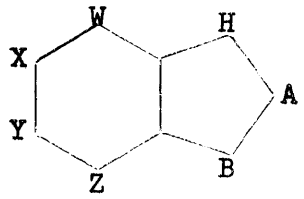
RESULTS

Preparation. - The molecule bis-(1-indenyl)mercury was prepared by the reaction of mercuric chloride with indenyllithium at about -78°C. It is crucial that all solvents and reagents be purged of water and peroxides or the yield will be drastically reduced - often to none. The substance is a white solid, though it is often obtained with a pale yellow coloration. It is insoluble in common non-polar organic solvents, but sparingly soluble in CH_2Cl_2, $CHCl_3$ and THF. The solid slowly decomposes on standing at 25°, and it decomposes rapidly at higher temperatures.

One previous attempt to prepare bis-(indenyl)mercury has been recorded but no product was isolated.[8] It is probable that failure in this case was due to a combination of at least the following two factors: (1) the use of insufficiently pure (i.e., peroxide-containing) solvent and (2) failure to cool the reaction mixture in the early stages.

Low Temperature Pmr Spectrum. - The 60 MHz spectrum recorded at -41° (Fig. IV-1) is the limiting low temperature spectrum since further

cooling caused no significant changes. This spectrum is very similar in its main features to that of the indenyl protons in ($\underline{h}^5$-C_5H_5)-($\underline{h}^1$-C_9H_7)$(CO)_2Fe$.[4] The complex multiplet of relative intensity 4 lying between 2.2τ and 2.9τ may be assigned to the aromatic protons, the WXYZ set shown in V. The proton bound to C1, the carbon atom to



V

which the Hg atom is also bound, gives a line well upfield, as is usual for such protons, at τ6.19, with a relative intensity of 1. The A and B protons have very similar chemical shifts and are coupled to each other with $J_{AB} \approx 5.7$ Hz; neither is strongly coupled (< 2 Hz) to the H proton. They therefore give rise to a relatively simple AB pattern centered at $\sim \tau 3.24$. All features of the limiting low temperature spectrum are thus in excellent accord with the bis-(1-indenyl)mercury structure. We can conceive of no other structure which accords with

the observed spectrum and consider the bis-(1-indenyl) structure to be conclusively proved.

There are two notable differences between this spectrum and the limiting spectra of $(\underline{h}^5\text{-}C_5H_5)(\underline{h}^1\text{-}C_5H_5)(CO)_2Fe$[5] and $(\underline{h}^5\text{-}C_5H_5)(\underline{h}^1\text{-}C_9H_7)\text{-}(CO)_2Fe$.[4] First, there is no observable difference between J_{HA} and J_{HB} and indeed both are very small ($\leq$ 2 Hz) and unresolved, whereas in both of the former compounds there was a distinct difference in these two J's. In the case of $(\underline{h}^5\text{-}C_5H_5)(\underline{h}^1\text{-}C_9H_7)(CO)_2Fe$ it was possible to show conclusively that $|J_{HA}| > |J_{HB}|$. The small magnitudes and lack of any distinct difference between $|J_{HA}|$ and $|J_{HB}|$ in $(\underline{h}^1\text{-}C_9H_7)$ are reminiscent of the situation of indene itself where Elleman and Manatt[9] found J_{HA}=2.02 Hz and J_{HB}=-1.98 Hz. These couplings are likely to be a moderately sensitive function of the angles between each of the several C-H bonds and the ring plane, and at least one of these angles, namely that involving C(1)-H, may in turn be sensitive to the nature of the substituent on C(1), viz., H-, $(\underline{h}^5\text{-}C_5H_5)(CO)_2Fe$- or $(\underline{h}^1\text{-}C_9H_7)Hg$-. Therefore, variation in the absolute and relative magnitudes of J_{HA} and J_{HB} with variation in substituent at C(1) is not unexpected. Conversely, however, it is plausible that compounds of indene and cyclopentadiene with the same substituent should exhibit parallel variations in J_{HA} and J_{HB}. It was on the basis of the latter assumption that the results for $(\underline{h}^5\text{-}C_5H_5)(\underline{h}^1\text{-}C_9H_7)\text{-}(CO)_2Fe$ were invoked[4] to support the assignment which had earlier been put forward[5] for $(\underline{h}^5\text{-}C_5H_5)(\underline{h}^1\text{-}C_5H_5)(CO)_2Fe$.

Temperature Dependence of Pmr Spectrum . - The 60 MHz pmr spectra of bis-(1-indenyl)mercury dissolved in CCl_3D at various temperatures are shown in Fig. IV-1. The changes have all been shown to be reversible with temperature. It is immediately obvious that, provided rapid intermolecular exchanges are not occurring (and this will be demonstrated later), the molecule is fluxional. We therefore eliminate Case 1 and Case 3 described above. Further, as we have just shown, the limiting low temperature spectrum is clearly that of the bis-(1-monohaptoindenyl)mercury structure, thus eliminating Case 4.

The three major changes which take place as the temperature is raised are as follows. (1) The H resonance and one half of the AB resonance collapse at the same rate, virtually disappearing around room temperature. At higher temperatures a new resonance of relative intensity 2 arises at a position ($\tau \approx 4.60$) which is the same (within experimental error and/or allowing for some small intrinsic dependence of chemical shifts on temperature) as the mean ($\tau \approx 4.68$) of the initial positions of the two separate resonances. Thermal decomposition of $(h^1\text{-}C_9H_7)_2Hg$ above about 70°C is too rapid to permit us to observe the further narrowing of this merged resonance.[10a] (2) At the same time, the fine structure of the non-collapsing half of the AB resonance changes and from about room temperature to +68° it approaches more and more closely a 1-2-1 triplet structure with a splitting ($\sim$ 3.5 Hz) which is, within experimental uncertainty, equal to the average[10b] of

the splittings ($|J_{AB}| = 5.7$, $|J_{HA}| \leq 2$ Hz) in the low temperature spectrum. (3) The multiplet due to the aromatic protons undergoes complex changes throughout the temperature range. These changes lead to sharpening and simplification and appear to be tending toward the development of a symmetrical XX'YY' spectrum at higher temperatures.

The changes just summarized are susceptible of only one explanation, namely, that the point of attachment of a mercury atom to the indenyl group shifts back and forth from the C(1) to the C(3) position more and more rapidly as the temperature increases. In this way a time-average plane of symmetry is established so that the H and B environments, the W and Z environments and the X and Y environments become nmr equivalent.

Rates and Activation Parameters. - Since there are only two exchanging protons in this case, and their coupling to each other is very much less than their chemical shift difference, the Gutowsky-Holm[11] treatment may be applied with reasonable accuracy to determine the thermodynamic parameters of activation. In the slow exchange region the line width of the singlet at τ6.2 was used. In the fast exchange (high temperature) region the width of the resonance at τ4.5 was used, with the assumption that this would have a width in the fast exchange limit (which could not be reached experimentally) equal to the average of the widths of the τ3.15 and τ6.2 resonances as observed in the -41° spectrum. Fitting a linear Arrhenius plot by the method of least

squares to the two sets of points led to the activation parameters Ea = 12.9 ± 0.6 Kcal/mol and Log A = 12.0 ± 0.5.

Concentration Independence. - As a means of determining whether the changes in the pmr spectrum which occur between -41 and +68°C (Fig. IV-1) are in fact due to an intramolecular process, the dependence of the spectrum upon concentration at room temperature was examined. Figure IV-2 shows two spectra each run at probe temperature (~ 25°C) on solutions which differ by a factor of 8 in concentration. For a bimolecular process the rates should differ by a factor of 64, but there is, in fact, no noticeable difference between the two spectra. Based on the previously determined rates we can estimate that the 25° spectrum at 1/64 the rate characteristic of the upper trace (which is for a saturated solution) should be similar in appearance to the trace given by the saturated solution at -20°C. Figure IV-1 shows that at this temperature the peaks for the H and B protons are still very prominent and the triplet structure of the A resonance is still very unsymmetrical. It is thus quite evident that the process responsible for the averaging is not bimolecular.[12]

DISCUSSION

The results reported here for bis-(1-indenyl)mercury complete the line of argument which was begun in the study[4] of ($\underline{h}^5$-C_5H_5)($\underline{h}^1$-C_9H_7)-$(CO)_2Fe$. The metal atom in the ($\underline{h}^5$-C_5H_5)$(CO)_2Fe$- group has all its valence shell orbitals engaged in bonding except for one, which con-

tains a single electron. It has only the possibility of interacting with univalent radicals, R· (such as Cl·, C_nH_{2n} + 1· or 1-indenyl) to form a simple two-center, two-electron bond. The position of this bond can move from one atom to another on R only if these atoms are adjacent and the pathway carried through a transition state or intermediate in which only two electrons are involved in the Fe-R interaction. This situation obtains in ($\underline{h}^5$-C_5H_5)($\underline{h}^1$-C_5H_5)$(CO)_2$Fe and the point of attachment to the ($\underline{h}^1$-C_5H_5) ring shifts rapidly. In the case of ($\underline{h}^5$-C_5H_5)($\underline{h}^1$-C_9H_7)$(CO)_2$Fe no shifting can occur because, on the one hand the intermediate of structural type III is too unstable while, on the other, the kind of greater-than-two-electron interaction involved in a transition state represented by IV is impossible for the ($\underline{h}^5$-C_5H_5)$(CO)_2$Fe group.

Conversely, when the metal-containing moiety has empty low-lying valence shell orbitals, which can be used in a transition state such as IV, the rapid interconversion of I and II <u>via</u> IV should be feasible. The mercury atom in ($\underline{h}^1$-C_9H_7)$_2$Hg, which has a linear, two-coordinate C-Hg-C ground state structure, the additional orbitals needed to form a transition state with multicenter bonding (i.e., one like IV) are most likely the two additional 6<u>p</u> orbitals, although the participation of outer d orbitals (5<u>d</u>) cannot be ruled out. Indeed, where such outer <u>d</u> orbitals are sufficiently low in energy, they alone may be adequate to permit the attainment of a transition state suitable for rapid 1,3 shifts.

The results of our study of $(\underline{h}^1\text{-}C_9H_7)_2Hg$ provide a basis for some comments on other fluxional molecules containing $(\underline{h}^1\text{-}C_5H_5)$ or $(\underline{h}^1\text{-}C_9H_7)$ groups. Interestingly, we can now adduce direct evidence against the validity of but an indirect argument for the ultimate correctness of the assignment of 1,3 shifts as proposed for $(C_2H_5)_3PCu(\underline{h}^1\text{-}C_5H_5)$ by Whitesides and Fleming.[3]

The conclusion that 1,3 shifts occur in $(C_2H_5)_3PCu(\underline{h}^1\text{-}C_5H_5)$ follows automatically from their assignment of the AA'BB' olefinic resonance in the low-temperature spectrum of that compound. A reversal of assignment necessitates a change in one's conclusion about the predominant shift (to 1,2) and, conversely, each of the two possible assumptions about the dominant kind of shift process demands, strictly, that one of the two possible assignments be made.

The basis for the assignment of Whitesides and Fleming was simply that for a series of $M\text{-}C_5H_5$ compounds they expected the spectral position (chemical shift) of the B protons (which are separated by four bonds from the metal atom) to be substantially constant while the position of the A protons (which are separated by only three bonds from the metal atom) would be more variable. It can now be demonstrated that this is an unsafe assumption. For $(\underline{h}^5\text{-}C_5H_5)(CO)_2Fe(\underline{h}^1\text{-}C_9H_7)_2$ and $Hg(\underline{h}^1\text{-}C_9H_7)$ we have found the following chemical shifts (in τ) all at 60 MHz in CCl_3D solution:

Compound	A Proton	B Proton
($\underline{h}^5$-C_5H_5)$(CO)_2$Fe(1-C_9H_7)	3.28	3.47
Hg($\underline{h}^1$-C_9H_7)$_2$	3.32	3.09

Clearly, the position of the B protons varies greatly, while the A protons have a substantially constant position.

The reason why the facts here are contrary to the expectation expressed by Whitesides and Fleming is that the chemical shifts of both A and B protons are affected significantly (perhaps predominantly) by the diamagnetic anisotropies of the $\underline{h}^5$-C_5H_5, CO and C_9H_7 groups, in a manner which cannot be simply predicted. In other words, the shifts do not depend simply upon the inductive influence of a metal acting solely through and being attenuated by the electron pairs of intervening chemical bonds.[15] The change from ($\underline{h}^5$-C_5H_5)$(CO)_2$Fe to $(C_2H_5)_3$PCu is such that constancy in the position of the B resonance of the $\underline{h}^1$-C_5H_5 group cannot be assumed, although it is possible. We must conclude therefore that on the experimental evidence per se, there is no basis for choosing between 1,2 shifts and 1,3 shifts to describe the rearrangement pathway in $(C_2H_5)_3$PCu($\underline{h}^1$-C_5H_5).

However, since Cu^I (like Hg^{II}) in a linear, two-coordinate complex has additional valence shell orbitals ($4\underline{p}$ orbitals for Cu^I) it may (like Hg^{II}) be able to participate in a transition state like that represented by IV and thereby permit 1,3 shifts to constitute the main

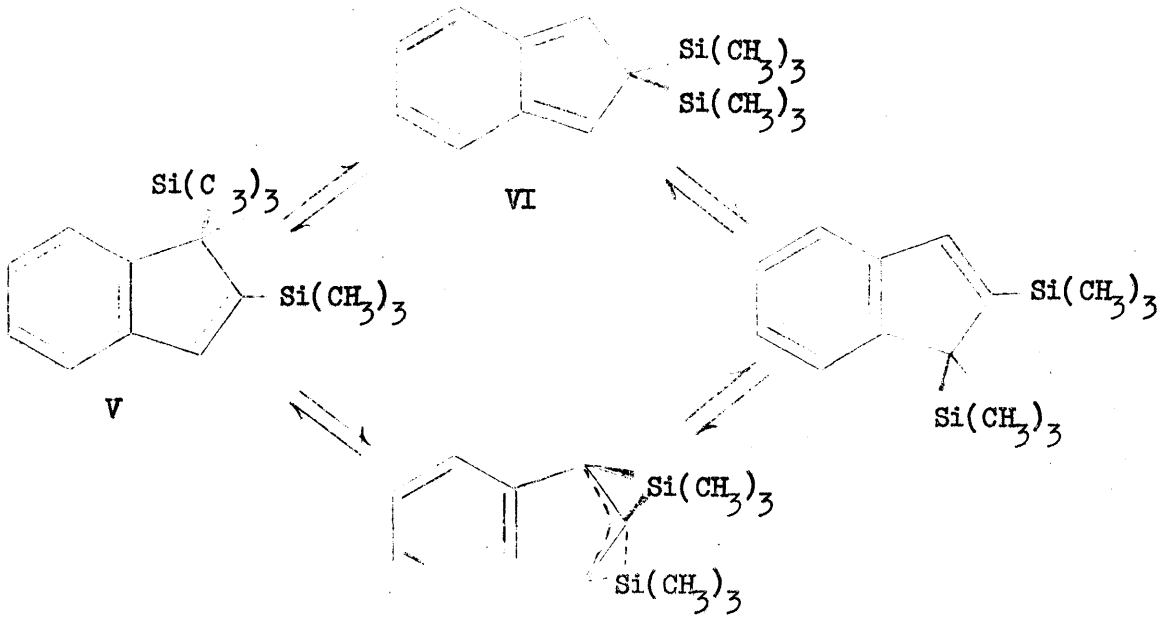
rearrangement pathway. Thus, the conclusion of Whitesides and Fleming may be correct but proof is lacking.

There have recently appeared several studies of the low-temperature pmr spectra of $(C_5H_5)_2Hg$.[18,19] Maslowsky and Nakamoto report that at -70° in SO_2 $(C_5H_5)_2Hg$ gives a spectrum indicative of slowly shifting $\underline{h}^1$-C_5H_5 rings. Their proposal that 1,2 shifts occur (based on the unsymmetrical shape of the AA'BB' signal) rests upon a direct deduction from Whitesides and Fleming's assignment for $(C_2H_5)_3PCu(\underline{h}^1$-$C_5H_5)$ and is therefore inconclusive. Indeed, if the relative positions of the A and B resonances in $(C_5H_5)_2Hg$ is taken to be the same as those in $(C_9H_7)_2Hg$, we must conclude that 1,3 shifts are occurring. We are not, however, espousing that conclusion because we have no firm faith in the premise.

Nesmeyanov *et al.* conclude that $(C_5H_5)_2Hg$ actually has a $(\underline{h}^5$-$C_5H_5)_2Hg$ structure apparently because ^{199}Hg-H coupling produces observable satellites in the room temperature pmr spectrum. Though the conclusion *might* be correct, the argument (as we understand it) is not. They also present evidence that Nakamoto's conclusions from SO_2 solutions are invalid.[20]

It is clear that much more thorough studies of cyclopentadienyl and indenyl compounds of the borderline metals such as mercury and copper are required in order to elucidate their structures, bonding and fluxional behavior.

Studies of Group IV indenyls have shown them to also be fluxional.[21-24] The fact that isoindenoid Diels-Alder adducts can be trapped[24] does not necessarily prove that the fluxional process proceeds *via* an isoindenoid intermediate. The unique molecule V has been synthesized[22] and it shows rapid exchange of the $Si(CH_3)_3$ groups in the high temperature pmr spectrum. One interpretation of this result



VII

is in terms of the C_{2v} isoindenoid intermediate (or transition state) VI but a displacement mechanism with a concerted movement of both $Si(CH_3)_3$ groups as in VIII is also conceivable. In any case, divalent mercury would appear to be more capable of expanding its coordination

sphere than is tetravalent silicon.[25]

It should be noted that bis(allyl)mercury appears to be static.[26] This may either be taken as evidence against the proposed 1,3 shift or may simply be explained by the greater difficulty in forcing the h^1-allyl moiety into a planar geometry. This could also be used as evidence that a pentahaptoindenyl configuration serves as the intermediate or transition state.

EXPERIMENTAL

Preparation. - Commercial butyllithium (0.042 moles) in hexane was used to metalate 5.4 g (0.047 mole) of indene in 140 ml of ether. The ether was freshly distilled from sodium/benzophenone. To the stirred solution of indenyllithium, which had been cooled to -78° (using an acetone/CO_2 bath) under nitrogen 6.05 g (0.0223 mole) of mercury(II) chloride in 60 ml of tetrahydrofuran was added dropwise over a period of 1.5 hrs. The THF was also freshly distilled from sodium/-benzophenone. The reaction mixture was stirred for an additional 0.25 hr and was then treated with 100 ml ether and 100 ml pentane, both precooled to -78°. This mixture was kept overnight (~ 16 hrs) at -78°, and the supernatant liquid was then siphoned from the reaction flask, leaving a pale yellow solid. This solid, still at -78°, was washed with two 80 ml portions of precooled ether, the ether being siphoned after each washing. Then 150 ml of methanol was added, the reaction flask

removed from the dry ice-acetone bath, and immediately 250 ml water (at 25°C) was added with rapid stirring. After 0.25 hr stirring, the flocculent precipitate was suction filtered, washed with 300 ml water and then with 60 ml ether. The pale yellow to pale gray solid was sucked dry and then collected and dried further under high vacuum.

Additional purification was achieved by extracting this crude product in air with 80 ml of 4:1 methylene chloride:hexane and filtering under nitrogen into a flask at -78°. The methylene chloride was then slowly removed under high vacuum at low temperature until the volume of the solution was reduced by about one third. The supernatant was then carefully removed with a syringe at -78°, and the pale yellow to white product was washed with several portions of pentane and dried under high vacuum at 0° in the dark. Yield: 1.1 g (12%) of pale yellow to white solid.

Anal. Calcd. for $C_{18}H_{14}Hg$: C, 50.16; H, 3.28. Found: C, 49.8; H, 3.04.

Pmr Spectra. - Spectra at 60 MHz were obtained with a Varian Associates A-60 nuclear magnetic resonance spectrometer. Temperature control was achieved with a V-6040 variable temperature controller and peak separations in methanol and ethylene glycol samples were used to calibrate the temperature. The 100 MHz spectra were recorded with a Varian HA-100 spectrometer equipped with a C-1024 time averaging computer.

FIGURE IV-1

Proton magnetic resonance spectra (at 60 MHz) of bis-(1-indenyl)mercury at various temperatures. An approximately 0.37M solution in CCl_3D was used. The small peak marked X is due to an impurity resulting from thermal decomposition at the highest temperature.

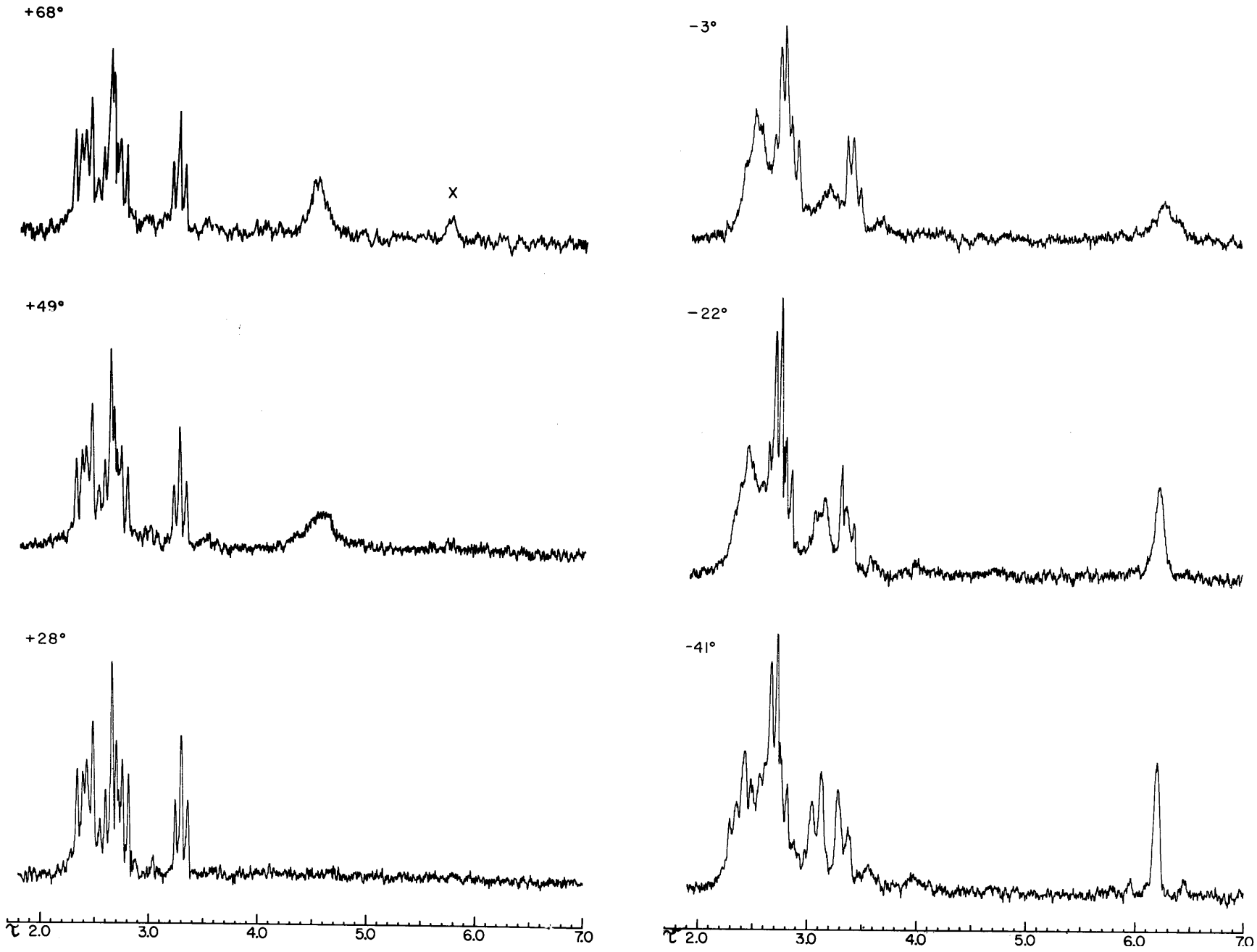
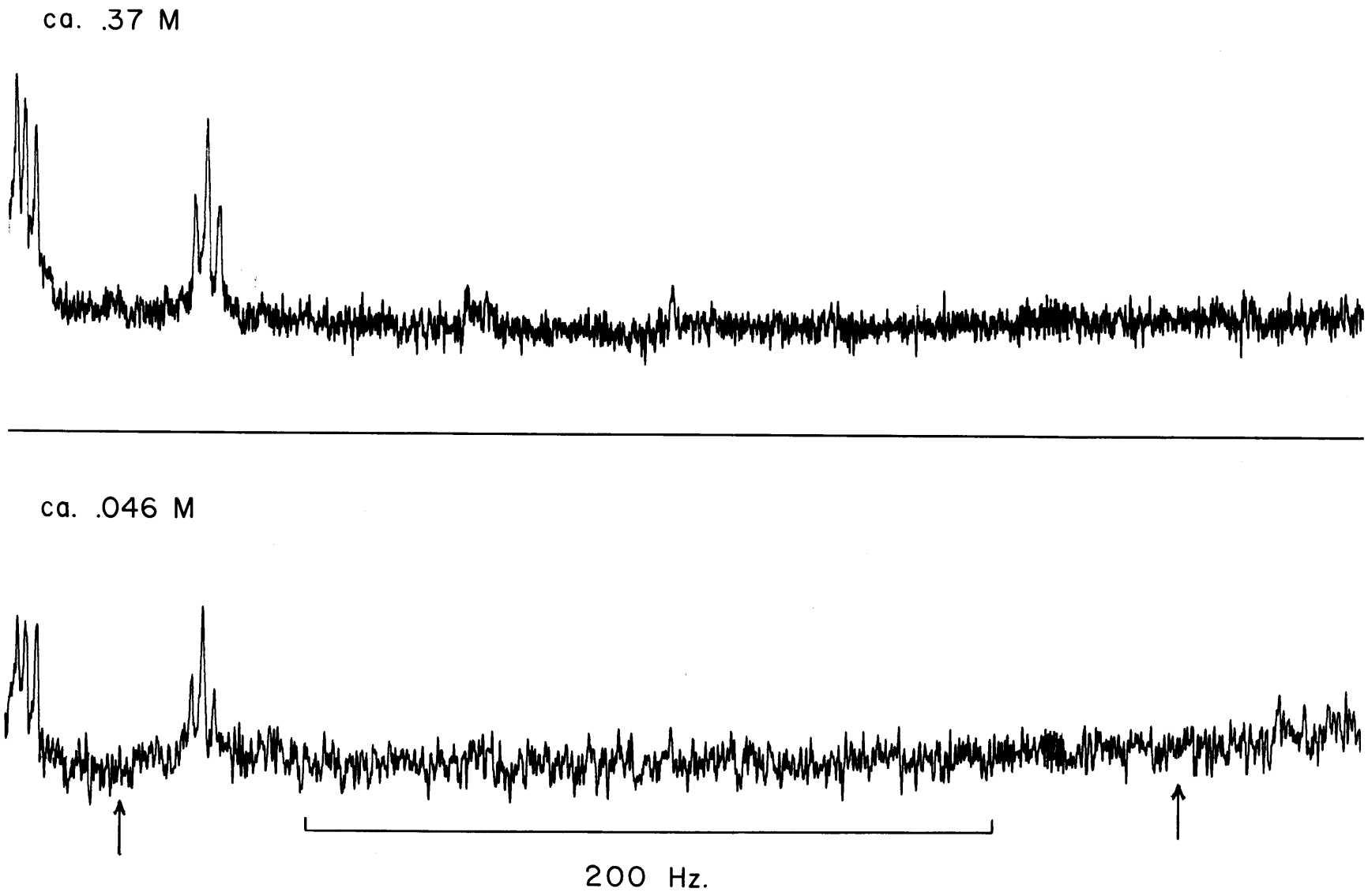

+68°
X
-3°
+49°
-22°
+28°
-41°
τ 2.0
3.0
4.0
5.0
6.0
7.0

FIGURE IV-2

Proton magnetic resonance spectra (at 100 MHz) of bis-(1-indenyl)mercury at 25° in CCl_3D as a function of concentration. The upper trace was recorded with a saturated solution (~ 0.37M) while the lower trace was obtained after dilution by a factor of 8. The lower trace is computer-averaged from 18 sweeps.


ca. .37 M
ca. .046 M
200 Hz.

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7. For the structure of this molecule see J. Trotter, Acta Cryst., 11, 355 (1958).
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10. (a) Pmr samples prepared in the presence of air are considerably more stable than those from which oxygen is rigorously excluded. The sample used for Fig. 1 also contained a trace of dihydroquinone, which improves stability. These observations are indicative of a free radical chain mechanism of decomposition.
    (b) Manatt and Elleman[9] have shown that in indene itself J_{HA} and J_{AB} have the same sign. Our results show that this is still true in $(C_9H_7)_2Hg$ since $|\pm 5.7 \pm J_{HA}|/2$ can equal $\sim |3.5|$ whereas $|\pm 5.7 \pm J_{HA}|/2$ cannot. Thus, the relative signs of two coupling

constants can be deduced by studying the high temperature spectrum of a fluxional molecule.

11. H. S. Gutowsky and C. H. Holm, J. Chem. Phys., 25, 1228 (1956).

12. The possibility of a two-step dissociation-recombination mechanism, probably involving a mixture of intra- and intermolecular exchanges, but following a rate law first order in $(C_9H_7)_2Hg$ is not directly disproved by the evidence at hand. We believe it will be generally recognized, however, that such a process is highly unlikely and have ruled it out. Direct evidence against (or for) it could be obtained from the presence (or absence) of satellite lines due to $^{199}Hg\cdots H$ couplings,[13] in the fast exchange limit. Unfortunately, thermal instability denies us the opportunity to reach this limit; the linewidth of the merged resonance at $+68^{\circ}$ is still too large to allow observation of the satellites which we believe to be present.

13. It has been noted[14] that the magnitudes of many $^{199}Hg\cdots H$ couplings in indenyl systems are unexpectedly large, but that some satellites may be discerned in the -41° spectrum of Fig. IV-1.

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15. For a very striking example of the effects of diamagnetic anisotropics see the nmr[16] and structural[17] data on $(C_5H_5)_3MoNO$.

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CHAPTER V

AN INFRARED STUDY OF THE STRUCTURES OF CYCLOPENTADIENYL COMPOUNDS OF COPPER(I) AND MERCURY(II)

The first description of a cyclopentadienylcopper compound outside of the patent literature was given by Wilkinson and Piper,[1] who isolated $(C_5H_5)[P(C_2H_5)_3]Cu$ from the reaction of Cu_2O with cyclopentadiene and triethylphosphine. These authors also made the suggestion, with reservations, that this molecule contains a monohaptocyclopentadienyl ring. This suggestion has been perpetuated by several subsequent publications.[2,3] However, in the course of a reinvestigation of the pmr spectrum of this compound, and homologous ones with different phosphines, we became doubtful about this structure. Close examination of the evidence for it from vibrational spectra[1] and indeed a review of the entire state of the published correlations[2] between ir spectra and cyclopentadienylmetal configurations indicated to us the need for a thorough, careful reexamination of this problem.

In view of contradictory claims[1,2,4-8] concerning the structures of cyclopentadienyl compounds of mercury(II) the study was extended to include $(C_5H_5)_2Hg$ and $(C_5H_5)HgCl$ as well.

EXPERIMENTAL

All organometallic compounds were prepared, stored, and handled in an atmosphere of prepurified nitrogen. Solvents were carefully dried in the manner appropriate to each and then distilled under nitrogen just prior to use. The organomercury compounds were stored at -78°, in the dark.

The $(C_5H_5)(PR_3)Cu$ compounds were prepared by reaction of C_5H_5Tl with the appropriate $[(PR_3)CuI]_4$ compound. The procedures will be described in detail in the following chapter.

Dicyclopentadienylmercury was prepared from TlC_5H_5 and $HgCl_2$ employing the procedure of Nesmeyanov, et al.,[9] and was recrystallized several times from ether at low temperature in the dark. Although manipulations involving this substance were performed in normal laboratory light, its exposure to light was otherwise restricted.

Cyclopentadienylmercury(II) chloride was prepared from TlC_5H_5 and $HgCl_2$ by the method of Kitching[8] and recrystallized several times from THF-pentane mixtures.

Triethylphosphineiodocopper(I) and tributylphosphineiodocopper(I) were prepared by methods in the literature.[10,11]

Spectroscopic Measurements. - Solutions of the mercurials were prepared in subdued light immediately before spectroscopic examination. Samples were monitored for decomposition by observing changes in the relative intensities of various peaks during the course of several scans.

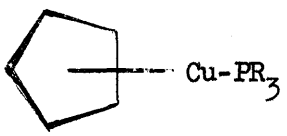
A nitrogen-filled glove bag was employed for the preparation of solutions and mulls of the copper compounds and for filling cells; samples were again monitored for decomposition. All solvents and mull media were examined by infrared spectroscopy to identify spurious peaks which might be present.

Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrometer, and frequency calibration was done with polystyrene film. The C-H stretching regions were also studied at higher resolution with a Perkin-Elmer 521 grating spectrometer which had previously been calibrated.

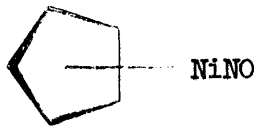
RESULTS

Reference Compounds. - The chief reference compound for pentahaptocyclopentadienylmetal group is ($\underline{h}^5$-C_5H_5)NiNO, the spectrum[12] of which is shown in the center of Fig. V-1. However, due consideration was also given to several other compounds, namely ($\underline{h}^5$-C_5H_5)$Mn(CO)_3$,[13] ($\underline{h}^5$-C_5H_5)$V(CO)_4$[14] and ferrocene.[15] A simple symmetry analysis in terms of internal coordinates for the C_5H_5 part of an M-C_5H_5 system with C_{5v} symmetry shows that there should be 14 normal modes of vibration, of which 7 will be infrared active. On the basis of the experimental observations and previously proposed assignments for the reference compounds just mentioned, the descriptions, intensities, and approximate frequencies of the infrared-active fundamentals localized in the C_5H_5 ring of an ($\underline{h}^5$-C_5H_5)M group are summarized in Table V-1.

From Table V-1 it is clear that the infrared spectrum expected for an ($\underline{h}^5$-C_5H_5)M system in the range of $\sim$ 600 to $\sim$ 3500 cm^{-1} is very simple indeed, consisting of a medium band at 3050-3100 cm^{-1}, a strong band at $\sim$ 1000 cm^{-1}, and a broad, very strong band at 800 $\pm$ 50 cm^{-1} with the possibility of two more bands, perhaps very weak, at $\sim$ 1400 cm^{-1} and $\sim$ 110 cm^{-1}. No further bands of appreciable intensity are to be expected, since the foregoing list accounts for all fundamentals. The spectrum of ($\underline{h}^5$-C_5H_5)NiNO seen in Fig. V-1 accords well with this symmetry.



I



II

For an ($\underline{h}^1$-C_5H_5)M system, which can have at best C_s symmetry, there are 24 normal modes of vibration arising in the C_5H_5 group itself and presumably all of them will have frequencies above 600 cm^{-1}. The only possible exceptions might be one or two of the four ring deformation modes. Five of the total of 24 modes are C-H stretches. One, the MC-H stretch, may be expected in the region of aliphatic C-H stretches, viz., 2800-3000 cm^{-1}, while the other four, the olefinic

C-H stretches, should come between 3000 and 3100 cm^{-1}. It would be entirely reasonable that of four such closely spaced bands only three might be resolved clearly. There should then be 18-20 fundamentals spread through the region from $\leq$ 1600 (C=C stretching) to $\geq$ 600 cm^{-1}. Thus a very rich and complex spectrum is to be expected in marked contrast to theory and observation for (g^5-C_5H_5)M systems.

As a reference standard for the monohaptocyclopentadienylmetal system we have used $(CH_3)_3GeC_5H_5$. It has been definitively shown by Davison and Rakita[16] that this is a fluxional molecule containing a monohaptocyclopentadienyl ring. The rate of rearrangement at room temperature is of the order of 10^2-10^3 sec^{-1}, that is, slow enough so that there can be no question of this rearrangement process significantly perturbing the vibrational spectrum. Figure V-2 shows the spectrum of $(CH_3)_3GeC_5H_5$. By comparison with numerous spectra of $(CH_3)_3Ge$ derivatives reported in the literature[17] and with the spectrum of $(CH_3)_3GeC{\equiv}CGe(CH_3)_3$ made available to us by Professor D. Seyferth and Mr. D. L. White, it is relatively easy to identify those bands which are due, at least in part, to vibrations essentially resident in the $(CH_3)_3Ge$ portion of the molecule. Such bands are indicated with crosses on the spectrum of $(CH_3)_3GeC_5H_5$ in Fig. V-2. It is clear that even when these bands are eliminated, the remaining spectrum is very rich and complex as expected.

Cyclopentadienylcopper Compounds. - Immediately above and below the reference spectrum ($(\underline{h}^5\text{-}C_5H_5)NiNO$) in Fig. V-1 are the spectra of the $C_5H_5CuPR_3$ compounds, and each of these is flanked by the spectrum of the corresponding $[R_3PCuI]_4$ compound. The spectra below 1400 cm^{-1} were recorded on mulls of the solid compounds because the $C_5H_5CuPR_3$ compounds are reactive toward CS_2 and halocarbons which would normally be used to get a complete record of the spectrum in the desired regions. In the C-H stretching region, however, solutions in perdeuteriotoluene were used.

The spectra of the $[R_3PCuI]_4$ compounds should be virutally identical with those parts of the $C_5H_5CuPR_3$ spectra which arise from the $CuPR_3$ portions of the molecules. Moreover, it seems safe to assume that there will be no more than slight interactions between the vibrations in the C_5H_5 portions of the molecules. Thus, by inspection, one may delete from the observed spectra of the $C_5H_5CuPR_3$ compounds the "PR_3 bands" so as to leave, barring some possible uncertainties caused by overlap, the spectra of the C_5H_5 rings in these molecules. Table V-2 lists the bands so identified. Overlap of PR_3 and C_5H_5 absorptions around 1400 cm^{-1} does, in fact, make it impossible to ascertain whether there is actually a medium or weak C_5H_5 band in this region, but otherwise the results are straightforward. It is abundantly clear that the $C_5H_5CuPR_3$ compounds possess extremely simple "C_5H_5 spectra" in the 600-1350 cm^{-1} region. The spectra are far too simple to be con-

sistent with the presence of monohaptocyclopentadienyl rings, but correlate satisfactorily with our expectations for a pentahapto ring as summarized in Table V-1.

The spectra in the C-H stretching region supply additional strong evidence that pentahapto rings are present. Only a single sharp peak is seen between 3000 and 3100 cm^{-1}. This is attributable to the e_1 mode, the a_1 mode being, as usual,[18] too weak to be seen. This result is in marked contrast to the multiple olefinic C-H stretching bands expected for a monohaptocyclopentadienylmetal system and clearly observed in $(CH_3)_3GeC_5H_5$ (see Fig. V-2).

Cyclopentadienylmercury Compounds. - The spectra of $(C_5H_5)_2Hg$ and C_5H_5HgCl, measured on CS_2 solutions, are shown in Fig. V-2. The spectrum of $(C_5H_5)_2Hg$ in CCl_4 was also recorded and it is essentially identical with that in CS_2. Two things are immediately clear; first, the spectra of the two mercurials are very similar to each other. Second, they are both very similar to what remains of the spectrum of $(CH_3)_3GeC_5H_5$ after bands due to the CH_3 groups have been deleted. In the region from 600 to 1350 cm^{-1} the general similarities of these three relatively complex spectra leave no doubt that the mercurials contain monohaptocyclopentadienyl groups.

The C-H stretching region again affords strong evidence for the type of cyclopentadienyl-metal configuration present. Both $(C_5H_5)_2Hg$ and C_5H_5HgCl show multiple absorptions in the olefinic C-H stretching

region, although the resolution is noticeably poorer in the case of $(C_5H_5)_2Hg$. Nevertheless, there is no doubt that the absorption here is multiple, closely akin to that in $(C_5H_5)HgCl$ and $(CH_3)_3GeC_5H_5$ and quite different from the single, sharp, peak at ~ 3085 cm^{-1} which is characteristic of ($\underline{h}^5$-C_5H_5)M systems. For a ($\underline{h}^1$-C_5H_5) ring there should also be an aliphatic C-H stretching band; presumably the bands occurring at 2960 cm^{-1} in $(C_5H_5)_2Hg$ and C_5H_5HgCl can be so assigned, although assignments in the 2800-2000 cm^{-1} region are somewhat ambiguous because the model compounds absorb here and because there is also a weak band at ~ 2850 cm^{-1}. The latter is, however, most likely an overtone or combination band and it may owe some of its intensity to Fermi resonance with the aliphatic C-H stretch.

The observed spectra for the $\underline{h}^1$-C_5H_5 compounds are summarized in Table V-3.

DISCUSSION

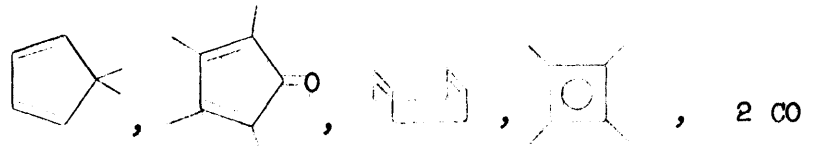
Cyclopentadienylcopper(I) Compounds. - The important conclusion, which emerges very clearly, is that these compounds contain pentahapto and not monohapto rings. It is certainly rather curious that the incorrect formulation has remained unchallenged for some 13 years. It should be noted that the original suggestion[1] of a monohapto ring was not supported by any strong experimental evidence and was put forth only in a qualified way. It would seem, however, that even at that

time the infrared data might have appeared more in support of a pentahapto ring, though material for comparison was considerably less abundant then. The subsequent assignment[2] of a monohapto structure on the basis of infrared data is more difficult to justify. In both of the earlier publications little attention was paid to the C-H stretching region (it was not even reported in one case).[2] This may have been due to the fact that the poor resolution (~ 20 cm^{-1}) obtainable in this region with a rock salt prism obscures significant structure. From the present study it is evident that this region of the spectrum, observed under adequate resolution, can be singularly informative.

It is worth commenting on the fact that the pentahapto structure, I, for $(C_5H_5)CuPR_3$ compounds need not be considered at all surprising. Such molecules are isoelectronic with ($\underline{h}^5$-C_5H_5)NiNO which has structure[19] II. The idea that d orbitals suitable for bonding interactions with the C_5H_5 ring will be markedly less available in $C_5H_5CuPR_3$ than in C_5H_5NiNO is certainly not plausible. Indeed, it is possible to view the ($\underline{h}^5$-C_5H_5)$CuPR_3$ molecules as members of a rather long isoelectronic sequence in which we have ($\underline{h}^5$-C_5H_5)M moieties interacting with 5-,4-,3-,2-, and, hypothetically as yet, 1-electron ligands, viz.

$(\underline{h}^5\text{-}C_5H_5)Fe(\underline{h}^5\text{-}C_5H_5)$ (ferrocene)

$(\underline{h}^5\text{-}C_5H_5)CoL$

L= , 2 CO

$(\underline{h}^5\text{-}C_5H_5)NiNO$, $(\underline{h}^5\text{-}C_5H_5)NiL$, L = 

$(\underline{h}^5\text{-}C_5H_5)Cu\ PR_3$

$[(\underline{h}^5\text{-}C_5H_5)Zn\text{-}R,\ R = \text{alkyl?}]$

$[(\underline{h}^5\text{-}C_5H_5)M,\ M = In, Tl, Ga?]$

From this point of view the pentahapto structure might be considered as that which is logically expected, rather than in any sense surprising. The question of whether the series does in fact extend to the zinc and gallium compounds is of some interest, and is under investigation.

It should be recognized, however, that the amount of d orbital participation in $(\underline{h}^5\text{-}C_5H_5)$-M bonding must decrease continuously in the above series, while the role of the e_1-type p orbitals (p_x and p_y when the 5-fold axis is called the z axis) will steadily increase as the p orbitals drop in energy and become less diffuse. In the case of $(\underline{h}^5\text{-}C_5H_5)Tl$, the 6p orbitals of thallium evidently are very well suited for overlap with the ring e_1 orbitals.[20] In $(\underline{h}^5\text{-}C_5H_5)In$, which is much less stable than the thallium compound, the p-orbital overlap may be

less effective. In any case, the inherent stability of the I oxidation state is lower for In than for Tl. The expected continuation of both trends as we go from In to Ga makes it problematical whether ($\underline{h}^5$-C_5H_5)Ga is capable of existence at ordinary temperatures, but experimental study seems worthwhile.

Another fact worthy of note in connection with the reasonableness of structure I is the remarkable chemical and thermal stability of the cyclopentadienylcopper(I) compounds; $C_5H_5CuP(C_2H_5)_3$ can be sublimed under vacuum at 70°, while other organocopper compounds decompose thermally well below 0°[21] and are rapidly hydrolyzed by water. Clearly, the enormously greater stability of the cyclopentadienyl compounds would be difficult to explain if conventional monohaptocyclopentadienylcopper structures were correct.

It is in fact an interesting historical irony that a precisely parallel situation prevailed with dicyclopentadienyliron. Immediately following Kealy and Pauson's report[22] of the isolation of $(C_5H_5)_2Fe$ and their discussion of it as a bis-($\underline{h}^1$-$C_5H_5)_2Fe$ molecule despite the fact that its "remarkable stability" was "of course, in sharp contrast to the failures of earlier workers to prepare similar compounds" with other R groups, Wilkinson, Rosenblum, Whiting and Woodward[23] rejected the monohaptocyclopentadienyl structure at least partly on the ground that the exceptional stability of ferrocene in comparison to other (nonexistent) organoiron species "led us to consider whether an alternative to the structure might be more nearly in accord with the unique

character of Kealy and Pauson's compound." The close similarity to the situation with $C_5H_5CuPR_3$ compounds has previously been overlooked.

In conjunction with the infrared studies, an X-ray structural investigation was undertaken by Dr. Josef Takats of These Laboratories on the compound, $C_5H_5CuP(C_6H_5)_3$,[25] whose preparation will be described in the following chapter. The most striking feature of this structure is that the copper is bonded to the cyclopentadienyl ring in the pentahapto configuration; the copper-ring moiety has nearly perfect C_{5v} symmetry. Figure V-3 illustrates the geometry of the molecule. Another important feature of this structure is that the metal-to-ring carbon distances show lengthening over those of analogous nickel compounds. This appears to reflect weakening of the metal-ring interaction due to the filling and contraction of 3d orbitals toward the right of the transition series.

Cyclopentadienylmercury(II) Compounds. - The spectra demonstrate unequivocally that these molecules do not contain pentahapto rings, as has been claimed by some workers.[7] Moreover, the spectra seem to us to be quite consistent with the presence of a monohapto ring in C_5H_5HgCl and with the presence of two such rings in $(C_5H_5)_2Hg$. The complexity of the $(C_5H_5)_2Hg$ spectrum requires the presence of at least one ($\underline{h}^1$-C_5H_5) ring. The possibility that the latter compound might contain one ($\underline{h}^5$-C_5H_5) and one ($\underline{h}^1$-C_5H_5) ring seems very remote indeed, since the differences between the $(C_5H_5)_2Hg$ and C_5H_5HgCl spectra are

minor and not consistent with the expected result of adding to the C_5H_5HgCl spectrum the bands arising from a ($\underline{h}^5$-C_5H_5)M group.

Shortly after the completion of our work, Maslowsky and Nakamoto[24] reported a study of the infrared spectra of $(C_5H_5)_2Hg$, C_5H_5HgCl, C_5H_5HgBr, and C_5H_5HgI. They have reached the same conclusions as we did, namely, that only ($\underline{h}^1$-C_5H_5) rings are present in these molecules. Their experimental data are in excellent agreement with ours. We have given the present brief account of our study of $(C_5H_5)_2Hg$ and C_5H_5HgCl since our approach, in terms of choice of reference compound ($C_5H_5Ge(CH_3)_3$, which we think is more appropriate in certain respects than C_5H_6), and emphasis on the C-H stretching region not only substantiates but supplements theirs.

In addition to these infrared studies, pmr studies[26] on C_5H_5HgX molecules, X = a halogen, show them to be <u>monohaptocyclopentadienyl</u> molecules, and fluxional. It appears that ($\underline{h}^1$-C_5H_5)$_2$Hg is rearranging at such a rapid rate that even at -140° (100 MHz)[26] in ethereal solvents, the single resonance is only somewhat broadened. This author confirms these observations by studies in Freon solvents down to -150° (60 MHz). Assuming log A $\approx$ 13 for this process, the activation energy must be quite small, implying that the slope of the Arrenhius plot is small. Hence, it may be impossible to reach the slow exchange limit by conventional nmr techniques since the rate is so insensitive to temperature changes.

TABLE V-1

Infrared-Active Fundamental Vibrational Transitions

for the C_5H_5 Ring in an ($\underline{h}^5$-C_5H_5)M System

Type of internal coordinate change[a]	Symmetry type	Approx frequency, cm^{-1}	Comments
C-H stretching	a_1	3050-3100	a_1 mode usually vw; only e_1 mode consistently seen
	e_1		
C-C stretching	a_1	~ 1100	Sym ring breathing; intensity highly variable; often vw usually m to w
	e_1	~ 1400	
C-H out-of-plane wagging	a_1	~ 800	Usually broad absorption; combined intensity very high; position varies greatly
	e_1		
C-H in plane wagging		~ 1000	Generally strong and close to 1000 cm^{-1}

(a) We follow here the original assignments of Lippincott and Nelson;[15] revisions have since been proposed.[2] Our structure conclusions are not altered by such changes, however.

TABLE V-2

Infrared Bands Assignable to C_5H_5 Groups

in the $C_5H_5CuPR_3$ Compounds[a]

$C_5H_5CuP(C_2H_5)_3$	$C_5H_5CuP(C_4H_9)_3$	Remarks
3085 m, sharp	3085 m, sharp	Spectrum measured in toluene-d_3
998 ms, sharp	997 ms, sharp	Mull spectrum
752 vs, vb	755 vs, vb	Mull spectrum

(a) m = medium; v = very; s = strong; b = broad

TABLE V-3

Infrared Spectra (cm^{-1}) of Monohapto cyclopentadienylmetal Groups

$(C_5H_5)_2Hg$[a]	C_5H_5HgCl[a]	$C_5H_5Ge(CH_3)_3$	$(CH_3)_3GeC{\equiv}CGe(CH_3)_3$[c]
3095 ms	3110 m	3110 m	
3088 ms	3095 m	3090 m	
3067 ms	3077 m	3070 m	
3040 w, sh	3070 m		
		2975 vs	2980 vs
		2910 vs	2915 vs
2960 m	2960 m		
2850 w	2855 w	2860 m	
		2800 w	2800 w
	1880 vw		
1800 m	1820 w	1838 vw	
1780 m	1805 w	1800 w	
1695 w	1700 vw		
1610 m	1645 w	1617 m	
1530 w	1543 w	1540 w	
1427 m	1461 m	1458 s	
1400 m		1420 m	1410 m
1370 s	1370 m	1378 m	
1282 w	1290 w	1295 m	
		1238 vs	1240 vs
1231 w	1222 w	1220 w	
1108 w		1110 m	
1082 m	1086 w	1087 m	
1023 m	1015 m	1015 w	
987 m	985 m	995 w	
995 m	958 w	960 m	
904 s	936 s	944 vs	
883 s	897 m	900 m	
		860 w	
		826 vs	
		826 vs	826 vs
820 m	812 m	817 vs	
		795 w	
	780 w	770 w	

TABLE V-3 (continued)

$(C_5H_5)_2Hg$[a]	C_5H_5HgCl[a]	$C_5H_5Ge(CH_3)_3$	$(CH_3)_3GeC{\equiv}CGe(CH_3)_3$[c]
		748 w	765 m
742 vs	750 vs	729 vs	
712 w	712 vw	710 vw	
665 vw	665 vw	672 vw	
641 m	649 m	650 vs	668 vs
		597 vs	608 s

(a) Measured in CS_2 solution.

(b) Measured as a neat liquid film.

(c) Combined data from CCl_4 solution and mineral oil mull.

FIGURE V-1

A. The infrared spectrum of $[(C_2H_5)_3PCuI]_4$. The high-frequency region was recorded as a Fluorolube mull and the low-frequency region as a Nujol Mull. B. The infrared spectrum of $(\underline{h}^5\text{-}C_5H_5)CuP(C_2H_5)_3$. The high-frequency region was studied in toluene-d_8 solution (the Fluorolube mull spectrum was essentially identical, but with a poorer signal to noise ratio) and the lower region as a Nujol mull. C. The infrared spectrum of $(\underline{h}^5\text{-}C_5H_5)NiNO$, redrawn from Ref. 12. D. The infrared spectrum of $(\underline{h}^5\text{-}C_5H_5)CuP(C_4H_9)_3$. The high-frequency region was studied as a solution in toluene-d_8 (the Fluorolube mull spectrum was essentially identical, but weaker) and the low-frequency region as a Nujol mull. E. The infrared spectrum of $[(C_4H_9)_3PCuI]_4$. The high-frequency region was recorded as a Fluorolube mull and the lower region as a Nujol mull.

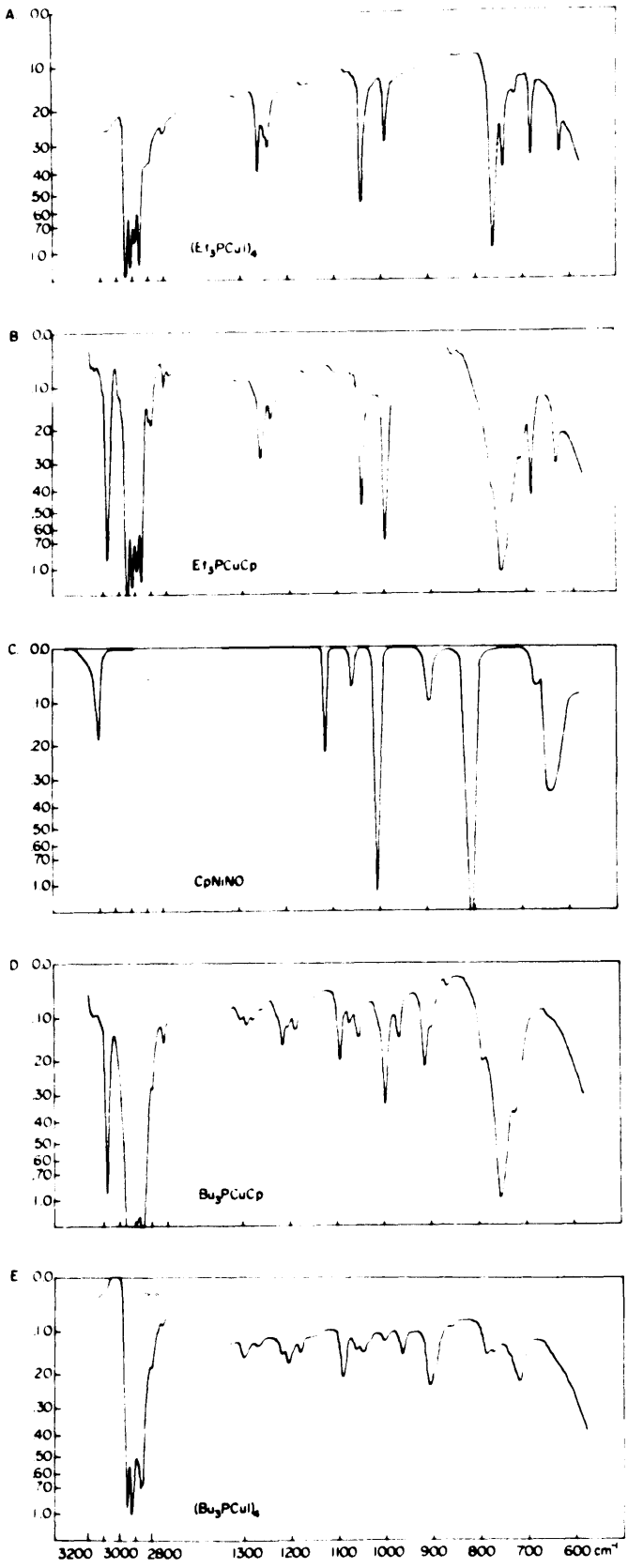

A
B
C
D
E
$(Et_3PCuI)_4$
Et_3PCuCp
CpNiNO
Bu_3PCuCp
$(Bu_3PCuI)_6$
3200 3000 2800 1300 1200 1100 1000 900 800 700 600 cm⁻¹

FIGURE V-2

A. The infrared spectrum of ($\underline{h}^1$-C_5H_5)$_2$Hg in carbon disulfide. B. The infrared spectrum of ($\underline{h}^1$-C_5H_5)HgCl in carbon disulfide. C. The infrared spectrum of ($\underline{h}^1$-C_5H_5)Ge(CH_3)$_3$ as a film of the pure liquid. This spectrum was supplied by Professor A. Davison and Mr. P. E. Rakita. Bands marked X are believed to be due to the Ge(CH_3)$_3$ part of the molecule.

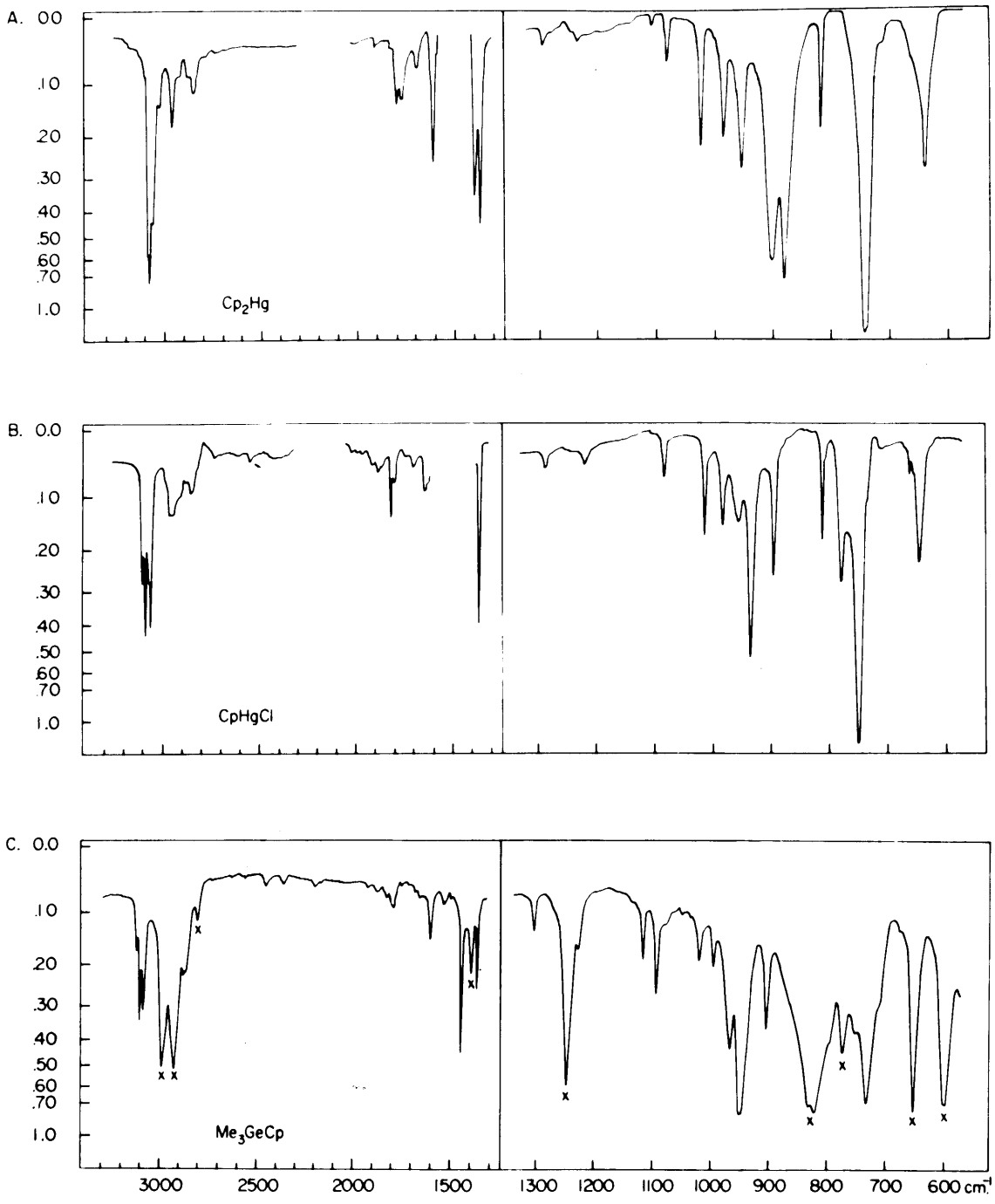
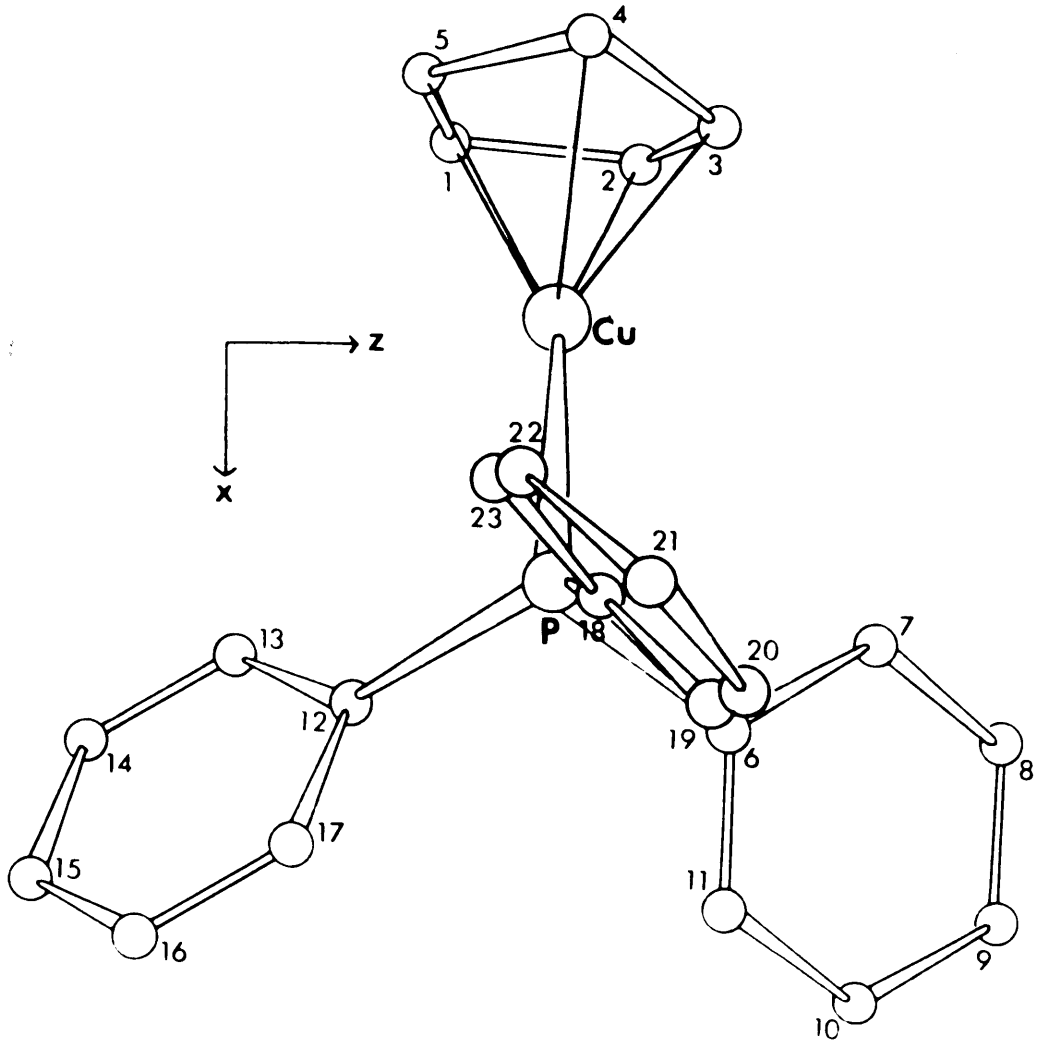

A. 00
.10
.20
.30
.40
.50
.60
.70
1.0
Cp2Hg
B. 0.0
.10
.20
.30
.40
.50
.60
.70
1.0
CpHgCl
C. 0.0
.10
.20
.30
.40
.50
.60
.70
1.0
Me3GeCp
3000
2500
2000
1500
1300
1200
1100
1000
900
800
700
600 cm-1

FIGURE V-3

The molecular structure of $C_5H_5CuP(C_6H_5)_3$ as shown in Ref. 25.


4
5
1
2
3
Cu
z
x
22
23
21
P
18
20
7
13
12
19
6
8
14
17
15
11
16
9
10

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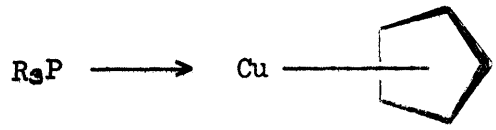
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CHAPTER VI

SYSTEMATIC PREPARATION AND CHARACTERIZATION OF PENTAHAPTOCYCLOPENTADIENYLCOPPER(I) COMPOUNDS

INTRODUCTION

Recent reports have presented infrared[1] and X-ray evidence[2] to show that $C_5H_5CuPR_3$ compounds have the structure, I, in which there is a pentahaptocyclopentadienyl ring. Our investigations were made



(I)

feasible by the development of a new general procedure for the preparation of such compounds.

Previously only the compound containing triethylphosphine was known;[3] it was prepared by the reaction of Cu_2O with cyclopentadiene and triethylphosphine. This type of reaction could, perhaps, be applied more generally, but it has practical disadvantages and a more straightforward, general route was sought.

This chapter describes such a route, illustrates its application by describing in detail the preparation and characterization of the five compounds ($\underline{h}^5$-C_5H_5)(L)Cu, where L = (1) $P(C_2H_5)_3$, (2) $P(C_4H_9)_3$, (3) $P(C_6H_5)_3$, (4) $P(OCH_3)_3$, (5) $CNCH_3$, and comments briefly on the properties, relative stabilities and bonding in these compounds.

The compound ($\underline{h}^5$-C_5H_5)(CO)Cu has also been prepared by a different method. It is much less stable than the phosphine compounds.

Studies by Whitesides and Fleming[4] presented evidence that in SO_2 solution, the nmr spectrum of $C_5H_5CuP(C_2H_5)_3$ was that of a fluxional monohaptocyclopentadienyl molecule. This led them to propose that the copper in $C_5H_5CuP(C_2H_5)_3$ was sigma-bonded to the C_5H_5 ring and that 1,3 shifts were occurring. It was of interest to us, in view of our infrared and X-ray findings, to investigate the behavior of some of these compounds in SO_2.

EXPERIMENTAL

The preparation and handling of all organometallics was carried out in an atmosphere of prepurified nitrogen, since the $\underline{h}^5$-cyclopentadienyl compounds are moderately air-sensitive as solids and extremely so when in solution. All solvents were carefully dried in an appropriate manner and were freshly distilled under nitrogen prior to use. Melting points were determined in sealed, nitrogen-filled capillaries.

Considerable difficulty was encountered in obtaining satisfactory elemental analyses, especially for carbon. Best results were obtained from Scandinavian Microanalytical Laboratories, Copenhagen, and Mrs. N. Alvord, of the M.I.T. Microanalytical Laboratory.

Triethylphosphineiodocopper(I),[5] tributylphosphineiodocopper(I),[6] triphenylphosphinebromocopper(I),[7] trimethylphosphiteiodocopper(I),[8] and methylisocyanideiodocopper(I)[9] were prepared by methods in the

literature. Mass spectra obtained by the direct injection technique were kindly provided by Dr. R. B. Moyes of Hull University.

(Pentahaptocyclopentadienyl)triethylphosphinecopper(I). - To 2.0 g (0.0065 mol) of triethylphosphineiodocopper(I) suspended in 100 ml pentane, was added 2.7 g (0.010 mol) thallium cyclopentadienide, and the mixture was stirred for 18 hr at 25°C. The reaction mixture was then filtered by suction, under nitrogen, and the residue was washed with two 20 ml portions of pentane. The total filtrate was reduced to 100 ml by evaporation under vacuum and the solution was then gradually (over 1 hr) cooled to -78°. After the solution had been allowed to remain at -78° for an additional two hours, the supernatant liquid was removed from the white crystalline product with a syringe and 25 ml pentane, precooled to -78°, was used to wash the product. Finally, the product was sublimed for 16 hr at 65°/0.01 Torr to yield 1.35 g (84%) of white, crystalline product, m.p. 122-124° (lit.[3] 127-128°).

Anal. Calcd. for $C_{11}H_{20}CuP$: C, 53.52; H, 8.18. Found: C, 53.5; H, 8.23.

The pmr spectrum of this compound dissolved in toluene-d_8 had the following resonances (τ values): sharp singlet at 3.85(5H) and complex multiplet at 9.0-9.5(15H). The h^5-cyclopentadienyl resonance shifts to τ4.30 in methylcyclohexane solution.

The mass spectrum showed prominent peaks for the parent ion at m/e 247 and 249 ($\frac{Cu^{63}}{Cu^{65}}$ = 2.24) and intense peaks corresponding to $(C_2H_5)_3PCu^+$ and $(C_2H_5)_3P^+$. As was reported by Whitesides and Fleming, peaks corresponding to $(C_5H_5)Cu^+$ were quite weak.

(Pentahaptocyclopentadienyl)tributylphosphinecopper(I). - The procedure just described for the preparation of the triethylphosphine analog was followed with 2.75 g (0.007 mol) of tributylphosphineiodocopper(I) and 2.16 g (0.008 mol) of thallium cyclopentadienide. Sublimation was accomplished at 70°/ 0.01 Torr for 36 hr, to yield 2.25 g (98%) of white, crystalline solid, m.p. 102-103°.

Anal. Calcd. for $C_{17}H_{32}CuP$: C, 61.68; H, 9.76. Found: C, 61.6; H, 9.75.

Pmr spectrum in toluene-d_8: τ3.83 (sharp singlet, 5H), τ8.6-9.2 (complex multiplet, 27H). In methylcyclohexane solution the sharp singlet appears at τ4.12.

The mass spectrum exhibited strong parent ion peaks at m/e = 331 and 333. Other prominent ions observed corresponded to $(C_4H_9)_3PCu^+$ and $(C_4H_9)_3P^+$.

(Pentahaptocyclopentadienyl)triphenylphosphinecopper(I). - To 1.70 g (0.0042 mol) of triphenylphosphinebromocopper(I) suspended in 100 ml of THF, was added 1.67 g (0.0062 mol) of thallium cyclopentadienide, and the mixture was stirred for 18 hr. Next, the mixture was filtered by suction, under nitrogen, and the residue washed with

25 ml of THF. The filtrate was evaporated to about 40 ml under high vacuum, 75 ml hexane were added and the solution was then cooled to -78°, which caused precipitation of ($\underline{h}^5$-C_5H_5)$CuP(C_6H_5)_3$ as a light tan solid. Supernatant liquid was removed with a syringe, the product was washed with 25 ml of hexane and then dried in high vacuum. This crude material was extracted with 300 ml of ether and the extract was filtered by suction under nitrogen through a small amount of decolorizing carbon. The filtrate was cooled at -78° for 28 hr, and the supernatant liquid was removed from the crystalline product with a syringe. The ($\underline{h}^5$-C_5H_5)$CuP(C_6H_5)_3$ was then washed with two 25 ml portions of ether which had been precooled to -78°, and was dried under high vacuum, yielding 1.0 g (61%) of white or nearly white crystals which exhibited no melting point and began to decompose at about 140°.

Anal. Calcd. for $C_{23}H_{20}CuP$: C, 70.66; H, 5.17; P, 7.92. Found: C, 70.6; H, 5.15; P, 7.50.

Pmr spectrum: τ2.6 (15H), τ4.09(5H) in tetrahydrofuran. The mass spectrum had parent ion peaks at m/e = 390 and 392. Strong peaks also occurred for the fragments $(C_5H_5)_3PCu^+$ and $(C_6H_5)_3P^+$.

This compound is less volatile than the alkylphosphine analogs and differs from them also in being virtually insoluble in nonpolar organic liquids.

(Pentahaptocyclopentadienyl)trimethylphosphitecopper(I). - To 1.6 g (0.0051 mol) trimethylphosphiteiodocopper(I) suspended in 100 ml pentane was added 1.48 g (0.0055 mol) thallium cyclopentadienide and the mixture was stirred for 16 hr at 25°. The reaction mixture was then filtered by suction under nitrogen and the residue washed with two 20 ml portions of pentane. Evaporation under high vacuum was employed to reduce the volume of the filtrate to 75 ml. Next, the solution was slowly cooled to -78° over a period of about 5 hr and was then kept at -78° for 16 hr. The supernatant liquid was removed from the white crystalline product by syringe and the product was washed with two 15 ml portions of -78° pentane and was dried under high vacuum. An additional recrystallization was employed to yield 1.00 g (78%) of pale-pink, air-sensitive oil, m.p. ca. -10°.

Anal. Calcd. for $C_8H_{14}O_3CuP$: C, 38.02; H, 5.59. Found: C, 37.8; H, 5.57.

Pmr spectrum, neat liquid: τ4.20 (sharp singlet, 5H), τ6.65 (doublet, J = 13.1 Hz, 9H). The ^{31}P splitting in $[(CH_3O)_3PCuI]_4$ is 12.0 Hz.

(Pentahaptocyclopentadienyl)methylisocyanidecopper(I).-To 1.6 g (0.0069 mol) of finely powdered methylisocyanideiodocopper(I) suspended in 100 ml pentane was added 1.97 g (0.0073 mol) of thallium cyclopentadienide. After 10 hr of brisk stirring, the reaction mixture was filtered by suction under nitrogen and the filtration residue was

extracted with two 20 ml portions of pentane. The combined filtrate was reduced under high vacuum to 100 ml, slowly cooled to -78° over a period of 5 hr and then allowed to remain at -78° for 16 hr. The supernatant liquid was then removed with a syringe and the crystalline product washed with two 20 ml portions of pentane, precooled to -78°. The crude product was purified by quickly extracting with 50, 20 then 20 ml portions of pentane in that order, treatment of the combined extracts with decolorizing carbon and then rapid suction filtration under nitrogen into a flask precooled to 0°. The filtrate was reduced to 60 ml under high vacuum and the product was crystallized as described above. Drying was carried out at -20° under high vacuum to yield 0.67 g (57%) of white or pale yellow crystalline product.

This compound is unstable at room temperature and rapidly turns brown, emitting the characteristic odor of methylisocyanide. Solutions appear to be slightly more thermally stable at room temperature, (although they are exceedingly air-sensitive) but then slowly deposit metallic copper.

An analysis was performed by rapidly transferring, under nitrogen, a sample into a tared weighing vessel equipped with a ground glass stopper, closing the vessel, weighing it and then decomposing its contents with nitric acid. Copper was determined iodometrically by standard volumetric procedures.[10]

Anal. Calcd. for C_7H_8NCu: Cu, 37.44. Found: Cu, 37.9.

Pmr spectrum in toluene-d_8: τ3.85 (sharp singlet, 5H), τ8.40 (broadened singlet, 3H). The low field singlet shifts to τ4.32 in methylcyclohexane.

(Pentahaptocyclopentadienyl)carbonylcopper. - To 1.5 g (0.016 mol) of finely powdered cuprous chloride suspended in 130 ml pentane, was added 4.85 g (0.018 mol) of thallium cyclopentadienide and one drop of $(C_4H_9)_3P$. The reaction vessel was maintained at 0° and with rapid stirring, carbon monoxide was bubbled into the mixture through a fritted glass gas inlet. The reaction was allowed to proceed at 0° for 10 days. During this time, pentane was periodically added to maintain the solution volume at about 130 ml. Toward the end of this period, a copper mirror was visible in some parts of the gas outlet system and the grease in the gound glass joints had turned dark red.

Under an atmosphere of carbon monoxide, the reaction mixture was filtered by suction and the residue washed with two 20 ml portions of pentane. The pale yellow filtrate was maintained at -55° and was distilled under high vacuum through a -78° trap. This process was repeated to yield finally about 20 ml of a colorless pentane solution of ($\underline{h}^5$-C_5H_5)CuCO which collected in the -78° trap. During the distillations, a pale-yellow, pentane-insoluble residue was observed to form in the distilling vessel and a white film formed in much of the distilling train. A stream of carbom monoxide swept much but not all of these residues into the collection flask, where the solution remained colorless.

The pentane solution of ($\underline{h}^5$-C_5H_5)CuCO began to slowly decompose at room temperature even under an atmosphere of carbon monoxide. Solutions maintained under nitrogen appeared to be considerably less stable. The solutions are air-sensitive, and deposit a copper-containing green precipitate on oxidation. These pentane solutions also react with phosphines with displacement of carbon monoxide to yield the corresponding ($\underline{h}^5$-C_5H_5)$CuPR_3$ derivative. In a typical experiment, 5 ml of a freshly distilled pentane solution of ($\underline{h}^5$-C_5H_5)CuCO, maintained at -78°, was treated with 0.20 ml $(C_4H_9)_3P$. Agitation of the solution caused gas evolution and the C≡O stretch of ($\underline{h}^5$-C_5H_5)CuCO disappeared from the infrared spectrum. After reduction of the solution volume (under high vacuum) to about 2 ml, cooling at -78° caused precipitation of a white crystalline product, which was recrystallized from pentane at -78°, sublimed at 68°/0.05 Torr, and identified as ($\underline{h}^5$-C_5H_5)Cu-[$P(C_4H_9)_3$] by its melting point and pmr spectrum. From the amount of phosphine adduct recovered, it is estimated that the total yield of ($\underline{h}^5$-C_5H_5)CuCO from the reaction was on the order of 100 mg.

The yellow-orange distillation residue, which always appears upon evaporation of ($\underline{h}^5$-C_5H_5)CuCO solutions invariably regenerates some ($\underline{h}^5$-C_5H_5)CuCO upon treatment with carbon monoxide. Extraction of this material with pentane (in which it is poorly soluble) under an atmosphere of carbon monoxide, yields a solution whose IR spectrum is characteristic of ($\underline{h}^5$-C_5H_5)CuCO. Extraction with more polar solvents (e.g., toluene or ether) produces orange solutions which are exceedingly

air sensitive and whose infrared spectra exhibit, besides the carbonyl stretch of ($\underline{h}^5$-C_5H_5)CuCO, other bands in the region of 2000 cm^{-1}. Even under an atmosphere of carbon monoxide, this yellow-orange residue is unstable, turning dark brown within several hours.

The preparation of ($\underline{h}^5$-C_5H_5)CuCO can also be achieved in anhydrous ether solution, using the same procedure as described above. The reaction proceeds much more rapidly than in pentane, but it is even more difficult to achieve any separation of solvent and product.

Sulfur Dioxide Experiments.

Anhydrous SO_2 was passed through conc. H_2SO_4 and then "Drierite" dessicant prior to use.[11]

The SO_2 adduct of $C_5H_5CuP(C_4H_9)_3$ was prepared in the following manner. A carefully weighed sample of $C_5H_5CuP(C_4H_9)_3$, 0.2141 g (0.646 mmol), was dissolved in 20 ml of pentane under nitrogen and the resulting solution was cooled in a dry ice-acetone bath to -40°. This caused some of the copper compound to crystallize from solution. Next, SO_2 was slowly distilled into the stirring soltuion. The solution became pale yellow immediately, and after continued SO_2 addition slowly turned orange, and the $C_5H_5CuP(C_4H_9)_3$ which had previously crystallized out, began to dissolve. A few minutes after all the $C_5H_5CuP(C_4H_9)_3$ had dissolved, a yellow solid began to precipitate. After it was certain that a very large excess of SO_2 had been distilled in, the mixture was allowed to stir for 2 hr at -50°. Next, the mixture was cooled to -78°, the colorless supernatant was removed from the yellow solid by syringe, and

the product was washed with three 5 ml portions of pentane, precooled to -78°. The yellow solid was dried under high vacuum for 3 hr at -50° and overnight at -78°.

The product was analyzed by attaching a dropping funnel and condenser to the reaction vessel and decomposing the adduct with "liquid fire".[12,13] The resulting $SO_4^=$ was determined gravimetrically[14] as $BaSO_4$. The result was that the ratio of $SO_4^=$ to copper is ca. 2.26. This result should not be taken as indicative of the exact stoichiometry of the complex since the purity of the adduct was not known and it is possible that both complexed and occluded SO_2 were present.

In attempts to recrystallize the SO_2 adduct of $C_5H_5CuP(C_4H_9)_3$, samples of the yellow solid were dissolved at low temperature in a minimum amount of ether and the resulting dark red-orange solution treated with pentane. Since this failed to precipitate the adduct, an attempt was made to reduce the volume by evaporation under high vacuum at -40°. The solution gradually became colorless and complete removal of the solvent yielded a white solid, identified as $C_5H_5CuP(C_4H_9)_3$ by its melting point and pmr spectrum. It was also noticed that when samples of the yellow solid were dried in vacuo at low temperature, spattered portions of the adduct adhering to the sides of the reaction flask just above the level of the cooling bath, slowly became white, presumably losing SO_2. Spattered portions at the top of the flask where it was nearly room temperature, decomposed to give the characteristic dark red oil.

The SO_2 adduct could be extracted with $C_6H_5CD_3$ at -30° and the pmr spectrum of the resulting solution exhibited a temperature dependence similar to that observed in pure SO_2, except that there appeared to be a symmetric collapse in the olefinic region. The rate of rearrangement appears to be slightly faster than in pure SO_2 but this may be due to differences in chemical shifts; in neither case is the slow exchange limit reached before freezing of the solution.

When pmr sample solutions are allowed to warm to room temperature, they decompose to yield dark red solutions (there is no evidence of metallic copper being formed). The pmr spectrum of the decomposed toluene solution is fairly straightforward with multiplets (besides those of the butyl groups) at τ3.50(2H), τ3.70(2H) and τ7.25(2H). This may be indicative of some sort of sigma-bonded cyclopentadienyl moiety. The pmr spectrum of the decomposed SO_2 solution showed singlets at τ3.4(2H) and τ7.05(1H) and aliphatic multiplets at τ8.4 and τ9.1(11H).

Spectroscopic Measurements

Proton nuclear magnetic resonance spectra were recorded on Varian Associates A-60 or T-60 spectrometers. The A-60, equipped with a V-6040 temperature controller, was employed for low temperature studies. Samples were prepared by either of two methods. In one, freeze-thaw degassed solvent and tetramethylsilane were distilled onto the solid sample and the nmr tube was sealed off under high vacuum. In the other method, the sample was placed in a nitrogen-flushed nmr tube, the tube was capped with a serum stopper and the degassed solvent was injected by

syringe. For thermally unstable compounds, sample solutions were prepared at low temperature and were transferred to cooled, serum-capped sample tubes either by quickly siphoning through stainless steel syringe needle tubing or by means of a syringe, which had been precooled by filling with -78° solvent. Sample solutions prepared by these procedures were stored at -78° until spectra were recorded, at which time the sample tubes were placed in the spectrometer probe, which had already equilibrated at low temperature.

Infrared spectra were obtained with a Perkin-Elmer 337 spectrophotometer and were calibrated with polystyrene film. Routine sample preparation has been described previously.[1] In the case of thermally unstable compounds, solutions were prepared at low temperatures and were kept at -78° until spectra were recorded. At this time, the sample solution was quickly injected into the IR cell by syringe and spectra were recorded immediately. Repeated scans were employed to monitor decomposition. In the case of mull spectra of ($\underline{h}^5$-C_5H_5)$CuCNCH_3$, mulls were prepared and spectra were taken as rapidly as possible. Decomposition was noted by successively recording spectra and observing any changes in various peaks.

RESULTS

All of the compounds except the carbonyl were prepared by a convenient procedure based on the reaction

$$\frac{1}{n}(LCuX)_n + C_5H_5Tl \longrightarrow C_5H_5CuL + TlX$$

where n presumably equals 4 and X is a halogen. The yields are generally quite high (57-98%) and the starting materials are readily available and easy to handle. The workup procedure is simple, generally involving filtration, crystallization and, possibly, sublimation. All five compounds are exceedingly air-sensitive in solution but the colorless solids can be handled in air for short periods of time without noticeable discoloration.

The carbonyl compound had to be prepared by a different procedure since no stable $(CuXCO)_n$ compound is known. The reaction used was

$$CuCl + C_5H_5Tl + CO \xrightarrow[0^{\circ}C]{\text{pentane}} C_5H_5CuCO$$

It appears that this reaction is catalyzed to some extent by added phosphines, which apparently form soluble CuCl species. This substance is highly unstable except under an atmosphere of carbon monoxide,[15] and even then it decomposes within an hour at room temperature. As expected, cyclopentadienylcarbonylcopper(I) is quite volatile and hence could not be completely separated from pentane by repeated trap-to-trap vacuum distillation at low temperatures. Distillations invariably leave an air-sensitive yellow residue remaining behind in the distilling vessel which appears to partially regenerate C_5H_5CuCO upon treatment with carbon monoxide. Treatment of a solution of C_5H_5CuCO at low temperature with tributylphosphine causes immediate displacement of CO and the compound $(\underline{h}^5\text{-}C_5H_5)[(C_4H_9)_3P]Cu$ can be isolated from the reaction.

The pmr spectra of all six compounds dissolved in saturated hydrocarbon solvents exhibit a sharp singlet at about $\tau 4.3$. The spectrum of C_5H_5CuCO was recorded at -20° to retard decomposition. The position of the cyclopentadienyl resonances in these compounds invariably shifts to lower field in toluene-d_8, sometimes by nearly 0.5 ppm. This displacement to lower field is unusual, since in our experience, aromatic solvents usually shift the proton resonance in $\underline{h}^5$-C_5H_5 molecules to higher field, sometimes by as much as 1 ppm. Also, resonance positions as low as $\tau 3.8$ are unusual[16] for $\underline{h}^5$-C_5H_5 complexes of metals with formal oxidation numbers of 0 or +1.

The infrared spectra of these molecules exhibit absorbances characteristic of a pentahaptocyclopentadienyl mode of bonding.[1] Infrared data are summarized in Table VI-1. The infrared spectrum of the carbonyl compound has a sharp band at 2093 cm^{-1}, assigned to CO stretching. This band rapidly decays at room temperature as the compound decomposes.

Within the series of ($\underline{h}^5$-C_5H_5)(L)Cu compounds, thermal stability varied greatly, depending upon L. ($\underline{h}^5$-C_5H_5)[$(C_6H_5)_3P$]Cu appears to be the most stable, decomposition beginning at about 130°. Both ($\underline{h}^5$-C_5H_5)-[$(C_2H_5)_3P$]Cu and ($\underline{h}^5$-C_5H_5)[$(C_4H_9)_3P$]Cu begin to darken in the region of their melting points (124° and 103° respectively). After several days at room temperature ($\underline{h}^5$-C_5H_5)[$(CH_3O)_3P$]Cu samples gave slight deposits of metallic copper. The least stable compounds are ($\underline{h}^5$-C_5H_5)(CH_3NC)Cu which darkens after several minutes at room temperature and

($\underline{h}^5$-C_5H_5)(CO)Cu which decomposes even more rapidly on warming to room temperature. The stabilities of the ($\underline{h}^5$-C_5H_5)(L)Cu compounds thus fall in the order (for L groups):

$$(C_6H_5)_3P \geq (C_2H_5)_3P \approx (C_4H_9)_3P > (CH_3O)_3P \gg CH_3NC > CO$$

The pmr spectra of $C_5H_5CuP(C_4H_9)_3$ and $C_5H_5CuP(C_2H_5)_3$ dissolved in SO_2 showed the same temperature dependence as reported by Whitesides and Fleming,[4] including asymmetric collapse in the olefinic region with the high field portion collapsing more rapidly. At low temperatures, the SO_2 solutions of these compounds are lemon yellow; above ca. 0° decomposition takes place to yield a dark red solution whose pmr spectrum is far more complex than that expected for a rapidly rearranging $\underline{h}^1$-C_5H_5 molecule. By reacting C_5H_5Cu-$P(C_4H_9)_3$ in pentane with SO_2 at low temperatures, a yellow adduct can be isolated which is stable at low temperatures but which decomposes to a dark red oil above about 0°. There appear to be ca. two SO_2 molecules per copper and these can be removed at low temperature to give back $C_5H_5CuP(C_4H_9)_3$. The pmr spectrum of a saturated toluene-d_8 solution of the SO_2 adduct is temperature dependent, but the collapse in the olefinic region is symmetric. The experimental difficulties inherent in a thorough investigation of this system are quite formidable and the most important facts have already emerged-- these copper compounds interact with SO_2 to form some type of adduct, which probably contains an $\underline{h}^1$-C_5H_5 ring.

DISCUSSION

As noted previously,[1] molecules of the type ($\underline{h}^5$-C_5H_5)(L)Cu fit naturally into the existing series of isoelectronic ($\underline{h}^5$-C_5H_5)(L)M molecules and therefore the presence of the pentahaptocyclopentadienyl ring in the copper compounds is not actually surprising, even though it went so long unrecognized. However, the contraction of the $\underline{3d}$ orbitals toward the right of the transition series leads to decreased

interaction between metal and cyclopentadienyl e_1 and e_2 orbitals and this is reflected in the relatively large distance of the metal atom from the center of the C_5H_5 ring, viz., 1.862(3) Å as compared with distances of about 1.75 Å for ($\underline{h}^5$-C_5H_5)Ni groups.[17] Since the $\underline{4s}$ and $\underline{4p}$ orbitals also decrease in energy toward the right of the transition series they presumably play an increasingly effective part in metal-ring bonding, ultimately, in ($\underline{h}^5$-C_5H_5)Tl becoming solely responsible for such bonding.[18]

The $\underline{d}$-orbital contraction must also affect the strength of the metal-L interaction, and it appears that the markedly variable stabilities of the complexes synthesized is a manifestation of a lack of available metal π back-bonding orbitals. This is evident in the case of the highly unstable ($\underline{h}^5$-C_5H_5)(CO)Cu where the CO stretching frequency of 2093 cm^{-1} is exceedingly high for a cyclopentadienyl metal carbonyl complex; the frequency in CO itself is 2143 cm^{-1}. The CO bond stretching force constant is calculated to be 17.7 millidynes/Angstrom. Table VI-2 compares this value to CO stretching force constants for isoelectronic ($\underline{h}^5$-C_5H_5)$M(CO)_n$ compounds. The force constant for ($\underline{h}^5$-C_5H_5)-$V(CO)_4$ is that calculated by Durig, et al. (Table VI-2); the others were calculated from the usual CO-factored secular equations.[19] It is quite apparent that back bonding, i.e., drift of electron density from filled metal 3d orbirals into C≡O π^* orbitals, decreases as ($\underline{h}^5$-C_5H_5)-CuCO is approached, and this is in spite of the fact that in the molecules with more than one CO group, there is greater competition for the

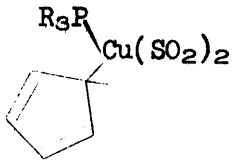
available π electron density on the metal. This correlation may, by extension, also explain why copper-carbonyl species in general are unstable and seldom isolated in the solid state.[20-21]

Infrared data on ($\underline{h}^5$-C_5H_5)$CuCNCH_3$ are informative as to the nature of the copper-isocyanide bond. Generally,[22] coordination to Lewis acids and metals which are poor π-donors (e.g., positively charged species) raises the C≡N stretching frequency above that found for the free isocyanide. On the other hand, coordination to metals which are good π-donors usually lowers the C≡N frequency. In ($\underline{h}^5$-C_5H_5)-$CuCNCH_3$, the ν(C≡N) is at 2190 cm^{-1}, which is distinctly higher than that found[22] for free $CNCH_3$, 2158 cm^{-1}. Thus, the interaction between the Cu 3d orbitals and the isocyanide π^* orbitals is weak, though it should be noted that considerably more stable Ci(1) isocyanide complexes with about the same $\Delta\nu$(C≡N) have been synthesized.[22] Although isocyanides, unlike CO, are capable of serving as good σ donors, often forming stable bonds to metal atoms in positive formal oxidation states, it must be concluded that dative σ bonding with the copper is not particularly strong in this case.

We are left, then, with some uncertainty as to why the ($\underline{h}^5$-C_5H_5)-(PR_3)Cu compounds are much more stable than the carbonyl and isocyanide complexes. It may be that the phosphines allow an optimum combination of σ-donor and π-acceptor functions which cannot be achieved with the other ligands. It is also possible that purely kinetic factors - especially those dependent on the escape of the ligand L because of its

volatility - lead to the greater practical stability of the phosphine complexes without their having any greater thermodynamic stability.

There can be little doubt that the species Whitesides and Fleming[4] observed in SO_2 solutions of $C_5H_5CuP(C_2H_5)_3$ was some sort of adduct. It is now well established that transition metal complexes can form 1:1[23,24] and 1:2[25] complexes with SO_2, in which there is a transition metal-sulfur bond and in which SO_2 complexation is usually reversible. A structure such as (II) explains the pmr spectra and satisfies the noble gas formalism. The SO_2 appears to dissociate readily, and rapidly



(II)

reversible dissociation may be involved in the fluxional behavior.

The decomposition of this complex may be due to a variety of reasons. Sulfur dioxide readily inserts into metal-carbon bonds,[26,27] reacts with phosphines[28] and acts as a dienophile.[29]

TABLE VI-1

Infrared Data for (h^5-C_5H_5)(L)Cu Molecules

L = $(C_2H_5)_3P$	$(C_4H_9)_3P$	$(C_6H_5)_3P$	$(CH_3O)_3P$	$CNCH_3$	CO	Assignments
3085[a] ms	3085[a] ms	g	3095[a] ms	3100[a] ms	h	E_1 C-H stretch
				2190 vs[a]		C≡N stretch
					2093 vs[c]	C≡O stretch
998[d] ms, sharp	997[d] ms, sharp	g	f	1000[d] m, b	h	C-H in-plane bending
752[d] vs, vb	755[d] vs, vb	g	ca. 775[b,e]	762[d] vs, vb	h	C-H out-of plane wagging

(a) toluene-d_8 solution
(b) neat liquid
(c) pentane solution
(d) mull
(e) ν_{P-O} interfers
(f) ν_{C-O} interfers
(g) phenyl group vibrations interfere
(h) not recorded because of instability of compound

m = medium
v = very
s = strong
b = broad

TABLE VI-2

CO Stretching Force Constants (Millidynes/Angstrom)

for $(\underline{h}^5\text{-}C_5H_5)M(CO)_n$ Species*

$(\underline{h}^5\text{-}C_5H_5)M(CO)_n$	k_{CO}	Reference
$(\underline{h}^5\text{-}C_5H_5)V(CO)_4$	15.6	a
$(\underline{h}^5\text{-}C_5H_5)Mn(CO)_3$	15.6	b
$(\underline{h}^5\text{-}C_5H_5)Co(CO)_2$	16.2	c
$(\underline{h}^5\text{-}C_5H_5)Cu(CO)$	17.7	this work
CO	18.6	

* All data are from solution spectra.

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CHAPTER VII

CYCLOPENTADIENYL COMPOUNDS OF GOLD(I)

INTRODUCTION

The phosphinegold(I) moiety is known to form alkyl and aryl compounds which have greater stability than those of phosphinecopper(I).[1] It is now known[2,3] that phosphinecopper(I) cyclopentadienyl molecules possess the pentahaptocyclopentadienyl structure both in solution and in the solid state. Whether or not gold can attain this geometry is not a trivial matter to predict. The fact that the simple two electron sigma bonds are so stable and the fact that the isoelectronic $(C_5H_5)HgX$ compounds are monohapto seems to speak for $C_5H_5AuPR_3$ being monohapto. However, the noble gas formalism, the known structures of the copper cyclopentadienyls, and the apparent pentahapto structure of isoelectronic C_5H_5PtNO[4] are in accord with a pentahapto configuration. Most intriguing is the possibility that the gold compounds might be at a cross-over point between monohapto and pentahapto, perhaps possessing the elusive intermediate polyhapto structure.

Triphenylphosphinecyclopentadienylgold(I) has been proposed[6] to have a monohaptocyclopentadienyl structure on the basis of infrared, UV and nmr measurements. The fact that previous infrared correlations[7] (those upon which Hüttel et al. based their conclusions) were partially incorrect, demanded a reconsideration of the infrared results. It was

also of interest to reexamine the pmr spectrum of $C_5H_5AuP(C_6H_5)_3$. As in the copper cyclopentadienyls,[8] it was felt that the influence of various phosphines on the properties of the molecules might afford some insight into the nature of the bonding.

EXPERIMENTAL

All organometallic compounds were prepared, stored and handled in an atmosphere of prepurified nitrogen. Solvents were carefully dried in the manner appropriate to each and then distilled under nitrogen just prior to use. The tributylphosphinecyclopentadienylgold(I) was stored at -78°.

Triphenylphosphinechlorogold(I) and tributylphosphinechlorogold(I) were prepared by methods in the literature.[10,11] In the case of the tributylphosphine compound, for purification, it was found that chromatography on alumina was superior to distillation.

Lithium cyclopentadienide was prepared by the reaction of commercial butyl lithium in hexane with freshly cracked cyclopentadiene in anhydrous ether. After removal of the solvent by distillation under nitrogen at atmospheric pressure, the pale pink powder was dried under high vacuum and was stored under nitrogen until used, at which time it was transferred by shaking through a glass connecting tube under nitrogen.

Triphenylphosphinecyclopentadienylgold(I). - This compound was prepared by the literature method[6] except that LiC_5H_5 was used instead of NaC_5H_5. The product was recrystallized from THF/acetone plus water

at 0° as described,[6] to yield well-formed crystals, m.p. darkening of the crystals beginning at ca. 100° (lit.[6] 100°d).

The room temperature pmr spectrum in $CDCl_3$ displays a multiplet centered at τ2.60(15H) and a singlet at τ3.75(5H). Dilution of the solution produces broadening of the singlet. It appears that this compound slowly decomposes at room temperature in solution to deposit a gold mirror.

Tributylphosphinecyclopentadienylgold(I). - To 2.00 g (4.6 mmol) of tributylphosphinechlorogold(I) dissolved in 100 ml ether at 0°, was added 1.51 g (5.6 mmol) of thallium cyclopentadienide. The reaction mixture was stirred for 40 hr at 0°, then for 5 hr at room temperature. Next, the ether was evaporated in vacuo, and the residue was extracted with 60 ml of pentane. After treating the extract with decolorizing carbon, it was suction-filtered under nitrogen and the residue was washed with three 10 ml portions of pentane. The filtrate was then cooled to -78° over a period of 2 hr, and was then maintained at -78° overnight. The supernatant was next removed from the crystalline product by syringe and the solid was washed with 20 ml of pentane, precooled to -78°. The recrystallization procedure was repeated and the pure product was dried under high vacuum at -10°, to yield 0.90 g (42%) of pale tan to white crystalline product.

This product begins to darken at room temperature under nitrogen (and in the dark) within an hour and eventually deposits a gold mirror. This compound was analyzed by quickly shaking a sample under nitrogen

into a tared weighing vessel equipped with a ground glass stopper. The weighed sample was dissolved in aqua regia and gold was determined gravimetrically after reduction with hydroquinone.[12]

Anal. Calcd. for $C_{17}H_{32}PAu$: Au, 42.41. Found: Au, 42.3.

The mass spectrum of this compound was recorded by the direct inlet method. It showed fragments corresponding to $C_5H_5AuP(C_4H_9)_3^+$, $AuP(C_4H_9)_3^+$ and $C_5H_5Au^+$. Qualitatively speaking, it appears that the metal $C_5H_5^+$ fragment is much more intense in the mass spectrum of the gold compound than in that of the analogous copper compound.[8]

The pmr spectrum of this compound in $C_6D_5CD_3$ consists of a doublet at τ3.50 (J = 3.2 Hz) (5H) and a complex multiplet at τ8.6-9.2 (27H). In methylcyclohexane solution, the doublet shifts to τ4.00 and appears to broaden somewhat. Decomposition to metallic gold was also noted in the samples.

Spectroscopic Measurements

Proton nuclear magnetic resonance spectra were recorded on Varian Associates A-60, T-60 or HA-100 spectrometers. Sample preparation followed the general procedure given in the experimental section of Chapter VI. The tributylphosphinecyclopentadienylgold(I) was stable enough to be quickly transferred in air to nitrogen-flushed sample tubes.

Infrared spectra were recorded with a Perkin-Elmer 337 spectrophotometer and were calibrated with polystyrene film. The procedure for sample preparation is that given in the experimental section of Chapter VI.

Mass spectra were kindly recorded by Mr. Charles M. Lukehart on a Perkin-Elmer Hitachi RMU6-D mass spectrometer. Samples were placed directly in the ionization chamber, rather than using the high temperature inlet system. This is a common procedure for organometallic samples.

RESULTS

Triphenylphosphinecyclopentadienylgold(I) was synthesized by the literature method,[7] substituting lithium cyclopentadienide for sodium cyclopentadienide. With thallium cyclopentadienide, the reaction was

$$(C_5H_5)_3PAuCl + LiC_5H_5 \xrightarrow{THF} (C_6H_5)_3PAuC_5H_5 + LiCl$$

impracticably slow. Tributylphosphinecyclopentadienylgold(I) was synthesized conveniently by the method employed for the copper compounds.[8]

$$(C_4H_9)_3PAuCl + TlC_5H_5 \xrightarrow[0^o]{Et_2O} (C_4H_9)_3PAuC_5H_5 + TlCl$$

Though the triphenylphosphine compound is perfectly stable at room temperature, the tributylphosphine compound noticeably darkens in the course of an hour and eventually deposits a gold mirror. The room temperature pmr spectrum of $C_5H_5AuP(C_6H_5)_3$ was reported to consist of a single, sharp resonance for the C_5H_5 ring at τ + 3.7 in $CDCl_3$.[6] This line is in reality not particularly sharp and dilution or lowering

of the temperature broadens it further; at low temperatures the C_5H_5 resonance is a doublet ($J \approx 1.9$ Hz).[9] The C_5H_5 resonance of $C_5H_5AuP(C_4H_9)_3$ is a sharp doublet at $\tau = 3.50$ in toluene-d_8 ($\tau = 4.00$ in methylcyclohexane). That the doublet is due to coupling to phosphorus was confirmed by demonstrating that the doublet separation ($J \approx 3.2$ Hz) was the same at 60 and 100 MHz. The room temperature spectrum of the triphenylphosphine compound is thus indicative of an intermolecular exchange process occurring at a rate, $1/\tau \geq J$ which is exchanging phosphines and thus wiping out the spin-spin coupling between the phosphorus and the ring protons. It should be noted that the chemical shift of the C_5H_5 ring protons of $C_5H_5AuP(C_4H_9)_3$ in $C_6D_5CD_3$ solution is even further down field than in ($\underline{h}^5$-C_5H_5)$CuP(C_4H_9)_3$,[8] which has an unusually low C_5H_5 resonance at $\tau = 3.8$.

The infrared spectra of $(C_6H_5)_3PAuCl$, $C_5H_5AuP(C_6H_5)_3$, $(C_4H_9)_3PAuCl$ and $C_5H_5AuP(C_4H_9)_3$ are shown in Fig. VII-1. The C_5H_5 spectrum in the C-H stretching region of $C_5H_5AuP(C_6H_5)_3$ was obscured by phenyl C-H stretches. It is significant in the case of $C_5H_5AuP(C_4H_9)_3$ that the C_5H_5 ring exhibits a single C-H stretch in $C_6D_5CD_3$ at 3080 cm^{-1}. The pattern is quite similar to that of ($\underline{h}^5$-C_5H_5-$Cu(C_4H_9)_3$[8] (3085 cm^{-1}) except that the C_5H_5 C-H stretching singlet of the gold compound is noticeably broader. The similarity between the gold and copper compounds is much less in the 600-1300 cm^{-1} region (see Fig. V-1). It is apparent that the mull spectra of the gold compounds are more complex than those of their copper analogues. The gold

compounds, after subtraction of bands in the corresponding R_3PAuCl molecules, show absorptions given in Table VII-1. It should be noted that, as in the case of the copper compounds, the gold compounds are too reactive toward the usual solvents for infrared spectroscopy (e.g., CS_2, CCl_4) to allow extensive infrared investigations in solution.

DISCUSSION

The principal objective of this study was to elucidate the structure of phosphinecyclopentadienylgold(I) molecules by spectroscopic means. This procedure was successful in the case of the copper analogs,[2,3] in which infrared spectra of model compounds and group theoretical arguments were employed. Table VII-2 summarizes the infrared-active vibrations expected for the ($\underline{h}^5$-C_5H_5)M (C_{5v} symmetry) system and empirical observations which have been made. In the case of the ($\underline{h}^5$-C_5H_5)$CuPR_3$ molecules, only three vibrations were observed for the C_5H_5 system (see Table V-2 and Table VI-1), i.e., the e_1 C-H stretching fundamental (ca. 3085 cm^{-1}, medium, sharp); the a_1 C-H in-plane wagging (ca. 1000 cm^{-1}, medium strong, sharp) and a_1 and e_1 C-H out-of-plane wagging (ca. 760 cm^{-1}, very strong and broad). These results were nicely in accord with an ($\underline{h}^5$-C_5H_5)M structure and bore little resemblence to ($\underline{h}^1$-C_5H_5)M model compounds (Fig. V-2 and Table V-3) which had far more complex spectra, as expected for molecules of lower symmetry.

As can be seen from Fig. VII-1, the infrared spectra of the $(C_5H_5)AuPR_3$ molecules also bear little resemblence to typical spectra of $(\underline{h}^1\text{-}C_5H_5)M$ compounds, e.g., the C-H stretch is a single band rather than a multiplet. Also the region from 600-1300 cm^{-1} is not nearly as complex, in spite of the fact that the gold spectra were taken of mulls, in which solid state effects might cause small splittings of some bands. Thus, it can be concluded with certainty that these compounds do not possess sigma-bonded cyclopentadienyl rings.

The C-H stretching region of $C_5H_5AuP(C_4H_9)_3$, in which the C_5H_5 e_1 mode is somewhat broad, is similar to that of $(\underline{h}^5\text{-}C_5H_5)CuP(C_4H_9)_3$. In both gold molecules, what apparently corresponds to the a_1 and e_1 out-of-plane C-H wagging modes at 790 (or 802) and 725 (or 732) cm^{-1} is accompanied by a ca. 65 cm^{-1} splitting of the bands (the bands cannot be resolved in $(\underline{h}^5\text{-}C_5H_5)Cu(PR_3)$.[2,8] The literature[7] indicates that this large a separation, though unusual, sometimes occurs for $\underline{h}^5\text{-}C_5H_5$ compounds such as those shown in Table VII-3. Since the data given were taken from tables of Ref. 7, rather than from published spectra, the assumption is made that these assignments are correct. One reason these data are given here is that the majority are spectra of polycrystalline samples and thus may better take into account any solid state effects which could perturb the $(C_5H_5)AuPR_3$ spectra. There seems to be no clear-cut pattern to the separation of the a_1 and e_1 modes; for example, within an isostructural series, there is no dependence on the mass of the metal. Other features of the $C_5H_5AuPR_3$ infrared spectra are two weak bands at

845 (or 845) and 825 (or 828) cm^{-1}. These are definitely not spurious, but cannot be easily accounted for within the simple C_{5v} $\underline{h}^5$-C_5H_5 model. What is presumably the a_1 C-H in-plane wagging mode occurs at 978 (or 970) cm^{-1} and is qualitatively weaker than in the copper compounds where it occurs at approximately 1000 cm^{-1}.

Thus, though the results are not entirely clear-cut, the infrared spectra of the $C_5H_5AuPR_3$ compounds are most in accord with a pentahapto-cyclopentadienyl configuration. While it is certain that the molecules are not monohapto, the possibility of a distortion from perfect C_{5v} symmetry cannot be excluded. The pmr spectra, especially the remarkable downfield shift in the C_5H_5 resonance on going to toluene solutions, are reminiscent of the ($\underline{h}^5$-C_5H_5)$CuPR_3$ compounds.[8] More exact structural details await an X-ray diffraction study.

The apparent thermal stabilities of $C_5H_5AuP(C_6H_5)_3$ and $C_5H_5AuP(C_4H_9)_3$ follow the same trend as in the copper series,[8] but the differences in stability are much greater in the gold series.

TABLE VII-1

Infrared Bands Assignable to C_5H_5 Groups

in the $C_5H_5AuPR_3$ Compounds[a]

$C_5H_5AuP(C_4H_9)_3$	$C_5H_5AuP(C_6H_5)_3$	Remarks
3085 m, fairly sharp	not observed	Spectrum measured in toluene-d_8
978 w	970 w	Mull spectrum
845 vw	845 w	Mull spectrum
825 vw	828 w	Mull spectrum
790 m	802 m	Mull spectrum
725 m	732 m	Mull spectrum

(a) m = medium; v = very; w = weak

TABLE VII-2

Infrared-Active Fundamental Vibrational Transitions

for the C_5H_5 Ring in an ($\underline{h}^5$-C_5H_5)M System

Type of internal coordinate change[a]	Symmetry type	Approx frequency, cm^{-1}	Comments
C-H stretching	a_1	3050-3100	a_1 mode usually vs; only e_1 mode consistently seen
	e_1		
C-C stretching	a_1	~ 1100	Sym ring breathing; intensity highly variable; often vw usually m to w
		~ 1400	
	e_1		
C-H out-of-plane wagging	a_1	~ 800	Usually broad absorption; combined intensity very high; position varies greatly
	e_1		
C-H in plane wagging	a_1	~ 1000	Generally strong and close to 1000 cm^{-1}

(a) We follow here the original assignments of Lippincott and Nelson; Spectrochim. Acta, 10, 307 (1958).

TABLE VII-3

Examples of ($\underline{h}^5$-C_5H_5)M Compounds

Showing Large Frequency Differences in C-H

Out-Of-Plane Wagging Modes[a]

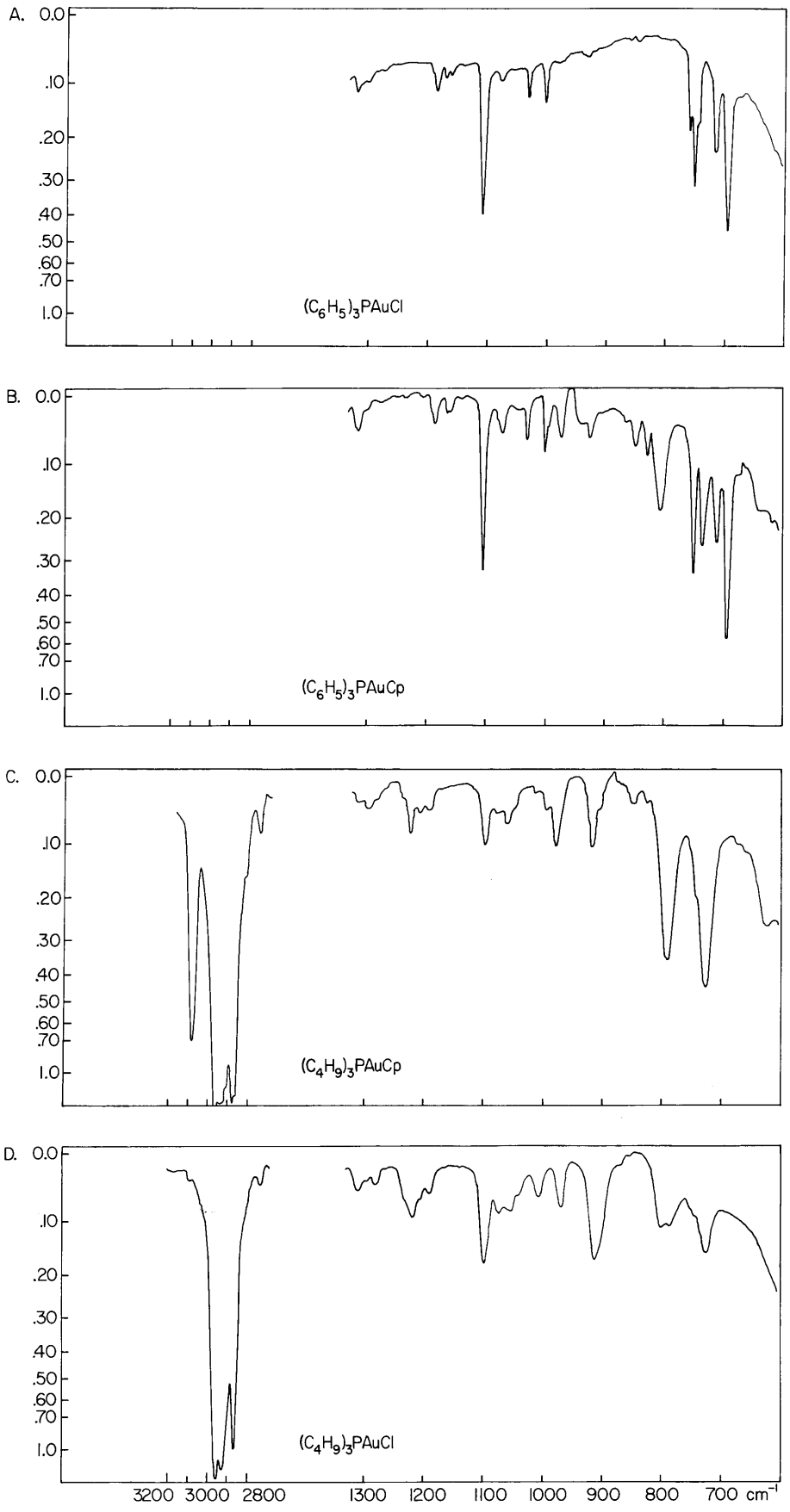
Compound	ν_8	ν_7	$\Delta\nu$
($\underline{h}^5$-C_5H_5)$Co(CO)_2$[b]	812	756	56
($\underline{h}^5$-C_5H_5)$_2$Ni	839	772	67
($\underline{h}^5$-C_5H_5)$_2$Fe	854	814	40
($\underline{h}^5$-C_5H_5)$_2$Cr	829	766	63

(a) Data in cm^{-1} from tables in Ref. 7. Spectra were of "polycrystalline samples". Vibration labels are also from Ref. 7.

(b) This is a liquid at room temperature.

FIGURE VII-1

A. The infrared spectrum of $(C_6H_5)_3PAuCl$ recorded as a Nujol mull. B. The infrared spectrum of $C_5H_5AuP(C_6H_5)_3$ studied in a Nujol mull. C. The infrared spectrum of $C_5H_5AuP(C_4H_9)_3$. The high-frequency region was recorded in toluene-d_8 solution and the low-frequency region as a Nujol mull. D. The infrared spectrum of $(C_4H_9)_3PAuCl$ recorded as a neat liquid.


A.
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
$(C_6H_5)_3PAuCl$
B.
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
$(C_6H_5)_3PAuCp$
C.
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
$(C_4H_9)_3PAuCp$
D.
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
$(C_4H_9)_3PAuCl$
3200 3000 2800
1300 1200 1100 1000 900 800 700 cm^{-1}

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BIOGRAPHICAL NOTE

The author was born on November 25, 1944, in Washington, D.C. After attending public schools in Arlington, Virginia, and Bethesda, Maryland, he graduated from Walter Johnson High School in June, 1962.

In September, 1962, the author entered the University of Maryland. There he was an N.S.F. Undergraduate Research Participant for three years, a Leidy Chemical Scholar, a junior year member of Phi Beta Kappa, a member of Phi Kappa Phi and a College of Arts and Sciences honors award winner. In June, 1966, the author received a B.S. degree from the University of Maryland with high honors and high honors in chemistry. During the summer of 1966, the author was employed as a chemist at the Harry Diamond Laboratories, where he received the Department of the Army Certificate of Achievement.

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The author is a member of the American Chemical Society, the Society of Sigma Xi and Phi Beta Kappa.