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# Phosphorus-31-Phosphorus-31 spin-spin coupling in metal complexes of phosphorus ligands

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 $^{31}\text{P}$ - $^{31}\text{P}$  SPIN-SPIN COUPLING IN METAL  
COMPLEXES OF PHOSPHORUS LIGANDS.**

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$^{31}\text{P}$ - $^{31}\text{P}$  SPIN-SPIN COUPLING IN METAL  
COMPLEXES OF PHOSPHORUS LIGANDS

by

Fredrick Bruce Ogilvie

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
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## INTRODUCTION

## Nature of the Metal-Phosphorus Link

In 1950 Chatt (1) proposed that co-ordination in transition metal complexes with phosphorus ligands occurs by two types of bonds: (a) a  $\sigma$ -bond formed by the overlap of a filled  $sp^3$  orbital of phosphorus with a vacant orbital of the metal, and (b) a  $\pi$ -bond formed by the overlap of a filled d orbital on the metal with vacant d orbitals on the phosphorus atom. He introduced this dative  $\pi$ -bonding concept to account for the fact that amines formed stable compounds with both  $BF_3$  and  $PtCl_2$  whereas  $PF_3$  formed a very stable complex with  $PtCl_2$  but no adduct with  $BF_3$ . Since that time considerable work and controversy has centered around the nature of the metal-phosphorus bond.

Chatt extended his interest in this problem and has done a broad study of the nature of the co-ordinate link between platinum and phosphorus (2-6). On the basis of the stability of binuclear complexes, trans- $[(R_3M)ClPtCl_2PtCl(MR_3)]$  ( $R = C_3H_7$ ;  $M = N, P, As, Sb, Bi$ ), Chatt concluded that the co-ordinating affinity of the ligands towards  $PtCl_2$  was  $PR_3 > AsR_3 > NR_3 > BiR_3$  (2). This is in contrast to the work by Coates (7) in which it was found that the co-ordinating affinity of  $MR_3$  ( $R = CH_3$ ;  $M = N, P, As, Sb, Bi$ ) towards  $Ga(CH_3)_3$  was  $NR_3 > PR_3 > AsR_3 > SbR_3 > BiR_3$ . It would thus appear that the effect of  $d\pi-d\pi$  bonding as far as gallium is concerned is subordinated

to the decrease of true donor tendency with increasing atomic weight whereas the relative importance of  $\pi$ -bonding is much greater in platinum complexes.

Further support for the importance of  $\pi$ -bonding in platinum complexes stemmed from the equilibrium studies between cis- and trans- $\text{PtCl}_2(\text{MEt}_3)_2$  ( $M = \text{P, As, Sb}$ ) (4, 5). After allowance was made for the possibly greater association of the solvent benzene with the cis-isomers and a large liberation of energy owing to favorable spatial redistribution of electric charge when the highly polar cis-isomers were converted to the non-polar trans-isomers, the cis-isomers were found to be more stable by approximately 10 kcal./mole. With  $\text{PtCl}_2(\text{PEt}_3)_2$  this was believed to represent the increase in bond energy when the phosphorus atoms are in a cis as compared with a trans configuration. If d orbitals in the phosphorus and platinum atoms play a part in the binding then in the cis-isomer each phosphorus atom can be bound by a different d orbital in the platinum atom whereas in the trans-isomer each phosphorus atom is competing for the same d orbitals leading to weaker binding. However since the total bond strengths of the cis-isomers of  $\text{PtCl}_2(\text{MEt}_3)_2$  ( $M = \text{P, As, Sb}$ ) are all approximately 10 kcal./mole higher than those in the trans-isomers, then the strength of the  $\pi$  component of the M-Pt bond must stay constant throughout the series if the difference is due to  $\pi$ -bonding. If this is so then the strength of the  $\sigma$  component must fall from P to Sb to account for the qualitatively observed weakening of the

M-Pt bond.

Redox potentials also indicate some degree of  $\pi$ -bonding (6). Upon varying the ligand in the couple  $L_2PtCl_4 - L_2PtCl_2$ , the only important factor would be the electron affinity of the metal as it is adjusted by the electron affinities of the ligands. If ligands withdraw electrons from the metal it should be more easily reduced. Electron withholding in the  $\sigma$  donating bond would be inductive while electron withdrawal through dative  $\pi$ -bonds would be mesomeric in character. Electron withholding will be similar in cis and trans compounds whereas mesomeric withdrawal will be less in cis compounds where the ligands can withdraw electrons from different d orbitals. Thus cis compounds should have a greater resistance to oxidation (redox potential higher) and this is found to be the case.

Craig et al. (8) have given a critical discussion of  $\pi$ -bonding in metal complexes. Overlap integrals were used as a criterion of bond strength in studying chemical bonds which may require the use of d orbitals. Overlap integrals were often found to be large enough to give quite strong  $\pi$ -bonds and were rather insensitive to differences in size of the bonded orbitals.

The dative  $\pi$ -bonding concept was used quite successfully in accounting for the trans-effect (3, 9, 10). At that time all the ligands of high trans-effect could form  $\pi$ -bonds by utilizing the d orbitals of the metal. Thus it was proposed

that the forces responsible for directing effects originate mainly in electron withdrawal occasioned by dative  $\pi$ -bond formation from a d orbital of the metal towards a ligand A of high trans effect. This electron withdrawal would increase the electron affinity of the metal atom and perhaps the strength of  $\sigma$  bonding to all other ligands B. However the electron withdrawal would decrease any tendency of the ligand B in the trans position to A to form a dative  $\pi$ -bond. The M-B bond would thus be weakened if the dative  $\pi$ -bond is an essential component. On the other hand if B, trans to A, has little tendency to form dative bonds, its attachment to the metal could be strengthened by the presence of A. However the discovery that the hydride ion (which cannot possibly form dative  $\pi$ -bonds) has a trans-effect comparable to the cyanide ion (11) casts some doubt on the importance of  $\pi$ -bonding in the trans-effect.

In conjunction with his other studies Chatt has determined the dipole moments of the cis platinum complexes (3, 5, 6). In most cases the high dipole moments indicate that the platinum-phosphorus link is mainly a single co-ordinate bond (5, 6). An exception to this is cis-PtCl<sub>2</sub>(PF<sub>3</sub>)<sub>2</sub> which has a low dipole moment and therefore the Pt-P bond may have some double bond character (3).

A great deal about the nature of metal-phosphorus bonding has been inferred from carbonyl stretching frequencies in substituted metal carbonyls although the conclusions reached by

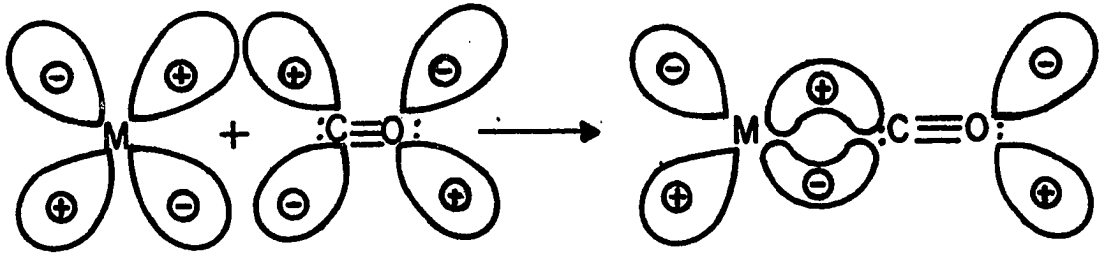
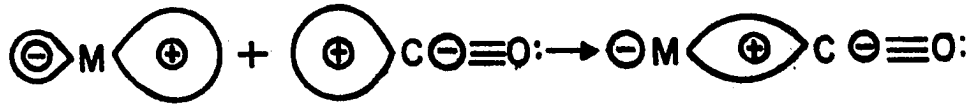


various authors on the interpretation of the results have not been consistent. Since there are several reviews dealing with metal carbonyl derivatives, (12-15) only the several explanations arising from the infrared studies will be discussed here. The basis for the various conclusions on metal-phosphorus bonding in carbonyl complexes is the generally accepted bonding model illustrated in Figures 1 and 2. Bonding involves both co-ordinate  $\sigma$ -bond formation in which the lone-pair electrons on the carbon atom interact with a vacant metallic orbital (Figure 1) and metal-ligand  $\pi$ -bonding in which filled metallic d orbitals interact with low-lying vacant antibonding  $\pi$  orbitals of the CO group (Figure 2). Trivalent phosphorus ligands which can participate in both  $\sigma$  and  $\pi$  bonding with vacant metal orbitals and filled metallic d orbitals respectively, would compete with the carbonyl ligands and would thus affect the carbonyl stretching frequencies.

Cotton and Kraihanzel have derived nonrigorous secular equations based on a simple force field model through which sets of force constants for the series of metal carbonyl derivatives may be obtained (16, 17). Although the absolute values for these force constants have no significance they are useful in assigning stretching frequencies and they are claimed to give internally consistent results for the series of derivatives  $M(\text{CO})_{6-n}L_n$ . Differences in force constants should therefore bear a direct relation to the actual numbers of  $\pi$  electrons involved in the M-C and C-O bonds and to the bond

Figure 1. CO→M  $\sigma$ -bond formation

Figure 2. M→CO  $d\pi$ - $p\pi^*$  "back-bonding"



orders. Cotton (17) has proposed that changes in C-O force constants (and stretching frequencies) with different donor groups are a function only of the  $\pi$ -accepting ability of the ligand in question and that all  $M(\text{CO})_5\text{L}$  complexes in which there is no M-L  $\pi$ -bonding should have roughly similar C-O force constants. Thus in a series of the type  $M(\text{CO})_5\text{PY}_3$ , a rise in the electronegativity of Y is accompanied by an increase in the metal phosphorus  $\pi$ -bonding. This in turn causes a depopulation of the CO antibonding orbitals and an increase in the CO force constants. From such studies of  $\nu(\text{CO})$ , a spectrochemical series of the  $\pi$ -bonding ability of a series of ligands has been proposed (18).

Bigorgne and co-workers have done an extensive study of carbonyl stretching frequencies in metal carbonyl derivatives (19-25). They have observed that the phenomenon of the lowering of the C-O frequencies is closely related to that of the raising of the M-C frequencies. In addition the curve of C-O force constants is linear with the degree of substitution for a given ligand  $\text{PY}_3$ . For all the ligands the slopes of these straight lines are a function of the effective electronegativity of Y and they vary linearly with Taft's polar substituent constant  $\sigma^*$ . Since their plot of  $\nu(\text{CO})$  versus  $\sigma^*$  was linear, they concluded that the lowering of the C-O stretching frequencies when the ligand varies from  $\text{PF}_3$  to  $\text{PR}_3$  is fundamentally an inductive phenomenon (24). Because  $\text{PR}_3$  has a donor capacity which is much larger than that of  $\text{PF}_3$  the

negative charge on the metal is distributed to the CO through the M-C-O  $\pi$  orbitals. From the observation that the plot of C-O force constants versus degree of substitution was a straight line they concluded that ligands in complexes cannot be characterized by definite donor-acceptor capacities but that this property varies in proportion to the degree of substitution (25).

Recently Darensbourg and Brown have concluded from infrared intensity studies of substituted metal carbonyls that there is appreciable  $\pi$ -bonding between metals and phosphorus or arsenic ligands (26). However they also conclude that there is no increase in  $\pi$ -bonding from the metal to the remaining CO groups when  $M(CO)_5L$  is formed from the parent carbonyl. The addition of negative charge on the metal from ligand L should weaken the metal-carbon  $\sigma$ -bond and thus lower the C-O force constant and stretching frequency by reducing the polarity of the C-O bond. This concept, however, seems to be at variance with the observations of Bigorgne (25) that M-C force constants increase while C-O force constants decrease.

If significant metal-phosphorus  $d\pi-d\pi$  bonding were occurring, such multiple bonding should manifest itself in the shortening of metal phosphorus bond length. Many metal phosphorus bond lengths are known (27-30) and indeed the bond lengths are shorter than the sum of the covalent radii. However difficulties are frequently encountered in choosing appropriate single-bond covalent radii. Most structures that

have been determined involve aryl or alkyl phosphines and there have been few extensions to analogous complexes containing more electronegative substituents on phosphorus wherein M-P  $\pi$ -bonding may be more important. It is highly probable that the metal phosphorus bond length is sensitive not only to substituents on phosphorus, but other ligands on the metal, geometrical structure, and structural distortions due to crystal packing. Thus, inferences about the metal-phosphorus bond from M-P bond lengths would necessitate the accurate determination of a very large number of structures.

It is noteworthy that most of the information about metal-phosphorus bonding has been gained from indirect evidence. Spectroscopic parameters which are directly associated with the metal-phosphorus link should yield more evidence that is less ambiguous. Thus studies have been carried out to determine ligand field splitting parameters ( $Dq$ ); metal-phosphorus stretching frequencies ( $\nu(MP)$ ); metal-phosphorus coupling constants ( $^1J_{MP}$ ); and phosphorus-phosphorus coupling constants through a metal ( $^2J_{PP}$ ). This dissertation is concerned with the determination and interpretation of  $^{31}P$ - $^{31}P$  coupling constants through metal atoms. Information about M-P bonds by other direct methods in conjunction with  $^{31}P$ - $^{31}P$  coupling constants will be discussed in the Results and Discussion. Studies of phosphorus-phosphorus coupling constants have an advantage over metal-phosphorus coupling

constants in that a wider variety of complexes can be studied since few metals have nuclear spins of  $1/2$  suitable for nuclear magnetic resonance studies. A brief background of n.m.r. spectroscopy and the basis for this study is given in the following subsection.

### Nuclear Magnetic Resonance Spectroscopy

The first n.m.r. signals were independently observed in 1945 by Bloch (31) and Purcell (32). Since that time nuclear magnetic resonance spectroscopy has grown until today about two thousand papers a year are published on the subject. Nuclear magnetic resonance studies can be divided into three parts: obtaining the spectra and analyzing them for chemical shifts and coupling constants; interpreting the spectra for the purpose of determining structural features of compounds; and the extension of the theory of nuclear magnetic resonance. There are numerous books that deal with obtaining and analyzing spectra (33-36). Therefore, except for the analysis of the  $X_n A A' X_n'$  system, this aspect will not be discussed here. Since the geometries of the systems studied in this work were determined independently, the use of n.m.r. techniques in elucidation of structures will not be treated. It might be mentioned that several excellent books have been published on the subject (33, 34, 37). Only one recent book (38) deals specifically with the theory of magnetic resonance and unfortunately it is already somewhat outdated. Since the theory

forms the basis of the interpretation of our results, certain key considerations will now be briefly developed.

There are four possible mechanisms by which two nuclei with spin can interact. In addition to direct dipolar interaction, nuclear spins in a molecule are coupled indirectly by a polarization of the electronic environment which is comprised of three contributions. In fluids the direct dipolar effect averages to zero and the residual interaction energy between nuclei A and B takes the form

$$E_{AB} = h J_{AB} I_A \cdot I_B \quad 1$$

in which  $I_A$  and  $I_B$  are the nuclear spin angular momenta (in units of  $h/2\pi$ ) and  $J_{AB}$  is the coupling constant in Hz. The theory for the three mechanisms contributing to  $J_{AB}$  was originally formulated by Ramsey (39) who also showed that there are no cross terms between these effects in  $E_{AB}$  so that the coupling constant may be written in terms of the three separate contributions

$$J_{AB} = J_{AB}^{(1)} + J_{AB}^{(2)} + J_{AB}^{(3)} \quad 2$$

$J_{AB}^{(1)}$  arises from the fact that a nuclear magnetic moment will affect the orbital motion of neighboring electrons. The induced electronic currents in turn produce magnetic fields which interact with other nuclear magnetic moments.



Nuclear magnetic moments will also interact by a dipole-dipole mechanism with spin magnetic moments of neighboring electrons giving rise to  $J_{AB}^{(2)}$ . This interaction produces spin polarization which leads to non-vanishing magnetic fields acting at other nuclei in the molecule.

A further term must be introduced to allow for the possibility that the electron may be in the same region of space as the nucleus. This term,  $J_{AB}^{(3)}$ , is known as the Fermi contact term and is non-zero only for s electrons. The Fermi contact term is the only one of importance in coupling with protons (40). Furthermore, there is considerable evidence that the contact term is dominant for coupling between all atoms (41-44).

Most theoretical studies are based on second-order perturbation theory. Early calculations involving both valence bond (45) and molecular orbital theory (46) used an average excitation energy approximation in which there was a degree of arbitrariness in the choice of an appropriate energy value. Using this approximation in molecular orbital theory necessarily leads to only positive coupling constants whereas many negative coupling constants are known experimentally. Pople and Santry (40) developed a molecular orbital theory which avoided the average excitation energy approximation and did predict both positive and negative signs. In their theory the Fermi contact term may be written in the form:

$$J_{AB}^{(3)} = - \frac{16}{9} \beta^2 \gamma_A \gamma_B h (s_A | \delta(r_A) | s_A) (s_B | \delta(r_B) | s_B) \Pi_{s_A s_B} \quad 3$$

where  $\beta$  is the Bohr magneton,  $\gamma_A$  and  $\gamma_B$  are the magnetogyric ratios for nuclei A and B respectively,  $h$  is Planck's constant,  $(s|\delta|s)$  are the values of the valence  $s$  atomic orbitals  $s_A$  and  $s_B$  at their respective nuclei and  $\Pi_{s_A s_B}$  is the mutual polarizability (47). Now  $\Pi_{s_A s_B}$  is given by

$$\Pi_{s_A s_B} = 4 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (\epsilon_i - \epsilon_j)^{-1} C_{is_A} C_{is_B} C_{js_A} C_{js_B} \quad 4$$

where  $(\epsilon_i - \epsilon_j)$  is the energy difference between occupied and unoccupied states, and  $C_{is_A} C_{is_B} C_{js_A} C_{js_B}$  is the product of the coefficients of the  $s$  atomic orbitals of the coupling sites in the molecular orbitals  $\psi_i$  (occupied) and  $\psi_j$  (unoccupied).

Problems arise with this treatment due to the sensitivity to cancellation of large terms of opposite sign. Recently Pople et al. (48) derived a self-consistent finite perturbation method using spin density matrices which quantitatively gives more accurate results than Equation 3. However for the qualitative treatment given here, Equation 3 is more appropriate.

Most of the compounds in this dissertation may be classified as  $X_n A A' X'_n$  spin systems. The analysis of this system has been worked out by Harris (49-52) and by Mowthorpe and Chapman (53). Although in theory it is possible to obtain the desired coupling constants from the A part of the n.m.r. spectrum, (53) in practice it is considerably more difficult than obtaining them from the X part and often it is impossible.

Unless  $J_{AX}$  is large or  $n$  is 1 or 2 there will be many overlapping lines in the A part of the spectrum. The splittings necessary to calculate the coupling constants are rarely observed because of these overlapping lines. In the following discussion only resonances of X nuclei are considered and it is assumed that all nuclei (X and A) have spin 1/2.

All transitions occur in pairs symmetrically disposed about  $\nu_X$  (the chemical shift) and so  $\nu_X$  may be deleted from all expressions. Furthermore it is convenient to describe two constants L and N:

$$L = |J_{AX} - J_{AX'}| \quad 5$$

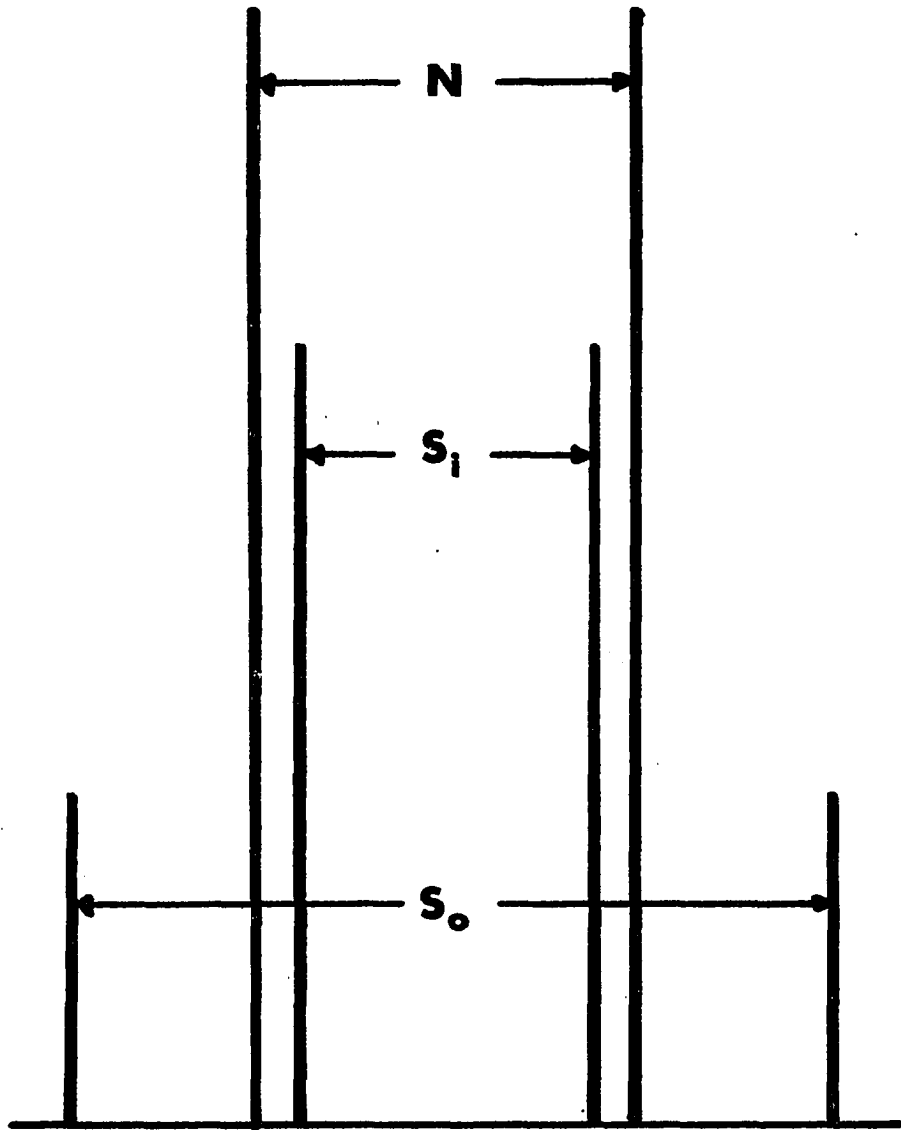
$$N = |J_{AX} + J_{AX'}| \quad 6$$

If we first assume that  $J_{XX'}$  is zero then  $J_{AA'}$ , L and N are the only parameters needed to describe the transition energies. In all spectra of this spin system there will be an intense doublet of separation N comprising half the total intensity. There will be  $2n$  pairs of other lines in each spectrum. A bar diagram of the typical spectrum when  $n = 1$  is given in Figure 3. The separation of the outer lines in the general  $X_n A A' X'_n$  system is given by

$$S_0(\chi) = [\chi^2 L^2 + J_{AA'}^2]^{1/2} + [(\chi - 1)^2 L^2 + J_{AA'}^2]^{1/2} \quad 7$$

where  $\chi$  is an integer between 1 and  $n$  inclusive. The separation

Figure 3. Bar diagram of the X part of an XAA'X' system in which  $N = 8$ ,  $L = 10$ , and  $J_{AA'} = 5$  Hz



of the inner lines is given by:

$$S_i(\chi) = [\chi^2 L^2 + J_{AA'}^2]^{1/2} - [(\chi - 1)^2 L^2 + J_{AA'}^2]^{1/2} \quad 8$$

The relative intensities of each inner and outer line are given by:

$$Z_i(\chi) = (1 + g)/2n \sum_{r=\chi}^n \frac{(r)n! \quad n!}{(n-r)!r!(n-r+\chi)!(r-\chi)!} \quad 9$$

$$Z_o(\chi) = (1 - g)/2n \sum_{r=\chi}^n \frac{(r)n! \quad n!}{(n-r)!r!(n-r+\chi)!(r-\chi)!} \quad 10$$

where  $g$  is a perturbation factor which arises due to mixing of the  $\alpha\beta$  and  $\beta\alpha$   $AA'$  spin states and is given by:

$$g = \frac{[\chi(\chi - 1)L^2 + J_{AA'}^2]}{([\chi^2 L^2 + J_{AA'}^2][(\chi - 1)^2 L^2 + J_{AA'}^2]^{1/2}} \quad 11$$

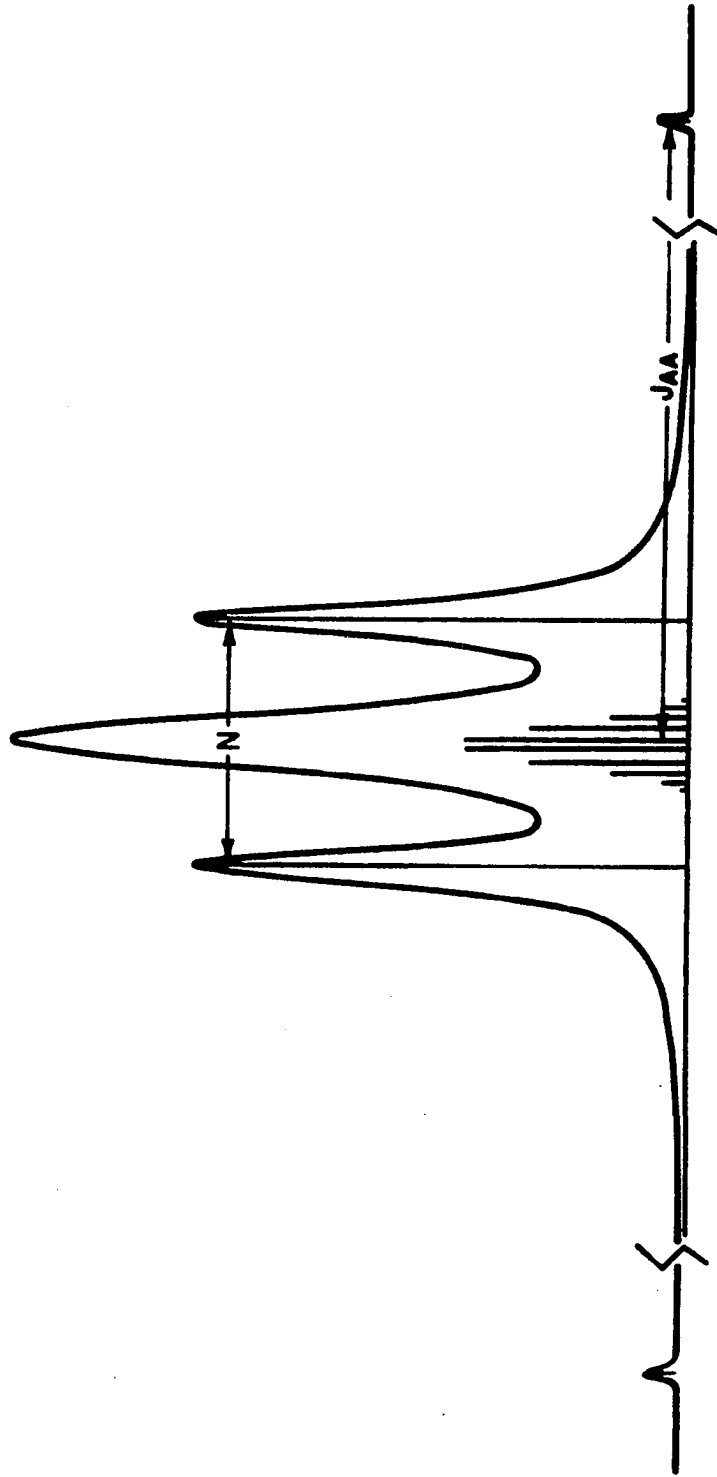
On this scale each line of the doublet of separation  $N$  will have intensity  $2^{2(n-1)}$ . If there is long range  $XX'$  coupling each line other than the intense doublet of separation  $N$  will be split into a 1:3:3:1 quartet with a separation equal to  $J_{XX'}$ .

Using Equations 9 and 10 it can be shown that the next most intense lines to the doublet of separation  $N$  are those when  $\chi = 1$  and that those lines when  $\chi > 1$  are much less intense and often not observed. Thus if the inner and outer lines due to  $\chi = 1$  are observed  $J_{AX}$ ,  $J_{AX'}$ , and  $J_{AA'}$  can be

calculated using Equations 5-8. However if  $J_{AA'}$  is large relative to  $L$ , the separation of the outer lines becomes greater and their relative intensity becomes much less while the separation of the inner lines becomes less and their relative intensity becomes greater. The outer lines become unobservable and the inner lines overlap giving rise to an apparent triplet as shown in Figure 4. If this occurs, the coupling constants can be obtained in three ways: (a) using high radio frequency power to saturate the inner lines which enhances the intensity of the outer lines and often makes them observable (b) using a computer program to simulate the observed band shape (see Appendix) and (c) using  $^{13}\text{C}$  sidebands in conjunction with double resonance techniques. Double resonance techniques furthermore often yield the signs of the coupling constants (52, 54). Of the three methods, observation of the outer lines gives the most accurate value of  $J_{AA'}$ . If  $J_{AA'}$  is greater than 100 Hz the intensities of the  $\chi = 1$  outer lines will be less than 1/1000 of the intensity of each line of the doublet of separation  $N$ . In these cases it is impossible to observe the outer lines with the present instrumentation at Iowa State University. The use of double resonance techniques in obtaining values of  $J_{AA'}$  is fully discussed elsewhere (54). The easiest method of obtaining values of  $J_{AA'}$ , which was used extensively in this work, is by computer simulation. A critique of this method is given in the Results and Discussion section.

Figure 4. Apparent triplet for the X part of an  $X_6AA'X_6'$  system arising from overlapping of the inner lines when  $J_{AA'} \gg L$ . The intensity of the  $\chi = 1$  outer lines has been exaggerated





### Purpose of Research

Because of the large confusion concerning the nature of the metal phosphorus link, it was believed that determination of  $^{31}\text{P} - ^{31}\text{P}$  coupling constants through metals would be useful in gaining further knowledge about metal-phosphorus bonding. This belief is based on the fact that coupling constants are dependent upon the electronic environment between the coupling sites. In complexes, this environment will be dependent upon: (a) the nature of the metal atom, (b) the stereochemistry of the complex, (c) the substituents on the phosphorus atoms, and (d) the other ligands in the complex. The results will be discussed using concepts derived from both valence bond and molecular orbital theories. The phosphorus ligands used in this work and by other authors are tabulated in Table 1.

Table 1. Phosphorus ligands used in complexes for which  $^{31}\text{P}$ - $^{31}\text{P}$  coupling constants have been determined.

(I) $\text{P}(\text{CH}_3)_3$	(XVI) $\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)$
(II) $\text{P}(\text{CH}_2\text{O})_3\text{CCH}_3$	(XVII) $\text{P}(\text{n-C}_4\text{H}_9)_2(\text{C}_6\text{H}_5)$
(III) $\text{P}(\text{CH}_2\text{Cl})_3$	(XVIII) $\text{PH}(\text{C}_6\text{H}_5)_2$
(IV) $\text{P}(\text{SCH}_3)_3$	(XIX) $\text{P}(\text{C}_6\text{H}_5)_3$
(VA) $\text{P}(\text{SCH}_2)_3\text{CCH}_3$	(XX) $\text{P}(\text{OC}_2\text{H}_5)_3$
(VB) $\text{P}(\text{SCH}_2)_3\text{CC}_5\text{H}_{11}$	(XXI) $\text{P}(\text{OC}_6\text{H}_5)_3$
(VI) $\text{P}[\text{N}(\text{CH}_3)_2]_3$	(XXII) $\text{P}(\text{CH}_2\text{Cl})\text{F}_2$
(VII) $\text{P}[\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5)]_3$	(XXIII) $\text{P}(\text{CCl}_3)\text{F}_2$
(VIII) $\text{P}(\text{OCH}_3)_3$	(XXIV) $\text{P}(\text{C}_6\text{H}_5)\text{F}_2$
(IXA) $\text{P}(\text{OCH}_2)_3\text{CCH}_3$	(XXV) $\text{P}[\text{N}(\text{CH}_3)_2]\text{F}_2$
(IXB) $\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$	(XXVI) $\text{P}[\text{N}(\text{C}_2\text{H}_5)_2]\text{F}_2$
(IXC) $\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7$	(XXVII) $\text{P}(\text{NC}_5\text{H}_{10})\text{F}_2$
(IXD) $\text{P}(\text{OCH}_2)_3\text{CC}_5\text{H}_{11}$	(XXVIII) $\text{P}(\text{OC}_6\text{H}_5)\text{F}_2$
(X) $\text{PF}_3$	(XXIX) $\text{P}(\text{O}_2\text{C}_6\text{H}_4)\text{F}$
(XI) $\text{PH}_3$	(XXX) $\text{C}_2\text{H}_5\text{N}(\text{PF}_2)_2$
(XII) $\text{P}(\text{C}_2\text{H}_5)_3$	(XXXI) $\text{P}(\text{CF}_3)_3$
(XIII) $\text{P}(\text{n-C}_3\text{H}_7)_3$	(XXXII) $\text{P}(\text{C}_6\text{H}_5)_2(\text{CF}_3)$
(XIV) $\text{P}(\text{n-C}_4\text{H}_9)_3$	(XXXIII) $\text{P}(\text{CF}_3)\text{F}_2$
(XV) $\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)$	

## EXPERIMENTAL

## Instrumentation

Infrared spectra were obtained on Perkin-Elmer Models 21 and 237B and Beckman Models 8 and 12 spectrometers. Proton n.m.r. spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as an internal standard or on a modified Varian HR-60 spectrometer using benzene as a locking signal. The  $^{31}\text{P}$  n.m.r. spectra were obtained on the Varian HR-60 spectrometer using 85% aqueous phosphoric acid as an external standard. Mass spectra were obtained on an Atlas CH-4 single focusing spectrometer at an energy of 70 ev.

## Analyses of Compounds

Micro-analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

## Analyses of N.M.R. Spectra

In cases where the outer peaks were unobservable, the spectra were analyzed either by double resonance techniques (54) or by using the computer program given in the Appendix which is written in Fortran IV for an I.B.M. 360/65 computer.

## Materials

Iron pentacarbonyl was purchased from Strem Chemicals Inc., chromium, molybdenum, and tungsten hexacarbonyls were purchased from Pressure Chemical Co.; and manganese decacarbonyl, palladium dichloride and potassium tetrachloroplatinate were

purchased from Alfa Inorganics Inc. Trimethyl phosphite (VIII) and hexamethylphosphorous triamide (VI) were purchased from Eastman Kodak Co.

#### Preparations of Intermediates

The preparations of the ligands (II) (55), (III) (56), (IV) (57), (V) (58), (IX) (59) have been reported previously as have the preparations of (I) and of AgI(I) (60). The preparations of chromium(nonbornadiene)tetracarbonyl (61), molybdenum-(nonbornadiene)tetracarbonyl (61), dichlorobis(benzonitrile)-palladium (62), and the manganese pentacarbonyl halides (63) have also been reported before. Tungsten (N, N, N', N'-tetramethyl-1, 3-diaminopropane) tetracarbonyl was a gift from Dr. G. R. Dobson of the University of South Dakota at Vermillion.

#### Preparation of N, N', N''-trimethyl-N, N', N''-triphenylphosphorous triamide (VIII)

Attempts to prepare this ligand by a previously reported synthesis (64) failed but the following procedure proved successful. In 100 ml. of liquid  $\text{NH}_3$  was dissolved 6.9 gm. (0.3 moles) of sodium. A crystal of  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were added to catalyze the formation of  $\text{NaNH}_2$ . To this was added dropwise 32.1 gm. (0.3 moles) of methylaniline. Anhydrous diethyl ether (125 ml.) was added dropwise and the ammonia was allowed to evaporate after which the mixture was refluxed for 30 min. to

insure complete removal of the ammonia. The mixture was then cooled to 0° and 13.7 gm. (0.1 moles) of phosphorus trichloride in 50 ml. of anhydrous ether was added dropwise. After stirring the mixture at 25° for 3 hrs. the sodium chloride was removed by filtration. The filtrate was taken to dryness yielding a white solid which was recrystallized from benzene in 34% yield. m.p. 208-210° (lit. 208-209°). The peak corresponding to the highest mass in the mass spectrum was at 106 (probably a  $N(CH_3)(C_6H_5)$  fragment). The n.m.r. spectrum consisted of a doublet at 2.67 p.p.m. ( $^3J_{PH} = 2.8$  Hz) and a multiplet at ca. 7.1 p.p.m.

#### Preparations of Complexes

The following compounds were a gift from Dr. R. J. Clark of Florida State University, Tallahassee, Florida (65-67):  $Cr(CO)_5(X)$ , cis- $Cr(CO)_4(X)_2$ ,  $Mo(CO)_5(X)$ , cis- and trans- $Mo(CO)_4(X)_2$ ,  $W(CO)_5(X)$ , cis- and trans- $Mo(CO)_4(X)_2$ ,  $Fe(CO)_4(X)$ ,  $Fe(CO)_3(X)_2$ ,  $Ni(CO)_2(X)_2$ , cis- $HMn(CO)_4(X)$ , trans- $HMn(CO)_4(X)$ , 1,2,3- $HMn(CO)_3(X)_2$ , 1,2,4- $HMn(CO)_3(X)_2$  and 1,2,6- $HMn(CO)_3(X)_2$ . The following compounds were a gift from Dr. J. M. Jenkins, Iowa State University, Ames, Iowa (68): cis- $PdCl_2(IXD)_2$ , trans- $PdI_2(IXD)_2$ , cis- $PtCl_2(IXD)_2$ , cis- $PtI_2(IXD)_2$ , cis- $PtCl_2(VIII)_2$ , cis- $PtI_2(VIII)_2$ , cis- $PtCl_2(VI)_2$ , trans- $PtCl_2(VI)_2$ , trans- $PtI_2(VI)_2$ , cis- $PdCl_2(II)_2$ , trans- $PdI_2(II)_2$ , trans- $PdCl_2(III)_2$ , trans- $PdI_2(III)_2$  and cis- $Mo(CO)_4(III)_2$ . The following compounds were a gift from Dr. A. C. Vandenbroucke,

Iowa State University, Ames, Iowa: cis-Cr(CO)<sub>4</sub>(IXA)<sub>2</sub>, trans-Cr(CO)<sub>4</sub>(IXB)<sub>2</sub>, trans-Fe(CO)<sub>3</sub>(IXB)<sub>2</sub> and Ni(CO)<sub>2</sub>(IXA)<sub>2</sub>. Cis- and trans-Mo(CO)<sub>4</sub>(VI)(IXB) were gifts from Mr. G. Wulfsberg and trans-Fe(CO)<sub>3</sub>(VI)(IXC) was a gift from Dr. R. L. Keiter, Iowa State University, Ames, Iowa.

The following compounds were prepared using the method of Stanclift and Hendricker (69): cis-Mo(CO)<sub>4</sub>(IXC)<sub>2</sub>, trans-Mo(CO)<sub>4</sub>(IXC)<sub>2</sub>, cis-W(CO)<sub>4</sub>(IXC)<sub>2</sub>, and trans-W(CO)<sub>4</sub>(IXC)<sub>2</sub>. The following compounds were synthesized using the method of Jenkins and Verkade (68): cis-Cr(CO)<sub>4</sub>(I)<sub>2</sub>, trans-Cr(CO)<sub>4</sub>(I)<sub>2</sub>, cis-Mo(CO)<sub>4</sub>(I)<sub>2</sub>, cis-PdCl<sub>2</sub>(VIII)<sub>2</sub>, PdI<sub>2</sub>(VIII)<sub>2</sub>, trans-PdCl<sub>2</sub>(VI)<sub>2</sub> and trans-PdI<sub>2</sub>(VI)<sub>2</sub>. The following compounds were prepared using the method of King (70): trans-Cr(CO)<sub>4</sub>(VI)<sub>2</sub>, trans-Mo(CO)<sub>4</sub>(VI)<sub>2</sub>, trans-Fe(CO)<sub>3</sub>(VI)<sub>2</sub> and Ni(CO)<sub>2</sub>(VI)<sub>2</sub>. The method of Poilblanc and Bigorgne (21) was used to prepare trans-Mo(CO)<sub>4</sub>(VIII)<sub>2</sub> while the method of Mathieu and Poilblanc (71) was used to prepare cis-Mo(CO)<sub>4</sub>(VIII)<sub>2</sub>. The method of Coates and Parkin was used to prepare trans-PdI<sub>2</sub>(I)<sub>2</sub> (72).

#### Preparation of cis-PdCl<sub>2</sub>(I)<sub>2</sub>

Although cis-PdCl<sub>2</sub>(I)<sub>2</sub> has been prepared previously by another route (72), the following method was used because of the ease in synthesizing the starting material PdCl<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>. One-half milliliter (ca. 6.6 mmoles) of trimethylphosphine was condensed onto a solution of 0.7 gm. (1.8 mmoles) PdCl<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub> in 25 ml. benzene at -196°. After stirring the mixture for

1 hr. at 25° the solvent was removed under reduced pressure. After extraction of the complex with chloroform and removal of the chloroform from the extract under reduced pressure, the complex was recrystallized from 50% ethanol-ether in 76% yield. The n.m.r. spectrum of the complex prepared in this manner was identical to the n.m.r. spectrum of cis-PdCl<sub>2</sub>(I)<sub>2</sub> prepared by the previously reported method.

Preparation of cis-Mo(CO)<sub>4</sub>(VI)<sub>2</sub>

To 0.6 gm. (2.0 mmoles) of molybdenum(norbornadiene)-tetracarbonyl in 25 ml. of pentane was added 1.0 gm. (6.1 mmoles) of hexamethylphosphorous triamide. After stirring the mixture at 25° for 30 min. the complex was filtered off in 88% yield. The carbonyl stretching frequencies observed in chloroform were at 1894(s), 1908(sh) and 2012(m) cm.<sup>-1</sup>

Preparation of cis-Mo(CO)<sub>4</sub>(VII)<sub>2</sub>

A mixture of 2.0 gm. (7.5 mmoles) of molybdenum hexacarbonyl and 6.0 gm. (17.2 mmoles) of (VII) in 125 ml. toluene was refluxed for 16 hrs. After cooling and filtering the mixture, its volume was reduced under reduced pressure until crystals began forming. Thirty milliliters of pentane was then added and the mixture was cooled to -20°. The complex, after separating by filtering, was recrystallized from toluene-pentane in ca. 20% yield. The carbonyl stretching frequencies observed in chloroform were at 1911(s), 1933(sh) and 2125(m)cm.<sup>-1</sup>



Preparation of  $\text{trans-W(CO)}_4(\text{VI})_2$

Although the preparation of this complex has been reported previously, (70) the ease of preparing the tungsten complex precursor makes the following method superior. To 0.86 gm. (2.0 mmoles) of tungsten(N,N,N',N'-tetramethyl-1,3-diaminopropane)tetracarbonyl in 50 ml. of toluene was added 1.0 gm. (6.1 mmoles) of hexamethylphosphorous triamide. After stirring for 48 hrs. at 25° the solvent was removed under reduced pressure. The residue was dissolved in hot pentane, the small amount of suspended material filtered, and the filtrate cooled to -78° giving pale yellow crystals in ca. 60% yield. The n.m.r. and infrared spectra were identical to those reported previously (70).

Preparation of  $\text{cis-W(CO)}_4(\text{I})_2$

Although the preparation of this complex has been reported previously (68) the ease of preparing the starting tungsten complex makes the following method superior. One-half milliliter (ca. 6.6 moles) of trimethylphosphine was condensed onto a solution of 0.86 gm. (2.0 mmoles) of tungsten(N,N,N',N'-tetramethyl-1,3-diaminopropane)tetracarbonyl in 30 ml. of benzene at -196°. After stirring at 25° for 48 hrs. the solvent was removed under reduced pressure. The residue was dissolved in hot pentane, the suspended solids filtered, and the filtrate cooled to -78° giving yellow crystals in 50% yield. The

n.m.r. spectrum of the compound was identical to the spectrum of an authentic sample.<sup>1</sup>

Preparation of *cis*- and *trans*-Mo(CO)<sub>4</sub>(VIII)(IXB)

The monosubstituted complex Mo(CO)<sub>5</sub>(IXB) was prepared as described by Verkade *et al.* (73). A solution of 8.2 gm. (20.6 mmoles) of Mo(CO)<sub>5</sub>(IXB) and 10.0 gm. (80.6 mmoles) of trimethylphosphite in 125 ml. methylcyclohexane was refluxed for 96 hrs. The solvent was removed under reduced pressure leaving an oily residue which was eluted with benzene on a silica gel column. Six compounds were obtained, of which, four were identified by comparison of their n.m.r. spectra with those of authentic samples. The products collected in order of their elution were: *trans*-Mo(CO)<sub>4</sub>(VIII)<sub>2</sub>, *cis*-Mo(CO)<sub>4</sub>(VIII)<sub>2</sub>, *trans*-Mo(CO)<sub>4</sub>(VIII)(IXB), (IXB), *cis*-Mo(CO)<sub>4</sub>(VIII)(IXB), and *trans*-Mo(CO)<sub>4</sub>(IXB)<sub>2</sub>. Mass spectra of both the *cis*- and *trans*-Mo(CO)<sub>4</sub>(VIII)(IXB) showed the expected parent ion patterns from 490 to 498 due to the various isotopes of molybdenum.

Preparation of *cis*-Cr(CO)<sub>4</sub>(VA)<sub>2</sub>

A solution of 0.41 gm. (1.6 mmoles) of chromium(norbornadiene)tetracarbonyl and 0.63 gm. (3.2 mmoles) of (VA) in 50 ml.

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<sup>1</sup>J. M. Jenkins, Ames, Iowa. N.M.R. data of transition metal complexes. Private communication. 1966.

benzene was stirred at 25° for 48 hrs. The solvent was removed under reduced pressure giving a pale greenish-yellow solid which was recrystallized from ca. 50% benzene-pentane in ca. 60% yield. The carbonyl stretching frequencies observed in chloroform were at 1931(s), 1957(sh) and 2033(m)cm<sup>-1</sup>.

Analysis: Calc'd. for Cr(CO)<sub>4</sub>(VA)<sub>2</sub>: C, 30.21; H, 3.26;  
S, 34.56

Found: C, 30.91; H, 3.70; S, 35.07

#### Preparation of trans-Cr(CO)<sub>4</sub>(VB)<sub>2</sub>

A solution of 0.41 gm. (1.6 mmoles) of chromium(norbornadiene)tetracarbonyl and 0.8 gm. (3.2 mmoles) of (VB) in 50 ml. benzene was stirred at 25° for 48 hrs. The solvent was removed under reduced pressure yielding an oil. Dissolving the oil in pentane and cooling to -20° gave a crystalline compound which melted below room temperature. The carbonyl stretching frequency observed in chloroform was at 1935(s)cm<sup>-1</sup>.

#### Preparation of trans-Cr(CO)<sub>4</sub>(IV)<sub>2</sub>

A solution of 0.41 gm. (1.6 mmoles) of chromium(norbornadiene)tetracarbonyl and 0.55 gm. (3.2 mmoles) of (IV) in 50 ml. of benzene was stirred at 25° for 48 hrs. The solvent was removed under reduced pressure yielding an oil. Attempts to form a crystalline compound failed. The carbonyl stretching frequency observed in chloroform was at 1925(s) cm<sup>-1</sup>.

Preparation of  $\text{cis-Mo(CO)}_4(\text{VA})_2$

A solution of 0.4 gm. (1.3 mmoles) of molybdenum-(norbornadiene)tetracarbonyl and 0.53 gm. (2.7 mmoles) of (VA) in 50 ml. of benzene was stirred at 25° for 12 hrs. The solvent was removed under reduced pressure giving a pale yellow solid which was recrystallized from ca. 50% benzene-pentane in ca. 60% yield. The carbonyl stretching frequencies observed in chloroform were at 1945(s), 1965(sh), and 2045(m)cm<sup>-1</sup>.

Analysis: Calc'd. for  $\text{Mo(CO)}_4(\text{VA})_2$ : C, 28.00; H, 3.02; S, 32.63.

Found: C, 28.73; H, 3.17; S, 33.04.

Preparation of  $\text{cis-Mo(CO)}_4(\text{VB})_2$

This compound was prepared in an analogous manner to that of  $\text{cis-Mo(CO)}_4(\text{VA})_2$  in ca. 60% yield. The carbonyl stretching frequencies observed in chloroform were at 1945(s), 1965(sh), and 2045(m)cm<sup>-1</sup>.

Preparation of  $\text{cis-Mo(CO)}_4(\text{IV})_2$

A solution of 0.4 gm. (1.3 mmoles) of molybdenum-(norbornadiene)tetracarbonyl and 0.46 gm. (2.7 mmoles) of (IV) in 50 ml. of benzene was stirred at 25° for 8 hrs. The solvent was removed under reduced pressure yielding an oil. Attempts to form a crystalline compound failed. The carbonyl stretching frequencies observed in chloroform were at 1945(s), 1955(s), and 2045(m)cm<sup>-1</sup>.

Preparation of  $\text{cis-W(CO)}_4(\text{VA})_2$

A solution of 0.4 gm. (1.0 mmoles) of tungsten(cyclo-octadiene)tetracarbonyl and 0.4 gm. (2.0 mmoles) of (VA) in 50 ml. of benzene was stirred at 25° for 8 hrs. The solvent was removed under reduced pressure giving a pale yellow solid which was recrystallized from ca. 50% benzene-pentane in ca. 60% yield. The carbonyl stretching frequencies observed in chloroform were at 1927(s), 1976(s), and 2041(m)cm<sup>-1</sup>.

Preparation of  $\text{cis-W(CO)}_4(\text{IV})_2$

A solution of 0.4 gm. (1.0 mmoles) of tungsten(cyclo-octadiene)tetracarbonyl and 0.35 gm. (2.0 mmoles) of (IV) in 50 ml. of benzene was stirred at 25° for 6 hrs. The solvent was removed under reduced pressure yielding an oil. Attempts to form a crystalline compound failed. The carbonyl stretching frequencies observed in chloroform were at 1920(s), 1935(sh), and 2035(m)cm<sup>-1</sup>.

Preparation of  $\text{cis-Mn(CO)}_4(\text{VI})\text{X}$  (X = Br, I)

A solution containing slightly greater than a 2:1 molar ratio of (VI) to manganese pentacarbonyl halide was refluxed in 30 ml. of pentane for 3 hrs. On cooling to -20° the product precipitated and was used without further purification. The carbonyl stretching frequencies observed in chloroform were at 1942(s), 2000(s), 2083(m)cm<sup>-1</sup> for X = Br and I, respectively.

Preparation of  $\text{cis-Mn(CO)}_4(\text{IXC})\text{X}$  (X = Cl, Br, I)

A solution containing slightly greater than a 2:1 molar ratio of (IXC) to manganese pentacarbonyl halide was refluxed in 30 ml. pentane for 4 hrs. at which time the cis complex had precipitated. The product was used without further purification. The carbonyl stretching frequencies observed in chloroform were at 1972(s), 2028(s), 2110(m)  $\text{cm}^{-1}$ ; 1980(s), 2020(s), 2105(m)  $\text{cm}^{-1}$ ; and 1984(s), 2020(s), 2105(m)  $\text{cm}^{-1}$  for X = Cl, Br, and I, respectively.

Preparation of  $1,2,4\text{-Mn(CO)}_3(\text{VI})_2\text{X}$  (X = Cl, Br)

A solution containing slightly greater than a 2:1 molar ratio of (VI) to manganese pentacarbonyl halide was refluxed in 30 ml. of pentane for 6 hrs. On cooling to  $-78^\circ$  the product precipitated and was used without further purification. The carbonyl stretching frequencies observed in chloroform were at 1887(s), 1946(s), 2024(w)  $\text{cm}^{-1}$  and 1901(s), 1938(s), 2020(w)  $\text{cm}^{-1}$  for X = Cl and Br, respectively.

Analysis: Calc'd for  $\text{Mn(CO)}_3(\text{VI})_2\text{Br}$ : C, 33.00; H, 6.00;  
Br, 14.67

Found: C, 32.92; H, 6.23; Br, 14.81.

Preparation of  $1,2,4\text{-Mn(CO)}_3(\text{VIII})_2\text{X}$  (X = Br, I)

A solution containing slightly greater than a 2:1 molar ratio of (VIII) to manganese pentacarbonyl was refluxed in 30 ml. of hexane for 6 hrs. On cooling to  $-20^\circ$  the product

precipitated and was used without further purification. The carbonyl stretching frequencies observed in chloroform were at 1890(s), 1976(s), 2058(w)cm<sup>-1</sup> and at 1942(s), 1965(s), 2045(w)cm<sup>-1</sup> for X = Br and I, respectively.

Analyses: Calc'd for Mn(CO)<sub>3</sub>(VIII)<sub>2</sub>Br: C, 23.17; H, 3.86; Br, 17.10.

Found: C, 23.29; H, 4.06; Br, 17.27.

Calc'd for Mn(CO)<sub>3</sub>(VIII)<sub>2</sub>I: C, 21.03; H, 3.53; I, 24.69.

Found: C, 21.20; H, 3.64; I, 24.89.

#### Preparation of 1,2,3-Mn(CO)<sub>3</sub>(VIII)<sub>2</sub>Br

A solution of 0.55 gm. (2.0 mmoles) of manganese pentacarbonyl bromide and 0.5 gm. (4.0 mmoles) of (VIII) in 30 ml. of pentane was refluxed for 4 hrs. On cooling to -20° crystals of the desired product formed. The carbonyl stretching frequencies observed in chloroform were at 1927(s), 1976(s), and 2041(s)cm<sup>-1</sup>.

Analysis: Calc'd for Mn(CO)<sub>3</sub>(VIII)<sub>2</sub>Br: C, 23.17; H, 3.86; Br, 17.10.

Found: C, 23.39; H, 3.98; Br, 17.20.

#### Preparation of 1,2,3-Mn(CO)<sub>3</sub>(IXC)<sub>2</sub>Br

A solution of 0.55 gm. (2.0 mmoles) of manganese pentacarbonyl bromide and 0.75 gm. (4.3 mmoles) of (IXC) in 30 ml. of benzene was heated to 40° for 6 hrs. On addition of pentane

and cooling to 0° the product precipitated and was used without further purification. The carbonyl stretching frequencies observed in chloroform were at 1946(s), 2000(s) and 2061(s)cm<sup>-1</sup>.

Analysis: Calc'd for Mn(CO)<sub>3</sub>(IXC)<sub>2</sub>Br: C, 35.72; H, 4.55; Br, 14.01.

Found: C, 35.94; H, 4.61; Br, 14.08.

#### Preparation of 1,2,4-Mn(CO)<sub>3</sub>(IXC)<sub>2</sub>Br

A solution of 0.55 gm. (2.0 mmoles) of manganese pentacarbonyl bromide and 0.75 gm. (4.3 mmoles) of (IXC) in 30 ml. of benzene was heated to 60° for 12 hrs. On addition of pentane and cooling to 0° the product precipitated and was used without further purification. The carbonyl stretching frequencies observed in chloroform were at 1953(s), 2000(s), and 2075(w)cm<sup>-1</sup>.

Analysis: Calc'd for Mn(CO)<sub>3</sub>(IXC)<sub>2</sub>Br: C, 35.72; H, 4.55; Br, 14.01.

Found: C, 35.90; H, 4.58; Br, 14.05.

#### Attempted Preparations

Because of the difficulties encountered in these attempted preparations the products were not characterized further.

#### PdCl<sub>2</sub>(VB)<sub>2</sub>

To a solution of 0.38 gm. (1.0 mmoles) of dichlorobis-(benzonitrile)palladium in 20 ml. of benzene was added a



solution of 0.5 gm. (2.0 mmoles) of (VB) in 10 ml. of benzene. A precipitate formed immediately. Attempts to dissolve the solid in various solvents failed and therefore it is believed to be polymeric.

PdCl<sub>2</sub>(IV)<sub>2</sub>

To a solution of 0.38 gm. (1.0 mmoles) of dichlorobis-(benzonitrile)palladium in 30 ml. of benzene was added 0.35 gm. (2.0 mmoles) of (IV). An orange solution resulted from which a yellowish-orange precipitate formed on the addition of pentane. This compound spontaneously decomposed.

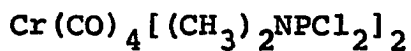
Fe(CO)<sub>3</sub>(VA)<sub>2</sub>

A solution of 1.0 gm. (5.1 mmoles) of iron pentacarbonyl and 2.0 gm. (10.2 mmoles) of (VA) in 125 ml. of toluene was irradiated with ultraviolet light (Hanovia lamp 654-A10) for 36 hrs. The solution was concentrated by removal of some of the solvent under reduced pressure, filtered, and pentane added to the filtrate. On cooling to -20° a precipitate formed which was found to be the ligand (VA).

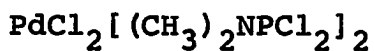
Mo(CO)<sub>4</sub>[(CH<sub>3</sub>)<sub>2</sub>NPCl<sub>2</sub>]<sub>2</sub>

The ligand, dichloro-N,N-dimethylaminophosphine was prepared by the method of Burg and Slota (74). A solution of 2.0 gm. (7.5 mmoles) of molybdenum hexacarbonyl and 2.2 gm. (15.0 mmoles) of (CH<sub>3</sub>)<sub>2</sub>NPCl<sub>2</sub> was refluxed in 40 ml. of hexane

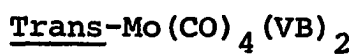
for 36 hrs. On removal of the solvent under reduced pressure a solid was obtained that fumed in air and decomposed under vacuum.



A solution of 2.2 gm. (10.0 mmoles) of chromium hexacarbonyl and 2.8 gm. (20.0 mmoles) of  $(\text{CH}_3)_2\text{NPCl}_2$  was refluxed in 40 ml. of heptane for 30 hrs. A black precipitate formed. Addition of water gave a green aqueous solution indicating that  $\text{Cr}^{+3}$  probably had formed.



To a suspension of 0.89 gm. (2.3 mmoles) of dichlorobis(benzonitrile)palladium in 70 ml. of diethyl ether was added 0.88 gm. (6.0 mmoles) of  $(\text{CH}_3)_2\text{NPCl}_2$ . A yellow precipitate immediately formed. Attempts to dissolve the solid in various solvents failed indicating that a polymer probably had formed.



Refluxing cis- $\text{Mo}(\text{CO})_4(\text{VB})_2$  in toluene for 24 hrs. in an attempt to isomerize it to the trans compound gave only the starting material. Refluxing cis- $\text{Mo}(\text{CO})_4(\text{VB})_2$  in diglyme decomposed the compound.

## RESULTS AND DISCUSSION

## Manganese Complexes

Although a number of manganese complexes of the types  $\text{Mn}(\text{CO})_4\text{LX}$  and  $\text{Mn}(\text{CO})_3\text{L}_2\text{X}$  ( $\text{L} = (\text{VI}), (\text{VIII}), (\text{IX})$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) were prepared, few n.m.r. spectra suitable for analysis by computer simulation could be obtained. This was due to the instability of the  $\text{Mn}^{+1}$  compounds to oxidation resulting in traces of paramagnetic impurities (probably  $\text{Mn}^{+2}$ ). Even when precautions were taken such as degassing the solvent with nitrogen prior to running the reaction, keeping the reaction mixture under nitrogen at all times, filtering under nitrogen, condensing benzene onto the sample in an n.m.r. tube under vacuum and sealing the n.m.r. tube under vacuum, paramagnetic impurities still formed which broadened the lines in the n.m.r. spectrum. It was also found that the more polar the solvent used to dissolve the sample, the more rapidly impurities formed.

Some interesting properties of these manganese compounds were observed. Angelici and Basolo have studied the kinetics of the substitution reactions of manganese pentacarbonyl halides with various phosphorus ligands (75-77). They had shown that substitution of the carbonyl trans to the halide did not occur and that cis- $\text{Mn}(\text{CO})_4\text{LX}$  formed first followed by the formation of 1,2,3- $\text{Mn}(\text{CO})_3\text{L}_2\text{X}$  which could be isomerized at higher temperatures to 1,2,4- $\text{Mn}(\text{CO})_3\text{L}_2\text{X}$ . In contrast to their work, we have found for the reaction of  $\text{Mn}(\text{CO})_5\text{Br}$  with (VI) that with varying

reaction times  $\text{Mn}(\text{CO})_4(\text{VI})\text{Br}$  formed followed by the appearance of  $1,2,4\text{-Mn}(\text{CO})_3(\text{VI})_2\text{Br}$  without any indication of the presence of  $1,2,3\text{-Mn}(\text{CO})_3(\text{VI})_2\text{Br}$ . This could be attributed to a steric effect due to the bulkiness of the ligand (70).

Another unusual property is the relative solubility of a complex with the bicyclic phosphite (IXA) compared to the analogous complex with the open chain phosphite (VIII). Thus  $1,2,3\text{-Mn}(\text{CO})_3(\text{IXA})_2\text{Br}$  precipitated out of a chloroform solution at  $40^\circ$  whereas it was often difficult to precipitate  $1,2,3\text{-Mn}(\text{CO})_3(\text{VIII})_2\text{Br}$  out of a pentane solution at  $-20^\circ$ .

#### Stereochemistry

Two unusual stereochemical properties of the molybdenum complexes were observed. One of these was with the ligands (VI) and (VII). King had been unable to prepare any cis complexes with (VI) (70). He had reacted molybdenum(norbornadiene)-tetracarbonyl and molybdenum(cycloheptatriene)tricarbonyl with (VI) and in both cases obtained trans- $\text{Mo}(\text{CO})_4(\text{VI})_2$  instead of the expected complexes cis- $\text{Mo}(\text{CO})_4(\text{VI})_2$  and fac- $\text{Mo}(\text{CO})_3(\text{VI})_3$ . He attributed the reluctance of (VI) to occupy cis positions to the bulk of the ligand. Although we have been able to prepare cis- $\text{Mo}(\text{CO})_4(\text{VI})_2$  we have found that it isomerizes to the trans isomer in benzene solution at room temperature in 30 min. In contrast, the ligand (VII) which should be similar to (VI) in chemical properties and almost as bulky readily forms cis- $\text{Mo}(\text{CO})_4(\text{VII})_2$ . Moreover cis- $\text{Mo}(\text{CO})_4(\text{VII})_2$  could not be

isomerized to trans-Mo(CO)<sub>4</sub>(VII)<sub>2</sub> by refluxing it for 24 hrs. in a toluene solution. Complexes of (VI) show other unusual properties which will be discussed later and it is possible that the bulk of (VI) is not the only reason for its reluctance to form cis complexes.

The other unusual stereochemical property observed occurred with the ligands (V) and (IX). With the bicyclic phosphites, the configuration of the complexes depended on the length of the alkyl chain in the 4 position. With (IXA) or (IXB) only the cis complexes could be obtained. With (IXC) a mixture of cis and trans-Mo(CO)<sub>4</sub>(IXC)<sub>2</sub> formed whereas the reaction of molybdenum(norbornadiene)tetracarbonyl with (IXD) at 25° gave only the trans isomer. The bicyclic thiophosphites on the other hand gave only cis complexes. Attempts to isomerize cis-Mo(CO)<sub>4</sub>(VB)<sub>2</sub> to the trans isomer by refluxing in toluene for 24 hrs. failed. It would appear that both steric and electronic effects determine the geometry of these complexes. With the bicyclic phosphites, steric effects appear to favor the trans isomer as the alkyl chain increases from methyl to pentyl. With the bicyclic thiophosphites, however, electronic effects of obscure origin must dominate the steric factor since the trans isomers of these ligands could not be prepared.

## N.M.R. Line Shapes and Computer Simulation

It has been found that if the coupling constants can be obtained by a method other than that of computer simulation of the envelope of overlapping lines, more accurate values are obtained. Anomalous line shapes in n.m.r. spectra can arise from a number of causes. The presence of paramagnetic impurities, as seemed to be the case with most manganese complexes, will cause a broadening of the lines. Although the line shape can be simulated for these cases it is doubtful that the coupling constants so derived have any significance.

Broadening of lines can also result from intermolecular exchange. Fackler et al. (78) have discussed this problem for the  $X_nAA'X'_n$  system. They have shown that a broad apparent triplet, a singlet or a doublet can result depending on the rate of exchange. Examples of this phenomenon were observed in this work with  $HgI_2(VI)_2$  in which a broad singlet was observed and probably with  $PdI_2(VIII)_2$ .

Difficulties in obtaining good line shapes can also arise from the instrumentation used. This is illustrated in Figures 5 and 6 with the  $^1H$  n.m.r. spectra of cis- $W(CO)_4(I)_2$  obtained on a Varian A-60 and an HR-60 spectrometer, respectively. The A-60 spectrum was obtained at a sweep rate of 0.1 Hz./sec. which is the slowest attainable with this instrument while the sweep rate used for the HR-60 spectrum was 0.023 Hz./sec. It is readily observed that the resolution of the A-60 spectrometer is not as good as that of the HR-60. More significantly,

Figure 5. N.M.R. spectrum of cis-W(CO)<sub>4</sub>(I)<sub>2</sub> obtained on a Varian A-60 spectrometer at a sweep rate of 0.1 Hz./sec.

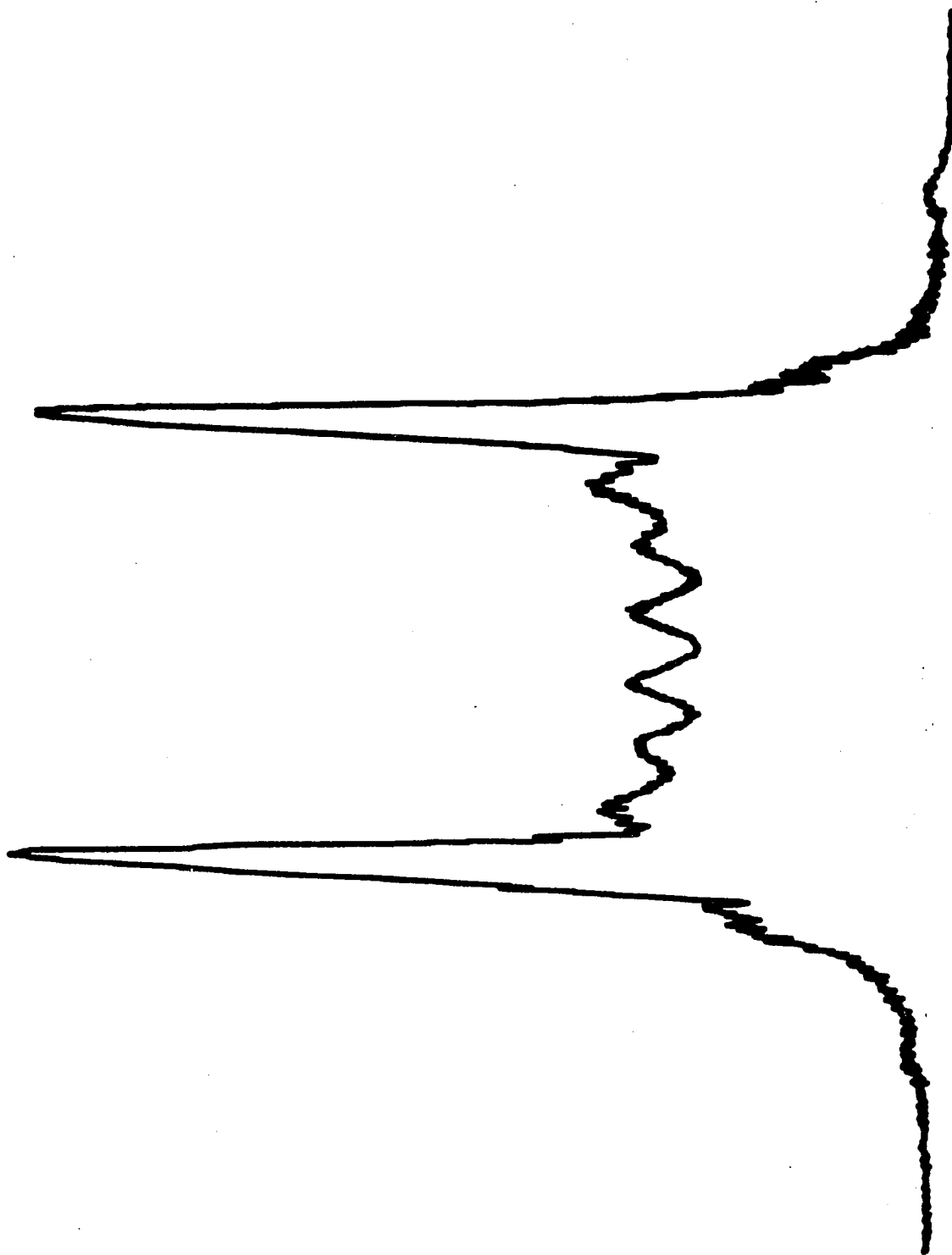
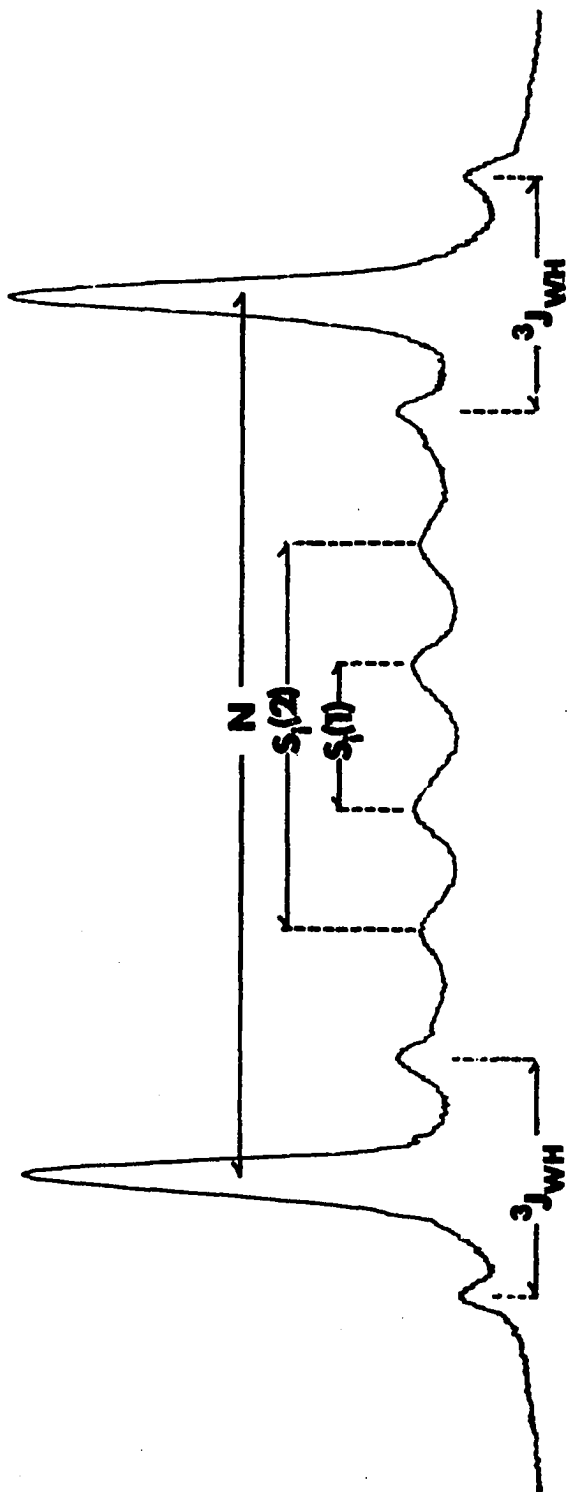




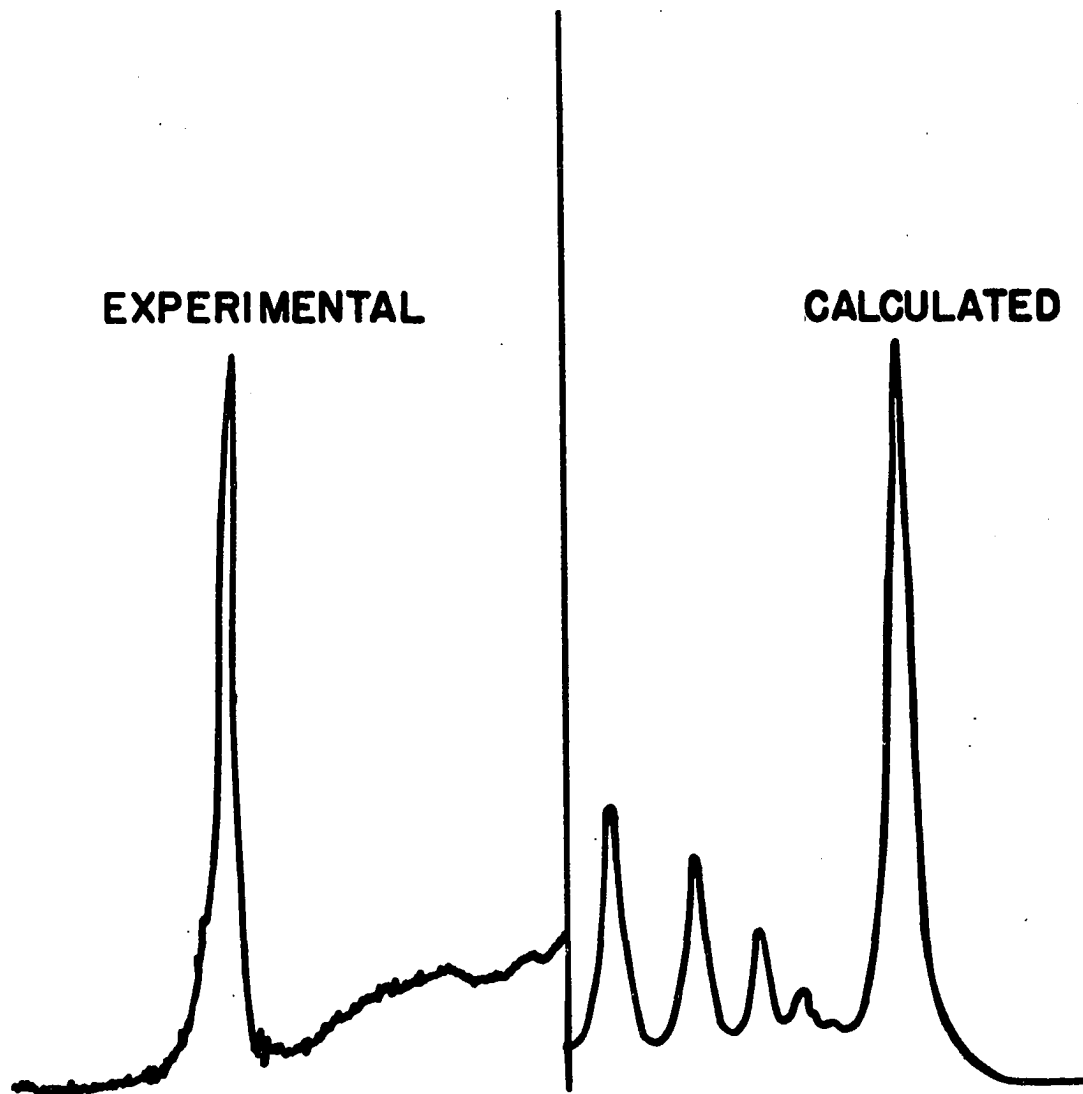
Figure 6. N.M.R. spectrum of cis-W(CO)<sub>4</sub>(I)<sub>2</sub> obtained on a Varian HR-60 spectrometer at a sweep rate of 0.023 Hz./sec.



ringing is observed for the intense lines in the spectrum obtained on the A-60. This means that the line shape is not truly Lorentzian since the ideally slow passage is not obtained. Thus the observed widths of these lines at half-height are smaller than the actual widths. Using these observed widths to calculate  $J_{AA'}$  by computer simulation leads to values that are greater than the true values by 5 to 10%.

The above causes for anomalous line shapes generally can be readily detected and their origins determined. Other anomalies in the line shapes are not so readily explained. In Figure 7 is a comparison of the experimental and calculated spectra for cis-Mo(CO)<sub>4</sub>(VIII)<sub>2</sub>. Although the width at half-height of the intense doublet is small in the experimental spectrum, the central lines are broad and lacking in resolution regardless of the instrument used to obtain the spectrum. Straightforward spectral calculations assuming uniform line widths do not account for the observed band shapes. Finer et al. (79) have observed this phenomenon with other compounds and have postulated a number of reasons for this phenomenon. Hindered internal rotation could cause variations in line width but in this case the n.m.r. spectrum would be temperature dependent. Due to a lack of time, temperature studies were not carried out on cis-Mo(CO)<sub>4</sub>(VIII)<sub>2</sub> or on the other compounds in which we noticed this phenomenon but Finer et al. did do temperature studies with their compounds and found that the spectra were temperature independent. Small non-zero XX' coupling would

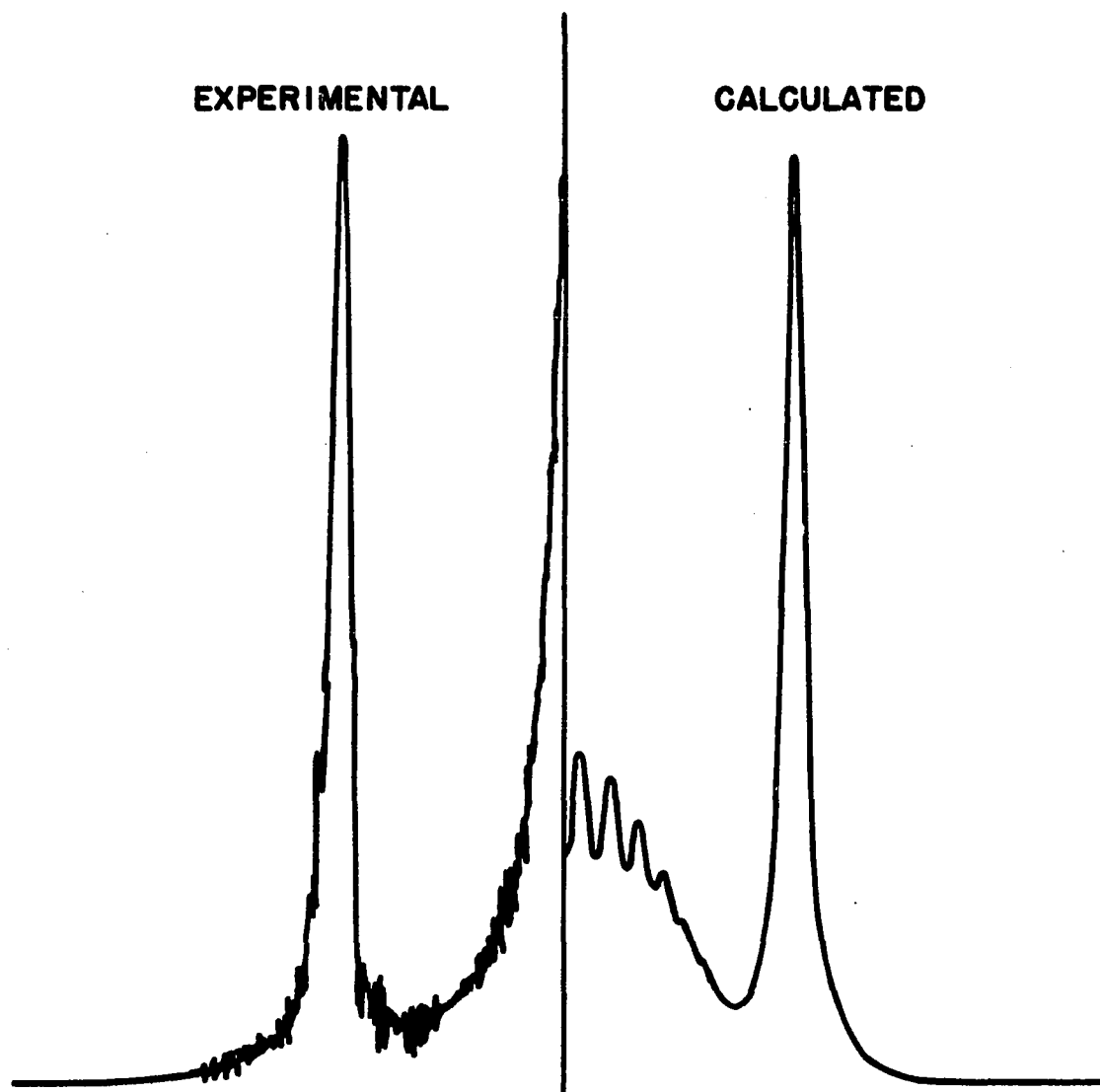
Figure 7. Comparison of experimental and calculated spectra  
for cis-Mo(CO)<sub>4</sub>(VIII)<sub>2</sub> using <sup>2</sup>J<sub>PP</sub> = 40 Hz



cause the inner lines to be broadened but it can be assumed for cis-Mo(CO)<sub>4</sub>(VIII)<sub>2</sub> that such coupling is negligible since even <sup>5</sup>J<sub>PH</sub> in cis-Mo(CO)<sub>4</sub>(VIII)(IXB) is zero. Thus it is unlikely that there is any XX' coupling through eight bonds in cis-Mo(CO)<sub>4</sub>(VIII)<sub>2</sub>. It is highly probable that quadrupolar broadening would account for this effect except that variations in line widths are known for cases in which no quadrupolar nuclei are present. Two of their postulates that seem most likely to account for the poor resolution of the central lines are that in theory each transition can have its own transverse relaxation time T<sub>2</sub>(80) and that off-diagonal elements of the relaxation matrix can cause overlapping lines to give band shapes which are not simply sums of Lorentzian lines (80).

A totally different phenomenon was observed for all the complexes of (VI). In the above cases the energies of the transitions were similar to those calculated in spite of the anomalous line shapes. In complexes of (VI), however, the energies of transition are not the same as those calculated. The result of this is that the values of J<sub>AA'</sub>, obtained by curve fitting are much larger than those obtained by the observation of the outer lines or by double resonance techniques. This is illustrated in Figure 8 which is a comparison of the experimental and calculated spectra for trans-Fe(CO)<sub>3</sub>(VI)<sub>2</sub> using a value of <sup>2</sup>J<sub>PP</sub> of 65 Hz obtained by double resonance techniques. A value of 320 Hz for <sup>2</sup>J<sub>PP</sub> is required to simulate

Figure 8. Comparison of experimental and calculated n.m.r. spectra for trans Fe(CO)<sub>3</sub>(VI)<sub>2</sub> using  ${}^2J_{pp} = 65$  Hz

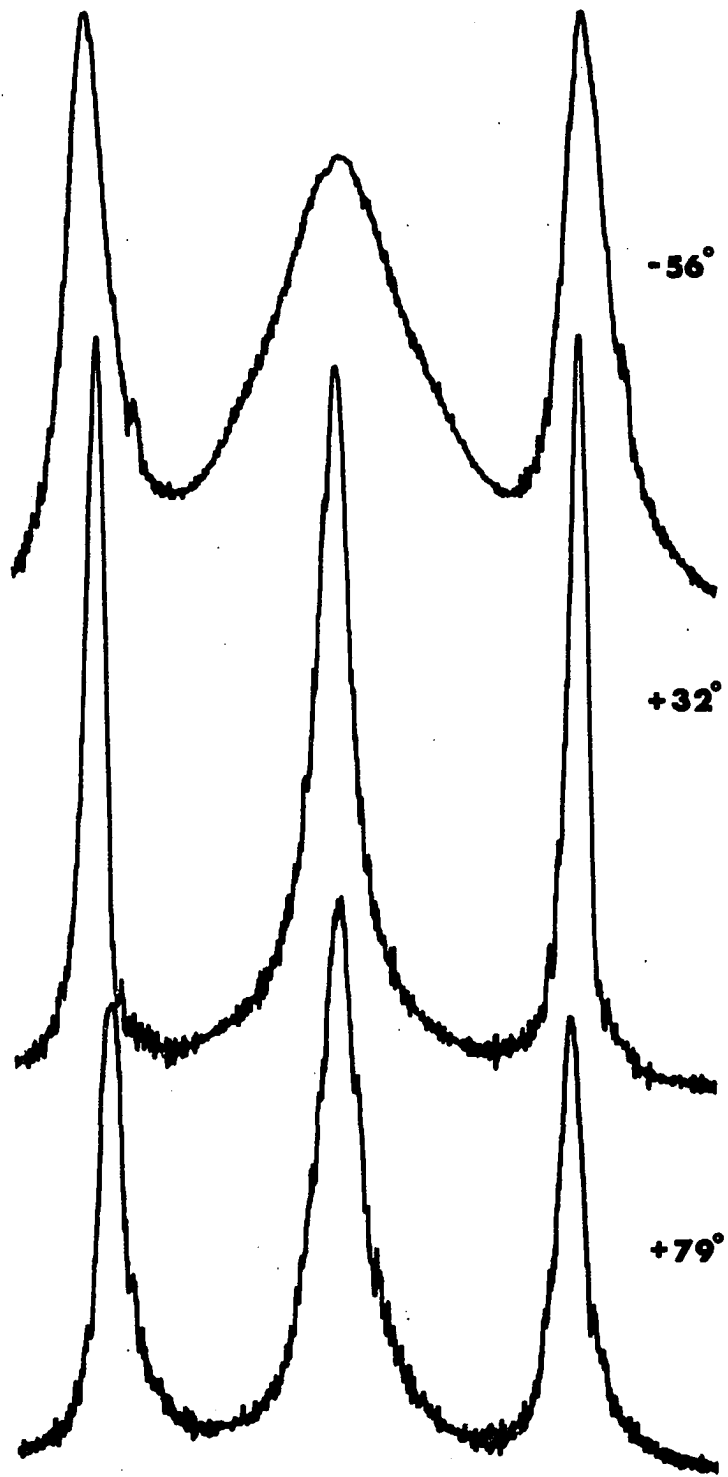




the observed spectrum. Values as high as 4500 Hz for  ${}^2J_{PP}$  in trans-PdCl<sub>2</sub>(VI)<sub>2</sub> were needed to simulate the observed spectra. For cis-Mo(CO)<sub>4</sub>(VI)<sub>2</sub> a value of 90 Hz was calculated for  ${}^2J_{PP}$  whereas a value of 12.4 Hz was obtained from the observation of the outer lines. In contrast, very good agreement was obtained between the calculated (20 Hz) and observed value (18.2 Hz) for  ${}^2J_{PP}$  in the similar complex cis-Mo(CO)<sub>4</sub>(VII)<sub>2</sub>.

Moreover the proton n.m.r. spectrum of trans-Fe(CO)<sub>3</sub>(VI)<sub>2</sub> is temperature dependent and it is probable that the spectra of all the complexes of (VI) would show a similar temperature dependence. The proton n.m.r. spectra of trans-Fe(CO)<sub>3</sub>(VI)<sub>2</sub> at -56°, +32°, and +79° are given in Figure 9. As the temperature decreases, the central portion becomes broader and the separation of the doublet increases. This separation which can be assigned to  ${}^3J_{PH}$  is 9.0 Hz at +79°, 9.5 Hz at +32° and 10.0 Hz at -56°. For this temperature dependence to be observed, some change in the molecule must be occurring during an interval which is of the order of n.m.r. detection time ( $10^{-2}$  sec.). An intermolecular exchange can be ruled out because as the temperature is increased, intermolecular exchange would increase causing the lines to broaden and not sharpen as is observed. Intramolecular exchange between cis- and trans-isomers is unlikely because the infrared spectrum at room temperature showed only one  $\nu(\text{CO})$  absorption at  $1876.5 \pm 1 \text{ cm}^{-1}$ . If a cis-trans-equilibrium were established it should be detected by infrared

Figure 9. Proton n.m.r. spectra of trans-Fe(CO)<sub>3</sub>(VI)<sub>2</sub> in toluene-d<sub>8</sub> at -56°, +32° and +79°C.



spectroscopy since infrared detection time is of the order of  $10^{-12}$  sec. This indeed is the case with  $\text{Fe}(\text{CO})_3(\text{X})_2$  which is known to undergo intramolecular exchange (81). Moreover the isomerization of cis- $\text{Mo}(\text{CO})_4(\text{VI})_2$  to trans- $\text{Mo}(\text{CO})_4(\text{VI})_2$  can be followed by nuclear magnetic resonance. If an exchange process were occurring it is unlikely that this could be done. It is possible that there is hindered internal rotation of the phosphorus substituents in the ligand. If this were the case, the rotation should stop upon sufficient cooling (perhaps below  $-56^\circ$ ) and the methyl groups should then become non-equivalent. Because of this, splitting of each line separated by N should be observed and it is probable that two apparent triplets would result. Moss and Shaw (82) have observed a similar effect in trans- $\text{NiBr}(\text{O-tolyl})[\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2]$  in which the phosphine-methyl resonances at room temperature consist of two well-defined 1:2:1 triplets showing that the two methyl groups on the same phosphine ligand differ considerably in their time-averaged magnetic environments. If hindered rotation occurs, however, it seems unusual that the value of  ${}^2J_{\text{pp}}$  obtained by computer simulation compared so well with the observed from the separation of the  $\chi = 1$  outer and inner lines in the spectrum of cis- $\text{Mo}(\text{CO})_4(\text{VII})_2$ .

It should be noted that since the inner lines show a temperature dependence, it is probable that the outer lines of weak intensity also are temperature dependent. Therefore any value obtained for  ${}^2J_{\text{pp}}$  from observation of these outer lines

or from double resonance methods may only be appropriate for the temperature at which they were obtained. Because of this, the comparison discussed later of  ${}^2J_{PP}$  values for complexes of (VI) with  ${}^2J_{PP}$  values for other complexes which are believed to be temperature independent may not be valid.

### Fluorine Spectra

The n.m.r. data other than phosphorus-phosphorus coupling constants for the complexes of (X) are given in Table 2. Although the changes in the  ${}^{19}\text{F}$  chemical shifts among the complexes of the same metal are relatively small, a consistent decrease in shielding is observed in all cases from mono to trans to cis. Because of the subtle factors capable of affecting such small changes in the dominant paramagnetic contribution to  ${}^{19}\text{F}$  shielding (34), it is presently not possible to interpret this trend.

While the  ${}^{19}\text{F}$  spectra of the mono-substituted complexes are characterized by a simple doublet due to P-F coupling, the general appearance of all the spectra of the disubstituted metal carbonyls is illustrated for the case of cis- $\text{W}(\text{CO})_4(\text{X})_2$  in Figure 10. In all the complexes of (X),  $L \gg J_{AA}$ , so that the coupling constants can be calculated from the  $\chi = 1$  lines. In many of the complexes, long-range fluorine-fluorine couplings were observed but the quartets could not be resolved sufficiently to calculate  ${}^4J_{FF}$ . Thus we can set an upper limit to  ${}^4J_{FF}$  in these complexes of 1 Hz.

Table 2. Fluorine n.m.r. data of complexes of (X)

Compound	$\delta F$ (p.p.m.) <sup>a</sup>	$^1J_{PF}$ (Hz)	$^3J_{PF}$ (Hz)	$^2J_{WF}$ (Hz)
Cr(CO) <sub>5</sub> (X)	2.06	1315		
<u>cis</u> -Cr(CO) <sub>4</sub> (X) <sub>2</sub>	-0.09	+1306	$\bar{F}$ 1.5	
<u>trans</u> -Cr(CO) <sub>4</sub> (X) <sub>2</sub>	1.28			
Mo(CO) <sub>5</sub> (X)	4.70	1310		
<u>cis</u> -Mo(CO) <sub>4</sub> (X) <sub>2</sub>	3.03	+1306	$\bar{F}$ 2.5	
<u>trans</u> -Mo(CO) <sub>4</sub> (X) <sub>2</sub>	3.99	+1320	$\bar{F}$ 37	
W(CO) <sub>5</sub> (X) <sup>b</sup>	7.89	1245		31
<u>cis</u> -W(CO) <sub>4</sub> (X) <sub>2</sub>	5.96	+1281	$\bar{F}$ 1.5	30
<u>trans</u> -W(CO) <sub>4</sub> (X) <sub>2</sub>	6.97	+1286	$\bar{F}$ 39	32
Fe(CO) <sub>4</sub> (X)	6.22	1329		
Fe(CO) <sub>3</sub> (X) <sub>2</sub>	5.59	+1322	$\bar{F}$ 26	
Ni(CO) <sub>2</sub> (X) <sub>2</sub>	18.87	+1357	$\bar{F}$ 34.5	
1,2,3-HMn(CO) <sub>3</sub> (X) <sub>2</sub> <sup>c</sup>		+1304.5	$\bar{F}$ 1.5	
1,2,4-HMn(CO) <sub>3</sub> (X) <sub>2</sub> <sup>d</sup>		+1311	$\bar{F}$ 27.5	

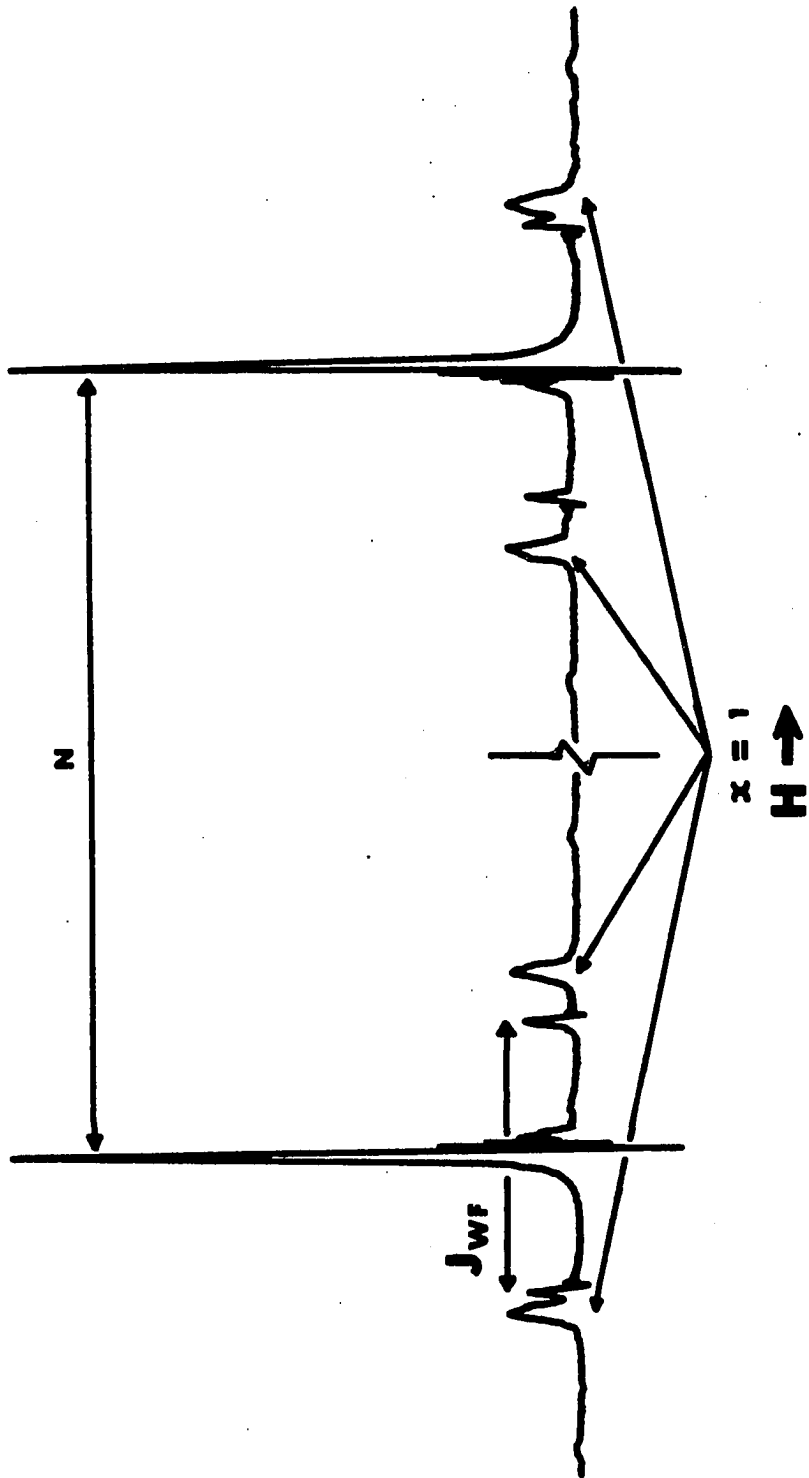
<sup>a</sup>Chemical shifts of neat samples or cyclohexane solutions relative to CFC1<sub>3</sub>.

<sup>b</sup> $^1J_{WP} = 485$  Hz.

<sup>c</sup> $^3J_{HF} = 10.0$  Hz.

<sup>d</sup> $^3J_{HF} = 12.0$  Hz;  $^4J_{FF} = 3.0 \pm 0.3$  Hz.

Figure 10. Fluorine n.m.r. spectrum of cis-W(CO)<sub>4</sub>(X)<sub>2</sub> obtained on a Varian HR-60 spectrometer at 56.4 MHz





Although only the relative signs of  $^1J_{PF}$  and  $^3J_{PF}$  could be calculated directly from the  $^{19}F$  spectra, it is probable that  $^1J_{PF}$  is negative (83). An interesting result is the large difference in  $^3J_{PF}$  between the cis and trans compounds. The magnitude of  $^3J_{PF}$  in the trans compounds is always larger than in the cis compounds. This shall be contrasted with the values of  $^2J_{PP}$  later in our discussion.

In the tungsten complexes  $^{183}W-^{19}F$  couplings of approximately 30 Hz were observed. To our knowledge these are the first values of  $^2J_{WF}$  reported. An attempt to determine the signs of  $^1J_{WP}$  and  $^2J_{WF}$  relative to  $^1J_{PF}$  in  $W(CO)_5(X)$  by double resonance INDOR techniques was unsuccessful because of the difficulty in matching the impedance of the frequency synthesizer at 2.47 MHz to the probe which must also have an input of 56.4 MHz. Moreover the frequency synthesizer did not generate sufficient power to irradiate  $^{183}W$ . The relative signs of  $^1J_{WP}$  and  $^2J_{WF}$  however were found to be the same.

### Proton Spectra

The n.m.r. data other than phosphorus-phosphorus coupling constants for compounds of (I) through (IX) are given in Tables 3-10. In general the chemical shifts of the protons on the carbons nearest to the phosphorus atom follow the trend  $L(\text{ligand}) < Cr, Mo \text{ and } W \text{ complexes of } L < Pd \text{ and } Pt \text{ complexes of } L < S=L < O=L$ . It is conceivable that the increased deshielding of these protons is a result of the increase in electronegativity of the metal moiety and the dominance of this

Table 3. Proton n.m.r. data of compounds of (I)

Compound	N (Hz)	$^2J_{PH}$ (Hz)	$^4J_{PH}$ (Hz)	$\delta H$ (p.p.m.) <sup>a</sup>	Solvent
(I) <sup>b</sup>		+2.7 $\pm$ 0.1		0.89	neat
<u>cis</u> -Cr(CO) <sub>4</sub> (I) <sub>2</sub>	-6.9 $\pm$ 0.1	-7.1 $\pm$ 0.2	+0.2 $\pm$ 0.2	0.99	C <sub>6</sub> H <sub>6</sub>
<u>trans</u> -Cr(CO) <sub>4</sub> (I) <sub>2</sub>	-7.4 $\pm$ 0.1	-7.7 $\pm$ 0.2	+0.3 $\pm$ 0.2	1.18	C <sub>6</sub> H <sub>6</sub>
<u>cis</u> -Mo(CO) <sub>4</sub> (I) <sub>2</sub>	-6.3 $\pm$ 0.1	-6.6 $\pm$ 0.2	+0.3 $\pm$ 0.2	0.99	C <sub>6</sub> H <sub>6</sub>
<u>cis</u> -W(CO) <sub>4</sub> (I) <sub>2</sub> <sup>c</sup>	-7.09 $\pm$ 0.02	-7.34 $\pm$ 0.05	+0.25 $\pm$ 0.05	1.08	C <sub>6</sub> H <sub>6</sub>
<u>cis</u> -PdCl <sub>2</sub> (I) <sub>2</sub> <sup>d</sup>	10.6	$\pm$ 11.7	$\bar{7}$ 1.1	1.73	CH <sub>2</sub> Cl <sub>2</sub>
<u>trans</u> -PdI <sub>2</sub> (I) <sub>2</sub>	-7.0 $\pm$ 0.1	-10.0 $\pm$ 0.2	+3.0 $\pm$ 0.2	1.85	CDCl <sub>3</sub>
O=(I) <sup>e</sup>		13.4		1.93	D <sub>2</sub> O
S=(I) <sup>b</sup>		-13.0 $\pm$ 0.1		1.74	neat

<sup>a</sup>Downfield from tetramethylsilane.

<sup>b</sup>Values from reference 84.

<sup>c</sup> $^1J_{WP} = \pm 209.8$  Hz;  $^3J_{WH} = \pm 1.9$  Hz.

<sup>d</sup>Values from reference 85.

<sup>e</sup>Values from reference 86.

Table 4. Proton n.m.r. data of compounds of (II)

Compound	N or ${}^2J_{\text{PH}}$ (Hz) <sup>a</sup>	$\delta\text{H}$ (p.p.m.) <sup>b</sup>	Solvent
(II)	8.0	4.30	$\text{CCl}_4$
<u>cis</u> - $\text{PdCl}_2(\text{II})_2$	0	4.70	$\text{CH}_3\text{CN}$
<u>trans</u> - $\text{PdCl}_2(\text{II})_2$	0	4.70	$\text{CH}_2\text{Cl}_2$
$\text{O}=(\text{II})^{\text{c}}$	7.3	4.40	$\text{CDCl}_3$
$\text{S}=(\text{II})^{\text{c}}$	5.6	4.49	$(\text{CH}_3)_2\text{CO}$

<sup>a</sup> $N = {}^2J_{\text{PH}} + {}^4J_{\text{PH}}$  for the palladium complexes;  $N = {}^2J_{\text{PH}}$  for the other compounds.

<sup>b</sup>Chemical shifts of the methylene protons downfield from tetramethylsilane. The chemical shifts of the methyl proton (ca. 1.3 p.p.m.) are not given.

<sup>c</sup>Values from reference 55.

Table 5. Proton n.m.r. data of compounds of (III)

Compound	N or ${}^2J_{\text{PH}}$ (Hz) <sup>a</sup>	$\delta\text{H}$ (p.p.m.) <sup>b</sup>	Solvent
(III)	6.1	3.78	$\text{CCl}_4$
<u>cis</u> - $\text{Mo}(\text{CO})_4(\text{III})_2$	0	3.38	$\text{C}_6\text{H}_6$
<u>trans</u> - $\text{PdCl}_2(\text{III})_2$	0	4.14	$\text{CH}_2\text{Cl}_2$
<u>trans</u> - $\text{PdI}_2(\text{III})_2$	0	3.77	$\text{C}_6\text{H}_6$

<sup>a</sup> $N = {}^2J_{\text{PH}} + {}^4J_{\text{PH}}$  for the complexes;  $N = {}^2J_{\text{PH}}$  for (III).

<sup>b</sup>Downfield from tetramethylsilane.

Table 6. Proton n.m.r. data of compounds of (IV)

Compound	$^3J_{PH}$ (Hz)	$\delta H$ (p.p.m.) <sup>a</sup>	Solvent
(IV)	10.0	2.26	CDCl <sub>3</sub>
<u>trans</u> -Cr(CO) <sub>4</sub> (IV) <sub>2</sub>	15.7	2.40	CDCl <sub>3</sub>
<u>cis</u> -Mo(CO) <sub>4</sub> (IV) <sub>2</sub>	15.5	2.03	C <sub>6</sub> H <sub>6</sub>
<u>cis</u> -W(CO) <sub>4</sub> (IV) <sub>2</sub>	15.7	2.38	CH <sub>2</sub> Cl <sub>2</sub>

<sup>a</sup>Downfield from tetramethylsilane.

Table 7. Proton n.m.r. data of compounds of (V)

Compound	$^3J_{PH}$ (Hz)	$\delta H$ (p.p.m.) <sup>a</sup>	Solvent
(VA)	2.1	2.87	CH <sub>2</sub> Cl <sub>2</sub>
<u>cis</u> -Cr(CO) <sub>4</sub> (VA) <sub>2</sub>	3.5	3.15	CH <sub>2</sub> Cl <sub>2</sub>
<u>trans</u> -Cr(CO) <sub>4</sub> (VB) <sub>2</sub>	3.5	3.10	CDCl <sub>3</sub>
<u>cis</u> -Mo(CO) <sub>4</sub> (VA) <sub>2</sub>	3.1	3.05	CDCl <sub>3</sub>
<u>cis</u> -W(CO) <sub>4</sub> (VA) <sub>2</sub>	3.5	3.11	CDCl <sub>3</sub>
O=(VA) <sup>b</sup>	11.6	3.38	C <sub>5</sub> H <sub>5</sub> N
S=(VA) <sup>b</sup>	10.0	3.32	C <sub>5</sub> H <sub>5</sub> N

<sup>a</sup>Chemical shifts of the methylene protons. The chemical shifts of the alkyl chains (ca. 1 p.p.m.) are not given.

<sup>b</sup>Values from reference 58.

Table 8. Proton n.m.r. data of compounds of (VI) and (VII)

Compound	$^3J_{\text{PH}}$ (Hz) <sup>a</sup>	$\delta\text{H}$ (p.p.m.) <sup>b</sup>	Solvent
(VI)	+8.8 $\pm$ 0.1 <sup>c</sup>	2.42 <sup>d</sup>	neat
(VII)	2.8	2.67 <sup>d</sup>	CDCl <sub>3</sub>
<u>trans</u> -Cr(CO) <sub>4</sub> (VI) <sub>2</sub>	+9.84 $\pm$ 0.02	2.65	C <sub>6</sub> H <sub>6</sub>
1,2,4-Mn(CO) <sub>3</sub> (VI) <sub>2</sub> Cl	9.2	2.70	C <sub>6</sub> H <sub>6</sub>
1,2,4-Mn(CO) <sub>3</sub> (VI) <sub>2</sub> Br	9.2	2.70	C <sub>6</sub> H <sub>6</sub>
<u>cis</u> -Mo(CO) <sub>4</sub> (VI) <sub>2</sub>	10.9	2.60	C <sub>6</sub> H <sub>6</sub>
<u>cis</u> -Mo(CO) <sub>4</sub> (VII) <sub>2</sub>	9.2	3.10 <sup>d</sup>	CDCl <sub>3</sub>
<u>trans</u> -Mo(CO) <sub>4</sub> (VI) <sub>2</sub>	+10.2 $\pm$ 0.1	2.67	C <sub>6</sub> H <sub>6</sub>
<u>trans</u> -W(CO) <sub>4</sub> (VI) <sub>2</sub>	+10.4 $\pm$ 0.1	2.56	C <sub>6</sub> H <sub>6</sub>
<u>trans</u> -Fe(CO) <sub>3</sub> (VI) <sub>2</sub>	+9.6 $\pm$ 0.1	2.67	C <sub>6</sub> H <sub>6</sub>
Ni(CO) <sub>2</sub> (VI) <sub>2</sub>	9.3	2.47	C <sub>6</sub> H <sub>6</sub>
<u>cis</u> -PdCl <sub>2</sub> (VI) <sub>2</sub>	9.7	2.63	C <sub>6</sub> H <sub>6</sub>
<u>trans</u> -PdCl <sub>2</sub> (VI) <sub>2</sub>	10.1	2.77	C <sub>6</sub> H <sub>6</sub>
<u>trans</u> -PdI <sub>2</sub> (VI) <sub>2</sub>	10.3	2.40	C <sub>6</sub> H <sub>6</sub>
<u>cis</u> -PtCl <sub>2</sub> (VI) <sub>2</sub>	9.4	2.78	CH <sub>2</sub> Cl <sub>2</sub>
<u>trans</u> -PtCl <sub>2</sub> (VI) <sub>2</sub>	10.1	2.83	CH <sub>2</sub> Cl <sub>2</sub>
<u>trans</u> -PtI <sub>2</sub> (VI) <sub>2</sub>	10.0	2.81	CH <sub>2</sub> Cl <sub>2</sub>
O=(VI)	+9.30 $\pm$ 0.03 <sup>c</sup>	2.62	neat
S=(VI) <sup>e</sup>	11.0	2.62	

<sup>a</sup>Values obtained at the ambient temperature of the probe (ca. 30°).

<sup>b</sup>Downfield from tetramethylsilane.

<sup>c</sup>Value from reference 54.

<sup>d</sup>Chemical shift of the methyl protons. The chemical shifts of the phenyl proton were ca. 7.1 p.p.m.

<sup>e</sup>Values from reference 87. The solvent used (if any) was not given.

Table 9. Proton n.m.r. data of compounds of (VIII)

Compound	$^3J_{\text{PtH}}$ (Hz)	$\delta\text{H}$ (p.p.m.) <sup>a</sup>	Solvent
(VIII) <sup>b</sup>	+10.0 $\pm$ 0.1	3.69	neat
1,2,3-Mn(CO) <sub>3</sub> (VIII) <sub>2</sub> Br	10.4	3.50	C <sub>6</sub> H <sub>6</sub>
1,2,4-Mn(CO) <sub>3</sub> (VIII) <sub>2</sub> I	10.7	3.51	C <sub>6</sub> H <sub>6</sub>
<u>cis</u> -Mo(CO) <sub>4</sub> (VIII) <sub>2</sub>	+11.6 $\pm$ 0.1	3.68	CDCl <sub>3</sub>
<u>trans</u> -Mo(CO) <sub>4</sub> (VIII) <sub>2</sub>	+11.6 $\pm$ 0.1	3.65	CDCl <sub>3</sub>
<u>cis</u> -PdCl <sub>2</sub> (VIII) <sub>2</sub>	+12.9 $\pm$ 0.2	3.89	CDCl <sub>3</sub>
PdI <sub>2</sub> (VIII) <sub>2</sub> <sup>c</sup>	broad	3.45	C <sub>6</sub> H <sub>6</sub>
<u>cis</u> -PtCl <sub>2</sub> (VIII) <sub>2</sub> <sup>d</sup>	12.7	3.88	CDCl <sub>3</sub>
<u>cis</u> -PtI <sub>2</sub> (VIII) <sub>2</sub> <sup>e</sup>	12.9	3.82	CH <sub>2</sub> Cl <sub>2</sub>
O=(VIII) <sup>b</sup>	+10.5 $\pm$ 0.1	3.46	neat
S=(VIII) <sup>f</sup>	+12.9 $\pm$ 0.1		neat

<sup>a</sup>Downfield from tetramethylsilane.

<sup>b</sup>Values from reference 84.

<sup>c</sup>Although cis in the solid state, the compound appears to be a cis-trans mixture in solution.

<sup>d</sup> $^4J_{\text{PtH}} = 2.5$  Hz.

<sup>e</sup> $^4J_{\text{PtH}} = 2.2$  Hz.

<sup>f</sup>Value from reference 84; the proton chemical shift was not reported.

Table 10. Proton n.m.r. data of compounds of (IX)

Compound	$^3J_{PH}$ (Hz)	$\delta H$ (p.p.m.) <sup>a</sup>	Solvent
(IXA)	2.00	3.93	$CDCl_3$
<u>cis</u> -Cr(CO) <sub>4</sub> (IXA) <sub>2</sub>	4.65	4.23	$(CH_3)_2CO$
<u>trans</u> -Cr(CO) <sub>4</sub> (IXB) <sub>2</sub>	4.11	4.29	$(CH_3)_2CO$
1,2,3-Mn(CO) <sub>3</sub> (IXC) <sub>2</sub> Br	4.7	4.30	$CHCl_3$
<u>cis</u> -Mo(CO) <sub>4</sub> (IXC) <sub>2</sub>	4.30	4.21	$(CH_3)_2CO$
<u>trans</u> -Mo(CO) <sub>4</sub> (IXC) <sub>2</sub>	4.20	4.28	$(CH_3)_2CO$
<u>cis</u> -W(CO) <sub>4</sub> (IXC) <sub>2</sub>	4.50	4.23	$(CH_3)_2CO$
<u>trans</u> -W(CO) <sub>4</sub> (IXC) <sub>2</sub>	4.40	4.17	$CDCl_3$
<u>trans</u> -Fe(CO) <sub>3</sub> (IXB) <sub>2</sub>	4.92	4.35	$(CH_3)_2CO$
<u>trans</u> -PdI <sub>2</sub> (IXD) <sub>2</sub>	$\sim 2^b$	4.37	$CH_2Cl_2$
<u>cis</u> -PdCl <sub>2</sub> (IXD) <sub>2</sub>	5.50	4.42	$CH_2Cl_2$
<u>cis</u> -PtI <sub>2</sub> (IXD) <sub>2</sub>	5.70	4.42	$CH_2Cl_2$
<u>cis</u> -PtCl <sub>2</sub> (IXD) <sub>2</sub>	5.65	4.47	DMSO
Ni(CO) <sub>2</sub> (IXA) <sub>2</sub>	4.00	4.10	$CDCl_3$
O=(IXA) <sup>c</sup>	6.00	4.48	$CH_3CN$
S=(IXA) <sup>c</sup>	7.00	4.48	$CH_3CN$

<sup>a</sup>Chemical shifts of the methylene protons downfield from tetramethylsilane. The chemical shifts of the alkyl chains (ca. 1 p.p.m.) are not given.

<sup>b</sup>Poor resolution of the apparent triplet did not permit the accurate determination of  $^3J_{PH}$ .

<sup>c</sup>Values from reference 88.

effect over any tendency toward back donation from the metal. The presence of several discrepancies in this trend, however, admits of the possibility of one or more subtle influences which at times may override the inductive effect. Moreover the use of different solvents may cause minor variations in the chemical shifts.

The general trend of the AX coupling constants  ${}^3J_{\text{POCH}}$  and  ${}^3J_{\text{PNCH}}$  as more electronegative groups are bound to the fourth site on phosphorus is toward increased frequency. McFarlane (84) has shown that  ${}^3J_{\text{POCH}}$  is positive in (VIII), and the oxide and sulfide of (VIII). Although the signs of  ${}^3J_{\text{POCH}}$  in derivatives of (IX) have not been determined, the values of  ${}^3J_{\text{POCH}}$  in analogous bicyclic compounds  $\text{XP}(\text{OCH}_2)_3\text{PY}$  ( $\text{X} = \text{e}^-$  pair, O, S;  $\text{Y} = \text{e}^-$  pair, O) have been shown to be positive and follow a trend similar to that of derivatives of (VIII) (54). It is therefore likely that  ${}^3J_{\text{POCH}}$  in derivatives of (IX) are positive. It has also been shown that  ${}^3J_{\text{PNCH}}$  in (VI) and its quinquivalent derivatives is positive (54). In trialkyl phosphines,  ${}^2J_{\text{PCH}}$  is positive (84, 89) or slightly negative (84) but it changes to negative in quinquivalent species such as  $\text{O}=\text{(I)}$  and  $\text{S}=\text{(I)}$  (84). Cullingworth et al. (90) have shown that  ${}^2J_{\text{PH}}$  in (I) reverses sign in forming complexes with organoaluminum compounds and Boros et al. (55) have presented evidence that the same phenomenon occurs when (II) is co-ordinated to a variety of acceptors. The sign determinations in the transition



metal complexes reported here is the first definitive proof that  ${}^2J_{PH}$  in (I) changes from positive to negative upon coordination.

It has also been found that there is AX' coupling in disubstituted complexes of (I). From the separation of the  $\chi = 1$  and  $\chi = 2$  inner lines in cis-W(CO)<sub>4</sub>(I)<sub>2</sub> (see Figure 6) it was possible to estimate  $J_{AX'}$  and  $J_{AA'}$  using Equations 12 and 13 (49).

$$|J_{AA'}| = [3S_i(1) + S_i(2)][S_i(1) - S_i(2)]/2[3S_i(1) - S_i(2)] \quad 12$$

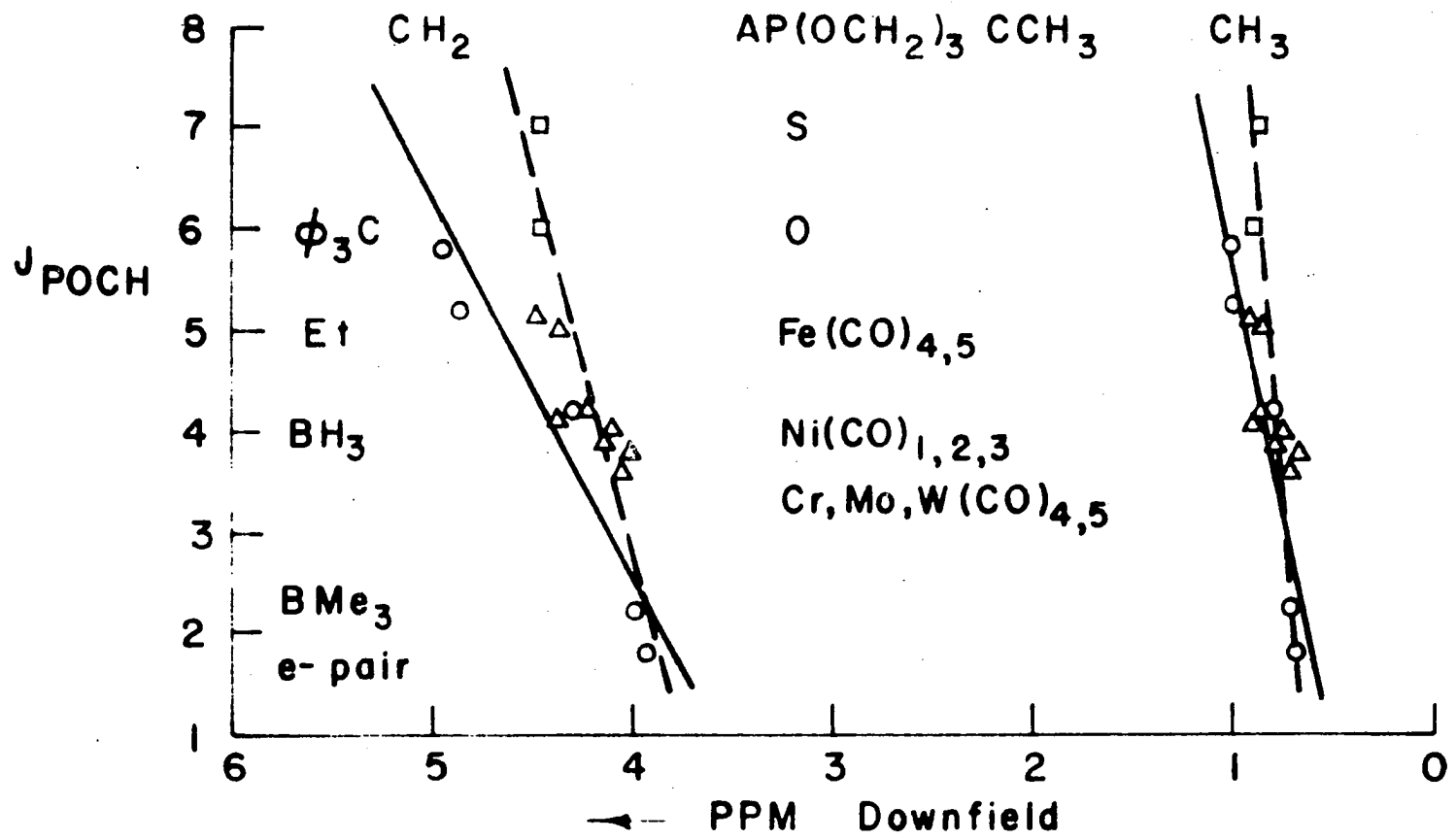
$$L^2 = [S_i(1)][S_i(2)][S_i(1) + S_i(2)]/[3S_i(1) - S_i(2)] \quad 13$$

Using these equations and the value of  $N = 7.09$  Hz, the following coupling constants were calculated:  $J_{AA'} = 22.9$  Hz,  $J_{AX} = \mp 7.22$  Hz and  $J_{AX'} = \pm 0.13$  Hz. The value of  $J_{AA'}$  from the separation of the  $\chi = 1$  inner and outer lines was 25.0 Hz. The values obtained from Equations 12 and 13 are rather imprecise since a change of 0.01 Hz in  $S_i(1)$  or  $S_i(2)$  changes  $J_{AA'}$  by ca. 3 Hz. Using 25.0 Hz for the value of  $J_{AA'}$ , the computer program given in the Appendix gave values of  $J_{AX} = -7.34 \pm 0.05$  and  $J_{AX'} = + 0.25 \pm 0.05$  Hz. The values of  $J_{AX}$  and  $J_{AX'}$  in the other complexes given in Table 3 were also obtained using the computer program. It is interesting that the values of  $J_{AX'}$  ( ${}^4J_{PH}$ ) in the palladium complexes is much larger than in the Group VI complexes and also that  $J_{AX'}$  is larger in

the trans complexes than in the cis analogs.

An attempt to correlate the chemical shifts of the protons and the values of  $^3J_{\text{PH}}$  in the complexes of (IXA) was of interest in view of the apparent linear correlations of these parameters in Y(IXA) where Y =  $e^-$  pair,  $\text{B}(\text{CH}_3)_3$ ,  $\text{BH}_3$ ,  $\text{CH}_3\text{CH}_2^+$ , and  $(\text{C}_6\text{H}_5)\text{C}^+$  (59). The plot in Figure 11 shows these correlations for the  $\beta$  and  $\gamma$  protons for the boron and carbon acceptor systems as solid lines and the new apparent linear correlations for some monosubstituted carbonyl complexes of (IXA) are shown as dashed lines. Although the monosubstituted carbonyl derivatives were chosen because of the better comparison of an  $\text{M}(\text{CO})_n$  than an  $\text{M}(\text{CO})_{n-1}\text{L}$  acceptor to systems like  $\text{BR}_3$  and  $\text{R}^+$ , the disubstituted derivatives also cluster on the dashed lines. Previously (59) it was noticed that the chalcogenides of (IXA) did not fall near the line generated by the  $\text{BR}_3$  and  $\text{R}^+$  adducts. These adducts, which fall on the solid lines, form single bonds with phosphorus whereas the chalcogenides form double bonds. The fact that there is a linear correlation of the transition metal complexes and the chalcogenides would seem to indicate that there is some degree of double bond character in the phosphorus-metal bond. The solid line correlations were obtained from the n.m.r. spectra taken in  $\text{CD}_3\text{CN}$  whereas the dashed line correlations were obtained using  $(\text{CH}_3)_2\text{CO}$ , DMSO,  $\text{CDCl}_3$  and  $\text{CH}_2\text{Cl}_2$  solutions because of solubility considerations. The observations are believed to be valid in spite of the variation

Figure 11. Correlation of proton chemical shifts with  $^3J_{\text{PH}}$  in derivatives of (IXA)



in solvents because the ligand shows only minor variations in its proton chemical shift in these solvents.

#### Mixed Ligand Complexes

Complexes containing two different phosphorus ligands are useful in that  $^{31}\text{P}$ - $^{31}\text{P}$  coupling constants can be obtained directly from the  $^{31}\text{P}$  spectrum since the phosphorus atoms are chemically non-equivalent. Prior to this, few bis-monodentate mixed ligand complexes have been prepared (91) because the synthesis of the desired complex is complicated by the formation of all other possible complexes.

The n.m.r. data other than the  $^{31}\text{P}$ - $^{31}\text{P}$  coupling values are given in Table 11. The proton n.m.r. spectra of the cis-molybdenum complexes and trans- $\text{Mo}(\text{CO})_4$  (VIII) (IXB) consist of two doublets (excluding the  $\text{C}_2\text{H}_5$  proton resonances) whose intensity ratio allowed their unique assignment to the  $\text{OCH}_3$ ,  $\text{N}(\text{CH}_3)_2$  or  $\text{OCH}_2$  groups each coupled over three bonds to a phosphorus atom. Although similar assignments could be made for the  $\text{OCH}_2$  and  $\text{N}(\text{CH}_3)_2$  proton resonances in the remaining two trans complexes, the doublets were significantly perturbed as shown in Figure 12.

The reason for the simple and perturbed doublets in the  $^1\text{H}$  n.m.r. traces of these compounds became clear upon observation of the  $^{31}\text{P}$  resonance absorptions. The two cis compounds exhibited simple AX patterns consisting of two doublets (broadened by  $^3J_{\text{PH}}$  coupling) in the  $^{31}\text{P}$  region whereas the

Table 11. N.M.R. data for mixed ligand complexes

Complex	Ligand	$\delta^1\text{H}^a$ (p.p.m.)	$^3\text{J}_{\text{PH}}^b$ (Hz)	$\delta^{31}\text{P}^c$ (p.p.m.)
<u>cis</u> -Mo(CO) <sub>4</sub> (VIII) (IXB)	(VIII)	3.61	11.7	-164.3
	(IXB)	4.17 <sup>d</sup>	4.2	-139.6
<u>trans</u> -Mo(CO) <sub>4</sub> (VIII) (IXB)	(VIII)	3.61	11.7	-176.4
	(IXB)	4.21 <sup>d</sup>	4.3	-148.0
<u>cis</u> -Mo(CO) <sub>4</sub> (VI) (IXB)	(VI)	2.60	10.0	-145.0
	(IXB)	4.16 <sup>d</sup>	4.2	-138.0
<u>trans</u> -Mo(CO) <sub>4</sub> (VI) (IXB)	(VI)	2.62	10.2	-153.7
	(IXB)	4.22 <sup>d</sup>	4.2	-147.9
<u>trans</u> -Fe(CO) <sub>3</sub> (VI) (IXC)	(VI)	2.60	10.0	-164.3
	(IXC)	4.21 <sup>d</sup>	4.9	-168.4

<sup>a</sup>Downfield from tetramethylsilane ( $\pm 0.01$  p.p.m.).

<sup>b</sup> $\pm 0.1$  Hz.

<sup>c</sup>Downfield from 85% aqueous phosphoric acid ( $\pm 0.5$  p.p.m.).

<sup>d</sup>Chemical shift of the methylene protons. The chemical shift of the alkyl chain (ca. 1 p.p.m.) is not given.

trans-Mo(CO)<sub>4</sub>(VIII) (IXB) although showing some AB character, was very nearly an AX spectrum. The <sup>31</sup>P spectra of the other two trans compounds were distinct AB patterns similarly broadened by <sup>3</sup>J<sub>PH</sub>. The spin classification of the pertinent

nuclei in the latter compounds (excluding the  $C_xH_{2x+1}$  protons) can be designated  $M_mABY_n$  where M and Y are the protons in (VI) ( $m = 18$ ) and (IX) ( $n = 6$ ) respectively, and A and B are the phosphorus nuclei in the aminophosphine and bicyclic phosphite. The amount of perturbation in the proton region depends on  $J_{AB}$  and the difference in chemical shift of the A and B nuclei ( $\nu_A - \nu_B$ ). If  $J_{AB} \ll (\nu_A - \nu_B)$  then no perturbation is observed as is the case in trans- $Mo(CO)_4$  (VIII) (IXB). If  $J_{AB} \approx (\nu_A - \nu_B)$  then the perturbation is similar to that observed for the other two trans compounds (Figure 12). If  $J_{AB} \gg (\nu_A - \nu_B)$  apparent triplets would be produced in the proton n.m.r. spectrum. In the two  $M_mABY_n$  systems reported here the AB coupling ( ${}^2J_{PP}$ ) results in  $2m + 1$  pairs of lines in the M region and  $2n + 1$  pairs in the Y portion of the spectrum even though  $J_{AY}$  and  $J_{BM}$  are zero. Hence the doublets in the proton spectra (Figure 12) reveal the envelopes of the  $2m + 1$  and  $2n + 1$  lines as a perturbation on the doublets.

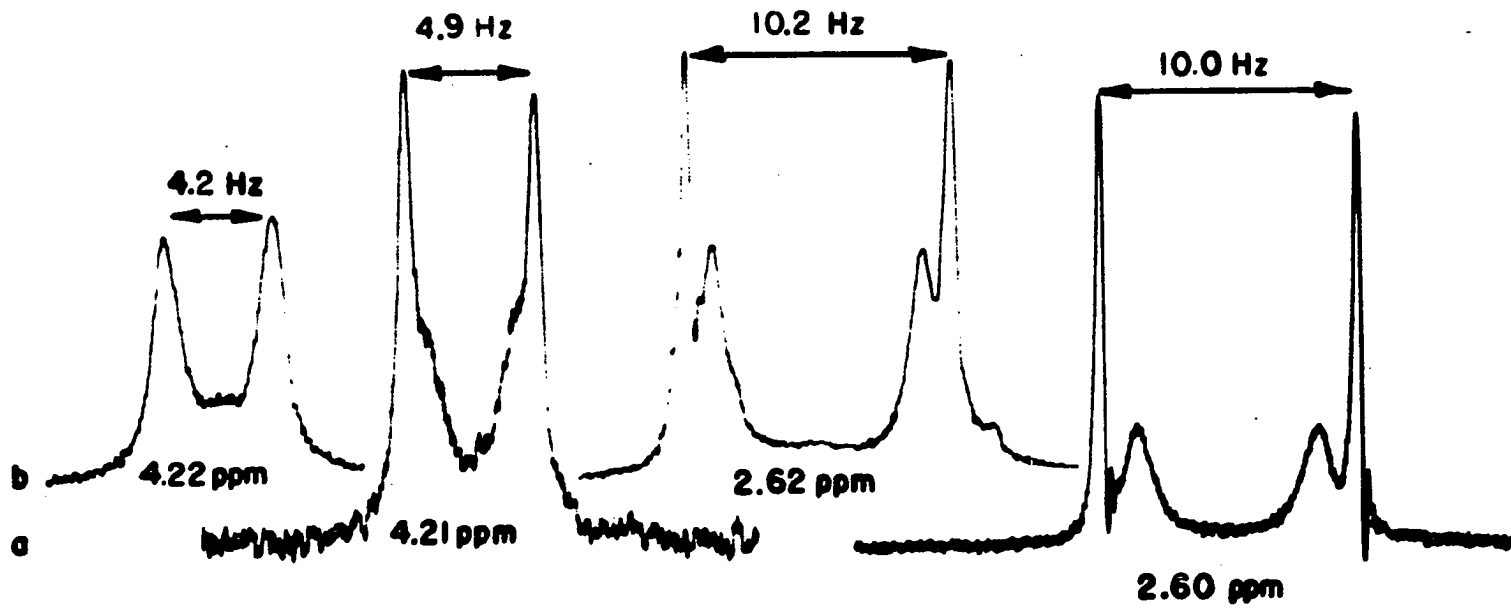
The observation that the n.m.r. spectrum of the protons on one ligand is not split by the phosphorus atom on the other ligand in these mixed ligand complexes is good evidence that  ${}^5J_{PH} = 0$  not only in these compounds but in complexes of (VI), (VIII) and (IX) in which both ligands are the same. The assumption that  $J_{AX}, ({}^5J_{PH})$  was zero was a requirement of the computer program in order to solve  $J_{AA}$ . Moreover  $N = J_{AX}$  so that our assignments of  ${}^3J_{PH}$  in Tables 6-10 are valid.

Figure 12. Proton n.m.r. spectra (not including  $C_xH_{2x+1}$  chain)

a. Trans-Fe(CO)<sub>3</sub>(VI)(IXC)

b. Trans-Mo(CO)<sub>4</sub>(VI)(IXB)





## Phosphorus-Phosphorus Coupling

The  $^{31}\text{P}$ - $^{31}\text{P}$  coupling constants that have been determined in this work and most of those that have been determined by other authors are given in Tables 12-20. The values for complexes of (VI) are only reported if they were obtained by double resonances techniques or by observing the outer lines. The values for complexes of (II) and (III) are not reported since  $N = 0$  and the apparent triplet was not observed.

The repeated observation in a variety of systems (92) that trans phosphorus-phosphorus couplings are large and are characterized by apparent triplets in the spectrum while cis couplings are small leaving the  $J_{\text{AX}}$  doublet unperturbed, has served as a criterion for determining the geometrical relationships of phosphorus ligands in many complexes. However considerable caution should be taken in using the observations of apparent triplets to assign the stereochemistry of complexes. Many cis complexes have appreciable phosphorus-phosphorus coupling and from the data available it appears that the magnitudes of  $^2J_{\text{PP}}$  in cis and trans manganese complexes are approximately equal and indeed in chromium complexes the magnitude of  $^2J_{\text{PP}}$  is even greater in cis compounds than in trans. Furthermore, weak  $^{31}\text{P}$ - $^{31}\text{P}$  coupling can lead to apparent triplets when  $J_{\text{AX}}$  is small. This was observed in cis- $\text{Mo}(\text{CO})_4(\text{VA})_2$ .

Other than in chromium and manganese compounds, phosphorus-phosphorus couplings are generally larger in trans compounds

Table 12.  $^{31}\text{P}$ - $^{31}\text{P}$  coupling constants in chromium complexes

Compound	$^2J_{\text{PP}}$ (Hz)	Method <sup>a</sup>
<u>cis</u> -Cr(CO) <sub>4</sub> (I) <sub>2</sub>	-36 ± 1	A
<u>trans</u> -Cr(CO) <sub>4</sub> (I) <sub>2</sub>	-28.5 ± 1	A
<u>trans</u> -Cr(CO) <sub>4</sub> (IV) <sub>2</sub>	~0	F
<u>cis</u> -Cr(CO) <sub>4</sub> (VA) <sub>2</sub>	~0	F
<u>trans</u> -Cr(CO) <sub>4</sub> (VB) <sub>2</sub>	~0	F
<u>trans</u> -Cr(CO) <sub>4</sub> (VI) <sub>2</sub>	-17 ± 5	C
<u>cis</u> -Cr(CO) <sub>4</sub> (IXA) <sub>2</sub>	70 ± 10	D
<u>trans</u> -Cr(CO) <sub>4</sub> (IXB) <sub>2</sub>	9 ± 3	D
<u>cis</u> -Cr(CO) <sub>4</sub> (X) <sub>2</sub>	78 ± 1	B
<u>trans</u> -Cr(CO) <sub>4</sub> (X) <sub>2</sub>	34 ± 1	B
<u>cis</u> -Cr(CO) <sub>4</sub> (XI) <sub>2</sub>	-26.2 <sup>b,c</sup>	A
<u>cis</u> -Cr(CO) <sub>4</sub> (XI)(XIX)	33.0 <sup>b</sup>	E
<u>trans</u> -Cr(CO) <sub>4</sub> (XIV)(XIX)	25 <sup>d</sup>	E
<u>trans</u> -Cr(CO) <sub>4</sub> (XIV)(XXI)	30 <sup>d</sup>	E
<u>cis</u> -Cr(CO) <sub>4</sub> (XXIII) <sub>2</sub>	67 ± 1 <sup>e</sup>	B
<u>cis</u> -Cr(CO) <sub>4</sub> (XXV) <sub>2</sub>	62 ± 2 <sup>e</sup>	B
<u>cis</u> -Cr(CO) <sub>4</sub> (XXX)	28.5 ± 0.5 <sup>e</sup>	B

<sup>a</sup>Methods of obtaining values of  $^2J_{\text{PP}}$  are:

- A - separation of  $\chi = 1$  inner and outer lines in the  $^1\text{H}$  spectrum
- B - separation of  $\chi = 1$  inner and outer lines in the  $^{19}\text{F}$  spectrum
- C - double resonance techniques
- D - computer simulation of the band shape
- E - direct observation in the  $^{31}\text{P}$  spectrum
- F - perturbation of main doublet was not observed.

<sup>b</sup>Values from reference 93.

<sup>c</sup>J. F. Nixon, Brighton, England. Sign determination of  $^2J_{\text{PP}}$  in cis-Cr(CO)<sub>4</sub>(XI)<sub>2</sub>. Private communication. 1969.

<sup>d</sup>Values from reference 91.

<sup>e</sup>Values from reference 94.

Table 13.  $^{31}\text{P}$ - $^{31}\text{P}$  coupling constants in molybdenum complexes

Compound	$^2J_{\text{PP}}$ (Hz)	Method <sup>a</sup>
<u>cis</u> -Mo(CO) <sub>4</sub> (I) <sub>2</sub>	-29.7 ± 0.1	A
<u>cis</u> -Mo(CO) <sub>4</sub> (IV) <sub>2</sub>	30 ± 10	D
<u>cis</u> -Mo(CO) <sub>4</sub> (VA) <sub>2</sub>	35 ± 10	D
<u>cis</u> -Mo(CO) <sub>4</sub> (VI) <sub>2</sub>	12.4 ± 0.2	A
<u>trans</u> -Mo(CO) <sub>4</sub> (VI) <sub>2</sub>	+101 ± 1	A
<u>cis</u> -Mo(CO) <sub>4</sub> (VII) <sub>2</sub>	18.2 ± 0.2	A
<u>cis</u> -Mo(CO) <sub>4</sub> (VIII) <sub>2</sub>	-40.5 ± 1	A
<u>trans</u> -Mo(CO) <sub>4</sub> (VIII) <sub>2</sub>	+162 ± 5	C
<u>cis</u> -Mo(CO) <sub>4</sub> (IXC) <sub>2</sub>	50 ± 10	D
<u>trans</u> -Mo(CO) <sub>4</sub> (IXC) <sub>2</sub>	210 ± 30	D
<u>cis</u> -Mo(CO) <sub>4</sub> (VI)(IXB)	39 ± 3	E
<u>trans</u> -Mo(CO) <sub>4</sub> (VI)(IXB)	141 ± 3	E
<u>cis</u> -Mo(CO) <sub>4</sub> (VIII)(IXB)	48 ± 3	E
<u>trans</u> -Mo(CO) <sub>4</sub> (VIII)(IXB)	185 ± 3	E
<u>cis</u> -Mo(CO) <sub>4</sub> (X) <sub>2</sub>	55 ± 1	B
<u>trans</u> -Mo(CO) <sub>4</sub> (X) <sub>2</sub>	312 ± 1	B
<u>cis</u> -Mo(CO) <sub>4</sub> (XI) <sub>2</sub>	18.3 <sup>b</sup>	A

<sup>a</sup>Methods of obtaining values of  $^2J_{\text{PP}}$  are:

- A - separation of  $\chi = 1$  inner and outer lines in the  $^1\text{H}$  spectrum
- B - separation of  $\chi = 1$  inner and outer lines in the  $^{19}\text{F}$  spectrum
- C - double resonance techniques
- D - computer simulation of the band shape
- E - direct observation in the  $^{31}\text{P}$  spectrum.

<sup>b</sup>Value from reference 93.

Table 13 (Continued)

Compound	${}^2J_{PP}$ (Hz)	Method <sup>a</sup>
<u>trans</u> -Mo(CO) <sub>4</sub> (XIV)(XIX)	50 <sup>c</sup>	E
<u>cis</u> -Mo(CO) <sub>4</sub> (XVII)(XIX)	21 <sup>c</sup>	E
<u>trans</u> -Mo(CO) <sub>4</sub> (XVII)(XIX)	49 <sup>c</sup>	E
<u>trans</u> -Mo(CO) <sub>4</sub> (XIV)(XXI)	112 <sup>c</sup>	E
<u>cis</u> -Mo(CO) <sub>4</sub> (XXII) <sub>2</sub>	42.5 ± 0.5 <sup>d</sup>	B
<u>cis</u> -Mo(CO) <sub>4</sub> (XXIII) <sub>2</sub>	-48.0 ± 0.5 <sup>d</sup>	B
<u>cis</u> -Mo(CO) <sub>4</sub> (XXV) <sub>2</sub>	38 ± 2 <sup>d</sup>	B
<u>cis</u> -Mo(CO) <sub>4</sub> (XXVI) <sub>2</sub>	38 ± 1 <sup>d</sup>	B
<u>cis</u> -Mo(CO) <sub>4</sub> (XXXIII) <sub>2</sub>	49 ± 1 <sup>d</sup>	B
<u>cis</u> -Mo(CO) <sub>4</sub> (XXX)	+121 <sup>e</sup>	B
<u>cis</u> -Mo(CO) <sub>4</sub> (XVIII) <sub>2</sub>	~19 <sup>f</sup>	A
<u>fac</u> -Mo(CO) <sub>3</sub> (X) <sub>3</sub>	56.4 ± 1.2 <sup>e</sup>	B
<u>fac</u> -Mo(CO) <sub>3</sub> (XXIV) <sub>3</sub>	43 ± 1 <sup>e</sup>	B
<u>fac</u> -Mo(CO) <sub>3</sub> (XXVIII) <sub>3</sub>	55.2 <sup>e</sup>	B
<u>fac</u> -Mo(CO) <sub>3</sub> (XXIX) <sub>3</sub>	51.0 <sup>e</sup>	B
<u>mer</u> -Mo(CO) <sub>3</sub> (VIII) <sub>3</sub>	47 <sup>g</sup>	E
<u>mer</u> -Mo(CO) <sub>3</sub> (XII) <sub>3</sub>	≤15 <sup>g</sup>	E
<u>mer</u> -Mo(CO) <sub>3</sub> (XX) <sub>3</sub>	51 <sup>g</sup>	E

<sup>c</sup>Values from reference 91.

<sup>d</sup>Values from reference 95.

<sup>e</sup>Values from reference 94.

<sup>f</sup>Value calculated from spectrum in reference 96.

<sup>g</sup>Values from reference 97.

Table 14.  $^{31}\text{P}$ - $^{31}\text{P}$  coupling constants in tungsten complexes

Compound	$^2J_{\text{PP}}$ (Hz)	Method <sup>a</sup>
<u>cis</u> -W(CO) <sub>4</sub> (I) <sub>2</sub>	-25.0 ± 0.1	A
<u>cis</u> -W(CO) <sub>4</sub> (IV) <sub>2</sub>	~0	F
<u>cis</u> -W(CO) <sub>4</sub> (VA) <sub>2</sub>	~0	F
<u>trans</u> -W(CO) <sub>4</sub> (VI) <sub>2</sub>	+81 ± 5	C
<u>cis</u> -W(CO) <sub>4</sub> (IXC) <sub>2</sub>	35 ± 5	D
<u>trans</u> -W(CO) <sub>4</sub> (IXC) <sub>2</sub>	140 ± 25	D
<u>cis</u> -W(CO) <sub>4</sub> (X) <sub>2</sub>	38 ± 1	B
<u>trans</u> -W(CO) <sub>4</sub> (X) <sub>2</sub>	315 ± 1	B
<u>cis</u> -W(CO) <sub>4</sub> (XI) <sub>2</sub>	13.4 <sup>b</sup>	A
<u>trans</u> -W(CO) <sub>4</sub> (XIV)(XIX)	65 <sup>c</sup>	E
<u>trans</u> -W(CO) <sub>4</sub> (XIV)(XXI)	120 <sup>c</sup>	E
<u>trans</u> -W(CO) <sub>4</sub> (XVII)(XXI)	112 <sup>c</sup>	E
<u>cis</u> -W(CO) <sub>4</sub> (XXII) <sub>2</sub>	33 ± 1 <sup>d</sup>	B
<u>cis</u> -W(CO) <sub>4</sub> (XXIII) <sub>2</sub>	38.0 ± 0.5 <sup>d</sup>	B
<u>cis</u> -W(CO) <sub>4</sub> (XXV) <sub>2</sub>	21 ± 1 <sup>d</sup>	B
<u>cis</u> W(CO) <sub>4</sub> (XXX)	155.3 ± 0.6 <sup>d</sup>	B

<sup>a</sup>Methods of obtaining values of  $^2J_{\text{PP}}$  are:

- A - separation of  $\chi = 1$  inner and outer lines in the  $^1\text{H}$  spectrum
- B - separation of  $\chi = 1$  inner and outer lines in the  $^{19}\text{F}$  spectrum
- C - double resonance techniques
- D - computer simulation of the band shape
- E - direct observation in the  $^{31}\text{P}$  spectrum
- F - perturbation of main doublet was not observed.

<sup>b</sup>Value from reference 93.

<sup>c</sup>Values from reference 91.

<sup>d</sup>Values from reference 94.

Table 15.  $^{31}\text{P}$ - $^{31}\text{P}$  coupling constants in manganese complexes

Compound	$^2J_{\text{PP}}$ (Hz)	Method <sup>a</sup>
1,2,3-Mn(CO) <sub>3</sub> (VIII) <sub>2</sub> Br	140 ± 20	D
1,2,4-Mn(CO) <sub>3</sub> (VIII) <sub>2</sub> I	170 ± 30	D
1,2,3-Mn(CO) <sub>3</sub> (IXC) <sub>2</sub> Br	110 ± 20	D
1,2,3-HMn(CO) <sub>3</sub> (X) <sub>2</sub>	125 ± 1	B
1,2,4-HMn(CO) <sub>3</sub> (X) <sub>2</sub>	155 ± 1	B

<sup>a</sup>Methods of obtaining  $^2J_{\text{PP}}$  are:

B - separation of the  $\chi = 1$  inner and outer lines in the  $^{19}\text{F}$  spectrum

D - computer simulation of the band shape.

Table 16.  $^{31}\text{P}$ - $^{31}\text{P}$  coupling constants in iron complexes

Compound	$^2J_{\text{PP}}$ (Hz)	Method <sup>a</sup>
<u>trans</u> -Fe(CO) <sub>3</sub> (VI) <sub>2</sub>	+65 ± 10	C
<u>trans</u> -Fe(CO) <sub>3</sub> (VI)(IXC)	183 ± 1	E
<u>trans</u> -Fe(CO) <sub>3</sub> (IXB)	300 ± 40	D
Fe(CO) <sub>3</sub> (X) <sub>2</sub> <sup>b</sup>	98 ± 1	B

<sup>a</sup>Methods of obtaining values of  $^2J_{\text{PP}}$  are:

B - separation of the  $\chi = 1$  inner and outer lines in the  $^{19}\text{F}$  spectrum

C - double resonance techniques

D - computer simulation of the band shape

E - direct observation in the  $^{31}\text{P}$  spectrum.

<sup>b</sup>Molecule is undergoing intramolecular exchange. Value obtained is a time average of all possible isomers.

Table 17.  $^{31}\text{P}$ - $^{31}\text{P}$  coupling constants in rhodium complexes

Compound	$^2J_{\text{PP}}$ (Hz)	Method <sup>a</sup>
<u>mer</u> -RhCl <sub>3</sub> (XIII) <sub>3</sub>	22 ± 3 <sup>b</sup>	E
<u>mer</u> -RhCl <sub>3</sub> (XIV) <sub>3</sub>	21 ± 3 <sup>b</sup>	E
<u>mer</u> -RhCl <sub>3</sub> (XVI) <sub>3</sub>	30 ± 8 <sup>b</sup>	E
1,2,4-RhCl <sub>3</sub> (XIV) <sub>2</sub> (XXI)	30.3 <sup>c</sup>	E

<sup>a</sup>Method of obtaining values of  $^2J_{\text{PP}}$  is:

E - direct observation in the  $^{31}\text{P}$  spectrum.

<sup>b</sup>Values from reference 98.

<sup>c</sup>Value from reference 99.

than in their cis isomers. This appears to be true especially with palladium and platinum complexes. Although  $|^2J_{\text{PP}}|$  is not always larger in trans compounds than in cis it does appear that  $|^3J_{\text{PP}}|$  in disubstituted complexes of (X) is larger in trans complexes than in cis.

The nature of the metal atom plays a definite role in determining  $^2J_{\text{PP}}$ . The most intensely studied series with the same stereochemistry consists of Group VI complexes. The data shows that the order of magnitude for cis couplings is Cr > Mo > W. For the trans couplings there appears to be less order other than that the  $^2J_{\text{PP}}$  values in Mo and W complexes are much larger than in their Cr analogues. From the few results for other groups, it is difficult to observe meaningful trends but



Table 18.  $^{31}\text{P}$ - $^{31}\text{P}$  coupling constants in nickel complexes

Compound	$^2J_{\text{PP}}$ (Hz)	Method <sup>a</sup>
$\text{Ni}(\text{CO})_2(\text{VI})_2$	$\sim 0$	F
$\text{Ni}(\text{CO})_2(\text{VIII})_2$	$10 \pm 3^{\text{b}}$	A
$\text{Ni}(\text{CO})_2(\text{IXA})_2$	$\sim 0$	F
$\text{Ni}(\text{CO})_2(\text{X})_2$	$38 \pm 1$	B
$\text{Ni}(\text{CO})_2(\text{XXV})_2$	$\sim 0^{\text{c}}$	F
$\text{Ni}(\text{CO})_2(\text{XXVI})_2$	$\sim 0^{\text{c}}$	F
$\text{Ni}(\text{CO})_2(\text{XXXI})_2$	$\sim 0^{\text{d}}$	F
$\text{Ni}(\text{CO})(\text{XXV})_3$	$\sim 0^{\text{c}}$	F
$\text{Ni}(\text{X})_4$	$< 19^{\text{c}}$	B
$\text{Ni}(\text{XXII})_4$	$< 15^{\text{e}}$	B
$\text{Ni}(\text{XXIII})_4$	$21 \pm 5^{\text{c}}$	B
$\text{Ni}(\text{XXVII})_4$	$\sim 15^{\text{c}}$	B
$\text{Ni}(\text{XXIX})_4$	$17.7^{\text{c}}$	B
$\text{Ni}(\text{XXXIII})_4$	$< 10^{\text{c}}$	B

<sup>a</sup>Methods of obtaining values of  $^2J_{\text{PP}}$  are:

- A - separation of  $\chi = 1$  inner and outer lines in the  $^1\text{H}$  spectrum
- B - separation of  $\chi = 1$  inner and outer lines in the  $^{19}\text{F}$  spectrum
- F - perturbation of main doublet was not observed.

<sup>b</sup>Value calculated from the spectrum in reference 100.

<sup>c</sup>Values from reference 94.

<sup>d</sup>Value from reference 101.

<sup>e</sup>Value from reference 102.

Table 19.  $^{31}\text{P}$ - $^{31}\text{P}$  coupling constants in palladium complexes

Compound	$^2J_{\text{PP}}$ (Hz)	Method <sup>a</sup>
<u>cis</u> -PdCl <sub>2</sub> (I) <sub>2</sub>	8 <sup>b</sup>	A
<u>trans</u> -PdI <sub>2</sub> (I) <sub>2</sub>	+572 ± 5	C
<u>cis</u> -PdCl <sub>2</sub> (VIII) <sub>2</sub>	+79.9 ± 0.2	A
<u>cis</u> -PdCl <sub>2</sub> (IXD) <sub>2</sub>	65 ± 10	D
<u>trans</u> -PdI <sub>2</sub> (I)(XII)	565 <sup>b</sup>	E
<u>trans</u> -PdI <sub>2</sub> (XIV)(XV)	551 <sup>c</sup>	E
<u>trans</u> -PdI <sub>2</sub> (XIV)(XXI)	758 <sup>c</sup>	E
<u>trans</u> -PdI <sub>2</sub> (XV)(XXI)	829 <sup>c</sup>	E
<u>trans</u> -PdCl <sub>2</sub> (XXXII) <sub>2</sub>	1100 ± 50 <sup>d</sup>	D

<sup>a</sup>Methods of obtaining values of  $^2J_{\text{PP}}$  are:

A - separation of the  $\chi = 1$  inner and outer lines in the  $^1\text{H}$  spectrum

C - double resonance techniques

D - computer simulation of the band shape

E - direct observation in the  $^{31}\text{P}$  spectrum.

<sup>b</sup>Values from reference 99.

<sup>c</sup>Values from reference 85.

<sup>d</sup>Value from reference 103. The value, however, is dubious since the author neglected the effect of  $^{31}\text{P}$ - $^1\text{H}$  coupling.

it does appear that couplings in palladium complexes are greater than in platinum complexes.

From the limited data available, the other ligands in a given complex appear to affect the value of  $^2J_{\text{PP}}$  relatively

Table 20.  $^{31}\text{P}$ - $^{31}\text{P}$  coupling constants in platinum complexes

Compound	$^2J_{\text{PP}}$ (Hz)	Method <sup>a</sup>
<u>cis</u> -PtCl <sub>2</sub> (VI) <sub>2</sub>	~0	F
<u>cis</u> -PtCl <sub>2</sub> (VIII) <sub>2</sub>	10 ± 2	D
<u>cis</u> -PtI <sub>2</sub> (VIII) <sub>2</sub>	~0	F
<u>cis</u> -PtCl <sub>2</sub> (IXD) <sub>2</sub>	35 ± 10	D
<u>cis</u> -PtI <sub>2</sub> (IXD) <sub>2</sub>	14 ± 5	D

<sup>a</sup>Methods of obtaining values of  $^2J_{\text{PP}}$  are:

D - computer simulation of the band shape

F - perturbation of main doublet was not observed.

slightly. Compounds in which only the halides are varied suggest that  $^2J_{\text{PP}}$  increases in magnitude from I to Cl. A similar small effect has been observed for  $^1J_{\text{PtP}}$  in some platinum complexes (104).

The most significant factor affecting phosphorus-phosphorus coupling is the electronegativity of the substituents on phosphorus. In most cases as the electronegativity increases,  $|^2J_{\text{PP}}|$  increases. The most notable exception to this is in the series of trans chromium complexes.

Up to now we have discussed the various trends considering only the magnitudes of  $^2J_{\text{PP}}$ . However coupling constants can have both negative and positive signs. For most coupling constants between two specified nuclei the sign is dependent only on the number of bonds between the nuclei. The observation

(105) that a sign change in  $^1J_{PP}$  took place upon altering the groups attached to phosphorus in diphosphorus compounds of the type  $R_2PPR_2$  made it of critical importance to determine the signs of  $^2J_{PP}$  in coordination complexes. The signs determined for cis compounds of Group VI indicate that all the signs are negative and that  $^2J_{PP}$  becomes more negative as the substituents on phosphorus become more electronegative. On the other hand  $^2J_{PP}$  for trans compounds of Group VI appears to become more positive as the electronegativity of the substituents increases. The signs of  $^2J_{PP}$  in trans-Cr(CO)<sub>4</sub>(I)<sub>2</sub> and trans-Cr(CO)<sub>4</sub>(VI)<sub>2</sub>, however, were also found to be negative. The apparent anomaly in the magnitudes of  $^2J_{PP}$  for the trans chromium compounds can thus be explained by assuming that  $^2J_{PP}$  goes through zero as the electronegativity of the substituents increases. The trends that can be formulated by considering both magnitudes and signs are illustrated in Figures 13 and 14. The one exception in Figure 13 is cis-Mo(CO)<sub>4</sub>(VI)<sub>2</sub>. This compound, however, readily isomerizes to trans-Mo(CO)<sub>4</sub>(VI)<sub>2</sub> and it is believed that the bulk of the ligand has distorted the molecule and that the P-Mo-P angle is greater than 90°. In light of the fact that complexes with tetrahedral symmetry have  $^{31}P$ - $^{31}P$  couplings of almost zero and that trans couplings are positive it is not unreasonable to expect  $^2J_{PP}$  in cis-Mo(CO)<sub>4</sub>(VI)<sub>2</sub> to be more positive than normally would be expected.

Figure 13. Variation of  ${}^2J_{PP}$  with the electronegativity of substituents on phosphorus for cis complexes of Group VI

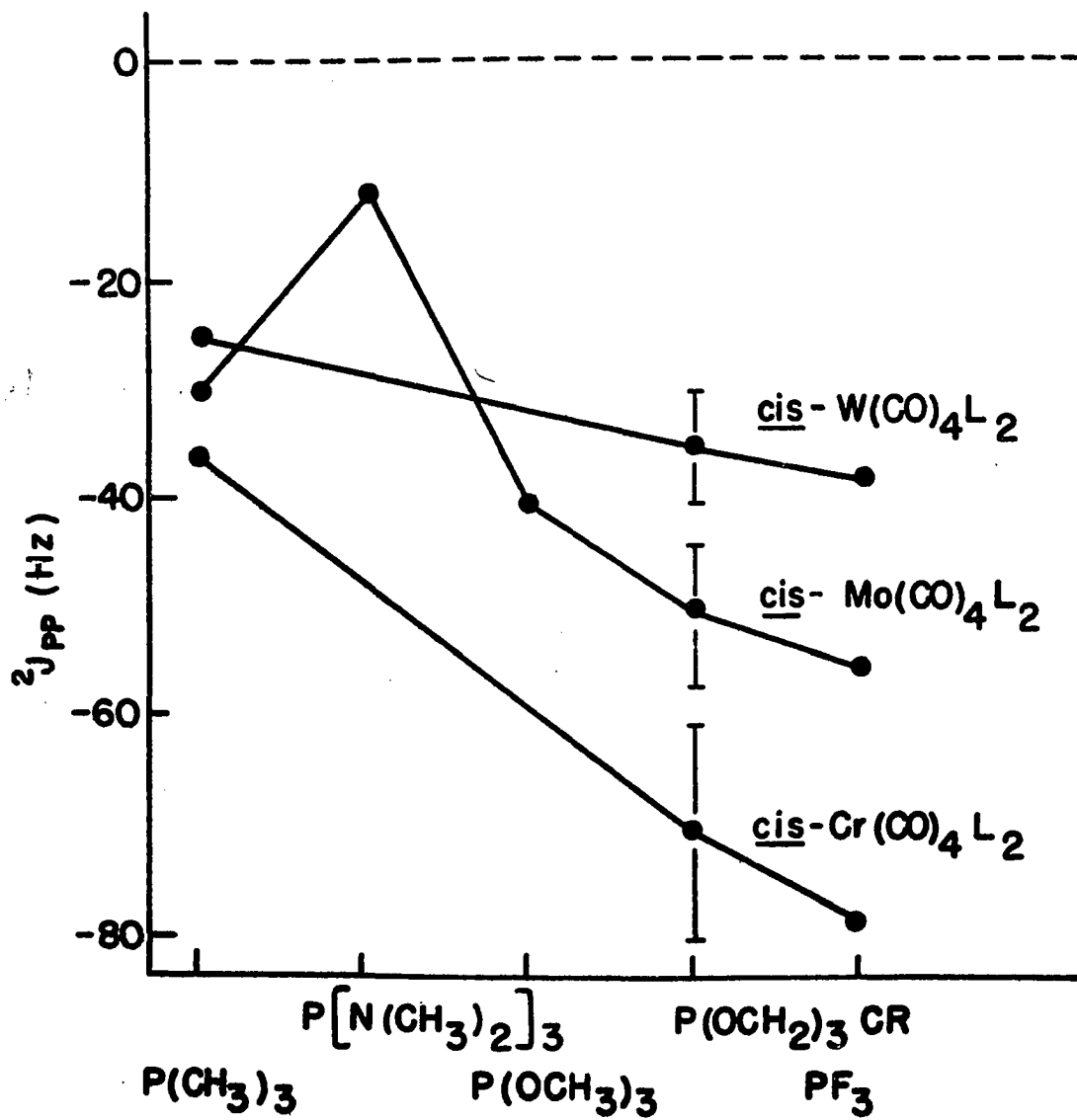
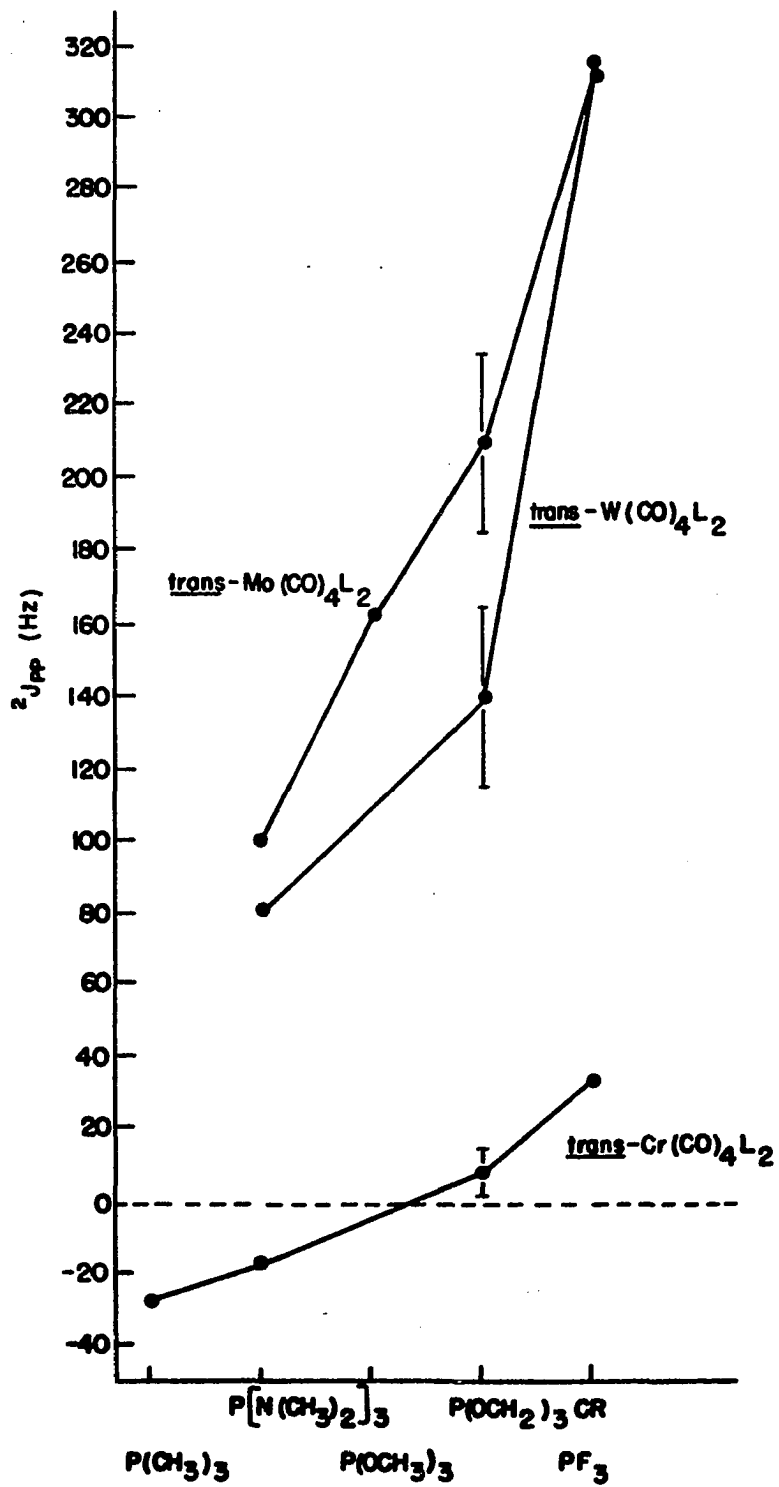


Figure 14. Variation of  ${}^2J_{pp}$  with the electronegativity of substituents on phosphorus for trans complexes of Group VI





The signs of  ${}^2J_{PP}$  in both cis-PdCl<sub>2</sub>(VIII)<sub>2</sub> and trans-PdI<sub>2</sub>(I)<sub>2</sub> were found to be positive. Trends can not be constructed from the limited data known for the palladium and platinum cases but it may be for these metals that the  ${}^2J_{PP}$  values for both the cis and trans configurations are positive, and become more positive as the electronegativity of the substituents on phosphorus increases.

Although signs of coupling constants could not be determined for complexes containing the bicyclic phosphite ligands, it is probable that our assignment in Figures 13 and 14 is correct. This conclusion is reached from the data obtained for the mixed ligand complexes. It is expected that the values of  ${}^2J_{PP}$  in the mixed ligand complexes should be intermediate in value between the values for the two analogous complexes in which both ligands are the same. If a sign change between complexes of (IX) and (VI) or (VIII) were occurring, the magnitudes of  ${}^2J_{PP}$  in the mixed ligand complexes should be less than  ${}^2J_{PP}$  in complexes in which both ligands are the same. Since this does not happen, our assignment is probably correct.

Since  ${}^{31}P$ - ${}^{31}P$  couplings found in co-ordination compounds are transmitted via the metal atom, metal-phosphorus couplings might be expected to parallel the trends found for the  ${}^2J_{PP}$  values. Although there are few metals with suitable nuclei in sufficient abundance for such studies, several papers dealing with metal-phosphorus couplings have been published (98, 104, 106-111). Indeed the values of  ${}^1J_{MP}$  are dependent upon the

substituents on phosphorus and the magnitudes of both  $^1J_{WP}$  and  $^1J_{PtP}$  in tungsten (106) and platinum (109) complexes, respectively, increase as the electronegativity of the substituents increase. Grim et al. (110) had ascribed their observed linear correlation of  $^1J_{WP}$  with  $\nu(\text{CO})$  in the series  $\text{W}(\text{CO})_5\text{L}$  [ $\text{L} = \text{PR}_3$ ,  $\text{PR}_2(\text{C}_6\text{H}_5)$ ,  $\text{PR}(\text{C}_6\text{H}_5)_2$ ,  $\text{P}(\text{C}_6\text{H}_5)_3$ ] to the increased  $\pi$  back bonding expected from  $\text{PR}_3$  to  $\text{P}(\text{C}_6\text{H}_5)_3$ . Over a larger range of electronegativity of substituents, however, the correlation between  $^1J_{WP}$  and  $\nu(\text{CO})$  breaks down (106).

Platinum-phosphorus coupling constants are greatly affected by the nature of the ligand trans to the phosphorus atom (104). Grim and coworkers (109) had discussed the large platinum-phosphorus coupling constants in terms of  $\pi$ -bonding. The concept of using  $\pi$ -bonding to explain coupling constants has been criticized by Schneider and Buckingham (41) who pointed out that the large  $^{195}\text{Pt}-^1\text{H}$  coupling constants are observed in platinum hydride complexes in which there can be no  $\pi$ -bonding. A similar criticism could be made for any explanation using  $\pi$ -bonding to account for  $^{31}\text{P}-^{31}\text{P}$  couplings since  $^2J_{\text{PH}}$  values in metal hydride complexes containing phosphorus ligands follow trends analogous to that observed for the  $^2J_{\text{PP}}$  values (112). If  $\pi$ -bonding were a significant factor,  $^2J_{\text{PP}}$  in cis complexes would be expected to be highly influenced by ligands trans to the phosphorus atoms. The closeness of  $^2J_{\text{PP}}$  in cis- $\text{Mo}(\text{CO})_4(\text{VIII})_2$  (40 Hz) and in mer- $\text{Mo}(\text{CO})_3(\text{VIII})_3$  (47 Hz) suggests that  $\pi$ -bonding is of little importance.

Pidcock and coworkers (104, 108) have suggested that the dependence of  ${}^1J_{PtP}$  on the ligand trans to phosphorus is due to an inductive effect. Ligands with a strong  $\sigma$  inductive character effectively reduce the positive charge on the platinum and thus weaken the overlap of the phosphorus and metal orbitals trans to the group in comparison to the case, where the phosphorus ligands are trans to one another. Thus in compounds of the type  $PtX_2(PR_3)_2$  where X is a phenyl or silyl group,  ${}^1J_{PtP}$  is greater in trans compounds than in the cis analogs whereas the opposite observations were made on these isomers when X is an electronegative group such as a halogen. These arguments are based on all  ${}^{195}Pt$ - ${}^{31}P$  coupling constants being positive which is likely (113). Inasmuch as a CO group is a poorer  $\sigma$  inducting group than a phosphine, the observation (114) that  ${}^1J_{WP}$  is larger in trans- $W(CO)_4(PR_3)_2$  than in the cis compound would suggest that  ${}^1J_{WP}$  is negative if the inductive arguments are correct.

In valence bond formalism the Fermi contact contribution to a coupling constant is dependent mainly upon the effective nuclear charges of the two coupling nuclei and the s character in the bonds between the nuclei (115). In the series (I), (VI), (VIII), (IX), (X) the effective nuclear charge on the phosphorus should increase as the electronegativity of the substituents increases. Thus the magnitude of  ${}^2J_{pp}$  should increase because of the effective nuclear charge as more electronegative substituents are placed on phosphorus. However, using

the arguments of Bent (116) an increase in the s character in the metal-phosphorus bond should also result in an increase in  $^2J_{PP}$ . Bent contends that hybridizational changes will occur such that s character concentrates in orbitals directed toward electropositive substituents. Changes in hybridization might reasonably be expected to cause changes in bond angles. Unfortunately few crystal structures have been determined on metal complexes containing the ligands used in this study. However the angles between the substituent atoms in the chalcogenide derivatives might reasonably be taken as indicative of the trend in metal complexes. In compounds of the type  $XPR_3$  (X = S, Se, or O) CPC bond angles are between  $106^\circ$  and  $108^\circ$  (27). The OPO angle in the oxide of (IXA) is  $104^\circ$  (117) while the FPF angles in the oxide and sulfide of (X) are  $102.5^\circ$  and  $100.3^\circ$  respectively (116). Although no structures of derivatives of (VI) have been determined, it is probable that the angles in the oxide are nearly tetrahedral. Thus both s character and effective nuclear charge can account for the trends observed and it is difficult to separate the two effects.

One criticism of the s character argument is that it does not readily take into account changes in signs of coupling constants. Thus an increase in s character is associated with an increase in the coupling constant. Manatt et al. (89), however, have shown that in the H-C-P fragment, the geminal coupling becomes smaller or more negative as the s character of the

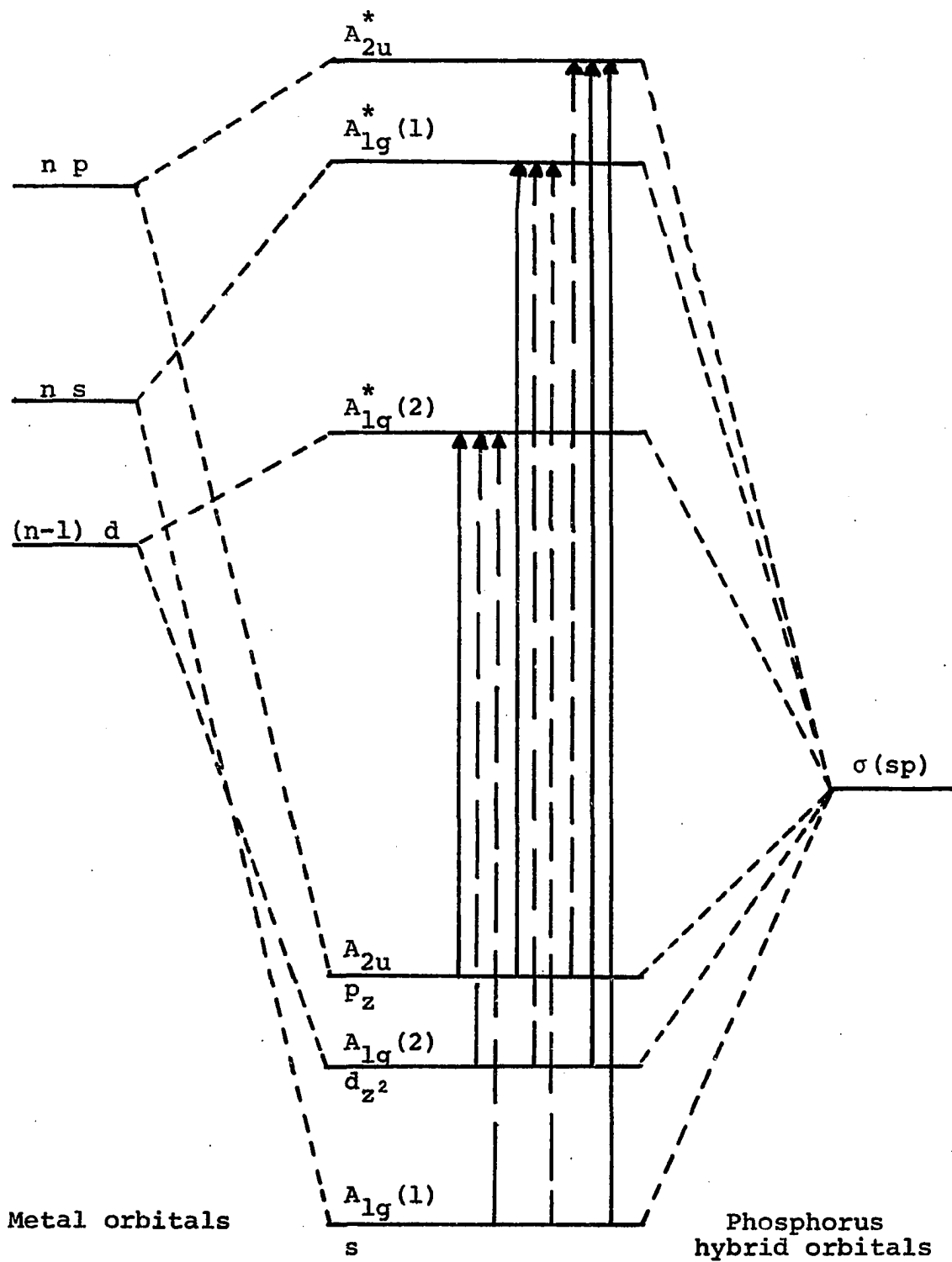
phosphorus atom bonding orbitals to carbon increases while the geminal coupling becomes greater or more positive as the s character of the carbon atom bonding orbital to phosphorus increases.

From Equations 3 and 4 it can be seen that in the molecular orbital theory of Pople and Santry (40), the Fermi contact contribution to a coupling constant is dependent on the magnitudes of the valence s orbitals at the coupling nuclei, the inverse of the energy difference  $(\epsilon_i - \epsilon_j)^{-1}$  and the product of the coefficients of the s atomic orbitals of the coupling sites in the molecular orbitals  $\psi_i$  (occupied) and  $\psi_j$  (unoccupied). Although the magnitude of the s electron density at the nucleus would be expected to increase with substituents of increasing electronegativity, causing an increase in  ${}^2J_{PP}$ , it is unlikely that the variation in coupling constants can be explained by this. It would appear that the dominant effect in determining coupling constants is the mutual polarizability. Good evidence for this is given by the molecule cis-PtCl(CH<sub>3</sub>)(XII)<sub>2</sub> which has two platinum-phosphorus coupling constants which differ widely (1719 Hz and 4179 Hz) (107). It is obvious that the s electron density at Pt must be the same for each coupling constant and that those at P will be nearly the same since identical ligands are involved. The large difference in  ${}^1J_{PtP}$  must therefore be due to differences in the orbitals used in the Pt-P bonds. Moreover, although the s electron densities at the nuclei can

affect the magnitudes of coupling constants they cannot affect the signs. Thus the change in sign for  ${}^2J_{PP}$  for the trans chromium complexes shows that changes in the coefficients of the s atomic orbitals must be dominating any change in the magnitudes of the s orbitals at the nuclei.

The difficulty in predicting even the sign of  ${}^2J_{PP}$  in coordination complexes is illustrated in the simple M.O. diagram in Figure 15. This diagram would be suitable for a trans disubstituted Group VI carbonyl complex assuming  $D_{4h}$  symmetry in which only the  $\sigma$ -bonds between the metal and the two phosphorus atoms have been considered and sp hybrids have been employed for the phosphorus orbitals. The arrows connect the molecular orbitals that contribute to the Fermi contact term. The solid and broken arrows represent transitions which give positive and negative contributions, respectively, to the Fermi term. Clearly the magnitude and sign of  ${}^2J_{PP}$  will depend on the order of these molecular orbitals, their energy differences and the magnitudes of the s atomic orbitals of phosphorus in the various molecular orbitals. Without detailed calculations, however, it is impossible to predict the signs of  ${}^2J_{PP}$ . As more electronegative substituents are placed on phosphorus the degree of s character in the sp hybrids of the phosphorus atoms should increase but it is not possible a priori to predict in which molecular orbitals this s character will concentrate. Thus even trends within a given series of the same metal with the same stereochemistry are not predictable. With cis compounds

Figure 15. Molecular orbital diagram for a disubstituted complex of  $D_{4h}$  symmetry considering only the  $\sigma$ -bonds formed with the phosphorus atoms. The positive and negative contributions to the Fermi contact term are illustrated by solid and broken arrows respectively





of lower symmetry prediction of signs of  ${}^2J_{PP}$  becomes even more difficult due to extensive configuration interaction.

Although the results do not indicate that metal-phosphorus  $\pi$ -bonding is important in affecting coupling constants this does not mean that metal-phosphorus  $\pi$ -bonding is absent. Indeed, far infrared studies (118, 119) indicate that  $\pi$ -bonding is significant in determining trends in metal-phosphorus stretching frequencies. This presents the intriguing possibility that n.m.r. in conjunction with far infrared studies may yield considerable information about metal-phosphorus bonding which might allow the separation of  $\sigma$  and  $\pi$  effects.

## SUGGESTIONS FOR FUTURE WORK

In this dissertation are reported the initial study of  $^{31}\text{P}$ - $^{31}\text{P}$  coupling in transition metal complexes. A large number of possibilities are open for future work. In any future determinations of  $^2J_{\text{PP}}$ , the signs of the coupling constants should be obtained whenever possible. Also the evaluation of  $^2J_{\text{PP}}$  by computer simulation should be done only if the values cannot be obtained by other methods.

Although paramagnetic impurities in solutions of  $\text{Mn}(\text{CO})_3\text{L}_2\text{X}$  (L = phosphorus ligand, X = halogen) caused slight broadening of the lines in the n.m.r. spectra making them unsuitable for analysis by computer simulation, it is probable that the signs and magnitudes of  $^2J_{\text{PP}}$  can be obtained by double resonance techniques. These and the analogous rhenium complexes should be studied. The effects of other ligands could be studied with these compounds since Cl, Br, I and other anionic ligands can be coordinated to the metal.

Effects of the electronegativity of substituents could be studied further by preparing complexes with ligands of the type  $\text{PRX}_2$ ,  $\text{PR}_2\text{X}$ ,  $\text{P}(\text{OR})\text{X}_2$ ,  $\text{P}(\text{OR})_2\text{X}$  and possibly  $\text{P}(\text{NR}_2)_2\text{X}$  (R = methyl, X = Cl, Br and perhaps I).

Complexes of other metals, notably the platinum metals Ru, Rh, Os and Ir, should be prepared. It would be advantageous to study the effect of the oxidation state of the metal on  $^2J_{\text{PP}}$  as well.

Trisubstituted meridial complexes of the Group VI metal carbonyls should be prepared to further test the hypothesis that  $\pi$ -bonding is of little importance in affecting  ${}^2J_{PP}$ . Preparation of these compounds however might be quite difficult.

More complexes of (II) and (III) should be prepared. Although the values of  $N({}^2J_{CH} + {}^4J_{CH})$  in complexes of these ligands were approximately zero, the expected values of  ${}^2J_{PP}$  are small enough that the outer lines should be detectable.

Mixed ligand complexes of Cr, Mo, W, Mn, Re and Fe should be prepared. The present instrumentation permits obtaining the  ${}^{31}P$  spectrum by INDOR techniques with sample quantities that are much smaller than those required to observe the  ${}^{31}P$  spectrum directly. Of primary interest would be mixed ligand complexes containing one of (I), (II), (III), (X) or (XI). With these ligands in a complex it should be possible to determine the signs of  ${}^2J_{PP}$  because the phosphorus atom in the other ligand will couple to the protons or fluorine in these ligands as well as the phosphorus atoms. It should be noted that preliminary studies have indicated that pure mixed ligand complexes of manganese could be obtained readily.

The dependence of the isomerization of cis- $Mo(CO)_4(IX)_2$  to the trans isomer on the length of the alkyl chain in the 4 position of the ligand and the failure of cis- $Mo(CO)_4(VA)_2$  to isomerize should be investigated more fully.

The unusual properties of (VI) should be examined by observing the effects of temperature, concentration and solvent on the n.m.r., near infrared and far infrared spectra of (VI), the oxide and sulfide of (VI), as well as mono and disubstituted complexes of (VI).

In order to further understand  $^{31}\text{P}$ - $^{31}\text{P}$  coupling in transition metal complexes it is necessary to carry out molecular orbital calculations. Unfortunately the symmetry of many of the complexes is too low to make this feasible and the spectra of complexes with more phosphorus ligands giving higher symmetry generally can not be analyzed.

Possibilities for molecular orbital calculations are nickel and platinum complexes of the type  $\text{ML}_2\text{L}'_2$  where L and L' are chemically similar ligands such as two phosphites or two phosphines. If the ligands were chosen such that the  $^{31}\text{P}$  chemical shifts were significantly different then the  $^{31}\text{P}$  spectrum with noise decoupling of the protons would be a simple  $\text{A}_2\text{X}_2$  system. However the ligands could be assumed to be identical for the purpose of the molecular orbital calculations resulting in a molecule of  $\text{T}_d$  symmetry.

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## APPENDIX

The computer program VIRCUP B. described here was written to analyze the  $X_n AA'X'_n$  spin system. From the input data the program will calculate the line positions and relative intensities using Equations 5 to 11, scale the intensities to correspond to the observed spectrum, and plot the band shape such that a direct comparison of the fit may be made with the observed spectrum. The following assumptions and restrictions have been made: (a) all nuclei have spin 1/2 (b)  $J_{XX'} = 0$  (c)  $J_{AX'} = J_{A'X} = 0$  (d)  $n \leq 18$  (e) all transitions have Lorentzian line shape with uniform line widths. Although the restriction that  $J_{AX'} = 0$  is not necessitated by the computer program it is required in order to determine  $J_{AA'}$  from Equations 7, 8 and 11. From these equations it can be seen that either  $L$  or  $J_{AA'}$  must be known in order to determine the other by a curve fitting procedure. In most of the complexes the assumption that  $J_{AX'} = 0$  is reasonable since the A and X' nuclei are separated by five bonds. When  $J_{AX'} = 0$ ,  $L = N = J_{AX}$  which is the separation of the intense doublet in the spectra. In the case where  $J_{AX'} \neq 0$ ,  $J_{AA'}$  must be determined by other means and then the program can be used to determine  $L$ .

A Lorentzian curve is given by the equation:

$$y = \frac{1}{a + bx^2}$$

The Bloch equations (120) describing the interaction of the nuclear magnetization with a radiofrequency field can be put in this form (for the absorption mode) if a steady state is assumed. Thus a Lorentzian line shape is valid only under slow passage conditions. From Equation 14 it can be shown that:

$$y_{\max.} = 1/a \quad 15$$

$$a = b(x_{1/2})^2 \quad 16$$

where  $x_{1/2}$  is the value of  $x$  at  $y = 1/2 y_{\max.}$ . Therefore the height and width at half height completely describe any Lorentzian curve.

In the following sections are given the input data, the computer listing and descriptions of operations performed, the output data and a curve matching. As an example throughout we shall use cis-PdCl<sub>2</sub>(IXD)<sub>2</sub>.

#### Input Data

##### Card 1

Columns 1-20 Alphameric label for x-axis of graph.

Columns 21-40 Alphameric label for y-axis of graph.

Columns 41-60 Alphameric label for graph identification.

Card 1 has FORMAT (16A4).

##### Card 2 to M-1

Columns 1-3 Job number to identify data set FORMAT (A3).

Columns 4-5 Value of  $n$  in  $X_n AA' X'_n$  (maximum value = 18)

FORMAT (I2).

Columns 6-11 Value of  $J_{AX}$  in Hz FORMAT (F6.2).

Columns 12-17 Value of  $J_{AX'}$  in Hz FORMAT (F6.2).

Columns 18-25 Estimated value of  $J_{AA'}$  in Hz FORMAT (F8.2).

Columns 26-30 Width of one line of the intense doublet separated by N at half height in Hz FORMAT (F5.2).

Columns 31-35 Height of one line of the intense doublet separated by N in cm. FORMAT (F5.2).

Columns 36-40 Scale factor - number of Hz/cm. in observed spectrum FORMAT (F5.2).

Columns 41-56 Name of complex FORMAT (4A4).

#### Card M

Columns 4-5 Value of 00 to stop.

#### Description of Program

Statements 1-5 Input data is read in.

Statements 6-10 Data set is defined for graph

Statements 11-15 If input for n in  $X_n AA' X'_n$  is zero the program stops. If input is greater than 18 the data set is rejected and an error message is printed out.

Statements 16-18 Values of N and L are calculated using Equations 5 and 6.

Statements 19-23 Input data is printed out.

Statements 24-29 Line positions and relative intensities of doublet separated by N is calculated.

Statements 30-31 DO loop is begun altering  $\chi$ .

Statements 32-40 Line positions for varying values of  $\chi$  are

determined using Equations 7 and 8.

Statements 41-42 Perturbation factor  $g$  is calculated using Equation 11.

Statements 43-57 Line intensities for varying values of  $\chi$  are calculated and normalized to a relative intensity of 1.0 for each line of intense doublet separated by  $N$ .

Statements 58-63 All line positions and relative intensities are printed out.

Statements 64-65 Line positions are scaled in cm. to fit observed spectrum.

Statements 66-75 Lorentzian line shape for each line is calculated using relative intensity of each line of main doublet of 1.0 and intensity due to overlapping lines are summed together at intervals of 0.0508 cm. over 15.24 cms.

Statements 76-80 The peak point of the main doublet is found.

Statements 81-83 The height of the main doublet, the calculated separation of the main doublet and the scale of the graph are printed out.

Statements 84-85 All intensities are normalized to the observed height of the main doublet.

Statement 86 The subroutine for the Simplotter is called. Input for the Simplotter is defined as follows.

## Simplotter Input

```
CALL GRAPH (NPTS, X, Y, KS, MODE, XSIZE, YSIZE, XSF, XMIN, YSF,
           YMIN, IXLB, IYLB, IGLB1, JLAB)
```

NPTS The magnitude represents the number of (x, y) points to be plotted; here 300.

X The name of the array containing the x- co-ordinates of the points.

Y The name of the array containing the y- co-ordinates of the points.

KS The plotting symbol to be used (if any); here none.

MODE This specifies the plotting method to be used; here straight lines are drawn from point to point but the points are not plotted.

XSIZE This defines the length of the x-axis in inches and whether a linear or log scale is wanted; here 6.0 inches, linear scale.

YSIZE This is similar to XSIZE for y-axis; here 10.0 inches, linear scale.

XSF This defines the scale factor (units/inch) on the x-axis; here 2.54 cm./inch.

XMIN The beginning point of the graph on the x-axis; here zero.

YSF This is similar to XSF on the y-axis.

YMIN This is similar to XMIN on the y-axis.

IXBL Alphabetic label for x-axis; here C.P.S. TIMES SCALE

IYLB Alphabetic label for y-axis; here LINE INTENSITY IN CM.



IGLB1 Alphabetic label for graph indentification; here VIRCUP

B.

JLAB Alphabetic label to identify data set.

```

C      VIRGUP B      OGILVIE
C      SYNTHESIS AND VARIABLE SCALE PLOTTING OF XNAAXN SPECTRUM
C      MAXIMUM VALUE OF N IS 18
C      DATA CARD FORMAT: COLS. 1-3 JOBNO,4-5 N, 6-11 JAX, 12-17 JAXPRIME
C      18-25 JAAPRIME, 26-30 WIDTH, 31-35 HIGH, 36-40 SCALE, 41-56 NAME
C      FIRST DATA CARD HAS ALPHAMERIC GRAPH LABELS. LAST MUST HAVE N=0.
      DIMENSION XLINE(74),XIN(74),X(300),Y(300),IXLB(5),IYLB(5),IGLB1(5)
      1,JLAB(5),NAME(4)
      READ (1,4) IXLB,IYLB,IGLB1
4  FORMAT (16A4)
      1 READ (1,2)JOBNO,N,AX,AXP,AAP,WIDTH,HIGH,SCALE,NAME(1),NAME(2),
      INAME(3),NAME(4)
      2 FORMAT (A3,I2,2F6.2,F8.2,3F5.2,4A4)
      JLAB(1)=JOBNO
      JLAB(2) =NAME(1)
      JLAB(3) =NAME (2)
      JLAB(4) =NAME(3)
      JLAB(5) =NAME(4)
      IF (N)30,30,33
33 IF (N-18)3,3,31
31 WRITE (3,32)JOBNO
32 FORMAT(1H1,10HDATA CARD ,A3,22H HAS N GREATER THAN 18)
      GO TO 1
      3 ENFL=FLOAT(N)
      EL=AX-AXP
      EN=AX+AXP
      WRITE (3,12) JOBNO,N,N,NAME(1),NAME(2),NAME(3),NAME(4)
      WRITE (3,13)AX,AXP,AAP,WIDTH
12  FORMAT(1H1,36X8HVIRGUP B,/9X,A3,52H COMPUTATION OF LINE POSITIONS
      1AND INTENSITIES FOR X,I2,3HAAX,I2,/25X,14H SPECTRUM OF ,4A4)
13  FORMAT (7X6HJAX = ,F6.2,12H JAXPRIME = ,F6.2,12H JAAPRIME = ,
      1F8.2,13H LINEWIDTH = ,F5.2//)
14  FORMAT(5X2HNO,5X8HPOSITION,4X9HINTENSITY,12X2HNO,5X8HPOSITION,
      14X9HINTENSITY)
      FNOR=2.**((2*(N-1)))
      XLINE(1)=EN/2.
      XLINE(2*N+2)=-EN/2.

```

```

XIA(1)=1.
XIN(2*N+2)=1.
WRITE (3,14)
CHI=1.
DO 99 I=1,N
PING=SQRT((CHI**2*EL**2)+AAP**2)
PONG=SQRT(((CHI-1.)**2*EL**2)+AAP**2)
XLINE(I+1)=(PING-PONG)/2.
J=I+N+1
K=2*N+I+2
M=3*N+I+2
XLINE(J)=(PING+PONG)/2.
XLINE(K)=-XLINE(I+1)
XLINE(M)=-XLINE(J)
PANG=CHI*(CHI-1.)*EL**2+AAP**2
GEE=PANG/(PING*PONG)
CCM=1.
IF (ENFL-CHI)21,21,22
22 TIMES=2.*ENFL-1.
23 CCM=CCM*TIMES
TIMES=TIMES-1.
IF (TIMES-ENFL-CHI)24,23,23
24 DIV=ENFL-CHI
25 CCM=CCM/DIV
DIV=DIV-1.
IF (DIV)21,21,25
21 XIN(I+1)=CCM*(1.+GEE)/(2.*FNOR)
XIN(J)=CCM*(1.-GEE)/(2.*FNOR)
XIN(K)=XIN(I+1)
XIN(M)=XIN(J)
99 CHI=CHI+1.
L=4*N+2
LC=2*N+1
DO 90 LA=1,LC
LB=LA+2*N+1
15 FORMAT(5XI2,2XF11.3,5XF6.4,14XI2,2XF11.3,5XF6.4)
90 WRITE (3,15)LA,XLINE(LA),XIN(LA),LB,XLINE(LB),XIN(LB)

```

```

      DO 101 I=1,L
101  XLINE(I)=XLINE(I)/SCALE
C    LINE POSITIONS NOW IN CENTIMETRES
      XCG=0.
      I=1
60   X(I)=XCG
      Y(I)=0.
      WID=4.*(SCALE/WIDTH)**2
      DO 66 K=1,L
66   Y(I)=Y(I)+XIN(K)/(1.+WID*(XLINE(K)-X(I))**2)
      XCG=XCG+.0508
C    STEP OF .0508 IS FOR 300 POINTS IN 15.24 CM (6 IN.)
      I=I+1
      IF (I-300)60,60,67
67   LIN=EN/(SCALE*.1016)+4.
70   IF (Y(LIN-1)-Y(LIN))72,72,71
71   LIN=LIN-1
      GO TO 70
72   FACT=HIGH/Y(LIN)
C    FINDS PEAK POINT OF MAIN DOUBLET-MAX ERROR 1 POINT,(.05*SCALE C/S)
      SPACE=2.*X(LIN)*SCALE
      WRITE (3,16)HIGH,SPACE,SCALE
16   FORMAT(1X31HIN PLOT MAIN DOUBLET PEAKS ARE ,F5.2,17H CM HIGH, SPAC
1ED ,F5.2,13H C.P.S. APART,/1X21H HORIZONTAL SCALE IS ,F5.2,15H C.P
2.S. PER CM.)
      DO 68 I=1,300
68   Y(I)=Y(I)*FACT
C    SPECTRUM HEIGHT NOW NORMALISED
      CALL GRAPH(300,X,Y,0.4,6.0,10.0,2.54,0.0,2.54,0.0,IXLB,IYLB,IGLB1
1,JLAB)
      GO TO 1
30   STOP 88
      END

```

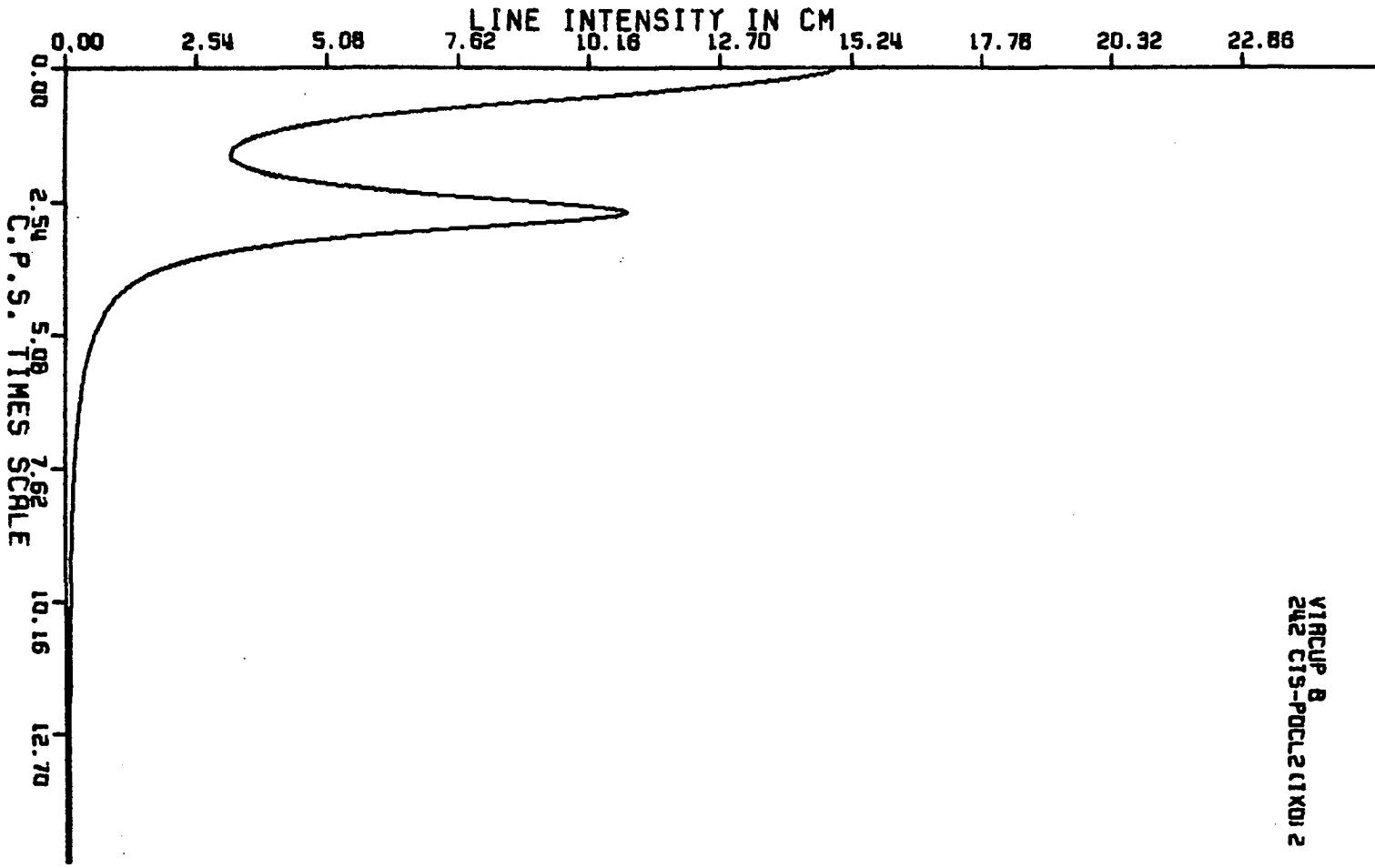
Figure 16. Computer output for cis-PdCl<sub>2</sub>(IXD)<sub>2</sub>. The line positions are given in Hz from  $\nu_X$  and the intensities are given relative to each line of the doublet of separation N having an intensity of 1

VIRCUP 3  
 242 COMPUTATION OF LINE POSITIONS AND INTENSITIES FOR X 6AAX 6  
 SPECTRUM OF CIS-POCL2(IXD)2  
 JAX = 5.50 JAXPRIME = 0.0 JAAPRIME = 65.00 LINEWIDTH = 0.90

NO	POSITION	INTENSITY	NO	POSITION	INTENSITY
1	2.750	1.0000	14	-2.750	1.0000
2	0.116	0.4504	15	-0.116	0.4504
3	0.346	0.3217	16	-0.346	0.3217
4	0.569	0.1609	17	-0.569	0.1609
5	0.780	0.0536	18	-0.780	0.0536
6	0.978	0.0107	19	-0.978	0.0107
7	1.160	0.0010	20	-1.160	0.0010
8	65.116	0.0008	21	-65.116	0.0008
9	65.578	0.0006	22	-65.578	0.0006
10	66.493	0.0003	23	-66.493	0.0003
11	67.842	0.0001	24	-67.842	0.0001
12	69.600	0.0000	25	-69.600	0.0000
13	71.738	0.0000	26	-71.738	0.0000

IN PLOT MAIN DOUBLET PEAKS ARE 10.90 CM HIGH, SPACED 5.49 C.P.S. APART  
 HORIZONTAL SCALE IS 1.00 C.P.S. PER CM.

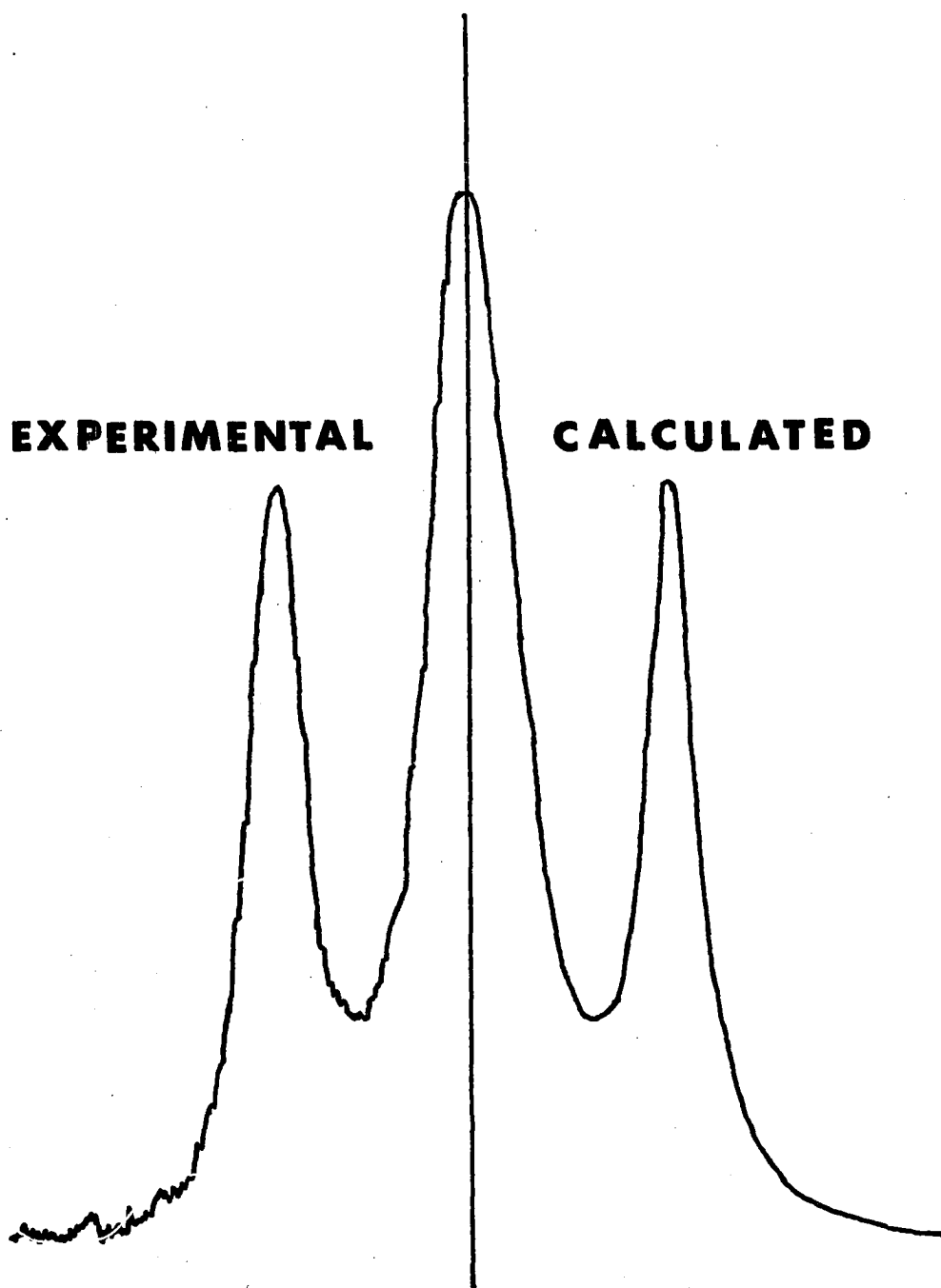
Figure 17. Simplotter output of the data given in Figure 16  
for cis-PdCl<sub>2</sub>(IXD)<sub>2</sub>



VIRCLIP 8  
242 CTS-POCL2 (1X0) 2



Figure 18. Comparison of the simplotter output in Figure 17 with the experimental spectrum of cis-PdCl<sub>2</sub>(IXD)<sub>2</sub>



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