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Structural and Conformational Studies of Selected Chelate Ring Systems

by

Joel M. Ressner

A Dissertation
Presented to the Graduate Committee
of Lehigh University
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Doctor of Philosophy
in
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1978

Certificate of Approval

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May 8, 1978
Date

Charles S. Kraihanzel
Professor in Charge

Accepted May 10, 1978
(Date)

Special committee directing the doctoral work of Mr. Joel M. Ressner.

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ABBREVIATIONS

Me	Methyl
Et	Ethyl
Ph	Phenyl
i-Pr	Isopropyl
Ac	Acetyl
Cp	Cyclopentadienyl
dpm	_bis_(diphenylphosphino)methane
dppe	1,2-_bis_(diphenylphosphino)ethane
dpp	1,3-_bis_(diphenylphosphino)propane
2,2-dmdpp	2,2-dimethyl-1,3-_bis_(diphenylphosphino)-propane
2,2-dmdap	2,2-dimethyl-1,3-_bis_(diphenylarsino)propane
2,2-dpp	2,2-_bis_(diphenylphosphino)propane
1,1-dpe	1,1-_bis_(diphenylphosphino)ethane

ABSTRACT

The ligands 2,2-dimethyl-1,3-bis(diphenylphosphino)propane (2,2-dmdpp) and 2,2-dimethyl-1,3-bis (diphenylarsino)propane (2,2-dmdap) have been synthesized. Metal tetracarbonyl derivatives of these ligands, $M(CO)_4(L\text{-}L)$, M=Mo,W are stereochemically nonrigid on the nmr time scale, as is the iron pentacarbonyl derivative, $Fe(CO)_3$(2,2-dmdpp). These systems provide examples of "virtual coupling;" the parameters for the $H_2PP'H_2'$ virtual coupled system are described, and are in line with values found by other researchers for similar systems. Manganese (I) tricarbonyl derivatives of both ligands, $XMn(CO)_3(L\text{-}L)$, (X = Cl,Br,I, Ac,Me) all exhibit facial geometry; the six-membered rings are stereochemically rigid. The axial methyl resonance appears upfield of that of the equatorial methyl, due to shielding by the phenyl rings on the donor atom. Four bond coupling of the equatorial methyl protons to the phosphorus atoms was noted, especially in the acetyl- and methyl- derivatives, where the equatorial methyl resonance appears as a triplet. Rings in πCpFe(2,2-dmdpp)X systems (X = Cl,Br,I), were also found to be stereochemically rigid.

Thiocyanate linkage isomerism in palladium (II) systems, $[(L\text{-}L)Pd(CNS)_2]$, (CNS does not specify the mode of attachment) was investigated by infrared spectroscopy with several chelating biphosphines. The results are somewhat ambiguous. The mode of thiocyanate coordination appears to change from S,S to S,N as the carbon-chain backbone of the ligand becomes more crowded. The complexes formed from 2,2-dmdpp and 2,2-dmdap appear to have "mixed" bonding (S,N), analogous to that of the 1,2-*bis*(diphenylphosphino)-ethane derivative rather than N,N-bonding found for the 1,3-*bis*(diphenylphosphino)propane derivative.

INTRODUCTION

The question of ascertaining molecular structure is one that concerns those working in many fields of science; for the chemist the molecular structure of compounds under study is of fundamental importance as physical properties, reactivity, possible medicinal properties or catalytic activity can all be structurally dependent phenomena.

Structural determination is most certainly an important aspect of chemistry. The possibilities of geometrical isomerism, stereoisomerism, coordination isomerism, and linkage isomerism can exist simultaneously in a given metal complex. Structural evidence has been cited, for example, as supporting evidence for electronic effects in molecules, such as $d\pi$-$d\pi$ bonding in metal carbonyls and relates *trans*- (or *cis*-) effects, and to support steric control of molecular geometry in some cases (one such case will be presented in Part II of this work). Structural analysis of obtainable reaction intermediates has aided in the elucidation of reaction pathways and rationalization of rates of reactivity. Structure elucidation has become important to almost every type of chemist; the organometallic or coordination chemist is no exception.

Methods of structural determination have become highly refined; physical methods such as dipole moment determination, nuclear magnetic resonance (nmr), electron spin resonance (esr), and infrared and laser Raman spectroscopy, mass spectrometry, and molecular weight determination (by various means) all contribute data by which a structure may be deduced; x-ray crystallography has become almost routine in the current decade; this technique, however, yields no information on the structure of molecules in solution.

Of the deductive methods of structural determination, nuclear magnetic resonance and infrared spectroscopy are both the most convenient and most widely used forms of instrumental structural analysis. The instrumentation is generally available, fairly simple to use, and the spectral results are often not overly difficult to interpret. Further, nuclear magnetic resonance is an excellent method for investigating time-related phenomena that cannot be explored by other instrumental methods. The time required for "sampling" in nmr is much longer than for other techniques (UV: 10^{-15} sec, visible: 10^{-14} sec, IR: 10^{-13} sec, nmr 10^{-1}-10^{-9} sec.[1]). Investigations of time/temperature related phenomena (reaction kinetics, ring inversion, etc.) have become fairly common in recent years.

Many systems, however, do not yield spectral data that is easily understood; infrared spectra can be of dubious interpretation due to non-resolvable absorptions, and nuclear magnetic resonance spectra, especially of chelate complexes, are often not first order and thus the resonances are not easily assigned. Methods such as spin decoupling, selective deuteration of sites on the ligand, and computer simulation of spectra must then be employed in the analysis of such magnetic resonance spectra.

The ideal system for structural investigation is therefore one in which the infrared data are non-ambiguous, and in which complex spin-coupling in the nmr spectra is minimized. A system with more than one magnetic nucleus can yield additional information if the instrumental capability of variable nucleus nmr is present; it can, however, lead to complications in the proton nmr spectra.

Transition metal carbonyl complexes are among the most investigated organometallic systems. The infrared properties of metal carbonyl complexes are fairly well known and spectral results can often be predicted on symmetry considerations alone. Furthermore, metal carbonyl absorptions (CO stretch) are usually relatively strong, fairly sharp, and fall within a well defined energy range, thus facilitating analysis.

Transition metal carbonyl compounds of phosphorus and arsenic donor ligands are quite well known; many of these complexes are hydrogenation or hydroformylation catalysts, and thus extensive investigations of the structures and reactive properties of these compounds have been conducted. The literature has been extensively reviewed.[2,3]

Use of a chelating biphosphine or biarsine ligand of appropriate chain length insures that the donor atoms will occupy cis positions in a metal complex. This limits to some extent the number of possible isomers a complex may form, an advantage not provided by the use of two monodentate ligands. In addition, the chelate effect[4] provides a certain amount of stabilization not present in cis complexes of two monodentate ligands.

Much of the work done in this area has involved the use of 1,2-bis(diphenylphosphines)ethane (dppe) as the chelating ligand, possibly because this chelating biphosphine is synthetically easy to obtain in high yields. The proton nmr spectra of metal carbonyl derivatives of the class of chelating biphosphine represented by the formula $Ph_2P(CH_2)_nPPh_2$, (n=2-4), do not, on the whole, yield a great deal of information because of their complexity.

The ligand systems $Ph_2PCR_1R_2PPh_2$ (R_1=R_2=H; R_1=H, R_2=Me, R_1=R_2=Me) have been investigated[9] and while the spectra are less complex the results in some cases are not unambiguous. For example, the complex

$CH_3Mn(CO)_3(Ph_2PCMe_2PPh_2)$ (Figure 1) can with certainty be assigned a facial configuration from infrared data alone; the resonances for the syn- and anti-methyl

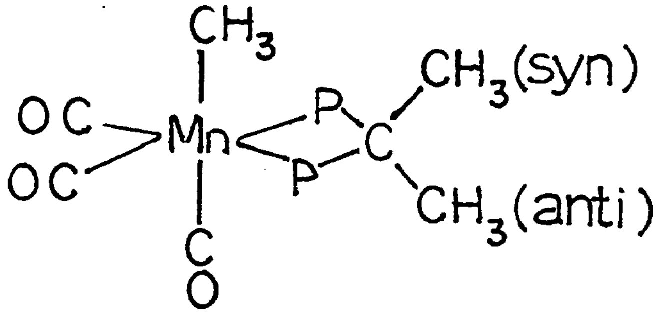


Figure 1. fac- $CH_3Mn(CO)_3(Ph_2PC(CH_3)_2PPh_2)$

groups cannot be assigned from the current data. This four membered ring system, moreover, shows a marked steric effect: $CH_3\overset{O}{\overset{\|}{C}}Mn(CO)_3(Ph_2PCMe_2PPh_2)$ has a meridional structure (Figure 2) while its decarbonylation product (above) is facial.

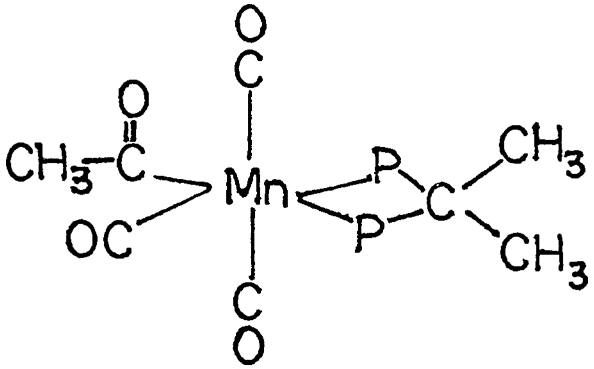
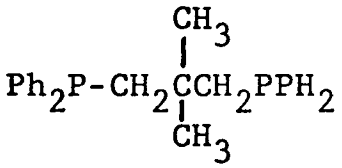


Figure 2. mer- $CH_3COMn(CO)_3(Ph_2PC(CH_3)_2PPh_2)$

This effect, could, perhaps, be avoided by use of a longer-chain ligand; however, the spectra of the phosphines in which n=2 or greater are complicated not only by spin coupling of non-equivalent protons, but by coupling of each of these protons to two phosphorus atoms. In some cases[5] the resonances cannot even be located with certainty. Attempts have been made to attack this problem by substitution of deuterium[6] or fluorine[7] for hydrogen atoms on the ligans.

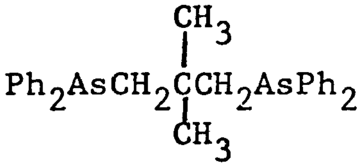
Other workers[8] have confronted this problem by designing ligands that are similar to the above mentioned phosphines but do not have the complex coupling problems inherent in their nuclear magnetic resonance spectra. If the steric demands made by these ligands are similar to that of the straight-chain chelating biphosphines yielding metal complexes of like symmetry, the wealth of infrared spectral information obtained for the well-known complexes of $Ph_2P(CH_2)_nPPh_2$ (n=2,3) can be complimented by the nuclear magnetic resonance data to yield definitive structural evidence.

The design of a ligand system that allows simplified structural analysis is a goal worth achieving. Thus, 2,2-dimethyl-1,3-bis(diphenylphosphino)propane (2,2-dmdpp,I) and 2,2-dimethyl-1,3-bis(diphenylarsino) propane (2,2-dmdap,II) (Figure 3) have been synthesized in these laboratories and several types of transition metal derivatives characterized. It is felt that the steric demands of these ligands will be quite similar



$\mathrm{Ph_2P\text{-}CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2PPH_2}$

I

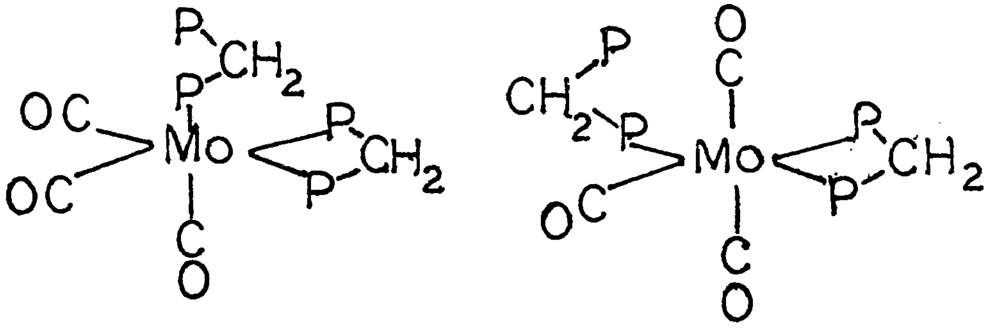


$\mathrm{Ph_2AsCH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2AsPh_2}$

II

Figure 3. 2,2-dimethyl-1,3-bis(diphenylphosphino)propane (I) and 2,2-dimethyl-1,3-bis(diphenylarsino)propane (II)

to those of the 1,3-bis(diphenylphosphino/arsino)propane analogs, and thus complexes of 2,2-dmdpp and 2,2-dmdap will be of like symmetry, facilitating interpretation of infrared data. The proton magnetic resonance spectra of these complexes should quite clearly indicate conformational mobility in the six-membered ring systems formed by these ligands, if such exists. By using these ligands to synthesize related series of complexes in which the electronic properties of the chelating ligand do not differ, one can address the questions of: (1) effect of overall complex geometry (i.e. octahedral vs. trigonal bipyramidal) on mobility of the chelate ring, (2) effect of the size of a third ligand, L, (L = halogen, hydride, alkyl , Ph_3P, Ph_3As, $(MeO)_3P$, $MeNH_2$, or other monodentate ligand) on the geometry of a six-coordinate metal complex (the question of meridional vs. facial geometry), (3) effect of this ligand, L, on the conformation and possible stereochemical non-rigidity of the six-membered chelate ring in facially substituted octahedral complexes, and (4) the effect, if any, of the size of the chelate donor atoms (P or As) on the geometry and possible conformational mobility of the complex. Experimental derivations of thermodynamic and kinetic parameters for ring inversion have not been performed in this work. The effect of the size of the groups bonded to the chelate donor atoms has not been investigated; diphenylchalcogenate moieties have been maintained throughout. This work presents no data on the effects of one chelate ring on the positioning of a second ring in an octahedral complex; though complexes such as $(CO)_2Mo(dppe)_2$ and both the facial and meridional isomers of $(CO)_3Mo$-$(dpm)_2$[11] (Figure 4) are known, all attempts to form



fac- mer-

Figure 4. fac- and mer $(CO)_3Mo(dpm)_2$

similar compounds $(CO)_2M(L-L)_2$ or $(CO)M(L)(L-L)_2$ with 2,2-dmdpp and 2,2-dmdap failed. Attempts to further elucidate the influence of substitution in the 2,2-positions of the ligand on the geometry of metal complexes were hindered by the inability to isolate ligands such as 2-methyl-2-tert-butyl-1,3-bis(diphenylphosphino)propane in pure form.

General comments on structural determination and conformational mobility of six-membered rings will be made in the next section of this work; each subsequent section will be devoted to the discussion of complexes of one specific type of geometric arrangement.

Part II of this work will concern the steric effects of a series of chelating ligands on the mode of bonding of the thiocyanate ion, an ambidentate ligand, in palladium complexes.

PART I

GENERAL CONSIDERATIONS

Infrared Analysis of the Six Coordinate Transition Metal Carbonyl Complexes: $(CO)_4M(L\text{-}L)$ and $(CO)_3M(L)(L\text{-}L)$

The frequencies of the vibrations of carbon monoxide moieties attached to a metal atom such that the CO-group is colinear with the M-C bond (a "terminal CO" group) fall in the region 1700-2200 cm^{-1}. The study of vibrational spectra of metal carbonyl compounds has long been an active field of inquiry; the experimental data are, in many cases, the basis for structural assignments, though incorrect assignments have, at times, been made. The literature is reviewed often, and at least one monograph[12] has appeared on the topic.

M. Bigorgne, in his excellent review of the vibrational spectroscopy of metal carbonyls[13], states that the following conditions must be fulfilled for vibrational spectroscopy to be a useful tool in structural determination:

1) The number of CO groups in the molecule must be known.
2) Two different bands must not have the same frequency.
3) A suitable, preferably non-polar, solvent must be used; failure results in altering of the spectrum (wide bands).

4) The spectrograph must have good resolution in the 2000 cm^{-1} region.

Consideration of molecular symmetry can often lead to prediction of the theoretical number of absorptions in the "CO stretch" energy region of the spectrum for a given complex; the use of Group Theory[14] can sometimes eliminate the need for a full normal coordinate analysis in assigning an absorption. If possible isomers of a complex have very different geometrics and thus dissimilar absorption patterns are predicted, molecular geometry can often be assigned on the basis of infrared evidence alone (assuming the absence of mixtures of isomers). A hazard inherent in this method of structural assignment is the possibility that two absorptions lie too close together to be resolved and only one apparent peak is observed, leading the researcher to erroneous deductions.

Comparison to the spectra of compounds of known geometry is a method frequently used in identifying structures when more than one is possible. This is often possible even when two complexes do not belong to the same symmetry point if one considers all of the atoms on the ligand, but do have similar symmetry if only the ligand donor atoms are considered. Thus, Cotton and Kraihanzel[15] were able to use theoretical considerations derived for C_2v symmetry to assign frequencies in the spectrum of $(CO)_4W(dppe)$ (dppe = 1,2-bis(diphenylphosphino)ethane) which, due to the non-planarity of the five-membered ring, is not rigorously C_2v symmetry. (Figure 5). That this method is reliable is shown by Table 1, which compares the frequencies of several metal tetracarbonyl compounds, all of which have localized C_2v symmetry about the metal atom.

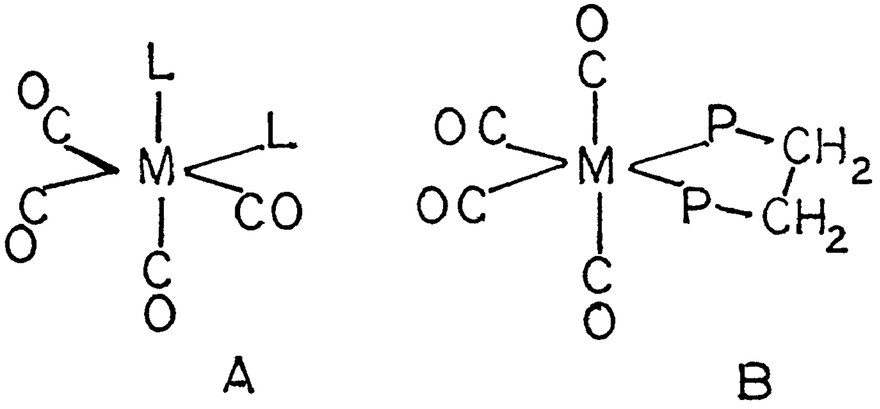


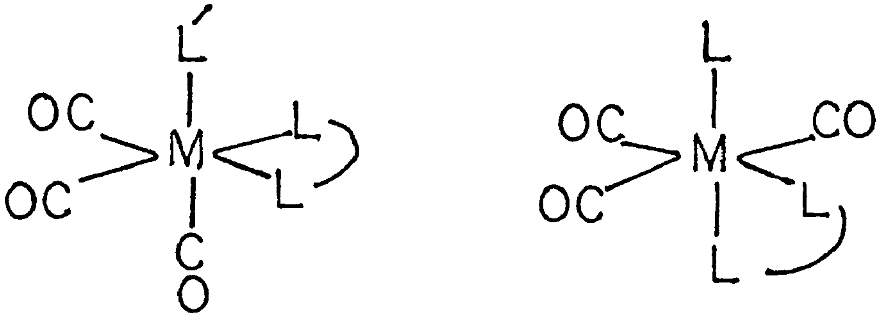
Figure 5. Idealized C_2v symmetry (A), $M(CO)_4$ (dppe) (B)

The interpretation of the infrared spectra of the tetracarbonyl derivatives is fairly straightforward; only one geometrical isomer is possible for a complex of this type. Tricarbonyl derivatives of six-coordinate metal complexes, however, can exist in two possible geometrical isomers: <u>fac</u>- (facial)- in which the carbonyl moieties are all located on the face of an octahedron, and thus are all mutually <u>cis</u>, or <u>mer</u>- (meridional)- in which the three carbon monoxide groups

Table 1. CO Stretch Frequencies for some Tetracarbonyl Compounds

Compound	Frequencies (cm^{-1})	Solvent	Ref.
$W(CO)_4(dppe)$	2016 1912 1091 1876	$CHCl_3$	15
cis-$Mo(CO)_4(AsPh_3)_2$	2023 1929 1915 1899	Saturated hydrocarbon	16
$Mo(CO)_4$-$(CH_3)_2As(CH_2)_3As(CH_3)_2$	2021 1925 1907 1899	Cyclohexane	6
$Mo(CO)_4$(2,2-dmdpp)	2018 1932 1914 1906	Methylcyclohexane	This work
$Mo(CO)_4$(2,2-dmdap)	2023 1930 1917 1900	Methylcyclohexane	This work

are located in the meridional plane of an octahedron, with two carbonyl groups cis to the third, but trans to each other. (Figure 6)



fac- mer-

Figure 6. Facial and meridional isomers of $M(CO)_3(L')(L\text{-}L)$

Both structures exhibit C_s symmetry, and three infrared-active fundamentals (2A' + A") are expected for both. In some complexes, as in the case of fac-$CH_3COMn(CO)_3(L\text{-}L)$, the two lower energy bands lie too close together to be resolved.[9] Kraihanzel and Maples[9] have found that the high energy CO stretch band in the infrared spectrum of a complex with a meridional structure is of low intensity relative to the other CO absorptions, whereas the high energy CO stretch absorption in a facial complex is as strong as, if not greater than, the intensities of the other carbonyl bands. The infrared data, coupled with nmr data, allowed these workers to deduce the structures of a great many complexes, including that of $CH_3COMn(CO)_3$ (dppe), which had previously been assigned an incorrect trans configuration.[5]

Conformational Analysis of the Six-Membered Ring

Conformation of the Ring

Of the three possible conformations of the six membered rings formed by metal chelates (Figure 7), the chair conformation seems to be preferred. The

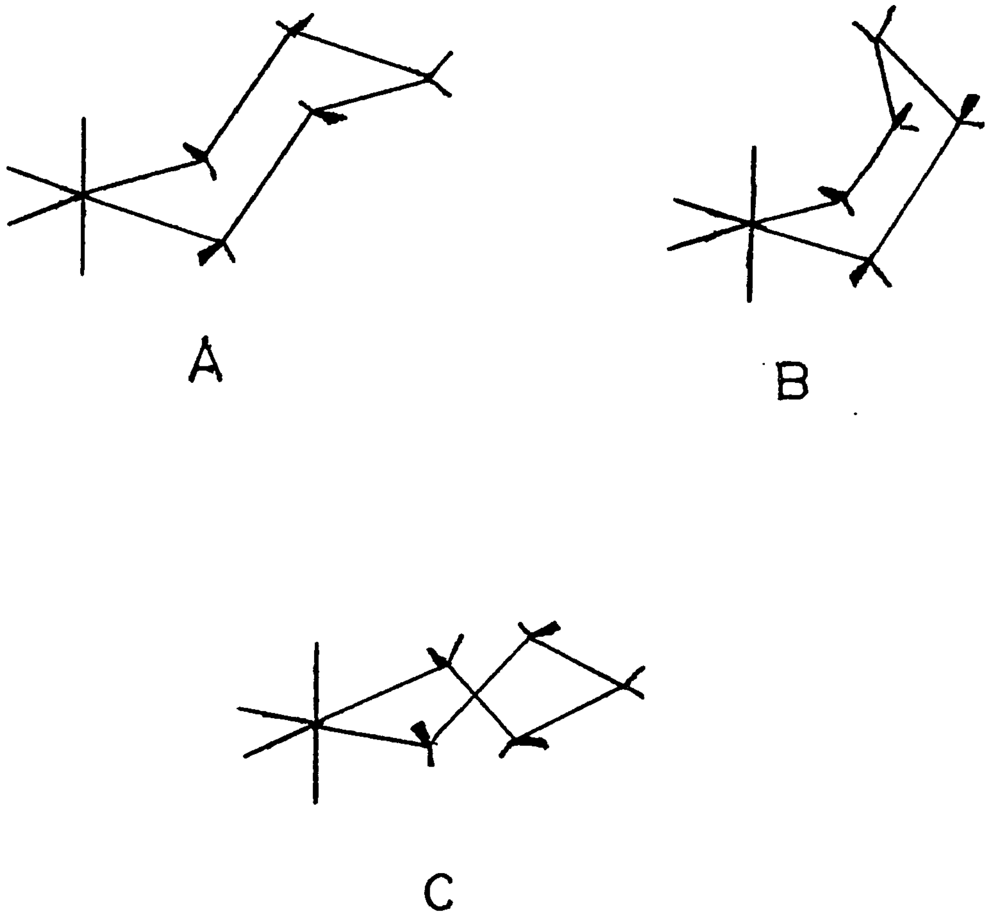


Figure 7. Chair (A), Boat (B), and Twist (C) Conformers

boat conformer is considerably more strained than the twist (skew boat) or chair conformers.[17,18] DeHayes and Busch[19] calculated that the chair conformation is energetically preferred over the twist or skew-boat conformations for diamine chelates. Axial substituents on the ring were found to interact with axial ligands on the metal ion, a flattening of the ring and causing the axial ligands to bend away from the ring.[19] Gollogly and Hawkins[17] predict a strong interaction between an apical group of an octahedral complex and the first and third carbon atoms of the chair conformation of the six-membered ring, resulting in a symmetrical flattening of the ring and a distortion of the apical group away from the ring. Calculations show the skew-boat form of the ring will interact with two different apical ligands, while the symmetric boat form of the ring will result in an even higher amount of ligand-ring interaction. Thus, these authors predict a symmetrical chair conformation will be preferred over the skew-boat and boat conformations, the chair being preferred over the skew-boat by over 8.4 kJoule/mol (2kcal/mol).

In the crystalline state, 1,3-diamine chelates have generally been found to have a chair conformation[17] though some systems have skew-boat conformations in the solid state.[20,21] This does not, however, predict their conformations in solution.

A square planar complex differs from an octahedral complex in that interactions external to the ring can be ignored, and the chelate ring can be considered as if it is isolated.[17] The conformation of lowest energy again is the symmetrical chair; chair-to-chair interconversion, however, proceeds through a skew-boat intermediate.[17] Appleton and Hall[22] found the nmr spectrum of $[Pd(dan)_2]Cl_2$, dan = 2,2-dimethyl-1,3-diaminopropane, to be two sharp peaks, in ratios 4:6, corresponding to the methylene and methyl resonances. Platinum satellites were observed in the spectra of N-deuterated $[Pt(dan)_2]Cl_2$ and $[Pt(dan)(NH_3)_2]Cl_2$, but no observable coupling between ^{195}Pt and the methyl group protons was found.

Dynamic Nuclear Magnetic Resonance (dnmr)

The use of nuclear magnetic resonance spectroscopy to investigate changes, both structural and chemical, compatible with the nmr time scale has blossomed with the introduction of instruments with ^{31}P, ^{19}F and ^{13}C capabilities, fft (fast Fourier transform) nmr, and prepackaged computer programs to fit calculated line shapes to those of the spectrum[23,24] to aid in the analysis of complex spectra. Many aspects of the subject popularly termed "dynamic nuclear magnetic resonance spectroscopy," have been detailed[25], including the study of inversion at metal sites, rotation about single bonds in organic molecules, cyclopolyenyl and cyclopolyenemetal systems, and conformational processes in rings. It is the last that is of interest here.

Inversion of a six-membered ring is not an energetically demanding process. Some free energies of activation for inversion of the chair conformation of six-membered rings with a dimethyl-substituted apical carbon atom, derived using nmr line shape techniques,[23] are listed in Table 2.

Table 2

Ring inversion barriers for selected six-membered rings

Compound	Solvent	$G^{\ddagger}$(kcal/mol)	$G^{\ddagger}$(kJoule/mol)
1,1-dimethylcyclohexane-d_4	CS_2	10.6	44.4
5,5-dimethyl 1,3-dioxan	$(CD_3)_2CO$	11.0,10.5	46.0,43.9
5,5-dimethyl-1,3-dithian	CS_2	10.6	44.4

(ref. 23)

Cyclohexane is an illustrative example of a ring system to which conformational study by variable temperature nmr is applicable. At temperatures above -50°C a solution of cyclohexane in carbon disulfide exhibits one sharp resonance; by -65°C this resonance has broadened considerably, and by -70°C two distinct, though incompletely resolved, resonances are seen (at 60 MHz).[26] Cooling the solution thus slows the rate of chair-chair interconversion to the point that the average lifetime of a conformer at about -70°C is of the same order of magnitude as the difference ($\nu_{axial} - \nu_{equatorial}$) (27.3 Hz[26]). Below -90°C the spectrum of the rigid chair isomer is obtained; at 40 MHz this consists of an unsymmetrical broadened quartet, which indicates an AB system.[27] Data from experiments such as this have led to values such as those listed in Table 2, by methods detailed in the literature.[23,25] Treatment of data by such methods is beyond the scope of this work, and will not be discussed.

Such experiments are not always successful; the nmr spectra of 1,1-dimethylcyclohexane, for example, shows little change to -120°C; mechanical problems often limit the range of temperatures that can be attained, and the coalescence temperature may never be reached.

Rings formed in many complexes of chelating ligands have been found to undergo rapid conformational inversion, making them ideal subjects for study. The conformational properties of 1,3-chelated ligands are expected to resemble the stereochemical features of the carbocyclic and heterocyclic six-membered ring systems mentioned above. The presence of a metal ion with its associated ligands as a participant in the six-membered ring introduces changes in ring dimensions due to the relatively long metal-donor bond distance[18] and steric interactions of other ligands with groups bonded to the donor atoms or with the ring itself.

Solvents seem to have some effect on the rate of conformational averaging; for the stereo-chemically non-rigid molecules trans-$[CO(tn)_2(NH_3)_2]^{3+}$ and $[CO(tn)_2(NO_2)_2]^+$, (tn = trimethylenediamine) conformational averaging in D_2O is faster than in 80% H_2SO_4 or DMSO-d_6.[28]

It is not the intent of this work to investigate the thermodynamics and kinetics of ring inversion. Variable temperature pmr experiments have been performed on some systems in order to determine the resonance patterns of the specific ligand systems designed for this work under several conditions, and thus to enable deduction of molecular structure from data taken directly from the spectra.

Ring Systems Formed from the Ligands 2,2-dmdpp and 2,2-dmdap

Conformationally Rigid or "Locked" Rings

A conformationally rigid six-membered chelate ring is shown in Figure 8. Arguments leading to conformational assignments for 1,3,2-dioxaphosphorinane systems[29] and their metal carbonyl derivatives[30] may be applied to these anlogous ring systems. The two methyl groups CH_{3a} (axial) and CH_{3e} (equatorial) are in different environments, and thus a singlet is expected for each. The axial methyl resonance is broader than that of the equatorial methyl, and is usually found at lower field.[29,30] The broadening is due to four bond HCCCH coupling of the axial methyl protons with the axial methylene protons of the ring, which is often found when the bonds linking the coupled nuclei form a planar W.[31,32] ("This [spatial] arrangement allows interaction between the antibonding lobes of the sp^3 orbitals on the appropriate carbon atoms leading to a pathway for the coupling to occur."[31,33]) (Figure 9).

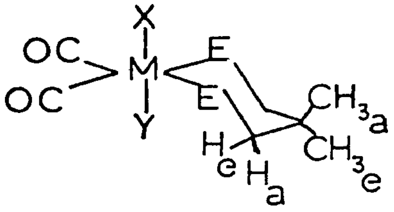


Figure 8. A conformationally locked chelate ring formed from the 2,2-dmdpp or 2,2-dmdap ligands.

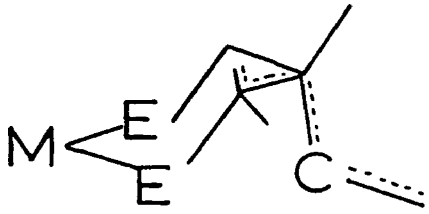


Figure 9. Four bond coupling of axial methyl and axial methylene protons

The methylene protons can be divided into axial and equatorial sets; in the absence of other magnetic nuclei (E≠P) an AB splitting pattern is found. Again, a planar W arrangement of atoms occurs (Figure 10); fine structure due to coupling between equatorial

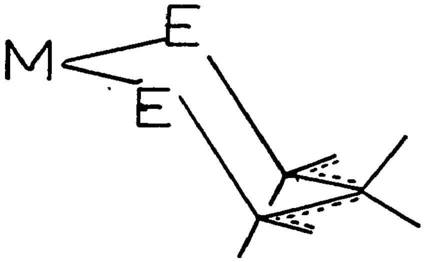


Figure 10. Four bond coupling of equatorial ring protons.

methylene protons has been noted in analogous systems.[30] Spin decoupling experiments have led to the assignment of the lower field methylene resonances in these systems to the axial protons,[29,30,33] which often appear to be broadened with no fine structure.[30] Figure 11 shows by means of a stick diagram the pattern of nmr resonances predicted for a locked ring formed by the 2,2-dmdap ligand. (Neither actual peak heights nor line width are considered in this diagram).

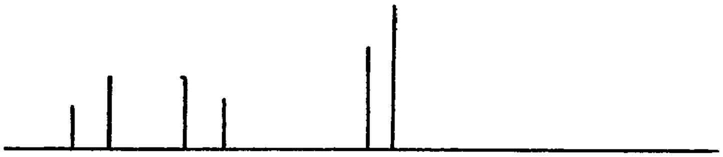
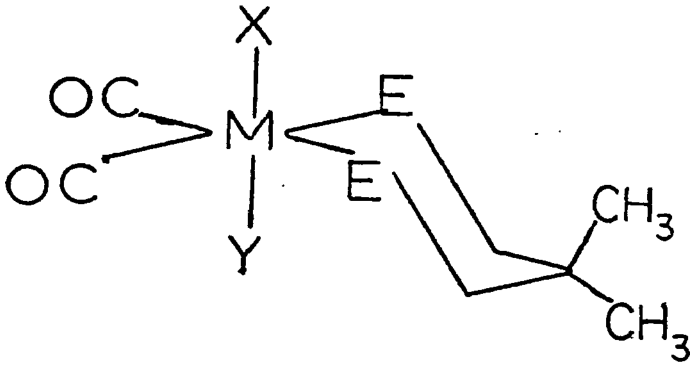


Figure 11. Resonances predicted for a locked ring formed for 2,2-dmdap.

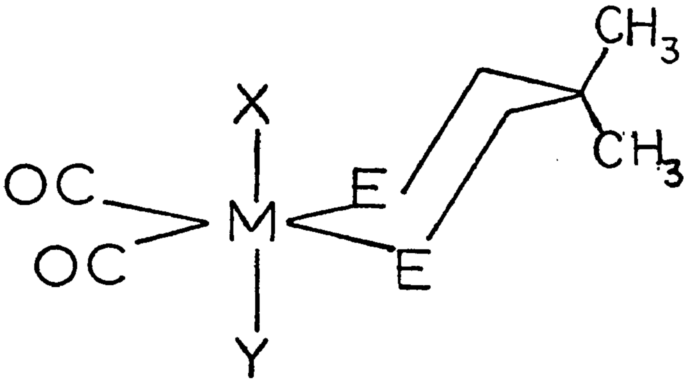
If the ligand donor atoms are phosphorus, coupling can occur to both the methyl and methylene protons. The resonances of methylene protons, now part of an AA'BB'XX' spin system, will appear as a complex multiplet, which requires spin-decoupling experiments and computer analysis to yield useful data. Analysis of the ring system formed by the chelating biphosphine ligand therefore depends solely on the methyl resonances which will, as in the case of the arsine, appear as two singlets.

The possibility of a mixture of conformers (Figure 12 A, B, X≠Y) of the conformationally rigid ring

Figure 12. Two possible conformers of XY(CO)$_2$M(L-L).



A



B

system must be considered. A spectrum following the patterns described above would result from each conformer; the spectra should be identical, but the chemical shift values will differ. Thus, the nmr spectrum of a mixture of two conformers of the six-membered ring derived from the 2,2-dmdap ligand would exhibit two AB quartets and two sets of two methyl resonances. If one conformer is preferred over the other and the two are present in unequal amounts the ratio of conformers can easily be obtained by the ratio of integrated intensities of the methyl resonances:

$$A/B = \frac{CH_3\ \text{axial(A)}}{CH_3\ \text{axial(B)}} = \frac{CH_3\ \text{equatorial(A)}}{CH_3\ \text{equatorial(B)}} .$$

Rapidly Interconverting Conformers

Rapid interconversion of the two possible chair conformationers will interchange the positions (relative to the ring) of both the methyl and the methylene groups. Two cases must now be considered.

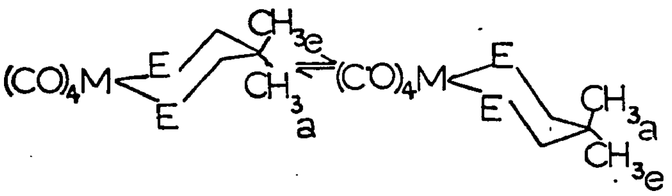


Figure 13. Rapidly interconverting conformers, X=Y=CO.

Ring inversion has caused $CH_3(1)$, which is axial in conformer A, to assume an equatorial position in conformer B. Likewise, $CH_3(2)$ changes from the equatorial to the axial position. Because both axial ligands on the metal are the same the chemical shift of $CH_3(1)$, axial, is the same as $CH_3(2)$, axial and the chemical shift of $CH_3(1)$, equatorial, is the same as that of $CH_3(2)$, equatorial. The rapid interconversion of the conformers will cause the resonance from $CH_3(1)$, axial, to be time-averaged with that of $CH_3(1)$, equatorial; thus only one methyl resonance for $CH_3(1)$ will be observed. The signals from $CH_3(2)$, axial, and $CH_3(2)$ equatorial will also be time-averaged, and as axial ligand X is the same as axial ligand Y, the chemical shift for the time averaged resonance for $CH_3(2)$ will be the same as that of the time averaged resonance of $CH_3(1)$.

The methylene protons of rapidly interconverting chair conformers H_{ax} and H_{eq} will become equivalent on the nmr time scale; the arguments given above for the interchange of axial and equatorial methyl groups hold equally for the methylene resonances. Rapidly interconverting rings formed from 2,2-dmdap, therefore, should exhibit only one methyl resonance and one methylene resonance (Figure 14).

Figure 14. Resonances predicted for a conformationally nonrigid ring formed from the 2,2-dmdap ligand; X=Y.

Rings derived from the chelating biphosphine 2,2-dmdpp will yield more complex spectra, due to the presence of the magnetic ^{31}P nucleus. The above argument holds for the methyl resonances; the methylene resonances, while still time averaged, will be more complex. Two phosphorus-hydrogen coupling constants -- $^{2}J_{PH}$ and $^{4}J_{PH'}$ -- plus the phosphorus-phosphorus coupling constant -- $^{2}J_{PMP}$ -- are required to describe this $A_2XX'A_2'$ spin system. This example of "virtual coupling" will be detailed more fully in the following chapter.

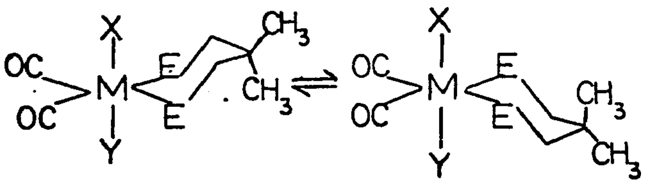


Figure 15. Rapidly interconverting conformers, X≠Y.

The spectra of the above systems assuming a locked ring were discussed in section 1. Rapid interconversion of conformers would result in spectra that represented a weighted time-average of the two conformers. Thus, if there is an X:1 ratio of the two conformers the chemical shifts of the methyl resonances is given by

$$\delta\mathrm{CH_3(1)} = [x/(x+1)\,\delta^{A}\mathrm{CH_3axial} + 1/(x+1)\,\delta^{B}\mathrm{CH_3equatorial}]$$

and

$$\delta\mathrm{CH_3(2)} = [x/(x+1)\,\delta^{A}\mathrm{CH_3equatorial} + 1/(x+1)\,\delta^{B}\mathrm{CH_3axial}]$$

(ref. 34).

Similar arguments hold for the methylene resonances. Thus, for the two sets of resonances of the two conformers (Figure 16, a, E=As) a time averaged spectrum would result.

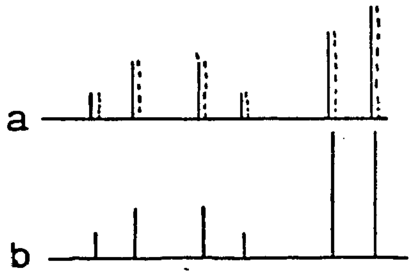


Figure 16. Resonances predicted for a conformationally non-rigid ring formed from the 2,2-dmdap ligand; X≠Y.
a. resonances for each conformer
b. time-averaged resonances

(For simplicity, Figure 16 assumes a 1:1 ratio of conformers.)

Similar arguments hold for the phosphine derivatives; the methylene resonances, however, would be too complex for straightforward interpretation.

Slowly Interconverting Conformers: The Variable Temperature NMR Experiment

Rapid interconversion of two conformers can often be slowed appreciably or halted by reducing the temperature of the solution. The previously cited work on cyclohexane is an example of this.

Variable temperature nmr experiments are often performed on ring systems to study the rate of interconversion. As the temperature of the solution under study is lowered the six-membered rings will interconvert less rapidly; each conformer will have a longer lifetime as there is now not enough energy to surmount the potential energy barrier to interconversion. Thus, the spectrum typical of the stereochemically non-rigid molecule will degenerate: resonances will broaden, becoming flatter as temperature decreases. As this spectrum collapses, a new spectrum -- that of the stereochemically rigid molecule -- will begin to appear as each conformer now has a lifetime comparable with the nmr time scale. At some temperature, called the limiting or coalescence temperature, the spectrum obtained will be that arising from only the rigid conformer(s);

lowering the temperature further will no longer affect the spectrum.

It is possible to run this experiment "in reverse" -- that is, to heat a solution of a molecule of a single conformer to see if interconversion to another conformer will occur. The possibility exists that bond breaking will occur before conformeric interconversion begins; this, however, is not an important piece of data. Temperature effects on chemical shifts are also seen at times.

Ligand Cone Angle

The ligand cone angle is a parameter useful in the discussion of comparative steric requirements of a ligand. Each ligand in a complex can be regarded as subtending a solid angle as viewed from the center of the metal atom; the ligand cone angle -- the apex of a cone, centered on the metal, just large enough to enclose the van der Waals radii of the outermost atoms of the ligand,[35] - is thus a measure of the ligand's ability to occupy space.

Ligand cone angles were orginally derived by measuring molecular models[35]; corrections have been made using an empirical correlation between the degree of substitution of CO on $Ni(CO)_4$ sealed with an eightfold excess of ligand L, measured by infrared spectroscopy.[2]

Cone angles derived for several ligands are listed in Table 3.

Table 3

Ligand Cone Angles (from reference 2)

X	θ, degrees
H	75
Me	90
$COCH_3$	100
Cl,Et	102
Br,Ph	105
I	107
$P(OMe)_3$	107
$Ph_2PCH_2CH_2PPh_2$	125
$Ph_2PCH_2CH_2CH_2PPh_2$	127
Cp	136
PPh_3	145

THE LIGANDS

The ligands 2,2-dimethyl-1,3-bis(diphenylphosphino) propane (2,2-dmdpp) and 2,2-dimethyl-1,3-bis(diphenylarsine)propane (2,2-dmdap) are synthesized by the method of Hewertson and Watson[58] involving cleavage of triphenylphosphine or triphenylarsine by sodium in anhydrous liquid ammonia (A) followed by reaction with an α,ω-dihalocarbon (C):

$$\text{(A)}\quad (C_6H_5)_3E + 2\,Na \xrightarrow{\text{liq } NH_3} (C_6H_5)_2ENa + C_6H_5Na$$

$$\text{(B)}\quad C_6H_5Na + NH_4Cl \xrightarrow{\text{liq } NH_3} C_6H_6 + NH_3 + NaCl$$

$$\text{(C)}\quad 2(C_6H_5)_2ENa + BrCH_2C(CH_3)_2CH_2Br \xrightarrow{\text{liq } NH_3}$$

$$(C_6H_5)_2ECH_2C(CH_3)_2CH_2E(C_6H_5)_2$$

The ligands crystallize as colorless plates from 2-propanol.

The proton nmr spectrum of 2,2-dmdpp in dichloromethane (Figure 17) appears as a singlet located at $\delta 1.11$ (6H) and a doublet centered at $\delta 2.41$ (4H, ${}^2J_{PH} = 3.1 \pm 0.2$ Hz). The spectrum of the diarsine in dichloromethane appears as two singlets resonating at 1.12 (6H) and 2.32 (4H).

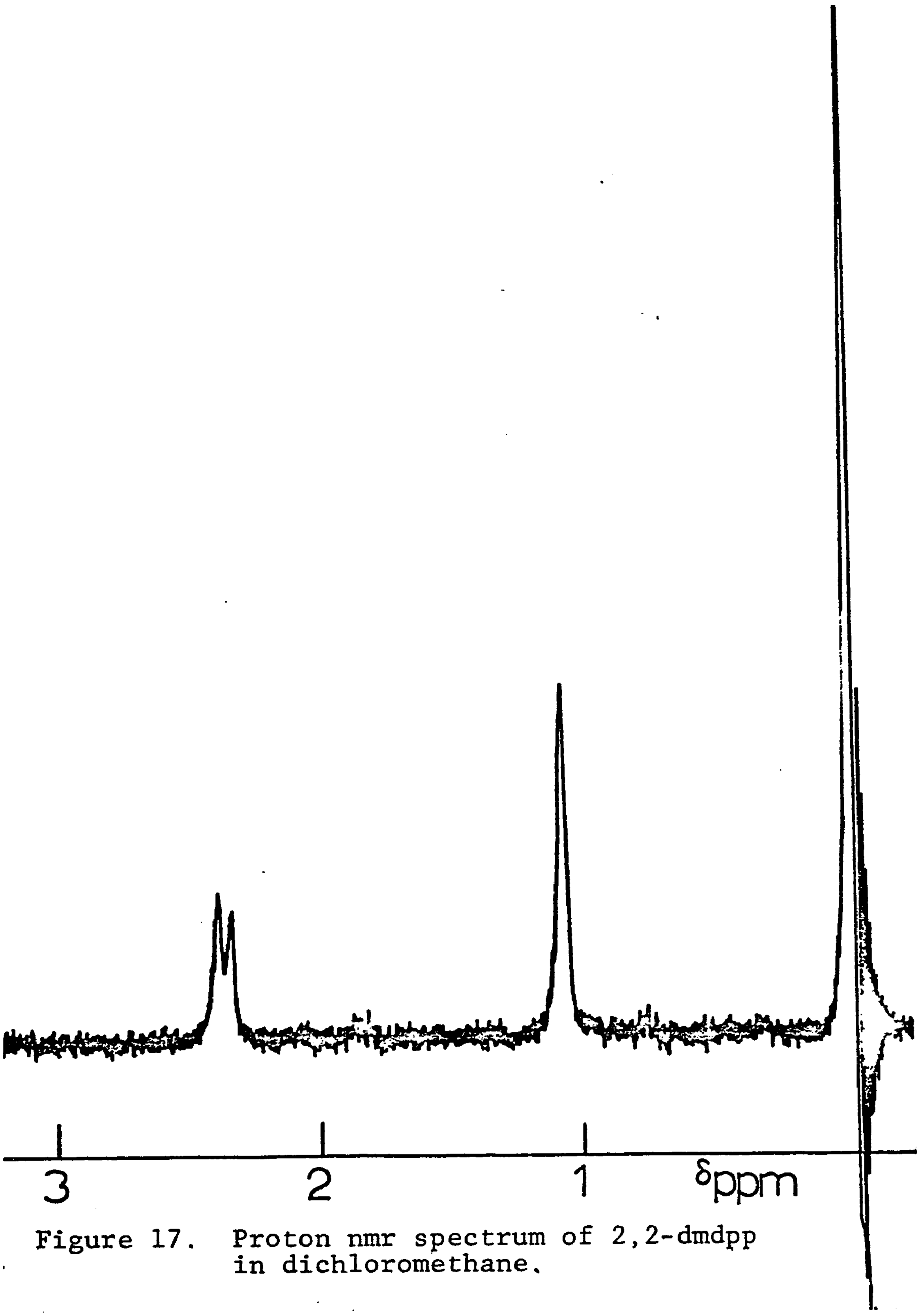


Figure 17. Proton nmr spectrum of 2,2-dmdpp in dichloromethane.

SYSTEMS WITH OCTAHEDRAL GEOMETRY: TETRACARBONYL DERIVATIVES

Introduction

The simplest complexes with chelating ligands that are derived from octahedral geometry are the tetracarbonyl derivatives of the Group VI metals molybdenum and tungsten: $M(CO)_4(L\text{-}L)$. This corresponds to a situation where X=Y=CO (see preceding chapter). Only one geometrical isomer is possible, though both conformations of this isomer can exist. As will be discussed later in this chapter, these compounds having C_{2v} local symmetry about the metal atom all are stereochemically non-rigid at ambient probe temperature and only the simple time-averaged spectra of the type discussed previously are observed.

Background

Hunter and Massey[8], working with the chelating ligand 1,3-bis(methylseleno)-2,2-dimethyl propane, found the Group VI carbonyl derivaties, $M(CO)_4(L\text{-}L)$, M=Cr, Mo, W, all exhibited temperature dependent stereochemical non-rigidity. Above room temperature the nuclear magnetic resonance spectrum consisted of three singlets; on lowering the temperature coalescence phenomena were seen, and below 240°K the spectra became "frozen out," and no further changes were seen. The "backbone methyl" group resonances appeared as a relatively broad singlet at approximately $\tau 8.7$ ($\delta 1.3$) and a doublet of lesser intensity centered slightly further upfield; two AB quartets of unequal intensity were observed in the methylene region. This was intepreted as being due to two unequally populated, *syn*-configured (the selenium methyl groups projecting on the same side of the ring; if the selenium methyls projected on opposite sides of the ring the system would be *anti*-configured), symmetric chair conformers. The broadened "backbone methyl" signal suggests that "increased nonbonding interactions between axial selenium-methyl groups causes some flattening of one of the chairm conformations,...displacing the equatorial geminal methyl group from the MSe_2 plane,...and giving it similar environment to its axial partner."[8] Flattening of the chair conformation should also affect the methylene signals; it was found that $\Delta\nu_{AB}$ was larger for one quartet than the other. The quartet with the smaller $\Delta\nu_{AB}$ "corresponded in intensity to that expected from the intensity of the geminal methyl singlet."

Cullen, *et al*.[6] investigated systems of the type $(CO)_4MAs(CH_3)_2CH_2CHRCD_2As(CH_3)_2$, where M = Cr, Mo,W and R=H, $C(CH_3)_3$. The metal carbonyl derivatives of the 1,3-*bis*(dimethylarsino)propane-d_2 ligand were found to be stereochemically non-rigid, yielding an AA'BB' spectrum. Two equivalent chair conformations are proposed, though skew-boat conformation cannot be discounted merely on the nmr evidence. It was also found that increasing bond lengths Cr-As $\overset{-}{<}$ MoAs W-As caused virtually no change in coupling constants, and thus changes in bond length are not reflected to any great extent by changes in the geometry of the ligand's backbone.

The tert-butyl derivative, however, forms complexes with a "locked" ring with the bulky tert-butyl group in an equatorial position. Only one conformer, the chair, was found.[6]

Cullen and Price[36] have synthesized the Group VI carbonyl derivatives of cis-1,3-bis(dimethylarsino)-2,2,4,4-tetramethylcyclobutane, forming complexes that have two six-membered rings as well as the cyclobutane ring inherent in the ligand. The presence of the cyclobutane ring in these complexes precludes the existence of skew-boat conformers, and as a result one of the six-membered rings has an unstable boat conformation if the other six-membered ring is in the more stable chair conformation (both conformations will have some distortion). If the complex is locked in one of the equivalent conformers two arsenic-methyl resonances and four ring-methyl resonances would be expected in solution.

The nmr spectra show only one arsenic-methyl resonance and two ring-methyl resonances; these results are consistent with rapid interconversion between equivalent conformers, or with a structure with a plane of symmetry through the C-As-M-As-C portion of the ring. The nmr spectrum shows no temperature dependence to -60°, suggesting that the symmetric structure may be favored in solution, as it lessens the repulsive force between the ring methyl groups and the axial metal carbonyl groups. (The crystal structure of the chromium derivative has been done; the C-As-Cr-As-C portion of the molecule has been found to be nearly planar.)

Stelzer and coworkers[37] have synthesized a six-membered ring compound with nitrogen and silicon in place of a carbon chain:

$$(CO)_4Mo(PMe_2NHSi(Me)_2NHPMe_2$$

Only one resonance was found for the $SiMe_2$ methyl groups; variable temperature studies, however, were not performed.

Synthetic Results

The 2,2-dmdpp and 2,2-dmdap derivatives of molybdenum hexacarbonyl are synthesized by direct substitution of the chelating ligand in refluxing methylcyclohexane (b.p. 101°C):

$$Mo(CO)_6 + L\text{-}L \xrightarrow{\Delta} Mo(CO)_4(L\text{-}L) + 2CO$$

L-L = 2,2-dmdpp, 2,2-dmdap

Derivatives of tungsten hexacarbonyl are synthesized by photolysis of the chelating ligand with the metal carbonyl in tetrahydrofuran (THF):

$$W(CO)_6 + L\text{-}L \xrightarrow{h\nu} W(CO)_4(L\text{-}L) + 2CO$$

L-L = 2,2-dmdpp, 2,2-dmdap

All four complexes are yellowish crystalline solids, obtainable in pure form by recrystallization from benzene/hexane mixtures. The complexes were identified by elemental analysis, infrared and nuclear magnetic resonance spectroscopy.

Discussion and Results

Infrared Spectral Analysis

The molybdenum and tungsten hexacarbonyl derivatives of 2,2-dimethyl-1,3-*bis*(diphenylphosphino)propane and 2,2-dimethyl-1,3-*bis*(diphenylarsino)propane exhibit infrared spectra typical of *cis*-disubstituted Group VI metal carbonyl compounds.[13]

If the carbon chain backbone of the ligand is ignored the complexes have approximate C_{2v} symmetry; four CO stretching modes are predicted, all of which are infrared and Raman active.[15]

Figure 18. Infrared absorptions in the CO stretch region of $Mo(CO)_4$(2,2-dmdpp) in methylcyclohexane.

Figure 19. Infrared absorptions in the CO stretch region of $W(CO)_4$(2,2-dmdap) in methylcyclohexane.

Table 4 lists the absorptions of the four metal carbonyl derivatives in methylcyclohexane solution, and their assignments, based on Cotton and Kraihanzel's analysis of $W(CO)_4(dppe)$[15] which also has localized C_{2v} symmetry about the metal atom.

Table 4

CO Stretching Frequencies for $M(CO)_4(L\text{-}L)$, (M=Mo,W, L-L=2,2-dmdpp or 2,2-dmdap)

Metal	Ligand	Absorptions (cm^{-1}) and Assignments			
		A_1	A_1	B_1	B_2
Mo	2,2-dmdpp	2018m	1932m	1914s,sh	1906vs
W	2,2-dmdpp	2018m	1929m		1902vs
Mo	2,2-dmdap	2023m	1930s	1917vs	1900vs
W	2,2-dmdap	2021m	1926s	1910vs	1897vs

intensities: m = medium, s - strong, vs = very strong
sh = shoulder

The *trans* pair of carbonyl groups give rise to the B_1 and the "almost forbidden" A_1 modes (Figure 20, a,b,), while the second A_1 and the B_2 modes are attributable to the *cis* carbonyl groups (Figure 20, c,d).[38]

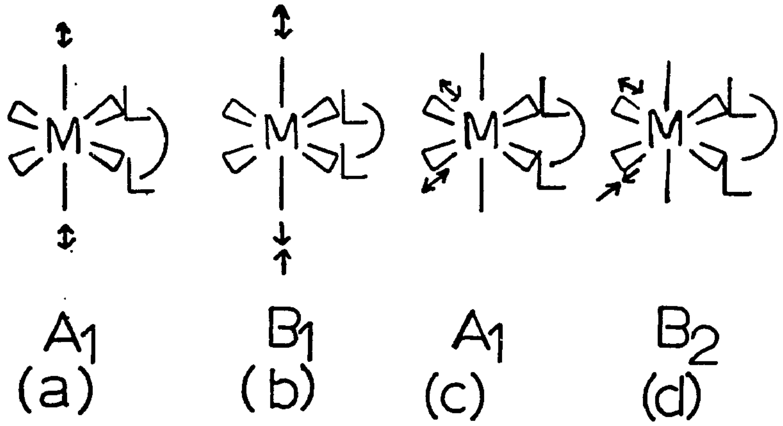


Figure 20. CO Stretching modes for $M(CO)_4(L-L)$

Note should be taken that while the weaker A_1 mode can definitely be assigned to the band at highest frequency and the B_1 mode to the band at lowest frequency,[39] the assignment of the second A_1 and the B_2

modes is solvent dependent in some cases.[40] The spectra obtained for the metal tetracarbonyl complexes of 2,2-dmdpp and 2,2-dmdap are so similar to those found by Cotton and Kraihanzel for $W(CO)_4(dppe)$[15] that the above assignments are felt to be justified.

Nuclear Magnetic Resonance Spectral Analysis

If the systems formed from the 2,2-dimethyl-1,3-dichalcogenatopropane ligands are stereochemically non-rigid, the axial and equatorial methylene protons interchange rapidly, and so are magnetically equivalent on the nmr time scale, and, assuming coupling to atom E does not exist and possible cross-ring coupling of methylene protons or long-range coupling to the methyl protons is too small to be resolved, a simple singlet would be expected for the methylene resonance. If, however, coupling of the methylene protons to nucleus E does exist (E=P), the methylene nuclei will exhibit a "virtual coupled" spectrum,[41-44] due to coupling of different magnitudes between the methylene protons and each E nucleus.

The appearance of this "virtually coupled triplet" depends largely upon the coupling between the two phosphorus atoms[41] and, as demonstrated by the work of King[45] and Jenkins and Shaw,[46] and will vary from metal to metal even with the same ligand. The phenomenon of virtual coupling will be discussed in greater detail later in this chapter.

If the system is stereochemically rigid each methylene resonance will, in the absence of coupling to atom E, appear as an AB quartet. If the ring is distorted, and the bond angle about one methylene carbon is not the same as the angle about the other methylene carbon, two AB quartets might be expected. In solution, however, it is possible that even slight mobility of the ring would negate this effect, and only one "time-averaged" quartet will be seen.

Again, if coupling exists to nucleus E (E=P), coupling of both the axial and equatorial methylene protons to both E nuclei would be expected, each coupling (*i.e.* J_{H_aE}, J_{H_eE}, $J_{H_aE'}$, $J_{H_eE'}$) being of a different magnitude. This, along with the possibility of cross-ring coupling of the methylene protons, leads to the prediction of a "complex multiplet" for the methylene resonances in this case, the form of which will depend on the previously mentioned coupling constants.

The methyl resonances will be a simple singlet if the molecule exhibits stereochemical non-rigidity, as the axial and equatorial methyl chemical shifts are time-averaged by the rapid interconversion of conformers relative to the nmr time scale. If the phosphine ligand is used, (E=P), any possible through-space coupling of the phosphorus atoms to the methyl groups will affect both groups equally. Coupling to the methylene protons will also be the same for both methyl groups.

As the temperature is lowered a stereochemically nonrigid molecule may lose some of its "fluxionality" until it will, at some temperature, become stereochemically rigid. At this coalescence (or limiting) temperature the nmr spectrum will be that of the stereochemically rigid system; no change will be observed in the spectrum at temperatures below the coalescence temperature. Two methyl resonances are expected, the resonance due to the axial methyl being of less height and broader than that of the equatorial methyl, due to far bond coupling to the axial methylene protons.

The ^1H nmr spectra of the metal carbonyl derivatives of 2,2-dimethyl-1,3-bis(diphenylarsino)propane (M = Mo,W) (Table 5) exhibit singlets for both the methyl and the methylene resonances in a 3:2 ratio.

Table 5

Proton nmr Resonances of $M(CO)_4$(2,2-dmdap) Complexes

	$^{\delta}$C-CH$_3$	$^{\delta}$As-CH$_2$-C	Solvent
Mo	0.99	2.31	CS_2
W	0.78	2.16	Toluene d_8

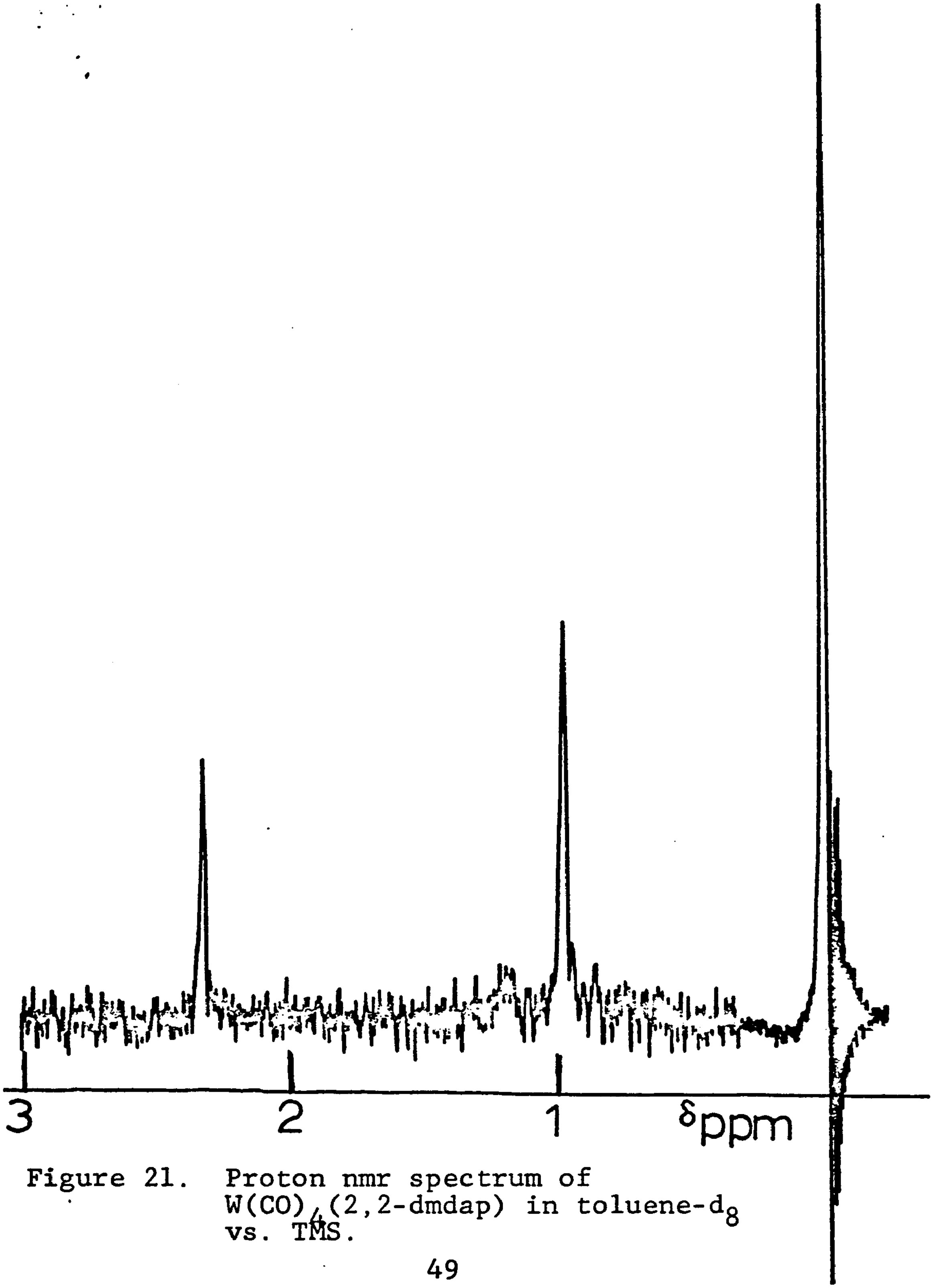


Figure 21. Proton nmr spectrum of $W(CO)_4(2,2\text{-dmdap})$ in toluene-d_8 vs. TMS.

Both of these compounds exhibit stereochemical non-rigidity at ambient probe temperature, as evidenced by both the methylene and methyl singlets; if the ring was locked an AB quartet would be expected for each methylene resonance (one AB quartet if both methylene groups are magnetically equivalent) and a singlet would be expected for each methyl group.

The nmr spectra of both the molybdenum and tungsten compounds exhibited some degree of temperature dependence. The resonances of the molybdenum compound showed some broadening and loss of peak height by -60°C in C S_2; by -80°C solid had precipitated from the dilute solution and further nmr spectral analysis was impossible. The tungsten analog, however, exhibited significant broadening by -20°C in toluene-d_8; by -60°C the original spectrum had completely collapsed, though no new resonances were seen.

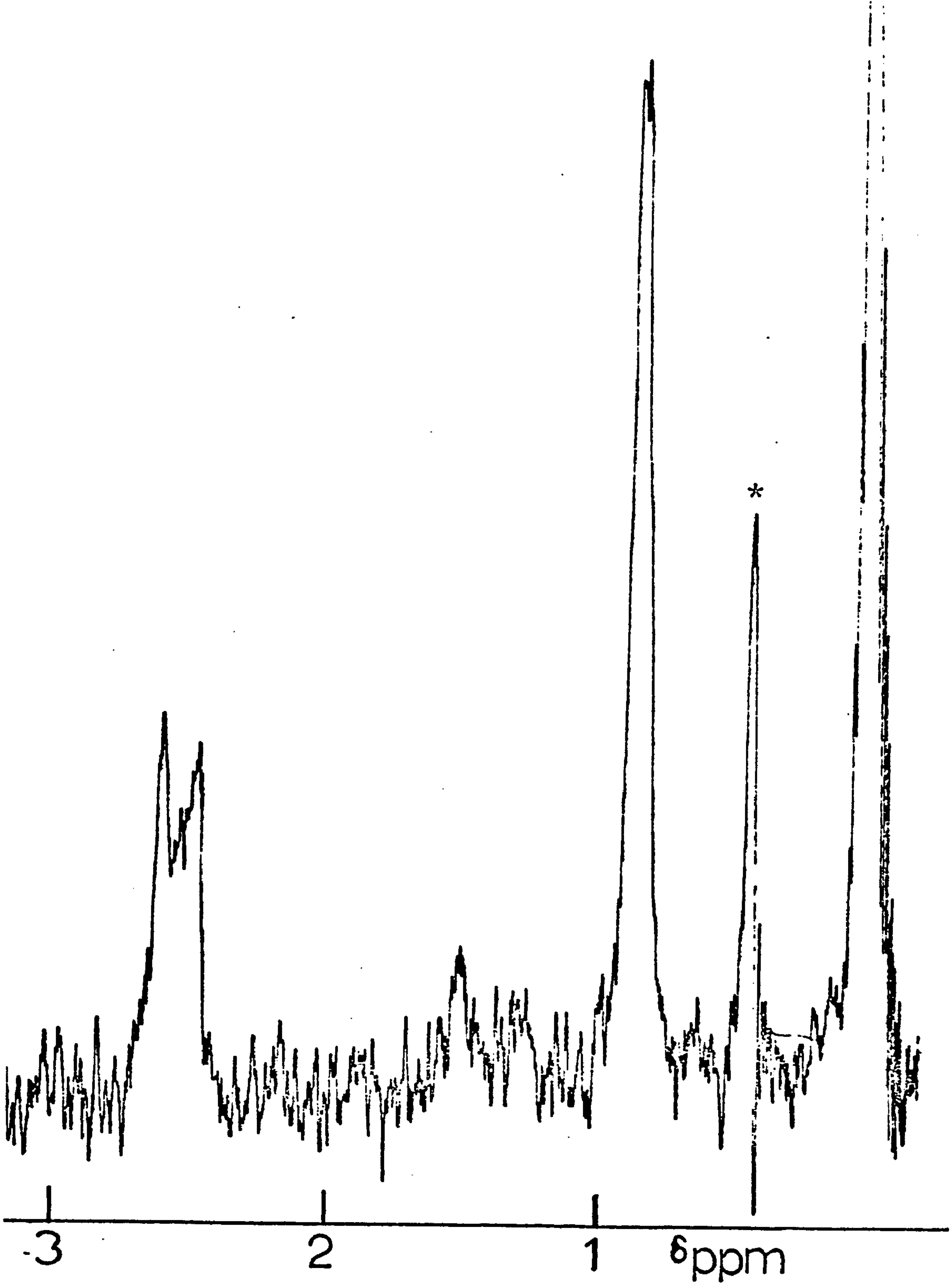
The ^1H nmr of 2,2-dimethyl-1,3-bis(diphenylphosphine)propane tetracarbonyl derivatives of molybdenum and tungsten exhibit one methyl resonance and a "virtual coupled triplet"[41], typical of an $X_nAA'X'_n$ system.

Table 6

Proton NMR Data for $M(CO)_4$(2,2-dmdpp) Complexes

Metal	$^{\delta}CCH_3$(ppm)	$^{\delta}P\text{-}CH_2\text{-}C$(ppm)	Solvent
Mo	0.83(singlet)	2.44(doublet)	$CDCl_3$
W	0.86(singlet)	2.56(doublet)	$CDCl_3$

Figure 22. Proton nmr spectrum of $W(CO)_4$(2,2-dmdpp) in $CDCl_3$. (* = spinning side band)



Once again, the absence of two distinct methyl resonances and the "simple" virtual coupled spectrum of the methylene protons indicates the systems are non-rigid at 34°C.

For a virtual coupled $X_nAA'X'_n$ system a total of (2n+1) pairs of lines symmetrically placed about ν_X is expected[41]. Two of these lines appear as a doublet (called the N-doublet; the lines are separated by a value of $N = |J_{AX} + J_{AX'}|$) with relative intensity equal to 2^{2n-1}. The remainder of the resonances are pairs of lines found both within and outside the N-doublet. As the value of $|J_{AX}-J_{AX'}|/|J_{AA}|$ decreases the intensities of the lines outside the N-doublet become very small and are usually not seen. The lines inside the N-doublet move closer together as the value of $|J_{AX}-J_{AX'}|/|J_{AA}|$ decreases, until the limiting case, $|J_{AA}|>>|J_{AX}-J_{AX'}|$, is reached and the resonance appears as a 1:2:1 triplet, as the central lines are now so close together they cannot be resolved. The remainder of the total intensity is spread over these 2n remaining pairs of lines.

Complexes of the chelating ligand 2,2-dimethyl-1,3-bis(diphenylphosphino)propane would be considered $X_2AA'X'_2$ systems; thus, five pairs of lines -- the N doublet, two inner pair, and two outer pair, would be expected. The separations of the outer and inner pairs of lines are given,[41] respectively, by

$$S_o(\chi) = \{\chi^2L^2+J_{PP}2\}^{\frac{1}{2}} + \{(\chi-1)^2L^2+J_{PP}^2\}^{\frac{1}{2}}$$

and

$$S_i(\chi) = \{\chi^2L^2+J_{PP}^2\}^{\frac{1}{2}} - \{(\chi-1)^2L^2+J_{PP}^2\}^{\frac{1}{2}}$$

where $\chi=1,2$ for the $X_2AA'X_2'$ system and $L=|{}^2J_{PH}-{}^4J_{PH'}|$ It is easily seen that $S_o(1) - S_i(1) = 2J_{PP}$. Thus if, as suggested by Finer and Harris[47], use of high radiofrequency power will sometimes allow the first set of outer resonances to be seen, and if the inner lines can be resolved, J_{PP} can be obtained directly from the spectrum. L can then be calculated from the value of J_{PP} thus obtained, and, if the probable signs of the coupling constants are known from similar compounds, the expressions for L and W can be mathematically combined to yield J_{AX} and $J_{AX'}$. (Computer simulation of nmr spectra is a useful tool in evaluating signs and magnitudes of coupling constants.) King[45] found that the methyl resonances in the nmr spectra of $[(Me_2N)_3P\ {}_2M(CO)_x]$(M=Cr,Mo,W,x=4; M=Ni,x=2; M=Fe,x=3) were virtual coupled; the phosphorus-phosphorus coupling, however, differed with the metal atom used. P-P coupling increased in series Ni<< Cr < Mo ≡ W < Fe.) The structures of all these complexes were found (by IR evidence) to be <u>trans</u>. The coupling, King states, is possibly related to the <u>trans</u> effect.

Table 7

Coupling Constants for *cis*-$(Me_3P)_2M(CO)_4$

Compound	N(Hz)	$^2J_{PH}$ (Hz)	$^4J_{PH'}$ (Hz)	$^2J_{PP}$ (Hz)	Solvent
cis-$Cr(CO)_4(Me_3P)_2$	-6.9±.1	-7.1±.2	+0.2±.2	-36±1	Benzene
cis-$Mo(CO)_4(Me_3P)_2$	-6.3±.1	-6.6±.2	+0.3±.2	-29.7±.1	Benzene
cis-$W(CO)_4(Me_3P)_2$	-7.09±.02	-7.34±0.05	+0.25± .05	-25.0±0.1	Benzene

(All data from ref. 49)

In the chelated system the phosphorus atoms are in <u>cis</u> positions; the P-P coupling would be expected to be small.[48] Ogilvie, Jenkins and Verkade[49] have measured $^{2}J_{PP}$ and N ($N = |^{2}J_{PH} + ^{4}J_{PH'}|$) and have thus obtained values of $^{2}J_{PH}$ and $^{4}J_{PH'}$ for <u>cis</u>-$M(CO)_4L_2$ systems (M=Cr,Mo,W) (Table 7).

Attempts were made to analyze the virtual coupled H_2PPH_2 systems and obtain similar data for the 6-membered ring systems. While N could be measured directly, the "inner lines" (those inside the N-doublet) could not be resolved (Figures 23,24). The N values for the molybdenum and tungsten complexes of 2,2-dmdpp are listed in Table 8.

Table 8

N values ($= |^{2}J_{PH} + ^{4}J_{PH'}|$) for Complexes of 2,2-dmdpp

Metal	N value
Mo	7.1 ± .2 Hz
W	7.4 ± .2 Hz

This is on the same order of magnitude as the values obtained by Verkade (Table 7 previous). Small peaks were observed symmetrically positioned about the methylene resonance in the molybdenum complex, though not in the tungsten complex on increasing the r.f. power. These peaks are separated by a distance of 54.6 ± 2 Hz.

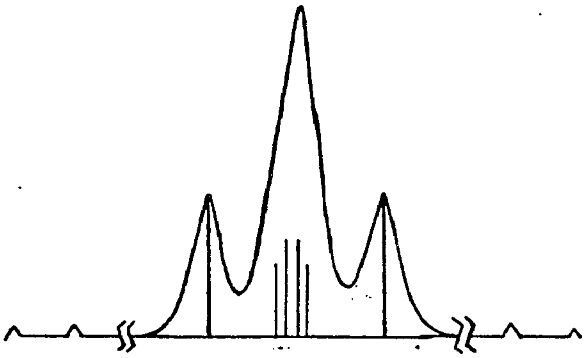


Figure 23. Predicted methylene resonances for the virtual coupled $H_2PP'H_2'$ system.

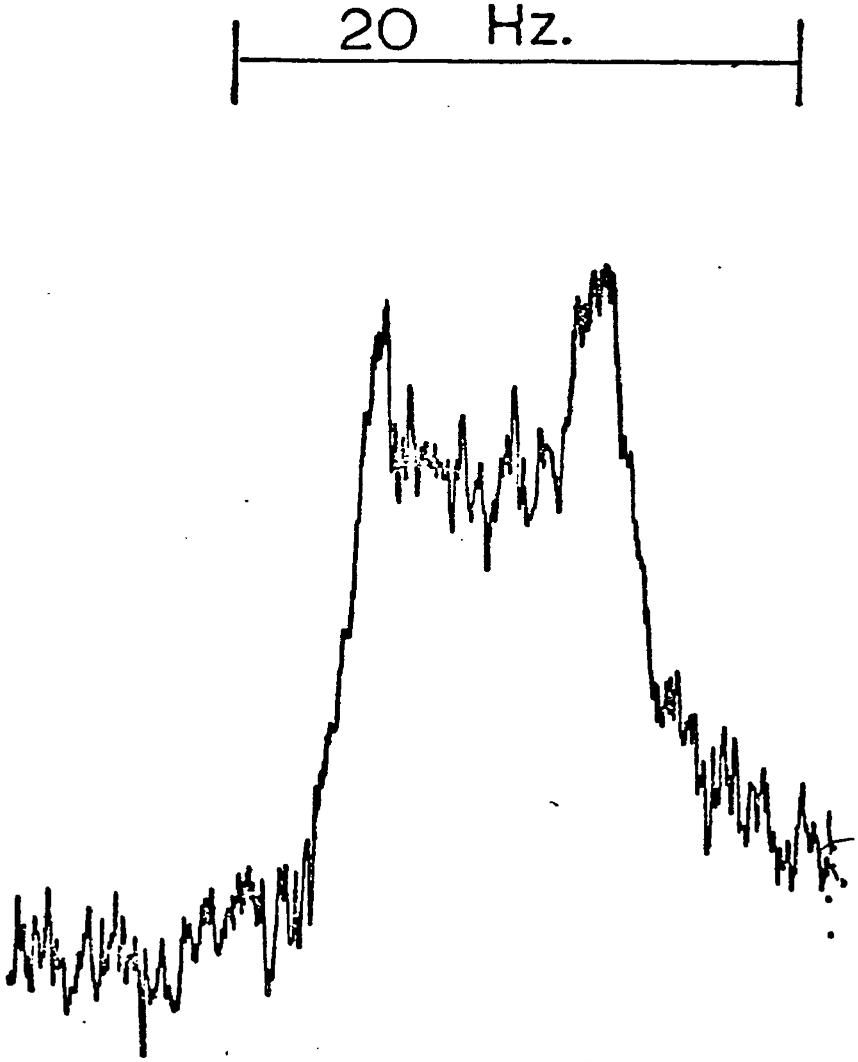


Figure 24. Methylene region of the proton nmr spectrum of $W(CO)_4$(2,2-dmdpp) in $CDCl_3$.

Although the inner peaks could not be resolved, it is reasonable to assume an inner peak separation, Si(1), of 1-2 Hz, based on the data presented by Ogilvie, *et al.*[49] for *cis* complexes of trimethylphosphine, as the N doublet values are similar. Thus, $^2J_{PP}$ for the molybdenum complex of 2,2-dmdpp is on the order of 25-27 Hz, which again is consistent with the order of magnitude of $^2J_{PP}$ found by Ogilvie for the *cis*-trimethylphosphine complexes and Grim[50] for complexes of $Ph_2P(CH_2)_3PPhR$ (R=Me,i=Pr). Lynden-Bell and Nixon[51] suggest that the sign of $^2J_{PMP}$ is likely to be negative in all *cis*-disubstituted octahedral complexes of Group VIB metals. A molecular orbital treatment of the origins and the signs of these coupling constants has been detailed.[48] Grim[50] has theorized that the phosphorus-phosphorus coupling in chelate rings is transmitted by two paths -- through the ligand backbone (J^B_{PP}) and through the metal center (J^M_{PP}), and the observed coupling is the sum of these two:

$$J_{PP} = J^B_{PP} + J^M_{PP} \ .$$

$^4J^B_{PP}$ is zero (or practically so) in the six-membered rings studied by Grim, and thus the equation reduces to $|J_{PP}| = |^2J^M_{PP}|$; a value of 28 Hz was found for $|^2J^{Mo}_{PP}|$, and 22 Hz for $|^2J^W_{PP}|$.

SYSTEMS WITH OCTAHEDRAL GEOMETRY: TRICARBONYL DERIVATIVES

Introduction

Two isomers are possible for octahedral metal carbonyl derivatives formed from a chelating ligand and a monodentate ligand: fac- (facial), in which the ligand moieties occupy the face of an octahedron, or mer- (meridional), in which all three ligand donor atoms are in a plane containing the metal atom.

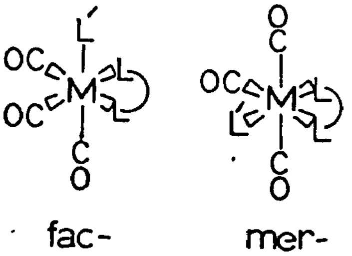


Figure 25. fac- and mer- isomers of $M(CO)_3(L')(L-L)$

If the six membered ring is locked, the fac-isomer will have two possible conformers; both conformers of the mer- geometry are equivalent.

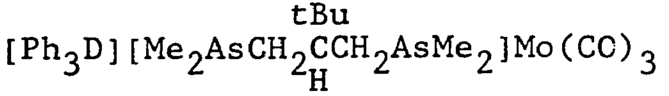
For transition metal carbonyl derivatives, the infrared spectra of the fac- and mer- structures in the 2000 cm^{-1} region are quite different and identification can often be made using infrared data alone, as discussed previously. Differentiation between the two facial conformers is more difficult; nmr techniques such as double resonance (i.e. decoupling experiments) or selective deuteration are often useful in this type of situation.

In this chapter several trisubstituted complexes derived from octahedral geometry are examined. Several aspects of the structures of these complexes are examined, with a view to addressing the questions posed in the introduction.

Background

Dobson and Houk[52] have found the geometry of the product formed from the reaction of (dppe)Mo$(CO)_4$ with monodentate phosphine, arsine and stibine ligands to be dependent on the steric demands of the incoming monodentate ligand. A carbonyl moiety trans to another carbonyl is expected to be more labile, according to π-bonding arguments[52,53] than a carbonyl trans to a phosphine, and the facial product is ordinarily to be expected. Ligands that are sterically demanding, however, result in crowding at the face of the octahedron, and thus the meridional product is formed. Dobson and Houk have found that reaction of Ph_3P and Ph_3As with (dppe)-Mo$(CO)_4$ yields the <u>mer</u>- isomer, whereas the product of the reaction with Ph_3Sb is the <u>fac</u>- isomer. This is attributed to reduction of the steric interaction between the phenyl groups of the Ph_3Sb ligand and the other moieties on the metal due to the larger size of the Sb atom.[52]

Cullen and Pomeroy[54] have investigated the effect of steric requirements on the six-membered rings formed by metal complexes of the chelating ligand $(CH_3)_2AsCH_2$-$CHRCH_2AS(CH_3)_2$, R = H, t-butyl. The steric requirements of the arsine seem to be less than those of dppe, due both to the larger size of the arsenic atom and the use of methyl instead of phenyl groups bonded to the arsenic atom. Thus, all of the compounds $(Ph_3P)[(CH_3)_2AsCH_2$-$CHRCH_2As(CH_3)_2]M(CO)_3$, M = Mo,W; R = H,t-butyl, are found to have fac- geometry.



Complexes with four, five, and six-membered rings formed from halomanganesepentacarbonyl are also found to exhibit fac- geometry.[9,54] The complex $(dppe)Mn(CO)_3$-$GeCl_3$, however, exhibits a meridional structure[55]; this is attributed to interaction between the bulky $GeCl_3$ moiety and the aryl groups attached to the phosphorus atoms. $[Ph_3D][Me_2AsCH_2\overset{tBu}{\underset{H}{C}}CH_2AsMe_2]Mo(CO)_3$ has facial geometry despite both the sterically bulky Ph_3P ligand and the large t-butyl group on the ring[54]; $(Me_2As(CH_2)_3$-$AsMe_2)Mn(CO)_3GeCl_3$ has also been found to have fac-geometry.[55] Kraihanzel and Maples[9] report that $(Ph_2PC$-$(Me)_2PPh_2)(Ac)Mn(CO)_3$ has meridional geometry but the decarbonylation product, $(Ph_2PCMe_2PPh_2)(Me)Mn(CO)_3$, has fac- geometry. The complex $ClMn(CO)_3(Ph_2PC(CH_3)_2PPh_2)$, which has facial geometry, isomerizes to mer-

$Cl_3SnMn(CO)_3(Ph_2PC(CH_3)_2PPh_2)$ on reaction with $SnCl_2 \cdot 6H_2O$.[59] Thus, overall, two trends are observed:

(1) interaction of the ring and other ligands on the metal atom decreases with increasing chain length, and

(2) for five- or six-membered rings, interaction between groups bonded to the chalcogen donor atom and the axial ligands on the metal seems to play an important role in determining the structure of the complex[56]; this interaction is dependent on the size of these groups, the size of the donor atom, and the size of the other ligands. Steric crowding on the carbon-chain backbone of the five- or six-membered ring, however, seems to play little part in determining whether the final complex will be in facial or meridional form.

Synthetic Results

The halomanganese pentacarbonyl derivatives of 2,2-dmdpp and 2,2-dmdap are synthetically obtainable by two routes: thermal reaction in refluxing methylcyclohexane (b.p. 101°C) (A) or photochemical reaction in THF (B). The product obtained from both reactions is the same.

$$\text{(A)} \quad X\,Mn(CO)_5 + L\text{-}L \xrightarrow[\text{methylcyclohexane}]{\Delta} XMn(CO)_3\text{-}(L\text{-}L) + 2CO$$

$$\text{(B)} \quad X\,Mn(CO)_5 + L\text{-}L \xrightarrow[\text{THF}]{h\nu} X\,Mn(CO)_3(L\text{-}L) + 2CO$$

The reaction in methylcyclohexane yields the pure product as needles on cooling the reaction mixture; the products are also purified by recrystallization from THF/methanol.

Acetylmanganesetricarbonyl derivatives of the chelating ligand were prepared by stirring methylmanganese pentacarbonyl[57] with the ligand in benzene solution for 24 hours under a nitrogen atmosphere. Hexane was added to the cloud point, then the solution was cooled, yielding the pure product as a yellow solid.

$$CH_3Mn(CO)_5 + L\text{-}L \xrightarrow{\text{benzene}} CH_3COMn(CO)_3(L\text{-}L) + CO$$

Heating a benzene solution of the acetylmanganesetricarbonyl derivative of either ligand under reflux for 72 hours under nitrogen caused decarbonylation of the acetyl moiety, yielding the methylmanganese-product.

$$CH_3COMn(CO)_3(L\text{-}L) \xrightarrow[\text{benzene}]{\Delta,\text{72 hr}} CH_3Mn(CO)_3(L\text{-}L)$$

The product is the same as that obtained by heating methylmanganesepentacarbonyl with the chelating ligand under nitrogen in benzene for 72 hours.

$$CH_3Mn(CO)_3 + L\text{-}L \rightarrow CH_3Mn(CO)_3(L\text{-}L) + 2CO$$

The pure product was obtained as golden crystals by recrystallization from benzene/hexane mixtures.

Infrared Spectral Results

Infrared data for trisubstituted complexes of 2,2-dmdpp and 2,2-dmdap are presented in Tables 9 and 10.

Both the fac- and mer- isomers of $XMn(CO)_3(L\text{-}L)$ have C_s symmetry; group theory predicts three CO-stretching modes -- 2A' + A'' (Figures 26 and 27). All three stretching modes are both infrared and Raman active.

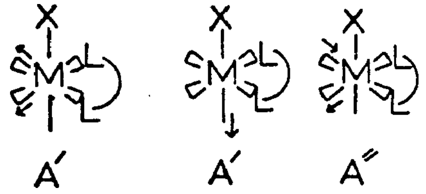


Figure 26. Normal modes of vibration of fac-$XM(CO)_3(L\text{-}L)$

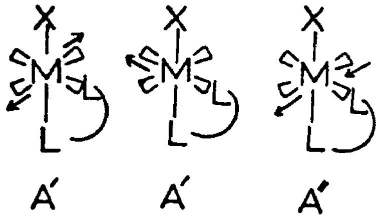


Figure 27. Normal modes of vibration of mer-$XM(CO)_3(L\text{-}L)$

The pattern of absorptions for the methyl-, acetyl- and halomanganesetricarbonyl derivatives of both the 2,2-dmdpp and 2,2-dmdap ligands corresponds closely to that found by Kraihanzel and Maples[9] for the facial

Table 9

Infrared CO absorptions and structural assignments for $XM(CO)_3(2,2\text{-dmdpp})$ complexes
M = Mn

X	Absorptions (cm^{-1})	Solvent	Structure
Cl	2027,1967,1892	Nujol	fac
	2029 s,sp; 1964 m,sp; 1905 m,sp	CH_2Cl_2	
Br	2023 1967 1894	Nujol	fac
	2026 s,sp; 1964 m,sp; 1904 m,sp	CH_2Cl_2	
I	2021 1964 1895	Nujol	fac
	2022 s,sp; 1961 m,sp; 1906 m,sp	CH_2Cl_2	
Acetyl	2010 s,sp; 1920 s,br (C=O, 1582,m,br)	CH_2Cl_2	fac
Methyl	1997 s,sp; 1920 m,sp; 1875 m,sp	CH_2Cl_2	fac

Intensities: s = strong, m = medium, sp = sharp, br = broad.

Table 10

Infrared absorptions and structured assignments for $XM(CO)_3(2,2\text{-dmdap})$ complexes.
M = Mn

X	Absorptions (cm^{-1})	Solvent	Structure
Cl	2029; 1965; 1896	Nujol	*fac*
	2028 s,sp; 1960 m,sp; 1908 m,sp	CH_2Cl_2	
Br	2026; 1966; 1897	Nujol	*fac*
	2038 s,sp; 1974 m,sp; 1927 m,sp	CH_2Cl_2	
I	2022; 1962; 1898	Nujol	*fac*
	2021 s,sp; 1958 m,sp; 1909 m,sp	CH_2Cl_2	
Acetyl	2000 s,sp; 1914 br,m (C=O, 1574, br)	CH_2Cl_2	*fac*
Methyl	1996 s,sp; 1920 m,sp; 1884 m,sp	CH_2Cl_2	*fac*

Intensities: s = strong, m = medium, sp = sharp, br = broad isomers of methylmanganesetricarbonyl complexes of chelating biphosphines, and these complexes are accordingly assigned a facial geometry. Typical spectra for the iodo-, acetyl-, and methyl-manganesetricarbonyl derivatives of both ligands are exhibited in Figures 28-33.

Figure 28. Infrared absorptions in the CO stretch region of $IMn(CO)_3$(2,2-dmdpp) in dichloromethane

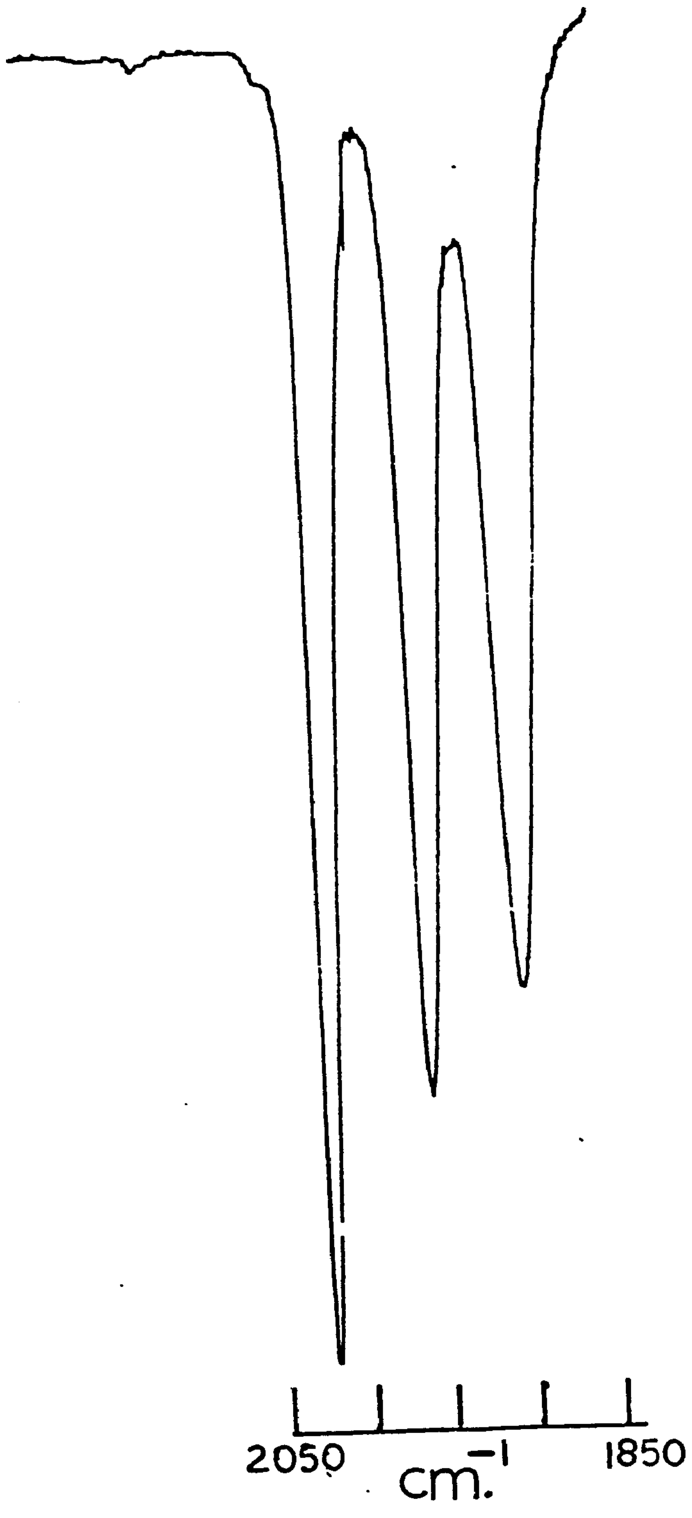
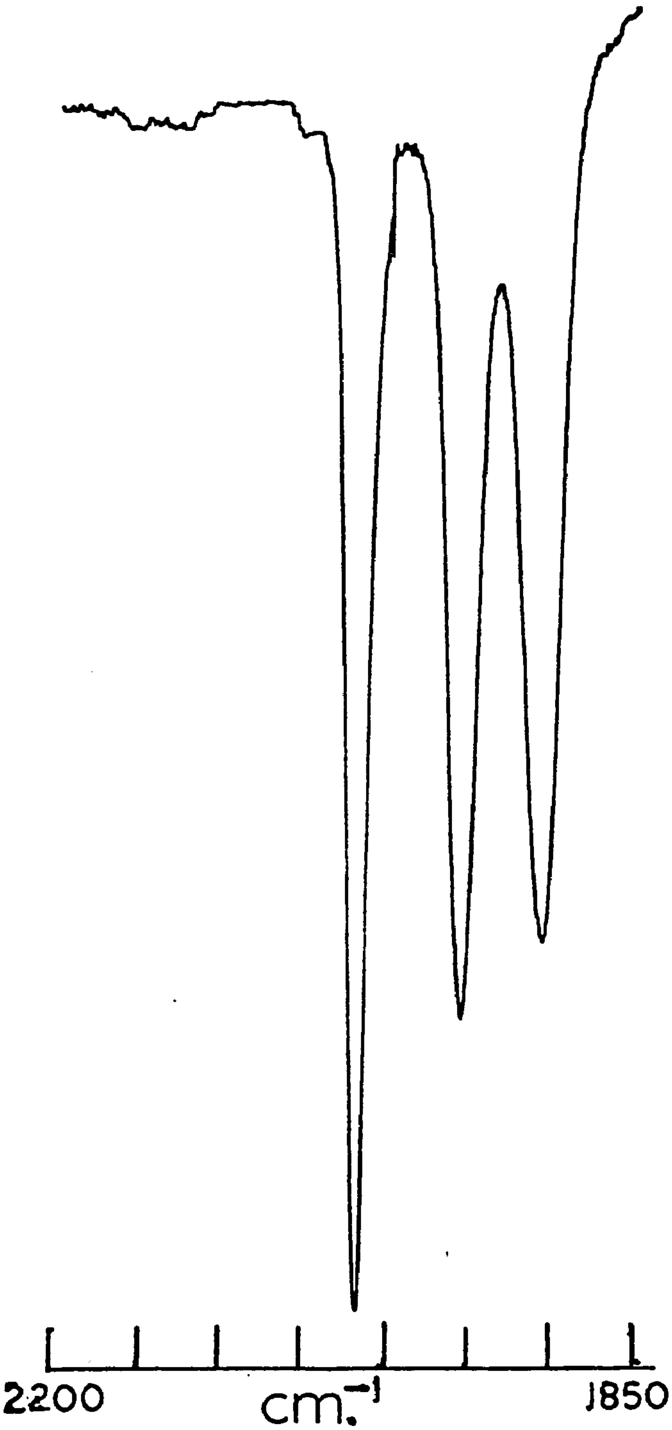


Figure 29. Infrared absorptions in the CO stretch region of $IMn(CO)_3$(2,2-dmdap) in dichloromethane



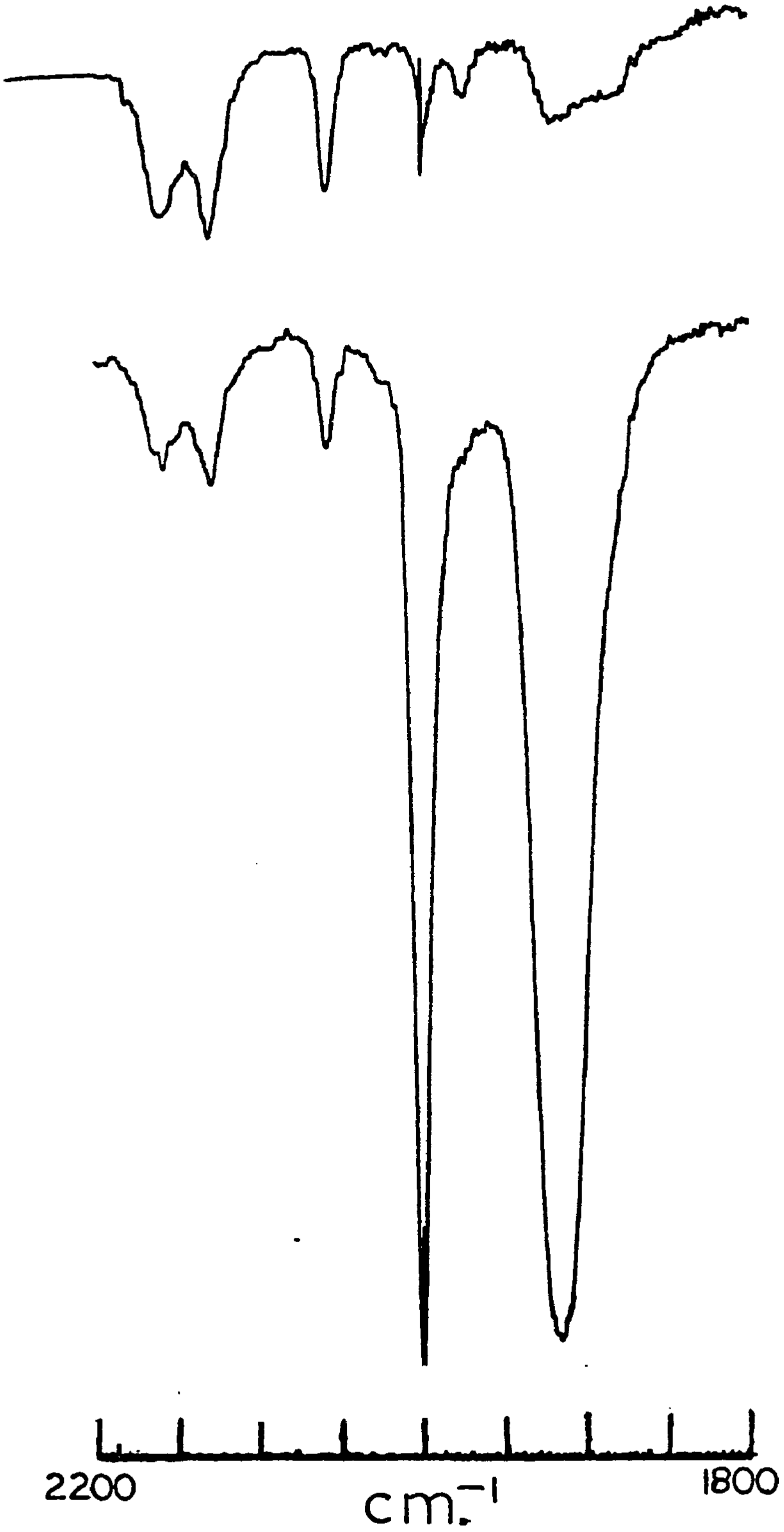


Figure 30. Infrared absorptions in the CO stretch region of AcMn(CO)$_3$(2,2-dmdpp) in dichloromethane

Figure 31. Infrared absorptions in the CO stretch region of AcMn(CO)$_3$(2,2-dmdap) in dichloromethane

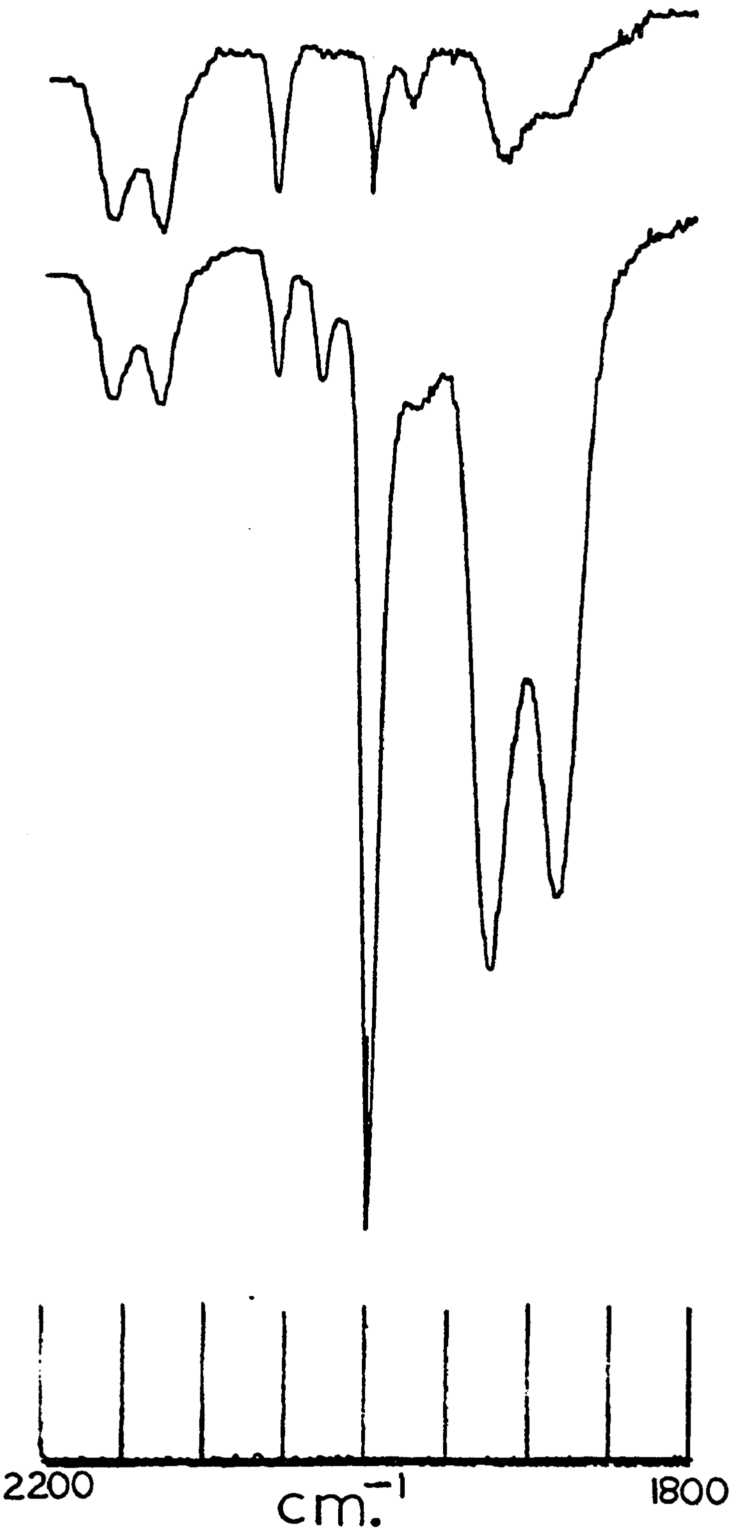


Figure 32. Infrared absorptions in the CO stretch region of MeMn(CO)$_3$(2,2-dmdpp) in dichloromethane

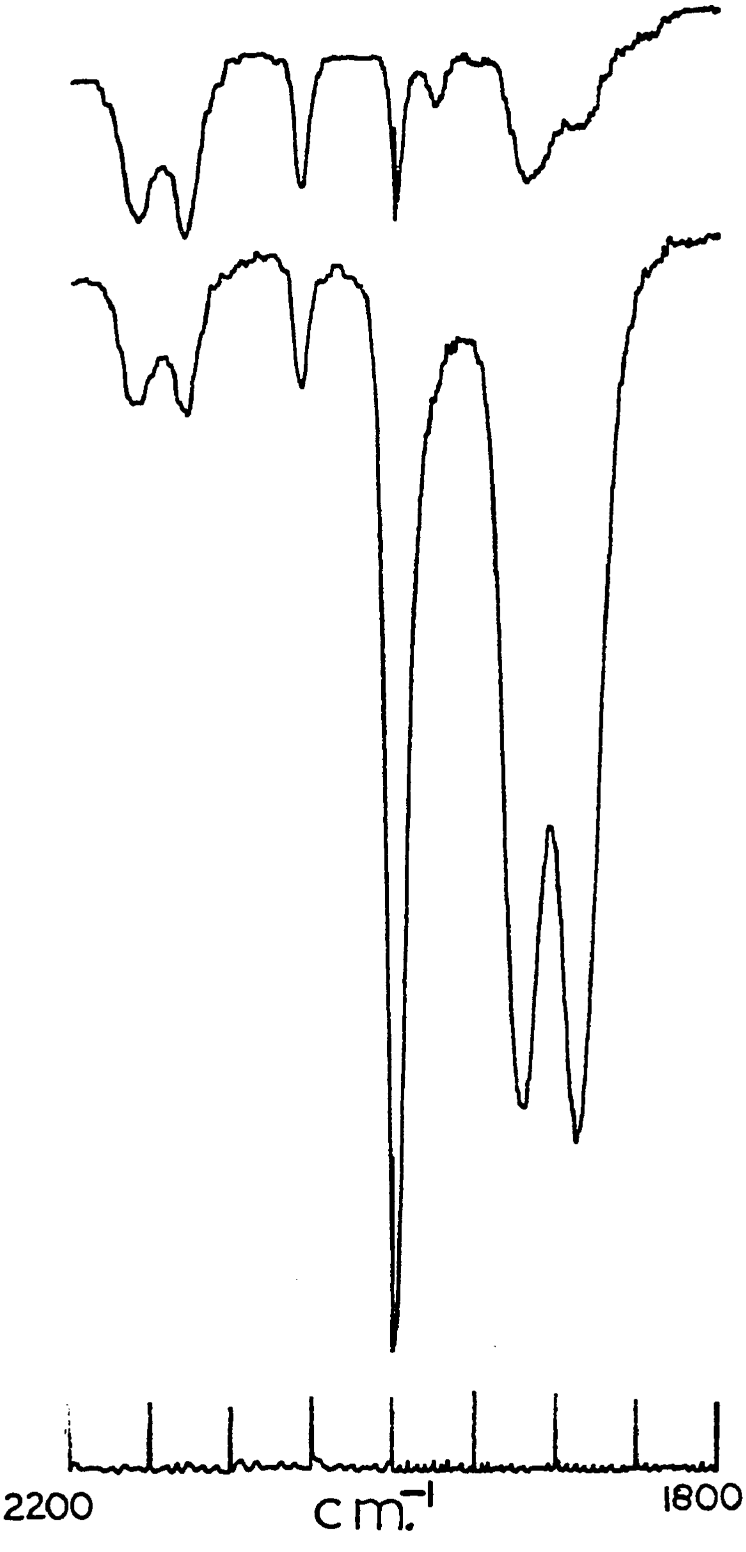


Figure 33. Infrared absorptions in the CO stretch region of $MeMn(CO)_3$(2,2-dmdap) in dichloromethane

NUCLEAR MAGNETIC RESONANCE SPECTRAL RESULTS

Halomanganese Tricarbonyl Derivatives

The 60 MHz proton nmr spectra of the halomanganese tricarbonyl complexes of 2,2-dmdpp, $XMn(CO)_3(2,2\text{-dmdpp})$, (X=Cl,Br,I) are all similar: two methyl resonances, the downfield resonance being the broader of the two, indicating a stereochemically rigid six-membered ring (Figure 34). The broad downfield resonance is assigned to the methyl group in the equatorial position. The methylene resonances appear as broad complex multiplets for the chloro- derivatives; they are not discernable from baseline noise in the spectra of the bromo- and iodo- derivatives. Chemical shift data are presented in Table 11.

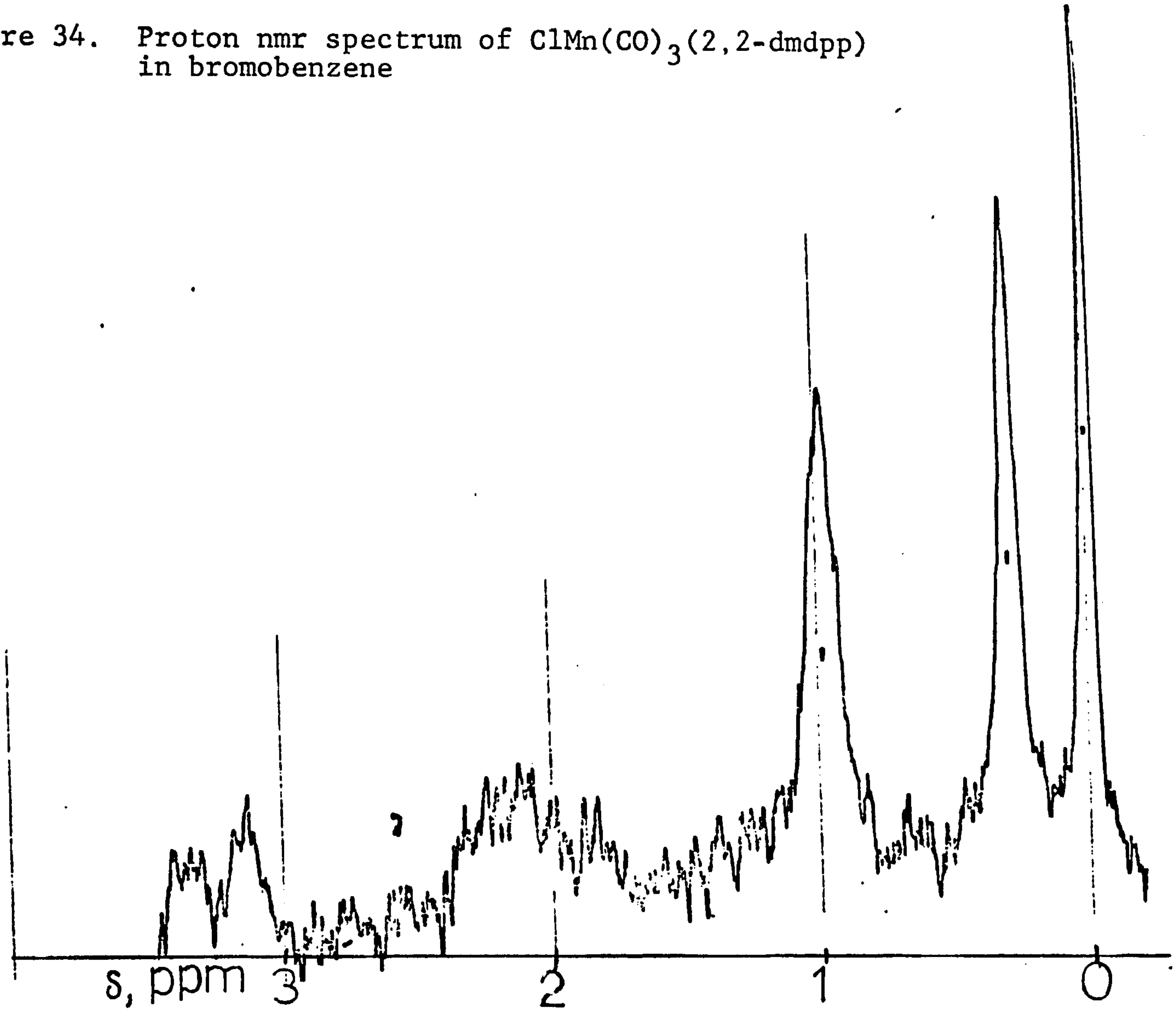
Table 11

Methyl Chemical Shift Data for $XMn(CO)_3(2,2\text{-dmdpp})$ Complexes (in bromobenzene, vs. TMS)

X	δCH_{3ax} (ppm)	δCH_{3eq} (ppm)	$\delta CH_{3eq} - \delta CH_{3ax}$	
			(ppm)	(Hz)
Cl	0.30	0.98	0.68	40.8
Br	0.22	1.03	0.81	48.6
I	0.14	1.08	0.94	56.4

The 60 MHz proton nmr spectra of the 2,2-dmdap derivatives of $XMn(CO)_5$, (X=Cl,Br,I) all have the same

Figure 34. Proton nmr spectrum of $ClMn(CO)_3(2,2\text{-dmdpp})$ in bromobenzene



general form: two singlets in the methyl region of the spectrum and an AB quartet arising from the methylene protons (Figure 35). The downfield methyl resonance is the taller and less broad of the two, and is thought to arise from the methyl group in the equatorial position. The assignment of axial and equatorial methylene resonances is uncertain. Proton nmr data for these systems are presented in Table 12.

Table 12

Proton nmr data for $XMn(CO)_3(2,2\text{-dmdap})$ Complexes (at 34° in bromobenzene)

X	δA (ppm)	δB (ppm)	$\delta CH_{3_{eq}}$ (ppm)	$\delta CH_{3_{ax}}$ (ppm)	$\delta CH_{3_{eq}} - \delta CH_{3_{ax}}$ ppm	Hz
Cl	3.06	2.14	1.05	0.39	0.66	39.6
Br	3.17	2.19	1.03	0.29	0.74	44.4
I	3.33	2.39	1.09	0.27	0.82	49.2

High temperature measurements on several compounds (Tables 13-16) show a large variation in the position of the axial one methyl resonance and in the spectra of the diarsine complexes, one set of methylene resonances, relative to TMS . In all cases the shifts are to lower field. The shifts appear to be linear with temperature (Figures 36-39). The coupling constant

Figure 35. Proton nmr spectrum of $BrMn(CO)_3$(2,2-dmdap) in bromobenzene.

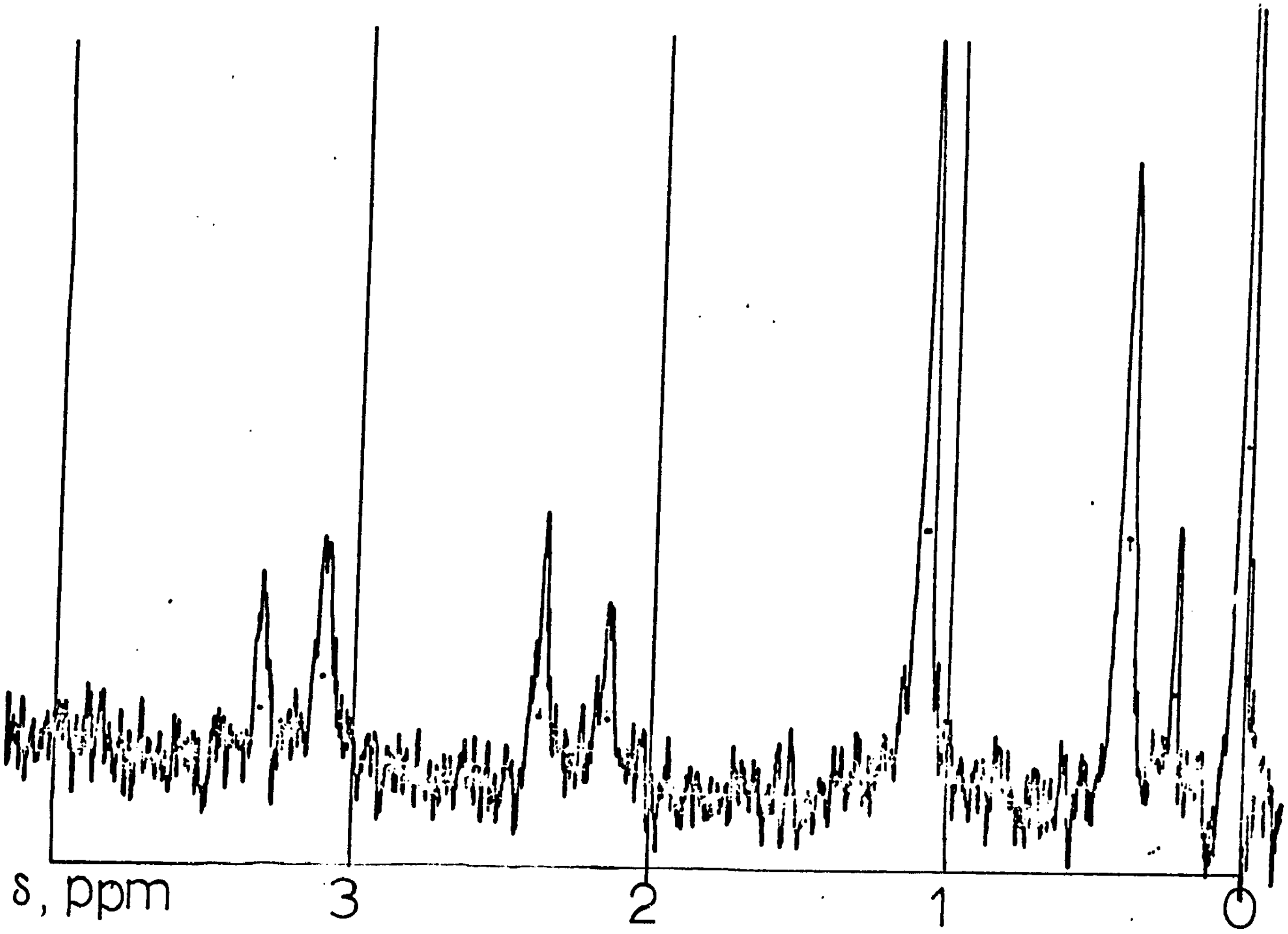


Table 13

Variable Temperature Data for $ClMn(CO)_3(2,2\text{-dmdap})$ (vs. TMS)

Temperature °C	$\delta CH_{3_{ax}}$ (ppm)	$\delta CH_{3_{eq}}$ (ppm)	δ_A(ppm)	δ_B(ppm)
34	.39	1.05	3.06	2.14
50	.42	1.06	3.07	2.19
80	.46	1.06	3.04	2.18
110	.51	1.07	3.07	2.23

J_{AB} = 13±1 Hz

Table 14

Variable Temperature Data for $BrMn(CO)_3(2,2\text{-dmdap})$ (vs. TMS)

Temperature °C	$\delta CH_{3_{ax}}$ (ppm)	$\delta CH_{3_{eq}}$ (ppm)	δ_A(ppm)	δ_B(ppm)
34	.29	1.03	3.17	2.19
50	.37	1.09	3.16	2.24
70	.39	1.07	3.17	2.27
90	.45	1.07	3.16	2.28
110	.47	1.09	3.17	2.29
130	.51	1.10	3.17	2.31

J_{AB} = 13±1 Hz

Table 15

Variable Temperature Data for $IMn(CO)_3(2,2\text{-dmdap})$ (vs CH_2Cl_2)

Temperature °C	δCH_{3ax} (ppm)	δCH_{3eq} (ppm)	δ_A (ppm)	δ_B (ppm)
34	.74	1.57	3.80	2.86
50	.77	1.57	3.78	2.86
70	.74	1.52	3.72	2.84
90	.78	1.54	3.73	2.85
110	.79	1.53	3.70	2.84

$J_{AB} = 13.0 \pm .5$ Hz

Table 16

Variable Temperature Data for $ClMn(CO)_3(2,2\text{-dmdpp})$ (vs.TMS)

Temperature (°C)	δCH_{3ax} (ppm)	δCH_{3eq} (ppm)
34	.30	.98
50	.35	1.02
80	.41	1.02
110	.44	1.00
130	.47	1.01

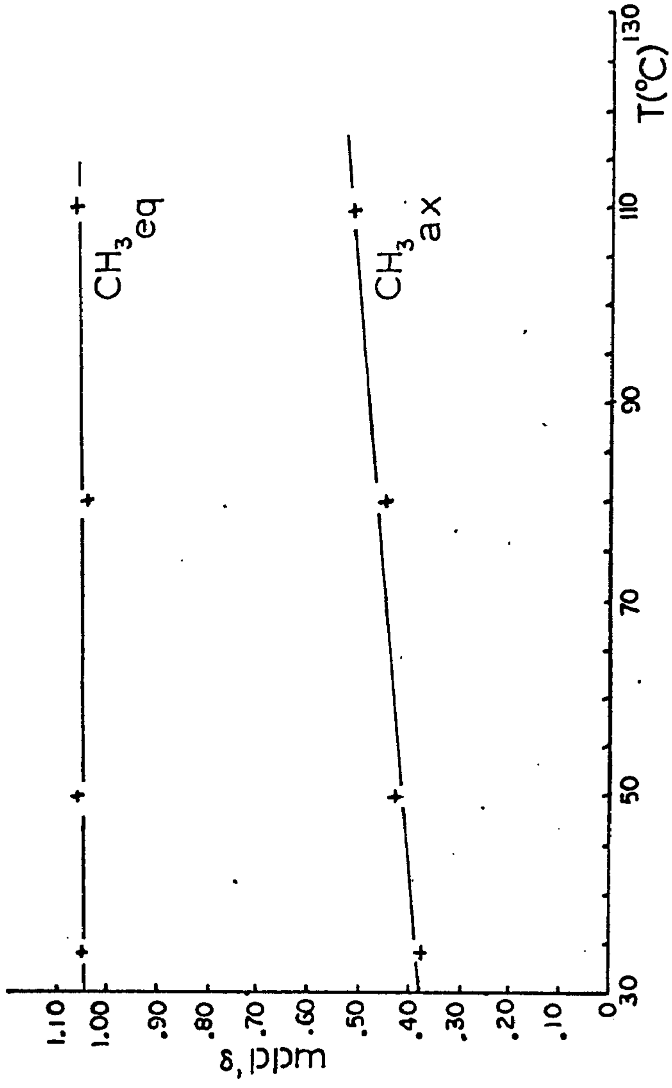


Figure 36. Graph of chemical shift vs. temperature for the ligand-methyl resonances of $ClMn(CO)_3$(2,2-dmdap)

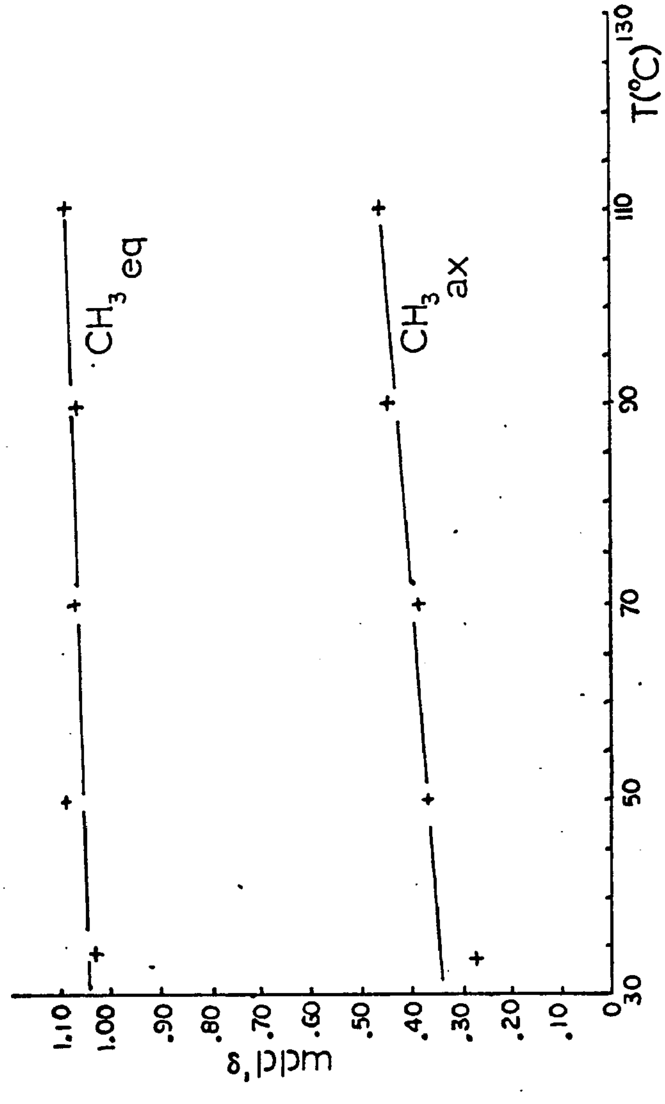


Figure 37. Graph of chemical shift vs. temperature for the ligand-methyl resonances of $BrMn(CO)_3$(2,2-dmdap)

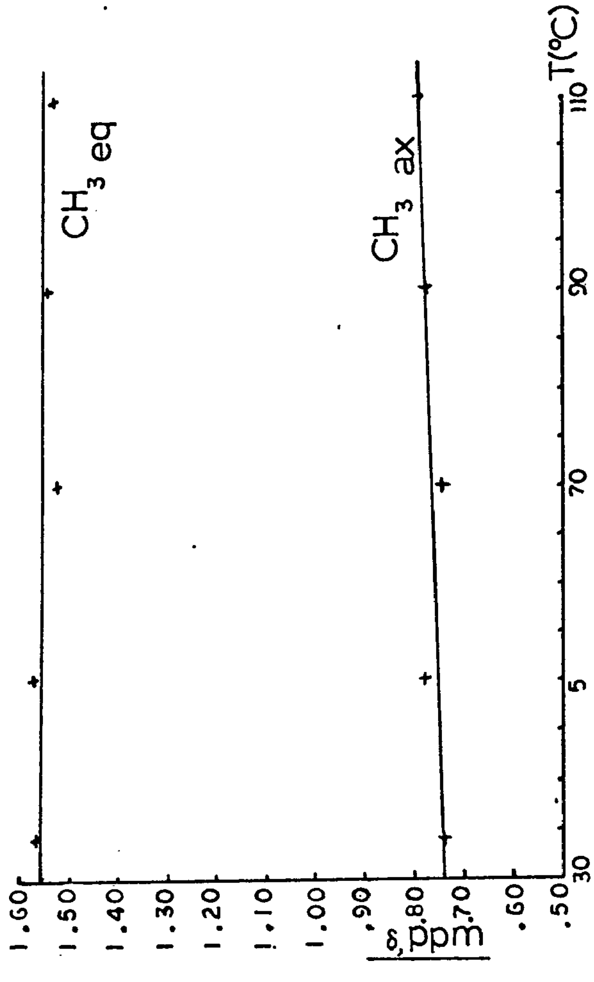


Figure 38. Graph of chemical shift vs. temperature for the ligand-methyl resonances of IMn(CO)$_3$(2,2-dmdap)

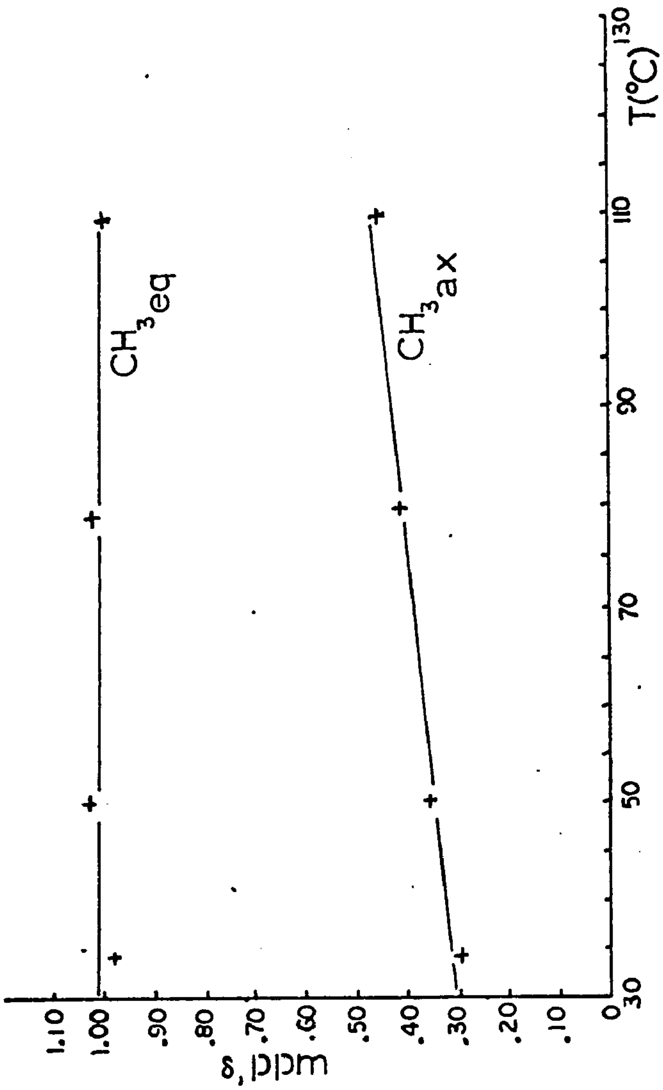


Figure 39. Graph of chemical shift vs. temperature for the ligand-methyl resonances of ClMn(CO)$_3$(2,2-dmdpp)

J_{AB} remains constant within experimental error for the AB quartets of the three diarsine complexes at all temperatures.

The coupling constant is the same to ±1 Hz for all three complexes.

Acetyl- and Methylmanganesetricarbonyl Derivatives

The nuclear magnetic resonance spectra of the acetyl- and methylmanganesetricarbonyl derivatives of 2,2-dmdpp and 2,2-dmdap (Table 17) are, with one exception, consistent with those recorded by Kraihanzel and Maples[5,9] for other complexes of this type having a facial geometry.

The acetyl complex of 2,2-dmdpp, $CH_3COMn(CO)_3(2,2\text{-dmdpp})$, exhibits two ligand-methyl resonances: the axial resonance appears as a singlet, but the equatorial methyl resonance is an apparent triplet, with peaks separated in both CS_2 and $CDCl_3$ by 3.0±.2 Hz (Figure 40).

As in the halomanganesetricarbonyl complexes, the equatorial methyl resonance appears at lower field than that of the axial methyl.

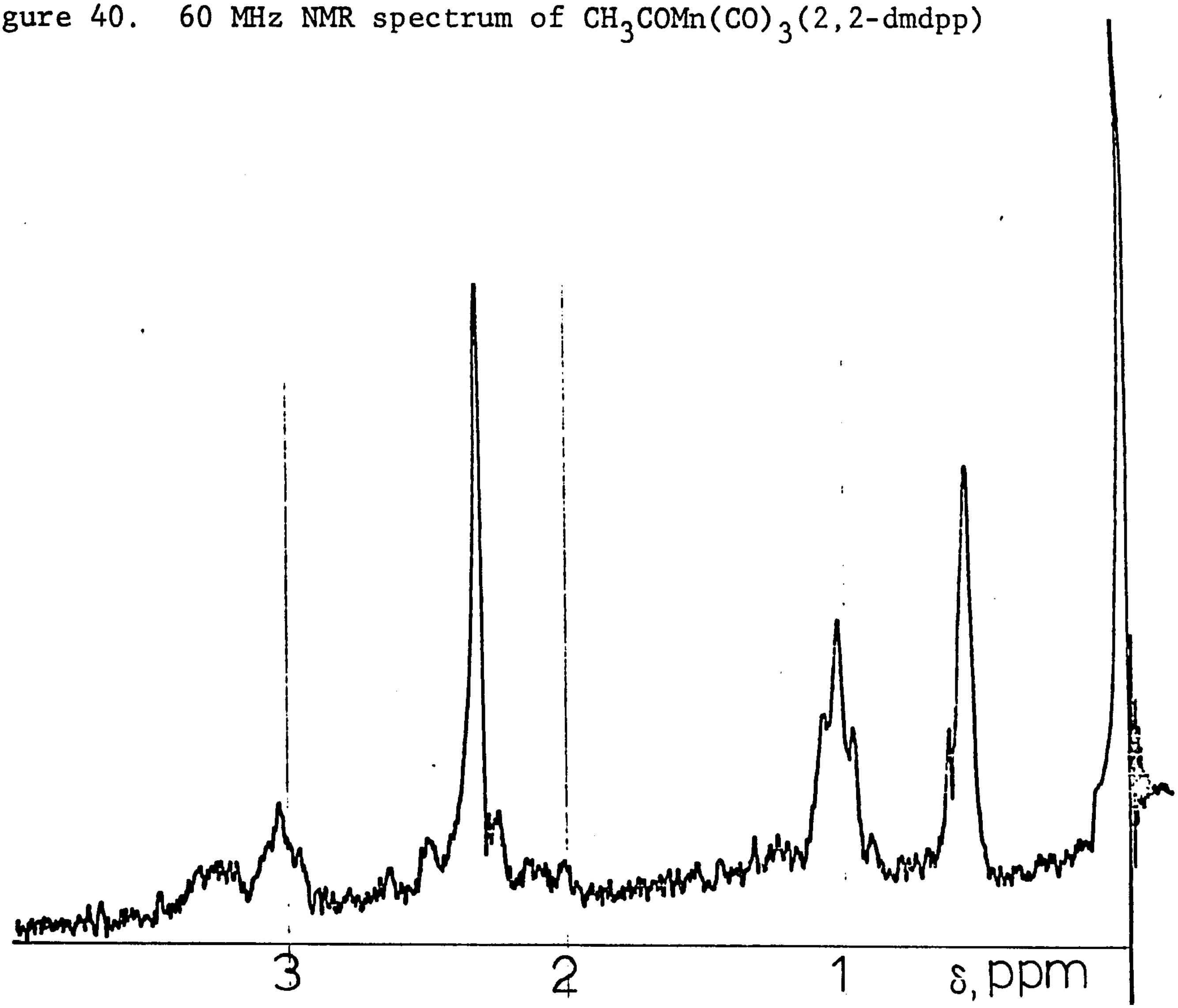
The acetyl-methyl resonance appears at lower field than either ligand-methyl resonance; this methyl group is bonded to a partially positive carbon atom in the acetyl moiety, and is thus deshielded to a greater extent than either ligand methyl.

Table 17

Proton nmr data for $CH_3Mn(CO)_3$(L-L) and $CH_3COMn(CO)$ (L-L) Complexes

Compound	Solvent	δCH_3CO (ppm)	δCH_3Mn (ppm)	Ligand Methyls $\delta {CH_3}_{eq}$ (ppm)	 $\delta {CH_3}_{ax}$ (ppm)	AB quartet (ppm) δ_1 δ_2 δ_3 δ_4
$CH_3COMn(CO)_3$(2,2-dmdpp)	CS_2	1.78		1.33	0.57	
	C_6H_6	2.34		1.03	0.57	
	$CDCl_3$	1.95		1.39	0.69	
$CH_3COMn(CO)_3$(2,2-dmdap)	C_6H_6	2.35		0.98	0.63	$^{3.08}2.87^{--}2.15$
$CH_3Mn(CO)_3$(2,2-dmdpp)	$CDCl_3$		-0.69	1.05	.38	
$CH_3Mn(CO)_3$(2,2-dmdap)	$CDCl_3$		-0.66	1.20	0.52	2.36 (singlet)

Figure 40. 60 MHz NMR spectrum of $CH_3COMn(CO)_3(2,2\text{-dmdpp})$



The methylene resonances appeared as two broad "humps" centered approximately at δ3.15 and δ2.85.

The position of the acetyl-methyl resonance is greatly solvent dependent, that of the ligand-methyl resonances less so. The solvent dependency of the chemical shifts does not correlate with the dipole moment, nor the dielectric constant, of the solvent.

The decarbonylation product of acetylmanganesetricarbonyl(2,2-dmdpp), methylmanganesetricarbonyl(2,2-dmdpp), $CH_3Mn(CO)_3$(2,2-dmdpp), gives rise to a spectrum in deuterochloroform which is quite similar in character (Figure 41) to that of the acetyl complex. Again, the equatorial methyl resonance is at lower field than the axial, and appears as an apparent triplet, with peaks separated by 2.2±0.2 Hz. The axial methyl resonance is a sharp singlet. The methyl moiety bonded to the metal atom gives rise to a 1:2:1 triplet ($^3J_{PH}$ = 9.0±0.2) due to coupling of the methyl protons with two equivalent phosphorus atoms, and appears upfield of TMS, as expected for a highly shielded methyl group bonded to a metal atom.

The methylene resonance appears as a broad hump centered at δ2.38.

The nmr spectrum of the acetyl manganese tricarbonyl derivative of 2,2-dmdap, $CH_3COMn(CO)_3$(2,2-dmdap), is similar to those of the halomanganesetricarbonyl derivatives of the same ligand: two methyl resonances are

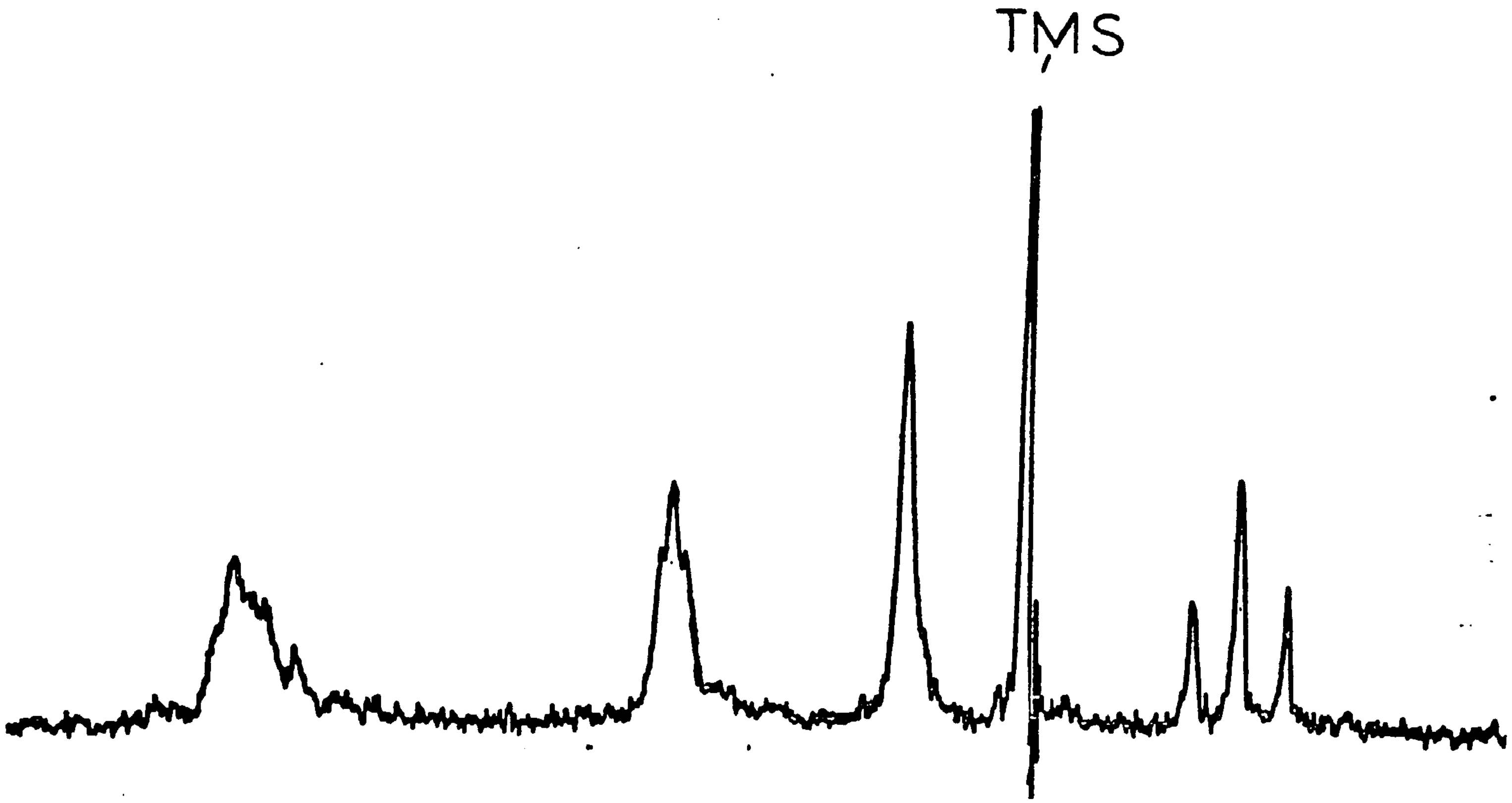


Figure 41. 60 MHz NMR spectrum of $CH_3Mn(CO)_3$(2,2-dmdpp)

observed, the broader (axial) methyl resonance being upfield of the sharper (equatorial) peak (Figure 42). The methylene protons give rise to an AB quartet (J_{AB} = 12.6 ±.5 Hz). The acetyl-methyl resonance, a sharp singlet, is found downfield of the ligand-methyl resonances and overlaps the upfield inner line of the AB quartet.

The proton nmr spectrum of methylmanganesetricarbonyl(2,2-dmdap), $CH_3Mn(CO)_3$(2,2-dmdap), (Figure 43), is unlike the spectrum of the other metal carbonyl derivatives of this ligand. The spectrum consists of four singlets: δ2.36 (As-CH_2-), δ1.20 (C-CH_3), δ0.52 (C-CH_3), and δ-0.66 (Mn-CH_3). Integration of the area under the resonances yields values of: 4.1:3.4:3.0:3.0, using the integrated value of the Mn-CH_3 resonance as equivalent to three protons. The value of 3.4 protons for one methyl resonance may be due to an impurity which gives rise to the broadened, uneven base of this resonance (Figure 43); this will be assumed to be the case in the discussion following.

Discussion

All of the compounds in the series $XMn(CO)_3$(2,2-dmdpp) and $XMn(CO)_3$(2,2-dmdap) (X=Cl,Br,I,CH_3CO,CH_3) have been assigned a facial geometry on the basis of infrared evidence. The absorption patterns are clearly in agreement with those found[9] for other facial manganese (I) tricarbonyl complexes of chelating ligands.

Figure 42. 60 MHz NMR spectrum of $CH_3COMn(CO)_3$(2,2-dmdap)

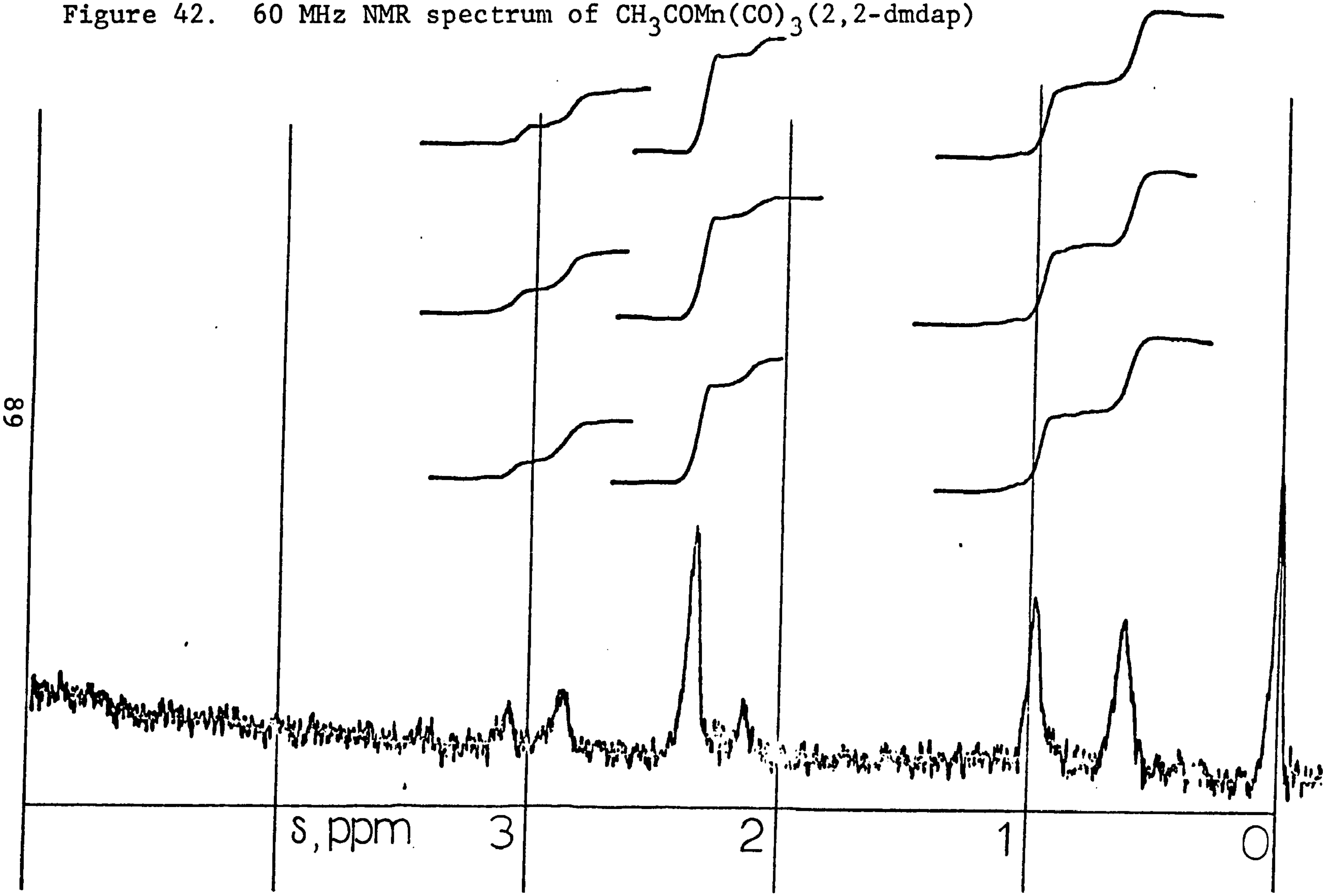
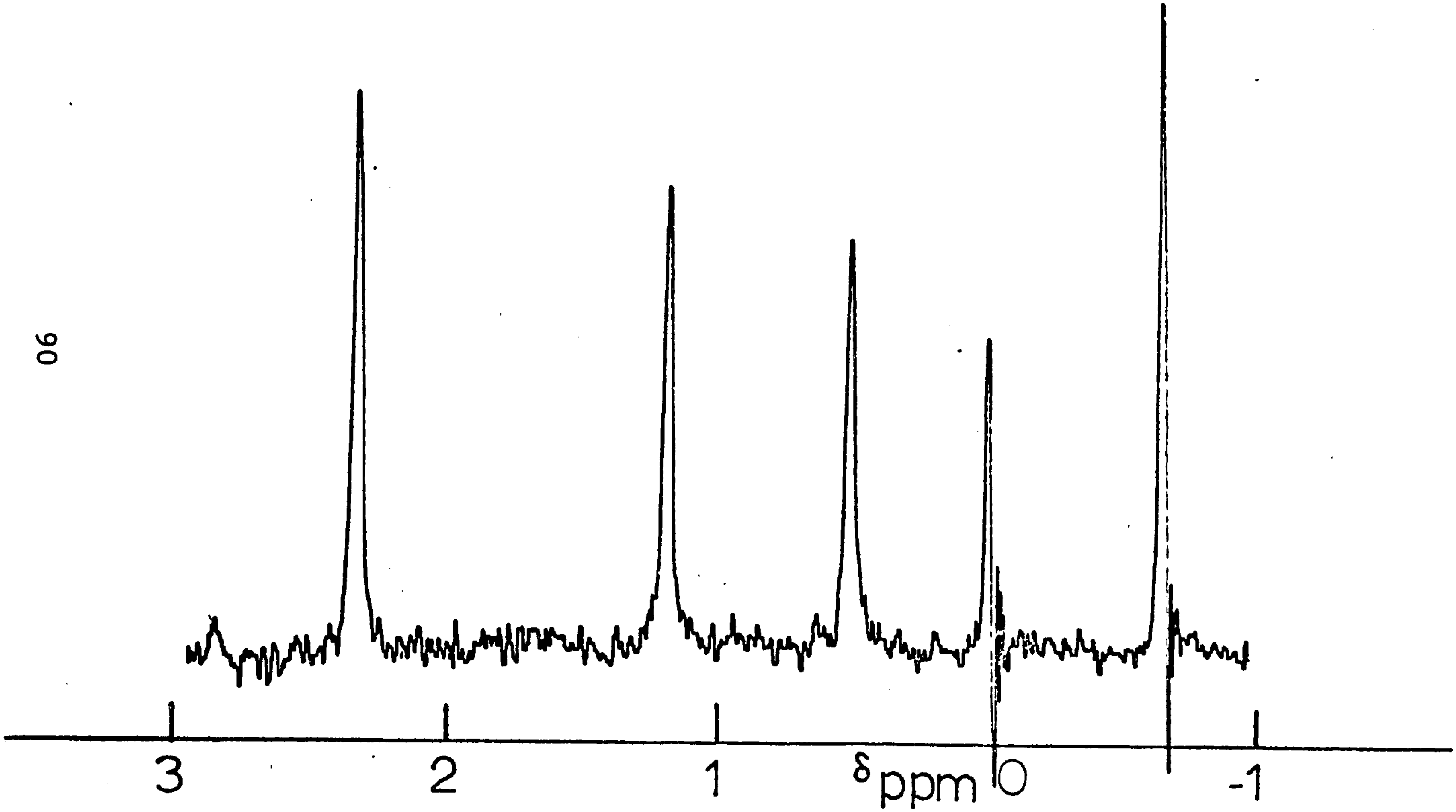


Figure 43. 60 MHz NMR spectrum of $CH_3Mn(CO)_3$(2,2-dmdap)



The proton nmr spectra of these complexes provide evidence for the conclusion that the six-membered ring systems formed from the 2,2-dmdpp and 2,2-dmdap ligands are conformationally rigid. The appearance of two methyl groups in the spectrum of each of these complexes plus the AB quartet arising from the methylene protons in complexes of the diarsine is indicative of a locked ring. This is in agreement with the results of Cullen and coworkers,[65] who have found the complexes of $XMn(CO)_3$-$As(CH_3)_2CH_2CHRCH_2As(CH_3)_2$ (R = H, t-butyl, X = Cl,Br,I) to be conformationally rigid.

The various types of spin-coupling exhibited in the proton nmr spectra of these manganese (I) complexes are of interest, as are the chemical shifts of the ligand-methyl resonances, in that they can be rationalized by considering the geometry of the ring and the steric effects of the ligand X.

Molecular and space-filling models of these complexes make clear some important spatial relationships in these ring systems. The phenyl groups appear to be hindered in their ability to freely rotate--those positioned closer to the ligand methyl groups moreso than those pointed away from this portion of the molecule. When arranging the phenyl moieties on the model in such a way that a minimal amount of steric interaction between them is obtained, it is found that the axial

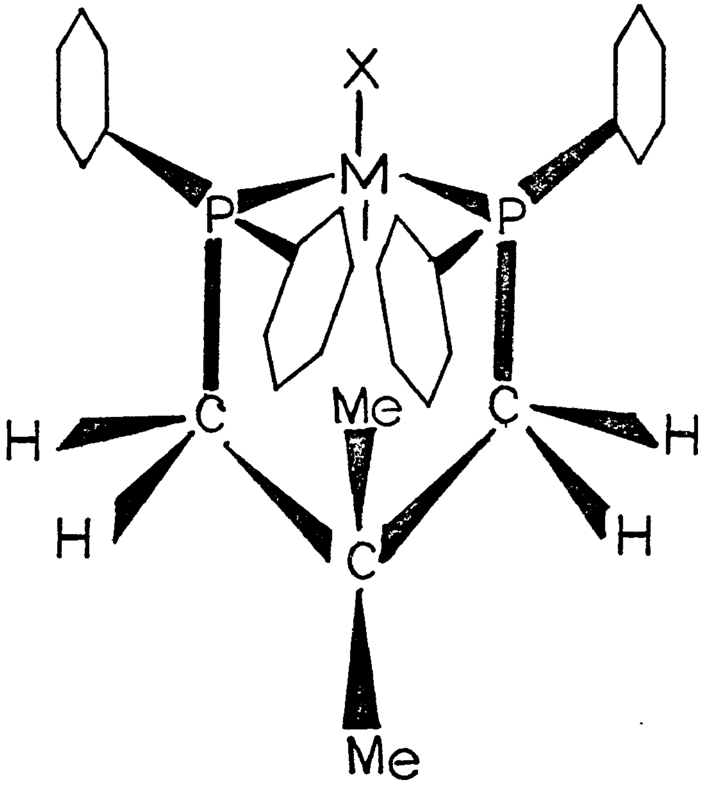
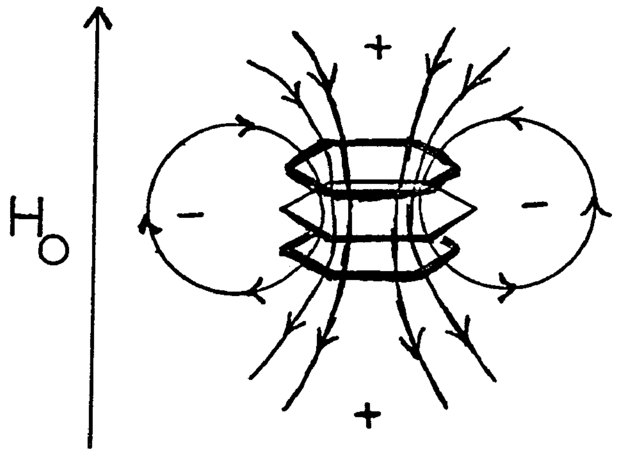


Figure 44. Spatial arrangement of the ligand methyl groups (from molecular models)

ligand-methyl group lies between the planes of the two rings (Figure 44). Aromatic rings are known to have an anisotropic shielding effect directed above and below the plane of the ring[66] (Figure 45); thus the protons

Figure 45

Anisotropic Shielding and Deshielding Effect About a Benzene Ring

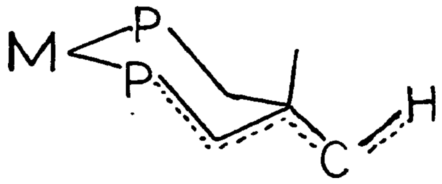


of the axial ligand-methyl group are shielded by the aromatic rings and their resonance is found upfield of that arising from the methyl group in the equatorial position, rather than downfield, as is found in many other ring systems.[29,30] The chemical shift of the axial methyl group decreases with increasing cone angle of ligand X in both the diphosphine and the diarsine complexes. This is possibly due to increased steric interaction of ligand X with either the chelating ligand's methylene protons[17] or, more likely, with the phenyl moieties bonded to the donor atoms. Distortion of the ring, caused by these steric interactions, could move the axial methyl group closer to the aromatic ring, increasing shielding, (shielding by aromatic rings is known to be a function of distance from the π electron cloud of the ring[67]) and thus moving the chemical shift of the axial methyl group closer to that of TMS.

It has been noted that two nuclei can spin-couple effectively over four bonds if the bonds are in a planar W arrangement.[31] Examination of molecular models of *fac*- $XMn(CO)_3$(2,2-dmdpp) and *fac*- $XMn(CO)_3$(2,2-dmdap) reveals three such planar W arrangements of bonds; coupling thus might be expected between the equatorial methylene atoms of the ring (see Figure 10), between the axial methyl protons and the equatorial methylene protons of the ring (see Figure 9), and, in the case of the diphosphine, between the equatorial methyl protons and the phosphorus atoms (Figure 46). In some ring systems coupling constants in the order of 2.5-2.9 Hz have been found for equatorial methylene-equatorial methylene proton coupling, while axial methyl-axial methylene coupling is often on the order of 0.7-0.8 Hz.[32]

Figure 46

Four Bond Coupling of Equatorial Methyl Protons and Ring Phosphorus Atoms



The resonances of the methylene protons of the ligand in complexes of 2,2-dmdpp could often not be discerned from baseline noise; an AB quartet, with no apparent fine structure, is, however, often found for the methylene resonances of complexes of 2,2-dmdap. Thus, coupling between the equatorial ring methylene protons must, if it exists, be quite small.

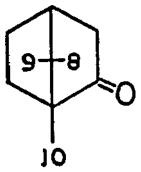
Coupling of the axial methyl protons to the axial methylene protons of the ring is apparent in the spectra, especially in the spectra of the diarsine complexes. The axial methyl resonance (the upfield methyl resonance) is always slightly broader and of less height than the equatorial methyl resonance due to this coupling, which, in other ring systems, is on the order of 0.7-0.8 Hz.[32]

Four bond coupling between the phosphorus nuclei and the equatorial methyl protons is seen in all of the proton nmr spectra of the complexes of 2,2-dmdap. The coupling seems to be fairly small in the halo-derivatives, as the methyl resonance appears as a broadened singlet. Coupling in the methyl- and acetyl- derivatives, however, seems to be larger, as the equatorial-methyl resonance appears as a well-defined triplet in both cases ($^4J_{PH}$ = 3.0±.2 Hz in $CH_3COMn(CO)_3$(2,2-dmdpp); $^4J_{PH}$ = 2.2±.2 Hz in $CH_3Mn(CO)_3$(2,2-dmdpp)).

The variation of methyl group chemical shifts of the halo-derivatives with temperature may be an example of a temperature-dependent "Aromatic Solvent Induced Shift" (ASIS),[62] and is due to interaction of the ligand methyl group with the aromatic solvent. A similar effect is seen in the temperature dependent nmr spectra of camphor, which is conformationally rigid,(Figure 47) in toluene.[63]

<u>Figure 47</u>

Camphor



The chemical shifts of methyls 8 and 9 show a linear variation with temperature, the resonances being displaced to higher field when the temperature is lowered, while the chemical shift of methyl 10 remains constant.

The variation of the acetyl resonance with solvent in the spectra of $CH_3COMn(CO)_3$(2,2-dmdpp) is another example of an aromatic solvent induced shift (ASIS).[60,61] The aromatic ring system interacts with a center of positive charge on the complex, resulting in deshielding of the protons at that site.[61]

The proton nmr spectrum of $CH_3Mn(CO)_3$(2,2-dmdap) is unlike the spectra obtained for any other complex of this ligand. While the elemental analysis indicates the complex is empirically as formulated, and infrared evidence supports a facial geometry for the complex, the methylene region appears as a simple singlet and two ligand-methyl resonances are observed. A single methylene resonance is typical of a conformationally non-rigid system; those systems with locked rings have, in previous examples, displayed an AB quartet in the methylene region. The appearance of two methyl singlets is indicative of a conformationally rigid system; the fact that the integrated areas under these resonances is the same as that for the methyl bonded to manganese indicates that each resonance represents only one methyl group. The appearance of only one resonance for the methyl group bonded to manganese indicates only one conformer is present; two different resonances would be expected if both conformers were present, as the ligand phenyl groups in one conformer would be much closer to this methyl group, influencing its chemical environment.

This spectrum does not lead to a clear interpretation. Based on the evidence of similar chelate systems and the appearance of two ligand-methyl resonances in the nmr spectrum, a conformationally rigid ring is postulated for this complex. It is doubtful that all of the methylene protons are magnetically equivalent; however, if $J/\Delta\nu$ is very large (i.e. if the chemical shift difference $\nu_A - \nu_B$ is very close to zero), the central resonances of the resultant AB quartet would be very close together and possibly unresolvable, with most of the total intensity of the AB system, while the outer lines would be very close to the inner lines and of very low intensity and may, in fact, be lost in the baseline noise.

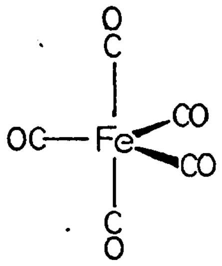
SYSTEMS WITH TRIGONAL BIPYRAMIDAL GEOMETRY: $Fe(CO)_5$ DERIVATIVES

Introduction and Background

It is well established that iron pentacarbonyl exists in a trigonal bipyramid configuration[68]

Figure 48

$Fe(CO)_5$



Gas phase electron diffraction studies have found the axial Fe-C bonds to be shorter than the equatorial by 0.045 Å.[68,69]

^{13}C nmr studies of pure iron pentacarbonyl have detected only one ^{13}C resonance,[70,71] though two resonances in a 3:2 (i.e. equatorial:axial) ratio would be expected for the trigonal bipyramidal structure.

Iron pentacarbonyl thus appears to be stereochemically non-rigid at ambient temperatures and below.[70,71,72] Several mechanisms have been postulated to explain this phenomenon, among them the Berry Pseudorotation mechanism[73] (Figure 49) and the turnstile rotation[74] (Figure 50).

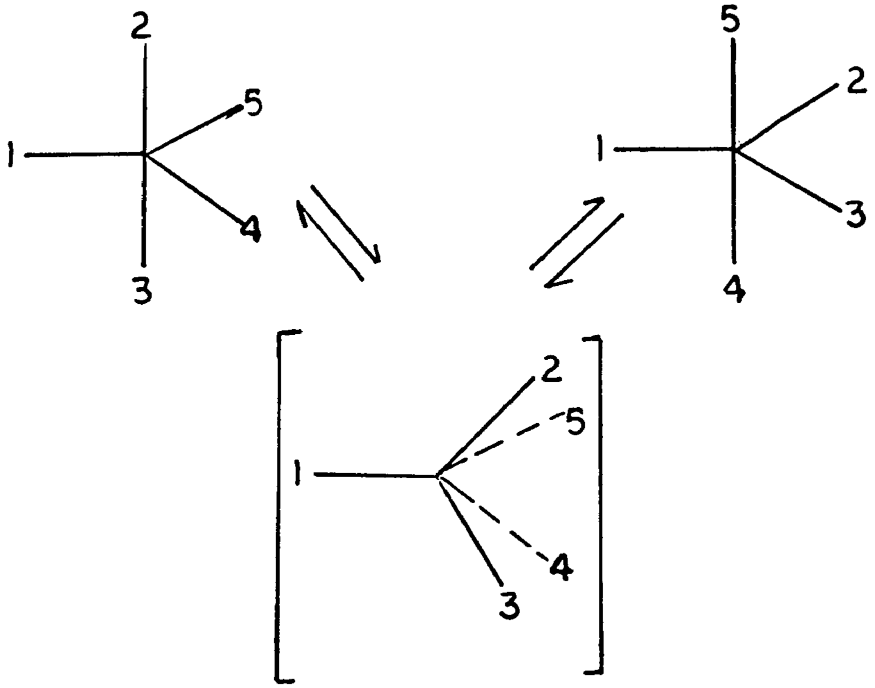
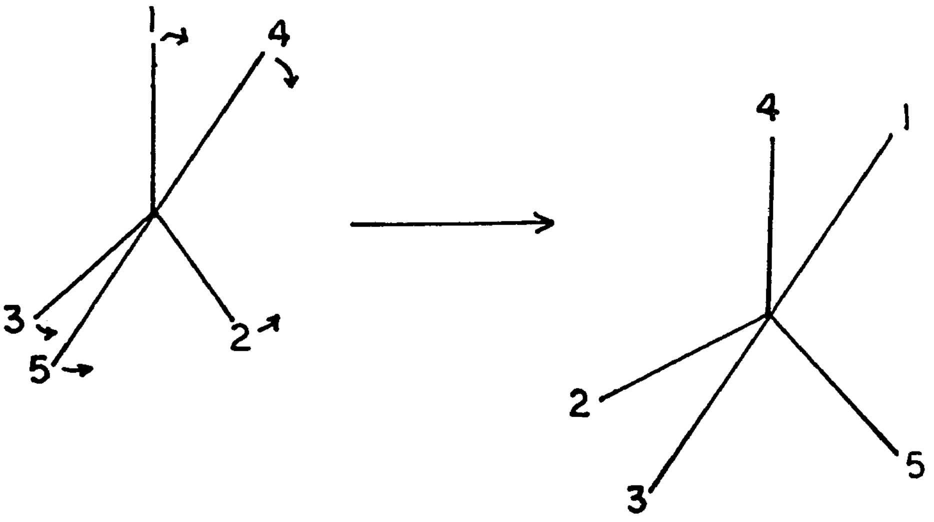


Figure 49. Berry pseudorotation mechanism

Figure 50. Turnstile rotation mechanism



Several monodentate derivatives of iron pentacarbonyl have also been found to undergo rapid intramolecular exchange.[72,75]

It seems reasonable to expect a greater barrier to intramolecular isomerization if one bidentate ligand, rather than two monodentate ligands, is used.[76] However, Odom, MacDiarmid and coworkers have found $Fe(Me_2PCH_2CH_2PMe_2)(CO)_3$non-rigid down to -80°,[77] while Cotton[78] has found the carbonyl groups of $Fe(Ph_2PCH_2PPh_2)(CO)_3$ to be equivalent on the nmr time scale down to -70°C. (A crystal structure of this compound[78] indicates the structure to be intermediate between trigonal bipyramidal and square pyramidal, eliminating the need for site permutation mechanisms. $Fe(diars)CO)_3$ (diars = o-phenylenebis(dimethylarsine)), however, was found to have trigonal bipyramidal structure[79]; the proton nuclear magnetic data is consistent with both stereochemical rigidity or non-rigidity). Odom, et al., in a later study, have shown this molecule to be non-rigid at temperatures as low as -140°C.[76] Iron pentacarbonyl derivatives of 1,2-bis(dimethylphosphino)-1,1-difluoroethane and 1,3-bis(diphenyl)phosphino)propane have been found to be non-rigid to -70° and -80°C, respectively, each having only one ^{13}C resonance.[76]

In this study two derivatives of iron pentacarbonyl have been synthesized and their proton nuclear magnetic resonance spectra examined. Two types of stereochemical non-rigidity might be expected in these complexes -- ring inversion and non-rigidity at the iron atom. Ring inversion does not require non-rigidity at the iron center, but non-rigidity at iron requires conformational mobility of the ring. Only the six-membered ring can be examined by proton nmr.

Synthetic Results

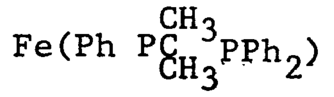
Reaction of the chelating biphosphines 2,2-bis(diphenylphosphino)propane (2,2-dpp), 2,2-dimethyl-1,3-bis-(diphenylphosphino)propane (2,2-dmdpp) with (cycloheptatriene)iron tricarbonyl[118] yields the product (L-L)-$Fe(CO)_3$ which was purified by chromatography.

$(C_7H_8)Fe(CO)_3 + L\text{-}L \rightarrow Fe(CO)_3(L\text{-}L) + C_7H_8$

Infrared Spectral Results

Infrared spectra of these complexes (Figure 51) exhibited the three absorptions expected for a structure in which one axial and one equatorial position of the trigonal bipyramid are occupied by the phosphorus atoms, and are in good agreement with the carbonyl stretching frequencies exhibited by other complexes of this type.[76] (Table 18)

Nuclear Magnetic Spectral Results

The proton nuclear magnetic resonance signal for the methyl groups of  $(CO)\ Fe(Ph\ P\overset{CH_3}{\underset{CH_3}{C}}PPh_2)$ appears as a

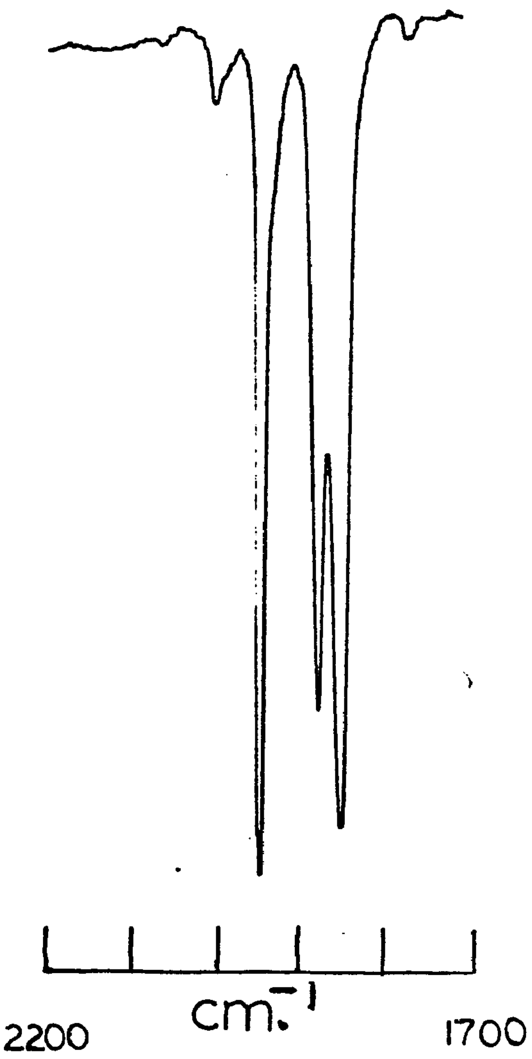


Figure 51. Infrared absorptions in the CO stretch region of $Fe(CO)_3$(2,2-dmdpp)

Table 18

Carbonyl Stretching Frequencies for $(L\text{-}L)Fe(CO)_3$

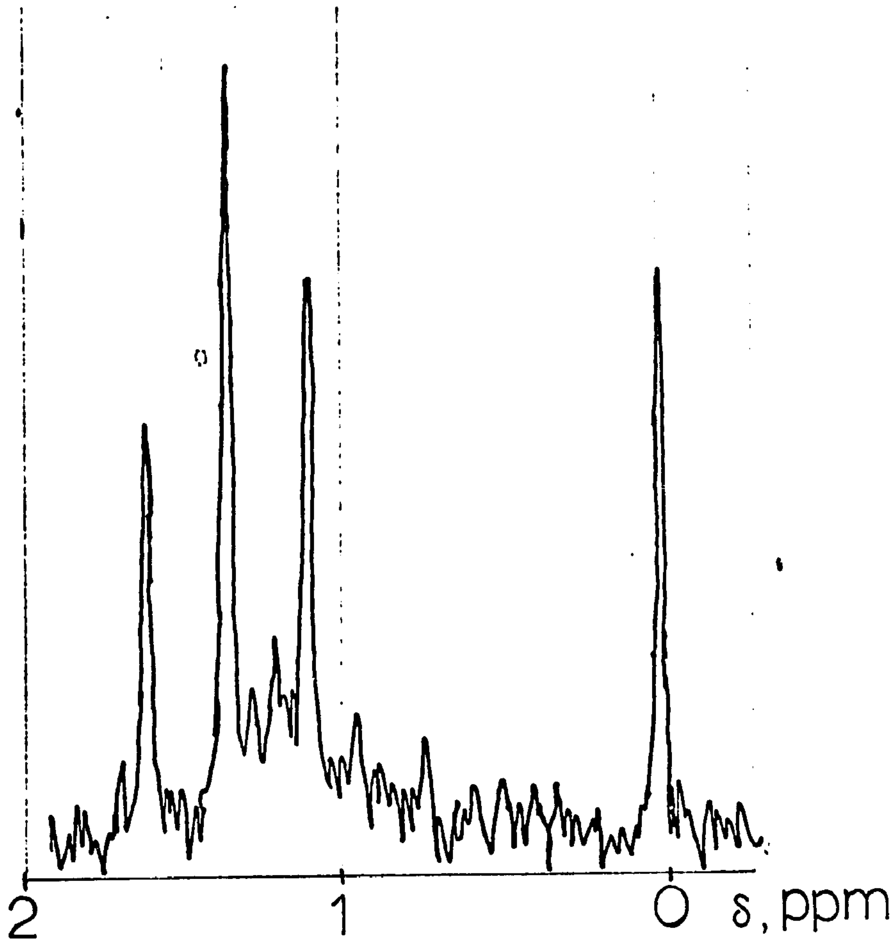
Compound	Phase	Freq. cm^{-1}
$(Ph\ PC(CH_3)_2PPh_2)Fe(CO)_3$	CH_2Cl_2sol'n	1986s,1909m,sh, 1898m
	hexane/ CH_2Cl_2(4:1)	1997s,1927m,sh, 1917m
(2,2-dmdpp)$Fe(CO)_3$	CH_2Cl_2sol'n	1990s,1918m, 1890s
	hexane/ CH_2Cl_2(4:1)	1995s,1925m, 1899s
$(Me_2PCH_2CH_2PMe_2)Fe(CO)_3$[a]	CH_2Cl_2sol'n	1970s,1896m,1877s
$(Ph_2PCH_2CH_2CH_2PPh_2)Fe\text{-}(CO)_3$[a]	CH_2Cl_2sol'n	1986s,1914m,1884vs

(a from ref. 76)

Notes: s=strong, m=medium, sh=shoulder, vs=very strong

triplet centered at $\delta 1.27$ $^3J_{PH} = 15.7 \pm .2$ Hz (benzene solution); this would be expected if both methyl groups coupled equally to both phosphorus atoms. (Figure 52) Low temperature studies in CS_2 solution produced some broadening of the resonances; solubility problems prevented effective study of this compound below -45°C. The proton nuclear magnetic resonance spectrum could be interpreted as arising from a non-rigid or from a planar four-membered ring; both interpretations are consistent with the observed triplet.

Figure 52. Methyl resonance of (2,2-dpp)$Fe(CO)_3$



The nuclear magnetic resonance spectrum of $(CO)_3Fe$-(2,2-dmdpp) consists of a singlet (0.39δ) and a virtual coupled triplet (centered at 2.17δ). The separation of the N doublet is 9.4±.2 Hz. (Figure 53)

The above spectrum is consistent with a non-rigid six-membered ring system. The presence of only one methyl absorption indicates the ring is not locked into one conformer. Furthermore, the appearance of only one virtual coupled triplet in the methylene region seems to indicate that the molecule is non-rigid at the metal atom; the axial and equatorial phosphorus nuclei would not be magnetically equivalent if the molecule were non-rigid, and the system would not be $X_nAA'X'_n$. The non-rigidity of the molecule of the iron atom is consistent with the results cited previously for other chelating biphosphines. The resonance signals did show broadening in CS_2 to -45°C, but again solubility problems prevented lower temperatures, and the limiting temperature was not found.

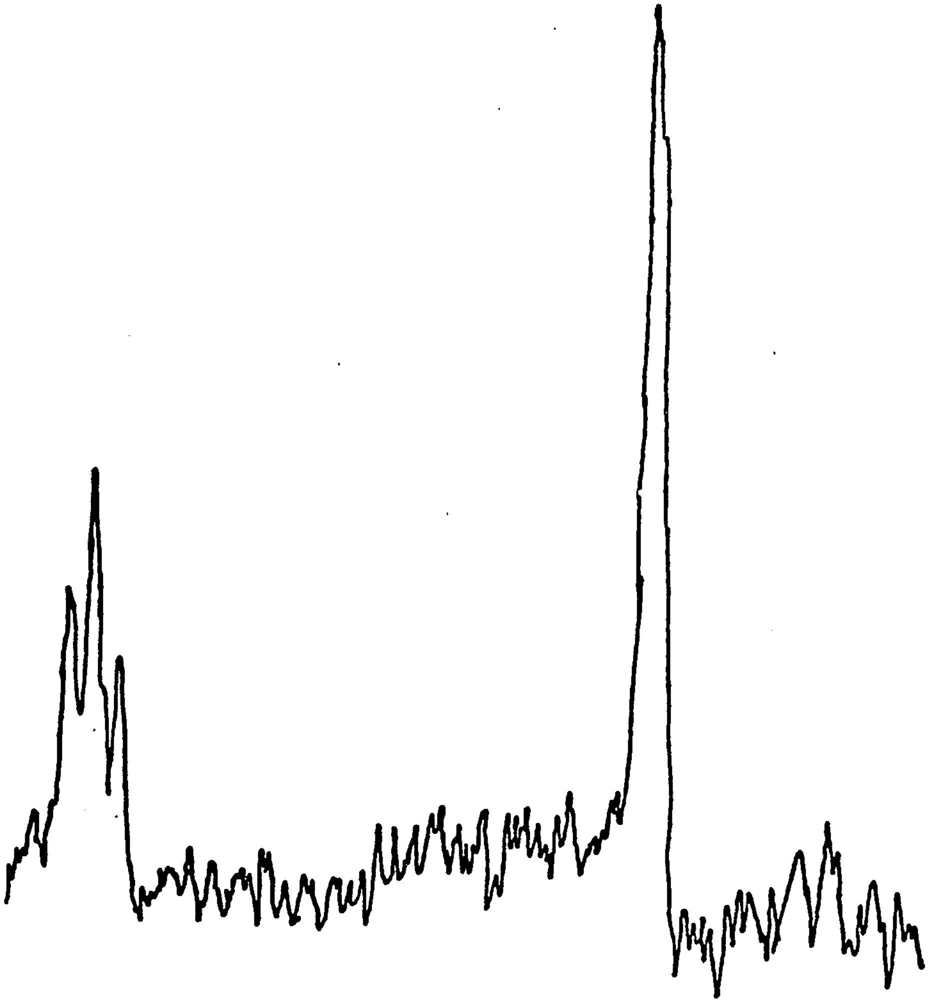


Figure 53. Trace of the proton NMR spectrum of (2,2-dmdpp)$Fe(CO)_3$

SYSTEMS WITH TETRAHEDRAL GEOMETRY: CYCLOPENTADIENYLIRON HALIDE DERIVATIVES

Compounds of the general formula πCpFe(CO)$_2$X often react with Lewis bases, B, to lose both carbonyl moieties and yield the corresponding πCpFeB$_2$X .

Previous studies have focused on the electronic effects, as reflected in the position of the π-cyclopentadienyl resonance, of replacing a strong π acceptor (CO) with a weaker one (P).[80] The only saturated chelating biphosphine used in these studies to date is 1,2-bis(diphenylphosphino)ethane (dppe); the X groups investigated are Cl, Br,[81] I,[82] Me$_3$Sn, Me$_3$Si,[80] Me, H,[83] CF$_3$, C$_2$F$_5$.[84] It is found that replacement of the carbonyl groups shifts the π-cyclopentadienyl resonance to higher field, i.e. lower chemical shift (δ) values. The replacement of the strongly π-accepting carbonyl moieties with phosphorus, a weaker π acceptor, results in increased electron density on the iron atom. This electron density is, in turn, transferred to the antibonding orbitals of the π-cyclopentadienyl ring, increasing the shielding of the ring's protons, and thus lowering the chemical shift.[80] Excess electron density can be fed into the X group if dπ-dπ bonding exists, as, for example, in the Me$_3$Sn and Me$_3$Si derivatives.[80] A saturation effect has been noted: substituting one CO group of πCpFe(CO)$_2$X with a tertiary phosphine can lower the chemical shift of the π-cyclopentadienyl ring as much as 0.5 ppm, while substitution of the second carbonyl group has only a very small additional effect.[84]

The 2,2-dimethyl-1,3-bis(diphenylphosphino)-propane derivatives of CpFe(CO)$_2$X (X = Cl,Br,I) have been synthesized in these laboratories, and nuclear magnetic resonance spectra at ambient probe temperature (34°C) and in some cases at other temperatures have been recorded. All attempts at synthesizing the 2,2-dimethyl-1,3-bis-(diphenylarsino)propane analogs of these compounds failed.

Proton nmr data for these complexes are given in Table 19. All show the characteristics expected for a rigid six-membered ring formed from the 2,2-dmdpp ligand; two methyl singlets and a complex multiplet in the methylene region

Table 19

Proton nmr Data for πCpFe(2,2-dmdpp)X Complexes

X	$\delta CH_{3\,ax}$ (ppm)	$\delta CH_{3\,eq}$ (ppm)	$\delta \pi C_5H_5$ (ppm)	Solvent	Ref.
Cl	0.15	0.84	3.96 (broad)	CH_2Cl_2	CH_2Cl_2
Br	0.16	0.93	3.79 (broad)	CH_2Cl_2	CH_2Cl_2
	0.15	0.94		CS_2	C_6H_6
I	0.18	0.95	4.18 (broad)	CH_2Cl_2	CH_2Cl_2

The downfield methyl resonance was the broader of the two and is thus assigned to the ligand-methyl group in the equatorial position. Little change is expected in the chemical shifts of the methyl resonances with change in ligand X as inductive effects would have to be felt over four bonds, and the change of cone angle is not very great in this series. Electronic effects are expected to influence the position of the π-cyclopentadienyl resonance; however, no correlation between $\delta(\pi Cp)$ and Pauling electronegativity values[85] for X (X = Cl,Br,I) have been observed.

No changes were observed in the proton nmr spectra of the chloro and iodo compounds to 90° (chloro) or 125° (iodo) in bromobenzene, indicating the ring remains locked, possibly due to the steric bulk of the π-cyclopentadienyl ring.

Resonances arising from the free ligand were not observed on heating; it can thus be assumed the phosphine remains bonded to the metal at all times to the decomposition point.

PART II

LINKAGE ISOMERISM: PALLADIUM (II) THIOCYANATE COMPLEXES

Introduction and Background

Linkage isomerism in metal complexes has been the object of a great deal of research activity during the last decade; the subject has been extensively reviewed several times.[86-89] The thiocyanate ion SCN^-, is an ambidentate ligand,[86] and can coordinate to a metal through either the sulfur or the nitrogen atom. If the thiocyanate ion is the only ligand present in a complex N-bonding predominates for hard metals[90] or class a metals such as Mo,W, or Mn[91]; soft metals such as Pd,Pt and Au produce S-bonded thiocyanate complexes. This trend in mode of bonding is generally followed throughout the periodic table.[92]

In 1961, Turco and Pecile[93] observed that the mode of coordination of thiocyanate toward palladium (II) or platinum (II) is dependent on the nature of the other ligands present. These authors point out that when two thiocyanate ions in $[Pd(SCN)_4]^{2-}$ are replaced by two ammine ligands the Pd-S linkage is maintained; however, when two organophosphine groups replace the thiocyanate ions the linkage is isomerized and an isothiocyanate complex results. Triphenyl phosphine yields the N-bonded palladium complex,[94] whereas triphenyl bismuth forms the S-bonded complex.[95] The mode of bonding in the triphenylarsine complex trans-[$Pd(Ph_3As)_2(CNS)_2$], is temperature sensitive. Infrared studies have shown the thiocyanate ion to be S-bonded when the complex is formed at low temperatures, but the complex is isomerized to the N-bonded species on heating or dissolution.[94,96] Dipole measurements proved to be inconclusive for this complex; the authors assign a trans structure on the basis of steric requirements.)

Several attempts have been made to explain the dependence of the mode of this cyanate bonding on the properties of other ligands in complexes. These explanations fall into two main categories: those that ascribe the mode of bonding to electronic effects, and those that focus on steric arguments. Both arguments have been thoroughly detailed in the cited literature and reviewed[87]; only a short summary will be given here.

Electronic effects. The π-bonding hypothesis is the rationalization found most often in the literature. Turco and Pecile,[93] for example, assumed that in $Pd(NH_3)_2(SCN)_2$ the $Pd-NH_3$ interaction is exclusively σ in character and results in a small further increase of electron density on the metal. Delocalization of this excess electron density through π-backbonding into the antibonding thiocyanate π orbitals localized on sulfur, along with sulfur's d orbitals, can enhance the stability of the metal-sulfur bond relative to that expected for N-bonding.[94] In the phosphine analog, π-backbonding can occur between the filled metal and empty phosphorus d orbitals. The resultant reduction in the electron density on the metal changes the character of the metal from "soft" (class b) to "hard" (class a). A strong π acceptor, such as a phosphine, thus makes metal d orbital electrons less available for π-back-bonding to the sulfur.[94,97] As observed before, the more ionic Pd-NCS linkage tends to form with class a metals.[90] The π-bonding hypothesis works well for amine complexes of palladium (II) such as nitro-substituted phenanthrolines, but does not always explain the results obtained for phosphine complexes.[87] For example, *cis*-$Ph_2PCH=CHPPh_2$ is a better π acceptor than dppe, as shown by the higher CO stretch frequencies of $M(CO)_4(L\text{-}L)$ (M=Cr,Mo,W) when L-L= *cis*-$Ph_2PCH=CHPPh_2$,[98] due either to the presence of empty -antibonding orbitals in the C=C bond or because the sp^2 carbon is more electronegative than the sp^3 carbon in dppe[98] yet its thiocyanate complex with palladium (II) exhibits only S-bonding: [Pd(*cis*-$Ph_2PCH=CHPPH_2$)$(SCN)_2$].[99]

Recent metal-phosphorus nmr coupling constant data have led many authors to question the existence of strong M-P π-bonding in square-planar complexes or to assume that M-P dπ-dπ bonding in these complexes is minimal.[100,101]

Steric Effects. The MSC bond angle is usually bent, often with a bond angle of about 100°, whereas the M-NCS system is usually linear[87,95] The S-bonded thiocyanate group therefore makes greater steric demands than the N-bonded group. The complex trans-[Pd$(Ph_3P)_2(NCS)_2$] exhibits N-bonded thiocyanate, while trans-[Pd$(Ph_3Sb)(SCN)_2$] exhibits S-bonding: the large Sb atom reduces the steric effects of the phenyl groups, allowing S-bonding, while the phenyls on the smaller P atom overcrows the metal and create greater steric interactions, thus promoting N-bonding.

Triphenylphosphite yields only the S-bonded complex trans-$[Pd\{P(OPh)_3\}_2(SCN)_2]$. Triphenylphosphite is less basic than triphenylphosphine, but has greater π-acceptor ability.[101] The presence of S-bonded thiocyanate in the triphenylphosphite complex is contrary to the π-bonding hypothesis (which predicts that ligands of greater π-acceptor ability should lead increasingly to N-bonding), but is consistent with steric control of coordination: triphenylphosphite has a smaller cone angle (121°) than triphenylphosphine (145°) and should therefore be less sterically demanding.[35]

Reaction of Ph_3As with $[Pd(SCN)_4]^{2-}$ at low temperatures yields the unstable S-bonded kinetic product, trans-$[Pd(Ph_3As)(NCS)_2]$. Triphenylarsine is thus a "borderline" ligand: the energy difference between the S-bonded and N-bonded isomers must be small.[96]

The tri-n-butylarsine ligand,which is less sterically demanding than triphenyl arsine, yields the S-bonded isomer in the solid state; on melting it partially isomerizes, yielding the mixed species: $[Pd(nBu_3As)_2(SCN)(NCS)]$, but reverts to the S-bonded form on cooling.[102] Possible explanations for this include increased steric effects on melting, and lattice effects favoring S-bonding in the solid state.[87]

Studies on $[Pd(Ph_3As)2(CNS)_2]$ systems have shown a solvent effect[103]; solvents with high dielectric constants favor S-bonding, while a mixture of S-bonding, N-bonding and thiocyanate bridge bonding is seen in solvents of low dielectric constant. Klopman[104] has shown that solvents with low dielectric constants favor charge-controlled reactions; thus, the low dielectric-constant solvents tend to promote the more ionic N-bonding.

Chelated Complexes.

As pointed out above, both the π-bonding and steric control hypotheses, and even combinations of the two, are used in the literature as explanations for the mode of thiocyanate bonding in complexes of monodentate ligands. Likewise, both arguments have been applied to complexes with chelating ligands. Thus, the existence of $[Pd(Ph_2AsCH_2CH_2NR_2)(SCN)_2]$, (R=H,Me,Et)[105] as the

S-bonded species and the "mixed" species [Pd($Ph_2PCH_2CH_2$-CH_2NMe_2)(SCN)(NCS)][106,107] with an N-bonded thiocyanate moiety <u>trans</u> to the phosphorus atom and an S-bonded <u>trans</u> to the nitrogen atom appear to support the effect of π-bonding on the mode of coordination of thiocyanate. Studies on complexes of chelating diphosphines and diarsines (with approximately constant π-bonding capabilities) support the theory that the mode of thiocyanate coordination is controlled by steric effects.

In the series [Pd($Ph_2P(CH_2)_nPPh_2$)$(CNS)_2$](n=1,2,3, CNS does not specify mode of coordination) it is found that the mode of thiocyanate bonding changes from S,S for n=1[108,109] to S,N for n=2[92,108,109,110,111] to N,N for n=3.[108,109] As the π-bonding capabilities for the ligands in this series remain constant, the mode of thiocyanate coordination must be sterically controlled. The Pd thiocyanate complex formed from 1,2-<u>bis</u>(diethylphosphino)ethene has also been found to have "mixed" thiocyanate bonding.[112] The complex formed from 1,3-<u>bis</u>-(diphenylstibino)propane, a less sterically demanding ligand, exhibits S-bonding only.[113]

Chow, McAuliffe, and coworkers have synthesized a series of complexes using diphosphines and diarsines with a vinylic carbon chain. Their results are shown in Table 20.

Table 20

Mode of Thiocyanate Coordination in Palladium (II) Complexes of Chelating Phosphorus Ligands with Vinylic Carbon Chain Backbones

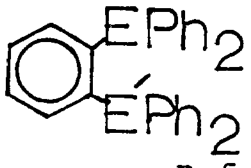
Ligand	Mode of Thiocyanate Coor.	Ref.
$Ph_2PCH{=}CHPPh_2$	S,S	99,115
$Ph_2PCH{=}CHAsPh_2$	S,S	115
$Ph_2AsCH{=}CHAsPh_2$	S,S	115
$Ph_2PCF{=}CFPPh_2$	S,N	114

The vinyl backbone is shorter than the dimethylene backbone in 1,2-bis(diphenylphosphino)ethane ($\sim$1.33 Å, cf. $-CH_2CH_2-$ in dppe = 1.58 Å).[115] The shorter ligand backbone pulls the phenyl groups away from the metal, decreasing the interaction with the CNS ligands. Thus, S,S-bonding becomes possible, in contrast to the S,N-bonding found with dppe. These data argue strongly for steric control of thiocyanate bonding: phosphorus ligands with vinylic backbones are believed to be better π-acceptors than their alkane analogs[116]; by the arguments of the π-bonding theory N-bonding would be promoted by these ligands. Instead, S-bonding is found.

Electronic effects are believed to be responsible for the N-bonding found with the fluorocarbon ligand,[114] though the authors do not go into a detailed explanation.

Levason and McAuliffe[116,117] have investigated the series of palladium thiocyanate complexes of ligands in which the donor atoms are in ortho positions on a benzene ring. Their results are tabulated in Table 21.

Table 21

Palladium (II) Thiocyanate Complexes of 

E	E'	Mode of Thiocy.Bdg.	Ref.
P	P	S,N	116
P	As	S,N	92,117
As	As	S,N	117
P	Sb	S,N	116
As	Sb	S,S	116

The o-phenylene linkage is intermediate in length between the dimethylene and vinyl backbone chains, and the data seem to support steric control of coordination. However, the authors report that preliminary data on platinum (II) complexes of these ligands are inconsistent with predictions based merely on steric control of coordination (due to lanthanide contraction the covalent radii of Pd (II) and Pt (II) are the same, 1.31 Å, and thus the same ligand should produce the same steric interactions, and thus the same modes of thiocyanate coordination, on both metals).[116] Thus, the authors argue that electronic effects cannot be completely ignored in determining the mode of thiocyanate coordination.

Interpretation of Data

The mode of thiocyanate coordination can be determined in several ways. The most accurate method is crystal structure determination; this, however, is costly, time consuming, and gives no information on the mode of thiocyanate bonding in solution (isomerization of thiocyanate compounds in solution has been noted in some cases).[92,116]

Infrared evidence is most often used in determining the mode of thiocyanate linkage; yet, even here, some uncertainty exists. Although some early workers in the field have used ν_{CS} (N-bonded: 870-820 cm^{-1}, S-bonded: 700-710 cm^{-1})[87,93] to determine the type of coordination, use of ν_{CN} has become standard. The criteria used by various authors are shown in Table 22.

Table 22

Frequency Ranges for Various Types of Thiocyanate Coordination

Compound Type	ν_{CN} (cm^{-1})
M-NCS	2100-2050 s,br[87,88,119]
	2080-2040[86]
M-SCN	2130-2085 s,sp[87,88,119]
	2120-2080[86]
M-NCS-M	2165-2065[87]
	$\geq$ 2140[88]

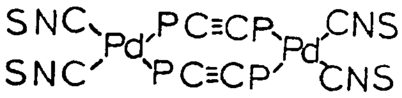
s = strong, br = broad, sp = sharp

It has also been noted[92] that ν_{CN} absorptions due to N-bonded thiocyanate tend to be broad (30-40 cm^{-1}), while those due to S-bonded thiocyanate are, in comparison, quite sharp (12-18 cm^{-1}). This is helpful in cases where the position of the absorption band does not yeild a clear cut assignment of the bonding mode.

Bridge bonding by the phosphine ligands is, of course, possible. Carty and Efraty[120] found absorptions at 2118 and 2072 cm^{-1} for $[Pd(Ph_2PC{\equiv}CPPh_2)(CNS)_2]$ indicating mixed thiocyanate bonding in this complex. Based on infrared CN stretch evidence alone it would be impossible to distinguish this bridged compound from a mononuclear complex.

Figure 54

$[Pd(Ph_3PC{\equiv}CPPh_2)(CNS)_2]$



Integrated absorption values of the peaks due to CN stretching have also been used to determine the mode of coordination of thiocyanate ion (cf. ref. 87, p. 252, and references therein). Values of 3-5 x 10^4 $M^{-1}cm^{-2}$ are found for the free thiocyanate ion; integrated intensities below this are found for the S-bonded thiocyanate ion, while N-bonded complexes yield values generally above 9×10^4 $M^{-1}cm^{-2}$. A variety of factors, however, can affect the results: dissociation in solution, hydrogen bonding solvents, which cause broadening of the peaks, and isomerization of the complex in solution to name a few.[87]

Solution infrared spectroscopy as a means of identifying modes of thiocyanate coordination has the disadvantage of not being able to distinguish between a species with "mixed bonding" --[(L-L)Pd(SCN)(NCS)]-- and a mixture of $[(L\text{-}L)Pd(SCN)_2]$ and $[(L\text{-}L)Pd(NCS)_2]$.[121,122]

Nuclear magnetic resonance spectroscopy has recently been introduced as a method of determining the mode of thiocyanate coordination in many cases. Anderson and Norbury[123] have used the lanthanide shift reagent tris-(7,7-dimethyl-1,1,1,2,2,3,3-heptafluorooctane-4,6-dionato)europium (III), $[Eu(fod)_3]$ to distinguish between N-bonded and S-bonded metal thiocyanate complexes.
The shift reagent, when added to an S-bonded thiocyanate complex produced a significant shift in the proton nmr of that complex (.3-.8 ppm), whereas the N-bonded thiocyanate complexes showed little or no shift (0.00-0.05 ppm). This is consistent with the tendency of a class a metal[91] like europium to coordinate readily with nitrogen (i.e. the terminal nitrogen of an S-bonded thiocyanate), but not with sulfur.

^{31}P nuclear magnetic resonance studies have been used to identify the mode of thiocyanate coordination in platinum (II)[121] and palladium (II)[122] complexes of phosphites and acetylenic phosphines. In these complexes the ^{31}P resonances of the thiocyanate, isothiocyanate, and mixed species are chemically shifted from one another; structural identification is aided by the occurrence of ^{14}N-^{31}P coupling in ^{31}P resonances of phosphorus nuclei bonded trans to N-bonded thiocyanate groups.[121] The spectra of the mixed platinum species often yield ^{31}P-^{31}P and $^{195}Pt^{31}P$ coupling constant data[121]; structural data have also been obtained by ^{15}N isotopic substitution and the resultant ^{15}N-^{31}P coupling constants.[122]

Goodfellow and coworkers[124,125] have used ^{1}H- ^{195}Pt internuclear double resonance (INDOR)[126] techniques to determine concentrations of linkage isomers in solutions of $Pt(CNS)_2L_2$ (L = NMe_3, PMe_3, PEt_3, $AsMe_3$, $AsEt_3$, etc.). Their data show the mode of thiocyanate coordination to be dependent on the size of the cis- ligands in these complexes.

(These nmr techniques require high sensitivity and often probes for nuclei other than hydrogen. FFT (fast Fourier transform) instrumentation is common in these studies.

Thus, in the opinion of this author, infrared spectroscopy remains the most practical method of elucidation of mode of thiocyanate coordination.)

Results

The infrared spectral characteristics of several palladium (II) thiocyanate complexes are shown in Table 23.

Four Membered Rings. $(\overline{\text{M-P-C-P}})$. The $[\mathrm{Pd(L\text{-}L)(CNS)_2}]$ complexes formed from the ligands bis-(diphenylphosphino)-methane, (dmp), and 1,1-bis-(diphenylphosphino)ethane, (1,1-dpe), both exhibit one CN stretch absorption above and one below 2100 cm^{-1} in both solution and the solid state (Figures 55-58). The product formed from 2,2-bis-diphenylphosphino)propane, (2,2-dpp), exhibits one absorption above 2100 cm^{-1} and one below this in solution, but both absorptions are below 2100 cm^{-1} in the solid state. (Figures 59,60).

According to the most generally used criterion S,N bonding is indicated in these complexes. However, as noted previously, there is some disagreement in the literature about the certainty of these criteria, and S-bonding has been found to exhibit a CN stretch absorption as low as 2080 cm^{-1}.[86] An additional criterion, peak width (at half height), was used to aid in identification of the mode of thiocyanate coordination.

The complex formed from dpm exhibits absorptions at 2116 and 2083 cm^{-1} in solution, 2108 and 2083 cm^{-1} in

Table 23

Infrared CN Stretching Frequencies of Pd(L-L)$(CNS)_2$ Complexes

Ligand	CN Stretch[a,b] (cm^{-1})		CN Stretch (lit.) (cm^{-1})		Bonding Assignment	Reference
	CH_2Cl_2	Nujol	CH_2Cl_2	Nujol		
$Ph_2PCH_2PPh_2$	2116,sp	2108,sp			S,S	108,109
	2083,sp	2083,sp				
$Ph_2PCH(CH_3)PPh_2$	2119,sp	2113,sp 2085,sp,sh			S,S(Nujol)	
	2085,br	2075,br			S,N(CH_2Cl_2)	
$Ph_2PC(CH_3)_2PPh_2$	2117,sp	2087,sp			S,S(Nujol)	
(2,2-dpp)	2081,br	2074,sp			S,N(CH_2Cl_2)	
$Ph_2PCH_2C(CH_3)_2$-CH_2PPh_2	2120,sp	2116,sp			S,N(Nujol)	
	2087,br	2083,br			S,N(CH_2Cl_2)	
$Ph_2AsCH_2C(CH_3)_2$-CH_2PPh_2	2117,sp	2115,sp			S,S(Nujol)	
	2084,br	2101,sp			S,N(CH_2Cl_2)	

Table 23 (Continued)

Ligand	CN Stretch[a,b] (cm^{-1})		CN Stretch(lit.) (cm^{-1})		Bonding Assignment	Reference
	CH_2Cl_2	Nujol	CH_2Cl_2	Nujol		
dppe	2117,sp	2126,sp	2120-2	2118-9	S,N	92,108,109
	2084,br	2099,sp	2086-93	2093-5		
dpp	2127,br	2088,br			N,N	108
	2091,br	2046,sp				
$Ph_2PCH_2CH_2NMe_2$	2123,sp	2118,br	2127	2126	S,N	92
	2082,br	2099,br	2087	2108		
$Ph_2PCH_2CH_2CH_2NMe$	2122,sp	2115,sp	2125,sp	2120,sp	S,N	92,108
	2085,br	2079,br	2087,br	2080,br		

NOTES:

a) "sp" indicates a peak width at half-height of 20 cm^{-1} or less.

b) "sh" = shoulder.

nujol mull. In all cases the absorptions are fairly sharp. Palenik and coworkers[109] have published the crystal structure of this compound and have found only S-bonding. (The infrared spectrum, however, has not been published.)

The complex formed from 2,2-dpe exhibits absorptions at 2119 and 2085 cm^{-1} in solution; the latter is fairly broad. In a nujol mull three absorptions are seen (2113, 2085 and 2075 cm^{-1}); the peak widths seem to indicate both S,S and S,N bonding. It is possible that an S,S-bonded form exists in the solid state which partially isomerizes to the S,N-bonded form in solution.

2,2-dpp forms a complex which has absorptions at 2117 and 2081 cm^{-1} in solution; the latter is broad. This is indicative of S,N bonding. The nujol mull spectrum, however, exhibits two very sharp absorptions, indicative of S,S-bonding, in the region normally assigned to the N-bonded CN stretch (2087 and 2079 cm^{-1}). These values, however, are close to the 2080 cm^{-1} lower limit given by Norby, et al.[86] Again, an S,S-bonded form is indicated by the nujol mullspectrum, and an S,N-bonded isomer by the solution spectrum.

Six Membered Rings. Palenik and coworkers[109] have found, through crystal structure studies, that 1,3-bis-(diphenylphosphino)propane, (dpp), yields a complex that has only N-bonded thiocyanate. (Again, the infrared

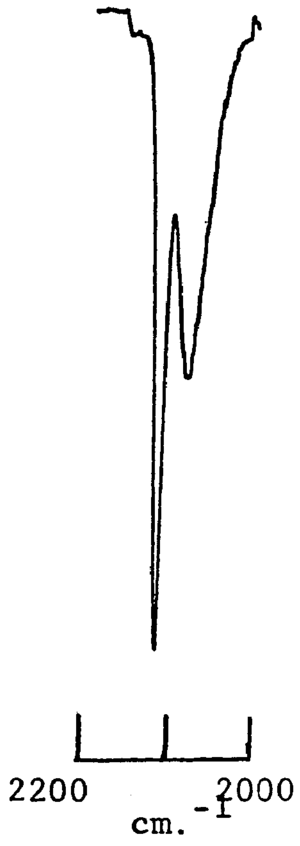


Figure 55.

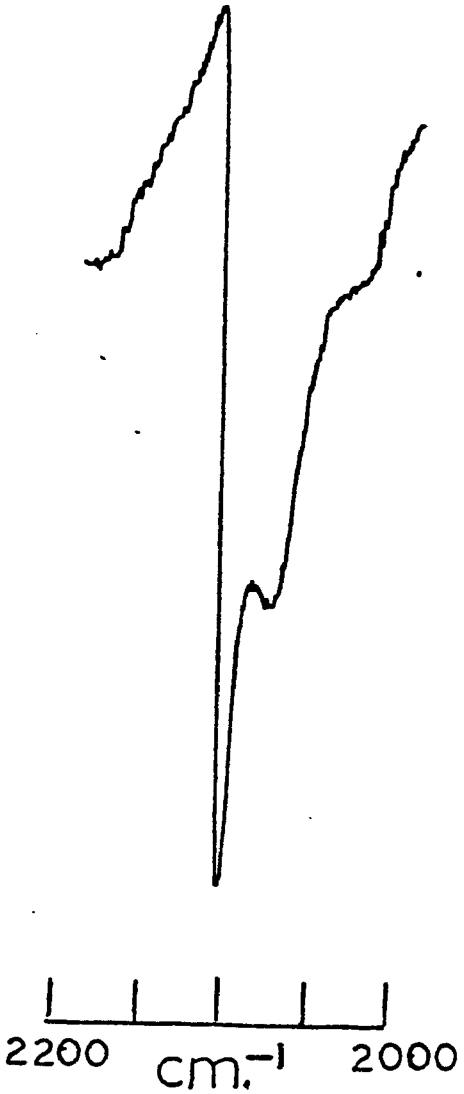


Figure 56.

Figure 55. Infrared absorptions in the CN stretch region of [Pd(dpm)$(CNS)_2$] in CH_2Cl_2

Figure 56. Infrared absorptions in the CN stretch region of [Pd(dpm)$(CNS)_2$] in Nujol.

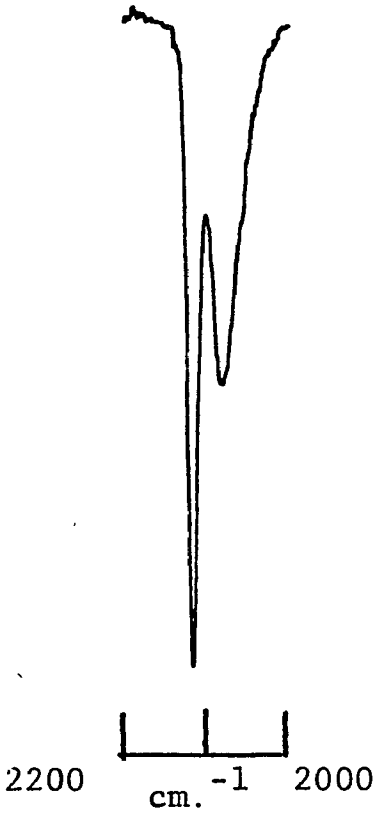


Figure 57.

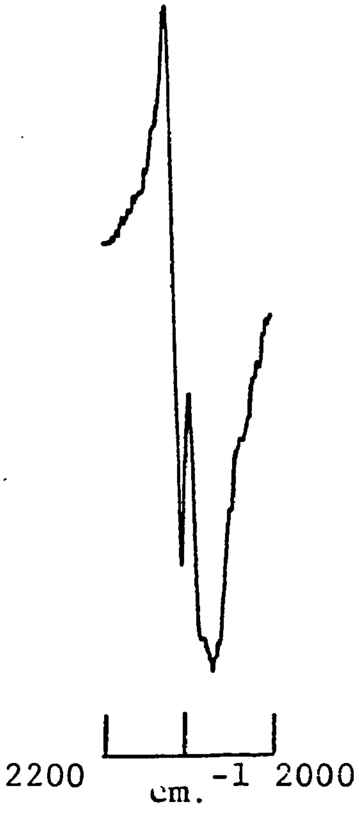


Figure 58.

Figure 57. Infrared absorptions in the CN stretch region of [Pd(1,1-dpe)(CNS)$_2$] in CH$_2$Cl$_2$.

Figure 58. Infrared absorptions in the CN stretch region of [Pd(1,1-dpe)(CNS)$_2$] in Nujol.

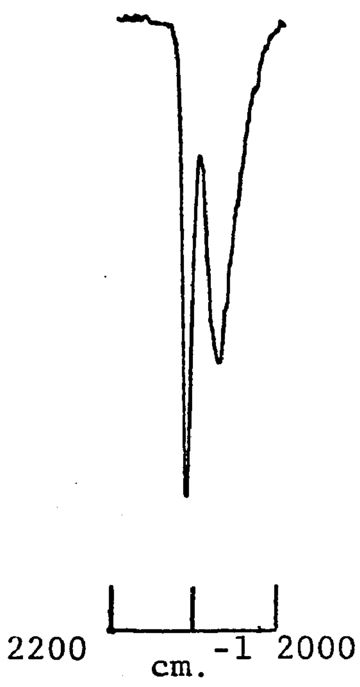


Figure 59

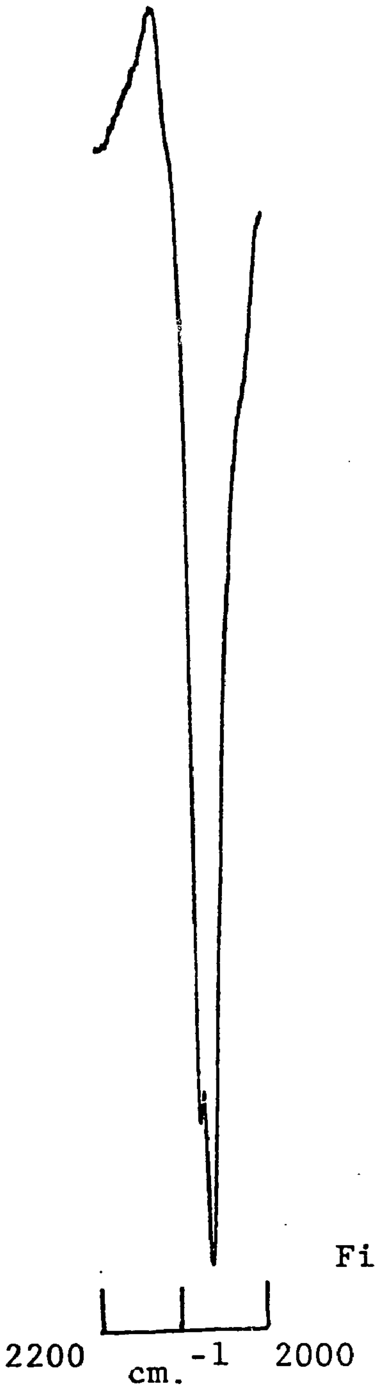


Figure 60

Figure 59. Infrared absorptions in the CN stretch region of [Pd(2,2-dpp)(CNS)$_2$] in CH$_2$Cl$_2$.

Figure 60. Infrared absorptions in the CN stretch region of [Pd(2,2-dpp)(CNS)$_2$] in Nujol.

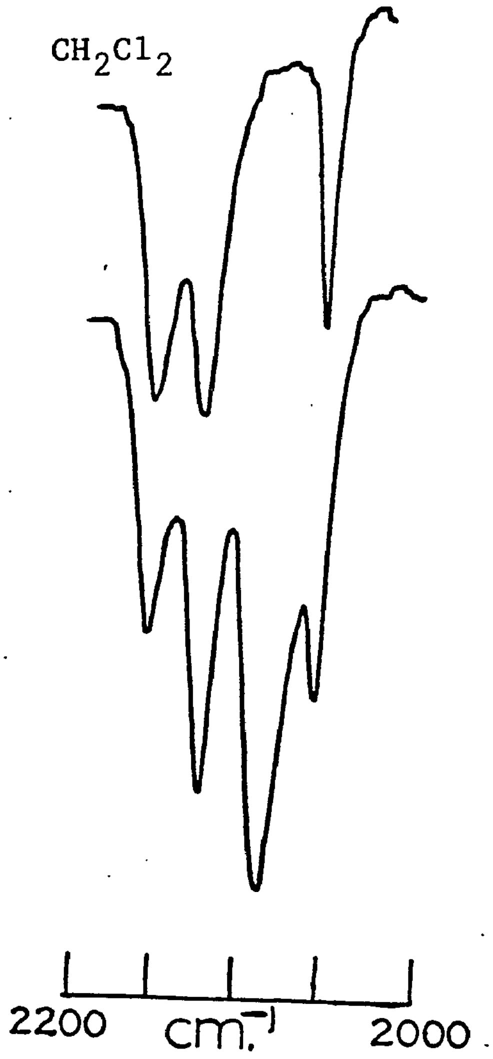


Figure 61. Infrared absorptions in the CN stretch region of $[Pd(dpp)(NCS)_2]$ in CH_2Cl_2.

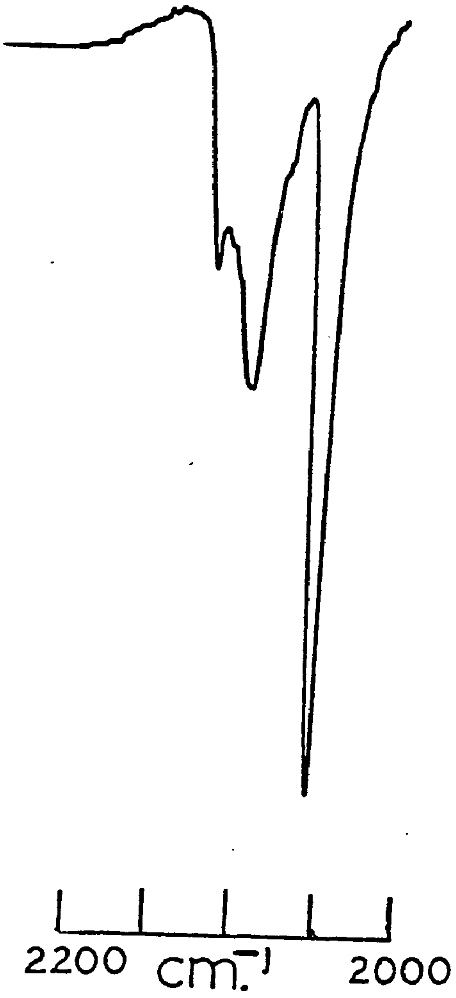


Figure 62. Infrared absorptions in the CN stretch region of $[Pd(dpp)(NCS)_2]$ in Nujol.

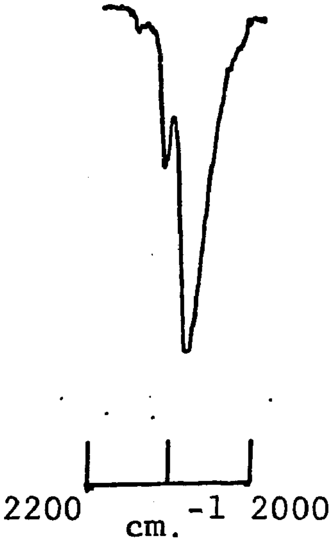


Figure 63.

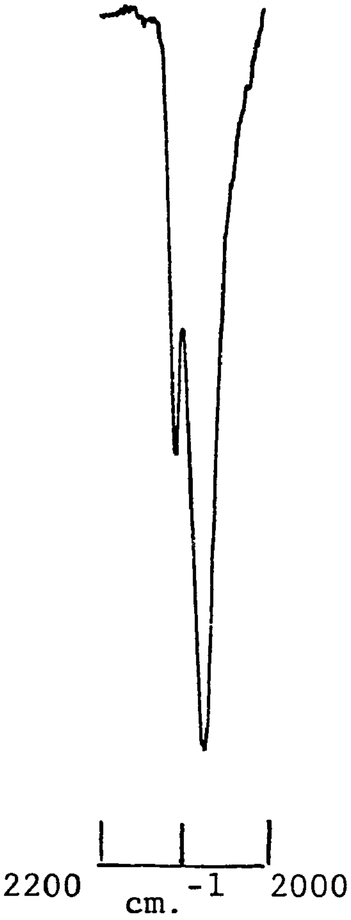


Figure 64.

Figure 63. Infrared absorptions in the CN stretch region of [Pd(2,2-dmdpp)(CNS)$_2$] in CH$_2$Cl$_2$.

Figure 64. Infrared absorptions in the CN stretch region of [Pd(2,2-dmdpp)(CNS)$_2$] in Nujol.

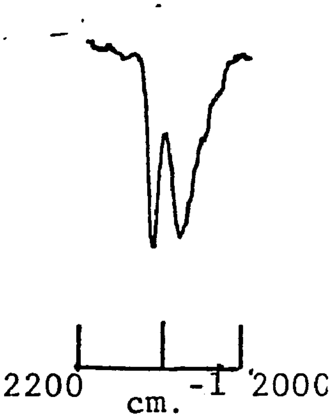


Figure 66.

Figure 66. Infrared absorptions in the CN stretch region of $[Pd(2,2\text{-}dmdap)(CNS)_2]$ in CH_2Cl_2.

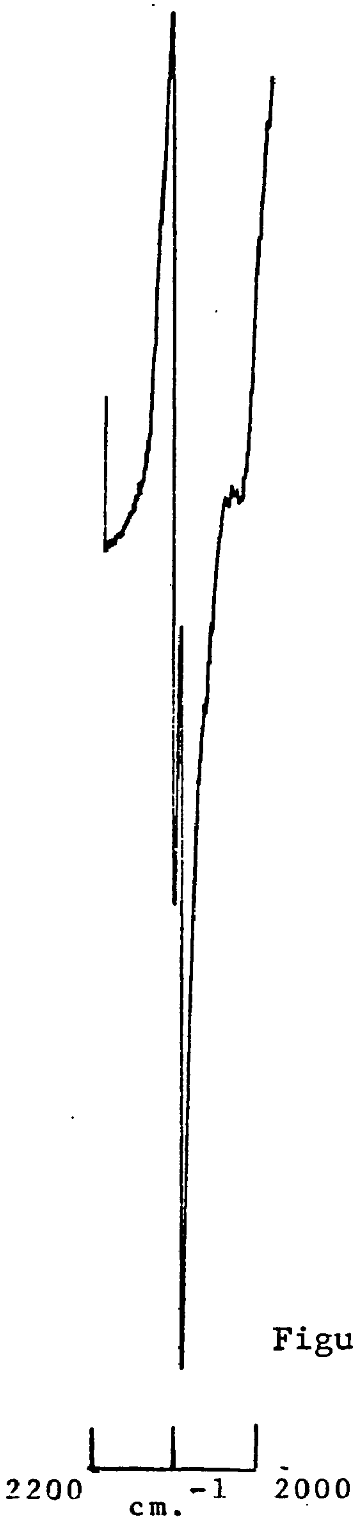


Figure 65.

Figure 65. Infrared absorptions in the CN stretch region of $[Pd(2,2\text{-}dmdap)(CNS)_2]$ in Nujol.

spectrum has not been published.) The infrared spectrum of this compound in the CN stretch region has been found in these laboratories to consist of two broad absorptions in methylene chloride, one above and one below (but close to) 2100 cm^{-1} (Figure 61). The spectrum in nujol consists of two much narrower absorptions, both below 2100 cm^{-1} (Figure 62). 2,2-dimethyl-1,3-bis(diphenylphosphino)-propane, (2,2-dmdpp), on the other hand, exhibits spectra both in solution and in the solid state (figures 63 and 64) that clearly are that of the S,N-bonded species. The arsenic analog of this ligand, 2,2-dimethyl-1,3-bis-(diphenylarsino)propane, (2,2-dmdap), yields a spectrum in nujol that is clearly the S,S-bonded form of the complex (Figure 65); in methylene chloride solution the spectrum (Figure 66) is that of the S,N form. 1,2-bis(diphenylarsino)ethane also exhibits this type of behavior: only the S,S-bonded form is found in the solid state, but some isomerization to the S,N-bonded form is found on dissolution of the complex in methylene chloride.[92]

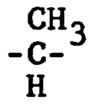
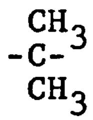
Discussion

Palenik, Meek and coworkers[108] have shown that increasing the chain length of a chelating biphosphine ligand, $Ph_2P(CH_2)_nPPh_2$, will cause the mode of thiocyanate coordination to change from S,S for n=1 through S,N (n=2) to N,N for n=3. They attribute this to an increased

P-Pd-P angle, leading to greater interaction between the phenyl groups and the coordinated thiocyanates.

In this study an attempt was made to determine the influence, if any, of groups on the carbon-chain backbone of the chelating ligand on the mode of thiocyanate coordination. This effect is especially to be looked for in the case where n=1: does increased crowding on the central carbon atom increase the interaction of the phenyls on phosphorus with the thiocyanate moiety to any great degree, causing a change from the S,S-bonded $[Pd(Ph_2PCH_2PPh_2)(SCN)_2]$ to, perhaps, a complex with "mixed" modes of thiocyanate coordination?

$[Pd(Ph_2P(CH_2)_3PPh_2)(NCS)_2]$ has already been shown to exhibit only N-bonding[108,109] in the solid state. Substitution of the central carbon atom of the ligand would not greatly change the geometry of this square planar complex, as shown by both theoretical considerations[17] and previous experimental evidence.[22] Thus, the work on the series of compounds where n=3 has been confined to differences between the compounds of 2,2-dimethyl-1,3-bis(diphenylphosphino)propane and its arsenic analog.

The bonding in the complexes containing four membered rings did seem to be sensitive to steric crowding on the methylene backbone, as the transition from S,S-bonding for the $-CH_2-$ backbone to S,N-bonding for the  $\overset{\displaystyle CH_3}{\underset{\displaystyle H}{-C-}}$ and  $\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{-C-}}$ backbones indicates. The spectra, however, are not without ambiguities, especially if the position of the CN stretch alone is used to assign coordination mode. That the dmp complex exhibits a spectrum in both solution and nujol mull that would be interpreted as "mixed" bonding is especially bothersome, in view of the results of the crystal structure showing only S-bonding in this complex. The mull spectrum of the 2,2-dpp is also rather unclear: the positions of the absorptions are in the region normally thought of as indicating N-bonding, yet the absorptions are far too sharp to be that of N-bonded thiocyanate. As the π-acceptor abilities for the three ligands are approximately equivalent, electronic effects cannot be put forward as an argument for the large frequency difference.

The crystal structure of the complex formed from 1,3-bis(diphenylphosphino)propane has proven the presence of N-bonding exclusively in the solid state. N-bonding is also indicated by the solution infrared spectrum of this complex. The analogous six-membered ring compounds formed from 2,2-dimethyl-1,3-bis(diphenylphosphino)-propane and its arsine analog both exhibit the infrared spectra typical of "mixed" bonding in solution; the phosphine also shows mixed bonding in nujol mulls, while the arsine exhibits S,S-bonding. These results are not surprising in the arsine case; the larger arsenic atom would move the phenyl groups attached to it further out in space, and this would result in less interaction with the thiocyanate ligands. The phosphine, however, would be expected to yield results similar to the straight-carbon-chain analog. The methyl groups on the ligand backbone would not be expected to lead to significant amounts of ring strain or deformation as compared to the straight chain analog, and thus similar steric interactions are expected.

In all, the results do seem to follow a general trend supporting steric control of thiocyanate coordination in these palladium complexes. There are, however, uncertainties in assignment of bonding mode that must be eliminated before a definite stand is taken.

EXPERIMENTAL

Materials

Solvents and reagents purchased from commercial supplies and used as received were methylcyclohexane (Matheson, Coleman, and Bell (M.C.B), East Rutherford, N. J.), methanol (Fisher Scientific Co,, Fairlawn, N.J.), 2-propanol (Fisher), Diethyl ether (Fisher), bromobenzene (J. T. Baker Chemical Co., Phillipsburg, N. J.), deuterochloroform (Stahler Isotope Chemicals, Rutherford, N.J.), dimethyl formamide (D.M.F.) (Baker), 95% and absolute ethanol (U.S. Industrial Chemicals Co., New York, N.Y.), triphenylphosphine (Strem Chemicals, Inc., Danvers, Mass.), gaseous ammonia (M.C.B.), sodium metal (Fisher), 2,2-dimethyl-1,3-propanediol (Aldrich Chemical Co., Cedar Knolls, N.J.), molybdenum hexacarbonyl (Strem), palladium dichloride (Fisher), potassium thiocyanate (Fisher), ammonium chloride (Fisher), and iron pentacarbonyl (Alfa Products, Beverly, Mass.).

Tetrahydrofuran (Fisher), hexanes (Fisher) and benzene (Mallinkrodt Chemical Works, St. Louis, Mo.) were distilled from CaH_2 under a nitrogen atmosphere before use. Dichloromethane (Fisher) was distilled from P_2O_5 under nitrogen before use.

Triphenylarsine was synthesized in these laboratories by the Grignard method.

Tungsten hexacarbonyl, a generous gift of the

Climax Molybdenum Co., Greenwich, Conn., was used as received.

Methylmanganese pentacarbonyl and the halomanganese pentacarbonyls (X=Cl,Br,I) were prepared by literature methods.[127,128]

Cyclopentadienyl irondicarbonyl halides were prepared by various students at Lehigh University by literature methods.[129]

Cycloheptatriene, a gift of the Shell Chemical Co., New York, N.Y., was used as received.

Experimental Techniques

Infrared Spectra

Infrared spectra were obtained with a Perkin-Elmer Model 283 spectrometer calibrated with polystyrene as a reference. Bond positions are ±1 cm^{-1}, and were read directly from the instrument's printout.

Proton Magnetic Resonance Spectra

All data were obtained with a Hitachi Perkin-Elmer R20A nuclear magnetic resonance spectrometer employing tetramethylsilane (TMS) (Aldrich) as an internal chemical shift standard. Chemical shift values are accurate to ±2 Hz. Coupling constant values are accurate to ±1 Hz (600 Hz scan), ±0.5 Hz (300 Hz scan), and ±0.2 Hz (120 Hz scan). Frequency measurements were taken with a Takeda Riken TR 3824X frequency counter.

Variable temperature experiments were performed using an R-202 VT variable temperature controller. Samples were allowed to equilibrate for 20 minutes at a given temperature before recording spectra.

Melting Points and Analyses

Melting points of metalcarbonyl complexes were determined in Kimax capillary tubes sealed under a nitrogen atmosphere using a "Mel-Temp" apparatus (Laboratory Devices, Cambridge, Mass.) and are uncorrected. (Those of the palladium thiocyanate complexes were taken in tubes open to the atmosphere.) Elemental analyses were performed by the Baron Consulting Co., Orange, Conn.

2,2-Dimethyl-1,3-dibromopropane

2,2-dimethyl-1,3-dibromopropane was prepared by the method of Whitmore, et al.[130] PBr_3 (162.6 g, 0.6 mol) was dropped onto 2,2-dimethyl-1,3-propanediol (52.0 g, .5 mol). The resultant mixture was heated to reflux 10 hrs with stirring. The reaction mixture was slowly poured onto 500 ml. ice, and the resultant mixture steam distilled. The lower (organic) layer was separated from the upper (aqueous) layer, washed with saturated potassium barbonate solution (2 x 100 ml.), and dried over anhydrous calcium chloride. The resultant liquid was distilled under reduced pressure; the fraction boiling 65°/13 torr was collected (Beilstein gives 68-71°/13 torr (I, 50) and $72^{o}/14$ for (1, 142) as boiling points). Yielding .493 grams (42%) of clear colorless 2,2-dimethyl-1,3-dibromopropane.

NMR spectrum (in CCl_4): 1.18 δ, (6H), 3.35 δ, singlet (4H).

2,2-dimethyl-1,3-bis(diphenylphosphino)propane.

The method of Hewertson and Watson[58] was used to prepare this ligand. A one liter, three-necked round-bottomed flask was equipped with mechanical stirrer and nitrogen inlet. The flask was flushed with dry nitrogen for ten minutes. Anhydrous ammonia (500 ml) was introduced via a tygon tube through the third neck. Sodium (1.84 g, 0.08 g atom) was dropped into the ammonia, resulting in a deep blue solution. This was stirred for thirty minutes. Triphenylphosphine (10.48 g, 0.04 mol) was then charged into the flask; the resultant deep red micture was stirred for thirty minutes. Ammonium chloride (1.87 g, 0.035 mol) was charged into the flask, turning the reaction mixture light orange. 2,2-dimethyl-1,3-dibromopropane (4.14 g, 0.018 mol) in 10 ml. anhydrous ether was then dropped into the reaction mixture. The reaction mixture was stirred overnight, allowing the ammonia to evaporate. The residues were extracted with methylene chloride, filtered; the solvent was removed and the residues recrystallized from 2-propanol, yielding 3.3 g (42%) of a white crystalline product, m.p. 86-87°C

NMR (CH_2Cl_2 solution): δ1.11, singlet, 6H; δ2.41, doublet, 4H, $^2J_{PH} = 3.1 \pm 0.2$ Hz.

Analysis: Calculated for $C_{29}H_{30}P_2$: C, 79.07; H. 6.86. Found: C, 78.68; H, 6.85.

2,2-Dimethyl-1,3-*bis*(diphenylarsino)propane

2,2-Dimethyl-1,3-*bis*(diphenylarsino)propane was prepared in a manner analogous to that of 2,2-dimethyl-1,3-*bis*(diphenylphosphino)propane, with the exception of the substitution of 12.24 grams (0.04 mol) of triphenylarsine for the equivalent molar amount of triphenylphosphine. Extraction of the product with methylene chloride and recrystallization from 2-propanol yielded 2.80 g (30.1%) of white crystalline product, m.p. 85-85.5°C.

Anal. Calculated for $C_{29}H_{30}As_2$: C, 65.92; H, 5.72. Found: C, 65.65; H, 5.71. NMR (CH_2Cl_2 solution): δ2.33 (singlet, 4H), δ1.12 (singlet, 6H).

(2,2-Dimethyl-1,3-*bis*(diphenylphosphino)propane)molybdenum tetracarbonyl

Molybdenum hexacarbonyl (0.264 g, 1 mmol) and 2,2-dimethyl-1,3-*bis*(diphenylphosphino)propane (0.440 g, 1 mmol) were mixed in a 50-ml round-bottomed flask. Methylcyclohexane (25 ml) was added after which the system was flushed with nitrogen. A condenser was attached to the flask, and the reaction mixture heated to gentle reflux. The volume of carbon monoxide evolved as a function of time was measured with a gas-measuring buret. When the evolution of gas had ceased, the reaction mixture was cooled to room temperature under nitrogen and then stored in a refrigerator. The precipitated solid was collected and dissolved in hot benzene, cleared with charcoal and filtered under nitrogen. Hexanes were added to the filtrants to give a cloud point after which the mixture was put in freezer. Pale yellow crystals formed and were collected under positive nitrogen pressure, washed with hexanes, and dried under high vacuum, yielding 0.38 g (58%) of a pale yellow crystalline product, m.p. 201-3.

Anal. Calculated for $C_{33}H_{33}MoO_4P_2$: C, 61.12; H, 4.66. Found: C, 60.96; H. 4.73.

[2,2-Dimethyl-1,3-*bis*(diphenylarsino)propane]molybdenum tetracarbonyl

Molybdenum hexacarbonyl (0.26 g, 1 mmol) and 2,2-dimethyl-1,3-*bis*(diphenylarsino)propane (0.53 g, 1 mmol) were charged into a Pyrex glass Schlenk tube. THF (30 ml) was added, and the stirred reaction mixture was irradiated for 2 hrs. During this time the reaction mixture was cooled by means of a water-cooled probe inserted in the solution. Gas evolved by the reaction as a function of time was trapped in a gas-measuring buret. After 2 hrs of irradiation the reaction mixture was cleared with charcoal, filtered under nitrogen, and reduced in volume, under a stream of nitrogen, with gentle heating. The volume of the solution was maintained at 15 ml. by continuous addition of absolute methanol during heating. At the first sign of precipitation of solid the process was halted, the solution allowed to cool to room temperature under nitrogen, then placed in a freezer, yielding 0.41 g (55%) of yellow crystals, m.p. 196-197°C.

Anal. Calculated for $C_{33}H_{30}MoO_4As_2$: C, 53.10; H, 4.15. Found: C, 53.54; H, 4.17.

<u>2,2-Dimethyl-1,3-bis(diphenylphosphino)propane tungsten-tetracarbonyl</u>

Tungsten hexacarbonyl (0.70 g, 2 mmol) and 2,2-dmdpp (0.88 g, 2 mmol) were irradiated in a Pyrex glass Schlenk tube for 4 hrs with stirring and cooling in 75 ml. THF. The crystallization procedure outlined in the synthesis of $MO(CO)_4$(2,2-dmdap) was then followed, yielding 0.65 g (44%) of product as yellow crystals, m.p. 191-194°C.

<u>2,2-Dimethyl-1,3-bis(diphenylarsino)propane tungsten tetracarbonyl</u>

Tungsten hexacarbonyl (0.70 g, 2 mmol) and 2,2-dimethyl-1,3-<u>bis</u>(diphenylarsino)propane (1.06 g, 2 mmol) in 25 ml. THF were irradiated for 5 hrs in a quartz tube with stirring and cooling. The reaction mixture was then cleared with charcoal and filtered under nitrogen.

The crystallization procedure outlined in the synthesis of $Mo(CO)_4$(2,2-dmdap) was then followed, yielding 0.73 g (44.5%) of yellow crystals, m.p. 211-213°C.

Acetylmanganesetricarbonyl (2,2-dimethyl-1,3-*bis*(diphenylphosphine)propane)

A mixture of 2,2-dimethyl-1,3-*bis*(diphenylphosphino) propane (0.55 g, 1.25 mmol) and methyl manganese pentacarbonyl[127] (0.26 g, 1.25 mmol) in oxygen-free, dry benzene was stirred under nitrogen for 24 hrs. The reaction mixture was then cleared with charcoal, filtered under nitrogen, and oxygen-free dry hexanes added to initiate crystallization of the product. Crystallization was completed by cooling the mixture below 0°C, yielding 0.37 g (48%) of tan solid, m.p. 193-4 d.

Anal. Calculated for $C_{34}H_{33}MnO_4P_2$: C, 65.60; H, 5.34. Found: C, 65.24; H, 5.17.

Acetylmanganesetricarbonyl (2,2-dimethyl-1,3-*bis*(diphenylarsino)propane)

Acetylmanganesetricarbonyl (2,2-dimethyl-1,3-*bis*(diphenylarsino)propane) was prepared in a manner similar to the preparation of the phosphine analog using 0.52 g (2.5 mmol) of methylmanganese pentacarbonyl and 1.32 g (2.5 mmol) of the diarsine, yielding 0.22 g (12.4%) of a yellow solid, m.p. 167-170°C.

Analysis Calculated for $C_{34}H_{33}MnO_4As_2$: C, 57.48;

H, 4.68. Found: C, 57.80; H, 4.93.

Methylmanganesetricarbonyl (2,3-dimethyl)-1,3-bis(diphenylphosphino)propane)

Acetylmanganesetricarbonyl (2,2-dimethyl-1,3-bis(diphenylphosphino)propane (1.41 g, 2.3 mmol) was heated to reflux in oxygen-free dry benzene (10 ml) for 72 hr. The reaction mixture was then cleared with charcoal, filtered under nitrogen and oxygen free dry hexanes were added to start crystallization. The mixture was cooled in the freezer to yield the product as golden yellow crystals which were collected under nitrogen, washed with hexanes and blown dry under a stream of nitrogen on a sinter, yielding 0.45 g (33%) of the pure product, m.p. 194.5-198d.

Anal. Calculated for $C_{34}H_{33}MnO_4P_2$: C, 65.60; H, 5.34. Found: C, 65.24; H, 5.17.

Acetylmanganesetricarbonyl (2,2-dimethyl-1,3-bis(diphenylarsino)propane

Acetylmanganesetricarbonyl (2,2-dimethyl-1,3-bis(diphenylarsino)propane) was prepared in a manner similar to the preparation of the phosphine analog using 0.52 g (2.5 mmol) of methylmanganese pentacarbonyl and 1.32 g (2.5 mmol) of the diarsine, yielding 0.22 g (12.4%) of a yellow solid, m.p. 167-170°C.

Analysis Calculated for $C_{34}H_{33}MnO_4As_2$: C, 57.48; H, 4.68 Found: C, 57.80; H, 4.93.

<u>Methylmanganesetricarbonyl (2,2-dimethyl)1,3-bis(diphenylphosphino)propane)</u>

Acetylmanganesetricarbonyl (2,2-dimethyl-1,3-<u>bis</u>(diphenylphosphino)propane (1.41 g, 2.3 mmol) was heated to reflux in oxygen-free dry benzene (10 ml) for 72 hr. The reaction mixture was then cleared with charcoal, filtered under nitrogen and oxygen free dry hexanes were added to start crystallization. The mixture was cooled in the freezer to yield the product as golden yellow crystals which were collected under nitrogen, washed with hexanes and blown dry under a stream of nitrogen on a sinter, yielding 0.45 g (33%) of the pure product, m.p. 194.5-198 d.

<u>Methylmanganesetricarbonyl (2,2-dimethyl-1,3-bis(diphenylarsino)propane)</u>

Methylmanganesetricarbonyl (2,2-dimethyl-1,3-<u>bis</u>(diphenylarsino)propane) was prepared from methylmanganese pentacarbonyl (0.21 g, 1 mmol) and 2,2-dimethyl-1,3-<u>bis</u> (diphenylarsino)propane (0.53 g, 1 mmol) by decarbonylation of the acetyl product in the manner of the 2,2-dmdpp analog, or by heating the reactants in refluxing benzene for 72 hr. The reaction mixture was cleared with charcoal, filtered under nitrogen, diluted with hexanes to the cloud point and then cooled to below 0° in the freezer. The yellow crystalline product was collected on a sintered glass filter under nitrogen, washed with hexanes and dried under high vacuum, yielding 0.52 g (76%) of the desired product, m.p. 181-185 d.

Analysis Calculated for $C_{33}H_{33}As_2MnO_3$: C, 58.08; H, 4.87. Found: C, 58.17; H, 4.98.

2,2-Dimethyl-1,3-*bis*(diphenylarsino)propanetricarbonylmanganese (I) halides

General Syntheses

2,2-Dimethyl-1,3-*bis*(diphenylarsino)propane (1.06 g, 2 mmol) and the halomanganese pentacarbonyl[128] (2 mmol) were heated in methylcyclohexane (20 ml) until evolution of gas ceased. The reaction mixture was cooled slowly to room temperature, then cooled to below 0°C in a freezer for 24 hours. The product was collected and recrystallized from CH_2Cl_2/MeOH.

2,2-Dimethyl-1,3-*bis*(diphenylphosphinopropanetricarbonylmanganese (I) halides

These compounds were synthesized in a manner similar to the arsine analogs.

Table 24. Characterization Data for $XMn(CO)_3$(2,2-dmdpp) and $XMn(CO)_3$(2,2-dmdap) Complexes.

Ligand	X	% Yield	M.P.(°C)	Color
2,2-dmdpp	Cl	90.5	190.5-196 d	Yellow
2,2-dmdpp	Br	94	200-204 d	Yellow-orange
2,2-dmdpp	I	43	201-205 d	Red-orange
2,2-dmdap	Cl	81	184 d	Yellow
2,2-dmdap	Br	69	194 d	Orange
2,2-dmdap	I	85	188-90 d	Red-orange

2,2-Dimethyl-1,3-bis(diphenylphosphino)propane iron tricarbonyl

The method of Odom, et al.,[76] was used to prepare this product. A 100 ml one necked, round-bottomed flask was flushed with nitrogen and charged with cycloheptatriene iron tricarbonyl[118] (0.928 g, 4 mmol), 2,2-dimethyl -1,3-bis(diphenylphosphino)propane (1.76 g, 4 mmol), and xylene (50 ml). The reaction mixture was heated to reflux temperature for 16 hr under a nitrogen atmosphere. The solvent was then removed under aspirator vacuum and the residues chromatographed on an alumina column using hexane/methylene chloride (4/1) as the eluting solvent. The first three 50 ml fractions were starting material, as shown by the infrared spectrum in the carbonyl region; the remainder was the desired product. Evaporation of the solvent yielded a 1.06 g (45.8%) of a yellow solid, m.p. 149-151 d.

2,2-bis(diphenylphosphine)propane irontricarbonyl

2,2-bis(diphenylphosphino)propane was synthesized in a manner analogous to the 2,2-dmdpp derivative, yielding 0.07 g (5%) of a yellow solid, m.p. 186-190 d.

Compounds of 2,2-dimethyl-1,3-bis(diphenylphosphino) propane and $CpFe(CO)_2X$

General Synthesis

The method of King, Houk and Pannel[81] was employed.

Table 25. Characterization Data for CpFe(2,2-dmdpp)X Complexes

X	Color	m.p.	% Yield	Analysis	Irradiation Time
Cl	Black (Powder)	181.3d	40		3 hr
Br	Black	187	69		6 hr
I	Gray Powder	212,217	58	Calc: C 59.33, H 5.13 Found: C 59.01, H 5.28	3 hr

Equimolar amounts of the chelating diphosphine and CpFe-$(CO)_2X$[129] were dissolved in THF (25 ml) and irradiated in a quartz tube with cooling and stirring. The THF was then reduced in volume under a stream of nitrogen with gentle heating and absolute methanol was slowly added to start crystallization of the product. In every preparation a greenish tinge to the mother liquor indicated the presence of the bridged compound:

$CpFe(CO)X\text{-}P(Ph)_2CH_2C(CH_3)_2CH_2P(Ph_2)X(CO)FeCp$

This compound, however, was not isolated. The black or gray product was collected on a sintered glass filter under nitrogen, washed with absolute methanol, and dried under high vacuum.

Palladium (II) thiocyanate complexes. General Synthesis.

These complexes were prepared by the method of Palinik, *et al.*[109] $K_2Pd(SCN)_4$ (0.42 g, 1 mmol) was dissolved in absolute ethanol (15 ml). The chelating ligand (1 mmol) was dissolved in dichloromethane (5 ml) and added rapidly to the stirred ethanol solution. A color change occurred; the red color rapidly changed to yellow. The reaction mixture was stirred until a solid precipitated (1-2 hrs). The solid was collected by suction filtration, washed with absolute ethanol, and dried under high vacuum.

(In the synthesis of [(dppe)Pd(SCN)(NCS)]: dppe, an orange solid ([Pd(dppe)$_2$][Pd(SCN)$_4$]) precipitated first. Recrystallization from hot DMF yielded the desired yellow product.)

Table 26. Characterization data for [Pd(L-L)(CNS)$_2$] Complexes

L-L	Color	Yield %	m.p. (°C)	Experimental Analysis					
				C		H		N	
				Calc.	Found	Calc.	Found	Calc.	Found
1,1-dpe	Bright Yellow	82	203-206	54.16	54.23	3.89	3.77	4.51	4.60
2,2-ddp	Beige	71	255-259d	54.85	54.49	4.13	4.16	4.41	4.27
2,2-dmdpp	Pale Yellow	80	285-289	56.15	56.07	4.56	4.42	4.22	4.22
2,2-dmdap	Bright Yellow	44	268	49.58	49.67	4.03	4.04	3.73	3.58
dpm	Light Yellow	83	178-9						
dppe	Light Yellow		267-270						
dpp	Bright Yellow	95	180-184d						
$Ph_2PCH_2CH_2NMe_2$	Bright Yellow	79	207-209						
$Ph_2PCH_2CH_2CH_2NMe_2$	Bright Yellow	93	126-129d						

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