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Studies in the coordination chemistry of phosphole

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STUDIES IN THE COORDINATION CHEMISTRY OF PHOSPHOLES

BY

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ABSTRACT

The chemical, physicochemical, theoretical and metal coordination studies of phospholes which have so far appeared in the literature are reviewed briefly with particular reference to the electronic structure of the system.

The coordinating properties of the simple phospholes 1-phenylphosphole (PP), 3-methyl-1-phenylphosphole (mPP), 3,4-dimethyl-1-phenylphosphole (dPP) and 3,4-dimethyl-1-n-butylphosphole (dBP) with the metal ions Re(III), Ru(III), Ru(II), Co(II), Rh(III), Ir(III), Ni(II), Pd(II), Pt(II), Cu(I) and Hg(II) and also with carbonyl complexes of Ru(II) and Rh(I) have been studied. In all of the complexes, including the carbonyl complexes, the ligands are bonded to the metals through the phosphorus lone pair electrons (σ bonded). The carbonyl stretching frequencies of the phosphole—metal carbonyl complexes resemble those of similar tertiary alkylarylphosphine complexes. Ru(III) can be reduced by the phospholes to Ru(II), Cu(II) is only partially reduced to Cu(I) and Rh(III) is stabilised.

In general, the phospholes appear to have about the same donor character as other tertiary phosphines although some of the complexes formed have unexpected structures. Detailed spectroscopic and magnetic studies of these complexes have been made.

Differences in the behavior of the various phospholes studied here, and also other phospholes, in complex formation are attributed to variations in the substitution pattern with the type of substitution at the phosphorus atom being apparently of particular importance.

The results are discussed in terms of orbital perturbation of a pyramidal phosphole in which the HOMO may not be the lone-pair orbital and also in terms of a pyramidal but aromatic phosphole system.

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ABBREVIATIONS

n-Bu	*n*-butyl
t-Bu	*tert*-butyl
Cy	cyclohexyl
DMA	dimethylacetamide
en	ethylenediamine
Et	ethyl
Me	methyl
Ph	phenyl
PNP	2,6-di(β-diphenylphosphinoethyl)pyridine
i-Pr	isopropyl
THF	tetrahydrofuran
VPP	1,2-bis(diphenylphosphino)ethylene

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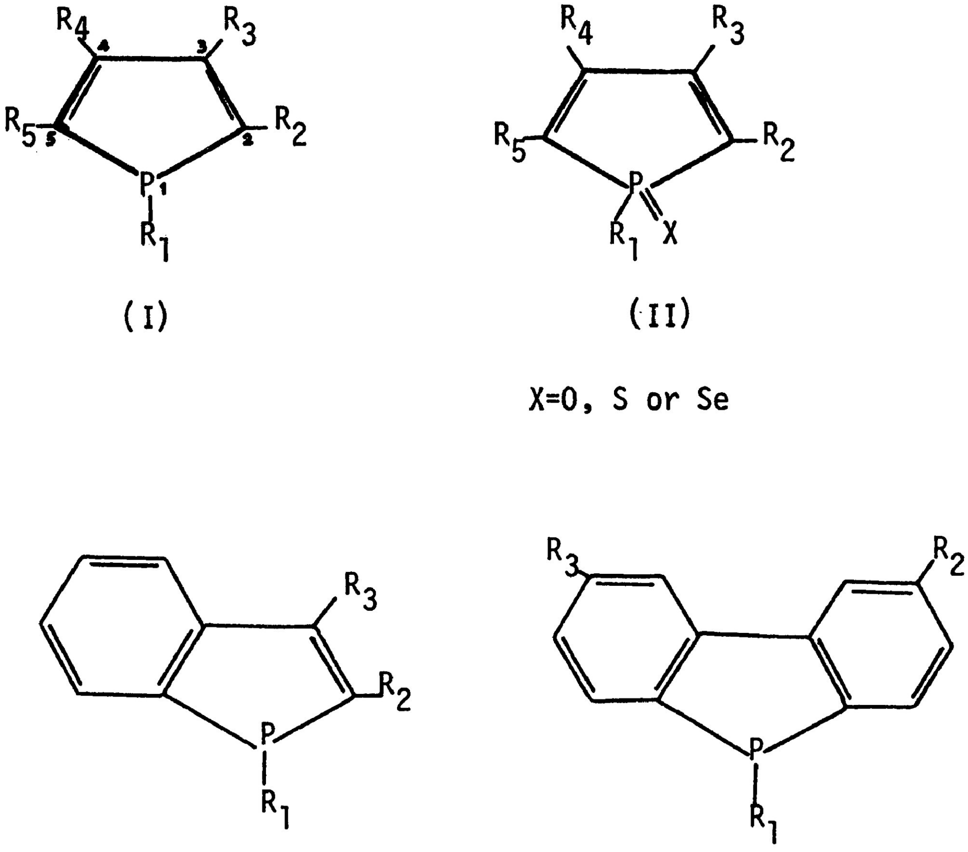
CHAPTER I

INTRODUCTION

The reactions of transition metals with tertiary phosphines have been well studied in the past twenty years (1,2). In general, metals that react readily with the phosphines have been classified as 'soft acids' by Pearson (3) and as class (b) acceptors by Chatt (4). The ability of the phosphorus atom to accept d electrons from group VIII and neighbouring elements into its empty, low energy, d orbitals is important in its bonding with the transition metals and easily accounts for the formation of the large number of well characterised complexes which are now known.

Recent new synthetic techniques have provided much easier routes for the synthesis of analogous cyclic phosphines, particularly the phospholes (I) which were unknown until 1959. The more readily accessible phospholes which have been synthesised are listed in Table (1), although it should be noted that phosphole itself (Fig. (1), structure I, $R_1=R_2=R_3=R_4=R_5=H$) remains unknown. In addition, functionally substituted phosphole derivatives have recently become available (9, 23-26). Furthermore, certain derivatives such as oxides, sulfides, selenides and related structures (II) of many of these phospholes have been well characterised. Finally, fused ring derivatives such as the benzophospholes (phosphindoles) (III) and the dibenzophospholes (IV) (Table 1) are known although, for the most part, they are outside the scope of this thesis. A discussion of synthetic approaches to phospholes and phosphole derivatives is not appropriate here and this topic has been thoroughly surveyed elsewhere (27, 28).

Fig. (1)



(I) (II)

X=O, S or Se

(III) (IV)

Table (1)

Phosphole and Fused-ring Phosphole Derivatives

Phosphole (I)

	R_1	R_2	R_3	R_4	R_5	Name	Abbr.	Ref.
a	Ph	Ph	Ph	Ph	Ph	1,2,3,4,5-pentaphenylphosphole	pPP	5,6
b	Ph	Ph	H	H	Ph	1,2,5-triphenylphosphole	TPP	7
c	Me	H	H	H	H	1-methylphosphole	MP	8
d	Me	Me	H	H	H	1,2-dimethylphosphole	$d^{12}MP$	9
e	Me	H	Me	H	H	1,3-dimethylphosphole	$d^{13}MP$	9
f	Me	H	Me	Me	H	1,3,4-trimethylphosphole	TMP	9
g	Ph	H	H	H	H	1-phenylphosphole	PP	10,11,12
h	Ph	H	Me	H	H	3-methyl-1-phenylphosphole	mPP	12,13
i	Ph	H	Me	Me	H	3,4-dimethyl-1-phenylphosphole	dPP	12,13
j	*n*-Bu	H	H	H	H	1-*n*-butylphosphole	BP	14
k	*n*-Bu	H	Me	H	H	3-methyl-1-*n*-butylphosphole	mBP	14
l	*n*-Bu	H	Me	Me	H	3,4-dimethyl-1-*n*-butylphosphole	dBP	12,14

Table (1) cont'd

m	t-Bu	H	Me	Me	H	3,4-dimethyl-1-t-butylphosphole	dtBP	15
n	CH_2Ph	H	H	H	H	1-benzylphosphole	ZP	9
o	CH_2Ph	H	Me	H	H	3-methyl-1-benzylphosphole	mZP	9
p	CH_2Ph	H	Me	Me	H	3,4-dimethyl-1-benzylphosphole	dZP	9

Phosphindole (III)

	R_1	R_2	R_3		
a	Ph	H	H	1-phenylphosphindole	16
b	Ph	Ph	n-Bu	3-n-butyl-1,2-diphenylphosphindole	17,18
c	Ph	Ph	PhC≡CPh	1,2-diphenyl-3-(o-phenylethinylphenyl)-phosphindole	19

Table (1) cont'd

Dibenzophosphole (IV)

	R_1	R_2	R_3			
a	Me	H	H	5-methyl-5*H*-dibenzophosphole	MDBP	19,20
b	Et	H	H	5-ethyl-5*H*-dibenzophosphole	EDBP	19,20
c	*i*-Pr	H	H	5-isopropyl-5*H*-dibenzophosphole	PDBP	21
d	*t*-Bu	H	H	5-*t*-butyl-5*H*-dibenzophosphole	BDBP	21
e	Ph	H	H	5-phenyl-5*H*-dibenzophosphole	DBP	19,20
f	Ph	OMe	OMe	2,8-dimethoxy-5-phenyl-5*H*-dibenzophosphole		21

Many papers have been published which are concerned directly or indirectly with the possible pyrrole-type aromatic character in the phosphole ring (29). Thus, one of the major areas of interest in phosphole chemistry is the extent to which the P lone-pair is delocalised into the ring and the possible aromatic properties of the system. The main thrust of this thesis is to gather chemical evidence regarding the electronic structure by studying the ability of certain phospholes to make available the P lone-pair for coordination to metals. It is appropriate therefore to review, in this chapter, the physical and chemical properties of phospholes, together with their coordination properties with special emphasis on the current views regarding the possible aromaticity of the phosphole system.

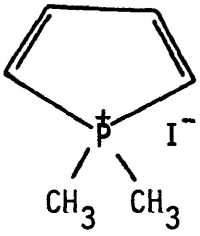
The Phospholes

It should be noted at the outset that several reviews (18,28,29,30) on various aspects of phosphole chemistry have appeared, mainly from workers in these laboratories, and a further review by another group will appear shortly (31). The material covered here, then, is a brief digest of the more important aspects of the topic to lay the ground work for the study to be described in the later chapters.

(i) Physical and Chemical Properties

If the nonbonding electron pair of the phosphorus atom in the phosphole system is significantly delocalised, the basicity, nucleophilicity and donor character should be low like those of pyrrole which has the pK_a value of -3.8 and which does not readily form quaternary salts. In this connection, Quin (8,33) observed that, unlike most simple tertiary phosphines, 1-methylphosphole is not extracted from pentane solution by 2N hydrochloric acid. It is however, removed from the pentane solution by stronger acid (6N) and therefore has a considerably lower basicity than the normal tertiary phosphines. The measurement of the pK_a value of 1-methylphosphole (the simplest phosphole yet prepared) was made by using ultraviolet absorption techniques and it was found that this phosphole has a pK_a value of 0.5. Although this value is higher than that of pyrrole, it is considerably lower that of triphenylphosphine (pK_a=2.73) (34) and also alkyl and vinylphosphines in general (8,33). This suggests that there is a considerable lone pair-diene interaction in the phosphole system which reduces the lone pair availability. However, a less readily apparent explanation of the results is that the non-bonding orbital of the phosphorus atom in a non-aromatic pyramidal ground state is possibly not the highest occupied molecular orbital (HOMO). This point will be returned to later.

In fact, most of the reactivity studies of phospholes have been concerned with the reactivity at the phosphorus atom. For example, simple and fused ring phospholes form methiodides (e.g. V) (8,14,22), P-haloalkylphospholium salts (e.g. VI) (8), P-aminophospholium salts (e.g. VII) (35) and phosphole P-dihalides (7). The formation of phospholium salts is apparently a typical phosphine characteristic but Quin (9,36) found that the rate of quaternisation of various phospholes depends markedly upon the substitution pattern on the ring. For example, 1-benzylphosphole (In) forms a salt with benzyl bromide very slowly (28% yield after 11 days) while with similar phospholes with substituents on the ring, e.g. methyl groups on the 3-(structure Io) and 3,4-(structure Ip) positions, the rate of quaternization increases significantly (2 days with 83% yield in both). This indicates substitution on the ring enhances the phosphine character and this has been attributed to electronic or steric effects (9) although, again, possible variations in orbital sequence cannot be ignored.



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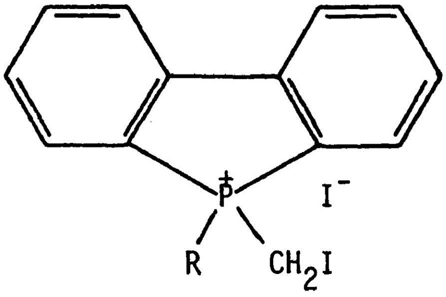

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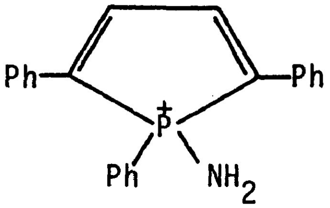
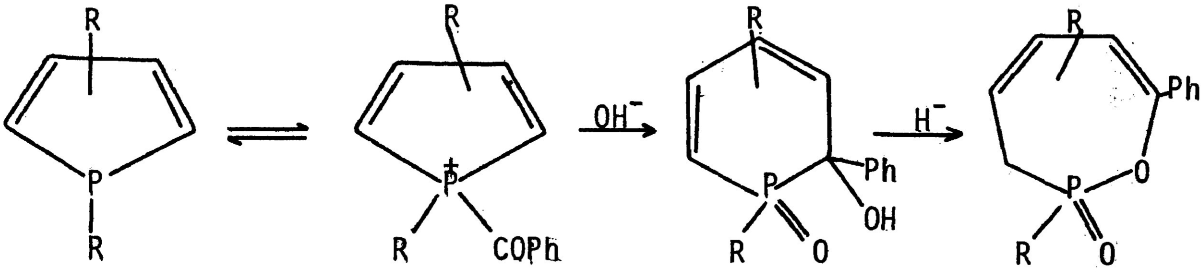


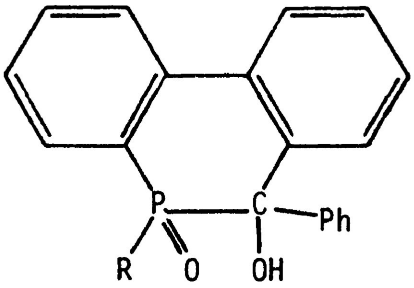
(VII)

In connection with quaternary salt formation by phospholes, Mathey (37-39) has developed a ring expansion of simple phospholes based upon the formation of 1-benzoylphospholium salts, in relatively low concentration, which undergo hydrolytic ring expansion under basic conditions to give six-membered rings as shown below. These too may be ring expanded by treatment with hydride ion.



(VIII) (IX) (X) (XI)

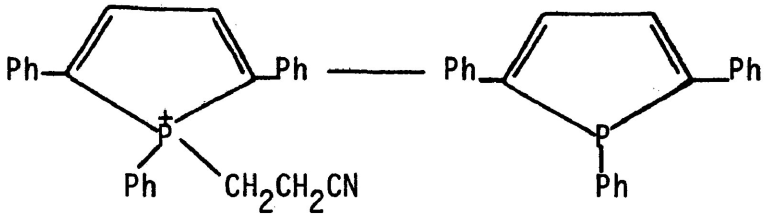
Allen (40) and also Hughes <u>et al.</u> (41) obtained similar results with fused-ring phospholes by treatment of certain phosphindoles and dibenzophospholes with benzoyl chloride to give ring expanded products such as the dibenzo[b,d]phosphorins XII.



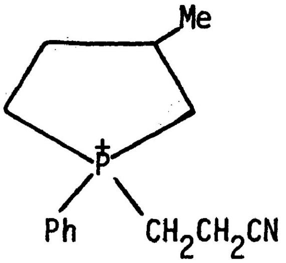
No dibenzophosphorin oxide was isolated with R=*t*-Bu and this indicates the steric inhibition of quaternisation by the bulky t-butyl group.

In other reactions of the phosphorus lone-pair, phospholes form oxides, sulfides or selenides readily (sometimes spontaneously) on treatment with hydrogen peroxide, sulfur or selenium in suitable solvents. This behavior is typical of tertiary phosphines and might be taken to indicate little or no lone-pair delocalisation in the phosphole system. However, Mortimer et al.(42) found that the P=O bond strength in 1,2,3,4,5-pentaphenylphosphole oxide is about 100 kcal/mole which is significantly lower than those of ordinary tertiary phosphine oxides (43) (120-150 kcal/mole) containing alkyl and aryl substituents. This implies possible lone-pair delocalisation in simple phospholes.

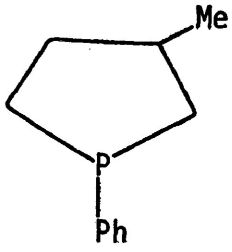
The studies discussed above concern reactions in which the lone-pair takes part. An interesting alternative approach by Mislow and his group (44) concerned the ease with which the lone-pair of phospholes may be regenerated from phospholium compounds. Thus, it was suggested (44) that if the lone-pair of phospholes is delocalised so that it is less readily available than that in ordinary tertiary phosphines in quaternary salt formation, heterolysis of the P-C bond in these quaternary salts to restore the lone-pair to the phosphorus atom should take place with a much faster rate in the phospholium system than in the phosphonium system. To test this hypothesis, these authors compared (44) the rate (at 41.6°C)of retrocyanoethylation of the phospholium salt XIII to give Ib with that of the cyclic salt XIV to give XV. The rate of retrocyanoethylation is considerably faster for XIII than for XIV and this supports the idea of a significant lone-pair delocalisation in phospholes.



(XIII) (Ib)



(XIV)



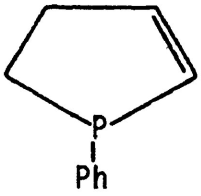
(XV)

Studies with cyanoethyl salts of a variety of cyclic and acyclic phosphines supported this view. One final point concerning phosphole lone-pair reactivity is the fact that 1,2,5-triphenylphosphole reacts as a very weak nucleophile with dimethyl acetylenedicarboxylate and this was taken also to indicate interaction of the phosphorus lone-pair with the π system of the ring (45).

Reactivity studies then suggest lone-pair delocalisation in phospholes although an abnormal orbital sequence may also explain the results and this point will be touched upon later. On the other hand, reactivity studies may be misleading to some extent since one is not dealing with isolated molecules but molecules at the moment of reaction where considerable electronic perturbation probably occurs. More reliable information might therefore be obtained from spectroscopic studies where perturbation is much less and from theoretical studies where it is nil although it will be seen later that theoretical studies of phospholes must be treated with caution.

Regarding NMR studies, Märkl (10) studied the PMR spectrum of 2,5-dimethyl-1-phenylphosphole and found that chemical shifts of the ring protons and methyl groups are similar to those in 2,5-dimethylthiophene which is undoubtedly aromatic. Later, this group (11) reported a marked similarity between the PMR spectrum of the ring unsubstituted phosphole, 1-phenylphosphole (Ig) in which the protons resonate in the aromatic region, and that of N-phenylpyrrole. Quin (8,9) observed a similar result with 1-methylphosphole. These studies suggested that there is some aromatic character in the phosphole system. Further studies of the PMR spectra of a wide range of phospholes were carried out by Mathey (12,14) who was able tentatively to relate the extent of the supposed aromatic character with the substitution pattern on the ring. It was found that with substituents on the 3- and the 3,4-positions of the phosphole system, both the ring proton signals and the methyl group proton signals shift to higher field. This would suggest that the substituents in the ring decrease the aromatic character and therefore substituent inductive effects and/or steric effects can not be ignored.

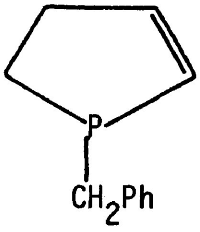
Further support for this idea comes from a ^{13}C NMR study of 1-phenylphosphole (46). Thus, the $^{2}J_{C(3)-P}$ value is greater than that in the corresponding 1-phenyl-2-phospholene (XVI) and this suggests a decrease in the average dihedral C-C-P



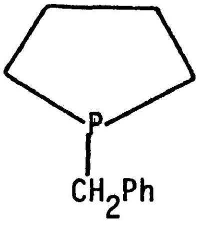
(XVI)

angle resulting from lowering of the barrier to pyramidal inversion (to be discussed later) at the phosphorus atom in phospholes. This in turn suggests some delocalisation of the lone-pair.

In further NMR studies, Quin (9,47) has found that phospholes possess a more deshielded ^{31}P atom than either 2-phospholenes (XVII) or phospholanes (XVIII). For example, the ^{31}P



(XVII)



(XVIII)

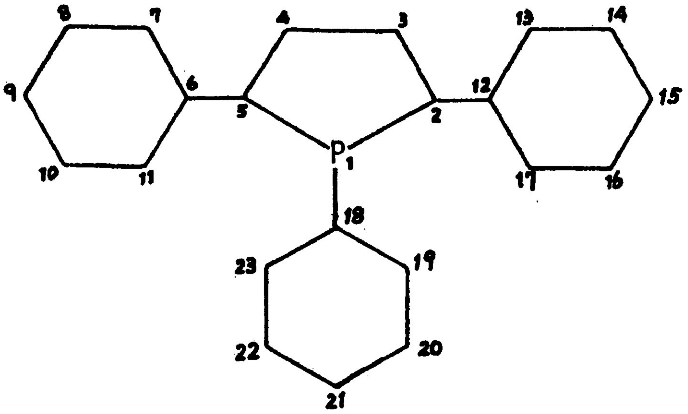
chemical shifts for 1-benzylphospholane (XVIII), 1-benzyl-2-phospholene (XVII) and 1-benzylphosphole (In) change markedly along the series and are +14.4, 0.0 and -7.9 ppm respectively. This is consistent with electron delocalisation from phosphorus <u>via</u> pπ - pπ (possibly with a dπ component) conjugation in the fully unsaturated system. However, conformational and ring size differences exist between the saturated and unsaturated rings and also the change in bond angles about the phosphorus atom must be considered. With the introduction of a methyl group into the

3-position a slightly deshielding effect at the phosphorus atom was observed (9), but introduction of a second methyl group into the 4-position causes the opposite effect and this was attributed to steric rather than electronic reasons. On the other hand, a carbomethoxy group introduced in the 3-position of the ring causes pronounced deshielding (9) of the phosphorus and this can be explained by resonance involving this group and the ring with further reduction of the electron density on the phosphorus atom. Thus, the bulk of the NMR evidence points to extensive delocalisation of the lone-pair on the phosphorus atom into the ring.

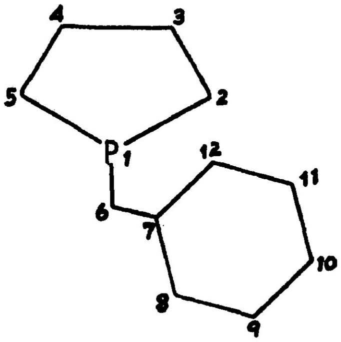
A much more precise and definitive NMR study was carried out by Mislow _et al._ who, studying the pyramidal inversion barriers in various phosphole derivatives (48-50), noted that the inversion barrier of acyclic phosphines is in the range of 29~36 kcal/mole and an increase in this energy barrier in non-aromatic cyclic phosphines would be expected because of angle strain. This is confirmed by an experimental value of 36 kcal/mole for 3-methyl-1-phenylphospholane (48). The same workers also found that the energy of the inversion barrier ($\Delta G^{\ddagger}_{25}$) about the phosphorus atom in 1-isopropyl-2-methyl-5-phenylphosphole is only about 16 kcal/mole at 42°C, compared to the expected value of over 36 kcal/mole for a non-aromatic model-_i.e._ the planar transition state is apparently of much lower energy than a non-aromatic model would require. This indicates significant interaction between the phosphorus lone-pair in phospholes and the π system in a pyramidal ground state and considerable aromatic character in the planar transition state which, according to Mislow, is ascribed to cyclic (3p-2p)π delocalisation. Fused rings in the phosphole system as in phosphindoles (III) and dibenzophospholes (IV) raise the inversion barrier 8-10 kcal/mole (49). The above result supports the earlier work of Brown (51) who, from molecular orbital (HMO) calculations, found that the energy difference between the tetrahedral state and planar state of phosphole is smaller than that for pyrrole. Theoretical calculations in general will be discussed shortly.

Besides nuclear magnetic resonance studies, ultraviolet spectroscopy has also been used in an attempt to assess the extent of delocalisation. Quin (8) observed that the ultraviolet spectrum of 1-methylphosphole possesses a single maximum absorption at 286nm which is different from the spectra of tertiary phosphines or divinylalkylphosphines both of which show absorptions in the range 200-246nm. The spectrum of the phosphole resembles that of N-methylpyrrole (λ_{max} 280nm) suggesting similar electronic excitation for the two ring systems but, in view of differences in molecular dimensions, inductive effects and other parameters between the two systems, this study can not be regarded as definitive.

In other studies, X-ray crystal structure determinations of simple phosphole derivatives have been carried out (52-54). In 1,2,5-triphenylphosphole (52) the molecule is pyramidal about the phosphorus atom and the ring P-C bond length is 1.822Å . There is therefore no significant bond shortening when compared with the P-C (phenyl) bond length of triphenylphosphine (1.828Å) (55). The $C_5P_1C_{18}$ bond angle is 106.2°.

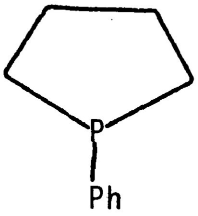


On the other hand, in 1-benzylphosphole, the ring P-C bond length is 1.783Å (53) which is slightly shorter than a normal P-C single bond length. There are no available data on phosphorus carbon double bond lengths with trivalent phosphorus atoms, but in $Ph_3P=CH_2$, which contains five valent phosphorus, the P=C length is 1.661A (56). Thus, the ring P-C bond length of 1-benzylphosphole is much longer than a P-C double bond of this type and even slightly longer than that with a bond order of 1.5. The bond angle of $C_2P_1C_6$ is 106.1° (53). Finally, the ring of 1-benzylphosphole is nonplanar and the phosphorus atom is pyramidal.

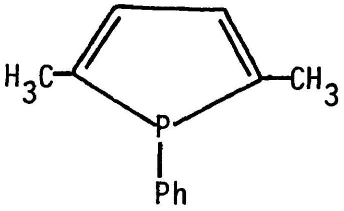


Several other conventional spectroscopic studies have been made including ESR studies of phosphole radical anions (57) and Faraday Effect investigations (58) but these have been adequately reviewed eleswhere (29) and no definite conclusion may be made from these studies.

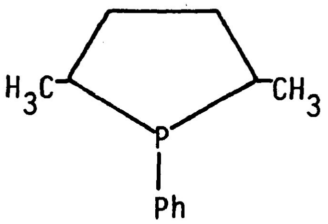
Using an entirely different spectroscopic approach, Schäfer <u>et al</u>.(59) carried out a photoelectron spectroscopic study of 1-phenylphosphole (Ig), 1-phenylphospholane (XIX), 2,5-dimethyl-1-phenylphosphole (XX) and



(XIX)



(XX)



(XXI)

2,5-dimethyl-1-phenylphospholane (XXI). In the case of (Ig), the ionization potentials of the n and highest π levels of the five-membered ring are virtually equal with values of 8.45 eV. The phenyl group shows an ionization potential of 9.25 eV (compared to the $e_{1g}(\pi)$MO in benzene which shows a band at 9.25 eV (60)) and is not split. This is different from <u>N</u>-phenylpyrrole where the corresponding band has a splitting of 0.6 eV (61). These results suggest that there is no conjugative interaction between the six and the five-membered ring in the phosphole Ig. With methyl substitution in the 2,5-positions of the phosphole ring, the highest π MO level drops to 8.0 eV which is the result of hyperconjugative interaction of the methyl groups with the π MO while the n level remains at 8.5 - i.e. in this system, the n-orbital is not the HOMO. In 2,5-dimethyl-1-phenylphosphole then, the highest occupied molecular orbital (HOMO) is one of the π levels of the five-membered ring and this is the same in energy as that of the corresponding 1,4-dimethyl-cis-butadiene MO (62). This was taken to suggest that the lone-pair of the phosphorus atom is not delocalised in the phosphole ring system (i.e. nonaromaticity). Indeed the ionization potential of the lone-pair remains virtually unchanged across the series Ig, XIX, XX, and XXI.

These results offer non-aromatic explanations for the reduced phosphorus lone-pair reactivity in phospholes in that since the lone-pair may not be the HOMO, it is not readily available for combination and orbital perturbation by an attacking species would be required in order for lone-pair reactions to occur. However, the further interpretation that phospholes are non-aromatic is open to doubt as later work by the same group suggests. This point will receive attention shortly.

Besides the above experimental work, recent theoretical studies have been directed towards the aromaticity problem in phospholes and the results of different studies are often mutually contradictory. For example Mislow's group (50,63) in connection with the pyramidal inversion approach, used the Pople CNDO/2 semiempirical molecular orbital theory to calculate the pyramidal inversion barrier of N,P and As compounds. Data for over 100 compounds were calculated and there is generally good agreement with experimental values (49) for both phospholes and phosphindoles.

The lower than normal inversion energy barrier in phospholes is said (44) to be due to (p-p)π conjugation of the lone-pair orbital with the adjacent pπ orbital in the ring system, and the influence of (2p-3d)π interaction is said to be unimportant in the determination of the barrier heights.

Schweig's group (64,65) using extended CNDO/2 methods to study the electronic structure of phospholes and arsoles, considered such factors as conformational effects, orbital energies, orbital sequences and orbital densities. In this case the difference in the energy of inversion barrier between phospholes and arsoles is calculated to be only 3.4 kcal/mole while Mislow's (50) calculations indicate a value of 14.8 kcal/mole. The apparent discrepancy is probably due to the different method of calculation and different assumptions regarding the various parameters used. Furthermore, in the ground state, the pyramidal molecules of phospholes and arsoles were said by Schweig _et al_. to have little n-π interaction (65). Clearly, the results of Mislow's group and Schweig's group are in serious disagreement.

In another approach, Mathey and Kaufmann (66) used the LCAO-MO-CNDO/2 method to study 1-methyl and 1-_tert_-butylphospholes in their pyramidal ground states and planar transition states. The 2pπ -3dπ conjugation was found by this method to play an important role in the ground state and even in the transition state (_i.e_. planar state). Generally, then, the results of Mislow _et al._ and Mathey _et al._ agree apart from the possible (2p-3d)π contribution. The substitution at the phosphorus atom also apparently influences the interaction of the lone-pair and diene system, in which the methyl group is a better electron donor than the tert-butyl group.

On the other hand, a very detailed treatment of the phosphole system by the linear combination of gaussian orbitals (LCGO) procedure was recently reported by Palmer et al. (67). On the basis of their studies, the phosphole system was deduced to be non-aromatic and non-planar and the contributions of the 3d orbital of the phosphorus atom to the system results in destabilising the planar arrangement rather than stabilising it (66). Since an aromatic system should have lower energy than a localised system, the low inversion barrier in the phospholes observed experimentally by Mislow's group can not be due (if Palmer's results are correct) to increased (2p-3p)π delocalisation in the transition state relative to the group state (50,63). In order to overcome this apparent contradiction, a vaguely defined valence force field effect was suggested as being responsible for the low inversion barrier. The calculated ionization potential (67) of 1-phenylphosphole is in good agreement with experimental observations (59) in which two bands (8.45 and 9.25 eV) of equal intensity were observed. It was also suggested (67) that PMR data are more similar to those of cyclopentadiene than those of pyrrole, furan and thiophen. Clearly the results of this study are in marked contrast to those of Mathey et al. and Mislow et al., although there is some agreement with Schweig's results.

Very recently Schweig's group (68) used the extended CNDO/S and MINDO/2 procedures to determine the electronic structures of a series of phospholes and, in contrast to the result of the earlier studies by this same group, concluded that despite the pyramidal ground state structure, phospholes are aromatic. The aromaticity is stabilised by the conjugative interaction of the cis-butadiene portion and the phosphorus atom in $n\pi^*$ conjugation and by P-C/π^* hyperconjugation. This interaction is due to the strong electron acceptance of the d-orditals of phosphorus atoms. This is consistent with the results observed in the photoelectron spectroscopic study (68) mentioned earlier and which was taken as "direct proof of the non-aromaticity of phosphole"! The results of theoretical studies must therefore be treated with caution. Other very recent theoretical studies essentially in agreement with Schweig's latest results (68) have been carried out but discussion of these is deferred until the next chapter.

The foregoing discussion summarises most of the chemical, spectroscopic and theoretical information regarding the electronic structure of phospholes available at this time. Obviously, many of the results are contradictory and no definite conclusion may be yet made. One thing is, however, clear and that is the lone-pair of phospholes is on the whole less readily available for chemical reaction than is the similar lone-pair of phosphines. One obvious probe of this reduced reactivity, whether it be due to aromatic character or an unusual orbital sequence or both, is metal complex formation. Certain studies in this area have already been carried out and, since they concern directly the main theme of the experimental work described later in this thesis, they are treated in a separate section below.

(ii) Coordination Chemistry of Phospholes and Related Systems

Although the reactions of cyclic phosphines with metals were reviewed (69) in 1975 and only a few additional papers have been published since then, it was felt that the coordination chemistry of phospholes and related compounds should be presented here in some detail since this topic forms the basis of the thesis. The discussion is not limited to simple phospholes here because, as will be seen in later chapters, the phospholes studied in this thesis show behavior which is frequently different from that of other phospholes in the literature and more like the behavior of other cyclic phosphines such as the dibenzophospholes.

The early studies on the coordination of simple phospholes (*i.e.* those without fused rings) involved reactions with metal carbonyls from which complexes with both M-P σ bonds and M-diene π -bonding was reported (6,15). Thus, this early work established the versatility of phosphole ligands, and the following section is a detailed discussion of the coordination properties of phosphole derivatives and fused-ring phospholes in general. Unlike the previous review (69), the following material is organized according to the metal involved rather than the nature of the ligand. It should, perhaps, be mentioned that much of the published work on phosphole coordination involves 1,2,5-triphenylphosphole because, until recently, this was the most readily available phosphole.

A. Group VB - Vanadium, Niobium and Tantalum

Both niobium and tantalum halides immediately react with 1,2,5-triphenylphosphole (TPP) to form the crystalline 1:1 adducts $(TPP)MX_5$ (M=Ta, X=Cl or Br; M=Nb, X=Cl) (70). Only oils are obtained with Nb(V) bromide and neither Nb(V) nor Ta(V) iodide react with TPP. This is believed to be due to steric effects arising from the large iodine atoms. The bond between the metal and the phosphorus atom is very weak and the ligand is readily replaced by coordinating solvents such as acetonitrile (70). The oxide TPPO (II, X=O), sulfide TPPS (II, X=S) and selenide TPPSe (II, X=Se) of TPP also give stable 1:1 adducts with Nb(V) and Ta(V) halides (70) under anhydrous conditions. When $(TPPO)TaCl_5$ is exposed to moisture, $(TPPO)TaOCl_3$ immediately forms; the oxygen atom coming from the moisture.

Since TPP is a weak base (8,33) as already mentioned, it is not easily protonated, even under anhydrous conditions, to form stable salts under normal conditions but this has been achieved by a number of routes which include the exposure of $(TPP)TaCl_5$ in benzene to ethanol vapour, the direct addition of a trace of ethanol to $(TPP)TaCl_5$ or by the passage of dry HCl gas into $(TPP)TaCl_5$ in benzene. All these reactions lead to the formation of an orange precipitate formulated as $[TPPH]^+[TaCl_6]^-$ (71). In addition to the simple phosphole, fused-ring phospholes such as 5-phenyl-5<u>H</u>-dibenzophosphole (DBP) (IVe) also react with Ta(V) halides to give well characterised stable complexes such as $(DBP)TaCl_5$ and the protonated species $[DBPH]^+[TaCl_6]^-$ (71). It is interesting to note that with $[TPPH]^+[TaCl_6]^-$, the protonation occurs at the phosphorus atom of the phosphole (71) whereas with the analogous pyrrole system, it occurs on one of the ring carbon atoms (32).

No cyclic phosphine complexes of vanadium are known.

B. Group VIB - Chromium, Molybdenum and Tungsten

The hexacarbonyls of chromium, molybdenum and tungsten react with 1,2,5-triphenylphosphole to give yellow crystalline monosubstituted complexes $(TPP)M(CO)_5$ (M=Cr, Mo or W) (72). Even under higher reaction temperatures, no further substitution occurs. However, with bismorpholine tetracarbonyls of molybdenum and tungsten, the triphenylphosphole displaces the two morpholine groups to form complexes of empirical formulae $(TPP)_3M(CO)_4$ (M=Mo or W) (72) which have been shown by infrared spectral studies to be more correctly formulated as $(TPP)_2M(CO)_4$ with the third phosphole molecule not directly coordinated to the metal. On the other hand, 1,2,5-triphenylphosphole oxide (TPPO) does not react with the hexacarbonyls of chromium and tungsten but does react with molybdenum hexacarbonyl to form $(TPPO)Mo(CO)_2$ which is not well characterised (72).

C. Group VIIB - Manganese, Technetium and Rhenium

Very recently, it has been shown that when mixtures of

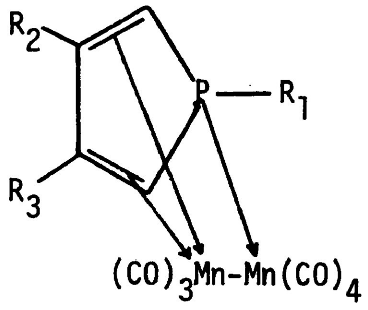
$Mn_2(CO)_{10}$ and certain simple phospholes are subjected to irradiation with UV light in hot cyclohexane solutions, a variety of complexes (listed in Table 2) are obtained (15,73). These include orange oils, σ complexes of formulae $L_xMn_2(CO)_{10-x}$ (x=1,2) and stable orange-red crystalline complexes $LMn_2(CO)_7$ in which the phosphole acts as a tridentate ligand via the phosphorus atom and diene system (15). Further irradiation of the complex $LMn_2(CO)_7$ (L=3,4-dimethyl-1-phenylphosphole) in the presence of $Mn_2(CO)_{10}$ cleaves the phosphorus-phenyl bond to give the σ , π complex $L'Mn_3(CO)_{12}$ (L'=3,4-dimethylphospholyl) in which a $P\text{-}Mn(CO)_5$ bond replaces the phosphorus-phenyl bond (15). Furthermore, when pyrolyzed at 150°C under reduced pressure, $L'Mn_3(CO)_{12}$ decomposes to give $L'Mn(CO)_3$ which is a typical aromatic π complex and which was characterised by PMR spectroscopic studies (15). The phospholyl manganese carbonyl complexes may also be synthesised by direct irradiation with UV light of certain phospholes with $Mn_2(CO)_{10}$ and also by heating the same mixture to give $L'Mn(CO)_3$ (Table 2) (73). The variation in donor properties of the various substituted phosphole ligands to the manganese has been estimated by the carbonyl stretching frequency which decreases in the series: Im $\approx$ Il $>$ Ii $\approx$ Io $>$ Ih $>$ Ig (see Table (1) for structures).

Earlier studies (70) showed that 1,2,5-triphenylphosphole does not react with $MnCl_2$ under normal conditions.

Turning now to studies with the borderline class (a)-class (b) acceptor rhenium, it has been found that rhenium(III) chloride reacts in dry methylene chloride under reflux with

Table (2)

Complexes of Formula $LMn_2(CO)_7$ (15)

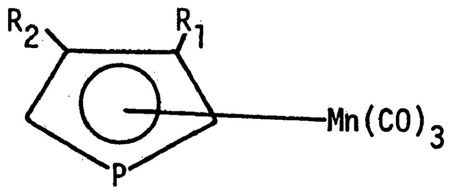


(XXII)

R_1	R_2	R_3
Ph	H	H
Ph	Me	H
Ph	Me	Me
n-Bu	Me	Me
t-Bu	Me	Me
CH_2Ph	Me	Me

Table (2) cont'd

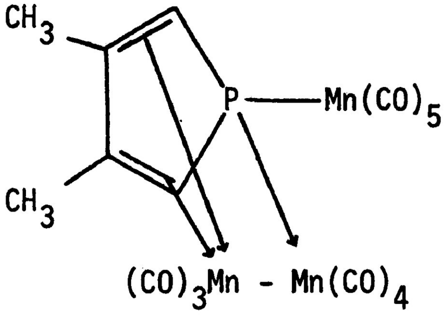
Complexes of Formula L'Mn(CO)$_3$ (15,73)



(XXIII)

R_1	R_2
H	H
Me	H
Me	Me

Complex of Formula L'Mn$_3$(CO)$_{12}$ (15)



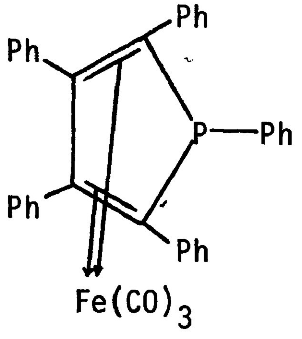
(XXIV)

1,2,5-triphenylphosphole, its oxide and its selenide and also with 5-phenyl-5H-dibenzophosphole to give compounds of the type $Re_3Cl_9L_2 \cdot CH_2Cl_2$ (74). The sulfide TPPS, however, produces a brown solid with Re_3Cl_9 which decomposes extremely readily even under dry nitrogen. If the reactions are carried out at room temperature, only one ligand is coordinated to the cluster forming the solvated $Re_3Cl_9L \cdot (CH_2Cl_2)_n$ (n=1 or 2) (74). The stretching frequencies of the Re-O and Re-Se bonds in the TPPO and TPPSe complexes show that, when compared with other related metal complexes (70), the phosphole derivatives are poor donors, although steric factors may also be important with these cluster compounds (74).

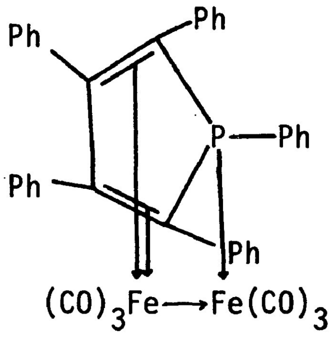
No cyclic phosphine complexes of technetium are known.

D. Group VIII - Iron, Ruthenium and Osmium

As was mentioned earlier, iron was the first metal used in the study of metal-phosphole complexes (6). Thus, iron pentacarbonyl in isooctane under reflux reacts with 1,2,3,4,5-pentaphenylphosphole (pPP) to give the σ bonded Fe-P complex (pPP)-$Fe(CO)_4$ (6). Under similar conditions (pPP) reacts with $Fe_3(CO)_4$ to form two products characterised as (pPP)$Fe(CO)_3$ (XXV) and (pPP)$Fe_2(CO)_6$ (XXVI) (6). In complex (XXV) the iron is π bonded (as shown in the structure below) to the diene system in a manner resembling that of the nonaromatic conjugated dienes which generally react readily with iron carbonyls. Both σ and π bonding are involved in complex (XXVI) with the ligand utilizing both the phosphorus lone-pair electrons and the diene system. The easy



(XXV)



(XXVI)

complex formation and the nature of the bonding suggest that the lone pair of electrons of the phosphorus atom is not delocalised into the ring but one must bear in mind that considerable electronic perturbation will occur during the reaction. Furthermore, the phosphole used here is heavily substituted and its behavior may not be typical. The oxide of this heavily substituted ligand only forms π bonds with iron through the diene system to give (pPPO)Fe$(CO)_3$ (6).

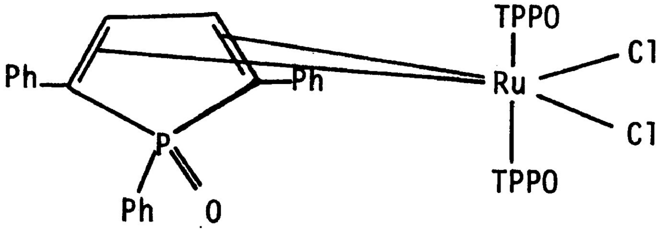
Similarly, 1,2,5-triphenylphosphole reacts with iron pentacarbonyl to give the monomeric crystalline π-(TPP)Fe$(CO)_3$ (72) and, in the case of TPPO, the absence of any shift in the P=O stretching frequency also points to the formulation π-(TPPO)Fe$(CO)_3$ (72). On the other hand, triphenylphosphole reacts with iron nonacarbonyl under mild conditions to give the poorly characterised σ-(TPP)Fe$(CO)_4$ (72) in which the CO stretching frequencies are similar to those of (pPP)Fe$(CO)_4$ (6).

It is interesting that neither triphenylphosphole nor 5-phenyl-5H-dibenzophosphole (DBP) react (70) with iron(II) halides but iron(III) reacts (70) with the oxides and sulfides TPPO, TPPS and DBPO in methylene chloride solutions to form the brown crystalline complexes L_2FeCl_3 (L=TPPO, TPPS or DBPO).

Regarding ruthenium systems, ruthenium(III) halides and phospholes form (75) a series of complexes of the type $RuCl_3L_n$ (n=1,2,3) depending upon the ratio of ligand to the metal halide. 1,2,5-Triphenylphosphole (TPP) or 5-phenyl-5H-dibenzophosphole (DBP) with ruthenium trichloride hydrate in ethanol in the ratio 3:1 give the air stable complexes L_2RuCl_3 (L=TPP or DBP) (75). When the ratio is increased to 6:1, DBP gives $(DBP)_3RuCl_3$ but the corresponding TPP complex could not be isolated. The complex $(DBP)_3RuCl_3$ is a monomer while the L_2RuCl_3 (L=TPP or DBP) complexes are probably dimeric. Even with large excesses of the ligands, ruthenium trichloride hydrate in ethanol under reflux with TPPO, TPPS or TPPSe only gives the 1:1 complexes $LRuCl_3$ (L=TPPO, TPPS or TPPSe) (75).

Unlike PPh_3, neither TPP nor DBP can reduce Ru(III) to form Ru(II) complexes and it is therefore necessary to prepare Ru(II) complexes of phospholes either directly from Ru(II) halides or by adding a reducing agent such as H_2, CO or $NaBH_4$ to the Ru(III) reactions. Thus, with an excess of DBP, the blue $[Ru_5Cl_{12}]^{2-}$ (generated by H_2 reduction) methanolic solution under reflux gives $(DBP)_3RuCl_2$, while if ethanol is used as solvent, $(DBP)_4RuCl_2$ (75) is formed. Under similar conditions, 1,2,5-triphenylphosphole gives $(TPP)_3RuCl_2$ (75). On prolonged reflux, a mixture of Ru(II) and TPPO in ethanol gives an air stable complex

$(TPPO)_3RuCl_2 \cdot EtOH$. From the stretching frequency of the P=O grouping it has been suggested (75) that one of the three TPPO ligands forms π bonds with the metal ion to give the six coordinate compound (XXVII). The oxide of DBP does not react



(XXVII)

with the Ru(II) solution and this is probably because of the absence of a stabilising π diene system in this ligand (75). Ruthenium carbonyl phosphole complexes (such as $(TPP)_2Ru(CO)_2Cl_2$ and $(DBP)_3Ru(CO)Cl_2$) can also be synthesed by using the red ruthenium carbonyl chloride (75). Similar reactions involving TPPO and TPPS produce uncharacterised brown oils (75). Ruthenium(II) complexes can also be obtained from Ru(III) by using $NaBH_4$ as a reducing agent - e.g. in the synthesis of the air sensitive hydride complex $(DBP)_4RuH_2$ (75).

No complexes of osmium with phospholes are known.

E. Group VIII - Cobalt, Rhodium and Iridium

Surprisingly, cobalt(II) chloride does not react with 1,2,5-triphenylphosphole (70) and only reacts weakly with triphenylphosphole oxide to give a green solid from which the ligands are lost on recrystallisation. The reflectance spectrum of this crude compound suggests the presence of a tetrahedral cobalt(II) complex with the possible formula of $(TPPO)CoCl_2$ (70). Normally, tertiary phosphines react readily with Co(II) to produce very stable four-coordinated complexes L_2CoX_2 (L=tertiary phosphine, X=halogen, NCO, NCS or CN) (2). Five-coordinated Co(II) tertiary phosphine complexes L_3CoX_2 (where X=Cl, Br or NCO) (76) have also been prepared but these are thermodynamically unstable. The bulky and undoubtedly non-aromatic substituted dibenzophospholes (RDBP) do, however, react with $CoBr_2$ to give stable green solids of formula L_3CoBr_2 (L=MDBP (IVa) or EDBP (IVb) (76). These low-spin five-coordinated Co(II) complexes have a magnetic moment of 1.95-2.0 B.M. and are nonelectrolytes, although a molecular weight determination in methylene chloride solution at 30°C indicates some dissociation (76). DBP (IVe) does not reduce Co(II) to Co(I) but the reduction can be effected by the use of a reducing agent such as $NaBH_3CN$ or $NaBH_4$ to give the well characterised Co(I) complexes $Co(BH_3CN)(DBP)_4$ and $CoCl(DBP)_3$ (77). Under more vigorous conditions in ethanol, $NaBH_4$ reduces Co(II) in the presence of DBP to the Co(0) complexes $Co(DBP)_4$ and $Co(DBP)_2$ (77).

Turning to rhodium, rhodium(III) chloride trihydrate reacts immediately with triphenylphosphole (TPP) to give the orange five-coordinated, dimeric, chloride bridged complex $[(TPP)RhCl_3]_2$ (78). There is no evidence for the formation of a reduced product (as occurs with PPh_3 (79)) even with a large excess of ligand. When the above reaction mixture is heated under reflux for periods of up to 24 hrs, a stable yellow-brown hydrido complex $RhHCl_2(TPP)_2$ is obtained (80). On the other hand, $RhCl_3 \cdot 3H_2O$ and 5-phenyl-5_H_-dibenzophosphole (DBP) or 1-phenylphosphole (PP) in ethanol under reflux for short periods of time produce the stable yellow solids L_3RhCl_3 (L=DBP or PP) (80). Again, no reduction of Rh(III) occurs under these conditions.

Rhodium(I) complexes can be synthesised either starting with rhodium(III) chloride or by ligand replacement on rhodium(I) complexes. When ethanol is replaced by chloroform in which TPP has a higher solubility, reduction of Rh(III) to Rh(I) occurs. Thus, TPP in chloroform reacts with $RhCl_3 \cdot 3H_2O$ in methanol under reflux to produce an orange solid RhCl(TPPO)(TPP) (80) in which, from i.r. data, the TPPO is π bonded to the rhodium. The strong affinity of the π system in TPPO for rhodium even in the presence of a large excess of TPP emphasises the relatively poor donor properties of the phosphorus atom in the phosphole system. TPPS, in ethanol, reacts with $RhCl_3 \cdot 3H_2O$ under reflux to give a brown solid which after recrystallisation from methylene chloride yields $RhCl(TPPS) \cdot CH_2Cl_2$ (80). The fact that rhodium bonds to sulfur is shown by the shift in the i.r. stretching frequency of the P-S bond. Rhodium carbonyl chloride $[RhCl(CO)_2]_2$ in alcoholic solution reacts with an excess of TPP, DBP or TPPS to give the yellow, well characterised solids $RhCl(CO)(TPP)_2$ and RhCl(CO)(DBP) and the black RhCl(CO)(TPPS). The chlorobis(ethylene)rhodium(I) dimer, $[RhCl(C_2H_4)_2]_2$, in methanol solution also reacts with DBP or TPP under reflux to produce the dimeric air-sensitive complexes $[RhCl(DBP)_2]_2$ and $[RhCl(TPP)_2]_2$ (80).

Finally in rhodium reactions, addition of an excess of DBP to $[RhCl(DBP)_2]_2$ in methanol under reflux yields an orange, air-stable solid $RhCl(DBP)_3$. The analogous complex $RhCl(TPP)_3$ is produced when a six-fold excess of TPP is treated under reflux with $[RhCl(C_2H_4)_2]_2$ in 1:1 chloroform/ethanol solution (80).

No complexes of phosphole derivatives with iridium are known.

F. Group VIII - Nickel, Palladium and Platinum

1,2,5-Triphenylphosphole (but not the oxide) reacts with nickel carbonyl to give the monosubstituted product, $(TPP)Ni(CO)_3$, which decomposes to a mixture of $(TPP)Ni(CO)_3$ and $(TPP)Ni(CO)_2$ during recrystallisation from benzene-methanol (72). As in the case of Co(II) neither TPP nor its oxide reacts with Ni(II). Also, phospholes with no ring substituents such as 1-methylphosphole (MP) (Ic) and 1-benzylphosphole (ZP) (In) do not react with nickel(II) chloride under normal conditions (8,53). However, the substituted phosphole 1-benzyl-3,4-dimethylphosphole does react to form the deep purple stable complex $(dZP)_2NiCl_2$ (81). The phosphole ligands are bound to the metal through σ bonds and rather surprisingly the complex shows an absence of ^{31}P-^{1}H coupling in the NMR spectrum. This difference in behavior has been attributed to steric interaction of the methyl groups which reduces the delocalisation in the phosphole ring. As noted earlier, 3,4-disubstitution causes marked modification in other phosphole chemical and physicochemical properties. However, again it may be variation in the orbital sequences which are responsible for the changes.

In contrast to the simple phospholes, dibenzophospholes are much better donors and form a large number of complexes with Ni(II), and these, together with those of other metals are listed in Table (3) (21,76). Complexes of DBP and substituted DBP (RDBP) occur in two stereochemistries: square planar, four-coordinate complexes of the type $(DBP)_2MX_2$, in both cis and trans configurations, and five-coordinate complexes of the type $(DBP)_3MX_2$.

X-ray crystal structure determinations on two complexes of the second type (Table (3), 1(a) R=Me, X=CN; and R=Et, X=CN) show that the first has a tetragonal pyramidal structure while the second adopts a trigonal bipyramidal configuration (82-84). These structural changes are also reflected in the different visible and near-infrared absorption spectra of the two compounds when mounted as Nujol mulls. When the phosphorus substituent of the dibenzophosphole is phenyl or a bulky alkyl group, only the four-coordinate complexes are formed.

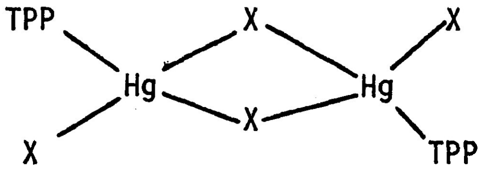
The nickel(I) complex, $(DBP)_3NiCl$, has been synthesised by reducing Ni(II) with $NaBH_4$ in ethanol solutions (77) at room temperature in the presence of DBP. Under reflux, the Ni(0) complexes $Ni(DBP)_2$ and $Ni(DBP)_4$ are formed depending upon the ratio between the metal and the ligand.

In contrast to Ni(II), the halides of palladium(II) and platinium(II) do react with TPP to give the stable complexes $(TPP)_2MX_2$ (M=Pd or Pt, X=Cl or Br). The infrared stretching frequencies in the M-X range show that the Pd(II) and Pt(II) chloride complexes are probably in _trans_-square planar configuration while the Pt(II) bromide assumes the _cis_-square planar configuration (77). The DBP and DBP related (RDBP) complexes are listed in Table (3) (21,76).

G. Group 1B and 11B - Copper, Silver, Gold, Zinc, Cadmium and Mercury

Certain other phosphole and DBP coordination studies have been made. For example, both TPP and DBP in methanol under reflux can reduce copper(II) chloride to form the copper(I) chloride complexes LCuCl (L=TPP or DBP) (70). Reactions between freshly prepared copper(I) chloride and the phospholes (TPP or DBP) in methanol under reflux yield the same compounds which have been identified by X-ray powder diffraction patterns (70).

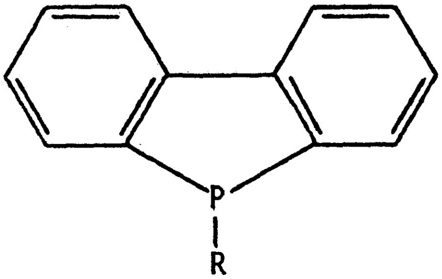
TPP also reacts with mercury(II) halides to give dimeric, yellow crystalline complexes $[(TPP)HgX_2]_2$ (X-Cl or Br) with halide bridges (XXVIII) (78). This is typical of phosphines. All of these



(XXVIII)

Table (3)

Complexes of the Dibenzophosphole System (21,76)



5-R-5H-Dibenzophospholes (RDBP)

1. $(RDBP)_3MX_2$	R=Me or Et
(a) M=Ni(II)	X=Cl, Br, I, SCN, CN
(b) M=Pd(II)	X=Br
(c) M=Pt(II)	X=Br, SCN
2. $(RDBP)_2MX_2$	R=Me or Et
(a) M=Ni(II)	X=Cl
(b) M=Pd(II)	X=CN, Br
(c) M=Pt(II)	X=CN, Cl

Table (3) cont'd

3. $(RDBP)_2MX_2$	R=Ph, *i*-Pr or *t*-Bu
(a) M=Ni(II)	X=Cl, Br, I, SCN
(b) M=Pd(II)	X=Br
(c) M=Pt(II)	X=Cl, Br

complexes are insoluble in nonpolar solvents and only slightly soluble in polar solvents.

No complexes of silver, gold, zinc and cadmium are known.

(iii) Aim of Work

It is clear from these introductory sections, that the question of the electronic structure of phospholes has not been unambiguously answered, although chemical, physico-chemical, spectroscopic, theoretical and coordination studies have significantly increased the knowledge on the subject. A great deal of the work done on phospholes in connection with coordination chemistry has been with either heavily substituted or fused ring systems and studies on simple phospholes are rare. Indeed, these have been restricted to a limited number of metal ions, namely Ni and Mn and much of the Mn work has been with Mn(0) systems. Only one complex (bis(1-benzyl-3,4-dimethylphosphole)nickel(II) chloride) (81) has been reported with the first row transition metals in oxidation states higher than one. Therefore, it was felt important to extend this work to cover the reactions between other transition metal ions and simple substituted phospholes in order to clarify their donor properties.

With these objectives in mind, this thesis will deal with a study of the coordination chemistry of simple phospholes. The systems studied include 1-phenylphosphole and its 3-methyl and

3,4-dimethyl derivatives and also 1-n-butyl-3,4-dimethylphosphole. A preliminary study of the previously unstudied related fused ring system 3-butyl-1,2-diphenylphosphindole (IIIb) with group VIII transition metal ions and some of their neighbours in the periodic table is also reported. The intention was to study the conditions under which complex formation occurs and in such cases, to study the electronic, magnetic and other physical properties of the complexes. From information gathered, it was hoped that some clarification can be made regarding the electronic structure of simple phospholes.

Ideally, phosphole itself or the simplest phosphole known (1-methylphosphole) should have been used but the former is as yet unknown and the latter is not easy to prepare in quantity. The decision was therefore made to use for the study those simple phospholes which are most easily synthesised in the quantities required.

CHAPTER II

RESULTS AND DISCUSSION

(i) Introduction

As already mentioned in Chapter I, tertiary phosphine complexes of transition metal ions have been extensively studied (1,2) and complex formation occurs readily with metal ions which fall in the category of class (b) acceptors. Furthermore, it was seen in Chapter I that the fused-ring phosphole, DBP (structure IVe), behaves similarly to triphenylphosphine and reacts with group VIII metal ions smoothly to give a variety of complexes the only peculiarity about which is that in some of them, the metal adopts less common coordination numbers.

On the other hand, the heavily substituted simple (*i.e*. non fused-ring) phosphole 1,2,5-triphenylphosphole is reluctant (70) to form complexes with such metals as Co(II) and Ni(II) and this appears also to be true of much simpler phospholes such as 1-benzylphosphole (8,53). However, substitution on the ring markedly changes the reactivity of the phosphole system such that with 1-benzyl-3,4-dimethylphosphole, complex formation with Ni(II) readily occurs (81).

A systematic study of simple phosphole coordination to transition metal halides has therefore been undertaken with three main objectives in mind. These are (a) to determine whether the observed lack of reactivity towards the normally good phosphine acceptors Co(II) and Ni(II) is general for most phospholes; (b) to determine how the substitution pattern affects the ease of complex formation (this has been done very recently to some extent by Mathey (73) using Mo carbonyls); (c) to attempt to make deductions regarding the electronic structure of phospholes. Reactions of the simple phospholes, PP(Ig), mPP(Ih), dPP(Ii) and dBP(Il) with the chlorides of Mn(II), Re(III), Fe(II), Ru(III), Co(II), Rh(III), Ir(III), Ni(II), Pd(II), Pt(II), Cu(II), Zn(II), Cd(II) and Hg(II) have therefore been studied and the results of these studies will be discussed in the following sections. The discussion will be arranged according to the metal involved and in the order in which these metals are discussed in Chapter I although not all of the metals mentioned in Chapter I were used in this study.

(ii) Phosphole Complexes of Metal Chlorides

A. Rhenium

Both the 3-substituted phosphole (mPP) and the 3,4-disubstituted phosphole (dPP) react immediately with Re_3Cl_9 in ethanol at room temperature to form purple or brown diamagnetic complexes $L_3Re_3Cl_9$ (L=mPP or dPP) as in the case of triphenylphosphine (85,86). This is different behavior from the more bulky

1,2,5-triphenylphosphole (TPP) and 5-phenyl-5H-dibenzophosphole systems which have been reported (74) to form the solvated complexes $L_2Re_3Cl_9 \cdot CH_2Cl_2$ (L=TPP or DBP).

The infrared spectra of $L_3Re_3Cl_9$ (L=mPP or dPP) are similar to the spectra of the ligands (with small shifts in some of the absorption bands and changes in their intensity) except for the region 400-200 cm^{-1} which is dominated by absorption bands at 280, 325 and 370 cm^{-1} for $(dPP)_3Re_3Cl_9$ and at 305 and 325 cm^{-1} for $(mPP)_3Re_3Cl_9$, tentatively assigned to the Re-Cl stretching frequency.

Table (4) records data on the electronic absorption spectra of these rhenium (III) chloride complexes. Comparison of these data with those of the analogous tris(triphenylphosphine)nonachlorotrirhenium shows a close similarity of all absorption bands. This strongly suggests that the phosphole complexes have a structure similar to that of the triphenylphosphine cluster complex and the spectra for all of these complexes are shown in Figure (2). The complexes $L_2Re_3Cl_9 \cdot CH_2Cl_2$ (L=TPP or DBP) have slightly different electronic absorption spectra (74) as would be expected.

Complex formation is extremely fast and no heating is necessary in contrast to the syntheses of $L_2Re_3Cl_9$ (L=TPP or DBP) which are prepared in methylene chloride under reflux. The much smaller size of the ligand eliminates any steric effect and this probably accounts for the fact that compounds of the stoichiometry $L_2Re_3Cl_9$ can not be isolated in these reactions. No apparent decomposition of the two phosphole complexes (derived from mPP and

Table (4)

Electronic Spectral and Infrared Data of Re(III) Complexes

Complex	Colour	Spectra, cm^{-1}		Ref.
		Electronic Absorption(a) (ε)	Infrared(c), ν_{Re-Cl}	
$(mPP)_3Re_3Cl_9$	purple	12300 (547)	305(sh)	
		18800 (1393)	325(s)	
		22300 (1386)		
$(dPP)_3Re_3Cl_9$	brown	12600 (490)	208(w)	
		18700 (803)	325(s)	
		22900 (sh) (754)	307(?)	
$(PPh_3)_3Re_3Cl_9$	red	13000 (490)		
		19200 (1960)		86
		22800 (sh) (1290)		

Table (4) cont'd

$(TPP)_2Re_3Cl_9 \cdot CH_2Cl_2$	brown	8000$^{(b)}$	
		12100	74
		18500	
$(DBP)_2Re_3Cl_9 \cdot CH_2Cl_2$	purple	7700$^{(b)}$	
		12600	74
		18900	

(a) Acetone was used as a solvent for the electronic absorption spectra; sh=shoulder

(b) Reflectane

(c) Nujol Mull; s=strong, w=weak

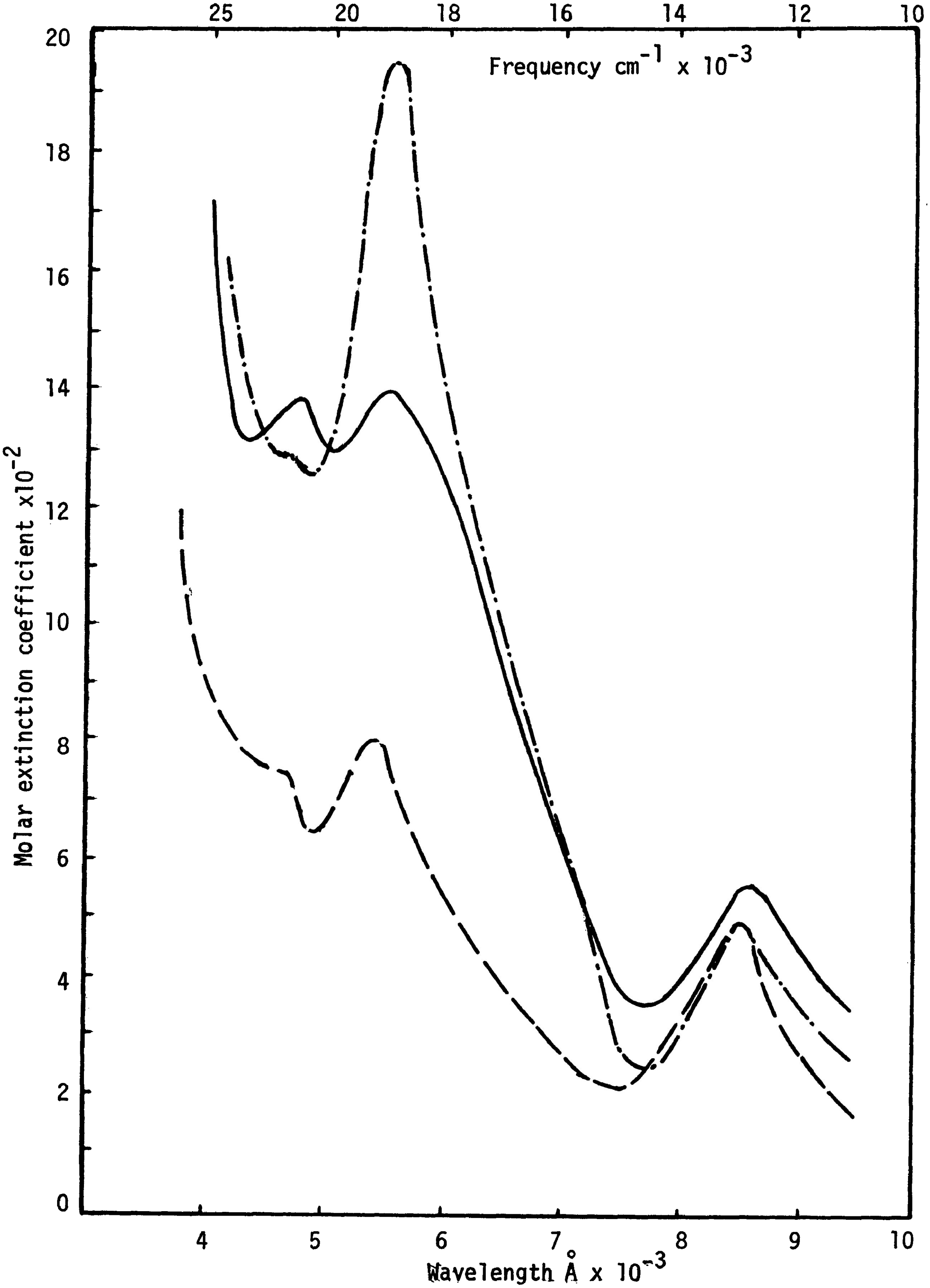


Fig. (2) Electronic Solution spectra of rhenium complexes in acetone, —— $(mPP)_3Re_3Cl_9$ (1.41×10^{-3}M); - - - $(dPP)_3Re_3Cl_9$ (1.82×10^{-3}M); —·— $(PPh_3)_3Re_3Cl_9$ ($\sim1\times10^{-3}$M) dPP) in solution has been observed since in acetone solutions the absorption spectra are similar to that of the PPh_3 complex. The TPP and DBP complexes, however, decompose immediately in acetone or ethanol (74). Thus, the simple phospholes are better donor ligands in this respect compared with DBP or TPP and, as DBP is normally a good donor, this could well be a steric effect since TPP, DBP and Re_3Cl_9 are all crowded systems.

Since these initial complexes with Re(III) were found to be conventional in all respects and since only limited amounts of each phosphole were available, no further reactions with Re(III) were undertaken so that more informative studies with other metals could be undertaken.

B. Ruthenium

An air-stable ruthenium(III) chloride complex of the 3,4-disubstituted phosphole (dPP) is readily prepared by stirring $RuCl_3 \cdot 3H_2O$ with a 4-fold excess of ligand in ethanol at room temperature. The crude product can be recrystallised from methylene chloride-hexane to give the reddish-brown crystalline complex, $(dPP)_3RuCl_3$. However, neither the ring unsubstituted phosphole (PP) nor the 3-substituted phosphole (mPP), under similar conditions give the analogous complexes. Greenish brown solids, which are insoluble in most common organic solvents, are obtained. The compounds analysed approximately as $LRuCl_3$ (L=PP or mPP) after successive washings with ethanol, methylene chloride and ether.

For all three phospholes, by prolonging the reaction time or by carrying out the reactions under reflux in ethanol with 4-fold excesses of ligand, the initially formed Ru(III) complexes are reduced to the +2 oxidation state. Thus, with PP and dPP, complete reduction of Ru(III) to Ru(II) is observed and the complexes L_3RuCl_2 (L=PP or dPP) are obtained in good yield. Surprisingly, only partial reduction of the Ru(III) occurs when mPP (5-fold excess) is used, and what appears to be a mixed-valent complex, $(mPP)_4Ru_2Cl_5$, results even after heating under reflux for 24 hours.

The Ru(III) complex $(dPP)_3RuCl_3$ is paramagnetic, with a magnetic moment of 1.78 B.M. consistent with low-spin d^5 metal ion (87). The complex $(mPP)_4Ru_2Cl_5$ was found to have a magnetic moment of 1.27 B.M. per Ru atom (theoretical value calculated on the basis of the root mean square of one typical Ru(III) atom of μ_{eff}=1.90 B.M. and one Ru(II) atom of μ_{eff}=0 gives μ_{eff}= 1.30 B.M. for a Ru(III)-Ru(II) system). The Ru(II) complexes are diamagnetic as expected.

The complex $(dPP)_3RuCl_3$ shows in the infrared spectrum, stretching absorption bands at 295 and 336 cm^{-1} while the two five-coordinated Ru(II) complexes have bands at 250 and 310 cm^{-1} for $(PP)_3RuCl_2$ and 270 and 325 cm^{-1} for $(dPP)_3RuCl_2$. These bands are presumably due to the Ru-Cl bonds. The mixed-valent $(mPP)_4Ru_2Cl_5$ also shows stretching frequencies at 235 and 320 cm^{-1}, assignable to Ru-Cl bands.

The electronic spectrum of the Ru(III) complex $(dPP)_3RuCl_3$ in methylene chloride solution (3 x 10^{-3} M) does not show any detectable d-d bands and this is probably due to the weak absorption of the d^5 system. Regarding the Ru(II) complexes, the electronic absorption spectra of $(dPP)_3RuCl_2$ are different in solution and in the solid state. Thus, in methylene chloride solution the spectrum (19600 cm^{-1} and 25000 cm^{-1}) of $(dPP)_3RuCl_2$ is similar to that of $(PPh_3)_3RuCl_2$ (19600 cm^{-1} and 25000 cm^{-1}) (89) (Fig. (3)) in DMA solution in which the bands are associated with the $(PPh_3)_2RuCl_2$ species which arises through dissociation. In methylene chloride solution, the complex is a non-conductor which suggests dissociation of the phosphole as follows:

$$(dPP)_3RuCl_2 \rightleftharpoons (dPP)_2RuCl_2 + dPP$$

The reflectance spectra of $(dPP)_3RuCl_2$, $(PP)_3RuCl_2$ and $(mPP)_4Ru_2Cl_5$ are very similar having a sharp band at 25000 cm^{-1} and a broad band at 8700 cm^{-1}. The complex $(PPh_3)_3RuCl_2$ has been found to give bands at $\sim$ 20800 cm^{-1} and 13300 cm^{-1} in DMA solution (89) in the presence of PPh_3 and they are probably similar in nature to those of the phosphole complexes.

The Ru(III) and Ru(II) complexes are probably monomeric involving 6-coordinated d^5 and 5-coordinated d^6 systems respectively as is the situation found in the analogous PPh_3 complexes $(PPh_3)_3RuCl_3$ (90) and $(PPh_3)_3RuCl_2$ (91). The apparent mixed-valent complex $(mPP)_4Ru_2Cl_5$ would be expected to have three chloride bridges as in the analogous n-butylphosphine complex (μ_{eff}=1.50 B.M.) which has been prepared (88) and the structure of which has been confirmed by X-ray single crystal diffraction studies (92).

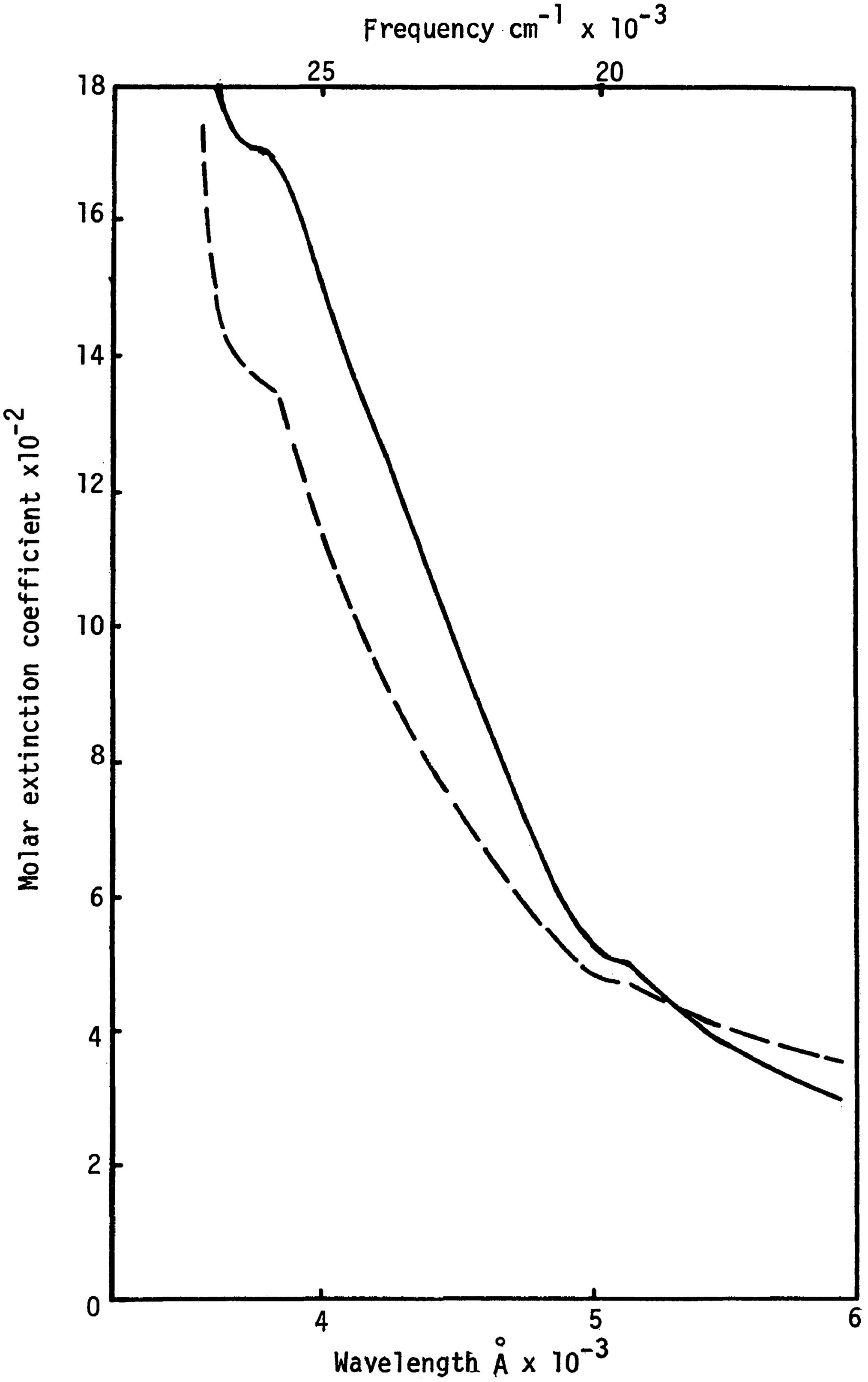


Fig. (3) Electronic solution spectra of ruthenium complexes, —— $RuCl_2(dPP)_3$ 1.60×10^{-3}M; – – $RuCl_2(PPh_3)_3$ 1.04×10^{-3}M

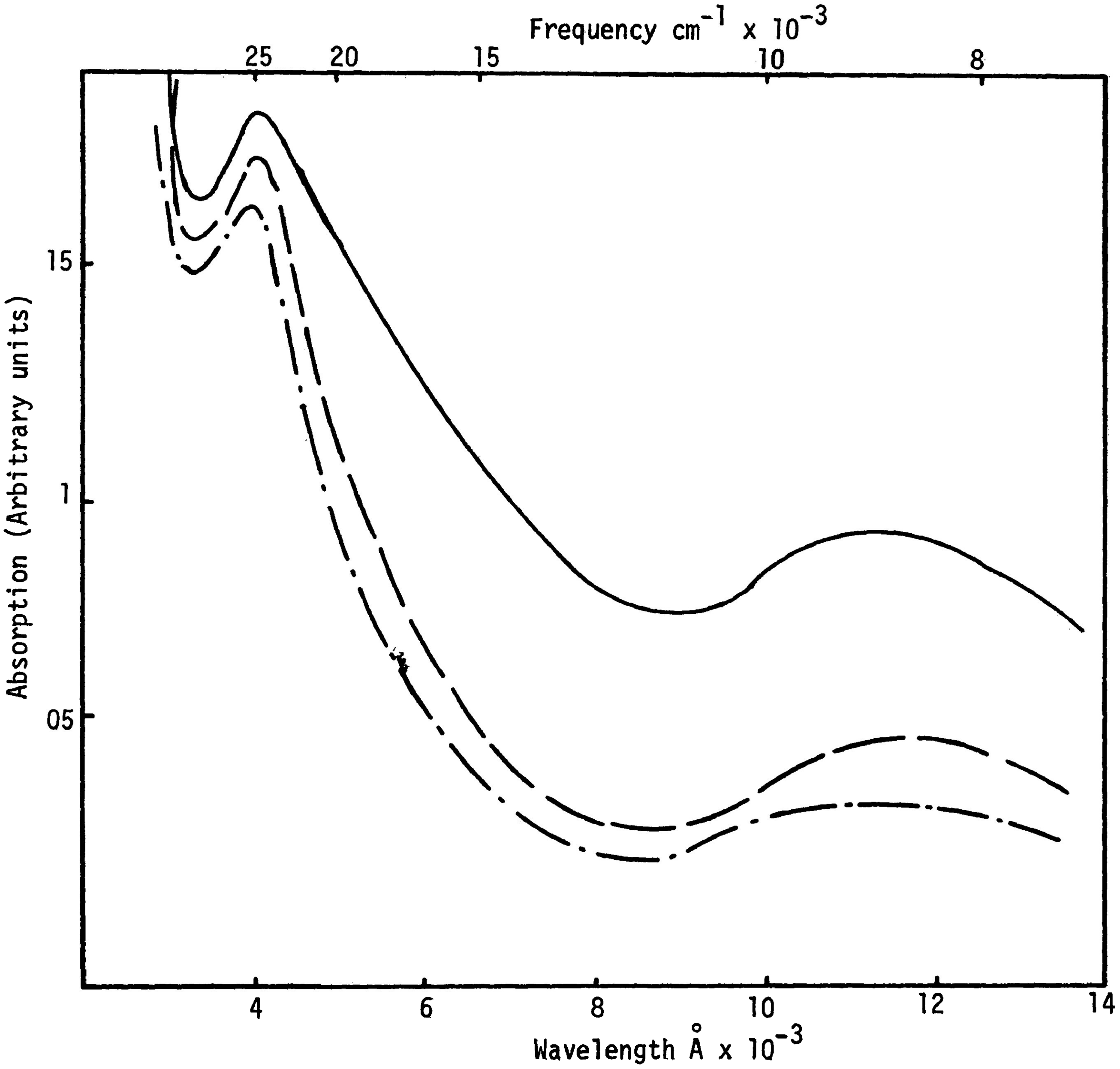
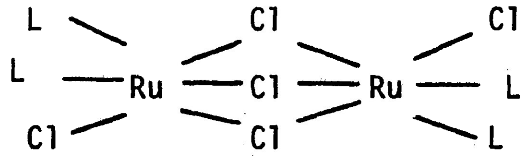


Fig. (4) Electronic reflectance spectra of ruthenium complexes,
— — $(PP)_3RuCl_2$; ——— $(mPP)_4Ru_2Cl_5$; —·— $(dPP)_3RuCl_2$



L=mPP or n-Bu_3P

(XXIX)

Thus, the simple phospholes PP and dPP behave in a similar manner to triphenylphosphine stabilising Ru(III) at room temperature and reducing Ru(III) to Ru(II) at higher temperatures. The 3-substituted phosphole (mPP), on the other hand, has similar properties to n-Bu_3P in partial reduction of Ru(III). This at least suggests the ready availability of the lone-pair phosphorus electrons in complex formation and subsequent reduction of the metal. The same situation is not found in DBP or TPP. While DBP and TPP complex with Ru(III) to form $RuCl_3(DBP)_3$ and $RuCl_3(TPP)_2$ respectively (75) and with Ru(II) to form $RuCl_2L_3$ (L=DBP or TPP) (75), no reduction of Ru(III) to Ru(II) has been observed. The reduction or otherwise of group VIII metal ions by various phosphines has been attributed (1,2) at least in part to steric effects and this has been discussed elsewhere (75).

The reason for the formation of $RuCl_3L$ with the ring unsubstituted (PP) and the 3-substituted (mPP) but the formation of a 6-coordinated complex $(dPP)_3RuCl_3$ with 3,4-disubstitution in the phosphole ring is not immediately clear. It certainly can not be attributed to steric effects since the steric bulk of the three ligands is about the same. However polymeric complexes of this type have been reported with TPP in connection with the Rh(III) complex $(TPP)RhCl_3$ (78) which is thought to involve chloride bridges and, in the case of the very bulky TPP, steric effects may well operate here. The differences between PP, mPP and dPP are more likely to be electronic and such electronic differences have been discussed in Chapter I.

C. Cobalt

Cobalt(II) chloride hexahydrate reacts smoothly with four-fold excesses of PP, mPP, dPP and dBP in ethanol under reflux to form air-stable, green, crystalline solids. These complexes of mPP, dPP and dBP can be recrystallised from methylene chloride-ether from which half a mole of methylene chloride is incorporated into the crystalline complex, even after pumping under greatly reduced pressure (10^{-5} torr), to give complexes of the formula $L_2CoCl_2 \cdot 0.5CH_2Cl_2$ (L=mPP, dPP or dBP). The unsubstituted phosphole, PP, forms the monohydrate, $(PP)_2CoCl_2 \cdot H_2O$ which is insoluble in benzene and ethanol and only slightly soluble in methylene chloride and acetone. It is moderately soluble in acetonitrile from which the complex can be recrystallised by the addition of ether, and subsequent drying under reduced pressure

(10^{-5} torr) still yields the monohydrate. It should, however, be noted here that the incorporation of solvents of recrystallisation is common with phosphole complexes (70,93). The presence of the solvents of crystallisation was confirmed by mass spectrometry (for CH_2Cl_2) and i.r. spectroscopy (for H_2O).

The infrared spectra of L_2CoCl_2 (L=PP, mPP, dPP or dBP) are similar to the spectra of the ligands (with small shifts in some of the absorption bands and changes in intensity) except in the region 200-400 cm^{-1}. The stretching absorption bands at 310 cm^{-1} for $(PP)_2CoCl_2 \cdot H_2O$, 300 cm^{-1} for $(mPP)_2CoCl_2 \cdot 0.5CH_2Cl_2$, 315 cm^{-1} for $(dPP)_2CoCl_2 \cdot 0.5CH_2Cl_2$ and 320 cm^{-1} for $(dBP)_2CoCl_2 \cdot 0.5CH_2Cl_2$ are presumably due to the Co-Cl bonds. The spectrum of $(PP)_2CoCl_2 \cdot H_2O$ even after recrystallisation from acetonitrile-ether also has a broad weak band between 3400 and 3600 cm^{-1} indicating that water is present probably in the crystal lattice as the complex is essentially tetrahedral (see later discussion).

The electronic absorption spectral data for the cobalt(II) complexes are shown in Table (5) and comparison of these data can be made with the analogous dichlorobis(triphenylphosphine)cobalt(II) (94,95). There are no spectral data reported for other Co(II) phosphole complexes. The similarity in the absorption bands of the phosphole complexes and the $(PPh_3)_2CoCl_2$ complex, which is known to be pseudotetrahedral with a C_{2v} symmetry, strongly indicates that these compounds are of very similar structure. Complexes of

Table (5)

Electronic, Infrared Spectral and Magnetic Moment Data of Co(II) Complexes

Complex	Medium	Spectra, cm^{-1}		μ_{eff} B.M.	Ref.
		Electronic Absorption (ε)	Infrared ν_{Co-Cl}		
$(PP)_2CoCl_2 \cdot H_2O$	solid	16700(sh)	310	4.12	
		15800			
		14700			
		6100			
$(mPP)_2CoCl_2 \cdot 0.5CH_2Cl_2$	CH_2Cl_2	16700 (165)	300	4.09	
	$4.03 \times 10^{-3}M$	14900 (234)			
		14700 (248)			
	solid	16700			
		15900			
		14800			
		6200			

Table (5) cont'd

$(dPP)_2CoCl_2 \cdot 0.5CH_2Cl_2$	CH_2Cl_2	16700(sh) (210)	315	4.14
	$3.23 \times 10^{-3}M$	15900 (289)		
		15200 (343)		
	solid	16700		
		15600		
		14800		
		6200		
$(dBP)_2CoCl_2 \cdot 0.5CH_2Cl_2$	CH_2Cl_2	26300 (1480)	320	3.90
	$8.609 \times 10^{-3}M$	15700 (441)		
		14900 (557)		
		14500 (563)		
	solid	26300		
		15700		
		14700		
		6100		

Table (5) cont'd

$(PPh_3)_2CoCl_2$	$CH_3COC_2H_5$	17200 (235)	4.41	94
	$2x10^{-3}M$	15700 (290)		
		14700 (310)		
	solid	15800		
		13000		
$(PPh_3)_2CoBr_2$	CH_2Cl_2	15600 (~740)	4.52	94
		14900 (970)		
		13100 (610)		
		10200 (80)		
		7700 (95)		
		6200 (110)		
	solid	15000		
		12800		

lower symmetry than tetrahedral, e.g. $CoCl_2L_2$ (C_{2v} symmetry), show (96) spectra rather similar to those of the CoX_4^{2-} species. Three transitions are allowed, namely ν_1: $^4A_2 \longrightarrow {}^4T_2$ (3000-5000 cm^{-1} usually not observed), ν_2: $^4A_2 \longrightarrow {}^4T_1(F)$ and ν_3: $^4A_2 \longrightarrow {}^4T_1(P)$. Lowering the symmetry from T_d to C_{2v} usually broadens the ν_2 transition. As the $^4A_2 \longrightarrow {}^4T_1(F)$ is split into three transitions $^4A_2 \longrightarrow {}^4B_2$, $^4A_2 \longrightarrow {}^4A_2$, $^4A_2 \longrightarrow {}^4B_1$, the $^4A_2 \longrightarrow {}^4T_1(P)$ band should be similarly split (97). Both reflectance and solution spectra were recorded and are reported here in order to detect any change in the electronic or geometrical structure which may occur in solution. No significant differences in the two spectra are observed except for typical lower resolution in the reflectance spectra. The weak, broad, near-infrared band due to the $^4A_2 \longrightarrow {}^4T_1(F)$ transition is observed at $\sim$ 6200 cm^{-1} while the $^4A_2 \longrightarrow {}^4T_1(P)$ transition is split into three components as predicted (97,98). The origin of the fine structure has also been attributed to spin-orbital coupling (87). The bands are slightly higher in energy ($\sim$ 1000 cm^{-1}) compared with those of $(PPh_3)_2CoCl_2$, probably indicating that the phospholes are comparable (perhaps slightly better) in donor strength with PPh_3.

The magnetic moments of each of the four complexes have been measured (Table (5)) and they are in the range of 3.9 to 4.15 B.M. which indicates three unpaired electrons in the Co(II) complexes with the electronic structure $e_g^4\ t^3_{2g}$. This is slightly smaller than the value of 4.41 B.M. found for $(PPh_3)_2CoCl_2$ (94). As has been mentioned before, the ligand field splitting

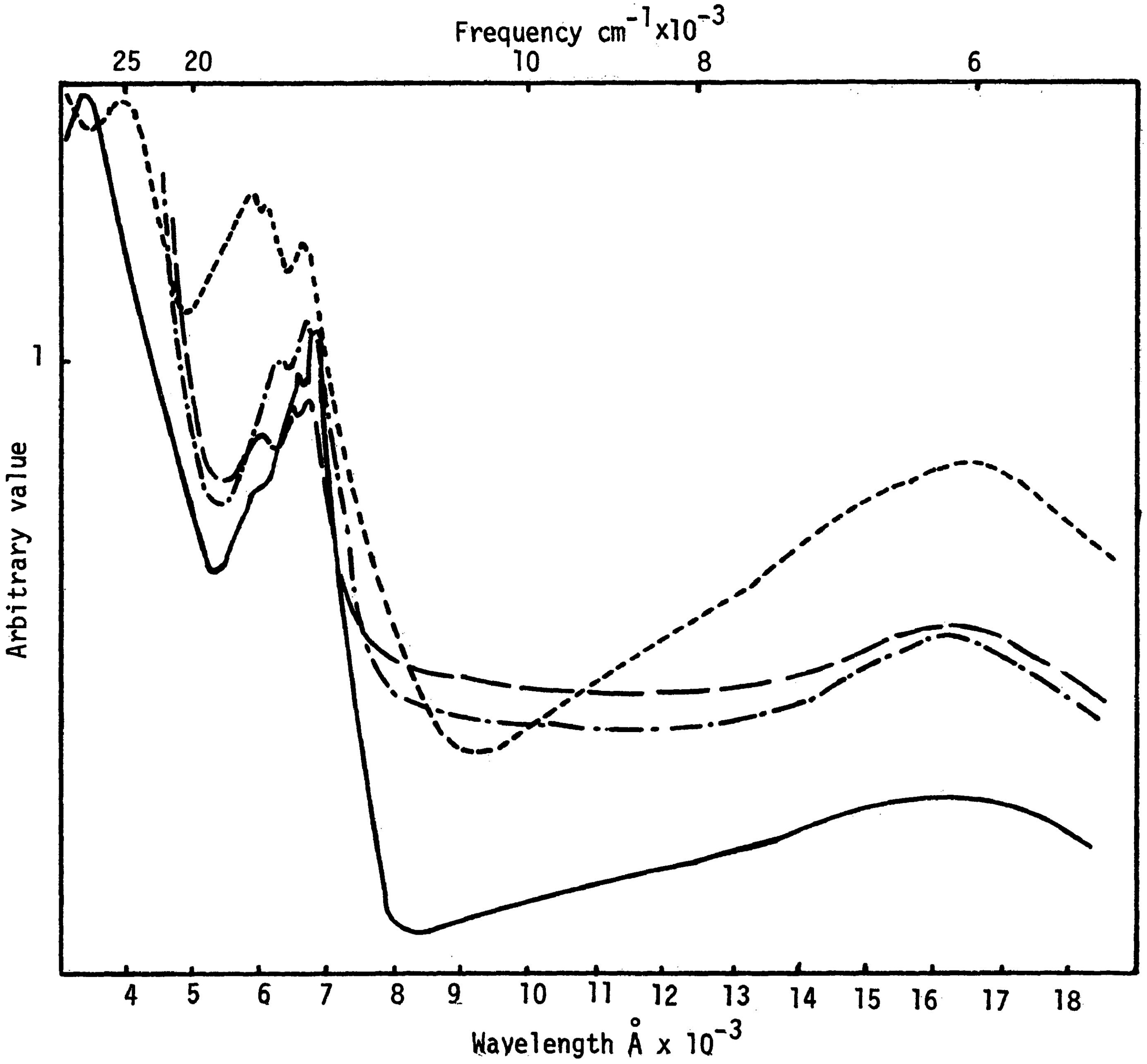


Fig. (5) Electronic reflectance spectra of Co(II) complexes,

—$CoCl_2(PP)_2 \cdot H_2O$; – –$CoCl_2(mPP)_2 \cdot 0.5CH_2Cl_2$;

–·–$CoCl_2(dPP)_2 \cdot 0.5CH_2Cl_2$; ····$CoCl_2(dBP)_2 \cdot 0.5CH_2Cl_2$

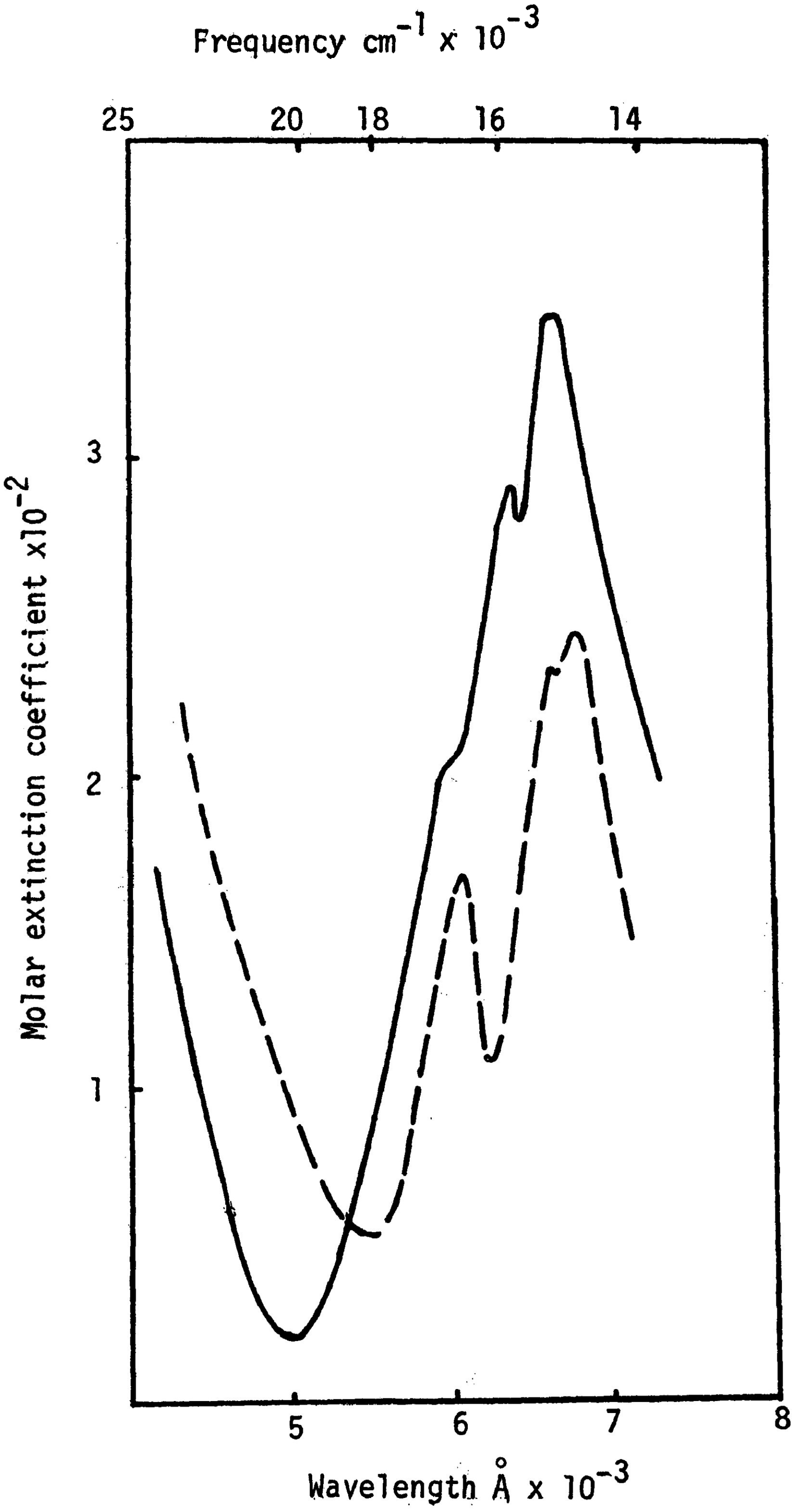


Fig. (6) Electronic solution spectra of Co(II) complexes in CH_2Cl_2,--($mPP)_2CoCl_2\cdot0.5CH_2Cl_2$ (4.03×10^{-3}M); —($dPP)_2CoCl_2\cdot0.5CH_2Cl_2$ (3.23×10^{-3}M)

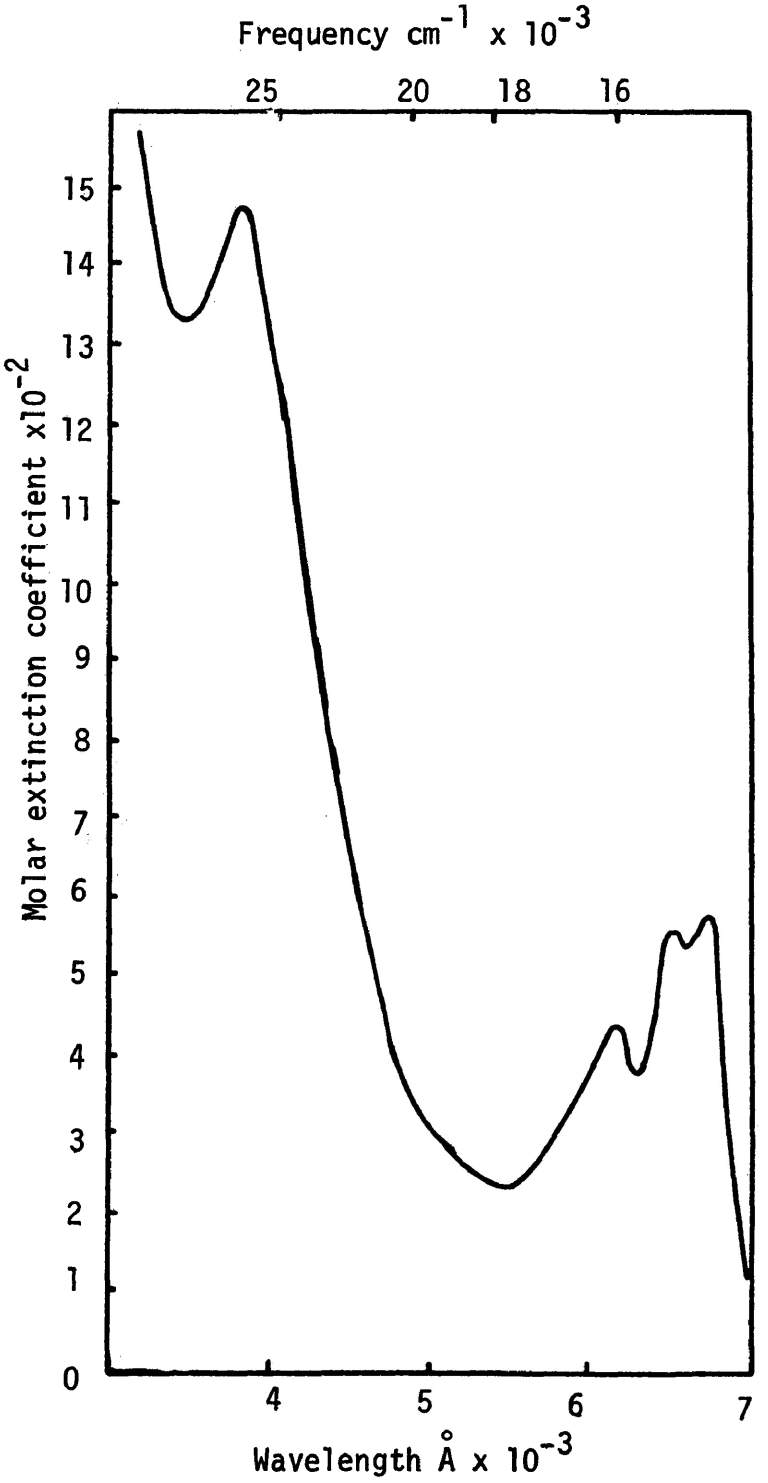


Fig. (7) Electronic solution spectrum in CH_2Cl_2 of $(dBP)_2CoCl_2 \cdot 0.5CH_2Cl_2$ (8.00×10^{-3}M) parameter Δ_t of PP, mPP, dPP and dBP is slightly larger than that of PPh_3. Since the orbital contributions to the magnetic moment vary inversely with the strength of the ligand field, the orbital contribution of PPh_3 to the metal ion would appear to be greater than that of each of the phospholes studied here. This again supports, as mentioned earlier, the idea that the phospholes are perhaps slightly better donors than PPh_3.

Thus, in contrast to the behavior of TPP and DBP, cobalt(II) chloride readily forms air-stable, high-spin complexes with PP, mPP, dPP and dBP which are analogous to those of tertiary alkyl and aryl phosphines (1,2). TPP does not complex with Co(II) (70), while no work has been done on Co(II)/DBP systems. The 5-alkyl-5H-dibenzophospholes (IV a,b; R=Me or Et) form 5-coordinated complexes of the type $CoCl_2L_3$ (76). With the simple phospholes, however no such complex can be obtained with $CoCl_2$ even in the presence of 4-fold excesses of ligand. It seems that, once again, the simple phospholes show more donor character than TPP.

It is surprising that the complex obtained from PP is different from the other three in that it is not soluble in methylene chloride and even after recrystallisation from acetonitrile-ether a monohydrate is still obtained. The water molecule is not coordinated to the cobalt since the electronic spectrum is typical of that of a tetrahedral system. Similar hydrated complexes have, however, been synthesised from other cyclic phosphines. For example, the hydrated 2-phenylisophosphindole Co(II) halide complexes $L_2CoX_2 \cdot H_2O$ (X=Cl, Br or I) (93) are prepared in and recrystallised from organic solvents. They are non-conductors in solution, and are therefore unlikely to be the ionic species $[L_2Co(H_2O)X]^+X^-$.

D. Rhodium

As has been found with PP(80), rhodium(III) chloride hydrate reacts readily with mPP and dPP in ethanol solution under reflux to give yellow, crystalline, air-stable complexes L_3RhCl_3 (L=mPP or dPP) which on recrystallisation from methylene chloride-ether, analysed as $(mPP)_3RhCl_3.0.5CH_2Cl_2$ and $(dPP)_3RhCl_3 \cdot CH_2Cl_2$ respectively. The presence of methylene chloride of crystallisation has been confirmed by solution PMR spectral studies with the methylene chloride peak appearing at δ =5.3. With dBP, only oils are obtained. No reduction of Rh(III) and no formation of hydrido complexes is observed on prolonging the reaction time to 4 days.

Little structural information is available from the infrared spectra which are similar to those of the ligands, mPP and dPP, except in the region between 400-200 cm^{-1}. The bands at 280 and 310 cm^{-1} for $(mPP)_3RhCl_3$ and at 290 and 320 cm^{-1} for $(dPP)_3RhCl_3$ are, as before, tentatively assigned to the Rh-Cl stretching mode. From the number of Rh-Cl bands in the infrared spectra of these complexes, they are probably octahedral with the chlorine atoms at the 1,2,6 positions (80).

The electronic absorption spectra of L_3RhCl_3 (L=mPP or dPP) in CH_2Cl_2 solution (3×10^{-3} M) do not show any appreciable d-d bands which may have been shifted to higher energy and therefore masked by the charge-transfer band which appears at $\sim$ 23000 cm^{-1}. The two Rh(III) complexes are diamagnetic.

The PMR spectrum of $(dPP)_3RhCl_3$ shows that the signal of the phenyl group protons (δ=7.33) shifts 7 Hz down field while that of the methyl group protons (δ=2.13) remains unchanged as compared with the spectrum of the ligand which shows the phenyl protons at δ=7.2 and the methyl protons at δ=2.13. This suggests that the phosphorus atom in the phosphole is bonded to the metal and that the lone-pair phosphorus electrons are readily available for coordination. The downfield shift of the phenyl group proton signals is consistent with a slightly positively charged coordinated phosphorus atom in the complex which is further evidence for σ-complex formation. Part of the shift may also be due to changes in the bond angles about the phosphorus atom in the complex.

Thus, PP, mPP, dPP and DBP (80) all form normal tris-complexes but with TPP, only $(TPP)RhCl_3$ is obtained (78). Steric bulk apparently is not the major reason for TPP forming the 1:1 complex with $RhCl_3$ since the dibenzophosphole DBP (which forms a tris-complex) is at least as bulky. In DBP, however, the two fused benzene rings are essentially coplanar with the phosphorus atom whereas in TPP, the two ring phenyl groups are skewed (52). It is possible therefore that this may produce sufficient steric interference to change the stoichiometry of the complexes formed with TPP.

It should also be noted that on prolonged heating under reflux (24 hrs.), TPP gives the hydrido Rh(III) complex $\mathrm{RhHCl_2(TPP)_2}$ (80), but this was not observed with the dPP system. Superficially, the electronic and steric properties of PP, mPP, dPP and DBP are similar but apparently different from those of TPP in reactions with Rh(III).

In related reactions, it is known that triphenylphosphine reduces Rh(III) instaneously to the Rh(I) system $\mathrm{RhCl(PPh_3)_3}$ (79) while the trialkyl phosphines (e.g. $\mathrm{PMe_3}$; $\mathrm{PEt_3}$ or $\mathrm{P(\underline{n}\text{-}Pr)_3}$ etc.) and $\mathrm{PCy_3}$ all form 1,2,6-$\mathrm{RhCl_3L_3}$ complexes (99). The mixed alkylarylphosphines (e.g. $\mathrm{PEtPh_2}$, $\mathrm{PEt_2Ph}$), however, form $\mathrm{RhHCl_2L_3}$ (99). Sacco (100) has postulated the following mechanism for the reaction of phosphines with $\mathrm{RhCl_3}$:

$$\mathrm{RhX_3} \xrightarrow[\mathrm{A}]{+\mathrm{L}} \mathrm{RhX_3L_3} \xrightarrow[\mathrm{B}]{+[\mathrm{H}],-\mathrm{X}^-} \mathrm{RhHX_2L_3} \underset{\substack{+\mathrm{HX}\\ \mathrm{C}}}{\overset{-\mathrm{HX}}{\rightleftharpoons}} \mathrm{RhXL_3}$$

In this sequence, the type of product formed depends upon the basicity of the phosphine ligand. Thus, with more basic (trialkyl) phosphines, the reaction stops at point A, but with less basic (e.g. triphenyl) phosphines, it goes completely to C. With phosphines of intermediate basicity (alkylaryl) it stops at B. It follows that PP, mPP, dPP and DBP are apparently comparable in basicity with trialkylphosphines whereas the behavior of TPP resembles that of mixed alkylarylphosphines in reactions with $RhCl_3$. This again suggests the ready availability of the lone-pair electrons (and perhaps non-aromaticity) in the simple phospholes. However, Shaw (101) has suggested that the type of product is due to steric rather than electronic factors as he has prepared hydrido complexes of the type $RhHCl_2L_2$ with bulky phosphine ligands such as $P\underline{t}\text{-}Bu\underline{n}\text{-}Pr_2$, $P\underline{t}\text{-}Bu_2Me$ or $P\underline{t}\text{-}Bu_2Et$ etc. It should also be remembered that Quin has found 1-methylphosphole to have an exceptionally low basicity (8).

While both electronic and steric factors may play important roles in deciding the nature of the products, steric effects alone can not account for the different products obtained with DBP and TPP. Therefore, it seems reasonable to conclude that at least in the case of phospholes, electronic factors may be dominant. However, the type of electronic factors which may operate in these reactions may not be a simple question of basicity, nucleophilicity or aromaticity. Thus, from Chapter I, it can be seen that certain phospholes at least may have an unusual orbital sequence which is not inconsistent with aromaticity (59) and in which the lone-pair orbital is not the HOMO. This and other facets of the electronic structure will be discussed at the end of this chapter.

E. Iridium

Both mPP and dPP in a 4-fold excess react smoothly with iridium(III) chloride trihydrate in ethanol on heating under reflux to give yellow solids L_3IrCl_3 (L=mPP or dPP). Surprisingly, under similar conditions, PP reduces Ir(III) to Ir(I) and the yellow solid obtained after recrystallisation from methylene chloride-ether analysed well for $(PP)_3IrCl$. However, in all cases, green solids are formed when the ligands are added to $IrCl_3$ in ethanol at room temperature. The crude products are insoluble in most common organic solvents and decompose in DMSO. Consequently, satisfactory elemental analysis could not be obtained for these products. From the limited data available these appear to be monophosphole complexes $LIrCl_3$ (L=mPP or dPP).

The trisphosphole-Ir(III) systems L_3IrCl_3 (L=mPP or dPP), show infrared stretching absorption bands at 315 and 310 cm^{-1} for the mPP and dPP complexes respectively, while the Ir(I) complex $(PP)_3IrCl$ has a single absorption at 320 cm^{-1}. The products which are probably monophosphole complexes exhibit bands at 295 and 320 cm^{-1}. These are again tentatively assigned to be the Ir-Cl bands.

All of the above complexes are diamagnetic, consistent with low-spin d^6(Ir(III)) or d^8(Ir(I)) arrangements in the metal ions. The electronic absorption spectra of these compounds in the solid state do not show any detectable d-d bands which is probably due to the weak d-d absorption of the third row transition metal ions of d^6 and d^8 configuration.

Thus, both mPP and dPP form the tris-complexes with Ir(III) chloride as has been observed before with Rh(III) chloride. On the other hand, with PP and Rh(III) chloride, only $(PP)_3RhCl_3$ is formed whereas Ir(III) is reduced to Ir(I) by PP. This is perhaps due to the lowering of the ionisation potentials on going from 4d to 5d transition metal ions. Tertiary phosphine ligands generally do not reduce Ir(III) and the Ir(I) complexes of alkyl or aryl phosphines have been prepared by substitution of the N_2 or cyclo-octadiene ligands of Ir(I) complexes (2).

Presumably, the differences between PP and the other phospholes are electronic and, as has been noted earlier, studies on the photoelectronic spectrum of PP (59) shows that the n-orbital and highest π orbital of PP have equal energy. This suggests, superficially, that the n-orbital is as readily available for bonding with the metal ions as those of the alkyl and aryl phosphines. Once again, this suggests that the lone-pair of electrons of the phosphorus atom is not entirely delocalised in the ring. Although, as mentioned before, the explanation of phosphole reactivity may not be as simple as this and the topic will be considered more thoroughly at the end of this Chapter.

The probable formation of $LIrCl_3$ (L=mPP or dPP) when the reaction is carried out at room temperature is not surprising since the poor donor TPP also forms $(TPP)RhCl_3$ (78). The poor analyses obtained for these monophosphole complexes is possibly due to contamination with some of the corresponding tris-complex.

If Sacco's theory (100) of complex formation and metal ion reduction in phosphine-Rh(III) systems also applies to Ir, it would appear that PP is less basic than either mPP or dPP.

F. Nickel

Nickel(II) chloride hexahydrate reacts smoothly with mPP, dPP and dBP in ethanol solution under reflux to form, after recrystallisation from methylene chloride-ether, air-stable, brown solids of the formula L_2NiCl_2 (L=mPP, dPP or dBP) which is apparently conventional phosphine behavior. However, under similar conditions, PP with $NiCl_2 \cdot 6H_2O$ gives the brown, apparently five-coordinate $(PP)_3NiCl_2$.

The stereochemistry of 4-coordinated Ni(II) complexes can generally be identified by the position and number of Ni-Cl bands in the infrared spectra (102). Thus, for complexes of the type L_2NiCl_2 a tetrahedral structure with C_{2v} symmetry exhibits 2 infrared-active bands at 298-340 cm^{-1}, a trans square-planar complex should show a single intense band at 400-410 cm^{-1}, while a cis square-planar arrangement shows 2 bands at lower frequencies than those of the trans compounds due to the trans effect and these can be found at 313-330 cm^{-1}. All of the phosphole complexes show two Ni-Cl stretchings in the 270-320 cm^{-1} region (Table 6), consistent with a tetrahedral or cis square-planar arrangement except the apparent five-coordinate PP complex which shows one such band at 320 cm^{-1}.

However, infrared data alone can not unambiguously assign a tetrahedral or <u>cis</u> square-planar structure to the 4 coordinate complexes and other data are required.

Table (6) also records the magnetic moments of all of the phosphole complexes determined by both Gouy's method and the solution PMR technique (103). The magnetic moments are slightly higher in the solid state in all instances. The L_2NiCl_2 (L=mPP, dPP or dBP) complexes have unusual magnetic properties with magnetic moments corresponding to between 1 and 2 unpaired electrons. The $(PP)_3NiCl_2$ complex, on the other hand, has a magnetic moment of only 1.49 B.M.. Magnetic susceptibility measurements on $(dPP)_2NiCl_2$ using PMR spectrometry over the range of temperatures 266-314°K shows that it is essentially temperature independent. Therefore, apparently none of the Ni(II) complexes synthesised are simple square-planar (which would give $\mu_{eff}=0$) or tetrahedral (which would give $\mu_{eff} = 3.0$ B.M.) complexes.

The electronic absorption spectral data of the Ni(II) phosphole complexes are shown in Table (7) and Figure (8). The electronic spectra of the apparent five-coordinated $(PP)_3NiCl_2$ in both the solid state and CH_2Cl_2 solution are typical of that of a d^8 square-planar system. In CH_2Cl_2 solution, it is a 1:1 electrolyte (Table 8), suggesting the presence of the species $[(PP)_3NiCl]^+Cl^-$. Both electronic spectral and magnetic moment data indicate that the same species is present in both solution and in the solid state, <u>i.e</u>. square planar $[(PP)_3NiCl]^+$. Certain square-planar Ni(II) complexes have been reported (104) to show anomalous magnetic

Table (6)

Infrared Data and Magnetic Moments of Ni(II)-Phosphole Complexes

Complex	Infrared ν(Ni-Cl)cm^{-1}(d)	μ_{eff} B.M.
$[(PP)_3NiCl]Cl$	320	1.49(a)
		1.45(b)
$[(mPP)_2NiCl_2]_2$	280	2.11(a)
	300	
$[(dPP)_2NiCl_2]_2$	270	2.12(a)
	320	1.90(b)(42°C)
		1.92(b)(35°C)
		1.94(b)(30°C)
		1.92(b)(21°C)
		1.90(b)(12°C)
		1.91(b)(6°C)
		1.89(b)(0°C)
		1.87(b)(-6°C)
		1.72(c)(42°C)
$[(dBP)_2NiCl_2]_2$	280	1.91(a)
	318	1.70(b)(decomposed after measurement)

Table (6) cont'd

(a) Solid state

(b) CH_2Cl_2 solution

(c) CH_2Cl_2 solution with ligand added

(d) Nujol Mull

Table (7)

Electronic Spectral Data of Nickel(II)-Phosphole Complexes

Complex	Medium	Absorption cm^{-1} (ε)	Ref.
$[(PP)_3NiCl]Cl$	solid	23800	
	CH_2Cl_2 $1 \times 10^{-3}M$	15300(10)	
$[(mPP)_2NiCl_2]_2$	solid	22700	
		15400	
		14500	
		7520	
$[(dPP)_2NiCl_2]_2$	solid	22700	
		15100	
		14300	
		7700	
	CH_2Cl_2	22800(898)	
	$1.95 \times 10^{-2}M$	15100(123)	
		14500(20)	
		7400(5)	
$[(dBP)_2NiCl_2]_2$	solid	23000	
		15400	
		14300	
		7550	

Table (7) cont'd

(PNP)NiCl$_2$	solid	25700	105
		18000	
		13200	
		7500	

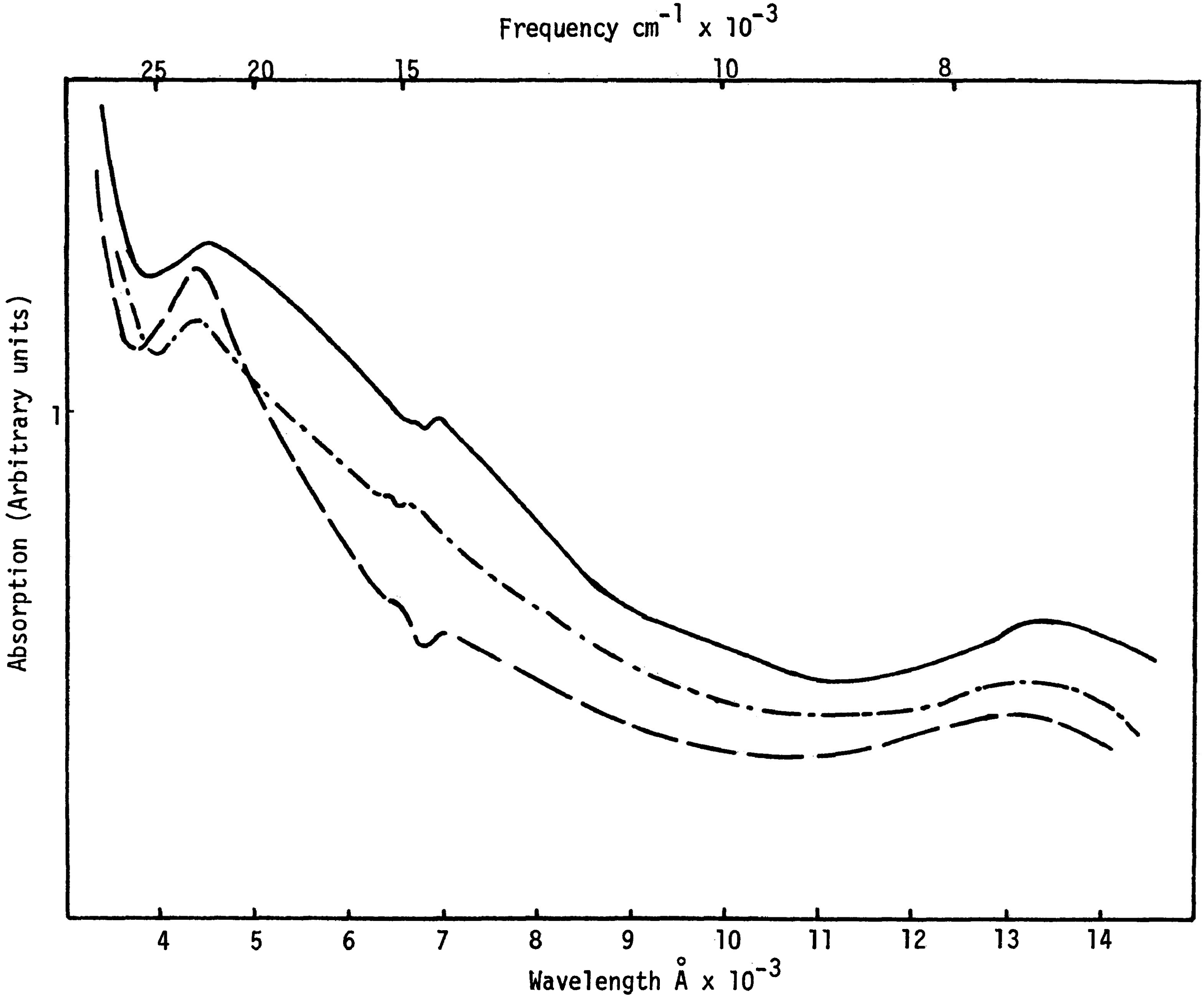


Fig. (8) Electronic Reflectance spectra of Ni(II) complexes,

—·—[(mPP)$_2$NiCl$_2$]$_2$; — [(dPP)$_2$NiCl$_2$]$_2$; — —[(dBP)$_2$NiCl$_2$]$_2$

Table (8)

Molar Conductivity Data

Complex	Concentration (M)	Λ (ohm^{-1} cm^2 mole^{-1})
$[(PP)_3NiCl]Cl$	1.00×10^{-3}(a)	7.7
$[(PP)_3PdCl]Cl$	1.17×10^{-3}(a)	9.4
$[(dPP)_3PtCl]Cl\cdot0.5CH_2Cl_2$	1.11×10^{-3}(a)	11.5
$[Et_4N]^+Cl^-$	1.16×10^{-3}(a)	8.3
$[Et_4N]^+I^-$	1.85×10^{-3}(a)	10.7
$(mPP)_5Rh_2(CO)Cl_4$	1.06×10^{-3}(b)	32.0
$(dPP)_5Rh_2(CO)Cl_4$	1.11×10^{-3}(b)	33.2
$(mPP)_5Rh_2Cl_4$	1.00×10^{-3}(b)	49.9
	1.14×10^{-3}(c)	46.6
$NaPF_6$	7.05×10^{-3}(b)	162.7
Ph_4PCl	0.96×10^{-3}(c)	148.8

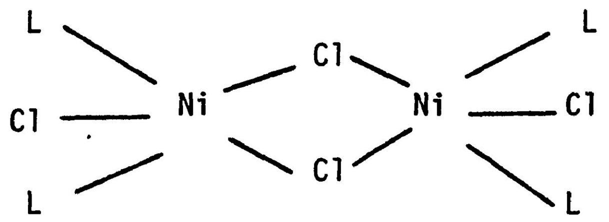
(a) Methylene chloride

(b) Acetone

(c) Acetonitrile

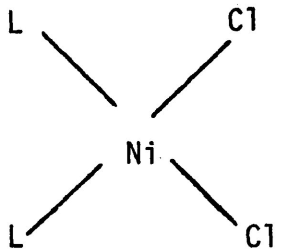
behavior, e.g. μ=1.50 B.M. for $(VPP)_2Ni(ClO_4)_2$ (VPP= 1,2-bis-(diphenylphosphino)ethylene) and this has been attributed to axial perturbations.

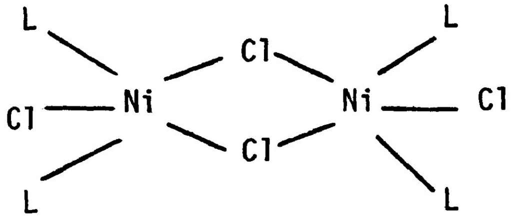
The apparent 4-coordinated complexes have electronic spectra entirely different from those of tetrahedral (105) or square-planar Ni(II) complexes. Surprisingly, the spectra resemble those of 5-coordinated high-spin complexes, e.g. $(PNP)NiCl_2$ (106) (for the structure of PNP, see list of abbreviations). In CH_2Cl_2 solution $(dPP)_2NiCl_2$ is a nonconductor and the molecular weight of the complex (by vapor pressure osmometry) was found to be 610 at 30°C which is considerably higher than that calculated for the monomer (MW=506). The mPP and dBP complexes decompose slowly in solution. Thus, the physical data suggest that the L_2NiCl_2 complexes are 5-coordinated dimers with chloride bridges as shown below.



L=mPP, dPP or dBP

Five-coordinated Ni(II) complexes have also been reported occasionally to be of intermediate spin and to have magnetic moments of 0.6-1.5 B.M., e.g. $(Ph_2PH)_3NiI_2$ (107) and $(DBP)_3NiX_2$ (X=Cl, Br, I or NCS) (76) which, however, have different electronic spectra to those of the phosphole complexes under study here (76). A study of the magnetic properties of these L_2NiCl_2 (L= mPP, dPP or dBP) complexes has shown that the magnetic moments are independent of temperature, indicating the absence of a thermal equilibrium between high and low-spin states. An alternative explanation which can satisfactorily account for the magnetic moments, electronic spectra and molecular weight data is that the complexes exist as equilibrium mixtures of 4-coordinated square-planar ($\mu_{eff}=0$) and 5-coordinated high spin complexes as shown below:





Such an equilibrium may not be very sensitive to temperature changes. The presence of free ligand, however, may shift the equilibrium in either direction and, indeed the magnetic moment drops to 1.72 B.M. (from 1.90 B.M.) when dPP is added to $(dPP)_2NiCl_2$ in CH_2Cl_2 solution.

Although the structures of the phosphole-Ni(II) complexes can not be regarded as unambiguously determined, it is clear that

PP, mPP, dPP and dBP all complex with $NiCl_2$ readily - a property not observed with TPP (70) or, surprisingly in view of these results, with 1-benzylphosphole (ZP) (81). Quin suggested (81) that the lone pair phosphorus electrons in ZP are involved in the formation of an aromatic system with the π electrons of the diene portion of the molecule and hence are not readily available for coordination. He also observed that upon introducing 3,4-dimethyl substituents (to give dZP) into the ring, complex formation with Ni(II) does occur and he suggested that this occurs because the substituents increase the electron density on the phosphorus atom (either by steric or electronic effects) and reduce the aromatic character. However, the work described in this thesis has shown that PP, which is similar to ZP in that it has no substituents in the ring, forms a stable ionic complex with Ni(II). This suggests the inductive and steric effects due to ring substituents are not the major factors which determine phosphole reactivity in complex formation and that reactivity (or lack of reactivity) may be due to other factors including, possibly the hybridization of the phosphorus atom. Again, this topic will be discussed later.

G. Palladium

Air-stable orange-yellow complexes of the formula L_2PdCl_2 (L=mPP or dPP) can be synthesised by heating a mixture of Pd(II) chloride and ligand (3-fold excess) in ethanol under reflux. However, under similar conditions, PP forms a brown solid, analysing as $(PP)_3PdCl_2$. Only oils are obtained with dBP. These complexes can be recrystallised unchanged from methylene chloride-ether.

The infrared spectra of these palladium(II) complexes are very similar to those of the ligands except in the far infrared region. The Pd-Cl bands are tentatively assigned at 295 and 310 cm^{-1} for $(PP)_3PdCl_2$, at 292 and 316 cm^{-1} for $(mPP)_2PdCl_2$ and at 290 and 314 cm^{-1} for $(dPP)_2PdCl_2$. The infrared stretching frequencies show that L_2PdCl_2 (L=mPP or dPP) are likely to be square-planar with the two chloride atoms cis to each other. The presence of two Pd-Cl stretching bands in $(PP)_3PdCl_2$ seems to indicate a 5-coordinate complex in the solid state. However, the reflectance spectrum and the solution electronic spectrum of this complex do not show any absorption bands in the visible region except a band at $\sim$ 30300 cm^{-1} (ε =1870) which probably is a charge-transfer band. Five-coordinate Pd(II) complexes normally only exhibit bands at 19000-23000 cm^{-1} (76). Similarly, $(mPP)_2PdCl_2$ only shows a band at $\sim$ 29500 cm^{-1}. On the other hand, the electronic spectrum of $(dPP)_2PdCl_2$ is typical of that of a square-planar d^8 system, with absorption bands at 16000 cm^{-1}(sh) (ε =8.7) and 20500 cm^{-1} (ε =29.4).

Although the stereochemistry of the $(PP)_3PdCl_2$ complex is unknown in the solid state, in CH_2Cl_2 solution, it is apparently square-planar due to the dissociation of the chloride ion:

$$(PP)_3PdCl_2 \rightleftharpoons [(PP)_3PdCl]^+Cl^-$$

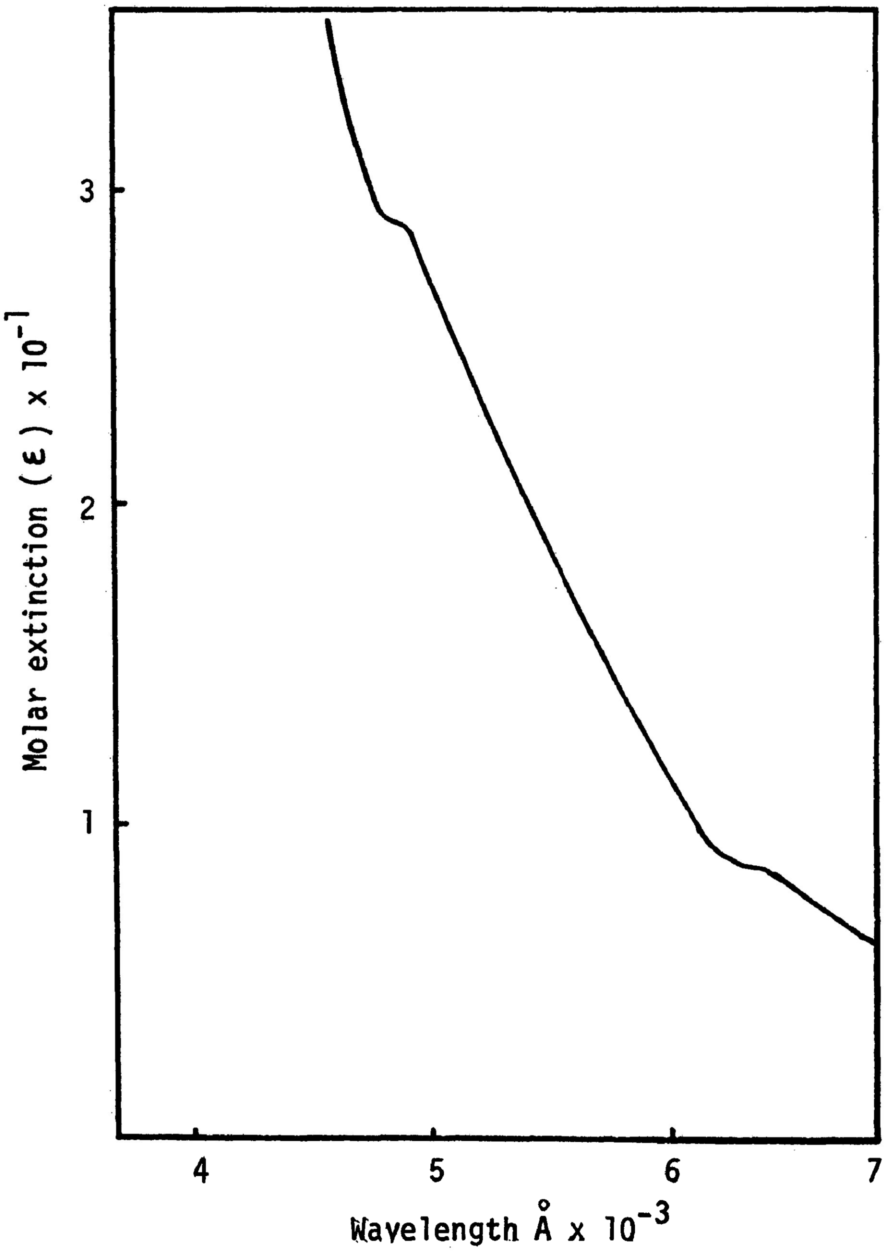


Fig. (9) Electronic solution spectrum of $(dPP)_2PdCl_2$ in CH_2Cl_2 solution (1.87×10^{-2}M)

This is supported by conductivity measurements (Table 8) in CH_2Cl_2 solution in which the complex is a 1:1 electrolyte.

The PMR spectrum of $(dPP)_2PdCl_2$ shows that the signal due to the CH_3 groups (δ =1.87) shifts 17.5 Hz upfield as compared with the spectrum of the ligand (δ =2.13) and the coupling constant $^4J_{(CH_3\text{-}C=C\text{-}P)}$ is 16 Hz. Alternatively, the two sets of CH_3 groups in the complex may be non-equivalent and not coupled with P as the above coupling seems rather high for $^4J_{P-H}$. This point will be discussed later for related Pt complexes. The phenyl proton signals (δ =7.3), as compared to the spectrum of the ligand (δ =7.2), shift 5 Hz downfield. Similarly, the signal of the CH_3 group of the mPP complex shifts 20 Hz (δ =1.89) upfield and that of the phenyl protons (δ =7.4) shifts 5 Hz downfield as compared with the spectrum of the ligand (δ =2.23 and δ =7.3 respectively). The small downfield shift of the phenyl protons may be accounted for by the change in P-Ph angle or by the slight positive charge on the phosphorus caused by coordination, but such a large upfield shift for the CH_3 groups on complex formation can not be explained by angular changes alone. While inductive effects on the methyl group in the complex should also be taken into consideration, the long range inductive effect due to an electron-poor P atom would be expected to deshield the CH_3 protons but obviously some shielding effect operates. It may be that the phosphole rings are not coplanar with each other due to steric interaction and torsion about the Pd-P bond and that the shielding is an orientation effect.

As noted in the introductory section, both TPP and PPh_3 palladium square-planar complexes prefer the trans configuration (78) but infrared spectral data for the mPP and dPP complexes suggest that the cis form predominates. Generally, the cis complex is more stable due to the trans effect of the phosphine ligands. However, with bulky ligands this is overcome by steric interaction and the trans isomer invariably forms. The characteristic of both mPP and dPP in forming the cis isomers is similar to that of secondary phosphines such as $(t\text{-Bu})_2PH$ (2) and also it is known that the preference for a trans arrangement follows the sequence Cl < Br < I (108).

Unlike the R-DBP complexes which form stable five-coordinated complexes of formula $(R\text{-DBP})_3PdX_2$ (R=Me or Et; X=Cl or Br), which has been attributed to the electron releasing properties of the alkyl group, PP in 4-fold excess gives with $PdCl_2$ the complex $(PP)_3PdCl_2$ which in CH_2Cl_2 solution is undoubtedly present largely as $[(PP)_3PdCl]^+Cl^-$. Ionic complexes of this type are well known (2) and the secondary phosphine complex $[(PPh_2H)_3PdBr]Br$ has been shown to dissociate reversibly in solution

$$[(PPh_2H)_3PdBr]Br \rightleftharpoons (PPh_2H)_2PdBr_2 + PPh_2H$$

In the presence of a large excess of free ligand (which shifts the equilibrium to the left) the conductivity is that of a 1:1 electrolyte (107).

Such an equilibrium is not observed in the PP system, possibly due to the smaller size of the ligand. Without X-ray crystallographic measurements, it is impossible to assign a structure to $(PP)_3PdCl_2$ in the solid state. The two ir bands at 295 and 310 cm^{-1} (tentatively assigned to Pd-Cl) can not be unambiguously assigned (note that the metal-P band also occurs in the same region (102)).

Even though doubt remains regarding the structures of certain of these Pd(II) complexes, undoubtedly the phosphole ligands are behaving in a similar manner to ordinary tertiary phosphines in complex formation.

H. Platinum

Both PP and mPP (in 3-fold excess) react with Pt(II) chloride in ethanol under reflux to form white solids L_2PtCl_2 (L=PP or mPP) but under similar conditions, dPP and $PtCl_2$ form an air-stable complex which, after recrystallisation from methylene chloride-ether, analysed as $(dPP)_3PtCl_2 \cdot 0.5CH_2Cl_2$. The incorporated CH_2Cl_2 in the crystal lattice was confirmed by a PMR spectroscopic study which showed that the CH_2Cl_2 peak absorbs at δ =5.3. All of the complexes are diamagnetic.

As in the palladium complexes, two metal-chloride stretching frequencies have been observed in the infrared spectra of $(PP)_2PtCl_2$ (308 and 320 cm^{-1}) and $(mPP)_2PtCl_2$ (300 and 315 cm^{-1}) indicating that the two chloride atoms are mutually cis. The $(dPP)_3PtCl_2$ complex also has two bands in the region 400-200 cm^{-1}

and these occur at 292 and 316 cm^{-1}.

The electronic absorption spectra (5500-33300 cm^{-1}) of all of these Pt(II) complexes do not show any d-d bands in both the solid state and in solution and the charge transfer bands appear at ~ 28600 cm^{-1}. In CH_2Cl_2 solution, the dPP complex is a 1:1 electrolyte indicating that the complex has a 4-coordinated structure $[(dPP)_3PtCl]^+Cl^-$ in solution at least.

The PMR spectrum of $(mPP)_2PtCl_2$ shows that the CH_3 groups of the two phospholes are 66 Hz apart. One of the CH_3 groups shifts 26 Hz upfield (δ =1.8) while the other shifts 40 Hz (δ =2.9) downfield as compared to the spectrum of the ligand (δ =2.23). This is, at first sight, surprising but the shifts may be accounted for in the following manner. The upfield-shift of one CH_3 group is possibly caused by the two five-membered rings of the <u>cis</u> ligands being mutually perpendicular (through steric interaction) such that the CH_3 group of one ligand is shielded by the π-electron cloud of the diene system of the neighboring ligand. The downfield shift may be due to the CH_3 group of the second ligand being effectively well above the plane of the square-planar ligand arrangement. The phenyl group protons shift 5 Hz (to δ =7.4) downfield when compared to the spectrum of the free ligand (δ =7.3). This again indicates that a Pt-P bond is formed in the complex and suggests that the lone-pair phosphorus electrons are readily available to form a metal-phosphorus σ bond as is the case with alkyl and aryl phosphines.

Walton (78) reported that TPP forms a bis-complex with

$PtCl_2$ in which the ligands are trans. In the present system with PP and mPP apparently only cis isomers are obtained. This is not unreasonable since Nelson (109) has postulated that the cis isomers of the tertiary phosphine complexes of Pd(II) and Pt(II) are thermodynamically more stable than the trans isomers and also in a mixture of isomers in solution cis-trans equilibria occur. The amount of trans isomer formed initially decreases as the basicity of the phosphine increases and it is known that the type of the product depends both upon the basicity and also the steric bulk of the phosphine ligand. The cis trialkyl and aryl phosphine complexes of these metals are predominant under normal conditions.

Once again this suggests that PP and mPP are more basic than TPP and in their behavior resemble tertiary phosphines in which the phosphorus is not part of an aromatic system. They are certainly less bulky than TPP. It should, however, be mentioned again that the true situation is probably not as simple as this as will be discussed later.

I. Copper and Mercury

Relatively few worthwhile results have been obtained with ions of these metals but air-stable, pale yellow solids are obtained by the reaction of CuCl with PP, mPP and dPP in chloroform-ethanol solution at room temperature. However, the crude products after recrystallisation from CH_2Cl_2-ether still had poor analyses and analysed only approximately as L_3CuCl (L=PP, mPP or dPP). No fully characterisable products could be obtained when $CuCl_2$ or CuCl were heated under reflux in ethanol or n-butanol with mPP or dPP although yellow crystalline solids were obtained in each case. Only oils are obtained when the reactions are carried out in benzene, THF or CH_2Cl_2 solutions.

The infrared spectra of the crude complexes L_3CuCl (L=PP, mPP or dPP) show one single Cu-Cl band 250 cm^{-1}.

Other cyclic phosphines do give characterisable Cu(I) complexes. For example both TPP and DBP reduce Cu(II) to Cu(I) under reflux in methanol to give monosubstituted complexes LCuCl (L=TPP or DBP) (70). While tris-complexes such as tris(triphenylphosphine) (110) or tris(isophosphindoline) (111) Cu(I) complexes have been reported from reactions in chloroform-ethanol or in ethanol, these complexes of formula L_3CuCl (L=PP, mPP or dPP) after recrystallisation from CH_2Cl_2-ether give unsatisfactory analyses and this is probably due to some dissociation of the phosphole ligands from the complex in solution as has been observed by Lippard (110).

Elemental analyses of the products obtained from $CuCl_2$ and mPP or dPP in ethanol show a Cu:Cl ratio of 1:1.3 even when the ligand is present in a 2-fold excess (only oils are obtained when a 3-4-fold excess of ligand is used). This suggests that reduction of Cu(II) to Cu(I) is incomplete and this, in turn, suggests that the reducing properties of these phosphole ligands may be due in large part to the steric bulk of the ligand rather than the availability of the P-lone pair electrons. This suggestion is supported by the fact that the bulky phosphole TPP reduces Cu(II) to Cu(I) rapidly and completely (70).

Turning briefly to mercury, air stable, white solid Hg(II) complexes of formula $LHgCl_2$ may be prepared by the reaction of PP, mPP, dPP or dBP with $HgCl_2$ in ethanol solution at room temperature. These crude products are insoluble in most organic solvents and thus, can only be purified by successive washings with water, ethanol, CH_2Cl_2 and ether to remove soluble impurities.

These complexes are apparently similar to $(TPP)HgCl_2$ (78) which has been assigned a conventional dimeric structure (XXVIII) on the basis of infrared data (ν_{Hg-Cl}=278 cm^{-1}). The stretching frequencies of Hg-Cl in the phosphole systems under study here occur at 280 cm^{-1} for $(PP)HgCl_2$, 282 cm^{-1} for $(mpp)HgCl_2$, 275 $cm^{-1}$for $(dPP)HgCl_2$ and 280 for $(dPP)HgCl_2$ and these are probably associated with the terminal Hg-Cl of a halogen-bridged system similar to XXVIII (Chapter I).

Since these complexes are insoluble in most common organic solvents, no PMR spectra could be obtained. The chloride analyses are poor even after prolonged treatment with ammonia in order to liberate chloride ion and this is possibly because the bridged chlorides are not completely liberated by this type of decomposition. The ease of complex formation of these phospholes with Hg(II) is comparable with that of TPP and other tertiary phosphines.

J. Other Metals

The chlorides of Mn(II), Fe(II), Zn(II) and Cd(II), under the same reaction conditions as those described for the other metals reported earlier in this Chapter, do not react with any of the phosphole ligands studied. Since the phosphole system may probably be classified as a class 'b' (4) type of ligand which prefers to form complexes with class 'b' metal ions, it is not surprising that they do not react with the above metal ions. Only a limited number of tertiary phosphine complexes of these metal ions have been reported (1,2) and these few complexes have polar metal-ligand bonds involving ligands of high electronegativity (1,2). Phosphine complexes of these metals would, therefore, not be expected to be very stable, particularly in the presence of donor solvents such as water, alcohol or acetone. Phosphole complexes of these metals are also expected to be unstable. It should be noted that earlier studies have shown that no complexes are formed between TPP and $MnCl_2$ or $FeCl_2$ (70).

(iii) Phosphole Complexes of Metal Carbonyls

The preceding studies with metal halides have shown that simple phospholes are reasonably good donors in complex formation and that, in many cases, the behavior of phospholes is quite similar to that of tertiary phosphines. However, although differences between the various phospholes have been observed, no reliable estimate of how different substitution patterns affect donor character may be made. It was felt that such information could possibly be obtained from complex formation studies with carbonyls of metals in a non-zero oxidation state and these studies are described in this section.

A. Ruthenium

A ruthenium carbonyl complex of 3-methyl-1-phenylphosphole (mPP) is formed by heating under reflux a mixture of the phosphole (4-fold excess) and $RuCl_3 \cdot 3H_2O$ in n-butanol solution for 12 hours. After recrystallisation of the brown, crude product from methylene chloride-ether, a complex was obtained which analysed as the Ru(II) system $(mPP)_3Ru(CO)Cl_2$.

The infrared spectrum shows an absorption band at 320 cm^{-1} which is presumably due to the Ru-Cl band and the intense stretching frequency of the carbonyl group occurs at 1960 cm^{-1}. The electronic absorption spectrum does not show any detectable d-d bands and the complex is diamagnetic.

Apparently similar monocarbonyl ruthenium(II) phosphine complexes such as $(PPhEt_2)_3Ru(CO)X_2$ (X=Cl, Br or I) (90) and $(PPhMe_2)_3Ru(CO)X_2$ (X=Cl, Br, I or SCN) (112) are well known and have been prepared in a similar manner except that 2-methoxyethanol was used as a solvent at room temperature. An alternative mode of reaction is in boiling ethanol in the presence of carbon monoxide. Undoubtedly the carbonyl group arises from the abstraction of CO from the solvent and such abstractions are common (90). The same reaction of the phosphole with $RuCl_3 \cdot 3H_2O$, when carried out in ethanol, only results in the formation of the mixed valent complex

$(mPP)_4Ru_2Cl_5$ and this complex has been discussed earlier.

The stretching frequency of the carbonyl group (ν_{CO}= 1960 cm^{-1}) is in the same range as that of the $(PPhMe_2)_3Ru(CO)Cl_2$ complex in which the chloride groups are in a trans arrangement (112). Cis complexes of $L_3Ru(CO)Cl_2$ (L=$PPhMe_2$, ν_{CO}=1928 cm^{-1}; $PPhEt_2$, ν_{CO}=1942 cm^{-1}) show CO stretching frequencies at slightly lower wave numbers and it therefore seems probable that the phosphole complex is a trans isomer and that the donor properties of mPP and $PPhMe_2$ are very similar. The preparation of other Ru(II) carbonyl-phosphole complexes was not attempted.

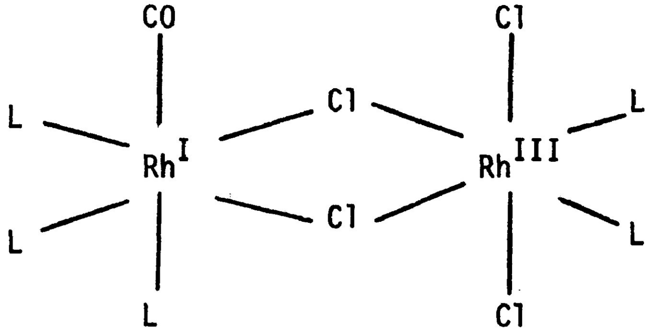
B. Rhodium

Rhodium(I) carbonyl phosphine complexes of the type $L_2Rh(CO)Cl$ are generally prepared by heating the respective ligand either with (A) a rhodium carbonyl containing solution prepared by passing carbon monoxide into an alcoholic solution of $RhCl_3 \cdot 3H_2O$ heated under reflux (113) or (B) $Rh_2(CO)_4Cl_2$ in a suitable solvent. Both synthetic routes have been attempted using phosphole ligands and found to give different products. Thus, when mPP or dPP is heated with the ethanolic solution of rhodium carbonyl chloride (as in method (A)) for 10-20 minutes, clear red solutions are obtained. Upon removing the solvent under reduced pressure followed by addition of ether, yellow monocarbonyl rhodium complexes analysing as $L_5Rh_2(CO)Cl_4$ (L=mPP or dPP) are obtained. On the other hand, with PP, the same treatment gives no rhodium carbonyl complex. Instead, what appears to be (on the basis of analyses and some spectroscopic data) the benzoyl complex $(PP)_3Rh(PhCO)Cl_2$ forms. The same product is obtained even if the reaction is carried out at room temperature. The carbonyl and the benzoyl complexes can be recrystallised unchanged from methylene chloride-ether except for the incorporation of 0.5 mole CH_2Cl_2 into the latter complex (confirmed by PMR spectrometry). With dBP, only oils are obtained in these reactions.

The infrared spectral data of the phosphole-Rh carbonyl and benzoyl complexes are recorded in Table (9). The two carbonyl complexes show stretching frequencies assignable to ν_{CO} and ν_{Rh-Cl} in the normal region, _i.e._ at 1970, 2050, 280 and 300 cm^{-1} for $(mPP)_5Rh_2(CO)Cl_4$ and at 1960, 285 and 320 cm^{-1} for $(dPP)_5Rh_2(CO)Cl_4$. The benzoyl complex shows a typical aryl ketonic group at 1680 cm^{-1} and Rh-Cl stretchings at 295 and 310 cm^{-1}. Attempts to confirm the presence of the benzoyl group by a mass spectrum of the complex gave no positive results since the expected peak at m/e 105 $(Ph-C\equiv O^+)$ was not observed but other evidence (to be presented later) appears to confirm the presence of this grouping.

If the reaction time in all of the above reactions is prolonged to ~1 hour or more, the carbonyl or benzoyl group is lost and $L_5Rh_2Cl_4$ (L=PP, mPP or dPP) are obtained. The infrared spectra only show the Rh-Cl and ligand vibrations (Table 9) and no bands are observed between 2200-1600 cm^{-1} assignable to ν_{CO}.

The complexes $L_5Rh_2(CO)Cl_4$ (L=mPP or dPP) and $L_5Rh_2Cl_4$ (L=PP, mPP or dPP) are nonconductors in acetone solution and are diamagnetic. Molecular weight determinations for the various complexes in CH_2Cl_2 by vapor pressure osmometry at 30°C give 983 for $(mPP)_5Rh_2(CO)Cl_4$ (MW calculated=1246), 600 for $(dPP)_5Rh_2(CO)Cl_4$ (MW=1316), 731 for $(PP)_5Rh_2Cl_4$ (MW=1148), 745 for $(mPP)_5Rh_2Cl_4$ (MW=1218) and 613 for $(dPP)_5Rh_2Cl_4$ (MW=1288). This indicates the possibility that these systems are mixed-valent Rh(I)-Rh(III) (XXX and XXXI) dimeric systems which dissociate in solution, e.g.



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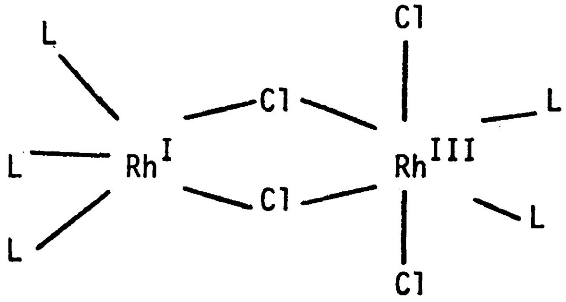
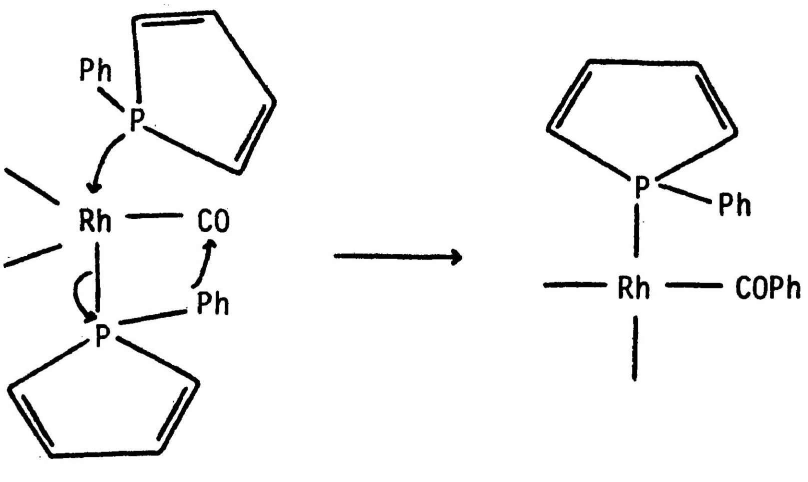


(XXXI)

The presence of two carbonyl stretching frequencies in the ir spectrum of $(mPP)_5Rh_2(CO)Cl_4$ at 1970 and 2050 is possibly due to the presence of 2 isomers in which CO is trans to Cl and L respectively.

Mixed-valent Rh(I)-Rh(III) complexes are fairly common-particularly with alkyaryl phosphine ligands such as PEt_2Ph or $PEtPh_2$ (100). However, the formation of dimeric carbonyl complexes has not been observed previously. The species present in the rhodium carbonyl ethanol solution used in the preparations are $Rh_2(CO)_4Cl_2$ and Cl^- before addition of the phosphole ligands (113). It therefore seems possible that subsequent reaction with the phosphole ligands results in the oxidation of one of the Rh(I) ions from +1 to +3 - probably by H_2O in the presence of Cl^- ions. How and why this reaction takes place remain unanswered.

The formation of the analogous benzoyl complex $(PP)_3Rh(PhCO)Cl_2$ possibly goes through some kind of Rh-CO intermediate followed by a phenyl migration as shown below



(XXXII) (XXXIII)

This reaction takes place at room temperature (or on heating under reflux for 10 min.) and is very fast making isolation of any Rh-CO complex impossible. As mentioned earlier, when the initial reactions are heated for a longer period (1 hr.), $L_5Rh_2Cl_4$ are produced in all three reactions. Clearly, with the CO complexes, CO is eliminated and it would seem likely that the benzoyl complex eliminates benzoyl chloride which then hydrolyses to benzoic acid.

The presence of benzoic acid in the reaction mixture is strongly suggested by the presence of a peak at m/e=121 in the mass spectrum of the residue remaining after the complex $(PP)_5Rh_2Cl_4$ is separated from the reaction mixture. The formation of $L_5Rh_2Cl_4$ from $L_5Rh_2(CO)Cl_4$ possibly goes through a similar phenyl migration (since an excess of ligand is required) forming a Rh-COPh linkage before the elimination of PhCOCl. The same complexes are obtained when the $L_5Rh_2(CO)Cl_4$ systems are heated with the respective ligand in CH_2Cl_2 or EtOH under reflux.

Other more heavily substituted phosphole Rh-carbonyl complexes are known and these are of a conventional nature. For example TPP and DBP form $(TPP)_2Rh(CO)Cl$ and $(DBP)Rh(CO)_2Cl \cdot MeOH$ (80) respectively from the rhodium carbonyl solutions. The anomalous behavior of these simple phospholes discussed in this thesis is of particular interest, and may possibly be attributed to the better donor properties of the simple ligands as compared with the bulky TPP and DBP. The stronger M-P bond may to some extent weaken the P-Ph bond making the phenyl group rather labile. In this connection, it should be noted (as discussed in Chapter I) that P-Ph cleavage in phospholes using Mo carbonyl has been observed. (15) although complexes of the type outlined above are unknown.

The synthesis of the same conventional type of phosphole complex $L_2Rh(CO)Cl$ (L=PP, mPP or dPP) can be achieved by reactions involving the addition of the ligands to $Rh_2(CO)_4Cl_2$ (method B) at room temperature in EtOH. A comparison of the ir spectra of $(PP)_2Rh(CO)Cl$ before and after recrystallisation shows that the intensities of both the carbonyl and the Rh-Cl bands change. Before recrystallisation, the two carbonyl bands at 1970 and 2060 cm^{-1} (Fig. 10) have the same intensity and the higher frequency Rh-Cl band (315 cm^{-1}) is a little more intense than the lower (290 cm^{-1}). After recrystallisation, however, the higher frequency carbonyl and Rh-Cl bands are more intense than the lower frequency bands. Similar observations have been made with $(mPP)_2Rh(CO)Cl$ but, in this case, the lower frequency carbonyl band (1970 cm^{-1}) is more intense than the higher (2070 cm^{-1}) carbonyl band while the higher frequency Rh-Cl (320 cm^{-1}) band is more intense than the lower before recrystallisation. After recrystallisation of $(mPP)_2Rh(CO)Cl$, the two carbonyl bands are of the same intensity as are the Rh-Cl bands.

The complexes $(PP)_2Rh(CO)Cl$ and $(mPP)_2Rh(CO)Cl$ both appear to be formed as mixtures of <u>cis</u> and <u>trans</u> isomers (shown below), as the infrared spectra show two distinct sets of ν_{CO} stretching frequencies at 1970 and 2060 cm^{-1} and 1970 and 2070 cm^{-1} respectively. The relative proportions of the two isomers change

Table (9)

Infrared Data for Rhodium Complexes

Complex	Colour	ν(CO)cm^{-1}	ν(Rh-Cl)cm^{-1}	Ref.
$(PP)_3Rh(PhCO)Cl_2 \cdot 0.5CH_2Cl_2$	yellow	1680	295,310	
$(mPP)_5Rh_2(CO)Cl_4$	yellow	1970,2050	280,300	
$(dPP)_5Rh_2(CO)Cl_4$	yellow	1960	285,320	
$(PP)_5Rh_2Cl_4$	yellow		305,325	
$(mPP)_5Rh_2Cl_4$	yellow		275,310	
$(dPP)_5Rh_2Cl_4$	yellow		280,320,340	
$(PP)_2Rh(CO)Cl$	yellow	1970,2060	290,315	
$(mPP)_2Rh(CO)Cl$	yellow	1970,2070	290,320	
$(dPP)_2Rh(CO)Cl$	yellow	1960	310	
$(mPP)_3RhCl \cdot 0.5CH_2Cl_2$	yellow		295	
$(dPP)_3RhCl$	yellow		280	

Table (9) cont'd

$(PMe_3)_2Rh(CO)Cl$	yellow	1954	113
$(PMe_2Ph)_2Rh(CO)Cl$	yellow	1970	113
$(PPh_3)_2Rh(CO)Cl$	yellow	1965	79
$(TPP)_2Rh(CO)Cl$	yellow	1985	80

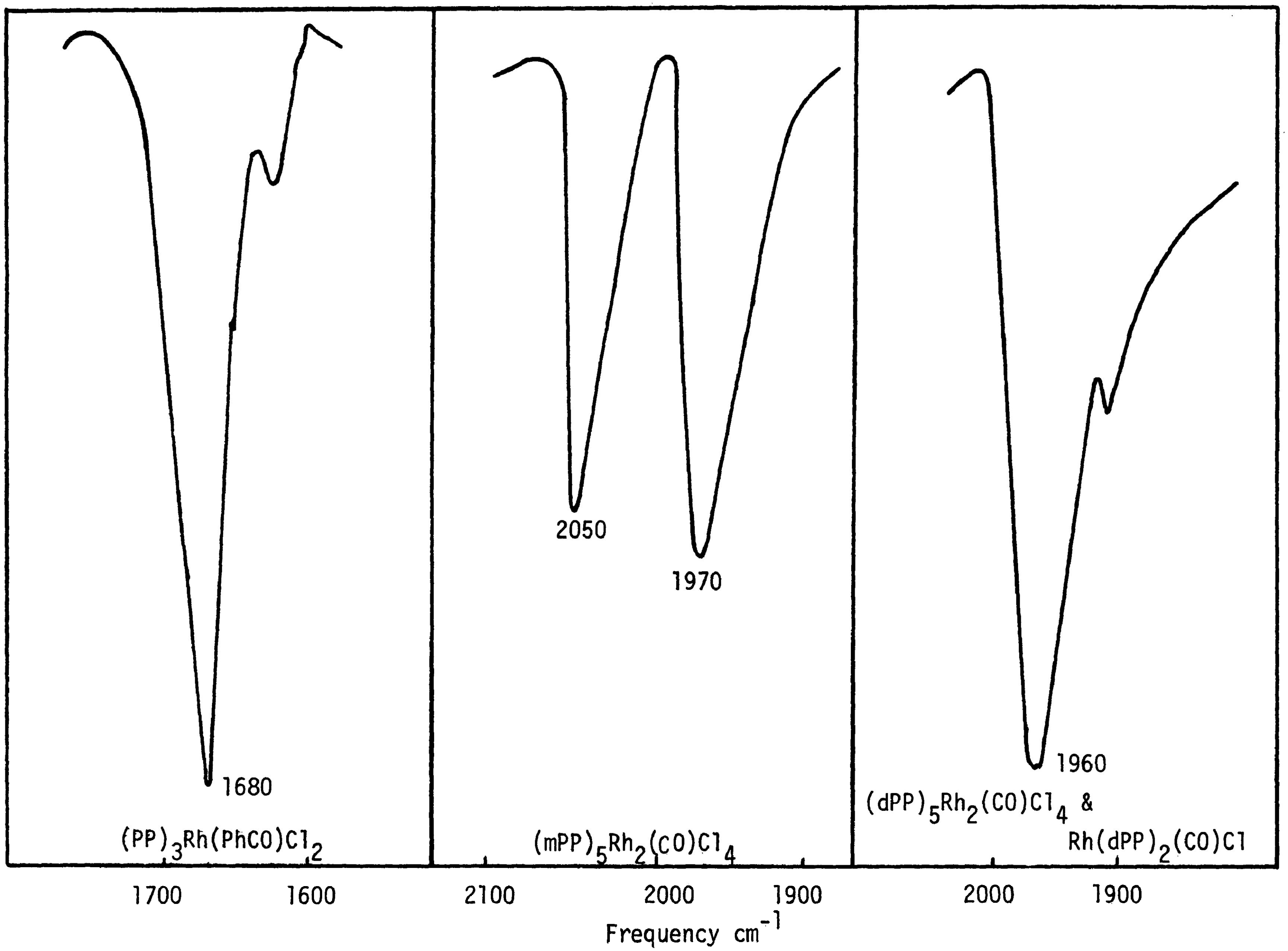


Fig. (10) Infrared spectra of rhodium carbonyl complexes in the CO stretching frequency region

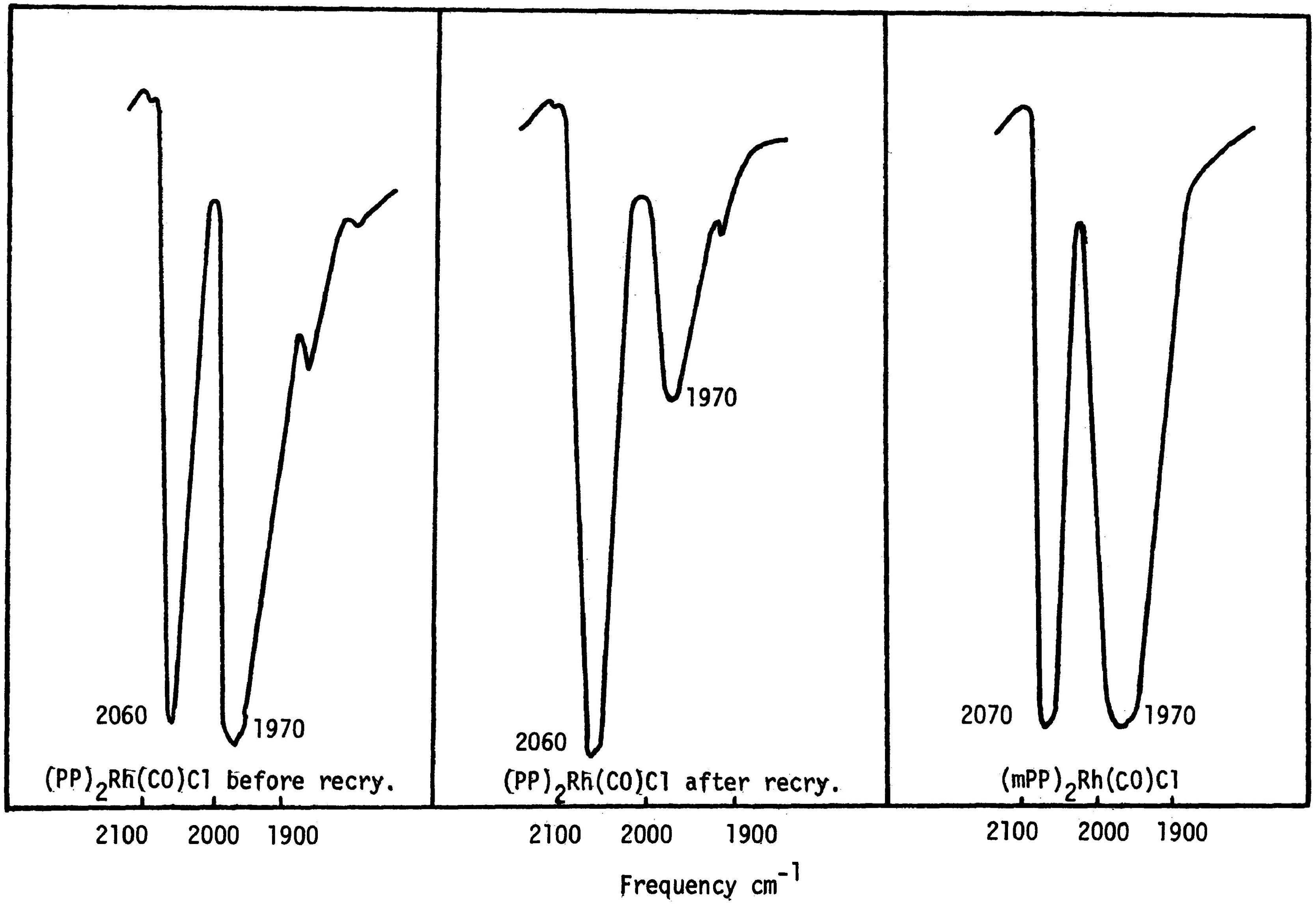
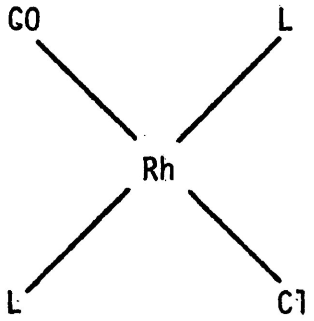
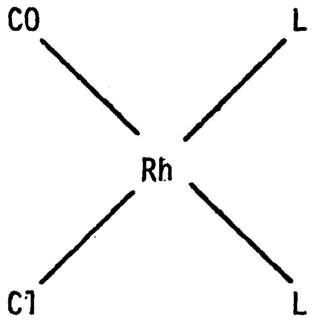


Fig. (10) Infrared spectra of rhodium carbonyl complexes in the CO stretching frequency region



<u>trans</u> ν_{CO}=1970 cm^{-1}

(XXXIV)



<u>cis</u> ν_{CO}=2060 or 2070 cm^{-1}

(XXXV)

upon recrystallisation as is shown by the changes in intensity which occur without frequency shifts. The <u>trans</u> assignment is made by analogy with $(PMe_2Ph)_2Rh(CO)Cl$ (113) (Table 9) and it follows that the other carbonyl frequency must be due to the <u>cis</u> arrangement although there are apparently no such systems in the literature.

The complex $(dPP)_2Rh(CO)Cl$ appears only to form the <u>trans</u> isomer since only one carbonyl frequency is observed with ν_{CO} at 1960 cm^{-1}. Comparison of ν_{CO} in the <u>trans</u> isomers mentioned above with those of the similar complexes containing PMe_3, PMe_2Ph and PPh_3 (Table 9) strongly indicates that these phospholes are of comparable donor character with the tertiary alkyl and aryl phosphines. Within these phosphole systems, the basicity or donor character seems to decrease in the order dPP$>$mPP$\approx$PP$>$TPP since ν_{CO} increases along this series as would be expected with such a change in donor character (78).

<u>Trans</u> complexes of this type are thought to be formed (79,113) as a result of the steric bulk of the ligand although the

cis form is expected to be more stable. As mentioned earlier only trans $(dPP)_2Rh(CO)Cl$ is formed when dPP is the coordinating ligand and this is likely to be associated with a steric effect since the more heavily substituted dPP is marginally more bulky than the other ligands. It should also be noted that as the steric bulk increases slightly along the series PP, mPP, dPP, so the amount of trans isomer initially formed also increases as is shown by the relative intensities of the carbonyl bands in the spectra.

These complexes, $L_2Rh(CO)Cl$, are again sensitive to heat. Thus, if the reactions of $Rh_2(CO)_4Cl_2$ and ligand in EtOH are carried out under reflux or if $L_2Rh(CO)Cl$ is heated with the ligand, L_3RhCl forms. The dPP complex $(dPP)_2Rh(CO)Cl$ seems to be more stable and decomposes only after heating for over 1 hour. The decarbonylation reaction again possibly takes place via migration of a phenyl group and elimination of $PhCO^-$ as PhCOOH although direct elimination of CO can not be excluded.

$$Rh_2(CO)_4Cl_2 \xrightarrow[-CO]{+L} L_2Rh(CO)Cl \xrightarrow[-CO]{+L} L_3RhCl\ (+\ PhCO^-\ ?)$$

(iv) Appendix

In addition to the work described in the previous sections, some trial experiments were carried out on the coordination properties of the fused-ring phosphole 3-n-butyl-1,2-diphenylphosphindole (IIIb) since no such studies of this system are in the limited literature on phosphindoles. Only a few experiments were carried out since the ligand can only be made in small quantities and a brief summary of these studies is given here.

The ligand is not very soluble in ethanol and ethanol-CH_2Cl_2 was therefore employed as a solvent throughout these reactions. The reagents were mixed at room temperature at which no reaction occurs and the mixture was then heated under reflux. A number of metal chlorides have been studied, including Re_3Cl_9, $CoCl_2$, $RhCl_3$, $IrCl_3$, $NiCl_2$, $PdCl_2$, $PtCl_2$, $CuCl_2$ and $HgCl_2$. Complex formation was observed in all cases but insufficient quantities for characterisation of the product were obtained in most of these reactions. However, satisfactory elemental analyses for the complexes of Ru(III),Rh(III), Cu(I) and Hg(II) were obtained.

The complex L_2RuCl_3 is prepared by heating $RuCl_3{\cdot}3H_2O$ and the ligand in a 1:3 ratio under reflux for 3 hours and the product was purified by washing with ethanol and then ether. The Cu(I) complex LCuCl was prepared from $CuCl_2{\cdot}2H_2O$ in the same manner as was the Ru(III) complex. This shows that the phosphindole is a reasonably good donor and acts in the normal manner as a reducing phosphine with Cu(II) to give a Cu(I) complex.

The Rh(III) complex L_2RhCl_3 was synthesised by stirring $RhCl_3{\cdot}3H_2O$ and the ligand at room temperature for 24 hours and the yellow product was purified by washing with ethanol and hexane. The Hg(II) complex, $LHgCl_2$ is obtained in the same manner except that the product precipitates immediately.

The infrared spectra (Table 10) of the complexes are, as expected, very similar to the spectrum of the free ligand except

Table (10)

Metal-Phosphindole Complexes

Complexes(a)	Colour	M.P.°C	Infrared ν(M-Cl)cm^{-1}(c)
L_2RuCl_3	brown	150(b)	280,335
L_2RhCl_3	yellow	138(b)	305,340
LCuCl	white	169	250
$LHgCl_2$	white	171	280

(a) L=3-*n*-Butyl-1,2-diphenylphosphindole

(b) Decomposed

(c) Nujol Mull

for the presence of typical metal-chloride stretching frequencies in the range 250-350 cm^{-1} depending upon the metal present.

Due to the lack of physical data obtained (because of the limited quantities of the products), it is impossible to make any comparison between this system and the other phospholes studied, but it appears that 3-n-butyl-1,2-diphenylphosphindole forms stable complexes with Ru(III), Rh(III), Cu(I) and Hg(II) and possibly several of the other metal ions investigated. Since the phosphindole is much more bulky than PP, mPP, dPP and dBP, it would be expected to be similar to TPP and DBP. It is not surprising, therefore, that only bis-complexes are obtained with Ru(III) and Rh(III). Cu(II) is reduced to Cu(I) as with TPP and DBP, and the reduction is accompanied by complex formation. By analogy with the simple phospholes, the adducts reported above clearly indicate complex formation via the phosphorus lone-pair and therefore there is appreciable donor character at the phosphorus atom in 3-n-butyl-1,2-diphenylphosphindole.

Further studies of this system would be desirable since similar studies with the related phosphindoline and isophosphindoline systems have given very interesting results (69). Further discussion of this topic would, however, be inappropriate here.

(v) Summary, Conclusions and Suggestions for Further Work

The coordinating properties of simple phospholes with metal ions have been examined and reported in Chapter (II). The simple phospholes, PP, mPP,dPP and dBP, all react smoothly with class 'b' metal ions to form stable complexes. In all of the complexes, including the carbonyl complexes, it appears that the ligands are bonded to the metals through the phosphorus lone pair electrons and the complexes are, in many ways, conventional σ-complexes. The compounds prepared generally adopt the most common coordination numbers, e.g. 4-coordinate, tetrahedral for Co(II), square-planar for Pd(II) and Pt(II), 5-coordinate for Ru(II) and 6-coordinate for Rh(III) etc. Only Ni(II) forms the apparently 5-coordinate, paramagnetic dimeric complexes.

It is most significant that both Ni(II) and Co(II) react readily with these phospholes while TPP and, more surprisingly, 1-benzylphosphole do not form any complex at all. As expected, Fe(II) does not react with these ligands due to the instability of the complexes in hydroxylic solvents.

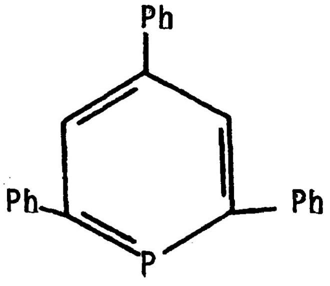
In general, the simple phospholes resemble the tertiary alkylaryl phosphines in behavior. Unlike PPh_3 which reduces Ru(III) to Ru(II), Rh(III) to Rh(I) and Cu(II) to Cu(I) instantaneously, these phospholes are not as good in reducing these metal ions. For example, Ru(III) can be reduced to Ru(II), Cu(II) is only partially reduced to Cu(I) and Rh(III) is stabilised. This is probably governed by both electronic and steric effects of the ligands. The bulky phospholes, TPP and DBP, only reduce Cu(II) to Cu(I) and no Ru(II) or Rh(I) complexes can be obtained from Ru(III) or Rh(III).

That these phospholes have similar donor properties as those of tertiary alkylaryl phosphines is again revealed by an examination of the carbonyl stretching frequencies of the ruthenium and rhodium carbonyl complexes. Undoubtedly, the simple phospholes are better donors than TPP possibly for steric reasons.

In summary, the present study indicates that although some unexpected and very interesting results have been obtained, the simple phospholes act, on the whole, in much the same manner as do ordinary tertiary phosphines in metal complex formation. Superficially, this might be taken as evidence for non-aromatic character. At several points in this Chapter, however, it has been stated that the situation may not be as simple as this and this will now be discussed.

In Chapter I, the question of the electronic structure of phospholes was discussed at some length and it is clear from that discussion that many of the arguments are mutually contradictory although the sum of the evidence tended to support some kind of aromatic character. One other noteworthy observation mentioned in Chapter I is that whatever the degree of delocalisation, in some phospholes at least, the n-orbital is not the HOMO as would be required for efficient complex formation although in other phospholes the n and highest π orbitals are comparable in energy. The exact orbital sequence depends upon the substitution pattern.

If such is the case, orbital perturbation by metal ions would need to occur if efficient complex formation were to take place and if stable complexes were to be formed. This would not be unreasonable since such orbital perturbations in phosphorus heterocycles of negligible basicity (such as the λ^3 phosphorins e.g. XXXVI, pK_a=-10 (114)), in which the n-orbital is most definitely not the HOMO, to give conventional metal complexes fairly easily have been observed (115).



(XXXVI)

If this is the situation, the ease with which complex formation of simple phospholes occurs may indicate only the rate at which orbital perturbation in a pyramidal ground state phosphole occurs rather than the actual electronic nature of the unperturbed ligand.

On the other hand, very recent work (not discussed in Chapter I) strongly indicates that the phosphole system may be both aromatic and pyramidal. This has very recently been postulated by Epiotis and Cherry (115) in a theoretical one-electron MO analysis aided by explicit SCF-MO-CNDO/2 calculations re-evaluation of the phosphole system including the photoelectron spectroscopic data obtained by Schäfer et al. (59). According to this treatment, there are significant lone-pair diene interactions in the pyramidal state (aromaticity) and the non-planarity (rather than the expected planar aromatic state) arises as a compromise geometry dictated by additional significant σ-interactions. This is in contrast to the analogous pyrrole system where, since aromaticity considerations are the only significant ones, the molecule is planar.

In the above mentioned study, no precise estimate of the degree of aromaticity was given although it was mentioned that further photoelectron spectroscopic information could give such an estimate. However, the results discussed in this Chapter show that complex formation by most simple phospholes is relatively easy and this might therefore indicate that the pyramidal aromatic system is easily perturbed. Whether this can be taken to imply that the degree of aromaticity in the pyramidal state is relatively low is debatable at present since, as Chapter I has shown, obvious deductions regarding the phosphole system are frequently incorrect.

If, however, the above suggestion is correct, one might ask why does 1-benzylphosphole not form a nickel(II) complex as mentioned earlier and as discovered by Quin (81) while 1-phenylphosphole does? The answer may lie in the observation of Epiotis and Cherry (116) that in 1-phenylphosphole, there is (contrary to Schäfer's suggestions (59)) a small interaction between the phosphorus lone-pair and the π system of the attached but twisted phenyl ring. This would possibly reduce the aromatic character in the five membered ring and this obviously could not occur in the 1-benzylphosphole system. On the other hand, the _n_-butyl substituted phosphole 1-_n_-butyl-3,4-dimethylphosphole does form metal complexes fairly readily and this too does not have a phenyl group upon the phosphorus. Whatever, the explanation, clearly much depends upon the substitution pattern and this observation has been made repeatedly in Chapter I in connection with other phosphole behavior.

Turning now to suggestions for further work, one obvious investigation to follow up is an extension of the studies with metal carbonyls - in particular Ru and Ir. A detailed analysis of the carbonyl stretching frequencies in these complexes may give information on the dependence of donor strength upon the substitution pattern of the phosphole ring.

A second point which merits study is that since simple phospholes readily form Rh and Ru complexes, the incorporation of phospholes into analogues of the homogeneously catalytically active Rh and Ru species such as $(PPh_3)_3RhCl$ (Wilkinson's catalyst (79)) would be worthwhile as these ligands may confer desirable activity or selectivity characteristics upon the catalysts.

Finally, the use of these phospholes in the possible stabilisation of unusual metal oxidation states generated by tetrahydroborate reduction of metal ions (as has been done with other phosphines (77)) would be worthy of study.

CHAPTER III

EXPERIMENTAL

(i) Materials

The chlorides of manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and cadmium(II) hydrate were purchased from British Drug House Chemicals Limited. Those of rhenium(III), ruthenium(III), rhodium(III), palladium(II) and platinum(II) were obtained from Alfa Inorganics while those of zinc(II) and mercury(II) were purchased from the J. T. Baker Chemical Co. 1,5-Diazabicyclo[5.4.0]-undec-5-ene (DBU) was purchased from the Aldrich Chemical Co., n-butyllithium from Alfa Inorganics and N, N, N', N'-tetramethyl-ethylenediamine (TMEDA) from the Eastman Kodak Co. These reagents were all used without further purification. Copper(I) chloride was prepared by the method of Keller (117) and $Rh_2(CO)_4Cl_2$ was synthesised as described in (87).

All reactions were carried out in a glove box constantly flushed with dry nitrogen (from the Canadian Liquid Air Company, Winnipeg, Manitoba), certified to contain not more than 20 parts per million of oxygen and not more than 10 parts per million of water. All solvents were distilled and degassed and stored over molecular sieves (4A) under nitrogen. All solid reagents weighed in air were crushed and pumped before use in the glove box.

(ii) Physical Measurements - Instrumental Procedures

Air-sensitive samples used in the physical measurements were suitably protected from atmospheric oxygen. Infrared studies were carried out on a Beckman IR12 infrared spectrophotometer. The samples were mounted as Nujol Mulls between polyethylene plates for the far infrared region (200-650 cm^{-1}) and sodium chloride plates for the normal infrared region (650-4000 cm^{-1}). The spectra were calibrated with a polystyrene reference film. Visible and ultraviolet spectra (reflectance and solution) were recorded on a Cary 14 recording spectrophotometer.

Mass spectra were recorded on a Hitachi-Perkin-Elmer Model RMU7 double focussing mass spectrometer. PMR spectra were obtained using a Varian Associates model A60-A spectrometer using deuterated chloroform or acetone as solvent with tetramethylsilane as internal standard.

Molar conductivities were measured on a YSI model 31 conductivity bridge at 25°C. The ground-glass stoppered conductivity cell was designed for use in the glove box and had a cell constant of 0.3671. Magnetic moments were measured either by the Gouy method (solid state) in a double-ended tube calibrated with $Nien_3(S_2O_3)$ or by the PMR method (solution) described by Evans (103).

All spectroscopic and magnetic data are recorded and discussed in Chapter II.

(iii) Elemental Analyses

Nickel, cobalt and copper were analysed by standard volumetric procedures using E.D.T.A. after the metal complexes were decomposed by treatment with concentrated HNO_3. Chloride ion was determined by potentiometric titration with $AgNO_3$ after the samples were digested with concentrated NH_3. Carbon-hydrogen analyses were carried out on a Perkin-Elmer model 240 CHN analyser in the Instrumentation Laboratory of this University. The molecular weight determinations were made using a Knauer electronic temperature measuring vapour pressure osmometer.

(iv) Syntheses of Ligands

A. PP, mPP and dPP

These ligands were prepared according Mathey's method (12,13,14) with slight modifications. A three-necked 1 liter flask was connected to a condenser and a N_2 bubbler and was flushed with dry N_2 for 1 hour. $PhPBr_2$ (46g., 0.17 moles) and liquified 1,3-butadiene (9.5g., 0.175 moles) were mixed in the flask which was immediately stoppered and stored in the refrigerator. When the mixture became solidified (approximately 2 weeks), it was removed from the refrigerator and dry benzene (200 ml) was directly distilled into the flask under N_2. DBU (52g., 0.34 moles) was quickly added at room temperature without any stirring. Dry methylene chloride (220 ml) was poured in slowly and the mixture was stirred gently. An exothermic reaction took place and it was necessary to cool the mixture with an ice-bath. The temperature was then progressively raised until the mixture was just refluxing gently. The reaction was completed in 5 hours and a clear, dark, reddish-brown solution resulted.

The flask was stoppered and transferred into the glove box and the solution was poured into a separatory funnel. It was then hydrolysed with 0.5N HCl (50 ml). The organic layer was separated and washed with dilute K_2CO_3 solution and dried over solid K_2CO_3. The organic layer was distilled at atmospheric pressure and the oily residue was extracted into degassed hexane and shaken with twice its volume of 0.5N HCl for 1 hour. The hexane layer was washed again with dilute K_2CO_3 and dried over solid K_2CO_3. The hexane was first removed under reduced pressure and the product was then distilled under reduced pressure (0.3 torr) at 60°C to give 1-phenylphosphole (PP) as an almost colourless liquid (1.5g., 6%).

The phospholes mPP and dPP were prepared in a similar manner from 2-methyl-1,3-butadiene (12g., 0.175 moles) and $PhPBr_2$ (46g., 0.17 moles) and from 2,3-dimethyl-1,3-butadiene (14.3g., 0.175 moles) and $PhPBr_2$ (46g., 0.17 moles) respectively. In these reactions, the initial reaction between the diene and $PhPBr_2$ required only 2-3 days in the refrigerator and the phospholes were obtained again as almost colourless liquids (mPP; 1.6g, 6%: dPP;

9g.,28%).

B. 1-n-Butyl-3,4-dimethylphosphole (dBP)

3,4-Dimethyl-1-phenylphosphole (5.5g., 0.029 moles) was poured at room temperature into a solution of n-BuLi (2M, 20 ml, 0.040 moles) and TMEDA (4.6g., 0.039 moles) in dry hexane (100 ml) under dry nitrogen. The initial reaction was extremely vigorous and the reaction mixture was then heated at the minimum temperature required for reflux for 4 hours. The mixture was then hydrolysed with 0.5N HCl and washed with K_2CO_3 solution and dried over solid K_2CO_3. It was distilled under reduced pressure (0.3 torr) at 50°C to give the phosphole as an almost colourless liquid (1.95g., 40%).

(v) Syntheses of Phosphole Complexes

The complexes were prepared according to the following methods and the yields were always in the range 60-80%.

A. The ligand was added dropwise to a stirred solution of metal chloride dissolved in ethanol at room temperature. The crude product was separated by centrifugation, washed with organic solvents and recrystallised from appropriate solvents.

B. The metal chloride was dissolved in ethanol to which the ligand was then added dropwise. The mixture was heated under reflux and then centrifuged. Any solid product was washed with organic solvents and recrystallised from suitable solvents. If no precipitation occurred during the reaction, the solvent was removed under reduced pressure and ether was added to precipitate the crude product which was then recrystallised from a suitable solvent and dried.

C. As described by Lippard (88), the metal chloride and the ligand were stirred together in chloroform for a suitable period of time. The solution was centrifuged and ethanol was then added. The crude product was obtained after the solvent was removed slowly under reduced pressure. The products obtained by this procedure were recrystallised from appropriate solvents.

(1) Rhenium Complexes

$(mPP)_3Re_3Cl_9$ ——— method A

The phosphole mPP (0.12g., 0.7 mmoles) and Re_3Cl_9 (0.15g., 0.17 mmoles) were used. After stirring the reaction mixture for 1/2 hour, the purple solid was separated by centrifugation and washed with ethanol and then ether. The complex was found to be pure and did not require further recrystallisation.

Anal:-Calculated:	C;28.3	H;2.4	Cl;22.8
Found:	C;28.8	H;2.8	Cl;22.9

$(dPP)_3Re_3Cl_9$ ——— method A

The phosphole dPP (0.18g., 0.95 mmoles) and Re_3Cl_9 (0.2g., 0.2 mmoles) were used and the procedure was the same as described for $(mPP)_3Re_3Cl_9$. The complex obtained was brown.

Anal:-Calculated:	C;30.0	H;2.7	Cl;22.1
Found:	C;30.2	H;2.9	Cl;21.9

(2) Ruthenium Complexes

$(PP)_3RuCl_2 \cdot 0.5CH_2Cl_2$ ——— method B

The phosphole PP (0.8g., 4.9 mmoles) and $RuCl_3 \cdot 3H_2O$ (0.25g., 0.96 mmoles) were allowed to react under the conditions of method B above. After heating the mixture under reflux for 10 hours, ether was added to the centrifuged brown solution, precipitating a brown solid which was recrystallised from CH_2Cl_2-ether and dried under reduced pressure.

Anal:-			
Calculated:	C;52.7	H;4.1	Cl:10.2
Found:	C;53.2	H;4.6	Cl;10.2

$(PP)RuCl_3$ ——— method A

Under the conditions of method A, PP (0.8g., 4.9 mmoles) and $RuCl_3 \cdot 3H_2O$ (0.25g., 0.96 mmoles) were allowed to react. After stirring the mixture for 1 hour, the resulting greenish brown solid was separated by centrifugation and washed with ethanol, CH_2Cl_2 and then ether.

Anal:-			
Calculated:	C;32.7	H;2.5	Cl;28.9
Found:	C;34.1	H;3.2	Cl;27.9

$(mPP)_4Ru_2Cl_5$ ——— method B

In this synthesis, mPP (0.8g., 4.6 mmoles) and $RuCl_3 \cdot 3H_2O$ (0.25g., 0.96 mmoles) were allowed to react under the conditions of method B above. After heating the mixture under reflux for 24 hours, the resulting brown solid was separated, washed with ethanol and ether and then recrystallised from CH_2Cl_2-ether.

Anal:-Calculated:	C;49.1	H;4.1	Cl;16.5
Found:	C;49.7	H;4.4	Cl;16.1

$(mPP)RuCl_3$ ——— method A

In instead of the above conditions, method A was used, mPP (0.8g., 4.6 mmoles) and $RuCl_3 \cdot 3H_2O$ (0.25g., 0.96 mmoles) gave, after stirring for 1 hour, a greenish brown solid which was separated and washed with ethanol, CH_2Cl_2 and ether. This solid analysed as $(mPP)RuCl_3$ as follows:

Anal:-Calculated:	C;34.6	H;2.9	Cl;27.9
Found:	C;34.7	H;3.6	Cl;28.0

$(dPP)_3RuCl_2$ ——— method B

In the usual manner, dPP (0.8g., 4.2 mmoles) and $RuCl_3 \cdot 3H_2O$ (0.22g., 0.85 mmoles) were used. After heating the mixture under reflux for 10 hours, ether was added to the centrifuged brown solution precipitating a brown solid which was recrystallised from CH_2Cl_2-ether.

Anal:-Calculated:	C;58.7	H;5.3	Cl;9.6
Found:	C;58.5	H;5.6	Cl;9.6

$(dPP)_3RuCl_3$ ——— method A

In contrast to method B, dPP(0.6g., 3.2 mmoles) reacts by method A with $RuCl_3 \cdot 3H_2O$ (0.2g., 0.77 mmoles) to give, after stirring for 2 hours, a reddish brown solid. This was separated and washed with ethanol and ether and then recrystallised from CH_2Cl_2-hexane.

Anal:-Calculated: C;56.0 H;5.1 Cl;13.8

Found: C;56.6 H;5.1 Cl;13.7

(3) Cobalt Complexes

$(PP)_2CoCl_2\cdot H_2O$ ——— method B

The phosphole PP (0.5g., 2.9 mmoles) and $CoCl_2\cdot 6H_2O$ (0.25g., 0.67 mmoles) were heated under reflux under the conditions of method B for 12 hours. The resulting green solid was separated and washed with ethanol, CH_2Cl_2 and ether and then recrystallised from CH_3CN-ether.

Anal:-Calculated: C;51.3 H;4.3 Co;12.6

Found: C;51.3 H;4.5 Co;11.9

$(mPP)_2CoCl_2\cdot 0\cdot 5CH_2Cl_2$ ——— method B

In the usual manner, mPP (0.5g., 2.8 mmoles) and $CoCl_2\cdot 6H_2O$ (0.25g., 0.67 mmoles) were used. After heating under reflux for 12 hours, the resulting green solid was separated and washed with ethanol and ether and then recrystallised from CH_2Cl_2-ether.

Anal:-Calculated: C;51.9 H;4.5 Co;11.3

Found: C;51.9 H;4.8 Co;11.9

$(dPP)_2CoCl_2\cdot 0\cdot 5CH_2Cl_2$ ——— method B

As above, the phosphole dPP(0.5g., 2.7 mmoles) was treated with $CoCl_2\cdot 6H_2O$ (0.25g., 0.67 mmoles). After heating under reflux for 12 hours, the resulting green solid was separated, washed with ethanol and ether and then recrystallised from CH_2Cl_2-ether.

Anal:-Calculated: C;53.6 H;5.0 Co;10.1

Found: C;53.6 H;5.1 Co; 9.4

$(dBP)_2CoCl_2 \cdot 0.5CH_2Cl_2$ ——— method B

The dBP complex corresponding to the dPP complex described above was prepared in the same manner using dBP (0.5g., 2.9 mmoles) and $CoCl_2 \cdot 6H_2O$ (0.25g., 0.67 mmoles).

Anal:-Calculated: C;48.4 H;6.9 Co;11.6

Found: C;48.7 H;7.1 Co;12.3

(4) Rhodium Complexes

$(mPP)_3RhCl_3$ ——— method B

The phosphole mPP (0.45g., 2.5 mmoles) and $RhCl_3 \cdot 3H_2O$ (0.2g., 0.75 mmoles) were treated according to method B. After heating under reflux for 1 hour, the yellow, crude product was separated and washed with ethanol and ether.

Anal:-Calculated: C;54.2 H;4.5 Cl;14.5

Found: C;54.1 H;4.7 Cl;14.5

After recrystallisation from CH_2Cl_2-ether and drying under reduced pressure, the complex gave the solvated complex $(mPP)_3RhCl_3 \cdot 0.5CH_2Cl_2$.

Anal:-Calculated: C;52.0 H;4.4 Cl;13.7

Found: C;51.6 H;4.8 Cl;13.5

$(dPP)_3RhCl_3$ ——— method B

Again using method B, the corresponding dPP complex was prepared using dPP (0.45g., 2.4 mmoles) and $RhCl_3 \cdot 3H_2O$ (0.2g., 0.75 mmoles) in the manner outlined above.

Anal:-Calculated: C;55.9 H;5.1

Found: C;55.9 H;5.2

After recrystallisation from CH_2Cl_2-ether and drying under reduced pressure, this too gave a solvated adduct $(dPP)_3RhCl_3 \cdot CH_2Cl_2$.

Anal:-Calculated: C;51.7 H;4.8 Cl;12.4

Found: C;51.3 H;4.7 Cl;11.9

(5) Iridium Complexes

$(PP)_3IrCl$ ——— method B

The phosphole PP (0.5g., 3.1 mmoles) and $IrCl_3 \cdot 3H_2O$ (0.22g., 0.6 mmoles) were treated according to method B. After heating the mixture under reflux for 12 hours, ether was added to the centrifuged orange solution precipitating a yellow solid which was washed with ether and then recrystallised from CH_2Cl_2-ether.

Anal:-Calculated: C;50.9 H;3.9 Cl;5.0

Found: C;50.5 H;4.4 Cl;5.4

$(mPP)IrCl_3$ ——— method A

The phosphole mPP (0.5g., 2.8 mmoles) and $IrCl_3 \cdot 3H_2O$ (0.22g., 0.6 mmoles) were treated by method A. After stirring the mixture for 1/2 hour, the green, crude product was separated and washed with ethanol, benzene, CH_2Cl_2 and ether.

Anal:-Calculated: C;27.9 H;2.4 Cl;22.5

Found: C;26.3 H;2.9 Cl;23.8

$(mPP)_3IrCl_3$ ——— method B

With method B, the tris adduct was obtained by using mPP (0.5g., 2.8 mmoles) and $IrCl_3 \cdot 3H_2O$ (0.22g., 0.6 mmoles). After heating under reflux for 12 hours, ether was added to the centrifuged yellow-brown solution precipitating an orange solid which was washed with ether and then recrystallised from CH_2Cl_2-ether.

Anal:-Calculated: C;48.3 H;4.1 Cl;13.0
Found: C;48.1 H;4.3 Cl;12.5

$(dPP)IrCl_3$ ——— method A

This was prepared in the same manner as $(mPP)IrCl_3$ using dPP (0.5g., 2.6 mmoles) and $IrCl_3 \cdot 3H_2O$ (0.22g., 0.6 mmoles).

Anal:-Calculated: C;29.6 H;2.7 Cl;21.9
C;30.3 H;2.9 Cl;19.6

$(dPP)_3IrCl_3$ ——— method B

This was prepared in the same manner as $(mPP)_3IrCl_3$ using dPP (05g., 2.6 mmoles) and $IrCl_3 \cdot 3H_2O$ (0.22g., 0.6 mmoles).

Anal:-Calculated: C;50.1 H;4.6 Cl;12.3
Found: C;50.8 H;4.9 Cl;11.6

(6) Nickel Complexes

$(PP)_3NiCl_2$ ——— method B

This tris-complex was prepared by treating PP (0.5g., 3.1 mmoles) with $NiCl_2 \cdot 6H_2O$ (0.18g., 0.78 mmoles) under the conditions of method B. After heating the mixture under reflux for 12 hours, the brown,crude product was separated and washed with ethanol and ether and then recrystallised from CH_2Cl_2-ether.

Anal:-Calculated:	C;59.1	H;4.5	Ni;9.6
Found:	C;59.6	H;5.4	Ni;8.8

$[(mPP)_2NiCl_2]_2$ ——— method B

Under similar conditions to those outlined above, mPP (0.5g., 2.8 mmoles) and $NiCl_2 \cdot 6H_2O$ (0.17g., 0.71 mmoles) reacted to give the bis-complex. Thus, after heating the mixture under reflux for 12 hours, ether was added to the centrifuged brown solution precipitating a brown solid which was washed with ether and recrystallised from CH_2Cl_2-ether.

Anal:-Calculated:	C;55.3	H;4.7	Ni;12.3
Found:	C;55.8	H;5.1	Ni;11.7

$[(dPP)_2NiCl_2]_2$ ——— method B

A similar bis-complex was obtained from dPP (0.55g., 2.9 mmoles) and $NiCl_2 \cdot 6H_2O$ (0.17g., 0.71 mmoles) and the procedure was the same as that described for $[(mPP)_2NiCl_2]_2$. The complex is brown.

Anal:-Calculated:	C;57.0	H;5.2	Ni;11.6
Found:	C;56.7	H;5.7	Ni;11.1

$[(dBP)_2NiCl_2]_2$ ——— method B

The phosphole dBP (0.5g., 2.9 mmoles) with $NiCl_2 \cdot 6H_2O$ (0.17g., 0.71 mmoles) also gives a bis-complex by the above procedure. As above, the complex is brown.

Anal:-Calculated: C;51.5 H;7.4 Ni;12.6

Found: C;52.7 H;8.1 Ni;11.9

(7) Palladium Complexes

$(PP)_3PdCl_2$ ——— method B

Treatment of PP (0.5g., 3.1 mmoles) with $PdCl_2$ (0.13g., 0.72 mmoles) by method B gave above tris-complex as follows. After heating the mixture under reflux for 12 hours, ether was added to the brown centrifuged solution precipitating a brown solid which was washed with ether and then recrystallised from CH_2Cl_2-ether.

Anal:-Calculated: C;54.8 H;4.2 Cl;10.8

Found: C;54.5 H;4.5 Cl;10.6

$(mPP)_2PdCl_2$ ——— method B

Only a bis complex was obtained by method B using mPP (0.5g., 2.9 mmoles) and $PdCl_2$ (0.17g., 0.96 mmoles). The procedure was the same as described for $(PP)_3PdCl_2$. The complex is orange.

Anal:-Calculated: C;50.3 H;4.2 Cl;13.6

Found: C;49.9 H;4.7 Cl;13.5

$(dPP)_2PdCl_2$ ——— method B

A similar bis-complex was obtained from dPP (0.5g., 2.6 mmoles) and $PdCl_2$ (0.16g., 0.88 mmoles) and the procedure was the same as described for $(PP)_3PdCl_2$. The complex is yellow-orange.

Anal:-Calculated: C;52.1 H;4.7 Cl;12.8

Found: C;52.2 H;4.9 Cl;12.5

(8) Platinum Complexes

$(PP)_2PtCl_2$ ——— method B

The phosphole PP (0.5g., 3.1 mmoles) and $PtCl_2$ (0.27g., 1.0 mmoles) were used. After heating the mixture under reflux, the white, crude product was separated, washed with ethanol and ether and then recrystallised from CH_2Cl_2-ether.

Anal:-Calculated:	C;41.0	H;3.1	Cl;12.1
Found:	C;40.9	H;3.1	Cl;12.1

$(mPP)_2PtCl_2$ ——— method B

A very similar bis-complex was obtained using mPP (0.5g., 2.9 mmoles) and $PtCl_2$ (0.25g., 0.96 mmoles) by using the same procedure as described for $(PP)_2PtCl_2$. The complex is white.

Anal:-Calculated:	C;43.6	H;4.3	Cl;11.5
Found:	C;43.1	H;4.1	Cl;11.3

$(dPP)_3PtCl_2 \cdot 0.5CH_2Cl_2$ ——— method B

In contrast to the above syntheses of Pt complexes, dPP (0.6g., 3.1 mmoles) and $PtCl_2$ (0.21g., 0.79 mmoles) give a tris-complex using method B. After heating under reflux for 12 hours, ether was added to the centrifuged solution precipitating a pale yellow solid which was washed with ether and then recrystallised from CH_2Cl_2-ether.

Anal:-Calculated:	C;50.0	H;4.6	Cl;8.1
Found:	C;49.9	H;5.0	Cl;8.6

(9) Copper Complexes

All of the copper complexes were pale yellow and prepared according to method C. However, analytical data were poor and could not be improved.

$(PP)_3CuCl$

This tris complex was obtained from PP (0.6g., 3.7 mmoles) and CuCl (0.12g., 1.2 mmoles).

Anal:-Calculated:	C;62.2	H;4.7	Cl;6.1
Found:	C;61.1	H;4.9	Cl;6.4

$(mPP)_3CuCl$

Using an identical method, a similar tris-complex was obtained from mPP (0.6g., 3.4 mmoles) and CuCl (0.11g., 1.1 mmoles).

Anal:-Calculated:	C;63.8	H;5.4	Cl;5.7
Found:	C;61.7	H;5.0	Cl;6.0

$(dPP)_3CuCl$

Again, a tris-complex was obtained by method C from dPP (0.6g., 3.1 mmoles) and CuCl (0.1g., 1.0 mmoles).

Anal:-Calculated:	C;65.2	H;5.9	Cl;5.3
Found:	C;63.9	H;5.9	Cl;5.7

(10) Mercury Complexes

All the complexes were white and were prepared according to method A. In all cases, chloride analyses were slightly low and this point has been treated in Chapter II.

(PP)$HgCl_2$

The phosphole PP (0.2g., 1.2 mmoles) and $HgCl_2$ (0.3g., 1.2 mmoles) were used. After stirring the mixture for 1/2 hour, the white, crude product was separated and washed with ethanol, CH_2Cl_2 and ether. The complex was found to be pure and did not require further recrystallisation.

Anal:-Calculated: C;27.8 H;2.1 Cl;16.3
Found: C;27.0 H;2.1 Cl;13.6

(mPP)$HgCl_2$

A very similar $HgCl_2$ complex was obtained from mPP (0.2g., 1.1 mmoles) and $HgCl_2$ (0.28g., 1.1 mmoles) and the detailed procedure was the same as described for (PP)$HgCl_2$.

Anal:-Calculated: C;29.6 H;2.5 Cl;15.9
Found: C;28.9 H;2.5 Cl;12.3

(dPP)$HgCl_2$

The phosphole dPP (0.2g., 1.0 mmoles) and $HgCl_2$ (0.26g., 1.0 mmoles) were used and the procedure was the same as described for (PP)$HgCl_2$.

Anal:-Calculated: C;31.4 H;2.9 Cl;15.2
Found: C;31.1 H;2.9 Cl;12.0

(dBP)$HgCl_2$

As with the other phospholes using method A, dBP (0.2g., 1.2 mmoles) reacts with $HgCl_2$ (0.3g., 1.2 mmoles) to give a mono-adduct.

Anal:-Calculated:	C;27.3	H;3.9	Cl;16.1
Found:	C;26.6	H;3.7	Cl;15.1

(11) Ruthenium Carbonyl Complex

$(mPP)_3Ru(CO)Cl_2\cdot CH_2Cl_2$

The phosphole mPP (0.5g., 2.8 mmoles) and Ru(III) in the form of $RuCl_3\cdot 3H_2O$ (0.18g., 0.7 mmoles) were used. The mixture was heated under reflux in n-butanol for 12 hours and ether was then added to the brown solution precipitating a brown solid which was washed with ether and then recrystallised from CH_2Cl_2-ether.

Anal:-Calculated:	C;52.1	H;4.4	Cl;8.8
Found:	C;51.7	H;4.7	Cl;8.7

(12) Rhodium Carbonyl Complexes

$(PP)_3Rh(PhCO)Cl_2\cdot 0.5CH_2Cl_2$

Carbon monoxide was passed into $RhCl_3\cdot 3H_2O$ (0.2g., 0.76 mmoles) in ethanol solution and the mixture was heated under reflux for 4 hours. The phosphole PP (0.49g., 3.0 mmoles) was added dropwise to the yellow rhodium carbonyl solution at room temperature and the mixture was heated for 10 minutes. The solvent was removed under reduced pressure and ether was added to precipitate the yellow product which was recrystallised from CH_2Cl_2-ether.

Anal:-Calculated:	C;54.7	H;4.2	Cl;8.8
Found:	C;54.3	H;4.7	Cl;9.5

$(mPP)_5Rh_2(CO)Cl_4$

The phosphole mPP (05g., 2.9 mmoles) and $RhCl_3\cdot 3H_2O$

(0.19g., 0.72 mmoles) were used and the procedure was otherwise the same as described for $(PP)_3Rh(PhCO)Cl_2$.

<u>Anal</u>:-Calculated: C;54.0 H;4.5 Cl;11.4

Found: C;53.9 H;5.0 Cl;11.9

$(dPP)_5Rh_2(CO)Cl_4$

A mixture similar to that described above was prepared from dPP (0.5g., 2.7 mmoles) and $RhCl_3 \cdot 3H_2O$ (0.17g., 0.66 mmoles) and the procedure was the same as that outlined above.

<u>Anal</u>:-Calculated: C;55.7 H;5.0 Cl;11.1

Found: C;55.3 H;5.4 Cl;11.2

$(PP)_5Rh_2Cl_4$

As described earlier for PP, carbon monoxide was passed into $RhCl_3 \cdot 3H_2O$ (0.2g., 0.76 mmoles) in ethanol solution and the mixture was heated under reflux for 4 hours. The phosphole PP (0.49g., 3.0 mmoles) was added dropwise to the yellow rhodium carbonyl solution at room temperature and then, unlike the earlier experiment, the mixture was heated under reflux for 2 hours. The solvent of the resulting clear reddish solution was removed under reduced pressure and ether was added to precipitate the yellow product which was recrystallised from CH_2Cl_2-ether.

<u>Anal</u>:-Calculated: C;52.3 H;4.0 Cl;12.4

Found: C;53.1 H;4.5 Cl;12.3

$(mPP)_5Rh_2Cl_4$

This complex may be prepared in two ways. Thus, mPP (0.5g., 2.9 mmoles) and $RhCl_3 \cdot 3H_2O$ (0.19g., 0.72 mmoles) were treated as described for $(PP)_5Rh_2Cl_4$.

Alternatively, mPP (0.1g., 0.5 mmoles) was added dropwise to $(mPP)_5Rh_2(CO)Cl_4$ (0.2g., 0.24 mmoles) in CH_2Cl_2 solution and the mixture was heated under reflux for 2 hours. Ether was added to the clear orange solution precipitating the yellow product.

Anal:-Calculated: C;54.2 H;4.6 Cl;11.6
Found: C;54.4 H;5.2 Cl;11.6

$(dPP)_5Rh_2Cl_4$

The phosphole dPP (0.5g., 2.7 mmoles) and $RhCl_3{\cdot}3H_2O$ (0.17g., 0.66 mmoles) were used and the procedure was the same as described for $(PP)_5Rh_2Cl_4$ or the second method described above for $(mPP)_5Rh_2Cl_4$.

Anal:-Calculated: C;55.9 H;5.1 Cl;11.0
Found: C;55.9 H;5.5 Cl;11.1

$(PP)_2Rh(CO)Cl$ ——— method A

The phosphole PP (0.18g., 1.1 mmoles) was added dropwise to $Rh_2(CO)_4Cl_2$ (0.2g., 0.51 mmoles) in ethanol at room temperature. The yellow, crude product was separated and recrystallised from CH_2Cl_2-ether.

Anal:-Calculated: C;51.8 H;3.7 Cl;7.3
Found: C;51.5 H;3.9 Cl;7.3

$(mPP)_2Rh(CO)Cl$ ——— method A

The phosphole mPP (0.19g., 1.1 mmoles) and $Rh_2(CO)_4Cl_2$ (0.2g., 0.51 mmoles) were used and the procedure was the same as described for $(PP)_2Rh(CO)Cl$.

Anal:-Calculated:	C;53.7	H;4.3	Cl;6.9
Found:	C;54.3	H;4.5	Cl;7.5

$(dPP)_2Rh(CO)Cl$ ——— method B

Using a slightly different method, treatment of dPP (0.34g., 1.8 mmoles) with $Rh_2(CO)_4Cl_2$ (0.2g., 0.51 mmoles) gave, after heating under reflux for 1/2 hour, the $(dPP)_2Rh(CO)Cl$ in solution. Ether was added to the centrifuged solution precipitating a yellow solid which was recrystallised from CH_2Cl_2-ether.

Anal:-Calculated:	C;55.3	H;4.8	Cl;6.5
Found:	C;55.5	H;4.8	Cl;6.8

$(mPP)_3RhCl \cdot 0.5CH_2Cl_2$ ——— method B

The solvated complex was prepared from mPP (0.32g., 1.8 mmoles) and $Rh_2(CO)_4Cl_2$ (0.2g., 0.51 mmoles). After heating the mixture under reflux for 1 hour, ether was added to the centrifuged solution precipitating a yellow solid which was recrystallised from CH_2Cl_2-ether.

Anal:-Calculated:	C;57.2	H;4.9	Cl;5.1
Found:	C;57.6	H;5.1	Cl;5.1

$(dPP)_3RhCl$ ——— method B

The phosphole dPP (0.21g., 1.1 mmoles) and $(dPP)_2Rh(CO)Cl$ (0.3g., 0.55 mmoles) in ethanol were heated under reflux for 2 hours. Ether was then added to the centrifuged solution precipitating a yellow solid which was recrystallised from CH_2Cl_2-ether.

Anal:-Calculated: C;61.5 H;5.6 Cl;5.0

Found: C;62.0 H;5.9 Cl;5.0

(13) 3-n-Butyl-1,2-diphenylphosphindole Complexes

L_2RuCl_3 ——— method B

The ligand (0.12g., 0.35 mmoles) in CH_2Cl_2 solution was added dropwise to $RuCl_3 \cdot 3H_2O$ (0.03g., 0.11 mmoles) in ethanol solution. After heating the mixture under reflux for 3 hours, the resulting brown solid was washed with ethanol and ether.

Anal:-Calculated: C;64.7 H;5.2

Found: C;64.1 H;5.4

L_2RhCl_3 ——— method A

The ligand (0.12g., 0.35 mmoles) in CH_2Cl_2 solution was added dropwise to $RhCl_3 \cdot 3H_2O$ (0.023g., 0.087 mmoles) in ethanol solution. After stirring for 24 hours, hexane was added to the centrifuged solution precipitating the yellow solid which was washed with hexane.

Anal:-Calculated: C;67.1 H;5.4

Found: C;67.9 H;5.6

LCuCl ——— method B

The ligand (0.099g., 0.29 mmoles) and $CuCl_2 \cdot 2H_2O$ (0.049g., 0.29 mmoles) were treated according to method B and the overall procedure was the same as that described for L_2RuCl_3.

Anal:-Calculated: C;65.3 H;5.2

Found: C;65.4 H;5.3

$LHgCl_2$ —— method A

The phosphindole (0.1g., 0.29 mmoles) in CH_2Cl_2 solution was added dropwise to $HgCl_2$ (0.08g., 0.29 mmoles) in ethanol solution. After stirring for 1/2 hour, the resulting white solid was washed with ethanol and ether.

Anal:-Calculated: C;47.0 H;3.8
Found: C;45.4 H;3.8

(vi) Attempted Syntheses

A variety of other reactions were attempted but, in each case either no complex was formed or no identifiable product could be obtained. These reactions included dPP with $MnCl_2$, dPP with $FeCl_2$, mPP or dPP with $CuCl_2$ or CuCl (products obtained but with highly variable analyses), dPP with $ZnCl_2$, dPP with $CdCl_2$ (product, but variable analyses), and the phosphindole with Re_3Cl_9, $CoCl_2 \cdot 6H_2O$, $IrCl_3 \cdot 3H_2O$, $NiCl_2 \cdot 6H_2O$, $PdCl_2$ and $PtCl_2$. In view of the mass of results obtained from other reactions described earlier, no further investigations were carried out on the above mentioned reactions.

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