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The reactions between four very simply substituted phospholes and the chlorides of Ni(II), Pd(II) and Pt(II) are described. The phospholes 1-phenylphosphole, 3-methyl-1-phenyl-phosphole and 3,4-dimethyl-1-phenylphosphole all readily form bis-complexes of formula L_2MCl_2 [L = phosphole ligand and M = Ni(II), Pd(II) or Pt(II)] or tris-complexes of formula L_3MCl_2. 1-n-Butyl-3,4-dimethylphosphole appears to form stable complexes only with Ni(II). Evidence is put forward which indicates that the L_2MCl_2 complexes exist in a four-coordinate, square-planar monomeric/five coordinate equilibrium while the L_3MCl_2 complexes are primarily the ionic species $[L_3MCl]^+$ Cl^- in solution. Comparisons are made with the behaviour of other simple phospholes which do not form Ni(II) complexes and the results are discussed briefly in terms of both aromatic and non-aromatic phosphole models.

The question of the electronic structure of the phosphole (I) system has occupied the attention of phosphorus chemists for eighteen years now but only recently has any general consensus of opinion (that the system is a somewhat unusual aromatic species) begun to appear. This topic has been reviewed elsewhere (1) and it
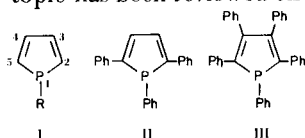
is only necessary to mention here that the results of many of the spectroscopic and theoretical studies carried out over the last five years are in serious conflict (1). Very recently, however, further studies (2,3,4) of primarily a theoretical nature have helped to explain some of these conflicts although, in view of past reevaluations of data, it would be unwise to assume that the matter is fully resolved.

Perhaps the clearest evidence for aromatic character is given by the nmr (pyramidal inversion) and kinetic (retrocyanoethylation) studies by Mislow's group (5,6), the basicity studies carried out by Quin, et al., (7) and the very recent detailed theoretical study by Epiotis and Cherry (4) although alternative explanations for some of the experimental data may be made. This latest theoretical study (4) strongly suggests that the phosphole system is pyramidal (rather than planar like pyrrole) but is also aromatic and the pyramidal arrangement in the ground state is a compromise geometry dictated by the various σ and π interactions present in the system. In pyrrole, the σ interactions are small and aromaticity considerations dominate the system to give a planar geometry. The unusually low pyramidal inversion barrier noted for phospholes (5) is therefore (as suggested by the authors) indicative of an increased degree of aromaticity in the planar inversion transition state.

The possible aromatic nature of the phosphole system

might be expected to affect the availability of the phosphorus lone-pair which would be required for the aromatic sextet. Furthermore, earlier studies (reviewed in reference 1) have shown that certain chemical and physical properties such as reactivity towards alkyl halides (8), ^{31}P nmr chemical shifts (7) and the energy of the phosphorus non-bonding orbital relative to the energies of the other orbitals (9), are sensitive to the substitution pattern in the phosphole ring. Some information regarding the nature of the phosphole system might therefore be obtained by a systematic study of the availability of the lone pair of electrons towards electrophiles of various types and the dependence of this availability upon the substitution pattern. We have carried out two such studies (initiated prior to the latest theoretical studies of the phosphole system (2,3,4)) concerning phosphole donor character towards various transition metal systems and phosphole reactivity towards dimethyl acetylenedicarboxylate. The results of the first of these studies forms the basis of two papers, of which this is the first, while the second investigation will be reported in a separate paper (10).

Several studies of phosphole coordination chemistry have been made and, for the most part, these have been reviewed elsewhere (11). These studies have been mainly of two types - i.e., studies of the coordination of phospholes with transition metal halides and with zero-valent transition metal carbonyls - and they have shown that the phospholes used have poor σ donor character and, in the complexes, the metal-phosphorus bonds are weak. However, in most of these investigations (11), heavily substituted phospholes such as II and III have been used and the behaviour of such phospholes may not be typical of simple phospholes in general for both steric and electronic reasons. This point has also been noted by others (12) and will be discussed more fully in a later paper.

Only three studies of the coordination chemistry of

very simple phospholes have been made although the results have been quite informative. The earliest significant result in this area was the observation (13) that whereas 1-methylphosphole (I, R = Me) and 1-benzylphosphole (I, R = CH$_2$Ph) do not form complexes with nickel(II) chloride (normally a very good phosphine acceptor), a property presumed (13) to be due to lone-pair delocalization into an aromatic ring, 1-benzyl-3,4-dimethylphosphole readily forms an apparently normal Ni(II) complex of formula L$_2$NiCl$_2$ (L = phosphole ligand). As mentioned elsewhere (11,13), this change in coordinating ability has been attributed to some kind of interaction between the 3- and 4-methyl groups in such a manner as to inhibit lone-pair delocalization in the ring and quaternization rates and nmr evidence (8) support this. An alternative explanation not considered by other authors arises from the observations of Schäfer, et al., (9) that variations in the substitution pattern in phospholes cause variations in the relative energies of the molecular orbitals such that whether the n-orbital or one of the π orbitals is the HOMO (highest occupied molecular orbital) may depend upon the substitution pattern. This, of course, would affect donor character, basicities and rates of quaternization and phosphole σ complexes would be expected to form most easily if the non-bonding orbital is the HOMO.

A second observation regarding complex formation by very simple phospholes is that 1-phenylphosphole (I, R = Ph) (designated here as PP) readily forms (14) an apparently conventional phosphine complex of Rh(III) chloride of composition (PP)$_3$RhCl$_3$. This is similar to the behaviour (14,15) of the much more hindered system 1,2,5-triphenylphosphole (II) (designated here as TPP) which forms (TPP)RhCl$_3$. The principal noteworthy feature of these Rh(III) reactions is that Rh(III) is not reduced to Rh(I) as occurs extremely readily with triphenylphosphine which gives (Ph$_3$P)$_3$RhCl (16).

The most detailed and systematic investigation of the coordination chemistry of simple phospholes so far recorded was very recently reported by Mathey (12) at about the same time as the present study commenced. Mathey's investigation concerned the reactions of six simple phospholes with the manganese carbonyl Mn$_2$(CO)$_{10}$ on heating in the presence of uv radiation. Three types of complex are formed under these conditions - i.e., the σ complexes L$_x$Mn(CO)$_{10-x}$ (L = phosphole ligand, x = 1 or 2), the σ,π (tridentate) complexes LMn$_2$(CO)$_7$ and the aromatic π-phospholyl complexes IV (R$_1$ = H or Me; R$_2$ = H or Me) in which the exocyclic phosphorus-carbon bond has been cleaved. The phospholes used

were V (R = Ph, n-Bu, t-Bu or CH$_2$Ph), VI and I (R = Rh). From small variations in the carbonyl stretching frequencies in the ir spectra of the complexes LMn$_2$(CO)$_7$, assumed to be due to ligand induced changes in polarization of the C=O bond, Mathey concluded (12) that the donor character of the phospholes decreases in the order V (R = t-Bu) ≈ V (R = n-Bu) > V (R = Ph) ≈ V (R = CH$_2$Ph) > VI > I (R = Ph).

In our investigation, we have studied the interaction of four simple phospholes with a wide range of transition metal chlorides and carbonyl chlorides in the +1, +2 or +3 oxidation states in reactions which produce only σ-bonded phosphole complexes (without uv activation of the systems) and which therefore use only the phosphorus lone pair of electrons. This paper concerns the reactions with nickel(II), palladium(II) and platinum(II) chlorides (a later paper (19) will deal with Re(III), Ru(III), Co(II), Rh(III) and Ir(III)) and these were chosen for initial investigation for two reasons. First, Quin's studies (13) indicated that complex formation between simple phospholes and nickel(II) chloride is the exception rather than the rule. Second, the isoelectronic Ni(II), Pd(II) and Pt(II) systems are what have been termed "class (b) acceptors" (17) or "soft acids" (18) - i.e., they are excellent phosphine acceptors and there is a wealth of literature on the phosphine complexes of these systems. Thus, comparisons of phosphole and conventional phosphine behaviour may readily be made. The phospholes chosen were 1-phenylphosphole (I, R = Rh) (designated here as PP), 3-methyl-1-phenylphosphole (VI) (mPP), 3,4-dimethyl-1-phenylphosphole (V, R = Ph) (dPP) and 1-n-butyl-3,4-dimethylphosphole (V, R = n-Bu) (dBP) on the basis that these should be adequate to demonstrate the dependence of behaviour upon the substitution pattern.

Reactions with Ni(II) Chloride.

Nickel(II) chloride hexahydrate reacts smoothly with the ring-carbon substituted phospholes mPP, dPP and dBP in ethanol solution under reflux to form, in 60-80% yield, air-stable brown solids of formula L$_2$NiCl$_2$ (L = phosphole ligand). The analytical data for (dBP)$_2$NiCl$_2$ are not quite as good as for the other complexes but could not be improved. On the other hand, other data to be discussed leave little doubt as to this formulation. In contrast, PP yields a complex of formula (PP)$_3$NiCl$_2$. These would therefore appear to be typical four-coordinate square planar and five-coordinate Ni(II)-tertiary phosphine complexes respectively. However, the physical properties of these systems show that the situation is considerably more complex.

Dealing first with the L$_2$NiCl$_2$ complexes, magnetic moment measurements (Table 1) in both the solid state and solution give values in the range 1.90-2.12 B.M. which correspond to the presence of one unpaired electron in each of the complexes. Square-planar complexes would
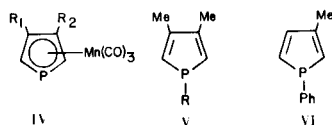

R$_1$ R$_2$ Me   Me   Me

—Mn(CO)$_3$

P   P   P
              R   Ph

IV   V   VI

Table 1

Ir and Magnetic Data for Metal(II)-Phosphole Complexes

Complex	Ir ν(M-Cl)cm^{-1} (a)	μ_{eff} B.M.
[(PP)$_3$NiCl]$^+$ Cl$^-$	320	1.49 (b)
		1.45 (c)
(mPP)$_2$NiCl$_2$	280, 300	2.11 (b)
(dPP)$_2$NiCl$_2$	270,320	2.12 (b)
		1.90 (c) (42°)
		1.92 (c) (35°)
		1.94 (c) (30°)
		1.92 (c) (21°)
		1.90 (c) (12°)
		1.91 (c) (6°)
		1.89 (c) (0°)
		1.87 (c) (-6°)
		1.72 (d) (42°)
(dBP)$_2$NiCl$_2$	280, 318	1.91 (b)
		1.70 (c)
[(PP)$_3$PdCl]$^+$ Cl$^-$	295, 310	--
(mPP)$_2$PdCl$_2$	292, 316	--
(dPP)$_2$PdCl$_2$	290, 314	--
(PP)$_2$PtCl$_2$	308, 320	--
(mPP)$_2$PtCl$_2$	300, 315	--
[(dPP)$_3$PtCl]$^+$ Cl$^-$	292, 316	--

(a) Nujol mull. (b) Solid state. (c) Dichloromethane solution. (d) Dichloromethane solution with added ligand (dec. after measurement).

Table 2

Electronic Spectral Data for Metal(II)-Phosphole Complexes

Complex	Medium	Absorption cm^{-1} (ϵ)
[(PP)$_3$NiCl]$^+$ Cl$^-$	solid	23800
	Dichloromethane (a)	15300 (10)
(mPP)$_2$NiCl$_2$	solid	22700
		15400
		14500
		7520
(dPP)$_2$NiCl$_2$	solid	22700
		15100
		14300
		7700
	Dichloromethane (a)	22800 (898)
		15100 (123)
		14500 (20)
		7400 (5)
(dBP)$_2$NiCl$_2$	solid	23000
		15400
		14300
		7550
(PNP)NiCl$_2$ (b)	solid	25700
		18000
		13200
		7500
(PP)$_3$PdCl$_2$	solid	30300
(mPP)$_2$PdCl$_2$	solid	29500
(dPP)$_2$PdCl$_2$	Dichloromethane (a)	20500 (29)
		16000 (9)
(dPP)$_3$PtCl$_2$	Dichloromethane	28600 (1890)

(a) Concentrations in the range 1×10^{-3} - $2 \times 10^{-2} M$.
(b) Reference 20.

normally have a moment of zero while the much less common tetrahedral Ni(II) systems would have moments in the range 3.5-4.0 B.M. Intermediate values of the type found for the phosphole complexes generally indicate the presence of equilibria between high-spin and low-spin species.

The electronic spectra of the L$_2$NiCl$_2$ complexes are all very similar in the solid state (Table 2) indicating basically the same type of structure is present in each case. Furthermore, in solution, the spectrum of the (dPP)$_2$NiCl$_2$ complex remains virtually unchanged suggesting that no significant structural change occurs upon dissolution. Unfortunately, it proved to be impossible to record solution spectra for the mPP and dBP complexes because of slow decomposition in solution. These spectra are unlike the spectra of four-coordinate, square-planar Ni(II) systems but are quite similar to the spectra of certain *five-coordinate*, high-spin Ni(II) complexes such as (PNP)NiCl$_2$ (PNP = the tridentate ligand 2,6-di(β-di-phenylphosphinoethyl)pyridine) (20), the spectrum of which is included in Table 2.

Further solution studies have been carried out on the solution stable (dPP)$_2$NiCl$_2$. For example, the complex is not ionic since it is a non-conductor in dichloromethane. Also, confirmation that (dPP)$_2$NiCl$_2$ is clearly not a simple monomeric square-planar structure (as indicated by the spectroscopic studies described earlier) comes from

molecular weight measurements which show the molecular weight to be 610 at 30°. This is considerably higher than that required (506) for a simple monomer and indicates that, in solution, the complex is a mixture of monomeric and polymeric species.

Ir spectra of the L$_2$NiCl$_2$ complexes are not very informative. Generally the spectra are very similar to those of the free ligands and the Ni-Cl stretching vibrations occur as two bands for all of the L$_2$NiCl$_2$ species in the 270-320 cm^{-1} range. This rules out a *trans* square-planar arrangement but is consistent (21) with a *cis* square-planar or a tetrahedral arrangement about the nickel. Ir data are listed in Table 1.

One might perhaps also expect to obtain structural information from nmr studies on the complexes but their paramagnetic nature makes it unlikely that very inform-ative ^{1}H nmr spectra could be obtained because of paramagnetic shifts of both sample and internal standard peaks. However, attempts to obtain ^{1}H nmr spectra were made but, because of the slow decomposition of (mPP)$_2$NiCl$_2$ and (dBP)$_2$NiCl$_2$ in solution mentioned earlier, this proved to be possible only for the complex of empirical formula (dPP)$_2$NiCl$_2$. As expected, the

spectrum provides little precise structural information. It does, however, show two distinct and broad methyl signals separated by 34 Hz in the range $\tau 8.0$ - $\tau 9.0$. Precise chemical shifts are impossible to determine because the TMS signal itself is paramagnetically shifted with this shift being almost certainly concentration dependent. The lower field peak has an extremely broad base with a long tail-off on the low-field side, and assuming that the tail-off is part of the lower-field methyl signal as seems likely, this signal is considerably greater in area than the higher field methyl signal. This implies that at least two distinct species are present in solution since magnetically non-equivalent methyl groups on the same ligand would give signals of equal area. As expected from a paramagnetic species, the aromatic proton signals are spread very widely - particularly on the low field side of the normal location of these signals.

The most reasonable interpretation of all of the foregoing information is that the L_2NiCl_2 species are actually equilibrium mixtures of diamagnetic cis square-planar systems of type VII (as indicated by ir measurements) and high-spin, five-coordinate, chloride-bridged dimers of type VIII (as indicated by electronic spectral

VII   VIII

and magnetic data). The molecular weight data, and perhaps also the magnetic and ir data, indicate that this equilibrium lies on the four-coordinate side at room temperature although the electronic spectrum of $(dPP)_2$-$NiCl_2$ indicates the reverse. It should however be noted that the more complex five-coordinate spectrum would probably mask the simpler four-coordinate spectrum, particularly at the higher frequency end of the spectrum.

This equilibrium is not sensitive to temperature changes over the range -6° to +42° as shown by the constant magnetic moment of $(dPP)_2NiCl_2$ over this temperature range. As expected, however, the equilibrium is apparently sensitive to the presence of added ligand. Thus, the solution magnetic moment of $(dPP)_2NiCl_2$ at 42° drops from 1.90 to 1.72 B.M. on addition of free ligand.

It appears, therefore, that the complexes initially formulated as conventional four-coordinate complexes L_2NiCl_2 (L = mPP, dPP, dBP) are, in fact, basically dimeric five-coordinate structures of an unusual, but not unknown, type existing in equilibrium with undetermined quantities of four-coordinate monomeric structures. X-ray crystal structure determinations would clearly be desirable here.

All of the above discussion raises questions regarding the exact nature of the complex of formula L_2NiCl_2 obtained by Quin (13) from 1-benzyl-3,4-dimethylphosphole (V, R = CH_2Ph) for which relatively little structural evidence was offered. It might be expected that this complex would be analogous to the above complexes rather than the simple monomeric, cis, slightly distorted, square-planar structure proposed by Quin (13). However, it does appear that Quin's complex is a monomeric, diamagnetic (and therefore square-planar) structure since it shows an extremely simple nmr spectrum in which all of the methyl protons are magnetically equivalent and appear as a slightly broadened singlet (^{31}P-H coupling is removed by complexation) inductively shifted slightly downfield (by 0.23 ppm) from the location of the methyl protons in the spectrum of the free ligand.

Furthermore, Quin's complex is purple while $(mPP)_2NiCl_2$, $(dPP)_2NiCl_2$ and $(dBP)_2NiCl_2$ described above are brown and, in addition, Quin's complex has a distinct melting point while all of the complexes described in this paper merely undergo decomposition between 100° and 200°.

Why 1-benzyl-3,4-dimethylphosphole should behave differently from the phospholes discussed earlier in this paper is not clear since two of these phospholes are 3,4-dimethyl substituted. It is true that in the 1-benzyl-phosphole, the phosphorus atom bears an alkyl substituent but this is true also of dBP (V, R = n-Bu) although the actual substituents are considerably different in structure. It is also true that Quin's complex was made in a somewhat different manner using a stoichiometric quantity of anhydrous $NiCl_2$ in absolute ethanol at room temperature but it is difficult to see that this would affect the nature of the product. For the moment, these differences in behaviour must remain unexplained but further discussion will be made in the summary and conclusions section of this paper.

Turning now to the apparently five-coordinate complex analyzing as $(PP)_3NiCl_2$, spectroscopic and magnetic data show quite clearly that the Ni(II) ion is a four-coordinate square-planar species. The infrared spectrum shows a single Ni-Cl band at 320-cm^{-1} which apparently rules out a trans L_2NiCl_2 type structure while a tetrahedral or cis square-planar geometry containing the L_2NiCl_2 unit would normally show two bands in this region.

The electronic spectra (Table 2) in the solid state and in solution are much more informative and are typical (22) of d^8 square-planar systems which suggests that one of the groupings present is dissociated from the Ni(II) ion. The ir spectrum discussed above suggests that this is a phosphole grouping since there is no good ir evidence for the L_2NiCl_2 unit in any geometrical arrangement and the presence of only one Ni-Cl band in the spectrum is consistent with the presence of only one Ni-Cl linkage. This suggests that the complex analyzing as $(PP)_3NiCl_2$ may be the ionic system $[(PP)_3NiCl]^+Cl^-$.

Very strong evidence for this solution state formulation is provided by conductance measurements (Table 3) in 1.00×10^{-3} M dichloromethane solution which show the complex to be a 1:1 electrolyte. For com-

Complex	Concentration (M)	$\Lambda(\text{ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1})$
$[(PP)_3NiCl]^+$ Cl^-	1.00×10^{-3} (a)	7.7
$[(PP)_3PdCl]^+$ Cl^-	1.17×10^{-3} (a)	9.4
$[(dPP)_3PtCl]^+$ Cl^-	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

(a) Dichloromethane.

parison purposes, molar conductivity data for typical 1:1 electrolytes are included in Table 3.

The only minor anomaly in this assignment comes from the magnetic moment (Table 1) which although low (1.49 B.M. in the solid state and 1.45 B.M. in solution) is not zero as would be expected for a square planar complex. However, certain square planar Ni(II) complexes have been reported (23) to show anomalous magnetic moments, e.g. μ_{eff} = 1.50 B.M. for $L'_2Ni(ClO_4)_2$ where L' = the bidentate bisphosphine IX. This has been attributed to axial perturbations and such perturbations may well occur in the phosphole complex $[(PP)_3NiCl]^+Cl^-$.

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Thus, although the structures of the phosphole Ni(II) complexes cannot be regarded as having been established beyond all possible doubt (X-ray crystal structures would be necessary for this), the formulations proposed in the foregoing discussion are entirely consistent with the available evidence. More important in the context of phosphole chemistry, it is clear that the phospholes PP, mPP, dPP and dBP behave primarily as normal phosphines in complex formation with Ni(II) chloride although some of the complex structures are a little unusual. The significance of these results will be discussed further later in this paper.

Reactions With the Chorides of Pd(II) and Pt(II).

Similar results were obtained in reactions with Pd(II) and Pt(II) systems although structures were less well established. Thus, air stable, orange-yellow complexes of formula L_2PdCl_2 (L = mPP or dPP) can be synthesized by heating a mixture of Pd(II) chloride and ligand (3-fold excess) in ethanol under reflux. However, under similar conditions, PP behaves with Pd(II) as it does with Ni(II) giving a brown solid analyzing as $(PP)_3PdCl_2$. Only oils were obtained with dBP. The complexes can be recrystallized unchanged from dichloromethane-ether solutions. Molecular weight data for the Pd(II) and Pt(II) complexes could not be obtained because of the small quantities of each complex available.

The infrared spectra of the complexes analyzing as

$(mPP)_2PdCl_2$ and $(dPP)_2PdCl_2$ are virtually identical (Table 1) in the Pd-Cl stretching region with two absorptions in the 290-316 cm^{-1} range. These are strongly suggestive of the presence of cis square-planar arrangements although it should be noted that the Pd-P vibration may appear in this region (20). This formulation is also strongly supported for $(dPP)_2PdCl_2$ by the solution (dichloromethane, 1.87 x 10^{-2} M) electronic spectrum which shows absorption at 16000 cm^{-1} (ϵ = 9) and 20500 cm^{-1} (ϵ = 29) entirely consistent with a square-planar d^8 system. The electronic spectrum of $(mPP)_2PdCl_2$ is less informative and shows, rather surprisingly, only one band at 29500 cm^{-1} which is possibly a charge-transfer band. The infrared spectra of the two complexes are so similar, however, that it is highly likely that, at least in the solid state, they have very similar basically cis square-planar structures. On the other hand, the possibility cannot be ignored that five-coordinate dimeric/four-coordinate monomeric equilibria of the type observed with the L_2NiCl_2 complexes occur also with Pd although the electronic spectra of $(dPP)_2PdCl_2$ indicate that the equilibrium is heavily on the monomeric side.

Unlike the Ni(II) complexes already discussed, the Pd(II) complexes are diamagnetic and it has therefore been possible to obtain a ^1H nmr spectrum for $(dPP)_2PdCl_2$. While the spectrum is poorly resolved and does not give any information of major importance, it does show interesting features and a brief description is therefore in order. Thus, in the spectrum of $(dPP)_2PdCl_2$, two sets of methyl signals appear at τ 8.01 and τ 8.27, with the higher field signal being broader and apparently of slightly (ca. 20%) greater area although signal overlap at the bases of the peaks and the presence of other weak signals in the same region makes accurate intergration difficult.

Both of these signals are shifted upfield relative to the corresponding methyl proton signal in the spectrum of the free ligand (τ 7.87) whereas a downfield shift due to the inductive effect of a coordinated phosphorus atom might have been expected.

The spectrum is therefore consistent with two possibilities. The first is that the two P atoms and the two Cl atoms are in a cis square-planar arrangement in which either the two five-membered rings are arranged identically but in such a manner that the two methyl groups on each ligand are magnetically non equivalent (e.g., with the two five-membered rings coplanar), or the planes of the two rings are arranged differently but each ring contains two magnetically identical methyl groups. The second possibility is that the two methyl signals are due to two different species present in similar quantities - i.e., a five-coordinate/four-coordinate equilibrium as observed with L_2NiCl_2. Further speculation at this stage is largely fruitless but the apparent inequality of the methyl proton peak areas in the spectrum is suggestive of an equilibrium

of the L_2NiCl_2 type. As will be seen shortly, similar effects are observed with the corresponding Pt(II) systems where two different species are clearly present.

The aromatic protons are, as expected, inductively shifted by 5 Hz to lower field and what appears to be two of the four ring olefinic protons appear as two very broad overlapping humps in the range τ 3.0-4.0.

Considering now the Pd(II) complex analyzing as $(PP)_3PdCl_2$, the presence of two probable Pd-Cl bands in the ir spectrum (Table 1) at 295 and 310 cm^{-1} suggest that the palladium atom may be five-coordinate. The electronic spectra of this complex (Table 2) (in both the solid state and in solution), however, do not yield any positive information in this respect as the spectra are relatively featureless except for a charge-transfer band at 30300 cm^{-1}. Five coordinate Pd(II) complexes normally show bands only at 19000-23000 cm^{-1} (26).

Conductance measurements (Table 3), on the other hand, strongly indicate that in solution, the species is a 1:1 electrolyte and the Pd(II) ion is therefore square planar due to the dissociation of chloride ion as occurs with the analogous Ni(II) system discussed earlier.

$$(PP)_3PdCl_2 \rightleftharpoons [(PP)_3PdCl]^+ \; Cl^-$$
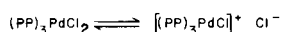
There is no way (short of X-ray crystallographic data) of estimating whether this ionization is significant in the solid state but the magnitude of the molar conductance shows that in solution, the dissociation lies far to the right. Ionic Pd(II) complexes of this type, e.g., $[(Ph_2PH)_3PdBr]^+$ Br$^-$, are well-known (24).

Regarding the Pt(II) complexes, the picture is broadly the same as with Pd(II). Thus, both PP and mPP (in 3-fold excess) react with Pt(II) chloride in ethanol under reflux to form white solids analyzing as L_2PtCl_2 (L= PP or mPP), but under similar conditions, the more heavily substituted dPP and PtCl₂ form an air stable complex analyzing (after recrystallization from ether-dichloromethane) as $(dPP)_3PtCl_2 \cdot 0.5CH_2Cl_2$. The presence of incorporated dichloromethane in the crystal lattice was confirmed by ^1H nmr spectrometry which showed the dichloromethane peak, as expected, at τ 4.70. All of the complexes are diamagnetic.

The ir spectra of the complexes (Table 1) are basically similar to those of the analogous Pd(II) complexes.

The electronic spectra of all three complexes show no d-d transitions in both the solid state and in solution and the only significant feature of the spectra is a charge-transfer band at around 28600 cm^{-1} (ϵ = 1890 for $(dPP)_3PtCl_2$). However, in dichloromethane solution, the dPP complex is a 1:1 electrolyte showing that like the similar complexes $(PP)_3NiCl_2$ and $(PP)_3PdCl_2$ already discussed, $(dPP)_3PtCl_2$ is an ionic species of the type $[(dPP)_3PtCl]^+ Cl^-$.

^1H nmr data were also obtainable for the $(mPP)_2PtCl_2$

complex and they show effects broadly similar to those observed with $(dPP)_2PdCl_2$. Thus, for $(mPP)_2PtCl_2$, two well separated methyl signals are observed with one 26 Hz upfield and the other 40 Hz downfield relative to the methyl proton signal in the spectrum of the free ligand. The lower field peak is extremely broad and poorly defined but is about 50% greater in area than the considerably sharper higher field peak. This is again strongly suggestive of the presence of a mixture of two complexes as observed with the Ni(II) and Pd(II) systems. There is no evidence for ^{195}Pt-CH_3 coupling unless the broadness of the lower field methyl signal is due to this. Such couplings should, however, be small since coupling would be through five bonds.

Thus, the behaviour of the phospholes PP, mPP and dPP with Pt(II) is apparently much the same as with Pd(II) except that with Pd(II) (and also Ni(II)) it is the least substituted ligand (PP) which forms the ionic complex $(PP)_3MCl^+Cl^-$, whereas with Pt(II), it is the most substituted ligand dPP which forms this type of complex.

It should be noted that, from ir evidence, the cis isomers of the square-planar components of the L_2PdCl_2 and L_2PtCl_2 mixtures appear to be favoured. This may be quite informative since it has been observed (25) that the cis isomers of Pd(II) and also Pt(II) are thermodynamically more stable than the trans isomers and, in solution, cis-trans equilibria occur. Furthermore, the amount of trans isomer initially formed depends upon two factors. First, as the basicity of the phosphine increases, the amount of trans isomer initially formed decreases. Also, the amount of trans isomer decreases with decreasing steric bulk of the ligand. One might tentatively deduce then that the phospholes PP, mPP and dPP are behaving as reasonably basic and compact normal secondary or tertiary phosphines.

Summary and Conclusions.

Although, as mentioned earlier, certain points regarding the inorganic chemistry of the complexes described in this paper remain to be clarified, some preliminary comments regarding the donor character of simple phospholes may be made.

For example, as mentioned above, the phospholes studied here appear to be reasonably nucleophilic, sterically relatively compact ligands which behave similarly to other phosphines in ease of complex formation although the type of complex formed is somewhat less common. On the other hand, on the basis of results reported in this paper, it is not possible to establish the relative donor character of the four phospholes studied although studies with Group VIII metal carbonyl chlorides (to be discussed in a later paper (19)) have yielded information of this type.

The most significant results have come from the studies with Ni(II). For example, it is clear that 3- or

3,4-disubstitution in the phosphole ring is not necessary for complex formation as might be implied from Quin's results (13) with 1-methylphosphole and 1-benzylphosphole since 1-phenylphosphole (PP) readily forms a nickel complex. Similarly, the fact that all four phospholes PP, mPP, dPP and dBP form Ni(II) complexes easily suggests that the substituent upon the phosphorus atom is not too critical. The one tentative generalization which fits all of the available data on Ni(II) is that only simple phospholes with alkyl substituents upon the phosphorus and no substituents upon the ring (i.e., as in 1-methylphosphole and 1-benzylphosphole but not 1-phenylphosphole) are resistant to complex formation with Ni(II).

Whether this means that 1-alkylphospholes are more aromatic than other phospholes is debatable. It may mean only that the non-bonding orbital is not the HOMO in these systems but is the HOMO in the phospholes used in the present study. Alternatively the ease of perturbation of an electronic structure in which the non-bonding pair is not the HOMO by a transition metal ion (already observed with phosphorins (26)) varies with the phosphole substitution pattern. Unfortunately, there is little data available on orbital sequences in phospholes but it is worth noting that in 1-phenylphosphole, photoelectron spectroscopic studies (9) indicate that the non-bonding orbital and the highest π-orbital are of virtually equal energy, i.e., the n-orbital is effectively the HOMO. The same study suggests that in 2,5-dimethyl-2-phenylphosphole, the n-orbital is not the HOMO by a large energy margin and complexation studies with this phosphole would be desirable.

As discussed in the introduction, however, it now seems probable that phospholes are indeed aromatic since recent theoretical studies by Epiotis and Cherry (4) strongly suggest that phospholes are both aromatic and pyramidal in the ground state and contradict the findings (later contradicted by Schäfer, et al., themselves (2)), of Schäfer, et al., (9) that ionization potential measurements of the non-bonding pairs indicate no aromaticity in phospholes. Apparently, it is the ionization potentials of the electrons in other orbitals which should give information of this type. Further support for aromaticity in 1-benzylphosphole, a phosphole particularly relevant to this discussion, comes from crystallographic studies (27) which show that the ring P—C bonds in the 1-benzylphosphole are unusually short.

What the study by Epiotis and Cherry did not show (as stated by the authors) is the degree of aromatic character in the pyramidal ground state although they did propose a method of establishing this. Clearly, this may be dependent upon the substitution pattern and, with regard to Quin's studies and our studies here with phosphole - Ni(II) systems, the available evidence would appear to indicate that the Ni(II) ion may be able to form complexes with phospholes which are only weakly aromatic in the

pyramidal ground state but not with phospholes which have a higher degree of lone pair diene interaction in this pyramidal state. In this connection, it may be significant that for 1-phenylphosphole, Epiotis and Cherry (4) found (contrary to previous findings by others (9)) that the phosphorus non-bonding pair interacts to some extent with the phenyl ring. Such interactions would be impossible with 1-alkylphospholes. Clearly this conclusion is only very tentative and further work on this intriguing problem is desirable.

EXPERIMENTAL

All reactions were carried out in a glove box (since the phospholes are air-sensitive) constantly flushed with dry, oxygen-free nitrogen. Yields were always in the range 60-80%. All solvents were distilled and degassed and stored over molecular sieves (Type 4A) under nitrogen. All solid reagents weighed in air were crushed and pumped to remove oxygen before use in the glove box.

The phosphole ligands were prepared by the method of Mathey, et al., (28), with only minor modifications to the procedure, and were used within a few hours of preparation.

The ir studies were carried out on a Beckman IR12 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 ir region (650-4000 cm^{-1}). The spectra were calibrated with a polystyrene reference film. Visible and ultraviolet spectra (reflectance and solution) were measured on a Cary 14 recording spectrophotometer. Nmr spectra were obtained using a Varian Associates model A60-A spectrometer using deuteriochloroform as solvent with tetramethylsilane as internal standard.

Molar conductivities were measured on a YSI model 31 conductivity bridge at 25°. 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$_2$O$_3$) (en = ethylenediamine) or by the nmr method described by Evans (29). The molecular weight determinations were made using a Knauer electronic temperature measuring vapour-pressure osmometer.

Nickel was analyzed by the standard volumetric procedure using EDTA after the metal complexes had been decomposed by treatment with concentrated nitric acid. Chloride ion was determined by potentiometric titration with silver nitrate after the samples had been digested with concentrated aqueous ammonia. It should be noted that in the case of the nickel complexes, chloride analyses were inexplicably variable and almost always slightly low. For the nickel complexes, therefore, only C, H and Ni analyses are quoted. These were accurately reproducible. Carbon-hydrogen analyses were carried out on a Perkin-Elmer model 240 CHN analyser. Melting points are not quoted since all of the complexes decompose slowly in the range 100-200°.

Nickel Complexes.

In a typical reaction, 3,4-dimethyl-1-phenylphosphole (dPP) (0.55 g., 2.9 mmoles) was added dropwise to nickel(II) chloride hexahydrate (0.17 g., 0.71 mmole) in ethanol (ca. 20 mL.) at room temperature. Upon completion of the addition, the mixture was heated under reflux for 12 hours. The cooled mixture was then centrifuged to remove small quantities of suspended material and the clear solution was treated with ether to precipitate the crude

complex. This complex was recrystallized from dichloromethane-ether to give the brown solid complex $(dPP)_2NiCl_2$ in *ca.* 70% yield.

Anal. Calcd. for $C_{24}H_{26}P_2NiCl_2$: C, 56.9; H, 5.2; Ni, 11.7. Found: C, 56.7; H, 5.7; Ni, 11.1.

Under similar conditions to those outlined above, 3-methyl-1-phenylphosphole (mPP) gave the complex $(mPP)_2NiCl_2$ while 1-*n*-butyl-3,4-dimethylphosphole (dBP) gave $(dBP)_2NiCl_2$ in comparable yields to those obtained with dPP.

Anal. Calcd. for $C_{22}H_{22}P_2NiCl_2$: C, 55.2; H, 4.6; Ni, 12.3. Found: C, 55.8; H, 5.1; Ni, 11.7.

Anal. Calcd. for $C_{20}H_{34}P_2NiCl_2$: C, 51.5; H, 7.3; Ni, 12.7. Found: C, 52.7; H, 8.1; Ni, 11.9.

In contrast, 1-phenylphosphole (PP) under virtually identical conditions gave $(PP)_3NiCl_2$ in similar yields.

Anal. Calcd. for $C_{30}H_{27}P_3NiCl_2$: C, 59.0; H, 4.5; Ni, 9.6. Found: C, 59.6; H, 5.4; Ni, 8.8.

Palladium and Platinum Complexes.

The palladium and platinum complexes were prepared by a virtually identical procedure to that outlined for the nickel complexes. Similar quantitites of reagents were used and similar yields were obtained. By this process, 3,4-dimethyl-1-phenylphosphole (dPP) gave, with $PdCl_2$, $(dPP)_2PdCl_2$ (orange solid), 3-methyl-1-phenylphosphole (mPP) gave $(mPP)_2PdCl_2$ (orange solid) and 1-phenylphosphole (PP) gave $(PP)_3PdCl_2$ (brown solid). 1-*n*-Butyl-3,4-dimethylphosphole (dBP) gave only uncharacterizable oils.

Anal. Calcd. for $C_{24}H_{26}P_2PdCl_2$: C, 52.0; H, 4.7; Cl, 12.8. Found: C, 52.2; H, 4.9; Cl, 12.5.

Anal. Calcd. for $C_{22}H_{22}P_2PdCl_2$: C, 50.3; H, 4.2; Cl, 13.5. Found: C, 49.9; H, 4.7; Cl, 13.5.

Anal. Calcd. for $C_{30}H_{27}P_3PdCl_2$: C, 54.8; H, 4.1; Cl, 10.8. Found: C, 54.5; H, 4.5; Cl, 10.6.

With Pt(II) chloride, the phospholes PP and mPP gave the colourless bis-adducts $(PP)_2PtCl_2$ and $(mPP)_2PtCl_2$ while dPP gave the pale-yellow, solvated tris-adduct $(dPP)_3PtCl_2 \cdot 0.5CH_2Cl_2$. Again, yields were in the 60-80% range and the presence of dichloromethane in the dPP adduct was confirmed by nmr spectrometry.

Anal. Calcd. for $C_{20}H_{18}P_2PtCl_2$: C, 41.0; H, 3.1; Cl, 12.1. Found: C, 40.9; H, 3.1; Cl, 12.1.

Anal. Calcd. for $C_{22}H_{22}P_2PtCl_2$: C, 43.0; H, 3.6; Cl, 11.6. Found: C, 43.1; H, 4.1; Cl, 11.3.

Anal. Calcd. for $C_{36}H_{39}P_3PtCl_2 \cdot 0.5CH_2Cl_2$: C, 50.2; H, 4.6; ionizable Cl, 8.1. Found: C, 49.9; H, 5.0; Cl, 8.6.

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