Ruthenium, Cobalt, Rhodium and Iridium Chlorides and of

Some Chlorocarbonyls of Ruthenium and Rhodium

*David G. Holah, Alan N. Hughes, Benjamin C. Hui and Pui-Kwan Tse*

Department of Chemistry, Lakehead University, Thunder Bay, Ontario, Canada P7B 5E1
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The reactions of 1-phenylphosphole (PP), 3-methyl-1-phenylphosphole (mPP), 3,4-dimethyl-1-phenylphosphole (dPP) and, in certain instances, 1-n-butyl-3,4-dimethylphosphole (dBP) with some transition metal chlorides and some metal-Cl-CO systems are reported. These reactions show that simple phospholes in general unexpectedly behave much like ordinary tertiary phosphines and that, unlike the reactions with Ni(II), Pd(II) and Pt(II), the complexes formed are conventional in most respects. However, a few unusual reactions were observed. For example, mPP partially reduces Ru(III) to give a mixed-valent Ru(III)-Ru(II) complex while PP reduces Ir(III) to Ir(I). From infrared spectroscopic studies of the square-planar Rh(I) complexes $L_2Rh(CO)Cl$ (L = phosphole), it appears that donor character decreases with decreasing substitution on the phosphole ring carbon atoms. Phosphorus-phenyl cleavage has been observed in reactions of 1-phenylphosphole with Rh-CO systems. The results are briefly discussed in relation to the behaviour of other phospholes in similar reactions and in the context of the electronic structure of phospholes.

In a previous paper (1) concerned with complexes of the simple phospholes, 1-phenylphosphole (I, R = phenyl, designated here as PP), 3-methyl-1-phenylphosphole (II, mPP), 3,4-dimethyl-1-phenylphosphole (III, R = phenyl, dPP) and 1-n-butyl-3,4-dimethylphosphole (III, R = n-butyl, dBP) with the chlorides of Ni(II), Pd(II) and Pt(II), we briefly surveyed the known coordination chemistry of simple phospholes (2) in the context of the possible aromatic nature of the phosphole system. In addition, it was found that, contrary to Quin's earlier observations (3) regarding the reluctance of 1-alkylphospholes to undergo Ni(II) complex formation unless 3,4-dialkyl substituted, simple phospholes in general behave as reasonably nucleophilic and sterically compact ligands which form σ complexes readily with Ni(II) and also with the isoelectronic Pd(II) and Pt(II) systems. On the other hand, the complexes formed are of unusual, but not unknown types and are apparently totally different from the only other known (3) simple phosphole-Ni(II) complex obtained from 1-benzyl-3,4-dimethylphosphole (III, R = benzyl).
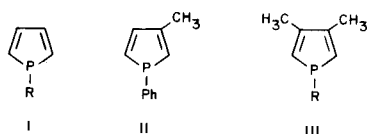
In short, III (R = CH₂Ph) behaves as a normal tertiary phosphine, PP, mPP, dPP and dBP, like phosphines in general, form Ni(II) complexes but these complexes have somewhat unusual structures, and 1-alkylphospholes without further ring substitution show no phosphine character in these reactions.

Apart from the observation that, as a general rule, most simple phospholes will form Ni(II) complexes fairly readily, only one tentative deduction was made from these results (1). Thus, to rationalize Quin's observations (3) that 1-alkylphospholes without further substituents in the ring will not form Ni(II) complexes while the phospholes PP, mPP, dPP and dBP clearly will, it was suggested (1) that the results of both studies may indicate that the degree of aromatic character in the phosphole system may be very sensitive to the substitution pattern with very simple 1-alkylphospholes having more aromatic character than more heavily substituted systems. Alternatively, as noted earlier, the results may simply reflect variations in the orbital sequences in the various phospholes with phospholes in which the phosphorus lone-pair is not in the HOMO being poorer donors in these reactions. That simple phospholes are pyramidal but at least to some degree aromatic molecules now appears to be beyond dispute (4,5) and further coordination studies would therefore have some bearing upon the aromaticity problem.

The results discussed above, of course, raise more questions than they answer. For example, does the unusual nature of the phosphole complexes produced with Ni(II) (as compared with those produced by normal tertiary phosphines) mean that simple phosphole complexes of transition metal systems in general will also have unusual characteristics? Also, will simple phospholes reduce systems like Rh(III) and Ru(III) to Rh(I) and Ru(II) respectively as do several more normal tertiary phosphines (6)? In addition, what factors determine the relative donor characters of the various simple phospholes studied and do these variations in donor character arise from variations in the degree of ground state aromatic character, variations

in the orbital sequences or some other electronic or steric property of phospholes?

It should be mentioned here that some information on the relative donor strengths of phospholes has already been obtained (7) from studies of complex formation with manganese carbonyls. Thus, simple phospholes react (7) with $Mn_2(CO)_{10}$ to give several different types of complex among which is the σ, π system IV in which the phosphorus atom is σ bonded to one manganese atom while the dienoid portion of the phosphole ring is π bonded to another manganese atom. Related σ, π complexes have been obtained (2b) from $Fe_3(CO)_{12}$. From variations in the several infrared carbonyl stretching frequencies of the complexes IV (decrease in CO frequency as a result of greater phosphole donor character), it was suggested (7)
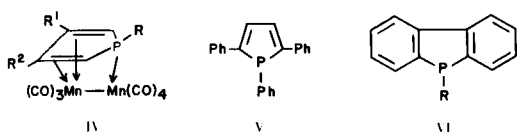
that phosphole donor strength decreases in the order III (R = t-butyl) $\simeq$ III (R = n-butyl) > III (R = phenyl) $\simeq$ III (R = benzyl) > II > I (R = phenyl) which is effectively the order of decreasing substitution of the ring carbon atoms. This was found (7) to agree with the apparent (8,9) order of decreasing basic character of these phospholes.

The system IV, however, is very complex and contains seven carbonyl groups. Moreover, both the phosphorus lone-pair electrons and the π system are involved in the bonding in the complex. It seemed desirable, therefore, in addition to the further coordination studies mentioned earlier, to measure variations in the CO stretching frequency in phosphole-metal carbonyl complexes in situations where only σ bonding of the phosphole occurs, where the geometry of the system is very simple (e.g., square-planar) and where very few (preferably only one) carbonyl groups are present. Furthermore, it seemed desirable to extend Mathey's studies (2,7,10) with metal(0) carbonyls to transition metal carbonyl systems in higher oxidation states.

Thus, this paper reports not only the coordination chemistry of simple phospholes with a variety of transition metal salts (chlorides of rhenium, ruthenium, cobalt, rhodium and iridium) and chlorocarbonyl systems but also the significance of these results to the chemistry of phospholes in general. As in the previous study (1), the phospholes used were PP (I, R = phenyl), mPP (II), dPP (III, R = phenyl), and, on occasion, dBP (III, R = n-butyl). In the later discussion, comparison with the known behaviour of the more complex phosphole derivatives 1,2,5-triphenylphosphole (V, designated here as TPP) and 5-phenyl-5H-dibenzophosphole (VI, DBP) will also be made. For convenience, the organization of this paper will be

by metal rather than by phosphole.

Results.

A. Rhenium.

Both mPP and dPP react immediately with Re_3Cl_9 in ethanol at room temperature to form stable, diamagnetic complexes of formula $L_3Re_3Cl_9$ (L = mPP or dPP) as occurs with more normal tertiary phosphines (11,12). This is different behaviour from the more bulky TPP and DBP systems which form (13) (under reflux) the less stable solvated bis-phosphole complexes $L_2Re_3Cl_9 \cdot CH_2Cl_2$ (L = TPP or DBP), implying that the simple phospholes are better donors than TPP or DBP although steric effects could also be involved since TPP, DBP and Re_3Cl_9 are all crowded systems. Reactions with PP were not attempted since relatively small amounts of this ligand were available and it seemed likely that more significant results would be obtained from other transition metal salts.

The spectroscopic properties of these products are entirely conventional and are very similar to those of the analogous triphenylphosphine complexes (11,12). Some infrared data are recorded in the Table.

B. Ruthenium.

The three phospholes dPP, mPP and PP, like triphenylphosphine, all stabilize Ru(III) in reactions with $RuCl_3 \cdot 3H_2O$ in ethanol at room temperature. With dPP, the $tris$-ligand complex $(dPP)_3RuCl_3$ is obtained but mPP and PP appear to give $LRuCl_3$ (L = mPP or PP) under these conditions. These last two complexes are insoluble in most common solvents and purification is difficult. However, purification of $(mPP)RuCl_3$ was effected by successive washings of the crude material with ethanol, dichloromethane and ether although the PP complex defied all efforts at further purification by this method. The dPP $tris$-ligand complex reported above is analogous to the well-known L_3RuCl_3 (L = PEt_2Ph (14) or PPh_3 (15)) and has similar magnetic properties (μ eff = 1.78 B.M.).

By prolonging the reaction time or by carrying out the reactions under reflux in ethanol with four-fold excesses of ligand, complete reduction of Ru(III) to Ru(II) by PP or dPP is observed and the complexes L_3RuCl_2 (L = PP or dPP) are obtained. Surprisingly, only partial reduction of Ru(III) occurs when mPP (five-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. This compound is analogous to the crystallographically characterised $(n-Bu_3P)_4Ru_2Cl_5$, the structure of which has been established (16,17) as VII. Again, magnetic data (μ eff = 1.27 B.M. per ruthenium atom) are consistent

Table

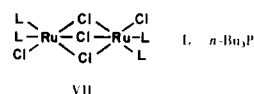Analytical and Spectroscopic Data

Complex	Color	Calculated C	Calculated H	Calculated Cl or Co (g)	Found C	Found H	Found Cl or Co (g)	ν M–Cl	Infrared Other
(mPP)₃Re₃Cl₉ (a,f)	purple	28.3	2.4	22.8	28.8	2.8	22.9	305sh, 325	
(dPP)₃Re₃Cl₉ (a,f)	brown	30.0	2.7	22.1	30.2	2.9	21.9	208, 325, 307?	
(PP)₃RuCl₂.0.5CH₂Cl₂ (b,c)	brown	52.7	4.1	10.2	53.2	4.6	10.2	250, 310	
(mPP)₄Ru₂Cl₅ (b,c)	brown	49.1	4.1	16.5	49.7	4.4	16.1	235, 320	
(mPP)RuCl₃ (a,f)	greenish brown	34.6	2.9	27.9	34.7	3.6	28.0		
(dPP)₃RuCl₂ (b,c)	brown	58.7	5.3	9.6	58.5	5.6	9.6	270, 325	
(dPP)₃RuCl₃ (a,d)	reddish brown	56.0	5.1	13.8	56.6	5.1	13.7	295, 336	
(mPP)₃Ru(CO)Cl₂.CH₂Cl₂	brown	52.1	4.4	8.8	51.7	4.7	8.7	320	1960 (M–CO)
(PP)₂CoCl₂.H₂O (b,e)	green	51.3	4.3	(12.6)	51.3	4.5	(11.9)	310	3400-3600 (H₂O)
(mPP)₂CoCl₂.0.5CH₂Cl₂ (b,c)	green	51.9	4.5	(11.3)	51.9	4.8	(11.9)	300	
(dPP)₂CoCl₂.0.5CH₂Cl₂ (b,c)	green	53.6	5.0	(10.8)	53.6	5.1	(9.4)(h)	315	
(dBP)₂CoCl₂.0.5CH₂Cl₂ (b,c)	green	48.4	6.9	(11.6)	48.7	7.1	(12.3)	320	
(mPP)₃RhCl₃ (b)	yellow	54.2	4.5	14.5	54.1	4.7	14.5	280, 310	
(mPP)₃RhCl₃.0.5CH₂Cl₂ (b,c)	yellow	51.9	4.4	13.8	51.6	4.8	13.5	280, 310	
(dPP)₃RhCl₃.CH₂Cl₂ (b,c)	yellow	51.7	4.8	12.4	51.3	4.7	11.9	290, 320	
(PP)₃Rh(PhCO)Cl₂.CH₂Cl₂?	yellow	54.0	4.1	8.4	54.3	4.7	9.5	295, 310	1680 (PhCO)
(mPP)₅Rh₂(CO)Cl₄	yellow	53.9	4.4	11.4	53.9	5.0	11.9	280, 300	1970, 2050 (Rh–CO)
(dPP)₅Rh₂(CO)Cl₄	yellow	55.6	5.0	10.8	55.3	5.4	11.2	285, 320	1960 (Rh–CO)
(PP)₅Rh₂Cl₄	yellow	52.3	4.0	12.4	53.1	4.5	12.3	305, 325	
(mPP)₅Rh₂Cl₄	yellow	54.2	4.6	11.7	54.4	5.2	11.6	275, 310	
(dPP)₅Rh₂Cl₄	yellow	55.9	5.1	11.0	55.9	5.5	11.1	280, 320, 340	
(PP)₂Rh(CO)Cl (cis-trans)	yellow	51.8	3.7	7.3	51.5	3.9	7.3	290, 315	1970, 2060 (CO)
(mPP)₂Rh(CO)Cl (cis-trans)	yellow	53.7	4.3	6.9	54.3	4.5	7.5	290, 320	1970, 2070 (CO)
(dPP)₂Rh(CO)Cl (trans)	yellow	55.3	4.8	6.6	55.5	4.8	6.8	310	
(mPP)₃RhCl.0.5CH₂Cl₂	yellow	57.2	4.9	5.1	57.6	5.1	5.1	295	
(dPP)₃RhCl	yellow	61.5	5.6	5.1	62.0	5.9	5.0	280	
(PP)₃IrCl (b,c)	yellow	50.9	3.9	5.0	50.5	4.4	5.4	320	
(mPP)₃IrCl₃ (b,c)	orange	48.3	4.1	13.0	48.1	4.3	12.5	315	
(dPP)₃IrCl₃ (b,c)	orange	50.1	4.6	12.3	50.8	4.9	11.6	310	

(a) Preparation method A. (b) Preparation method B. (c) Recrystallized from dichloromethane/ethyl ether. (d) Recrystallized from dichloromethane/hexane. (e) Recrystallized from acetonitrile/diethyl ether. (f) Compound obtained pure after initial washing. (g) Ionizable chloride: Co analyses in parentheses. (h) This anomalously low cobalt analysis could not be improved.

with such a dimeric, mixed-valent structure for (mPP)$_4$-Ru$_2$Cl$_5$.

In contrast, when the reaction between Ru(III) chloride and mPP is carried out in n-butyl alcohol under reflux, complete reduction of Ru(III) to Ru(II) and also abstraction of CO from the solvent occur with formation of the chlorocarbonyl species (mPP)$_3$Ru(CO)Cl$_2$. Similar Ru(II) complexes of ordinary tertiary phosphines such as (PPh-Et$_2$)$_3$Ru(CO)X$_2$ (X = Cl, Br, I) (15) and (PPhMe$_2$)$_3$Ru-(CO)X$_2$ (X = Cl, Br, I or SCN) (18) are well known and have been prepared using 2-methoxyethanol as a solvent at room temperature.

Some infrared spectroscopic data for these ruthenium complexes are recorded in the Table. In addition, it should be noted that the electronic spectra in solution and in the solid state for (dPP)$_3$RuCl$_2$ are different. Thus, in dichloromethane solution, the spectrum (19,600 cm^{-1} and 25,000 cm^{-1}) of (dPP)$_3$RuCl$_2$ is very similar to that of the analogous complex (PPh$_3$)$_3$RuCl$_2$ (19) in dimethyl-acetamide (DMA) solution in which the bands are associated with the (PPh$_3$)$_2$RuCl$_2$ species which arises through dissociation. In dichloromethane solution, the dPP complex is a non-conductor and this is consistent with a similar dissociation of a phosphole molecule from the complex to give the species (dPP)$_2$RuCl$_2$.

Considering briefly the infrared spectrum of (mPP)$_3$-Ru(CO)Cl$_2$ (Table), the fact that the stretching frequency of the carbonyl group falls in the same range as that of (PPhMe$_2$)$_3$Ru(CO)Cl$_2$, in which the chloride groups are in a *trans* arrangement, suggests that the phosphole complex has a similar structure. *Cis*-isomers of L$_3$Ru(CO)Cl$_2$ (L = dimethylphenylphosphine, ν CO = 1928 cm^{-1}; di-ethylphenylphosphine, ν CO = 1942 cm^{-1}) show CO stretching frequencies at slightly lower wavenumber values.

C. Cobalt.

From reactions between cobalt(II) chloride hexahydrate and PP, mPP, dPP and dBP, air-stable, crystalline solids of formula L$_2$CoCl$_2$·0.5CH$_2$Cl$_2$ (L = mPP, dPP or dBP) and (PP)$_2$CoCl$_2$·H$_2$O have been isolated. Even after re-crystallization and prolonged drying under reduced pressure (10^{-5} torr), the solvent of crystallization could not be removed as is often the case with phsophole and related complexes (20,21). The presence of the solvents of crystallization was confirmed by mass spectrometry (for di-chloromethane) and ir spectrophotometry (for water).

The similarity of the spectroscopic (electronic) and magnetic (μ eff = *ca.* 4 B.M.) data for these compounds with such data for the known tetrahedral dichlorobis(tri-phenylphosphine)cobalt(II) (22,23) leaves little doubt that the phosphole complexes have the same type of structure as the triphenylphosphine complex and this implies that the phosphole and phosphine ligands have similar donor strengths.

In contrast, TPP does not complex with Co(II) (20) and it seems that once again the simple phospholes show greater donor character than TPP. No work has been done on Co(II)/DBP systems but the related 5-alkyl-5H-dibenzo-phospholes (VI, R = Me or Et) form five-coordinated complexes of the type L$_3$CoCl$_2$ (24). With the simple phospholes, however, no such complex can be obtained even in the presence of four-fold excesses of ligand.

It is surprising that the complex obtained from PP is different from the other three in that it is not soluble in dichloromethane and, even after recrystallization from acetonitrile-ether, a monohydrate is still obtained. The water molecule is not coordinated to the cobalt atom since the electronic spectrum of the complex is typical of a tetrahedral system. Similar hydrated complexes have, however, been synthesized from other cyclic phosphines. For example, the hydrated 2-phenylisophosphindoline com-plexes L$_2$CoX$_2$·H$_2$O (X = Cl, Br or I) are prepared (21) in and recrystallized from organic solvents. They are non-conductors in solution and are therefore unlikely to be the ionic species [L$_2$Co(H$_2$O)X]$^+$ X$^-$.

D. Rodium.

Two different types of reaction, namely those between the phospholes and rhodium(III) chloride and those be-tween the phospholes and Rh-Cl-CO systems, have been studied. In the first case, reactions with mPP and dPP produce L$_3$RhCl$_3$ (L = mPP or dPP) while the correspond-ing PP complex has already been reported (25). As with the cobalt complexes, solvent of recrystallization is in-corporated into the crystal lattices upon recrystallization from dichloromethane and this appears in the solution nmr spectrum at $\bar\tau$ 4.7. 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 four days.

From the number of Rh-Cl bands in the infrared spectra of these complexes (Table) they are probably octahedral with the chlorine atoms at the 1,2,6 positions (25). The nmr spectrum of (dPP)$_3$RhCl$_3$ shows that the signal of the phenyl group protons (τ 2.67) shifts 7 Hz down field while that of the methyl group protons (τ 7.87) remains unchanged as compared with the spectrum of the free ligand. This is consistent with σ coordination of the phos-phorus atom to the metal.

Thus, PP, mPP, dPP and DBP (25) all form normal *tris*-complexes but with TPP, only (TPP)RhCl$_3$ is obtained (26). Steric bulk apparently is not the major reason for TPP forming the 1:1 complex with RhCl$_3$ since the di-benzophosphole 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 phenyl groups are skewed (27). 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 hours), TPP gives the hydrido Rh(III) complex $(TPP)_2RhHCl_2$ (25), but this was not observed with the dPP system. Superficially then, PP, mPP, dPP and the dibenzophosphole DBP have similar electronic and steric properties but are different in some way from TPP.

Considering now rhodium carbonyl systems, rhodium(I) carbonyl complexes of the type $L_2Rh(CO)Cl$ are generally prepared by heating the respective ligand either with (i) a rhodium carbonyl containing solution prepared by passing carbon monoxide into an alcoholic solution of $RhCl_3 \cdot 3H_2O$ heated under reflux (28) or (ii) $Rh_2(CO)_4Cl_2$ 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 used in method (i), the monocarbonyl complexes $L_5Rh_2(CO)Cl_4$ (L = mPP or dPP) are obtained. On the other hand, the reaction using PP proceeds differently and produces what appears to be the benzoyl complex $(PP)_3Rh(PhCO)Cl_2 \cdot CH_2Cl_2$. The same product is obtained even if the reaction is carried out at room temperature. With dBP, only oils are obtained in these reactions.

The infrared spectra of the two carbonyl complexes (Table) show ν CO and ν Rh-Cl in the normal regions and the benzoyl complex shows a typical aryl ketonic group at 1680 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 was not observed.

If the reaction time in all of the above reactions is prolonged to one 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 of these binuclear complexes show only the Rh-Cl and ligand vibrations (Table) and no bands are observed in the range $2200\text{-}1600 \text{ cm}^{-1}$ assignable to ν CO. In the conversion of the benzoyl complex to $(PP)_5Rh_2Cl_4$, the reaction mixture residue shows a peak in the mass spectrum at m/e 121 consistent with the presence of benzoic acid. This could possibly arise by elimination of benzoyl chloride from the complex followed by hydrolysis to benzoic acid.

Little more can be said about the benzoyl complex at this stage and no further characterization of the complex was attempted. However, the improtant point here is not so much the structure of the complex but the fact that the benzoyl group can only arise from P-Ph cleavage in the phosphole. This means that the P-Ph cleavages observed by Mathey (2c,7,10) in reactions of simple phospholes with metal(0) carbonyls are not, in fact, restricted to metal(0) systems. Also, the interaction of the cleaved phenyl group with carbon monoxide is of considerable interest. Further study of this benzoyl complex and of

the generality of this type of reaction will form the basis of a separate investigation.

The complexes $L_5Rh_2(CO)Cl_4$ (L = mPP or dPP) and $L_5Rh_2Cl_4$ (L = PP, mPP or dPP) are non-conductors in acetone solution and are diamagnetic. Molecular weight determinations for the various complexes in dichloromethane at 30° 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 $(mPP)_5Rh_2-Cl_4$ (MW = 1218) and 613 for $(dPP)_5Rh_2Cl_4$ (MW = 1288). This indicates that these systems are probably mixed-valent Rh(I)-Rh(III) dimeric systems (e.g., VIII or IX) which dissociate in solution. Such dissociations are not uncommon for halogen-bridged dimeric species (1).
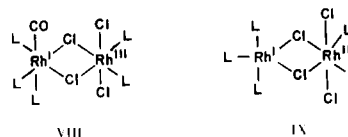
The presence of two carbonyl stretching frequencies (Table) in the ir spectrum of $(mPP)_5Rh_2(CO)Cl_4$ is possibly due to the presence of two isomers in which CO is trans to Cl and L, respectively.

The formation of mixed-valent Rh(I)-Rh(III) complexes is fairly common, particularly with alkylaryl phosphine ligands such as $PPhEt_2$ or PPh_2Et (29). However, the formation of dimeric carbonyl complexes of this type has apparently not been observed previously. The species present in the rhodium carbonyl ethanol solution used in the preparations are (30) an Rh(I) carbonyl system and possibly also some unreduced Rh(III) before addition of the phosphole ligands and it therefore seems that subsequent reaction with the phosphole could well lead to the formation of an Rh(I)-Rh(III) mixed-valent product. Alternatively, oxidation of Rh(I) to Rh(III) by some as yet unknown process could occur during reaction with the phosphole.

Other more heavily substituted phosphole-Rh(I)-carbonyl complexes are known and these have more conventional structures. For example, TPP (V) and DBP (VI, R = phenyl) form the square-planar species $(TPP)_2Rh(CO)Cl$ and $(DBP)Rh(CO)_2Cl \cdot MeOH$ respectively (25) from the rhodium carbonyl solutions referred to earlier. Clearly, simple phospholes in the reactions described above behave quite differently from the more complex phospholes TPP and DBP, possibly because of better donor character and a consequent increase in the lability of the P-phenyl group.

The synthesis of the same conventional type of complex $L_2Rh(CO)Cl$ (L = PP, mPP or dPP) can, however, be achieved using simple phospholes by reactions involving the addition of the ligands to solutions of $Rh_2(CO)_4Cl_2$ (method (ii)). A comparison of the ir spectra of $(PP)_2-Rh(CO)Cl$ before and after recrystallization shows that the intensities of both the carbonyl and the Rh-Cl bands

change. Before recrystallization, the two carbonyl bands (Table) have the same intensity and the higher frequency Rh-Cl band (Table) is a little more intense than the lower but, after recrystallization, the higher frequency carbonyl and Rh-Cl bands are more intense. With (mPP)$_2$Rh(CO)Cl, the lower frequency carbonyl band and the higher frequency Rh-Cl band are the more intense before recrystallization while, after recrystallization, the two carbonyl bands are of the same intensity as are the Rh-Cl bands. The fact that these complexes show two distinct sets of carbonyl frequencies whose intensities but not positions change on recrystallization suggests the formation of mixtures of isomers in which the phosphole ligands are cis or trans to one another with the relative proportions of the two isomers altering during recrystallization. The trans assignment to the lower carbonyl frequency is made by analogy with (PPhMe$_2$)$_2$Rh(CO)Cl (28a) and (PPh$_3$)$_2$Rh-(CO)Cl (28a) and (PPh$_3$)$_2$Rh(CO)Cl (28b) and it follows that the higher carbonyl frequency must be due to the cis arrangement. There are apparently no such cis-phosphine-Rh-CO systems known although cis-trans equilibria have been postulated (31).

With dPP only the trans isomer of (dPP)$_2$Rh(CO)Cl is formed (as is the case with all other phosphines previously studied (28)) and this is possibly associated with a steric effect since the more heavily substituted dPP is marginally more bulky than the other simple phospholes. It should also be noted that, as the steric bulk increases along the series PP, mPP, dPP, so the amount of trans isomer formed upon initial isolation of the product also increases as is shown by the relative intensities of the carbonyl bands in the ir spectra. The even more bulky TPP, of course, also forms only the trans complex. However, if this argument is correct, it is not clear why the very compact PMe$_3$ also apparently (28) only forms the trans isomer.

These complexes L$_2$Rh(CO)Cl are sensitive to heat and, if the reactions of Rh$_2$(CO)$_4$Cl$_2$ and ligand (mPP or dPP) in ethanol are carried out under reflux or if L$_2$Rh(CO)Cl is heated with the free ligand, L$_3$RhCl forms. The dPP complex (dPP)$_2$Rh(CO)Cl seems to be more stable and decomposes only after heating for more than 1 hour. The decarbonylation probably occurs by direct displacement of CO.

E. Iridium.

Both mPP and dPP react with iridium(III) chloride trihydrate in ethanol on heating under reflux to give L$_3$IrCl$_3$ (L = mPP or dPP) while, surprisingly, under similar conditions, PP reduces Ir(III) to Ir(I) giving (PP)$_3$IrCl. However, in all cases, green solids are formed when the ligands are added to IrCl$_3$ in ethanol at room temperature. Although these products could not be purified satisfac-

torily, they appear to be monophosphole complexes LIrCl$_3$ similar to the analogous (TPP)RhCl$_3$ (26) prepared under similar mild conditions.

Thus, both mPP and dPP form the tris complexes with Ir(III) chloride as has been observed with Rh(III) chloride. On the other hand, with PP and Rh(III) chloride, only (PP)$_3$RhCl$_3$ is formed whereas Ir(III) is reduced to Ir(I) by PP. This is perhaps due to the lowering of the ionization potentials on going from 4d to 5d transition metal ions. Tertiary phosphines generally do not reduce Ir(III) but Ir(I) complexes of alkyl or aryl phosphines have been prepared by direct replacement of N$_2$ or cyclooctadiene ligands in suitable Ir(I) complexes (32).
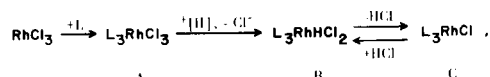
Discussion.

The most obvious and most significant deduction from this investigation and our earlier study (1) is that simple phospholes of the type studied here behave much like normal tertiary phosphines towards a fairly wide variety of transition metals in a variety of oxidation states. For example, with Re(III) which is only a borderline class (b) acceptor (33) (i.e., a relatively poor phosphine acceptor) and also a crowded system, the phospholes mPP and dPP form conventional tris-ligand complexes L$_3$Re$_3$Cl$_9$ under very mild conditions as do other normal tertiary phosphines (11,12) but not the bulky phosphole derivatives TPP and DBP as mentioned earlier. Furthermore, with Ru(III) in ethanol, PP and dPP behave in a similar manner to triphenylphosphine stabilizing Ru(III) at room temperature and reducing Ru(III) to Ru(II) at higher temperatures. The 3-substituted phosphole mPP, on the other hand, while stabilizing Ru(III) under mild conditions, has similar properties to n-Bu$_3$P in that partial reduction to a mixed-valent Ru(III)-Ru(II) system occurs at higher temperatures. Again, this is not the case with the more heavily substituted systems TPP and DBP which give (34) with Ru(III) (TPP)$_2$RuCl$_3$ and (DBP)$_3$RuCl$_3$, respectively, without reduction while with Ru(II) these two phosphole derivatives give (34) L$_3$RuCl$_2$ (L = TPP or DBP). The reduction of transition metal ions by phosphines has been discussed in terms of steric effects (35) and basicity effects (29) and this point will be returned to shortly. In addition, as already remarked, mPP behaves like a mixed alkyl-aryl phosphine in reactions with Ru(III) chloride in hot n-butyl alcohol to give the Ru(II) system (mPP)$_3$Ru(CO)Cl$_2$.

With Co(II) the phosphole complexes obtained are entirely analogous to other tetrahedral Co(II) phosphine complexes and again, the readiness with which these phospholes react is much greater than TPP which forms no complexes with Co(II).

The most specific information comes from the rhodium-phosphole reactions described earlier. Thus, PP, mPP and

dPP do *not* reduce Rh(III) under the conditions employed. In contrast, triphenylphosphine reduces Rh(III) instantly to $(PPh_3)_3RhCl$ (6) while trialkylphosphines (*e.g.*, PMe_3, PEt_3 or $P(n\text{-}Pr)_3$) and $P(C_6H_{11})_3$ all form $1,2,6\text{-}L_3RhCl_3$ complexes (35a). Mixed aryl-alkyl phosphines (*e.g.*, $PEtPh_2$ and PEt_2Ph), however, form L_3RhHCl_2 (35a). While reduction of species such as Rh(III) has been suggested to be dependent, at least to some extent, upon steric factors (35) it seems more likely that basicity plays a more important role. In this connection, Sacco, *et al.*, (29), has postulated the following mechanism for the reaction of $RhCl_3$ with phosphines:

$$RhCl_3 \xrightarrow{+L} \underset{A}{L_3RhCl_3} \xrightarrow{+HL, -Cl^-} \underset{B}{L_3RhHCl_2} \underset{+HCl}{\overset{-HCl}{\rightleftharpoons}} \underset{C}{L_3RhCl} ,$$

In this sequence, the type of product formed depends largely upon the basicity of the phosphine ligand. Thus, with more basic (*e.g.*, trialkyl) phosphines, the reaction stops at point A, but with much less basic (*e.g.*, triaryl) phosphines, it stops at point C. With phosphines of intermediate basicity (*e.g.*, alkylaryl) it stops at point B. If this argument is correct as seems highly likely, it follows that PP, mPP, dPP and DBP are apparently comparable in basicity with trialkylphosphines whereas the behaviour of TPP resembles that of mixed alkylarylphosphines in reactions with $RhCl_3$.

That steric bulk does, at least occasionally, play some role in these reactions is, however, shown by the fact that $RhCl_3$ forms complexes of the type L_2RhCl_2 with the very bulky trialkylphosphines $P(t\text{-}Bu)(n\text{-}Pr)_2$, $P(t\text{-}Bu)_2Me$ and $P(t\text{-}Bu)_2Et$ (36) but it should be borne in mind that our earlier study (1) with Ni(II), Pd(II) and Pt(II) has shown that the phospholes studied in this paper act as sterically compact ligands.

The square-planar Rh-CO systems, $L_2Rh(CO)Cl$ (L = PP, mPP or dPP), as well as demonstrating the conventional donor character of the phospholes, provide information regarding the dependence of donor character upon the substitution pattern of the phosphole ring. Comparison of ν CO in the spectra of the *trans* isomers mentioned earlier with those of the similar complexes containing PMe_3, PMe_2Ph and PPh_3 (28) 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 ≅ PP > TPP since ν CO increases along this series as would be expected (7) with such a change in donor character. This sequence is in agreement with the deductions of Mathey (7) referred to in the introduction to this paper.

That reduction of Ir(III) to Ir(I) by PP but not by mPP or dPP occurs is consistent with the above deductions since, if Sacco's theory (29) relating reduction to phosphine basicity is correct, and applies also to Ir(III), then

reduction of Ir(III) by PP would be more likely than with mPP or dPP since the ir studies of $L_2Rh(CO)Cl$ (L =phosphine ligand) indicate that PP is less basic than the other phospholes.

In summary, the phospholes described in this paper are surprisingly good donors and the phosphorus lone-pair of electrons is readily available for reactions with transition metal systems. On the other hand, the very simple systems 1-methylphosphole (I, R = methyl) and 1-benzylphosphole are rather poor donors as is the heavily substituted TPP as discussed elsewhere (1,37). Clearly, the variations in behaviour and donor character shown by the various simple phospholes discussed in this and other papers (1,3,38) must arise from variations in the electronic structure of the phosphole ring since all of the simple phospholes are sterically very similar. Equally clearly, if simple phosphole derivatives are aromatic in the pyramidal ground state as now seems highly probable (4,5), this aromatic character is easily perturbed in many cases. Whether this marked donor character of an otherwise aromatic system arises from strong electronic perturbations by metal ions as occurs with λ^3-phosphorins (39) or is due to a relatively high lone-pair electron density upon the phosphorus atom in the unperturbed phosphole cannot be determined from the information presented in this paper but in another paper (40) we will show that simple phospholes are also surprisingly good nucleophiles in reactions with organic electrophiles such as dimethyl acetylenedicarboxylate.

EXPERIMENTAL

Physical measurements and analyses were carried out as described previously (1) as were the syntheses of the phospholes used. As with the Ni(II) complexes (1), the Co(II) complexes gave more reproducible metal than chloride analyses. Melting points are not reported here since all of the complexes described decompose slowly between 100° and 200°.

It should be noted that for several complexes, the C and H analytical values are slightly higher than would normally be expected. In virtually all such cases, the product was obtained by precipitation from dichloromethane solution with ether (hexane in one instance) and residual precipitating solvent was occluded in the crystals. The presence of this solvent was shown by mass spectral analysis but attempts to remove the solvent by pumping at room temperature had no effect. Pumping at higher temperatures was not possible because of thermal instability of the complexes.

Syntheses of Metal Complexes.

As before (1), the syntheses of the various metal complexes were carried out in a glove box constantly flushed with dry, oxygen-free nitrogen. The solvents used were distilled, degassed and stored over molecular sieves (Type 4A) while solid reagents were crushed, degassed and stored in the glove box.

### I. From Metal Halide-Phosphole Reactions.

The complexes were prepared usually by either of two methods (A and B described below) and yields were always in the range 60-80%. Analytical data, the method of preparation and other data for each complex are recorded in the Table.

Method A.

The ligand (in 1-5 molar excess) was added dropwise to a stirred solution of metal chloride in ethanol (typically 0.25 g. in ca. 15-20 ml.) at room temperature. The crude product precipitated after a short time (1-2 hours) and was separated by centrifugation, washed with organic solvents such as ethanol or dichloromethane and recrystallized (if necessary) from suitable solvents (Table).

Method B.

The metal chloride was dissolved in ethanol as above and the phosphole (in 1-5 molar excess) was then added dropwise. After the addition, the mixture was heated under reflux for 1-24 hours (usually 10-12 hours) and then centrifuged. Any solid product was washed with organic solvents as before and recrystallized from a suitable solvent. If no precipitation occurred during the reaction, the solvent volume was decreased under reduced pressure and ether was added to precipitate the crude product. This was washed in the usual manner if necessary.

$(mPP)_3Ru(CO)Cl_2 \cdot CH_2Cl_2$.
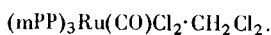
The phosphole mPP (0.5 g., 2.8 mmoles) and $RuCl_3 \cdot 3H_2O$ (0.18 g., 0.7 mmole) were heated together under reflux in n-butyl alcohol ($\sim$20 ml.) for 12 hours. After cooling the brown solution, ether was added to precipitate the crude complex as a brown solid (ca. 70% yield) which was purified by recrystallization from dichloromethane-ether.

II. From Metal Halid-Carbonyl Systems.

$(PP)_3Rh(PhCO)Cl_2 \cdot CH_2Cl_2$ and $L_5Rh_2(CO)Cl_4$ (L = mPP or dPP).

Carbon monoxide was passed into $RhCl_3 \cdot 3H_2O$ (0.2 g., 0.76 mmole) in ethanol ($\sim$ 20 ml.) and the mixture was heated under reflux for 4 hours. The phosphole PP (0.49 g., 3.0 mmoles) was then added dropwise to the resulting yellow rhodium carbonyl solution at room temperature and the mixture was again heated under reflux for 10 minutes. The solvent volume was decreased under reduced pressure and ether was added to precipitate the yellow complex $(PP)_3Rh(PhCO)Cl_2$ which was recrystallized from dichloromethane-ether to give the solvated complex $(PP)_3Rh(Ph-CO)Cl_2 \cdot CH_2Cl_2$.

Using the same procedure, the phospholes mPP and dPP gave $L_5Rh_2(CO)Cl_4$ (L = mPP or dPP).
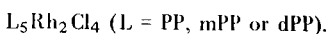
$L_5Rh_2Cl_4$ (L = PP, mPP or dPP).

Carbon monoxide was passed into $RhCl_3 \cdot 3H_2O$ (0.2 g., 0.76 mmole) in ethanol ($\sim$ 20 ml.) and the mixture was heated under reflux for 4 hours. The phosphole PP (0.49 g., 3.0 mmoles) was then added dropwise to the yellow rhodium carbonyl solution at room temperature and then, in contrast to the earlier experiment, the mixture was heated under reflux for 2 hours. Solvent was removed under reduced pressure from the resulting clear reddish solution and ether was added to precipitate $(PP)_5Rh_2Cl_4$ which, as before, was recrystallized from dichloromethane-ether.

The complexes $(mPP)_5Rh_2Cl_4$ and $(dPP)_5Rh_2Cl_4$ were prepared in a virtually identical manner but these complexes can also be prepared by treating $L_5Rh_2(CO)Cl_4$ (L = mPP or dPP) in dichloromethane ($\sim$ 10 ml.) with an excess of the appropriate phosphole followed by heating the solution for 2 hours under reflux. The product was isolated and purified in the usual manner.

$L_2Rh(CO)Cl$ (L = PP or MPP).
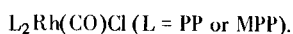
The phosphole PP (0.18 g., 1.1 mmole) was added dropwise to $Rh_2(CO)_4Cl_4$ (0.2 g., 0.51 mmole) in ethanol ($\sim$10 ml.) at room temperature. The crude yellow product $(PP)_2Rh(CO)Cl$ precipi-

tated and was separated and recrystallized from dichloromethane-ether. The complex $(mPP)_2Rh(CO)Cl$ was prepared in a virtually identical manner.

$(dPP)_2Rh(CO)Cl$.
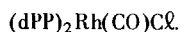
This complex was prepared in a slightly different manner from the corresponding PP and mPP complexes. Thus, treatment of dPP (0.34 g., 1.8 mmoles) with $Rh_2(CO)_4Cl_2$ (0.2 g., 0.51 mmole) in ethanol as before gave, after heating the mixture under reflux for 0.5 hour, an almost clear yellow solution. The complex $(dPP)_2Rh(CO)Cl$ was precipitated by adding ether to the centrifuged solution and recrystallization was carried out in the usual way.

$(mPP)_3RhCl \cdot 0.5CH_2Cl_2$ and $(dPP)_3RhCl$.
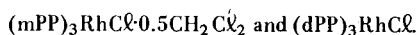
The solvated complex $(mPP)_3RhCl \cdot 0.5CH_2Cl_2$ was prepared from mPP (0.32 g., 1.8 mmoles) and $Rh_2(CO)_4Cl_2$ (0.2 g., 0.51 mmole) in ethanol under reflux for 1 hour. The centrifuged solution was then treated with ether to precipitate the crude yellow complex which was recrystallized from dichloromethane-ether.

The unsolvated dPP complex $(dPP)_3RhCl$ was prepared similarly except that a 2-hour period of heating under reflux was required and preparation was directly from the complex $(dPP)_2-Rh(CO)Cl$ by treatment with free dPP.

Acknowledgment.

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