

THE REACTIONS OF
1,2,5-TRIPHENYLPHOSPHOLE AND ITS OXIDE
SULFIDE AND SELENIDE
WITH
Nb(V) and Ta(V) HALIDES

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ABSTRACT

The coordination chemistry of Nb(V) and Ta(V) with phosphines and phosphine oxides, sulfides and selenides is reviewed briefly, as are the electronic properties and coordination reactions of phospholes.

In this work, a systematic investigation of the reactions of 1,2,5-triphenylphosphole (TPP) and its oxide (TPPO), sulfide (TPPS) and selenide (TPPSe) with the halides of Ta(V) and Nb(V) was carried out. Despite the weak basic character of TPP relative to other tertiary phosphines, TPP reacted readily and the crystalline compounds TPP.TaCl₅, TPP.TaBr₅, and TPP.NbCl₅ were isolated. However, the low stability of these adducts relative to their triphenylphosphine analogues further indicates the poor accessibility of the phosphorus lone electron pair in TPP which may be due to the partial delocalization of the lone pair into the heterocyclic ring.

The P-protonated salts of TPP, [TPPH]⁺[TaCl₆]⁻ and [TPPH]⁺[NbCl₆]⁻ were formed by reactions of the 1:1 adducts TPP.TaCl₅ and TPP.NbCl₅ with small amounts of ethanol and with anhydrous hydrogen chloride. The salt [TPPH]⁺[TaCl₆]⁻ is remarkably stable in the solid

state in view of the weak basicity of TPP. The more basic ligands 5-phenyl-5-*H*-dibenzophosphole and triphenylphosphine also formed 1:1 adducts with TaCl_5 and these reacted readily with anhydrous HCl to give P-protonated salts.

1:1 Adducts and solvated 1:1 adducts of TPPO with MX_5 (M=Ta, Nb; X=Cl, Br) in several crystalline forms were isolated, with the large shift of the P=O stretching frequency indicating coordination through the oxygen atom. TaI_5 appears to cleave the P=O bond of TPPO to form TPP and an unidentified TPPO-tantalum oxyiodide complex, while NbI_5 with TPPO appears to form a simple 1:1 adduct. Neither TaCl_5 nor NbCl_5 appear to abstract oxygen from TPPO, but when the $\text{TPPO}\cdot\text{MCl}_5$ adducts are allowed to react slowly with water, $\text{TPPO}\cdot\text{MOCl}_3$ adducts are produced. With TPPS, the adducts $\text{TPPS}\cdot\text{MCl}_5$ in two crystalline forms were isolated but with TPPSe the adducts $\text{TPPSe}\cdot\text{MCl}_5$ gave only one crystalline phase. There was no evidence of abstraction of either chalcogenide by the metal halides, but traces of moisture in the $\text{TPPSe}\cdot\text{NbCl}_5$ reaction led to formation of $\text{TPPO}\cdot\text{NbCl}_5$.

Data on the infrared spectra, X-ray powder diffraction patterns, NMR spectra and visible absorption spectra of the complexes is discussed.

ACKNOWLEDGEMENTS

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INTRODUCTION

Phosphines as Donor Ligands

The largest portion of the known coordination chemistry of the transition metals is that occupied by ligands where oxygen and nitrogen are the donor atoms. This is the result of their "hard" donor character (1) which makes them suitable σ donors for the majority of the transition metals in their common oxidation states. These "hard" donor atoms are characterized by their high electronegativity, low polarizability and their possession of empty orbitals of only very high energy. The transition metals with which these ligands interact most strongly have been classified as "hard" acids by Pearson (1) and as class (a) acceptors by Chatt *et al.* (2).

Following complexes with oxygen and nitrogen donor ligands, the next largest group of transition metal complexes are those with substituted phosphines where phosphorus is the donor atom. Phosphine complexes of many transition metals are now known, with most of the investigation centred on the class (b) acceptors, with which phosphines appear to react most readily. The

class (b) acceptors include most of the group VIII transition metals and some of their immediate neighbours in the Periodic Table (2). Both Chatt *et al.* and Pearson have observed that these metals have a preference for the "soft", more easily polarizable donor atoms such as phosphorus and sulfur. The ability of phosphorus and sulfur atoms to accept electrons into empty d orbitals of relatively low energy may be important in their bonding with these transition metals. The group VIII metals can donate electrons from filled d orbitals of suitable symmetry into the empty donor atom d orbitals to form a π bond. This may be why, for example, there is an abundance of phosphine complexes with d^8 metal ions such as Ni(II), Pd(II), Pt(II), Rh(I), and Ir(I) (See for example (3), (4), (5) and references cited therein).

With transition metals having lower numbers of d-electrons, such as the group VIb, Vb, and IVb metals, one finds that the number of complexes with phosphine donors decreases sharply. This apparent relationship between the number of d-electrons on the metal atom and the number of phosphine complexes may be an indication of the importance of $d\pi-d\pi$ interaction in stabilizing the metal-phosphorus bond. Aslanov *et al.* (6) found, from X-ray studies of a series of phosphine complexes of W(IV), Re(IV), Os(IV), Ir(IV), Re(III), Os(III) and

Ir(III), that there is a significant shortening of the metal-phosphorus bond in going from a d^2 to a d^5 configuration ($2.55\overset{\circ}{\text{Å}} \rightarrow 2.39\overset{\circ}{\text{Å}}$) in the same oxidation state, but very little change in the bond length between different oxidation states of the same d-configuration (e.g. Os(III): $2.41\overset{\circ}{\text{Å}}$, Ir(IV): $2.39\overset{\circ}{\text{Å}}$). The contraction of the metal-phosphorus bond with increasing d-electron population on the metal ion suggests that π bonding may be involved. Venanzi (7) on the other hand, has argued, on the basis of ^{195}Pt -NMR data, that π bonding is relatively unimportant in class (b) metal-phosphine complexes, and that changes in bond strength arise directly from changes in the character of the M-P σ bond.

With the transition metals of low d-electron population, most of the phosphine complexes which are known are with the zero-valent metals. The group Vb elements vanadium, niobium and tantalum readily illustrate this pattern. The most stable oxidation state of vanadium, V(IV), is dominated by vanadyl compounds such as $(\text{PEt}_3)_2\text{VOCl}_2$ (8). Other than these, phosphine complexes of simple V(III), V(IV) or V(V) halides have not been reported. The only other vanadium-phosphine complexes are with V(-I), V(0) and V(I) (Table I).

Niobium and tantalum, at first glance, would appear to follow the same pattern as a number of M(-I) and M(I)

Table I

Vanadium, Niobium and Tantalum Phosphine
Complexes

<u>Oxidation State</u>	<u>Complex</u>	<u>Reference</u>
V(-I)	$[\text{Et}_4\text{N}][\text{Ph}_3\text{PV}(\text{CO})_5]$	9
V(0)	$(\text{Ph}_3\text{P})_2\text{V}(\text{CO})_4$	9
	$(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_3\text{V}$	10
V(I)	$(\text{C}_5\text{H}_5)\text{V}(\text{CO})_3\text{PH}_3$	11
	$(\text{C}_5\text{H}_5)\text{V}(\text{CO})_3\text{PR}_3$, R=alkyl, aryl	12
M(-I)	$\text{Ph}_3\text{SnM}(\text{CO})_5\text{PPh}_3$	13
	$[\text{Et}_4\text{N}][\text{M}(\text{CO})_5\text{PPh}_3]$, M=V, Nb, Ta	13
Ta(I)	$(\text{C}_5\text{H}_5)\text{Ta}(\text{CO})_3\text{PPh}_3$	14
	$(\text{C}_5\text{H}_5)\text{Ta}(\text{CO})_2(\text{PPh}_3)_2$	14
Nb(IV)	$(\text{Ph}_3\text{P})_{3/2}\text{NbCl}_4$	16
Nb(V)	$(\text{Ph}_3\text{P})\text{NbCl}_5$	15
Ta(V)	$(\text{Bu}_3\text{P})\text{TaCl}_5$	17

phosphine complexes with these metals are now known (Table I). However, in contrast to vanadium, phosphine adducts with the higher oxidation states of these metals have also been reported. For example, 1:1 and 1:2 adducts of triphenylphosphine with NbCl_5 have been reported (15) (although the chloride analysis reported for the 1:1 adduct is too low to allow positive identification of this species). A Nb(IV) adduct formulated as $(\text{Ph}_3\text{P})_{3/2}\text{NbCl}_4$ has been reported (16) and a Ta(V)-tributylphosphine adduct, $(\text{Bu}_3\text{P})\text{TaCl}_5$ is mentioned briefly as an intermediate in the thermal reaction of TaCl_5 with Bu_3P (which gives TaPCl_2 and BuCl as end products) (17). Thus, Nb(V) and Ta(V) appear to possess a small amount of "soft" acceptor character. In the case of these d^0 metal ions, $d\pi-d\pi$ bonding cannot be responsible for stabilizing the metal-phosphorus bond, and thus the stabilities of the complexes are determined by the M-P σ bond strength.

An important stimulus in the coordination work with phosphines has been the catalytic activity which some of the phosphine-class (b) metal complexes possess. Perhaps the most widely known of these is "Wilkinson's Catalyst", $(\text{Ph}_3\text{P})_3\text{RhCl}$ (3), which shows a high activity in the homogeneous hydrogenation of olefins. A related complex, $(\text{Ph}_3\text{P})_3\text{RhH}(\text{CO})$ shows a high selectivity for the

hydrogenation of 1-alkenes and is also active in the hydroformylation of alkenes (4). The triphenylphosphine substituent appears to play a significant part in these complexes as a change in the substituents on the phosphine alters the catalytic activity. Thus, with $(R_3P)_3RhCl$, the rate of hydrogenation is considerably lower when R is an alkyl group than when R is an aryl group (5). It has been suggested that the observed activity might be due to the phenyl groups acting as "reservoirs" for electronic charge during critical stages in the catalysis sequence. It is possible that this could involve $d\pi-d\pi$ interaction between the metal ion and the phosphorus atom.

Phosphine Oxides as Donor Ligands

Because of the "hard" donor character of oxygen, the phosphine oxides are considerably better electron donors to the class (a) metals than the phosphines themselves. The oxide can be thought of as formed from the parent phosphine by σ donation of a phosphorus 3p electron pair into an oxygen 2p orbital with simultaneous π back donation of an oxygen 2p electron pair into a phosphorus 3d orbital (18). This back donation is strong enough to give the PO link considerable double bond character although the bond remains quite polar. The

Table II

Transition Metal-Phosphine Oxide Adducts

<u>Compound</u>	<u>Reference</u>
L_2CdI_2	(20)
L_2ZnI_2 ; $(Me_3PO)_2ZnCl_2$	(20, 21)
L_2CoX_2 , X=Cl, Br, I; $(Me_3PO)_2CoCl_2$	(20, 21)
$L_4Cu(ClO_4)_2$	(20)
$L_4Ni(ClO_4)_2$	(20)
$L_4Mn(ClO_4)_2$	(20)
L_2FeBr_2 ; $L_4Fe(ClO_4)_3$	(20)
L_2SnX_4 , X=Cl, Br; $(Me_3PO)_2SnCl_4$	(20, 21)
L_2TiCl_4 ; $((PhO)_3PO)TiCl_4$	(20, 23)
$(Me_3PO)_2GeCl_4$	(21)
L_2ZrCl_4 ; $(Me_3PO)ZrCl_4$	(25, 21)
$((PhO)_3PO)_2VCl_3$	(23)
L_2VCl_4 ; $((NMe_2)_3PO)_nVCl_4$, n=1, 2	(23)
L_2VOCl_2 ; $L_4VO(ClO_4)_2$	(24)
$LMCl_n$, $MCl_n=VCl_3$, $NbCl_5$, $TiCl_4$, $ZrCl_4$, $FeCl_3$	(22)
$(R_3PO)MX_5$, R=Ph, NMe_2 ; M=Nb, Ta; X=Cl, Br	(26, 27, 28)
$LM(OEt)_2X_3$, M=Nb, Ta; X=Cl, Br	(29)
L_2NbOCl_3	(26, 27, 30)
L_2TaOCl_3	(30)
L_2MoOCl_3	(31)

L= Ph_3PO

nature of the $d\pi-p\pi$ overlap and the evidence for it is reviewed in considerable detail by Hudson (19). The remaining electron pair on the oxygen is readily available for σ -coordination and this is evident in the number of complexes formed with class (a) acceptors. It is readily apparent from Table II that adducts of phosphine oxides with a wide variety of metals have now been characterized.

In contrast to the relatively few phosphine complexes of niobium and tantalum in their higher oxidation states, the complexes with phosphine oxides are much more numerous. Thus, 1:1 complexes of triphenylphosphine oxide and hexamethylphosphoramide, $[(Me_2N)_3PO]$, have been reported by a number of authors (22, 26-29). A particularly interesting aspect of the phosphine oxide complexes is the oxygen abstraction observed in some instances. For example, when $NbCl_5$ reacts with a two to four-molar excess of Ph_3PO , the product is $(Ph_3PO)_2NbOCl_3$ (26,27,30). However, with 1:1 molar ratios under strictly anhydrous conditions, only the 1:1 adduct $(Ph_3PO)NbCl_5$ is obtained (26). Oxygen abstraction by $TaCl_5$ under similar conditions has not been proven conclusively. Whereas only the 1:1 adduct $(Ph_3PO)TaCl_5$ has been reported by several authors (26,27), Fairbrother *et al.* (30) did obtain the oxytrichloride adduct $(Ph_3PO)_2TaOCl_3$,

but only by reacting TaCl_5 with the hydrogen peroxide adduct of triphenylphosphine oxide $(\text{Ph}_3\text{PO})_2 \cdot \text{H}_2\text{O}_2$. Here the peroxide could, and almost certainly does, serve as the oxygen source for the oxytrichloride. This would appear to indicate a small difference in the affinity of oxygen for Nb(V) and Ta(V) and thus a trend of decreasing class (a) acceptor character down the series of vanadium, niobium and tantalum. The slightly weaker $\text{R}_3\text{PO} \rightarrow \text{M}$ bond for tantalum can be deduced from the shifts of the P=O stretching frequency in the infrared spectrum on coordination. Thus, in $\text{Ph}_3\text{PO} \cdot \text{NbCl}_5$ and $\text{Ph}_3\text{PO} \cdot \text{TaCl}_5$, the P=O shifts are 215 cm^{-1} and 205 cm^{-1} respectively to lower energy (26).

Other metals such as Mo and W also effect oxygen abstraction from phosphine oxides. Using an excess of Ph_3PO , Horner and Tyree (31) found that MoCl_5 reacts to give $(\text{Ph}_3\text{PO})_2\text{MoOCl}_3$. Lindner *et al.* (22) found that $[\text{Ph}_3\text{PP}(\text{O})\text{Cl}_2]\text{Cl}$ reacts with VCl_3 , NbCl_5 , TiCl_4 , ZrCl_4 and FeCl_3 to give 1:1 Ph_3PO adducts (Table II), but that MoCl_5 and WCl_6 react to give $\text{Ph}_3\text{PCl}_2 \cdot \text{MoOCl}_3$ and $\text{Ph}_3\text{PCl}_2 \cdot \text{WOCl}_4$ respectively.

Phosphine Sulfides and Selenides as Donor Ligands

Although they are electronically similar to the phosphine oxides, the phosphine sulfides and selenides

Table III

Transition Metal-Phosphine Sulfide Complexes

<u>Complex</u>	<u>Reference</u>
$L_2PdCl_2^*$	(32)
$L_2PtCl_2^*$	(32)
$LAuCl_3^*$; $LAuCl^*$	(32)
$LHgX_2^*$, $X=Cl, Br, I$	(32, 36)
$(Me_3PS)_2HgCl_2^*$; $L_2HgCl_2^*$	(33, 35)
$(Me_3PS)_2CdI_2$; $[LCdI_2]_2$	(33, 37)
$(Me_3PS)_2ZnI_2$	(33)
L_2SnCl_4	(27)
$L(TiCl_4)_2$; $LTiBr_4$	(27)
$LSbCl_5$	(27)
$LNbCl_5$	(27, 28)
$LTaCl_5$	(27, 28)
$L(FeCl_3)_n$, $n=1-1.5$	(27)
$L(AlCl_3)_n$, $n=1-3$	(27)
$LAlBr_3$	(27)
$LCuX^*$, $X=Cl, Br$	(36)
$(Me_3PS)_4Co(ClO_4)_2$; $(Me_3PS)_2CoX_2$, $X=Cl, Br, I$	(35)
$LWCl_5$; $LWBr_4$	(37)

$L=Ph_3PS$

* - Complexes with "soft" acceptors

have received much less attention as donor ligands, and it is only in the last few years that their coordination reactions have been investigated. Since sulfur is a "soft" donor, it would be expected to bond most readily with the "soft" metal acceptors and complexes with a number of these are now known (Table III). However, complexes with the "borderline" metals, Cd(II) and Zn(II) and with the "hard" acceptors Al(III), Fe(III), Sn(IV), Ti(IV), Sb(V), Nb(V), Ta(V), W(V), and W(IV) are also known (Table III). This overlap in bonding character could be due to less efficient $p\pi-d\pi$ back-bonding from sulfur to phosphorus, thus giving the P=S bond some contribution from the form $\overset{\dagger}{P} \rightarrow \bar{S}$. The intermediate position of the P=S bond energy (~ 90 kcal/mole) (38) between that of $\overset{\dagger}{N} \rightarrow \bar{O}$ (50 - 70 kcal/mole) (19), where there is virtually complete charge separation, and that of P=O ($\sim 125 - 140$ kcal/mole) (19) is an indication of the less efficient π bonding in the P=S system. This may increase the electron density at the sulfur atom, giving it some "hard" donor character.

Although complexes with the phosphine selenides are fewer in number (Table IV), the same generalizations can be made. Most of the complexes are with the "soft" acceptors with the exceptions of Ta(V), Nb(V), and W(V). As noted earlier, Ta(V) and Nb(V) appear to have some

Table IV

Transition Metal-Phosphine Selenide Complexes

<u>Complex</u>	<u>Reference</u>
L_2PdCl_2	(32)
L_2PtCl_2	(32)
$LAuCl$	(32)
$LHgX_2$, X=Cl, Br, I	(32)
$LAgClO_4$	(34)
$[(C_4H_9)_3PSe]_2CdI_2$	(34)
LMX_5 , M=Ta, Nb; X=Cl, Br	(28)
$LWCl_5$	(37)

$L=Ph_3PSe$

"soft" acceptor character. With the "hard" acceptor vanadium, however, there are no reported phosphine sulfide or selenide adducts, even for low oxidation states of the metal. A number of diphosphine disulfide complexes with different transition metals have also been prepared, and these are reviewed by Slinkard (39).

Although the group Vb metals of the Periodic Table, vanadium, niobium and tantalum have similar outer electron configurations, they show distinct differences in their chemical behaviour. As previously mentioned, vanadium is usually found in the 4+ oxidation state, while niobium and tantalum prefer the 5+ state. Nb(V), however, is more easily reduced to Nb(IV) than is Ta(V) to Ta(IV). Thus, NbCl₅ is reduced by pyridine (py) to give (py)₂NbCl₄, but TaCl₅ forms only the 1:1 adduct (py)TaCl₅ (40). Similarly NbCl₅ is reduced by red phosphorus to NbCl₄, but reduction of TaCl₅ under the same conditions is negligible (41).

The reduction tendencies appear to parallel the affinity of the metal halide for oxygen. Vanadium readily complexes with oxygen donors, and also forms the very stable V=O bond. NbCl₅ appears to abstract oxygen from phosphine oxides under suitable conditions, but TaCl₅ does not appear to do so (26,27). Ta(V) and Nb(V) react with the "soft" donor atoms phosphorus,

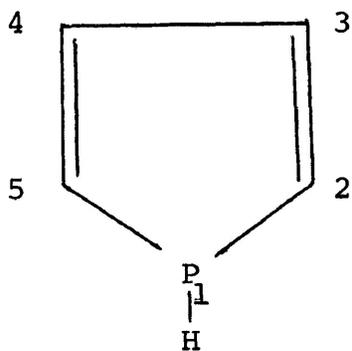
sulfur and selenium, but V(IV) does not. This rather peculiar reactivity of the Nb(V) and Ta(V) halides has made them suitable for the investigation of their reactions with 1,2,5-triphenylphosphole and its oxide, sulfide and selenide.

The Phospholes: Physical and Chemical Properties

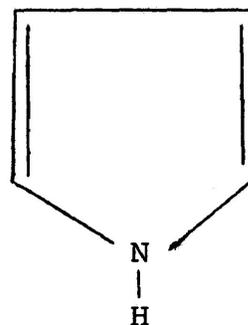
Phosphole (I) is the phosphorus analogue of the aromatic heterocycle pyrrole (II), and because of the apparent structural similarity between the two systems, they have often been compared and contrasted. In comparison with the phosphines, the donor properties of the phospholes have received little attention. This is because their syntheses have been more recent than those of the phosphines and because they appear to have a weaker basic character than the corresponding phosphines (42). This last fact has a bearing on the possible aromaticity of the phosphole ring, which will be discussed shortly.

The unsubstituted phosphole (I) has not yet been synthesized, but 1-methylphosphole (III) (42) and 1-phenylphosphole (IV) (43) are now known. The first phospholes synthesized were more highly substituted in nature, such as 1,2,3,4,5-pentaphenylphosphole (V) (44,45) and 1,2,5-triphenylphosphole (TPP) (VI) (46). A

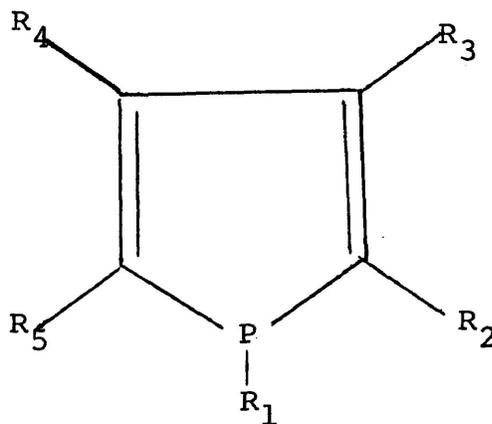
Figure I



I
Phosphole



II
Pyrrole



- III: $R_1 = \text{Me}; R_2, R_3, R_4, R_5 = \text{H}$ 1-Methylphosphole
IV: $R_1 = \text{Ph}; R_2, R_3, R_4, R_5 = \text{H}$ 1-Phenylphosphole
V: $R_1, R_2, R_3, R_4, R_5 = \text{Ph}$ 1,2,3,4,5-Pentaphenylphosphole
VI: $R_1, R_2, R_5 = \text{Ph}; R_3, R_4 = \text{H}$ 1,2,5-Triphenylphosphole (TPP)

number of different phospholes have now been prepared, and their syntheses are reviewed by Hughes and Srivnavit (47).

It is well known that the heterocycle pyrrole possesses considerable aromatic character due to delocalization of the nitrogen lone electron pair into the five-membered ring (48). Thus, pyrrole, and pyrrole derivatives behave chemically as aromatic systems, are planar in structure (49) and have a weakly acidic proton at the nitrogen atom.

In the analogous phosphole ring, the question of aromaticity has not been unambiguously answered. There was considerable debate as to whether phosphole molecules are planar as are pyrrole molecules. Until quite recently, the general consensus (47) appeared to be that the phosphole ring possesses some aromaticity, but that the phosphorus electron pair is not completely delocalized as in pyrroles.

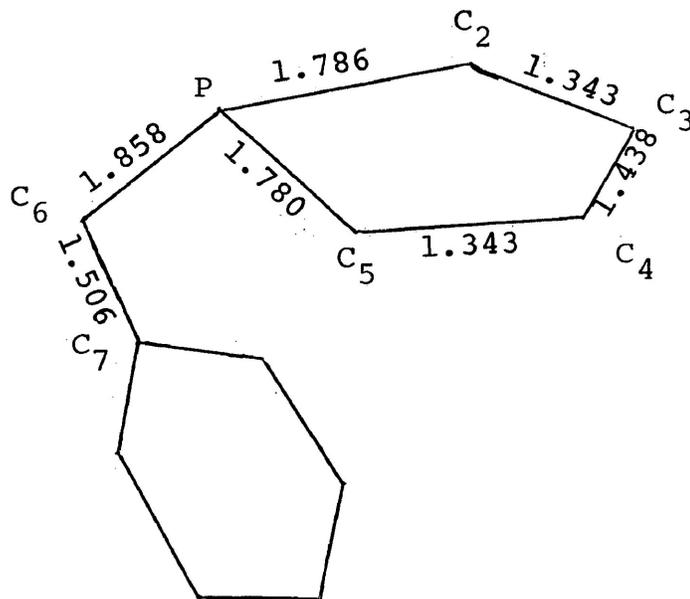
Evidence for delocalization is both physical and chemical. For example, the P=O bond strength in 1,2,3,4,5-pentaphenylphosphole oxide was found by Millar *et al.* (50) to be about 100 kcal/mole whereas it is of the order of 125 - 140 kcal/mole for tertiary phosphine oxides with alkyl and aryl substituents. Märkl (43) found that the ring protons of 1-phenylphosphole resonate in the aromatic region and that the phosphole gives an NMR spec-

trum very similar to that of *N*-phenylpyrrole. Quin *et al.* (51) made similar observations about 1-methylphosphole and found that it is considerably less basic than most normal tertiary phosphines, having a pK_a value of about 0.5, as compared to a pK_a value of 5.2 estimated for a non-aromatic model of the phosphole. The pK_a of 0.5 is still higher than that estimated for pyrrole (-3.8) (52), and indicates that delocalization is not nearly as complete as in pyrrole. The fact that 1,2,5-triphenylphosphole reacts as a very weak nucleophile with dimethylacetylenedicarboxylate further indicates interaction of the phosphorus lone pair with the π system of the ring (53). On the other hand, chemical reactions of phospholes, such as oxide formation, quaternary salt formation and metal coordination do not parallel pyrrole reactions and superficially would tend to indicate that the phosphorus lone pair is not significantly delocalized.

This issue has been clarified somewhat through Mislow's studies of the pyramidal inversion barriers in phospholes (54,55) and (to a lesser extent) through the recent X-ray structure determinations of 1-benzylphosphole (56) and 1,2,5-triphenylphosphole (57). Mislow (54) found that the energy of the inversion barrier about the phosphorus atom in 1-isopropyl-2-methyl-5-

Figure II

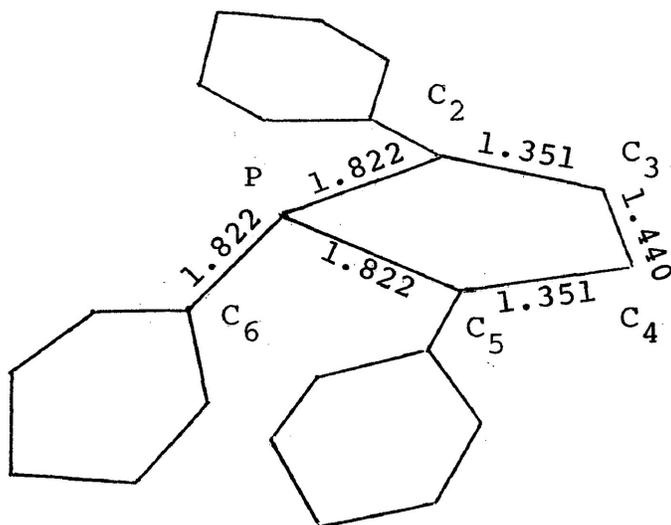
The Crystal Structure of
1-Benzylphosphole (56)



<	C ₂ PC ₅	=	90.7°
<	C ₂ PC ₆	=	106.1°
<	C ₅ PC ₆	=	105.9°
<	PC ₆ C ₇	=	116.4°

Figure III

The Crystal Structure of 1,2,5-Triphenyl-
phosphole (57)



$$\begin{aligned} \angle C_2PC_6 &= 104.4^\circ \\ \angle C_5PC_6 &= 106.2^\circ \end{aligned}$$

phenylphosphole is about 16 kcal/mole, as opposed to 29 - 36 kcal/mole for alkyl and aryl phosphines. This again indicates substantial interaction of the phosphorus non-bonding electron pair with the π system in a pyramidal ground state and probably considerable aromatic character in the planar inversion transition state. According to Mislow, these results are consistent with $(3p-2p)\pi$ delocalization. This supports the earlier conclusions reached by Brown (58) who found, from simple Molecular Orbital calculations, that the energy difference in going from the planar configuration of pyrrole and an aromatic phosphole to the tetrahedral configuration is much greater for pyrrole than it is for phosphole.

Thus, while the configuration about the phosphorus atom in phospholes is pyramidal in the ground state, accounting for their observed donor activity, there is still considerable interaction between the phosphorus lone pair and the π system of the ring and this accounts for the low basicity and poor donor character of the phosphole system.

The crystal structures of 1-benzylphosphole (Figure II) and 1,2,5-triphenylphosphole (Figure III) both indicate that the arrangement about the phosphorus is pyramidal in the ground state when the molecules are "frozen"

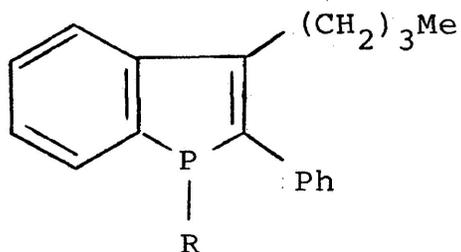
in a crystal lattice. Microwave studies on the free molecules, such as those done on pyrrole (49), may give significant information regarding the dimensions of the free phosphole molecule.

The heterocyclic ring in 1-benzylphosphole (56) is not planar, but slightly puckered with the phosphorus atom lying 0.21\AA above the plane of the rest of the ring. This puckering could be due in part to the torque exerted on the phosphorus atom from repulsion between the phosphole and phenyl rings (see Figure II). It is interesting to note that whereas there is a significant shortening of the P-C bonds within the phosphole ring of 1-benzylphosphole ($\sim 1.783\text{\AA}$), no significant difference was noted between the three P-C bond lengths of 1,2,5-triphenylphosphole ($\sim 1.822\text{\AA}$) (57).

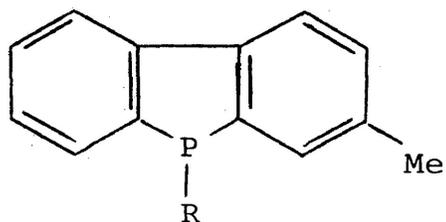
Fused-ring phospholes appear to have much less aromatic character than the simple phospholes and behave more like tertiary phosphines. They should therefore be better donors. Whereas the inversion barrier energy for a number of simple phospholes is 15 - 16 kcal/mole (55), that for the phosphindole VII (Figure IV) is about 23 kcal/mole, and that for the dibenzophosphole VIII is about 26 kcal/mole. These values are approaching the inversion barrier energies of tertiary phosphines and of saturated phosphorus - containing heterocycles such as 3-methyl-1-phenylphospholane, IX, (~ 36 kcal/mole) and 3-methyl-

Figure IV

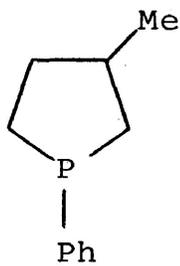
Fused Ring Phospholes



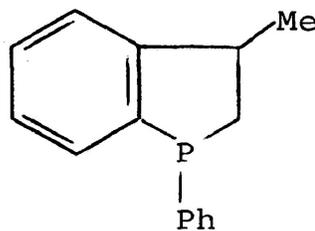
VII: R = (dl) -CD₂ -CH(OMe) Ph



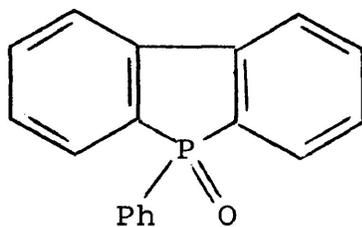
VIII: R = (dl) -CD₂ -CH(OMe) Ph



IX



X



XI

phenylphosphindoline, X (~ 35 kcal/mole) (55).

Thermochemical measurements of the P=O bond strength in 5-phenyl-5*H*-dibenzophosphole oxide, XI, by Millar (50) support this conclusion. The value of 126 ± 9 kcal/mole obtained is roughly comparable with that of triphenylphosphine oxide (128 ± 5 kcal/mole) and much higher than that of 1,2,3,4,5-pentaphenylphosphole oxide (100 ± 10 kcal/mole).

The Phospholes: Coordination Chemistry

The known coordination chemistry of the simple phospholes (*i.e.* those without fused rings) is not very extensive. The first metal adducts were reported by Braye *et al.* in 1961 (59). They found that 1,2,3,4,5-pentaphenylphosphole reacts with $\text{Fe}(\text{CO})_5$ to give pentaphenylphosphole - iron tetracarbonyl, with the phosphole coordinating through the phosphorus atom. Reaction with $\text{Fe}_3(\text{CO})_{12}$ gives, in addition, pentaphenylphosphole - iron tricarbonyl where bonding to the metal occurs through the diene π system of the phosphole ring, and also pentaphenylphosphole - $\text{Fe}_2(\text{CO})_6$ where coordination occurs through both the diene π system and the phosphorus atom, but with each entity bonded to a different iron atom. Reaction of pentaphenylphosphole oxide with $\text{Fe}(\text{CO})_5$ gives the π -bonded pentaphenylphosphole oxide - iron

tricarbonyl complex. From this evidence, Braye *et al.* concluded that there is little interaction between the phosphorus lone pair and the diene π system of the heterocyclic ring, the phosphole molecule acting much like a tertiary phosphine with an attached conjugated diene system.

Four years later, Cookson *et al.* (60) made similar observations about 1,2,5-triphenylphosphole (TPP). This reacts with $\text{Fe}_2(\text{CO})_9$ to give the P-bonded $\text{TPPFe}(\text{CO})_4$, but with $\text{Fe}(\text{CO})_5$ the π -bonded $\text{TPPFe}(\text{CO})_3$ complex is obtained. The hexacarbonyls of chromium, molybdenum and tungsten give P-bonded complexes of the type $\text{TPPM}(\text{CO})_5$, and reaction with $\text{Ni}(\text{CO})_4$ gives $\text{TPPNi}(\text{CO})_3$. Attempted recrystallization of the nickel complex results in decomposition to what appears to be $(\text{TPP})_2\text{Ni}(\text{CO})_2$. Attempts to produce disubstituted molybdenum and tungsten complexes by reacting triphenylphosphole with the bis-morpholine tetracarbonyls, $(\text{C}_4\text{H}_9\text{ON})_2\text{M}(\text{CO})_4$ give mixed-ligand products of the form $(\text{TPP})(\text{C}_4\text{H}_9\text{ON})\text{M}(\text{CO})_4$, and also tris-phosphole complexes of the form $(\text{TPP})_3\text{M}(\text{CO})_4$, where the authors feel that one of the phosphole molecules is not directly coordinated to the metal.

Cobalt carbonyl complexes of phospholes and phospholenes have been used successfully as catalysts in the

hydroformylation reactions of alkenes to aldehydes and alcohols (61).

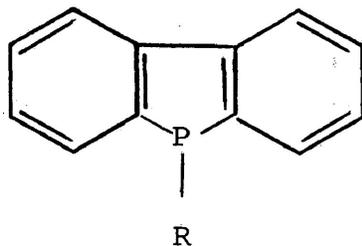
Walton (62) found that 1,2,5-triphenylphosphole reacts with the halides of Pd(II), Pt(II), Hg(II) and Rh(III) to give the complexes $(\text{TPP})_2\text{MX}_2$, $\text{M} = \text{Pd}, \text{Pt}$, $\text{X} = \text{Cl}, \text{Br}$; $(\text{TPP})\text{HgX}_2$, $\text{X} = \text{Cl}, \text{Br}$ and $(\text{TPP})\text{RhCl}_3$. In all of these complexes, coordination appears to be through the phosphorus atom.

Up until the work described in this thesis, these appear to be the only reported complexes with simple phospholes. It is noteworthy that in all of the above reports the "soft" phosphole donor reacts with the "soft" acceptors Rh(III), Pt(II), Pd(II) and Hg(II) and the zero-valent carbonyls of Fe, Cr, Mo, W and Ni.

A number of Ni(II), Pd(II) and Pt(II) complexes of fused ring phospholes have been synthesised by Allen *et al.* (63) and these are listed in Table V. The substituted dibenzophosphole (Phos) complexes occur in two stoichiometries: square-planar, four-coordinate complexes of the type $(\text{Phos})_2\text{MX}_2$, in both *cis* and *trans* configurations, and five-coordinate complexes of the type $(\text{Phos})_3\text{MX}_2$. An X-ray crystal structure determination on two complexes of the second type (Table V, 1(a): $\text{R}=\text{Me}$, $\text{X}=\text{CN}$ and 1(a): $\text{R}=\text{Et}$, $\text{X}=\text{CN}$) shows that the former has a tetragonal pyramidal structure while the latter

Table V

Complexes of Fused Ring Phospholes (63)



5-R-5-H-Dibenzophospholes (Phos)

1. (Phos)₃MX₂ R=Me or Et
 - a) M=Ni(II), X=Cl, Br, I, NCS, CN
 - b) M=Pd(II), X=Br
 - c) M=Pt(II), X=Br, SCN
 - d) M=Co(II), X=Br

2. (Phos)₂MX₂ R=Me or Et
 - a) M=Ni(II), X=Cl
 - b) M=Pd(II), X=CN, Br
 - c) M=Pt(II), X=CN, Cl

3. (Phos)₂MX₂ R=Ph, Prⁱ, Bu^t
 - a) M=Ni(II), X=Cl, Br, I, NCS
 - b) M=Pd(II), X=Br
 - c) M=Pt(II), X=Cl, Br

adopts a trigonal bipyramidal configuration (64). Initial evidence for these differing structures came from the different visible and infrared absorption spectra of the two compounds when mounted as Nujol mulls. In methylene chloride solution, however, both exhibit identical visible spectra and are thought to assume identical configurations. More recently, Powell *et al.* (65) have shown that the first compound (1(a): R=Me, X=CN) can be crystallized into either configuration by using different solvents.

When the phosphorus substituent of the dibenzophosphole is a phenyl group, or a bulky alkyl group, only the four-coordinate complexes are formed. With small alkyl substituents, three dibenzophosphole molecules coordinate to form the five-coordinate complexes. The higher coordination is attributed to the electron-releasing effect of the alkyl group, making the P-alkyl-dibenzophospholes better donors than 5-phenyl-5-H-dibenzophosphole. With very bulky alkyl groups, steric requirements are thought to force four-coordination. The same authors (63) have also prepared some Ni(II), Pd(II) and Pt(II) complexes with cyclic six and seven-membered ring phosphines containing fused benzene rings. No other complexes of fused ring phospholes have been reported.

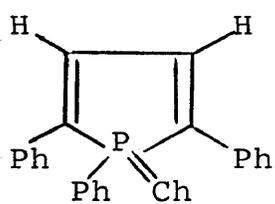
Phosphole oxides, sulfides and selenides have received almost no attention as donor ligands, even though they should be better electron donors than the phospholes themselves. Braye *et al.* (59) formed the π -bonded 1,2,3,4,5-pentaphenylphosphole oxide-iron tricarbonyl complex, and Cookson *et al.* (60) formed a similar complex with 1,2,5-triphenylphosphole oxide (TPPO). They also found that triphenylphosphole oxide does not react with $\text{Ni}(\text{CO})_4$, $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$, but does react with $\text{Mo}(\text{CO})_6$ to give small amounts of a product thought to be $(\text{TPPO})_2\text{Mo}(\text{CO})_2$. No other complexes of phosphole oxides have been reported before this present work. The only mention of phosphole sulfides or selenides is by Braye *et al.* (59) who found that when pentaphenylphosphole sulfide reacts with iron carbonyls, complete cleavage of the P=S bond occurs to give the pentaphenylphosphole - iron tetracarbonyl complex. In one of these reactions, a small amount of $\text{Fe}_3\text{S}_2(\text{CO})_9$ was isolated.

It is apparent, therefore that the known coordination chemistry of phospholes and their chalcogenides is very limited. The complexes which are known are all with "soft" metal acceptors. Further study and characterization of the donor properties of these molecules may provide more information on the steric and electronic effects of the phosphole ring, and perhaps on the catalytic

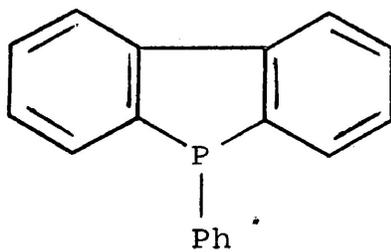
activity of phosphole complexes. Furthermore, useful information regarding the electronic structure of phospholes could possibly be obtained, although Mislow's recent measurements (54,55) (published after the work described here was started) have gone a long way towards providing a more accurate picture of the phosphole system.

With these objectives in view, this thesis will deal with a study of the reactions of the readily available (66) 1,2,5-triphenylphosphole and its oxide, sulfide and selenide with the halides of Nb(V) and Ta(V).

For the sake of brevity in the Experimental and Discussion sections which follow, abbreviations have been used for the ligands. 1,2,5-Triphenylphosphole (Figure III) is abbreviated to TPP and triphenylphosphine to Ph_3P as already mentioned. The other ligands (Figure V) are abbreviated as follows: 1,2,5-triphenylphosphole oxide: TPPO (XII); 1,2,5-triphenylphosphole sulfide: TPPS (XIII); 1,2,5-triphenylphosphole selenide: TPPSe (XIV); 5-phenyl-5H-dibenzophosphole: DBP (XV). Where a formula involves both a niobium halide and the corresponding tantalum halide, M is used in the formula to refer to both metals.

Figure V

XII: Ch=O
XIII: Ch=S
XIV: Ch=Se



XV

EXPERIMENTAL

Chemicals

Niobium and tantalum pentachloride were purchased from Alfa Inorganics. The pentabromides and pentaiodides of both metals were made by direct reaction of the appropriate elements in evacuated sealed tubes as outlined by Fairbrother (40). All pentahalides were purified by vacuum sublimation prior to use.

1,2,5-Triphenylphosphole (TPP) was prepared by the method of Campbell *et al.* (66) from the reaction of 1,4-diphenyl-1,3-butadiene with dichlorophenylphosphine. It was purified by several recrystallizations from chloroform, and in some cases by vacuum sublimation (10^{-6} Torr, 120°C). The phosphole oxide (TPPO), sulfide (TPPS), and selenide (TPPSe) were prepared by the reaction of the parent phosphole with hydrogen peroxide in ethanol/ethyl acetate, flowers of sulfur in boiling xylene and powdered selenium (also in boiling xylene) respectively, the products being recrystallized from 1:1 ethanol-ethyl acetate (TPPO),

acetonitrile (TPPS) and benzene (TPPSe).

5-Phenyl-5*H*-dibenzophosphole (DBP), a dibenzophosphole derivative (XV), was prepared by the method of Hoffmann (67). Triphenylphosphine was purchased from Eastman Organic Chemicals and triphenylphosphine oxide from the J.T. Baker Chemical Company. Both were used without further purification.

All subsequent reactions were carried out in a glove box 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. The oxygen content of the glove box was kept below 100 p.p.m. and was monitored using the Hersch Cell type (68) of oxygen meter. All solvents were degassed by flushing with dry nitrogen and stored over freshly pumped (10^{-6} Torr) molecular sieves (Fisher, Type 4A) under nitrogen. As a further precaution against moisture, methylene chloride, benzene and n-pentane were distilled from calcium hydride prior to degassing. All solid reactants prepared in air were crushed and pumped under low vacuum (10^{-3} Torr) before use in the glove box.

Deuterated sulfuric acid (99% D) was purchased from Stohler Isotope Chemicals. DCl was generated as needed by the reaction of degassed D_2SO_4 on dried

sodium chloride under nitrogen. D₂O (99.7% D) was purchased from Merck, Sharp and Dohme Limited.

Instrumental Procedures

Samples used in the physical measurements were suitably protected from atmospheric moisture. 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 between 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 were recorded on a Cary 14 recording spectrophotometer using 1.0 cm. and 0.1 cm. stoppered cells and a Holmium filter for calibration. Intensity measurements were calibrated against a standard solution of 1,2,5-triphenylphosphole oxide ($\lambda_{\max} = 394\text{m}\mu$, $\log \epsilon = 4.16$) (66) in methylene chloride.

Samples for X-ray powder diffraction photography were sealed in Lindemann X-ray capillaries and the photographs were recorded on Debye-Scherrer type cameras (114.6 mm. dia.) using Ni-filtered copper K_α radiation from a Phillips PW 1130 3KW X-ray Generator. Mass spectra were recorded on a Hitachi-Perkin-Elmer

Model RMU-7 double focussing mass spectrometer. NMR spectra were obtained using a Varian Associates model A60-A spectrometer using deuterated chloroform or methylene chloride as solvent with tetramethylsilane as the internal standard where needed.

Molar conductivities were measured on a YSI model 31 conductivity bridge at line frequency (60 Hz) and room temperature (20°C). The ground-glass stoppered conductivity cell was designed for use in the glove box and had a cell constant of 0.33.

Elemental Analyses

Metal analyses of tantalum and niobium were performed gravimetrically by hydrolysis of the complexes in ethanal-aqueous ammonia solution (4:1 by vol.) followed by ignition of the precipitated hydroxide to the oxide M_2O_5 . Chloride in the supernatant liquid was determined gravimetrically as silver chloride. Carbon-hydrogen analyses were carried out under the supervision of W.J. Buis, at the Institute for Organic Chemistry, TNO, Utrecht, the Netherlands, and also on a Perkin-Elmer model 240 CHN analyser in the Instrumentation Laboratory of this University. In some cases, where the ligand was not decomposed on hydrolysis, it was extracted into methylene chloride and

determined spectrophotometrically using a characteristic visible absorption band (TPPO:394 $m\mu$, $\log \epsilon = 4.16$; TPPS:385 $m\mu$, $\log \epsilon = 4.10$) (66).

Syntheses

1a. TPP.TaCl₅. A mixture of TaCl₅ (0.65 g) and TPP (0.60 g) was heated under reflux for 2 1/2 h. in methylene chloride-pentane (8:1, 9 ml). The resulting dark brown solution was quickly centrifuged, stoppered and cooled overnight. This resulted in the deposition of large, dark brown crystals, yield 0.8 g (66%). These crystals were vacuum dried.

Calc'd. for (C₂₂H₁₇P).TaCl₅:

C:39.41, H:2.56, Ta:26.97, Cl:26.44

Found: C:39.2, H:2.7, Ta:26.0, Cl:25.5

1b. (TPP.NbCl₅*). Reaction of NbCl₅ (0.41 g) with TPP (0.47 g) as above gave a dark green solution. Slow evaporation of the solvent yielded dark green crystals (0.5 g, 60%).

*Compounds in parentheses were identified from the fact that they have identical X-ray powder diffraction patterns with the first member in the series and are therefore probably isostructural with the first compound.

1c. (TPP.TaBr₅). TaBr₅ (0.92 g) was heated under reflux with TPP (0.51 g) in methylene chloride (10 ml) for 2 h. The resulting dark purple crystals were centrifuged and vacuum dried, yield 1.1 g (70%).

2. DBP.TaCl₅. A mixture of TaCl₅ (0.60 g) and DBP (0.32 g) was heated under reflux in benzene (5 ml) for 1 h. The pale yellow solution obtained was centrifuged and evaporated slowly under vacuum to 1/4 volume, giving orange crystals which were pumped under high vacuum (10⁻⁶ Torr, 6 h.) to give a yellow solid, yield 0.45 g (60%).

Calc'd. for (C₁₈H₁₃P).TaCl₅:

C:34.94, H:2.12, Ta:29.29, Cl:28.68

Found: C:34.8, H:2.3, Ta:29.5, Cl:27.6

3. Ph₃P.TaCl₅. A mixture of TaCl₅ (0.96 g) and Ph₃P (0.75 g) was heated under reflux in benzene (6 ml) for 1 1/2 h. The resulting yellow solution was centrifuged, and pentane (1 ml) added, precipitating a bright yellow crystalline solid which was vacuum dried, yield 0.95 g, (60%).

Calc'd. for (C₁₈H₁₅P).TaCl₅:

Ta:28.86, Cl:28.28

Found: Ta:28.7, Cl:28.1

4a. $[\text{TPPH}]^+ [\text{TaCl}_6]^-$. Anhydrous HCl was bubbled through a benzene solution (8 ml) of TPP.TaCl₅ (0.5 g) immediately producing an orange precipitate. This was washed with benzene (2x5 ml), vacuum dried and dissolved in methylene chloride. Slow addition of pentane precipitated an orange solid which was quickly centrifuged and vacuum dried, yield 0.15 g (30%). If the methylene chloride solution was allowed to stand for any length of time (more than five minutes), an unidentified yellow precipitate was formed.

Calc'd. for (C₂₂H₁₈P).TaCl₆:

C:37.37, H:2.57, Ta:25.58, Cl:30.09

Found: C:36.9, H:2.5, Ta:25.7, Cl:29.6

4b. $[\text{TPPH}]^+ [\text{NbCl}_6]^-$. When anhydrous HCl was bubbled through a benzene solution (6 ml) of TPP.NbCl₅ (0.5 g) a purple precipitate was formed. Attempted recrystallization of this in methylene chloride resulted in extensive decomposition.

4c. $[\text{TPPD}]^+ [\text{TaCl}_6]^-$. Anhydrous DCl was bubbled through a benzene solution (6 ml) of TPP.TaCl₅ (0.4 g) producing an orange precipitate; this was

washed with benzene and recrystallized from methylene chloride, yield 0.15 g (35%).

5. $[\text{DBPH}]^+[\text{TaCl}_6]^-$. Anhydrous HCl was bubbled through a benzene solution (8 ml) of $\text{DBP} \cdot \text{TaCl}_5$ (0.65 g). The resulting white precipitate was washed with benzene (2x5 ml), dried and recrystallized from methylene chloride-pentane, yield 0.45 g (65%).

Calc'd. for $(\text{C}_{18}\text{H}_{14}\text{P}) \cdot \text{TaCl}_6$:

Ta:27.62, Cl:32.49

Found: Ta:27.0, Cl:31.7

6. $[\text{Ph}_3\text{PH}]^+[\text{TaCl}_6]^-$. Anhydrous HCl was bubbled through a benzene solution (8 ml) of $\text{Ph}_3\text{P} \cdot \text{TaCl}_5$ (0.60 g), producing immediately a white precipitate. This was washed with benzene, dried and recrystallized from methylene chloride-pentane, yield 0.55 g (86%).

Calc'd. for $(\text{C}_{18}\text{H}_{16}\text{P}) \cdot \text{TaCl}_6$:

Ta:27.53, Cl:32.39

Found: Ta:27.0, Cl:31.2

7a. $\text{TPPO} \cdot \text{TaCl}_5 \cdot \text{CH}_2\text{Cl}_2$. A mixture of TaCl_5 (0.65 g) and TPPO (0.67 g) was heated under reflux in methylene chloride (10 ml) for 2 h. A bright red crystalline solid (~1 g) was produced. This was

dissolved in hot methylene chloride and recrystallized by slow evaporation to 1/3 volume, yield 0.81 g (65%). If the solid was recrystallized by precipitating from methylene chloride solution with pentane, the solvent content was found to vary from 0.5 to 1.5 moles.

Calc'd. for $(C_{22}H_{17}PO).TaCl_5.(CH_2Cl_2)$:

C:35.81, H:2.48, Ta:23.45, Cl:22.98

Found: C:36.0, H:2.6, Ta:23.4, Cl:22.6

7b. $(TPPO.TaBr_5.CH_2Cl_2, TPPO.NbX_5.CH_2Cl_2, X=Cl, Br)$.

The pentahalides were heated under reflux with TPPO in 1:1 molar ratios in methylene chloride for 1 1/2 - 3 h. to produce red solids. These were recrystallized from methylene chloride, yield 70 - 85%.

8a. $\alpha-TPPO.TaCl_5$. The solvated adduct (7a.), (0.5 g), when washed with acetonitrile (5 ml) changed from a bright red (scarlet) to a flocculent orange-red solid which was then vacuum-dried, yield 0.38 g (95%).

Calc'd. for $(C_{22}H_{17}PO).TaCl_5$:

C:38.49, H:2.50, Ta:26.35, Cl:25.83

Found: C:38.9, H:2.6, Ta:26.9, Cl:25.6

8b. (α -TPPO.NbCl₅). The adduct TPPO.NbCl₅.-CH₂Cl₂ (0.5 g) was washed with acetonitrile (2x5 ml) and vacuum dried, yield 0.40 g (91%).

9a. β -TPPO.TaCl₅. (I) When the solvated adduct (7a.) was heated (85°C) under vacuum (10⁻⁶ Torr) for 16 h., the β -phase was obtained in quantitative yield. Alternatively, sublimation of the adduct (7a.) under high vacuum (10⁻⁶ Torr) at 230 - 250°C also gave the β -phase and some free TPPO.

(II) To a suspension of TaCl₅ (0.87 g) in benzene (10 ml) was added TPPO (0.82 g) and the mixture was heated under reflux for 2 1/2 h. The red crystalline solid deposited (~1.3 g, 80%) was recrystallized in small quantities (50 mg) from hot benzene (10 ml).

Calc'd. for (C₂₂H₁₇PO).TaCl₅:

C:38.49, H:2.50, Ta:26.35, Cl:25.83

Found: C:38.7, H:2.7, Ta:26.3, Cl:25.3

9b. (β -TPPO.NbCl₅). A mixture of NbCl₅ (0.50 g) and TPPO (0.63 g) was heated under reflux in benzene for 1 1/2 h. depositing a dark red solid which was vacuum-dried, yield 0.95 g (85%).

10a. TPPO.TaOCl₃. A methylene chloride solution of the adduct (7a.), (0.25 g) was set aside in a rubber-stoppered tube. After two weeks, the orange solid deposited was removed, washed with methylene chloride and vacuum-dried, yield 0.15 g (70%).

Calc'd. for (C₂₂H₁₇PO).TaOCl₃:

C:41.83, H:2.71, Ta:28.64, Cl:16.84

Found: C:41.7, H:2.9, Ta:27.3, Cl:17.3

10b. (TPPO.NbOCl₃). A methylene chloride solution of the adduct TPPO.NbCl₅.CH₂Cl₂ (0.3 g) was allowed to stand for two weeks in a rubber-stoppered test tube. The dark orange solid which precipitated was washed with methylene chloride (2x5 ml) and vacuum dried, yield 0.15 g (55%).

11a. TPPS.TaCl₅.C₆H₆. A mixture of TaCl₅ (0.64 g) and TPPS (0.56 g) was heated under reflux in benzene (5 ml) for 2 h. The resulting deep red solution was set aside for several hours, during which time large, dark red crystals were deposited, yield 0.60 g (50%). Slow evaporation of the solution to 1/3 volume yielded more product, but of lower purity.

Calc'd. for (C₂₂H₁₇PS).TaCl₅.(C₆H₆):

Ta:23.17, Cl:22.71

Found: Ta:23.4, Cl:22.3

11b. $(\text{TPPS} \cdot \text{NbCl}_5 \cdot \text{C}_6\text{H}_6)$. A mixture of NbCl_5 (0.51 g) and TPPS (0.60 g) was heated under reflux in benzene for 1 1/2 h. The dark green solution was set aside to cool, depositing green crystals, yield 0.65 g (60%).

12a. $\alpha\text{-TPPS} \cdot \text{TaCl}_5$. The benzene adduct (11a.) was pumped under high vacuum (10^{-6} Torr) at 85°C for 6 h., giving a red-brown solid in quantitative yield. Calc'd. for $(\text{C}_{22}\text{H}_{17}\text{PS}) \cdot \text{TaCl}_5$:

TPPS*:49.02, Ta:25.75, Cl:25.24

Found: TPPS*:49.0, Ta:25.6, Cl:25.0

*Ligand percentages determined spectroscopically.

12b. $(\alpha\text{-TPPS} \cdot \text{NbCl}_5)$. The adduct (11b.) (0.3 g) was washed with pentane (3x5 ml) giving a flocculent green solid which was vacuum dried, yield 0.25 g (94%).

13a. $\beta\text{-TPPS} \cdot \text{TaCl}_5 \cdot 0.5(\text{C}_6\text{H}_6)$. A suspension of TaCl_5 (0.55 g) and TPPS (0.58 g) was heated under reflux in benzene (7 ml) for 1 1/2 h. The dark red solution was stoppered and left overnight, depositing red crystals which were vacuum dried, yield 0.85 g (78%).

Calc'd. for $(C_{22}H_{17}PS).TaCl_5 \cdot 0.5(C_6H_6)$:

Ta:24.43, Cl:23.95

Found: Ta:24.46, Cl:23.65

13b. $(\beta\text{-TPPS}.TaCl_5 \cdot 0.5(CH_2Cl_2))$. A mixture of $TaCl_5$ (1.0 g) and TPPS (1.0 g) was heated under reflux for 2 1/2 h. On cooling the mixture a dark red crystalline solid was deposited. This was vacuum dried, yield 1.2 g (60%).

13c. $(\beta\text{-TPPS}.TaCl_5)$. The adduct (13b.) was pumped under high vacuum (10^{-6} Torr) at 85°C for 14 h.

Calc'd. for $(C_{22}H_{17}PS).TaCl_5$:

TPPS:49.02, Ta:25.75, Cl:25.24

Found: TPPS:48.1, Ta:25.8, Cl:24.5

13d. $(\beta\text{-TPPS}.NbCl_5)$. A mixture of $NbCl_5$ (0.33 g) and TPPS (0.43 g) was heated under reflux in methylene chloride (8 ml) for 1 1/2 h. Slow evaporation to 1/4 volume yielded a dark green crystalline solid. This was dried under high vacuum (10^{-6} Torr, 85°C, 16 h.), yield 0.5 g (67%).

13e. $(\beta\text{-TPPSe}.TaCl_5 \cdot 0.5(C_6H_6))$. A mixture of $TaCl_5$ (1.1 g) and TPPSe (1.3 g) was heated under

reflux in benzene (10 ml) for 2 1/2 h. The red-brown solid formed was recrystallized from benzene, yield 1.5 g (60%).

Calc'd. for $(C_{22}H_{17}PSe).TaCl_5.0.5(C_6H_6)$:

C:38.08, H:2.56, Ta:22.94, Cl:22.48

Found: C:37.8, H:2.7, Ta:23.1, Cl:21.1

13f. $(\beta-TPPSe.NbCl_5.0.5(C_6H_6))$. Reaction of $NbCl_5$ (0.8 g) with TPPSe (1.2 g) in benzene (10 ml) under reflux for 2 h. produced a dark green solid. This was dried under vacuum, yield 1.2 g (60%).

Attempted Reactions

1. Tantalum and Niobium Iodides. When NbI_5 and TaI_5 were heated under reflux with TPP, TPPS, and TPPSe in methylene chloride or benzene, only the starting materials were recovered. There was no evidence of reaction of the pentaiodides with these ligands. With TPPO, reactions did occur and these are outlined later in this section.

2. $NbBr_5 + TPP$. The reaction of $NbBr_5$ with TPP in a 1:1 molar ratio in methylene chloride produced an oil which could not be crystallized.

3. [TPPH]⁺[TaCl₆]⁻ + NaPh₄B. Attempts were made to replace the [TaCl₆]⁻ ion in the phospholium salt with the [Ph₄B]⁻ ion and thus stabilize the protonated phosphole with a different anion. A reaction did occur between the two salts when suspended in benzene, but with decomposition of the P-protonated phosphole as indicated by the disappearance of the P-H⁺ stretching frequency. The products formed were mixtures as Ta-Cl vibrations appeared in all products isolated. No pure tetraphenyl boron salt was obtained.

4. ZnCl₂ + TPP + HCl. In an attempt to stabilize a protonated phosphole with [ZnCl₄]⁼, anhydrous HCl was bubbled through a suspension of ZnCl₂ and TPP in 1:2 molar ratios in methylene chloride. There was no reaction of ZnCl₂ and TPP alone, but on addition of HCl, an orange solution and a gummy orange solid were obtained. However, neither the orange solid nor the solid precipitated from solution showed a P-H⁺ stretching frequency in their infrared spectra. The spectra indicated that the solids were not very pure. Attempts to recrystallize the products resulted in oils. Analyses of the yellow-orange solid from different reactions were not reproducible.

5. TaCl₅ + Ph₃PO (an excess). A mixture of TaCl₅ (0.19 g) and Ph₃PO (0.45 g) was heated under reflux in benzene (6 ml) for 15 h. About 10 mg of a white insoluble solid, identified from its infrared spectrum as the oxytrichloride adduct (Ph₃PO)₂.TaOCl₃ (30) was obtained. Evaporation of the remaining benzene solution to dryness yielded a mixture of unreacted Ph₃PO and the 1:1 adduct Ph₃PO.TaCl₅, identified by their infrared spectra.

6. TaCl₅ + TPPO (an excess). A mixture of TaCl₅ (0.21 g) and TPPO (0.57 g) was heated under reflux in benzene (6 ml) for 16 h. A small amount (~100 mg) of the oxytrichloride adduct TPPO.TaOCl₃ was obtained, but the major products were the 1:1 adduct TPPO.TaCl₅ and unreacted TPPO, as identified by their infrared spectra.

7. NbCl₅ + TPPO (an excess). A mixture of NbCl₅ (0.25 g) and TPPO (0.94 g) was heated under reflux for 14 h. in benzene (9 ml). A dark red solution and a small amount (~40 mg) of orange, insoluble solid were obtained. Infrared measurements showed that the orange solid was the oxytrichloride adduct and that the solution contained a mixture of the 1:1 adduct TPPO.NbCl₅ and unreacted TPPO.

8. TPPO.TaCl₅ + Moisture. When the solvated adduct TPPO.TaCl₅.CH₂Cl₂ was dissolved in wet acetonitrile, or when a benzene solution of β-TPPO.TaCl₅ was exposed to the atmosphere, a yellow-orange insoluble solid was formed. This exhibited a strong Ta=O band, contained TPPO and gave a Ta:Cl ratio of about 1:2. However no consistent analyses could be obtained for this compound.

9. TaI₅ + Ph₃PO (an excess). A mixture of TaI₅ (0.65 g) and Ph₃PO (0.45 g) was heated under reflux in benzene for 24 h., producing a grey, insoluble product. The infrared spectrum of this indicated a Ph₃PO complex was formed. There was no infrared evidence for formation of Ph₃P or of Ta=O, or Ta-O-Ta bonds.

10. TaI₅ + TPPO (an excess). A mixture of TaI₅ (0.50 g) and TPPO (0.44 g) was heated under reflux for 26 h., forming a black insoluble product exhibiting strong absorption bands at 1083 cm⁻¹ and 730 cm⁻¹ in its infrared spectrum. Evaporation of the benzene solution yielded over 100 mg of TPP.

11. NbI₅ + TPPO (an excess). A mixture of NbI₅ (0.54 g) and TPPO (0.51 g) was heated under reflux

in benzene for 24 h. The infrared spectrum of the black, insoluble solid formed exhibited a strong absorption band at 1040 cm^{-1} . Evaporation of the benzene solution yielded unreacted TPPO.

12. $\text{NbCl}_5 + \text{TPPSe} + \text{Moisture}$. In several reactions of NbCl_5 , with TPPSe, where the mixture was heated under reflux in benzene overnight, it was found that if moisture was not rigorously excluded from the glove box atmosphere, then some $\beta\text{-TPPO.NbCl}_5$ was formed, as confirmed by the fact that the dark red product has an identical infrared spectrum and X-ray powder diffraction pattern as an authentic sample of $\beta\text{-TPPO.NbCl}_5$ (see subsection 9b. of the preceding section). The strong absorption at about 1055 cm^{-1} in the infrared spectrum of the product (where only weak ligand absorptions are found in $\beta\text{-TPPSe.NbCl}_5$) can only be attributed to coordinated P=O (see Table VIII in the Discussion).

RESULTS AND DISCUSSION

The Reactions of TPP, Ph₃P and DBP with Nb(V) and Ta(V)

(a) Phosphole and Phosphine Complexes

Despite the weaker basicity noted (51) for the simple phospholes such as TPP relative to tertiary phosphines, TPP was found to react surprisingly readily with the chlorides and bromides of Ta(V) and Nb(V). The three crystalline adducts formed, TPP.TaCl₅, TPP.TaBr₅ and TPP.NbCl₅ are very sensitive to moisture and solvent vapours and although the analyses were not all ideal, they showed clearly that the complexes had 1:1 stoichiometries. The three complexes have identical X-ray powder diffraction patterns, thus confirming their similar stoichiometries.

There was no reaction between TPP and the penta-iodides of both metals, probably because the greater steric interaction between the phosphole molecule, with its three bulky phenyl groups (see Introduction, Figure III), and the large iodide ions is enough to offset the relatively weak bonding interaction between the phosphorus and the metal. This steric interaction

may also account for the lower stability of the pentabromide adducts relative to the pentachloride ones. The weak nature of the metal-phosphorus bond is evident in that all three crystalline adducts are decomposed by traces of moisture and that coordinating solvents such as ethanol, acetonitrile and even the weak donor ether, readily displace TPP from the complexes.

The weakness of the metal-phosphorus bond in these adducts is consistent with $(3p - 2p)\pi$ interaction between the phosphorus lone electron pair and the diene π system of the phosphole ring as suggested by Mislow (54, 55). Further evidence for the poor accessibility of the phosphorus lone pair has come from other work in this laboratory (69) which has shown that TPP does not react with the chlorides of Ag(I), Mn(II), Fe(II), Cd(II), and Ni(II), although phosphine complexes of these metal halides are well known (70).

That the phosphole molecule is not changed structurally on coordination is shown by the fact that TPP is immediately displaced from the complex by ether and by hydrolysis in ethanol-aqueous ammonia. Although the adduct $\text{TPP} \cdot \text{TaCl}_5$ sublimes unchanged under high vacuum (10^{-6} Torr, 140°C), attempts to determine its molecular weight by mass spectrometry at a low ionizing voltage gave only the TPP molecular ion ($m/e = 312$).

1:1 Complexes of Ph_3P and DBP with TaCl_5 were made in a similar manner to the TPP complexes. The complex $\text{Ph}_3\text{P} \cdot \text{TaCl}_5$ (which has since been reported in the literature (71)) is much more stable than the corresponding TPP complex as would be expected from the greater basicity of the phosphine. Thus, $\text{Ph}_3\text{P} \cdot \text{TaCl}_5$ is stable indefinitely in dry ether and is hydrolysed more slowly in air than is $\text{TPP} \cdot \text{TaCl}_5$. The $\text{DBP} \cdot \text{TaCl}_5$ complex exhibits an intermediate stability, decomposing in dry ether over a period of several hours. Although the basicity of DBP is similar to that of Ph_3P , a greater steric interaction due to the more rigid nature of the system may weaken its bonding to the metal ion.

The infrared spectrum of $\text{TPP} \cdot \text{TaCl}_5$ is somewhat similar to the ligand spectrum (with small shifts in some of the absorption bands, and changes in their intensity) except for the region $400 - 300 \text{ cm}^{-1}$ which is dominated by the strong Ta-Cl stretching absorption, centred at 355 cm^{-1} . $\text{TPP} \cdot \text{NbCl}_5$ gives a very similar infrared spectrum, but with the Nb-Cl stretching band at 365 cm^{-1} . Metal chloride vibrations in other TaCl_5 and NbCl_5 adducts have been recorded as having similar locations (26, 28). No M-Cl vibrations, however, have been reported for the other phosphine complexes

of these metals. The complexes $\text{Ph}_3\text{P} \cdot \text{TaCl}_5$ and $\text{DBP} \cdot \text{TaCl}_5$ show strong M-Cl absorptions at 345 and 350 cm^{-1} respectively.

Because of the lower stability of $\text{TPP} \cdot \text{TaBr}_5$, it could not readily be purified and a clear infrared spectrum of this adduct was not obtained. The spectrum of the crude $\text{TPP} \cdot \text{TaBr}_5$ is however similar to that of $\text{TPP} \cdot \text{TaCl}_5$ except that the Ta-Br stretching band is at 240 cm^{-1} .

In the reaction of TPP with NbBr_5 , the oil which was obtained exhibited a strong absorption band at 268 cm^{-1} , attributable to an Nb-Br vibration, but also had a strong band at 1045 cm^{-1} which is not present in the crystalline 1:1 complexes. This band is however similar to that due to coordinated P=O in the adduct $\text{TPPO} \cdot \text{NbBr}_5 \cdot \text{CH}_2\text{Cl}_2$ (1049 cm^{-1} , Table VII). It is thus probable that in this reaction, the 1:1 adduct $\text{TPP} \cdot \text{NbBr}_5$ is initially formed but then reacts with trace moisture to form a mixture of $\text{TPP} \cdot \text{NbBr}_5$, $\text{TPPO} \cdot \text{NbBr}_5$ and some decomposition products. The 1:1 adduct $\text{TPP} \cdot \text{NbBr}_5$ can probably be obtained in relatively pure form by a reaction under very rigorously water-free conditions. This reaction is not unique to NbBr_5 as in one instance of a reaction of TPP with NbCl_5 where special precaution against moisture was not taken,

an oil was produced which showed a strong absorption band at 1056 cm^{-1} in its infrared spectrum. The remainder of the spectrum was also similar to that of $\text{TPPO}\cdot\text{NbCl}_5\cdot\text{CH}_2\text{Cl}_2$ (P=O band at 1058 cm^{-1} , Table VII).

It is interesting that where moisture is present, the oxygen prefers to bond to the phosphorus atom to form the P=O link rather than bond to the niobium to form either Nb=O or Nb-O-Nb bonds. The infrared spectra of the oils showed the presence of neither Nb=O nor Nb-O-Nb groups which absorb at about 922 cm^{-1} and 767 cm^{-1} respectively (72). It would appear, then, that the P=O bond is stronger than the Nb=O bond. This conclusion is further supported by evidence from TPPO and TPPSe reactions with Nb(V) to be discussed later.

A number of workers have assigned metal-phosphorus stretching vibrations in phosphine complexes, and these cover a wide frequency range ($460 - 90\text{ cm}^{-1}$; see (73), (74) and references cited therein). This wide variation has been attributed to: differences in the nature of the metal, differences in the nature of the phosphine and differences in the structure of the complexes (73). Shobatake and Nakamoto (75) have assigned metal-phosphorus stretching vibrations in a number of Ni(II) and Pd(II) phosphine complexes on the basis of

metal isotope shifts and found these to lie in the narrower range of $273 - 164 \text{ cm}^{-1}$.

An attempt was made to identify M-P vibrations in the tantalum - phosphole complexes by a comparison of the far-infrared region ($600 - 200 \text{ cm}^{-1}$) of analogous phosphole ($\text{TPP} \cdot \text{TaCl}_5$), phosphole oxide ($\text{TPPO} \cdot \text{TaCl}_5$) and protonated phosphole ($[\text{TPPH}]^+ [\text{TaCl}_6]^-$) complexes. However, no reasonable assignment could be made. The complexity of the spectra of all three types of complexes in the $600 - 400 \text{ cm}^{-1}$ region precludes any positive assignment. The strong M-Cl band in the $400 - 300 \text{ cm}^{-1}$ region obscures bands of low intensity and the complexes exhibit no strong band in the $300 - 200 \text{ cm}^{-1}$ region. The low sensitivity of the instrument in this last region results in the poor resolution of absorption bands of weak intensity.

(b) Phospholium and Phosponium Salts

The discovery of a second series of phosphole complexes was made, quite by accident, when the 1:1 adducts were found to react with traces of ethanol vapour in the glove box atmosphere to give an orange product. It was subsequently found that $\text{TPP} \cdot \text{TaCl}_5$ in benzene reacts with several drops of ethanol to produce a similar orange precipitate which, when

purified, was identified as $[\text{TPPH}]^+ [\text{TaCl}_6]^-$ where $[\text{TPPH}]^+$ represents P-protonated 1,2,5-triphenylphosphole (*i.e.*: a 1H-phospholium salt is formed). The same compound was then also made by the addition of several drops of water to $\text{TPP} \cdot \text{TaCl}_5$ and also by passing anhydrous HCl through a solution of $\text{TPP} \cdot \text{TaCl}_5$ in benzene.

In the case of the ethanol and water additions, the phospholium salt is probably formed by the initial reaction of the ethanol or water with $\text{TPP} \cdot \text{TaCl}_5$ to produce HCl which then reacts with more $\text{TPP} \cdot \text{TaCl}_5$ units, giving the salt. When ethanol was used, an infrared spectrum of the material obtained from benzene washings of the salt showed the presence of free TPP and of a tantalum - ethoxy product, possibly $\text{Ta}(\text{OEt})_2\text{Cl}_3$, which is well known (40). When water was used, an insoluble, unidentified residue exhibiting Ta=O and Ta-OH absorptions in its infrared spectrum was obtained as one of the products.

The identify and structure of the 1H-phospholium salt, $[\text{TPPH}]^+ [\text{TaCl}_6]^-$ was proven by satisfactory analyses and by infrared spectral evidence. The salt exhibits a strong Ta-Cl absorption band at 325 cm^{-1} in its infrared spectrum, characteristic of the $[\text{TaCl}_6]^-$ ion (76). The remainder of the spectrum is similar to that of TPP with small band shifts and intensity

Table VI

Infrared Data on Protonated Phospholes

<u>Compound</u>	ν (P-R) (cm^{-1})	ν (M-Cl) (cm^{-1})	<u>Reference</u>
PH_3	2327	-	(78)
PH_4^+	2304	-	(78)
PD_3	1694	-	(78)
PD_4^+	1625	-	(78)
$[\text{Ph}_3\text{PH}]^+ \text{Cl}^-$	2418	-	-
$[\text{TPPH}]^+ [\text{TaCl}_6]^-$	2410	325	-
$[\text{TPPH}]^+ [\text{NbCl}_6]^-$	2385	340	-
$[\text{Ph}_3\text{PH}]^+ [\text{TaCl}_6]^-$	2430	330	-
$[\text{DBPH}]^+ [\text{TaCl}_6]^-$	2395	330	-
$[\text{TPPD}]^+ [\text{TaCl}_6]^-$	1753	325	-
$[\text{NH}_4]^+ [\text{TaCl}_6]^-$	-	321	(76)
$[\text{NH}_4]^+ [\text{NbCl}_6]^-$	-	333	(76)

*R=H, D

changes, except that, in the spectrum of the salt, a sharp peak of medium intensity is found at 2410 cm^{-1} . This band can be attributed to an $\text{R}_3\text{P}^+-\text{H}$ stretching vibration as such vibrations are typical of this type of system (77) and almost unique to this region of the infrared spectrum.

More conclusive evidence for this assignment came from the formation of the complex $[\text{TPPD}]^+[\text{TaCl}_6]^-$ by the reaction of DCl with TPP.TaCl_5 . This salt, which is X-ray isostructural with $[\text{TPPH}]^+[\text{TaCl}_6]^-$, has no absorption band at 2410 cm^{-1} , but a sharp peak of medium intensity at 1753 cm^{-1} , characteristic of an $\text{R}_3\text{P}^+-\text{D}$ stretching vibration (see (77) and examples in Table VI)). The same deuterated salt was also produced by the reaction of TPP.TaCl_5 in benzene with small amounts of D_2O .

A strong band at 890 cm^{-1} in the infrared spectrum of $[\text{TPPH}]^+[\text{TaCl}_6]^-$, which becomes very weak in the spectrum of $[\text{TPPD}]^+[\text{TaCl}_6]^-$, is probably associated with a $\text{P}-\text{H}$ bending vibration. Apart from the above differences, the infrared spectra of the protonated and deuterated salts are almost identical. The shift of the 2410 cm^{-1} band on deuteration strongly indicates that protonation is occurring at the phosphorus atom of TPP.

There is the possibility that the P-H bond arises⁺ from a structural change in the phosphole molecule, but this can be discounted, as the evidence available indicates that the phosphole molecule remains intact. For example, acetonitrile displaces TPP from the salt, a low voltage mass spectrum gave a peak at $m/e = 312$ due to $[\text{TPP}]^+$ and an attempted high vacuum sublimation of $[\text{TPPH}]^+[\text{TaCl}_6]^-$ produced $\text{TPP} \cdot \text{TaCl}_5$ as the sublimed phase.

A molar conductivity measurement on a freshly-prepared methylene chloride solution of $[\text{TPPH}]^+[\text{TaCl}_6]^-$ gave a value of $6.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ (Table VII). This decreased rapidly, even as the measurement was being made, indicating the instability of the salt in solution. The value of 6.6 is comparable with that of $[\text{Et}_4\text{N}]^+\text{Cl}^-$ (8.25) and $[\text{Et}_4\text{N}]^+\text{I}^-$ (10.7) in methylene chloride and supports the formulation of the salt as a 1:1 electrolyte. The conductivity values in methylene chloride are significantly lower than those in more polar solvents such as nitromethane which gives values of 0-50 $\text{ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ for non-electrolytes and 80-100 $\text{ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ for 1:1 electrolytes at 10^{-3}M concentrations (79). In methylene chloride it was found that non-electrolytes such as $\text{Fe}(\text{S}_2\text{CNET}_2)_3$ and $\beta\text{-TPPO} \cdot \text{TaCl}_5$ give very low conductivity values

Table VII

Molar Conductivity Data
(methylene chloride solution)

<u>Complex</u>	<u>Concentration</u> (M)	<u>Molar</u> <u>Conductivity</u> (ohm ⁻¹ cm ² mole ⁻¹)
[TPPH] ⁺ [TaCl ₆] ⁻	7.5 X 10 ⁻⁴	6.6
[Et ₄ N] ⁺ Cl ⁻	1.16 X 10 ⁻³	8.25
[Et ₄ N] ⁺ I ⁻	1.85 X 10 ⁻³	10.7
β-TPPO.TaCl ₅	5.5 X 10 ⁻³	0.060
Fe(S ₂ CNEt ₂) ₃	1.07 X 10 ⁻³	0.061

($\sim 0.06 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$). Other workers (23) have similarly found very low values for non-electrolytes in methylene chloride solution.

An attempt was made to determine the P-H coupling constant of $[\text{TPPH}]^+ [\text{TaCl}_6]^-$ by NMR measurements. These were unsuccessful due to the low solubility of the complex in suitable NMR solvents and its instability in solution which prevented the use of multiple-scan signal averaging techniques.

The corresponding niobium phospholium salt, $[\text{TPPH}]^+ [\text{NbCl}_6]^-$ was made by treating $\text{TPP} \cdot \text{NbCl}_5$ in benzene either with anhydrous HCl or with several drops of ethanol. The addition of water produced only a messy oil, possibly because of the competing tendency to form the P=O bond noted earlier. The niobium salt is less stable than the tantalum one and decomposes extensively when recrystallization is attempted.

In one case of ethanol addition an orange precipitate was formed, which, in addition to having the absorption pattern due to $[\text{TPPH}]^+$ in its infrared spectrum, also had several extra bands which corresponded closely to the ethoxy absorptions of $[\text{Et}_4\text{N}]^+ [\text{Nb}(\text{OEt})_2\text{Cl}_4]^-$ (29). It would appear that in this instance the salt $[\text{TPPH}]^+ [\text{Nb}(\text{OEt})_2\text{Cl}_4]^-$ was produced. Attempts to recrystallize this product resulted

only in decomposition. The amount of ethanol added and perhaps the concentration of TPP.NbCl_5 in the benzene solution thus appear to be critical in determining whether the $[\text{NbCl}_6]^-$ or $[\text{Nb}(\text{OEt})_2\text{Cl}_4]^-$ salt is formed.

The salts $[\text{Ph}_3\text{PH}]^+[\text{TaCl}_6]^-$ and $[\text{DBPH}]^+[\text{TaCl}_6]^-$ were made from the corresponding TaCl_5 adducts by treating these with anhydrous HCl in benzene. The $^+$ P-H stretching absorption in their infrared spectra (Table VI) again indicates that protonation occurs at the phosphorus atom. In the case of Ph_3P and DBP , protonation at the phosphorus atom is to be expected because of the greater basicity of these ligands relative to TPP . The higher stability of these salts is shown by the fact that $[\text{Ph}_3\text{PH}]^+[\text{TaCl}_6]^-$ in the solid state is air stable for several days while $[\text{TPPH}]^+[\text{TaCl}_6]^-$ hydrolyses within several hours. Triphenylphosphine also reacts readily with HCl to form $[\text{Ph}_3\text{PH}]^+\text{Cl}^-$ but TPP shows no immediate reaction. Over a period of several days, however, with frequent bubbling of dry HCl , TPP in benzene solution did produce an orange oil which could be pumped under reduced pressure to give a yellow solid. Although the chloride content of this solid ($\sim 14\%$) would indicate that a salt is formed, the infrared spectrum indicated that the material

was not a pure product and it displayed no P-H stretching absorption. Attempts to purify this material resulted only in further decomposition.

The stability of the protonated phosphole in the salt $[\text{TPPH}]^+[\text{TaCl}_6]^-$ thus appears to be at least partly due to a favourable lattice energy for the solid, which is highly crystalline, as indicated by its strong X-ray powder diffraction pattern. Another probable stabilizing factor in the salt is the stability of the $[\text{TaCl}_6]^-$ ion, which is known to form readily under several different circumstances (76, 80).

Attempts at stabilizing the protonated phosphole with other large anions were unsuccessful. A reaction did occur between a suspension of ZnCl_2 and TPP in benzene through which HCl was passed and it would appear that at least some ionic product is formed, as indicated by an infrared absorption band at 285 cm^{-1} in the product, typical of the $[\text{ZnCl}_4]^{2-}$ ion (81). However, the product showed no P-H stretch in its infrared spectrum, was extremely moisture-sensitive, and could not be purified.

A reaction also occurred between $\text{Na}^+[\text{Ph}_4\text{B}]^-$ and $[\text{TPPH}]^+[\text{TaCl}_6]^-$, but again none of the products of this reaction showed a P-H absorption. B. Hui (82) did obtain a compound with a P-H absorption from a reaction of FeCl_3 with TPP and HCl, but again this

proved to be extremely moisture-sensitive and could not be purified adequately for analysis.

The protonated phosphole salts of Ta(V) and Nb(V) are unique in that this is the first known work on protonation of the phosphole ring and the major results described in the foregoing discussion have been the subject of a recent communication (82).

It is interesting to compare these results with the protonation work which has been done on the pyrrole system. The position of protonation in pyrrole itself has not been clearly established because of the tendency of pyrrole to form a trimer under acidic conditions, possibly through the initial formation of an *N*-protonated pyrrole (83). 2,4-Dimethyl-3-ethylpyrrole was found by Bullock (84) to form a monomeric hydrochloride under anhydrous conditions which is claimed to have an *N*-protonated structure on the basis of its infrared spectrum. Although this appears to be the only *N*-protonated pyrrole reported, this paper has received little attention in the literature. In a later paper, Bullock *et al.* (85) found that a number of other alkyl pyrroles form hydrochlorides where, on the basis of their NMR spectra in concentrated HCl, protonation is assigned at the α carbon atom of the pyrrole ring. Chiang and Whipple (52) have found that in 12 - 16 M H_2SO_4 solutions, the pyrrole ring of

some substituted pyrroles protonates at either the α or β ring carbon atom, depending on the number of substituents and their position on the ring. In a later paper Chiang *et al.* (86) report similar protonation reactions with substituted *N*-phenylpyrroles.

A reaction was tried in this present work between pyrrole and HCl under the anhydrous, oxygen-free, non-polar solvent (benzene) conditions used for TPP. A product was obtained for which analyses tentatively indicate the formation of a pyrrole dimer hydrochloride. This reaction thus appears to be different from the trimerization reaction of pyrrole observed in concentrated aqueous HCl and in an ether-gaseous HCl system (83). No attempt was made to determine the site of protonation in this product. Perhaps a more meaningful comparison with TPP could be gained from a study of the reaction of 1,2,5-triphenylpyrrole with HCl under anhydrous, non-polar solvent conditions.

The Reactions of TPPO with Nb(V) and Ta(V)

Because of its good σ donor properties, TPPO, as expected, reacts readily with the chlorides and bromides of Nb(V) and Ta(V) to form 1:1 adducts which crystallize from methylene chloride solution with 0.5 to 1.5 moles of the solvent. Washing the solvated

pentachloride adducts with dry acetonitrile removes the methylene chloride to give the 1:1 adducts, TPPO.MCl₅, in the α crystalline form. The 1:1 complexes were also isolated in a second (β) crystalline form by pumping the solvated adducts under high vacuum and by 1:1 molar reactions of TPPO and the pentachlorides in benzene. In making the analogous Ta(V) and Nb(V) complexes of Ph₃PO, Brown *et al.* (28) obtained only one crystalline form.

Coordination through the oxygen atom of TPPO is readily apparent from the large shift of the P=O stretching frequency in the complexes (Table VIII). Although the shifts are large ($\sim 120 \text{ cm}^{-1}$), they are still only approximately half as large as the P=O shifts in the corresponding Ph₃PO complexes (Table VIII). This indicates that a weaker PO→M donor bond is formed by the phosphole oxide than by the phosphine oxide perhaps because of an electron-withdrawing effect of the phosphole ring on the oxygen electrons. The weaker metal-oxygen bond may also be due partly to a greater steric interaction in the case of TPPO coordination than in the case of Ph₃PO coordination. The α and β TPPO complexes have identical P=O shifts and identical infrared spectra except that the β complexes exhibit a broader M-Cl absorption band.

Table VIII

Infrared Data on TPPO Complexes

<u>Compound</u>	ν (P=O) (cm^{-1})	$\Delta\nu$ (P=O)	ν (M-X) (cm^{-1})	<u>Reference</u>
TPPO	1181	-	-	-
α -TPPO.TaCl ₅	1064	117	332	-
β -TPPO.TaCl ₅	1064	117	336,342	-
TPPO.TaBr ₅ .CH ₂ Cl ₂	1053	128	235	-
α -TPPO.NbCl ₅	1058	123	355	-
β -TPPO.NbCl ₅	1058	123	350,365	-
TPPO.NbBr ₅ .CH ₂ Cl ₂	1049	132	-	-
TPPO.TaOCl ₃	1089 (800)*	92	338	-
TPPO.NbOCl ₃	1081 (930)*	100	335	-
Ph ₃ PO.NbCl ₅	977	215	344	(28)
Ph ₃ PO.NbBr ₅	970	222	247	(28)
Ph ₃ PO.TaCl ₅	987	205	377,333,327	(28)
Ph ₃ PO.TaBr ₅	975	217	-	(28)
(Ph ₃ PO) ₂ .NbOCl ₃	1167	25	-	(26)

*M=O absorption

The TPPO complexes are much more stable than the corresponding TPP complexes and are not decomposed by either dry acetonitrile or dry ether. In air and in solvents containing small amounts of water, slow decomposition of the TPPO.TaCl₅ complexes occurs to produce an unidentified oxychloride compound still retaining coordinated TPPO (as evident from the P=O shift of 42 cm⁻¹) but having a Ta:Cl ratio of between 1:1 and 1:2.

If the 1:1 TPPO adducts are allowed to react very slowly with moisture (such as by diffusion through a rubber stopper), oxytrichloride adducts of the type TPPO.MOCl₃ are formed. These adducts could not be well purified because of their low solubility and their tendency to undergo further decomposition in the presence of an excess of moisture. However, analyses did give a M:Cl ratio of close to 1:3 and the infrared spectra exhibited strong absorptions at 800 cm⁻¹ in the tantalum adduct and 930 cm⁻¹ in the niobium adduct, both assignable to M=O vibrations (72). The remainder of the spectra are very similar to those of the corresponding pentachloride complexes but with smaller P=O shifts. TPPO was recovered on hydrolysis of the complexes, indicating that the ligand has not undergone any structural change.

The weaker PO→M bond formed in the oxytrichloride complexes relative to the pentachloride complexes, as indicated by the lower P=O frequency shifts, is due no doubt to the formation of the M=O bond. A much smaller P=O shift was observed in $(\text{Ph}_3\text{PO})_2 \cdot \text{NbOCl}_3$, but this may be because of weakened PO→M bonds due to the coordination of two ligand molecules.

The source of the oxygen atom in the oxytrichlorides is of considerable interest in view of the fact that NbCl_5 appears to abstract oxygen from Ph_3PO (26, 27, 30). With a weaker P=O bond in the phosphole oxides, one would expect that oxygen abstraction from TPPO would occur more readily than from Ph_3PO .

Oxygen abstraction by TaCl_5 from Ph_3PO has not been proven conclusively and when attempted in this work (see Experimental Section, Attempted Reactions, #5) there was no evidence of oxygen abstraction. Brown *et al.* (28) report inconclusive results for a reaction of TaBr_5 with an excess of Ph_3PO .

In the present work, it was found that neither TaCl_5 nor NbCl_5 abstract oxygen from TPPO when heated under reflux for extended periods with a two-molar excess of the ligand in dry benzene. Dry oxygen gas also failed to react with solutions of the 1:1 pentachloride adducts, thus leaving water as the probable source of the oxytrichloride oxygen.

The above reactions would tend to indicate that the P=O bond is more stable than the M=O bond in the oxytrichlorides. The reported heats of formation of the pentachlorides and oxytrichlorides (40) of niobium and tantalum indicate that the M=O bond strengths lie in the range of 90-100 kcal/mole, or slightly lower than the 100 kcal/mole reported for the P=O bond strength in phosphole oxides (50). This would tend to support the observed results, and make the oxygen abstraction reaction of NbCl_5 and Ph_3PO , where the P=O bond strength is about 128 kcal/mole (87), the exception rather than the rule.

The only situation in which any cleavage of the P=O bond was observed in the pentachloride complexes was under the more extreme conditions of high vacuum sublimation. In the high vacuum sublimation of $\text{TPPO} \cdot \text{TaCl}_5 \cdot \text{CH}_2\text{Cl}_2$ (10^{-6} Torr, 235°C), a small amount of $\text{TPP} \cdot \text{TaCl}_5$ was produced as a sublimed phase.

Although TPPO does react readily with the pentaiodides of both niobium and tantalum, no pure complexes were isolated because of the difficulty of preparing very pure pentaiodides and because of the insoluble nature of the products formed. However, much information can be gained from the infrared spectra of the reaction products.

TPPO reacts with NbI_5 in a 1:1 ratio and also with an excess of the ligand to form a dark brown insoluble solid, having a strong absorption band at 1040 cm^{-1} , attributable to coordinated P=O . The remainder of the infrared spectrum is identical to that of the $\beta\text{-TPPO.TaCl}_5$ complex except for the absence of a M-Cl vibration. (The M-I vibrational absorptions are just below the range of the infrared instrument used). The P=O shift of 141 cm^{-1} fits into the trend of increasing shift from the chloride to the bromide 1:1 complexes (Table VIII) and indicates that a 1:1 TPPO-NbI_5 complex is probably formed.

With TPPO and TaI_5 , the infrared data indicates that a more complex reaction occurs. When TPPO is treated with TaI_5 in 1:1 stoichiometries, the insoluble product formed has two strong absorptions at 1083 cm^{-1} and at 1031 cm^{-1} , probably due to coordinated P=O , and another strong band at 730 cm^{-1} , possibly due to a bridging Ta-O-Ta vibration (29, 72).

With a 2:1 ratio of TPPO to TaI_5 and a longer reflux time, the insoluble product exhibits only the strong 1083 cm^{-1} and 730 cm^{-1} absorptions while evaporation of the benzene solution yields relatively large amounts of TPP. It appears then, that TaI_5 does abstract oxygen from TPPO to give a TPPO-tantalum

oxyiodide adduct and TPP. The P=O shift of 98 cm^{-1} in this adduct is similar to that in TPPO.TaOCl_3 . The initial formation of a P=O band at 1031 cm^{-1} indicates that a 1:1 TPPO-TaI_5 adduct probably forms first, but decomposes quickly to the oxyiodide adduct. Because of this oxygen abstraction reaction, attempts to isolate a 1:1 adduct were unsuccessful.

When TaI_5 was treated with an excess of Ph_3PO , no oxygen abstraction was observed, as indicated by the large P=O shift ($1185 \rightarrow 990\text{ cm}^{-1}$) and the absence of any Ta=O or Ta-O-Ta absorption bands in the infrared spectrum of the product. This can be accounted for by the higher P=O bond strength of the phosphine oxide relative to the phosphole oxide. The difference in the NbI_5 and TaI_5 reactions with TPPO indicates that TaI_5 has the higher affinity for oxygen. This is the reverse of the order indicated by the pentachlorides of the two metals from their reactions with TPPO and Ph_3PO as already discussed.

Metal-oxygen stretching vibrations have been assigned in the region of $500 - 300\text{ cm}^{-1}$ for various oxygen donor complexes (81). An attempt was made to assign M-O vibrations in the TPPO complexes, but because of the complexity of the spectra in the $500 - 300\text{ cm}^{-1}$ region, a reasonable assignment could not be made.

The Reactions of TPPS and TPPSe with Nb(V) and Ta(V)

TPPS reacts readily with TaCl_5 and NbCl_5 to give solvated complexes of two stoichiometries, from which 1:1 adducts in two crystalline forms were isolated. Crystalline 1:1 adducts containing one mole of benzene are obtained from reactions in benzene where a slight excess of the metal halide is used. High vacuum pumping removes the benzene to give TPPS.MCl_5 adducts in the α crystalline form. When the same reactions are carried out in benzene or methylene chloride using a slight excess of the ligand, 1:1 complexes containing half a mole of the solvent are formed. Removal of the solvent by high vacuum pumping gives the TPPS.MCl_5 complexes in the β crystalline form. If the α -TPPS.- TaCl_5 adduct is dissolved in methylene chloride and recrystallized, the solvated β 1:1 adduct is obtained. Brown *et al.* (28) also made 1:1 adducts of Ph_3PS and TaCl_5 in two different crystalline forms. With Ph_3PS and NbCl_5 , however, they obtained only one crystalline phase.

Table IX summarizes the infrared data of the TPPS complexes and provides a comparison with the corresponding Ph_3PS complexes of Brown *et al.* (28). The P=S stretching vibration in the free ligand is assigned to

Table IX

Infrared Data on TPPS and TPPSe Complexes

<u>Compound</u>	<u>ν (P=A*) (cm⁻¹)</u>	<u>$\Delta\nu$ (P=A*) (cm⁻¹)</u>	<u>ν (M-Cl)</u>	<u>Reference</u>
TPPS	637	-	-	-
α -TPPS.TaCl ₅	613/625	24/12	342	-
β -TPPS.TaCl ₅	613/625	24/12	340	-
α -TPPS.NbCl ₅	611/623	26/14	365	-
β -TPPS.NbCl ₅	611/623	26/14	355,375	-
α -Ph ₃ PS.TaCl ₅	580	48	379,347,327	(28)
β -Ph ₃ PS.TaCl ₅	580	48	321	(28)
Ph ₃ PS.NbCl ₅	575	53	370,347,333	(28)
TPPSe	555	-	-	-
β -TPPSe.TaCl ₅	550	5	342	-
β -TPPSe.NbCl ₅	548	7	355	-
α -Ph ₃ PSe.TaCl ₅	536	19	376,347,327	(28)
β -Ph ₃ PSe.TaCl ₅	536	19	323	(28)
Ph ₃ PSe.NbCl ₅	533	22	376,364,345	(28)

*A=S, Se

a band of medium intensity at 637 cm^{-1} , on the basis of similar assignments in tertiary phosphine sulfides (77). In the complexes, however, the P=S stretching frequency cannot be assigned unambiguously because with the disappearance of the 637 cm^{-1} band, two new bands of equal intensity appear at 625 cm^{-1} and 613 cm^{-1} in the tantalum complex and 623 cm^{-1} and 611 cm^{-1} in the niobium complex. Thus, the P=S frequency shift could be either about 24 cm^{-1} or about 12 cm^{-1} .

Different frequency shifts in the NbCl_5 complex (26, 14 cm^{-1}) and in a crude TPPS-TaBr₅ product (29, 16 cm^{-1}) do not resolve this problem as both new bands appear to shift by the same amount. This would suggest that both bands are associated with the P=S vibration. The reason for the splitting of the band is not known, but a similar phenomenon has been observed in Th(IV) and U(IV) TPPO complexes where the P=O band is also split (69).

The infrared spectra of the α and β phases of the TPPS complexes are identical except in the $500\text{-}400\text{ cm}^{-1}$ region where the α phase has absorptions of medium intensity at 485 cm^{-1} and 450 cm^{-1} while the β phase has only very weak absorptions in these locations. The spectra of the solvated adducts are identical to their corresponding non-solvated adducts

except for the presence of extra bands associated with the solvent (methylene chloride: 1270, 740 cm^{-1} ; benzene 1480, 690 cm^{-1}).

Although the P=S bond is weaker than the P=O bond, there was no evidence of sulfur abstraction by TaCl_5 or NbCl_5 from TPPS. Fairbrother *et al.* (30) and Brown *et al.* (28) found similarly that sulfur is not abstracted from Ph_3PS by Ta(V) and Nb(V) halides. This would indicate a weaker affinity of the Ta(V) and Nb(V) halides for the "soft" sulfur donor atom than for the "hard" oxygen donor atom and the lower stability of the TPPS complexes compared to the TPPO complexes supports this view. For example, TPPS is readily displaced from the complexes by coordinating solvents such as ethanol and acetonitrile and also by moisture from air and from wet solvents. The weaker bonding interaction would also account for the lack of any reaction with the tantalum and niobium pentafluorides, where bonding would be offset by greater steric interactions.

TPPSe also reacts readily with NbCl_5 and TaCl_5 in benzene, producing 1:1 solvated complexes, which are X-ray isostructural with the corresponding β -TPPS complexes. Attempts to produce the α crystalline form of the TPPSe complexes by use of an excess of the metal halide produced only oils.

In several instances of reactions with NbCl_5 where the solvent was not rigorously dried, a red product was formed and identified by its infrared spectrum and X-ray powder pattern as $\beta\text{-TPPO.NbCl}_5$. This would indicate that, in the presence of moisture, the P=Se bond is cleaved and the P=O bond formed to produce coordinated TPPO. This supports earlier conclusions from TPP and TPPO reactions that the P=O bond strength is greater than that of M=O, at least in the case of the chlorides of Nb(V) and Ta(V).

The instability of the TPPSe complexes towards coordinating solvents and moisture is similar to that of the TPPS complexes already discussed. This would be expected as the "soft" donor character of the selenium atom is comparable with that of the sulfur atom.

The P=Se stretching frequency in the free ligand is assigned to a sharp absorption band of medium intensity at 555 cm^{-1} , on the basis of similar assignments in tertiary phosphine selenides (77). On complexation, this band disappears, and a band of very weak intensity appears at 500 cm^{-1} . This would imply a frequency shift on complexation of 5 cm^{-1} , which is not unreasonable in view of the P=Se frequency shifts of 19 cm^{-1} and 22 cm^{-1} reported for Ph_3PSe

complexes of Ta(V) and Nb(V) (Table VIII). The reason for the large decrease in intensity is not known. The only other possible band which could be assigned to a P=Se absorption in the complexes is a band of medium intensity at 500 cm^{-1} , but this would mean a P=Se frequency shift of 55 cm^{-1} , which is highly unlikely.

Because of the complexity of the infrared spectra in the $500 - 200 \text{ cm}^{-1}$ region, no attempt was made to assign either metal-sulfur or metal-selenium absorptions in the TPPS and TPPSe complexes.

Other Physical Data

(a) NMR Measurements

Table X summarizes the NMR data obtained for some of the complexes described in the foregoing discussions. Included for comparison are the ligand proton resonances and those of the methiodide of 1,2,5-triphenylphosphole, $[\text{TPPMe}]^+\text{I}^-$, prepared after Campbell *et al.* (66). In the methiodide, where the bonding to the phosphorus is quaternary, the phosphorus atom has a full positive charge. A similar electronic arrangement would be expected in the TPP complexes, though perhaps with less complete electron withdrawal from the phosphorus. The deshielding effect of electron withdrawal is evident for $[\text{TPPMe}]^+\text{I}^-$ and $\text{TPP} \cdot \text{TaCl}_5$

Table X
NMR Data of TPP and TPP Adducts

<u>Compound</u>	<u>Ligand Proton Resonances</u>			
	<u>Phenyl Protons</u> (τ)	<u>β-Ring Protons</u> (τ)	$^3J_{PH}$ (Hz)	<u>Others</u> (τ)
TPP	2.35 - 2.90	2.64, 2.83, * [2.73]	11	-
[TPPMe] ⁺ I ⁻	1.45 - 2.75	1.43, 2.08, [1.80]	38	6.91, 7.14, ² J _{PH} =14Hz (methyl group)
TPP.TaCl ₅	1.76 - 2.80	2.32, 2.78, [2.52]	24	-
TPPO	2.21 - 2.80	1.90, 2.50, [2.19]	36	-
β -TPPO.TaCl ₅	1.65 - 2.78	2.39, 3.01, [2.71]	37	-
TPPS	2.24 - 2.80	2.33, 2.77, [2.55]	26	-
		2.03, 2.62, [2.33]	35	
	2.24 - 2.80	2.32, 2.93, [2.62]	36	-
β -TPPS.TaCl ₅ .0.5CH ₂ Cl ₂	1.98 - 2.88	2.43, 2.84, [2.62]	24	4.70 (CH ₂ Cl ₂)
		2.14, 2.76, [2.47]	36	

*Values in square parenthesis represent average (*i.e.* : non-coupled) β -proton resonance positions.

where the phenyl protons resonate at lower field than in TPP alone (Table X). The phenyl protons of the methiodide show a greater downfield shift than those of TPP.TaCl₅. Similar, but smaller, downfield shifts of the phenyl protons occur in the TPPO and TPPS complexes. The phenyl protons showing the largest shift appear to be the α protons on the phenyl ring attached to the phosphorus atom. These resonate as a complex multiplet at the downfield end of the phenyl proton resonances of the complexes and of the methiodide. Such a complex splitting pattern for these protons would be expected due to their coupling to the phosphorus atom, to the other phenyl protons on the same ring and, possibly, to each other due to non-equivalent orientations if rotation of the P-phenyl group is seriously restricted.

Of particular interest in these complexes are the resonance positions of the two protons at the β positions on the phosphole ring, and the magnitude of the spin coupling between these protons and the phosphorus nucleus. In TPP, the two β protons resonate in the aromatic region, and cannot be readily distinguished from the phenyl protons on the basis of their 60 MHz NMR spectrum alone. They have been identified, however, through a comparison of the 60 MHz

and 100 MHz NMR spectra of TPP (51) and their coupling constant to the phosphorus atom, $^3J_{PH}$, is 10.8 Hz (51). Although the resonance positions are not reported, the most likely assignment in the spectrum of TPP recorded in this laboratory is to two sharp resonance peaks at τ 2.64 and 2.83. In the phosphole methiodide, the β protons apparently shift downfield to τ 1.43 and 2.08, presumably because of the inductive effect of electron withdrawal by the phosphorus atom. The coupling constant for these β protons, $^3J_{PH}$, also undergoes a large increase to 38 Hz compared with 10.8 Hz in the parent phosphole (51). Quin (51) has studied the $^2J_{PH}$ and $^3J_{PH}$ coupling constants in 1-methyl phosphole and has pointed out that in this and other phospholes where the phosphorus is tri-coordinated, the consensus is that $^2J_{PH}$ is high (~ 38 Hz) while $^3J_{PH}$ is much smaller (~ 14 Hz), although the reverse seems to be the case for acyclic phosphorus compounds. Mislow's 1-isopropyl-2-methyl-5-phenylphosphole (54) similarly shows a low $^3J_{PH}$ coupling constant of 9.5 Hz.

In phosphole adducts where the phosphorus is tetra-coordinated, the magnitudes of the coupling constants appear to reverse, with the β ring protons having $^3J_{PH}$ values of 35 - 40 Hz and the α ring protons having $^2J_{PH}$ values of 10 - 15 Hz. This is evident in the

methiodide of TPP where the two sharp resonance peaks at τ 1.43 and 2.08, integrating for two protons out of the 17 in that region, are clearly due to the phosphole ring β protons. Märkl *et al.* (43) similarly report that the coupling constant, ${}^3J_{\text{PH}}$, of the β ring protons in the quaternary benzyl bromide salt of 1-phenyl-2,5-dimethylphosphole is large (>30 Hz). The exact value is not reported since one of the β proton resonances is obscured by the phenyl protons. In the spectrum of the sulfide of 1-phenyl-2,5-dimethylphosphole where the phosphorus is again tetra-coordinated, Märkl *et al.* (43) report a ${}^3J_{\text{PH}}$ value of 13 Hz for the exocyclic methyl protons and a ${}^3J_{\text{PH}}$ value of 40 Hz for the β ring protons. 1-Phenyl-3-phospholene oxide similarly has a high splitting of the ring β proton signal (${}^3J_{\text{PH}} = 29.5$ Hz) relative to the parent phospholene (${}^3J_{\text{PH}} = 8$ Hz) (43).

More information on the ring proton coupling constants in quaternary phosphole systems could be gained from a study of the quaternary salts of 1-methylphosphole and 1-phenylphosphole. Low temperature studies on the parent phospholes themselves may prove helpful as this would "freeze" the orientation of the lone electron pair on the phosphorus, preventing pyramidal inversion. It is known that in cyclic phos-

phines, the magnitudes of $^2J_{PH}$ and $^3J_{PH}$ are strongly dependent on the dihedral angle between the C-H bond and the phosphorus lone pair (See the discussion by Tebby (88)).

In TPPO, one would expect the β ring protons to resonate in much the same position as in TPP, since the inductive effect of electron withdrawal by the oxygen is effectively neutralized by the π -electron back-donation from the oxygen to the phosphorus. One of the β proton resonance peaks occurs as a sharp singlet at τ 3.01, separate from the main phenyl resonances. The second is assigned to a sharp peak at τ 2.39 in the phenyl resonance region, to give a $^3J_{PH}$ coupling constant of 37 Hz and an average resonance position (non-coupled) of τ 2.71, very similar to that of TPP (τ 2.73). Since the bonding in TPPS is similar to that in TPPO, a coupling constant of similar magnitude would be expected and the β proton resonances are assigned to peaks at τ 2.32 and 2.93, giving $^3J_{PH} = 36$ Hz. Since back-donation from the sulfur to the phosphorus is less efficient than from oxygen to phosphorus, inductive deshielding of the β protons would be expected to be greater in TPPS and the mean resonance position of the β protons in TPPS, τ 2.62, is about 0.1 ppm downfield from that in TPPO.

For the complexes, of which $\text{TPP} \cdot \text{TaCl}_5$, β - $\text{TPPO} \cdot \text{TaCl}_5$ and β - $\text{TPPS} \cdot \text{TaCl}_5 \cdot 0.5\text{CH}_2\text{Cl}_2$ are taken as representatives, the assignment of resonance positions for the β protons is more difficult due to the greater complexity of the spectra, and the fact that the β proton resonances occur in the same region as the phenyl resonances. Possible assignments are listed in Table X, but on the basis of the NMR spectra available, no definite assignments can be made. For the $\text{TPP} \cdot \text{TaCl}_5$ complex, the deshielding effect of electron donation by the phosphorus would be expected to be similar to that in the methiodide, though perhaps not quite as large. This would favour the assignment at τ 1.90 and 2.50, which gives a $^3J_{\text{PH}}$ coupling constant of 36 Hz - about what would be expected for a quaternary system. In the TPPO and TPPS complexes, the electron donation by the oxygen and sulfur would be expected to have a much lower influence on the electron environment of the β ring protons and, thus, smaller downfield shifts would be expected. Since the phosphorus atom remains tetra-coordinated, no large changes in the magnitudes of the coupling constants would be expected either. The complexity of peaks in the NMR spectra of these complexes makes even a tentative assignment difficult and the values

quoted should be considered more as extreme possibilities rather than definite assignments.

It is clear that more work with tetra-coordinated phospholes and phosphole complexes in this area is necessary to establish better the deshielding effects and spin interactions on the phosphole ring protons.

(b) Visible Spectra

The visible absorption bands of the ligands and of their $TaCl_5$ complexes are given in Table XI. In all cases of complexation, the absorption band shifts to longer wavelength and decreases slightly in intensity.

Since Ta(V) and Nb(V) have d^0 configurations, the visible bands are due to electron transitions on the ligands. The visible band cannot be due to an $n \rightarrow \sigma^*$ transition of the phosphorus lone pair as this lies below $210 \text{ m}\mu$ in tertiary phosphines (89). The shift of the visible band to longer wavelength when the phosphorus lone pair is bonded rules out the non-bonding pair as the chromophoric group. However, it does indicate some interaction of the lone pair with the main absorbing group of the phosphole ring (which may be taken as an indication of some aromaticity in the parent phosphole) since, clearly, the energy difference

Table XI

Visible Absorption Spectra Data

<u>Compound</u>	<u>Solvent</u>	λ_{max} ($\text{m}\mu$)	<u>Log. ϵ</u>	<u>Reference</u>
TPP	EtOH	369	4.25	(66)
[TPPMe] ⁺ I ⁻	EtOH	380	4.14	(66)
TPP.TaCl ₅	CH ₂ Cl ₂	391	3.99	-
TPPO	EtOH	394	4.16	(66)
TPPO.TaCl ₅ .CH ₂ Cl ₂	CH ₂ Cl ₂	439	3.99	-
α -TPPO.TaCl ₅	C ₆ H ₆	439	3.93	-
β -TPPO.TaCl ₅	C ₆ H ₆	439	4.05	-
TPPS	C ₆ H ₆	385	4.10	-
α -TPPS.TaCl ₅	C ₆ H ₆	403	4.04	-
TPPSe	EtOH	380	4.14	(66)
β -TPPSe.TaCl ₅	CH ₂ Cl ₂	390	4.05	-

between the ground and excited states of the unsaturated system is decreased on bonding of the phosphorus lone pair. On the other hand, the shift may be largely due to inductive effects although it would seem to be rather large for this in certain cases.

It is probably dangerous to think of an actual isolated chromophoric group within the phosphole molecule, and the electron transition can best be thought of as occurring between molecular orbitals which encompass the whole phosphole ring with some contribution from the phenyl rings. However, some idea of the nature of these orbitals can be gained from examining chromophoric systems.

The diene system alone cannot be responsible for the electron transition ($\pi \rightarrow \pi^*$). 1,3-Butadiene absorbs at about 217 $m\mu$ (90) and cyclopentadiene absorbs at about 238 $m\mu$ (90). The effect of conjugation with a phenyl system is pronounced, and shifts the band to much longer wavelength. 1,4-Diphenyl-1,3-butadiene absorbs at 334 $m\mu$ ($\log. \epsilon = 4.60$) (91) and, when the diene system is incorporated into a five-membered ring, 1,4-diphenyl-1,3-cyclopentadiene absorbs at 346 $m\mu$ ($\log. \epsilon = 4.36$) (91). This compares favourably in both position and intensity with TPP, where a hetero atom is incorporated into the ring. The molecular orbitals involved in this electron transition thus appear

to be primarily associated with the 2,5-diphenyl-2,4-diene system of the ring, perturbed by the phosphorus hetero atom.

A bathochromic shift of 11 $m\mu$ is observed in the visible band of TPP on formation of the methiodide where the phosphorus lone pair is completely bonded. This removes the interaction of the lone pair with the hetero ring and may also increase the interaction between the ring carbon p electrons and the empty phosphorus d orbitals thus changing the conjugation within the "chromophore" system. In TPP.TaCl₅, a larger bathochromic shift (22 $m\mu$) is observed, which may indicate that further interaction occurs between the TaCl₅ and TPP other than the effect of electron donation at the phosphorus atom. Direct interaction between the d orbitals on the tantalum and the p electrons of the heterocyclic ring is not likely as the distance between the two would be relatively large. An interaction between a chlorine atom of TaCl₅ and the π electrons, or between a chlorine atom and an α hydrogen on one of the three phenyl rings in close proximity to the TaCl₅ is more feasible.

TPPO, on complexation, also shows a relatively large bathochromic shift (35 $m\mu$) in its visible absorption band. This again may indicate some interaction between the TaCl₅ and the TPPO other than through

the oxygen atom, although the affinity of tantalum for oxygen is strong. With TPPS and TPPSe, progressively smaller red shifts are observed on complexation, and this may be an indication of two factors: a decreasing bonding interaction between the sulfur, and the selenium with the tantalum, and a progressively weaker $p\pi-d\pi$ interaction in the P=S and P=Se bonds.

(c) X-Ray Powder Diffraction Data

Table XII lists the partial X-ray powder diffraction pattern data for the more highly crystalline adducts obtained. The intensities were estimated visually on an arbitrary scale of 0-10, the value 10 being assigned to the most intense line of the powder pattern. Most of the very weak lines are omitted.

Summary

This thesis has examined the reactions of some of the Ta(V) and Nb(V) halides with 1,2,5-triphenylphosphole, its oxide, sulfide and selenide derivatives. The reactions and properties of the TPP complexes are consistent with the known properties of the phosphole system. The low stability of the TPP complexes relative to the Ph_3P complexes shows the weak basic

Table XII

Partial X-Ray Powder Diffraction Patterns for the Complexes

TPP.TaCl ₅ (TPP.TaBr ₅ , TPP.NbCl ₅)	DBP.TaCl ₅	Ph ₃ P.TaCl ₅	[TPPH] ⁺ [TaCl ₆] ⁻ ([TPPH] ⁺ [NbCl ₆] ⁻ , [TPPD] ⁺ [TaCl ₆] ⁻)	[DBPH] ⁺ [TaCl ₆] ⁻
$\frac{\sin^2 \theta}{I}$	$\frac{\sin^2 \theta}{I}$	$\frac{\sin^2 \theta}{I}$	$\frac{\sin^2 \theta}{I}$	$\frac{\sin^2 \theta}{I}$
0.0036 1	0.0038 5	0.0063 10	0.0040 4	0.0062 4
0.0071 10	0.0049 7	0.0078 10	0.0066 9	0.0073 7
0.0104 10	0.0077 10	0.0109 4	0.0070 4	0.0117 10
0.0113 0.5	0.0116 7	0.0123 5	0.0109 10	0.0125 3
0.0144 5	0.0129 9	0.0172 4	0.0138 1	0.0149 0.5
0.0167 3	0.0138 5	0.0197 1	0.0152 1	0.0227 6
0.0180 4	0.0168 1	0.0209 1	0.0168 2	0.0249 8
0.0225 1	0.0223 5	0.0244 4	0.0181 1	0.0278 4
0.0252 7	0.0253 6	0.0266 2	0.0207 9	0.0290 4
0.0283 0.5	0.0276 3	0.0354 1	0.0221 1	0.0322 1
0.0324 0.5	0.0299 6	0.0393 1	0.0241 1	0.0377 2
0.0403 4	0.0336 1	0.0443 0.5	0.0272 0.5	0.0412 3
0.0437 3	0.0384 5	0.0576 1	0.0316 8	0.0573 3
0.0519 1	0.0451 4		0.0342 0.5	0.0648 1
0.0614 0.5	0.0565 1		0.0450 6	0.0813 2
	0.0670 6		0.0695 4	0.0893 4
	0.0786 1			

Table XII (cont'd)

$[\text{Ph}_3\text{PH}]^+ [\text{TaCl}_6]^-$		$\alpha\text{-TPPO.TaCl}_5$ ($\beta\text{-TPPO.NbCl}_5$)		$\beta\text{-TPPO.TaCl}_5$ ($\beta\text{-TPPO.NbCl}_5$)		$\alpha\text{-TPPS.TaCl}_5$ ($\alpha\text{-TPPS.NbCl}_5$)		$\beta\text{-TPPS.TaCl}_5$ ($\beta\text{-TPPS.NbCl}_5$, $\beta\text{-TPPSe.MCl}_5$)	
$\frac{\text{Sin}^2 \theta}{I}$	$\frac{\text{Sin}^2 \theta}{I}$	$\frac{\text{Sin}^2 \theta}{I}$	$\frac{\text{Sin}^2 \theta}{I}$	$\frac{\text{Sin}^2 \theta}{I}$	$\frac{\text{Sin}^2 \theta}{I}$	$\frac{\text{Sin}^2 \theta}{I}$	$\frac{\text{Sin}^2 \theta}{I}$	$\frac{\text{Sin}^2 \theta}{I}$	$\frac{\text{Sin}^2 \theta}{I}$
0.0078	10	0.0095	10	0.0044	1	0.0032	10	0.0035	3
0.0109	0.5	0.0113	2	0.0055	1	0.0060	4	0.0059	10
0.0123	8	0.0127	5	0.0077	2	0.0072	4	0.0071	3
0.0151	1	0.0142	1	0.0083	10	0.0090	3	0.0094	5
0.0172	1	0.0158	2	0.0100	8	0.0110	4	0.0118	1
0.0200	6	0.0174	0.5	0.0119	10	0.0128	3	0.0132	4
0.0215	2	0.0193	0.5	0.0172	2	0.0147	2	0.0168	8
0.0247	10	0.0216	1	0.0183	1	0.0163	5	0.0218	6
0.0295	5	0.0236	1	0.0234	8	0.0193	0.5	0.0244	1
0.0325	0.5	0.0249	3	0.0271	8	0.0233	7	0.0263	3
0.0360	3	0.0276	2	0.0295	2	0.0296	6	0.0290	2
0.0493	4	0.0309	3	0.0315	0.5	0.0349	3	0.0338	5
0.0686	1	0.0353	0.5	0.0336	0.5	0.0394	1	0.0469	2
0.0856	1	0.0397	1	0.0370	0.5	0.0417	1	0.0688	1
0.0933	1	0.0452	1	0.0392	0.5	0.0444	0.5	0.0759	1
		0.0473	1	0.0423	2				

character of TPP and thus tends to support the view that partial delocalization of the phosphorus lone pair into the heterocyclic ring occurs in the phosphole system. In this respect, the stability of the P-protonated phosphole with the $[\text{TaCl}_6]^-$ ion is exceptional.

With respect to the protonation of phospholes and of pyrroles, it appears that more protonation work on pyrrole and substituted pyrroles under strictly anhydrous conditions is necessary as these reactions may not parallel the protonation reactions (52, 86) in an aqueous, acidic medium. The formation of a protonated phosphole by TPP makes a study of similar reactions with other phospholes having both more and less highly substituted heterocyclic rings seem worthy of investigation.

The predominantly "hard" acceptor character of Ta(V) and Nb(V) is evident in the greater stability of the TPPO complexes relative to the TPPS and TPPSe complexes, but the fact that the latter two do react does indicate that these metal ions have a certain "soft" character as well. The bond strengths of the P=O bond in TPPO and of the M=O and M-O-M bonds in the oxyhalide adducts of Ta(V) and Nb(V) are very similar in magnitude. The latter two appear to vary with the halide and the metal with the result that

formation of the P=O bond is indicated in some reactions, formation of the M=O bond in others and oxygen abstraction from TPPO with formation of an M-O-M bond in one other.

The reactions of TPP and its derivatives with Ta(V) and Nb(V) have given both expected and unexpected results as outlined above. Since this work was done, studies of phospholes and phosphole derivatives with other metal systems have been carried out in this laboratory (92) giving other interesting results and further characterizing the properties of phospholes as donor ligands with the transition metals.

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