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Advances in the Study of Metal Complexes with Tervalent Phosphorus Amides

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Data on the synthesis, structure, and chemical properties of complexes of non-transition and transition metals with tervalent phosphorus amides are surveyed. An attempt is made to trace the influence of the amide functional group of the ligand on the properties of these compounds. The literature data on the practical use of the metal complexes with formamides are analysed in the review.
The bibliography includes 265 references.

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I. INTRODUCTION

The metal complexes of ligands containing a tervalent phosphorus atom are being vigorously investigated. Studies have been made of their synthesis, structure, physiological activity, chemical properties, and catalytic properties. Analysis of the existing publications has shown that the vast majority of the latter are devoted to complexes with phosphine ligands, namely with triphenylphosphine. Apparently, the availability of triphenylphosphine, the convenience with which it can be employed, as well as Wilkinson's succesful synthesis of effective catalytic systems based on this phosphine, dictated the choice of the ligands. Overall, the tendency to employ a narrow group of well known ligands arose from the passive attitude of organophosphorus chemists to the new field in the boundary region where the interests of coordination chemistry and the chemistry of organophosphorus compounds are interlinked. In recent years the situation changed and complexes with a wide variety of phosphorus ligands—phosphites, phosphonites, phosphinites, phosphorofluoridites, etc.—began to be investigated and fundamentally new results have been obtained. Together with the ligands already enumerated, tervalent phosphorus acid amides (TPAA), which are very interesting from the chemical standpoint, began to be used as ligands. Initially such derivatives were regarded as kinds of "hybrids" of two popular classical ligands—phosphines and amines. Subsequently, novel qualities of formamides, which make the complexes obtained from them very unusual, were discovered.

The field of science devoted to the study of metal complexes of TPAA is at present still in the stage of its establishment. More than 350 articles and patents have been devoted to it. However, it is significant that the existing publications do not as yet constitute a stream of relevant information and chemical ideas. As a rule, they report only new facts which are not compared to any great extent with facts known from related studies and studies on other phosphorus-containing complexes. In view of this, we aimed to prepare the first review in the world literature on metal complexes of TPAA. For this purpose, we have given a systematic account of published data and have analysed (insofar as this is at present possible) the influence of the phosphamide fragment of the ligand on the synthesis, structure, and properties of new coordination systems. It is essential to note the characteristic feature of this review. The relevant problems are considered from the standpoint of organophosphorus chemistry which in our view should have full parity with coordination chemistry in the study of the systems mentioned.

II. SYNTHESIS

1. Non-transition Metal Complexes

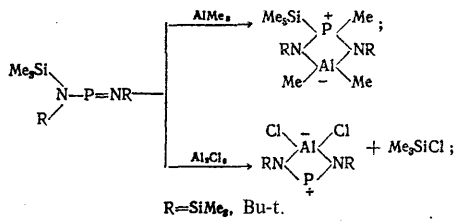
There are only very brief mentions in the literature of the preparation of complexes of TPAA with zinc and cadmium. The complexes $ZnCl_2L_2.2H_2O$ have been obtained from the triethyleneamide of phosphorous acid.[1] The mode of coordination and other structural problems have not been reported. The reactions of the hexamethyltriamide of phosphonous acid (I) and of the tetramethyldiamide of phenylphosphonous acid (II) with CdI_2 have been described;[2] according to the authors, the products $CdI_2.(I)_2$ and $CdI_2.(II)_2$ were obtained. It has been assumed[3] that the coordination of the ligand in the interaction of $Cd(NO_3)_2$ with the di(butylamide) of cyclohexylphosphonous acid is effected via the unshared electron pair of the nitrogen atom. We may note that the structures were not rigorously demonstrated in the above studies.[2,3]

The complexes of bivalent mercury with mono- and bi-dentate ligands have been investigated in greater detail.[2,4-7] It has been established that compounds having the compositions HgX_2L_2 and HgX_2L can then be formed. The coordination of the ligands to the phosphorus atom was elucidated on the basis of ^{31}P NMR data and in addition the *trans*-configuration of the complexes HgX_2L_2 was demonstrated. The formation of the mercury complexes can be accompanied by unusual reactions, for example, the formation of P—P bonds.[2]

Among Group III metals, only aluminium has been studied in reactions with TPAA. Vigorous complex formation by triethylaluminium via phosphorus in interaction with equimolar amounts of amides or imides or phosphinous acid has been demonstrated.[8] In the latter case adducts were obtained in which the two phosphorus atoms are equivalent according to NMR data, indicating the parallel binding of the aluminium atom with two phosphorus atoms. When *HN*-phosphimides are used, the complex formation reaction is supplemented by the metallation of nitrogen. TPAA react also with $AlCl_3$: the formation of monoadducts in this process has been indicated.[9] On dissolution in methylene chloride, the latter can

react with formation of phosphorus–phosphorus systems.[10,11] The reaction dynamics has been investigated by ^{31}P NMR. Analogous derivatives can be more simply obtained by the reaction of $AlCl_3$ with phosphoramidochloridites, Salts whose cations have a discoordinate phosphorus atom are then formed initially. Subsequently, they disproportionate or add to the electron-donating TPAA.[9,10,12]

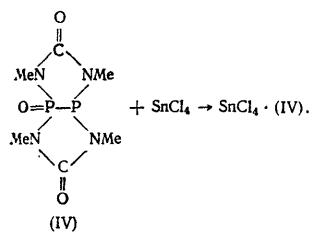
Very interesting results have been obtained[13,14] in the study of *N*-silylated amides of phosphorimidic acids (III):



R=SiMe$_3$, Bu-t.

The difference between the reactions of the amidoimide (III) with trimethylaluminium and trimethylboron is noteworthy; the latter reaction leads only to a linear system with the boron atom at one of its ends.[14]

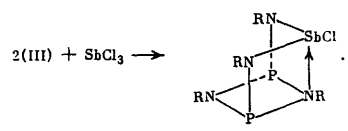
The wide-scale study of the synthesis of phosphorus complexes based on tin halides has been initiated. Compounds having the composition $SnCl_4L_2$ have been obtained from the full amides and amidoesters of phosphorous acids[15,16] and the amides of phosphonous[17,18] acids. The complex $SnCl_4L$ has been synthesised from the complex P–P ligand (IV):[19]



(IV)

The study of the structure of the complexes by ^{31}P NMR, ^{1}H NMR, and infrared spectroscopy led to the conclusion that the ligand is coordinated to the phosphorus atom. It has been shown that the stability of the test substances is determined by the electron-donating capacity of the substituents at the phosphorus atom.[16]

Derivatives of Group V non-transition metals have been little studied in their complex formation reactions with TPAA. It has been reported that $SbCl_5$ chlorinates these compounds, being reduced at the same time to $SbCl_3$. The second stage of the process involves the formation of aminochlorophosphonium hexachloroantimonates.[20] Furthermore, the possibility of the usual complex formation reaction between $SbCl_5$ and the P–P ligand (IV) has been indicated.[19] An unusual reaction involving a stage in which the nitrogen atom of the phosphamide centre is coordinated to SbCl has been described:[21]



The mode of coordination is determined by stereochemical factors, namely by the mutual approach in space of the antimony and nitrogen atoms. The use of $AsCl_3$ does not lead to the closure of the skeletal system.[21]

2. Transition Metal Complexes

The study of transition metal complexes with TPAA was begun comparatively recently, but it is being prosecuted vigorously and is distinguished by highly novel synthetic features. One may say that a much greater number of different types of complexes have been created in this field than in other related fields of coordination chemistry. This situation can apparently be accounted for by the structural variety of the ligands related to TPAA and the wide variety of their chemical properties: the synthesis of complexes of each group will accordingly be considered in a way emphasising the role not only of the metal but also of the corresponding type of phosphamide ligand.

The complexes of metals of the first Groups have been investigated relatively modestly. On the other hand, those of Group VI, VII, and VIII metals have been widely studied and the characteristic features of the individual classes of compounds have been elucidated.

(a) *Complexes of metals in the first Groups.* Among the phosphamide complexes of copper, silver, and gold, derivatives of univalent copper have been investigated in greatest detail. The first representatives of compounds of this class have been obtained[22] by the interaction of the salt CuX with the simplest amides of alkylene phosphorous acids. Subsequently the reaction was extended to a wide range of phosphamides,[4,23,24] including cyclic phosphoramidites of carbohydrates.[25,26] The structures of the majority of the complexes obtained have been investigated by NMR and X-ray diffraction, which demonstrated that the ligand is coordinated to the phosphorus atom. In complexes of the phosphorinane type, it was shown that the metal occupies an axial position and that the six-membered ring has the chair conformation.[24]

Certain phosphamide complexes of copper hydride[27] and organocopper compounds[28] have also been studied.

Silver complexes of different composition have been obtained by the reaction of the salts AgX with the phosphamide (I). When X = Cl, CN, or NO_3, the compounds $AgXL_2$ are formed and, in the case where X = BPh_4, systems in which three molecules of the ligand (I) are incorporated in the central nucleus can be isolated. The same picture has been noted in a study with the bicyclic compound $P(NMeCH_2)_3$. .CMe (V) using salts with different anions. The triethyleneamide of phosphorous acid gives rise to the complexes $AgXL_4$ regardless of the type of anion. In all cases the ligand is coordinated to the phosphorus atom, which has been demonstrated by X-ray diffraction.[29] The difference noted in the behaviour of formally similar ligands is apparently associated with the appreciable difference between their geometrical parameters and the wide variety of the electronic effects in the P–N fragment.[30] In confirmation of the latter postulate, we may note that sterically hindered phosphamides are only singly bound to silver salts.[31]

Bidentate ligands have also been investigated in reactions with silver salts.[6,32] The iminodiphosphines (VI) have been studied in special detail:[32]

$$\underset{\text{(VI)}}{MeN(PPh_2)_2} + AgBr \rightarrow [MeN(PPh_2AgBr)_2]_2 .$$

The structure of the adduct whose molecule is based on the $Ag_4Br_2^{2+}$ octahedron has been demonstrated by X-ray diffraction. We may draw attention to the specific influence of the amide unit, manifested in the formation of the octahedral structure. If instead of this unit, two phosphorus atoms are linked by a methylene group, a different polyhedron, namely $Ag_3Br_2^{+}$, is formed.[32]

Complexes of univalent and tervalent gold with TPAA began to be investigated only in very recent years. The amides of phosphinous acids[31] and azaphospholes[33] have been used as monodentate ligands. The problem of the mode of coordination of the ligand still remains controversial in this instance. Iminodiphosphines[34] and the corresponding anions[35] have been used as bidentate ligands.

The study of the complexes of TPAA with Group IV and V metals has been fragmentary. There exists a brief communication about the chelation of the central atom in $TiCl_4$ by 1,3-di-t-butyl-2,4-dichloro-1,3,2,4-diazadiphosphetidine (VII).[36] There has been a very interesting study of the oxidative addition of phosphorous acid triisocyanate to $TiCl_4$ and $ZrCl_4$:[37]

$$MCl_4 + P(N{=}C{=}O)_3 \rightarrow MCl_3P(N{=}C{=}O)_2 + ClN{=}C{=}O.$$

The diethylamides of dimethyl phosphorous and phenylphosphonous acids add to VCl_4; 1:1 and 2:1 adducts are formed in the former case and only 1:1 atoms in the latter.[38] A series of complexes have been synthesised by ligand transfer reactions between $CpV(CO)_3L$ and the full amides of phosphorous,[39,40] and dimethylphosphinous[41] acids:

$$CpV(CO)_4 + L \rightarrow CpV(CO)_3L.$$

$CpNb(CO)_4$ reacts in accordance with an analogous scheme but with more extensive substitution.[42]

(*b*) *Complexes of Group VI metals.* Almost all the studies published on this question have been devoted to the derivatives of metals in the lowest oxidation states. A common feature of these investigations is the use of identical or structurally similar initial metal-containing compounds. These are usually hexacarbonyls or mixed carbonyls. The substances mentioned are made to react with TPAA and one mole of carbon monoxide is readily evolved.† When special rules are fulfilled, even more complete substitution of the carbonyl ligand may take place. Acetonitrile, olefins, etc. are displaced from the coordination sphere more readily than carbon monoxide. The principle of ligand displacement constitutes the basis of the most popular direct method of synthesis of the complexes considered. However, this method can be supplemented successfully in many instances by a second, combined procedure. Complexes of the metal with phosphorus acid chlorides or other phosphorus compounds capable of reacting with nucleophiles are obtained in a preliminary step. In the concluding stage the intermediate complexes are made to react with nitrogen-containing bases to form the required products.

Direct synthesis. Chromium and molybdenum complexes may be obtained by electrophilic substitution at the metal atom, i.e. by the reaction of carbonylate anions with aminohalogeno-derivatives of phosphorous acid.[43-45] Substitution takes place readily, since the aminohalogeno-derivatives, especially 2-fluoro-1,3-dimethyl-1,3,2-diazaphospholan (VIII), readily give rise to highly electrophilic phosphamide cations. This results in the formation of phosphometallic systems, for example:

$$NaCpMo(CO)_3 + F{-}P\langle N(Me)\rangle N(Me) \rightarrow (CO)_3CpMo{-}P\langle N(Me)\rangle N(Me)$$

(VIII)

†In the interaction of ionic reagents, carbon monoxide may not be evolved.

The chemical structure of the substances obtained has been demonstrated by X-ray diffraction. The final conclusion about the electronic structure has not yet been reached, although this problem is the subject of a lively discussion.[45,46]

Carbonylate ions have been made to interact with the tetrafluoride of *N*-methyldiphosphorimidic acid (IX):[47]

$$MeN(PF_2)_2 + NaCpMo(CO)_3 \xrightarrow{1:1} F_2PN(Me){-}PF[MoCp(CO)_3];$$
(IX)
$$\xrightarrow{1:2} F_2PN(Me){-}P[MoCp(CO)_3]_2.$$

The reaction proceeds in a more complex manner in another instance:[48]

$$(Me_3Si)_2NPCl_2 + Na_2Cr(CO)_5 \rightarrow Cr(CO)_5[P{-}N(SiMe_3)_2]_2 +$$
$$+ [Cr(CO)_5]_2PN(SiMe_3)_2 + \{Cr(CO)_4[PN(SiMe_3)_2]_2\}[Cr(CO)_5]_2.$$

All the substances indicated have been isolated from the reaction mixture by fractional recrystallisation and their structures have been determined by X-ray diffraction. The chemistry of these reactions has not been discussed. Carbonylate anions have been made to react with the aminofluoroderivatives of phosphorous acid in the presence of mercury(II) chloride, which is an oxidant. Derivatives of zero-valent metals are formed in this case:[49]

$$M_2(CO)_{10}^{2-} + F_2PNEt_2 + HgCl_2 \rightarrow M(CO)_5(F_2PNEt_2);$$
$$M{=}Cr, Mo, W.$$

TPAA manifest much more frequently only a ligand transferring activity without the loss of their structural elements, as shown above. We shall consider this possibility in relation to the employment of derivatives of zero-valent metals of different chemical nature—neutral complexes of the type $M(CO)_6$, ionic complexes of the type $[M(CO)_5X]^-$, and other related compounds. These substances effectively undergo ligand transfer reactions with full amides,[1,5,50-55] ester amides,[56] mixed amide–acid halides,[5,57-59] and iminoamides [60,61] of phosphorous acid, the amides of phosphonous and phosphinous acids,[23,41,50,60,62,63] diazaphospholes,[64] and the amides of hypodiphosphorous and other branched P–P acids.[19,65-67] The amides of diphosphonous acids and other bidentate ligands[68-72] as well as cyclic[73,74] and bicyclic[51,56,75] phosphamides play an important role in these reactions.

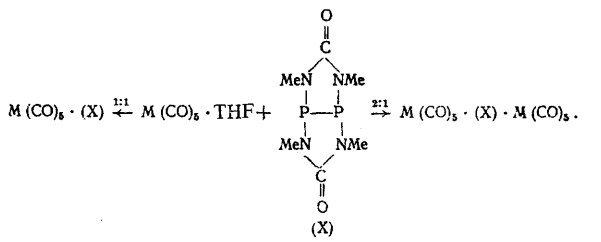
Monosubstitution of the carbonyl ligand takes place under relatively mild conditions. For this purpose, metal hexacarbonyls or other related substances are heated with an equimolar amount of TPAA in an organic solvent.[41,56,60,76-78] It is useful to carry out the reaction in its photochemical version:[49]

$$M(CO)_6 + THF \xrightarrow{h\nu} M(CO)_5 \cdot THF \xrightarrow{L} M(CO)_5L.$$

In studies with enantiomeric TPAA and prochiral complexes, diastereoisomers were synthesised[61,62,79] and it proved possible to separate them by the usual methods.

The reactions of ligands with molecules containing two phosphorus atoms, including phosphorus atoms linked directly to one another, have been investigated in various laboratories. If one of these atoms is tervalent and the other pentavalent, the process takes place only once.[19] If both phosphorus atoms are tervalent, as in the ligand (X), then the monosubstitution of the metal can proceed with participation

of one or both[65,67] phosphorus centres:



(X)

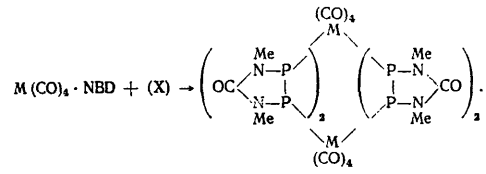
An analogous situation arises in diazadiphosphetidines.[73,77]

In the reactions examined above the difference in the complex formation reactions of chromium, molybdenum, and tungsten carbonyls was hardly manifested. Nevertheless, such a difference can be found by analysing the reactions of these carbonyls with the bidentate phosphimide ligand $(Ph_2P)_2NCH(R)COOMe$ (XI). Tungsten carbonyls react mainly with monosubstitution, while chromium and molybdenum carbonyls react with disubstitution.[80,81]

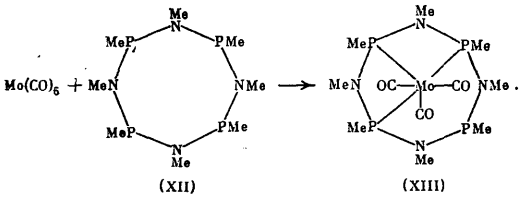
The bis-ligand transfer reaction has also been studied in detail. In order to achieve a satisfactory result, an excess of the ligand is normally employed.[5,52] The synthesis of disubstituted products is of special interest since generally speaking it can lead to geometrically isomeric complexes. It has been noted that the *cis*-forms are formed preferentially in the initial stage and can be converted on heating into the *trans*-forms.[5,57,59] In a number of experiments it proved possible to separate these isomers and to investigate their specific properties.[5,52]

It is essential to consider specially the ligand transfer reactions of phosphamides with other electron-donating centres. The hydrazide of diphenylphosphinous acid reacts with metal hexacarbonyls to form chelates.[82] An analogous result has been achieved with the full amides of αω-alkylenediphosphonous acids. When the distance between the phosphorus atoms in the molecules of the latter reaches a specific value, dinuclear systems are formed.[68,69,72]

Iminodiphosphine ligands of types (VI), (IX), and (XI) have been studied more widely in metallocycle formation.[80–86] Interesting results have also been obtained for the interaction of the norbornadiene (NBD) complexes of chromium and molybdenum carbanions with the P–P ligand (X):[67]



The tris-ligand transfer reaction has been studied relatively little. In relation to metal hexacarbonyls, this reaction yields positive results only when a specific TPAA are used. Such a ligand is the eight-membered phosphazane (XII):[87]

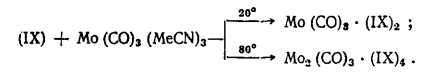


(XII) (XIII)

The fourth phosphorus atom is not coordinated to molybdenum. It is of interest that this phosphorus atom forms the longest bonds with the neighbouring nitrogen atoms (1.742 and 1.728 Å); the lengths of other bonds in the ring are much shorter (1.699 and 1.712 Å). The phosphorus atom not involved in coordination has the smallest endocyclic angle (107.13° against 109.02–110.5°).

On reaction with MeI, the neutral compound $(MeNPMe)_4 \cdot Mo(CO)_3$ (XIII) forms the corresponding ionic complex, which can also be prepared by the reaction of the ligand (XII), MeI, and $Mo(CO)_6$.

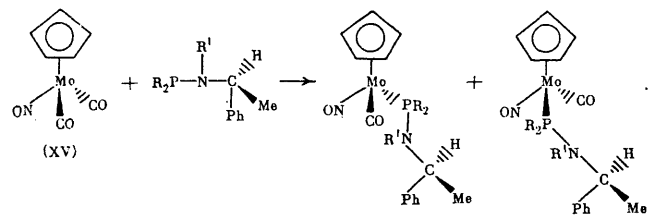
A study of the tris-ligand transfer reaction of hexacarbonyls with the dimethyl hydrazide of diphenylphosphonous acid has been published.[82] The ligand is bound in this reaction to the metal only via the phosphorus atoms. Nevertheless, in synthesis involving phosphorylated α-aminopyridine, coordination with participation of both the phosphorus atoms and the nitrogen atoms of the pyridine rings has been noted.[89,90] Very interesting results have been obtained[91] in a study of the interaction of the bidentate ligand (IX) with a mixed molybdenum carbonyl:



The structure of the dinuclear complex was demonstrated by X-ray diffraction. The difference in the ligand environment of the molybdenum atoms and the presence of a direct bond between them are noteworthy. Both these factors are not characteristic of the dinuclear complex obtained from the ligand (X).[66]

There are isolated mentions in the literature of the possibility of the hexa-ligand transfer reactions of the carbonyls of the metals considered. Thus, when the ligand (IX) is used under the conditions of photochemical stimulation, a spirotricyclic complex is readily formed.[92] Analogous substitution takes place with the tetrafluoride of *N*-phenyldiphosphorimidous acid (XIV).[93] A spirotricyclic complex of chromium has been obtained also on cocondensation of the metal vapour with the ligand (IX), while the monodentate mixed acid amides and fluorides give rise to symmetrical acyclic adducts under conditions of this reaction.[94,95] The cocondensation of chromium vapour with a mixture of ligands gives rise to a set of complexes of different ligand composition, from which the product $[(IX)_2 \cdot Cr(F_2PNMe)_2]$ has been isolated in a pure form.[95]

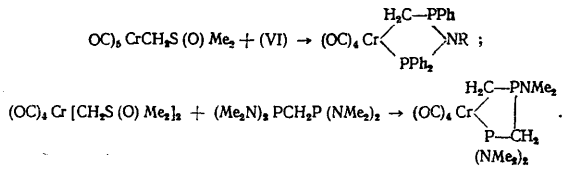
We shall now turn to studies on ligand transfer reactions in which derivatives of Group VI metals in the +1 or +2 oxidation states are used as starting materials. This possibility has been demonstrated in two investigations:[62,96]



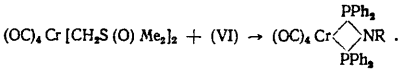
It is significant that the diastereoisomers are formed in unequal amounts; the ratio of the products depends on the type of the groups R and R'. Apparently this result is determined by an associative mechanism; in this case the transition states arising when the ligand attacks via two enantiomeric directions need not necessarily have the same energies.

There are also literature data on the ligand transfer reactions involving bidentate ligands. Thus one carbonyl ligand is displaced from a carbonyl of type (XV) on treatment with the tetrafluoride (IX).[97] It has been established very recently that the complexes of chromium carbonyl with the

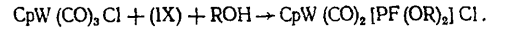
imides of diphenylphosphinous acid of type (VI) and the octamethyltetramide of methylenediphosphonous acid[98–100] form novel chromium-containing phosphaheterocycles:



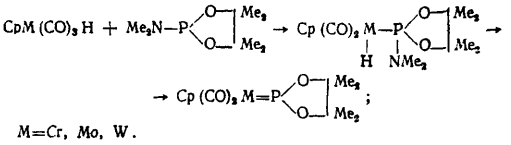
It has been concluded that the chromylide $(CO)_4Cr{=}CH_2$ is probably formed as an intermediate. However, this pathway is not obligatory:[99]



Systems in which the oxidation state of the metal is +2, namely cyclopentadienylmetal tricarbonyl chlorides,[97,101] readily interact with bidentate ligands of types (IX) and (XI) to form chelates. In the complex formation reaction in alcohol, the bidentate ligand (IX) can undergo alcoholysis:[97]

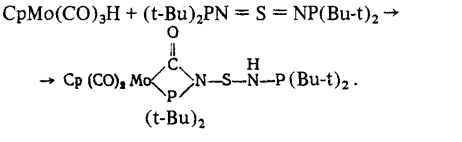


We may mention specially the non-trivial reactions of hydride complexes. The following reactions have been discussed:[102]



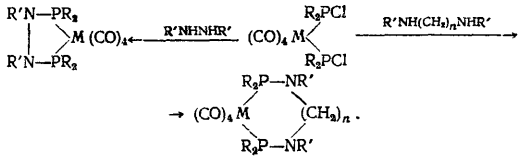
M=Cr, Mo, W.

The structure of compounds with a phosphorus–metal double bond had been demonstrated by X-ray diffraction. The phosphamide (I) enters into similar reactions. The hydrides considered react in an even more complex manner with phosphoiminosulphites:[103]

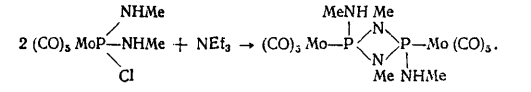


2,8-Dioxa-5-aza-1-phosphabicyclo[3.3.0]octane has been used as a ligand in complex formation reactions of neutral tungstates. It has been suggested that the overlap of the nitrogen and phosphorus orbitals is difficult in this compound for geometrical reasons, so that the phosphorus centre is less electron-donating, as a result of which tungsten is coordinated to the nitrogen atom. If the *P*-borate derivative is used in the complex formation reaction, then a stable *N*-tungsten adduct is formed.[104]

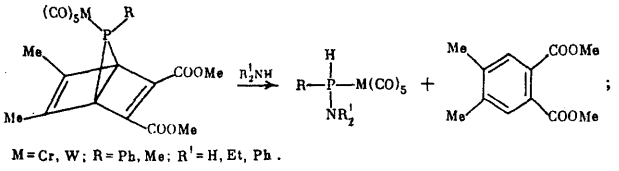
Combined synthesis of phosphamide complexes. Within the framework of this approach, the amido-group is introduced as a result of the substitution of the halogen atoms in halogenophosphine complexes. The simplest version of the synthesis consists in the interaction of monochlorophosphine systems with secondary amines.[105] More complex reactions involving secondary diamines and dialkylhydrazines can also be included here:[106]



The reaction of halogenophosphine complexes with ammonia and primary amines#,[77,107–110] including primary diamines,[106] with other functional groups[108,111] is widely used. We may mention specially the dehydrochlorination of chloramide complexes which can lead to dinuclear complexes inaccessible by other procedures, for example:[107]



The reactions of nitrogen-containing bases with halogenophosphine complexes proceed in an unusual manner in many instances. Thus the coordination compounds of molybdenum with CCl_3PF_2 phosphorylate very readily secondary amines via the P–CCl_3 bonds and not the P–F bonds.[112] The synthesis of hydrogen-containing aminophosphine complexes is chemically even more interesting:[113]



M=Cr, W; R=Ph, Me; R'=H, Et, Ph.

The possible mechanisms of this reaction have been analysed.[113]

In the course of studies designed to demonstrate the structures of the complexes investigated using physicochemical methods, certain interesting rules have been established. Thus it has been shown that the direct coordinate bonds ($^{97}Mo-^{31}P$ [114] and $^{183}W-^{31}P$ [51]) depend on the electronegativity of the atoms linked to the phosphorus atoms. In the ligand sequence obtained, phosphamides are located between phosphines and phosphites. Qualitatively the same picture can be traced in coordination shifts.[51] It is of interest that each type of complex (phosphine, phosphite, and phosphamide) constitutes a specific family when the direct coordinate bonds ($^{183}W-^{31}P$) are correlated with the $\nu(CO)$ frequencies in the IR spectra.[55]

(c) Complexes of Group VII metals. The general postulates which we have already mentioned in relation to the synthesis of Group VI metals hold also in relation to the synthesis of complexes of Group VII metals. One can only point to the smaller number of the relevant studies and the fact that they are almost all devoted solely to manganese derivatives. The principal method of synthesis of these compounds is the

#The reactions can have specific pathways. In contrast to other primary amines, the interaction of t-$BuNH_2$ with the complex $(CO)_5MoPCl_3$ leads to the formation of a diphosphorus cyclic derivative and not a monophosphorus derivative.[77]

ligand transfer reaction. The dinuclear zero-valent manganese carbonyl complex $Mn_2(CO)_{10}$ has been used in reactions with the phosphamides (I) [115] and (VII).[36] The cyclic iron–arsenic–manganese cluster reacts with the ligand (I) via the dissociation of the manganese–iron bond.[116]

The readily available derivatives of metals in the +1 oxidation state of the type of $CpMn(CO)_3$ [57,117] and $Mn(CO)_5Br$ [41] have been most often used as the initial compounds. One and sometimes also two of their ligands are readily substituted by the simplest TPAA. More complex reactions have also been described, for example:[118]

$$CpMn(CO)_2THF + Ph_2PN{=}CMn(CO)_2Cp \rightarrow Cp(CO)_2Mn{-}PPh_2N{=}CMn(CO)_2Cp.$$

Interesting data have been obtained using tetraphenyldiazaphospholes.[119] The *trans*-isomer ensures the mono-ligand transfer reaction involving $Mn(CO)_5Br$. The *cis*-isomer is capable of double substitution to give *mer*-$Mn(CO)_3L_2Br$. If one begins with the corresponding rhenium derivative, then double substitution takes place with both ligands.

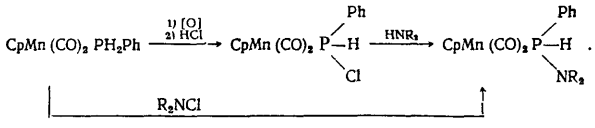
Bidentate ligands have also been used in a series of studies. Thus treatment of $Mn(CO)_5Br$ with the ligand (XI) results in the effective substitution of two carbonyl groups,[80] while in the interaction of $[Re(CO)_3(THF)_2Br]_2$ with 1,3-di-t-butyl-2,4-dimethyl-1,3,2,4-diazadiphosphetidine [120] two THF molecules are substituted. Similar processes also occur in the $CpMn(CO)_3$–ligand (IX) system.[97]§

TPAA with the α-pyridyl residue incorporated in the phosphamide fragment are also capable of single or double insertion in the coordination sphere as a result of the displacement of carbon monoxide.[76]

In the reactions described above coordination involved the phosphorus centre of the ligand. It has been shown[122] that, for the dinuclear complexes of rhenium, there is a possibility of the parallel *PN*-coordination when phosphineiminoamide ligands are used.

Derivatives of manganese in the +2 oxidation state have also been investigated in ligand transfer reactions.[57,123,124] Here we may mention the synthesis of diastereoisomeric components using optically active phosphamides.[123,124]

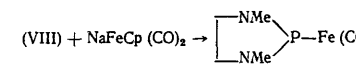
The synthesis of the phosphoramidite complexes of Group VII metals by the combined method has been little studied. Only one communication on this topic has been published:[125]



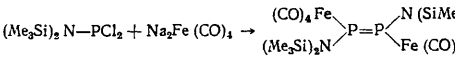
We may mention that the chlorophosphine derivative formed in the first stage is labile and rapidly disproportionates, while the corresponding phosphamide product is stable.

(d) *Complexes of Group VIII metals.* The greatest number of studies have been devoted to the synthesis of the phosphamide complexes of Group VIII metals. Bearing this in mind and also the known specific features of the individual families of elements of this Group, we have divided the entire data into sections in terms of three triads.

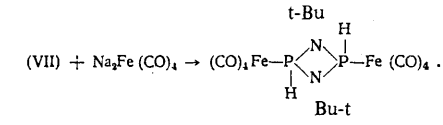
The metals of the first triad (Fe, Ru, Os) exhibit widely the 0, +1, and +2 oxidation states. The coordination systems in which we are interested have been obtained only by direct synthesis. Electrophilic substitution at the metal atom incorporated in the structure of the carbonylate anion has been used within the framework of this method, for example:[43]



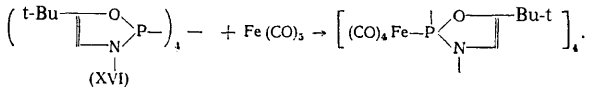
The employment of carbonylates with the more electron-donating iron atom in the interaction with the same acid fluoride (VIII) leads to the formation of a complex of the corresponding amide of hypodiphosphorus acid.[43] An even more complex compound has been obtained in the related reaction based on phosphoramidous chlorides:[48]



The author did not consider the chemistry of this process. An unusual derivative of the diamide of hypophosphorous acid has been obtained by treating the above carbonylate with the ligand (VII).[126] The traces of water present are apparently the source of hydrogen:



The ligand transfer reactions of the simplest complexes of the metals in the triad have been studied in greater detail on treatment with TPAA. In these reactions the TPAA usually do not lose any atoms or groups, as mentioned above. In individual experiments, such loss nevertheless occurs, but the structural element separated from the phosphorus remains part of the composition of the complex. We may mention the principal aspects of the investigations. The phosphamide (I) [127] and monoaminophosphines[41,128] react with $Fe(CO)_5$ to form monosubstitution products. Apart from monodentate ligands, bidentate[129,130] and tetradentate[131] ligands have been used in the reactions with $Fe(CO)_5$. As an illustration, we may quote the reaction



It is significant that the initial tetramer (XVI) behaves differently in the complex formation reactions—in its reaction with boron trifluoride ether, it is converted into the monomeric form and gives rise to a boron complex of a derivative of dicoordinate phosphorus, while in the example quoted only carbon monoxide is displaced from the four $Fe(CO)_5$ molecules. The structure of the iron complex has been demonstrated by X-ray diffraction and a significant difference between the lengths of the P–N bonds has been demonstrated (the distance is 1.737 Å for the bonds involved in both the small and the large rings, while the distance is 1.676 Å for the bonds in the large ring only). This difference is apparently determined by the different interactions of the unshared electron pairs of the nitrogen atoms with the electrons of the two phosphorus–iron coordinate bonds conjugated with them.

Phosphoramidous halides have also been introduced into the ligand transfer reaction.[132–134] If Lewis acids are added to the reaction mixture, then the primary adduct can ionise. In the synthesis of complexes of the type $Fe(CO)_4L$, one may begin with cluster carbonyls whereupon structurally simpler iron carbonyls are usually formed as side products (they sometimes also undergo ligand transfer reactions).[19,53,75,93,]

§ The carbene complexes of manganese behave analogously.[121]

[132,135–137] It has been suggested that complexes of zero-valent iron with TPAA be synthesised also by the cocondensation of the metal vapour with monodentate[95] and bidentate[95,138] ligands. The iron atoms in these compounds are linked to five phosphorus atoms having identical or different substituents.

The coordination compounds of TPAA with zero-valent ruthenium and osmium have been little studied. The following methods of their synthesis have been described in the literature:[139–141]

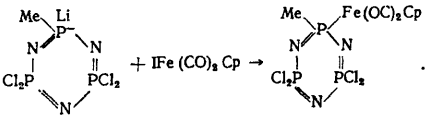
$$RuH(O_2CMe)(PPh_3)_3 + F_2PNMe_2 \rightarrow \underset{(XVII)}{Ru \cdot (XVII)_6};$$

$$Ru_3(CO)_{12} + \underset{(XVIII)}{(RO)_2P(R')N-P(OR)_2} \rightarrow Ru_3(CO)_{10}[\mu\text{-(XVIII)}] \rightarrow Ru_2(\mu\text{-CO})(CO)_4[\mu\text{-(XVIII)}].$$

The reactions of $Os(CO)_{11}(NCMe)$ and $H_2Os(CO)_{10}$ with the phosphoiminosulphite $(t\text{-}Bu_2PN)_2S$ have been carried out for osmium.[142]

The coordination compounds of iron and the +1 oxidation state having phosphamide ligands have been studied non-systematically. The possibility of the exchange of carbon monoxide for an optically active phosphamide in the prochiral allylnitrosodicarbonyliron complex has been reported.[143] The reaction resulted in the formation of a mixture of two diastereoisomers, which was resolved by the usual procedures.

The synthesis of complexes in the molecules of which the central atom is in the +2 oxidation state has been studied relatively widely. The preparation of coordination compounds by nucleophilic substitution at the metal atom has been described:[144]



The mode of coordination and other related questions have been analysed using X-ray diffraction data. In addition, the usual ligand transfer reactions of carbonylcyclopentadienyliron derivatives, accompanied by the displacement of one or two carbon monoxide molecules on treatment with phosphorous triamide[127] or phosphoramidous fluorides,[57,97] the tetrafluorides of diphosphorimidous acids,[97] and phosphinous acid amides[145–147] have been used in a series of studies. Among the reagents mentioned, optically active substances have been frequently used, which made it possible to obtain systems with a chiral iron atom. The possible epimerisation and migration of the carbonyl in these derivatives has been discussed in a number of studies.[145,147,148]

If the ligand transfer reaction is carried out in its photochemical version, then other profound changes in the system are possible together with the exchange processes, for example:

$$\underset{R=Me,\ Ph.}{Ph_2P-NH-CH_2R} + \underset{|}{CpFe(CO)_2}PhCHOMe \rightarrow \underset{|\quad|}{(OC)CpFe-PPh_2}PhCH-NCH_2R;$$

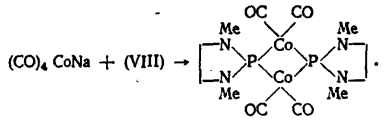
When R = Ph, the iminophosphine complex is obtained.[149]

Ruthenium complexes of the phosphoramidous difluoride (XVII) are readily formed from chlorides stabilised by triphenylphosphine. In the course of the synthesis triphenylphosphine is partly displaced:[150,151]

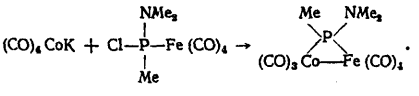
$$RuCl_2(PPh_3)_3 + (XVII) \rightarrow RuCl_2(PPh_3)_2(XVII)_2.$$

The adducts with different TPAA based on the chloroarene-ruthenium derivatives[152–154] as well as the corresponding hydrides[155] have been obtained analogously.

The Co, Rh, Ir triad. It has been suggested that electrophilic substitution at the metal atom be used to obtain the cobalt complexes. The carbonylate anions are usually made to react with phosphoramidous halides for this purpose, for example:[156]



Above we considered the analogous reactions of phosphorodiamidous fluoride (VIII) with iron and other transition metal carbonylates and noted that they all lead to mononuclear complexes. It is of interest that the phosphonamidous chloride derivative of iron tetracarbonyl gives rise to a heterometallic complex on interaction with cobalt carbonylate:[137]



Dinuclear carbonyls, for example $Co_2(CO)_8$ (XIX), can also be involved in the cyclic cluster formation reaction.[157] The cluster obtained proved to be an extremely promising initial compound for the synthesis of other skeletal systems.[158,159]

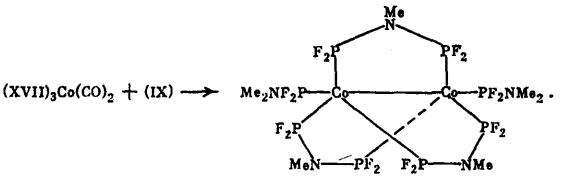
Together with the electrophilic substitution method, the ligand transfer method has also been used to synthesise cobalt complexes of TPAA, for example:[41,127]

$$CpCo(CO)_2 + \underset{(XX)}{Me_2PNMe_2} \rightarrow CpCo(CO)(Me_2PNMe_2);$$

$$Hg[Co(CO)_4]_2 + (I) \rightarrow Hg[Co(CO)_3 \cdot (I)]_2.$$

Ligand transfer reactions of this type with structurally similar cobalt complexes $Cp(CO)_2Co(R_F)I$, whose molecules contain the metal atom in the +3 oxidation state, have been achieved using optically active phosphinous amides. Two diastereoisomers are formed in this instance, their ratio being determined by the perfluoroalkyl group R_F.[160]

A relatively complex instance of the ligand transfer reaction makes it possible to obtain a dinuclear complex in a photochemical experiment from a phorphorus-containing mononuclear complex and the ligand (IX):[161]



Cobalt octacarbonyl (XIX) has been studied more widely in the ligand transfer and accompanying reactions. It has been stated that this compound reacts with the ligands (XX) [41] and (I) [127] to give ionic products. The structure of the compounds has not been demonstrated in detail. Subsequently this reaction was investigated in another study[78] where the formation of paramgnetic mononuclear products (A) was established for the full amides of phosphorous acids, while dinuclear diamagnetic substances (B) were found to be produced in the reactions involving the phosphoramidous esters (cyclic and linear):

$$(XIX) + L \begin{cases} \xrightarrow{\text{(A)}} Co(CO)_3L; \\ \xrightarrow{\text{(B)}} [Co(CO)_3L]_2. \end{cases}$$

The octacarbonyl (XIX) has been studied in detail in the reaction with the bidentate ligand (IX). The reaction at 20 °C leads to the formation of the dinuclear dicarbonyl $[Co_2(CO)_2(IX)_3]$.¶ On photochemical activation and when an excess of the ligand is used, the product of the full ligand transfer reaction $[Co_2(IX)_5]$ is obtained.[162] There are three chelating ligands in the molecules of each of these complexes, which give rise to five-membered rings with two cobalt atoms. A similar result has been noted also in the reaction of the octacarbonyl (XIX) with the phosphoimine (XIV).[93] Dinuclear systems have also been obtained by the cocondensation of cobalt vapour with the corresponding ligands.[95,161]

The synthesis of cationic cobalt phosphamide complexes by the reaction of cobalt(II) perchlorate with the bidentate ligand $(Ph_2P)_2NPh$ has been reported.[163] Analogous cobalt compounds with α-diphenylphosphamidopyridine have been described.[6] The reactions leading to cobalt–aluminium complexes are chemically more involved:[164]

$$CoCl_2[P(NR_2)_3]_2 + AlCl_3 + P(NR_2)_3 \rightarrow CoCl[P(NR_2)_3]_3[AlCl_4].$$

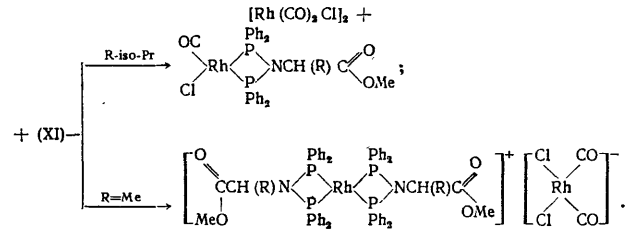
The oxidative addition of the triisocyanate of phosphorous acid to the simplest cobalt complexes merit special attention:[165]

$$(Me_5Cp)Co(CO)_2 + P(N{=}C{=}O)_3 \rightarrow (Me_5Cp)Co\begin{matrix}CO\\ \diagup\\ -N{=}C{=}O\\ \diagdown\\ P(N{=}C{=}O)_2\end{matrix}.$$

Particularly numerous studies have been devoted to the rhodium complexes of TPAA, which can be accounted for by their catalytic activity. The latter factor affects also the character of the investigations carried out: the published articles frequently describe not individual coordination compounds but compositions comprising them, which are designed for catalysis (such compositions were examined in the Section devoted to catalysis). In contrast to cobalt complexes, the above compounds are more homogeneous in terms of the principal chemical features. As a rule, the central atom of the molecule is in the +1 oxidation state. The methods of synthesis of these systems are also relatively similar. They usually consist in the interaction of carbonyl or olefinic dinuclear complexes with TPAA and the process involves either the substitution of the ligand or the breaking of the $[\mu\text{-}X_2]$ bridges. We shall consider the latter possibility. In many studies the formation of the *trans*-complexes from μ-dichlorotetracarbonyldirhodium has been investigated:

$$[Rh(CO)_2Cl]_2 + 4L \rightarrow \begin{matrix}OC & L\\ & Rh\\ L & CL\end{matrix}.$$

The ligands employed were the full amides of phosphorous,[166,167] alkyl phosphorous†,[168–171] and phosphinous[23,172] acids. The bidentate TPAA behave in a complex manner. The cyclodiphosphazan (VII) and the corresponding difluoride give rise to different types of complexes depending on the reactant ratio.[36,173] The ligand (XI) and its analogues ensure the chelation of the metal:[80,81]



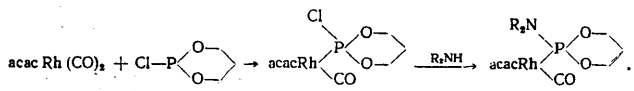
This example demonstrates the detailed influence of structural factors on the course of the complex formation reaction. It has been shown in a number of studies that the interaction of μ-dichlorotetracarbonyldirhodium can lead to not only the mononuclear complexes already examined but also to dinuclear complexes.[166,171,173] According to Nifant'ev et al.[171] such a process involving monodentate phosphamides takes place when the reaction is carried out in the presence of oxygen.

Bidentate ligands make it possible to obtain dinuclear rhodium complexes more frequently than the monodentate ligands. A dinuclear complex with a ruptured chlorine bridge has been obtained from the hard ligand (X),[67] while a complex with the intact bridge has been obtained from the relatively labile imide of diphenylphosphinous acid.[174,175] A result close to the latter case has been obtained in a study with the ethylimides of dimethyl-[176] and diphenyl-phosphorous acids (XVIII),[177] although here too the influence of the ester group on the details of the structure of the dinuclear complexes was manifested.

We shall consider the ligand transfer reactions of olefinic π-complexes of rhodium(I) chloride. These substances can be converted into mono- and di-nuclear coordination systems. Thus, according to the data of Aresta et al.[178], the ethylene π-complex and the phosphamide (I) react at 20 °C to form a product resulting from the rupture of the chlorine bridge. In other studies[179,180] dinuclear complexes were synthesised. Phosphoramidous fluorides of type (XVII) have been introduced into the ligand transfer reaction; the possibility of the complete substitution of the ethylene ligand by phosphamide ligands was demonstrated.[181]

Cyclo-octadiene derivatives of rhodium(I) chloride react with bidentate ligands of type (VII) to form dinuclear complexes in the molecules of which the metal atoms are coordinated to different phosphorus atoms.[82] Extensive, including complete, substitution of primary ligands by the bidentate ligands occurs upon the addition of tetrafluoroborates.[22]

The readily available acetylacetonatodicarbonylrhodium, which readily reacts with a wide variety of 2-amino-1,3,2-dioxaphosphorinanes[183] and 2-amino-1,3,2-oxazaphosphorinanes,[184] can be used for the synthesis of stable mononuclear complexes of univalent rhodium with one phosphamide ligand. The axial orientation of the metal relative to the six-membered ring of the ligand has been established in the complexes obtained. Some of the phosphamide complexes of the type considered have been synthesised in accordance with a two-stage scheme:[183]



On interaction with phosphamide in the presence of perchloric acid, the acetylacetonatorhodium(I) derivative with the cyclo-octadiene ligand exchanges the acetylacetonato-group and not the olefin group.[185]

¶The ligand transfer reaction of cobalt dodecacarbonyl has also been described briefly in the literature.[93]

†The results of the study of Grishina et al.[170] have been partly revised.[171]

In conclusion of the consideration of the synthesis of rhodium coordination compounds, we shall deal with the interconversions of the phosphorus-containing complexes. The partial displacement of PF_3 from the coordination sphere on treatment with the ligand (I) has been reported.[167] The reduction of phosphamide complexes of rhodium(I) is also of great interest.[186,187]

The synthesis of coordination compounds of iridium with TPAA has been little studied.

Complexes with the bidentate ligand (VI), obtained from the cyclooctadiene (COD) derivatives of iridium, have been reported:[188]

$$[Ir(COD)Cl]_2 + (VI) \rightarrow [Ir\cdot(VI)_2]Cl.$$

The reaction of the complex $[Ir(C_8H_{14})_2Cl]_2$ with an excess of PF_2NMe_2 leads to the formation of the complex $IrCl.(PF_2NMe_2)_3$, in which there are no intermolecular Ir–Ir contacts, in contrast to the PF_3 derivatives.[189]

The Ni, Pd, and Pt triad. The study of the synthesis of complexes of the metals of the last triad with TPAA has its characteristic features. Thus, the relevant derivatives of all the elements of this family have been investigated to approximately the same extent. The second feature is manifested in the relative chemical paucity of the field considered. Thus there are virtually no reactions involving the formation and decomposition of clusters on complex formation, there are almost no unexpected reactions, and the syntheses in the coordination sphere of the metal have been little developed.

We shall consider the formation of phosphamide complexes of zero-valent metals. A series of studies on the ligand transfer reactions of $Ni(CO)_4$ have been published. The process involving the monodentate ligands (I),[2,5,127,190] (V),[75] and (XX),[41] phosphoramidous halides,[2,191] and the complex cyclic phosphamides $P_4(NMe)_6$ [192] and $MeP[N(R)SiMe_2]_2$ [193] is accompanied by the substitution of one or two carbonyl groups. The reaction with the bidentate ligand (IX) can be more far reaching and may even involve complete substitution.[130] The silylated amidoimide complex of zero-valent nickel (XXI) has been synthesised with the aid of the ligand transfer method:[194]

$$Ni(COD)_2 + R_2N{-}P{=}NR \rightarrow \left(\begin{array}{c} R_2N \\ \diagdown \\ P{-} \\ \diagup \\ RN \end{array}\right)_3 {-}Ni;$$

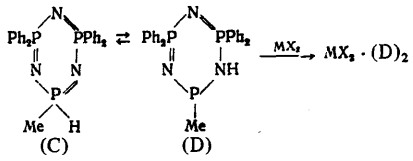
$R=SiMe_3$. (XXI)

Nickel complexes containing only phosphamide ligands have also been obtained from the metal vapour.[95]

Coordination compounds of platinum have been studied in greatest detail by Scherer, who showed that biscyclooctadieneplatinum reacts with amidoimides of type (III) to form substances having the composition $Pt(III)_3$.[195] The interaction of the ligand (III) with cyclic platinum clusters has also been achieved:[196]

$$Pt_3(\mu\text{-}CNR)_3(CNR)_3 + (III) \rightarrow Pt_3(\mu\text{-}CNR)(CNR)_3\cdot(III)_2.$$

The preparation of complexes of bivalent metals has been described fairly extensively. Nickel, palladium, and platinum salts or their benzonitrile and similar derivatives form complexes effectively with various full amides[1,5,75,78,197,198] and amidoesters[104,199–202] of tervalent phosphorus acids and the amidoimides (III).[202] The reaction of acetonitrile solutions of palladium and platinum halides with an unusual cyclotriphosphazene is of special interest:[203]



(C) (D)

According to ^{31}P NMR data, the initial phosphazene exists almost fully in the form (C), which, however, being a prototropic system can be converted into the form (D) to form a complex.

The study of the interaction of triethylphosphine derivatives of platinum and palladium dichlorides with di- and triazaphospholes established that the primary adducts can have different compositions. It has been suggested that the ligand is coordinated with both phosphorus and nitrogen atoms.[204]

Bivalent metal salts have been made to react with bidentate ligands (VII),[205] (XI),[80,81] (VI),[85] and (XVIII) [71] and mononuclear, including chelate, and dinuclear complexes were obtained. Nickelocene, π-allylpalladium chloride, Zeise's salt, and other similar organometallic compounds have been widely investigated in reactions with TPAA. The full amides[206,207] and amidoesters[202,208,209] of phosphorus acid, including those containing carbohydrate residues in their molecules,[168,210] as well as the bidentate ligands (VII) [211] and (VI) [212] have been resorted to as the latter.

In conclusion we shall deal with the intracoordination synthesis of phosphamide complexes. Phosphatrihalogeno-,[197,213–215] phosphamidohalogeno-,[216] and phosphinohalogeno-derivatives[80,214,217] of metals react satisfactorily with amines, being converted into the required complexes. Unfortunately the reaction is not of general importance.[213,214] Metal amides are phosphorylated more effectively than amines.[214,215]

III. CHEMICAL PROPERTIES

The publications on this question are divided into three groups. The first, main group includes studies on reactions involving the phosphamide (phosphimide) fragment of the ligand without affecting the coordination sphere. The data obtained are important for the synthesis of new types of phosphorus-containing complexes. At the same time they are of fundamental significance in a general chemical sense, because they demonstrate the influence of the metal on the reactivity of coordinated organophosphorus systems. The second group includes studies devoted to the preparation of complex organic compounds, the phosphorus-containing and metallic components of the complexes fulfilling only auxiliary functions. Studies on the last group are concentrated on the inorganic aspect of the chemistry of complexes—oxidation-reduction processes, additional complex formation via the functional groups in the side chains, and ligand transfer reactions.

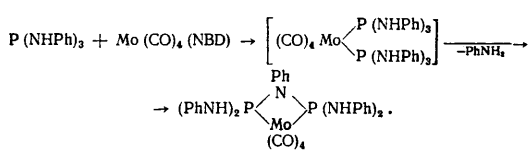
1. The Reactions of the Coordinated Ligand Via the Phosphamide (Phosphimide) Bond

In the first place we shall consider the reactions of complexes involving a single P–N bond. TPAA are known to be labile and to undergo readily reactions via the phosphamide functional group on treatment with reagents whose molecules contain a mobile hydrogen atom or a polar double bond.[218] The possibility of involving also metallic complexes of TPAA

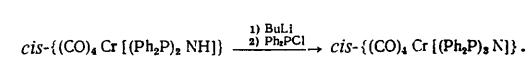
in similar reactions has been discussed in a series of studies in recent years. It has been established that their P–N bond is cleaved by hydrogen chloride with formation of phosphochloro-[41,59,62,113,117,135,136,219,220] or amidophosphochloro-complexes.[107,137]# In many cases hydrochlorination is accompanied by profound skeletal rearrangements.[91] Overall, the hydrochlorination of the complexes proceeds readily, although it requires more severe conditions than the corresponding reactions of the free ligands.[136] The complexes synthesised, which are as a rule difficult to obtain by other methods, are widely used for the preparation of a wide variety of types of phosphorus-containing coordination systems (see, for example, Refs.113, 137).

The phosphamide complexes also react with hydrogen bromide,[69,72,107,113,117,136,219] hydrogen iodide,[107,113,117,219] and hydrogen fluoride.[117,146] Instead of the last compound, it is sometimes convenient to use benzoyl fluoride.[117] The deamination reaction considered makes it possible to solve simply certain coordination-chemical problems; for example, it permits the synthesis of enantiomeric complexes with a chiral metal atom.[146]

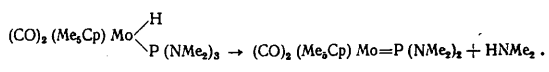
The hydrolysis[59,162] and alcoholysis[24,59,77,199] of the phosphamide complexes have been reported. The influence of the nature of the metal on the ease of the process has been established in relation to these reactions. Thus it has been shown that the copper complexes react more readily than the platinum complexes. In the latter case a positive effect is achieved only when acid catalysts are employed.[199] A characteristic reaction of the complexes, which has not been very widely investigated, is transamidation.[107] It leads to the disproportionation of the ligands:[221]



Thus the metal is a factor promoting the conversion of the trianilide of phosphorous acid into bis(phosphorodianilidato)-phenylamine and aniline. We may point out another possibility of inner-sphere phosphorylation:[222]

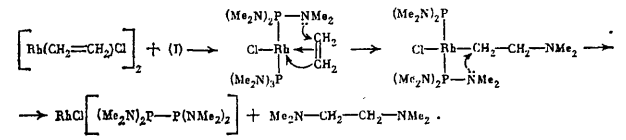


It is significant that this process is more effective than the analogous reaction without the participation of the metal. Phosphorylation accompanied by the formation of the P=M double bond is of great interest:

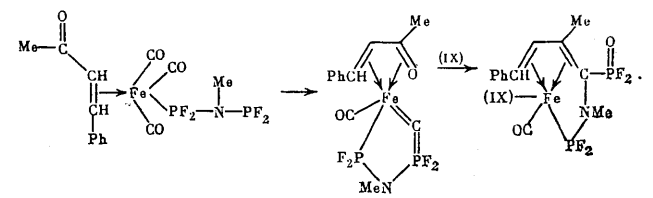


In the compounds obtained, sulphur, diazomethane, carbon disulphide, and iron carbonyls are inserted in this bond with formation of novel three- and four-membered cyclic derivatives.[102] The interaction of the phosphamide complexes with carbon dioxide, accompanied by the insertion of the reactant in the P–N bond, is no less important.[178]

The reaction of the phosphamide complexes with ethylene which has no analogy in the series of phosphamides, merits special attention:[178]

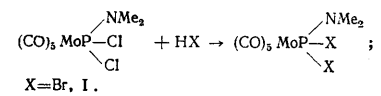


The reactions of benzylideneacetone, carbon monoxide, and the ligand (IX) coordinated jointly to the iron atom are formally similar to the above reaction:[129]



Individual motifs of this scheme can also be found in the paper of Newton and King.[223] On the basis of the data analysed, one may conclude that the possibilities of metal complex synthesis have begun to extend also to the synthesis of organic compounds which are difficult to obtain, including compounds which are extremely complex. Further development of this field of study is already urgently required. Success can be ensured only by a close cooperation between organophosphorus chemists and specialists in metal complex reactions.

The reactions of the coordinated phosphamide are not manifested solely by the degradation of the P–N bond. It is extremely significant that this structural unit can facilitate the substitution of other groups linked to the phosphorus atom. Thus the molybdenum complex with PCl_3 does not exchange chlorine atoms on treatment with hydrogen bromide and iodide. However, this reaction does occur with the corresponding phosphoramidous chloride complex:[107]

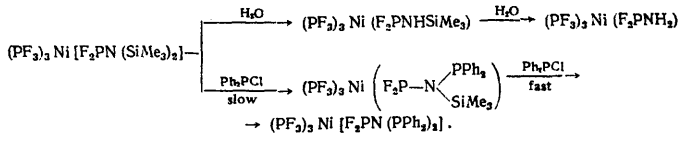


The amido-group probably exhibits a mesomeric electron-donating capacity in relation to the phosphorus atom, which promotes the heterolysis of the P–Cl bond.§ Nevertheless the unshared electron pair of the amido-group can ensure the formation of borate complexes[77] and protonation products. A stable ammonium compound has been detected only in a study involving a complex in which effective d_π, p_π-conjugation in the phosphamide fragment was not ensured for geometrical reasons.[220]

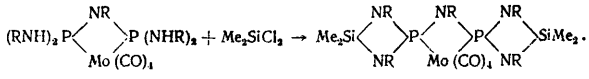
#For the description of the anomalous course of this reaction, see Müller and Vahrenkamp.[137]

§In relation to the hydrogen atom in the amidophosphohydride complexes, the amido-group exhibits electron-accepting properties. These complexes are readily deprotonated with formation of phosphorus-centred anions, which readily enter into reactions with electrophiles, forming various substances, including those which are virtually unobtainable in other ways.[224]

Among other reactions involving nitrogen, we may mention the desilylation of coordinated *N*-silylphosphamides:[214]

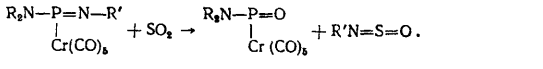


Heterocyclic condensations are of interest,[106,110,222] for example:



The reactions of phosphimide complexes, i.e. systems with a P=N double bond, should be considered separately. These compounds are readily hydrated[202,225] and combine with alcohol,[202] forming the usual phosphamide coordination compounds. Certain complexes of Group VI metals with cyclic phosphimides readily undergo cyclo-oligomerisation.[74]

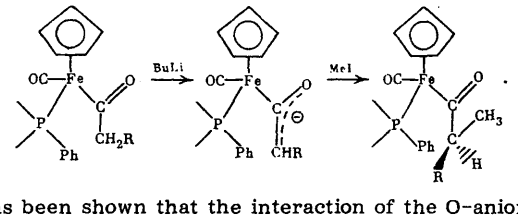
The deimidation of chromium complexes of the amidoimides of phosphorous acid is a reaction without analogy in the chemistry of classical organophosphorus compounds:[60]



2. The Use of the Phosphamide Complexes in Fine Organic Synthesis

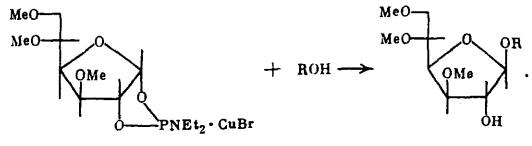
It has been shown[28] that the copper-lithium complexes stabilised by the hexaethyltriamide of phosphorous acid yield very satisfactory results in the specific α-alkylation of αβ-unsaturated ketones. The hydrolysis of the reaction mixture entails in this instance the complete decomposition of the complex and the decomposition of the ligand to water-soluble substances, which ensures the preparative employment of this important reaction.

The alkylation of Fe-acyl derivatives stabilised by phosphorus-containing ligands is of interest:[226]



It has been shown that the interaction of the O-anionic end of the ambident component of the side group with the benzene ring results in a definite diastereoselectivity. The most marked manifestation of this effect has been noted when phenylphosphamide ligands were employed.

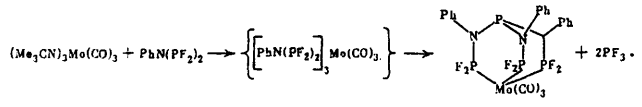
It has been suggested that the copper complexes of cyclic phosphoramidites (derivatives of carbohydrates) be used in glycosylation,[26] for example:



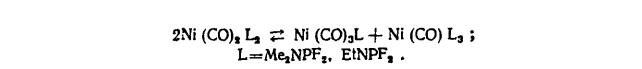
The cyclic phosphoramidites themselves behave in this reaction as phosphorylating agents. Thus complex formation involving the phosphorus atom alters significantly the nature of these derivatives.

3. Other Reactions

We shall consider the reactions involving the metal atom in the phosphamide complexes. The disproportionation of asymmetric ligands is sometimes observed. The disproportionation yields especially satisfactory results and the formation of highly symmetrical skeletal systems is possible, for example:[227]

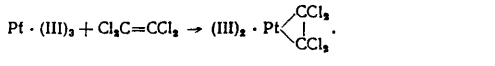


Another type of disproportionation has been described. It reduces to the redistribution of the ligands between individual molecules of the complex without altering their structure. As an illustration, we may mention the equilibrium established over a year at 20 °C:[191]

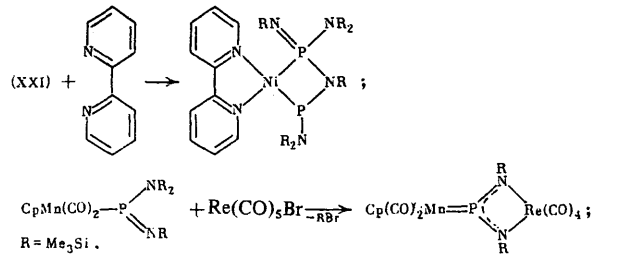


The displacement of one phosphamide ligand by another[228] or by P-ligands of a different chemical type[145,195] from the complexes has also been reported. Ligand transfer may be accompanied by profound changes in the structure of the coordination compound, for example, by the migration of the organophosphorus ligand from the metal to the π-bound benzene ring.[154]

We shall now turn to reactions accompanied by a change in the oxidation state of the metal. The complexes may be reduced by chemical and electrochemical methods[15,115,229,230] and can be oxidised. The latter is especially interesting, because it can lead to structurally unusual results, for example:[225]



In conclusion of this Section, we may point to the reactions of complexes having ligands with C–N groups in the side chains. These compounds can react with the simplest derivatives of metals, forming complex dinuclear systems.[231] The reactions of complexes whose ligands have P–N groups are even more interesting. In this case complex formation is accompanied by a far-reaching intracoordination rearrangement:[194,232]



IV. THE SEARCH FOR PRACTICAL APPLICATIONS

1. Catalysis

Functioning as ligands in metal complex catalysts, TPAA are in principle analogous to phosphines. Nevertheless, they are characterised by a wide variety of electronic and steric parameters to a greater extent in phosphines and other

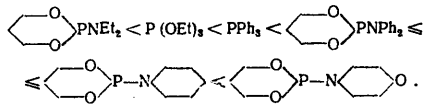
derivatives of tervalent phosphorus, which leads to very realistic prospects for the regulation of the activity and selectivity of catalytic systems. An important factor is also the availability of many TPAA.

Hydrogenation processes in the presence of complexes with phosphamide ligands have been studied in greatest detail. The first communications[233,234] on this question were devoted to the hydrogenation of styrene in the presence of the [RhCl.$(C_2H_4)_2]_2$ + nL system. It has been established that the activity of the catalysts increases significantly on passing to phenylphosphamides whose molecules contain piperidine, pyrrolidine, or morpholine residues. The use of derivatives of less basic amines or amines with branched groups weakens sharply the catalytic properties. The general activity series summarised by James[235] are as follows:

$$PPhA_2,\ PPh_2A > PPh_3 > PA_3 \geqslant PAlk_3;$$
$$PPh_3 > PPh_2Alk \approx PAlk_2A > PPhAlk_2 > PAlk_3.$$

where A is the residue of the main and sterically unhindered secondary amine.

The influence of the nature of the ligands on the rate of hydrogenation has been observed in greater detail in a study[183] devoted to the acetylacetonate derivatives acacRh.(CO)L. The activity of the catalysts increases in the sequence



In many cases interesting results were obtained also with complexes having bidentate phosphamide ligands, for example, the ligand (XI).[80]

The substrate and the solvent[234,236] and also admixtures of oxygen play an important role in hydrogenation in the presence of various phosphamide complexes of rhodium. Oxygen oxidises the phosphamide ligands in mononuclear *trans*-complexes, which leads to the appearance of dinuclear complexes having a comparatively high catalytic activity.[171]

The use of optically active phosphamides to synthesise enantio-selective rhodium catalysts proved to be extremely fruitful. A wide variety of monodentate[237,238] and bidentate[239–248] ligands¶ were used for this purpose, the latter exhibiting the best activity overall. Optically active phosphoramidite complexes immobilised on mineral carriers have also been investigated, but their application does not yield appreciable advantages.[253]

The enantioselectivity of the phosphamide complexes and the configuration of the products of asymmetric hydrogenation probably depend on the nature of the amido-groups at the phosphorus atom.[240,245,254] Thus when the compounds $[Rh(CO)L]ClO_4$ are used in the hydrogenation of *N*-acylaminocinnamic acid, the transition from (1*R*, 2*R*)-bis(diphenylphosphinoamino)cyclohexane to (1*R*, 2*R*)-bis(diphenylphosphino-*N*-methylamino)cyclohexane leads to the inversion of the stereochemical result of the reaction.[254]

The use of palladium complexes with TPAA in hydrogenation is less well known. The full amides of phosphorous acid exhibited a high activity in the C_3H_5PdLCl–$NaBH_4$–O_2 system in the reduction of nitrobenzene, alkenes, and alkynes.[206,255] Systems obtained from phosphoramidites (derivatives of carbohydrates)[168,210,256] and cyclophosphorylated ephedrine[208,209] showed some catalytic activity. The possibility of using ruthenium complexes with the ligand (VII) in the hydrogenation of oct-1-ene has been indicated in the literature.[257]

The rhodium(I) complexes of TPAA yielded satisfactory results in the catalysis of hydroformylation.[172,258,259] The influence of the ligand on the direction of the process has been traced in relation to the hydroformylation of hex-1-ene. It has been shown that the increase of the π-acceptor capacity of the phosphoramidite, observed when aryl residues are introduced at the nitrogen atom, leads to an increase of the yield of the aldehyde having the normal structure. A decrease of π-acceptor capacity entails the formation of large amounts of the isomeric aldehyde. The use of polymeric complexes of the type $P–OC_6H_4NMePPh_2.RhCl(CO)$ has been reported.[172] It has been indicated that there is a possibility of the enantioselective hydroformylation of prochiral alkenes and of the hydrosilylation of ketones using rhodium complexes with optically active ligands.[249] The carboxylations of propene in the presence of a palladium catalyst, promoted by the full alkylamides of phosphorous acid, has also been described. The process selectivity reaches 79.5% with respect to isobutyric acid, which exceeds the selectivity of the catalytic system using PPh_3.[260]

We shall now turn to the catalysis of oligomerisation and polymerisation. A number of nickel and cobalt complexes containing the hexaalkyltriamides of phosphorous acid[164,261,262] and phosphamide bidentate ligands[163] are of technical interest for the polymerisation and oligomerisation of α-olefins and dienes. It is significant that nickel catalysts of this type can be used in an aqueous medium.[263] The oligomerisation of acetylenes in the presence of the $Pd(acac)_2.AlEt_3.L$ system has been investigated.[264] When $L = Ph_2PNMe_2$, the amount of dimer formed is smaller by a factor of two and the amount of higher oligomers is twice as great as in the case where $L = PPh_3$.

Among other possibilities of catalysis using the above complexes, we may point to the conversion of methanol into ethanol[89] and to the acceleration of diffusional photographic processes in sensitive layers of polymers.[265]

2. The Synthesis of Medicinal Drugs

Data on the synthesis of platinum complexes and positive results of their tests in the treatment of oncological affectations have been published.[1,200] Studies initiated at the present time are being extended to the field of complex biogenic systems.[199] It has been suggested that gold complexes based on azaphospholes be used in chrysotherapy.[33,204]

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Thus metal complexes of TPAA constitute a large class of coordination compounds which are constantly attracting increasing attention. An important feature of these systems is that their ligands are chemically varied. They are frequently extremely labile or do not exist at all as individual substances but are entirely stable in the coordinated state. Consequently the only source of any information about these phosphorous compounds is the study of their metal derivatives.

Complexes with TPAA enter into a wide variety of reactions in the coordination sphere of the metal. An important role is due in this instance to the phosphamide component of the molecule which either changes as a result of the dissociation of the P–N bond, or activates a neighbouring group, or

¶Recently, particular attention has been devoted to ligands obtained by phosphorylating optically active aminoalcohols.[249–252]

influences the properties of the metal. In other words, the behaviour of the complex is not determined simply by the central ligand atom but also by the functional group based on it.

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