Russian Chemical Reviews **65** (3) 225–247 (1996)
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UDC 541.49 + 546.97

Coordination chemistry of hydrophosphorane compounds

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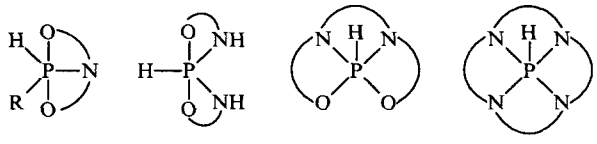
Abstract. The overall results of the study of hydrophosphorane compounds as ligands for metal complex synthesis and catalysis are summarised and discussed. The principal types of coordination of hydrophosphoranes, the structure of their metallo-derivatives, and the possible mechanism of the complex formation reaction are examined. The prospects for the employment of hydrophosphoranes in modern coordination design are demonstrated. The bibliography includes 102 references.

I. Introduction

The current range of phosphorus-containing ligands is exceptionally varied and in many respects determines the progress in the field of metal complex design. Many phosphorus-containing ligands are involved in the construction of tens and perhaps hundreds of coordination compounds. Thus the Cambridge Structural Database contains information about the structures of 720 complexes based on one of the simplest organophosphorus compounds — triphenylphosphine,[1] and this does not constitute the maximum information available since new studies are being regularly published. After all, there has been no flagging of interest for more than 30 years in perhaps the most popular P, N-bidentate ligand — 2-diphenylphosphinopyridine. We may also point to the outstanding range of complex chiral systems which have found application in asymmetric catalysis.[2,3] Overall, the stream of information about the coordination compounds of phosphorus has recently assumed an avalanche-like character. Nevertheless, the notable event which occurred towards the end of the 1970s is outstanding even against this background — the introduction into practical metal complex synthesis of a fundamentally new class of phosphorus-containing ligands — hydrophosphoranes.

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Received 28 July 1995
Uspekhi Khimii **65** (3) 242–265 (1996); translated by A K Grzybowski



At first sight, the structure of hydrophosphoranes contains no potential donor centres — their phosphorus atom has no lone pair (LP) and those of the nitrogen and oxygen atoms should be involved in $p\pi-d\pi$ conjugation with the *d* orbitals of the phosphorus atoms. However, these compounds are in fact the most variable phosphorus-containing ligands capable of P-, N-, P,N-, P,O-, and N,N-coordination. Furthermore, many new metal complexes have been obtained precisely in the study of the reactivities of hydrophosphoranes (HP), whereupon a whole series of unusual coordination polyhedra were synthesised. Any complex reaction involving hydrophosphoranes is a nontrivial phenomenon in coordination chemistry from the standpoint both stet its products and of the initial compounds. Indeed hydrophosphoranes can quite justifiably be called paradoxical ligands: they are formally incapable of binding Lewis acids but exhibit an extremely wide range of coordination possibilities.

Nowadays hydrophosphoranes constitute an independent, unique class of phosphorus-containing ligands. They have occupied this position as a result of deliberate efforts by two leading research teams: the French school under the leadership of Professor Riess, who were involved in the initiation of the coordination chemistry of hydrophosphoranes, and the American school led by Professor Lattman.

The reactivity of hydrophosphoranes has been investigated in considerable detail from the standpoint of organophosphorus chemistry and several thorough reviews have been published on this topic (see, for example, Nifant'ev and Kukhareva[4]). However, many new data concerning the formation of complexes by hydrophosphoranes have appeared since their publication and, furthermore, the data on the chemistry of hydrophosphoranes presented in these reviews are either very scanty[5,6] or are invoked merely to illustrate certain fundamental concepts: the relation between organometallic and coordination chemistry,[7] the characteristics of phosphoranide coordination,[8] the characteristics of complex formation in systems with a phosphorus–nitrogen bond,[9] and the structural characteristics of metallated phosphoranes.[10] The present review is the first attempt at a systematic consideration of the coordination properties of hydrophosphoranes and of their role and position in the series of phosphorus-containing ligands. We have tried to compare the reactivities of various groups of

hydrophosphoranes, to differentiate within each group the principal types of bonding to the central atom, to discuss certain spectroscopic features (primarily ^{31}P NMR and IR spectroscopic data concerning metallo-derivatives of hydro-phosphoranes), and to indicate the prospects for the use of hydrophosphoranes in modern coordination design.

The data presented in this review have been divided into sections in accordance with the number of phosphorus-containing rings in the initial hydrophosphoranes and the nature of the junctions between them: bicyclic systems (condensed and spiro-systems) were examined initially and then tricyclic and tetracyclic systems.

II. The formation of complexes by bicyclic hydrophosphoranes

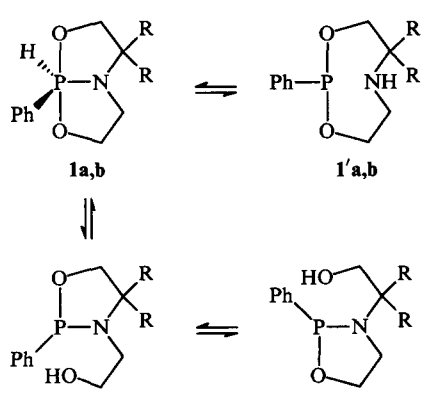
1. Processes involving bicyclic aminophosphoranes with condensed rings

Complexes of bicyclic aminophosphoranes (BAP) with condensed rings containing Rh, Pd, Ru, Mo, W, Fe, and Co are known at present. In the arrangement of the data for this part of the review, account was taken primarily of the nature of the central metal atom. An attempt was made to demonstrate strikingly the principal types of coordination of the ligands under discussion and as far as possible to reflect the history of the development of the branch of the chemistry of hydrophosphoranes considered. In view of the last factor, the discussion is initiated by considering compounds of platinum metals.

a. Rhodium complexes of bicyclic aminophosphoranes

A communication [11] concerning the coordination of BAP, which in historical terms proved to be the first group of ligands of a fundamentally new class, was published in 1978.

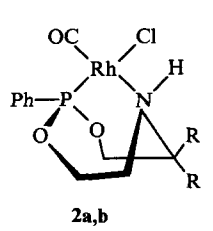
A general scheme for a possible tautomeric equilibrium involving BAP was presented [11] and, although only forms with pentacoordinate phosphorus **1a,b** were detected spectroscopically in solution, the presence of two donor centres — the phosphorus and nitrogen atoms in the potential phosphocane tautomers **1'a,b** — led the authors to carry out complex formation reactions with BAP.



1a,b **1'a,b**

R = H (**a**) (Phoran), Me (**b**)

It was found that compounds **1a,b** react rapidly under mild conditions with $[Rh(CO)_2Cl]_2$ (P : Rh = 1 : 1), forming compounds **2a,b** in yields exceeding 95%.



2a,b

Parameter	Compound	
	2a	**2b**
ν(NH)/cm^{-1}	3195	3178
ν(CO)/cm^{-1}	1991	1985
ν(RhCl)/cm^{-1}	290	285
δ_P/ppm	162.0	160.8
^1J(P,Rh)/Hz	190.5	197

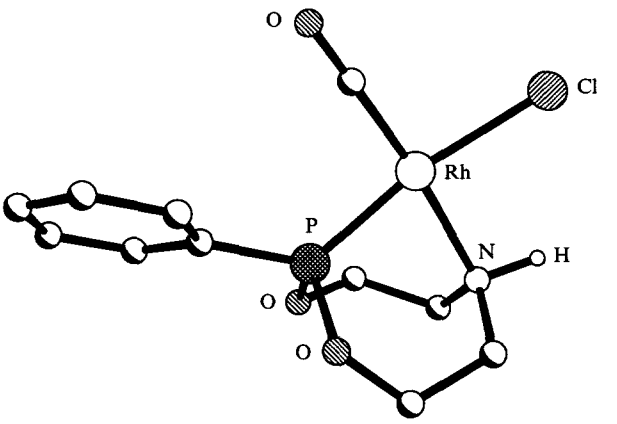


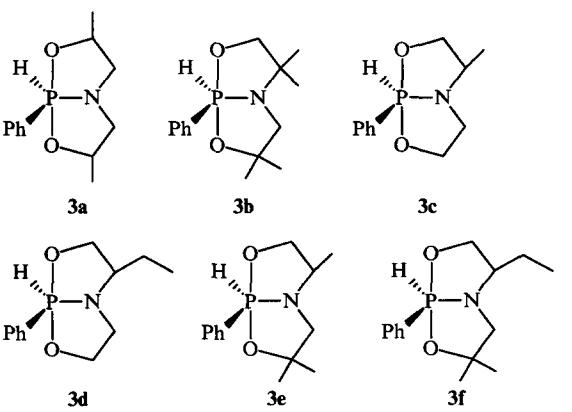
Figure 1. The structure of complex **2a**.

We may note that the IR and ^{31}P NMR spectroscopic parameters [especially ν(CO), ν(RhCl), and the spin–spin coupling constants (SSCC) ^1J(P,Rh)] quoted for complexes **2a,b** are typical (taking into account the nature of the phosphorus centre) for mononuclear chlororhodium(I) carbonyl compounds with various chelating P,N-bidentate ligands.[12–14] On the other hand, the chemical behaviour of complexes **2a,b** differs appreciably from that of the rhodium complexes with trivial phosphorus-containing ligands. Thus the formation of a 2 : 1 complex is not observed on interaction of compounds **1a,b** with $[Rh(CO)_2Cl]_2$ in the molar proportions P : Rh = 2 : 1. The reactions of compound **2b** with an excess of triphenylphosphine affords *trans*-$[RhCl(CO)(PPh_3)_2]$ with displacement of the P,N-bidentate ligand, but this time in the form of the initial pentacoordinate structure **1b** and not the phosphocane form **1'b**.

X-Ray diffraction study of complexes **2a,b** (Fig. 1)[15] revealed distances between the rhodium atom and its nearest neighbours typical of those for chelate chlororhodium carbonyl compounds with P,N-bidentate ligands as well as normal intramolecular Cl···H–N hydrogen bonds. The phosphorus–nitrogen atom distances of 2.793 and 2.788 Å (for compounds **2a** and **2b** respectively), are much less than the sum of the van der Waals radii (3.4 Å). This indicates the occurrence of the intramolecular P···N attractive interaction.

Ethene-containing analogues of compounds **2a,b**, formed by the reaction of compounds **1a,b** with $[Rh(C_2H_4)_2Cl]_2$ in the molar proportions P : Rh = 1 : 1, are also known. The same reaction, but with a molar ratio of P : Rh = 2 : 1, leads to the cationic complexes $[RhL_2]^+Cl^-$ (L = bicyclic aminophosphorane) with a *cis*-configuration of the phosphorus atoms. We may note the presence of the N–H···Cl^-···H–N hydrogen bonds between the nitrogen centres of the coordinated phosphocyclanes and the counterion.

The interaction of $[Rh(CO)_2Cl]_2$ with a series of new BAP (compounds **3a–f**) was investigated subsequently.[16,17]



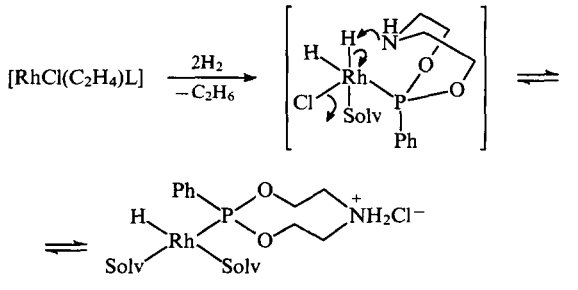
3a **3b** **3c**

3d **3e** **3f**

Compounds **3c–f** were synthesised in a homochiral form from L-alaninol or D-ethylalaninol. The rhodium complexes [RhCl(CO)L] obtained from compounds **3a–f** have the same structures as complexes **2a,b** mentioned above, which follows from their ^{31}P NMR and IR spectra: δ_P = 147–161 ppm, ^1J(P,Rh) = 180–190 Hz; ν(CO) = 1995–2003 cm^{-1}, ν(RhCl) = 280–300 cm^{-1}, ν(NH) = 3190–3203 cm^{-1}. One of the possible diastereoisomers of the complex based on the phosphorane **3c**, used as the catalyst of the enantioselective hydrogenation of (*Z*)-α-acetamidocinnamic acid with a chemical yield of 92% and an optical yield of 18%, has been isolated by fractional crystallisation from solution in acetonitrile.

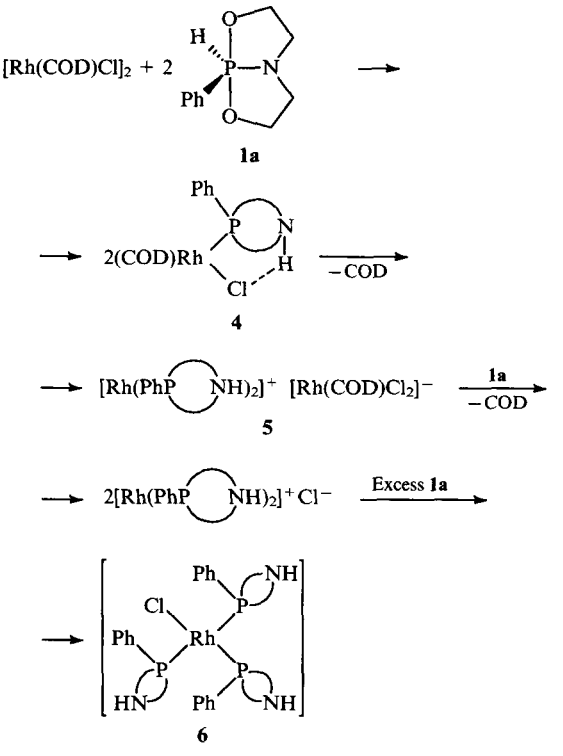
Catalysis involving rhodium complexes of BAP merits special consideration. They are all coordination systems of the metal in a 'cradle' type, formed by the phosphocane bound as a P,N-bidentate species. The more labile nitrogen centre under these conditions is the hydrophilic NH group, capable of binding a proton in the course of the catalytic cycle. The binding of a proton is accompanied by the freeing of a coordination vacancy at the central atom. These structural features make it possible to regard the rhodium derivatives of BAP as promising metal complex catalysts. Several attempts have been made to use such compounds as catalysts. In particular, in the hydroformylation of hex-1-ene, complex **2b** ensures under comparable conditions a higher degree of conversion than $RhCl(CO)(PPh_3)_2$ (85% and 52% respectively).[16] The cationic systems $[Rh(CO)L(MeCN)]^+PF_6^-$, obtained from compounds **2a,b** and $AgPF_6$ in acetonitrile, catalyse the hydrogenation of (*Z*)-α-acetamidocinnamic acid to *N*-acetylphenylalanine.[18] The yield of the product was not indicated.

The hydrogenation of hex-1-ene in the presence of the ethene complex $[RhCl(C_2H_4)L]$ has been investigated in detail.[19] It was shown that its activity in hydrogenation and isomerisation is somewhat superior to that of the familiar Wilkinson catalyst $RhCl(PPh_3)_3$. This applies particularly to the isomerisation process. The above feature is due to the role played by the nitrogen centre in the catalytic cycle, since the monohydride complex formed with its participation is in fact the true catalyst of the isomerisation of the alkene.



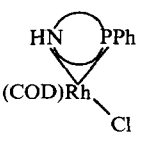
Overall, the study of the catalytic properties of the rhodium derivatives of BAP has been fragmentary and limited. Thus, in the light of the latest advances in asymmetric catalysis,[3] it is evident that the hydrogenation of the prochiral precursors of aminoacids is by no means the only field where rhodium complexes with P,N-bidentate optically active ligands can be used. Apparently, this catalyst may be expected to exhibit a much higher asymmetrising activity in, for example, hydroformylation and isomerisation processes. One thing is clear, the search for a due place for BAP in modern metal complex catalysis (especially enantioselective) has only just begun and requires further efforts.

The study of the interaction of compound **1a** (Phoran) with $[Rh(COD)Cl]_2$ (COD = cycloocta-1,5-diene)—a familiar precursor of active catalytic systems—is of special interest in this connection.[20] The reaction is monitored by IR, ^{31}P NMR, and UV spectroscopic methods.



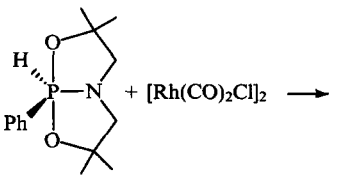
Complex **4**, formed initially with the phosphocane coordinated as a P-monodentate species, is subsequently transformed into the unusual ionic adduct **5** with a *cis*-disposition of the phosphorus atoms in the cation, which has been characterised by X-ray diffraction. The ν(NH) absorption band of a single crystal of complex **5** is in the region of 3190 cm^{-1}. Only one N–H···Cl hydrogen bond was detected under these conditions. It is of interest that a further two forms of compound **5**, characterised by ν(NH) frequencies of 3205 and 3215 cm^{-1}, have been isolated. According to the authors, the difference between the ν(NH) absorption frequencies is due to the different orientations of the cation and the anion in the crystals of these forms.

The indication of the P-monodentate binding of the phosphocane in complexes **4** and **6** is of fundamental importance. However, this important conclusion appears inadequately justified. Firstly, these compounds were not isolated from the reaction mixture. Secondly, the spectroscopic data presented are clearly insufficient for a rigorous demonstration of their structure. Thus the structure of compound **6** was postulated solely on the basis of UV spectroscopic data. For complex **4**, it is possible to put forward a structure in which the coordination number (CN) of rhodium is five with a consequent apical coordination of the amino-group. Such a structure does not conflict with the spectroscopic parameters of this complex: δ_P = 140.0 ppm, ^1J(P,Rh) = 210 Hz; ν(NH) = 3140 cm^{-1}, and λ_{max} = 404 nm. Indeed such a low ν(NH) frequency is more likely to indicate direct coordination of the nitrogen centre to rhodium than the presence of the N–H···Cl bond involving a noncoordinated amino-group.

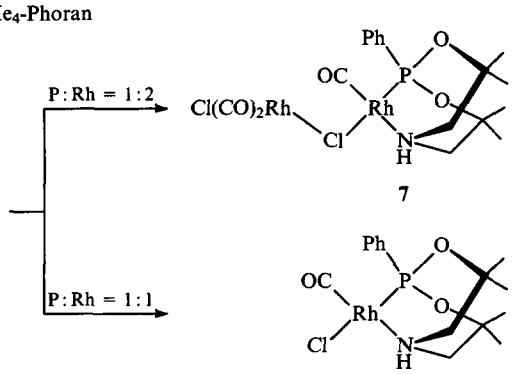


Considerable attention has been devoted to the detailed study of the reaction of BAP with another rhodium catalyst popular in metal complex synthesis and catalysis—$[Rh(CO)_2Cl]_2$. A series of chelate chlororhodium carbonyl complexes, obtained by the interaction of various BAP with this precursor, have already

been mentioned. An important discovery was made in the course of a detailed study of this process with participation of BAP such as Phoran[21] and especially Me_4-Phoran:[22] the stable dinuclear rhodium(I) complexes **7** with one chloride bridge were obtained unexpectedly.



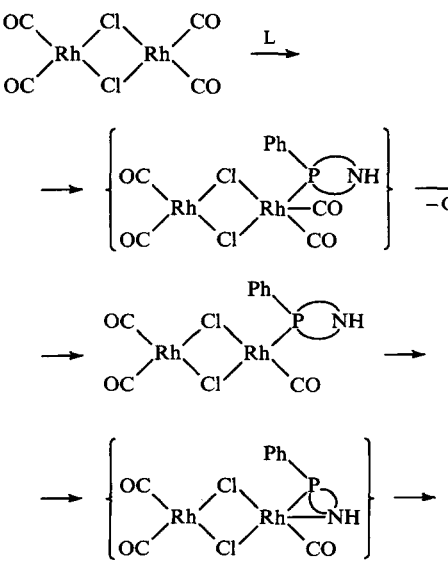
Me_4-Phoran

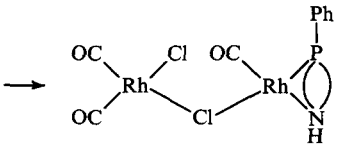


Compound **7** was characterised by ^1H and ^{31}P NMR and IR spectroscopic methods, by field desorption mass spectrometry, and by X-ray diffraction. The N–H···Cl intramolecular hydrogen bond between the nitrogen centre and the chloride ligand of the $[Cl(CO)_2Rh]$ fragment was detected. The distance between the phosphorus and nitrogen atoms (2.705 Å) is appreciably shorter than in complexes **2a,b**, which indicates a more pronounced attractive N···P interaction in the case of complex **7**. The further reaction between complex **7** and Me_4-Phoran leads to a mononuclear complex. It is of interest that the coordination of unsubstituted Phoran is not quite so selective, since for the molar ratio P : Rh = 1 : 2 a mixture of products is formed: compound **2a**, already known, and an analogue of compound **7**, namely $[Cl(CO)_2Rh(\mu\text{-}Cl)Rh(CO)(Phoran)]$. Attempts at a preparative separation of the latter product were unsuccessful.

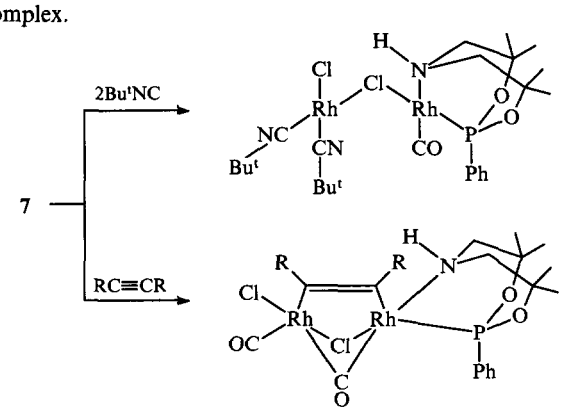
A general mechanism of the interaction of BAP (L) with $[Rh(CO)_2Cl]_2$ has been proposed.

The dirhodium complex with one chloride bridge is a stable intermediate in this process on the way to chelate mononuclear compounds.





Study of the reactivity of complex **7** revealed an appreciable stability of the chloride bridge:[23] reactive compounds such as O_2, CO, CO_2, CS_2, CH_3I, $CH_2{=}CH_2$, and HC≡CH do not interact with compound **7** even under conditions of thermal or photochemical activation. Only Bu^tNC or activated alkynes are capable of modifying the structure of this unusual dinuclear complex.



R = CO_2Me, CO_2Bu, CF_3

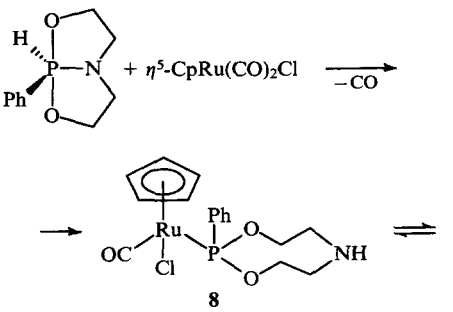
In considering the structures of new rhodium compounds ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy and, in the case of the *tert*-butyl isocyanide derivative, ^{15}N NMR spectroscopy were used. In the last case, direct binding of the nitrogen centre of the phosphocane to the metal was demonstrated by use of the naturally abundant ^{15}N isotope and the INEPT method [$\delta_N = -370.0$ ppm, $^1J(N,Rh) \approx {}^2J(N,P) \approx 11.8$ Hz]. This is an extremely rare and elegant experiment involving the application of ^{15}N NMR spectroscopy to determine the nature of the coordination of the P,N-containing ligand. We may note that the study of Brun et al.[23] is the latest of a series of studies carried out over a decade and devoted to the rhodium derivatives of BAP.

Summarising, we may note that chelate P,N-bidentate coordination of BAP in the phosphocane form is characteristic of rhodium. There exists indirect evidence for the possibility of their P-monodentate binding, but this type of coordination has been established reliably only in relation to complexes of other transition metals.

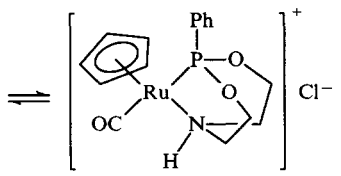
b. Ruthenium and palladium compounds

We are aware of only one study[24] devoted to the interaction of BAP (specifically Phoran) with the ruthenium complex $CpRu(CO)_2Cl$.

The ionic complex **9**, which according to ^1H and ^{31}P NMR spectroscopic data is in equilibrium with the neutral complex **8**, was isolated from the reaction mixture in an almost quantitative yield. The ion-exchange reaction between $NaBPh_4$ and compound

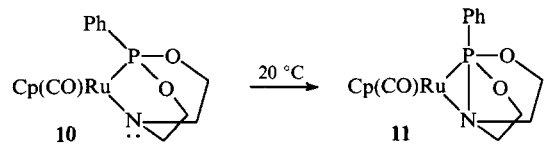


8



9

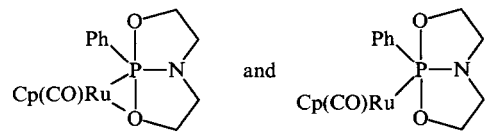
9 afforded an analogue of the latter complex, containing tetraphenylborate as the anion. Its deprotonation by treatment with MeLi at −100 °C leads to the amide adduct **10**, which is stable only at low temperatures, being transformed gradually at 20 °C into the phosphoranide complex **11**.



10 11

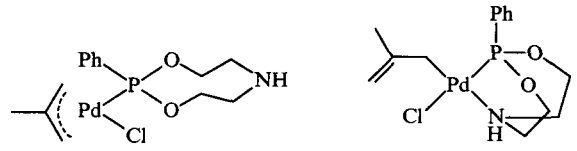
δ_P = 181.0 ppm δ_P = 69.0 ppm

The structures of complexes **8**–**11** have been established by means of ^1H and ^{31}P NMR and IR spectroscopy and, in the case of compounds **10** and **11**, by comparing their ^{31}P NMR spectroscopic parameters with those of the Mo- and W-containing analogues, which have been investigated in detail by X-ray diffraction. Later in this review we shall discuss further the characteristics of the phosphoranide type of binding of BAP to metals. For the moment, we may note that Vierling et al.[24] postulated the existence of equilibrium (even at −100 °C) between complex **11** and its isomers **11′** and **11″** with P,O-bidentate or P-monodentate phosphoranide coordination.

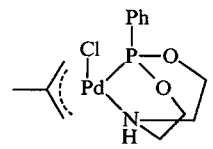


11′ and 11″

Like ruthenium and rhodium, palladium is capable of P-monodentate and P,N-bidentate binding of BAP in the phosphocane form. In particular, the reaction between $[CH_2CMeCH_2PdCl]_2$ and Phoran (P:Pd = 1:1) affords a complex mixture of isomers.[25]



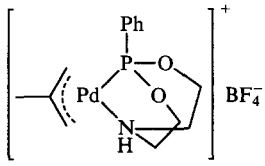
12 12′



12″

The IR spectrum of the reaction solution contains three absorption bands at 3400, 3280, and 3200 cm^{-1}, corresponding to the NH group, the highest frequency band referring to the noncoordinated amino-group of complex **12**. It has been suggested that complexes **12′** and **12″** are stabilised by the formation of intramolecular hydrogen bonds. There is apparently a dynamic equilibrium between the three isomers, as a consequence of which a poor resolution is observed in the ^{31}P NMR spectrum. On the whole, one may agree with Agbossou et al.[25] that a more correct description of the reaction under consideration requires additional studies.

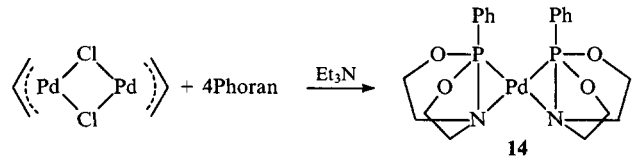
Apart from complexes **12**, **12′**, and **12″**, the chelate cationic complex **13** is also known.



13

According to conductimetric data, complex **13** is an electrolyte of a type intermediate between 1:1 and 1:2. This is apparently associated with the existence of equilibrium between complex **13** and the dimer $[CH_2CMeCH_2Pd(\mu\text{-}L)_2PdCH_2CMeCH_2](BF_4)_2$, in which the phosphocane ligands are of the bridging P,N-bidentate type. The high activity of complex **13** in the catalysis of the oligomerisation of butadiene is noteworthy (a mixture of C_8, C_{12}, and C_{16} products with 100% conversion was obtained).

It has been stated[26] that an unstable palladium phosphoranide derivative **14** is formed.[26]



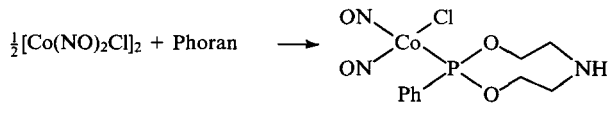
14

Since the structure of complex **14** was postulated solely on the basis of ^{31}P NMR spectroscopic data, further experimental data for its confirmation appear necessary.

Summarising, we may note that the ruthenium and especially the palladium derivatives of BAP are represented by few examples and have been investigated fairly superficially. This field of BAP coordination chemistry still awaits its investigators.

c. Cobalt and iron complexes

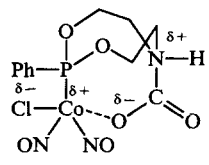
We are aware of only one complex formation reaction between BAP and a cobalt compound, namely $[Co(NO)_2Cl]_2$.[27,28]



15

According to X-ray diffraction data, although the distance between the P and N atoms in the phosphocane ring (2.978 Å) in complex **15** is greater than in the case of the chelate rhodium complexes **2a,b**, it is again appreciably less than the sum of the van der Waals radii. By virtue of the noncoordinated peripheral amino-group, compound **15** enters into an interesting reaction with carbon dioxide, leading to the formation of the carbamate-like adduct **16**.[28]

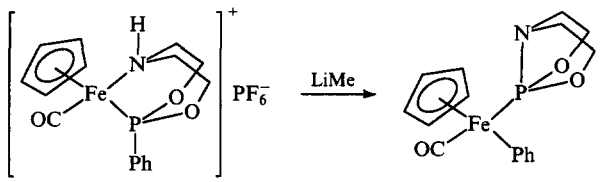
During storage under an argon atmosphere, complex **16** gradually loses the CO_2 group with regeneration of the initial



16

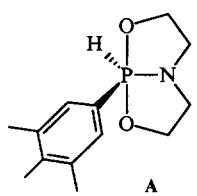
compound **15**. The reversible binding of CO_2 observed here models to some extent biosynthetic carboxylation processes with participation of biotin.

In contrast to the cobalt-containing complexes, the iron-containing BAP complexes have been investigated fairly widely. The first step in the study of their chemical properties already led to the discovery of the unique reversible migration of the phenyl group from phosphorus to the metal without change in the oxidation state and the coordination number of the latter.[29] The deprotonation of complex **17** [obtained from $CpFe(CO)_2Br$ and Phoran], carried out for the synthesis of a phosphoranide derivative, led to the formation of complex **18** with a bicyclophosphoramidite ligand.



17 **18**

The structure of complex **18** has been demonstrated by X-ray diffraction. The deprotonation process is reversible: the passage of gaseous HCl through a solution of complex **18** in tetrahydrofuran (THF) in the presence of NH_4PF_6 regenerates complex **17** with a 60% yield. It has been suggested that the transannular N → P interaction in the structure of complex **17** facilitates the 1,2-shift of the phenyl group attached to the P–Fe bond. Subsequently a similar reversible migration was observed [24] also for a homologue of Phoran (compound **A**),where precisely the carbon atom which had been previously linked to phosphorus was found to be bound to iron, which agrees well with the concept of a 1,2-sigmatropic shift of the aryl group.



A

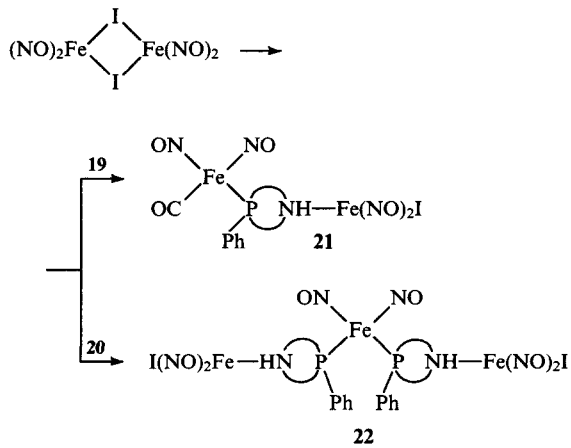
As a result of the successful choice of the initial iron compounds, it proved possible to obtain, via a two-stage synthesis, systems with bridging P,N-bidentate binding of the phosphocane ring.[30,31] We may note that this type of unusual coordination of BAP was observed for the first time. Complexes with the P-monodentate coordination of the ligand were obtained initially.

$Fe(CO)_2(NO)_2$ + Phoran →

P:Fe = 1:1 → $Fe(CO)(NO)_2[PhP(OCH_2CH_2)_2NH]$ **19**

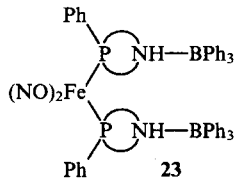
P:Fe = 2:1 → $Fe(NO)_2[PhP(OCH_2CH_2)_2NH]_2$ **20**

A weak broad ν(NH) absorption band at 3400 cm^{-1}, characteristic of a noncoordinated secondary amino-group, was observed in the IR spectrum of compound **19**. Two weak, narrow, ν(NH) bands at 3400 and 3300 cm^{-1} were recorded for complex **20**, the presence of the latter band being tentatively attributed to the existence of intermolecular hydrogen bonds. Subsequently the dinuclear and trinuclear iron complexes **21** and **22** were obtained from complexes **19** and **20**.



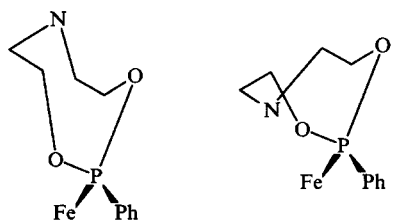
Unfortunately compounds **21** and **22** have been studied inadequately. Thus only fragment peaks were detected in their mass spectra, although an extremely mild method (chemical ionisation) was used. Nothing is said in the communication of Mordenti et al.[31] about attempts to determine the molecular structures of compounds **21** and **22** by independent methods.

The peripheral amino-groups in complex **20** are capable of coordinating various Lewis acids, for example the proton (in the HCl–$NaBPh_4$–EtOH system) or BPh_3.[32] In the latter case, an interesting three-centre adduct of the P–Fe–P type (compound **23**) was obtained from BAP.



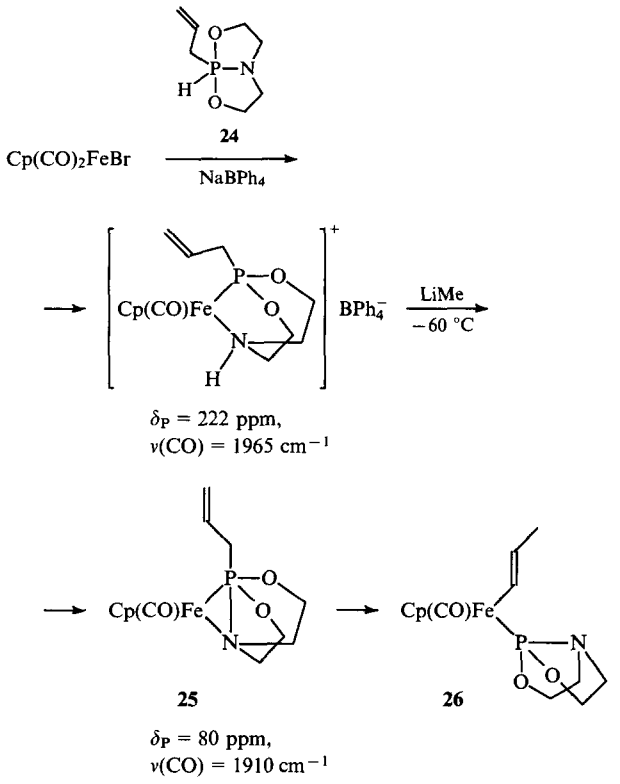
23

The structures of compounds **20** and **23** were established by X-ray diffraction. A tetrahedral coordination of the iron atom was observed in both cases. The distances between the phosphorus and nitrogen atoms in the phosphorus-containing rings are 3.647 and 3.616 Å for compound **20** and 3.590 Å for compound **23**, which appreciably exceeds the sum of the van der Waals radii. The conformations of the phosphocane rings in compounds **20** and **23** can be described as 'chair-boat'.



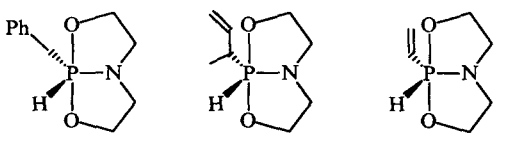
The O···H–N hydrogen bond involving the amino-group of one molecule and the nitrosyl oxygen atom of another was detected in complex **20**. It had been postulated previously on the basis of IR spectroscopic data. A weak N–H···N contact was also found. These hydrogen bonds apparently actually stabilise the novel ligand conformations.

Iron phosphoranide complexes are also known. In particular, such an adduct has been detected by ^{31}P NMR spectroscopy as an intermediate in the unprecedented process involving the reorganisation and migration of the allyl group from phosphorus to iron.[34,35]

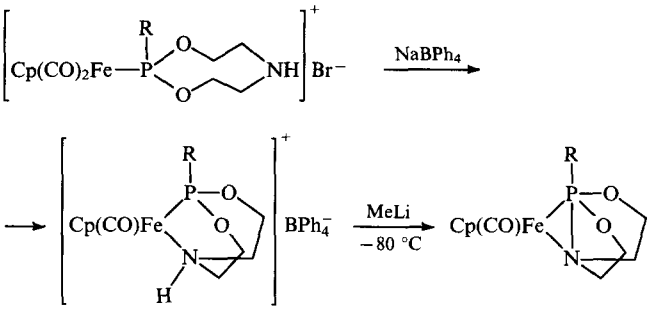


The coordination of the allyl-substituted BAP (compound **24**) leads not to a σ-allyliron complex, which might be formed as a result of the direct migration of the allyl group from phosphorus to iron, but to the σ-vinyliron compound **26** as a result of the isomerisation of this substituent accompanying the transfer process. The phosphoranide adduct **25** is stable in solution only at temperatures below 0 °C. At 60 °C, it is fully converted into compound **26** in 1 h. The structure of complex **26** was established by ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopy. Whereas the migration of the phenyl group is known to be a reversible process, the reverse transfer of the vinyl group from iron to phosphorus is not observed even when complex **26** is treated with hydrogen chloride. It has been suggested that the phosphoranide coordination of compound **25** increases the electron density on the metal and hence its basicity, activating the insertion of iron into an allyl or vinyl C–H bond with the subsequent 1,3-shift of a proton and dissociation of the P–C bond. In fact the decrease in the ν(CO) frequency by 55 cm^{-1} on passing from the cationic complex to the phosphoranide adduct **25** agrees well with an increase in electron density on the iron atom in the adduct. Thus the migration of the allyl group differs radically both from the transfer of the phenyl group (accompanied by dissociation of the P–C bond alone) and from the known *ortho*-metallation reactions (involving only the insertion of the metal in a C–H bond).

Apart from the allylphosphorane **24**, several further related BAP were used to investigate the fine details of the migration of organic groups from phosphorus to iron.[35]



The interaction of these compounds with $Cp(CO)_2FeBr$ leads in the first stage to ionic complexes and then to phosphoranide complexes.



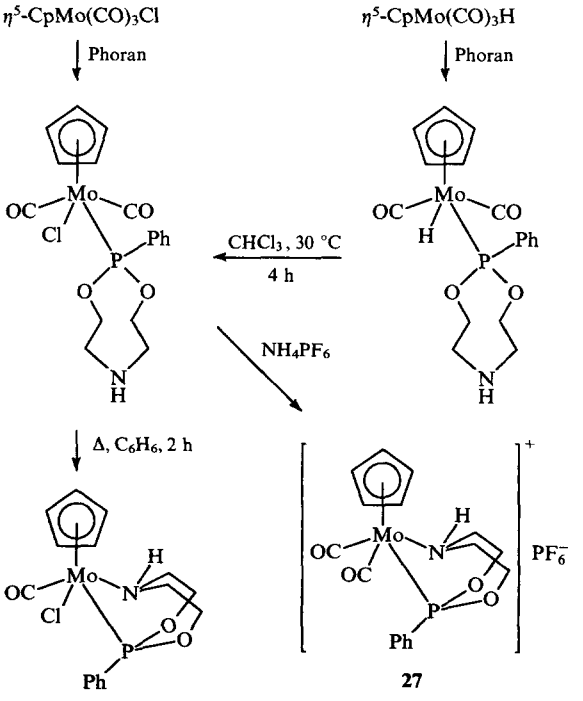
The phosphoranide complexes exist in solution only at temperatures below 0 °C. It is of interest that the iron-containing analogue of the ruthenium amide intermediate **10** has not been detected spectroscopically even at −100 °C, apparently as a consequence of its short lifetime. Since the structures of the phosphoranide complexes have been discussed only on the basis of ^{31}P NMR and IR spectroscopic data, one cannot rule out the possibility of the existence in solution of their isomers with P-monodentate and P,O-bidentate coordination, analogous to the ruthenium derivatives **11** and **11′**.

An attempt to isolate the iron phosphoranide compounds led to their further reactions. The complex with a methylallyl group rearranges smoothly after refluxing in THF for 1 h into the σ-vinyliron compound (like compound **25**), while the remaining compounds form complex mixtures of products under these conditions.

Thus the study of the iron complexes has been an important stage in the development of the coordination chemistry of BAP: the P-monodentate and P,N-bidentate bridging types of binding of the phosphocane forms have been clearly demonstrated and a series of phosphoranide adducts have been characterised spectroscopically.

d. Molybdenum and tungsten compounds

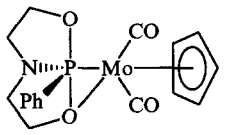
Virtually all the data obtained on the formation of complexes by BAP with molybdenum and tungsten compounds refer to molybdenum complexes. There are very few tungsten adducts of BAP. In particular, the interaction of compound **3c** with $M(CO)_6$ (M = Mo, W) at 120–150 °C for 24 h leads to the products $M(CO)_5L$ with P-monodentate coordination of the phosphocane.[16] The use in this process of the sterically less



hindered ligand Phoran made it possible to obtain the disubstituted compounds $M(CO)_4L_2$, but complexes of the type $M(CO)_4L$ in which the phosphocane is bound as a P,N-bidentate species have not been obtained.

Both P-monodentate and P,N-bidentate coordination has been achieved by employing more reactive molybdenum compounds initially.[36] All these complexes were investigated by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy, mass spectrometry, and by vapour phase osmometry.

The deprotonation of compound **27** by treatment with LiMe (ether/THF, 60 °C) leads to a molybdenum compound with P,O-bidentate phosphoranide coordination of the ligand.[37]



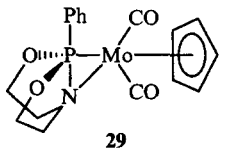
δ_P = 23.8 ppm,
ν(CO) = 1925 and 1835 cm^{-1}

28

This is the first example not only of the phosphoranide type coordination of BAP but also of the synthesis of a metallated phosphorane.[10]

It has been shown by X-ray diffraction that the P–O bond involved in the formation of a three-membered metallocycle is significantly lengthened compared with the second P–O bond (1.893 and 1.653 Å). We may note that the usual BAP geometry is retained in complex **28**: the oxygen atoms being axial and the nitrogen atoms and the phenyl group equatorial.

The first transition metal complex containing the N–P–M cyclic fragment was synthesised by the deprotonation of compound **27** with methyllithium under mild conditions (THF, −20 °C).[38]

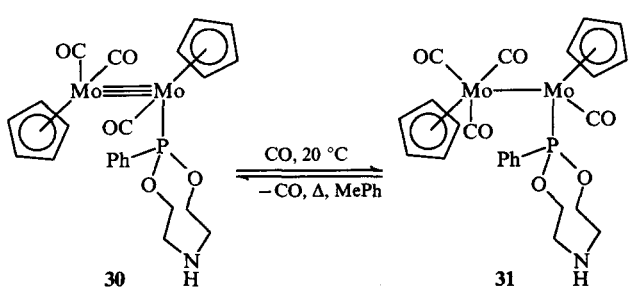


δ_P = 43.9 ppm,
ν(CO) = 1945 and 1855 cm^{-1}

29

According to X-ray diffraction data, the P–N bond in complex **29** is one of the longest (1.91 Å) of this type. The equatorial orientation of the oxygen atoms, unusual for trigonal-bipyramidal phosphorus, and the axial orientation of the phenyl group are also noteworthy. It is of interest that complex **29** isomerises readily to complex **28** (on heating in solution in THF to 60 °C). When hydrogen chloride was passed through a THF solution of complex **29**, an analogue of complex **27** was obtained in a quantitative yield (the counterion is the chloride anion). The tungsten analogue of compound **29** has also been obtained.

The dimeric molybdenum complex $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ has also been resorted to in order to investigate the coordination of BAP. In this case, the lack of information about its interaction with potentially chelating ligands and also the presence of the highly reactive Mo≡Mo bond are of interest. It has been found that the reaction of this complex with Phoran leads to two main products — **30** and **31**.[39,40]



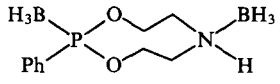
30 **31**

Both substances were characterised by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy and by field desorption mass spectrometry, while complex **30** was characterised in addition by X-ray diffraction. Compound **30** was the first example of the direct substitution of a CO ligand in $Cp_2Mo_2(CO)_4$ with retention of the Mo≡Mo bond and at the same time it was the first BAP complex where the P-monodentate coordination of the phosphocane form was confirmed by X-ray diffraction.

A methylated analogue of compound **30** — the complex $(C_5Me_5)Mo_2(CO)_3L$ — has been synthesised and investigated[41] by X-ray diffraction. Its synthesis requires more severe conditions and the yield is much lower than that of compound **30**. This is associated with the large steric factor for the η^5-C_5Me_5 ligand compared with η^5-C_5H_5. The special importance of molybdenum in the coordination chemistry of BAP is noteworthy because unique phosphoranide complexes with three-membered metallocycles have in fact been obtained precisely with this metal and characterised by X-ray diffraction.

e. The adducts of BAP with BH_3

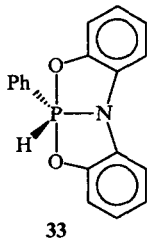
Apart from the formation of complexes between BAP and transition metal compounds, the interaction of the former with certain borane complexes has bean investigated. Thus the reaction of Phoran with $BH_3 \cdot SMe_2$ affords compound **32** as the main product (for the molar ratio B : P = 2 : 1).[42]



32

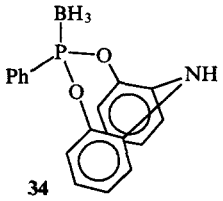
The adduct **32** was characterised reliably by spectroscopic methods: ^1H, ^{11}B, and ^{31}P NMR and IR spectroscopic, as well as mass-spectrometric data have been published. The stereospecificity of the above reaction has been demonstrated because compound **32** is characterised by a *cis*-disposition of the BH_3 fragments relative to the phosphocane ring.

Special mention should be made of an unusual BAP, the bicyclic skeleton of which contains condensed benzene rings.[43]



33

In contrast to Phoran, compound **33** exhibits a high chemical stability: it does not hydrolyse, it does not undergo deuterium exchange with D_2O in the presence of either triethylamine or toluene-*p*-sulfonic acid, and it does not react with the NaH/MeI system. The phosphorane **33** hardly interacts with $BH_3 \cdot SMe_2$. Its reaction with $BH_3 \cdot THF$ takes place in the course of a week and leads to a complex mixture of products, among which compound **34** was identified by the ^{31}P and ^{11}B NMR methods.



34

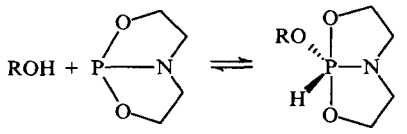
The attempt to isolate compound **34** was unsuccessful: the initial BAP was isolated in ~90% yield. Such a low reactivity of compound **33** can be accounted for by the marked delocalisation

of the lone pair of nitrogen through interaction with phosphorus and the benzene rings (all four rings are coplanar). This stabilises additionally the phosphorane structure in relation to the possible phosphocane tautomer and is also responsible for the absence of donor centres. Unfortunately we do not possess literature data on the formation of complexes between compound **33** and transition metals. In our view, it would be interesting in this instance to compare the reactivities of compound **33** and other BAP, in the first place Phoran, which would assist in a better understanding of the mechanism of the coordination of hydrophosphorane compounds.

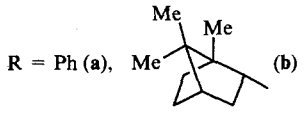
f. The formation of BAP complexes *in situ*

There exists a nonstandard approach to the synthesis of BAP involving the interaction, under mild conditions, of the corresponding proton-donor reagent (ROH, ArOH, R_2NH) with bicyclo[3.3.0]-1-phospha-2,8-dioxa-5-azaoctane in an organic solvent.[44,45] The BAP is then characterised in situ without isolation from the solution.

It is surprising that this very convenient method of synthesis of a wide variety of BAP as potential ligands has been introduced only quite recently into practice in coordination synthesis. Compounds **35a,b** have been synthesised by this method in CH_2Cl_2.[46]

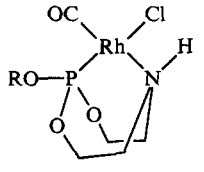


35a,b



R = Ph (**a**), (**b**)

The addition of solutions containing compounds **35a,b** to $[Rh(CO)_2Cl]_2$ (P/Rh = 1) led to the formation of the chelate mononuclear rhodium complexes **36a,b**.

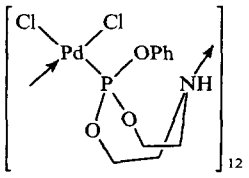


36a,b

Parameter	Compound	
	36a	**36b**
ν(NH)/cm^{-1}	3230	3148
ν(CO)/cm^{-1}	2012	1996
ν(RhCl)/cm^{-1}	294	300
δ_P/ppm	128.3	133.5
^1J(P,Rh)/Hz	291	262

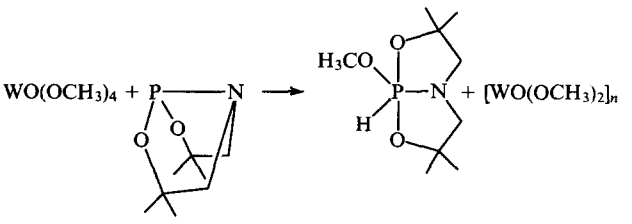
Compounds **36a,b** are insoluble in organic solvents, except DMSO, but at 80 °C they undergo vigorous solvation followed by degradation. For this reason, the final confirmation of the structure of compounds **36a,b** was achieved by ^{13}C solid-state NMR spectroscopic and ESCA methods.

The complex formation reaction between compound **35a** and $Pd(COD)Cl_2$ resulted in the formation of a polynuclear palladium complex with a bridging phosphocane ligand.[47]



The complex was characterised in detail by IR and ^{31}P and ^{13}C NMR spectroscopy, ESCA, and ultracentrifugation; its nonstereoregular structure was established.

We may note an important feature—in contrast to other BAP, the coordination of compounds **35a,b** leads to complexes with a phosphite, and not phosphonite, phosphorus centre.



It is of interest that a reaction formally the reverse of the processes mentioned above had been achieved earlier.[48]

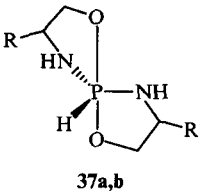
The formation of the free phosphorane is treated as a result of the intracomplex oxidative addition of methanol to the N-coordinated phosphoramidite catalysed by the traces of H^+ present in the reaction medium.

It follows from the foregoing that the BAP function either as precursors of the phosphocanes (chelating or bridging) bound via P-monodentate or P,N-bidentate linkages or as P,N- or P,O-bidentate phosphoranide ligands. In the coordination of BAP in the phosphocane form, the differentiation of P-monodentate and P,N-bidentate binding is made feasible by a reliable criterion—the absorption frequency of the NH group in the IR spectra of these complexes. Thus a wide range of vibrational frequencies (3050–3320 cm^{-1}) is characteristic of the coordinated amino-group, but the unusually high values of ν(NH) = 3280–3320 cm^{-1} are observed only in the spectra of the cationic compounds and are associated with the presence of a positive charge on the metal atom, while the anomalously low frequencies 3050–3080 cm^{-1} are known only for $[RhL_2]^+Cl^-$, which contains strong hydrogen bonds with the counterion. On the other hand, the typical values of ν(NH) are in the range 3140–3260 cm^{-1}. The free peripheral amino-group is characterised by the frequency range 3340–3400 cm^{-1}. Occasionally a decrease to 3300 cm^{-1} is observed owing to the participation of this group in hydrogen bonds.

2. Processes with participation of hydrospirophosphoranes

a. Rhodium complexes of hydrospirophosphoranes

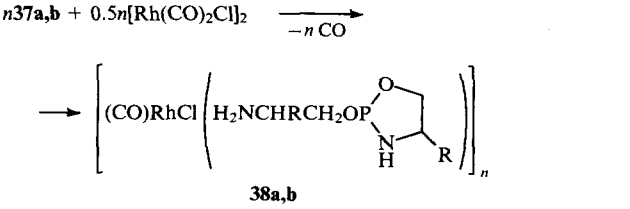
Hydrospirophosphoranes (HSP) constitute the most thoroughly investigated group of hydrophosphoranes,[49] but their coordination chemistry began to develop comparatively recently.[50,51]



37a,b

R = H (**a**), Et (**b**)

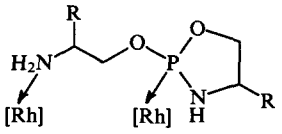
As in the case of BAP, the first transition metal complexes with HSP ligands were those of rhodium.



38a,b

n = 4 (**a**), 6 (**b**)

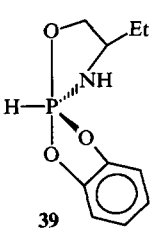
It has been established that processes involving HSP are much slower than those involving organic phosphorus(III) ligands. Thus, in complex formation with the oxazahydrospirophosphorane **37a**, the residual signal of this ligand persists in the ^{31}P NMR spectrum of the reaction solution for 30 min even at 20 °C, whereas in complex formation with the aminophosphite under the same conditions the free ligand signal is recorded only at −70 °C.[52] It follows from the ^{31}P and ^{15}N NMR data (compound **37a** with 96.4% enrichment in the ^{15}N isotope) and IR spectroscopy that the key factor in the coordination of HSP is the opening of the oxazaphospholane ring with liberation of the peripheral amino-group bound to the metal.



The polynuclear nature of these complexes, where the phosphorus-containing ligand functions as a bridging P,N-bidentate species, has been established by sedimentation analysis of solutions of compounds **38a,b** in DMSO. The elementary units of compounds **38a,b** have *trans*-orientation of the phosphorus and nitrogen centres in the coordination sphere of rhodium. This is yet another distinctive feature of the complexes based on HSP: the chlororhodium carbonyl complexes of aminophosphites and aminophosphoramidites are as a rule mononuclear with a *cis*-disposition of the phosphorus and nitrogen atoms.[52–54]

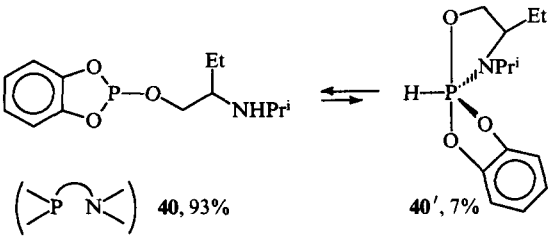
Despite thorough investigation of complexes **38a,b**, the driving force of the formation of the polynuclear structures remained unelucidated. It is also not known whether these compounds are linear or cyclic oligomers. At the present time, we are inclined to regard them as cyclooligomers, since signals due to the noncoordinated phosphorus or nitrogen centres have not been detected in the ^{31}P and ^{15}N NMR spectra.

The use of the chiral HSP **37b** and **39** in the asymmetric hydrosilylation of acetophenone by diphenylsilane [both ligands were obtained from (*R*)-2-aminobutanol] has been reported.[55]

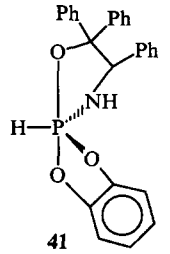


39

The $2L/[Rh(CO)_2Cl]_2$ (L = compound **39**) catalytic system ensures an optical yield of the reaction product of 9%. Unfortunately, the use of chiral HSP in asymmetric catalysis has not received due development and only the studies concerned with the synthesis and coordination of optically active HSP with a catechol fragment have been continued.[56] This concerns the synthesis of the aminophosphite **40**, which is in equilibrium with its P(V) tautomer **40'** (this is typical for aminophosphites and aminophosphoramites with a secondary peripheral amino-group), and also of the hydrophosphorane **41**.

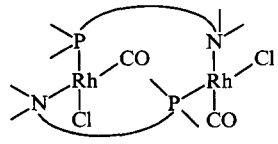


40, 93% **40'**, 7%

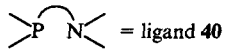


41

The complex formation reaction between compound **40** and $[Rh(CO)_2Cl]_2$ (P : Rh = 1 : 1) leads to the formation of the dinuclear rhodium compound **42**.

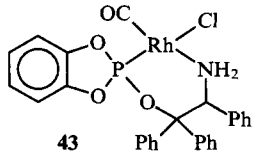


42



= ligand **40**

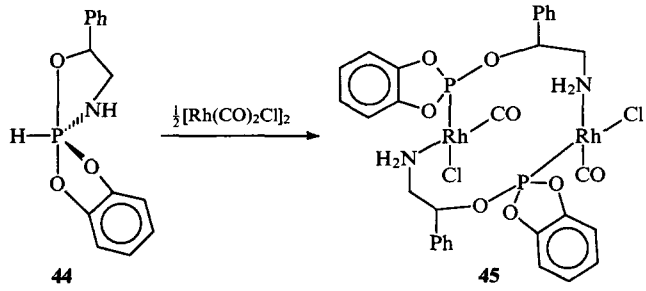
It was shown that the structure of compound **42** contains the N–H···Cl intramolecular hydrogen bonds. Under the same conditions, the ligand **41** forms the mononuclear chelate complex **43**.



43

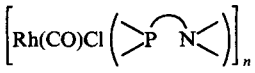
It exists in the form of two conformers: pseudotetrahedral and pseudosquare, which follows from ^{13}C NMR and IR spectroscopic data. The tendency of compound **43** to isomerise to the form with a *cis*-disposition of the carbonyl and amino-groups in the coordination sphere of the rhodium has been discovered.

In contrast to compound **41**, the sterically less hindered HSP **44** forms a dinuclear, and no longer a mononuclear, rhodium complex.[57]



44 **45**

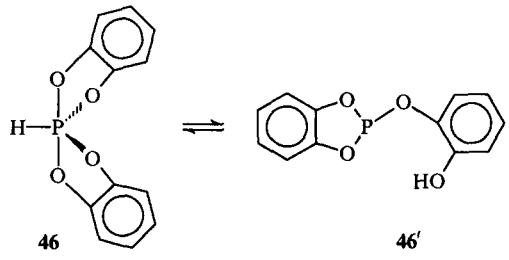
We may note that compound **45** is perhaps the most thoroughly investigated complex based on HSP: ^{31}P NMR (including the low-temperature version), ^{1}H NMR, ^{13}C NMR (including the version in the solid state), ^{14}N NMR, and ^{103}Rh NMR spectroscopy, IR spectroscopy, ESCA, and desorption mass spectrometry were resorted to in the consideration of its structure. The dissolution of compound **45** in acetone is accompanied by its reorganisation; fragments with a *cis*-orientation of the carbonyl and amino-groups at the rhodium atom appear in solution and ultimately a polynuclear compound with $n = 12$



(according to ultracentrifugation data) is formed.

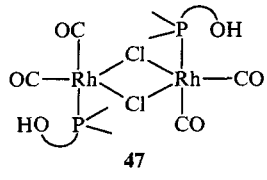
In all probability, for the rhodium derivatives of HSP with a catechol fragment there is a definite relation between the steric factor associated with the ligand and the nature of the coordination compound: less sterically hindered ligands give rise to metal complexes with a larger number of rhodium centres.

The study[58] of the interaction of 2,2′-spirobis(1,3,2-benzodioxaphosphole) **46** with $[Rh(CO)_2Cl]_2$ is of special interest because this is the only example of complex formation involving tetraoxohydrospirophosphoranes. The HSP **46** is known[49] to be in equilibrium with its tricoordinate tautomer **46′**.

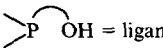


46 **46′**

The rhodium complex formed with the ligand **46′** in CH_2Cl_2 is a dimer with a rhodium coordination number of five (the rhodium coordination polyhedron is a trigonal bipyramid with an apical phosphorus atom).

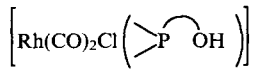


47


= ligand **46′**

The peripheral OH group is not then bound to the metal.

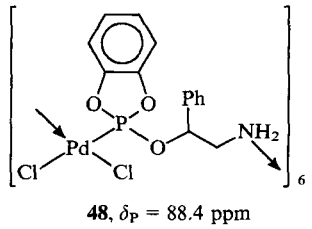
In the crystalline complex **47**, the phosphorus-containing ligands function as P-monodentate and P,O-bidentate species, the phosphorus centre now occupying an equatorial position. It has been suggested that the fragments



can combine into a polynuclear aggregate as a result of the bridging function of both the chloride ligands and the ligands coordinated as P,O-bidentate species.

b. Palladium and platinum derivatives of hydrospirophosphoranes

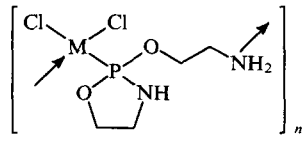
At the present time, we know of only three metal complexes of hydrospirophosphoranes. In particular, the reaction between $Pd(COD)Cl_2$ and the HSP **44** gave compound **48**, which was initially described as mononuclear.[59] However, measurement of the molecular mass of this complex by ultracentrifugation revealed its hexanuclear nature.[60]



48, δ_P = 88.4 ppm

The terminal positions of the chloride ligands in the structure of compound **48** have been reliably established by three independent physical methods — ESCA, IR, and X-ray emission spectroscopy. Hence it follows that the bridging ligands in the polynuclear complex **48** are in fact the phosphorus — containing ligands.

The polynuclear metal complexes **49** and **50** have been synthesised by the reaction of the HSP **37a** with $M(COD)Cl_2$ (M = Pd, Pt).[47,61]



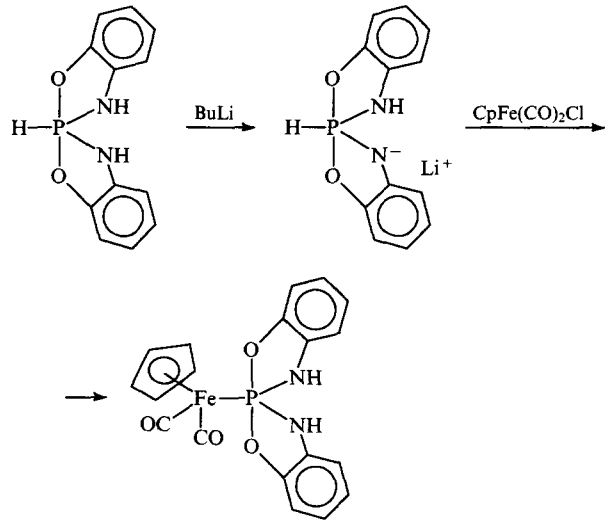
49: M = Pd, n = 4

50: M = Pt, n = 6

49, 50

Their structures were established from ^{31}P, ^{13}C, and IR spectroscopic, ESCA, and flame-desorption mass-spectrometric data and by sedimentation analysis.

Instead of the initial hydrospirophosphorane, its amide derivative has been used[62] in the complex formation reaction, which led unexpectedly to the formation of a phosphoranide adduct.

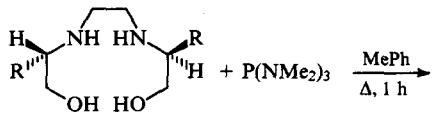


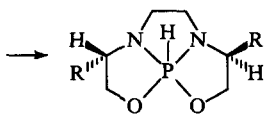
The information accumulated hitherto on the coordination behaviour of HSP permits the following conclusions: (1) these ligands do not tend to undergo coordination of the phosphoranide type and hence the spectroscopic parameters of their metal complexes are close to those for compounds based on organophosphorus(III) P,N-bidentate ligands — aminophosphites and aminophosphoramidites; (2) the majority of HSP complexes are polynuclear, but the available data on the molecular masses of the metal derivatives of HSP have been obtained mainly in the study of their solutions, so that direct structural investigations of solid-state specimens of these substances are needed.

III. The formation of complexes by tricyclic hydrophosphoranes

There are as yet few publications on this topic, but we are devoting to it a separate section of the present review because it is one of the most rapidly developing fields of modern coordination chemistry of hydrophosphorane compounds.

In 1990 Vannoorenberghe and Buono[63] reported the synthesis of the first representatives of a new group of hydrophosphoranes — tricyclic hydrophosphoranes which they called 'triquinphosphoranes'.

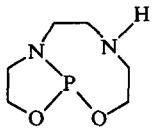




51a–d

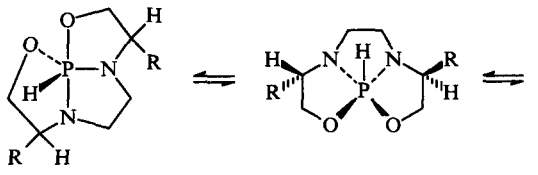
R = H (**a**), Me (**b**), Pr^i (**c**), CH_2Ph (**d**)

The ^{31}P NMR spectrum of a solution of compound **51a** in deuteriated DMSO in the temperature range 20 to 80 °C did not reveal the presence of the potential P(III)-tautomer **51'a**.

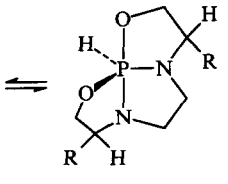


51'a

It was shown that rapid pseudorotation is characteristic of the 'triquinphosphoranes', the difference between the conformational energies of the trigonal bipyramid (TBP) and the square pyramid (SP) being small — 2.0 ± 1.5 kcal mol^{-1}.

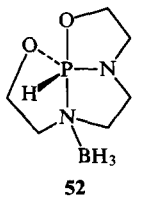


TBP1 **SP**



TBP2

It is extremely significant that one nitrogen atom in the TBP is in the unusual apical position, so that it is displaced from the $p\pi-d\pi$ conjugation with the phosphorus atom and is an independent donor centre. Indeed, the interaction of compound **51a** with $BH_3 \cdot SMe_2$ in the molar proportions P : B = 1 : 1 leads to the formation of the stable crystalline adduct **52** in 90% yield.

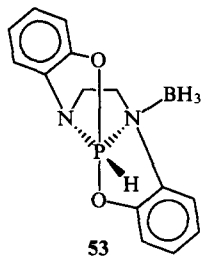


52

δ_P = 24.5 ppm, ^1J(P,H) = 820 Hz;
δ_B = 15.6 ppm, ^1J(B,H) = 93 Hz

We may recall that the P,N-bidentate phosphoranide coordination of the BAP is also characterised by an apical nitrogen atom.

The synthesis of tricyclic hydrophosphoranes from ephedrine and compounds with condensed benzene rings has also been reported.[64] The latter hydrophosphorane is known in the form of a stable monoborane complex, for which the structure **53** has been proposed.

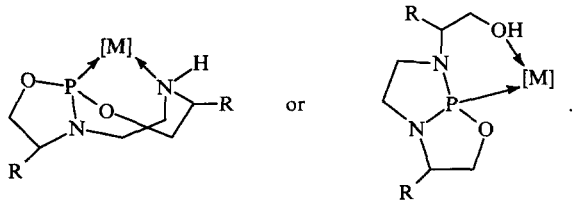


53

However, this structure is surprising, since no hydrophosphoranes in which an equatorial nitrogen atom functions as a donor centre are known. Since the above communication[64] contains no rigorous evidence for the structure **53**, one may suppose that the compound is more likely to have a structure similar to that of the boron-containing adduct, mentioned above, with an axial orientation of the P—N—B fragment.†

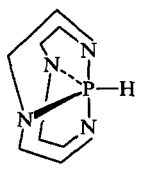
Subsequently the synthesis of yet another chiral 'triquinphosphorane' **51e** (R = Et) was described.[65] Despite the use of the less reactive phosphorylating agent $P(NEt_2)_3$ and the fact that the reaction was carried out without a solvent, the yield of compound **51e** proved to be not less than that of compounds **51a–d**. The first transition metal complex with a tricyclic phosphorane was obtained from compound **51e**. The reaction of compound **51e** with $Pd(COD)Cl_2$ (P : Pd = 1 : 1) proceeds under mild conditions. According to ^{31}P NMR data, phosphoranide coordination of the ligand takes place in this complex.

There is no doubt that there are satisfactory prospects for the coordination chemistry of 'triquinphosphoranes'. One can postulate that, by varying the metallic matrix and (or) the reaction conditions, it is possible to control the complex formation process involving tricyclic hydrophosphanes and achieve not only phosphoranide coordination but also other types, for example,



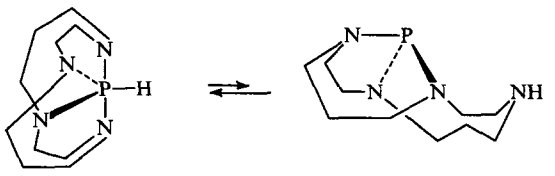
IV. The formation of complexes by tetracyclic hydrophosphoranes

The synthesis of a series of polycyclic and tetraamino-substituted phosphorus compounds, two of which (cyclenPH and cyclamPH) have found applications in coordination chemistry, was reported in 1978.[66,67]



54 (cyclenPH)

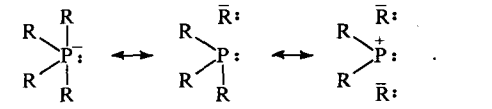
† The P—N—B fragment in compound **53** does indeed occupy an axial position, which has been demonstrated by X-ray diffraction (personal communication by Dr Contreras).



55a, (cyclamPH), 82%

55b, 18%

Several years later, the structure of the hydrophosphorane cyclenPH was refined with the aid of X-ray and electron diffraction.[68] This compound has the structure of a distorted trigonal bipyramid with a large equatorial N–P–N angle (137.9° according to X-ray diffraction data) as a consequence of the small steric effect of the hydrogen atom. The anion of **54** with Li^+ as the counterion was described in the same study, while the polymeric complex $[Li(THF)cyclenP]_n$ was investigated by X-ray diffraction. The structure of this unusual compound merits a detailed discussion because the coordination of compound **54** to transition metals is achieved as a rule in the phosphoranide form. Furthermore cyclenPH is the first hydrophosphorane for which a direct structural comparison with the phosphoranide anion has been carried out. We may note that the linking units between the fragments in the polymer $[Li(THF)cyclenP]_n$ are lithium cations. Despite the presence of a formal negative charge on the phosphorus atom, lithium is bound directly to the axial nitrogen atoms of two neighbouring fragments in this instance. This indicates the greater nucleophilicity of the axial nitrogen atoms compared with phosphorus. Furthermore, the axial bonds are lengthened by 0.21 Å compared with the initial cyclenPH and exceed by 0.1 Å the sum of the covalent radii. Overall, the phosphoranide ion may be described as resonance hybrid of three canonical forms:



Phosphoranide Phosphine Phosphenium ion

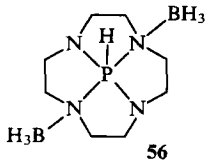
The contribution of each of these forms is determined by the specific ligand environment at the phosphorus atom.

Although the study of the complex formation reactions of tetracyclic tetraazahydrophosphoranes (TTP) was initiated somewhat later than that of the BAP, at the present time two representatives of this group of ligands (compounds **54** and **55**) proved to be the most thoroughly investigated among hydrophosphorane ligands. The complexes of the ligands **54** and **55** will be considered simultaneously. The order in which they are described is based on the structure of the product of the coordination of the phosphorane and the type of complex-forming atom. Reactions involving the simultaneous occurrence of processes in which the hydrophosphorane structure is preserved and transformed will be discussed in one section.

1. Coordination with retention of the hydrophosphorane structure

a. Boron complexes

The pioneering communication concerning the coordination possibilities of the hydrophosphorane **54** appeared in 1983. It was found that the hydrophosphorane **54** readily reacts with diborane to form complex **56** in an almost quantitative yield.[69]



56

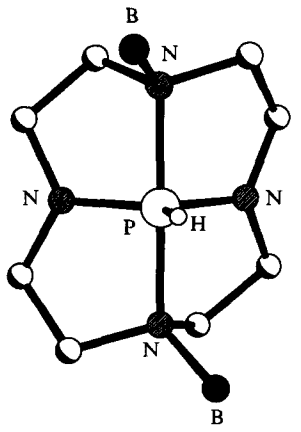
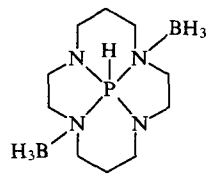


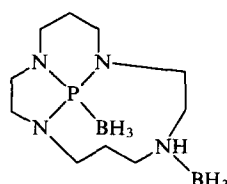
Figure 2. The structure of compound **56**.

Compound **56** has a high decomposition temperature and a high stability in air, which distinguishes it favourably from the few other borane adducts constructed from the usually unstable strained phosphorus-containing structures. The monoborane complex has not even been detected: when 0.5 mol of B_2H_6 is added, the same compound (compound **56**) is formed, whilst half of the initial compound **54** remains unreacted. The difference in the behaviour of the phosphoranes cyclenPH and Phoran in relation to BH_3 is determined both by the strong macrocyclic effect, which in the case of compound **54** favours the formation of the 'closed' form, and by the presence in compound **54** of the more basic axial nitrogen atoms.

The interaction of cyclamPH with B_2H_6 was described in the same study. It proceeds less unambiguously and leads to a mixture of products, from which only two were isolated and identified: compounds **57** and **58** (in 40% and 15% yields respectively).



57



58

Both compounds can be stored in the solid state for several months without appreciable changes, but, when compound **57** is allowed to stand at room temperature in a sealed tube in solution in CD_2Cl_2, it is fully converted into compound **58** in several weeks.

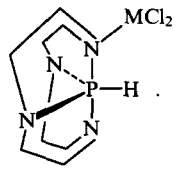
The structures of complexes **56** and **58** have been demonstrated by X-ray diffraction.[70,71] The molecule of compound **56** (Fig. 2) can be regarded as a trigonal bipyramid with a slight deviation towards a square pyramid. Lengthening of the apical P–N bonds and the shortening of the equatorial P–H and P–N bonds compared with the initial cyclenPH is observed. Although both BH_3 groups are coordinated to the apical nitrogen atoms, the B–N bonds are not located in a single plane owing to the slight helical distortion of the molecule. It was established that compound **58** exists in the form of only one of the two possible diastereoisomers, in which the P–B and N–B bonds are in the *trans*-positions relative to one another.

b. Transition metal complexes

Before beginning the consideration of transition metal complexes of cyclenPH, we may note that one or both apical nitrogen centres in the molecule of compound **54** can be easily protonated by strong acids (for example, CF_3CO_2H or HBF_4).

On the other hand, the quaternisation reaction leads only to the monoalkylated product even on treatment with an excess of MeI.[72]

In order to synthesise N-linked metallo-derivatives of cyclenPH, a study has been made [73] of its interaction with $ZnCl_2$ and $CdCl_2$. On the basis of spectroscopic data, similar to those obtained for the monoprotonated and monoalkylated adducts, the following structure was attributed to the zinc (compound **59**) and cadmium (compound **60**) complexes of cyclenPH:

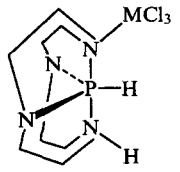


59: M = Zn

60: M = Cd

59, 60

Attempts to isolate 1:2 compounds by treatment with an excess of zinc or cadmium chloride were unsuccessful. Both complexes give rise to derivatives on treatment with strong acids. Thus treatment of compounds **59** and **60** with one equivalent of HCl led to the formation of compounds **61** and **62**.



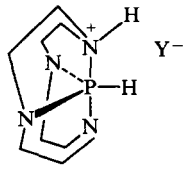
61: M = Zn

62: M = Cd

61, 62

X-Ray diffraction of complex **61** showed that it exists in the form of a 'head to tail' dimer stabilised by two N–H···Cl hydrogen bonds.

The interaction of compound **54** with cobalt, molybdenum, manganese, iron and tungsten carbonyls and hydrides has been examined in an extensive investigation.[74] The reaction of compound **54** with $HWCp(CO)_3$ proceeds as an acid–base process with formation of the salt **63**.



63: Y = $WCp(CO)_3$

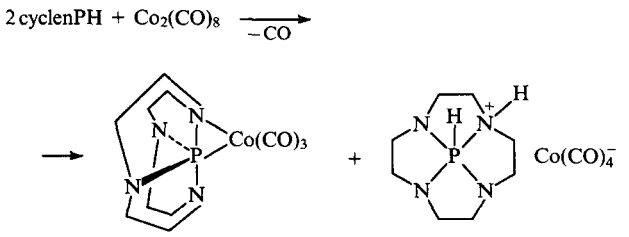
64: Y = I

63, 64

Its treatment with MeI leads to the replacement of the anion: $MeWCp(CO)_3$ and compound **64** are formed. Similarly to the reaction involving compound **54**, only fairly strong nitrogen-containing bases (in particular NEt_3) react with $HWCp(CO)_3$, whereas weaker bases, for example pyridine, do not react.

Here it is appropriate to mention that all the monoprotonated nitrogen-monocoordinated cyclenPH adducts give rise to a single signal in the ^{13}C NMR spectra (at room temperature) in the range 42.8–45.0 ppm. However, the low-temperature (at −76 °C) ^{13}C NMR spectrum of compound **64** contains five signals. These spectroscopic features can be explained, according to Lattman et al.[74], by two different exchange processes: pseudorotation with proton transfer between the nitrogen atoms and the dissociation of the P–N bond in the P–N–H fragment accompanied by the transfer of a proton and the reduction of the P–N bond. However, the available data are insufficient for the identification of these two mechanisms, although it has been stated[66] that compound **54** undergoes pseudorotation.

The interaction of compound **54** with metal carbonyl dimers proceeds in a much more complex manner.



65 **66**

The salt **66** is stable in solution in THF at room temperature under an inert atmosphere, but an increase in temperature to 55 °C leads to the spontaneous loss of H_2 and CO molecules by the salt and the formation of the covalent derivative **65**. The corresponding reaction of compound **54** with $[MoCp(CO)_3]_2$ affords analogous products: (cyclenP)$MoCp(CO)_2$ **67** and $(cyclenPH_2)^+[MoCp(CO)_3]$ **68**. However, in this case even prolonged refluxing of a mixture of compounds **67** and **68** in THF does not lead to the transformation of the salt into the covalent derivative. The only product of the reaction of compound **54** with $Mn_2(CO)_{10}$ (refluxing in THF) which was isolated proved to be the salt $(cyclenPH_2)$ $[Mn(CO)_5]$.

The covalent derivative of manganese analogous to compounds **65** and **67** is apparently unstable under the reaction conditions and decomposes, while the reaction of cyclenPH with $[FeCp(CO)_2]_2$ does not occur at all even after prolonged refluxing in THF or dioxane.

According to Lattman et al.[74], the behaviour of compound **54** in the reaction with dinuclear transition metal carbonyls is very similar to the behaviour of phosphines under the same conditions. For example, the interaction of PR_3 with $Co_2(CO)_8$ leads to the initial formation of the salt $[Co(CO)_3(PR_3)_2]^+[Co(CO)_4]^-$, which then loses a CO molecule and is converted into $Co_2(CO)_6(PR_3)_2$. The structures of compounds **67**, and later[75] also of **65**, were confirmed by X-ray diffraction. Their principal feature is the presence of the three-membered ring



with a greatly lengthened P–N bond. Such compounds will be examined in greater detail in the next section.

Thus the TTP are capable of both N-monodentate and N,N-bidentate coordination to the corresponding Lewis acids. Coordination of this structural type is reflected in the length of the apical and equatorial bonds in the hydrophosphorane (the former are lengthened and the latter are shortened) and is manifested spectroscopically by a downfield shift of δ_P and an increase in the spin–spin coupling constants $^1J(P,H)$ in the ^{31}P NMR spectra.

In a number of instances, N-monodentate and N,N-bidentate binding is accompanied by the occurrence of parallel processes leading to P,N-bidentate coordination. This is caused either by the existence of a tautomeric equilibrium (as in the case of cyclamPH) or by the nature of the initial metal complex.

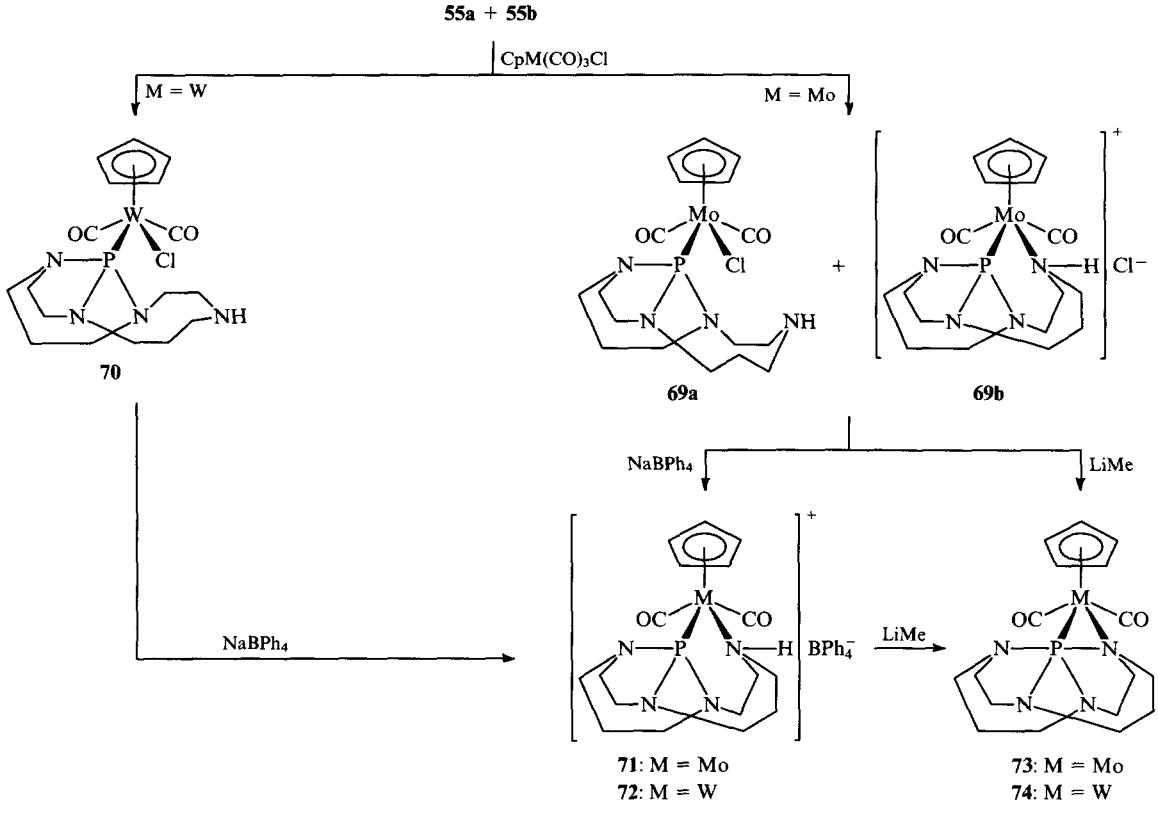
2. Coordination with transformation of the hydrophosphorane structure

a. Molybdenum and tungsten complexes

The first communication concerning the use of tetracyclic hydrophosphoranes in coordination chemistry dates back to 1982.[76] A series of molybdenum and tungsten complexes obtained from cyclamPH are described in this paper and X-ray diffraction data are presented for one of them. An extensive study, in which all the aspects of the synthesis, reactivity, and structural features of these compounds are analysed in detail, was published much later (Scheme 1).[77]

As stated above, cyclamPH exists as an equilibrium mixture of the closed and open forms. On addition of this mixture of the molybdenum and tungsten complexes, the equilibrium is

Scheme 1



quantitatively displaced to the right and compounds **69** and **70** are formed respectively. According to ^{31}P NMR and conductimetric data, complex **69** exists in solution as a mixture of the covalent form **69a** (75%) and the ionic form **69b** (25%).

Only complex **69a** is present in the solid phase, which is indicated by the ν(NH) = 3297 cm^{-1} absorption band, characteristic of a noncoordinated secondary amino-group. The conductimetric data obtained for compound **70** also indicate the absence of any appreciable amounts of the ionic product. On treatment with $NaBPh_4$, complexes **69** and **70** are readily converted into compounds **71** and **72** respectively. Unfortunately, compounds **71** and **72** have been less fully characterised spectroscopically than compounds **69** and **70**. Thus, in the description of their IR spectra, the frequencies ν(NH) are not indicated. Furthermore, only δ_P = 118 ppm is quoted for complex **72** without an indication of the value of the spin–spin coupling constant ^1J(P,W). The reactions of compounds **71** and **72** with MeLi lead to compounds **73** and **74** with P,N-bidentate phosphoranide coordination. Complex **73** can also be obtained from compound **69**, but its yield is then low (20%), since in this case mainly unidentified decomposition products are formed. The transition to phosphoranide coordination is accompanied by an appreciable upfield shift of δ_P in the ^{31}P NMR spectra (by more than 170 ppm). In the IR spectra of complexes **73** and **74**, the frequencies ν(CO) are reduced by $\sim$50 cm^{-1} compared with compounds **71** and **72** as a consequence of the decrease in the positive charge on the metal atom. The structure of compound **73** has been demonstrated by X-ray diffraction (Fig. 3). The environment of the phosphorus atom constitutes an almost regular trigonal bipyramid. Thus the N(1), P, and N(3) atoms lie virtually on a single straight line (176°), while the angles in the equatorial plane are close to 120°. The greater length of the P–N(1) bond (1.85 Å) and, conversely, the small lengths of the remaining three P–N bonds are striking. The P–Mo and N–Mo bonds have the usual lengths.

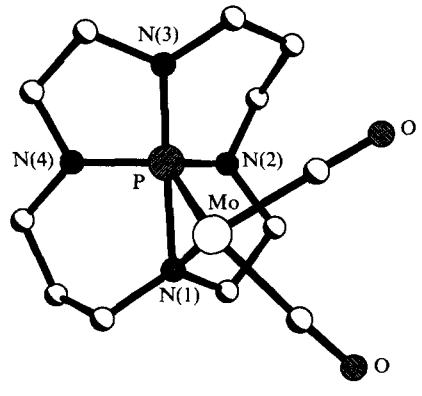
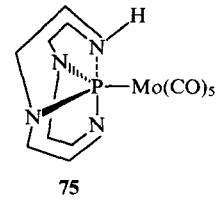


Figure 3. The structure of complex **73** (the η^5-C_5H_5 ring has been omitted for clarity).

It is of interest that the structure of compound **73** shown an unusual 'negative' distortion of the trigonal-bipyramidal configuration, which means that it is not intermediate between the ideal trigonal bipyramidal and square pyramidal configurations.[77]

Several studies have been devoted to the complex of cyclenPH with $Mo(CO)_6$ and its reactivity.[78–81] It was established[78] that treatment of compound **54** with the complex $Mo(CO)_6$ in boiling toluene affords HcyclenPMo$(CO)_5$ **75**, in which cyclenPH is linked to the metal only via the phosphorus atom.

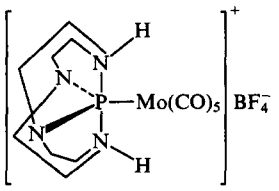


75

δ_P = 116 ppm,
ν(NH) = 3400 cm^{-1}

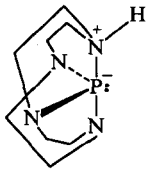
NMR and IR spectroscopic data indicate unambiguously the presence of a noncoordinated secondary amino-group in the structure of compound **75**. However, treatment of it with HBF_4 leads to the formation of a product with a pentacoordinate

phosphorus atom, where both axial nitrogen atoms are protonated, and not a simple ammonium salt.

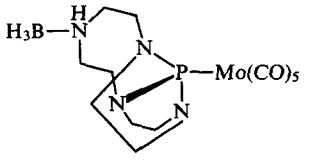


76

The cause of such unusual reactivity was deduced with the aid of X-ray diffraction. The geometry of the phosphorus atom in compound **75** is unique: instead of the tetrahedral configuration, a distorted trigonal bipyramidal coordination obtains (Fig. 4). The Mo, N(2), and N(4) atoms are in the equatorial positions, whilst the N(1) atom is in one of the axial positions. The other axial position is occupied by the N(3) atom, which interacts with phosphorus via the lone pair. Although P–N(3) = 2.356 Å, a distance which exceeds by ~0.4 Å the lengths of the axial P–N bonds in other cyclenPH derivatives, it is nevertheless less than the sum of the van der Waals radii. A more important feature is that the phosphorus atom is almost in the plane of the Mo, N(2), and N(4) atoms, while the equatorial and axial N–P–N angles are typical of those for other trigonal-bipyramidal derivatives of cyclenPH, in which all four nitrogen atoms form with the phosphorus atom bonds having 'normal' lengths. It is more correct to regard the 'cyclenPH' fragment as a phosphoranide zwitterion.



The reactions of compounds **75** with Lewis acids are unusually sensitive to the nature of the acid. It has been reported [79] that the interaction of compound **75** with THF · BH_3 affords the product **77**, in which the coordination number of phosphorus is four and there is an unusual conformation of the cyclenP ring.



77

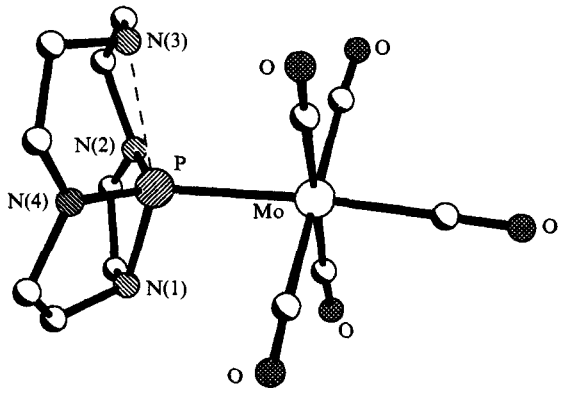
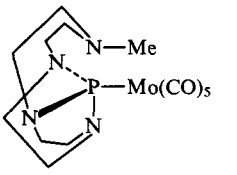


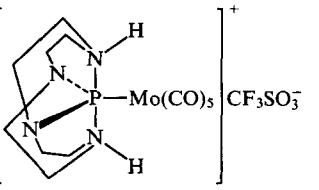
Figure 4. The structure of compound **75**.

The structure of compound **77** was established from ^{31}P, ^{13}C, ^{11}B, and ^{1}H NMR and IR spectroscopic data and was confirmed by X-ray diffraction. Treatment of complex **75** with $Me_3O^+BF_4^-$ leads to the analogue **76**, where one of the apical nitrogen atoms is not protonated but methylated. Unfortunately, this structure has been discussed only on the basis of ^{31}P NMR spectroscopic data.

The interaction of compound **75** with CF_3SO_3Me led to the formation of two products — **78** and **79**.[80]



78



79

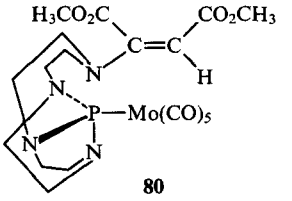
The same compounds, **78** and **79**, were isolated also after carrying out the reaction with the molar ratio **75**: CF_3SO_3Me = 2 : 1. The authors put forward two different mechanisms of the interaction of compound **75** with HBF_4, methyl triflate, and THF · BH_3. According to the first mechanism, the Lewis acid reacts initially with the lone pair of the second amino-group, which is followed by proton transfer. This process is analogous to the addition of alkyl halides to secondary amines.

$$RX + R_2NH \longrightarrow R_3NH^+X^-,$$

$$R_3NH^+X^- + R_2NH \rightleftharpoons R_3N + R_2NH_2^+X^-.$$

In the case of the complex with borane, the proton transfer is unfavourable and the corresponding structure may be isolated.

The other mechanism involves the initial protonation of the second axial nitrogen atom in the *trans*-position relative to NH. This results in the immediate formation of the salt **76**.

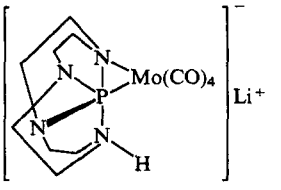


80

The similarity of compound **75** to a secondary amine is also indicated by its interaction with $CH_3O_2CC{\equiv}CCO_2CH_3$ giving rise to compound **80**.

The structure of compound **80** was established by X-ray diffraction. Overall, the complex formation reaction between cyclenPH and $Mo(CO)_6$ demonstrates the ability of the 'cyclen' fragment to stabilise the trigonal bipyramidal geometry around the phosphorus atom as a result of a transannular interaction. This interaction is fairly weak and in subsequent reactions the complex may behave as a secondary amine.

The deprotonation of compound **75** by BuLi led to the formation of a phosphoranide adduct.[81]

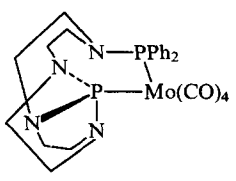


81, δ_P = 20 ppm

We may note that the transition from the transannular P···NH contact in compound **75** to the direct P–N bond in compound **81** is accompanied by a pronounced (96 ppm) upfield shift of the δ_P resonance signal of compound **81** compared with the

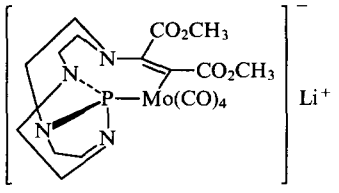
signal of complex **75**. The presence of both carbonyl ligands and of a secondary amino-group in complex **75** makes it necessary to think about the mechanism of the formation of complex **81**. It is well known that the reactions of metal carbonyls with alkyllithium compounds lead to acyl complexes. If this reaction path is followed, the acyl complex should split off pentanal with formation of compound **81**. However, if compound **75** undergoes direct deprotonation by butyllithium with subsequent attack by the nitrogen on the metal, butane and CO are formed. Since butane was in fact isolated from the reaction mixture, the occurrence of the process via the second path was confirmed.

We have frequently noted a fundamental feature of the three-membered phosphoranide rings P—N—M, namely the presence in the latter of a lengthened P—N bond, which, together with the negative charge of the complex ion of compound **81**, increases significantly the reactivity of the compound. Thus the addition of $ClPPh_2$ to the latter leads to a derivative with two different phosphorus atoms.



82

The structure of compound **82** was confirmed by IR and ^{31}P, ^{13}C and ^{1}H NMR spectroscopic data and X-ray diffraction. Treatment of compound **81** with $H_3CO_2CC{\equiv}CCO_2CH_3$ also induces the dissociation of the Mo—N bond, which results in the formation of the metallated enamine **83**.

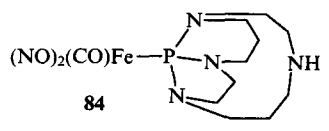


83

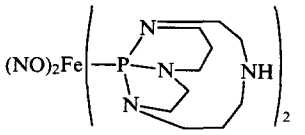
Thus the reactions of tricyclic hydrophosphoranes with molybdenum and tungsten complexes take place with dissociation of the P—H and P—N bonds accompanied by the P-monodentate binding of the ligand in the open form. The products obtained may undergo further reactions accompanied by the transition to the P,N-bidentate (including phosphoranide) and the P-monodentate phosphoranide coordination of the ligand.

b. Iron and rhodium complexes

In contrast to the bicyclic hydrophosphoranes, TTP have not been widely employed in the coordination chemistry of iron and rhodium. Only four iron and rhodium complexes with the cyclamPH and cyclenPH ligands are known at present. The interaction of cyclamPH with $Fe(NO)_2(CO)_2$ for different ligand : metal molar ratios was investigated in the study [77] already mentioned above. It was established that the reaction proceeds with formation of monosubstituted or disubstituted products (**84** and **85**), in which the ligand is bound exclusively via the phosphorus atom.



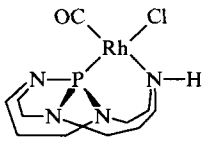
84



85

The structures of these substances were confirmed by ^{31}P NMR and IR spectroscopic data as well as mass-spectrometric data (chemical ionisation method). Compared with the initial complex $Fe(NO)_2(CO)_2$, the IR spectra of complexes **84** and **85** exhibit a bathochromic shift of ν(CO) (for compound **84**) and ν(NO) (for compounds **84** and **85**). This finding indicates that the aminophosphoramidite ligand is a pronounced σ-donor and a weak π-acceptor, apparently owing to the strong $p\pi-d\pi$ interaction characteristic of this compound. The presence of two ν(NH) bands in the spectrum of compound **85** (3120 and 3340 cm^{-1}) may be caused, according to the authors, by intermolecular hydrogen bonds.

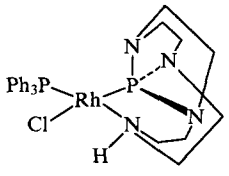
The synthesis of the chlororhodium carbonyl complex **86** from $[Rh(CO)_2Cl]_2$ and cyclamPH was described in the same study.



86

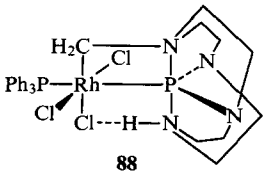
The ^{31}P NMR and IR spectroscopic characteristics of compound **86** are analogous to those of the rhodium(I) carbonyl-containing complexes with P,N-bidentate ligands already mentioned.

An attempt has been made [70] to initiate the tautomeric rearrangement of the phosphorane by treating cyclenPH with the complex $[Rh(CO)_2Cl]_2$, which was unsuccessful. However, the authors do not state what the particular result of this interaction was, so that such a claim can be treated in extremely broad terms, for example, as one implying the complete absence of the occurrence of any reaction. Nevertheless, the latter appears most improbable, since one is dealing with contact between a reactive phosphorane and a reactive rhodium substrate, particularly since cyclenPH interacts readily [82] with $[Rh(PPh_3)_3Cl]$ with formation of compound **87**.



87

It was found that complex **87** reacts slowly (in two days) with methylene chloride, affording the unique rhodium complex **88** with pentacoordinate phosphorus atom and the four-membered ring P—N—C—Rh.



88

The structures of compounds **87** and **88** were established by use the ^{31}P and ^{1}H NMR methods, while that of compound **88** was further confirmed by X-ray diffraction. The coordination

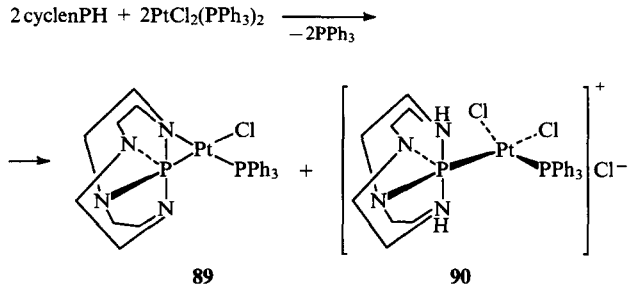
polyhedra in complex **88** are a distorted octahedron for the rhodium atom and a distorted trigonal bipyramid for the phosphorus atom. The formation of compound **88** apparently includes the oxidative addition of CH_2Cl_2 to rhodium and a subsequent rearrangement of the 'cyclenP' fragment accompanied by a change in the coordination number of phosphorus from 4 to 5 and attack by the nitrogen atom on a carbon atom with displacement of a chloride anion. It is of interest that a compound similar to compound **88** is formed in $CDCl_3$ immediately after the dissolution of complex **87**.

Thus the coordination of the tetracyclic hydrophosphoranes to iron and rhodium proceeds with decomposition of the hydrophosphorane structure of the ligand and by their P-monodentate (in the case of iron) or P,N-bidentate (in the case of rhodium) binding.

c. Platinum complexes

Platinum complexes are in fact most widely used in the study of the coordination possibilities of tetracyclic hydrophosphoranes. An impressive diversity of interconversions of complexes of one kind into others has been observed for these complexes. However, only cyclenPH has been used in most of these complexes; only one compound with cyclamPH is known.

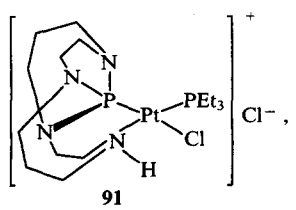
The pioneering communication[83] published in 1987 discusses an unusual reaction between cyclenPH and *cis*-$PtCl_2(PPh_3)_2$.



89 **90**

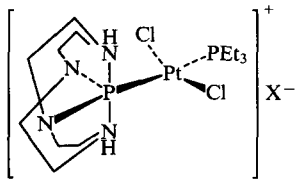
The very high value of the spin–spin coupling constant ^1J(P,Pt) = 5567 Hz for compound **90** (for compound **89**, it is 3672 Hz) and the anomalously low frequency ν(Pt–Cl) = 249 cm^{-1} for complex **89** (for complex **90**, its values are 275 and 300 cm^{-1}) are noteworthy. Such a low frequency ν(Pt–Cl) corresponds as a rule to a considerable lengthening of the Pt–Cl bond. Indeed, X-ray diffraction of compound **89** showed that the Pt–Cl distance in this compound is 2.44 Å. The geometry of the 'cyclenP' ligand in complex **89** is of the 'usual' type: the distance from the phosphorus to the nitrogen atom in this three-membered ring is very large (1.872 Å), whereas the length of the three other P–N bonds are in the range 1.68–1.70 Å. Owing to the strain in the metallocycle, all four bond angles in the plane of the platinum square deviate appreciably from 90°. We may note that lengthening of the Pt–Cl bond is as a rule caused by the strong *trans*-influence of the corresponding substituent. However, the authors did not decide to account for this anomaly by the pentacoordinate state of the phosphorus atom, because the frequencies ν(Pt–Cl) in complex **90** and *cis*-$PtCl_2(PPh_3)_2$ are fairly close. In their view, long Pt–Cl bond and the low frequency ν(Pt–Cl) may be dictated to a large extent by steric and/or electronic requirements of the three-membered metallocycle. We shall return later to the analysis of this problem.

The reaction between cyclamPH and the dinuclear compound $[Pt_2Cl_4(PEt_3)_2]$ leads to the cationic complex **91**,[84]



91

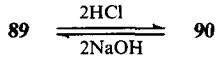
whereas the only product of the reaction of the same platinum dimer with cyclenPH which has been isolated proved to be complex **92**.



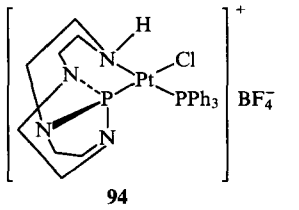
92: X = Cl^-
93: X = PF_6^-

Analogue **93** of compound **92** was obtained by ion exchange of the latter with KPF_6. The structures of the salts **92** and **93** are similar to the structure of complex **90**, but in the latter the chloride ligands have the *cis*-configuration. In the determination of the structures of compounds **91**–**93**, the ^1H, ^{13}C, ^{31}P, and ^{195}Pt NMR methods and conductimetry were used, whilst in the case of compound **91** X-ray diffraction was also employed. All the bond lengths in the first coordination sphere of the platinum atom in compound **91** are within the standard ranges of values. Unfortunately, the comparison of the complex formation reactions of cyclenPH and cyclamPH with the same metallic substrate was not developed further.

Subsequent studies were devoted to further reactions of compounds **89** and **90**. Thus their tendency towards the interconversion has been demonstrated.[85]

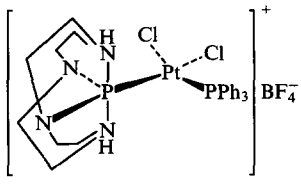


It is noteworthy that the monoprotonated intermediate was not isolated or even detected in this reaction. Thus the interaction of compound **89** with less than two equivalents of HCl nevertheless leads to the product **90** and part of the initial complex does not react. This is apparently associated with the fact that the chloride anion is a strongly coordinating ligand, which may displace the mode of reaction towards double protonation. Consequently the use of a noncoordinating anion can ensure the isolation of the monoprotonated derivative. Indeed, the reaction of compound **89** with one equivalent of HBF_4 affords compound **94**.



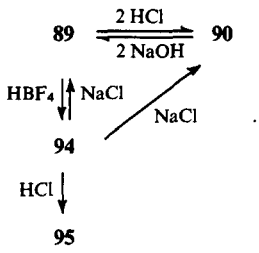
94

The cation of compound **94** is apparently a key intermediate in the conversion of compound **89** into compound **90**. In fact, treatment of compound **94** with HCl results in the immediate formation of the diprotonated adduct **95**.



95

Furthermore, when a source of chloride ions (NaCl) is added to compound **94**, compounds **89** and **90** are formed. Taken all together, the interconversions of complexes **89**, **90**, **94**, and **95** can be represented by the following scheme:



The structures of compounds **90** and **94** were confirmed by X-ray diffraction. The phosphorus centre in complex **90** has the configuration of a distorted trigonal bipyramid with lengthened axial P–N bonds, while that in compound **94** has a distorted tetrahedral configuration (Fig. 5). The dissociation of the P–N bond increases the phosphorus–nitrogen distance to 2.775 Å and the P(1)–Pt–N(1) angle by 28.2° compared with the analogous angle in compound **89**. The appreciable similarity of the ligand structures in compounds **89**, **90**, and **94** indicates the tendency of the 'cyclenPH' fragment to retain the trigonal bipyramidal geometry.

Systematic studies of the reactivity of compound **89** towards various nucleophiles and electrophiles were carried out subsequently.[86,87] The results are presented in Scheme 2.

The reactions of compound **89** with $Na[Co(CO)_4]$, NaSMe, KI, and KBr afford the substitution products **96**–**99** respectively. The NMR spectra of compounds **89**, **98**, and **99** are virtually identical with the exception of small differences in δ_P and $^1J(P,Pt)$. The $\nu(CO)$ frequencies in the spectrum of compound **96** are significantly lower than in those of other compounds of the type $LCo(CO)_4$. This indicates a markedly ionic character of the Pt–Co bond and the presence of a partial negative charge on the $Co(CO)_4$ group. In fact, the interaction of compound **96** with Me_3SiI leads to the formation of complex **98** and $Me_3SiCo(CO)_4$.

On the other hand, the reaction of compound **89** with $Ph_2PCH_2PPh_2$ leads to the substitution of a triphenylphosphine ligand and the attempts to displace the chloride ligand outside the coordination sphere of platinum by treatment with $NaBPh_4$ were unsuccessful. Treatment of compound **89** with electrophiles such as MeI and Bu^nBr also leads to compounds **98** and **99**. The exchange reactions between platinum complexes and RHal (Hal = Br, I), involving the exchange of chlorine at the platinum atom, usually proceed via oxidative addition and reductive elimination with participation of the metal atom. However, no evidence in support of this reaction mechanism was found even in a low-temperature experiment. An alternative to this mechanism may be the formation of a *N*-alkylated derivative with subsequent substitution of the halogen and the elimination of an alkyl halide. Indeed, metallation of compound **89** by MeO_3SCF_3 leads to the salt **101**, whilst its treatment with KI affords compound **98**.

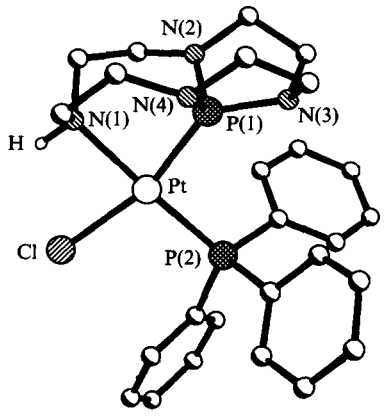
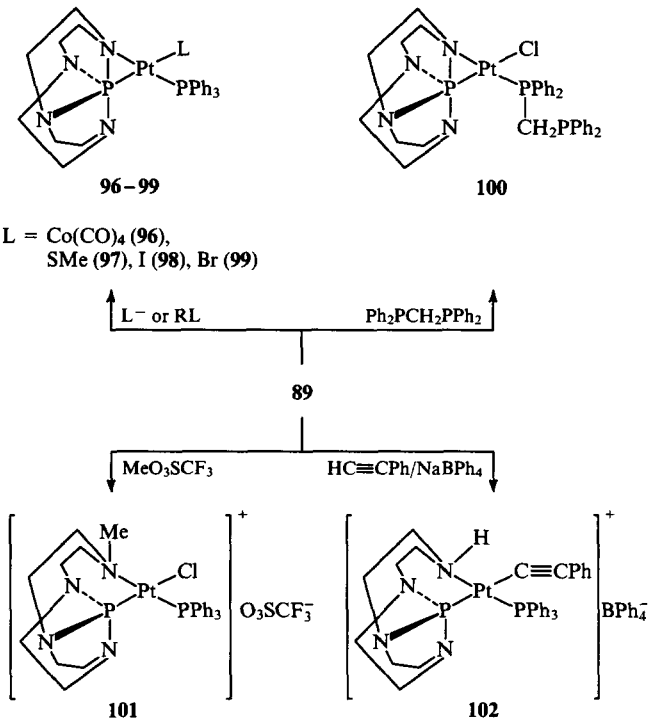


Figure 5. The structure of the cation of compound **94**.

Scheme 2



Very weak electrophiles do not react with compound **89**. For example, the interaction of compound **89** and HC≡CPh does not take place even in boiling THF. However, after the addition of $NaBPh_4$ to the reaction mixture, compound **102** is formed. Various possible mechanisms of the formation of compound **102** have been compared.[87] According to the authors *N*-protonation takes place and is followed by the coordination of the alkyne with substitution of the chloride ion.

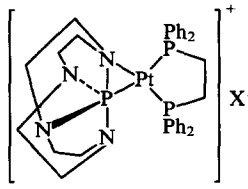
It follows from the scheme presented above that anionic nucleophiles substitute Cl^-, whilst neutral nucleophiles substitute PPh_3. Cationic electrophiles with noncoordinating anions attack the nitrogen atom, which leads to the dissociation of the P–N bond, whereas electrophiles with coordinating anions induce the dissociation of the Pt–N bond.

The structures of compounds **96**, **98**, and **99** have been demonstrated by X-ray diffraction.[88] The cause of the lengthening of the Pt–Cl bond and of the low $\nu(Pt-Cl)$ frequency was again discussed in this connection. The cause may not be solely the strain in the three-membered ring or solely the strong *trans*-effect of the pentacoordinate phosphorus. According to the authors, the principal difference between the structures of compounds **89** and **90** consists in the orientation of the N–P–N axis with participation of the axial nitrogen atoms: in the plane of the platinum square in compound **89** and at right angles to this square in compound **90**. It may be that in the former case the trigonal-bipyramidal phosphorus atom exerts a stronger *trans*-influence. However, the question arises of the legitimacy of such comparison, since in fact one is dealing with completely different ligands: one nitrogen centre is coordinated in compound **89**, whereas in compound **90** both axial nitrogen atoms are protonated. For this reason, the limited *trans*-influence of 'H_2cyclenP' in complex **90** does not permit conclusions concerning such influence of 'cyclenP' in compound **89**. Furthermore, in compound **90** 'H_2cyclenP' exhibits a fairly strong *trans*-influence, although not as strong as in complex **89**. Indeed, the length of the Pt–Cl bond in the *trans*-position relative to the phosphorus atom of 'H_2cyclenP' in compound **90** is 2.386 Å, whereas in compound **94** it is 2.353 Å. The Pt–Cl bond in the *trans*-position relative to the triphenyl phosphine ligand in compound **90** is shorter still (2.343 Å). The conclusion that the *trans*-influence of the pentacoordinate phosphorus atom is

greater than that of the tetracoordinate phosphorus atom follows from these data. Whereas the Pt–Cl distance in compound **94** may be regarded as 'normal' on the basis of the nature of the phosphorus centre, in compound **90** the distance is anomalously large.

It is also scarcely possible to agree with the treatment of the unusually high spin–spin coupling constant ^1J(P,Pt) in complex **90** by Siriwardane et al.[88] In their view, the bonding σ orbital used by phosphorus to form a bond with platinum is approximately sp^2-hybridised. It was then concluded that the high level of *s* character leads to a high value of ^1J(P,Pt). However, increase in the *s* character of the σ-bond should inevitably lead to the shortening of the Pt–P bond. However, the Pt–P bond in compound **90** is very long (2.289 Å). Complexes of platinum with phosphites are also characterised by high spin–spin coupling constants ^1J(P,Pt) (from 5600 to 6000 Hz) and short Pt–P bonds (~2.20 Å).[89–92] Thus metallated phosphoranes exhibit a whole series of spectroscopic and structural anomalies. The characteristics established for complexes with trivial organophosphorus(III) ligands are not always confirmed in the case of pentacoordinate phosphorus. Specific syntheses of a whole series of homologous structures and a thorough spectroscopic and structural study are apparently needed for the determination of the mutual correlations.

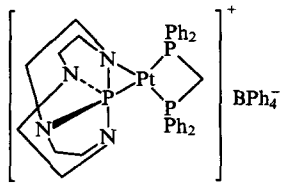
In the latest experimental study[93] devoted to platinum complexes, investigation of the reactions of compound **89** with various phosphines was continued. Thus the interaction of compound **89** with $Ph_2P(CH_2)_2PPh_2$ afforded the ionic product **103**.



X = Cl^- (**103**), PF_6^- (**104**)

103, 104

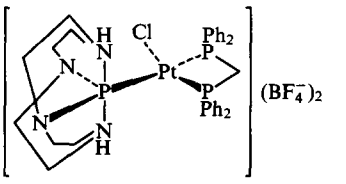
The ionic nature of compound **103** was established both spectroscopically and chemically: the exchange of the chloride ion for PF_6^- with formation of compound **104**, which has ^{31}P NMR characteristics almost identical with those of complex **103**, was carried out. The structure of complex **103** differs sharply from that of compound **100**. It is extremely likely that the monodentate coordination of the ligand $Ph_2PCH_2PPh_2$ is associated with its small chelate angle (73°), whereas in $Ph_2P(CH_2)_2PPh_2$ the angle is 85°. In most cases, this difference is of no fundamental importance. However, the presence of the three-membered phosphoranide ring in compound **100** apparently inhibits the formation of the second small ring. As already mentioned, the attempts to coordinate the free phosphorus centre in compound **100** by treatment with $NaPF_6$ or $NaBPh_4$ were on the whole unsuccessful. This results in the formation of a mixture of adducts, which could not be separated, but the authors[93] nevertheless postulated the formation of complex **105**.



105

In support of their view, they quote only the values of δ_P for the three different phosphorus atoms and the spin–spin coupling constant ^2J(P,P). The spin–spin coupling constant ^1J(P,Pt) could not be determined owing to the presence of numerous signals due to impurities.

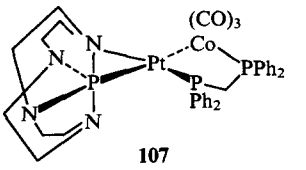
It was found that the free phosphorus centre in compound **100** can be coordinated via another path — the decomposition of the three-membered ring. This aim was achieved by a procedure already tested, by treatment with HBF_4.



106

Again, as in the synthesis of compound **90**, the monoprotonated adduct could not be obtained.

The presence of the noncoordinated phosphorus atom in the structure of compound **100** raised the possibility that interaction with another metal complex would yield a heterobinuclear compound. In fact, the reaction of compound **100** with $Na[Co(CO)_4]$ led to the formation of the bimetallic complex **107** with a Pt–Co bond.



107

The structures of compounds **106** and **107** were established by X-ray diffraction. The geometry around the phosphorus atom in compound **106** can be described as distorted trigonal bipyramidal (Fig. 6). The lengths of the axial P–N bonds not only exceed by 0.25–0.30 Å the lengths of the equatorial bonds, but they are also greater than the sum of the covalent radii. Apparently only the unusual geometry of the 'cyclenP' ring prevents the dissociation of these bonds. Both N–H groups form hydrogen bonds with the counterion.

The facts mentioned above indicate that platinum can be readily incorporated in both three- and five-membered rings simultaneously, whereas the inclusion of the metal in three- and four-membered rings is very difficult to achieve.

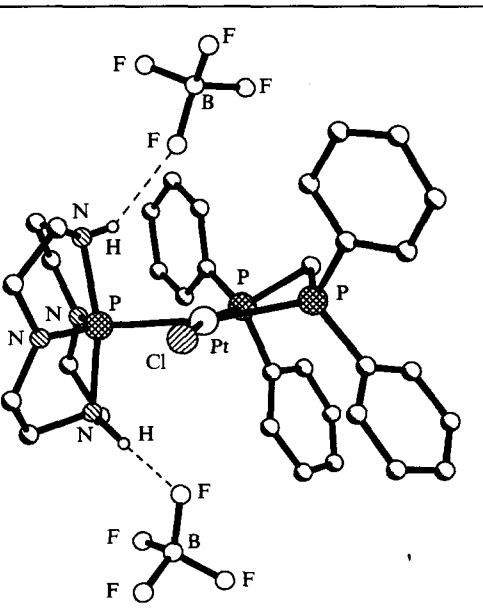


Figure 6. The structure of compound **106**.

On the whole, the coordination of cyclenPH to platinum leads to metallated phosphoranes with P-monodentate or P,N-bidentate binding of the ligand. On treatment with appropriate reagents, the compounds obtained can be interconverted or they can be converted into a multiplicity of different metal complexes with P,N-bidentate coordination, in which the coordination number of phosphorus is smaller. The interaction of cyclamPH and platinum has been clearly inadequately investigated. Nevertheless, the available data indicate the displacement of the **55a** ⇄ **55b** equilibrium towards the open form with P,N-bidentate binding of the ligand.

Evidently TTP are the most versatile ligands in the coordination chemistry of hydrophosphoranes. They are capable of N- and P-monodentate and N,N- and P,N-bidentate coordination, including coordination of the phosphoranide type.

The tetracyclic hydrophosphoranes can behave as amines, phosphoramidites, aminophosphoramidites, or as hydrophosphoranes proper depending on the type of Lewis acid, forming at the same time unique metal complexes. When bound to a metal, they sometimes assume the functions of the latter, interacting with reagents of different nature. However, reactions in which TTP are coordinated solely in the P-monodentate or the P,N-bidentate phosphorane form, without the occurrence of parallel reactions or without treatment by deprotonating agents, are so far unknown. The search for processes of this kind is still to be carried out.

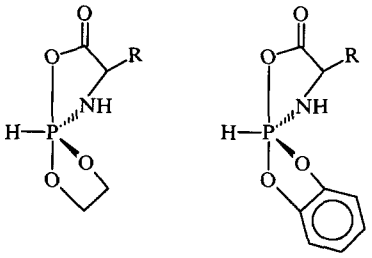
V. Conclusion

It is seen from the data presented that considerable advances have been made in the chemistry of metallo-derivatives of hydrophosphoranes. The bicyclic and tetracyclic hydrophosphoranes were found to be the most thoroughly investigated groups of compounds, whilst a new aspect—the study of a complex formation reaction by 'triquinphosphoranes'—has only just become outlined but promises to be continued on a duly impressive scale. At the same time the extensive coordination possibilities of hydrophosphoranes have not yet been utilised to the extent that they deserve. We may point to certain fundamental problems the solution of which we believe to be of current interest.

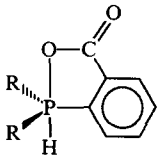
1. Comparison of the reactivities of various groups of hydrophosphoranes employing a specific metallic substrate and standard complex formation conditions. So far, there have been few such studies—only $[Rh(CO)_2Cl]_2$ is known as a general partner in the complex formation reactions involving BAP, HSP, and TTP. The remaining platinum metals have been used to a lesser extent. Rhodium complexes have been thoroughly investigated for the BAP, while the palladium complexes have been studied very superficially and there are no examples whatever of platinum adducts. On the other hand, the platinum derivatives of the tetracyclic hydrophosphoranes have been investigated in detail, while the studies on the rhodium complexes have been fragmentary and the palladium complexes are unknown. So far, the chemistry of the HSP is in many respects the chemistry of one metal, namely of rhodium. Palladium and especially platinum have clearly not been employed adequately. Furthermore, it would be useful to investigate the interaction of a specific phosphorane with a series of analogous metal complexes, for example $M(COD)Cl_2$ (M = Pd, Pt), $M(CO)_n$, etc. This would assist in a better understanding of the mechanism of the coordination of the hydrophosphoranes. Such studies are also extremely few in number.

2. The extensive employment of all groups of hydrophosphoranes in catalysis, especially asymmetric catalysis. Nowadays this field has already been outlined—certain BAP and HSP have been involved in catalytic processes, whereas the tetracyclic hydrophosphoranes have been completely ignored by specialists in catalysis. Clearly extraordinary results may be expected for ligands with superior coordination and stereochemical properties of the kind possessed by hydrophosphoranes.

HSP with aminoacid residues,[94,95] i.e.

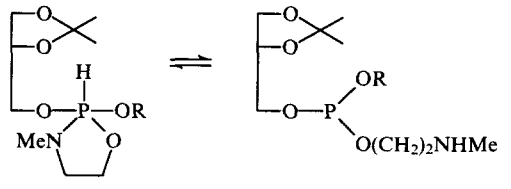


may be of special interest primarily for metal complex asymmetric catalysis because these stable compounds are obtained in satisfactory yields by the direct phosphorylation of readily available chiral precursors—natural aminoacids. The authors of the present review have begun studies on the employment of such HSP in coordination design. We may also mention a novel hydrophosphorane with an unusual axial orientation of the P–H bond.[96]



It is significant that an active catalyst of the oligomerisation of ethene has been obtained from this compound by treatment with KOH, $NiCl_2$, and $NaBH_4$.

3. The expansion of the range of hydrophosphorane ligands by resorting to new systems, for example, monocyclic hydrophosphoranes.[97]



R = Me, CH_2Ph

Tetraoxohydrophosphoranes, on the coordination chemistry of which only one study has been published, merit more constant attention.

It is essential to state that the field of synthesis of a wide variety of BAP with additional coordination centres by the interaction of proton-donating reagents with derivatives of bicyclo[3.3.0]-1-phospha-2,8-dioxa-5-azaoctane has been developing vigorously in recent times.[98] These systems can also be regarded as promising polyfunctional ligands.

4. The study of the mechanism of complex formation reactions of hydrophosphoranes. The interaction of the tautomer having a tricoordinate phosphorus atom with a metal-containing substrate has been traditionally postulated. However, in a whole series of cases the existence of such a tautomer is doubtful. Thus NMR and IR spectroscopic studies of solutions of oxazahydrospirophosphoranes did not reveal the presence of the phosphorus(III) form.[51,99,100] Furthermore, these HSP do not react under mild conditions with $(acac)Rh(CO)_2$ and $BF_3 \cdot Et_2O$, atypical of organophosphorus(III) compounds. The tautomeric equilibrium postulated for Phoran has also not been detected spectroscopically[11] [the phosphorus(III) isomer has been found only in the gas phase]. Finally, cyclenPH exists in the phosphorus(V) form in solution, in the solid state, and in the gas phase,[78] although a whole series of metallo-derivatives are known

where it is coordinated in the open form. On the other hand, the interaction of cyclenPH with B_2H_6 leads to a bisborane adduct with pentacoordinate phosphorus. All these facts indicate the active role of the transition metal in the complex formation reaction involving the hydrophosphorane and hence the existence of a mechanism involving the formation of a metal hydride intermediate (in accordance with the same principle as in the reactions of silanes, secondary phosphines, or hydrophosphoryl compounds).[51, 101] At the same time, one cannot exclude from discussion the mechanism with participation of the phosphorus(III) tautomers of hydrophosphoranes. We may recall that a bisborane adduct has been obtained for Phoran, in which the latter exists in an open form let alone the fact that phosphorus(III) isomers have been detected spectroscopically for many hydrophosphoranes. Both mechanisms apparently operate, their contributions depending on the nature of the hydrophosphorane, the Lewis acid, and the reaction conditions. However, additional studies are needed to justify this view.

The interest in the employment of hydrophosphoranes in metal complex design has not weakened. A review by Lattman and co-workers, containing a brief survey of the ligand properties of cyclenPH, has been published recently.[102] We believe that the current achievements in the coordination chemistry of hydrophosphoranes constitute merely a prologue to its further development.

In the preparation of the figures, the facilities of the Cambridge Structural Database (1995 release) were employed. These permit a graphical representation of molecules on the basis of the atomic coordinates of the crystals of the test compounds deposited in the Database.

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