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Phospha-alkynes—Compounds of Monocoordinate Phosphorus

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The review gives a systematic account of and surveys the results of studies on compounds of monocoordinate phosphorus. The methods of synthesis of phospha-alkynes from phosphines and phospha-alkenes (by pyrolysis or low-temperature elimination), their structure and physico-chemical properties, and also their chemical behaviour in complex-formation and cycloaddition reactions are examined.
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I. INTRODUCTION

The synthesis of phosphaethyne (H−C≡P) in 1961[1] laid the foundation of the class of organophosphorus compounds (OPC) which are derivatives of monocoordinate phosphorus (phospha-alkynes). The first communication about the synthesis of a compound of this type (NaCP) dates back to 1894,[2] but subsequent attempts to reproduce the experiments described in that report were unsuccessful.[1]

The development of the chemistry of monocoordinate phosphorus was inhibited by the Mulliken–Pitzer hypothesis, according to which the existence of phosphorus derivatives resembling cyanides is impossible owing to the presence of vacant *d* orbitals in the phosphorus atom. Gier's study[1] disproved these views. When PH_3 was passed through a low-intensity electric arc between graphite electrodes, phosphaethyne (H−C≡P) was obtained. It is a colourless reactive gas, stable at temperatures below the triple point (−124° ± 2 °C) and at a reduced pressure (<30 mmHg).[1] The molecular weight, determined mass-spectrometrically, confirmed its composition and the addition of HCl at −110 °C with formation of dichloromethylphosphine confirmed the presence of a C≡P triple bond. The infrared spectrum of the solid specimen at −196 °C also corresponded to the H−C≡P structure.[1]

However, owing to the extreme instability of derivatives of monocoordinate phosphorus, only little attention has been devoted to their investigation during the last 15 years. Gier's data[1] have been confirmed and deuteriophosphaethyne has been obtained by an analogous procedure;[3] the microwave,[3] ultraviolet, infrared (IR), and NMR spectra[4-7] of phosphaethyne as well as its photoelectron spectrum (PES)[8] have been investigated and quantum-chemical calculations have been performed for the H−C≡P molecule.[9-11] As a result of the discovery of new methods of synthesis of phospha-alkynes, studies in this field have been developing at a higher rate only since the middle 1970's. Ten compounds of monocoordinate phosphorus and some of their deuteriated derivatives are now known; approximately 50 communications devoted to their synthesis and the study of their physicochemical properties have been published. The possibility of using phospha-alkynes in organic synthesis and in the chemistry of transition metal complexes has aroused much interest in the vigorous research into this class of OPC prosecuted at the present time.

Some information on the chemistry of phospha-alkynes is contained in reviews[12,13] devoted mainly to compounds of dicoordinate phosphorus. This review gives a systematic account and a survey of the results of studies on phospha-alkynes both in terms of the synthetic aspect and as regards their structure, physicochemical properties, and reactivity. It is noteworthy that experimental data on the synthesis and properties of phospha-alkynes have been frequently reproduced and have been confirmed by different groups of investigators. In this respect, the results of Matveev and coworkers[14-19] differ from them sharply, cannot be accepted as reliable, and are not considered in this review.

II. SYNTHESIS

Phospha-alkynes (I)–(X) (Table 1) are thermally unstable and very reactive compounds. With the exception of 3,3-dimethyl-1-phosphabutyne (VII), they are gases which are stable only at low temperatures in an inert atmosphere or at room temperature in a state of high rarefaction.

The methods of synthesis of phospha-alkynes known at present are based on the elimination of hydrogen halides, trialkylchlorosilane, or hexa-alkyldisiloxanes from substituted phosphines and compounds of dicoordinate phosphorus (phospha-alkenes). These methods can be divided into two groups: high-temperature pyrolysis and low-temperature elimination in the presence of solid alkali (Table 1). In cases where the starting compounds are di- or tri-halogenophosphines, a two-stage reaction has been proposed with formation of an intermediate phospha-alkene.

The majority of phospha-alkynes have been synthesised by high-temperature pyrolysis. Thus phosphaethyne (I) has been obtained by passing dichloromethylphosphine through a quartz tube 8 mm in diameter and 150 mm long, heated to 1000 °C, at a pressure of 2 mmHg.[20,21] 1-Phosphapropyne (II) has been synthesised analogously:[22,23]

$$MePCl_2 \xrightarrow[-HCl]{\Delta} \underset{(I)}{H-C\equiv P};$$

$$MeCH_2PCl_2 \xrightarrow[-HCl]{\Delta} [MeCH{=}PCl] \xrightarrow[-HCl]{\Delta} \underset{(II)}{Me-C\equiv P}.$$

Westwood et al.,[23] who used photoelectron spectroscopy as an

identification procedure, note that the formation of phosphapropyne (II) and HCl is not the only pathway to the decomposition of the initial dichloroethylphosphine. According to PES (the reaction products were introduced directly into the ionisation chamber of the spectrometer), the reaction mixture also contains the initial phosphine, PCl_3, C_2H_2, C_2H_4, and C_2H_6.[23] The isolation of compound (II) in a pure form therefore requires the successive employment of three low-temperature traps at −78 °C (for the separation of the initial phosphine), −126 °C (for the separation of PCl_3), and at the temperature of liquid nitrogen. When the last trap is heated, traces of C_2H_6 appear and these are followed by C_2H_4 and HCl, in order of their volatilities. Further heating yields phosphapropyne alone. Its yield is not more than 10%. As the pressure is reduced, the yield of compound (II) with respect to C_2H_4 increases. Phosphapropyne specimens can be stored without any changes at the temperature of liquid nitrogen in the course of a month.[23]

Table 1. The synthesis of phospha-alkynes (I)–(X).

Compound	Method of synthesis*	Reaction conditions		Refs.
		t, °C	p, mmHg	
HC≡P (I)	P	1000	2	[20]
DC≡P	P	1000	2	[20]
$CH_3C{\equiv}P$ (II)	P	900	0.05	[22,23]
$CD_3C{\equiv}P$	P	900	0.05	[22,23]
F—C≡P (III)	E	20	30	[32,33]
NC—C≡P (IV)	P	700	50	[20]
$CH_2{=}CH{-}C{\equiv}P$ (V)	P	1000	30—60	[24]
HC≡C–C≡P (VI)	P	1100	30—60	[25]
DC≡C–C≡P	P	1100	30—60	[25]
$Me_3C{-}C{\equiv}P$ (VII)	E	20	in solution	[34]
Ph—C≡P (VIII)	P	700—800	—	[26—28]
$Me_3Si{-}C{\equiv}P$ (IX)	P	750	$2{\cdot}10^{-6}$	[29]
$CF_3C{\equiv}P$ (X)	P	—	—	[31]

*P = pyrolysis; E = elimination under the influence of alkali.

Cyanophosphaethyne (IV) has been synthesised from phosphaethyne (I).[20] The unpurified compound (I), obtained by pyrolysing dichloromethylphosphine, is passed through a trap, containing KOH pellets and cooled to −78 °C, in order to remove HCl and is then transferred together with cyanogen azide to a furnace at 700 °C and a pressure of 50 mmHg:

$$MePCl_2 \xrightarrow[-HCl]{\Delta} \underset{(I)}{HC{\equiv}P} \xrightarrow{\Delta,NCN_3} \underset{(IV)}{N{\equiv}C{-}C{\equiv}P}.$$

The authors suggest that pyrolysis of NCN_3 results in the formation of nitrile radicals which undergo a substitution reaction with phosphaethyne, giving rise to the final product (IV) in ~1% yield.[20]

Vinylphosphaethyne (V)[24] and ethynylphosphaethyne (VI)[25] have been obtained by the pyrolysis of the corresponding dichlorophosphines. In the latter case the initial phosphine is formed immediately in the reaction zone on pyrolysing a 2:1 mixture of 3-chloropropyne and phosphorus trichloride:

$$CH_2{=}CH{-}CH_2PCl_2 \xrightarrow[-HCl]{\Delta} \underset{(V)}{CH_2{=}CH{-}C{\equiv}P};$$

$$HC{\equiv}CCH_2Cl + PCl_3 \xrightarrow{\Delta} [HC{\equiv}CCH_2PCl_2] \xrightarrow{\Delta} \underset{(VI)}{HC{\equiv}C{-}C{\equiv}P}.$$

In the syntheses of phenylphosphaethyne (VIII)[26–28] and trimethylsilylphosphaethyne (IX),[29] the starting materials were compounds of dicoordinate phosphorus, both phospha-alkynes are formed in quantitative yields:

$$(Me)_3Si(Ph)C{=}PCl \xrightarrow[-(Me_3)SiCl]{\Delta} \underset{(VIII)}{Ph{-}C{\equiv}P};$$

$$[(Me)_3Si]_2C{=}PCl \xrightarrow[-(Me_3)SiCl]{\Delta} \underset{(IX)}{(Me)_3SiC{\equiv}P}.$$

Appel et al.[26] noted that the method of synthesis which they proposed makes it possible to isolate phenylphosphaethyne (VIII) in a pure form, which was impossible when benzyldichlorophosphine was used as the starting material owing to the large amount of impurities formed during its pyrolysis. However, even in the absence of impurities, the phospha-alkyne (VIII) is stable only at a low temperature, decomposing slowly above −50 °C (the half-life at 0 °C was 7 min).[26] The trimethylsilyl derivative (IX) is somewhat more stable and begins to decompose only at −10 °C; the half-life at room temperature is 50 min.[29] This compound can also be obtained by the pyrolysis of *P*-chlorobis(methylene)phosphorane:[30]

$$[Me_3Si]_2C{=}\overset{Cl}{\overset{|}{P}}{-}C[SiMe_3]_2 \xrightarrow{\Delta} \underset{(VIII)}{Me_3SiC{\equiv}P}.$$

The available information about the synthesis of trifluoromethylphosphaethyne (X) is extremely scanty.[31] The compound has been obtained by the pyrolysis of pentafluoroethylphosphine:

$$CF_3CF_2PH_2 \xrightarrow[-HF]{\Delta} \underset{(X)}{CF_3C{\equiv}P}.$$

The low-temperature elimination method makes it possible to synthesise phospha-alkynes which are unstable at high temperatures. Fluorophosphaethyne (III)[32,33] and 3,3-dimethyl-1-phosphabutyne (VII)[34] have been obtained in this way. Compound (III) is formed when the vapour of the initial trifluoromethylphosphine is passed through a spiral glass tube 10 mm in diameter and 400 mm long filled with solid potassium hydroxide, at room temperature and a pressure of 30 mmHg:

$$CF_3PH_2 \xrightarrow[-HF]{KOH} [CF_2{=}PH] \xrightarrow[-HF]{KOH} \underset{(III)}{FC{\equiv}P}.$$

An increase of the contact time between the initial phosphine and the alkali and a decrease of pressure lead to an increase of the content of fluorophosphaethyne (III) relative to the phospha-alkene.[32]

The initial reactant in the synthesis of the t-butyl derivative (VII) is a compound of dicoordinate phosphorus:[34]

$$\begin{matrix} Me_3SiO \\ Me_3C \end{matrix}\!\!\diagdown\!\!C{=}PSiMe_3 \xrightarrow[-[Me_3Si]_2O]{NaOH} \underset{(VII)}{Me_3C{-}C{\equiv}P}.$$

At room temperature solid sodium hydroxide is added slowly into a solution of the disilyl derivative in diethylene glycol dimethyl ether; the yield of compound (VII) is 76%. 3,3-Dimethyl-1-phosphabutyne (VII) is a colourless mobile liquid with a b.p. 61 °C and is the only representative of phospha-alkynes stable under normal conditions known at the present time.

The phospha-alkynes (I)–(IV), (VIII), and (IX) have been obtained by methods analogous to those described above.[35]

The high reactivity and thermal instability of phospha-alkynes precludes the synthesis of most of them by these methods in preparative amounts. Phospha-alkynes are even more unstable in the presence of the numerous impurities formed in the pyrolysis of the initial phosphines. In this sense the search for new methods of synthesis is undoubtedly an urgent problem in the chemistry of compounds of monocoordinate phosphorus.

III. STRUCTURE AND PHYSICOCHEMICAL PROPERTIES

The phospha-alkynes (I)–(X) have been investigated with the aid of various physicochemical methods: mass-spectrometry and microwave, photoelectron, IR, and NMR spectroscopy. Mass spectra have been used to identify the compounds and to determine their molecular weights. Microwave and photoelectron spectra have also been employed successfully for the same purpose. The microwave spectroscopic and PES methods, which make it possible to transfer in the course of experiments the substances from the synthetic zone directly into the spectrometer cell with rarefaction and at a low temperature, are the most convenient and in many instances the only methods available for the identification and analysis of compounds as unstable as phospha-alkynes. Because of the low stability of phospha-alkynes, IR and NMR spectroscopy are used to investigate them to a much lesser extent.

Table 2. The structural parameters of phospha-alkynes RCP.

Compound	R	$r(X^*-C_{sp})$, Å	$r(C\equiv P)$, Å	Refs.
(I)	H	1.0667	1.5421	[3, 36]
(II)	Me	1.465	1.544	[37]
(III)	F	1.285; 1.270	1.541; 1.547	[38], [32]
(IV)	NC	1.382	1.544**	[20]
(V)	CH_2=CH	1.432	1.544**	[24]
(VI)	CH≡C	1.382	1.544**	[25]
(VII)	Me_3C	1.473	1.536	[39]
(VIII)	Ph	1.467	1.544**	[28]
(X)	CF_3	1.460	1.542	[31]

*X = atom of group R linked to the C_{sp} carbon atom.
**The parameter was taken from data for compound (II).[37]

The steric structure of phospha-alkynes has been established by a microwave spectroscopy (Table 2); they are structural analogues of the corresponding nitriles. Thus, like hydrogen cyanide, phosphaethyne has a linear structure and in both molecules the shortening of the C≡P and C≡N bonds[40] relative to single C–P and C–N bonds is almost the same (0.31 and 0.32 Å). The C–N [and C–P?] bond lengths in these compounds also differ little (1.0632 Å in HCN). A similar situation has been noted also[28,37,39] for alkyl and phenyl derivatives of phosphaethyne [compounds (II), (VII), and (VIII)] and the corresponding nitriles: the values of $r(C-C_{sp})$, namely 1.458 Å in MeCN and 1.451 Å in PhCN, differ little from those for the phospha-alkynes (II) and (VIII) (Table 2). On the other hand, the F–C bond in the F–C≡P molecule is much longer than in F–C≡N (1.262 Å) and is close to the value 1.279 Å observed in the F–C≡CH molecule.[38] A characteristic feature of phospha-alkynes which distinguishes them from nitriles is a weak sensitivity of the C≡P bond length to the substituent at the carbon atom (Table 2) – some shortening of the bond is observed only for the t-butyl derivative (VII). It has been noted[39] that, although the opposite tendency is observed in the series of a corresponding nitriles [$r(C\equiv N)$, Å: 1.156 in HCN, 1.157 in MeCN, and 1.159 in Me_3CCN], it is difficult to draw definite conclusions on this basis because of the assumptions made for phospha-alkynes (see the footnote to Table 2) and the possible experimental errors. However, the main tasks in the analysis of microwave spectra, namely the identification of representatives of the new class of OPC and an unambiguous demonstration of the structure with a C≡P triple bond, have been carried out.

Six phospha-alkynes have been investigated by PES (Table 3). In all the compounds, the first ionisation potential (IP) corresponds to the removal of an electron from a bonding π orbital localised predominantly at the C≡P group and the second ionisation potential corresponds to the removal of a non-bonding *n* electron localised at the phosphorus atom. The results of a comparative analysis of the PES of phospha-alkynes and the corresponding nitriles indicate the similarity of the electronic structures of the RC≡P and RC≡N molecules.[41] This is shown, for example, by the influence of substituents on the orbital characteristics, which are virtually identical in the series of phospha-alkynes and nitrides (Fig.1). Thus the stabilisation of the bonding π orbital is observed in both series and the observed order in the variation of the π(C≡)IP, namely H > F > Me > Me_3C, is due to the mesomeric (+*M*) effect of the substituents.[41] In both phospha-alkynes and nitriles, the IP of the *n* orbital decreases consistently in the sequence R = F, H, Me, Me_3C, in conformity with the increase of the +*I* effect of the substituent R.[41] On the other hand, in all the phospha-alkynes there is a greater shift towards lower ionisation potentials compared with nitriles than might have been supposed to result from substitution of the nitrogen atom by the less electronegative phosphorus atom.[41] Evidently the most important feature of phospha-alkynes is the increase in the latter of the $\pi - n$ separation compared with nitriles, which is a quantitative indication of the decrease of the $2p\pi-3p\pi$ overlap in these compounds compared with the $2p\pi-2p\pi$ overlap in the RC≡N molecules.[41] These data are clearly illustrated by the correlation orbital diagram (Fig.1).[41] The difference in the separation of the π and *n* levels between phospha-alkynes and nitriles noted above is manifested also in their chemical properties (Section IV).

Table 3. PES data for phospha-alkynes RCP.

Compound	R	IP[π(C≡P)], eV	IP[*n*(P)], eV	Refs.	Compound	R	IP[π(C≡P)], eV	IP[*n*(P)], eV	Refs.
(I)	H	10.79	12.86	[8]	(VII)	Me_3C	9.61	11.44	[41]
(II)	Me	9.89	12.19	[23]	(VIII)	Ph	8.68	11.76	[41]
(III)	F	10.57	13.55	[32]	(IX)	Me_3Si	9.9	10.9	[42]

There is very little information about the IR spectra of phospha-alkynes, probably because of experimental difficulties. The ν(C≡P) stretching vibration frequency varies within fairly broad limits: 1265 cm^{-1} for HC≡P,[1] 1660 cm^{-1} [33] or 1670.8 cm^{-1} [43] for FC≡P, and 1533 cm^{-1} for $Me_3C-C\equiv P$.[34] There are contradictions in the literature data for ν(C≡P) in the infrared spectrum of phosphaethyne. Johns et al.[4] altogether failed to observe the band at 1265 cm^{-1} and concluded that its assignment to ν(C≡P) was erroneous. A similar doubt was expressed also by Becker et al.[34] in connection with a comparison of the IR spectra of HC≡P[1] and $Me_3CC\equiv P$. In the light of the available limited data, the ν(C≡P) band in the IR spectra of phospha-alkynes appears to be non-characteristic.

Studies of the phospha-alkynes (I), (III), and (VII)–(IX) by ^{31}P and ^{13}C NMR have shown (Table 4) that, whereas the range of variation of the chemical shift of the signal due to the phosphorus nucleus in these compounds is about 300

p.p.m., the $\delta^{13}C$ chemical shift for the *sp*-hybridised carbon atom is more characteristic ($\Delta\delta \cong 50$ p.p.m.). It has been noted[7] that the spin–spin coupling constant $^1J(CH) = 211$ Hz in the ^{13}C NMR spectrum of phosphaethyne is directly related to the nature of the C≡P triple bond and shows that the hybridisation of the carbon atom in the HC≡P molecule is close to *sp* (calculation yields 43% of *s* character).

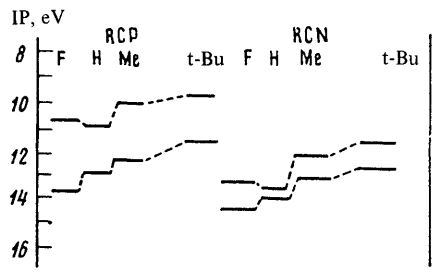


Figure 1. Orbital correlation diagram for the first two ionisation potentials of RCP and RCN.[41]

Table 4. NMR data for phospha-alkynes RCP.

Compound	R	$\delta^{31}P$, p.p.m.*	$\delta^{13}C_{sp}$, p.p.m.**	$^1J(P\text{-}C_{sp})$, Hz	Refs.
(I)	H	−32	154	54	[7]
(III)	F	−206.4	—	—	[33]
(VII)	Me_3C	−69.2	184.8	38.5	[34]
VIII	Ph	−32	164.9	48.3	[26]
(IX)	Me_3Si	96	201.4	13.9	[29]

*Relative to 85% H_3PO_4.
**Relative to Me_4Si.

Important information about the polarity of phospha-alkynes has been obtained in their investigation by microwave spectroscopy. The experimental dipole moments of the compounds (μ_{exp}, D) are 0.39 for HCP,[3] 1.499 for MeCP,[37] 0.279 for FCP,[38] 3.44 for NCCP,[20] 1.183 for $CH_2=CHCP$,[24] and 0.745 for HC≡CCP.[25] The significant difference between the dipole moments of HCP and HCN ($\mu_{exp} = 3$ D) has been explained[3] by the lower electronegativity of the phosphorus atom compared with the nitrogen atom (2.1 and 3.0 respectively) and by the diffuseness of the unshared (lone) electron pair (LEP) of the phosphorus atom. Analysis of the dipole moments of the phospha-alkynes (I)–(VI) in terms of the vector-additive scheme made it possible to determine the polarity of the C≡P triple bond.[44] It has been noted[44] that the data for the polarity of the phospha-alkynes fit satisfactorily within the framework of the additive computational scheme after the correct selection of the corresponding models despite the view[20] that there are no signs of additivity. The polarity of the C≡P bond is almost independent of the substituent at the *sp* hybridised carbon atom and is characterised by a dipole moment of 0.7 ± 0.1 D in the direction from phosphorus to carbon. The opposite polarity of the C≡P bond in phospha-alkynes compared with the C≡N bond in nitriles is also indicated by the results of a quantum-chemical calculation for the HCP molecule,[10] according to which the carbon atom constitutes the negative end of the C≡P bond dipole: the charges on the H, C, and P atoms are respectively +0.226 e, −0.307 e, and +0.081 e.

IV. CHEMICAL PROPERTIES

The chemical properties of phospha-alkynes have been little investigated. It is known that these compounds rapidly polymerise on raising the temperature, forming solid resins.[1] At temperatures somewhat above those corresponding to their stability, phospha-alkynes interact with hydrogen halides to form halogenophosphines and phospha-alkenes:[1,26]

$$\underset{(I)}{H{-}C{\equiv}P} + HCl \xrightarrow{-110^\circ} MePCl_2;$$

$$\underset{(VIII)}{Ph{-}C{\equiv}P} + HCl \rightarrow PhCH{=}PCl.$$

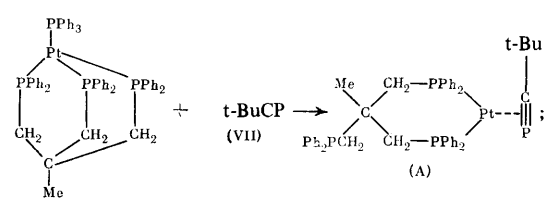
These reactions have been used to demonstrate the structure of the phospha-alkynes (I)[1] and (VIII)[26] obtained. In many of the studies quoted above the possibility of using phospha-alkynes in synthetic chemistry and in the transition metal complex chemistry is discussed. For example, it has been suggested that, owing to the large positive charge on the phosphorus atom (+0.48 e on P, −0.09 e on C, and −0.39 e on F), fluorophosphaethyne can function as an electron density acceptor in chemical reactions.[32] However, the low thermal stability of phospha-alkynes and the impossibility of synthesising them in preparative amounts preclude their wide-scale employment in practical chemistry. Only a series of transition metal complexes of the only phospha-alkyne stable under normal conditions, namely the t-butyl derivative of compound (VII),[45–49] and the cycloaddition reaction involving PhC≡P[27] have so far been investigated.

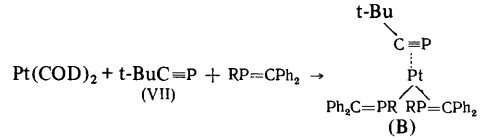
3,3-Dimethyl-1-phosphabutyne taken in excess forms cream-coloured semitransparent crystals of a 1:1 complex with zerovalent platinum at room temperature in benzene in a quantitative yield:[45]

$$Pt(C_2H_4)(PPh_3)_2 + t\text{-}BuC{\equiv}P \rightarrow Pt(PPh_3)_2(t\text{-}BuC{\equiv}P).$$

X-Ray diffraction analysis of the complex showed that the phospha-alkyne (VII) is coordinated "sideways" to the platinum atom, so that the LPE of the phosphorus atom hardly interacts with the metal (Fig. 2).[45] It was of interest that the C–P bond (1.672 Å) in the coordinated t-BuCP is appreciably longer than that in the free molecule of compound (VII) (1.544 Å). Elemental analysis of the ^{31}P NMR spectra of the complex are consistent with the structure presented.[45]

The synthesis of two new complexes of t-BuCP with zerovalent platinum, in which the phospha-alkyne is also coordinated "sideways" to the platinum atom, has been recently reported:[46,47]





Here COD = cyclo-octa-1,5-diene and R = mesityl. Structure (B) is the first example of a complex containing only

phospha-alkyne and phospha-alkene molecules as ligands, both molecules of the latter compound being coordinated to the platinum atom via the LEP of the phosphorus atom, in contrast to t-BuC≡P. A characteristic feature of the NMR spectra of all three complexes of compound (VII) with zerovalent platinum is the very low spin–spin coupling constant ^1J(Pt, P), which is 62 Hz for $Pt(PPh_3)_2$(t-BuCP),[45] 144 Hz for structure (A), and 115 Hz for structure (B),[46] which indicates a greater amount of *s* character of the LEP of the phosphorus atom in the coordinated phospha-alkyne (VII).[46]

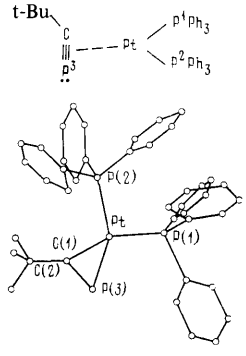
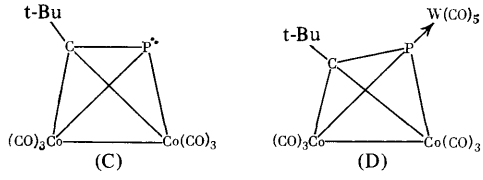


Figure 2. The structure of the complex of t-BuCP with zerovalent platinum.[45]

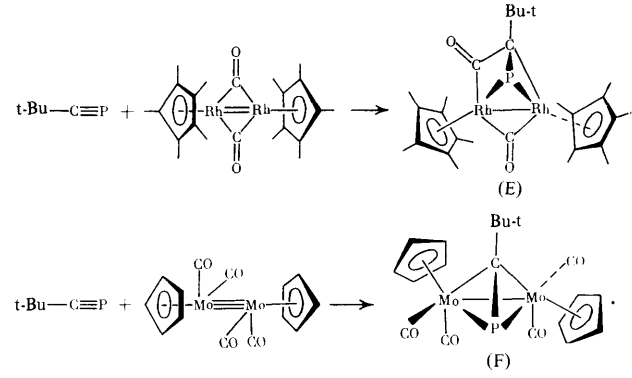
Equimolar amounts of t-BuCP and $Co_2(CO)_8$ react in tetrahydrofuran at room temperature with formation of the complex $Co_2(CO)_6$(t-BuCP) (C); it is a blood-red oil, which readily decomposes in air and in the light.[46] When the reaction is carried out in toluene with subsequent addition of tungsten pentacarbonyl, the crystalline complex $Co_2(CO)_6$(t-BuCP). .$W(CO)_6$ (D), which is stable in air and has m.p. 109–110 °C, is formed:[48]



Its structure, in which t-BuCP is a donor of six electrons, has been established by X-ray diffraction:[48] the bridging phospha-alkyne fragment and the two $Co(CO)_3$ groups form a tetrahedron, the phosphorus atom being coordinated to $W(CO)_5$. The C–P bond in the coordinated phospha-alkyne (VII) (1.695 Å) is much longer, as in the platinum complex, than in the free ligand. The shorter W–P bond in this complex compared with that in the familiar complex cis-$W(CO)_4$. .$(PMe_3)_2$ (2.502 Å) reflects, according to the authors,[48] an unusual hybridisation of the phosphorus atom in complex (D).

At −60 °C t-BuCP adds quantitatively to the metal–metal Rh=Rh and Mo≡Mo multiple bonds with formation of complexes (E) and (F), which are resistant to oxygen and atmospheric moisture:[49]

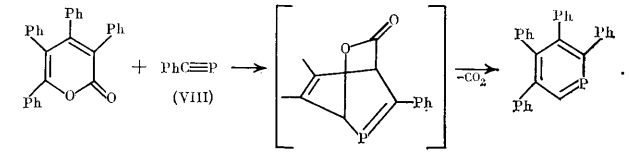
Scheme



The addition takes place in both cases at right angles to the metal–metal bond. X-Ray diffraction analysis of complex (F) showed[49] that its molecule contains the Mo_2PC tetrahedron; the length of the P–C bond increases to 1.713 Å, which is characteristic of a double bond.

The chemistry of the complexes of phospha-alkynes with transition metals constitutes a clear manifestation of an important feature of their electronic structure, noted in the analysis of the PES:[41] the much more significant separation of the π and *n* levels in phospha-alkynes than in nitriles. It is known for the majority of nitriles that they are coordinated to transition metals via the LEP of the nitrogen atom and that only some of them, having a powerful electron-accepting group at the carbon atom (for example, $CF_3C{\equiv}N$) add "sideways".[41] On the other hand, the coordination of the metal to the C≡P triple bond is characteristic of phospha-alkynes. The unshared electron pair of the phosphorus atom is involved only in complex (D) on formation of a bond with a tungsten atom, because the possibilities for coordination with participation of the π electrons of the C≡P bond have already been exhausted.[48]

An example of the involvement of a phospha-alkyne as a dienophile in the diene synthesis is provided by the [4 + 2]-cycloaddition of phenylphosphaethyne to α-pyrone and cyclopentadienone.[27] In both cases PhCP reacts at the instant of its evolution on thermolysis of the phospha-alkene $Ph(Me_3Si)C$ = PCl with the corresponding diene to form λ^3-phosphorines after the elimination of CO_2 or CO,[27] for example:



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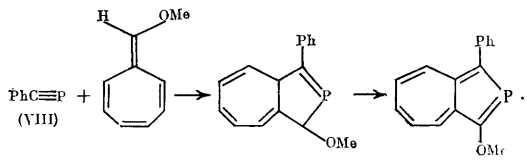
The data presented illustrate the first advances achieved in the chemistry of derivatives of monocoordinate phosphorus. The search for new methods of synthesis of stable phospha-alkynes and the improvement of the physicochemical experimental techniques will undoubtedly promote further successful development of research into this new and interesting field of the chemistry of OPC.

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During the preparation of the manuscript for the press, several new publications appeared on the subject of this review.[50–52] A study of the PES of phosphaethyne and fluorophosphaethyne by the method of Green functions

showed that the ionisation of the 1π and 3σ MO in HCP and also of the 2π, 4σ, and 1π MO in FCP can be described within the framework of a one-particle ionisation pattern.[50] The vibrational-rotational spectrum of fluorophosphaethyne has been investigated.[51] The observed frequency $\nu(C\equiv P) = 1670.842\ cm^{-1}$ agrees with $\nu(C\equiv P) = 1670.8\ cm^{-1}$ determined previously.[43]

The reaction involving the [8 + 2]-cycloaddition of phenylphosphaethyne to 8-methoxyheptafulvene leads to the formation of the previously unknown 2-phospha-azulene:[52]



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