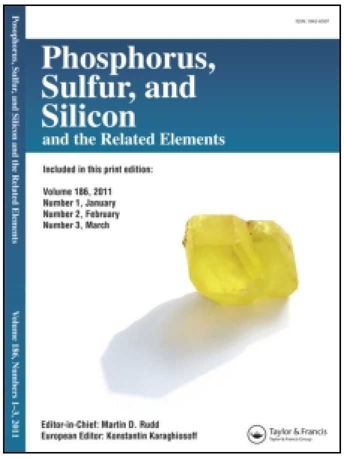


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

METAL AND ORGANOMETALLOIDAL PHOSPHITES AND PHOSPHONATES

P. N. Nagar[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

To cite this Article Nagar, P. N.(1993) 'METAL AND ORGANOMETALLOIDAL PHOSPHITES AND PHOSPHONATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 79: 1, 207 — 237
To link to this Article: DOI: 10.1080/10426509308034414
URL: http://dx.doi.org/10.1080/10426509308034414

Phosphorus, Sulfur, and Silicon, 1993, Vol. 79, pp. 207–237
Reprints available directly from the publisher
Photocopying permitted by license only

METAL AND ORGANOMETALLOIDAL PHOSPHITES AND PHOSPHONATES

P. N. NAGAR
Department of Chemistry, University of Rajasthan, Jaipur 302004, India

(Received December 5, 1988; in final form December 21, 1992)

Dialkyl phosphonates are versatile chemical reagents in which existence of phosphonate and phosphite equilibrium makes them an interesting series of ambidentate ligands. The mode of chemical bonding in their metal and organometal derivatives offers interesting possibilities. Phosphorus-31 NMR spectroscopy provides convincing evidence regarding the chemical bonding modes. The present review article describes the reactions of metal and organometal halides with dialkyl phosphonates (e.g., Li, Na, K, Ag, Ca, Zn, Cd, Co, Ti, Zr, V, Nb, Ta, Ru, Ir, W, Ni, Pd, Pt, B, Al, Si, Ge, Sn, Pb, P, As, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Yb, etc.).

Key words: Dialkyl phosphonates; dialkyl thiophosphonates; triorganometal dialkyl phosphites; triorganotin dialkyl(alkylene)thiophosphites; 2-dialkyl phosphonato-1,3,2-dioxaarsolanes and -arsenanes.

A. INTRODUCTION

Dialkyl phosphonates have a long history, having been described for the first time in 1905.[1] These are versatile chemical reagents which undergo a wide variety of reactions in which phosphorus acts either as a nucleophilic or an electrophilic center.

The structure of phosphorous acid [$P(OH)_3$ or $H(O)P(OH)_2$] as well as of its diester [$(RO)_2POH$ or $(RO)_2P(O)H$][2] was a subject of considerable controversy in the early days of phosphorus chemistry which was resolved with the development of spectroscopic techniques. It was established that phosphorus acid remains in the phosphonic acid, $H(O)P(OH)_2$ form and similarly its diester also remains in the phosphonate, $(RO)_2P(O)H$ form. The name suggested by the nomenclature commission of IUPAC for the diester of phosphonic acid is dialkyl phosphonate[3] although the names dialkyl hydrogenphosphonate and dialkyl phosphite continue to be equally popular in the literature. Alkali metal derivatives exist in the phosphite [$(RO)_2POM$] form.[2] The phosphonate (P^V)-phosphite (P^{III}) equilibrium in dialkyl phosphonates makes them an interesting series of ambident ligands. Dialkyl phosphonates also have a wide range of industrial applications.[4–8] The mode of chemical bonding in metal and organometalloidal derivatives offers interesting possibilities, and the formations of M—P(O), M—O—P, M—O—P=O, and M—O—P=O → M, (M = metal) bonded derivatives have been postulated. In fact, there was considerable confusion in the early literature regarding the structural features of these compounds. Phosphorus-31-NMR spectroscopy, however, has been able to resolve many of these problems and it may be considered as probably the most informative technique for distinguishing the above types of chemical bonding modes.

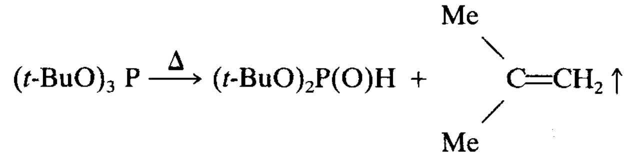
In view of their interesting structural features, a brief review is presented here on metal and organometalloidal phosphites and phosphonates, emphasizing the work carried out during the last two decades. For the sake of comparison, the derivatives of dialkyl thiophosphonates, trialkyl phosphites, dialkyl alkylphosphonates and dialkyl phosphinic acids will also be discussed briefly.

B. GENERAL

Several methods for the synthesis of dialkyl phosphonates have been recommended in the literature[9–36] but, for all practical purposes, lower dialkyl phosphonates are obtained in excellent yields by adding an alcohol to phosphorus trichloride in refluxing *n*-hexane.[9,10]

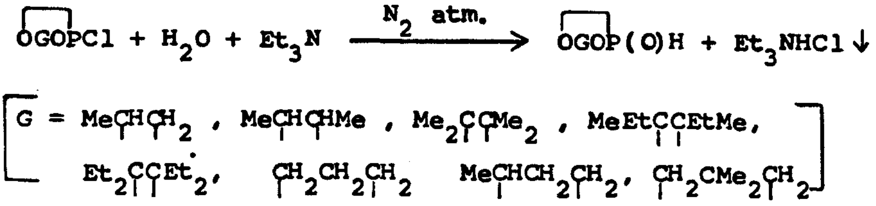
$$PCl_3 + 3ROH \rightarrow (RO)_2P(O)H + 2HCl\uparrow + RCl\uparrow$$

Ditertiary-butyl-phosphonate can be obtained by thermal decomposition of tri-*t*-butyl phosphite under reduced pressure.[11,12]

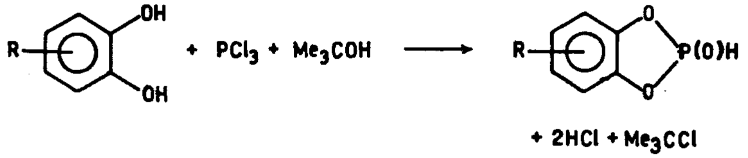


$$(t\text{-}BuO)_3\,P \xrightarrow{\Delta} (t\text{-}BuO)_2P(O)H + Me_2C{=}CH_2\uparrow$$

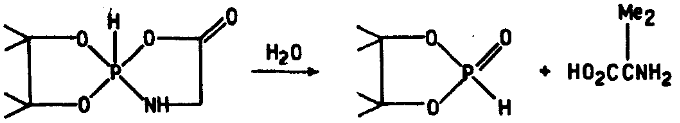
O,O-Alkylene phosphonates[30–35] are synthesized by the controlled hydrolysis of 2-chloro-1,3,2-dioxaphospholanes and phosphorinanes in the presence of a suitable base.



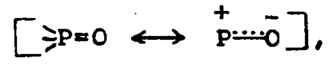
O,O-Arylene phosphonates[36] are synthesized by the reaction of phosphorus trichloride with a mixture of substituted catechols and *t*-butanol.



It is also of interest to note that water reacts with spiro phosphoranes that contain the P—H bond to displace the amino acid and form cyclic phosphonates.[37]



Dialkyl phosphonates are generally volatile liquids and, due to the dipole-dipole interactions between the phosphoryl groups

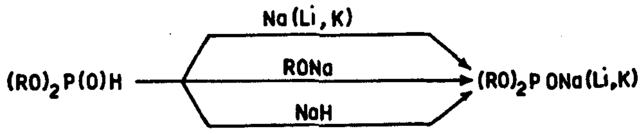


such esters have higher boiling points than the corresponding trialkyl phosphites.[38–42] On the basis of detailed spectroscopic studies [Raman,[43], IR,[44–46], UV,[47] ^{1}H,[48,49] ^{31}P,[50–54] and ^{13}C, spectra], it was concluded that dialkyl phosphonates exist entirely in the phosphonate form $(RO)_2P(O)H$ to the exclusion of the phosphite structure, $(RO)_2POH$.[53] The existence of a phosphonate-phosphite equilibrium has also been postulated in the literature to explain certain reactions.[2,55,57,58]

C. DIALKYL PHOSPHONATE DERIVATIVES OF MAIN GROUP ELEMENTS

(i) Alkali Metals (Li, Na and K)

The alkali metal derivatives of dialkyl phosphonates are prepared by this interaction with alkali metals, sodium alkoxide or by sodium hydride in organic solvents.[59–63] The lithium salts have also been prepared by the interaction of trialkyl phosphites with lithium bromide.[63]



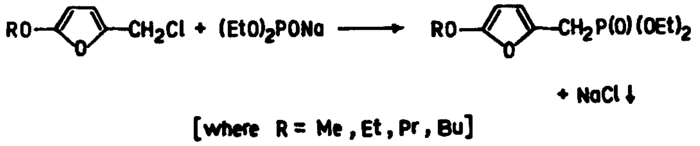
$$(RO)_3P + LiBr \xrightarrow{C_6H_6} (RO)_2POLi + RBr$$

The alkali metal salts are white powdery solids soluble in organic solvents (e.g. ether, cyclohexane, light petroleum, etc.). The IR spectra of these salts are devoid of a phosphoryl (νP=O) absorption band but show the presence of a strong absorption at 1050 cm^{-1}, which is characteristic of both P—$\bar{O}$ and P—O—R groups. Daasch[58] favors a structure containing the covalent oxygen-metal bond [P—O—M]. The ^{31}P NMR shift values have been found in the range 139 to 153 ppm which corresponds to the ^{31}P NMR shift values found in phosphite structure.[50]

The alkali metal salts are powerful nucleophilic reagents and react with a wide variety of substances which contain electrophilic centers. Sodium dialkyl phosphites react with organic halides to yield compounds each of which contain a carbon-phosphorus bond (Michaelis-Becker reaction).[64]

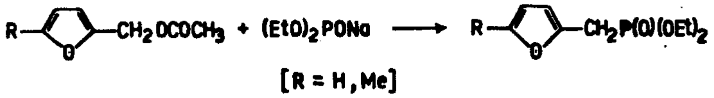
$$(RO)_2PONa + R'X \rightarrow (RO)_2P(O)R' + NaX\downarrow$$

The Michaelis-Becker reaction[64] with non-activated alkyl halides in the presence of crown ethers gives only moderate yields of dialkyl alkylphosphonates. Little or no reaction appears to take place in the absence of crown ethers.[65] Crown ethers behave as phase transfer catalysts. The reaction of 5-substituted-2-(chloromethyl)furanes with sodium dialkyl phosphite in benzene gives 38–57% phosphonylated compounds[66]:



[where R = Me, Et, Pr, Bu]

When R is an acyl group, the reaction gives diphosphonylated products. A similar reaction with furfuryl alcohol derivatives also gives phosphonylated products in 10–23% yields.[66]



[R = H,Me]

Methylene diphosphonic tetraalkyl esters are prepared by condensing sodium dialkyl phosphites with an excess of dichloromethane.[67]

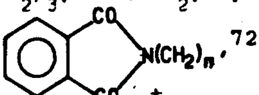
$$2(RO)_2PONa + CH_2Cl_2 \xrightarrow[C_6H_6/\text{Hexane}]{40°C} [(RO)_2P(O)]_2CH_2 + 2NaCl\downarrow$$

On acid hydrolysis these esters yield methylene diphosphonic acid.[68] The acid as well as the ester are used as components and intermediates in the manufacture of metal sequestrants, polymer plastisizers, fire retardants for polymers, antioxidizing agents and components of detergents.[67,68]

An extensive survey of the literature published during the last two decades on the reactions of sodium dialkyl phosphites with organic moieties is summarized below.

$$(RO)_2PONa + R'X \longrightarrow (RO)_2P(O)R' + NaX\downarrow$$

where R' = $Cl(CH_2)_3$,[62] $MeOCH_2$,[69] $MeC(O)(CH_2)_n$,[70] Ph_3C,[71] $H_2N(CH_2)_n$,[72]



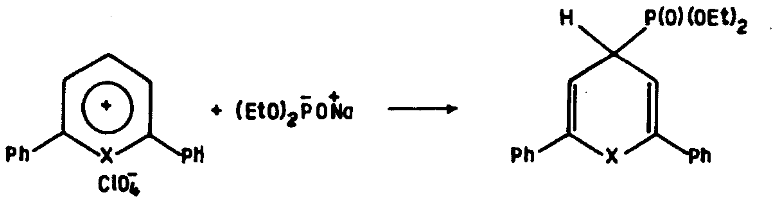
,[72] $EtCO_2CH_2$,[73] $ClCH_2C(O)$,[73] $R_2NC(O)CH_2$,[74] $(Me_2C{=}CHCH_2)_2\overset{+}{N}Me_2$,[75] $EtCO_2(CH_2)_n$,[73,76] C_6Cl_5,[77]

Sodium dialkyl phosphites react with oximes to give diphosphonates in 14–30% yields.[78]

$$R^1R^2C{=}NOH + (RO)_2\bar{P}O\overset{+}{N}a \rightarrow R^1R^2C[P(O)(OR)_2]NHP(O)(OR)_2$$

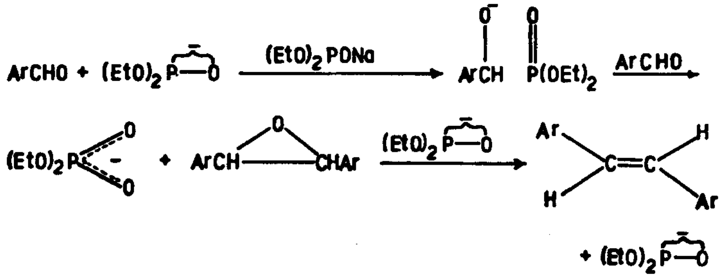
$$\left[\begin{array}{l}\text{where } R = Et, Pr, Me_2CH;\ R^1 = Me, Et, Ph;\\ \quad R^2 = H, Me;\ R^1R^2 = (CH_2)_5\end{array}\right]$$

Diethyl(2,6-diphenyl-4H-pyran-4-yl) phosphonate was prepared by adding an equimolar amount of a benzene solution of sodium diethyl phosphite to 2,6-diphenylpyrylium salt suspended in dry THF at −78°C. The purity of the product was judged by its NMR and TLC assay with those of an analytical sample[79]



[X = O or S]

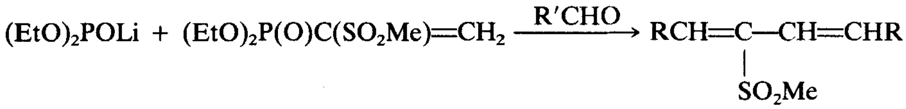
Full details about the synthesis of stilbenes by the reaction of sodium diethyl phosphite with aromatic aldehydes are available in the literature. The suggested mechanism involves the formation of an oxiran intermediate followed by a further attack of a diethyl phosphite anion to give a Wadsworth Emmons intermediate leading to a stilbene.[80]



The electrochemical oxidation of sodium dialkyl phosphites on a platinum electrode in dry acetonitrile, in the presence of 0.1 M $NaClO_4$, and aromatic or heteroaromatic compounds at ambient temperature in an inert environment yields compounds of the type, $RP(O)(OR')_2$, (R = thienyl furyl, naphthyl, anisyl, quinolinyl; R′ = Et, Pr, Bu).[81] In the presence of aromatic or heterocyclic compounds, 15–30% yields of $(RO)_2P(O)R'$ were obtained. Similar oxidation in the presence of $ET_4\overset{+}{N}B\overset{-}{F}_4$ gave the following products[82]:

$$(RO)_2PONa \xrightarrow{MeCN} (RO)_2P(O)H + RP(O)(OR)_2 + (RO)_3P{=}O + (RO)_2P(O)F + (RO)_2PF$$

Functionalized dienes (and tetraenes) were synthesized (in 26–63% yield) by the one pot reaction of phosphoryl stabilized carbanions (prepared by the Michael addition of diethyl lithiophosphite to vinyl phosphonates) with aromatic aldehydes.[83]



$$(EtO)_2POLi + (EtO)_2P(O)C(SO_2Me){=}CH_2 \xrightarrow{R'CHO} RCH{=}\underset{\displaystyle SO_2Me}{\underset{|}{C}}{-}CH{=}CHR$$

[where R′ = Ph, p-ClC_6H_4, styryl, 2-thienyl]

(ii) *Alkaline Earth Metals and Group IIB Metals*

The reactions of dialkyl phosphonates with II-A and II-B metal salts[84] give oligometric products. The nature of the reaction is dependent upon the substituents present in the phosphonate as well as on the nucleophilicity of the metal salts.

$$n(RO)_2P(O)H + nMX_2 \rightarrow [ROPH(O)OM]_nX + nRX$$

$$2(RO)_2P(O)H + MX_2 \rightarrow [RPO(O)HO]_2M + 2RX$$

$$\begin{bmatrix} \text{where R = Me, Et, Bu; M = Ca, Zn, Cd, Mn, Co;} \\ \text{X = Cl, NO}_3\text{, Ac} \end{bmatrix}$$

Phosphonate salts of divalent metal ions (Mg, Mn, Zn and Ca) have also been synthesized by combining aqueous solutions of phosphonic acid and solutions of metal salts. In this way salts of the type, $M[O_3PC_nH_{2n+1}].H_2O$ (M = Mg, Mn, Zn, n = 1–12; M = Ca, Cd, n = 1–4); $M[O_3PPh].H_2O$ (M = Mg, Mn, Zn); $Ca[HO_3PPh]_2$ and $Ca[HO_3PC_nH_{2n+1}]_2$ ($n \geq 5$) have been prepared. The structure of $Mn[O_3PPh].H_2O$ has been solved by X-ray crystallography.[85]

(iii) Derivatives of Group IIIA Elements (B and Al)

Boron trichloride[86] forms 1:1 adducts with dialkyl phosphonates at lower temperatures (−80°). These adducts decompose at ambient conditions with the evolution of an alkyl chloride. In contrast to the above, the reactions between aluminium (III) chloride and dialkyl phosphonates[87] in different molar ratios proceed with the evolution of hydrogen chloride and the formation of white insoluble products.

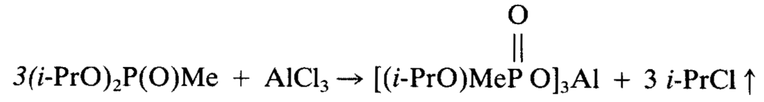
$$2(RO)_2P(O)H + AlCl_3 \rightarrow Al[OP(O)(OR)R]_2Cl + 2HCl\uparrow$$

$$3(RO)_2P(O)H + AlCl_3 \rightarrow Al[OP(O)(OR)R]_3 + 3HCl\uparrow$$

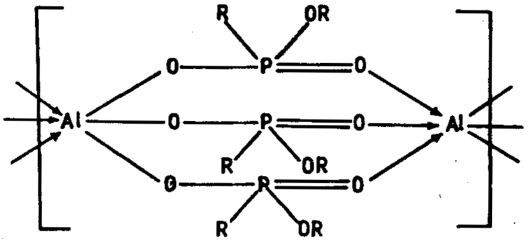
[where R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu]

The IR spectra show the presence of νAl—O—P(O) (590–362 cm^{-1}) νP—C (715 cm^{-1}) and νP=O (1200–1215 cm^{-1}) characteristic absorption bands. The phosphoryl absorption band is shifted towards lower wave numbers due to intermolecular coordination of the phosphoryl group with aluminium.

Interestingly, similar reactions of $AlCl_3$,[88] $EtAlCl_2$[89] and $Al(OR)_3$[90,91] with dialkyl alkylphosphonates and trialkyl phosphites proceed with the evolution of an alkyl chloride and coordination polymers of the following type are formulated:



$$3(i\text{-}PrO)_2P(O)Me + AlCl_3 \rightarrow [(i\text{-}PrO)Me\overset{\overset{\displaystyle O}{\|}}{P}O]_3Al + 3\ i\text{-}PrCl\uparrow$$



$$n(R'O)_2P(O)R'' + nEtAlCl_2 \xrightarrow{N_2} [EtAlCl_2(O)PR''(OR')_2]_n \rightarrow$$

$$[(R'O)R''P(O)OAlEtCl]_n + (2n-1)R'Cl\uparrow$$

$$(RO)_3P + EtAlCl_2 \rightarrow [(RO)_3PAlEtCl_2] \rightarrow [(RO)RP(O)AlEtCl] + RCl\uparrow$$

$$3(RO)_2P(O)R'' + (R'O)_3Al \xrightarrow{N_2} [(RO)R''P(O)O]_3Al + 3R'OR$$

The products thus formed have been characterized by elemental analyses and IR measurements.[88-91]

(iv) *Derivatives of Group IVA Elements (Si, Ge, Sn and Pb)*

The Michaelis Becker[64] and Michaelis Arbuzov[92] reactions constitute a very convenient method for the synthesis of dialkyl alkylphosphonates. The work on Si, Sn, Ge and Pb appears to be mainly confined to the triorganometal derivatives.

(a) *Triorganosilicon derivatives.* Organosilicon and organophosphorus chemistry are probably the most thoroughly studied areas of elemento organic chemistry. In recent years there has been a rapid increase in the study of both synthetic methods and the properties of compounds containing the Si—O—P linkage.

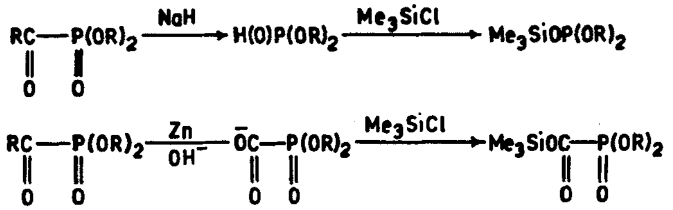
The first inorganic compound containing the Si—O—P[93,94] unit was synthesized in 1800. Apparently, the first organosilicon compound containing a Si—O—P unit was $[(CH_3)_3SiO]_3P{=}O$.[95] But later on, Voronkov[96] reported a number of compounds containing Si—O—P linkages.

The reactions of sodium dialkyl phosphites and trialkyl phosphites with triorganosilicon halides were reviewed[97] in 1968. However, the structural features of the product [e.g. phosphite, Si—O—P or phosphonate, Si—P(O)] were not fully established at that time. In recent years, different spectroscopic techniques have been employed to identify the silicon phosphites and, on that basis; a phosphite structure [Si—O—P, $\delta\ ^{31}P = 113 \pm 3$ ppm] has been established.

$$R_3SiX + (RO)_2PONa \rightarrow R_3SiOP(OR)_2 + NaX\downarrow$$

$$R_3SiX + (RO)_3P \rightarrow R_3SiOP(OR)_2 + RX\uparrow$$

Alternatively, these were also synthesized by the reactions mentioned below:



$$\underset{\substack{\| \\ O}}{RC}-\underset{\substack{\| \\ O}}{P}(OR)_2 \xrightarrow{NaH} H(O)P(OR)_2 \xrightarrow{Me_3SiCl} Me_3SiOP(OR)_2$$

$$\underset{\substack{\| \\ O}}{RC}-\underset{\substack{\| \\ O}}{P}(OR)_2 \xrightarrow[OH^-]{Zn} {}^-\underset{\substack{\| \\ O}}{OC}-\underset{\substack{\| \\ O}}{P}(OR)_2 \xrightarrow{Me_3SiCl} Me_3SiO\underset{\substack{\| \\ O}}{C}-\underset{\substack{\| \\ O}}{P}(OR)_2$$

$$\longrightarrow Me_3SiOP(OR)_2 + CO_2\uparrow$$ (Reference 99, 100)

$$(RO)_2P(O)H + Na \xrightarrow{CO_2} (RO)_2P(O)CO_2Na \xrightarrow{Me_3SiCl}$$

$$(RO)_2POSiMe_3 + CO_2\uparrow$$ (Reference 101)

Chojnowski *et al.*[102,103] and Pudovik *et al.*[104] reported the formation of phosphite derivatives in the following reactions:

$$(MeO)_3P + Me_3SiI \xrightarrow{N_2} (MeO)_2POSiMe_3$$

$$+ MeI[\delta\ ^{31}P = 126.7\ ppm(sept);\ J(POCH)\ 11\ Hz]$$

$$\overline{X_1XX_2}PCl + MeC(O)N(SiMe_3)_2 \rightarrow \overline{X_1XX_2}POSiMe_3$$

In contrast, similar reactions were claimed by Newlands[105] and by Glidewell *et al.*[106] to have yielded silyl phosphonate [SiP(O) ~ $\delta\,^{31}P = 6.5$ ppm] derivatives:

$$(i\text{-PrO})_2PONa + Ph_3SiCl \rightarrow (i\text{-PrO})_2P(O)SiPh_3 + NaCl\downarrow$$

$$(i\text{-PrO})_3P + Ph_3SiCl \rightarrow (i\text{-PrO})_2P(O)SiPh_3 + i\text{-PrCl}\uparrow$$

$$(i\text{-PrO})_2P(O)Cl + LiSiPh_3 \rightarrow (i\text{-PrO})_2P(O)SiPh_3 + LiCl\downarrow$$

$$(i\text{-PrO})_2PCl + KOSiPh_3 \rightarrow (i\text{-PrO})_2P(O)SiPh_3 + KCl\downarrow$$

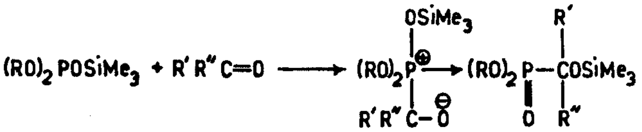
$$(i\text{-PrO})_2PCl + NaOSiMe_3 \rightarrow (i\text{-PrO})_2P(O)SiMe_3 + NaCl\downarrow$$

The reaction of diisopropyl phosphonate with hexamethyldisilazane was also reported to yield a phosphonate product.[106]

$$2(i\text{-PrO})_2P(O)H + HN(SiMe_3)_2 \text{ light petroleum} \rightarrow 2(i\text{-PrO})_2P(O)SiMe_3 + NH_3\uparrow$$

It seems that the above results require rechecking under rigorous conditions (e.g., inert atmosphere etc.) particularly in view of the more recent and thorough studies of Chojnowski *et al.* which favor the formation of phosphite derivatives.[102,103]

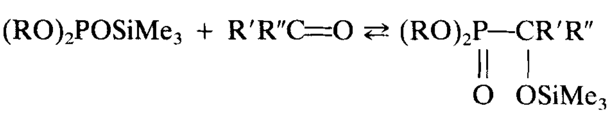
The triorganosilyl phosphites behave as strong nucleophilic reagents and are widely used in organic synthesis. They react with a wide variety of saturated and unsaturated carbonyl compounds. Dialkyl trimethylsilyl phosphites readily add to the carbonyl groups of aldehydes and ketones with the formation of α-trialkylsiloxy alkylphosphonates.[107-114]



$$(RO)_2POSiMe_3 + R'R''C{=}O \longrightarrow \underset{R'R''C-\overset{\ominus}{O}}{\overset{OSiMe_3}{(RO)_2\overset{\oplus}{P}}} \longrightarrow (RO)_2\underset{O}{P}-\underset{R''}{\overset{R'}{C}}OSiMe_3$$

It has been suggested[110,113,115] that the reaction begins with a nucleophilic attack of the phosphorus atom on a carbonyl carbon atom. These adducts are found to be thermally unstable and decompose upon heating to the starting materials.[116,117]

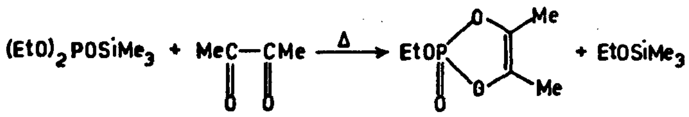
The silyl phosphites add vigorously to the esters and nitriles of pyruvic acids,[118] acetyl phosphonates,[119] benzoyl phosphonates[120] and biacetyl[121-123] with the formation of the corresponding phosphonate.



$$(RO)_2POSiMe_3 + R'R''C{=}O \rightleftarrows (RO)_2\underset{O}{\overset{}{P}}\!-\!\underset{OSiMe_3}{CR'R''}$$

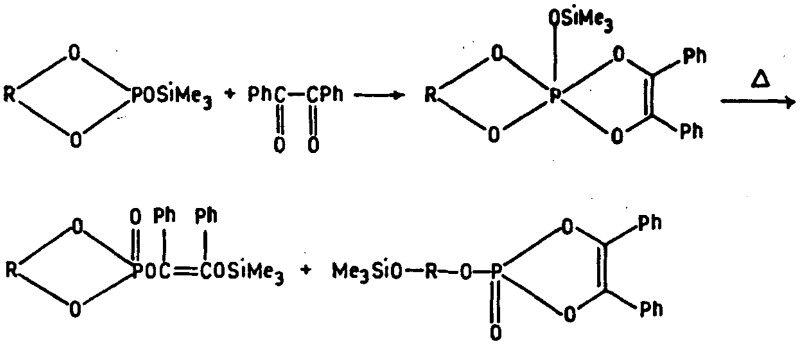
$$\left[\begin{array}{l} \text{where } R = Et, Me_3Si;\ R' = Me, Ph; \\ \qquad\quad R'' = CO_2Me, CN, P(O)(OEt)_2, Ac \end{array}\right]$$

As a result of silotropic transformations and phosphonate-phosphate rearrangements, dioxaphospholen and trimethylsilicon ethoxide are formed from diethyl trimethylsilyl phosphite and diacetyl.[123]



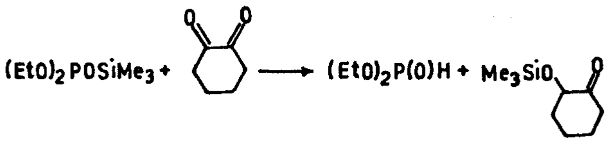
Similarly, in the reactions of silyl phosphite with benzyl, the phosphonate phosphate rearrangement is faster than the migration of the silyl group and the consequent adduct upon heating is converted to a dioxaphospholen.[122,124]

The silylated spiro phosphoranes[125] are formed at low temperatures (~ –50°C) which, upon heating are transformed into corresponding cyclic phosphates.



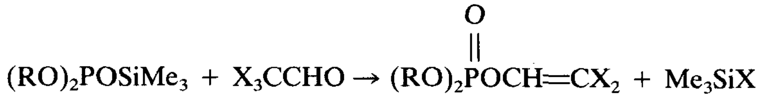
[where R = –CH(Me)CH(Me)–, o-C_6H_4–]

The attempts to obtain adducts of silyl phosphites and cyclohexane 1,2-dione were unsuccessful. The reaction results in the quantitative formation of diethyl phosphonate and α-trimethylsiloxycyclohexanone.[126]



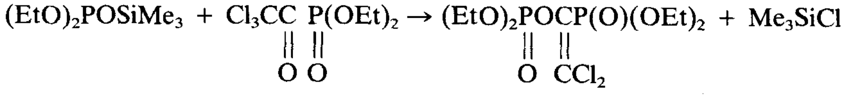
Contrary to the above, the reaction between silyl phosphite and acetoacetic ester exclusively yields an adduct.[109,127]

The interaction of silyl phosphite with trihalogenoacetaldehyde initially leads to phosphonates which decompose on heating into vinyl phosphonates.[128,129]



$$(RO)_2POSiMe_3 + X_3CCHO \rightarrow (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}OCH{=}CX_2 + Me_3SiX$$

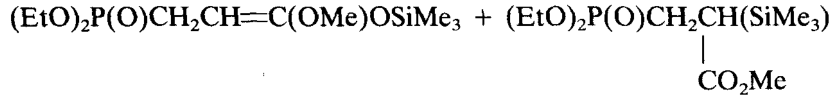
The reaction of silyl phosphite with trichloroacetyl phosphonate yields unsaturated phosphoryloxy phosphonates.[130]



$$(EtO)_2POSiMe_3 + Cl_3C\underset{\underset{\displaystyle O}{\|}}{C}\underset{\underset{\displaystyle O}{\|}}{P}(OEt)_2 \rightarrow (EtO)_2\underset{\underset{\displaystyle O}{\|}}{P}O\underset{\underset{\displaystyle CCl_2}{\|}}{C}P(O)(OEt)_2 + Me_3SiCl$$

The silyl phosphites react vigorously with α,β-unsaturated carbonyl compounds via both 1,2- and 1,4-addition pathways.[131]

$(EtO)_2POSiMe_3 + CH_2{=}CHCO_2Me \rightarrow$

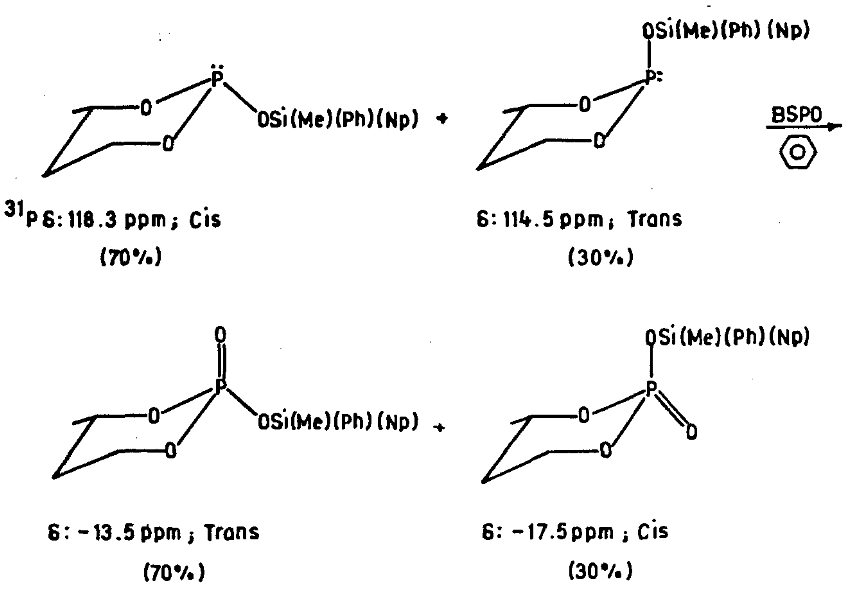


$$(EtO)_2P(O)CH_2CH{=}C(OMe)OSiMe_3 + (EtO)_2P(O)CH_2\underset{\displaystyle CO_2Me}{\underset{|}{C}}H(SiMe_3)$$

The trimethylsilyl diethylphosphite also reacts with 5-benzylidene barbituric acid and the reaction proceeds by 1,4-shift mechanism.[132,133]

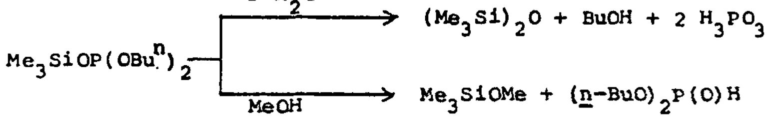
The reactions of silyl phosphites with *p*-quinones,[122,134] cyclohexanethione,[135] nitrosoalkanes,[136] heterocumulenes[137,138] diaza compounds,[139,140] phenyl azide,[141] epoxides[142] and diketene[143] have been recently reported in the literature and all yield adducts.

Certain silyl phosphites are selectively oxidized by bis(trimethylsilyl)peroxide at room temperature to respective oxyphosphoryl derivatives with retention of configuration at the phosphorus atom.[144]



The fast oxygen transfer to P(III) compounds and high stereospecificity was explained by the ionic character of the process.[144]

Keeber *et al.*[145] studied the fission reactions of a silyl phosphite with water and methanol.



$$Me_3SiOP(OBu^n)_2 \xrightarrow{5\,H_2O} (Me_3Si)_2O + BuOH + 2\,H_3PO_3$$

$$Me_3SiOP(OBu^n)_2 \xrightarrow[MeOH]{} Me_3SiOMe + (\underline{n}\text{-}BuO)_2P(O)H$$

Cyclic silyl phosphites undergo the Arbuzov reaction with halo acetones and forms cyclic acetonyl phosphonates. The reaction in propylene oxide gives 24%

yields while in MeCN/cyclohexene oxide gives 43% yields of cyclic acetonyl phosphonates.[146]

$$\overline{OCH_2CR_2CH_2OP}OSiMe_3 + MeC(O)CH_2X \rightarrow$$

$$\overline{OCH_2CR_2CH_2OP}(O)CH_2C(O)Me + Me_3SiX$$

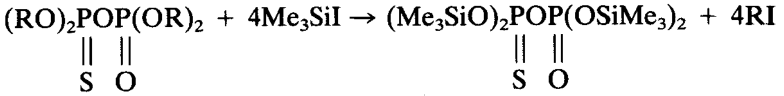
$$[\text{where } R = H, Me;\ X = Br, I]$$

Michalski *et al.*[147,148] and Olah *et al.*[149] studied the transesterification reactions of $(R'O)_2P(O)X'$, with Me_3SiI.

$$X'(O)P(OR')_2 + 2Me_3SiI \rightarrow X'(O)P(OSiMe_3)_2 + 2R'I$$

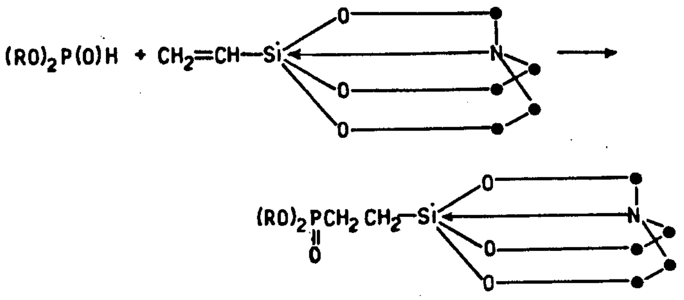
$$\left[\begin{array}{l}\text{where } X' = H, Cl, Br, NH_2, NHR, NR_2, SR, BrCH\pi 2CH_2\text{—}\\ \quad \text{—}HC = CCH_2\text{—}, (EtOOC)_2CHCH_2\text{—}, PhCH_2\text{—}\end{array}\right]$$

A similar reaction is also used for ester of polyphosphoric acid with the preservation of the P—O—P linkage.



$$(RO)_2\underset{\underset{S}{\|}}{P}O\underset{\underset{O}{\|}}{P}(OR)_2 + 4Me_3SiI \rightarrow (Me_3SiO)_2\underset{\underset{S}{\|}}{P}O\underset{\underset{O}{\|}}{P}(OSiMe_3)_2 + 4RI$$

Phosphinosilatranes[150] have been prepared by heating 1-vinyl silatrane with dialkyl phosphonates.



[where R = Me, Et, Pr]

Pudovik *et al.* have recently synthesized dialkyl trimethylsilyl dithiophosphites $[(RS)_2POSiMe_3]$ in 53–55% yields by heating $(RS)_2PCl$ with $(Me_3Si)_2NAc$.[151]

(b) *Triorganogermanium derivatives.* The reactions of sodium dialkyl phosphites with trialkylgermanium halides and of tetraalkyl pyrophosphites with trialkyl germanium alkoxides have been shown by Novikova *et al.*[152] to give trialkylgermanium dialkyl phosphites.

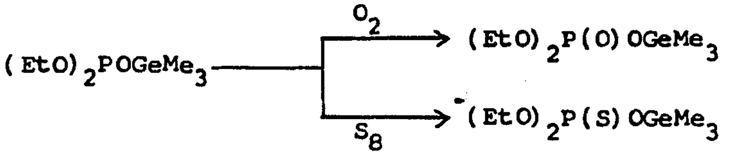
$$(RO)_2PONa + R_3'GeX \xrightarrow{\text{argon}} (RO)_2POGeR_3' + NaX\downarrow$$

$$[\text{where } R = Et,\ R' = Me, Et,\ X = \text{halogen}]$$

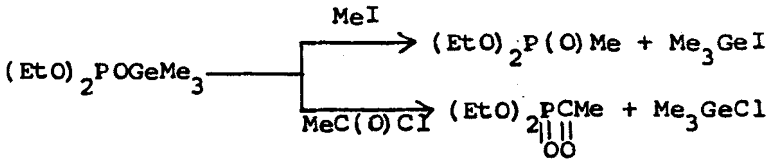
$$(RO)_2POP(OR)_2 + R_3'GeOR \rightarrow (RO)_2POGeR_3' + (RO)_3P$$

The phosphite structure of the product [e.g. $(EtO)_2POGeMe_3$, $\delta\ ^{31}P = 126$ ppm] has been confirmed on the basis of its ^{31}P NMR chemical shift which is in the region of tricoordinated phosphorus atom.

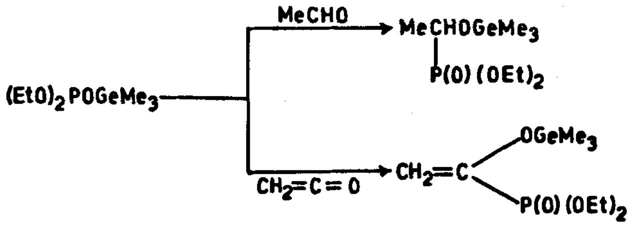
Trimethylgermanium diethyl phosphite readily combines with oxygen and sulfur and forms the corresponding phosphate and monothiophosphate derivatives, respectively.



The germanium phosphite shown, undergoes the Arbuzov reaction with alkyl and acyl halides with the liberation of heat.



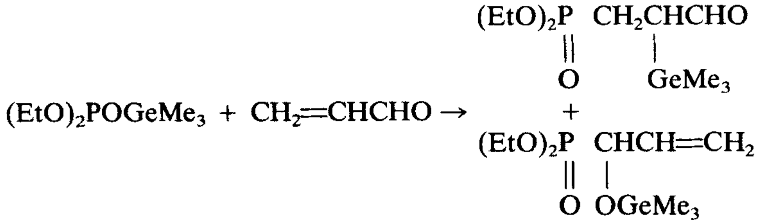
An exothermic reaction occurred between a germanium phosphite and a saturated or an unsaturated carbonyl compound yielding the adducts shown below:



2

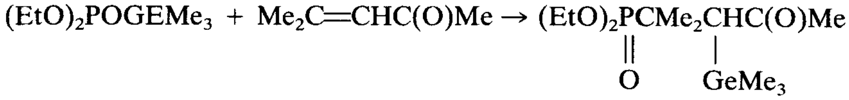
These adducts have been characterized by IR and NMR spectral data.[152]

The reaction of the same germanium phosphite with acrolein yields a 1,2 ($\delta\ ^{31}P = 23$ ppm) and a 3,4 addition product ($\delta\ ^{31}P = 19$ ppm).



$$(EtO)_2POGeMe_3 + CH_2{=}CHCHO \rightarrow \underset{\substack{\| \\ O}}{(EtO)_2P}\ \underset{\substack{| \\ GeMe_3}}{CH_2CHCHO} + \underset{\substack{\| \\ O}}{(EtO)_2P}\ \underset{\substack{| \\ OGeMe_3}}{CHCH{=}CH_2}$$

The reaction between the germanium phosphite and mesityl oxide requires heating (130°C, 1.5 hr.) to form a 1,2-addition product.



$$(EtO)_2POGEMe_3 + Me_2C{=}CHC(O)Me \rightarrow (EtO)_2\underset{\displaystyle O}{\overset{}{\underset{\|}{P}}}CMe_2\underset{\displaystyle GeMe_3}{\underset{|}{C}}HC(O)Me$$

Similarly the α,β-unsaturated nitriles, carboxylic esters and diethyl vinylphosphonate also yield adducts with germyl phosphites.[152]

(c) *Organotin(IV) and allied derivatives.* Arbuzov and Pudovik[153,154] in 1948 used the Arbuzov reaction for the preparation of $R_3SnP(O)(OR)_2$ and postulated the formation of a direct tin phosphorus [Sn—P(O)] linkage in these derivatives. The products reported were not characterized by spectroscopic techniques.

Novikova *et al.*[152] in 1975 studied the reactions of sodium dialkyl phosphites with triorganotin halides and of tetraalkyl pyrophosphites with triorganotin alkoxides and postulated the formation of direct tin oxygen phosphorus [Sn—O—P] linkages in these derivatives.

$$(RO)_2PONa + R'_3SnX \xrightarrow[\text{atm.}]{\text{argon}} (RO)_2POSnR'_3 + NaX\downarrow$$

$$(RO)_2POP(OR)_2 + R'_3SnOR \rightarrow (RO)_2POSnR'_3 + (RO)_3P$$

$$[\text{where } R = Et,\ R' = Me,\ Et,\ X = \text{halogen}]$$

Alternatively tin phosphites can also be prepared by the exchange reaction.

$$Me_3SiOP(OEt)_2 + EtOSnEt_3 \rightarrow Et_3SnOP(OEt)_2 + Me_3SiOEt$$

The structure of triethyltin diethyl phosphite was supported by ^{31}P NMR spectroscopy ($\delta\ ^{31}P = 76$ ppm).

P. N. Nagar[155] carried out detailed investigations on the reactions of anions of dialkyl phosphonates with tri- and diorganotin chlorides. Sodium dialkyl phosphites were prepared *in situ* and were allowed to react with organotin chlorides at room temperature to yield organotin dialkyl phosphites.

$$(RO)_2PONa + R'_3SnCl \rightarrow (RO)_2POSnR'_3 + NaCl\downarrow$$

$$[\text{where } R = Me,\ Et,\ n\text{-}Pr,\ i\text{-}Pr,\ n\text{-}Bu;\ R' = Me,\ Et,\ n\text{-}Pr,\ n\text{-}Bu]$$

$$2(RO)_2PONa + R'_2SnCl_2 \rightarrow [(RO)_2PO]_2SnR'_2 + 2NaCl\downarrow$$

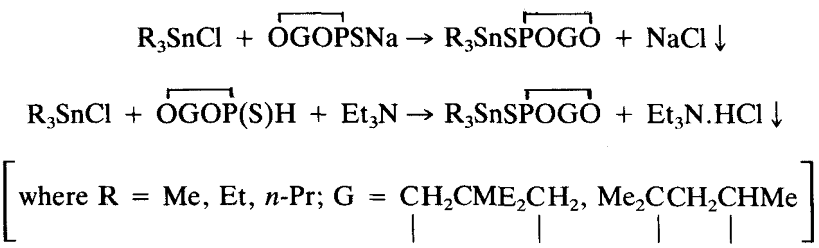
$$[\text{where } R = Me,\ Et,\ n\text{-}Pr;\ R' = Me,\ Et]$$

Identical products were also obtained when organotin chlorides were complexed with dialkyl phosphonates and then heated with triethylamine. Organotin dialkyl phosphites were volatile liquids (except R′ = Ph). IR spectra of organotin dialkyl phosphites are devoid of a phosphoryl (P=O) absorption band in the region 1270 ± 10 cm^{-1}. A new band is present at 680–630 cm^{-1} which is assigned for a νSn—O—P absorption. The ^1H spectra have no P—H proton signal and ^{31}P spectra show resonance peaks in the region of 139 ± 2 ppm, characteristic of a phosphite structure. The ^{119}Sn NMR spectrum of tripropyltin dipropyl phosphite shows a resonance signal at 137.38 ppm which supports the tetracoordinate nature of tin.[155]

For the sake of comparison triorganotin dialkyl thiophosphites have also been synthesized by the methods described below.[156]

$$R_3SnCl + (EtO)_2PSNa \rightarrow R_3SnSP(OEt)_2 + NaCl\downarrow$$

$$R_3SnCl + (EtO)_2P(S)H + Et_3N \rightarrow R_3SnSP(OEt)_2 + Et_3N.HCl\downarrow$$



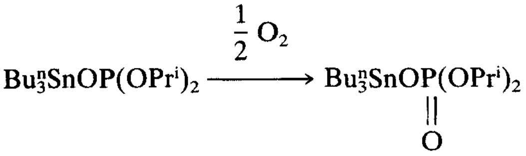
$$R_3SnCl + \overline{OGOP}SNa \rightarrow R_3SnS\overline{POGO} + NaCl\downarrow$$

$$R_3SnCl + \overline{OGOP}(S)H + Et_3N \rightarrow R_3SnS\overline{POGO} + Et_3N.HCl\downarrow$$

$$\left[\text{where } R = Me, Et, n\text{-}Pr;\ G = \underset{|}{C}H_2CME_2\underset{|}{C}H_2,\ Me_2\underset{|}{C}CH_2\underset{|}{C}HMe\right]$$

The products thus obtained are also colorless volatile liquids having a pungent odor and are found to be monomeric in nature. The δ ^{31}P for these compounds ranges between 109–116 ppm. On the basis of spectroscopic properties (IR, NMR (^1H and ^{31}P) the mode of chemical bonding with tin appears to occur through the sulfur atom.[156]

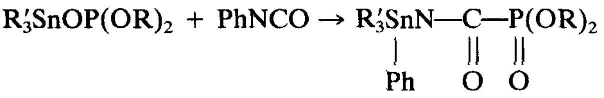
Quantitative oxidation can be carried out by passing dry oxygen through a benzene solution of tributyltin diisopropyl phosphite (volatile) which yield tributyltin diisopropyl phosphate (nonvolatile). The phosphorus-31-NMR resonance peak present at 139.44 ppm in the phosphite structure [Sn—O—P] disappears and a new resonance peak appears at 4.2 ppm in the oxidized product, which correspond to the phosphate structure [Sn—O—P=O].



$$Bu^n_3SnOP(OPr^i)_2 \xrightarrow{\frac{1}{2}O_2} Bu^n_3SnO\underset{\overset{\|}{O}}{P}(OPr^i)_2$$

Similar to the oxidation of organotin phosphites, triphenyltin diphenyl phosphinite[157] [$Ph_3SnOPPh_2$] is also extremely sensitive to oxygen and is readily converted into the phosphinate [$Ph_3SnO_2PPh_2$].

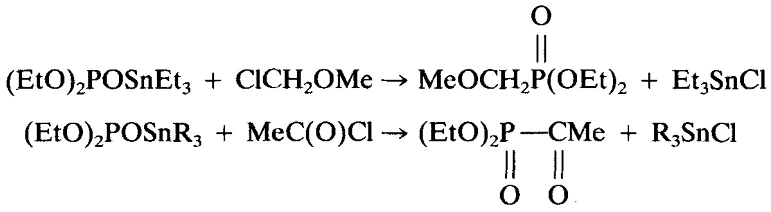
A mild exothermic reaction occurs on mixing phenyl isocyanate and triorganotin dialkyl phosphite which goes to completion after refluxing and yields inserted products which are characterized by IR and NMR (^1H, ^{31}P and ^{119}Sn) spectroscopic techniques.[155]



$$R'_3SnOP(OR)_2 + PhNCO \rightarrow R'_3Sn\underset{\overset{|}{Ph}}{N}—\underset{\overset{\|}{O}}{C}—\underset{\overset{\|}{O}}{P}(OR)_2$$

[where R′ = *n*-Pr, *n*-Bu; R = *n*-Pr, *i*-Pr]

Novikova *et al.*[152] have studied the Arbuzov reaction of organotin phosphites with chloromethyl methyl ether and acetyl chloride.

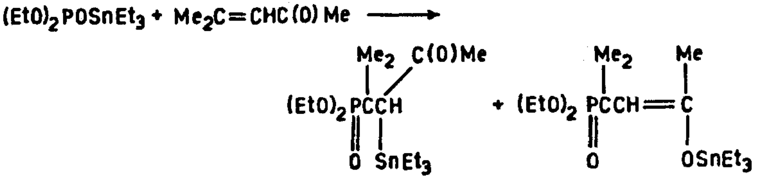


$$(EtO)_2POSnEt_3 + ClCH_2OMe \rightarrow MeOCH_2\overset{O}{\overset{\|}{P}}(OEt)_2 + Et_3SnCl$$

$$(EtO)_2POSnR_3 + MeC(O)Cl \rightarrow (EtO)_2\underset{O}{\underset{\|}{P}}-\underset{O}{\underset{\|}{C}}Me + R_3SnCl$$

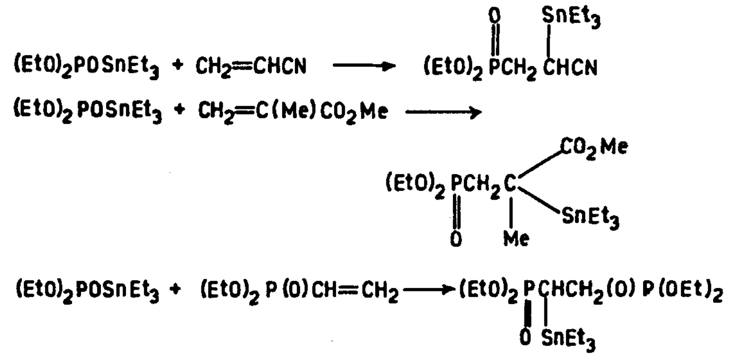
[where R = Me, Et]

An exothermic reaction occurred on mixing organotin phosphite with mesityl oxide and resulted in the formation of addition compounds.



(C Isomer, 92%) (C Isomer, 8%)

The α,β-unsaturated nitriles carboxylic esters and diethyl vinyl phosphonate add to tin phosphites with the liberation of heat.[152]



The above adducts were characterized by NMR measurements.

Dialkyl phosphonate reacts with tin tetrachloride in refluxing benzene to yield a rearranged product.[158]

$$(RO)_2P(O)H + SnCl_4 \rightarrow [RP(O)(OR)O]_2SnCl_2 + 2HCl\uparrow$$

Similar types of products have also been obtained in the reactions of trialkyl phosphites with tin tetrachloride.[159] The structure elucidation of the above products is based on IR and TGA measurements. On this basis the formation of Sn—O—P linkages have been established.

In contrast to sodium dialkyl phosphites, sodium-O-alkyl phosphonates (which are readily obtained by hydrolysis of dialkyl phosphonates in the presence of sodium hydroxide) were caused to react with triorganotin chlorides, yielding *O*-triorgano-

O-alkyl phosphonates as nonvolatile viscous liquids (Except R′ = Ph) stable up to 225°C.[160]

$$(RO)_2P(O)H + NaOH \rightarrow ROP(O)(H)ONa + ROH$$

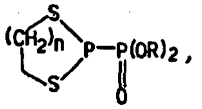
$$ROP(O)(H)ONa + R'_3SnCl \rightarrow R'_3SnOP(O)(H)OR + NaCl\downarrow$$

$$[\text{where } R = Me, Et;\ R' = Me, n\text{-}Bu, Ph]$$

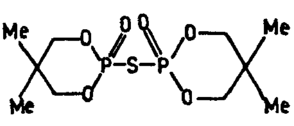
On the basis of IR and multinuclear NMR (^1H, ^{13}C, ^{31}P and ^{119}Sn) data, a polymeric structure was suggested for these compounds.

(v) *Derivatives of Group V Elements (P and As)*

The reactions of sodium dialkyl phosphites (dialkyl phosphonate anions) with dialkyl phosphorochloridate, yield P—P bonded hypophosphates.[161,162] Cyclic hypophosphates are also synthesized by similar reactions using their cyclic analogues.[163,164] Cyclic dithiophosphates are synthesized by condensing their thio analogues.[165] Alcoholysis, cleavage and hydrolysis reactions of 2-(dialkyl phosphoryl) 1,3,2-dithiaphospholane (I)[166] and the mechanism of isomerization of symmetrical monothio pyrophosphates (II)[167] have also been recently reported in the literature.



(I)



(II)

The reactions of dialkyl phosphonate anions with chlorophenyl phosphines[168] and condensation reactions between chloro and methoxy phosphines[169,170] yield P—P[172,173] bonded derivatives as shown by 31-phosphorus NMR measurements of the products.

$$n\,(RO)_2P\cdots\cdots\overset{-}{O} + Ph_{3-n}PCl_n \longrightarrow Ph_{3-n}P\left[P(O)(OR)_2\right]_n + nCl^-$$

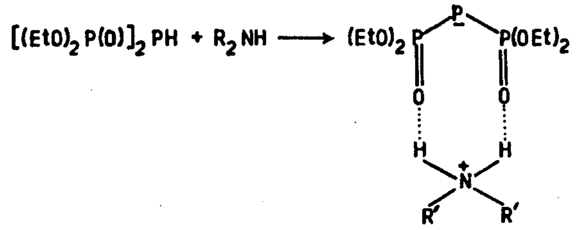
A simple bond energy calculations by Glidewell *et al.*[168] shows that the Δ°H term associated with the isomerization of ⟩POP⟨ to ⟩P—P(O)⟨ linkage is -93 KJ mol^{-1}. Hence, the P—O—P bridged isomer in this series of compounds is thermodynamically less stable and thus converts into P—P(O) bonded species.

Tris(diethylphosphito)phosphine which is obtained by reaction of PCl_3 and $(EtO)_2P(O)H$ in the presence of triethylamine at -50°C, is split by ammonia or amines to give the corresponding ammonium bis(diethylphosphito)phosphinidene, the first compound known to contain a phosphorus atom with coordination number two and connected to two other phosphorus atoms.[171] The reaction pathway has been investigated by NMR measurements.[172]

$$PCl_3 + 3(EtO)_2P(O)H + 3C_5H_5N \rightarrow [(EtO)_2P(O)]_3P + 3C_5H_5NHCl\downarrow$$

Ammonium bis(diethylphosphito)phosphinidene was obtained by treating $[(EtO)_2P(O)]_3P$ with R_2NH.[173,174]

$$[(EtO)_2P(O)]_3P + R_2NH \rightarrow HP[P(O)(OEt)_2]_2 + R_2NP(O)(OEt)_2$$



(III)

The product (III) reacts with diethyl chlorophosphate to give tris(diethylphosphito)phosphane.

$$\text{(III)} + (RO)_2P(O)Cl \rightarrow [(RO)_2P(O)]_3P + R_2NH_2Cl\downarrow$$

$$[\text{where } R = Et,\ R' = C_5H_{10}]$$

Analogous reactions have also been reported with halogen derivatives of non-metals [e.g. Ph_2PCl, $PhPCl_2$, R—X, $RCHX_2$, XCH_2—CH_2X] and in certain cases with metals [e.g. $HgCl_2$, PhHgCl].

Tris(diethylphosphito)phosphane reacts with trialkyl phosphine to give the following products.[173]

$$[(EtO)_2P(O)]_3P + R_3P \rightarrow R_3P{=}P{-}P(O)P(OEt)_2 + (EtO)_2POP(O)(OEt)_2$$

$$[\text{where } R = Et,\ n\text{-}Bu]$$

The product III also reacts with Cl—Z [Z = $P(OEt)_2$, $SiMe_3$] and

$$[(EtO)_2(O)PPP(O)(OEt)_2][H_2NC_5H_{10}] + Cl{-}Z \rightarrow$$

$$Z{-}P[P(O)(OEt)_2]_2 + C_5H_{10}NH_2Cl\downarrow$$

is able to function as a ligand in coordination compounds. It is able to replace carbon monoxide to yield anionic metal carbonyls (IV).[174]

$$[H_2NH_5H_{10}][(CO)_5Mo{-}P\{P(OEt)_2\}_2]\ \text{(IV)}$$

The 31-phosphorus NMR spectral data for all the above products have been reported.[172,174]

The reactions of $(EtO)_3P$ and $(EtO)_2PONa$ with dialkyl (or aryl) iodo arsines yield derivatives containing an arsenic-phosphorus linkage.[175]

$$EtBuAsI + (EtO)_3P \rightarrow EtBuAs{-}P(O)(OEt)_2 + EtI$$

$$R^1R^2AsI + (EtO)_2PONa \rightarrow R^1R^2As{-}P(O)(OEt)_2 + NaI\downarrow$$

$$[\text{where } R^1 \text{ and } R^2 = \text{alkyl, alkenyl, aryl}]$$

These compounds are volatile under reduced pressure and decompose on heating at 150°C with 15% HCl. No spectroscopic data were reported for these compounds.

Van Wazer *et al.*[169,176,177] carried out detailed investigations on the reactions of

$P(OMe)_3$ with different haloarsines and have observed the Arbuzov type reaction with the formation of a direct arsenic-phosphorus $[\mathrm{As{-}P{=}O}]$ linkage.

$$\mathrm{RAsX_2 + 2P(OMe)_2 \xrightarrow[\text{room temp.}]{N_2\ \text{atm.}} RAs[P(O)(OMe)_2]_2 + 2MeX}$$

$$[\text{where } \mathrm{R = Me, Ph;\ X = Cl, I}]$$

Structural evidence for the compounds was obtained from ^{31}P NMR spectra. The ^{1}H decoupled ^{31}P NMR spectrum exhibits a singlet at δ 30.9 ppm. These values support formation of a direct arsenic-phosphorus linkage. Although 75-arsenic has a spin of 3/2, it does not show coupling with the phosphorus due to a large quadrupolar interaction. In the ^{1}H NMR spectrum of bis(dimethylphosphonato)-methylarsine, $CH_3As[P(O)(OCH_3)_2]_2$ a triplet is observed for the arsenic-methyl group, which results from the coupling of two phosphorus atoms with the methyl proton. The J value of 16.5 Hz is additional evidence for an As—P bond.[176]

Dialkyl phosphonate derivatives of arsenic (III) have been obtained by the reaction of arsenic trichloride with dialkyl phosphonates in the presence of a base. The reactions are exothermic and proceed to completion at ambient temperature.[178]

$$\mathrm{3(RO)_2P(O)H + AsCl_3 + 3Et_3N \rightarrow [(RO)_2P(O)]_3As + 3Et_3N.HCl\downarrow}$$

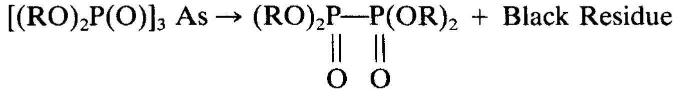
$$[\text{where } \mathrm{R = Me, Et,}\ n\text{-Pr},\ i\text{-Pr},\ n\text{-Bu}]$$

The reactions of arsenic chloride isopropoxides with dialkyl phosphonates yield the corresponding mixed isopropoxide dialkyl phosphonates as moisture sensitive colored oily liquids.

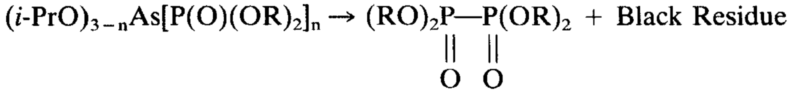
$$(i\text{-PrO})_{3-n}\mathrm{AsCl_n + n(RO)_2P(O)H + nEt_3N \rightarrow}\ (i\text{-PrO})_{3-n}\mathrm{As[P(O)(OR)_2]_n + nEt_3N.HCl\downarrow}$$

$$[\text{where } \mathrm{R = Et,}\ n\text{-Pr},\ i\text{-Pr},\ n\text{-Bu};\ \mathrm{n = 1\ or\ 2}]$$

These compounds show a tendency to decompose on being kept at ambient temperatures, yielding tetraalkyl hypophosphates.

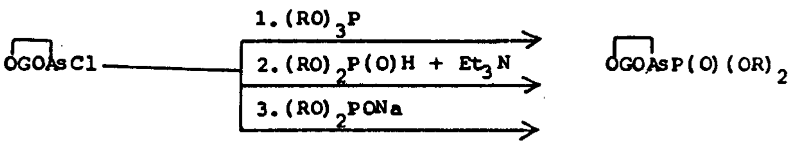


$$\mathrm{[(RO)_2P(O)]_3\,As \rightarrow (RO)_2\underset{\underset{\displaystyle O}{\|}}{P}{-}\underset{\underset{\displaystyle O}{\|}}{P}(OR)_2} + \text{Black Residue}$$



$$(i\text{-PrO})_{3-n}\mathrm{As[P(O)(OR)_2]_n \rightarrow (RO)_2\underset{\underset{\displaystyle O}{\|}}{P}{-}\underset{\underset{\displaystyle O}{\|}}{P}(OR)_2} + \text{Black Residue}$$

The reactions of $(RO)_3P$, $(RO)_2P(O)H$ (in the presence of base) and $(RO)_2PONa$ with 2-chloro-1,3,2-dioxaarsolanes and -arsenanes in an inert atmosphere yield 2-dialkyl phosphonato-1,3,2-dioxaarsolanes and -arsenanes as light yellow to dark red oily liquids which show a tendency to decompose under ambient conditions and are susceptible to hydrolysis even by atmospheric moisture. On pyrolyzing these compounds under reduced pressure tetraalkyl hypophosphates are obtained.[179]



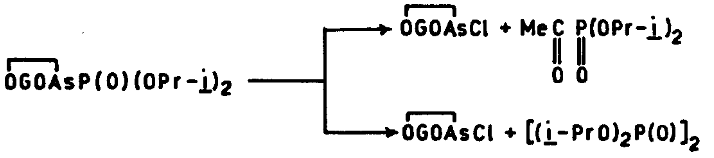
$$\text{OGOAsCl} \xrightarrow[\substack{2.\ (RO)_2P(O)H\ +\ Et_3N \\ 3.\ (RO)_2PONa}]{1.\ (RO)_3P} \text{OGOAsP(O)(OR)}_2$$

where 1. G = CH_2CH_2, $MeCHCH_2$, Me_2CCH_2CHMe
R = Et, i-Pr

2. G = CH_2CH_2, $MeCHCH_2$, Me_2CCH_2CHMe
Me_2CCMe_2, $CH_2CH{=}CHCH_2$
R = Me, Et, n-Pr, i-Pr, allyl

3. G = Me_2CCH_2CHMe
R = i-Pr

2-Diisopropyl phosphonato-1,3,2 dioxaarsolanes and -arsenanes react with acetyl chloride and dialkyl phosphorochloridate yielding the following products[178]:

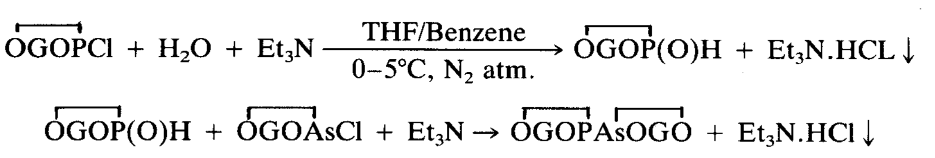


$$\text{OGOAsP(O)(OPr-}i)_2 \rightarrow \text{OGOAsCl} + \text{MeC(O)P(O)(OPr-}i)_2$$
$$\text{OGOAsP(O)(OPr-}i)_2 \rightarrow \text{OGOAsCl} + [(i\text{-PrO})_2P(O)]_2$$

[where G = $MeCHCH_2$, Me_2CCMe_2]

The above products have been characterized by elemental analysis, molecular weight determinations, IR and NMR (^1H and ^{31}P) measurements.[178]

A new 2-oxy-1,3,2-dioxaphosphorinane has been synthesized and caused to react with 2-chloro-1,3,2-dioxarsenane in the presence of triethylamine to yield the first cyclic analogue.[180]



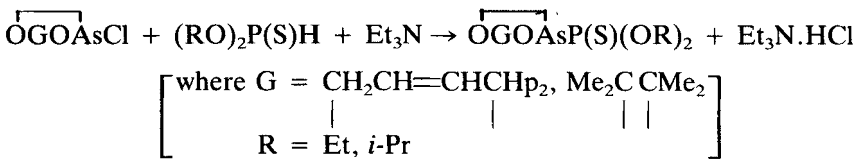
$$\text{OGOPCl} + H_2O + Et_3N \xrightarrow[0\text{–}5^\circ C,\ N_2\ \text{atm.}]{\text{THF/Benzene}} \text{OGOP(O)H} + Et_3N.HCL\downarrow$$

$$\text{OGOP(O)H} + \text{OGOAsCl} + Et_3N \rightarrow \text{OGOPAsOGO} + Et_3N.HCl\downarrow$$

[where G = Me_2CCH_2CHMe]

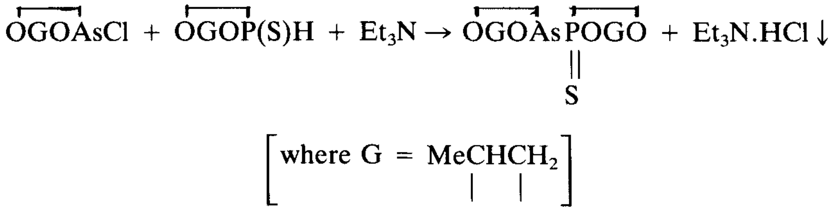
The product is a white crystalline solid, soluble in common organic solvents, highly susceptible to hydrolysis. It was characterized by IR and ^1H NMR measurements.

The reactions of dialkyl thiophosphonates with arsenic(III) chlorides also yield arsenic-phosphorus [As—P=S] bonded derivatives which appear to be less stable than their dialkyl phosphonate analogues.[180]



$$\overline{\mathrm{OGOAs}}\mathrm{Cl} + (\mathrm{RO})_2\mathrm{P(S)H} + \mathrm{Et_3N} \rightarrow \overline{\mathrm{OGOAs}}\mathrm{P(S)(OR)_2} + \mathrm{Et_3N.HCl}\downarrow$$

$$\left[\begin{array}{l}\text{where } \mathrm{G} = \mathrm{CH_2CH{=}CHCHp_2},\ \mathrm{Me_2C\,CMe_2} \\ \qquad \mathrm{R} = \mathrm{Et},\ i\text{-}\mathrm{Pr}\end{array}\right]$$



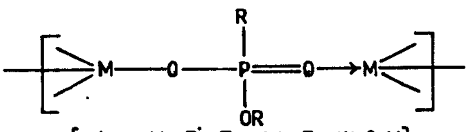
$$\overline{\mathrm{OGOAs}}\mathrm{Cl} + \overline{\mathrm{OGOP}}\mathrm{(S)H} + \mathrm{Et_3N} \rightarrow \overline{\mathrm{OGOAs}}\,\overset{\displaystyle\|}{\underset{\mathrm{S}}{}}\!\overline{\mathrm{POGO}} + \mathrm{Et_3N.HCl}\downarrow$$

$$\left[\text{where } \mathrm{G} = \mathrm{MeCHCH_2}\right]$$

D. TRANSITION METAL DERIVATIVES OF DIALKYL PHOSPHONATES

In comparison to dialkyl phosphonate derivatives of main group elements, the corresponding derivatives of transition metals are less well known. Among the transition metal derivatives, the published work appears to be confined to Ti, Zr, V, Nb, Ta and W.

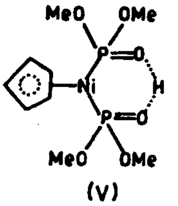
Puri *et al.* have carried out an extensive study of the reactions of a number of metal halides [e.g. $TiCl_4$,[181] $ZrCl_4$,[182] $VOCl_3$,[183] $NbCl_5$,[184] $TaCl_5$,[184] WCl_5[185]] with dialkyl phosphonates in refluxing benzene and observed the formation of hydrogen chloride with stepwise replacement of chlorine moieties from the metal chloride; the products are generally insoluble solids, the IR spectra of which indicate the presence of bands due to metal-oxygen-phosphorus, phosphorus-carbon, and co-ordinated phosphoryl (P=O) linkages. The formation of coordinated polymeric structures having the following type of bridges has been suggested for the above products.



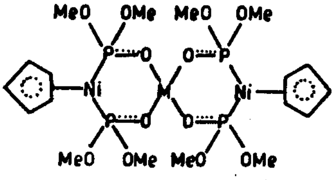
[where M=Ti, Zr, Nb,Ta,W & V]

Clevage reactions of dialkyl alkylphosphonates, $(RO)_2P(O)R$ with some metal halides and alkoxides [$ZrCl_4$,[186] VCl_3, $Ti(OR)_4$,[187] Ti(III),[188] V(III), Cr(III)] at elevated temperatures have been reported to proceed with the evolution of alkyl chloride or ether, and the formation of coordination polymers.

Metal π-complexes have been shown to form 2,4-trinuclear complexes[189] of the super sandwich type with a spiro center and are synthesized by reacting nickelocene with dimethyl phosphonate. Complex V was prepared in 38% yield. When this was treated with ammonia, it gave $Cp{-}Ni[P(O)(OMe)_2]_2NH_4^+$, which with MCl_2 gave complex VI (M = Co, Zn).



(V)

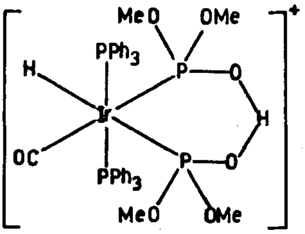


(VI)

Nickelocene[190] reacts with $(RO)_2P(O)H$ R = Me, Et to form $[CP—Ni[P(OR)_2]_2H]$ which contains a six membered NiP_2O_2H ring with a presumably symmetrical OH. . .OH bond. Reactions of this compound with HBF_4, NH_4, Tl and HgI_2 are also discussed.

The P—H bond of dialkyl phosphonates (open chain and cyclic) oxidatively adds to $IrCl_2.L_2$[191] [L = PPh_3, $AsPh_3$] and $IrCl(PMe_2Ph)_3$ to give six-coordinate hydrido(dialkylphosphonato)iridium(III) complexes e.g. $IrHCl(PMe_2Ph)_3[P(O)(OMe)_2]$. All the complexes have been characterized by IR and NMR (^1H and ^{31}P) measurements.

Treatment of $[\{IrCl(1,5\text{-}C_8H_{12})\}_2]$ with Ph_2PCl and water gave $[IrCl(1,5\text{-}C_8H_{12})\{(PPh_2O)_2H\}]$. In the presence of bidentate ligands, complexes $IrHCl(L—L)\{(PPh_2O)_2H\}$(L—L = $Ph_2As(CH_2)_2$, $PhS(CH_2)_2SPh$ or $Ph_2P(CH_2)_2PPh_2$) were formed while in the absence of ligand, dissociation of diene readily occurs and polymeric materials were obtained. Heterobimetallic and heterotrimetallic compounds have also been reported. In contrast to the above, the addition of $(RO)_2P(O)H$, (R = Me, Et or Ph) and $Ph_2P(O)H$ to, $[IrCl(CO)(PPh_3)_2]$ yield unstable hydrides. The structural characterization of the complexes were carried out by IR and NMR (^1H and ^{31}P) spectroscopy. Several geometrical and linkage isomers of the complex, $[IrHCl(CO)(PR_2O)(PPh_3)_2]$ (R = OMe, OEt, OPh and Ph) and their distribution has been estimated by the relative integration of their IrH resonances. The NMR (^1H and ^{31}P) spectra of the isomers in $CDCl_3$ as well as in excess of $(RO)_2P(O)H$, (R = Me, Et) have also been studied.[192]



(VII)

The P—H bond of the cyclic phosphonate $\overline{OCH_2CMe_2CH_2OP}(O)H$ reacts with chlorobis(cyclo-octene)rhodium (I) dimer to give $RhX(R_2POHOPR_2)_2(R_2POH)$, (X = H, Cl) and $RhCl_2$ $(R_2POHOPR_2)(R_2POH)_2$, where, R_2PO = $\overline{OCH_2CMe_2CH_2OPO}$. The iridium analogue also yields the corresponding products. The complexes have been characterized by NMR (^1H and ^{31}P) data. It was reported that some of the complexes act as catalysts or catalytic precursors for the stereoselective reduction of 4-t-butyl cyclohexanone.[193]

Venezky *et al.*[194] studied the murcuration of dialkyl phosphonates and obtained crystalline derivatives of mercury.

$$2(RO)_2P(O)H + HgO \xrightarrow{\text{slow}} [(RO)_2P(O)]_2Hg + H_2O$$

$$[(RO)_2P(O)]_2Hg + HgX_2 \rightarrow 2(RO)_2P(O)HgX$$

[where R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *t*-Bu]

Pidcock *et al.*[195] determined the $^{199}Hg—^{31}P$ coupling constants in the diethyl phosphonato complexes $[HgX\{(EtO)_2PO\}]$ [X = Cl, Br, I, $MeCO_2$ or $(EtO)_2PO$] and the crystal structure of the chloro complex. Chloro diethyl phosphonato)-mercury(II) crystallizes in the monoclinic system, space group CO with Z = 16 in a cell of dimensions, a = 17.43, b = 17.47, c = 12.59A°, β = 90.15. The mercury atoms in two of the four molecules comprising the asymmetric unit have a distorted trigonal-bipyramidal environment, while the coordination around the mercury atoms of the other two molecules is distorted octahedral. The $^{199}Hg—^{31}P$ coupling constant value for the complexes $[HgX\{(EtO)_2PO\}]$ ranges between 7.5 to 12.97 KHz. ^1J (Hg—P) and ^{31}P chemical shift ranges between +5.2 to +53.8 ppm. Although the molecular weight measurements for the complexes $[Hg(EtO)_2PO]$ suggest a dimeric structure, the complex has only one ^{31}P resonance. This indicates the probability of exchange of the bridging and the terminal phosphonate groups.

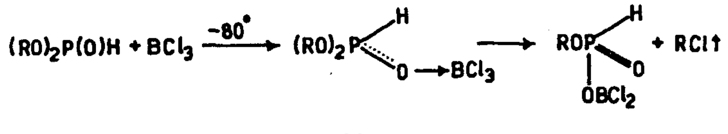
On the other hand UV irradiation of $M_2(CO)_{10}$ [M = Mn, Re] in the presence of $Hg[P(O)(OR)_2]_2$ gave $[M(CO)_4.P(O)(OEt)_2]_2$.[196] On the basis of elemental analyses and IR, mass and ^{31}P NMR spectral data, a ring structure consisting of $2M(CO)_4$ units and alternating M—P—O bonds was suggested.

Guangzhi *et al.* have recently studied the photolysis of the dialkyl phosphonates and their mercury derivatives of the type $(RO)_2P(O)HgX$ (X = OAc, Cl and Br) by spin trapping techniques and ESR spectroscopy. The results showed that radical $(RO)_2P\dot{O}$ were formed during UV irradiation and could be trapped by N-tert.-butylphenyl nitrone. From these investigations it was found that homolysis of the P—Hg link is much easier than the P—H bond.[197]

E. ADDITION COMPLEXES OF DIALKYL PHOSPHONATES

Dialkyl phosphonates exhibit a variety of modes of coordination in complexes. The proton attached to phosphorus may be retained or lost, and the neutral and anionic forms can coordinate to the metal atom through either phosphorus[56] or oxygen or both the phosphorus atom and the terminal oxygen atom. The class (a) or hard acceptors from group IA and IIA form compounds in which the phosphorus atom has been shown to be trivalent by ^{31}P NMR spectroscopy $[(RO)_2P—O—M]$[198] [soluble in organic solvents] while class (b) acceptors e.g. Ag^+ and Cu^+ are formulated as $(RO)_2P—O—M$ in the solid state [insoluble in organic solvents].

Gerrard *et al.*[86] reported the formation of 1:1 addition complexes of BCl_3 with $(RO)_2P(O)H$, which extrude alkyl chloride at −80°C or hydrogen chloride (R = aryl).



$$(PhO)_2P(O)H + BCl_3 \xrightarrow{-20°} (PhO)_2POBCl_2 + HCl\uparrow$$

Puri *et al.*[87] reported the formation of a 1:3 addition complex of $(EtO)_3Al$ with $(EtO)_2P(O)H$ as a colorless liquid (jelly like), which on extended storage (~3 months) at ambient temperatures changed into a light green solid.

$$3(EtO)_2P(O)H + Al(OEt)_3 \rightarrow (EtO)_3Al.3(EtO)_2P(O)H$$

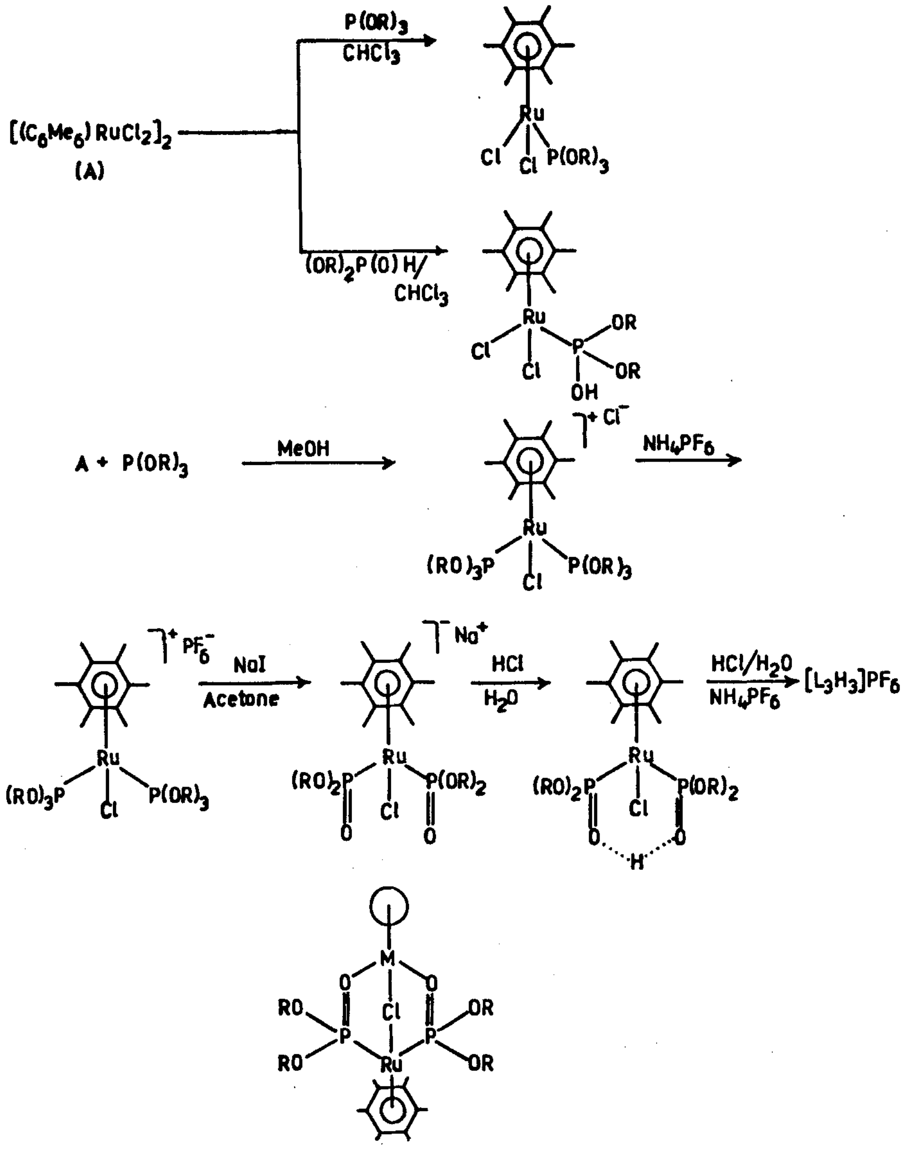
Pudovik *et al.*[199] have studied the stoichiometries and equilibrium constants of the addition complexes of the type $Me_mSnCl_{4\text{-}m}$ $n(RO)_2P(O)H$, by IR spectroscopy and have shown that the νP—H absorption frequency shifts towards higher wave numbers while νP═O moves towards lower wave numbers on complexation. The NMR (^1H, ^{31}P and ^{119}Sn) spectral data of the complexes were not reported.

Yarakova *et al.*[200] studied the thermodynamic parameters for the complexation and Reiter *et al.*[201] determined the formation constants as a function of nuclear spin coupling constants from NMR data at 35°C for the complexes of the type, R_mSnCl_4 $n(R'O)_2P(O)H$ (where R = Me, R' = Me, Et, Ph, m = 2, 3; n = 1).

Addition complexes of SnX_4 with $Et(RO)O(O)H$[202], $(RO)_3P$[154], and $(i\text{-}PrO)_2P(O)Me$[203] have also been reported in the literature. A variety of addition complexes of tin(IV) and organotin(IV) chlorides with dialkyl phosphonates have been synthesized, $R_nSnCl_{4\text{-}n}.m(R'C)_2P(O)H$ [where R = Me, Et, *n*-Pr, Ph; R' = Me, Et, *n*-Pr, *i*-Pr; n = 0, 2, 3; m = 1 or 2].

On heating $SnCl_4 \cdot 2(R'O)_2P(O)H$, evolve hydrogen chloride and are converted to white glassy solids that are insoluble in organic solvents, while organotin(IV) complexes were found to show higher thermal stability. On the basis of spectroscopic studies IR and NMR (^1H, ^{31}P and ^{119}Sn) deshielding of the phosphorus atom and shielding of the tin atom was established. The ^{119}Sn NMR signal of $Me_3SnCl(MeO)_2P(O)H$ which appeared at 78.79 ppm in benzene shifts further upfield in dimethyl phosphonate as a solvent appearing at 6.5 ppm indicating fast exchange between the bonded and free phosphonate molecule.[155]

$(MeO)_3P$ reacts with $[\{(C_6Me_6)RuCl_2\}_2]$ in methanol to yield $[(C_6Me_6)RuCl\{P(OMe)_3\}_2]^+$ which has been isolated as a chloride salt, and undergoes the Michaelis Arbuzov reaction to give neutral complexes as $[(C_6Me_6)RuCl\text{-}\{P(O)(OMe)_2\}\{P(OMe)_3\}]$ and the anion $[(C_6Me_6)RuCl\{P(O)(OMe)_2\}_2]^-$. The anion acts potentially as a bi- or tridentate ligand and are structurally analogous to oxygen tripod ligands. The complexes have been characterized by spectroscopic data. The above anion reacts with transition metal and main group metal ions e.g., Mn^+, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+} or Fe^{3+} to give 2:1 (n–2) complexes of the composition $[ML_2]$. HL also oxidatively adds to the metal(O) complexes to yield metal hydride complexes of the composition $[LM(CO)_3H]$. The copper carbonyl complex, LCu(CO) is the first neutral complex of this type. The author has also isolated the cationic complexes of the type (ring ML^+ (where (ring) M = $(C_5Me_5)Rh$ or $(C_6Me_6)Ru$ (last structure) in which L^- exclusively reacted as a tridentate O, O, Cl ligand.[204]



Trotskaya *et al.*[205] have obtained bis(dialkyl phosphonato)bis(dialkyl phosphito)platinum complexes of the type $[Pt\{(RO)_2PO\}_2\{(RO)_2POH\}_2]$ (R = Me and Et) from tetrachloroplatinate(II) and trialkyl phosphite in aqueous solution or dialkyl phosphonate in alcohol. All the phosphorus atoms in the complexes are equivalent in the ^{31}P NMR spectra indicating that proton exchange occurs in solution.

$$(RO)_2POM + PtCl_2L_2 \rightarrow Pt\{(RO)_2PO\}_2L_2 \text{ (trans)}$$

[where M = Na or Ag, L = Et_3P, Et_3As and C_5H_5N]

$$\mathrm{Pt\{(PhO)_2PO\}_2(Et_3As)_2}$$

$$+\ \mathrm{cis\text{-}[PtCl_2(Et_3As)_2]} \xrightarrow[\text{Reflux}]{\text{Toluene}} 2\ \mathrm{trans\text{-}[PtCl\{(PhO)_2PO\}\ (Et_3As)_2]}$$

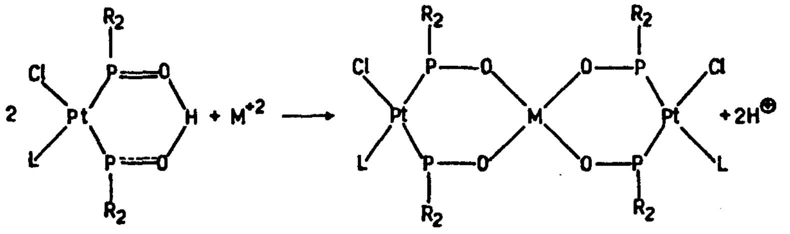
$$\mathrm{cis\text{-}[PtCl_2L_2]} + \mathrm{(PhO)_2POH} \rightarrow \mathrm{trans\text{-}[PtCl\{(PhO)_2PO\}L_2} + \mathrm{HCl}\uparrow$$

In the following reaction the phosphite complex product initially rearranged from trans to cis. It was investigated by UV spectrometry.

$$2\mathrm{(RO)_2POH} + \mathrm{Pt_2Cl_4L_2} \rightarrow 2\mathrm{[PtCl_4\{(RO)_2POH\}L]}$$

$$\mathrm{[PtCl_4\{(RO)_2POHL]} + \mathrm{(RO)_2POH} \rightarrow \mathrm{[PtCl\{(RO)_2PO\}(RO)_2POHL]} + \mathrm{HCl}\uparrow$$

The platinum complexes of the type $\mathrm{PtCl[OP(OMe)_2]HOP(OMe)_2]L}$[206] (L = $\mathrm{PEt_3}$, $\mathrm{PPh_3}$) were found to be acidic in nature and the proton bonded to oxygen can be removed by titration with sodium methoxide or 1,5 diazabicyclo[4.3.0]non-5-ene. The anionic compound can chelate to Cu(II), Co(II), $\mathrm{UO_2IV}$) and Th(V) through the oxygen and given mixed metal complexes,[207] $\mathrm{\{[PtCl][OP(OR_2]_2L\}_nM}$, (n = 2, R = Me, L = $\mathrm{PEt_3}$, M = Cu, $\mathrm{UO_2}$ and L = $\mathrm{PPh_3}$, M = Co; n = 2, R = Ph, L = $\mathrm{PEt_3}$, M = Th). By treating $\mathrm{PtCl[OP(OMe)_2]_2\ [HOP(OMe)_2]PEt_3}$ with $\mathrm{BF_3Et_2O}$ a complex $\mathrm{PtCl[OP(OMe)_2]\ [F_2BOP(Me)_2].PEt_3}$ was isolated. Mixed metal trimetallic compounds were also reported. Electronic spectra of mixed metal complexes show a square planar geometry about Cu(II) and Ni(II) and a tetrahedral geometry about Co(II). NMR, EPR spectra and low temperature magnetic studies have been reported for the above complexes.[207]

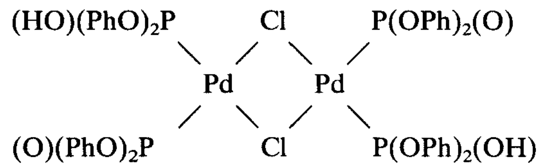


where

R = OMe; L = $\mathrm{PEt_3}$; M = Cu
R = OMe; L = $\mathrm{PEt_3}$; M = $\mathrm{UO_2}$
R = OMe; L = $\mathrm{PPh_3}$; M = Co
R = OPh; L = $\mathrm{PEt_3}$; M = Cu

Troitskaya *et al.*[208] in 1966 isolated two complexes of palladium, $\mathrm{[Pd\{(EtO)_2PO\}_2]}$ and $\mathrm{[PdCl\{(EtO)_2PO\}\{(EtO)_2POH\}]}$ but no structural formulas were proposed at that time. In 1970 Pidcock *et al.*[209] have studied the reaction between $\mathrm{Na_2[PdCl_4]}$

and $(PhO)_2P(O)H$ and postulated the following structure on the basis of ^{31}P NMR studies.



Several attempts were made to prepare the complex $[PdCl\{(PhO)_2PO\}L_2]$ and $[Pd\{(PhO)_2PO\}_2L_2]$, ($L = R_3P$) but only intractable oils were obtained.

By analogy a rhodium complex of the type $[RhCl_3(Bu_3P)_2\{(PhO)_3P\}]$ has been prepared and on the basis of NMR results a meridional configuration was assigned.

Pidcock *et al.*[209] have also carried out detailed NMR investigations of the complexes of Rh, Pd and Pt with triphenyl phosphite and diphenyl phosphonate. The coupling constants were examined in terms of Fermi contact interaction.

Andrew *et al.*[210] studied rhodium(I) and -(III) complexes of diphenyl phosphinous acid and of secondary phosphites. These were prepared by shaking $[\{RhCl(C_8H_{12})\}_2]$, (C_8H_{12} = cyclo-octa-1,5-diene) with Ph_2PCl in CH_3OH/H_2O and then adding MCl. This gave a high yield of the triple-chloride-bridged anionic complex $M[Rh_2Cl_5\{(PPh_2O)_2H\}]_2$, ($M = AsPh_4$ or $PPh_3(CH_2Ph)^+$. The structure of $Ph_4As[Rh_2Cl_5\{(PPh_2O)_2H\}_2]$ (A) (CH_2Cl_2 trisolvate) has been verified by X-ray analysis. The crystals are triclinic, space group $\bar{P}1$ with a = 12.157(A), b = 16.191(5), c = 20.523(8)A°; $\alpha = 96.02(3)$, $\beta = 99.88(2)$, $\gamma = 96.10(2)°$ and Z = 2. The variable temperature ^{31}P—^1H NMR spectroscopy results indicate that the above complex (A) undergoes facile intramolecular scrambling of the phosphorus nuclei at ambient temperature.

Addition complexes of the type LnL_mCl_3[211] [where Ln = La, Pr, Nd, Sm and Eu, m = 6, Ln = Gd, Tb, Dy, Yb, m = 5; L = $(EtO)_2P(O)H$ and $(i\text{-}PrO)_2(O)H$] were prepared by the reaction of $LnCl_3$ and dialkyl phosphonates in dry ethanol and isopropanol respectively. On the basis of elemental analysis and spectroscopic studies (IR, ^1H NMR, ^{31}P NMR) it was shown that dialkyl phosphonates coordinate to the lanthanide metal atom through the phosphoryl (P=O) oxygen atom.

Uranyl complexes $[UO(NO_2)_2.2H_2O]$ with phosphate, phosphonate, phosphinate and phosphine oxide,[212] have been studied by spectroscopy. It was found that the decrease in stretching frequency (νP=O) on complexation is related to increasing metal extracting ability. The ^{31}P—^1H coupling constants increase on complexation. There appears to be no marked trend relating the change in coupling constant to complexing ability of the parent compound, although J(P—O—C—H) increases from 0.4 to c.p.s. in $(RO)_3P=O$ to 0.7 c.p.s. in $(RO)_2P(O)R'$. No change in proton-proton coupling constants is observed upon complexation.

ACKNOWLEDGEMENT

The author is extremely indebted to Professor R. C. Mehrotra and Dr. G. Srivastava for their inspiring guidance and critical suggestions.

REFERENCES

1. A. E. Arbuzov, *Dissertation*, Kazan, USSR (1905).
2. G. O. Doak and L. D. Freedman, *Chem. Revs.*, **61,** 31 (1961).
3. J. Rigaudy and S. P. Klesney, Nomenclature of Organic Chemistry, Pergamon Press, Ed. (1979) pp. 400.
4. J. R. Van Wazer, Phosphorus and Its Compounds (Interscience, London, 1961), Vol. II, pp. 1267, 1933.
5. W. Lorenz, US Pat., 2, 701, 255 (1955).
6. W. F. Barthel, P. A. Giand and S. A. Hall, *J. Am. Chem. Soc.*, **76,** 4186.
7. P. M. Vyacheslavov, G. K. Burkat, M. L. Petrov, A. E. Tsil'ko and B. G. Karbasov, *Otkrytiya Izobret Prom. Obraztsy Tovarnyl Znaki*, **19,** 79 (1983); *Chem. Abstr.*, **99,** 60929 (1983).
8. M. I. Kabachnik, *Izvest Akad. Nauk SSSR Otdel. Khim. Nauk*, 233 (1947).
9. J. C. Bailar Jr., Inorg. Synthesis, (McGraw Hill, New York, 1953), Vol. IV, pp. 61.
10. P. R. Napier, N. T. Williams Jr., E. B. Johnston and M. J. Horn, Eur. Pat., 33, 999; *Chem. Abstr.*, **96,** 6868t (1982).
11. V. Mark and J. R. Van Wazer, *J. Org. Chem.*, **29,** 1004 (1964).
12. H. Goldwhite and B. C. Saunders, *J. Chem. Soc.*, 2409 (1957).
13. E. A. Arbuzov and V. S. Vinogradova, *Izvest Akad. Nauk SSSR*, **83,** 79 (1952).
14. A. G. Hoechst, *Japan*, **77,** 27141 (1977).
15. E. N. Walsh, *J. Am. Chem. Soc.*, **81,** 3023 (1959).
16. K. Trove, E. Iashev and G. Borisov, *Phosphorus and Sulfur*, **12,** 313 (1982).
17. L. V. Nesterov and R. A. Sibirova, *Zh. Obshch. Khim.*, **31,** 897 (1961).
18. V. S. Kuskov and G. Kh. Gradis, *Doklady Akad. Nauk SSSR*, **92,** 323 (1953).
19. M. G. Imaev, V. G. Maslennikov, V. M. Gorina and O. S. Krashenmikova, *Zh. Obshch. Khim.*, **35,** 75 (1965).
20. K. A. Petrov, E. E. Nifant'ev and B. Ya. Kibman, *Zh. Prikl. Khim.*, **36,** 1853 (1963).
21. V. Tichy and S. Truchlik, *Chem. Zvesti*, **12,** 345 (1958).
22. K. A. Petrov, E. E. Nifant'ev and R. G. Gol'tsova, *Zh. Obshch. Khim.*, **32,** 3723 (1962).
23. E. H. Fields, *J. Am. Chem. Soc.*, **74,** 1528 (1952).
24. K. A. Petrov and R. G. Gol'tsova, *Russ. Chem. Revs.*, **35,** 622 (1966).
25. A. A. Oswald, *Can. J. Chem.*, **37,** 1498 (1959).
26. C. Brown, *J. Chem. Soc. (Chem. Commun.)*, 7 (1978).
27. J. Michalski and Cz. Krawiecki, *Chem. and Ind.*, 1323 (1954).
28. G. Aksnes and D. Aksnes, *Acta Chem. Scand.*, **18,** 38 (1964).
29. A. E. Arbuzov and M. G. Imaev, *Izvest Akad. Nauk SSSR Otdel. Khim. Nauk*, 171 (1959); *Chem. Abstr.*, **53,** 16039 (1959).
30. A. Zwierzak, *Can. J. Chem.*, **45,** 2501 (1967).
31. A. E. Arbuzov and N. A. Razumova, *Izvest Akad. Nauk SSSR Otdel. Khim. Nauk*, 187 (1956).
32. N. J. Lucas, F. M. Mitchell Jr. and C. N. Scully, *J. Am. Chem. Soc.*, **72,** 5491 (1950).
33. A. E. Arbuzov, V. M. Zorastrova and N. I. Rizpolozhenskii, *Izvest Akad. Nauk SSSR Otdel. Khim. Nauk*, 208 (1948).
34. A. E. Arbuzov and M. M. Azanoveskaya, *Izvest Akad. Nauk SSSR Otdel. Khim. Nauk*, 473 (1949); 544 (1951).
35. B. A. Arbuzov and V. M. Zorastrova, *Izvest Akad. Nauk SSSR Otdel. Khim. Nauk*, 770 (1952); 779 (1952).
36. N. K. Bliznyuk, T. A. Bondareva and L. D. Protasova, *Otkrytiya Izobret Prom. Obraztsy Tovarnyl Znaki*, **9,** 61 (1984); *Chem. Abstr.*, **100,** 210159t (1984).
37. B. Garrigues, A. Munoz and M. Mulliew, *Phosphorus and Sulfur*, **9,** 183 (1980).
38. C. D. Millar, R. C. Millar and W. Rogers Jr., *J. Am. Chem. Soc.*, **80,** 1562 (1958).
39. J. R. Van Wazar, Phosphorus and Its Compounds (Interscience, Inc., New York, 1958) Vol. I.
40. A. E. Arbuzov and P. I. Rakov, *Izvest Akad. Nauk SSSR Otdel. Khim. Nauk*, 237 (1950); *Chem. Abstr.*, **44,** 8713 (1950).
41. R. L. McConnell and H. W. Coover Jr., *J. Org. Chem.*, **24,** 630 (1959).
42. C. P. Smith, *J. Am. Chem. Soc.*, **60,** 183 (1953).
43. A. E. Arbuzov, M. I. Batuev and V. S. Vinogradova, *Doklady Akad. Nauk SSSR*, **54,** 599 (1946).
44. E. M. Popov, M. I. Kabachink and L. S. Mayants, *Russ. Chem. Revs.*, **30,** 362 (1961).
45. L. C. Thomas, Interpretation of IR Spectra of Organophosphorus Compounds, (Heydon & Sons Ltd., London, 1974), pp. 58, 213–215.
46. L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23,** 853 (1951).
47. R. P. Bucx, S. Singnadbja and L. B. Rogers, *Anal. Chem.*, **26,** 1240 (1954).
48. L. J. Goodell and J. T. Yoke, *Can. J. Chem.*, **47,** 2461 (1969).
49. G. Mavel, *Compt. Rend.*, **248,** 3699 (1959).
50. M. M. Crutchfield, C. H. Dungan, J. H. Lether, V. Mark and J. R. Van Wazer, Topics in

Phosphorus Chemistry, (Interscience, Publisher John Wiley & Sons, New York, 1967), Vol. V, pp. 48, 236, 260, 261, 291.
51. C. F. Callis, J. R. Van Wazer, J. N. Shoolery and W. A. Anderson, *J. Am. Chem. Soc.*, **79,** 2719 (1957).
52. H. Finegold, *Ann. N.Y. Acad. Sci.*, **70,** 875 (1958).
53. N. Muller, P. C. Lauterbur and J. Goldenson, *J. Am. Chem. Soc.*, **78,** 3557 (1956).
54. J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, *J. Am. Chem. Soc.*, **78,** 5715 (1956).
55. R. H. Williams and L. A. Hamilton, *J. Am. Chem. Soc.*, **74,** 5418 (1952).
56. M. I. Kabachnik and E. I. Golubeva, *Doklady Akad. Nauk SSSR*, **105,** 1258 (1955); *Chem. Abstr.*, **50,** 11232 (1956).
57. M. I. Kabachnik and Yu. M. Polikarpov, *Doklady Akad. Nauk SSSR*, **115,** 2512 (1957); *Chem. Abstr.*, **52,** 5327 (1958).
58. L. W. Daasch, *J. Am. Chem. Soc.*, **80,** 5301 (1958).
59. G. M. Kosolapoff, *J. Am. Chem. Soc.*, **67,** 1180, 2259 (1945).
60. G. M. Kosolapoff and A. D. Brown Jr., *J. Chem. Soc. (D) Commun.*, **21,** 1266 (1969).
61. B. A. Arbuzov and N. P. Grechkin, *Izvest Akad. Nauk SSSR Otdel. Khim. Nauk*, 440 (1956); *Chem. Abstr.*, **50,** 16661 (1956).
62. R. G. Harvey, T. C. Myers, H. J. Jacobs and E. V. Jensen, *J. Am. Chem. Soc.*, **79,** 2612 (1957).
63. V. S. Abramov and O. D. Somoilova, *J. Gen. Chem.*, **22,** 912 (1952); *Chem. Abstr.*, **47,** 4838 (1953).
64. G. M. Kosolapoff, Organophosphorus Compounds, (John Wiley & Sons, Inc., New York, 1950), pp. 121–125.
65. Y. Weizhen, S. Guiyun and Y. Chengyl, *Huaxue Xuebao*, **45,** 622 (1987); *Chem. Abstr.*, **108,** 221784j (1988).
66. L. M. Pevzner, V. M. Ignat'ev and B. I. Ionin, *Zh. Obshch. Khim.*, **57,** 2259 (1987); *Chem. Abstr.*, **110,** 8284 (1989).
67. J. W. Stec and A. Okruszek, Pol. (Pat.), 130983 (1980); *Chem. Abstr.*, **109,** 211219k (1989).
68. J. W. Stec and A. Okruszek, Pol. (Pat.), **131,** 549 (1986); *Chem. Abstr.*, **109,** 211220b (1989).
69. A. E. Arbuzov and V. S. Abramov, *Izvest. Akad. Nauk SSSR Otdel Khim. Nauk*, 35 (1959); *Chem. Abstr.*, **53,** 15956i (1959).
70. H. Normant and G. Sturtz, *Compt. Rend.*, **253,** 2366 (1961); *Chem. Abstr.*, **56,** 8739 (1962).
71. A. E. Arbuzov and C. L. Chang, *Izvest. Akad. Nauk SSSR Ser. Khim.*, 1934 (1963); 1941 (1963); 1945 (1963).
72. M. I. Kabachnik, T. Yu. Medved, N. M. Dyatlova, O. G. Arkhipova and M. V. Rudominov, *Russ. Chem. Revs.*, **37,** 1 (1968).
73. K. Huang, B. Wang and G. Yigao, **3,** 5 (1984); *Chem. Abstr.*, **101,** 55224k (1984).
74. M. K. Kern, V. N. Nguyen and J. D. Cross, *J. Org. Chem.*, **46,** 5188 (1981).
75. L. L. Nikogosyan, K. A. Nersesyan, T. Ya. Satina and M. G. Indzhikyan, *Arm. Khim. Zh.*, **36,** 267 (1983).
76. A. N. Pudovik and G. E. Yastrebova, *Russ. Chem. Revs.*, **39,** 562 (1970).
77. W. Boenigk and G. Haegele, *Chem. Ber.*, **117,** 2287 (1984); *Chem. Abstr.*, **101,** 55235q (1984).
78. M. G. Zimin, A. R. Burilov and A. N. Podovik, *Zh. Obshch. Khim.*, **50,** 751 (1980).
79. C. H. Chen and G. A. Reynolds, *J. Org. Chem.*, **45,** 2449 (1980).
80. T. Minami, N. Matsuzaki, Y. Ohshiro and T. Agawa, *J. Chem. Soc. Perkin Trans.*, **1,** 1731 (1980).
81. A. S. Romakin, Yu. A. Babkin, E. V. Nikitin, O. V. Parakin, Yu. A. Ignat'ev, G. V. Romanov, Yu. M. Kargin and A. N. Pudovik, *Otkrytiya Izobret*, **21,** 281 (1987); *Chem. Abstr.*, **108,** 150714y (1988).
82. E. V. Nikitin, A. S. Romakhim, O. V. Parakin, Yu. A. Ignat'ev, G. V. Romanov, Yu. M. Kargin and A. N. Pudovik, *Doklady Akad. Nauk SSSR*, **258,** 678 (1981); *Chem. Abstr.*, **95,** 204064r (1981).
83. T. Minami, S. Tokumasu and I. Hirao, *Bull. Chem. Soc. Jpn.*, **58,** 2139 (1985).
84. K. Trove and G. Borisov, *Phosphorus and Sulfur*, **17,** 257, 267 (1983); *Chem. Abstr.*, **100,** 149970, 209993 (1984).
85. G. Cao, H. Lee, M. V. Lynch and E. T. Mallouk, *Inorg. Chem.*, **27,** 2781 (1988).
86. R. Bedell, M. J. Frazer and W. Gerrard, *J. Chem. Soc.*, 4037 (1960).
87. D. M. Puri and A. Parkash, *J. Indian Chem. Soc.*, **49,** 7 (1972).
88. C. M. Mikulski, N. M. Karayannis, J. V. Minkiewicz, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta*, **3,** 523 (1969).
89. B. M. Cohen and J. D. Smith, *J. Chem. Soc. A*, 2087 (1969).
90. K. A. Andrianov, A. S. Shapatin and V. V. Ponomarev, *Izvest Akad. Nauk SSSR Ser. Khim.*, **1,** 187 (1965); *Chem. Abstr.*, **62,** 11846 (1965).
91. K. A. Andrianov and A. S. Shapatin, *Izvest. Akad. Nauk SSSR Otdel. Khim. Nauk*, 1753 (1962); *Chem. Abstr.*, **58,** 7965 (1963).

92. B. A. Arbuzov, *Pure Appl. Chem.*, **9,** 307 (1964).
93. P. Hautefeuille and T. Margottet, *Compt. Rend.*, **96,** 1052 (1883).
94. P. Hautefeuille, *Compt. Rend.*, **99,** 789 (1884).
95. R. O. Sauer, *J. Am. Chem. Soc.*, **66,** 1707 (1944).
96. M. G. Voronkov, *Zh. Obshch. Khim.*, **25,** 469 (1955).
97. E. A. Chernyshev and E. F. Bugerenko, *Organomet. Chem. Revs.*, **3,** 469 (1968).
98. M. Sekine, H. Mori and T. Hata, *Bull. Chem. Soc. (Jpn.)*, **55,** 239 (1982).
99. M. Sekine, K. Okimoto, K. Yamada and T. Hata, *J. Org. Chem.*, **46,** 2097 (1981).
100. M. Fujii, K. Ozaki, A. Kume, M. Sekine and T. Hata, *Tetrahedron Lett.*, **27,** 3365 (1986).
101. K. Issleib, M. Bubner and A. Balszuweit, *Z. Anorg. Allg. Chem.*, **546,** 142 (1987); *Chem. Abstr.*, **108,** 6115g (1988).
102. J. Chojnowski, M. Cypryk and J. Michalski, *J. Organomet. Chem.*, **215,** 355 (1981).
103. J. Chojnowski, M. Cypryk, M. Michalski and L. Woznik, *Macro-Mol. Stud. Pol. Akad. Sci.*, **90,** 362 (1981); *Chem. Abstr.*, **96,** 122887 (1982).
104. A. N. Pudovik, M. A. Pudovik, L. K. Kibardina and M. D. Medvedeva, *Otkrytiya Izobret Prom. Obraztsy Tovarnyl Znaki*, **53,** 62 (1976); *Chem. Abstr.*, **86,** 72858 (1977).
105. M. J. Newlands, US Pat., 3164, 622; *Chem. Abstr.*, **62,** 16297 (1965).
106. I. G. T. Ferguson and C. Glidewell, *J. Chem. Soc. Dalton*, 2071 (1977).
107. Z. S. Novikova, S. N. Mashonina and I. F. Lutsenko, *Zh. Obshch. Khim.*, **41,** 2110 (1971).
108. Z. S. Novikova and I. F. Lutsenko, *Zh. Obshch. Khim.*, **40,** 2199 (1970).
109. Z. S. Novikova, S. N. Mashonina, T. A. Sapozhnikova and I. F. Lutsenko, *Zh. Obshch. Khim.*, **41,** 2622 (1971).
110. I. V. Nesterov, N. E. Krepysheva, R. A. Sabirov and G. N. Romanova, *Zh. Obshch. Khim.*, **41,** 2449 (1971).
111. Z. S. Novikova, S. N. Mashonina and I. F. Lutsenko, Symposium (The Chemistry and Application of Organophosphorus Compounds), pp. 86 (1974).
112. A. N. Pudovik, T. Kh. Gazizov and Yu. I. Sudarov, *Zh. Obshch. Khim.*, **43,** 2886 (1973).
113. A. M. Kibardin, T. Kh. Gazizov and A. N. Pudovik, Symposium (The Chemistry of Organomet. Compounds), *Izv. Nauka, Leningrad*, pp. 167 (1976).
114. D. A. Evans, K. M. Hurst, L. K. Truesdale and J. M. Takecs, *Tetrahedron Letters*, 2495 (1977).
115. D. A. Evans, K. M. Hurst and J. M. Takecs, *J. Am. Chem. Soc.*, **100,** 3467 (1978).
116. A. N. Pudovik, Yu. I. Sudarev, A. P. Pashinkin, V. I. Kovalenko, A. M. Kibardin and T. Kh. Gazizov, *Doklady Akad. Nauk SSSR*, **218,** 359 (1974).
117. M. A. Pudovik, L. K. Kibardina, M. D. Medvedeva, T. A. Pestova, Kh. E. Kharlampidi and A. N. Pudovik, *Zh. Obsch. Khim.*, **46,** 1944 (1976).
118. I. V. Konovalova, L. A. Burnaeva, N. Sh. Saefullina and A. N. Pudovik, *Zh. Obshch. Khim.*, **46,** 18 (1976).
119. A. N. Pudovik, E. S. Batyeva and G. C. Zamaletdinova, *Zh. Obshch. Khim.*, **43,** 680 (1973).
120. M. Sekine and T. Hata, *Chem. Comm.*, 285 (1978).
121. T. Kh. Gazizov, A. M. Kibardin, A. P. Pashinkin, Yu. I. Sudarev and A. N. Pudovik, *Zh. Obshch. Khim.*, **43,** 679 (1973).
122. A. N. Pudovik, A. M. Kibardin, A. P. Pashinkin, Yu. I. Sudarev and T. Kh. Gazizov, *Zh. Obshch. Khim.*, **44,** 522 (1974).
123. T. Kh. Gazizov, A. M. Kibardin and A. N. Pudovik, **46,** 926 (1976).
124. M. Sekine, M. Nakajima and T. Hata, *J. Org. Chem.*, **46,** 4030 (1981).
125. V. V. Ovchinnikov, Yu. G. Evstaf'eva, R. A. Cherkasov and A. N. Pudovik, *Zh. Obshch. Khim.*, **53,** 1923 (1983).
126. A. N. Pudovik, T. Kh. Gazizov and A. M. Kibardin, *Zh. Obshch. Khim.*, **45,** 2094 (1975).
127. E. Kh. Ofitserova, O. E. Ivanova, E. N. Ofitserov, I. V. Konovalova and A. N. Pudovik, *Zh. Obshch. Khim.*, **51,** 505 (1981).
128. T. Kh. Gazizov, Yu. I. Sudarev, A. M. Kibardin, A. V. Belyalov and A. N. Pudovik, *Zh. Obshch. Khim.*, **51,** 8 (1981).
129. A. M. Kibardin, T. Kh. Gazizov, P. I. Gryaznov and A. N. Pudovik, *Izvest Akad. Nauk. SSSR Ser. Khim.*, 1095 (1981).
130. I. V. Konovalova, L. A. Burnaeva and A. N. Pudovik, *Zh. Obshch. Khim.*, **45,** 2567 (1975).
131. M. Sekine, M. Nakajima and T. Hata, *Bull. Chem. Soc. (Jpn).*, **39,** 918 (1981).
132. A. N. Pudovik, E. S. Batyeva and G. V. Zamaletdinova, *Zh. Obshch. Khim.*, **43,** 947 (1973).
133. D. Liotta, V. Sunay and S. Ginsberg, *J. Org. Chem.*, **47,** 2227 (1982).
134. A. N. Pudovik, E. S. Batyeva and G. V. Zamaletdinova, *Zh. Obshch. Khim.*, **42,** 2577 (1972).
135. M. G. Zimin, A. R. Burilov and A. N. Pudovik, *Zh. Obshch. Khim.*, **51,** 2140 (1981); *Chem. Abstr.*, **97,** 110195 (1982).
136. L. V. Nesterov and N. A. Aleksandrova, *Izvest Akad. Nauk SSSR, Ser. Khim.*, 971 (1978).
137. I. F. Lutsenko, Symposium (The Chemistry and Application of Organophosphorus Compounds), *Izd. Nauka, Moscow*, p. 172 (1974).

138. S. V. Ponomarev, A. I. Moskalenko and I. F. Lutsenko, *Zh. Obshch. Khim.*, **48,** 296 (1978).
139. A. N. Pudovik and R. D. Gareev, *Zh. Obshch. Khim.*, **45,** 235 (1975).
140. R. D. Gareev and A. N. Pudovik, *Zh. Obshch. Khim.*, **46,** 1717 (1976).
141. R. D. Gareev, *Zh. Obshch. Khim.*, **45,** 1155 (1975), **46,** 2662 (1976); *Chem. Abstr.*, **86,** 140135 (1977).
142. A. Toshio and O. Yoshiki, *Synthesis*, **11,** 916 (1983); *Chem. Abstr.*, **101,** 7276 (1984).
143. A. N. Pudovik, A. A. Sobanov, I. V. Bakhtiyarova and M. G. Zimin, *Zh. Obshch. Khim.*, **53,** 2665 (1983); *Chem. Abstr.*, **100,** 121227w (1984).
144. L. Wozniak, J. Kowalski and J. Chojnowski, *Tetrahedron Lett.*, **26,** 4965 (1985).
145. W. H. Keeber and H. W. Post, *J. Org. Chem.*, **21,** 509 (1956).
146. I. Morita, S. Chokai, T. Masami, K. Masahira and S. Makoto, *Chem. Pharm. Bull.*, **36,** 1135 (1988); *Chem. Abstr.*, **110,** 24007y (1989).
147. J. Chojnowskii, M. Cypryk and J. Michalski, *J. Organomet. Chem.*, **215,** 355 (1981).
148. B. Borecka, J. Chojnowski, J. Michalski and J. Zielinska, *J. Organomet. Chem.*, **171,** 17 (1979).
149. G. A. Clah and S. C. Narang, *Tetrahedron*, **38,** 2225 (1982).
150. M. G. Voronkov, V. M. D'Yakov, N. M. Kudyokov and M. V. Sigalov, *Zh. Obshch. Khim.*, **49,** 1525 (1979).
151. V. A. Al'fonsov, A. M. Pudovik, I. S. Nizamov, A. G. Trusenev and A. N. Pudovik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **12,** 2868 (1987); *Chem. Abstr.*, **110,** 57744q (1989).
152. Z. S. Novikova, S. N. Mashoshina and I. F. Lutsenko, *Zh. Obshch. Khim.*, **45,** 1486 (1975).
153. B. A. Arbuzov and N. P. Grechkin, *ibid.*, **17,** 2166 (1947); *Chem. Abstr.*, **42,** 4522 (1948), *Doklady Akad. Nauk SSSR*, **59,** 1433 (1948), *Chem. Abstr.*, **47,** 4281 (1953).
154. B. A. Arbuzov and A. N. Pudovik, *J. Gen. Chem.*, **17,** 2158 (1947); *Chem. Abstr.*, **42,** 4522 (1948).
155. P. N. Nagar, Ph.D. Thesis, University of Rajasthan, Jaipur (1988), India, *J. Indian Chem. Soc.*, **67,** 703 (1990). First Indo-Soviet Symposium on Organomet. Chem., PO-23 (1988).
156. P. N. Nagar, Phosphorus and Sulfur, **40,** 177 (1988).
157. H. Schuman, *Angew. Chem. Internat. Edit.*, **8,** 937 (1969).
158. D. M. Puri, S. N. Dubey, A. Parkash and S. M. Singh, *Indica Acta Cienc.*, **4,** 224 (1978).
159. M. M. Labes, C. Owens, N. M. Karayannis and L. Pytlewski, *J. Phys. Chem.*, **75,** 637 (1971).
160. J. N. Pandey, G. Srivastava, *J. Organomet. Chem.*, **354,** 301 (1988).
161. J. Michalski and A. Zwierzak, *Bull. Akad. (Polon.) Sci. Ser. Sci. Chim.*, **13,** 253 (1965).
162. R. L. McConnel and H. W. Coover, *J. Org. Chem.*, **24,** 630 (1959).
163. R. S. Edmundson, *Tetrahedron*, **21,** 2379 (1965).
164. W. Stec and A. Zwierzak, *Can. J. Chem.*, **45,** 2513 (1967).
165. M. Mikolajojczyk and B. Ziemnicka, *J. Chem. Soc. Perkin Trans.*, **2,** 501 (1983).
166. L. V. Ermanson, N. N. Godovikov and V. S. Blagoveshchenski, *Izvest Akad. Nauk SSSR Ser. Khim.*, **2,** 423 (1986); *Chem. Abstr.*, **106,** 5146u (1987).
167. J. Michalski, W. Reimschussel, R. Kaminski and P. Paneth, *Phosphorus and Sulfur*, **30,** 257 (1987); *Chem. Abstr.*, **108,** 75494 (1988).
168. C. Glidewell, *J. Organomet. Chem.*, **142,** 171 (1977).
169. K. M. Abraham and J. R. Van Wazer, *Inorg. Chem.*, **13,** 2346 (1974); **14,** 1099 (1975).
170. K. M. Abraham and J. R. Van Wazer, *Phosphorus Compounds*, **1,** 402 (1972).
171. D. Weber, G. Heckmann and E. Fluck, *Z. Naturforsch*, **31,** 81 (1976).
172. D. Weber and E. Fluck, *Z. Naturforsch*, **30,** 60 (1975).
173. D. Weber and E. Fluck, *Z. Anorg. Allg. Chem.*, **424,** 103 (1976).
174. D. Weber and E. Fluck, *Inorg. Nucl. Chem. Lett.*, **12,** 515 (1976).
175. G. Kamai and O. N. Belorossova, *Bull. Akad. Sci. URSS Classe Sci. Khim.*, 191 (1946); *Chem. Abstr.*, 4133 (1948).
176. K. M. Abraham and J. R. Van Wazer, *Inorg. Chem.*, **15,** 857 (1976).
177. K. M. Abraham and J. R. Van Wazer, *J. Organomet. Chem.*, **113,** 265 (1976).
178. P. N. Nagar, G. Srivastava and R. C. Mehrotra, *Synth. React. Inorg. Met.-Org. Chem.*, **13,** 249 (1983).
179. P. N. Nagar, G. Srivastava and R. C. Mehrotra, *Synth. React. Inorg. Met.-Org. Chem.*, **12,** 749 (1982).
180. P. N. Nagar, G. Srivastava and R. C. Mehrotra, *Phosphorus and Sulfur*, **18,** 145 (1983).
181. D. M. Puri and A. Parkash, *J. Indian Chem. Soc.*, **49,** 833 (1972).
182. D. M. Puri and A. Parkash, *Indian J. Chem.*, **13,** 384 (1975).
183. D. M. Puri and S. Singh, *Indian J. Chem.*, **20,** 375 (1981).
184. D. M. Puri and S. Singh, *J. Indian Chem. Soc.*, **58,** 327 (1981).
185. D. M. Puri and S. Singh, *Indian J. Chem.*, **19,** 1021 (1980).
186. C. Owens, L. L. Pytelowski, N. M. Karaynnis, J. Wysoczanski and M. M. Labes, *J. Polymer Science (Part B)*, **8,** 81 (1970).

187. G. H. Dahl and B. P. Block, *Inorg. Chem.*, **6**, 1439 (1967).
188. C. M. Mikulski, N. M. Karayannis, M. J. Strocko and M. M. Labes, *Inorg. Chem.*, **9**, 2053 (1970).
189. H. Werner and K. N. Tri, *Angew. Chem.*, **80**, 323 (1977); *Chem. Abstr.*, **89**, 23465 (1977).
190. H. Werner and K. N. Tri, *Z. Anorg. Allg. Chem.*, 475 (1981); *Chem. Abstr.*, **95**, 204122 (1981).
191. M. A. Bennett and T. R. B. Mitchell, *J. Organomet. Chem.*, **250**, 499 (1983).
192. J. Andrew, S. Duncan and T. A. Stephensen, *J. Chem. Soc., Dalton Trans.*, 1755 (1983).
193. M. A. Bennett and T. R. B. Mitchell, *J. Organomet. Chem.*, **295**, 223 (1985).
194. D. L. Venezky and R. B. Fox, *J. Am. Chem. Soc.*, **78**, 1664 (1956).
195. J. Bennett, A. Pidcock, C. R. Waterhouse, P. Coggon, A. T. McPhail and M. Paul, *J. Chem. Soc. (A)*, 2094 (1970).
196. P. Jaither and P. Peringer, *Transition Met. Chem.*, **9**, 325 (1984).
197. E. Li, J. Zhou, G. Xu, Bopuxue Zazhi, **5**, 15 (1988); *Chem. Abstr.*, **110**, 24008z (1989).
198. K. Modedritzer, *J. Inorg. Nucl. Chem.*, **19**, 22 (1961).
199. A. N. Pudovik, A. A. Muratova, N. P. Safiullina, E. G. Yarakova and V. P. Plekhov, *Zh. Obshch. Khim.*, **45**, 520 (1975).
200. E. G. Yarkova, N. R. Safiullina and A. A. Muratova, *Izvest. Vyssh. Uchebn. Zaved. Khim. Technol.*, **24**, 1314 (1981); *Chem. Abstr.*, **96**, 34400 (1982).
201. C. R. Reite, N. Takahashi, K. R. Bunting and W. G. Caldwell, *Inorg. Chim. Acta*, **64**, L45–L46 (1982).
202. A. A. Muratova, E. G. Yarkova, V. P. Plekov, A. A. Mushina and A. N. Pudovik, *Zh. Obshch. Khim.*, **40**, 19 (1970).
203. C. Owens, L. L. Pytlewski, C. M. Mikulski and N. M. Karayanis, *J. Inorg. Nucl. Chem.*, **41**, 1261 (1979).
204. K. Wolfgang and B. Elke, *Inorg. Chem.*, **27**, 3500 (1988).
205. A. A. Grinberg and A. D. Troitskaya, *Bull. Akad. Sci. USSR*, 178 (1944), *Trudy Kazan Khim., Teknol Inst. S. M. Kovova*, **18**, 59 (1953).
206. A. Pidcock and C. R. Waterhouse, *J. Chem. Soc. (A)*, 2080 (1970).
207. R. P. Sperline and D. M. Roundhill, *Inorg. Chem.*, **16**, 2612 (1977).
208. G. A. Levishina, A. D. Trotskaya and R. R. Shagidullin, *Russ. J. Inorg. Chem.*, **11**, 985 (1966).
209. F. A. Allen, A. Pidcock and C. R. Waterhouse, *J. Chem. Soc. (A)*, 2087 (1970).
210. J. Andrew, S. Duncan, T. A. Stephenson, D. M. Roundhill and D. Hedden, *J. Chem. Soc. (Dalton Trans)*, 801 (1984).
211. N. P. Kapoor and R. Saraswati, *Inorg. Chim. Acta*, **126**, 125 (1987).
212. J. L. Burdett and L. L. Burger, *Canadian J. Chem.*, **44**, 111 (1966).