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C–ELEMENT-SUBSTITUTED PHOSPHORUS YLIDS

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INTRODUCTION

The chemistry of phosphorus ylids containing different elements (metals and metalloids) at the α-carbon atom has attracted considerable interest in the last few years. Almost all elements of the periodic system, with the exception of inert gases and unstable radioactive elements, have been used as substituents at the ylidic carbon atom. Addition of different elements to the ylidic carbon creates a large group of compounds possessing various properties, most notably with respect to the element–carbanion bond. Consideration of the properties of C–element-substituted phosphorus ylids offers a unique opportunity to explain the influence of the different heteroatoms on carbanion properties.

Unfortunately, C–element-substituted phosphorus ylid chemistry has not yet been reviewed despite the extensive literature on the subject. There are only summarizing articles on certain of the problems of the interesting types of ylids,[1–4] for instance, the short review published by Schmidbaur in 1975 on inorganic phosphorus ylid chemistry.[1] The properties of C–element-substituted ylids are mentioned in passing in reviews devoted to various aspects of organic phosphorus ylids.[5–13] It is hoped that the present review will fill this gap in ylid chemistry. It summarizes data in the chemistry of C–element-substituted phosphorus ylids, containing elements of the main and side groups of the periodic system at the α-carbon atom described up to 1993.

1. YLIDS CONTAINING METAL ATOMS OF THE MAIN GROUPS AT THE α-CARBON ATOM

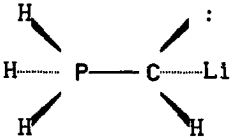
This section is concerned with the synthesis and properties of ylidic compounds substituted at the carbanionic centre by metal atoms of the main group.

1.1. *Ylids containing metal atoms of the IA and IIA groups*

The ionic degree of the Li–C bond depends on the negative charge value of the carbon atom. An electron-withdrawing phosphonium group at the ylidic carbon atom raises the ionic character of the Li–C bond in comparison with standard organolithium compounds. McDowell and Streitwieser[14] have reported *ab initio* SCF-MO calculations of the simplest phosphonium lithium methylid **1**. They found that the C–Li bond of **1** has ionic character and the molecule has to exist in solution in an associated state. Calculations by Bestmann indicate a pyramidal structure for **1**, with a small (0.8 kcal mol^{-1}) inversion barrier.[15]

$$H_3P{=}CH^{-}Li^{+} \longleftrightarrow H_3P^{+}\text{-}CH^{2-}Li^{+}$$

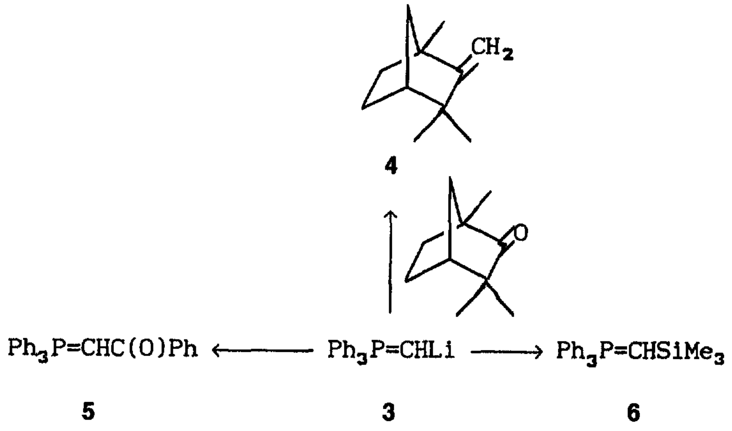
1



These theoretical calculations were confirmed by Corey and Kang who recently synthesized triphenylphosphonium α-lithium methylid and showed it to possess high reactivity. Interaction of butyllithium with triphenylphosphonium methylid (**2**) in THF solution at −78 to 40°C gave an intensively red coloured reaction mixture containing the lithium methylid **3** in a concentration of 0.2 mol l^{-1}. Ylid **3** may also be obtained as an orange-coloured suspension by reaction of methyltriphenylphosphonium bromide with two equivalents of *sec*-butyllithium in ether at temperatures from −78 to +20°C[16] (eq. 1):

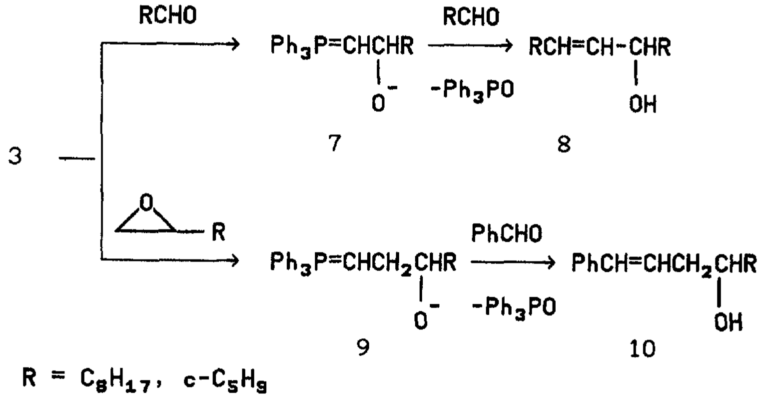
$$\underset{\mathbf{2}}{Ph_3P{=}CH_2} + t\text{-BuLi} \longrightarrow \underset{\mathbf{3}}{Ph_3\overset{+}{P}\text{-}\overset{-}{C}HLi} \longleftrightarrow Ph_3\overset{+}{P}\text{-}\overset{-}{C}H\ \underset{-}{}Li^{+} \qquad (1)$$

The lithium methylid **3** is significantly more nucleophilic than the initially formed triphenylphosphonium methylid. For example, sterically hindered fenchone does not react with triphenylphosphonium methylid even on heating to 50°C in different solvents. However, it can be easily olefinated by the lithium methylid in 1 h at temperatures from −50 to 20°C giving the exomethylene derivative **4** in 87% yield.[16] The reaction of lithium methylid **3** with benzoyl chloride or trimethylchlorosilane leads to the formation of the C-substituted ylids **5** and **6** (Scheme 1).



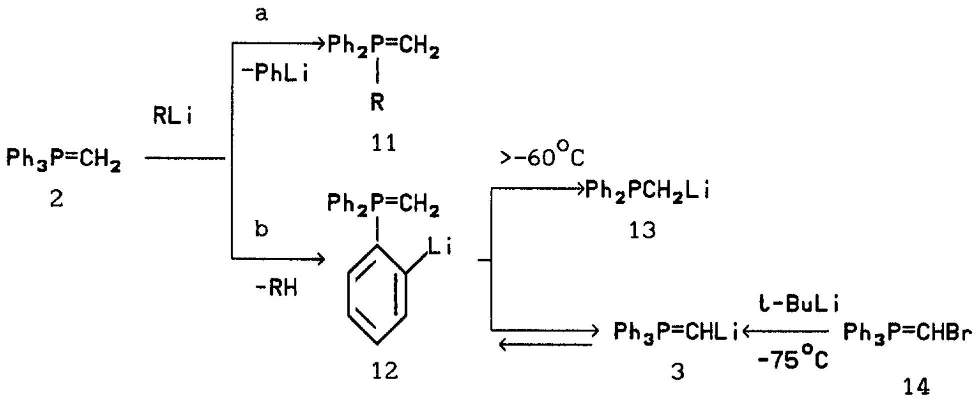
Scheme 1.

Double Wittig reactions can be carried out with α-lithiated ylids. Thus, reaction of the lithium methylid (**3**) with aldehydes affords α-oxido ylids **7**, which then react with a second molecule of aldehyde to provide the homoallylic alcohols **8**. The reaction of lithium methylid (**3**) with epoxides proceeds similarly via formation of an α-oxido ylidic intermediate **9**. Reaction of the latter with benzaldehyde gives *trans,trans*-homoallylic alcohols **10**[16] (Scheme 2).



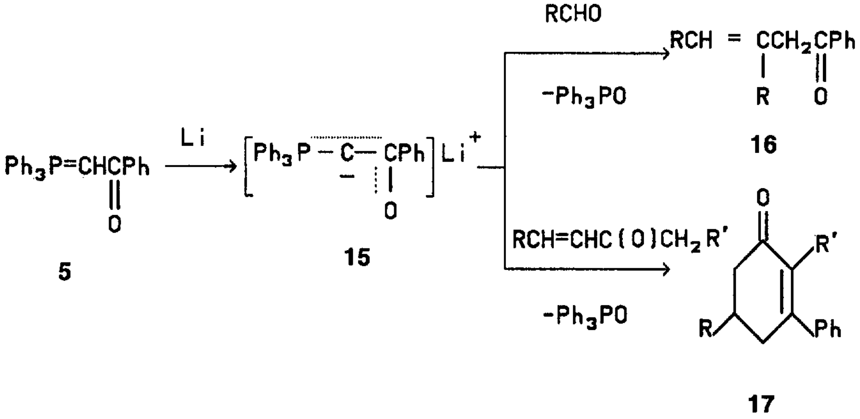
Scheme 2.

Schlosser showed by means of NMR at low temperature that the reaction of the triphenylphosphonium methylid with lithium alkyls is followed either by substitution of a phenyl group at the phosphorus atom by an alkyl group with formation of compound **11** (R = Alkyl, path α) or by metallation of the benzene ring with formation of compound **12** (path b, Scheme 3). However, the lithiated ylid **3** is not formed. Thus, reaction between the triphenylphosphonium methylid **2** and *tert*-butyllithium leads to the formation of ylid **12**, which is unstable, and above −60°C transformed into the lithiated phosphine **13** (Scheme 3).[17–19] Schlosser obtained the lithium methylid (**3**) by reaction of triphenylphosphonium bromomethylid (**14**) with *tert*-butyllithium in hexane at −75°C and confirmed its structure by means of NMR ($\delta_{H}\alpha$ −1.51 ppm, J_{HP} 14.0 Hz; $\delta_{C}\alpha$ 5.3 ppm, J_{CH} 108.0 Hz, J_{CP} 14.2 Hz; δ_{p} 9.5 ppm).[19] The spectral characteristics of the ylid **3** obtained by this method differed from those for the ylid obtained by the reaction of triphenylphosphonium methylid (**2**) with lithium alkyls.[19] Later, Corey described in detail the preparation of the lithium methylid (**3**) by reaction of triphenylphosphonium methylid (**2**) with *tert*-butyllithium. The high chemical reactivity of this reagent was demonstrated by several examples of reactions with different electrophiles.[20] Corey assumed the existence of a metallotropic tautomeric equilibrium between the lithium methylid (**3**) and the benzene ring lithiated species **12**, which explains the results obtained by Schlosser[17,19] (Scheme 3).



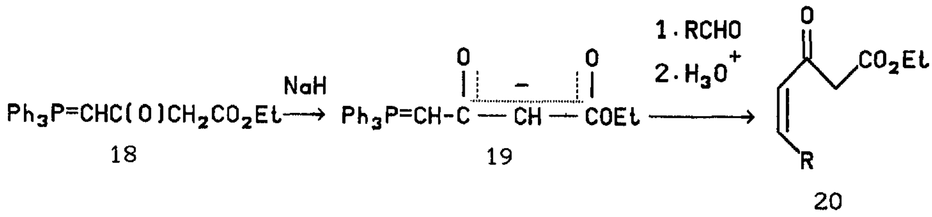
Scheme 3.

Lithiation is an important means of activating phosphorus ylids, thereby greatly extending their synthetic utility.[21] Thus, the triphenylphosphonium phenacylid **5** reacts easily with aldehydes, and does not react with ketones. However, the interaction of ylid **5** with lithium in HMPA leads to the formation of the highly active ylid **15**, which easily converts both aldehydes and ketones into olefins **16** and **17**. With α,β-unsaturated ketones the ylid **15** reacts first by Michael addition to give a betaine, intramolecular cyclization of which gives substituted cyclohexenones **17**[22,23] (Scheme 4).



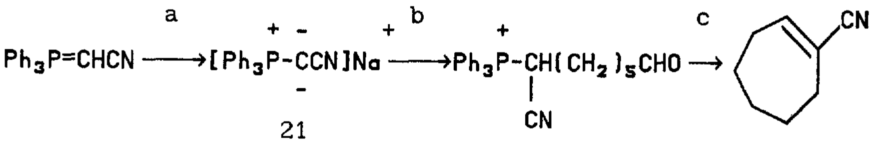
Scheme 4.

Under normal conditions the stabilized ylid **18** does not react with aldehydes even at reflux in THF. However, it readily forms anion **19** on treatment with sodium hydride in THF containing traces of moisture and anion **19** undergoes Wittig reaction with carbonyl compounds to give conjugated β-ketoesters **20**. The overall process is (*Z*)-selective and proceeds in excellent yield (60–98%)[24,25] (eq. 2).



(2)

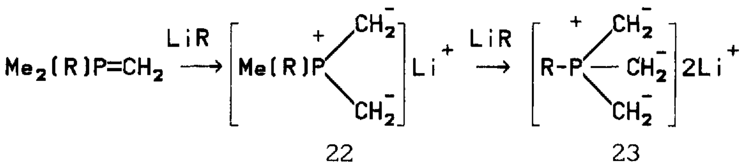
The sodium derivative of triphenylphosphonium cyanomethylid (**21**) was prepared by Bestmann and Schmidt and used for the preparation of cyclic compounds[26] (eq. 3).



(3)

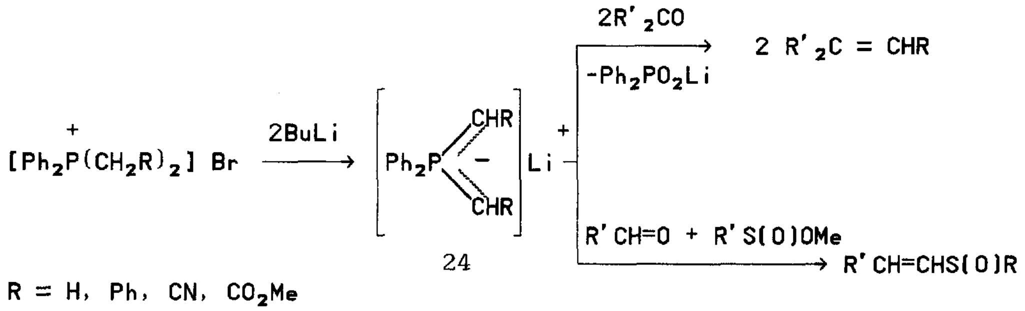
a – $NaN(SiMe_3)_2$; b – $Br(CH_2)_5CHO$; c – $NaN(SiMe_3)_2$

The reaction of trialkylphosphonium alkylids with excess of methyl- or butyllithium leads to lithiation of one or two of the alkyl groups at the phosphorus atom to afford highly reactive ylid-anions **22** and **23** (eq. 4).[27–37] These can be used as ligands in ylid complexes with transition metals[2,3] (see Section 2).



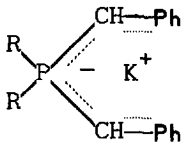
(4)

Ylid-anions of the type **24**, R = H, synthesized by Cristau and co-workers, react at room temperature with sterically hindered ketones such as di-*tert*-butyl ketone, fenchone, which triphenylphosphonium methylid does not olefinate (eq. 13).[38–49] The anions **24** react with carbonyl compounds in 1 : 2 proportion and as a result the yields of olefins with respect to ylid can reach 180–200%. The reactions of the ylid-anions with carbonates, thiocarbonates, isocyanates, carbodiimides and sulfinates proceeds with formation of the (*E*)-isomers of α,β-unsaturated derivatives of carbonic and sulfinic acids[47–49] (Scheme 5).

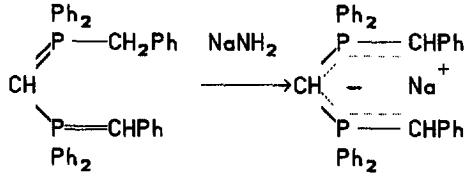


Scheme 5.

X-Ray structure analysis of the potassium derivative **25** shows strong coordinative interaction of the metal atom with the ylidic carbon atom and the *ortho*-carbon atoms of the benzylid groups.[50,51] Bis-ylid **26** reacts with sodium amide to form coloured sodium complexes **27** in which the metal is bonded via the benzylid positions. NMR spectra indicate a symmetrical coordination site for Na^+ above the benzylid rings (eq. 5).[50]

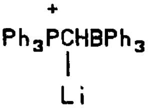


25



26 27 (5)

Lithiated ylids are versatile reagents for the preparation of other phosphorus ylids by exchange of the metal atom for different groups.[52] The adduct of triphenylborane with α-lithium-substituted triphenylphosphonium methylid **28** described by Seyferth is especially interesting.[53]



$$Ph_3\overset{+}{P}\underset{\underset{\displaystyle Li}{|}}{C}HBPh_3$$

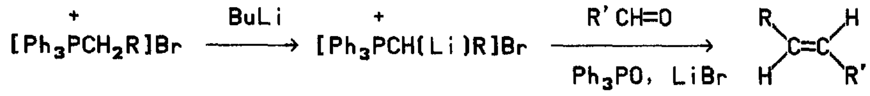
28

Ylidic complexes with alkali and alkaline earth metals. Phosphorus ylids react with alkali metal salts to form stable complexes. The most stable complexes were obtained with lithium halides (eq. 6); their stability is so high that isolation of 'salt-free' ylids can be a problem.[3,13,54–58] The structures of ylidic complexes with alkali metals halides have been studied but are still not completely clarified.[54] Ylidic complexes with lithium salts, **29**, are very reactive, and they undergo Wittig reaction with carbonyl compounds in a manner similar to that of the initially formed phosphorus ylids (eq. 7). Ylidic complexes with alkali metals differ from salt-free ylids in Wittig reaction stereochemistry.[58,59] Thus, reaction of 'salt-free' non-stabilized phosphorus ylids with carbonyl compounds usually give *cis*-olefins, while the lithium complexes give stereochemically pure *trans*-olefins:[13]

$$Me_3P{=}CH_2 \xrightarrow{Li^+X^-} [Me_3\overset{+}{P}CH_2Li]LnX^- \qquad (6)$$

29

Ln-solvent



(7)

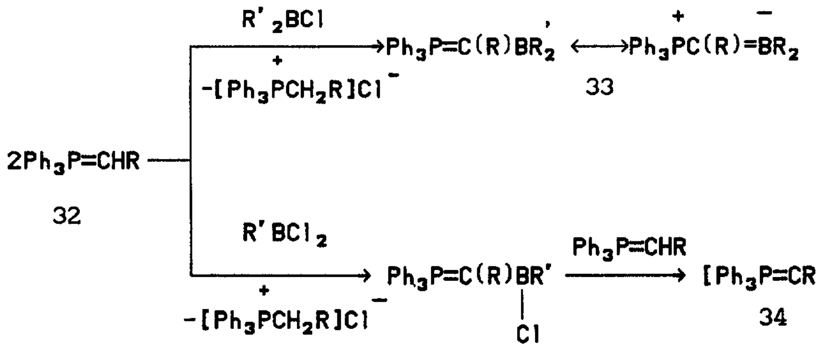
Salt-like ylidic complexes with heavy alkali metals possess lower thermal stability. Caesium derivatives, probably containing true anions $[(CH_3)_2P^+(CH_2^-)_2]Cs^+$, have been isolated.[3,50,51] Alkaline earth metals, being rather strong Lewis acids react with phosphorus ylids to form stable salt-like complexes having cyclic structures with coordinate bonds.[1,61] Some ylidic complexes with alkali earth metals are coordination polymers.[62–64] Free ylids of the type $R_3P = CHM$, substituted by an alkaline earth metal at the α-carbon atom, have not been described.

1.2. *Ylids containing metal atoms of the IIIA group*

Being strong Lewis acids, the elements of the third group of the periodic system readily interact with phosphorus ylids possessing basic properties. Reaction of phosphorus ylids with boron compounds usually gives simple 1 : 1 addition products such as **30** and **31**, while aluminium, gallium, indium and thallium compounds give more complex products. Betaines **30** and **31** are salt-like thermally stable compounds, the structures of which have been confirmed by NMR spectra and X-ray analysis.[63–66] The reaction of triphenylphosphonium alkylids **32** or benzylids with dialkyl chloroboranes in benzene result in transylidation and formation of ylids **33**, R = Me, Et, Ph; R′ = c-C_5H_9, C_5H_{11}, c-C_6H_{11}, which can be isolated in crystalline form.[67] Reaction of the phosphorus ylids with alkyl dichloroboranes gives bisylid-alkylboranes (**34**), as a result of transylidation where R′ is cycloalkyl or sterically hindered alkyl[67–69] (Scheme 6). *Ab initio* calculations on boron-substituted ylids have been reported.[15]

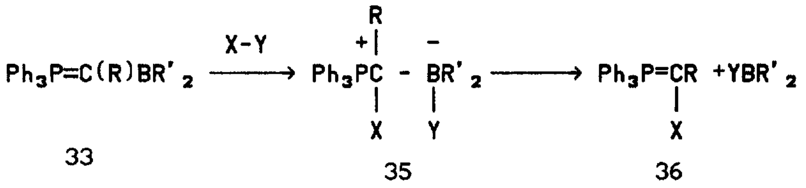
$Ph_3\overset{+}{P}CH_2\overset{-}{B}H_3$ $Ph_3\overset{+}{P}CH_2\overset{-}{B}F_3$

30 31



Scheme 6.

The highly reactive C–boron-substituted ylids **33** react with polar or polarized compounds X–Y to give ylids **36** and boranes through an intermediate onium complex (eq. 8). The reaction of ylids **33** with deuteromethanol leads to the formation of ylids **37** that have been used for the preparation of deuterated olefins. Reaction of ylids **33** with bromine gives phosphonium salts **38** which can be converted into ylids **39** by treatment with butyllithium[69] (eq. 9).



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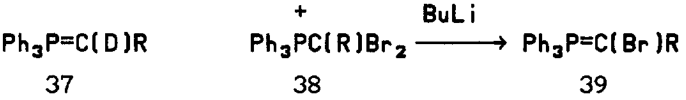
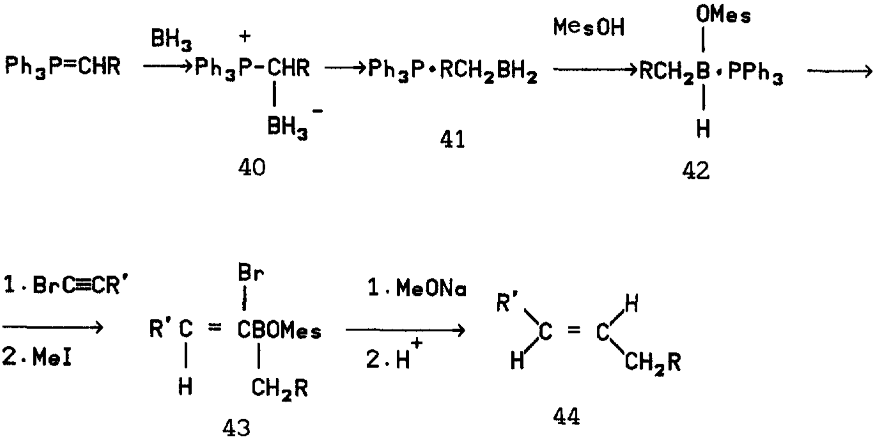


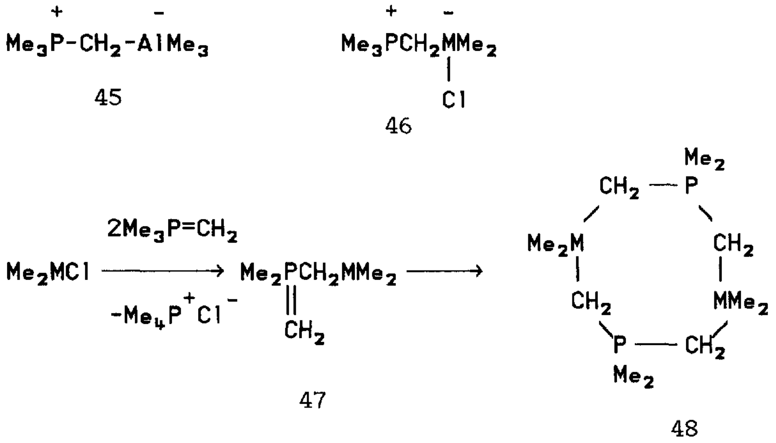
(9)

Stereoselective syntheses of olefins, in particular of (*E*)-unsaturated pheromones, have been developed based on hydroboronated adducts of phosphorus ylids. Thus reaction of phosphorus ylids **32** with borane gives betaines **40** which easily rearrange to the adducts **41**.[66] Reaction of **41** with 2,4,6-trimethylphenol affords adducts **42** (Mes = 2,4,6-$Me_3C_6H_2$) which react with bromoacetylene in the presence of methyl iodide to give the vinylboranes **43**. Treatment of the latter with sodium methoxide followed by protonolysis yields olefin **44**, with 99% of (*E*)-selectivity[66,70] (Scheme 7).



Scheme 7.

Dialkyl and trialkyl derivatives of aluminium, gallium, indium and thallium react with phosphorus ylids to form betaines of the types **45** and **46** (M = Ga, In, Tl), which have been isolated and purified by crystallization (eq. 10). Aluminium, gallium, indium and thallium dialkylhalides react with trimethylphosphonium methylid in a 1 : 2 ratio to afford the tetramethylphosphonium chloride and ylids **47** as a result of transylidation. Ylids **47**, which contain a coordinatively unsaturated metal atom in the chain, very easily dimerize to the stable cyclic products **48** (eq. 10).[1,3,74]



(10)

1.3. *Ylids containing metal atoms of the IVA group* [C–Si, C–Sn *and* C–Ge *substituted ylids*]

C-Silylated phosphorus ylids have been studied in detail because of their great preparative importance, availability, stability and reactivity. C–Germanium and C–tin-substituted phosphorus ylids have been studied in less detail.

1.3.1. *Synthesis.* Phosphorus ylids react with silicon, germanium and tin halides in a 2 : 1 ratio to give C–element-substituted phosphorus ylids **50** (M = Si, Ge, Sn) and phosphonium salts as a result of transylidation between the intermediate phosphonium salt **49** and the starting ylid (eq. 11).[75,76] Many examples of syntheses of cyclic and acyclic C–element-substituted phosphorus ylids **50** by this method have been described.[1,77–80]

$$R_3P{=}CH_2 \xrightarrow{R'_3MCl} \underset{49}{[R_3PCH_2MR'_3]^{+}Cl^{-}} \xrightarrow[-[R_3PMe]^{+}Cl^{-}]{R_3P=CH_2} \underset{50}{R_3P{=}CHMR'_3} \qquad (11)$$

Di- and tricarbanions of the types **51** and **53** react with silicon, germanium, tin and lead halides in 1 : 1 proportion to form C-substituted phosphorus ylids of the types **52** and **54** (M = Ge, Si, Sn, Pb)[71,81,83] (eq. 12, 13).

$$R_2(Me)P{=}CH_2 \xrightarrow{BuLi} \underset{51}{[R_2P(\overset{-}{C}H_2)_2]^{-}Li^{+}} \xrightarrow{Me_3MCl} \underset{52}{R_2(Me)P{=}CHMMe_3} \qquad (12)$$

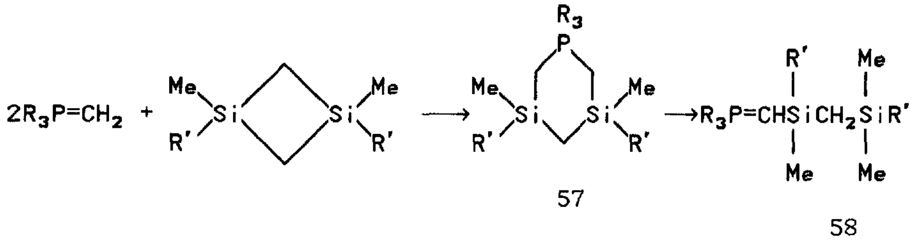
$$Me_3P{=}CH_2 \xrightarrow{2BuLi} \underset{53}{[MeP(\overset{-}{C}H_2)_3]^{-}2Li^{+}} \xrightarrow{Me_3MCl} \underset{54}{Me_3P{=}C(MMe_3)_2} \qquad (13)$$

Reaction of trimethylphosphonium trimethylsilylmethylid (**55**) with heterosiloxanes provides an elegant route to the simple phosphonium ylid **56** with trimethylgermanium, trimethyltin and trimethyllead substituents. The driving force for this transformation has been attributed to the propensity for disiloxane formation[71,84] (eq. 14).

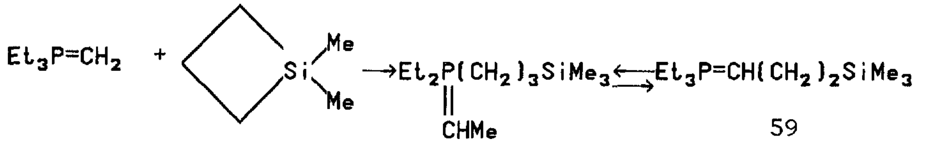
$$\underset{55}{Me_3P{=}CHSiMe_3} + Me_3SiOMMe_3 \longrightarrow \underset{56}{Me_3P{=}CHMMe_3} + (Me_3Si)_2O \qquad (14)$$

M = Ge, Sn, Pb

C-Silylated phosphorus ylids have been obtained from phosphonium alkylids and derivatives of sila- or disilacyclobutane. The mechanism of this reaction probably includes formation of pentaalkylphosphorane intermediates **57**[84a–86] (eq. 15, 16).



(15)



(16)

Treatment of α-silylalkylphosphonium salts with organolithium bases leads to the formation of ↑ ylids in which the silicon substituent is directly attached to the ylidic carbon atom. This type of reaction has been widely used for the preparation of silylated ylids[75,87] (eq. 17).

$$R^1_3P + ClCH(R^2)SiR^3_3 \longrightarrow [R^1_3\overset{+}{P}CH(R^2)SiR^3_3]Cl^- \longrightarrow R^1_3P{=}C(R^2)SiR^3_3 \qquad (17)$$

In some cases α-silylalkylphosphonium salts can be converted into phosphorus ylids on heating and without added organolithium bases. For example, thermolysis of trimethylsilylmethyltrimethylphosphonium chloride leads to the elimination of trimethylchlorosilane and formation of trimethylphosphoniumtrimethylsilylmethylid (**55**), which was collected by vacuum distillation as a colourless liquid[75] (eq. 18).

$$2[Me_3\overset{+}{P}CH_2SiMe_3]Cl^- \xrightarrow[-Me_3SiCl]{\Delta} \underset{55}{Me_3P{=}CHSiMe_3} + Me_4\overset{+}{P}Cl^- \qquad (18)$$

Reaction of C-silyl-substituted P-chloroylids with organolithium compounds proceeds by replacement of the chlorine atom by an alkyl group and gives C-silylated phosphorus ylids in very good yields[80] (eq. 17).

$$t\text{-}Bu_2PCH_2SiMe_3 \xrightarrow{CCl_4} t\text{-}Bu_2P(Cl){=}CHSiMe_3 \xrightarrow{RLi} t\text{-}Bu_2P(R){=}CHSiMe \qquad (19)$$

1.3.2. *Properties*. Phosphorus ylids stabilized by silicon, germanium and tin atoms are rather stable, and they can be easily purified by distillation under vacuum or crystallization from organic solvents. Silicon atoms at the ylidic carbon reduce the basicity and nucleophilicity of C-silyl-substituted phosphorus ylids and induce a pronounced stabilizing effect on the carbanion. Among the most striking consequences of this stabilizing effect is the course of transylidation reactions in the case of C-silylated phosphorus ylids, which testifies to the higher CH-acidity of the C-silyl-substituted phosphonium salts **49**[75] (eq. 11). Transylidation is not directly dependent on the size of substituents, because SiH_3 shows the same stabilizing effect as more sterically demanding groups.[87,88] Replacement of the trimethylsilyl group at the ylidic carbon atom with the *tert*-butyl group, however, leads to a significant increase in ylid basicity, i.e. to anion destabilization.[89] Germanium and tin show similar effects.[75] The stabilizing effect of the silicon and the related reduction of ylid basicity may be explained in terms of the participation of d-orbitals in delocalization of the negative charge of the ylidic carbon atom.[87]

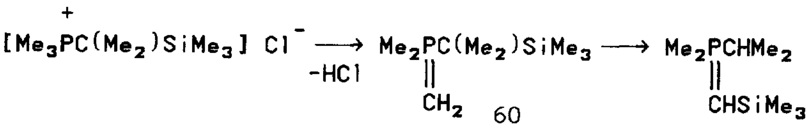
$$R_3\overset{+}{P}{-}\overset{-}{C}HSiMe_3 \longleftrightarrow R_3\overset{+}{P}CH{=}\overset{-}{Si}Me_3$$

The modern concept uses the idea of electrostatic charge interaction and redistribution of the charge of the ylidic carbon atom. This concept implies an increase in space around the carbanionic centre and a corresponding decrease in the repulsive forces between the high electron density of the ylidic carbanion and the bonding electrons of the σ-framework upon introduction of the larger third-row elements.[62] The π-interaction between the phosphorus atom and the ylidic carbon atom is described as negative hyperconjugation. This interaction transfers electron density from the occupied p-orbital on the carbon atom to the unoccupied σ*-orbitals of the phosphorus ligand. The d-orbitals on phosphorus exert only a polarizing function.[91] This concept has to a certain extent been confirmed by experimental investigation of phosphorus ylids by means of photoelectron spectroscopy. On the basis of the experimental values for P=C π-ionization and CNDO/2 calculations of C-silyl-substituted phosphorus ylids Bock and co-workers came to the conclusion that silicon stabilization is not the consequence of a π-energy lowering but of a decrease of the MO coefficient at the ylidic, quasi-anionic carbon atom.[92,93] IR and NMR spectroscopic studies of C-silyl-substituted phosphorus ylids have been performed in detail.[1,52,75] The absorption frequency value of the P=C group in triphenylphosphonium trimethylsilylmethylid is 1150 cm^{-1}.[52,81] X-Ray analyses show the pyramidal configuration of the ylidic carbon atom of silylated ylids.[94]

The trimethylsilyl group at the ylidic carbon atom is remarkable for its high lability. C-Silyl-substituted phosphorus ylids are easily desilylated on reactions with hydroxyl-containing compounds, in particular alcohols or silanols, and give salt-free ylids, R = Alk, Ph, in a very pure state[74] (eq. 25).

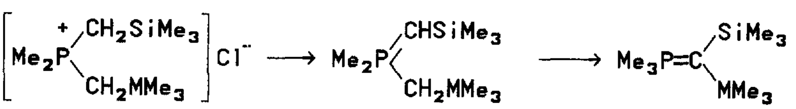
$$R_3P{=}CHSiMe_3 + MeOH \longrightarrow R_3P{=}CH_2 + Me_3SiOMe \qquad (20)$$

The trialkylsilyl group in the C-silylated ylids **60** can migrate to carbanion centres which leads to lower basicity and nucleophilicity (eq. 21).[71] Trialkylstannyl- and trialkylgermyl groups in the ylids **61** also migrate easily (eq. 22). Consequently, C-monostannyl-substituted phosphorus ylids **62** which undergo facile disproportionation into distannyl-substituted ylids **63** have only been detected spectroscopically (eq. 23).[81,84] The analogous lead derivative was found to be even more sensitive. Silicon and to some extent germanium atoms stabilize ylidic carbanions, whereas the latter are destabilized and thus enhanced in reactivity by tin- and lead-containing substituents. The increased acceptor abilities of tetracoordinated tin and lead species, compared with the silicon and germanium analogues, facilitate nucleophilic attack at the ylid, inducing disproportionation.[71,75,84]



$$[Me_3\overset{+}{P}C(Me_2)SiMe_3]\,Cl^- \xrightarrow[-HCl]{} \underset{\underset{\textstyle CH_2}{\|}}{Me_2PC(Me_2)SiMe_3} \longrightarrow \underset{\underset{\textstyle CHSiMe_3}{\|}}{Me_2PCHMe_2} \qquad (21)$$

60



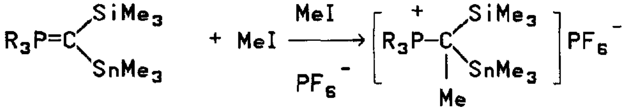
61 (22)

$$2[Me_3\overset{+}{P}CH_2SnMe_3]Cl^- \longrightarrow \underset{62}{2Me_3P{=}CHSnMe_3} \longrightarrow \underset{63}{Me_3P{=}C(SnMe_3)_2} + Me_3P{=}CH_2 \qquad (23)$$

The susceptibility to disproportionation exhibited by the higher homologues contrasts sharply with the behaviour of trimethylphosphonium trimethylsilylmethylid, which is accessible via disproportionation according to equation 24.[71,75,84]

$$Me_3P{=}CH_2 + Me_3P{=}C(SiMe_3)_2 \longrightarrow 2Me_3P{=}CHSiMe_3 \qquad (24)$$

The ylid carbon atom in the organosilyl-substituted ylids shows nucleophilic character and reacts with methyl iodide[96] (eq. 25).

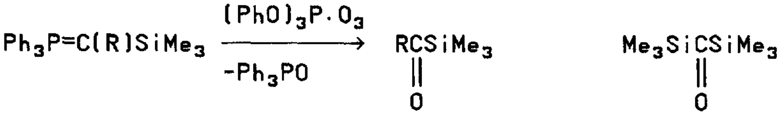

(25)

Silyl-substituted ylids are used as starting materials for the preparation of new C-substituted phosphorus ylids, in particular cyclic and acyclic difunctional ylids.[63,74] Trimethylsilyl groups at the ylidic carbon atom are easily exchanged for various substituents by reactions with chlorine-containing electrophiles, including polychlorosilanes, chlorophosphines, PCl_3, chloroarsines and chlorostibines. A wide variety of phosphorus, arsenic and antimony-substituted ylids **64** have been obtained in this way[71,75,90,95] (eq. 26), including silyl-containing heterocycles.[52,76]

$$R_3P{=}C(R')SiMe_3 \xrightarrow[-Me_3SiCl]{R''Cl} \underset{64}{R_3P{=}CR'R''} \tag{26}$$

$$R''{=}SiMe_nCl_{3-n},\ Me_2P,\ PCl_2,\ Me_2As,\ Me_2Sb,\ \pi\text{-}Cp(CO)FeSi(Me_2)$$

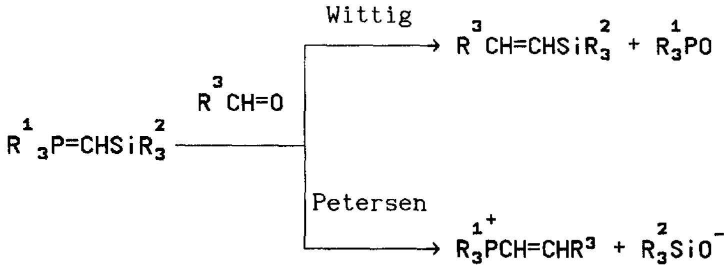
The oxidation of triphenylphosphonium bis(trimethylsilyl)methylid, by the triphenylphosphite/ozone adduct yields silyl ketones **65**, R = $SiMe_3$, Ph, 4-BrC_6H_4, 4-$MeOC_6H_4$, including bis-trimethylsilyl ketone[97–99] (eq. 27).


(27)

65

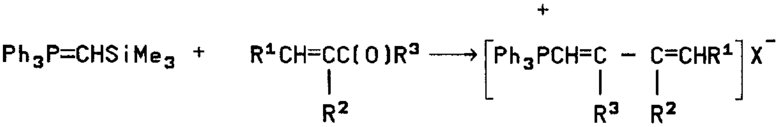
$$Ph_3P{=}C(R)SiMe_3 \xrightarrow[-Ph_3PO]{(PhO)_3P\cdot O_3} RC({=}O)SiMe_3 \qquad Me_3SiC({=}O)SiMe_3$$

Due to competition between silicon and phosphorus for the carbonyl oxygen atom the reaction of the C-silyl-substituted ylids with carbonyl compounds may proceed in two ways, i.e. by the Wittig and Petersen reactions (Scheme 8).[65,100–102] The reaction of C-silyl-substituted phosphorus ylids with aldehydes and ketones usually results in formation of mixtures of compounds, and hence is not of wide synthetic application.[3]



Scheme 8.

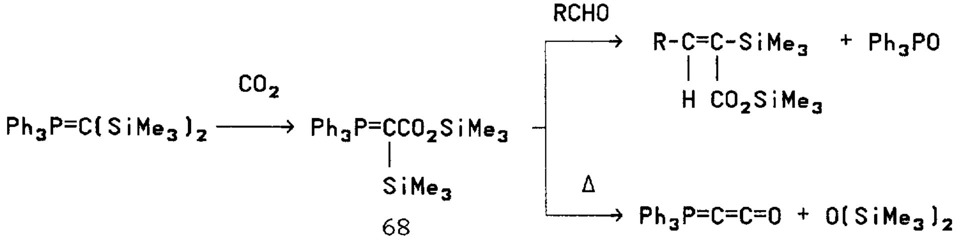
Sometimes, however, the reaction proceeds regioselectively. For example, reaction of the triphenylphosphonium trimethylsilylmethylid (**6**) with unsaturated carbonyl compounds **66** gives conjugated phosphonium salts **67** with R^1 = H, Ph; R^2 = H, Me; R^3 = H, Me; X = Br, Me_3SiO in 50–100% yields[103a] (eq. 28).



$$Ph_3P{=}CHSiMe_3 + R^1CH{=}C(R^2)C(O)R^3 \longrightarrow [Ph_3\overset{+}{P}CH{=}C(R^3){-}C(R^2){=}CHR^1]X^- \quad (28)$$

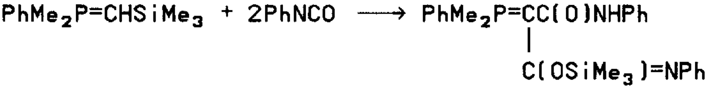
6 66 67

The reaction of bis-silylated phosphorus ylids with carbon dioxide to give silylated acyl ylids **68** was described recently by Bestmann and co-workers. These react smoothly with aldehydes to provide α,β-unsaturated silylesters in good yields and with high stereoselectivity. Alternatively, their thermolysis affords ketenylids.[103b,108] (Scheme 9).



Scheme 9.

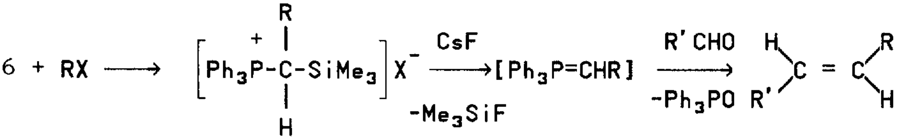
Insertion products **69** are also formed with isocyanates, isothiocyanates and carbon disulfide[103] (eq. 29).



$$PhMe_2P{=}CHSiMe_3 + 2PhNCO \longrightarrow PhMe_2P{=}C(C(O)NHPh)C(OSiMe_3){=}NPh \quad (29)$$

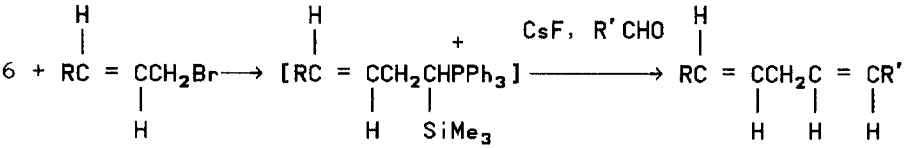
69

The cleavage of the Si–C bond of α-silylated phosphonium salts by treatment with caesium fluoride is a convenient method for generation of phosphorus ylids, and has been used for preparation of naturally occurring compounds. Thus, alkylation of triphenylphosphonium trimethylsilylmethylid (**6**) with alkyl halides affords C-silylated phosphonium salts **70** which on subsequent reaction with fluoride anion undergo desilylation and formation of substituted ylids. The latter compounds in turn then undergo Wittig reaction to provide disubstituted *Z*-alkenes **71** in high yields (eq. 30).[97,100,104–108] This reaction sequence has been applied for the synthesis of homoconjugated pheromones of Lepidoptera.[104–108] In similar fashion the alkylation of ylids **6** with allylic bromides leads to skipped *Z*,*E*-dienes **72** (eq. 31).[108]



$$6 + RX \longrightarrow [Ph_3\overset{+}{P}{-}CH(R){-}SiMe_3]X^- \xrightarrow[-Me_3SiF]{CsF} [Ph_3P{=}CHR] \xrightarrow[-Ph_3PO]{R'CHO} (H)(R')C{=}C(R)(H) \quad (30)$$

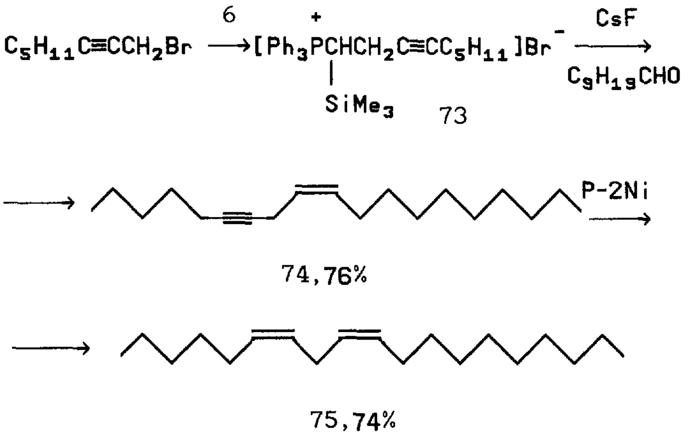
70 71



$$6 + RCH{=}CHCH_2Br \longrightarrow [RCH{=}CHCH_2CH(SiMe_3)\overset{+}{P}Ph_3] \xrightarrow{CsF,\ R'CHO} RCH{=}CHCH_2CH{=}CHR' \quad (31)$$

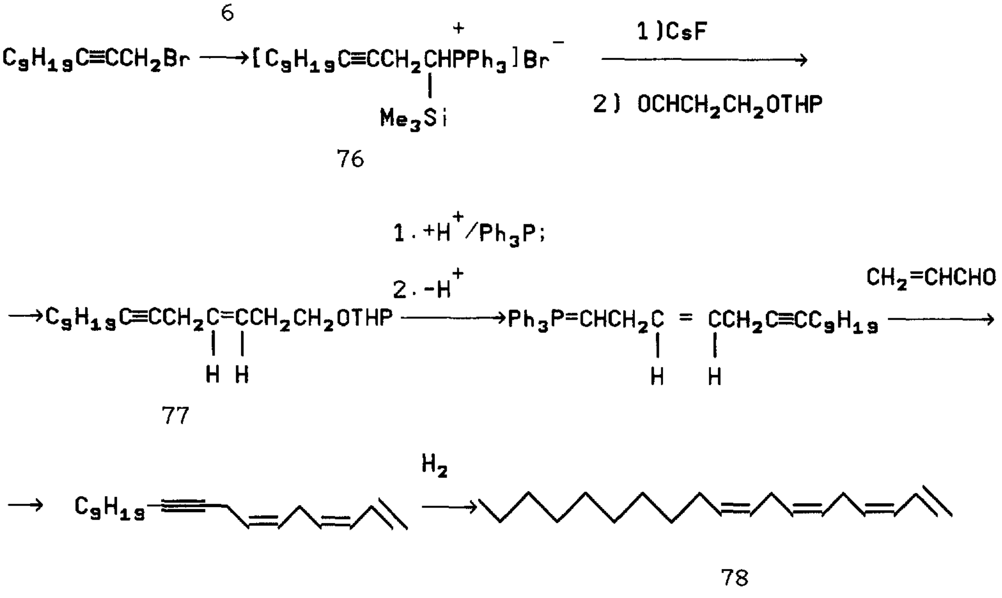
72

Alkylation of triphenylphosphonium trimethylsilylmethylid (**6**) with the propargylic halide shown gives the salt **73** which can be subsequently desilylated by caesium fluoride in the presence of the aldehyde to afford the ene-yne **74** with 98% *Z*-stereoselectivity. The ene-yne **74** can then be reduced with P-2 nickel to yield the *Z*,*Z*-diene **75** in which the multiple bonds are separated by a methylene group as shown in Scheme 10.[108]



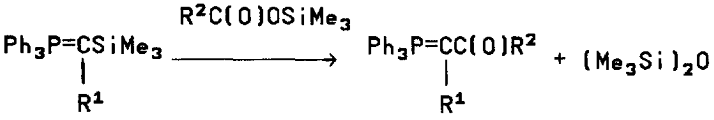
Scheme 10.

This highly stereoselective approach has been particularly useful for preparation of pheromones, in particular of the (*Z*,*Z*)-6,9-nonadecadiene, a component of the pheromone complex of *Bupalus piniarius*.[109,110] A second example involving formation of the salt **76** from an acetylenic bromide and the ene-yne **77** is shown in Scheme 11. The latter was transformed into tetra-ene **78**, which is a pheromone component of *Operophtera brumata*.[108,109]



Scheme 11.

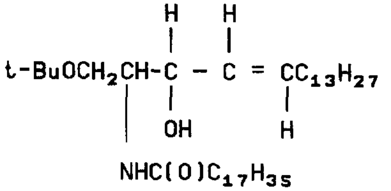
The reaction of C-silyl-substituted phosphorus ylids with silyl esters followed by elimination of hexamethyldisiloxane is a convenient method for the preparation of acyl-alkylids **79** (eq. 32).[79,98,104] The reaction of the C-silyl-substituted phosphorus ylids with carbonic acids proceeds analogously. Based on this reaction methods for the replacement of the OH-group by the ylid function were developed.[98] Acyl-ylids **79** prepared in this way in 88% yield were applied for the synthesis of *N*-tert-butoxy-carbonyl-substituted merucatinone, a starting compound for the preparation of drugs.[98,111] They have also been used for the synthesis of disubstituted acetylenes,[105] by treatment with trifluoromethanesulfononic anhydride to obtain O-substituted vinylphosphonium salts followed by reduction with sodium amalgam.



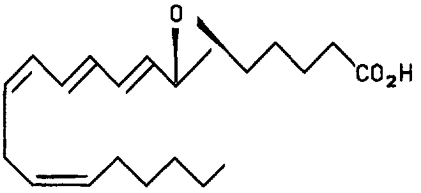
$$Ph_3P{=}\underset{\displaystyle R^1}{\underset{|}{C}}SiMe_3 \xrightarrow{R^2C(O)OSiMe_3} \underset{\textbf{79}}{Ph_3P{=}\underset{\displaystyle R^1}{\underset{|}{C}}C(O)R^2} + (Me_3Si)_2O \qquad (32)$$

79

The reaction of the C-silylated phosphorus ylids with silyl esters has been applied in the synthesis of ceramide (**80**), leukotriene A_4 (**81**),[112,113] and components of the gland secretion of the ant *Manica rubida*.[104]



80



81

C-Silylated phosphorus ylids have been used as versatile ligands for transition metals in their various oxidation states. With copper, silver and gold halides and their phosphine complexes they form a variety of stable coordination compounds, containing metal–carbon bonds.[114–116] Neutral phosphorus ylid complexes have been obtained by reaction of trimethylphosphonium trimethylsilylmethylid with iron, chromium, molybdenum and tungsten carbonyls.[117–122] The examples of C-silyl-substituted complexes are described in the literature[1–4] and discussed in the next section of this review.

2. YLIDS CONTAINING TRANSITION METALS AT THE α-CARBON ATOM

Metal atoms directly bonded to an ylidic carbon atom may interact with an ylidic carbanion in two ways. Thus, metals with σ-donor properties (+I-effect) would induce an increased electron density at the ylidic carbon atom and thereby enhance the ylid nucleophilicity (eq. 33, structure B). This effect would make the ylid more reactive as in the case of a lithiated phosphorus ylid. Contrastingly, main group metals possessing suitable acceptor orbitals, for example metals of the silicon group, may interact with the filled carbon centred p-orbitals of the ylid. The resulting carbon–metal bond with π-back donation possibly creating a partial metal–carbon double bond, would then decrease the electron density at the ylidic carbon and thus lead to reduced ylid nucleophilicity (structure C). The relative contribution of these two opposing effects will certainly depend on the nature of the metal centre as well as on the surrounding ligands.

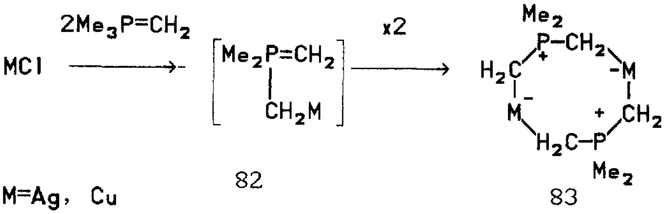
$$R_3P{=}CH{-}M \longleftrightarrow R_3\overset{+}{P}{-}\overset{-}{C}H{\leftarrow}M \longleftrightarrow R_3\overset{+}{P}{-}CH{=}\overset{-}{M} \qquad (33)$$

$$\text{A} \qquad\qquad \text{B} \qquad\qquad \text{C}$$

Transition metals possessing a high π-acceptor capacity consequently manifest a pronounced stabilizing effect on the ylidic carbanion. Transition metals of almost all groups of the periodic table have been sited at the α-carbon atom within the last few years. However, because of their propensity to form a high coordination number, many of the transition metals interact readily with the ylidic carbon atom to form dimers and oligomers. Indeed many examples shown in this section of the review illustrate the potential variety of synthetic possibilities achieved by substitution of the ylid hydrogen atoms with transition metal atoms. Some ylidic complexes may serve as excellent catalysts while others may be useful in pharmacology.[123–125] The chemistry of such ylid complexes with metals has been described in several articles.[1–4]

2.1. *Ylids containing metal atoms of the IB and IIB groups*

The reaction of phosphorus ylids with copper(I), silver(I) and gold(I) halides proceed with 2 : 1 stoichiometry to give ylids **82**, as a result of transylidation. These are easily converted into linear or cyclic dimers **83**. The compounds **83** have a high stability toward hydrolysis, oxidation and heating (eq. 34). Various complexes of this kind have been described. However, free ylids bearing metals of group IB at the α-carbon atom have not been isolated.[115,116,126–128]



(34)

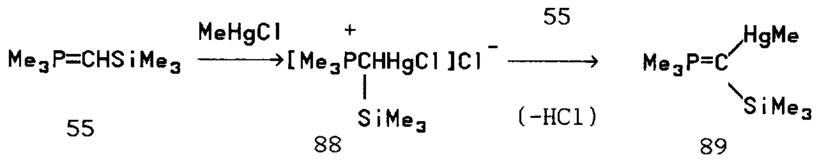
In contrast to the group IB elements ylid derivatives of the second sub-group elements (mercury and cadmium) form stable σ-bonds and have a low coordination number. Consequently C–mercury-containing phosphorus ylids may exist in the monomeric non-associated state. The mercury atom is generally not capable of acidifying adjacent hydrogen atoms in mercurated onium salts, but as with other d^{10}-systems it tends to do the reverse. Mercurated ylids are therefore accessible when an anion-stabilizing substituent at the ylidic carbon compensates for this retarding influence of the metal. Thus, the successful syntheses of C-mercurated phosphorus ylids depends on the electron-withdrawing capacity of the second substituent at the α-carbon atom. Stabilized phosphorus ylids, containing benzoyl, cyano- or carbomethoxy groups at the α-carbon atom add mercuric acetate as well as mercuric chloride to form compounds **84** with a mercury–carbon bond. Treatment of these compounds with liquid ammonia or sodium methoxide gives C-mercurated phosphorus ylids such as **85** or **86** in high yields. These undergo Wittig reaction with aldehydes to form olefins **87**[129–131] (eq. 35, 36).

$$\underset{32}{Ph_3P{=}CHR} \xrightarrow{Hg(OCOMe)_2} \underset{84}{[Ph_3PCH(R)HgOCOMe]^{+}OCOMe^{-}} \xrightarrow{B} \underset{85}{Ph_3P{=}C(R)HgC(R){=}PPh_3} \qquad (35)$$

$B = NaOMe/MeOH,\ NH_3;\ R = CN,\ COPh,\ CO_2Me$

$$\underset{86}{[Ph_3P{=}C(CO_2Me)]_2Hg} + RCHO \longrightarrow \underset{87}{[RCH{=}C(CO_2Me)]_2Hg} \qquad (36)$$

The C-silylated phosphorus ylid **55** reacts with methylmercury chloride to give a C-mercurated derivative **88** which is easily dehydrochlorinated by an excess of the phosphorus ylid with resultant formation of ylid **89**, containing both a C–Hg and a C–Si bond (eq. 37). Ylid **89** was also obtained from C-lithiated phosphorus ylids and methylmercury chloride (eq. 38). Ylid **89** is a stable liquid which may be distilled under vacuum.[130]



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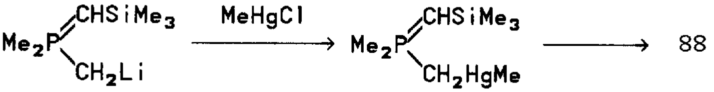
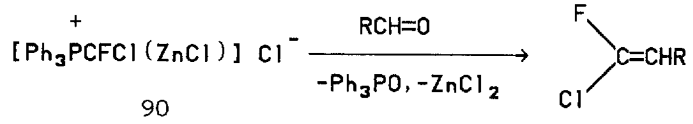


(38)

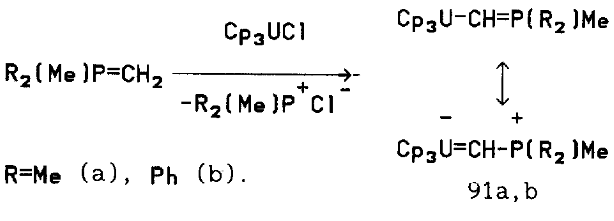
A variety of ylid complexes with metals of group IIB have been described.[132–145] These complexes cannot be considered as true ylids, although they readily undergo the Wittig reaction and are widely used for the preparation of olefins. Ylid complexes such as **90** are obtained by reaction of triphenylphosphine with tetrahalogenomethanes and zinc, and are important starting reagents for the preparation of halo-olefins (Scheme 39).[63,143–145]



(39)

2.2. *Ylids containing metal atoms of the actinium group*

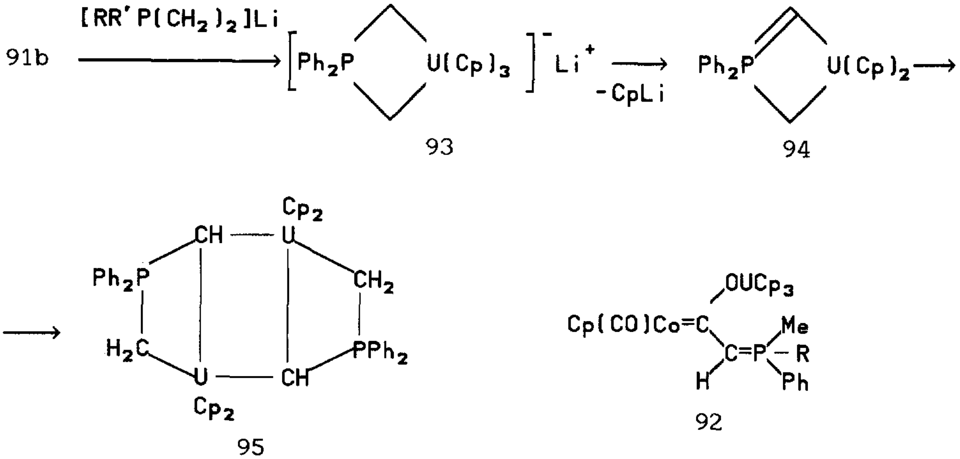
The high stability of transition metal complexes has also stimulated studies of phosphorus ylids, containing elements of the actinium group at the α-carbon atom, particularly uranium. The reaction of tris(cyclopentadienyl)uranium chloride with phosphorus ylids or their lithium derivatives gives flammable, dark green crystalline complexes (**91**) which are sensitive to moisture and oxygen. X-Ray analyses[146–148] and electronic diffraction studies[149] show the metallocene structure of ylids **91** (eq. 40). The short U–C 2.293(1) Å and C–P 1.692(2) Å distances of the compounds **91a** are indicative of delocalization of the negative charge in the U–C–P triad.[147–149] These ylids display nucleophilic properties and react with polar unsaturated compounds such as RNCO, RCN, RNC and metal carbonyls.[148]



$$R_2(Me)P{=}CH_2 \xrightarrow[-R_2(Me)\overset{+}{P}\overset{-}{Cl}]{Cp_3UCl} Cp_3U{-}CH{=}P(R_2)Me \leftrightarrow Cp_3\overset{-}{U}{=}CH{-}\overset{+}{P}(R_2)Me$$

(40)

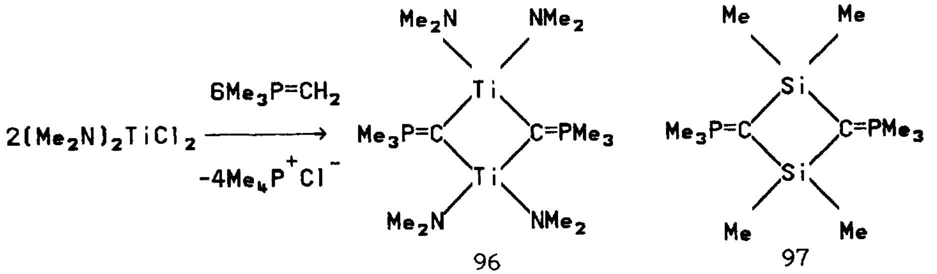
Thus, reaction of the compound **91b** with cobalt cyclopentadienyl dicarbonyl leads to the formation of ylid **92**. Excess of $[Ph_2P(CH_2)_2]Li$ metallates the ylid **91b** to afford cyclic compound **93** transforming into cyclic metallocene ylid **94**. The latter easily dimerizes to afford red crystalline complex **95**. The structure of compounds **95** was determined by X-ray analysis[31,150] (Scheme 12).



Scheme 12.

2.3. *Ylids containing metal atoms of the IIIB and IVB groups*

Uncompleted orbitals of the elements of IVB group (Ti, Zr, Hg) determine their capacity to form donor–acceptor bonds. Often the chemistry of d-configurated tetravalent titanium parallels that of the d^0 elements of group IVa. In their ability to stabilize an ylidic carbanion tetravalent titanium and zirconium are similar to silicon and tin. Thus, the preparations and structures of 1,3-dititanocyclobutane (**96**) and the silicon derivative **97** are comparable (eq. 41).[151,152] C–Titanium-substituted bis-ylid **98** has been obtained by reaction of titanium tetrachloride with tris-(diethylamino) phosphonium methylid and its structure has been determined by X-ray analysis.[153,154] The interaction of diethylaminodimethylphosphonium methylid with diethylzirconium leads, as a result of the transylidation, to the formation of stable four-membered cyclic ylid **99**.[153]



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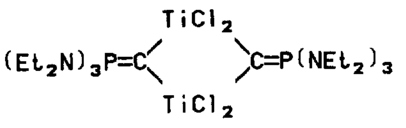
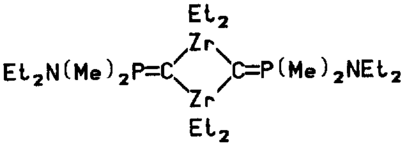
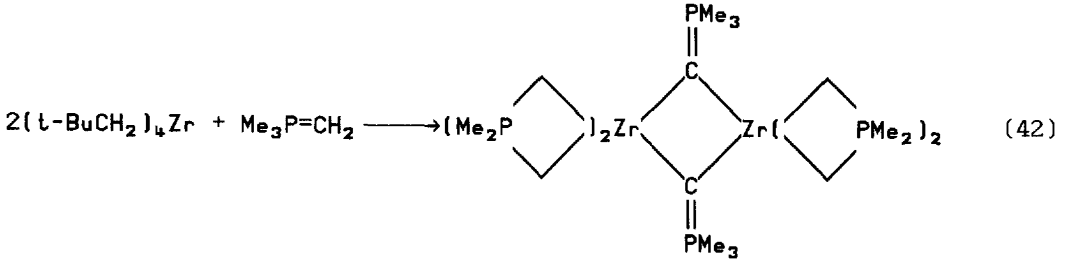


98



99

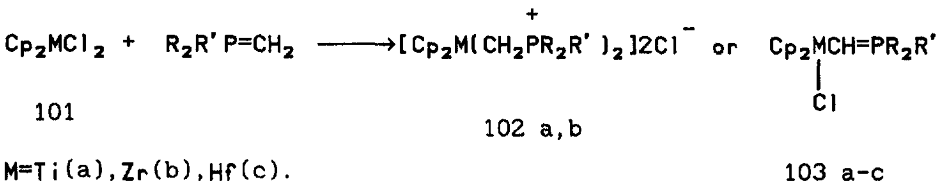
The reaction of tetraneopentylzirconium with trimethylphosphonium methylid gives the four-membered cyclic bis-ylid **100**, containing two zirconium atoms at the ylid carbon atoms, which was isolated as yellow monoclinic crystals. An X-ray structure analysis of the 1,3-dizirconiocyclobutanic ylid **100** revealed that the Zr–C distances were shortened[152] (eq. 42).



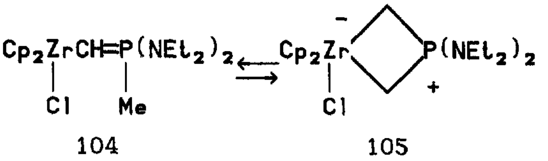
100

(42)

Bis(λ^5-cyclopentadienyl)titanium, zirconium and hafnium halogenides (**101**) with appropriately substituted phosphorus ylids provide 1 : 2 addition products **102** (R, R′ = Me) or via the trans-ylidation yield C-metallated ylids **103** (R = R′ = Ph, Et_2N or R = Et_2N, R′ = Me).[151–159] The molecular structure of the yellow crystalline complex **103a** (R = R′ = Ph) shows an approximately tetrahedral environment of ligands around the zirconium atom and the existence of delocalized multiple Zr–C–P bonds (eq. 43).[155,157,158] Zirconium ylid **104** exists in a tautomeric equilibrium with the chelate ylid complex **105** (eq. 44).[155] The tautomeric equilibrium **104** ⇆ **105** depends on the nature of the solvent.

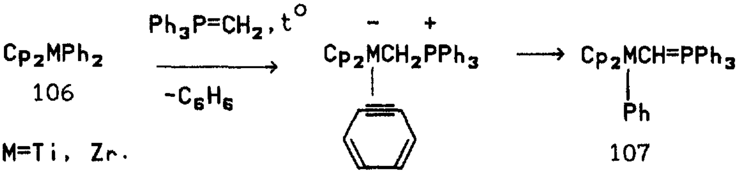


$$\mathrm{Cp_2MCl_2 + R_2R'P{=}CH_2 \longrightarrow [Cp_2M(CH_2\overset{+}{P}R_2R')_2]2Cl^- \text{ or } Cp_2\underset{Cl}{\underset{|}{M}}CH{=}PR_2R'} \quad (43)$$



(44)

Metallocene titanium, zirconium and hafnium ylids **107**, **109** are obtained by reaction of triphenylphosphonium methylid with thermally generated (η^2-ethene) or (η^2-aryne) metallocenes (eq. 45). The reaction occurs by exchange of the ethene or aryne ligands on the phosphorus ylid ligand and a proton shift from the methylene group to the aryne ligand. The reaction of triphenylphosphonium methylid with di(η^4-cyclopentadienyl)hafnium-cyclopentane (**108**) proceeds in a similar fashion[160,161] (eq. 46). The reaction of dicyclopentadiendiphenyl zirconium with triphenylphosphonium ethylid gives the cyclic metallocene ylid **110**[161] (eq. 47).



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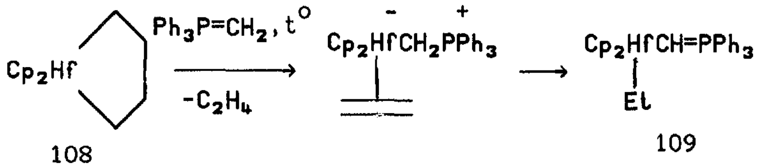
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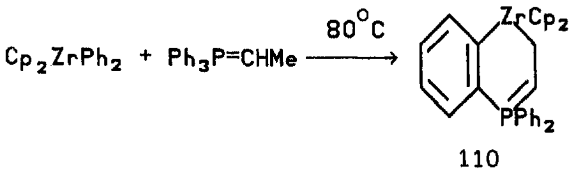
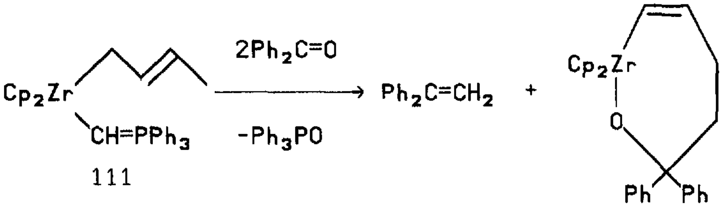
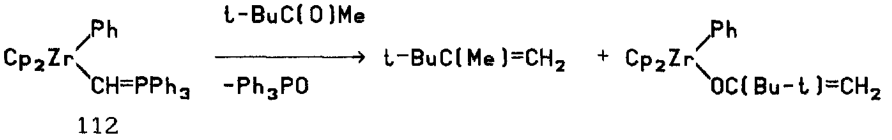

(47)

The nucleophilicity of metallocene ylids (M = Ti, Zr, Hf) is reduced due to high electron accepting ability (by pπ-mechanism) of the transition metals.[160]

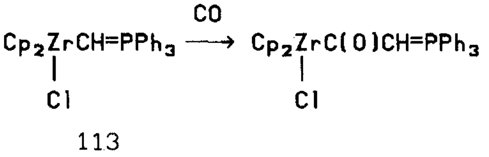
$$R_3MCH{=}PPh_3 \longleftrightarrow R_3\overset{-}{M}{=}CH\text{-}\overset{+}{P}Ph_3 \longleftrightarrow R_3M\text{-}\overset{-}{C}H\text{-}\overset{+}{P}Ph_3$$

Nevertheless the metallocene ylids **111**, **112** react with ketones as shown in eqs 48, 49.[160] Carbon monoxide easily inserts into the metal–carbon bond of zirconium ylid **113**[159] (eq. 50).


(48)


(49)

$$Cp_2Zr(Ph)CH{=}PPh_3 \xrightarrow[-Ph_3PO]{t\text{-}BuC(O)Me} t\text{-}BuC(Me){=}CH_2 + Cp_2Zr(Ph)OC(Bu\text{-}t){=}CH_2$$


(50)

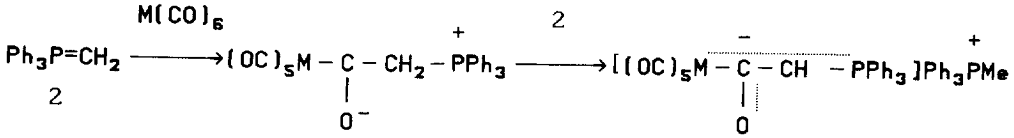
$$Cp_2Zr(Cl)CH{=}PPh_3 \xrightarrow{CO} Cp_2Zr(Cl)C(O)CH{=}PPh_3$$

2.4. *Ylids containing metal atoms of the VB group*

Ylids, containing a metal atom of the vanadium subgroup at the α-carbon of the P═C group are unknown although a few vanadium ylid complexes have been described.[33,34]

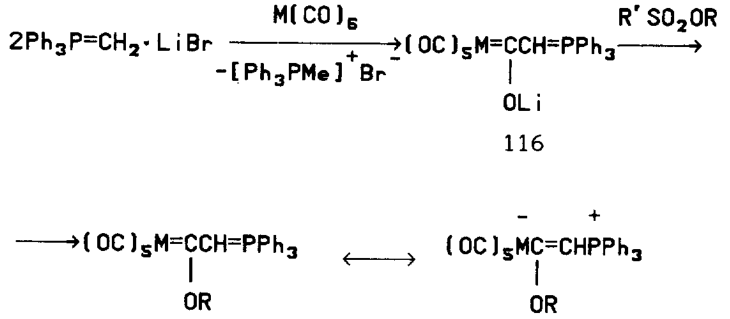
2.5. *Ylids containing metal atoms of the VIB group*

The reaction of phosphorus ylids with metal carbonyls is a convenient method for the preparation of various ylid complexes with transition metals. The product of reaction between phosphorus ylids and metal carbonyls depends on the nature of the metal, the surrounding ligands, the structure of the phosphorus ylid and the reaction conditions.[3] Phosphorus ylids with carbonyls of chromium, molybdenum, tungsten and iron usually form the products of addition of the ylid carbanion to the C═O group, while with magnesium, cobalt and nickel carbonyls give the products of replacement of the C═O group on the phosphorus ylid ligand. Angelicci[162] and Darensbourg[163] came to the conclusion that the addition of the ylid to the C═O group of metal carbonyls depends on the C═O ligand force constant. Salt-free phosphorus ylids add to the C═O group of metal carbonyls to form, via intermediates **114**, ylid-phosphonium salts **115**, M = Cr, W, Mo (eq. 51).[164–166] In the presence of lithium bromide the reaction between triphenylphosphonium methylid (**2**) and chromium or tungsten hexacarbonyls gives phosphorus ylids **116** (eq. 52), which are easily silylated by trimethylsilyl triflate or alkylated by fluorosulphonic acid methyl ether to form ylids **117**.[164] IR, NMR spectra and X-ray analysis reveal the essential contribution of the vinylphosphonium structure to compounds **118**.[119,164]



$$\underset{2}{Ph_3P{=}CH_2} \xrightarrow{M(CO)_6} (OC)_5M-\underset{O^-}{C}-CH_2-\overset{+}{P}Ph_3 \xrightarrow{2} [(OC)_5M-\underset{O}{C}\overset{-}{-}CH-PPh_3]\overset{+}{Ph_3PMe}$$

114 115 (51)



$$2Ph_3P{=}CH_2\cdot LiBr \xrightarrow[-[Ph_3PMe]^+Br^-]{M(CO)_6} (OC)_5M{=}\underset{OLi}{C}CH{=}PPh_3 \xrightarrow{R'SO_2OR}$$

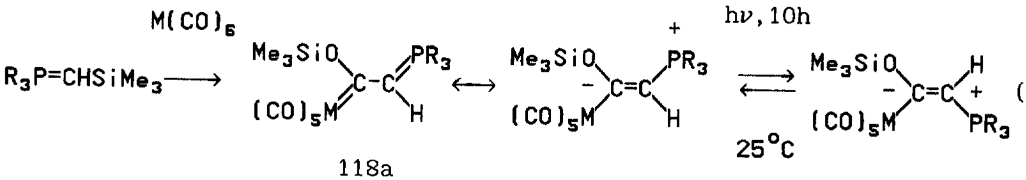
116 (52)

$$\longrightarrow (OC)_5M{=}\underset{OR}{C}CH{=}PPh_3 \longleftrightarrow (OC)_5M\overset{-}{\underset{OR}{C}}{=}CH\overset{+}{P}Ph_3$$

117a,b

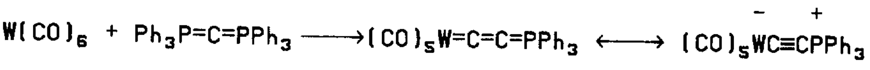
(a) R=Me₃Si, R′=CF₃ ; (b) R=Me, R′=F

The neutral products of addition **118a**, M = Cr, Mo, W, existing as *Z*- and *E*-geometric isomers were obtained by reaction of metal carbonyls with C-silylated ylids.[117] The initial reaction results in the formation of the thermodynamically stable (*E*)-isomers, which are further transformed into (*Z*)-isomers by UV-irradiation in benzene (eq. 53).[118,119]



118a

The UV-irradiation of tungsten hexacarbonyl and hexaphenylcarbodiphosphoranes provides the cumulenylids **119**. This reaction proceeds via the Wittig olefination of one of the C═O groups of the hexacarbonyl[166] (eq. 54).



$$W(CO)_6 + Ph_3P{=}C{=}PPh_3 \xrightarrow[-Ph_3P=O]{} (CO)_5W{=}C{=}C{=}PPh_3 \longleftrightarrow (CO)_5\overset{-}{W}C{\equiv}C\overset{+}{P}Ph_3 \qquad (54)$$

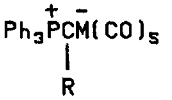
119

The heating of chromium or molybdenum hexacarbonyls with allylylids **120** at 50–60°C in petrol or under UV-irradiation gives complexes **121**.[167–170] More severe reaction conditions provide η^3-phosphonium allylylid complex **122a,b**. X-Ray analysis shows the distorted octahedral structure of complexes **122a** with the metal atom coordinated to the planar allyl ligand.[170]

$Ph_3P{=}CHR$

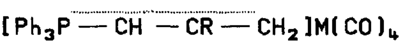
120

R=Ph, CH=CH$_2$, CH=CHPh, CH=CHMe



$Ph_3\overset{+}{P}\underset{\displaystyle R}{C}\overset{-}{M}(CO)_5$

121 M=Mo, Cr



$[Ph_3P-CH-CR-CH_2]M(CO)_4$

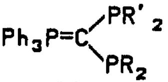
122

R=CH-CH=CH$_2$, CH-CMe=CH$_2$
M=Mo (a), W (b),

C–Phosphine-substituted ylids **123** and **124** easily exchange ligands in carbonyl chromium complexes **125** to form phosphorus ylids with a phosphine–metal bond. Triphenylphosphonium diphenylphosphinomethylid **123** replaces THF in chromium pentacarbonyl complex **125**, L = THF, to form the linear ylid **126**. Bis-phosphine-substituted phosphorus ylid **124** reacts with chromium pentacarbonyl complex **125**, L = C_7H_8, to form cyclic ylids **127**. The chromium atom of which is connected to two tervalent phosphorus atoms.[171] The compounds **127** are diamagnetic, soluble in organic solvents, and stable to moisture and oxygen. Complexes **125**, L = $CH_2S(O)Me_2$, react with bis-phosphine-substituted phosphorus ylids **124**, R = Me or Ph; R′ = Me or Ph, to form five-membered metallocycles **128**, containing an exocyclic P=C bond.[172,173]

$Ph_3P{=}CHPPh_2$

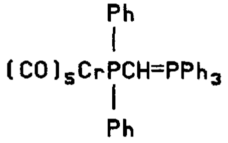
123



124

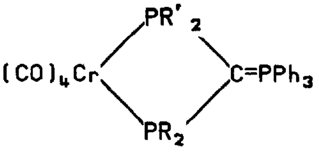
$Cr(CO)_5L$

125

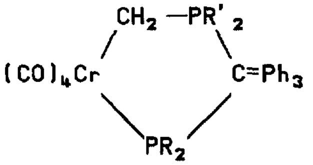


$(CO)_5Cr\underset{\displaystyle Ph}{\overset{\displaystyle Ph}{P}}CH{=}PPh_3$

126



127



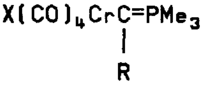
128

Tertiary phosphines at −60°C add chromium, tungsten and molybdenum complexes **129** to form metal-substituted phosphorus ylids **130** and **131**.[174]

$X(CO)_4M{\equiv}CR$

129

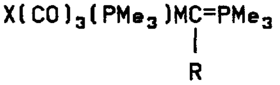
X=Cl, Br, I;



$X(CO)_4Cr\underset{\displaystyle R}{C}{=}PMe_3$

130

R=Me, Ar, SiMe$_3$,



$X(CO)_3(PMe_3)M\underset{\displaystyle R}{C}{=}PMe_3$

131

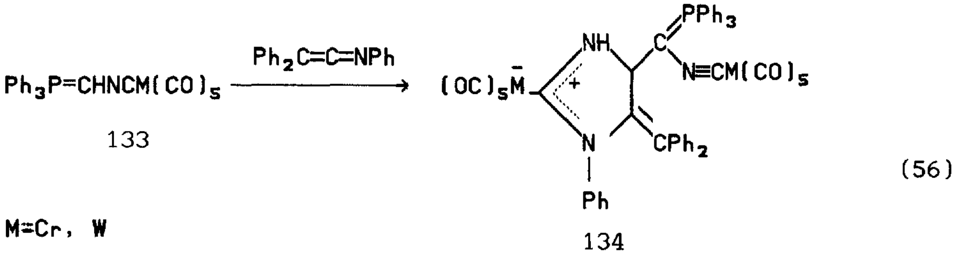
R=Ph, 4-MeC$_6$H$_4$, SiPh$_3$
M= Mo, W

The metal-containing ylids **132** (eq. 55) were obtained by reaction of triphenylphosphonium methylid with chromium nitrile complexes. The reaction occurs by a proton shift from the ylid carbon atom to nitrogen.[175]

$$(CO)_5Cr\overset{+}{N}{\equiv}CR + CH_2{=}PPh_3 \longrightarrow (CO)_5CrNH{=}C(R)CH{=}PPh_3 \qquad (55)$$

132

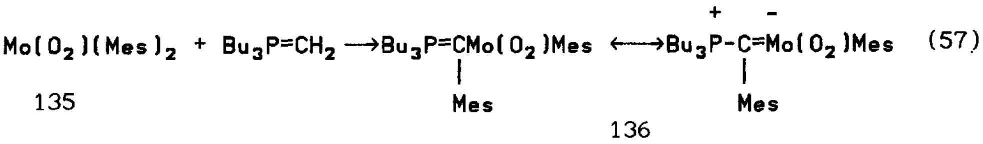
Ylid **133** adds triphenylketenimine in a ratio of 2 : 1 to form the cyclic ylid **134**[176] (eq. 56). The reaction of metallonitrile ylids with isocyanates and carbon disulphide proceeds in a similar fashion.[175–177]



133 134 (56)

M=Cr, W

Dioxomolybdenum ylid **136** is synthesized by reaction of the complex **135** with tributylphosphonium methylid. ^{13}C and ^{31}P NMR spectra as well as X-ray analysis show the structure to contain a molybdenum–carbon double bond in the ground state (eq. 57).[178,179]



$$Mo(O_2)(Mes)_2 + Bu_3P{=}CH_2 \longrightarrow Bu_3P{=}\underset{\displaystyle Mes}{\underset{|}{C}}Mo(O_2)Mes \longleftrightarrow Bu_3\overset{+}{P}{-}\underset{\displaystyle Mes}{\underset{|}{\overset{-}{C}}}{=}Mo(O_2)Mes \qquad (57)$$

135 136

Phosphine-phosphonium ylids **138** containing a chromium or tungsten atom at the tervalent phosphorus atom were obtained by the reaction of chlorodiphenylphosphine-pentacarbonyl metals **137** with triphenylphosphonium methylid[171] (eq. 58).

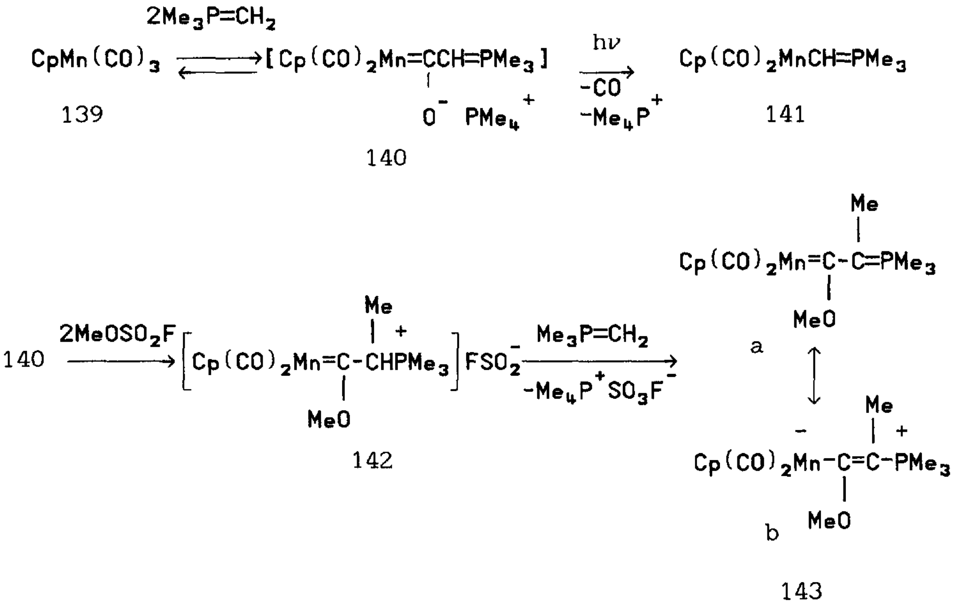
$$(CO)_5MPPh_2Cl + 2CH_2{=}PPh_3 \longrightarrow (CO)_5MP(Ph_2)CH{=}PPh_3 + [Ph_3\overset{+}{P}Me]Cl^- \qquad (58)$$

137 2 138

M = Cr, W

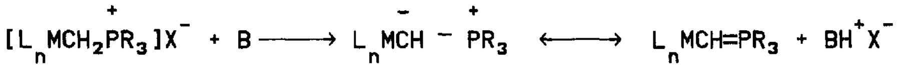
2.6. *Ylids containing metal atoms of the VIIB group*

As with chromium hexacarbonyl, the manganese complexes **139** add phosphorus ylids to form mesomeric ylid complexes **140**, existing in equilibrium with the starting compounds.[181,182] Photolysis of compound **140** with elimination of carbon monoxide leads to formation of the neutral ylid **141**, containing a manganese atom at the α-carbon.[183] Alkylation of ylid complex **140** by methyl fluorosulphonate gives the manganese-phosphonium salt **142**, treatment of which with trimethylphosphonium methylid provides ylid **143**.[182] X-Ray analysis of compound **143** shows that the phosphonium formula b predominates in the ground state and that the carbon fragment is planar with a double bond of C_α–C_β. The P–C distance (1.76 Å) is longer than the average value for phosphorus ylids[183,190] (Scheme 13).

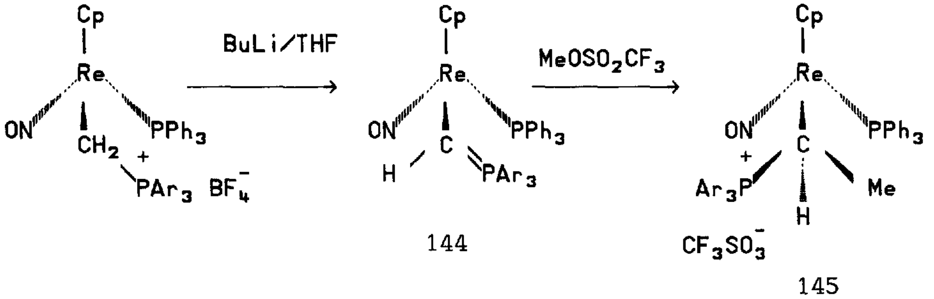


Scheme 13.

Deprotonation of ylid complexes provides opportunities to obtain phosphorus ylids substituted by a transition metal at the α-carbon atom[184,185] (eq. 59). Reaction of the optically active rhenium ylid complex with butyl lithium in THF in the presence of TMEDA provided the phosphorus ylid **144**, which is chiral around the rhenium atom. The ylid **144** reveals nucleophilic properties in the reaction with methyltriflate in THF at −78°C to form the (*S,S,R,R*) α-rhenium substituted phosphonium salt **145**[186] (eq. 60).

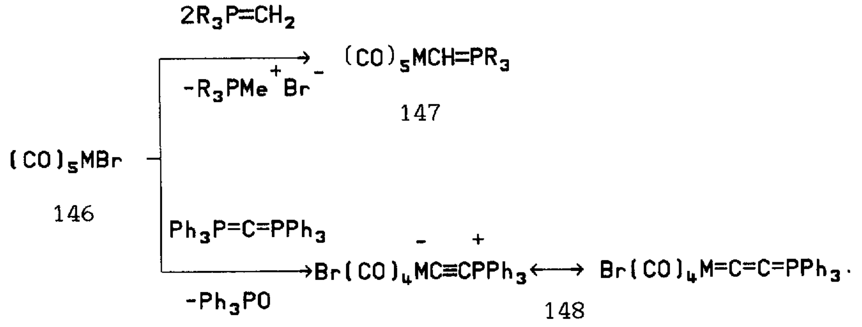


$$[L_nMCH_2\overset{+}{P}R_3]X^- + B \longrightarrow L_nM\overset{-}{C}H - \overset{+}{P}R_3 \longleftrightarrow L_nMCH{=}PR_3 + BH^+X^- \qquad (59)$$



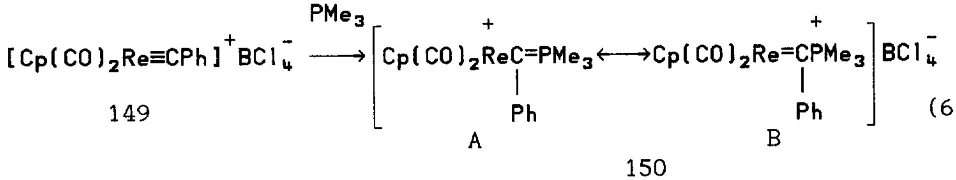
(60)

As shown in Scheme 14, bromopentacarbonyl complexes of manganese and rhenium **146** undergo transylidation with phosphorus ylids to afford C-metalcarbonyl-substituted phosphorus ylids **147**, M = Mn, Re.[157,187,188] At the same time the reaction of the hexaphenylcarbodiphosphorane with complexes **146** is accompanied by Wittig olefination to provide the cumulene ylids **148**, M = Mn, Re.[188,189] X-Ray analysis shows that the negative charge of the conjugated bond system in ylids **148** is localized on the metal atom and the contribution of the resonance structure with the triple C≡C bond in the ground state is comparatively high. The compound **148** is relatively unreactive to moisture, oxygen, strong acids and alkylation[190] (Scheme 14).

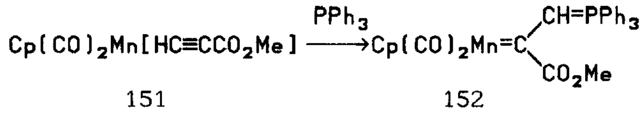


Scheme 14.

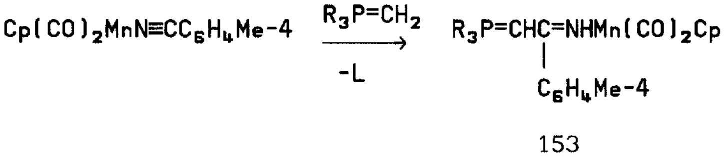
Cationic complex **149** adds trimethylphosphine to form a C–metal-substituted phosphorus ylid **150**. The short bond distance between the rhenium atom and the ylid carbon atom (1.97 Å) shows that structure B predominates in the ground state of the compound **150** (eq. 61).[174,184,191–194] Triphenylphosphine adds to alkyne complex **151** to provide a metal-containing acyl ylid **152** (eq. 62). Phosphorus ylids having hydrogen atoms at the α-carbon are added to the C═N bond of nitrile manganese complexes to form phosphorus ylids **153** with the metal atom bonded to the nitrogen atom[194] (eq. 63).



$$\underset{149}{[\mathrm{Cp(CO)_2Re{\equiv}CPh}]^{+}\mathrm{BCl_4^{-}}} \xrightarrow{\mathrm{PMe_3}} \underset{150}{\left[\underset{A}{\mathrm{Cp(CO)_2\overset{+}{Re}\underset{\underset{Ph}{|}}{C}{=}PMe_3}} \longleftrightarrow \underset{B}{\mathrm{Cp(CO)_2Re{=}\underset{\underset{Ph}{|}}{C}\overset{+}{P}Me_3}}\right]\mathrm{BCl_4^{-}}} \qquad (61)$$



$$\underset{151}{\mathrm{Cp(CO)_2Mn[HC{\equiv}CCO_2Me]}} \xrightarrow{\mathrm{PPh_3}} \underset{152}{\mathrm{Cp(CO)_2Mn{=}C(CH{=}PPh_3)(CO_2Me)}} \qquad (62)$$

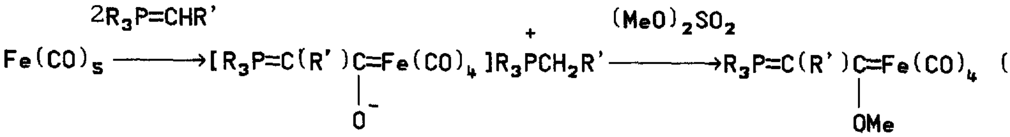


$$\mathrm{Cp(CO)_2MnN{\equiv}CC_6H_4Me\text{-}4} \xrightarrow[-L]{R_3P{=}CH_2} \underset{153}{\mathrm{R_3P{=}CH\underset{\underset{C_6H_4Me\text{-}4}{|}}{C}{=}NHMn(CO)_2Cp}} \qquad (63)$$

2.7. *Ylids containing metal atoms of VIIIB group*

Transition elements of the eighth group form various complexes with ylid ligands many of which are widely applied in organic synthesis.

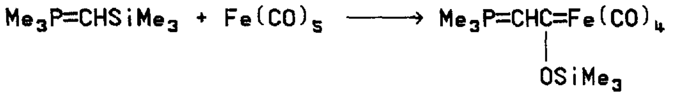
2.7.1. *Iron subgroup.* Different phosphorus ylids containing a metal atom at the α-,β-carbon atoms or in the side chain have been synthesized. The most general method for preparation of such ylids is the reaction of iron carbonyls with phosphorus ylids proceeding via either C═O group replacement for phosphorus ylid ligands or addition of the ylid carbon atom to the C═O groups. As shown in eq. 64, iron pentacarbonyl adds phosphorus ylids to form betaines which are easily deprotonated by the starting ylid to form stable anionic organoiron phosphorus ylids **154**. The negative charges of the ylid carbon atom and the oxygen atom of compound **154** are delocalized over the system including the phosphonium cation, two sp^2-hybridized carbon atoms, the oxygen atom and the iron atom, which is a strong acceptor of electrons via the pd_π-mechanism. The alkylation of compound **154** by dimethylsulphate results in a neutral phosphorus ylid **155** isolated as a yellow crystalline compound.[195,196]



$$Fe(CO)_5 \xrightarrow{2R_3P=CHR'} [R_3P=C(R')\underset{O^-}{C}=Fe(CO)_4]\overset{+}{R_3PCH_2R'} \xrightarrow{(MeO)_2SO_2} R_3P=C(R')\underset{OMe}{C}=Fe(CO)_4 \tag{64}$$

154 155

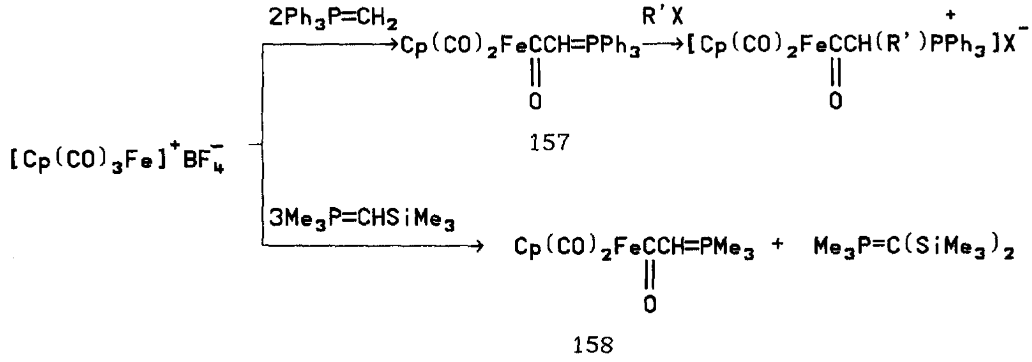
Reaction of iron pentacarbonyl with C-silyl-substituted phosphorus ylids leads directly to the formation of the neutral ylid **156** via the migration of the trimethylsilyl group to the negatively charged oxygen atom[117,188] (eq. 65).



$$Me_3P=CHSiMe_3 + Fe(CO)_5 \longrightarrow Me_3P=CH\underset{OSiMe_3}{C}=Fe(CO)_4 \tag{65}$$

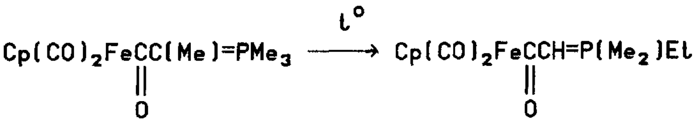
156

Reaction of cationic cyclopentadienyl-tricarbonyl iron complexes with phosphorus ylids via transylidation affords iron-containing phosphorus acylylids **157**, R = H, Me, Ph.[119] The compound **157** displays nucleophilic properties reacting with hydrogen chloride, trimethylchlorosilane and alkyl halides at the α-carbon atom with formation of phosphonium salts (Scheme 15). Ylid **158** was obtained by reaction of **156** with a C-silylated phosphorus ylid (Scheme 15).[119]



Scheme 15.

Upon heating the compound **159** rearranges into compound **160** as a result of methyl group migration from the ylid carbon atom to one of the methyl groups on the phosphorus atom (eq. 66).[119,196–198]

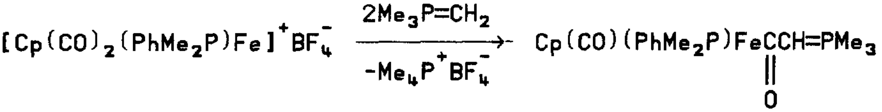


$$\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{Cp(CO)_2FeC}}\mathrm{C(Me)=PMe_3} \xrightarrow{t^\circ} \underset{\substack{\| \\ \mathrm{O}}}{\mathrm{Cp(CO)_2FeC}}\mathrm{CH=P(Me_2)Et} \qquad (66)$$

159 160

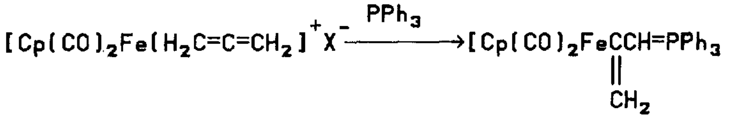
The reaction of phosphorus ylids with iron complexes modifies their structure as shown in eqs 67, 68.[119,171,197,198,208]

$$\mathrm{(CO)_nMPPh_2Cl} \xrightarrow[-\,\mathrm{[Ph_3PCH_2R]Cl^-}]{\substack{\mathrm{2Ph_3P{=}CHR} \\ 32 \\ +}} \mathrm{(CO)_nMPPh_2CR{=}PPh_3} \qquad (67)$$



$$\mathrm{[Cp(CO)_2(PhMe_2P)Fe]^+BF_4^-} \xrightarrow[-\mathrm{Me_4P^+BF_4^-}]{\mathrm{2Me_3P{=}CH_2}} \mathrm{Cp(CO)(PhMe_2P)Fe}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{CH{=}PMe_3} \qquad (68)$$

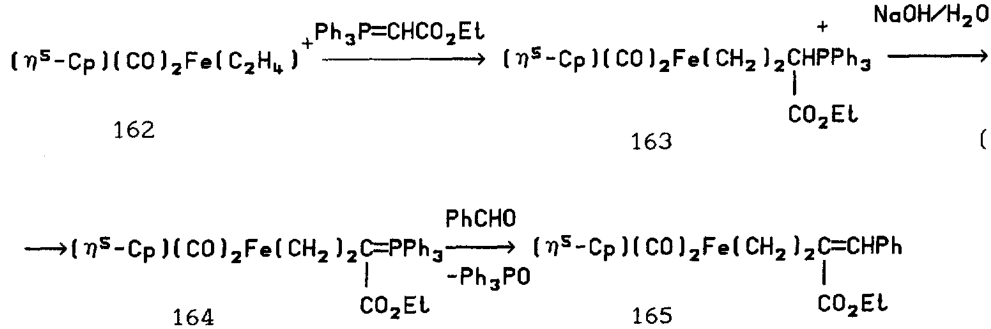
The ylid complex **161**, containing an iron atom at the β-position, was obtained by reaction of triphenylphosphine with alkene, allene and alkyne complexes of iron (eq. 69).[199–201]



$$\mathrm{[Cp(CO)_2Fe(H_2C{=}C{=}CH_2)]^+X^-} \xrightarrow{\mathrm{PPh_3}} \mathrm{[Cp(CO)_2Fe}\underset{\substack{\| \\ \mathrm{CH_2}}}{\mathrm{C}}\mathrm{CH{=}PPh_3} \qquad (69)$$

161

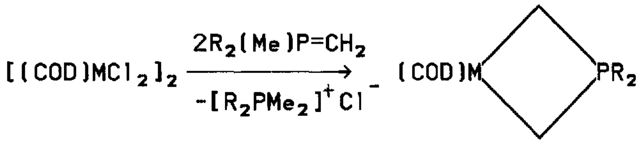
The addition of triphenylphosphonium carboethoxymethylid to complex **162** provides phosphonium salt **163**, treatment of which by aqueous sodium hydroxide solution leads to the organoiron ylid **164**. The latter smoothly undergoes a Wittig reaction with formation of iron-containing alkenes **165**[202] (eq. 70).



$$\underset{162}{\mathrm{(\eta^5\text{-}Cp)(CO)_2Fe(C_2H_4)^+}} \xrightarrow{\mathrm{Ph_3P{=}CHCO_2Et}} \underset{163}{\mathrm{(\eta^5\text{-}Cp)(CO)_2Fe(CH_2)_2}\underset{\substack{| \\ \mathrm{CO_2Et}}}{\mathrm{C}}\mathrm{H\overset{+}{P}Ph_3}} \xrightarrow{\mathrm{NaOH/H_2O}} \qquad (70)$$

$$\xrightarrow{} \underset{164}{\mathrm{(\eta^5\text{-}Cp)(CO)_2Fe(CH_2)_2}\underset{\substack{| \\ \mathrm{CO_2Et}}}{\mathrm{C}}\mathrm{{=}PPh_3}} \xrightarrow[-\mathrm{Ph_3PO}]{\mathrm{PhCHO}} \underset{165}{\mathrm{(\eta^5\text{-}Cp)(CO)_2Fe(CH_2)_2}\underset{\substack{| \\ \mathrm{CO_2Et}}}{\mathrm{C}}\mathrm{{=}CHPh}}$$

2.7.2. *Platinum and palladium subgroups.* Over the last few years different cyclic and acyclic complexes of platinum group metals with phosphorus ylid ligands have been synthesized, some of them being of practical significance.[122] However, among these complexes there are a few compounds containing multiple P–C bonds. Halides of the platinum subgroup elements undergo transylidation with phosphorus ylids, resulting in metal-containing phosphorus ylids which easily dimerize to cyclic or acyclic ylid metal complexes. Alternatively, they undergo intramolecular cyclization to afford complexes of the type **166**[37,203–206] (eq. 71).



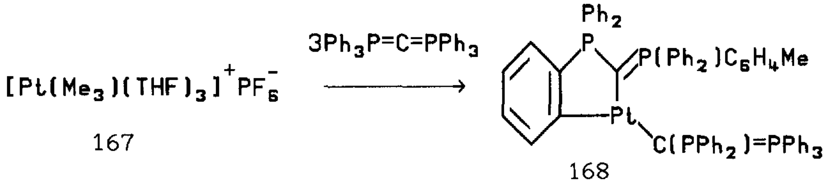
(71)

166

M=Ir, Rh;

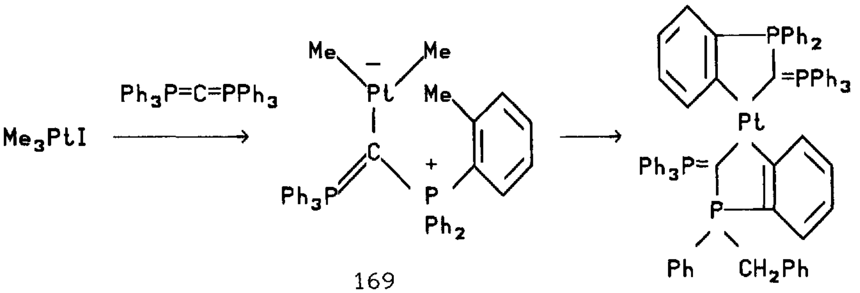
R=Me, t-Bu, -(CH$_2$)$_4$-, -(CH$_2$)$_5$-; L=CO, PMe$_3$.

One of the few examples of phosphorus ylids, containing a platinum atom at the α-carbon is compound **168** obtained by the reaction of hexaphenylcarbodiphosphorane with platinum complex **167**. This reaction involves not only substitution of THF ligands and methyl groups at the platinum atom but also *ortho*-metallation of the benzene ring at the phosphorus atom (eq. 72).[207] In some cases phosphorus ylids may substitute methyl groups at the platinum atom. Reaction of trimethylplatinum iodide with hexaphenylcarbodiphosphorane leads to the formation of bis-ylid **170** probably via intermediate **169** (eq. 73).[207]



167 168

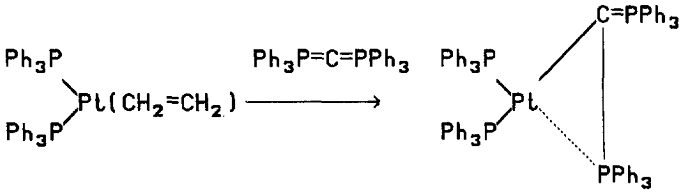
(72)



169 170

(73)

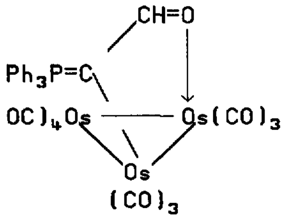
Hexaphenylcarbodiphosphorane displaces ethylene from platinum complexes **171** to form the cyclic ylid **172** with a platinum atom at the α-carbon (eq. 74).[18]



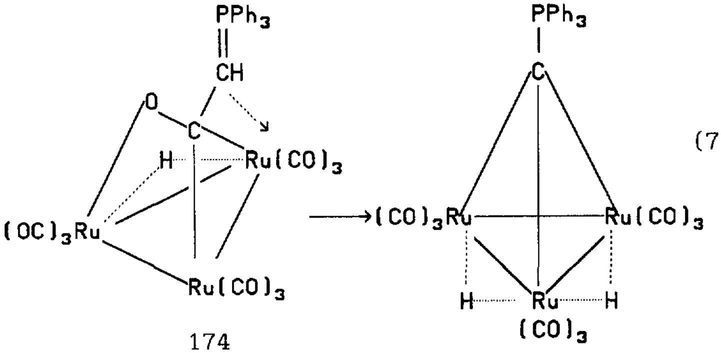
171 172

(74)

Deeming and co-workers have shown that rapid oxidative addition of $Ph_3P{=}CHCHO$ to $[Os_3(CO)_{10}(MeCN)_2]$ gives ylid complexes of osmium **173**, which decarboxylate to give clusters containing triply-bridging ligands whose X-ray analysis was reported.[209] Bogle and co-workers described interesting examples of syntheses of phosphorus ylids containing platinum group metals. By reaction of triphenylphosphonium methylid with $[(CO)_4Ru]_3$ in THF at $-20°C$ they obtained ylid complex **174**, which was converted to an osmium cluster by reflux in cyclohexane[210] (eq. 75).



173



174

(75)

Thus, transition metals can effectively stabilize an ylid carbanion, thereby reducing its nucleophilicity. Nevertheless, in some cases ylids stabilized by transition metals show comparatively high reactivity. Some ylidic complexes serve as excellent catalysts and others may be useful in pharmacology.[123–125] Further developments in their chemistry, especially in the field of the synthesis using new interesting complexes of transition metals, may be expected.

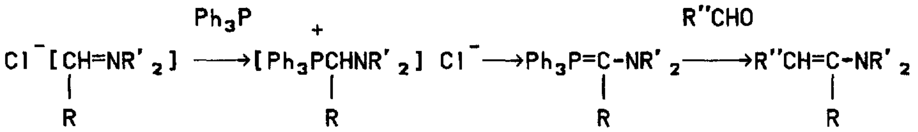
3. YLIDS CONTAINING ELEMENTS OF V–VII GROUPS AT THE α-CARBON ATOM

Phosphorus ylids containing elements of the V–VII main groups at the α-carbon atom are the most important from a synthetic point of view. These phosphorus ylids are used for the preparation of many biologically active and naturally occurring compounds and are of interest for theoretical studies. The phosphorus ylids stabilized by elements of the V–VII groups have a covalent carbon–element bond and are typical in terms of their reactivity to organic phosphorus ylids.

3.1. *C–N, C–P, C–As and C–Sb substituted ylids*

The structure and properties of phosphorus ylids stabilized by nitrogen, phosphorus and arsenic are very varied due to the variable valences and coordination states of the fifth group elements. These ylids are used widely in organic synthesis for preparation of many important compounds. Today they rank among the most important tools of the preparative organic chemist both in research and in industry as, e.g., in the Wittig olefin synthesis.

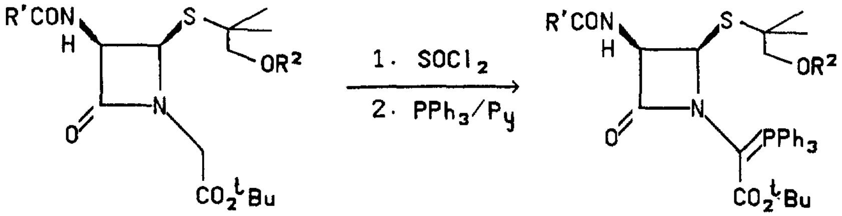
3.1.1. *Synthesis.* C–N Ylids can be obtained via the dehydrohalogenation of corresponding phosphonium salts (eq. 76). However, dialkylamino groups at the ylidic carbon atom are generally not capable of rendering the adjacent hydrogen atoms in the corresponding phosphonium salts sufficiently acidic. Not surprisingly, the *ab initio* calculation fulfilled by Bestmann and co-workers showed that a tervalent nitrogen atom destabilizes the ylid carbanion.[15] Efforts to obtain non-stabilized C–N ylids of the type **176** (R = H or alkyl) via dehydrohalogenation of the corresponding phosphonium salts were unsuccessful.[211,212] C-Amino-substituted ylids **176** are accessible only when anion-stabilizing substituents R at the ylid carbon atom compensate for the retarding influence of the nitrogen atom (eq. 77). Thus, Wittig reaction of C–N ylids **176** generated *in situ* from *β*-enamino phosphonium salts **175** with base followed by addition of aldehydes leads to 2-functionalized 1,3-butadienes.[213]



$$\mathrm{Cl^-[\underset{\underset{R}{|}}{C}H{=}NR'_2]} \xrightarrow{\mathrm{Ph_3P}} \mathrm{[Ph_3\overset{+}{P}\underset{\underset{R}{|}}{C}HNR'_2]\,Cl^-} \longrightarrow \mathrm{Ph_3P{=}\underset{\underset{R}{|}}{C}{-}NR'_2} \xrightarrow{\mathrm{R''CHO}} \mathrm{R''CH{=}\underset{\underset{R}{|}}{C}{-}NR'_2} \qquad (76)$$

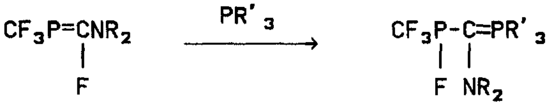
175 176

Methods for synthesis of ylids **177** containing the 4-thioacetylazetidinone group at the α-carbon atom are very important from a preparative point of view and were extensively used by Woodward in the β-lactam antibiotic area (eq. 77).[214]



177

The reaction of two-coordinate phosphorus compounds **178** with lower trialkylphosphines provides representatives of phosphorus ylids containing a dialkylamino group at the α-carbon **179** (eq. 78). The reaction occurs by replacement of the fluorine atom at the sp^2-hybridized carbon atom with subsequent migration of the fluorine atom to the phosphorus atom. X-Ray analysis revealed that the high stability of the phosphorus ylid **179** is due to delocalization of the negative charge of the ylid carbon atom by both the CF$_3$ group and the fluorine atom.[215]

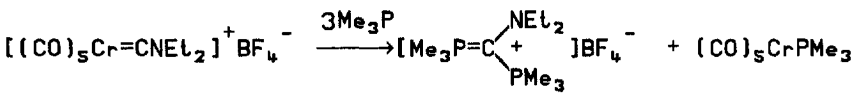


$$\mathrm{CF_3P{=}\underset{\underset{F}{|}}{C}NR_2} \xrightarrow{\mathrm{PR'_3}} \mathrm{CF_3\underset{\underset{F}{|}}{P}{-}\underset{\underset{NR_2}{|}}{C}{=}PR'_3} \qquad (78)$$

178 179

R=Me, Et; R'=Me, Et

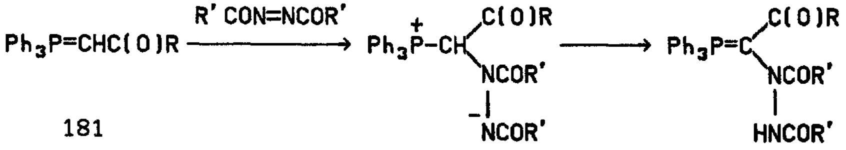
By the reaction of the trimethylphosphine with a carbene–chromium complex Kreissl and co-workers obtained ylid-phosphonium salt **180** bearing a dialkylamino group at the central carbon atom (eq. 79).[216]



$$\mathrm{[(CO)_5Cr{=}CNEt_2]^+BF_4^-} \xrightarrow{\mathrm{3Me_3P}} \left[\mathrm{Me_3P{=}C}\begin{smallmatrix}\mathrm{NEt_2}\\ +\\ \mathrm{PMe_3}\end{smallmatrix}\right]\mathrm{BF_4^-} + \mathrm{(CO)_5CrPMe_3} \qquad (79)$$

180

A convenient method for C–N ylid syntheses is the Michael addition of acyl ylids **181** to cyclic[217,218] or acyclic compounds,[219] containing a multiple N=N bond activated by carbonyl groups. A likely reaction mechanism involves the formation of a betaine intermediate, which is transformed into ylid **182** by a prototropic shift. The yields of ylids are very good (eq. 80).



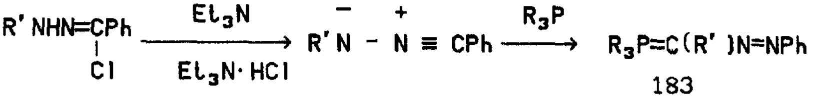
181

R=Alk, Ph, AlkO

182

(80)

Triphenylphosphine and amides of tervalent phosphorus acids react with C-ethoxycarbonyl- and C-acetyl-*N*-nitrylimines to form stable azomethylenephosphonium ylids **183**, R = Ph, $(C_5H_{10})_2N$, R′ = CO_2Et, C(O)Me[220–222] (eq. 81). The ylid **185** was obtained by reaction of the ylid **184** with a diazonium salt followed by treatment with sodium ethoxide.[222] Ylid **186** bearing two azo-groups at the α-carbon atom was obtained by reaction of bis(phenylazo)methane with triphenyldichlorophosphorane in the presence of triethylamine.[223,224]

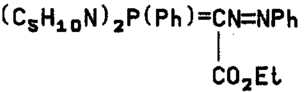


183

(81)

$(C_5H_{10}N)_2P(Ph)=CHCO_2Et$

184



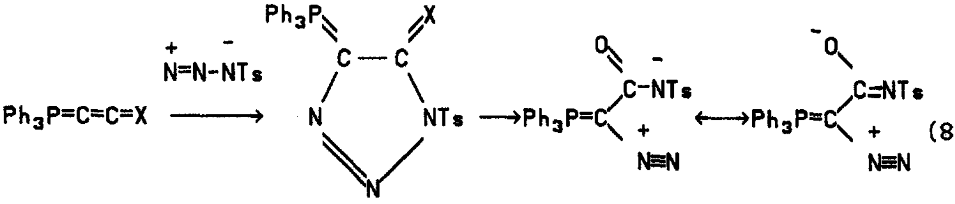
$(C_5H_{10}N)_2P(Ph)=C(CO_2Et)N=NPh$

185

$Ph_3P=C(N=NPh)_2$

186

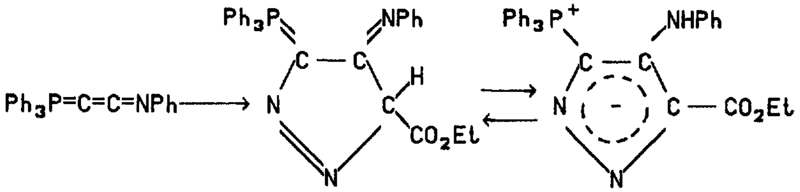
Phosphacumulenylids undergo 1,3-dipolar cycloaddition reaction with sulphonylazides to form ylids **187**, X = O, S, NPh, containing triazolidic rings (eq. 82). Opening of the five-membered ring of the ylids **187**, X = O, gives ylids **188** bearing a diazo group at the α-carbon atom.[225] The reaction of diazoacetic ester with triphenylphosphonium *N*-phenyliminoketenylid results in the stable 1,3-dipolar pyrazole cycloaddition product **189**. Delocalization of the negative charge of the ylidic carbanion atom by the aromatic heterocycle leads to high stability and low reactivity for compound **189** (eq. 83).



187

188

(82)


(83)

189

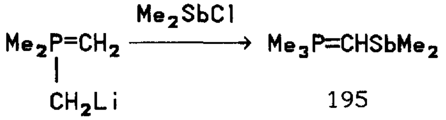
Unlike the nitrogen atom the tervalent phosphorus and arsenic atoms effectively stabilize the ylid carbanion and as a consequence the transylidation method is the most important method for preparation of C-phosphino-C-arsino- and C-stibino-substituted phosphorus ylids.[84] Alkyldichlorophosphines and phosphorus trichloride react with simple phosphorus ylids to form compounds **190**, **191**, R = Ph, Alk_2N ; R′ = H, Alk, containing two or three ylid groups at the tervalent phosphorus atom.[228] The phosphine-phosphonium ylids **192**, having R^1 = H, Me, Ph, CO_2Me, PPh_3 ; R^2 = Ph, C_6H_{11}, were obtained in high yields by reaction of stabilized and non-stabilized ylids with diaryl- and dialkylchlorophosphines[155,226–230] (Scheme 16).

$$\begin{tikzcd}
(R_3P{=}CR')_3P & R_3P{=}CHR' \arrow[l, "PCl_3"'] \arrow[r, "AlkPCl_2"] \arrow[d, "R^2_2PCl"] & (R_3P{=}CR')_2PAlk \\
190 & R_3P{=}C(R^1)PR^2_2 & 191 \\
 & 192 &
\end{tikzcd}$$

Scheme 16.

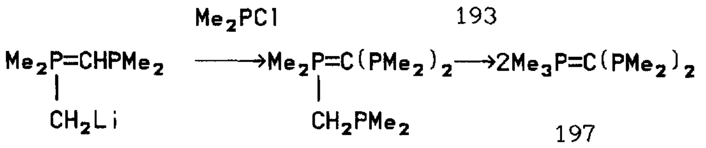
A convenient method for the preparation of phosphorus ylids **193**–**195** bearing phosphorus, arsenic or antimony atoms at the ylidic carbon atom is the reaction of C-silyl-substituted ylids with chlorophosphines, chloroarsines and chlorostibines, which involves elimination of trimethylchlorosilane. Instead of chloroarsines the arsenic trimethylsilyl ethers may be successfully used[84,153] (eq. 84). C–Phosphine- and C–arsine-substituted phosphorus ylids **193** and **194** are stable vacuum-distillable liquids crystallizing below 0°C. The reaction of lithiated trimethylphosphonium methylid with dimethylchlorostibine leads to the formation of trimethylphosphonium dimethylstibinomethylid **195** in a yield of 40%[84] (eq. 85).

$$\underset{193}{Me_3P{=}CHPMe_2} \xleftarrow[-Me_3SiCl]{Me_2PCl} Me_3P{=}CHSiMe_3 \xrightarrow[-(Me_3Si)_2O]{Me_2AsOSiMe_3} \underset{194}{Me_3P{=}CHAsMe_2} \qquad (84)$$



$$\underset{\substack{|\\CH_2Li}}{Me_2P{=}CH_2} \xrightarrow{Me_2SbCl} \underset{195}{Me_3P{=}CHSbMe_2} \qquad (85)$$

The reaction of a C–lithium-substituted phosphorus ylid with an excess of dimethylchlorophosphine gives bis-phosphine-substituted ylid **196**.[231–235] On heating ylid **196** with trimethylphosphonium dimethylphosphinemethylid **193**, two molecules of trimethylphosphonium bis(dimethylphosphine) methylid **197** are produced via recombination of dimethylphosphino groups (eq. 86).[71,150,231]

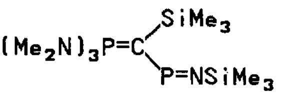


$$\underset{\mathrm{CH_2Li}}{\mathrm{Me_2P{=}CHPMe_2}} \xrightarrow{\mathrm{Me_2PCl}} \underset{\mathrm{CH_2PMe_2}}{\mathrm{Me_2P{=}C(PMe_2)_2}} \longrightarrow \mathrm{2Me_3P{=}C(PMe_2)_2} \qquad (86)$$

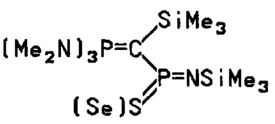
193 197

196

In recent years considerable attention has been devoted to the syntheses of phosphorus ylids possessing a low-coordinate phosphorus atom at the ylidic carbanion. Phosphorus ylid **198** containing two-coordinated phosphorus atoms at the α-carbon was obtained by the reaction of a (dichlorophosphinyl)methylphosphonium salt with sodium bis(trimethylsilyl)amide. The addition of sulphur or selenium to the phosphorus ylid **198** leads to ylids **199** containing a pentavalent tricoordinated phosphorus atom at the α-carbon.[236]

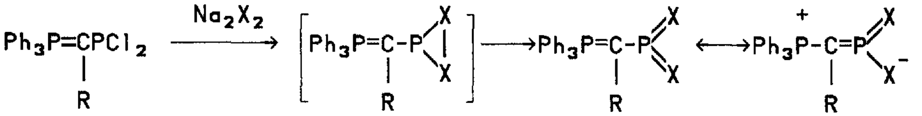


198



199

Dichloro[organo(triphenylphosphonio)methanylid]phosphines smoothly react with sodium diselenide as well as with sodium sulfide to give ylids such as **200** containing a tricoordinate pentavalent phosphorus atom at the α-carbon, which may be isolated as yellow crystals. The NMR spectra [δ_P 214 ppm (X = Se) and 243 ppm (X = S)] and X-ray analysis (eq. 87) confirmed the structure of these compounds.[237,238]

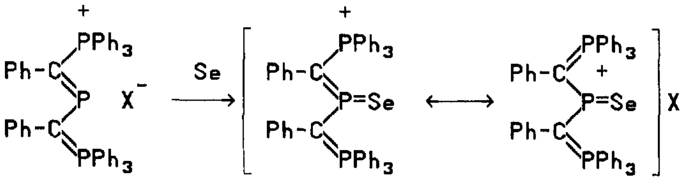


(87)

200

X= S, Se; R= Me, Et, Ph, 3-MeC$_6$H$_4$

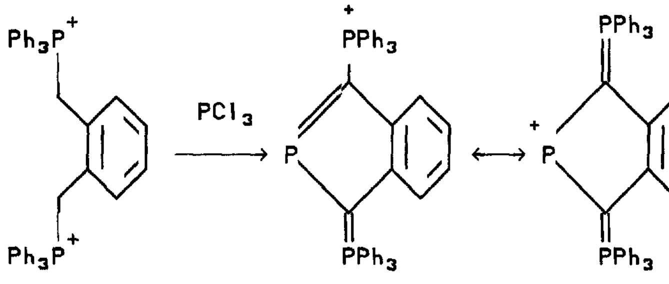
Schmidpeter showed recently that bis-ylidochlorophosphine exists as the bis-ylidylphosphenium cation, which may be regarded as a derivative of phosphacyanines. It reacts with selenium to form monomeric bis-ylid-substituted selenophosphonium chloride **201**—the first chalcogenic ion with trigonal planar phosphorus[150,238-240] (eq. 88).



(88)

201

The phosphorus ylid containing a two-coordinate phosphorus atom at the ylid carbon atom was also synthesized by reaction of the bis-phosphonium salt **202** with phosphorus trichloride in the presence of triethylamine. The NMR spectrum shows that the ylid structure predominates in the ground state of the compound **203**[226] (eq. 89).



202 203

(89)

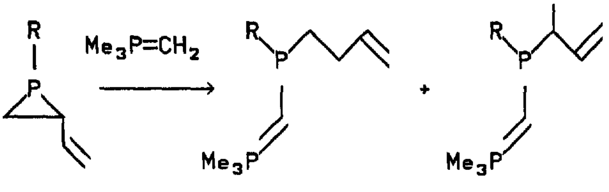
By means of the reaction of trimethylphosphine with fluorinated phosphalkenes Grobe and co-workers obtained phosphorus ylids **204**, X = F, OMe, OEt, bearing a tervalent phosphorus atom on the ylid carbon atom. The formation of the ylid **204** illustrates the electrophilic nature of the sp^2 hybridized carbon atom of the phospha-alkene containing a π-donor substituent X[241] (eq. 90).

$$\mathrm{Me_3P + F_3CP{=}C(F)X \xrightarrow[CH_2Cl_2]{-196-\ -80^{\circ}C} \underset{204}{Me_3P{=}C(X)P(F)CF_3}} \qquad (90)$$

Majoral and co-workers described a synthesis of the phosphorus ylid **205** containing two-coordinated phosphorus atoms at the ylid carbon. The reaction of triphenylphosphonium methylid with chlorophospha-alkenes proceeds in a reagent ratio of 2 : 1[242] (eq. 91).

$$\mathrm{2Ph_3P{=}CH_2 + ClP{=}C(SiMe_3)_2 \longrightarrow \underset{205}{Ph_3P{=}CHP{=}C(SiMe_3)_2} + [Ph_3\overset{+}{P}Me]Cl^-} \qquad (91)$$

An original method for the preparation of C-phosphine-substituted phosphorus ylids has been described by Benn *et al.*[243] Reaction of trimethylphosphonium methylid with 1-alkyl-2-vinylphosphiranes is followed by both opening of the three-membered ring and proton migration to afford the isomeric C-phosphine-substituted ylids **206** and **207**, R = t-Bu, c-C_6H_{11} (eq. 92).



206 207

(92)

Triphenylphosphonium oxyphosphinemethylids (**208**), R = H, Me, Ph, are obtained in yields of 70–95% by heating dialkyl and diarylphosphinic acid chlorides with triphenylphosphonium ylids. The reaction of chloroanhydrides of dialkyl and diaryl esters of phosphorus acid with triphenylphosphonium methylid proceeds in tetrahydrofuran at room temperature and gives ylids **209**, R = Alk, Ph in good yields.[153,244] The reaction of a phosphorus ylid with mono- and dichlorides of phosphorus thioacids as well as with thiophosphoryl chloride leads to the replacement of the chlorine atoms to provide ylids **210** possessing one, two or three C–P bonds[153,228,245] (eq. 93).

$Ph_3P{=}C(R){-}P(O)R'_2$

208

$Ph_3P{=}CHP(O)(OR)_2$

209

$$2n\ Ph_3P{=}CHR \xrightarrow{Ph_nP(S)Cl_{3-n}} (Ph_3P{=}CR)_{3-n}P(S)Ph_n \qquad (93)$$

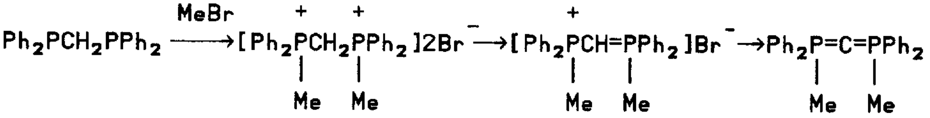
210

Triphenylphosphonium diphenylphosphonomethylid **211** can be obtained in high yield by quaternization of triphenylphosphine with diphenylchloromethylphosphonate (175°C, 4 h, yield 77%).[248] Upon heating to 100–110°C ylid **211** reacts with aromatic and aliphatic aldehydes to form the diphenyl *trans*-vinylphosphonates (eq. 94).

$$(PhO)_2P(O)CH_2Cl \xrightarrow{Ph_3P} [(PhO)_2P(O)CH_2\overset{+}{P}Ph_3]Cl^- \longrightarrow (PhO)_2P(O)CH{=}PPh_3 \qquad (94)$$

211

Bis(diorganylphosphine)methanes react with alkyl halides to form methylenphosphonium salts, dehydrohalogenation of which affords an ylid-phosphonium salt and then carbodiphosphoranes (eq. 95).[249] Tris(phosphonium)methanes, being strong CH-acids are easily transformed into ylid-bis-phosphonium salts **212**[231,250–253] (eq. 96).

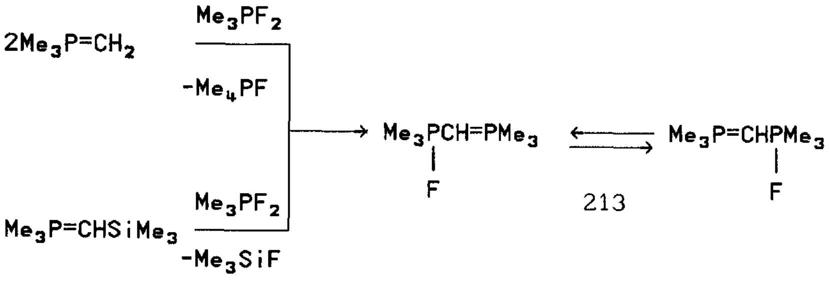


$$Ph_2PCH_2PPh_2 \xrightarrow{MeBr} [Ph_2\underset{Me}{\overset{+}{P}}CH_2\underset{Me}{\overset{+}{P}}Ph_2]2Br^- \longrightarrow [Ph_2\underset{Me}{P}CH{=}\underset{Me}{\overset{+}{P}}Ph_2]Br^- \longrightarrow Ph_2\underset{Me}{P}{=}C{=}\underset{Me}{P}Ph_2 \qquad (95)$$

$$CH(PMe_2)_3 \xrightarrow{MeI} [CH(\overset{+}{P}Me_3)_3]3I^- \xrightarrow[-HI]{} [Me_3\overset{+}{P}{=}C(PMe_2)_2]2I^- \qquad (96)$$

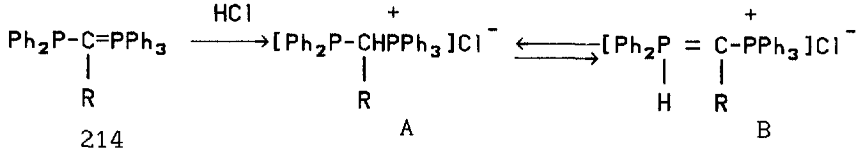
212

Trimethylphosphonium methylid reacts with trimethylfluorophosphorane to form the C-fluorophosphorane substituted ylid **213**. NMR studies established the fast migration of the fluorine atom between the two phosphorus atoms. The same ylid was also obtained by reaction of the C-silyl-substituted phosphorus ylid with trimethyldifluorophosphorane.[229,230] (Scheme 17).



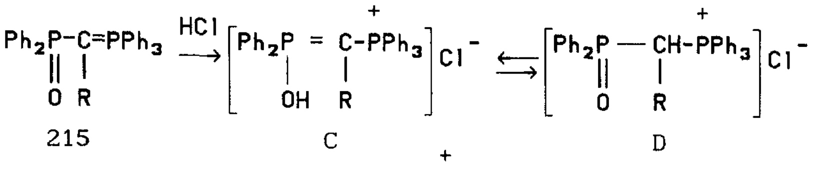
Scheme 17.

3.1.2. *Properties*. The phosphorus ylids stabilized by phosphorus, arsenic, and antimony atoms are rather stable. These compounds can be easily purified by distillation under vacuum or crystallization from organic solvents. Ter- and pentavalent phosphorus atoms at the ylid carbon reduce both the basicity and the nucleophilicity of C–phosphorus substituted ylids. The influence of the substituent on the basicity of ylids is decreased in the sequence: $Ph_3P^+ > CO_2Et > P(O)(OR)_2 >$ $(O)Ph_2 > P(S)Ph_2$.[245,254] Two or three phosphonium groups at the ylid carbon atom greatly reduce the basicity of these compounds. For instance, tris(triphenylphosphonium)methylid is not protonated even by strong acids. Bis(triphenylphosphonium)diphenylphosphinomethylid **214**, $R = [PPh_3]X^-$ with hydrogen chloride gives the P-protonated form B,[255,256] while in the case of the ylid **214**, $R = CO_2Et$, both C- and P-protonated forms A and B are found in solution.[257] NMR spectroscopy shows the existence of an equilibrium between the A and B prototropic forms of compound **214** in methylene chloride at $-80°C$. The concentration of the A form increases when the concentration of hydrogen chloride is raised[258] (eq. 97).



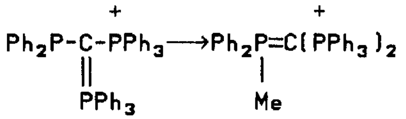
(97)

The protonation of ylid **215**, containing a P=O group at the α-carbon atom, proceeds with formation of either the OH- and CH-protonated form depending on the nature of the substituents R. If R is a triphenylphosphonium or tosyl group the OH-protonated form C is formed; if R is CO_2Et both OH- and CH-protonated forms exist in tautomeric equilibrium in solution[259] (eq. 98).



(98)

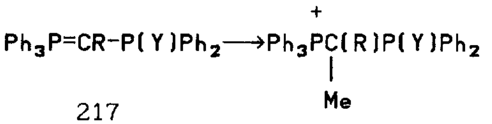
Alkylation of phosphine-phosphonium ylids **216** affords P-alkylated phosphonium salts,[245,254,260] while alkylation of phosphoryl or thiophosphoryl substituted phosphorus ylids **217**, X = O, S, gives C-substituted phosphonium salts (eq. 99, 100). The reaction of C–bis-phosphine substituted ylid **218** with 1,4-dibromobut-2-ene gives cyclic ylid-phosphonium salts **219** in very good yield[246,247] (eq. 101).



$$\mathrm{Ph_2P\text{-}\underset{\underset{PPh_3}{\|}}{C}\text{-}\overset{+}{P}Ph_3 \longrightarrow Ph_2\underset{\underset{Me}{|}}{P}{=}C(\overset{+}{P}Ph_3)_2}$$

216

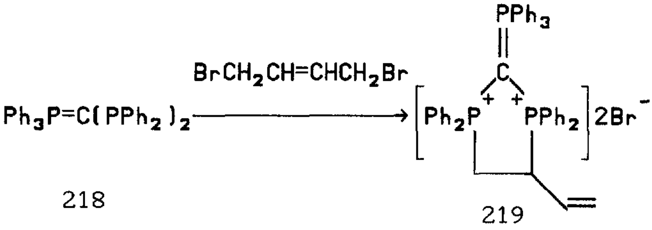
(99)



$$\mathrm{Ph_3P{=}CR\text{-}P(Y)Ph_2 \longrightarrow Ph_3\overset{+}{P}\underset{\underset{Me}{|}}{C}(R)P(Y)Ph_2}$$

217

(100)

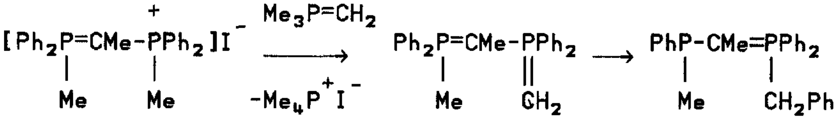


218

219

(101)

Some C–phosphorus-containing phosphorus ylids undergo interesting rearrangements. Thus, treatment of the phosphonium salt **220** with trimethylphosphonium methylid causes rearrangement into the C-phosphine-substituted phosphorus ylid **221** as a result of phenyl group migration from the phosphorus atom to the ylid carbon[261] (eq. 102).

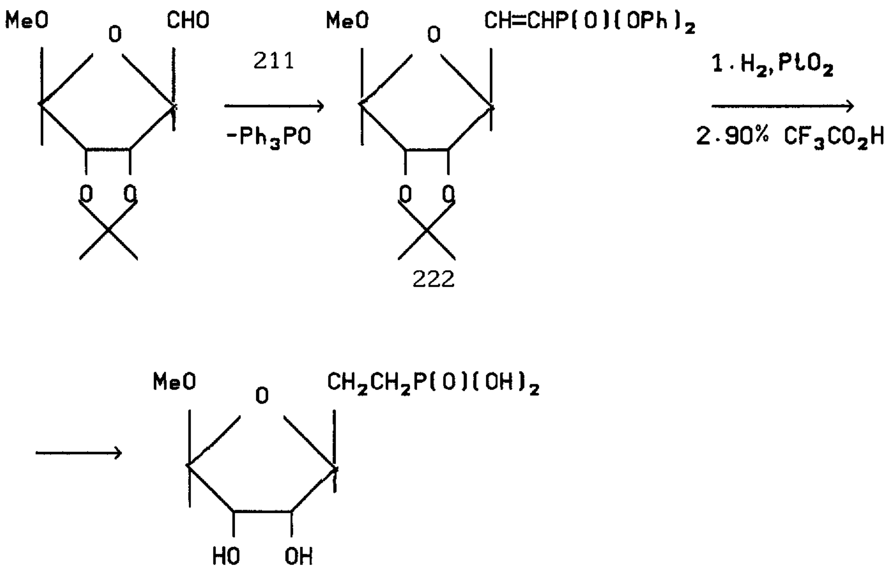


$$\mathrm{[Ph_2\underset{\underset{Me}{|}}{P}{=}CMe\text{-}\underset{\underset{Me}{|}}{\overset{+}{P}}Ph_2]\overset{-}{I} \xrightarrow[-Me_4\overset{+}{P}\overset{-}{I}]{Me_3P{=}CH_2} Ph_2\underset{\underset{Me}{|}}{P}{=}CMe\text{-}\underset{\underset{CH_2}{\|}}{P}Ph_2 \longrightarrow Ph\underset{\underset{Me}{|}}{P}\text{-}CMe{=}\underset{\underset{CH_2Ph}{|}}{P}Ph_2}$$

220 221

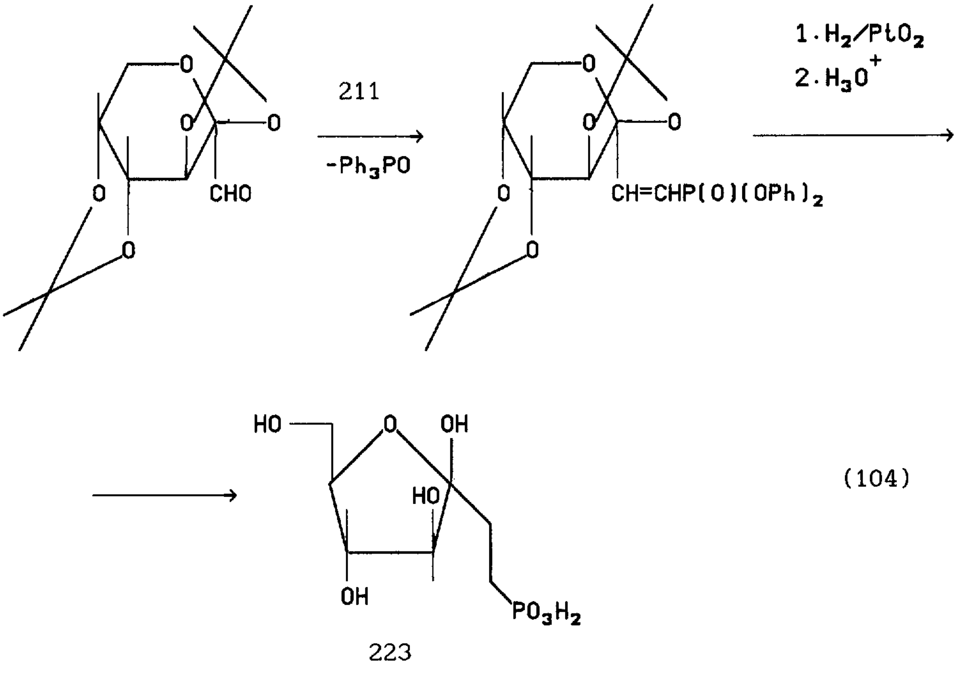
(102)

Despite their relatively low nucleophilicity ylids stabilized by a tetracoordinated phosphorus atom undergo the Wittig reaction with aldehydes to provide phosphorylated olefins. By means of C–phosphorus-substituted ylids one can obtain, in particular, isosteric analogs of naturally occurring phosphates differing by the presence of a P–C bond. The replacement of P–O bond in phosphates with a P–C bond provides biologically active compounds capable of inhibiting physiological processes in which natural phosphates take part.[263,264] Carbohydrates containing protected hydroxyl groups, are easily olefinated by triphenylphosphonium diphenylphosphonomethylid (**211**) with formation of vinylphosphonates **222**. When compound **222** was hydrogenated over platinum or palladium oxide and hydrolysed, phosphonic acids were obtained[265] (eq. 103).



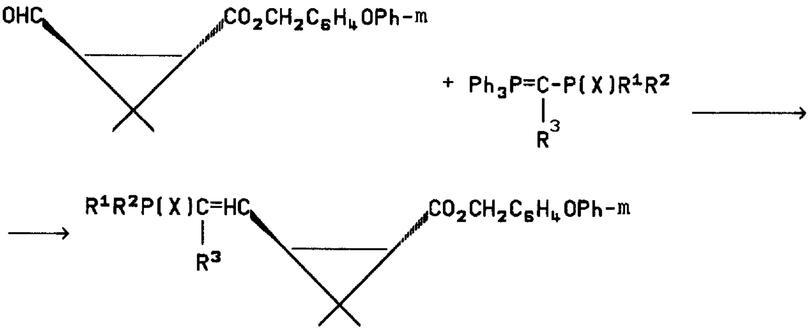
(103)

Using triphenylphosphonium diphenylphosphonomethylid (**211**), the synthesis of a fructose-1-phosphate phosphonic analogue **223** which appeared to possess bioregulatory properties with respect to hexosophosphate transport systems was achieved[266] (eq. 104).



(104)

Similarly the isosteres of ribose-5-phosphate-5-dioxo, 2,3,4,5-di-*O*-isopropylidene-D-arabinose, 2,3,4,5,6-penta-*O*-acetyl-dehydro-D-glucose, etc. were obtained.[267–269] Huang and co-workers synthesized phosphorus containing pyrethroids **224** using C-phosphorylated ylids[270] (eq. 105).

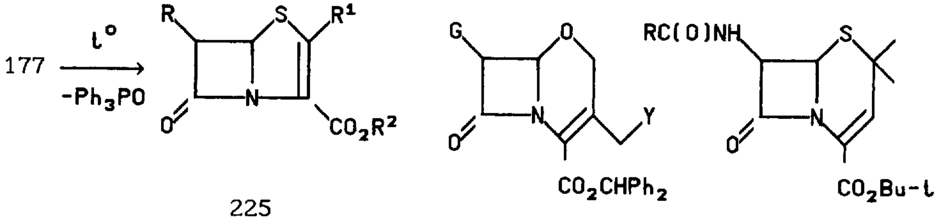


(105)

224

R^1=AlkO, PhO, Ph; R^2=AlkO, ArO; R^3=H, Me;

Phosphorus ylids **177** containing the 4-thioacetylacetydinone group at the α-carbon atom have found numerous applications in the synthesis of β-lactam antibiotics. Upon heating for several hours in toluene, they form penemates **225** in good yields via an intramolecular Wittig reaction.[271] A variety of the other β-lactam antibiotics, derivatives of the penem and cephem acids **226, 227**, were synthesized in analogous fashion[271–279] (eq. 106).



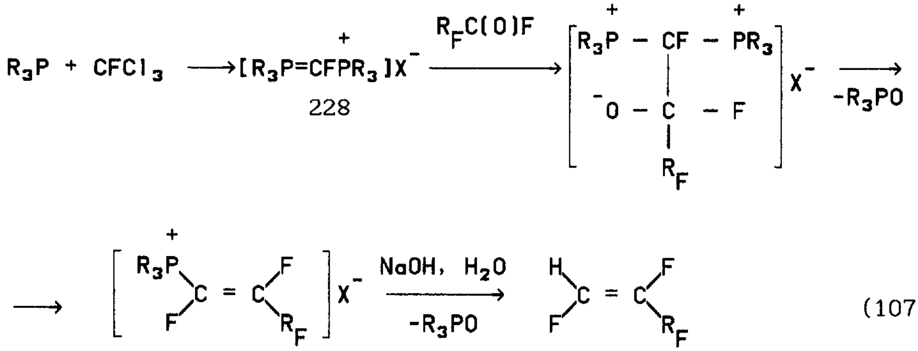
(106)

225

226

227

Barton developed a method for preparation of fluoroolefin **230** as shown in eq. 107. Evidently the reaction proceeds via a mechanism close to that of the Wittig reaction and includes the formation of a betaine, which is decomposed to give the phosphine oxide and vinylphosphonium salt **229**. Cleavage of the C–P bond in the phosphonium salt **229** is then achieved by treatment with aqueous sodium hydroxide solution. The yields of fluoroolefins **230** are in the range 45–62%.[280,281]



228

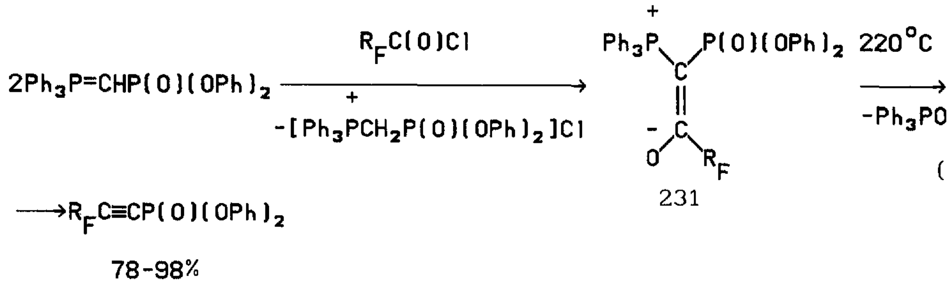
229

230

(107)

R=Bu, Ph; R_F=CF_3, CF_2CF_3, $CF_2CF_2CF_3$, CF_2Cl, $CF_3(CF_2)OCF(CF_3)_2$

The synthesis of 1-perfluoroalkynylphosphonates is achieved by the pyrolysis of 2-oxyalkylidene triphenylphosphonium ylids **231** via an intramolecular Wittig reaction[282] (eq. 108).



231

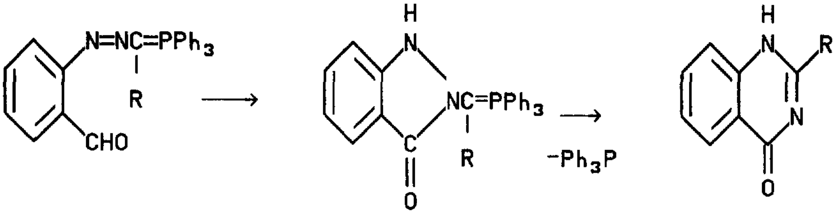
(108)

$R_F = CF_3, CF_3CF_2, CF_3CF_2CF_2$

In some cases the ylids bearing a phosphine group at the α-carbon atom rearrange into trisphosphinemethanes[231] (eq. 109).

$$[Ph_2P\overset{-}{C}HPPh_2]\overset{+}{Li} \xrightarrow{R_2PCl} R_2P(PPh_2){=}CHPPh_2 \longrightarrow R_2PCH(PPh_2)_2 \qquad (109)$$

The thermolysis of *O*-formylarylazomethylid affords ylids **232** which are further transformed into quinazolines[283,284] (eq. 110).

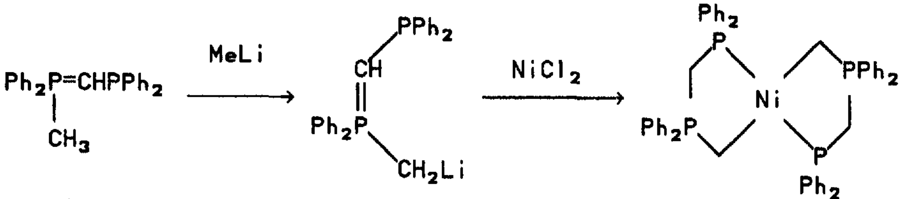


232

(110)

R= CO_2Me, $C(O)Me$, SO_2Ph, $SO_2C_6H_4Me$-4, $C(S)SMe$

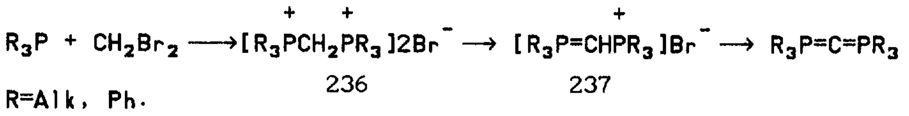
The ylid **233** reacts with methyllithium to provide the carbanions **234**, which are used as ligands for ylid complexes with transition metals.[232–235] Thus, the stable nickel complexes **235** are obtained by the reaction of nickel dichloride with 2 equivalents of **234**[217,285] (eq. 111).



233 234 235

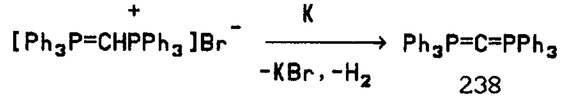
(111)

3.1.3. *Carbodiphosphoranes*. Carbodiphosphoranes are an interesting class of C–phosphorus-substituted ylids having on the α-carbon two negative charges stabilized by two phosphonium groups.[286] Carbodiphosphoranes are derivatives of ylid-phosphonium salts **237** formed by dehydrohalogenation of **236** using weak bases (eq. 112). The reaction of salts **237** with sodium amide or butyllithium leads to the abstraction of the second proton from the α-carbon atom and formation of carbodiphosphorane. Heating of bis(triphenylphosphonium)methylid bromide with potassium in dimethoxyethane provides the hexaphenylcarbodiphosphorane **238**[287-289] (eq. 113).



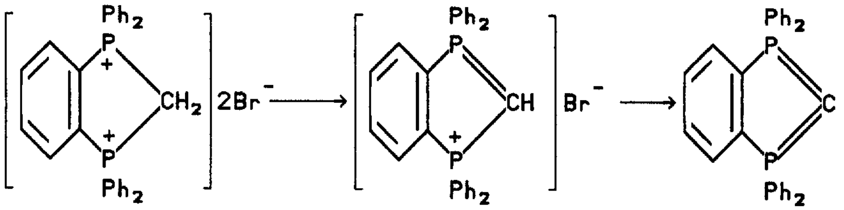
$$R_3P + CH_2Br_2 \longrightarrow \underset{236}{[R_3\overset{+}{P}CH_2\overset{+}{P}R_3]2Br^-} \longrightarrow \underset{237}{[R_3P{=}CH\overset{+}{P}R_3]Br^-} \longrightarrow R_3P{=}C{=}PR_3 \qquad (112)$$

R=Alk, Ph.



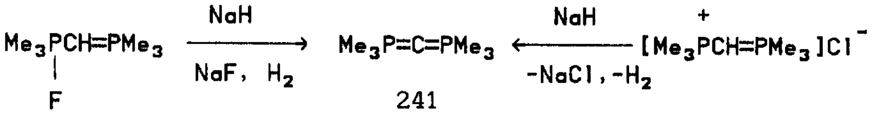
$$[Ph_3P{=}CH\overset{+}{P}Ph_3]Br^- \xrightarrow[-KBr,\,-H_2]{K} \underset{238}{Ph_3P{=}C{=}PPh_3} \qquad (113)$$

The treatment of cyclic bis-phosphonium salts with ammonia or butyllithium affords ylid-phosphonium salts **239** which may be deprotonated by means of the triethylphosphonium ethylid. The resulting cyclic carbodiphosphorane **240** was isolated as a yellow crystalline solid stable at −40°C (eq. 114).[290]



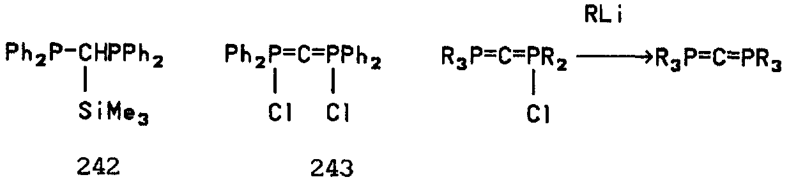
239 240 (114)

Heating the trimethylfluorophosphorane-stabilized ylid with sodium hydride provides hexamethylcarbodiphosphorane **241** in good yield (eq. 115). The exchange of the fluorine atom in the ylid-phosphorane for a chlorine atom, and subsequent heating of ylid-phosphonium salt with sodium hydride also gives **241** in very good yield[230,292] (eq. 115).



$$Me_3\underset{\underset{F}{|}}{P}CH{=}PMe_3 \xrightarrow[NaF,\ H_2]{NaH} \underset{241}{Me_3P{=}C{=}PMe_3} \xleftarrow[-NaCl,\,-H_2]{NaH} [Me_3\overset{+}{P}CH{=}PMe_3]Cl^- \qquad (115)$$

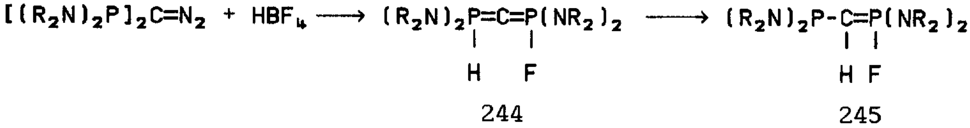
Ylid-phosphonium salts formed upon treatment of triphenylphosphine with carbon tetrachloride may be easily dehydrochlorinated by the tris(dimethylamino)phosphine to furnish carbodiphosphoranes in good yields.[289] The reaction of tervalent phosphorus compounds **242** containing a trimethylsilyl group at the α-carbon with tetrachloromethane leads to the P-chlorocarbodiphosphoranes **243**.[293,294] The chlorine atoms of P-chloroylids are easily replaced by alkyl groups on reaction with organolithium compounds (eq. 116).[295a] P-Fluoroylids react with butyllithium in the presence of TMEDA to form carbodiphosphoranes.[295b]



$$Ph_2P\text{-}\underset{SiMe_3}{\underset{|}{C}}HPPh_2 \qquad Ph_2\underset{Cl}{\underset{|}{P}}=C=\underset{Cl}{\underset{|}{P}}Ph_2 \qquad R_3P=C=\underset{Cl}{\underset{|}{P}}R_2 \xrightarrow{RLi} R_3P=C=PR_3 \tag{116}$$

242 243

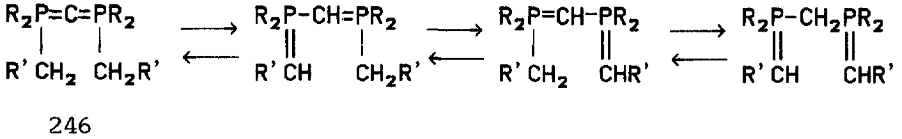
Bertrand and Baceiredo found that carbodiphosphorane with a P–H bond can be directly obtained by addition of tetrafluoroboric acid to diphosphinodiazomethane. Carbodiphosphorane is thermally quite stable as a solid (mp 116°C); in solution it slowly rearranges into the isomeric phosphorus ylid **245** (eq. 117).[296]



$$[(R_2N)_2P]_2C=N_2 + HBF_4 \longrightarrow (R_2N)_2\underset{H}{\underset{|}{P}}=C=\underset{F}{\underset{|}{P}}(NR_2)_2 \longrightarrow (R_2N)_2P\text{-}\underset{H}{\underset{|}{C}}=\underset{F}{\underset{|}{P}}(NR_2)_2 \tag{117}$$

244 245

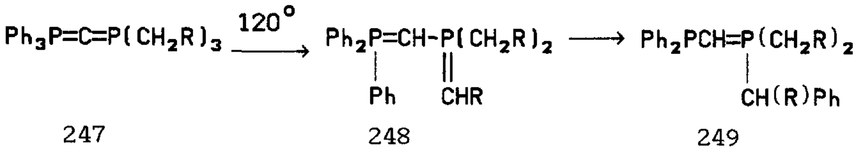
NMR spectra show that carbodiphosphoranes **245** bearing alkyl groups at the phosphorus atom exist as an equilibrium mixture of prototropic tautomers (eq. 118).[297,298] The position of the tautomeric equilibrium depends on the acidifying effect of the substituents. Electron-withdrawing substituents shift the equilibrium towards the bis-ylid form. The prototropic exchange between tautomers probably proceeds through a six-membered transition state.[291,297–301]



$$R_2\underset{R'CH_2}{\underset{|}{P}}=C=\underset{CH_2R'}{\underset{|}{P}}R_2 \rightleftarrows R_2\underset{R'CH}{\underset{\|}{P}}\text{-}CH=\underset{CH_2R'}{\underset{|}{P}}R_2 \rightleftarrows R_2\underset{R'CH_2}{\underset{|}{P}}=CH\text{-}\underset{CHR'}{\underset{\|}{P}}R_2 \rightleftarrows R_2\underset{R'CH}{\underset{\|}{P}}\text{-}CH_2\underset{CHR'}{\underset{\|}{P}}R_2 \tag{118}$$

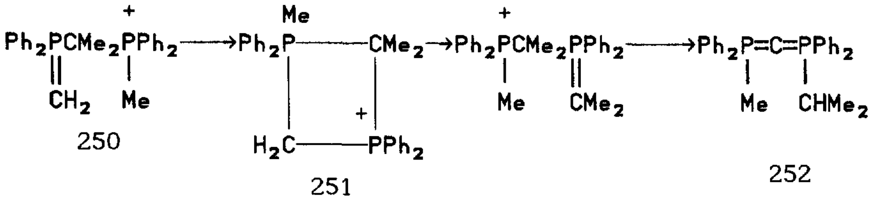
246

Some carbodiphosphoranes undergo rearrangement accompanied by migration of alkyl or phenyl groups. Thus, on heating to 120°C, asymmetric trialkyl-substituted carbodiphosphoranes **247** give ylids **249** via the formation of bis-ylids **248** as a result of phenyl group migration from the phosphorus atom to the ylid carbon atom (eq. 119).[214,302] Ylid-phosphonium salts **250** bearing a dimethylmethylene group between the two phosphorus atoms are unstable and rearrange through a four-membered transition state **251** into carbodiphosphoranes **252** (eq. 120). As a result of the rearrangement less sterically hindered compounds are formed.[261] Transylidation of 1,2-bis-phosphonium benzene **253** with excess triethylphosphonium ethylid provides an unstable bis-ylid **254** which easily rearranges into the carbodiphosphorane[303] (eq. 121).



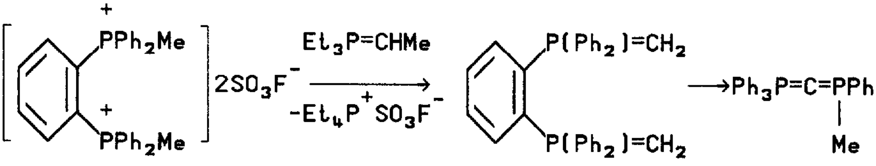
$$Ph_3P=C=P(CH_2R)_3 \xrightarrow{120^\circ} Ph_2\underset{Ph}{\underset{|}{P}}=CH\text{-}\underset{CHR}{\underset{\|}{P}}(CH_2R)_2 \longrightarrow Ph_2PCH=\underset{CH(R)Ph}{\underset{|}{P}}(CH_2R)_2 \tag{119}$$

247 248 249



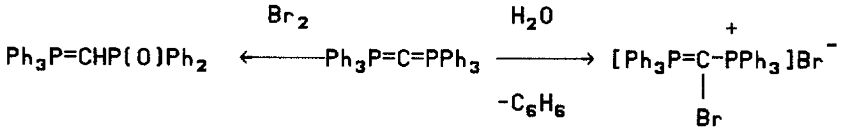
$$Ph_2\underset{CH_2}{\underset{\|}{\overset{+}{P}}}CMe_2\underset{Me}{\underset{|}{P}}Ph_2 \longrightarrow \begin{array}{ccc} Ph_2\overset{Me}{P} & \text{—} & CMe_2 \\ | & & {}^{+}| \\ H_2C & \text{—} & PPh_2 \end{array} \longrightarrow Ph_2\underset{Me}{\underset{|}{\overset{+}{P}}}CMe_2\underset{CMe_2}{\underset{\|}{P}}Ph_2 \longrightarrow Ph_2\underset{Me}{\underset{|}{P}}=C=\underset{CHMe_2}{\underset{|}{P}}Ph_2 \tag{120}$$

250 251 252



253 254 (121)

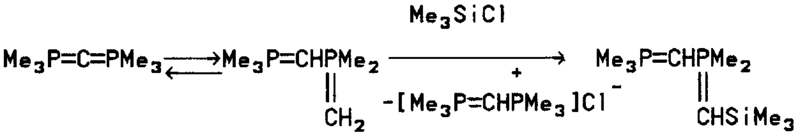
Hydrolysis of hexaphenylcarbodiphosphorane proceeds with elimination of benzene and formation of the triphenylphosphonium oxidiphenylphosphinomethylid **255**. The reaction of hexaphenylcarbodiphosphorane with bromine leads to the bromomethylid **256**[249,288] (eq. 122).



$$\mathrm{Ph_3P{=}CHP(O)Ph_2} \xleftarrow{\mathrm{Br_2}} \mathrm{Ph_3P{=}C{=}PPh_3} \xrightarrow[-\mathrm{C_6H_6}]{\mathrm{H_2O}} [\mathrm{Ph_3P{=}}\underset{\displaystyle |\atop \mathrm{Br}}{\overset{+}{\mathrm{C}}}\mathrm{{-}PPh_3}]\mathrm{Br^-} \quad (122)$$

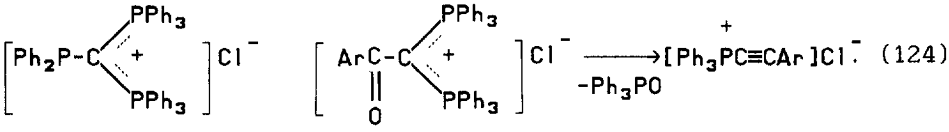
255 256

Carbodiphosphoranes possess high basicity and nucleophilicity. The reaction between carbodiphosphoranes and electrophiles gives products of replacement at the central or lateral carbon atom. For instance, reaction of hexamethylcarbodiphosphorane with trimethylchlorosilane affords ylid **257** bearing the trimethylsilylgroup at the lateral carbon atom (eq. 123). Alkylation of carbodiphosphorane usually proceeds at the ylidic carbon atom to form ylid-phosphonium salts. Hexaphenylcarbodiphosphorane adds diphenylchlorophosphine to the ylid carbon atom to form the phosphonium salt **258**. The X-ray analysis and NMR spectrum show that the compound possesses non-equivalent triphenylphosphonium groups because of the hindered rotation of the diphenylphosphine group.[253] Hexaphenylcarbodiphosphorane reacts with aromatic acyl chlorides to form C-acylated ylid-phosphonium salts **259**, which upon heating undergo an intramolecular Wittig reaction to provide arylethynylphosphonium salts **260**[304] (eq. 124).



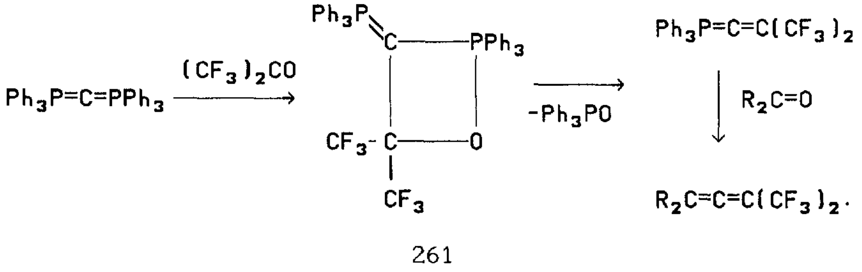
$$\mathrm{Me_3P{=}C{=}PMe_3} \rightleftarrows \mathrm{Me_3P{=}CH}\underset{\displaystyle \| \atop \mathrm{CH_2}}{\mathrm{P}}\mathrm{Me_2} \xrightarrow[-[\mathrm{Me_3P{=}CH\overset{+}{P}Me_3}]\mathrm{Cl^-}]{\mathrm{Me_3SiCl}} \mathrm{Me_3P{=}CH}\underset{\displaystyle \| \atop \mathrm{CHSiMe_3}}{\mathrm{P}}\mathrm{Me_2} \quad (123)$$

257



258 259 260 (124)

Carbodiphosphoranes react readily with aldehydes and ketones. The reaction proceeds through the formation of the four-membered cyclic oxaphosphetanes **261**, which are stable at room temperature and can be isolated and characterized by NMR. Upon heating the oxaphosphetanes **261** are transformed into allenylids which undergo Wittig reaction with the formation of allenes (eq. 125). With carbon dioxide, carbodiphosphoranes form betaines **262** which may be isolated, characterized and after heating, transformed into phosphonium ketenes **263** (eq. 126). Analogously, phosphonium thioketenes **264** and phosphonium keteneimines **265** were obtained.[306-308] The reaction of carbodiphosphorane with diphenylketene yields cumulenylid **266**, which readily undergoes Wittig reactions with aldehydes to form cumulenes **267**[309] (eq. 127).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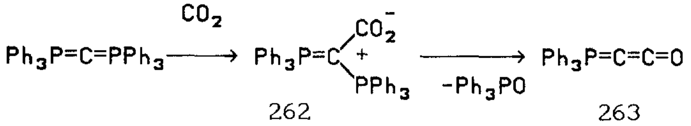
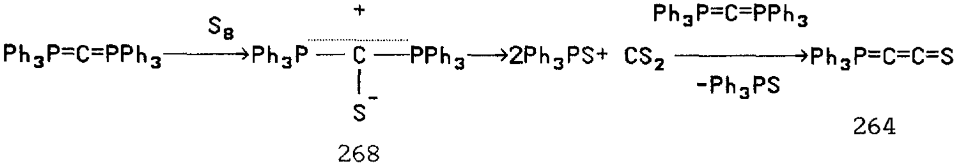

(126)

$$\underset{264}{Ph_3P{=}C{=}C{=}S} \quad \underset{265}{Ph_3P{=}C{=}C{=}NAr} \quad \underset{266}{Ph_3P{=}C{=}C{=}CPh_2} \xrightarrow[-Ph_3PO]{ArCHO} \underset{267}{Ph_2C{=}C{=}C{=}CHAr} \qquad (127)$$

In THF at −50°C hexaphenylcarbodiphosphorane adds sulphur to form betaine **268** in solution at 0°C and which may be crystallized at −50°C as a red solid. At room temperature betaine **268** eliminates carbon disulphide which reacts with the starting hexaphenylcarbodiphosphorane to afford phosphonium ketene **264** (eq. 128).[310] Alkylation of betaine **268** proceeds with the formation of phosphonium salt **269** (eq. 129). Addition of selenium to hexaphenylcarbodiphosphorane leads to the formation of betaine **270** stable at room temperature and identified by X-ray analysis.[310]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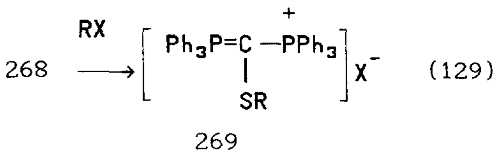
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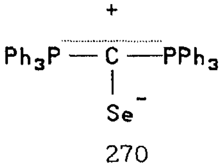
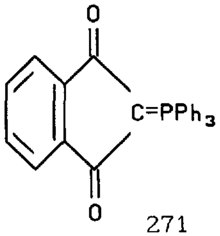


R=Me, CH_2Ph, $SnMe_3$; X=SO_2F, Cl

The reaction of hexaphenylcarbodiphosphorane with aromatic dicarboxylic acid and anhydrides such as phthalic acid anhydride proceeds with exchange of the anhydride oxygen atom for the ylid function to form cyclic ylids **271**.[304,305] Hexaphenylcarbodiphosphorane reacts with the salicylaldehyde to give the six-membered cyclic oxaphosphorane **273**. The reaction probably proceeds via intermediate **272**.[311]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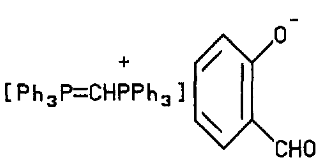
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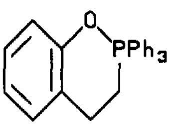
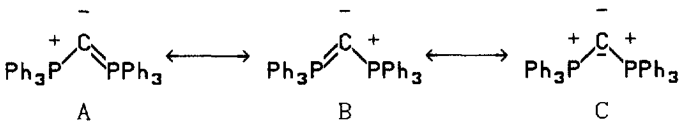

273

Carbodiphosphoranes are widely used as ligands for the preparation of transition metal complexes.[312-317] Ylid complexes containing carbodiphosphorane ligands are described in detail in other reviews.[1-4,316] The chemical and physico-chemical properties show that the diylid resonance formula C predominates in the ground state of carbodiphosphoranes.

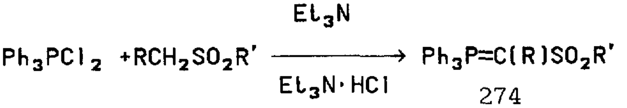


Thus, the molecular structure of hexamethylcarbodiphosphorane in the gas state was identified by electronography. The distance of the P═C bond is shortened to 1.594(3) Å while the distance of the C–P bond is 1.814(3) Å. The P═C═P angle is equal to 147.6(5)° greatly differing from that of C═C═C in allenes which is close to 180°. The central carbon atom of carbodiphosphoranes has hybridization close to sp^2.[318] Dipole moments of carbodiphosphoranes have also been determined, μ (benzene) 4.69 ± 0.05 D.[319,320] The structure of hexaphenylcarbodiphosphorane was studied in detail because of its interesting triboluminescent properties.[323-325] Triboluminescence is the ability of substances to generate light under mechanical stimulation. Hexaphenylcarbodiphosphorane forms polymorphic crystalline forms, in particular rhombic crystals without triboluminescent properties and microcrystalline triboluminescent monoclinic crystals. The main difference between these crystalline forms is related to the values of the P═C═P angles and C–P······P–C dihedral angles.[326,327]

3.2. *C–O, C–S and C–Se substituted ylids*

Ylids stabilized by sixth group elements (oxygen, sulphur, selenium) are very different in their structures and properties. The chemistry of these ylids has been intensively studied and synthetic methods and chemical properties have been developed and studied in detail.

3.2.1. *Synthesis.* Among this group of phosphorus ylids the C-sulphonyl-substituted ylids are the most accessible. Due to the efficient stabilization of the negative charge on the ylid carbon by the hexavalent sulphur atom, these ylids are characterized by high stability. They can be obtained by such simple methods as the direct phosphorylation of a polyhalogenphosphorane with a sulphonyl methane in the presence of triethylamine (eq. 130). Ylids **274**, R = H, SO_2Ar; R′ = CF_3, Ar, were isolated in high yields as stable crystalline substances.[328] Ylids **275**, R = CF_3, Me, Bu, Ph, were obtained by the reaction of triphenylphosphine with alkyl and arylsulphonylhalogenomethanes in the presence of organic bases (eq. 131).[329-331] Heating of phenyl iodonium ylids with triphenylphosphine in the presence of copper acetyl-acetonate as a catalyst provides phosphonium ylids **276** in high yields[332] (eq. 132).



$$Ph_3PCl_2 + RCH_2SO_2R' \xrightarrow[Et_3N\cdot HCl]{Et_3N} \underset{274}{Ph_3P{=}C(R)SO_2R'} \qquad (130)$$

$$Ph_3P \xrightarrow{RSO_2CH_2X} [Ph_3\overset{+}{P}CH_2SO_2R]\;X^- \xrightarrow{B} \underset{275}{Ph_3P{=}CHSO_2R} \tag{131}$$

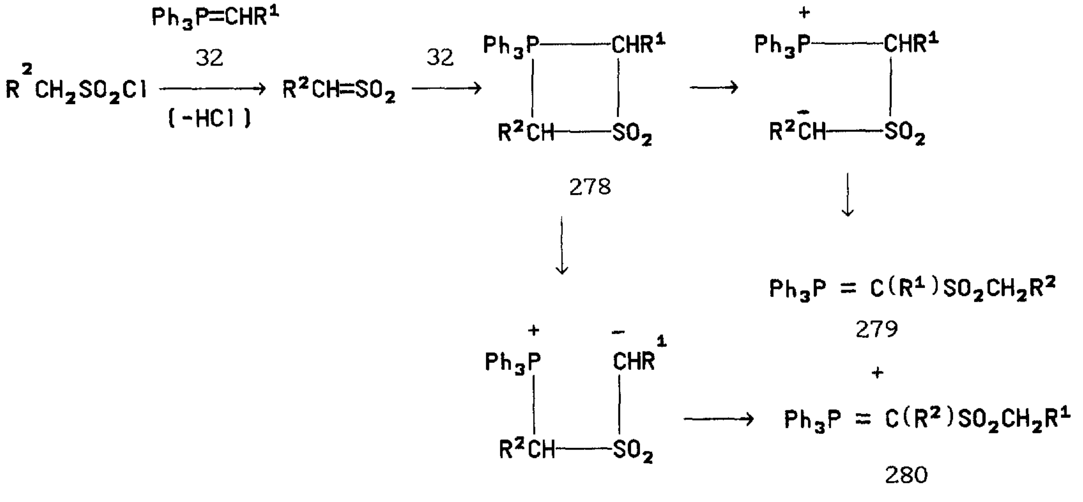
$$\underset{R=Me,\ Ph}{PhI{=}C(SO_2R)_2} + Ph_3P \longrightarrow \underset{276}{Ph_3P{=}C(SO_2R)_2} + PhI \tag{132}$$

A common method for preparation of sulfonylmethylid **274** is the reaction of simple phosphorus ylids **32**, containing hydrogen atoms at the ylidic carbon atom, with sulfonyl fluorides or sulfonyl sulfonates, X = F, $R'SO_3^-$ (eq. 133).[330,331] The reaction of phosphorus ylids with sulfonyl chlorides, however, leads to the formation of chlorinated phosphorus ylids **277** without formation of sulfonyl-substituted ylids **275** as shown in eq. 134.[330]

$$\underset{32}{2Ph_3P{=}CHR} + R'SO_2X \longrightarrow 274 + [Ph_3\overset{+}{P}CH_2R]X^- \tag{133}$$

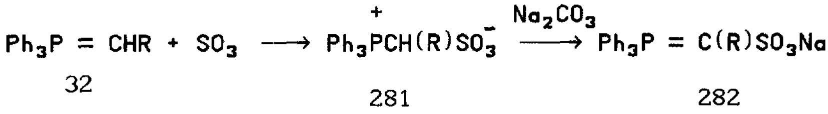
$$RSO_2Cl \xrightarrow{Ph_3P=CH_2} RSO_2^-[Ph_3\overset{+}{P}CH_2Cl] \xrightarrow{Ph_3P=CH_2} \underset{277}{Ph_3P{=}CHCl} + [Ph_3\overset{+}{P}Me]\;RSO_2^- \tag{134}$$

The reactions of a phosphorus ylid with alkylsulfonyl halides is followed by rearrangement as a result of which substituent R^1 passes from the ylid carbon atom to the sulphur atom and R^2 from the hexavalent sulphur atom to the ylid carbon atom. The ylid probably dehydrohalogenates the sulfonylhalide to form a sulfene, which as a result of subsequent [2+2] cycloaddition to the phosphorane gives the four-membered cyclic intermediate **278**. Cleavage of one of the two C–P bonds in intermediate **278** then provides isomers of the ylids **279** and **280**. The ratio of isomers **279** and **280** depends on the nature of the substituents R^1 and R^2 [332a] (Scheme 18).



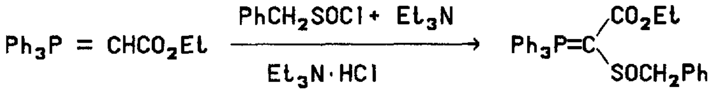
Scheme 18.

Electrophilic addition of sulfur trioxide to phosphorus ylids **32** proceeds in dichloroethane with formation of stable crystalline betaines **281** in 40–95% yields. These may be deprotonated by an aqueous solution of sodium carbonate to furnish ylids **282**[333] (eq. 135).



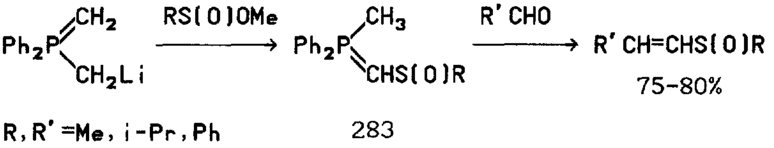
$$\underset{32}{Ph_3P=CHR} + SO_3 \longrightarrow \underset{281}{Ph_3\overset{+}{P}CH(R)SO_3^-} \xrightarrow{Na_2CO_3} \underset{282}{Ph_3P=C(R)SO_3Na} \quad (135)$$

The introduction of the sulfinyl group to phosphorus atom is also easily achieved by reaction of stabilized ylids with sulfinyl chlorides in the presence of triethylamine[333a,334a] (eq. 136).



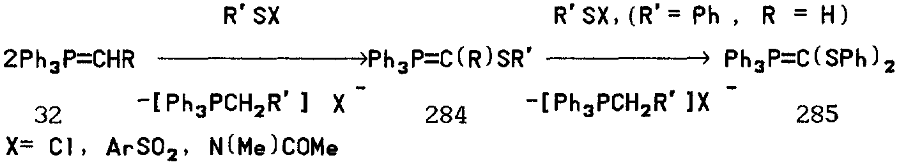
(136)

The reaction of diylids with sulfinates leads to the formation of C–sulfinylylids **283**, which undergo Wittig reaction with aldehydes with excellent stereoselectivity ($E/Z > 91/9$). The same reaction with a chiral sulfinate leads to chiral *E*-vinylsulfoxides ($E/Z > 99/1$), with inversion of configuration at the sulfur atom greater than 96%[48] (eq. 137).



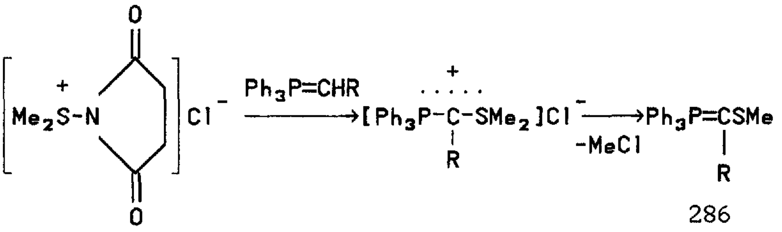
(137)

There are several convenient methods for the synthesis of phosphorus ylids bearing a divalent sulfur atom at the α-carbon. The simplest method for the preparation of such ylids is the reaction of stabilized and non-stabilized phosphorus ylids **32** with sulfenylchlorides. Reaction proceeds in benzene or THF at 20°C with reagent ratios of 2 : 1 or 3 : 1 to afford ylids **284** and **285** bearing one or two *RS*-groups at the α-carbon atom (eq. 138).[334,335,372a] *p*-Tolyl-*p*-toluenesulfonate and *N*-methyl-*N*-phenylthioacetamide can also be used.[334a] Reaction of stabilized phosphorus ylids with dimethylsuccinimidosulfonium chloride gives the ylid **286** as shown in eq. 139.[334,336]



$$\underset{32}{2Ph_3P=CHR} \xrightarrow[-[Ph_3PCH_2R']\,X^-]{R'SX} \underset{284}{Ph_3P=C(R)SR'} \xrightarrow[-[Ph_3PCH_2R']X^-]{R'SX,\,(R'=Ph\,,\ R=H)} \underset{285}{Ph_3P=C(SPh)_2} \quad (138)$$

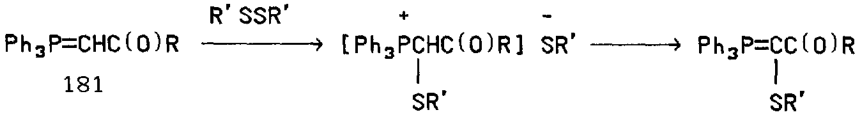
X= Cl, $ArSO_2$, N(Me)COMe



(139)

R = CO_2Et, CO_2Me, C(O)Ph, CN

The reaction of phosphorus ylids **181** with disulfides in benzene affords C–thioalkyl ylids **287** in about 90% yields[334,337] (eq. 140).



$$\underset{181}{Ph_3P{=}CHC(O)R} \xrightarrow{R'SSR'} [Ph_3\overset{+}{P}\underset{\displaystyle SR'}{\underset{|}{C}}HC(O)R]\ \overset{-}{SR'} \longrightarrow \underset{287}{Ph_3P{=}\underset{\displaystyle SR'}{\underset{|}{C}}C(O)R} \qquad (140)$$

$R = Me,\ MeO;\ R' = R_2NC(S),\ EtO_2C$

The syntheses of ylids **288** and **289**, R = Bu, Ph, bearing two thioether groups at the α-carbon atom can be accomplished by reaction of tertiary phosphines with carbenes, generated by the action of sodium hydride on tosylhydrazones (eq. 141)[338] or by decomposition of tris(phenylthio)methyllithium (eq. 142). Ylids **289** were isolated in the crystalline state.[339–341]

$$TsNHN{=}C(SEt)_2 \xrightarrow{NaH} [:C(SEt)_2] \xrightarrow{Ph_3P} \underset{288}{Ph_3P{=}C(SEt)_2} \qquad (141)$$

$$(PhS)_3CLi \xrightarrow[-PhSLi]{} [(PhS)_2C:] \xrightarrow{R_3P} \underset{289}{R_3P{=}C(SPh)_2} \qquad (142)$$

Iodine-containing phosphonium salts react with both sodium thiophenolates and sodium salts of dithiocarbonic salts to give phosphorus ylids, which undergo *in situ* Wittig reactions with aldehydes to form vinylsulfides[334] (eq. 143).

$$[Ph_3\overset{+}{P}CH_2I]\overset{-}{I} + 2RSNa + ArCHO \longrightarrow ArCH{=}CHSR + Ph_3PO \qquad (143)$$

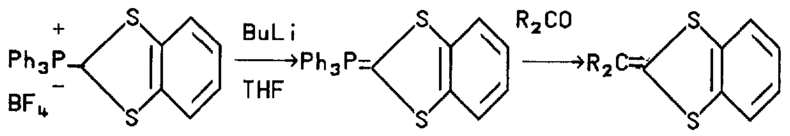
$RS = Me_2NC(S)S,\ Ar$

The most important method for the synthesis of ylids **290**, containing thioalkyl groups at the α-carbon atom consists of dehydrohalogenation of phosphonium salts with organolithium compounds. Ylids **290** synthesized by this method were used in Wittig reactions without prior isolation[342] (eq. 144).

$$[Ph_3\overset{+}{P}CH_2SR]\overset{-}{Cl} \xrightarrow{PhLi} Ph_3P{=}CHSR \xrightarrow{R'CHO} RSCH{=}CHR' \qquad (144)$$

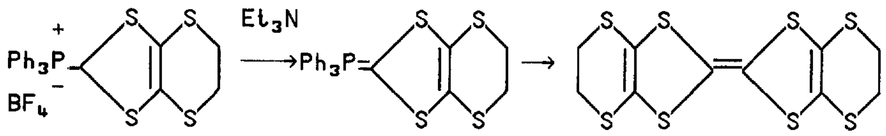
290

The ability of dithia- and tetrathiafulvalene derivatives to generate electroconductive salts has stimulated great interest in the phosphorus ylids **291** and **292** bearing the corresponding thiafulvalene groups.[343–348] Ylids containing the 1,3-dithiol-2-yliden moiety were used for the preparation of the corresponding polyformyl-tetrathiafulvalenes which possess powerful donor ability and form the 2-D cation-radical salt **293**[312,346] (eq. 145, 146).



291

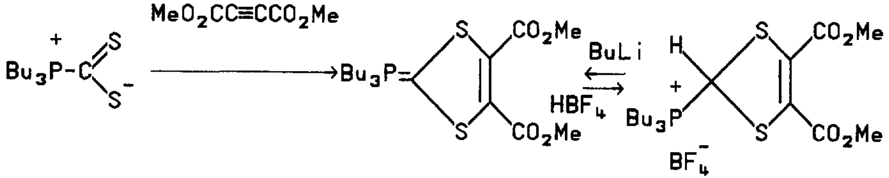
(145)



292 293

(146)

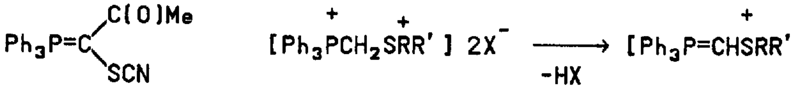
The tributylphosphonium-carbon disulfide adduct adds dimethylacetylene dicarboxylate to form cyclic ylid **294**, which reacts with fluoroboric acid to afford crystalline salt **295**. The treatment of phosphonium salt **295** with butyllithium yields a red solution of the highly reactive ylid **294** which undergoes Wittig reactions with aldehydes and ketones to form various dithiafulvenes possessing π-donor properties[343] (eq. 147).



294 295

(147)

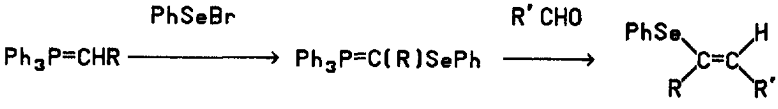
Triphenylphosphonium 2-oxo-1-thiacyanopropylid **296** was obtained by the reaction of triphenylphosphonium methoxycarbonylmethylid with thiocyanogen in 65% yield.[336] Alkylation of the *R*-thiomethyl triphenylphosphonium salts with R′X gives phosphonium-sulfonium salts **297**. These are easily dehydrohalogenated into ylids **298**, which are stabilized by the sulfonium group[349] (eq. 148). Petragnani *et al.* obtained C–seleno-substituted ylids **299** by the reaction of phosphorus ylids with phenylselenylbromide.[350] C–Seleno-substituted ylids **299** undergo Wittig reaction with aldehydes to furnish various phenylselenoalkenes[350–356] (eq. 149).



$$\mathrm{Ph_3P{=}C}\begin{matrix}\mathrm{C(O)Me}\\ \mathrm{SCN}\end{matrix} \qquad [\overset{+}{\mathrm{Ph_3P}}\mathrm{CH_2}\overset{+}{\mathrm{S}}\mathrm{RR'}]\ 2X^- \xrightarrow[\mathrm{-HX}]{} [\mathrm{Ph_3P{=}CH}\overset{+}{\mathrm{S}}\mathrm{RR'}]X^-$$

296 297 298

(148)

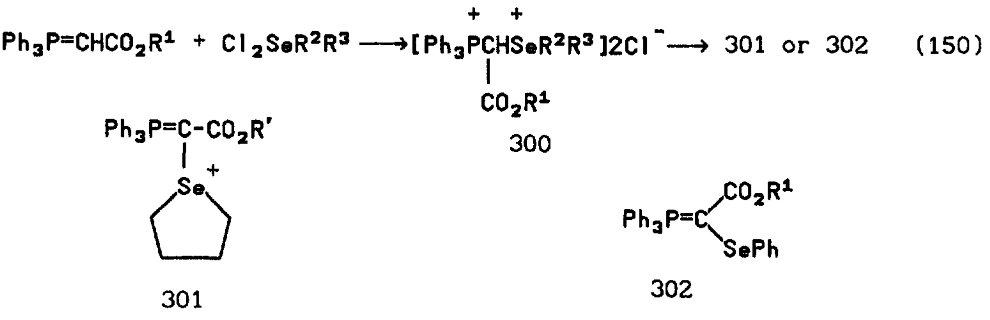


299

(149)

The reaction of selenium dichloride with triphenylphosphonium alkoxycarbonylmethylids leads to the formation of either phosphonium-selenonium ylids **301** or C–seleno-substituted ylids **302**.

Intermediate salts **300** are stable if they contain two alkyl groups, R^2, $R^3 = (CH_2)_4$. In this case, salts **300** are dehydrochlorinated by an excess of the phosphorus ylid to form the ylidonium salts **301**. However, the salts **300** containing a phenyl and an alkyl group at the selenium atom easily eliminate the alkyl halide to form ylid **302**[357,358] (eq. 150).



$$\mathrm{Ph_3P{=}CHCO_2R^1} + \mathrm{Cl_2SeR^2R^3} \longrightarrow [\mathrm{Ph_3\overset{+}{P}\underset{\substack{|\\ CO_2R^1}}{C}H\overset{+}{Se}R^2R^3}]2\mathrm{Cl^-} \longrightarrow 301 \text{ or } 302 \qquad (150)$$

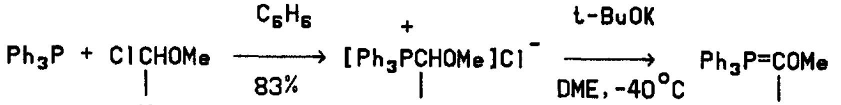
300

301

302

Phosphorus ylids **304** and **306** bearing R = AlkO or ArO at the α-carbon atom are of great preparative importance and may be obtained by dehydrohalogenation of phosphonium salts.[360,361] The treatment of a fine suspension of phosphonium salts **303** in ether with phenyllithium provides a bright red solution of ylids **306**, R = Me, Ph, Tol, which react with aldehydes and ketones to form vinyl ethers (eq. 151).[342,360] Triphenylphosphonium α-methoxymethylid (**306**) was obtained in very good yield from phosphonium salt **305**, which was suspended in dimethoxyethane at −40°C and then treated with potassium *tert*-butoxide for 5 min to give a red solution of the unstable, highly reactive ylid **306**, which reacts readily with aldehydes and ketones[362] (eq. 152).

$$\underset{303}{[\mathrm{Ph_2\overset{+}{P}CH_2OR}]\mathrm{Cl^-}} \xrightarrow{\mathrm{PhLi}} \underset{304}{\mathrm{Ph_3P{=}CHOR}} \xrightarrow{\mathrm{R'_2C{=}O}} \mathrm{R'_2C{=}CHOR} \qquad (151)$$

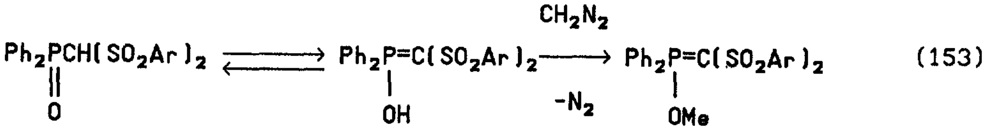


$$\mathrm{Ph_3P} + \mathrm{Cl\underset{\substack{|\\ Me}}{C}HOMe} \xrightarrow[83\%]{\mathrm{C_6H_6}} [\mathrm{Ph_3\overset{+}{P}\underset{\substack{|\\ Me}}{C}HOMe}]\mathrm{Cl^-} \xrightarrow[\mathrm{DME},\,-40^\circ\mathrm{C}]{t\text{-BuOK}} \mathrm{Ph_3P{=}\underset{\substack{|\\ Me}}{C}OMe} \qquad (152)$$

305

306

3.2.2. *Properties*. C–Sulfonyl-substituted phosphorus ylids are very stable compounds. Ylids bearing oxygen or divalent sulfur at the α-carbon atom are more unstable and should be used *in situ* for chemical transformations. The structure of triphenylphosphonium toluolsulfonylmethylid has been determined by X-ray analysis. The P═C distance (1.709 Å) and the average C–(Ph)–P–C angle of the molecule have values close to those observed in a number of other triphenylphosphonium ylids.[330,363] IR spectra of ylids bearing sulfonyl or sulfinyl groups at the α-carbon atom reveal a shift of the S═O and SO_2 frequencies to longer wavelength the effective delocalization of the carbanion negative charge by these groups.[364–367] The high thermodynamic stability of the sulfinylylid group allows the existence of triadic prototropic tautomerism in bis(arylsulfonyl)methylphosphine oxides **307**. In the crystalline state they exist in the CH-phosphine oxide form, but in solution tautomeric mixtures of the OH-ylid and CH-phosphine oxide forms are easily detected by spectroscopic methods. The chemical properties of the methylphosphine oxides are similar to those of the OH-acids of tetracoordinate phosphorus[368,369] (eq. 153).



$$\underset{\overset{\|}{\mathrm{O}}}{\mathrm{Ph_2PCH(SO_2Ar)_2}} \rightleftarrows \underset{\mathrm{OH}}{\mathrm{Ph_2P{=}C(SO_2Ar)_2}} \xrightarrow[-N_2]{CH_2N_2} \underset{\mathrm{OMe}}{\mathrm{Ph_2P{=}C(SO_2Ar)_2}} \qquad (153)$$

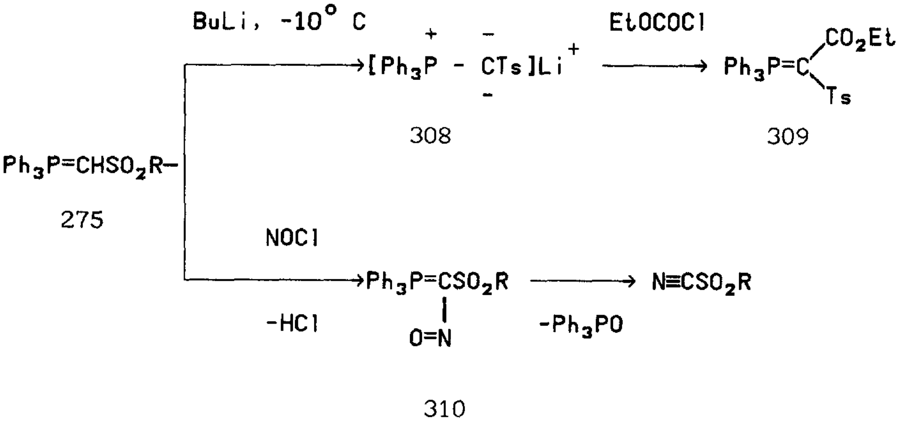
307

Ab initio calculations show that the presence of an oxygen atom at the ylid carbon atom stabilizes singlet carbenes but not ylids; such ylids have an enhanced tendency to dissociate into carbenes and tertiary phosphines.[15] These ylids can be considered to be carbene complexes of tertiary phosphines. The transition state for carbene formation has been determined using the *ab initio* RHF/6-31G*/6-31G* method. The intramolecular rearrangement of such ylids to 1,2-diketones has been described[370] (eq. 154, 155).

$$Ph_3P{=}CR^1OR^2 \longrightarrow :CR^1OR^2 + Ph_3P \qquad (154)$$

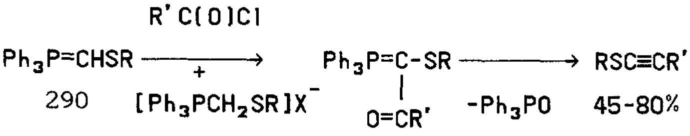
$$Ph_3P{=}C(R^1)OC(O)R^2 \xrightarrow{-30^\circ C} Ph_3P + :C(R^1)OC(O)R^2 \longrightarrow R^1C(O)C(O)R^2 \qquad (155)$$

The hydrogen atom at the α-carbon of C-sulfonyl-stabilized phosphorus ylids **275** is comparatively mobile. The treatment of ylids **275** with butyllithium gives dianion **308**, which easily reacts with chlorine-containing electrophiles to provide new ylids **309**.[330] The interaction of the ylid with nitrosyl chloride in pyridine causes the replacement of the hydrogen atom at the α-carbon by the nitrosyl group with formation of ylid **310** which readily breaks down to the sulfonyl cyanide[330,371] (Scheme 19).



Scheme 19.

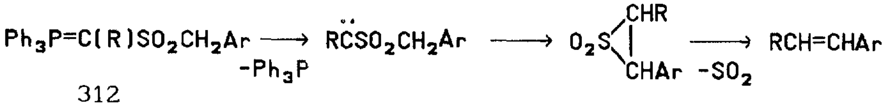
Ylids **290** with acyl chlorides yield acylmethylids **311** which on vacuum pyrolysis, 0.005 mm Hg at 230°C, form thioacetylenes in good yields by intramolecular Wittig reaction[372] (eq. 156).



$$\underset{290}{\mathrm{Ph_3P{=}CHSR}} \xrightarrow[\substack{+\\ \mathrm{[Ph_3PCH_2SR]X^-}}]{\mathrm{R'C(O)Cl}} \mathrm{Ph_3P{=}\underset{\substack{|\\ O{=}CR'}}{C}{-}SR} \xrightarrow[\mathrm{-Ph_3PO}]{} \underset{45\text{-}80\%}{\mathrm{RSC{\equiv}CR'}} \qquad (156)$$

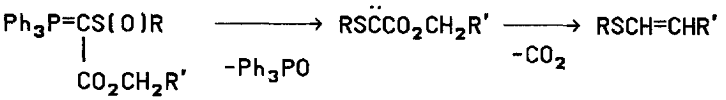
311

Flash vacuum pyrolysis of sulfonyl- and sulfinyl-stabilized phosphorus ylids **312** and **313** results in loss of either phosphine or phosphine oxide to generate thio-, sulfinyl- and sulfonyl-carbenes which undergo a variety of rearrangements and insertion processes to give various products[373] (eq. 157, 158).



(157)

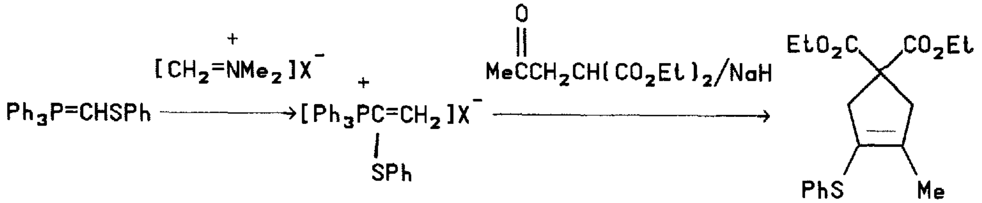
312



$$\mathrm{Ph_3P{=}\underset{\substack{|\\ CO_2CH_2R'}}{C}S(O)R} \xrightarrow[\mathrm{-Ph_3PO}]{} \mathrm{RS\ddot{C}CO_2CH_2R'} \xrightarrow[\mathrm{-CO_2}]{} \mathrm{RSCH{=}CHR'} \qquad (158)$$

313

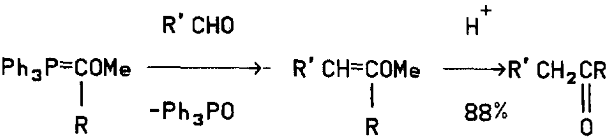
Substituted phosphonium salts **314** are obtained by the reaction of an iminium salt with phenylthiomethylid and may then be used for cyclopentene synthesis[374] (eq. 159).



(159)

314

The basicity and nucleophilicity of C-sulfonyl-substituted ylids are not high and hence they show low reactivity in the Wittig reaction. Monosulfonyl-substituted ylids react only with aldehydes but not with ketones. Triphenylphosphonium bis(sulfonyl)methylids do not undergo the Wittig reaction with either aldehydes or ketones. Contrastingly, phosphorus ylids bearing thioalkyl, alkoxyl and aroxyl groups at the α-carbon easily undergo the Wittig reaction with different carbonyl compounds.[375–383] Ylids bearing alkoxyl groups at the ylid carbon atom olefinate both aldehydes and ketones to form vinyl ethers **315** in high yields. The hydrolysis of the latter compounds provides aldehydes (R = H) or ketones (R = Me), respectively[375,376] (eq. 160).

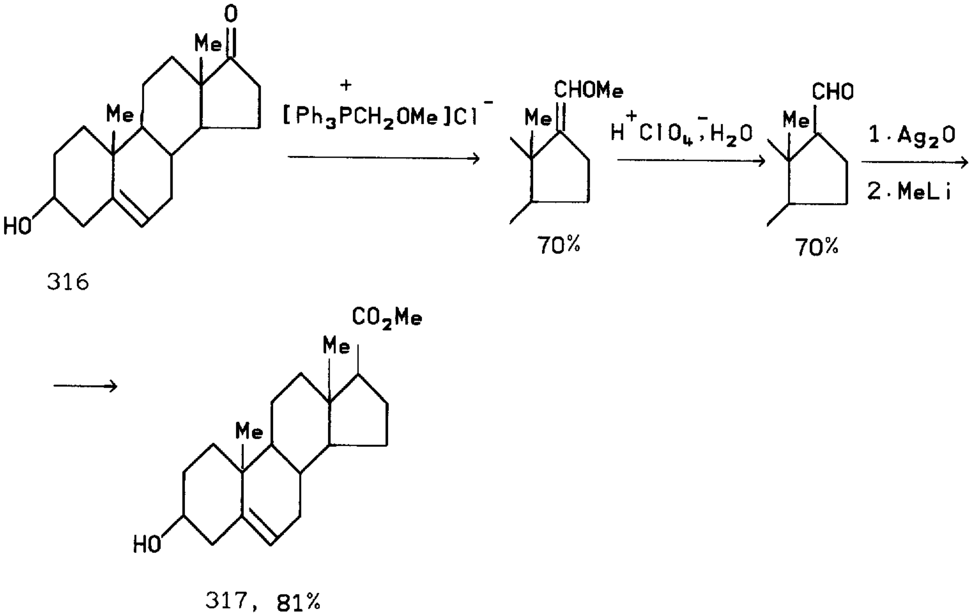


$$\mathrm{Ph_3P{=}\underset{\substack{|\\ R}}{C}OMe} \xrightarrow[\mathrm{-Ph_3PO}]{\mathrm{R'CHO}} \mathrm{R'CH{=}\underset{\substack{|\\ R}}{C}OMe} \xrightarrow[88\%]{\mathrm{H^+}} \mathrm{R'CH_2\underset{\substack{\|\\ O}}{C}R} \qquad (160)$$

R=H, Me

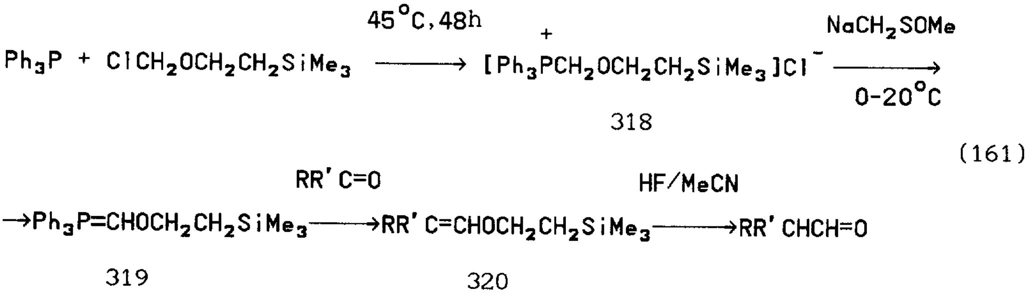
315

The aldehydes formed in these reactions can then again undergo a further Wittig reaction with triphenylphosphonium methoxymethylid to homologate the chain. By this method steroidal aldehydes were obtained (Scheme 20).[384,385] Danishevsky *et al.* developed a simple method for the preparation of pregenenolone **317** by reaction of androstenolone **316** using dehydrohalogenation of the methoxymethyltriphenylphosphonium salt with sodium hydride in dimethyl sulfoxide.[384,385]



Scheme 20.

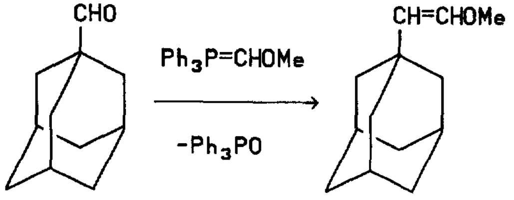
Silicon-containing α-alkoxymethylids **319** are especially convenient for the transfer of an aldehydic carbon atom. They undergo Wittig reaction with different carbonyl compounds as shown in eq. 161. Vinyl ethers **320** formed in this case may be converted to aldehydes either by treatment with a 5% solution of hydrogen fluoride in acetonitrile or via reaction with perchloric acid.[377–383]



$$Ph_3P + ClCH_2OCH_2CH_2SiMe_3 \xrightarrow{45^\circ C, 48h} \underset{318}{[Ph_3\overset{+}{P}CH_2OCH_2CH_2SiMe_3]Cl^-} \xrightarrow[0\text{-}20^\circ C]{NaCH_2SOMe} \qquad (161)$$

$$\rightarrow \underset{319}{Ph_3P{=}CHOCH_2CH_2SiMe_3} \xrightarrow{RR'C{=}O} \underset{320}{RR'C{=}CHOCH_2CH_2SiMe_3} \xrightarrow{HF/MeCN} RR'CHCH{=}O$$

Highly active triphenylphosphonium methoxymethylid easily undergoes Wittig reaction with sterically hindered carbonyl compounds. For instance, it olefinates 1-adamantanecarboxaldehyde **321** in ether at −40°C (eq. 162).[386]



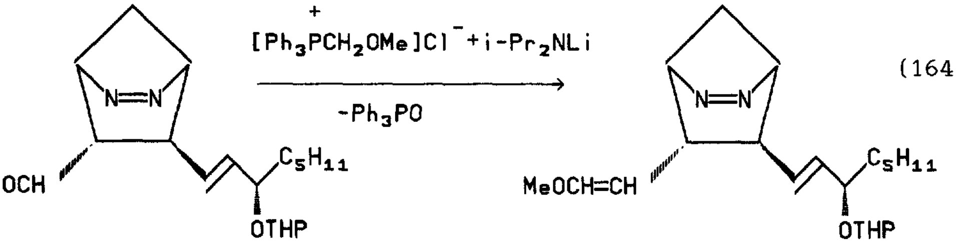
321

(162)

The reaction between alkoxymethylid and chlorodifluoromethane has been found to be a useful alternative to the Wittig reaction for the synthesis of many difluoromethylene olefins[387] (eq. 163).

$$2Ph_3P{=}CHOR + HCF_2Cl \longrightarrow F_2C{=}CHOR \qquad (163)$$
$$R{=}Me,\ i\text{-}Bu$$

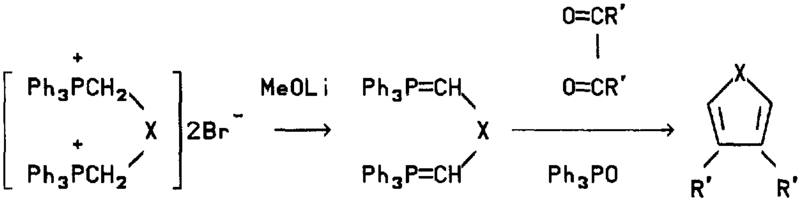
Corey and co-workers showed that dehydrochlorination of α-methoxyalkyl phosphonium salts proceeds smoothly using lithium diisopropylamide. Ylids obtained by this method were used for the synthesis of 9,11-azo-analogue of prostaglandin-endoperoxide PGH$_2$ **322**[388] (eq. 164).



(164)

322,70%

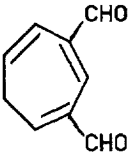
Lithium methoxide transforms bis(triphenylphosphoniummethyl)oxide and sulfide dibromides into bis-ylids **323** bearing oxygen or sulfur atoms at the α-carbon atoms. Ylids **323** undergo the Wittig reaction with dialdehydes to form various heterocycles including macrocycles.[389] For example, by reaction of ylids **323** with β-diketones furane and thiophene derivatives **324** (X = O, S) are obtained; and by reaction of **323** with cycloheptatriene-1,6-dialdehyde **325**—4,9-methanooxa (or thia)[22]annulenes **326** are prepared.[390] The reaction of ylids **323** with biphenyl-2,2′-dialdehyde **327** provides the nine-membered ring **328**.[391,392] The reaction of ylids **323** with dialdehyde **329** gives the [13]-annulenes **330**, possessing conjugated double and triple bonds[393] (eq. 165).



323

324

(165)



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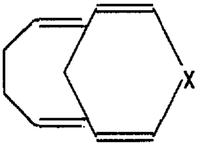

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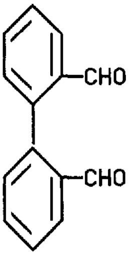

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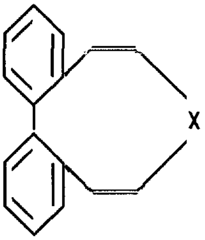
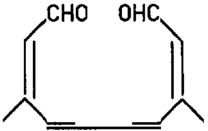


328

X= O, S



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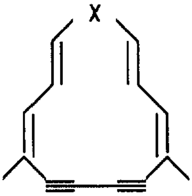


330

3.3. *C–Halogen-substituted phosphorus ylids*

The considerable interest in C–halogen-substituted phosphorus ylids has been created by the synthetic importance of halogenolefins.[394]

3.3.1. *Synthesis*. C–Halogenated ylids may be obtained by dehydrohalogenation of phosphonium salts or by reaction of a tertiary phosphine with a source of mono- or dihalogenomethylene fragment. The addition of a halocarbene or carbenoid to a tertiary phosphine is one of the most important methods for the synthesis of phosphorus ylids bearing one or two halogen atoms at the α-carbon atom. The oldest methods for the synthesis of C–halogenated ylids is the treatment of polyhalogenomethanes with strong bases in the presence of a tertiary phosphine.[395-397] In this way Seyferth and co-workers,[398] and Wittig and Schlosser[399] obtained triphenylphosphonium chloromethylid (**277**) from methylene chloride, butyllithium and triphenylphosphine in 65% yield (eq. 166). Generation of dichlorocarbene from chloroform and potassium *tert*-butoxide in the presence of triphenylphosphine affords a yellow suspension of triphenyl phosphonium dichloromethylid (**331**) which may be used for the Wittig reaction without isolation from the reaction mixture.[395] Similarly ylids **332** bearing chlorine and fluorine atoms at the ylidic carbon were prepared (eq. 167).

$$Ph_3P + CH_2Cl_2 \xrightarrow{BuLi} \underset{277}{Ph_3P{=}CHCl} \qquad (166)$$

$$Ph_3P + CXCl_3 \xrightarrow{t\text{-}BuOK} Ph_3P{=}CXCl \xrightarrow{RCHO} RCH{=}CXCl \qquad (167)$$

331 (X=Cl);
332 (X=F)

Triphenylphosphonium dichloromethylid **331** can be obtained easily underphase transfer conditions from chloroform, and 50% aqueous sodium hydroxide solution in the presence of a phase transfer catalyst (TEBA). The dichlorocarbene initially formed is trapped by triphenylphosphine and ylid **351** can then undergo the Wittig reaction *in situ*. Thus, by this method α,α-dichlorostyrene was obtained in 47% yield (eq. 168).[400] In similar fashion, vigorous stirring of a benzene solution of dichlorothioether, triphenylphosphine, benzaldehyde and TEBA for 90 min at room temperature with a 40% aqueous solution of sodium hydroxide gives α-dialkyl-thio-α-chlorostyrenes **333**, R^1 = Me, i-Bu; R^2 = Ph; R^3 = H, Me, in yields of about 40% (eq. 169). This reaction was used for the preparation of pyrethroids.[401,402]

$$Ph_3P + CHCl_3 \xrightarrow{NaOH/H_2O} 331 \xrightarrow[-Ph_3PO]{RCHO} RCH{=}CCl_2 \qquad (168)$$

$$R^1SCHCl_2 + Ph_3P + R^2CHO \xrightarrow[-Ph_3PO]{NaOH/H_2O} \underset{333}{R^2CH{=}C(Cl)SR^1} \qquad (169)$$

With heating, salts of trihalogenoacetic acids decarboxylate to form dihalogenocarbene which may be trapped by a tertiary phosphine to provide phosphorus ylids. Thus, decarboxylation of salts of trihalogenoacetic acids **334**, M = Li, Na, K, $SnMe_3$, in the presence of tertiary phosphines yields phosphorus ylids **335**, R = Bu, Ph (eq. 170).[403–406] A variant of this method is reaction of triphenylphosphine with methyl dichlorofluoroacetate and lithium chloride (eq. 171).[407–410] The heating of triphenylphosphine with fluorodichloromethylphenylmercury, probably proceeds via the formation of chlorofluorocarbene and provides triphenylphosphonium fluorochloromethylid **332** (eq. 172).[411] However, some trihalogenoacetates, for example sodium fluorodichloroacetate, with triphenylphosphine give a betaine, which is converted to ylid **332** without formation of the dihalogenocarbene (eq. 173).[397,398,404] Chlorofluorocarbene has also been generated by the addition of methanol to a mixture of sodium hydride and methyl dichlorofluoroacetate. *In situ* trapping with triphenylphosphine followed by direct reaction with a carbonyl compound without isolation of the ylid was demonstrated.[412]

$$\underset{334}{ClCF_2CO_2M} \xrightarrow[-MCl,\,-CO_2\cdot]{} [:CF_2] \xrightarrow{R_3P} \underset{335}{R_3P{=}CF_2} \qquad (170)$$

$$FCCl_2CO_2Me \xrightarrow{LiCl} Cl_2CFCO_2Li \xrightarrow[-LiCl,\,-CO_2]{Ph_3P} \underset{332}{Ph_3P{=}CClF} \qquad (171)$$

$$Ph_3P + PhHgCFCl_2 \xrightarrow{80^{\circ}C} 332 + PhHgCl \qquad (172)$$

$$Ph_3P + Cl_2CFCO_2Na \xrightarrow[-NaCl]{} \left[Ph_3\overset{+}{P}CFClCO_2^{-}\right] \xrightarrow[-CO_2]{} 332 \qquad (173)$$

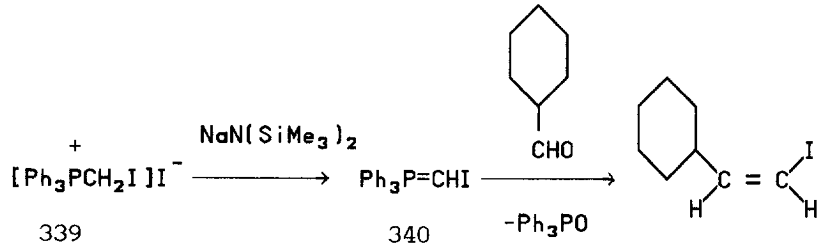
The dehydrohalogenation of halogenomethyltriphenylphosphonium salts is widely used for the obtention of C–halogen-substituted phosphorus ylids **336**. Dehydrohalogenating agents used include butyllithium, phenyllithium, lithium diisopropylamide, and potassium *tert*-butoxide (eq. 174).[375,413–420] However, it should be noted that, in some cases butyl- and phenyllithium may not only deprotonate phosphonium salt but also exchange the halogen atom at the α-carbon for lithium resulting in mixtures of two ylids, and hence, after reaction with the carbonyl compound, of two olefins (eq. 175). The ability of organolithium compound to interact with the halogen atom increases in the sequence: Cl < Br < I. For example, dehydrohalogenation of an iodomethylene salt phosphonium by phenyllithium yields 70% of triphenylphosphonium methylid and only 30% of the iodine methylid.[419,420] Sometimes dehydrohalogenation of halogenomethylphosphonium salts is followed by replacement of the halogen atom by a butyl group to form ylid **338** as shown in eq. 176.[144]

$$\mathrm{Ph_3P + CH_2FI \xrightarrow{PhLi} [Ph_3\overset{+}{P}CH_2F]I^- \longrightarrow \underset{336}{Ph_3P{=}CHF}} \qquad (174)$$

$$\underset{X=Br,\ Cl,\ I}{\mathrm{[Ph_3\overset{+}{P}CH_2X]X^-}} \longrightarrow \mathrm{\underset{337}{Ph_3P{=}CHX} + Ph_3P{=}CH_2} \qquad (175)$$

$$\mathrm{[Ph_3\overset{+}{P}CH_2F]I^- \xrightarrow{BuLi} \underset{336}{Ph_3P{=}CHF} + \underset{338}{Ph_3P{=}CHBu} \xrightarrow{R_2C=O} R_2C{=}CHF + R_2C{=}CHBu} \qquad (176)$$

The replacement of butyllithium and phenyllithium by the sterically hindered base sodium bis(trimethylsilyl)amide avoids almost all side reactions. In this case dehydrohalogenation of the phosphonium salt proceeds smoothly to yield pure triphenylphosphonium halogenomethylids in high yield.[414] Stork and Zhaoh showed that the reaction of iodomethyltriphenylphosphonium iodide **339** with sodium bis(trimethylsilyl)amide in THF at −60°C in the presence of cyclohexylcarboxaldehyde yields 71% of the synthetically useful vinyl iodide (eq. 177).[415]



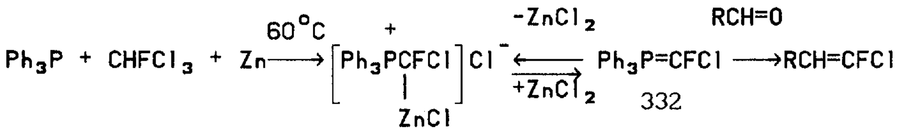
(177)

Non-stabilized phosphorus ylids may be used instead of organolithium compounds for dehydrohalogenation of phosphonium salts. Transylidation of phosphonium salts by means of trimethylphosphonium methylid proceeds smoothly and results in pure triphenylphosphonium chloromethylid (**277**) which was isolated as an orange crystalline solid in high yield (eq. 178).[414] The dehydrochlorination of dichloromethyltriphenylphosphonium chloride by hexaphenylcarbodiphosphorane in a solvent incapable of protonating the strongly basic ylid gives triphenylphosphonium dichloromethylid (**331**)[414,416] (eq. 179).

$$\overset{+}{[Ph_3PCH_2Cl]}Cl^- \xrightarrow[-\overset{+}{[Ph_3PMe]}Cl^-]{Ph_3P{=}CH_2} 277 \tag{178}$$

$$\overset{+}{[Ph_3PCHCl_2]}Cl^- \xrightarrow[-\overset{+}{[Ph_3P{=}CHPPh_3]}Cl^-]{Ph_3P{=}C{=}PPh_3} 331 \tag{179}$$

Another important method for the preparation of C–halogen-substituted phosphorus ylids relies on formation of trihalogenomethylphosphonium salts, which can be obtained by reaction of tertiary phosphine with tetrahalogenomethanes. Thus, the reaction of triphenylphosphine with dibromodifluoromethane yields the stable bromodifluoromethyltriphenylphosphonium bromide[419] while the fluorotrichloromethane and triphenylphosphine do not form the corresponding phosphonium salt.[420a] The reaction of tris(dimethylamino)phosphine with mixed fluorine-containing tetrahalogenomethanes provides phosphonium salts in high yields, dehalogenation of which leads to the formation of phosphorus ylids which are useful sources of the difluoro-, chlorofluoro-, or bromofluoromethylene fragments.[421] Burton and Van Hamme introduced the dehalogenation of phosphonium salts by reductive elimination with a second transition group metal (zinc, cadmium, mercury) which can be considered to produce an organometallic phosphonium salt capable of undergoing the Wittig reaction with aldehydes and ketones.[422] In another example, heating of triphenylphosphine with trichlorofluoromethane in the presence of zinc leads to the formation of a stable 'quasi-complex' organometallic compound **341** which may be isolated. In solution this complex dissociates into the phosphorus ylid **332** and zinc chloride and so readily undergoes the Wittig reaction (eq. 180).[420a] Similarly, triphenylphosphine with diiodofluoromethane yields a stable iodofluoromethyltriphenylphosphonium iodide which can be transformed into triphenylphosphonium fluoromethylid (**336**) on treatment with zinc–copper couple[144,417] (eq. 181).



$$Ph_3P + CHFCl_3 + Zn \xrightarrow{60^\circ C} \underset{341}{\left[\overset{+}{Ph_3P}\underset{\displaystyle ZnCl}{\underset{|}{C}}FCl\right]Cl^-} \underset{+ZnCl_2}{\overset{-ZnCl_2}{\rightleftarrows}} \underset{332}{Ph_3P{=}CFCl} \xrightarrow{RCH{=}O} RCH{=}CFCl \tag{180}$$

$$Ph_3P + CHFI_3 \longrightarrow \overset{+}{[Ph_3PCHFI]}I^- \xrightarrow{Zn/Cu,\,0^\circ C} \underset{336}{Ph_3P{=}CHF} \tag{181}$$

Tertiary phosphines [Ph_3P or $(Me_2N)_3P$] are also convenient reagents for dehalogenation of polyhalogenophosphonium salts **342**[421–424] (eq. 182). The reaction is usually carried out without isolation of the phosphonium salts by treatment of the tetrahalogenomethane $CX_4 = CCl_4$, CBr_4, CBr_2Cl_2, CCl_2F_2, CBr_2F_2, $CBrCl_3$ with an excess of the tertiary phosphine.[416,425–429] Highly reactive ylids **343** may be generated by reaction of tris(dimethylamino)phosphine or triphenylphosphine with mixed fluorine-containing tetrahalogenomethanes or bromotrichloromethane in a 2:1 ratio[421,425–428] (eq. 183). This method was used to obtain dichloromethylids immobilized on a polymeric support (eq. 184).

$$\underset{342}{[R_3\overset{+}{P}CCl_3]Cl^-} \xrightarrow[-R'_3PCl_2]{R'_3P} R_3P{=}CCl_2 \qquad (182)$$

$$2R_3P + CX_4 \longrightarrow \underset{343}{R_3P{=}CX_2} + R_3PX_2 \qquad (183)$$

$$\textcircled{P}{-}PPh_2 \xrightarrow{CCl_4} \textcircled{P}{-}\overset{+}{P}(Ph_2)Cl]CCl_3^- \longrightarrow \textcircled{P}{-}P(Ph_2){=}CCl_2 + \textcircled{P}{-}P(Ph_2)Cl_2 \qquad (184)$$

Ylids formed in the reaction of triphenylphosphine with tetrahalogenomethanes are capable of reacting with chlorotriphenylphosphonium chloride to form the ylid-phosphonium salts **344**[430,431,431a] (eq. 185).

$$2Ph_3P + CCl_4 \longrightarrow \underset{331}{Ph_3P{=}CCl_2} + Ph_3PCl_2 \longrightarrow [Ph_3\overset{+}{P}CCl_2\overset{+}{P}Ph_3]2Cl^- \xrightarrow[-Ph_3PCl_2]{Ph_3P} \qquad (185)$$

$$\longrightarrow \underset{344}{[Ph_3P{=}CCl\overset{+}{P}Ph_3]Cl^-}$$

NMR spectroscopy shows that the reaction of a trihalogenomethyl phosphonium salt with zinc gives a zinc–organic complex **345** which dissociates to $ZnCl_2$ and the phosphorus ylid **346**.[360] In the stationary state the equilibrium is strongly shifted towards the salt **345**, and the ylid cannot be detected by spectroscopic methods. However, in the presence of a carbonyl compound the equilibrium is displaced towards the ylid **346** which can then undergo the Wittig reaction to form olefins in high yield[29,387] (eq. 186).

$$[(Me_2N)_3\overset{+}{P}CFCl_2]Cl^- \xrightarrow{M} \underset{345}{[(Me_2N)_3\overset{+}{P}CFCl(MCl)]Cl^-} \underset{MCl_2}{\overset{+MCl_2}{\rightleftarrows}} \underset{346}{(Me_2N)_3P{=}CFCl} \longrightarrow \qquad (186)$$

$$\xrightarrow[-(Me_2N)_3PO\cdot]{R_2CO} R_2C{=}CFCl$$

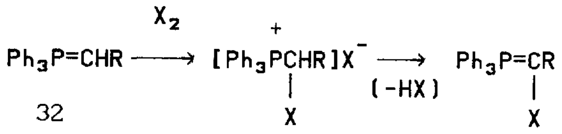
M=Zn, Cd, Hg

Electrochemical reduction of dihalogenomethylphosphonium salts has also been used to generate ylids **343**. In an aprotic medium (DMF, MeCN) this ylid reacted with aldehydes in the cell to give the corresponding olefin[431] (eq. 187).

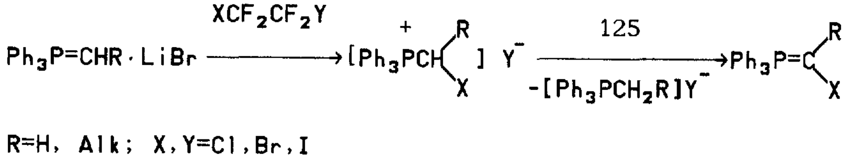
$$[R_3\overset{+}{P}CX_2Y]Y^- \xrightarrow{2e} \underset{343}{R_3P{=}CX_2} \xrightarrow{R'CHO} R'CH{=}CX_2 \qquad (187)$$

X=Y=Cl; X=F, Y=Br

C–Halogen-substituted phosphorus ylids can also be obtained by treatment of phosphorus ylids **32**, containing hydrogen atoms at the ylid carbon atom, with a halogenating agent. The reaction proceeds in a reagent ratio of 2 : 1, because the starting ylid **32** readily deprotonates the intermediate phosphonium salt where CH-acidity increased because of the electron acceptor ability of the halogen atom (eq. 188). In the case of ylids **32** bearing strong electron acceptors at the α-carbon [R = CO_2Alk, C(O)Alk, C(O)Ar] the dehydrochlorination of an intermediate phosphonium salt is carried out in the presence of triethylamine.[433] Halogenating reagents which have been used include chlorine, bromine,[433] phenyliododichloride[434] and chloramine T.[435,436] Non-stabilized phosphorus ylids can be halogenated by means of perhalofluoroalkanes (eq. 189).[437] Fluorination of triphenylphosphonium methylid **2** by $FClO_3$ gives a fluoromethylphosphonium salt which on dehydrohalogenation yields triphenylphosphonium fluoromethylid (**336**) in good yield. The latter undergoes the Wittig reaction with aldehydes to form (*Z*)- and (*E*)-isomers of the vinylfluorides in 50% yields in a 1 : 1 ratio[438] (eq. 190).

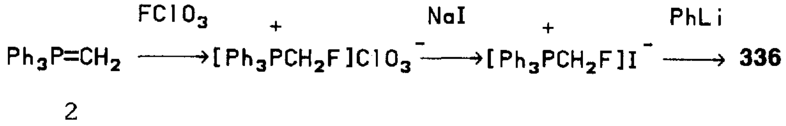


$$\underset{32}{\mathrm{Ph_3P{=}CHR}} \xrightarrow{X_2} [\mathrm{Ph_3\overset{+}{P}\underset{\substack{|\\X}}{C}HR}]X^- \xrightarrow[(-HX)]{} \mathrm{Ph_3P{=}\underset{\substack{|\\X}}{C}R} \qquad (188)$$



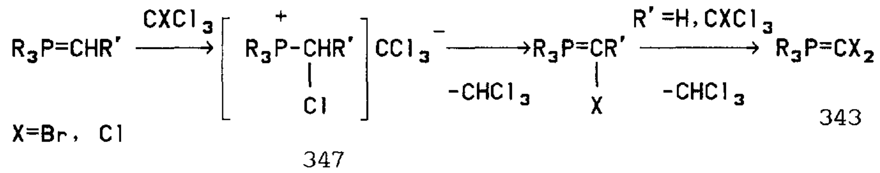
$$\mathrm{Ph_3P{=}CHR\cdot LiBr} \xrightarrow{XCF_2CF_2Y} [\mathrm{Ph_3\overset{+}{P}CH(R)(X)}]\,Y^- \xrightarrow[-[Ph_3PCH_2R]Y^-]{125} \mathrm{Ph_3P{=}C(R)(X)} \qquad (189)$$

R=H, Alk; X,Y=Cl,Br,I



$$\underset{2}{\mathrm{Ph_3P{=}CH_2}} \xrightarrow{FClO_3} [\mathrm{Ph_3\overset{+}{P}CH_2F}]ClO_3^- \xrightarrow{NaI} [\mathrm{Ph_3\overset{+}{P}CH_2F}]I^- \xrightarrow{PhLi} \mathbf{336} \qquad (190)$$

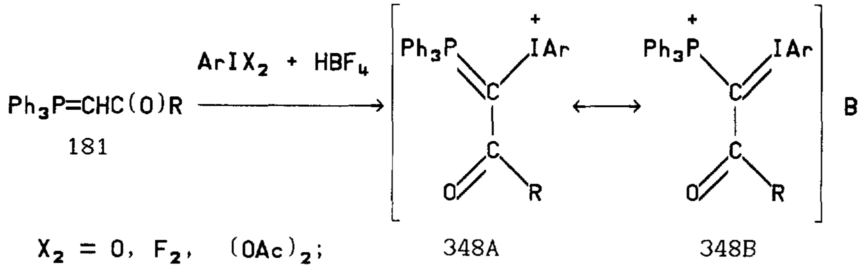
The replacement of hydrogen atoms at the α-carbon for chlorine or bromine atoms can be achieved by the reaction of phosphorus ylids with tetrachloro- or tetrabromomethane.[439] Phosphorus ylids with tetrahalogenomethane form an ionic pair **347** which easily eliminates chloroform to form ylid **343**[440] (eq. 191).



$$\mathrm{R_3P{=}CHR'} \xrightarrow{CXCl_3} \underset{347}{\left[\mathrm{R_3\overset{+}{P}{-}\underset{\substack{|\\Cl}}{C}HR'}\right]\mathrm{CCl_3^-}} \xrightarrow[-CHCl_3]{} \mathrm{R_3P{=}\underset{\substack{|\\X}}{C}R'} \xrightarrow[-CHCl_3]{R'=H,\,CXCl_3} \underset{343}{\mathrm{R_3P{=}CX_2}} \qquad (191)$$

X=Br, Cl

Phosphonium-iodonium ylids **348** were obtained by the reaction of stabilized phosphorus ylids **181** with tervalent iodine derivatives. X-Ray analysis showed that the ylid-iodonium structure **348B** predominates in the ground state of the molecule[441] (eq. 192).



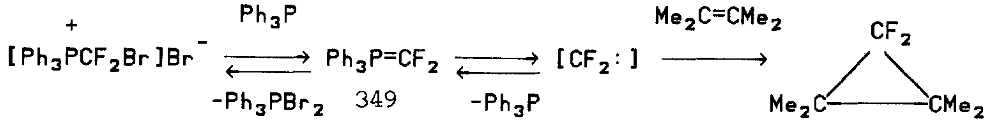
(192)

X_2 = O, F_2, $(OAc)_2$;
R = EtO, Ph, 4-MeC_6H_4; Ar= Ph, 2-MeC_6H_4

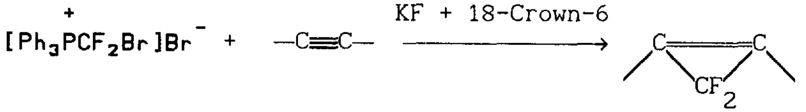
Halogen atoms at the α-carbon of tertiary alkylphosphines are very mobile and easily migrate to the phosphorus atom [by a 1,2(C → P)-halogenotropic shift] with formation of the corresponding P-halogenoylids. α-Halogenoalkyl-phosphines bearing electron accepting substituents at the α-carbon atom are comparatively easily rearranged to phosphorus ylids, X = Cl, Br, in very good yields. The mobile halogen atom of the P-halogenoylids may be replaced with different substituents. Various examples of the preparation of phosphorus ylids by this method have been described[442–450] (eq. 193).

$$R_2\underset{X}{\underset{|}{\ddot{P}}}C(R)Cl \longrightarrow R_2\underset{X}{\underset{|}{P}}{=}C(R)Cl \qquad (193)$$

3.3.2. *Properties. Ab initio* calculations carried out by Dixon[452] and Bestmann[15] show that the C–fluorine-containing ylid $H_3P{=}CHF$ has a non-planar P=C group with an inversion barrier of about 2.8 kcal mol^{-1}.[15] Francl and co-workers concur with the results of Dixon and suggest that the zwitterionic character of the P=C bond in $H_3P{=}CF_2$ molecules is minimal. The π-character of the P=C bond in the pentavalent systems can be increased by fluorine substitution at C as evidenced by charge density difference plots.[453] The stability of C–halogen-containing phosphorus ylids is very different and depends on the electron-withdrawing capacity of the second substituent at the ylid carbon atom. C–halogenoylids stabilized by strong electron accepting substituents may be successfully isolated and purified while the non-stabilized ylids bearing one or two halogen atoms at the α-carbon are used, as a rule, in solution without isolation and purification.[414,416] Only triphenylphosphonium chloromethylid[414] and dichloromethylid[416] have been isolated. Triphenylphosphonium difluoromethylid (**349**) generated either by the reaction of bromodifluoromethyl triphenylphosphonium bromide with tertiary phosphines or by treatment with potassium fluoride and 18-crown-6 readily dissociates into difluorocarbene and triphenylphosphine. The difluorocarbene may be trapped by tetramethylethylene with formation of 1,1-difluoro-2,2,3,3-tetramethyl cyclopropane[454] (eq. 194). Schlosser and co-workers have recently found that difluoromethylid adds to terminal and internal acetylenes to afford difluorocyclopropenes in good yields[455] (eq. 195).



(194)



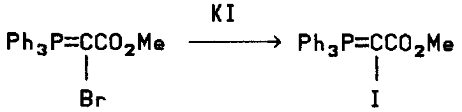
(195)

Alkylation, acylation or arylation of simple fluoromethylids followed by transylidation gives a direct entry into α-fluorosubstituted ylids and provides a useful and convenient way to a variety of fluoroolefins[433] (eq. 196). Reaction of triphenylphosphonium dichloromethylid with ethylchloroformate and carbamoyl chlorides leads to acyl ylids **350**, R = Ph_2N, EtO[433] (eq. 197). Substitution reactions of ylids with potassium iodide or potassium thiocyanate lead to replacement of the bromine atom at the ylid carbon by iodine or thiocyanate (eq. 198, 199).[456]

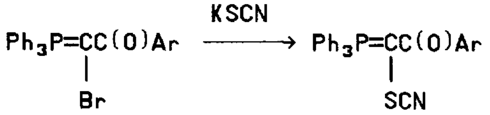
$$2R_3P{=}CHX + R'C(O)Cl \longrightarrow R_3P{=}CXC(O)R' \xrightarrow{RCHO} RCH{=}CXC(O)R' \quad (196)$$

$$X = Cl,\ F$$

$$Ph_3P{=}CCl_2 + ClC(O)R \xrightarrow[-Cl_2]{} \underset{350}{Ph_3P{=}C(Cl)C(O)R} \quad (197)$$

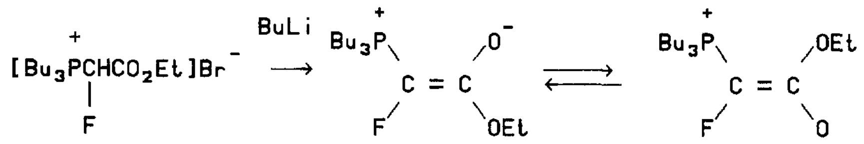


$$Ph_3P{=}\underset{Br}{C}CO_2Me \xrightarrow{KI} Ph_3P{=}\underset{I}{C}CO_2Me \quad (198)$$



$$Ph_3P{=}\underset{Br}{C}C(O)Ar \xrightarrow{KSCN} Ph_3P{=}\underset{SCN}{C}C(O)Ar \quad (199)$$

Tributylphosphonium ethoxycarbonylfluoromethylid exists as a mixture of two geometric isomers **352A** and **352B** due to hindered rotation around PC═C bond caused by partial enolization[413] (eq. 200).



351 352A 352B

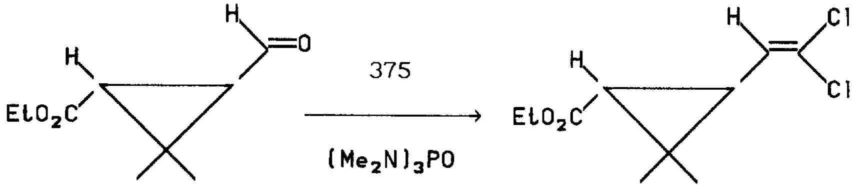
α-Chloroalkylphosphines exist in tautomeric equilibrium with the corresponding ylids bearing a halogen atom at the phosphorus atom. Diad phosphorus–carbon halogenotropy proceeds through the formation of a phosphinium cation **354**.[371] Hence, α-chloroalkylphosphines show chemical properties typical of both tervalent phosphorus compounds and ylids.[2,121,457–459]

$$\underset{353A}{R_2PCHCl_2} \rightleftarrows \underset{354}{[R_2\overset{+}{P}{=}CHCl]Cl^-} \rightleftarrows \underset{353B}{R_2P(Cl){=}CHCl} \quad (201)$$

$$R = i\text{-}Pr_2N$$

The major use for C–halogen-substituted phosphorus ylids lies in the synthesis of halogenolefins. As the electron-accepting halogen atoms at the ylid carbon atom decrease the nucleophilicity of phosphorus ylids, triphenylphosphonium halogenoylids readily olefinate aldehydes and activated ketones but do not interact with non-activated ketones and esters. Contrastingly electron-donating substituents at the phosphorus atom, and in particular the dimethylamino group, decrease the electrophilicity of the phosphonium group and raise the activity of halogenoylids. As olefinating reagents, which are sources of dihalogenmethylene groups, the tris(dialkylamino)phosphonium ylids and their stable complexes with metals have advantages over their triphenylphosphonium counterparts. Tris(dimethylamino)phosphonium dichloromethylid (**355**) is significantly more reactive than the corresponding triphenylphosphonium ylid **331** (eq. 202). Thus, unlike the latter, tris(dimethylamino)phosphonium dichloromethylid (**355**) transforms ethyl *cis,trans*-carbonaldehyde into the chrysanthemic acid analogue **356** in high yield (eq. 203).[421,425–427]

$$(Me_2N)_3P \xrightarrow[-76^\circ C,\ CH_2Cl_2]{BrCCl_3} \underset{355}{(Me_2N)_3P{=}CCl_2} \xrightarrow{Me_2CHCHO} Cl_2CH{=}CHPr\text{-}i \qquad (202)$$



356 (203)

The yields and stereochemistry of the Wittig reaction in the case of tris(dimethylamino)phosphonium halogenylids depend on the method of phosphonium salt dechlorination. Thus, the dechlorination of salt **357** by triphenylphosphine or tris(dimethylamino)phosphine proceeds via the formation of ylid **346**, which on reaction with isopropyl trifluoroacetate affords (*Z*)-1-chloro-2-propoxyperfluoropropene in good yield (eq. 204).[421,424] Zinc–copper couple exothermically dehalogenates phosphonium salts **357** in the presence of carbonyl compounds RR′C=O, where R = Ph, C_6H_{13}, CF_3; R′ = H, Ph, CF_3, Me, AlkO to form 1-chloro-1-fluoroalkenes. In the case of aldehydes and activated ketones the yields of olefins are almost quantitative, for ketones of the acetophenone type, about 70%, and for esters the yields are 21–95%. The reaction of ylid **346** with esters preferentially yields the (*Z*)-isomers of alkylpolyfluoroalkenyl esters **358** (eq. 205). However, monofluoro-, fluorochloro-, bromofluoromethylids with aldehydes and unsymmetrical ketones yield, as a rule, a mixture of the (*Z*)- and (*E*)-olefins.[421,423,424]

$$\underset{357}{\overset{+}{[}(Me_2N)_3PCFCl_2]\,Cl^-} + R_3P + CF_3CO_2Pr\text{-}i \longrightarrow \underset{40\text{-}65\%}{CF_3(i\text{-}PrO)C{=}CFCl} \qquad (204)$$

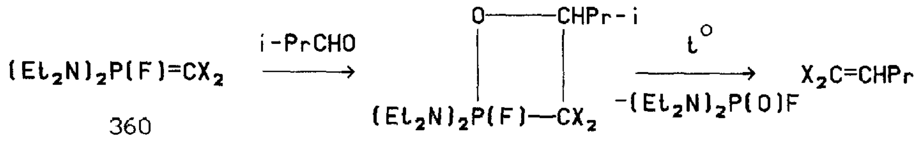
$$\Big\downarrow$$

$$\underset{346}{(Me_2N)_3P{=}CFCl} + R_F(RO)C{=}O \xrightarrow{60^\circ C} \underset{358}{R_F(RO)C{=}CFCl} + (Me_2N)_3PO \qquad (205)$$

A convenient source of the difluoromethylene group is difluoromethylid **359**, generated from tris(dimethylamino)phosphine and dibromofluoromethane, which undergoes Wittig reactions with cyclohexanone, acetophenone and propiophenone[421,423,424] (eq. 206).

$$\underset{359}{(Me_2N)_3P{=}CF_2} + RR'C{=}O \xrightarrow{20^\circ C} RR'C{=}CF_2 + (Me_2N)_3PO \qquad (206)$$

In the case of the ylid **360** bearing a fluorine atom at phosphorus, the four-membered cyclic products **361** of [2+2]-cycloaddition to aldehydes may be isolated and studied by means of NMR spectroscopy. On further heating to 60–80°C these adducts decompose with formation of 1,1-dihalogenalkenes and fluorophosphonates[462] (eq. 207).


360

X=Cl, Br.

361

(207)

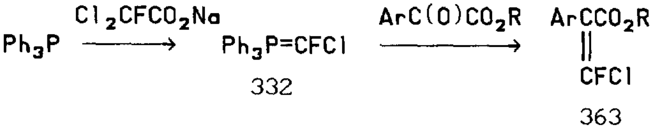
Triphenylphosphonium fluoromethylid (**336**) olefinates aliphatic and aromatic aldehydes, activated and non-activated ketones. However, the reaction is not stereospecific and mixtures of (*Z*)- and (*E*)-olefin are formed in a 1 : 1 ratio (eq. 208).[144,418] Ylid **362**, which transforms aldehydes and activated ketones to α,α-difluoroolefins in good yields did not, however, react with cyclohexanone and acetophenone (eq. 209). Triphenylphosphonium fluorochloromethylid (**332**) generated by reaction of triphenylphosphine with the sodium salt of dichlorofluoroacetic acid is very reactive and undergoes Wittig reactions with aldehydes and activated ketones to yield both the (*Z*)- and (*E*)-isomers of fluoro-olefins in a 1 : 1 ratio. Ylid **332** also olefinates α-ketoesters to form α-aryl-β-fluoro-β-chloroacrylic acids **363**[396,397,407,409,463,464] (eq. 210).

$$\underset{336}{Ph_3P{=}CHF} + RR'C{=}O \longrightarrow RR'C{=}CHF + Ph_3PO \qquad (208)$$

$R = H;\ R' = C_5H_{11}, C_6H_{13}, Ph, 3\text{-}ClC_6H_4, 3\text{-}CF_3C_6H_4, C_6F_5;$

$RR' = -(CH_2)_5-, Ph, Ph(Me), Ph(CF_3)$

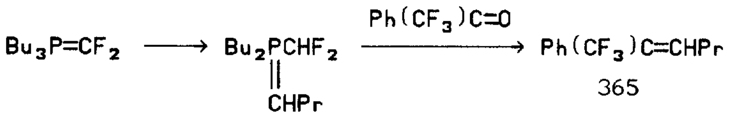
$$\underset{362}{Ph_3P{=}CF_2} \xrightarrow{RR'C{=}O} RR'C{=}CF_2 \qquad (209)$$



$$Ph_3P \xrightarrow{Cl_2CFCO_2Na} \underset{332}{Ph_3P{=}CFCl} \xrightarrow{ArC(O)CO_2R} \underset{363}{ArC(CO_2R){=}CFCl} \qquad (210)$$

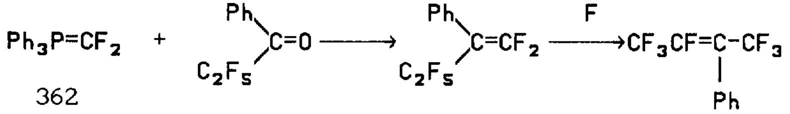
Tributylphosphonium difluoromethylid is remarkable for its high reactivity due to the electron-donating effect of the butyl groups. This ylid generated *in situ* by means of the halogenoacetate method olefinates such unreactive ketones as benzophenone, cyclohexanone and methylketones RC(O)Me, where R = C_5H_{11}, Ph, 2-furyl, 2-thienyl, etc. (eq. 211).[407,408] However, there are examples of deviation from the normal Wittig reaction. Thus, the reaction of tributylphosphonium difluoromethylid with trifluoroacetophenone affords the olefin **365**, which is formed by prototropic rearrangement of the difluoromethylid into the butylid **364** (eq. 212).[403,407] The Wittig reaction of C–fluoro-substituted ylids **362** with ketones bearing perfluoroalkyl groups is sometimes followed by isomerization with migration of a fluorine atom (eq. 213, 214).[404] In the absence of strong bases the isomerization of fluoro-olefins is less marked.[403]

$$Bu_3P{=}CF_2 + RR'C{=}O \xrightarrow{1h,\ 180^{o}C} RR'C{=}CF_2 + Bu_3P \qquad (211)$$

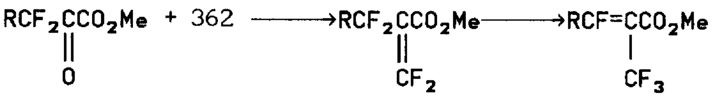


$$Bu_3P{=}CF_2 \longrightarrow \underset{CHPr}{\underset{\|}{Bu_2PCHF_2}} \xrightarrow{Ph(CF_3)C{=}O} \underset{365}{Ph(CF_3)C{=}CHPr} \qquad (212)$$

364



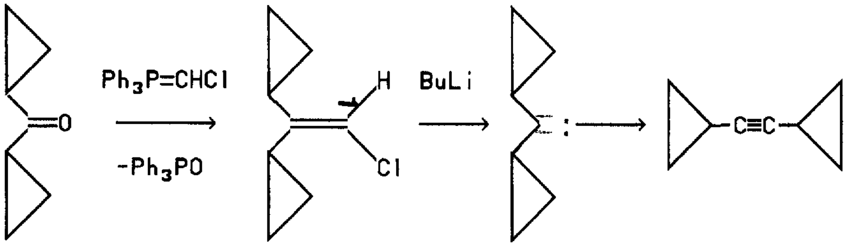
(213)



$$\underset{O}{\underset{\|}{RCF_2CCO_2Me}} + 362 \longrightarrow \underset{CF_2}{\underset{\|}{RCF_2CCO_2Me}} \longrightarrow \underset{CF_3}{\underset{|}{RCF{=}CCO_2Me}} \qquad (214)$$

$R{=}CF_3,\ C_2F_5$

C–Halogen-substituted phosphorus ylids are widely used in organic synthesis. Thus, the reaction of triphenylphosphonium chloromethylid with dicyclopropylketone affords chloro-olefin **366** in 81% yield and after treatment with butyllithium at room temperature provides a convenient route to dicyclopropyl acetylene via the carbenoid[451] (eq. 215).



(215)

366

Triphenylphosphonium dichloromethylid (**331**) has been used for the modification of polymeric reagents, and in particular to produce insoluble polymeric ynamines **367**[458,459] (eq. 216).

$$\textcircled{P}{-}C_6H_4CHO \xrightarrow{Ph_3P{=}CCl_2} \textcircled{P}{-}C_6H_4CH{=}CCl_2 \xrightarrow{LiNEt_2} \textcircled{P}{-}C_6H_4C{\equiv}CNEt_2 \qquad (216)$$

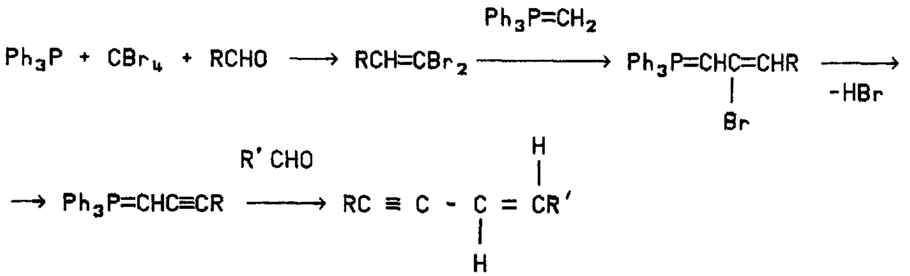
367

In the reaction between protected 17-keto-3-β-oxi-6-androstenone ether and the triphenylphosphonium fluoromethylid the 17-fluoromethylene-substituted steroid was obtained.[439] A convenient method for halo-olefin synthesis developed by Corey involves the reaction of triphenylphosphine with tetrabromomethane in the presence of zinc powder (eq. 217).[460] Dibromomethylid **368** reacts *in situ* with aldehydes to give bromo-olefins[463] which were used for the synthesis of retinoids,[463] and acetylenic acids,[460,461] by reaction of the dibromo-olefin with butyllithium and subsequent treatment of the resultant lithium acetylide with carbon dioxide as in the case of **369** which was formed in 82–90% yield (eq. 218).

$$\mathrm{Ph_3P + CBr_4 + Zn} \xrightarrow[\mathrm{CH_2Cl_2}]{25^{\circ}\mathrm{C}} \underset{368}{[\mathrm{Ph_3P{=}CBr_2}]} \xrightarrow{\mathrm{RCHO}} \mathrm{RCH{=}CBr_2} \qquad (217)$$

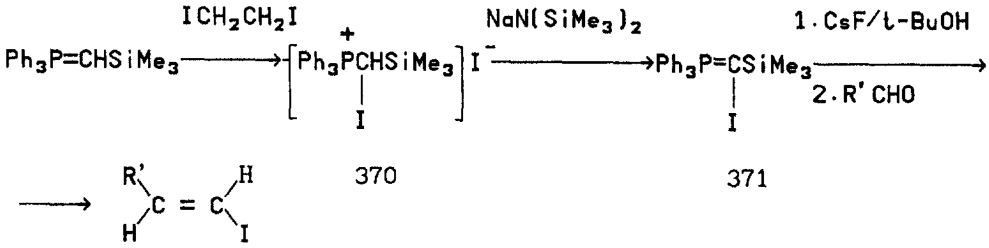
$$368 \xrightarrow{\mathrm{RCHO}} \mathrm{RCH{=}CBr_2} \xrightarrow{\mathrm{BuLi}} \mathrm{RC \equiv CLi} \xrightarrow[2\cdot \mathrm{H^+}]{1\cdot \mathrm{CO_2}} \underset{369}{\mathrm{RC \equiv CCO_2H}} \qquad (218)$$

Bestmann has developed syntheses of some pheromone synthons from C–halogen-substituted ylids (eq. 219).[465]



(219)

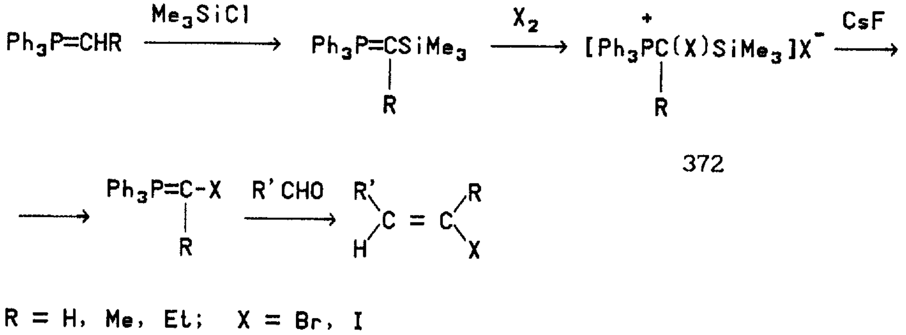
Methods for the preparation of α-halo-olefins based on C–silicon-substituted ylids have been described. The soft iodination of triphenylphosphonium trimethylsilylmethylid by means of 1,2-iodoethane gives iodoalkylphosphonium salt **370** in high yield. The dehydroiodination of **370** with sodium bis(trimethylsilyl)amide leads to the formation of ylid **371**. Treatment of the latter with caesium fluoride in *tert*-butanol in the presence of a carbonyl compound furnishs α-iodo-olefins in a highly stereoselective manner (eq. 220).[466]



370 371

(220)

Consecutive treatment of non-stabilized phosphorus ylids with trimethylchlorosilane and a halogen affords phosphonium salts **372** which are easily desilylated by caesium fluoride to form phosphorus ylids. These latter compounds react *in situ* with aldehydes to provide halo-olefins as shown in eq. 221.[467]



372

(221)

4. CONCLUSIONS

It is therefore clear that heteroatoms, directly bonded to the ylid carbon atom, may play a considerable role in determining the properties of these phosphorus ylids. Two distrint subclasses may be defined. In one of these, substituents (for example, metal atoms of the IA and IIA groups, nitrogen atoms, tin and lead atoms) increase electron density at the carbon atom and lead to more reactive reagents, while in the second class other heteroatoms (for example, silicon and germanium atoms, elements of V–VII groups, transition metals) effectively stabilize the ylid carbanion, and by virtue of reduced electron density at the α-carbon atom reduce ylid nucleophilicity. In both cases, new and useful synthetic possibilities have emerged and further developments in this area of chemistry can be clearly expected.

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