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PERSPECTIVE

Sterically protected organophosphorus compounds in low co-ordination states

Masaaki Yoshifuji

*Department of Chemistry, Graduate School of Science, Tohoku University, Aoba,
Sendai 980-8578, Japan*

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The chemistry of sterically protected low co-ordinate organophosphorus compounds is described; these compounds comprise diphosphenes, phosphaethenes, phosphaallenes, phosphabutatrienes, phosphinidenecyclobutenes, and so forth, and are discussed in terms of syntheses, ^{31}P NMR analyses, X-ray crystallographic structure analyses, as well as physical and chemical properties.

1 Introduction

One hundred and twenty years ago, Köhler and Michaelis[1] reported on phosphobenzene 'PhP=PPh', as a phosphorus analogue of azobenzene, as a reaction product of dichlorophenylphosphine and phenylphosphine. This was the first report on a compound containing the P=P bond, but later it was shown that the compound was actually oligomers of PhP units, being a tetramer or pentamer in solution[2] and a pentamer or a hexamer in the solid state.[3] Subsequently, chemists generally believed that compounds such as 'phosphobenzene' cannot exist as stable entities, since according to the 'classical double-bond rule' double bonding involving the heavier main group elements is unstable,[4] due to the hypothesis that the energy gain on formation of π bonding with vast but dilute electron lobes is not large through a long bond distance; *i.e.* electrons in the 3s, 3p or 3d orbitals do not form a strong bond because of the long bond length and unfavourable hybridization of the sp^2 configuration. Thus much effort had been paid to thermodynamic stabilization of these multiple bonds by electronic or delocalization effects; indeed, Dimroth and Hoffmann[5] reported phosphacyanins and Märkl[6] reported phosphabenzenes, both having a delocalized P=C bond.

However, in 1978, utilizing the mesityl group as a sterically protecting moiety (hereafter abbreviated to Mes), Bickelhaupt and co-workers[7] reported on a phosphaethene with a P=C bond (**1**), and in 1981, utilizing the 2,4,6-tri-*tert*-butylphenyl group I reported on a diphosphene with a P=P bond (**2**).[8] It should be noted that, in 1981, Becker *et al.*[9] reported a phosphaalkyne with a P≡C bond protected with the *tert*-butyl group (**3**), and that in the field of silicon chemistry West *et al.*[10] reported the first isolated disilene with a Si=Si bond (**4**) bearing four mesityl groups (Scheme 1).

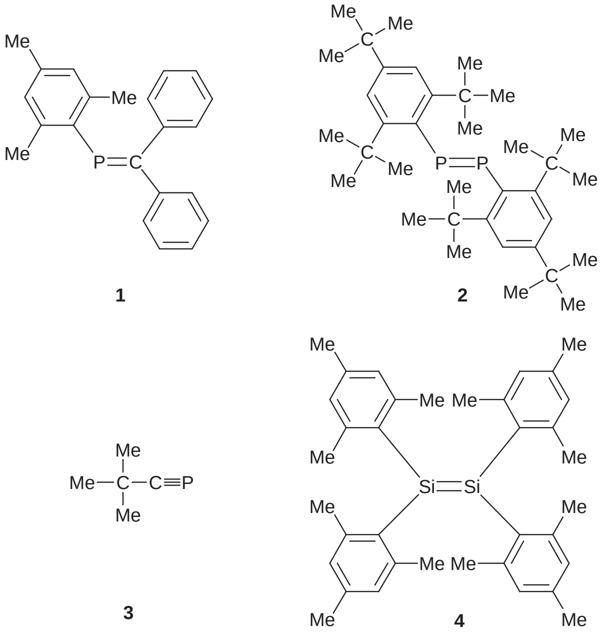
These compounds are the earliest examples of localized multiple bonding which violates the classical 'double bond rule'. Since they involve interesting bonding and novel structures, studies on the chemistry of multiple bonds of the heavier main-group elements have been carried out in various fields of chemistry including theory, chemical reactions, photochemistry, co-ordination chemistry and electrochemistry. The chemistry thus newly created for multiply bonded phosphorus compounds was generally regarded as a renaissance of phosphorus chemistry. Indeed, there have been several review articles and books[11–21] dealing with this new chemistry, since these compounds are supposed to be highly reactive unless reasonably protected, and even when being sufficiently protected to be analysed they are still chemically reactive.

2 Low co-ordinated organophosphorus compounds

Thus, this article focuses on the chemistry of sterically protected organophosphorus compounds in low co-ordination states, but mainly limited to my results concerning the bonding

Masaaki Yoshifuji was born in Tokyo in 1941. He received a bachelor degree in 1966, master degree in 1968, and Doctor of Science in 1971 from The University of Tokyo. He was appointed as Research Associate in 1971 and was promoted to Associate Professor at Tokyo (Faculty of Science) in 1988. He has been Professor at Tohoku University (Graduate School of Science) since 1989. His research interests are unusual organic compounds including heteroatoms in terms of structure, chemical reactivities and physical properties.

Masaaki Yoshifuji

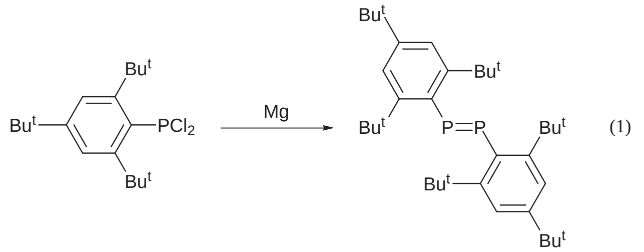


Scheme 1

with P=X (X = P, C, As or Si), P=C=X (X = P, C or N), P=C=C=X (X = P or C) and C≡P.

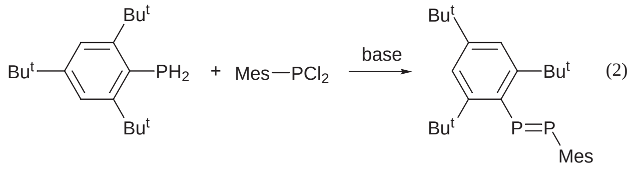
2.1 Diphosphenes

The sterically protected diphosphene **2** was prepared as a stable compound by dechlorination reaction of the corresponding phosphonous dichloride **5** with magnesium metal for the first time, as shown in equation (1).[8] Electron transfer reagents such as lithium dihydronaphthylide can be used in place of magnesium for the dechlorination of phosphonous dichlorides.



5 **2**

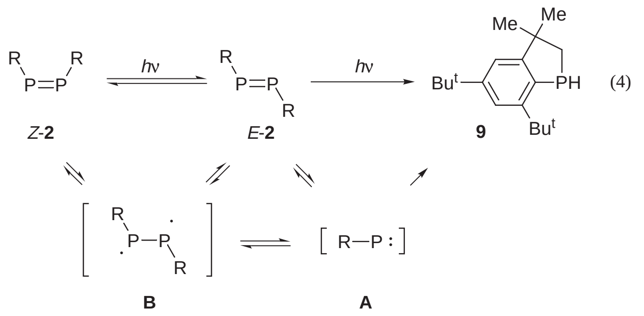
There are several other methods to prepare diphosphenes especially for unsymmetrical diphosphenes such as **6**. Starting from the corresponding primary phosphine **7** and phosphonous dichloride **8**, the unsymmetrical diphosphene **6** is available in the presence of a base such as triethylamine or 1,8-diazabicyclo-[5.4.0]undec-7-ene (dbu), as shown in equation (2).[22] From a mixture of two different phosphonous dichlorides, unsymmetrical diphosphenes can be obtained by dechlorination reaction, together with the symmetrical diphosphenes, but careful purification such as column chromatography is required, to obtain the desired unsymmetrical diphosphenes, where R, R′ = 2,4,6-$Bu^t_3C_6H_2$, tri-*tert*-pentylphenyl,[23] 2,6-dimesityl-4-methylphenyl,[24] and so on, as shown generally in equation (3).

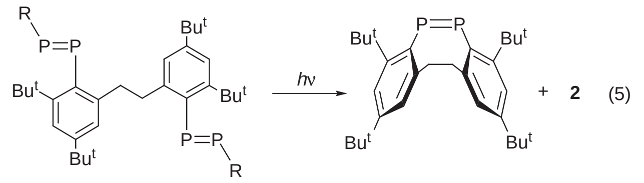


7 **8** **6**

$$RPCl_2 + R'PCl_2 \xrightarrow{Mg} R'P{=}PR' + RP{=}PR' + RP{=}PR \quad (3)$$

At the beginning of my research on diphosphenes a reaction mechanism was postulated which involves the corresponding phosphinidene as an intermediate,[8] a phosphorus analogue of nitrene, which subsequently forms the diphosphene, a formal dimer of the phosphinidene. However, it is now known that phosphinidenes such as 2,4,6-tri-*tert*-butylphenylphosphinidene (**A**), if formed, tend intramolecularly to insert into the C–H bond of one of the methyl groups of the *ortho tert*-butyls of the protecting group to form a phosphaindane derivative **9**,[25] rather than dimerize to the diphosphene. Thus the formation of a diphosphene, through a formal dimerization of diphosphene, might be explainable by an alternative intermediate such as a 'phosphinidenoid', RP(Cl)MgCl. Photolysis of diphosphenes has been investigated to determine whether the products depend on the wavelength of irradiation; irradiation with a mercury lamp without a filter causes the formation of phosphaindane **9**, while irradiation through a Pyrex filter[25] or 514.5 nm laser light[26] causes *E*/*Z* isomerization at low temperature [equation (4); R = 2,4,6-$Bu^t_3C_6H_2$]. The isomerized *Z*-**2** returns to *E*-**2** upon warming, due to enormous steric congestion between the two aryl groups in the *Z* isomer. However, it is not yet clear whether a biradical **B** is really involved in the *E*/*Z* isomerization of **2**, while Bickelhaupt and co-workers[27] experimentally determined the activation parameters for the thermal isomerization reaction of 1-(2,4,6-tri-*tert*-butylphenyl)-2-(2,4,6-triisopropylphenyl)diphosphene, as $\Delta H^\ddagger = 29.5 \pm 1.4$ kcal^{-1} and $\Delta S^\ddagger = 38 \pm 6$ cal K^{-1} mol^{-1} (cal = 4.184 J). Although a nitrogen atom is directly attached to one of the phosphorus atoms, Niecke *et al.*[28,29] reported preparations and X-ray analyses of *Z*-aminodiphosphenes, which are stable at room temperature. Very recently, utilizing 1,2-bis(2-bromo-3,5-di-*tert*-butylphenyl)ethane as a protecting group, an internal *cis*-diphosphene *Z*-**10** of the *o*-cyclophane type was prepared together with **2** from a bis(diphosphene) *E*,*E*-**11**, as shown in equation (5),[30] where the reaction might proceed intramolecularly *via* olefin metathesis or similar mechanism. The structure of *Z*-**10** was confirmed by X-ray analysis of the tungsten complex of the ligand. Under certain conditions, unsymmetrical diphosphenes RP=PR′, where R = 2,4,6-$Bu^t_3C_6H_2$, R′ = Mes,[31] 2,4,6-tris(trifluoromethyl)phenyl,[32] pentamethylcyclopentadienyl,[33] $(Me_3Si)_2N(Me_3Si)N$[28] or *tert*-butylamino,[29] gave **2** (RP=PR), indicating that disproportionation occurred upon irradiation or warming in solutions. Although Gaspar and co-workers[34] reported direct observation of mesitylphosphinidene by ESR spectroscopy, I could not obtain any proof to support the generation of phosphinidene species, even at cryogenic temperature during the photolysis of the phosphinidene precursors.[35] On the other hand, diphosphenes of the Group 6 metal carbonyls also caused *E*/*Z* photoisomerization upon irradiation by UV light.[36]





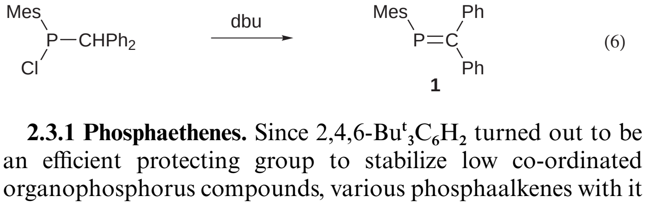
E,*E*-**11** *Z*-**10**

2.2 Phosphaarsenes

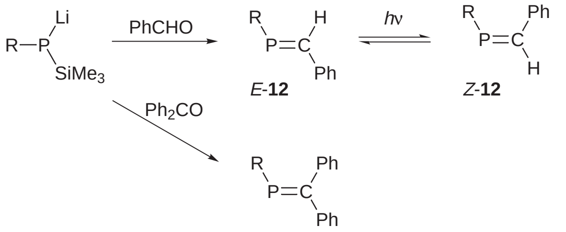
Phosphorus compounds with P=As bonding can be prepared by the reaction of primary phosphines with dichloroarsines in the presence of a base such as dbu.[37] Using an *o*-diarylphenyl substituent, such as the 2,6-dimesityl-4-methylphenyl, the phosphaarsene was prepared as a stable orange solid material.[24]

2.3 Phosphaalkenes

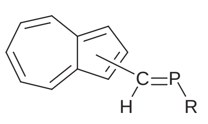
A sterically protected phosphaalkene, 1-mesityl-2,2-diphenyl-1-phosphaethene (**1**), was prepared by Bickelhaupt and co-workers[7,38] as the first example of the phosphaethene with a localized P=C bond [equation (6)].



2.3.1 Phosphaethenes. Since 2,4,6-$Bu^t_3C_6H_2$ turned out to be an efficient protecting group to stabilize low co-ordinated organophosphorus compounds, various phosphaalkenes with it have been prepared from the corresponding silylphosphide and aldehydes or ketones [equation (7)], by the phospha-Peterson reaction.[39,40] Furthermore, photoisomerization of *E*-**12** was attained to give *E*/*Z* isomers.[40–42] This method can generally be applied to the preparation of phosphaethenes and was useful to prepare phosphaalkene **13** bearing the novel aromatic compound azulene.[43] Geoffroy and co-workers[44–46] and I[47] reported the formation of 1,2-, 1,3- and 1,4-bis(2-phosphaethenyl)benzene derivatives **14**, prepared from the corresponding dialdehydes.



(7)



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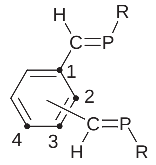
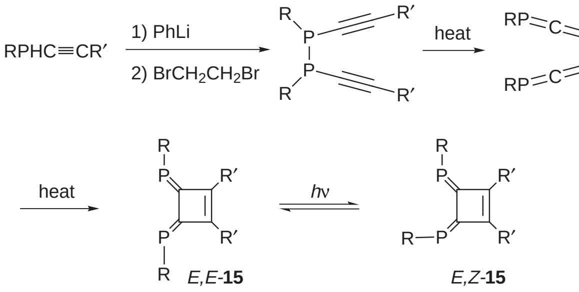


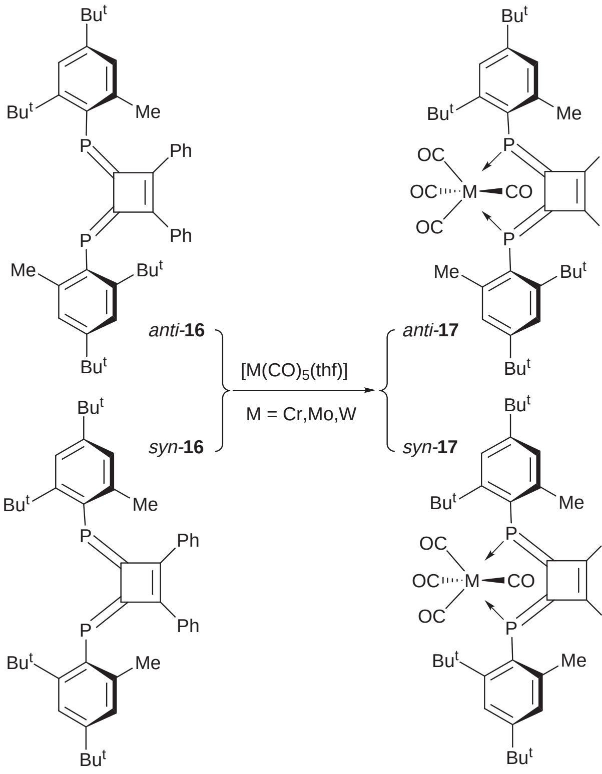
14

2.3.2 Diphosphinidenecyclobutenes. Appel *et al.*,[48] Märkl[49] and I[50,51] reported the synthesis and structure of diphosphinidenecyclobutene **15** (R = 2,4,6-$\mathrm{Bu^t{}_3C_6H_2}$, R′ = Ph or $\mathrm{SiMe_3}$), as shown in equation (8). The system seems to involve both the buta-1,3-diene and the hexa-1,3,5-triene system, within a molecule. Furthermore, the 2,4,6-$\mathrm{Bu^t{}_3C_6H_2}$ groups can take both the *E* and *Z* configuration. It is of interest that the direction of photoequilibrium depends on the substituents; if R′ = $\mathrm{SiMe_3}$ or Ph, the *E*,*E* configuration is major, while if R′ = H the *E*,*Z* configuration is major, probably due to steric congestion between the two R groups and the substituents R′. Needless to say, the *Z*,*Z* configuration is hard to achieve because of the serious steric congestion between the two R groups. Iodine-induced *E*/*Z* isomerization was observed in the case of diphosphinidenecyclobutene, and this is a good method for preparation of *E*,*Z*-phosphinidenecyclobutenes.[52]



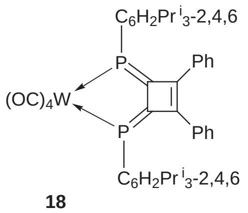
(8)

On the other hand, we have developed several protecting groups other than 2,4,6-$\mathrm{Bu^t{}_3C_6H_2}$ and found that 2,4-di-*tert*-butyl-6-methylphenyl is useful to stabilize the diphosphinidenecyclobutene system. In addition to the *E*/*Z* configurational isomerism, as mentioned above, conformational isomerism was observed, due to the restricted rotation around the two P–C bonds at the edges of the system. The compound **16** consisted of two rotamers, *syn* and *anti* isomers, and after addition of $[\mathrm{M(CO)_5(thf)}]$ to this mixture, where M is a Group 6 metal, the ^{31}P NMR of the reaction products appeared as a mixture of *syn*-**17** and *anti*-**17** with complete retention of conformation [equation (9)]. The structure of *syn*-**17**, where M = W, was unambiguously determined by X-ray analysis.[53] On the other hand, *anti*-**17**, where M = W, was analysed by HPLC using a chiral column and a baseline separation was attained; each separated enantiomer showed a symmetrical CD spectrum. These results indicate that an asymmetric environment can be created in the diphosphinidenecyclobutene due to the restricted rotation.



(9)

It is interesting that diphosphinidenecyclobutenes have various possible co-ordination modes toward transition metals. Indeed, some of them give σ- and π-co-ordinated complexes with Group 6 metal carbonyls, as shown in **18** and **19**.[54] A similar complex was obtained in the case of 2,4,6-$\mathrm{Bu^t{}_3C_6H_2}$ at the phosphorus and H at the cyclobutene ring. Although Rau and Behrens[55] reported on the formation and structural analysis of tricarbonyl(η^6-dimethylenecyclobutene)chromium(0) and tricarbonyl(η^6-diisopropylidenecyclobutene)chromium(0), **19** is the first example of the diphosphinidenecyclobutene–tungsten carbonyl system, where the ligand is doubly co-ordinated with tungsten metals, and of the bidentate ligation in **18**.



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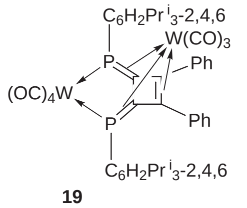


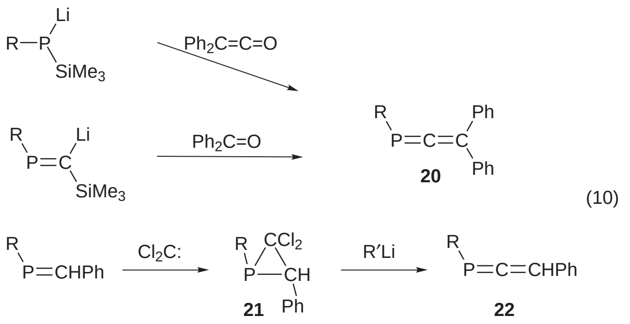
19

2.3.3 Phosphasilene. Compounds with a P=Si bond have been prepared, however they are not so stable even when sufficiently protected with bulky substituents,[56] probably due to a weak π bond (29 kcal $\mathrm{mol^{-1}}$) as calculated by an *ab initio* method.[57]

2.4 Phosphacumulenes

Phosphacumulenes, such as phosphaallenes, diphosphaallenes, phosphabutatrienes and diphosphabutatrienes, were prepared by various methods.

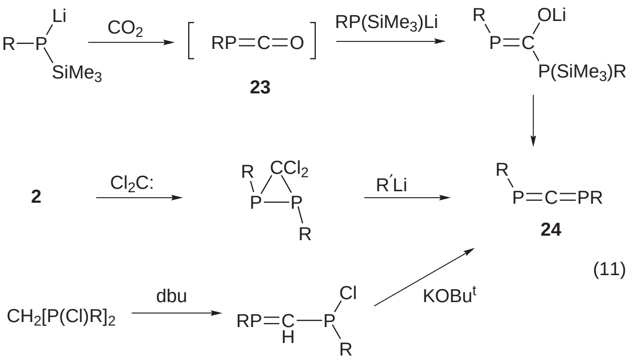
2.4.1 Phosphaallenes. 1-Phosphaallene **20** can be prepared by either the Peterson reaction,[58] the phospha-Peterson reaction,[59,60] or the phosphorus version of the Doering–Moore–Skattebøl reaction (DMS reaction)[61] as shown in equation (10),



(10)

R = 2,4,6-$Bu^t_3C_6H_2$. It should be mentioned here that stereochemistry is not preserved during the DMS reaction, since the dichlorophosphirane **21**, obtained as a reaction intermediate, was identical either starting from *E*- or *Z*-phosphaethene. Furthermore, axial chirality exists around the P=C=C bond of phosphaallene **22**, and the separation of enantiomers by a chiral HPLC column was successful, indicating that the racemization is not fast in the dark, while it is almost instantaneous upon irradiation with light.[62]

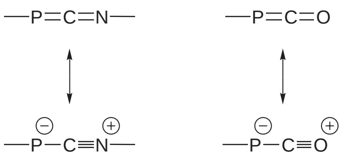
2.4.2 Diphosphaallenes. 1,3-Diphosphaallene **24**[63] can be prepared by various methods, as shown in equation (11),



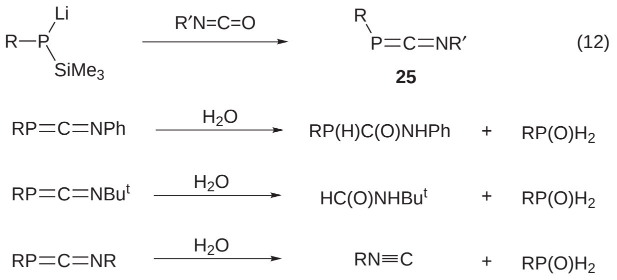
(11)

R = 2,4,6-$Bu^t_3C_6H_2$. For the first time the compound was prepared from the reaction of silylphosphide with carbon dioxide, *via* a phosphaketene **23**[64] as an intermediate. Alternatively, it was prepared by the reaction of halogenophosphino-substituted phosphaalkenes with potassium *tert*-butoxide.[65] Recently we have developed a phosphorus version of the DMS reaction of diphosphenes with dichlorocarbene, followed by ring opening of dihalogenodiphosphiranes with alkyllithium reagents [equation (11)].[66] Thus an unsymmetrical diphosphaallene was prepared from the corresponding unsymmetrical diphosphene.[23] The structure of the 1,3-diphosphaallene **24** was determined by X-ray analysis by Karsch *et al.*[67] It should be noted that similar axial chirality exists around the P=C=P bond, and the separation of enantiomers through a chiral HPLC column was successful,[68] though the racemization took place on irradiation with light.

2.4.3 P=C=N. Phosphorus compounds with the P=C=N bond can be prepared by the reaction of silylphosphides with isocyanates, as shown in equation (12).[59,69] This type of compound protected by the *tert*-butyl group was first reported by Kolodiazhnyi.[70] The reaction of the azaphosphaallene with water depends on the substituents R′ on the nitrogen.[71] Phosphorus chemical shifts of azaphosphaallenes **25** appear at high field: δ −106.2 for R′ = Ph, −101.9 for R′ = Bu^t and −135.3 for R′ = R, probably due to the existence of a canonical structure with negative charge on the phosphorus, as depicted in Scheme 2. A similar high field shift is observed for **23**.[64]

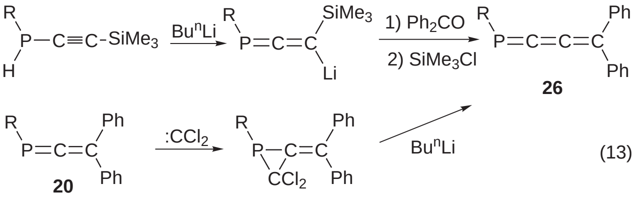


Scheme 2



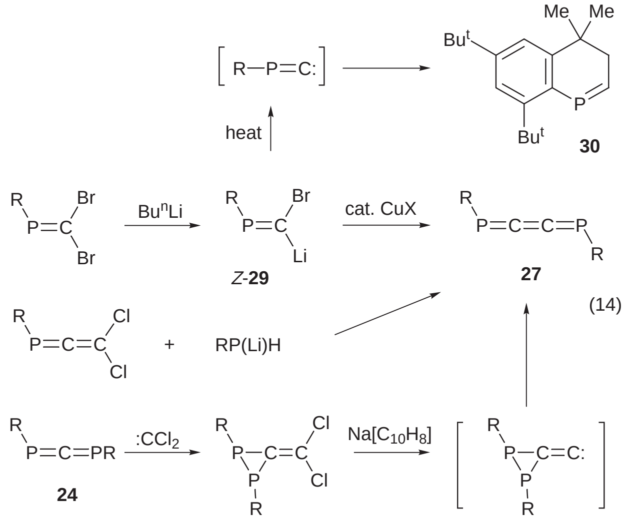
(12)

2.4.4 Phosphabutatrienes and diphosphabutatrienes. 4,4-Diphenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphabuta-1,2,3-triene **26** can be prepared by either the method reported by Märkl[72] (Peterson reaction) or that by the phospha-DMS reaction[73] from **20**, as shown in equation (13) (R = 2,4,6-$Bu^t_3C_6H_2$).



(13)

On the other hand, 1,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,4-diphosphabuta-1,2,3-triene **27** was similarly prepared; coupling reactions mediated with copper halides are useful to obtain 1,4-diphosphabutatrienes **27** [equation (14)].[74–76] Furthermore, the



(14)

phospha-DMS reaction, stating from 1,3-diphosphaallene **24**, also gave **27** *via* dichloromethylenediphosphirane indicating generation of a carbene intermediate. It is noteworthy that the corresponding bromo derivative *Z*-**29** gave the 3,4-dihydro-1-phosphanaphthalene derivative **30** upon warming, indicating a carbene intermediate.[77]

2.5 Diphosphabutadienes

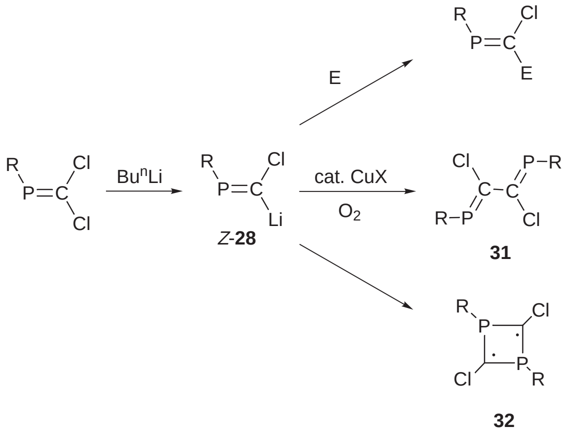
As a conjugated system containing low co-ordinated phosphorus atom(s), 2,3-dichloro-1,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,4-diphosphabuta-1,3-diene **31** was obtained as a coupling product of the reaction of 2-chloro-2-(2,4,6-tri-*tert*-butyl-

Table 1 The ^{31}P NMR chemical shifts, δ_P, and bond lengths *d*(P=X) of some organophosphorus compounds in low co-ordination states

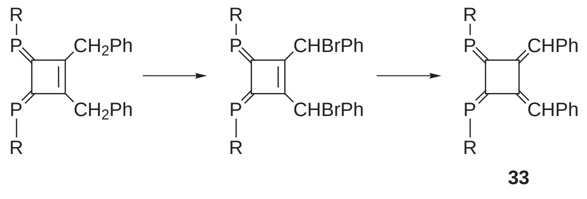
Compound	R′	System	δ_P	*d*(P=X)/pm	Ref.
E-**2**	—	P=P	492.4	203.4(2)	8
Z-**2**	—	P=P	368	204.1(4)[a]	25, 26
1	—	P=C	233.0	169.2(3)	7, 38
E-**12**	—	P=C	259.3	166.0(6)	40, 41
Z-**12**	—	P=C	241.6	167.4(2)	40, 41
20	—	P=C=C	72.1	162.5(4)	59, 60
24	—	P=C=P	142.7	163.5(8), 163.0(8)	63, 67
23	—	P=C=O	−207.4	—	64
25	Ph	P=C=N	−106.2	165.1(3)	69
26	—	P=C=C=C	156.7	164.7(8)	73
E,*E*-**15**	$SiMe_3$	P=C–C=P	162.5	167.8(6), 167.6(5)	50, 51
E,*Z*-**15**	$SiMe_3$	P=C–C=P	197.4, 176.6	166.5(7), 166.2(7)	50
E-**27**	—	P=C=C=P	180.6	165.6(6)[b]	74, 75, 76
Z-**27**	—	P=C=C=P	170.0	—	75, 76
31	—	P=C–C=P	248.0	169.1(4)	78
33	—	P=C–C=P	190.7	168.3(5), 166.9(5)	83
3	—	P≡C	−69.2	152.0(12)[c]	9
34	—	P≡C	34.4	151.6(13)	88, 89

[a] X-Ray data taken from ref. 30 for [$\{W(CO)_5\}_2$(*Z*-**10**)]. [b] X-Ray data taken from ref. 74 for [$\{W(CO)_5\}_2$(*E*-**27**)]. [c] X-Ray data taken from ref. 86 for *trans*-[$Mo(R'C{\equiv}P)_2(Et_2PCH_2CH_2PEt_2)_2$] (R′ = adamantyl).

phenyl)phosphaethenyllithium *Z*-**28** in the presence of copper chloride and the yields are higher in the presence than in the absence of oxygen.[78] In the case of the bromo derivative, a similar reaction of *Z*-**29** occurs to give the corresponding dibromodiphosphabutadiene. However, when *Z*-**28** was allowed to react with electrophiles, such as alkyl halides, aldehydes, ketones, isocyanates and acid chlorides, nucleophilic reactions took place to give multifunctionalized methylenephosphines in good yield [equation (15)].[79,80] However, in both cases, diphosphabutatriene **27** was obtained as a by-product due to dehalogenation of the dihalogenobutadienes. Under similar reaction conditions except for the absence of copper halide, or oxygen bubbling, the formation and crystal structure of the dichlorodiphosphacyclobutanediyl **32** was reported by Niecke *et al.*[81] On the other hand Appel *et al.*[82] reported formation of 1,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,4-diphosphabuta-1,3-diene by the elimination reaction of ethylenebis[chloro(2,4,6-tri-*tert*-butylphenyl)phosphine] with 1,5-diazabicyclo[4.3.0]non-5-ene. Furthermore, we have prepared a 4-radialene,[83] the dimethylenediphosphinidenecyclobutane **33**, as shown in equation (16). In contrast to the instability of the isomer *E*-**28**, as mentioned below, *Z*-**28** gave the corresponding alkylation products by reaction with various electrophiles even at room temperature.



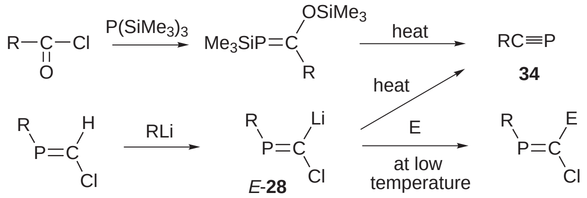
(15)



(16)

2.6 Phosphaalkynes

A sterically protected phosphaalkyne **3** of co-ordination number 1 was reported by Becker *et al.*[9] in 1981 for the first time, carrying *tert*-butyl as a protecting group. Phosphaalkynes are phosphorus analogues of nitriles and their chemistry has been developed not only as ligands of transition metal complexes, but also as a building block for further interesting phosphorus-containing heterocyclic compounds.[84–87] The 2,4,6-tri-*tert*-butylphenyl derivative **34** has been prepared by the two different methods, by the elimination of a siloxane from phosphaalkenes[88,89] and by the 1,2-aryl migration from phosphorus to carbon, which can be considered as a phosphorus version of the Fritsch–Buttenberg–Wiechell reaction (FBW reaction) of *E*-**28**, as shown in equation (17).[80,90] In contrast, the isomer *Z*-**28** did not form phosphaalkyne, indicating that some stereoelectronic effect might be operating during this FBW reaction, as has been postulated by Köbrich and Trapp[91] for the original FBW reactions.



(17)

3 Conclusion

Studies on low co-ordinate organophosphorus compounds have extensively been developed since the first findings were disclosed that those kinds of compounds can be kinetically stabilized efficiently by bulky substituents, such as the 2,4,6-tri-*tert*-butylphenyl group. As a result, they have stimulated many chemists in the field of organic, inorganic as well as theoretical chemistry. As has been shown for almost two decades, various kinds of unusual compounds have been isolated and characterized involving not only phosphorus but also Group 14 and 16 elements, utilizing bulky substituents as well as special substituents with electronic effects.[92] Table 1 lists ^{31}P chemical shifts for some selected low co-ordinated phosphorus compounds, together with the observed lengths for the P=X bonds d(P=X) determined by X-ray analyses. The chemical shifts change sensitively depending on the substituents, as well as on the bonding systems,[93] although the bond lengths are almost constant: *ca.* 200 pm for the P=P bonds and 160–170 pm for the P=C bonds. The reactivities of highly protected low co-ordinated organophosphorus compounds are to some extent similar to those of the corresponding C=C systems rather than the N=N or N=C systems. Since such organophosphorus compounds involve phosphorus atom(s) in low co-ordination states with lone-pair electrons, the unsaturated systems are expected potentially to include novel and unusual characters, which are hitherto unknown and far beyond our common concept of either unsaturated carbon compounds or organophosphorus compounds. Thus a breakthrough is awaited as to the application of those compounds in the direction of materials or drugs.

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