Chemistry of 3-Membered Carbon–Phosphorus Heterocycles

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I. Introduction

The parent oxirane (ethylene oxide) was discovered as early as 1859 by Wurtz. Today, millions of tons of oxirane are produced each year by the chemical industry. The compound is mainly used in the preparation of ethylene glycols and poly(ethylene glycols) and for the manufacture of polymers. The story of aziridines also started very early. In 1888, Gabriel prepared the parent compound, which he formulated as vinylamine. The correct formulation was soon established by Marckwald. Today, some aziridines are produced commercially and are used in textiles, plastics, coatings, and drugs (e.g., anticancer drugs). These brief considerations underline the paramount importance of 3-membered heterocycles in organic chemistry.

As already stated in a previous review on phosphole chemistry,[1] the heterocyclic chemistry of phosphorus is deeply underdeveloped by comparison with its oxygen, nitrogen, and sulfur counterparts. In the case of three-membered heterocycles, the story started in 1963 with the discovery of phosphiranes by Wagner.[2] To say the least, this discovery was considered with some skepticism[3] until it was confirmed in 1967.[4] Then, Baudler succeeded in preparing the first stable diphosphirane in 1978.[5] The next breakthrough came in 1982 when Marinetti and Mathey unambiguously characterized the phosphirene ring.[6] The story was completed with the discovery of the first stable 2*H*-phosphirene by Regitz in 1987 and by the characterization of the diphosphirene ring by Niecke in 1989 (see sections II.B.2 and II.D). Several reviews have been already written on three-membered phosphorus rings,[7-12] but they are now obsolete because progress in the field is extremely fast. In this review, we have

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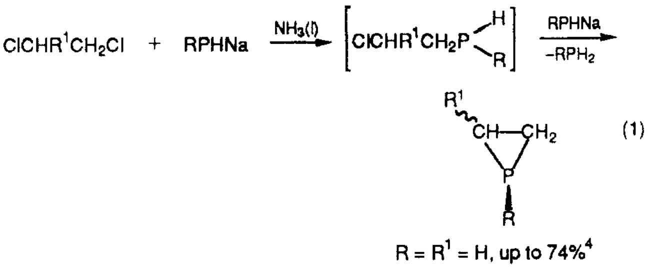
attempted to comprehensively cover the literature until the middle of 1989.

II. Synthesis

A. Phosphiranes

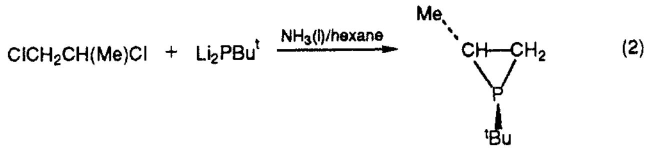
1. From P and C_2 Units

The original synthesis by Wagner[2,4,13] relies on the reaction of the sodium derivatives of PH_3 or RPH_2 with a 1,2-dichloroalkane in liquid ammonia (eq 1).


(1)

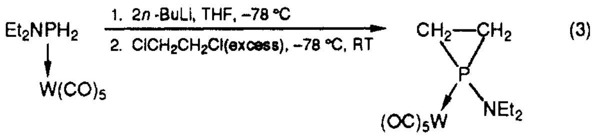
R = R^1 = H, up to 74%[4]
R = Me, R^1 = H, 30%[13]
R = Ph, R^1 = H, 60%[13]
R = H, R^1 = Me, 30%[13]
R = H, R^1 = Et, 25%[13]

The reaction has also been performed in HMPA as the solvent in order to get P–D and C–D derivatives.[14] In one case, it proved possible to replace chlorine by the mesyloxy $MeSO_2O$ leaving group.[15] Recently, Baudler[16] extended the reaction to the synthesis of the thermally stable 1-*tert*-butyl-2-methylphosphirane (eq 2).


(2)

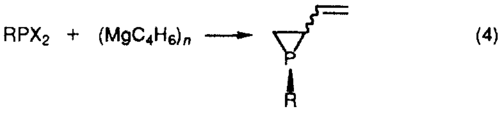
14%

Finally, similar chemistry has been carried out in the coordination sphere of tungsten[17] (eq 3).


(3)

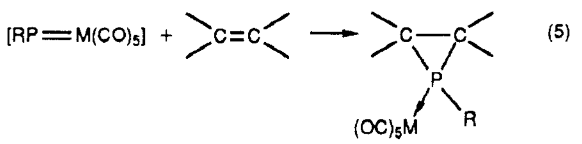
40%

A second synthesis of phosphiranes relying on the combination of P and C_2 units was devised by Richter.[18,19] It takes advantage of the existence of polymeric magnesium–butadiene adducts[20] (eq 4).


(4)

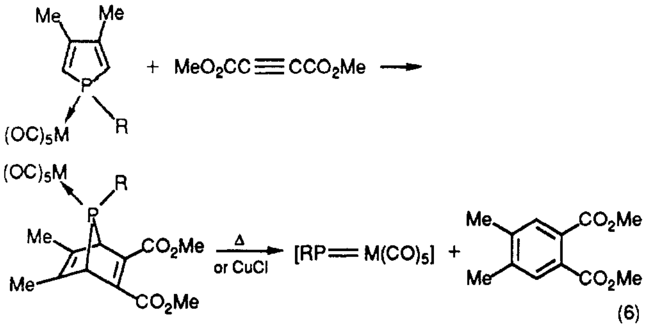
The reaction gives the vinyl-substituted phosphiranes as a mixture of cis (major) and trans (minor) isomers. The yields are good (36–58%) only when bulky alkyl P substituents are used (*tert*-butyl, cyclohexyl, menthyl).

A third route was discovered more recently by Marinetti and Mathey.[21] It involves the concerted [1+2] cycloaddition between transient singlet terminal phosphinidene complexes and olefins (eq 5). The reaction takes place with full retention of stereochemistry at the C=C double bond.

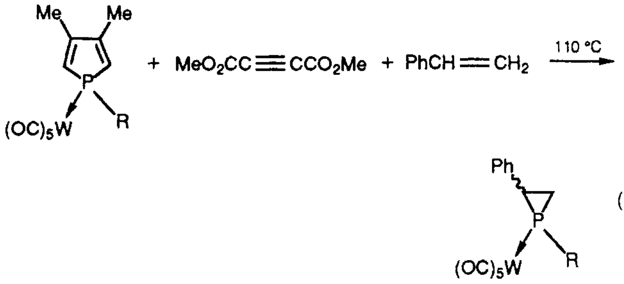

(5)

M = Cr, W; R = Me,[21] Ph,[21] allyl,[23] MeO,[24] $-CH_2CH_2-$[25]

The terminal phosphinidene complexes are generated by thermal or catalytic decomposition of the appropriate 7-phosphanorbornadiene complexes[26] (eq 6).

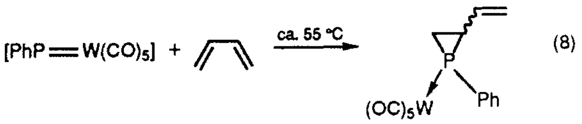

(6)

It proved possible to combine the synthesis of the phosphinidene precursors with the [1+2] cycloaddition[27] (eq 7).

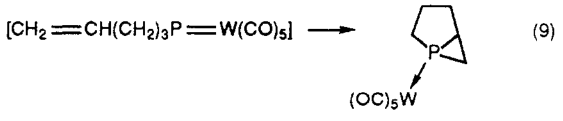

(7)

R = Ph, 80%
R = Me, 64%

The decomplexation of some of the phosphirane rings thus obtained has been successfully carried out[28] by an already described procedure working for phosphirene complexes (see later text). Functional olefins such as enol ethers,[21] enamines,[22] acrylic esters,[21] or conjugated dienes[21] can be used in lieu of ordinary olefins, for example with dienes[21] in eq 8.

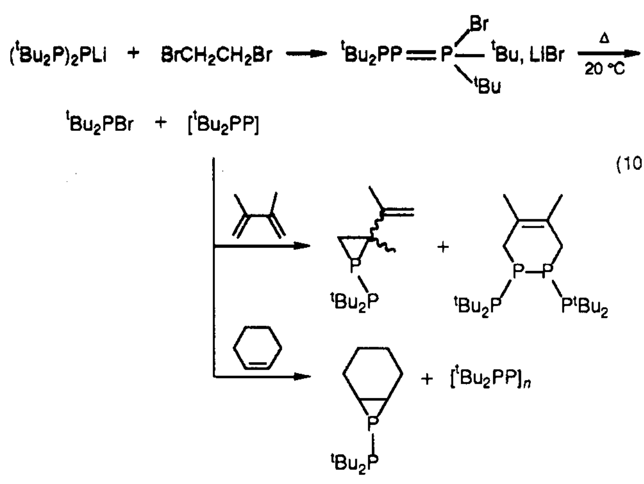

(8)

Finally, self-condensation can be observed with phosphinidenes bearing olefinic substituents[23] (eq 9).


(9)

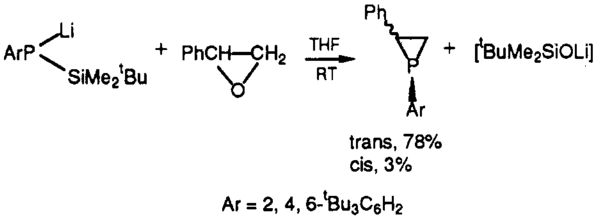
100%

A theoretical study has shown that free singlet phosphinidenes could react with olefins without activation energy.[29] Whereas the ground state of phosphinidenes is normally a triplet, it is a singlet for phosphinophosphinidenes[30] due to the very efficient stabilization of this state by the lone pair at the phosphino phosphorus. In a very recent work,[31,32] Fritz has been able to generate a phosphinophosphinidene and has shown that it reacts with olefins to give phosphiranes, in agreement with the theoretical predictions (eq 10).

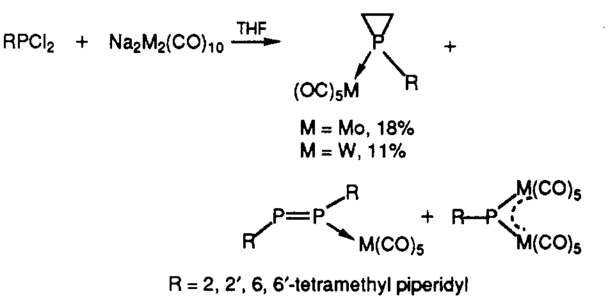

(10)

It may prove difficult to generalize these exciting results to other types of free phosphinidenes. In retrospect, the successful condensation of terminal phosphinidene complexes with olefins (eq 5) may be ascribed to the stabilization of the singlet state and to the enhancement of the electrophilicity of phosphorus upon complexation.[33,34]

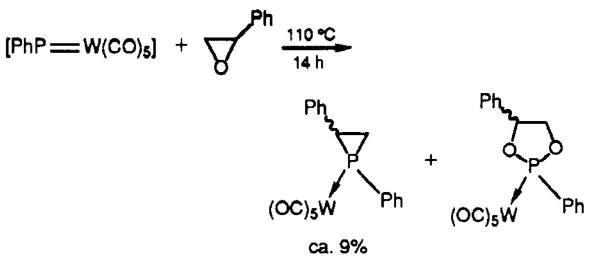
Still another method was introduced by Yoshifuji in 1985.[35] It involves the reaction of lithium silylphosphides with epoxides (eq 11).

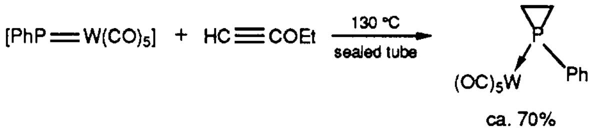

(11)

Phosphiranes were also formed via other routes formally involving the condensation of P and C_2 units. However, the 3-membered ring was either a side product or a transient poorly characterized species. For example, Huttner[36] noticed the formation of phosphiranes in the reaction of an aminodichlorophosphine with $Na_2M_2(CO)_{10}$ in THF (eq 12). The tungsten complex was characterized by X-ray crystal structure analysis. The molecule of ethylene involved in formation of the ring comes from decomposition of THF after α-metalation.

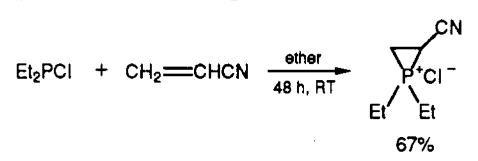

(12)

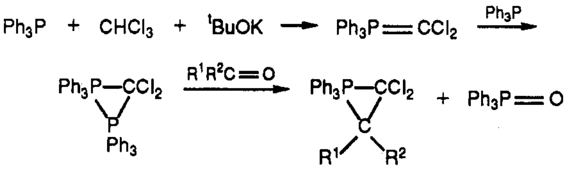
Phosphiranes were also obtained in the reaction of terminal phosphinidene complexes (eq 6) with oxiranes[37] (eq 13) or ethoxyacetylene[38] (eq 14). At lower temperature in the second case, the main product of the reaction is the 3,4-bis(ethoxyphosphole) complex formed via a formal [1+2+2] cycloaddition between the phosphinidene complex and the alkyne.


(13)

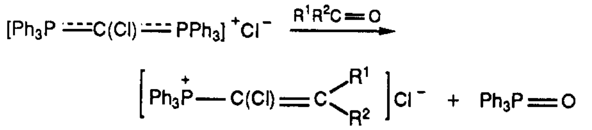

(14)

Phosphiranes were also mentioned in two earlier works. First, Gundermann and Garming described a 1:1 adduct between diethylchlorophosphine and acrylonitrile[39] (eq 15). This crystalline water-sensitive adduct was characterized by Cl and P elemental analysis, IR, and ^{1}H NMR spectroscopy. Its definitive formulation as a phosphiranium salt would need more data. The same statement can be made concerning the work of Indian chemists[40–43] who proposed the following synthetic scheme on the basis of very limited evidence (IR and elemental analysis):

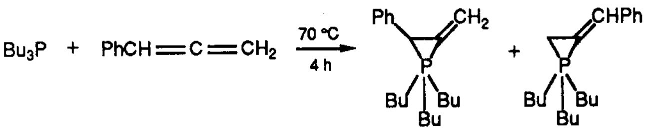

(15)


(16a)

According to a thorough investigation of the CCl_4/PPh_3 system by Appel and his group,[44] the reaction of $Ph_3P{=}CCl_2$ with triphenylphosphine in fact gives the stable [chloro(triphenylphosphoranylidene)methyl]triphenylphosphonium chloride. Thus, the correct scheme is probably as follows:

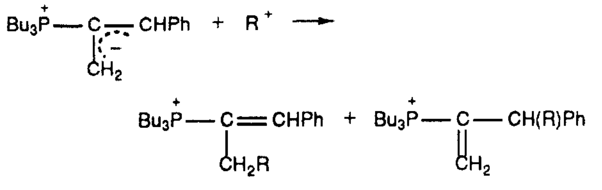

(16b)

It must be pointed out here that all the available data (see later) indicate that both phosphiranium salts and pentacoordinate phosphiranes are, normally, highly unstable species. Thus, a more recent work of Russian chemists[45] must also be taken with care (eq 17). These species were allowed to react with HBr and MeBr to give open-chain phosphonium salts. A delocalized zwitterion could also explain the formation of these products (eq 18).


(17)

2. From PC and C Units

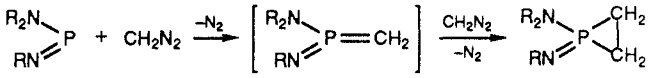
The availability of phosphaalkenes allowed the development of another route to the phosphirane ring, implying the condensation of a carbenoid species with



(18)

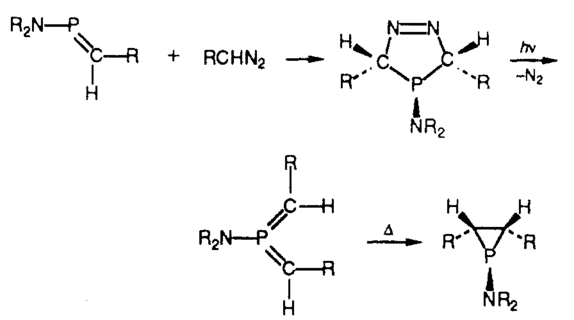
R = H, Me

a phosphorus–carbon double bond. This route was independently proposed by Niecke and Arbuzov. The work of Arbuzov is reported in section 5. The work of Niecke is summarized in eqs 19 and 20. With substituted diazoalkanes, the reaction stops at the phosphorane stage.[47] The electrocyclic closure of the phosphorane involves four electrons and is conrotatory according to the Woodward–Hoffmann rules.[48] This kind of chemistry has been extended by Appel,[50] Märkl,[51] and Regitz.[52] It has allowed the first characterization of stable 1-chlorophosphiranes[51,52,101] (eq 21)



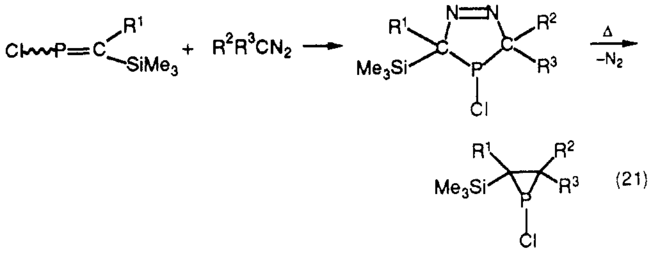
(19)[46]

R = SiMe3



(20)[48,49]

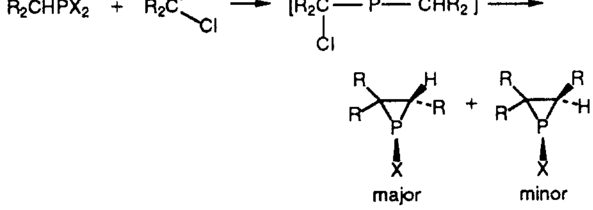
R = SiMe3



(21)

R^1 = Ph, SiMe$_3$; R^2 = H, Me, Ph; R^3 = ^{t}Bu, Ar

(see also eq 57). The source of the one-carbon unit may also be an organometallic carbenoid as demonstrated by Niecke,[53] who used this technique to prepare 1-chloro or 1-bromophosphiranes (eq 22).

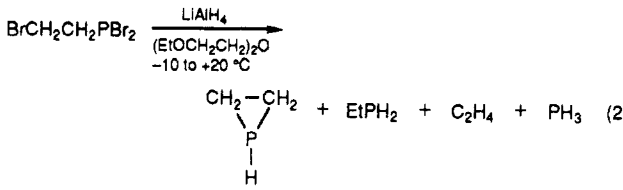


(22)

R = SiMe$_3$, X = Cl, Br, X = Cl, 55%, major : minor = 6:1

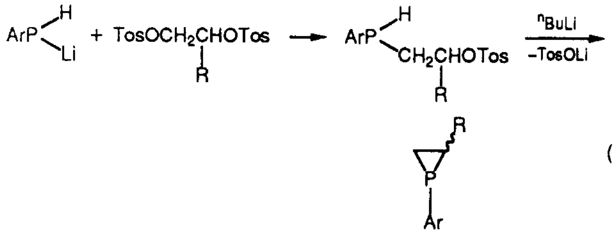
3. By Cyclization of a P–C–C Unit

The pioneering synthesis of phosphiranes by Wagner[4] (eq 1) involves the transient formation of a (β-chloroethyl)phosphine. Besides, Wagner et al.[4] also showed that the reduction of (β-bromoethyl)dibromophosphine by LiAlH$_4$ affords some phosphirane (eq 23).



(23)

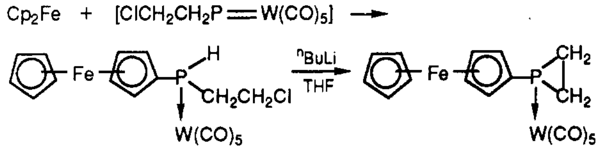
These observations paved the way for another type of phosphirane synthesis, implying the cyclization of a preformed XCCPH unit. Such a route was first proposed by Oshikawa[54] (eq 24).



(24)

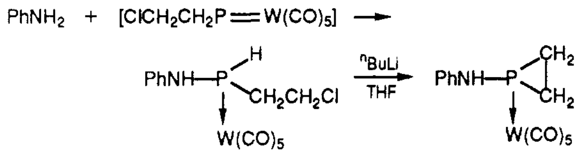
Ar = 2, 4, 6-^{t}Bu$_3$C$_6$H$_2$, R = H, 43%
Ar = 2, 4, 6-^{t}Bu$_3$C$_6$H$_2$, R = Me, 11%
Ar = 2, 4, 6-Me$_3$C$_6$H$_2$, R = H, 60%
Ar = 2, 4, 6-Me$_3$C$_6$H$_2$, R = Me, 43%

The availability of a precursor of [ClCH$_2$CH$_2$P=W(CO)$_5$] via the route depicted in eq 6 allowed derivation of a related approach in the coordination sphere of tungsten (eqs 25 and 26).



(25)

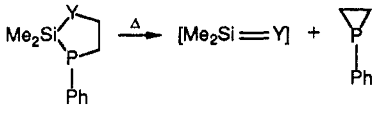
step 1, 31%[55]
step 2, 81%



(26)

step 1, 80%[56]
step 2, 77%

Finally, another related synthesis of 1-phenylphosphirane involving contraction of a five-membered ring containing a PCC unit was briefly mentioned by Satgé[57] (eq 27).

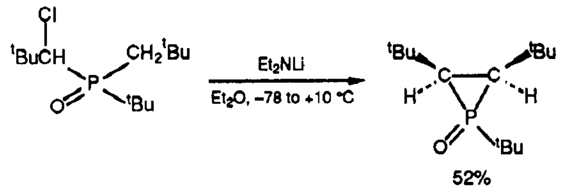


(27)

Y = O, S

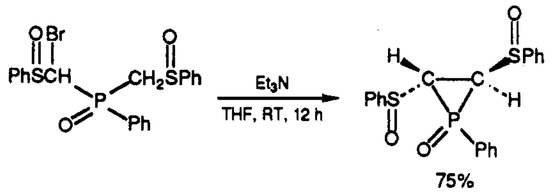
4. By Cyclization of a C–P–C Unit

The last route to build the phosphirane ring was apparent in section 2. The cyclization of bisylides as depicted in eq 20 indeed involves formation of a C–C bond in a C–P–C unit. This scheme was first successfully used by Quast[58,59] (eq 28). The cis configuration of the resulting phosphirane oxide was proposed on the basis of ^{1}H and ^{13}C NMR spectral data. The stability



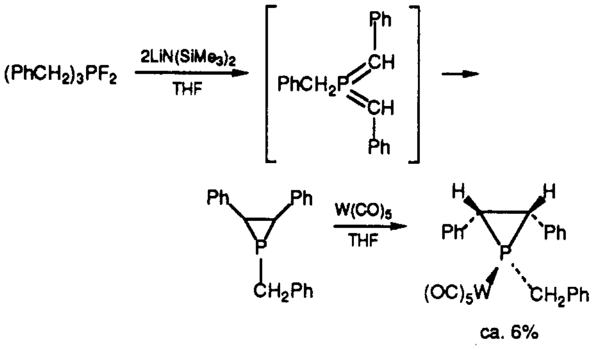
(28)

of this species obviously results from steric protection of the ring by the three bulky *tert*-butyl groups since an analogous 1,2,3-triphenyl-substituted phosphirane oxide was shown to be unstable.[60] More recently, Oshikawa[61] devised a similar scheme using phenylsulfinyl as the sterically protecting group (eq 29). In that case, the phosphirane oxide had the trans configuration.

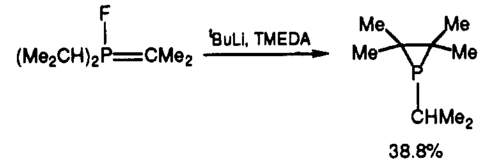


(29)

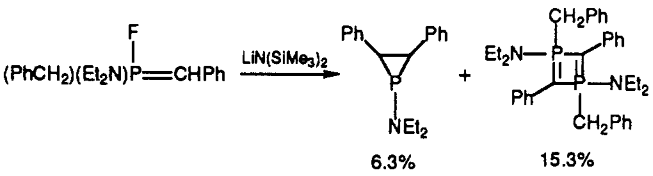
A different approach relying on transient formation of a bisylide as in eq 20 was also recently proposed by Fluck[62] (eq 30). A similar route was investigated some time later by the same group[63] using fluorinated monoylides as the starting products (eq 31). The course of the reaction depends on the substitution scheme of the starting ylide as shown in eq 32. Metalation takes place at either the benzyl or benzylidene group and yields either a phosphirane or a 1,3-diphosphete.



(30)



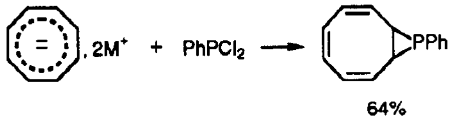
(31)



(32)

5. Synthesis of Polycyclic Phosphiranes

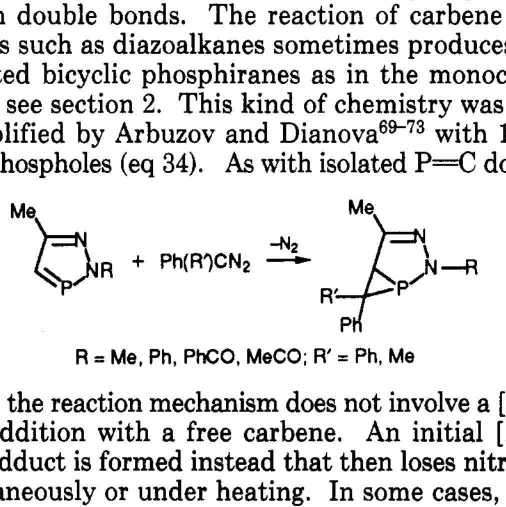
In several instances, specific syntheses of polycyclic phosphiranes have been described. The first one was depicted by Katz in 1966[64] soon after the discovery of the phosphirane ring. It takes advantage of the existence of cyclooctatetraene dianions (eq 33). The method was subsequently extended to a variety of dihalophosphines RPX$_2$ by Märkl[65] (R = alkyl, alkoxy, dialkylamino). Then, Richter[66] repeated the reaction with magnesium cyclooctatetraene and R = *tert*-butyl, cyclohexyl, and menthyl. Very recently, the use of calcium, strontium, and barium derivatives was also proposed.[193] Recently too, Quin[67] used the same scheme to prepare a 9-phosphabicyclo[6.1.0]nona-2,4,6-triene stabilized by the very bulky 2,4,6-tri-*tert*-butylphenyl substituent at phosphorus. Finally, the phenyl derivative was also mentioned in an earlier paper[68] describing an improved procedure for the preparation of potassium cyclooctatetraenide.



(33)

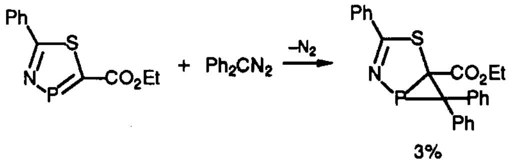
M = Li, K

Another preparation of bicyclic phosphiranes takes advantage of the ready availability of delocalized phosphorus heterocycles with accessible phosphorus–carbon double bonds. The reaction of carbene precursors such as diazoalkanes sometimes produces the expected bicyclic phosphiranes as in the monocyclic series; see section 2. This kind of chemistry was first examplified by Arbuzov and Dianova[69–73] with 1,2,3-diazaphospholes (eq 34). As with isolated $P{=}C$ double bonds, the reaction mechanism does not involve a [2+1] cycloaddition with a free carbene. An initial [2+3] cycloadduct is formed instead that then loses nitrogen spontaneously or under heating. In some cases, such an adduct was fully characterized.[74] A similar reaction was recently performed with a 1,3,4-thiazaphosphole,[73] although in very low yield (eq 35).



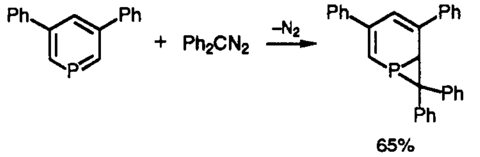
(34)

R = Me, Ph, PhCO, MeCO; R′ = Ph, Me

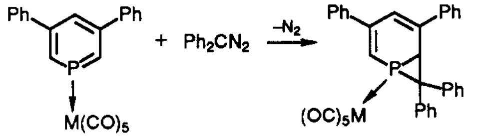


(35)

A more significant extension of this chemistry to free or complexed phosphinines was described by Märkl[75,76] (eqs 36 and 37). In the first case, other diazoalkanes such as CH$_2$N$_2$, MeCHN$_2$, Me$_2$CN$_2$, ..., lead to structurally complex diphosphachiropteradienes[75] whereas,



(36)

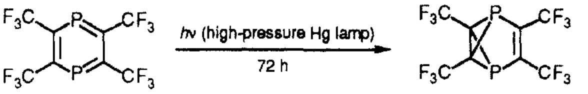


(37)

M = Cr, Mo, W

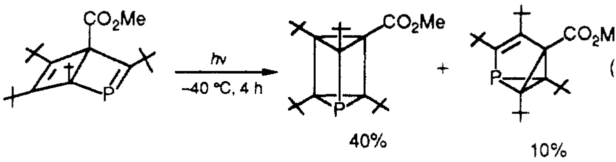
in the second case, the same diazoalkanes lead to the normal [2+3] cycloadducts with a 1,2,4-diazaphospholene ring.[76]

Several other less general syntheses of polycyclic phosphiranes have been reported in the literature. The first one was described by Kobayashi et al.[77-79] and provided the first known access to a phosphorus analogue of benzvalene (eq 38). Much more recently, various other syntheses of polycyclic phosphiranes have been reported. The self-condensation of a 4-pentenylphosphinidene complex[23] has already been depicted in eq 9. On the other hand, Regitz and co-workers[80] have described the first synthesis of a phosphaprismane via a photochemical intramolecular [2+2] cycloaddition. A phosphabenzvalene is formed as a byproduct (eq 39).



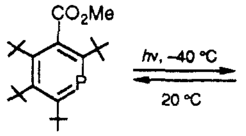
41% from precursor of 1, 4-diphosphinine

(38)

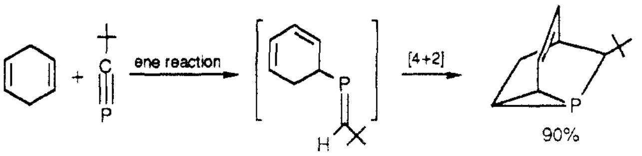


(39)

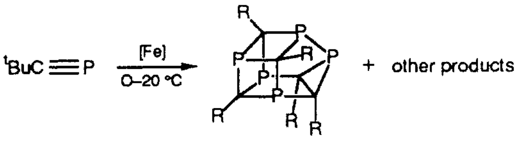
Another isomer of the phosphabenzvalene is made by irradiation of the corresponding phosphinine at low temperature (eq 40). The reverse transformation takes place at room temperature. Subsequently, Regitz et al.[81] also showed that the ene reaction between 1,4-diene and *tert*-butylphosphaalkyne produces a polycyclic phosphirane (eq 41). Finally, the reaction of (η^4-1-methylnaphthalene)(η^6-toluene)iron with *tert*-butylphosphaalkyne affords a very small yield (ca. 1%) of a polycyclic phosphirane[82] (eq 42). The structure of this cage was established by X-ray analysis.



(40)



(41)



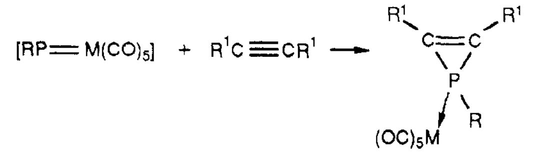
R = ^{t}Bu

(42)

B. Phosphirenes

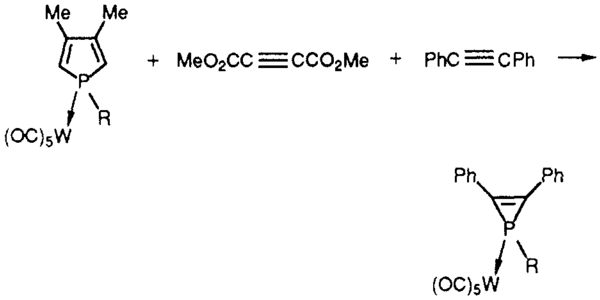
1. From P and C$_2$ Units

The first unambiguous synthesis of the phosphirene ring was reported by Marinetti and Mathey.[6] It relies on the reaction of transient terminal phosphinidene complexes with alkynes (eq 43). The terminal phosphinidene complexes are generated from the appropriate 7-phosphanorbornadiene complexes as shown in eq 6 or from the phosphirane complex when R = Et$_2$N or Cl; see eq 3. It proved possible to combine the synthesis of the 7-phosphanorbornadiene precursors with the [1+2] cycloaddition (eq 44). The decomplexation of some of the phosphirene rings thus obtained has been successfully carried out by an oxidative procedure (eq 45). Mono- and disubstituted alkynes have been used in this synthesis. In one case, a functional alkyne has also been successfully condensed with a terminal phosphinidene complex[86] (eq 46). On the contrary, electron-rich alkynes such as alkoxyacetylenes or ynamines directly give phosphole complexes via a formal [1+2+2] cycloaddition.[38] A related synthesis of 1-(dialkylamino)phosphirene complexes was depicted some time later.[89] It only differs from the previous one by the technique used to generate the transient terminal



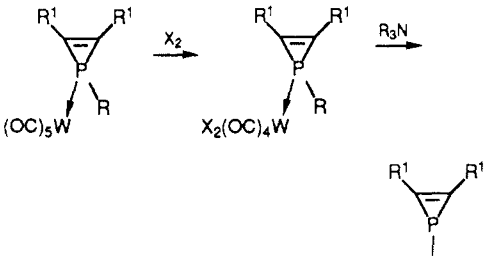
(43)

M = Cr, Mo, W; R = Me,[6] Ph,[6] allyl,[23] butenyl,[23] MeO,[24] (CH$_2$)$_2$,[25] (CH$_2$)$_3$,[25] Et$_2$N,[17] (CH$_2$)$_2$Cl,[83] CH$_2$Cl,[84] CO$_2$Et,[85] CN,[85] ^{t}BuO,[85] 9-fluorenyl,[85] Cl[17]



(44)

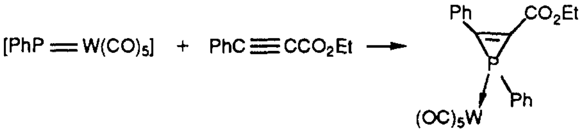
R = Ph, 75%[86]
R = (CH$_2$)$_2$Cl, 70%[83]
R = CN, 40%[85]
R = 9-fluorenyl, 80%[85]



(45)

R = R^1 = Ph, 60%[87]
R = Ph, R^1 = Et, 39%[86]
R = (CH$_2$)$_2$Cl, R^1 = Ph; 65%[88]
R = Cl → –O–, R^1 = Ph, 55%[88]

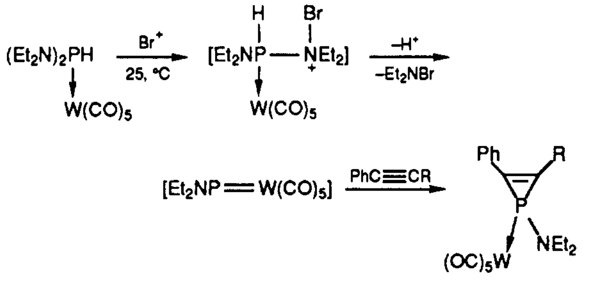
X$_2$ = I$_2$, Br$_3^-$; R$_3$N = *N*-methylimidazole, 2,2′-bipyridyl



(46)

ca. 50%

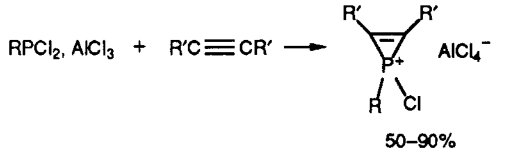
phosphinidene complex (eq 47). The scheme reproduces the postulated mechanism. The bromination is carried out by pyridinium tribromide in the presence of α-picoline. The bromodiethylamine has not been characterized.



(47)

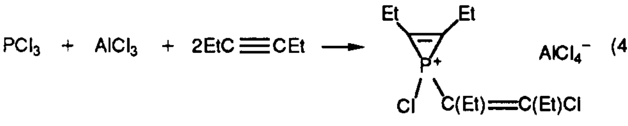
R = H, 60%
R = Ph, 20%

A completely different approach was devised by Hogeveen.[90] It involves the direct reaction of RPCl$_2$–AlCl$_3$ complexes with alkynes (eq 48). The phosphirenium salts thus obtained have been completely characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. They show limited thermal stability. The method was subsequently extended to monohalophosphines by Breslow.[91] The reaction also works with phosphorus trichloride.[92] In that case, the reaction involves a second molecule of alkyne (eq 49).



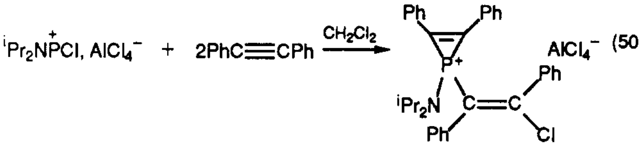
(48)

R = Me, Ph; R′ = H, Me

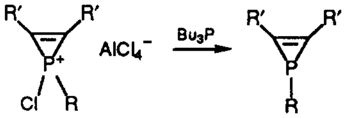


(49)

On another side, Cowley[93] has demonstrated that it is possible to replace the RPCl$_2$–AlCl$_3$ adducts by well-defined phosphenium cations (eq 50). In this case, the phosphirenium salt has been characterized by X-ray crystal structure analysis. In spite of their limited thermal stability, it proved possible to reduce in situ the chlorophosphirenium salts into the corresponding tervalent phosphirenes[92] (eq 51).



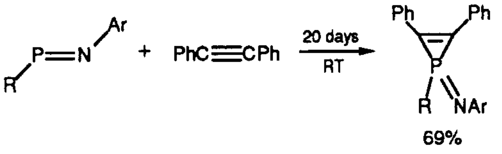
(50)



(51)

R = Ph, Me, ᵗBu, C(Et)═C(Et)Cl; R′ = Ph, Et

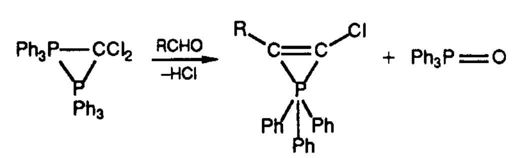
Finally, another approach to tetracoordinate phosphirenes was very recently proposed by Niecke[94] (eq 52). This reaction underlines the carbenic behavior of this iminophosphane.



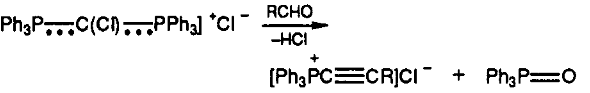
(52)

R = ᵗBu, Ar = 2, 4, 6-ᵗBu$_3$C$_6$H$_2$

Presently, no other reliable route to the phosphirene ring via a C_2 + P condensation is known. Indeed, the work of Indian chemists,[40–43] already discussed in section II.A.1 (eq 16), is probably erroneous. The proposed scheme is depicted in eq 53a, and the alternate explanation is given in eq 53b.

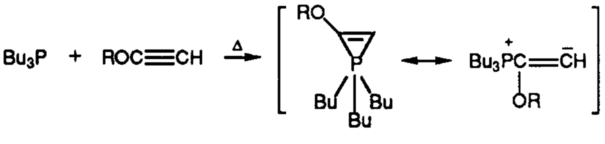


(53a)



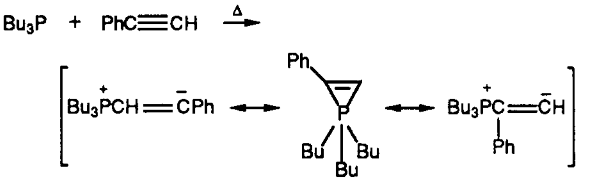
(53b)

On the other hand, mention by Russian chemists[95–98] of 1:1 adducts between tributylphosphine and alkoxy- or phenylacetylenes with pentacoordinate phosphirene structures (eq 54a,b) is not convincing. Indeed, these adducts were not characterized by modern spectroscopic techniques but were only allowed to react in situ with various electrophiles (HBr, MeC(O)Br, MeI, C_3H_5Br, ...) to give open-chain phosphonium salts.



(54)

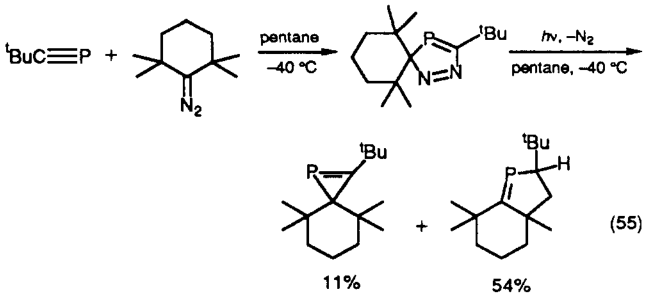
R = Et, Bu



(54a)

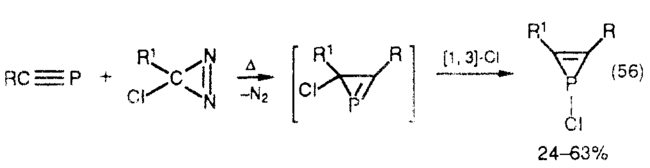
2. From PC and C Units: Synthesis of 2*H*-Phosphirenes

The availability of stable phosphaalkynes opened other possibilities for the synthesis of phosphirenes. It became theoretically possible to prepare 2*H*-phosphirenes by condensation of a carbene precursor with a $P\equiv C$ triple bond. This possibility was proved feasible by Regitz and his group,[99] leading to the discovery of the first stable 2*H*-phosphirene (eq 55). The 1-phos-



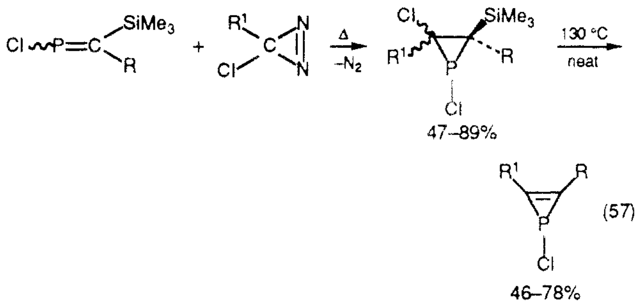
(55)

pha-1-cyclopentene formed as the major product of the photolytic reaction probably results from insertion of the transient carbene into one of the C–H bonds of a vicinal methyl group. The 2*H*-phosphirene has been fully characterized by NMR spectroscopy, and the structure of its $PW(CO)_5$ complex has been established by X-ray analysis. When now chlorocarbene precursors are used in similar condensations, the transiently formed 2*H*-phosphirenes rearrange via formal chlorine 1,3-shifts from carbon to phosphorus to give the first free 1-chlorophosphirenes[100] (eq 56). The same 1-chlorophosphirenes were also obtained in two steps by condensation of the same chlorocarbene precursors with silylated chlorophosphaalkenes[101] (eq 57). Previously, 1-chlorophosphirenes were only known as their $PW(CO)_5$ complexes.[83,89]



(56)

R = ᵗBu, adamantyl, CMe₂Et; R¹ = Ph, ᵗBu, PhO, MeO

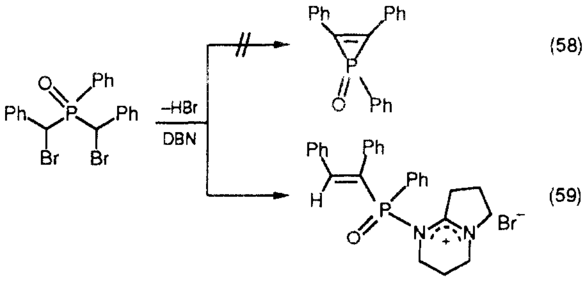


(57)

R = Ph, SiMe₃; R¹ = Ph, OPh

3. By Cyclization of a C–P–C Unit

In 1972, Stille[102] proposed what appeared to be the first synthesis of a stable phosphirene derivative at the moment. The scheme relied on the cyclization of a C–P–C unit as shown in eq 58. The cyclic structure was assigned to the product on the basis of its mass spectrum, its conversion into diphenylacetylene upon pyrolysis at 120 °C, and its opening into (*E*)-(1,2-diphenylvinyl)phenylphosphinic acid upon hydrolysis. However, the product could not be obtained in the pure state, and it was proved later by Quast[103] that the compound was an open-chain derivative containing 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (eq 59). The probable intermediacy of the genuine phosphirene oxide in this reaction nevertheless demonstrates that the cyclization of C–P–C units has some potential in the synthesis of phosphirene derivatives.



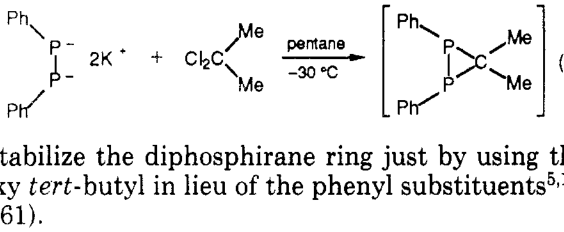
(58)

(59)

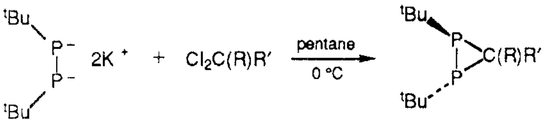
C. Diphosphiranes

1. From P_2 and C Units

The pioneering work of Baudler started with a preliminary observation.[104] An unstable diphosphirane was detected via its high-field ^{31}P nuclear resonance (−122 ppm) in the reaction of 2,2-dichloropropane with K(Ph)PP(Ph)K (eq 60). Subsequently, it proved possible to stabilize the diphosphirane ring just by using the bulky *tert*-butyl in lieu of the phenyl substituents[5,105] (eq 61).



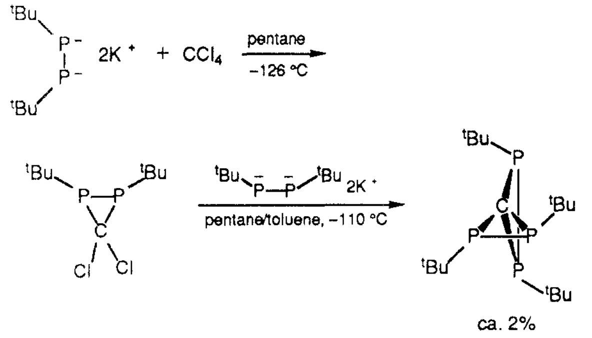
(60)



(61)

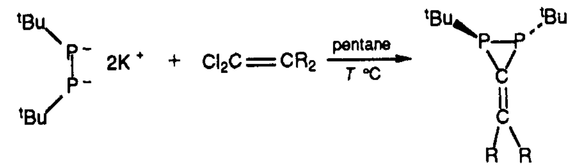
R = R′ = H, 11.3%
R = H, R′ = Me, 19%
R = R′ = Me, 32.8%

It must be stressed here that an apolar medium such as pentane is a prerequisite for the successful formation of the 3-membered ring. The compound with R, R′ = H slowly dimerizes at room temperature to give the corresponding 1,2,4,5-tetraphosphacyclohexane. It soon appeared that this synthetic methodology was very general provided that the bulky *tert*-butyl protecting groups were kept. At low temperature, a similar reaction with carbon tetrachloride affords a low yield of tetraphosphaspiro[2.2]pentane[106] (eq 62). The method was also successfully extended to 1,1-dichloroalkenes,[107] isocyanide dichlorides,[108] and (dichloromethylene)-phosphines[109] (eqs 63–65). With isocyanide dichlorides, two isomers of the corresponding 1,3-diphosphetane-2,4-diimines are also formed. In the latter case, among the interesting byproducts are a phosphinidenetetraphospholane with an exocyclic C=P double bond and a diphosphinyl-substituted phosphindole. As evidenced by the low yields, this kind of chemistry needs some skill to be successfully carried out.



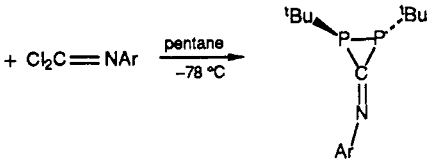
(62)

The availability of stable phosphorus–phosphorus double bonds since the pioneering work of Yoshifuji in 1981 opened another route to the diphosphirane ring via the condensation of P=P units with carbenoids. This possibility was first realized by Huttner[110] with a diphosphene complex (eq 66). Soon afterward, a sim-



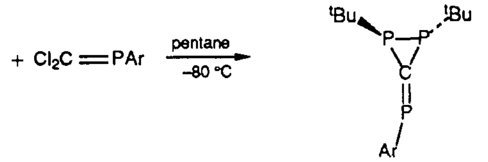
(63)

$R = H$, $T = -78$
$R = Me$, $T = 0$, 13%
$R = 4\text{-}ClC_6H_4$,
$T = -33$, 8%



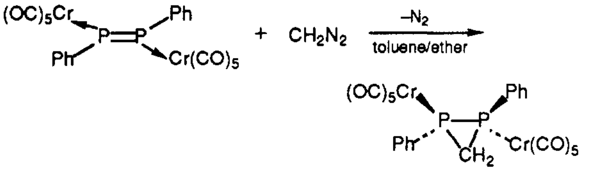
(64)

$Ar = 2,4\text{-}{}^tBu_2C_6H_3$, 4%
$Ar = 2\text{-}{}^tBuC_6H_4$, 5%



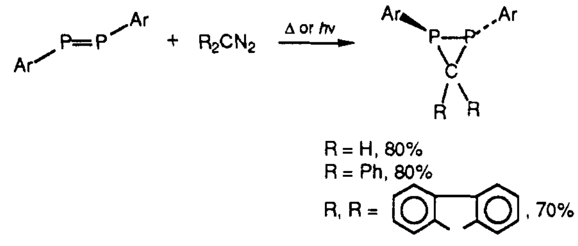
(65)

$Ar = 2,4\text{-}{}^tBu_2\text{-}6\text{-}MeC_6H_2$, ca. 5%



(66)

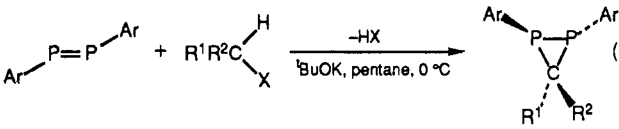
63%



(67)

R = H, 80%
R = Ph, 80%
R, R = , 70%

$Ar = 2,4,6\text{-}{}^tBu_3C_6H_2$

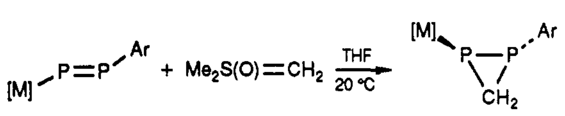


(68)

$R^1 = R^2 = X = Cl$, 80%
$R^1 = R^2 = X = Br$, 80%

$Ar = 2,4,6\text{-}{}^tBu_3C_6H_2$

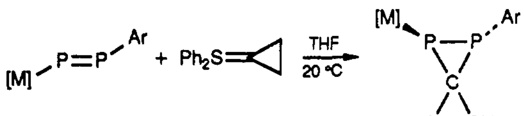
ilar scheme was applied to a free diphosphene by Koenig[111,112] (eq 67). Koenig[112] also showed that organometallic carbenoids could be used for the same purpose (eq 68). Still another carbenoid generated from 1,1-dichloroethane and butyllithium at 0 °C was shown to react with the same diphosphene to give the corresponding diphosphirane in 75% yield.[113] All these diphosphiranes are thermally stable. The corresponding phosphaalkenes $ArP{=}CR_2$ are obtained as byproducts in every cases. A related chemistry was reported by Weber[114,115] with transition-metal-substituted diphosphenes and sulfur ylides as the carbene precursors (eq 69). 1,2-Diphosphaspiro[2.2]pentanes were also obtained with diphenylsulfonium cyclopropanide[115] (eq 70). A completely different approach, but always involving the condensation of P_2 and C units, was described by Schmidpeter.[116,117] With this approach, triphosphenium salt is allowed to react with dichloromethane (eq 71). Finally, the work of Indian chemists[40–43,118] on pentacoordinate diphosphiranes has already been refuted (see section II.A.1, eqs 16a,b).



(69)

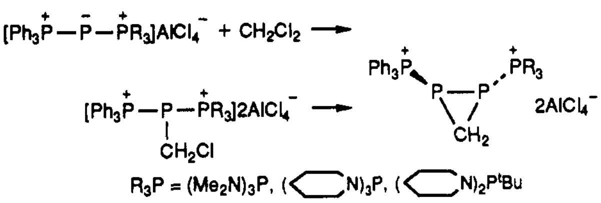
[M] = Fe, 45%
[M] = Ru, 32%

$Ar = 2,4,6\text{-}{}^tBu_3C_6H_2$; $[M] = (\eta^5\text{-}C_5Me_5)(CO)_2Fe$, $(\eta^5\text{-}C_5Me_5)(CO)_2Ru$



(70)

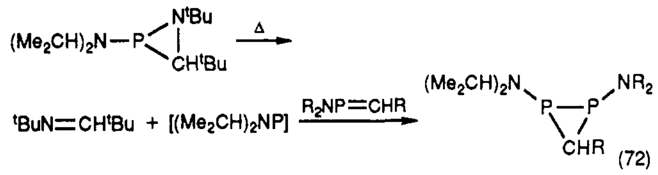
[M] = Fe, 37%
[M] = Ru, 21%



(71)

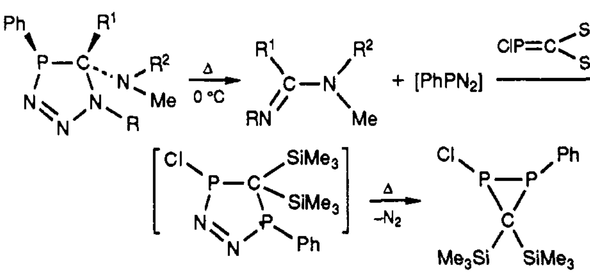
2. From PC and P Units

The condensation of phosphinidenes with phosphaalkenes as a route to diphosphiranes was first mentioned by Niecke[119,120] (eq 72). The experimental details have not been published. Obviously, this route is hampered by the lack of convenient phosphinidene precursors working under mild conditions. A second illustration of this scheme was very recently proposed by Carrié[121] (eq 73). The various intermediates have been postulated on the basis of MNDO calculations. Even more recently, a similar reaction has been described by Niecke in a preliminary communication[122] (eq 74). Finally, another related scheme was depicted

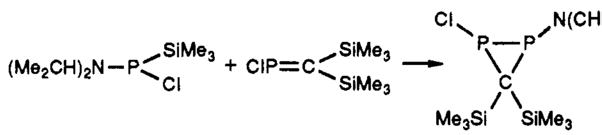


(72)

$R = SiMe_3$

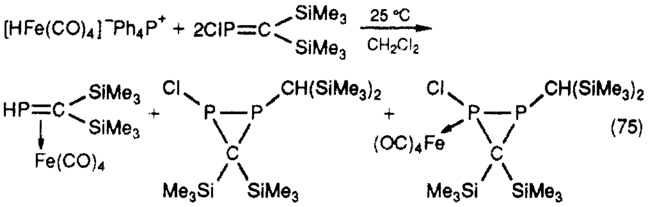


(73)



(74)

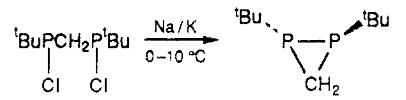
by Majoral and Mathieu[123] (eq 75). Al least formally, this reaction can be viewed as the [1+2] cycloaddition of a terminal phosphinidene complex [$(Me_3Si)_2CHP{=}Fe(CO)_4$] with the starting phosphaalkene. The uncomplexed diphosphirane was characterized by mass and NMR spectroscopy. The base peak in the mass spectrum corresponds to the diphosphirene formed by loss of Me_3SiCl.



(75)

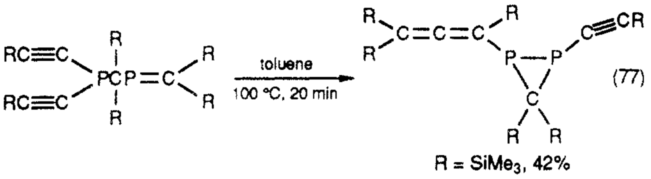
3. By Cyclization of a P–C–P Unit

This approach in eq 76 was very early proposed by Lutsenko.[124] The 3-membered ring was obtained as a 80:20 mixture with its dimer. Much more recently,



(76)

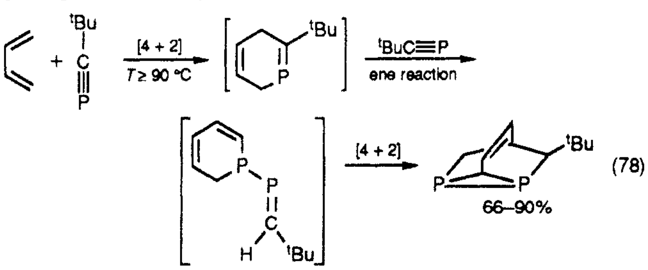
Appel described the pyrolysis of a 2,4-diphospha-1-butene, which yields a diphosphirane via a P–C–P cyclization[125] (eq 77). The proposed mechanism involves an intramolecular C≡C + P=C [2+2] cycloaddition. Apparently, no other use was ever made of this P–C–P approach.



(77)

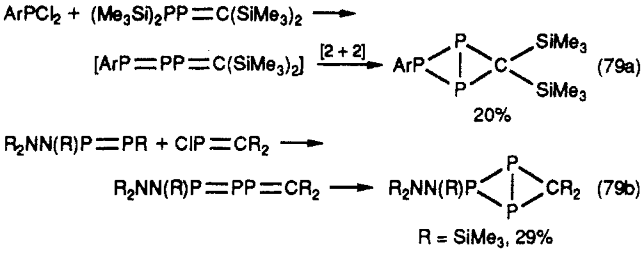
4. Synthesis of Polycyclic Diphosphiranes

As in the case of phosphiranes, several specific syntheses of polycyclic diphosphiranes have been described in the literature. For example, Regitz[81] has studied the reaction of conjugated dienes with phosphaalkynes, which yields polycycles containing a diphosphirane ring (eq 78).

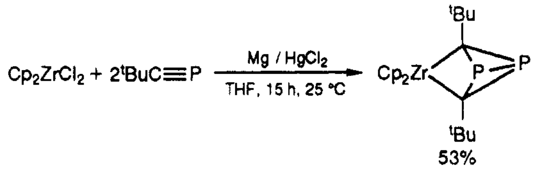


(78)

The parallel between this scheme and eq 41 must be underlined. Triphosphabicyclobutanes were also prepared very recently by Appel[126a] and Niecke[126b] via the isomerization of transient 1,2,3-triphosphabutadienes (eqs 79a,b). The postulated mechanism involves an intramolecular P=P + P=C [2+2] cycloaddition. Several other syntheses of polycyclic diphosphiranes rely on the cyclotelomerization of a phosphaalkyne in the coordination sphere of a transition metal. For example, Binger and Regitz studied the reactions of *tert*-butylphosphaacetylene with zirconocene[127] (eq 80) and with (η^5-pentamethylcyclopentadienyl)(η^6-naphthalene)vanadium[128] (eq 81). In both cases, peculiar structures containing the diphosphirane ring were obtained.



(79a)
(79b)



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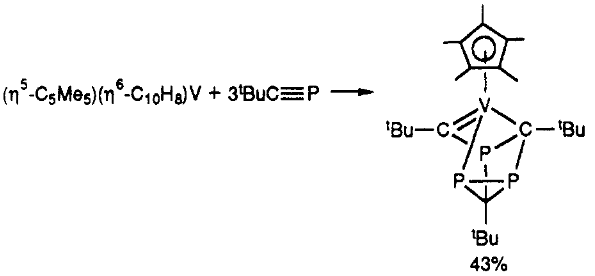
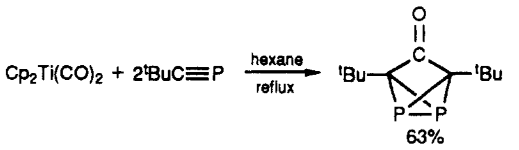


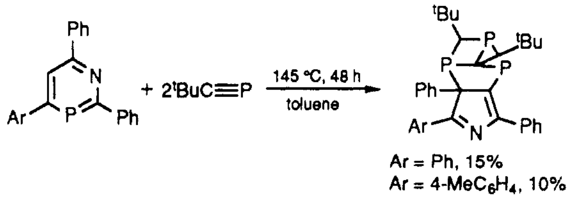
(81)

Both structures were established by X-ray analysis. Another work of Cowley[129] followed the same guidelines, but in that case, the phosphaalkyne telomer spontaneously leaves the coordination sphere of the transition metal (eq 82).



(82)

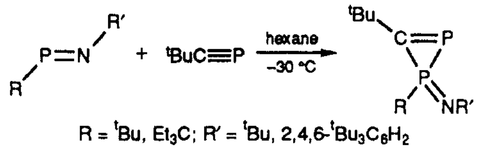
Finally, still another reaction of *tert*-butylphosphacetylene with a 1,3-azaphosphinine was shown by Märkl[130] to give a polycyclic diphosphirane (eq 83). The structure of one of the compounds with Ar = Ph was determined by X-ray analysis. The postulated mechanism is rather complicated.



(83)

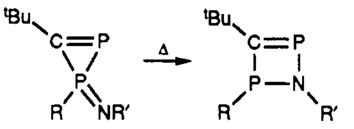
D. Diphosphirenes

At the beginning of 1989, Niecke[131] reported the reaction of carbene-like iminophosphanes with *tert*-butylphosphaacetylene (eq 84). This reaction again un-



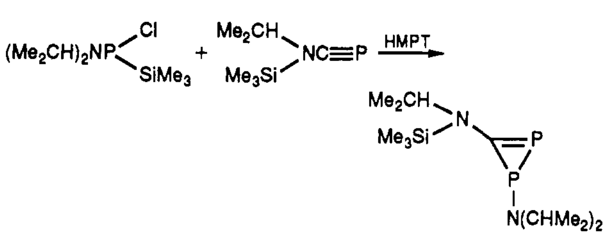
(84)

derlines the parallelism between alkyne and phosphaalkyne chemistry; see eq 52. The 1,2-diphosphirenes thus obtained are unstable, air- and moisture-sensitive red compounds that have been characterized by elemental analysis and mass and ^{31}P NMR spectroscopy. These compounds readily rearrange under heating to give the corresponding 4-membered rings (eq 85). This rearrangement is easily followed by ^{31}P NMR spectroscopy: the high-field resonance of the λ^5-phosphorus between −41 and −43 ppm is drastically shifted downfield (→+160 ppm), and the P–P coupling constant drops from ca. 180 to ca. 68 Hz whereas the resonance of the 2-coordinate phosphorus remains at very low fields (ca. 350 to ca. 330 ppm).

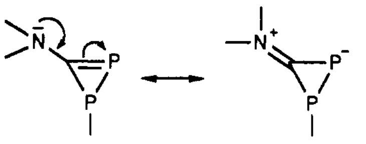


(85)

Even more recently, Niecke[132] allowed an aminophosphinidene precursor to react with an amino-substituted phosphaalkyne and obtained a stable diphosphirene (eq 86). The ^{31}P resonances are observed at −118.7 and +14.9 ppm with ^1J(P–P) = 105 Hz. The X-ray crystal structure analysis indicates a planar P–C–N–Si system with a relatively long P=C double bond (1.702 Å). Obviously, the compound shows some zwitterionic character, which partly explains the stability of the ring (eq 87).



(86)



(87)

III. Physicochemical Data and Theoretical Problems

A. Phosphiranes

1. Structural Data

The available data are collected in Table I. With an intracyclic CPC angle lying ca. 49°, the phosphirane ring is obviously very strained. The high pyramidality of phosphorus suggests a large inversion barrier (which has never been measured until now) and a pronounced s character for the lone pair at phosphorus. The comparison between the various data shows that the ring can "breathe" easily. Whereas the intracyclic CPC angle remains remarkably constant, the internal P–C and C–C bond lengths, respectively, vary in the ranges 1.78–1.89 and 1.46–1.59 Å. Apparently, the complexation of phosphorus stabilizes the ring whereas the presence of bulky substituents at the ring carbons destabilizes it.

2. Spectroscopic Data

The ^{1}H, ^{13}C, and ^{31}P NMR spectra of parent phosphirane have been the subject of a detailed study.[134] The most noteworthy spectroscopic feature of C_2H_4PH is the extreme high-field shift of the ^{31}P resonance: $\delta(^{31}P) = -341$ ppm (vs H_3PO_4). This trend has been found for all the phosphiranes studied so far. In Figure 1, the variations of the ^{31}P chemical shift for a series of RP-substituted phosphiranes are plotted against the corresponding data for $RPPh_2$.[53] This upfield shift of the heteroatom resonance is observed in all the 3-membered heterocycles. For example, it has been found for $\delta(^{15}N)$ in aziridines[135] and $\delta(^{29}Si)$ in siliranes.[136] From another standpoint, it has been shown that a linear relationship exists between the ^{31}P magnetic shielding anisotropy and the intracyclic CPC angle; see Figure 2. As a consequence, a characteristic high value of $\Delta\sigma(^{31}P)$ (566 ppm) has been found for phosphirane 4[137] (see Table I).

Other characteristic NMR features of the phosphirane ring include the following.

(1) Ring carbon resonances at high fields: $\delta(^{13}C)$ = 0.7 ppm for C_2H_4PH[134] and 11.04 ppm for C_2H_4PPh[138] vs 27.15 ppm in $(CH_2)_4PPh$.[138] This shift is typical of other organic 3-membered rings as well.

(2) Low ^1J(P–H) couplings: 158.34 Hz in C_2H_4PH vs 169–217 Hz for acyclic secondary phosphines.[134] According to the authors,[134] this low value reflects the low s character of the P–H bond, but this suggestion does not agree with the results of theoretical calculations on the relationship between ^1J(P–H) coupling and s character.[139]

(3) Highly negative ^1J(P–C) couplings within the ring: −39.7 Hz in C_2H_4PPh vs a typical −14 Hz in $(CH_2)_4PPh$.[138] Absolute values in the range 37.9–82.1 Hz have been recorded for the series of tervalent phosphiranes whose ^{31}P chemical shifts are plotted in Figure 1.[53] On the contrary, much lower absolute values have been recorded for phosphirane complexes and oxides: $(C_2H_4PH)W(CO)_5$, ^1J(P–C) = 10.4 Hz[56] vs 33 Hz in the free species;[134] ^1J(P–C) = 12.5 Hz for 1,2,3-tri-*tert*-butylphosphirane oxide[58,59] (see eq 28) vs 58.8 Hz for the open-chain analogue.[59]

An infrared and Raman study of the parent phosphirane and its deuterated derivatives[140] have yielded some interesting information. The P–C stretching vibrations are shifted toward lower frequencies in the 3-membered ring when compared to analogous vibrations in Me_2PH: 598.1 and 656.7 cm^{-1} vs 664 and 710 cm^{-1} in Me_2PH. This clearly indicates that the P–C bonds are weaker than usual in phosphiranes. On the contrary, the 3-membered ring has no influence on the P–H stretching frequency.[140]

Other spectroscopic studies of the phosphirane ring include IR,[141,142] microwave,[143] and ion cyclotron resonance spectrometry.[144] Thermodynamic functions of phosphirane have been calculated and compared with those of aziridine.[145]

3. Theoretical Calculations

Numerous theoretical calculations have been performed on the phosphirane ring.[29,146–154] The first self-consistent field calculations at the experimental geometry (STO-4-31G) have been carried out by Aue et al.[151] The results have been correlated with the

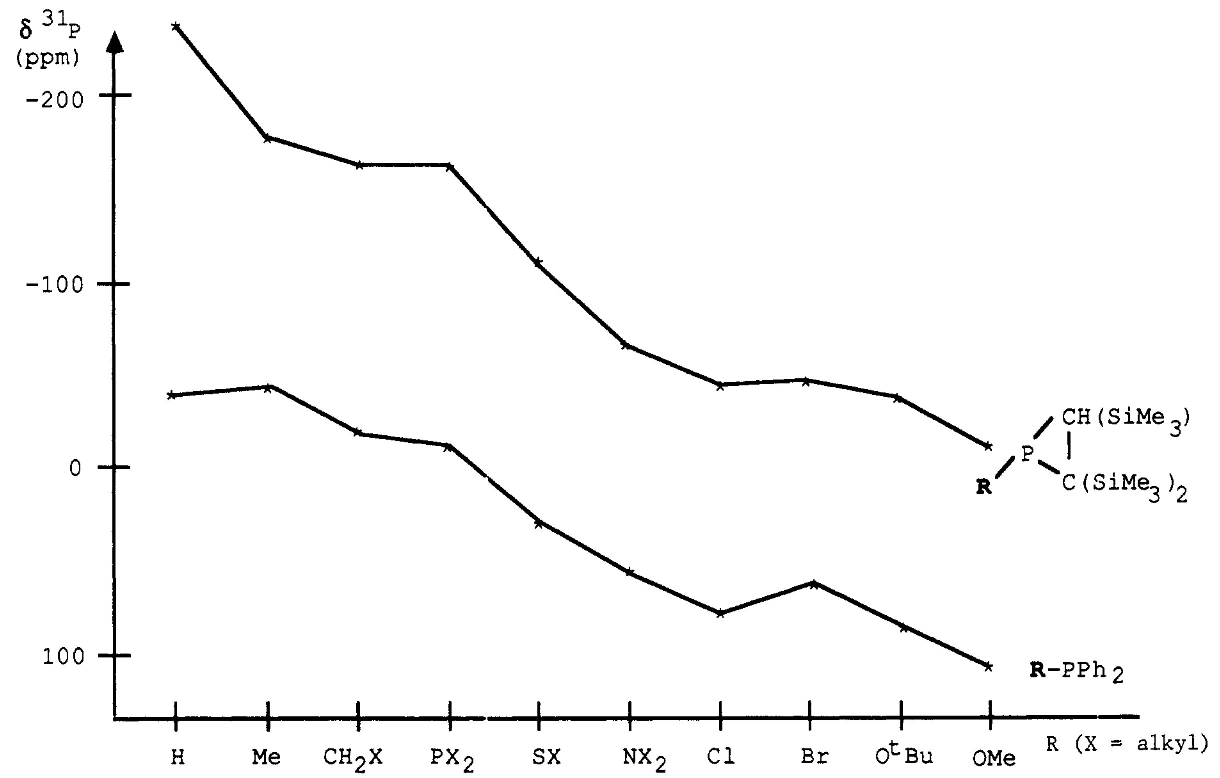


Figure 1. ^{31}P chemical shifts of a series of P-substituted phosphiranes and diphenylphosphanes (reprinted from ref 53; copyright 1989 VCH).

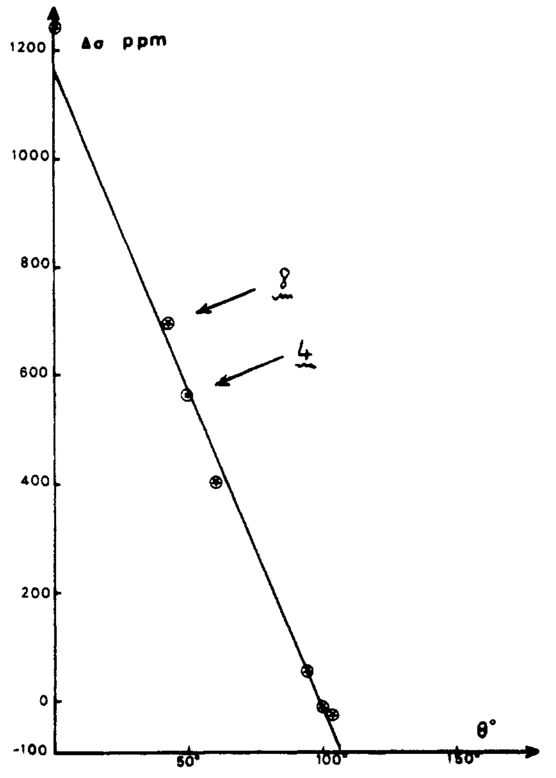
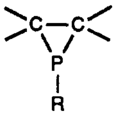
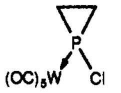
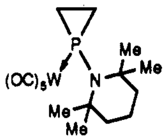
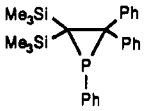
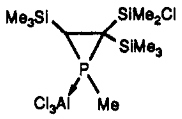
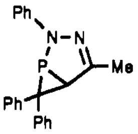
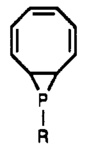
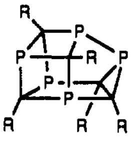


Figure 2. Experimental anisotropy $\Delta\sigma(^{31}P) = \sigma_{11} - \sigma_{33}$ of several phosphines as a function of the strain angle θ at the phosphorus (reprinted from ref 137; copyright 1988 Elsevier).

photoelectron spectra. When dimethylphosphine and phosphirane are compared, the energy of the HOMO that has predominantly lone-pair character in both cases is lower by 15.4 kcal/mol for the heterocycle. The s character of the lone pair increases from 43 to 49%. The second highest occupied orbital (σ_a) is an antisymmetric combination of the p orbitals of the carbon atoms and is well localized in the two intracyclic P–C bonds. The decrease of the CPC angle from 99° in dimethylphosphine to 47.4° in phosphirane increases the corresponding antibonding CC interaction and raises the energy of σ_a from −11.8 eV in Me_2PH to −10.21 eV in phosphirane. A significant shift of electron density from phosphorus to carbons takes place in order to minimize the Coulombic repulsion between the two intracyclic P–C σ bonds. This electron shift together with the increased s character of the lone pair combined with a destabilization of the corresponding $^{+}$PH salt by ring strain explains why the proton affinity of phosphirane is lower by 23.2 kcal/mol than that of dimethylphosphine. The subsequent calculations of Cowley[153] (RHF/6-31G* and MP$_2$/6-31G*) slightly alter this picture. The HOMO of phosphirane is now presented as a mixture of the lone pair on phosphorus (an sp hybrid) with the symmetric combination found in the degenerate 3e′ orbitals of cyclopropane; see Figure 3. In fact, the lone pair at phosphorus is predicted to be partially delocalized over the ring. The replacement of hydrogen by chlorine as the phosphorus substituent leads to a shortening of the calculated P–C bond lengths by 0.013 Å due to a larger charge separation between the phosphorus and carbon centers: $q_p = +0.24$, $q_c = -0.51$ for PH; $q_p = +0.50$, $q_c = 0.53$ for PCl. An attempt to calculate the inversion barrier about phosphorus by constraining the P–H bond to lie within the plane of the ring, perpendicular to the C–C bond, and then optimizing the remaining geometrical parameters led to the dissociation of the molecule into phosphinidene and ethylene.[153] This result clearly shows that the previous estimates of the phosphirane inversion barrier (33,[142] 39.9,[146] 80.4 kcal/mol[155]) must be taken with care. The already-mentioned calculations of Gonbeau and Pfister-Guillouzo[29] mainly led to the conclusion that singlet phosphinidene could react with ethylene to give phos-

TABLE I. Structural Data for Phosphiranes[a]



compd	no.	bond angles, deg			bond lengths, Å			ref
		C-P-C	C-P-R	P-C-C	P-C	C-C	P-R	
	1	47.4	95.2	66.3	1.867	1.502	1.428 (P-H)	14
	2	49.2	102.6 104.3	64.6 66.2	1.78 1.81	1.49	2.037 (P-Cl)	56
	3	48.5		65.3 66.2	1.80 1.82	1.49	1.667 (P-N)	36
	4	49	110.6 115.1		1.87 1.89	1.56		50
	5	51.1	112.7 113.9	63.7 65.2	1.797 1.820	1.559	1.818 (P-C)	53
	6	47.8	88.2 101.1	65.7 66.5	1.87 1.88	1.52	1.72 (P-N)	133
 R = Ph$_2$C(C$_5$H$_4$N-2)	6a	47.1	105.8 108.9		1.813 1.842	1.460	1.951 (P-C)	193
 R = ^{t}Bu	7	49.7		65.2		1.588	2.175 (P-P)	82

[a] All data are from X-ray crystal structure analyses except for the parent species (microwaves).

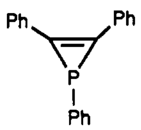
phirane without activation energy. Other series of calculations tried to predict the values of the ^1J(C-C) and ^1J(C-H) couplings in phosphirane and phosphirene[156] or the structure and stability of the phosphiranium cation.[157]

B. Phosphirenes

1. Structural, Spectroscopic, and Theoretical Data

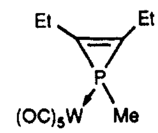
Several structural studies of the phosphirene ring have been carried out. The corresponding data are collected in Table II. As phosphiranes, phosphirenes are characterized by a very small CPC intracyclic angle in the range 42-46°. The phosphirene ring is also able to "breathe" as its saturated analogue: intracyclic P—C and C═C bond lengths, respectively, vary in the ranges 1.71-1.82 and 1.30-1.36 Å. Apparently, these ranges are as large as in the phosphirane case, but a direct comparison is inappropriate because no phosphiranium salt nor pentacoordinate phosphirane is known.

As a result of the smaller CPC intracyclic angle, the ^{31}P nucleus of phosphirenes tend to resonate at higher field than that of comparable phosphiranes. For example, for (Ph$_2$C$_2$PPh)W(CO)$_5$: $\delta(^{31}P) = -161.4$ ppm[6] and for (Ph$_2$C$_2$H$_2$PPh)W(CO)$_5$ $\delta(^{31}P) = -120.8, -127.5$, or -143 ppm according to the isomer.[21] For the same reason, the ^{31}P magnetic shielding anisotropy is higher for phosphirenes than for phosphiranes; e.g., $\Delta\sigma(^{31}P) = 694$ ppm for 8[161] (Table II; Figure 2). As tervalent phosphiranes, tervalent phosphirenes are also characterized by a huge intracyclic ^1J(C-P) coupling constant that drastically decreases when the phosphorus coordination number increases from 3 to 4:



8

^1J(P-C ring) = 43.9 Hz[87]



^1J(P-C ring) = 13.4 Hz[6]

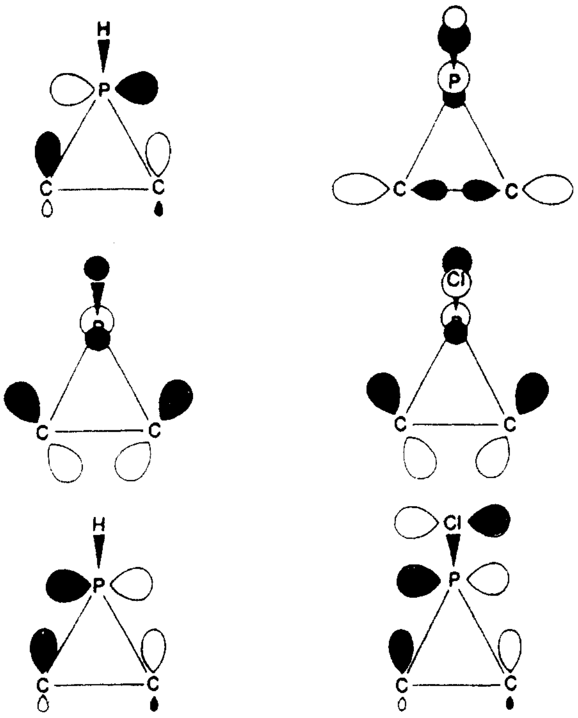
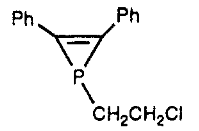
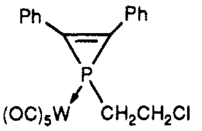


Figure 3. Molecular orbitals for $HPCH_2CH_2$ (left) and $ClPCH_2CH_2$ (right): top, LUMO; middle, HOMO; bottom, second highest MO (reprinted from ref 153; copyright 1988 American Chemical Society).

This trend is even greater for the external ^1J(C–P) coupling:



^1J(P–CH$_2$) = 57.4 Hz[88]



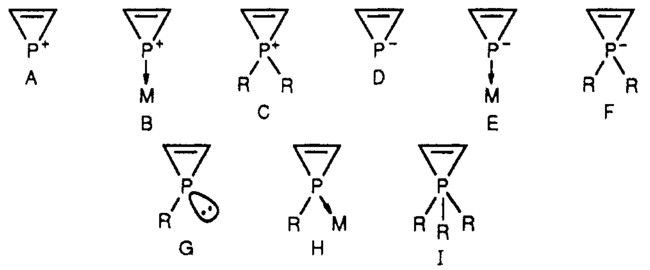
^1J(P–CH$_2$) = 0.8 Hz[83]

The phosphirene ring has been studied from a theoretical standpoint by Gonbeau and Pfister-Guillouzo.[162] The results of this study are graphically depicted in Figure 4. The ring is considered as the combination of a phosphinidene unit and a C≡C triple bond. The most significant orbital of this system is the second highest occupied molecular orbital $p^*_{(P)} + \pi^*_2$(C≡C), which can be viewed as an asymmetric combination of the two intracyclic P–C bonds (as in phosphirane). The occupancy of this orbital corresponds to an electronic transfer from the heteroatom into one of the antibonding orbitals of the former C≡C triple bond. This σ delocalization weakens the C=C bond. It depends on the respective energetic levels of $p^*_{(P)}$ and π^*_2(C≡C). A similar description is valid for all the heterocyclopropenes, XC_2H_2. The higher the electronegativity of X, the lower the energy of $p^*_{(X)}$, the higher the gap between $p^*_{(X)}$ and π^*_2(C≡C), and the lower the σ delocalization from X to C=C and the stability of the heterocyclopropene. This picture explains well why thiirenium salts should be less stable than phosphirenes and phosphirenium salts less stable than silirenes.

On the other hand, the enormous stabilizing effect of complexation on the phosphirene ring has been rationalized as follows:[33] The destabilization of the ring by the 4-electron interaction between the lone pair at phosphorus and the occupied π orbital of the C=C bond is weakened upon complexation. Then, the level of $p^*_{(P)}$ is raised when the phosphinidene unit is bonded to a transition metal. Thus, the σ delocalization increases. Table II indeed shows a lengthening of the C=C bond in phosphirene complexes.

2. *Aromaticity Problem*

One of the most intriguing problems in phosphirene chemistry is the question of phosphirene aromaticity or antiaromaticity. At first sight, phosphirenyl cations (A), their complexes (B), and phosphirenium cations (C)



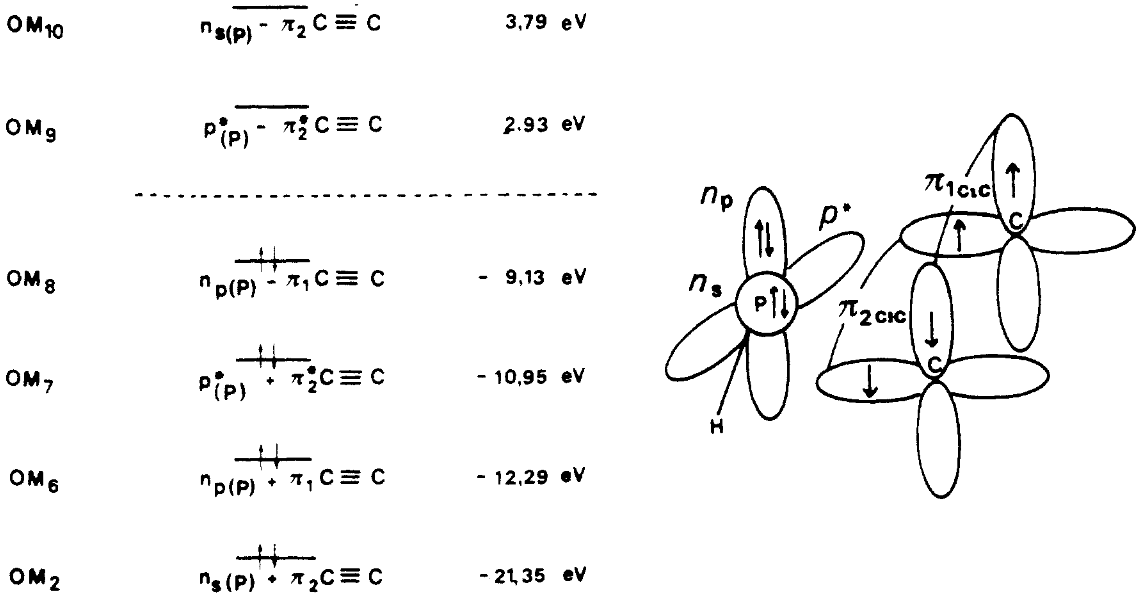
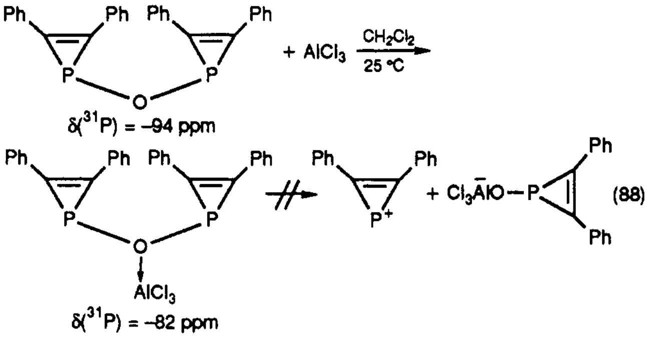


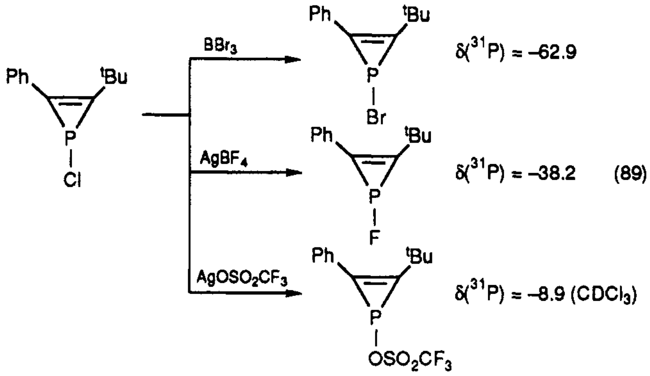
Figure 4. Molecular orbitals of phosphirene (reprinted from ref 162; copyright 1985 CDR).

could be aromatic species. On the contrary, phosphirenyl anions (D), their complexes (E), and phosphirenium anions (F) could be antiaromatic species. The situation is still different in tervalent phosphirenes (G), their complexes (H), and pentacoordinate phosphirenes (I). These questions are far from being solved. What follows is a summary of the few indications that can be found in the literature concerning these problems. Apparently, the aromaticity of phosphirenyl cation (A) is weak. Indeed, the interaction of $AlCl_3$ with bis(phosphirenyl) ethers yields stable complexes via their oxygen atom; no dismutation is observed[88] (eq 88).



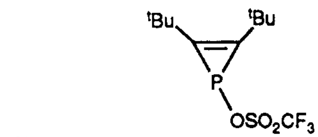
(88)

On the other hand, the reaction of 1-chlorophosphirenes with BBr_3, $AgBF_4$, or $AgOSO_2CF_3$ give the covalent 1-bromo-, 1-fluoro-, or 1-[[(trifluoromethyl)sulfonyl]oxy]phosphirenes[158] (eq 89). In all these



(89)

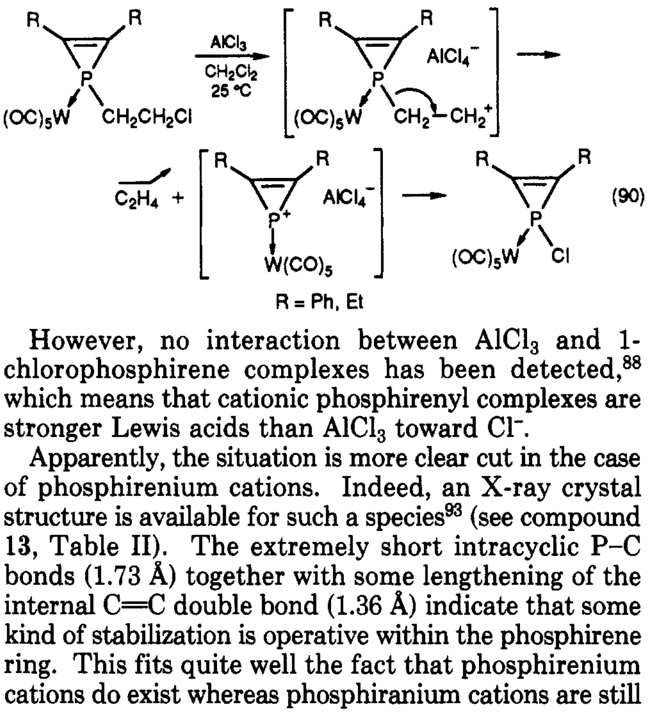
compounds, the absolute value of the ^1J(P–C ring) coupling constants are very high (60–70 Hz) but the covalent nature of the 1-fluorophosphirene is easily established by the huge ^1J(P–F) coupling (1062 Hz). The only point suggesting the possibility of a limited ionization in such compounds is the great sensitivity of the ^{31}P chemical shift of the 1-[(trifluoromethyl)sulfonyl]oxy derivatives to the nature of the solvent. For example



δ(^{31}P) = −8.5 (CCl_4), +6.3 ($CHCl_3$), +13.4 (CH_2Cl_2)[158]

At this point, it must be mentioned that the first ab initio calculations (HF, MP2, MP3, MP4SDQ/6-31G*) on the phosphirenyl cation ($C_2H_2P^+$) have been published very recently.[163] The cyclic structure is the most stable isomer. The reaction of P^+ with acetylene is predicted to be exothermic. The preferred calculated geometry (P–C = 1.728 Å and C–C = 1.350 Å (MP3/6-31G*)) suggests a strong aromaticity, but the author of the paper has not specifically discussed this question.

The situation also appears somewhat unclear for the complexes of phosphirenyl cations (B). The synthesis of 1-chlorophosphirene complexes from the corresponding 1-β-chloroethyl derivatives via the loss of ethylene[83] (eq 90) implies some stabilization of the cationic phosphirenyl complexes, which serves as a driving force for this abnormal reaction.

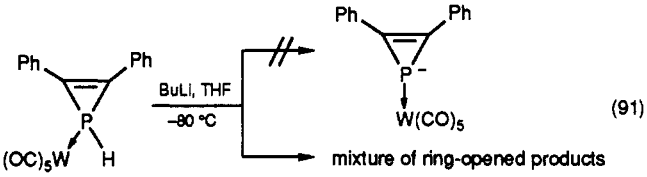


(90)

However, no interaction between $AlCl_3$ and 1-chlorophosphirene complexes has been detected,[88] which means that cationic phosphirenyl complexes are stronger Lewis acids than $AlCl_3$ toward Cl^-.

Apparently, the situation is more clear cut in the case of phosphirenium cations. Indeed, an X-ray crystal structure is available for such a species[93] (see compound 13, Table II). The extremely short intracyclic P–C bonds (1.73 Å) together with some lengthening of the internal C=C double bond (1.36 Å) indicate that some kind of stabilization is operative within the phosphirene ring. This fits quite well the fact that phosphirenium cations do exist whereas phosphiranium cations are still unknown and, in any case, are probably highly unstable. However, a predominant Hückel-type 3d–2p π interaction seems difficult to admit since the neutral pentacoordinate species 14 (Table II) appears even more stabilized if the same criteria are used (1.71 and 1.36 Å for the intracyclic P—C and C=C bonds[160]). These observations may be easier to rationalize if using the concept of σ delocalization, which has already been discussed for tervalent phosphirenes (G) and their complexes (H).[33,162]

At the moment, the possible antiaromaticity of anions such as D–F, is still a matter of conjecture since such species have never been characterized. The only available indication in the literature concerns the complexed anions (E). An attempt to metalate a P–H-substituted phosphirene complex led to the opening of the ring even at −80 °C[88] (eq 91). Thus, the instability

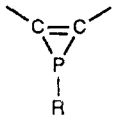


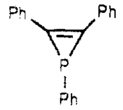
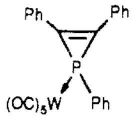
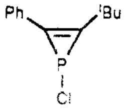
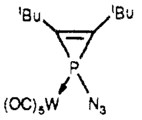
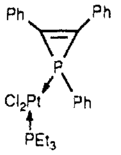
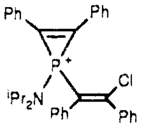
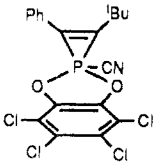
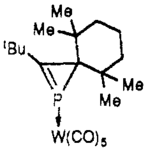
(91)

of E seems well established. Only phase-transfer conditions allowed condensation in basic medium of the PH complex with aldehydes or electron-poor alkenes and alkynes.

As already stated at the beginning of this section, much work remains to be done in order to understand the parameters governing the stability of the various phosphirene derivatives.

TABLE II. Structural Data for Phosphirenes[a]



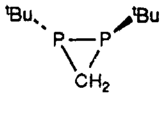
		bond angles, deg			bond lengths, Å			
compd	no.	C-P-C	C-P-R	P-C-C	P-C	C-C	P-R	ref
	8	41.8	104.0 104.4	69.1	1.820 1.821	1.299	1.842 (P-C)	87
	9	42.8	106.6 108.6	68.4 68.7	1.787 1.790	1.307	1.831 (P-C)	6
	10	42.9	103.7 104.2	68.4 68.7	1.781 1.784	1.303	2.166 (P-Cl)	158
	11	44.4	110.0 110.6	66.9 68.8	1.764 1.789	1.342	1.763 (P-N)	158
	12	44.0	109.4 111.7	67.8 68.3	1.776 1.782	1.332		159
	13	46.1		66.9 67.0	1.730 1.732	1.36	1.640 (P-N) 1.799 (P-C)	93
	14	46.8		66.3 66.9	1.709 1.715	1.360	1.784 (P-C) 1.668 (P-O) 1.700	160
	15	49.2		56.7 74.1	1.634 1.881	1.482		99

[a] All the data are from X-ray crystal structure analyses. The structure of the 2*H*-phosphirene **15** has been incorporated in the table for comparison.

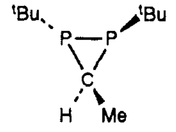
C. Diphosphiranes

Structural, Spectroscopic, and Theoretical Data. Several structural studies of species containing the diphosphirane ring have appeared in the literature. The corresponding results are summarized in Table III. As already noted for phosphirane and phosphirene rings, the diphosphirane ring is very flexible. The ring P-P and P-C bond lengths and the internal P-C-P angle indeed vary in wide ranges: 2.118-2.238 Å, 1.794-1.915 Å, and 71.5-75.2°, respectively. At the bottom of the range, the P-P bond seems to have some double-bond character (compound **22**[129]). As proposed by Dewar,[150] a 3-membered ring can also be viewed as a π complex. It would be perhaps interesting in some cases to think of diphosphiranes as donor-acceptor π complexes between diphosphenes and carbenes. In fact, one of the syntheses of diphosphiranes involves such an interaction (see section II.C.1, eqs 66-70).

As far as NMR spectroscopy is concerned, diphosphiranes behave like phosphiranes and phosphirenes. Some representative data from the work of Baudler are listed below:



$\delta(^{31}P) = -168.8$ ppm[5]
$\delta(^{13}C(CH_2)) = +6.2$ ppm
$^{1}J(P-CH_2) = 53$ Hz



$\delta(^{31}P) = -129.4, -138.5$ ppm[105]
$^{1}J(P-P) = -162.4$ Hz
$\delta^{13}C(CH) = +21$ ppm
$^{1}J(P-CH) = -55.9, -52.0$ Hz
$^{1}J(P-CMe_3) = -39.2, -33.3$ Hz

In line with the observations made on the other 3-membered carbon-phosphorus rings, the ^{31}P and ^{13}C

resonances appear at high fields and the ^1J(C–P) couplings are huge for tervalent phosphorus derivatives.

Diphosphiranes have been studied from a theoretical standpoint by a combination of semiempirical calculations and photoelectron spectroscopy.[152,165] The first spectral bands were assigned to linear combinations of the phosphorus lone pairs and to Walsh orbitals. A strong mixing of these orbitals was predicted. In the case of spiro compounds such as **19**, no spiro interaction could be detected by similar techniques.[166]

IV. Chemical Properties

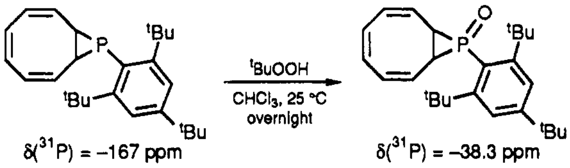
A. Phosphiranes

The first known phosphiranes[2,4,13] were only weakly substituted and displayed great instability. For example, parent phosphirane completely decomposes at room temperature within 24 h to give ethylphosphine, ethylene, and polymeric products.[4] For a long time, this instability precluded any serious investigation of the chemical properties of this ring. In the 1980s, various investigators started to apply to phosphiranes the two stabilization techniques that had already been successfully used in the case of phosphaalkenes and diphosphenes. Both phosphiranes with bulky substituents at phosphorus and phosphirane complexes proved to be perfectly stable. An in-depth study of phosphirane chemistry thus became possible and was rapidly developed.

1. Reactions with Retention of the Ring

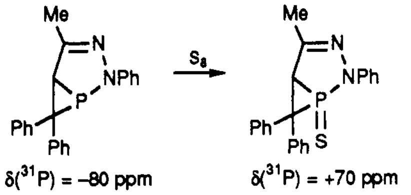
As rationalized on the basis of theoretical arguments, the nucleophilicity of the lone pair at phosphorus is very low. Thus, phosphiranes do not react with acids to give the corresponding $^+$PH salts nor with quaternizing agents (RX) to give the corresponding $^+$PR salts. Decomposition takes place instead. It must be stressed here that no stable phosphiranium salt is known at the moment.

Very recently, Quin[67] was able to perform the oxidation of a sterically protected phosphirane without cleavage of the ring (eq 92).



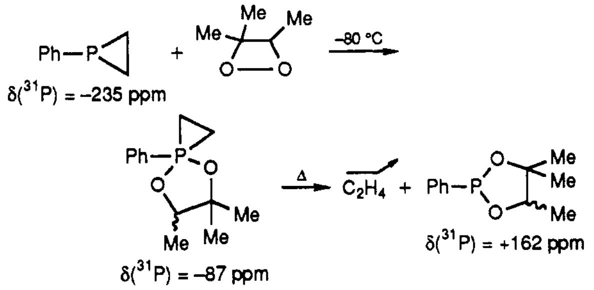
(92)

The oxide shows a ^{17}O chemical shift at high field for a phosphine oxide. The range recorded so far was from 39.6 to 116.4 ppm (vs H_2O). In that case, the ^{17}O resonance appears at +18 ppm. This phosphirane oxide slowly decomposes at room temperature in chloroform solution (90% after 3 days). The only two other known phosphirane oxides[58,61] have been obtained by cyclization of acyclic P=O precursors; see eqs 28 and 29. In the same vein, but some time earlier, Arbuzov[70] reported the synthesis of a phosphirane sulfide by sulfurization of the corresponding tervalent phosphirane (eq 93). In that case, the nitrogen substituent (NPh) probably plays a role in the increased reactivity of the lone pair. The ^{31}P chemical shift of the resulting phosphirane sulfide looks surprisingly "normal". A reorganization of the bicyclic structure upon sulfurization is not excluded.



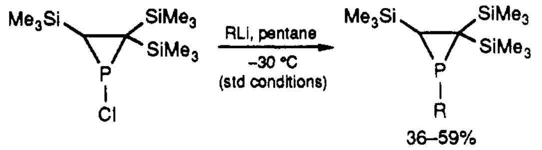
(93)

Another reaction involving a phosphirane lone pair was described by Denney.[167] The only reported pentacoordinate phosphirane was observed at low temperature when a dioxetane was allowed to react with 1-phenylphosphirane (eq 94). The pentacoordinate



(94)

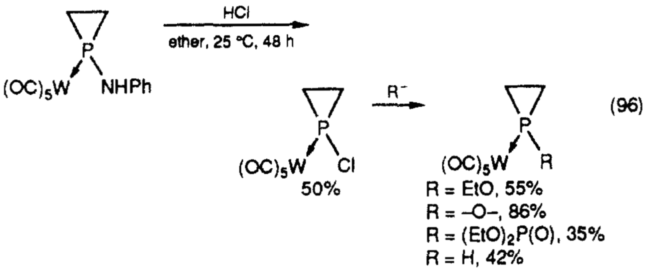
species is stable at −80 °C (no evolution after 2 weeks) but decomposes on warming with loss of ethylene. A similar reaction was observed with 3,4-bis(trifluoromethyl)dithiete, but in that case, the transient pentacoordinate phosphirane decomposes even at −80 °C.[15] In some instances, complexation of a phosphirane lone pair was performed in order to gain additional ring stability. Examples have been described with $Mo(CO)_{3-5}$[168] and $W(CO)_5$.[62] However, in most instances, such complexes with $M(CO)_5$ (M = Cr, W) were directly synthesized from acyclic precursors; see eq 5. The complexing ability of phosphiranes seems to be rather high, probably because their Tolman cone angle is small. Whereas the nucleophilic reactivity of the phosphirane phosphorus is low, conversely its electrophilic reactivity appears to be high. However, if the reaction with a nucleophile is performed without care, the phosphirane ring tends to cleave (see later text). The recent availability of stable hindered 1-chlorophosphiranes[51-53] has allowed numerous substitution reactions to be performed with ring retention. Examples are given in eq 95.[53]



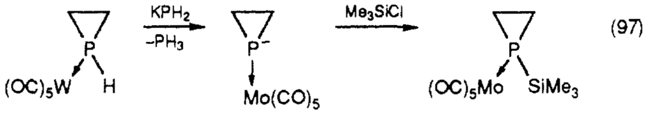
(95)

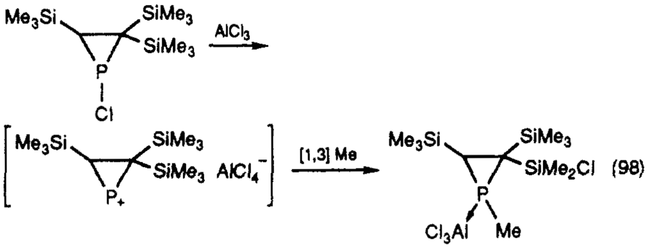
R = Me, ᵗBu, ⁿBu, ˢBu, Me_3SiCH_2, $(Me_3Si)_2CCl$, Et_2N, ^{i}Pr_2N, MeO, ᵗBuO, ᵗBuS, ⁿBu_2P, $(Me_3Si)_2P$, H

The reaction of dry HCl with the 1-aminophosphirane complexes obtained as described in eqs 3[17] and 26[56] has allowed preparation of a stable complex of the parent 1-chlorophosphirane. This complex can also undergo nucleophilic substitutions at phosphorus with mild nucleophiles[56] (eq 96). In that case, the opening of the ring appears to be very easy. Attempts to get stable phosphirane anions (P$^-$) or cations (P$^+$) have been rather frustrating until now. The metalation of the P–H bond of P-unsubstituted phosphiranes by various metalating agents (RLi, K/NH_3)[51,168] has always led to complicated mixtures of acyclic phosphides. The only successful metalation experiment has been carried out



in the coordination sphere of a transition metal[168] (eq 97). On the other hand, an attempt to get a phosphirane cation by reaction of AlCl$_3$ with a 1-chlorophosphirane has led to a curious rearrangement[53] (eq 98). The structural parameters of the final product (5) are given in Table I.

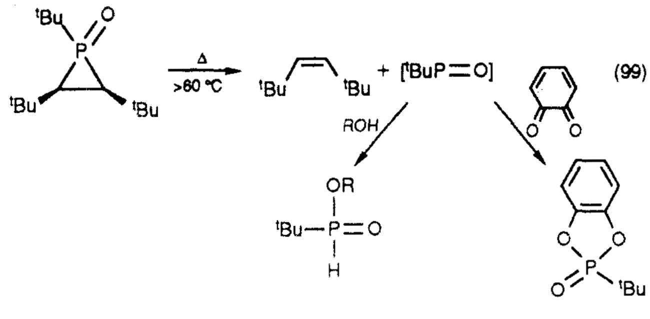




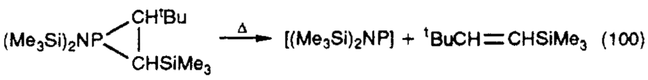
5

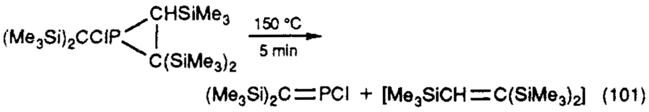
2. *Reactions with Cleavage of the Two P–C Bonds of the Ring*

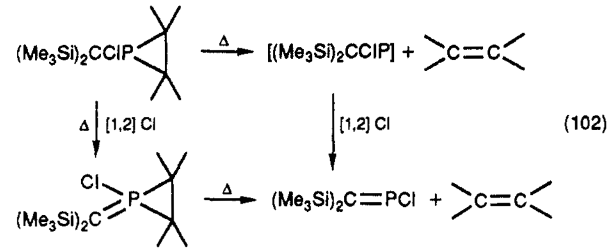
The simultaneous thermal cleavage of the two P–C bonds of the phosphirane ring with the release of an alkene and a phosphinidene fragment was first demonstrated by Quast[169] with the 1,2,3-tri-*tert*-butylphosphirane oxide made according to eq 28. The phosphinidene oxide thus generated was trapped by water, methanol, or *o*-quinones (eq 99). It failed to react with Me$_3$SiC≡CSiMe$_3$, 2,3-dimethylbutadiene, and MeC(O)C(O)Me. The retention of the stereochemistry of the ethylenic fragment suggests a concerted cleavage reaction.



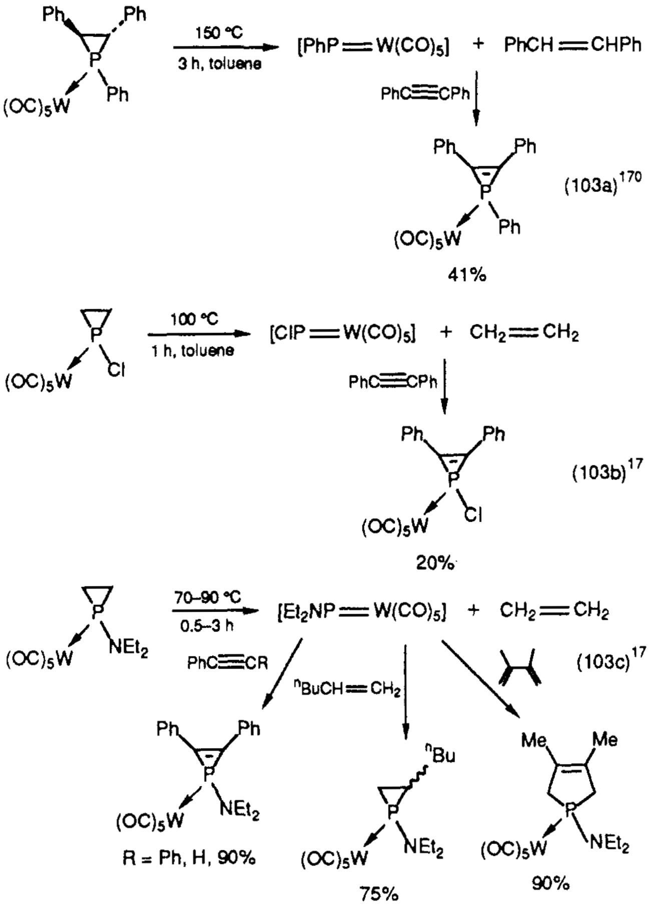
The same possibility was also briefly mentioned by Niecke for a 1-amino-[119] and a 1-chloro[bis(trimethylsilyl)methyl]phosphirane[53] (eqs 100 and 101). In the latter case, the chlorophosphaalkene was characterized by its NMR parameters. Two possible mechanisms were proposed for its formation (eq 102). Finally, the simultaneous thermal cleavage of the two P–C bonds of the phosphirane ring was also demonstrated for a series of phosphirane complexes[17,170] (eqs 103a–c, Scheme I).





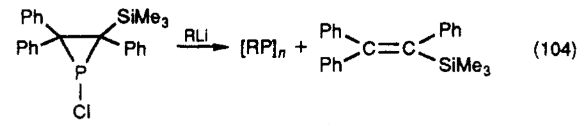


SCHEME I

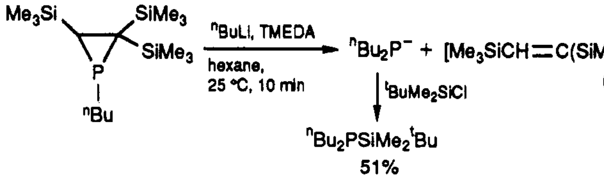


In all cases, the formation of a transient terminal phosphinidene complex was postulated on the basis of trapping experiments. The higher thermal lability of the 1-aminophosphirane complex was assigned to the stabilization of the singlet state of the phosphinidene fragment by the nitrogen lone pair. The thermal cleavage thus becomes symmetry-allowed; see ref 29.

In some instances, the complete collapse of the phosphirane ring was also observed upon reaction with nucleophiles. This was demonstrated by Märkl[51] and Niecke[53] for tervalent phosphiranes (eqs 104 and 105).



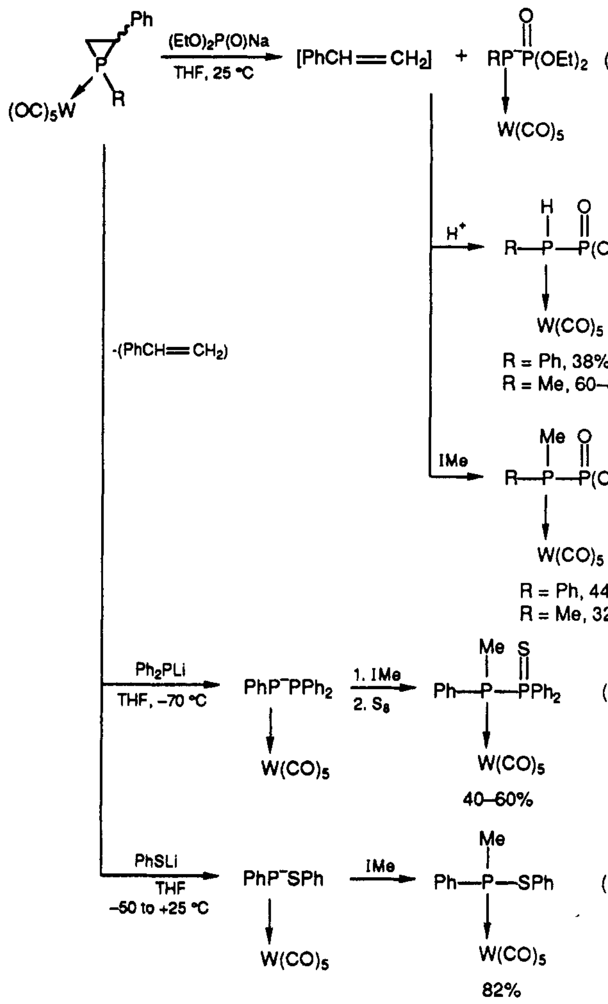
R = Ph, (Me$_3$Si)$_3$C (n = 2), 2,4,6-^{t}Bu$_3$C$_6$H$_2$ (n = 2)



(105)

Apparently, the collapse of the ring in nucleophilic medium is even easier with the P complexes. Several soft nucleophiles were shown to induce the cleavage of the two P–C ring bonds[27] (eqs 106–109, Scheme II).

SCHEME II

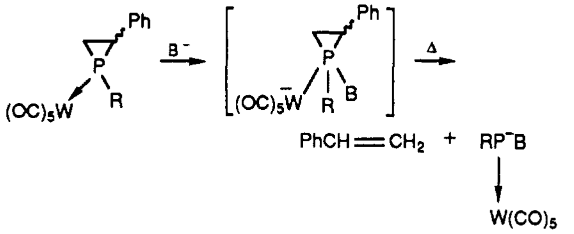


(106)

(107)

(108)

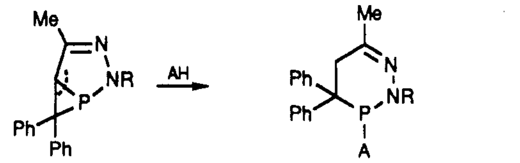
The proposed mechanism involves the formation of a transient pentacoordinate phosphirane that collapses as previously shown in eq 94 (eq 109). With harder nucleophiles such as RO⁻ and R_2N^-, the transient pentacoordinate phosphirane is apparently more stable and the reaction follows another path; see later text.



(109)

3. Reactions with Cleavage of One P–C Bond of the Ring

The cleavage of one of the ring P–C bonds can take place with either protic reagents or nucleophiles. The first possibility was demonstrated by Arbuzov with bicyclic phosphiranes[70,73] (eq 110).

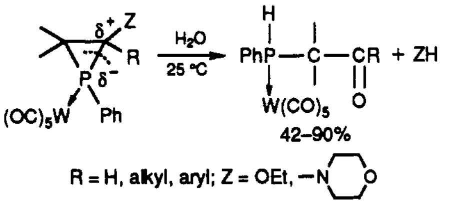


(110)

R = R′ = Me, 81% after 10 days at 25 °C[73]

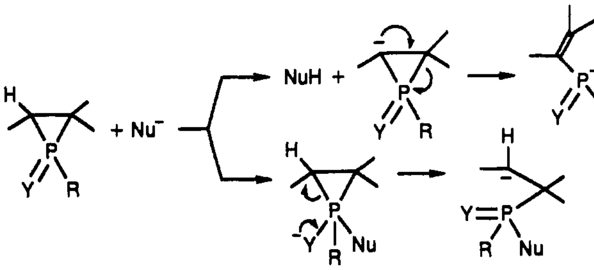
R = Me, Ph, MeC(O), PhC(O); A = R′O, Cl

Once again, it is possible to relate this kind of chemistry to phosphirane complexes. When one of the P–C ring bonds is activated (polarized) by an electron-releasing substituent such as alkoxy or amino, the cleavage takes place by simple hydrolysis at room temperature[21,22] (eq 111). The easy polarization of these P–C ring bonds results from the high energy of the corresponding orbitals; see section III.A.3. It is interesting to note that the polarity of these bonds has been inverted by Z and $W(CO)_5$ (compare eqs 110 and 111).

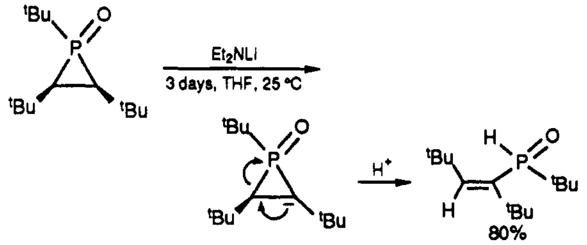


(111)

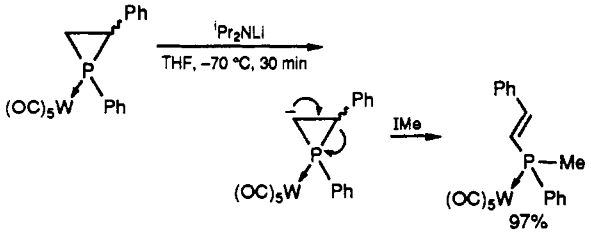
The selective cleavage of one of the P–C ring bonds can also take place either via the abstraction of a proton at a carbon of the ring or via the attack of a nucleophile at phosphorus (eq 112). The path followed depends on the basicity of the nucleophile, its steric bulk, the electron-attracting power of Y, and the steric bulks of R and Y. When these parameters are high, metalation is favored. Such a situation has been depicted by Quast[59] and Marinetti[27] (eqs 113 and 114). The other situation has been illustrated by Richter with vinylphosphiranes[171] and Marinetti with phosphirane complexes[27] (eqs 115–118, Scheme III). The obtention of a cyclic carbene complex in the latter case is especially noteworthy. Why hard nucleophiles such as RO⁻ and



(112)

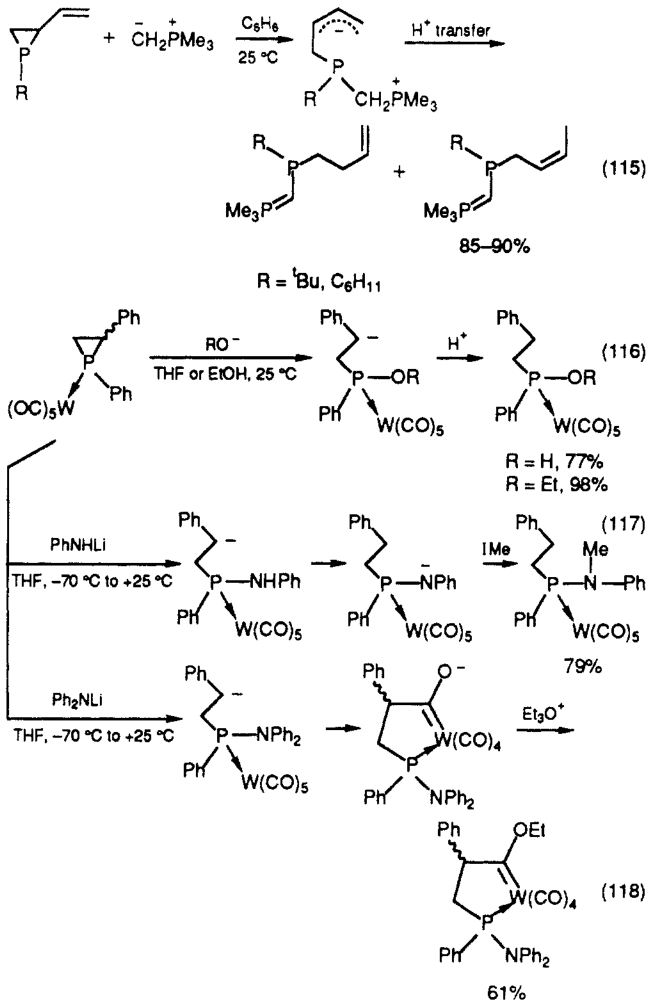


(113)



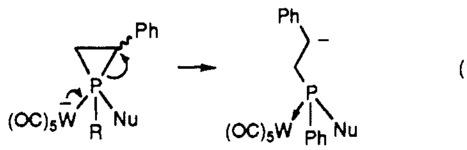
(114)

SCHEME III



(115) (116) (117) (118)

R_2N^- cleave only one P–C ring bond whereas soft nucleophiles such as R_2P^- and $R_2P(O)^-$ cleave both ring bonds (eqs 106–108) is explained by the relative stability of the transient pentacoordinate phosphiranes in the first case (see the work of Denney[15,167] and eq 94). Since the stability is sufficient, the reorganization of the transient phosphoranes can occur (eq 119).

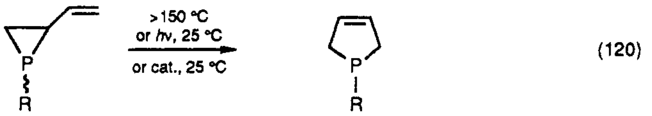


(119)

4. Ring Expansions

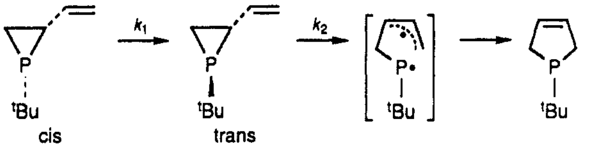
The ring expansions of phosphiranes can occur either via an internal reorganization of the molecule or via an insertion reaction.

The only known intramolecular ring expansion of monocyclic phosphiranes was first described by Richter[18,19] with 2-vinylphosphiranes (eq 120). A thorough kinetic study of the thermal isomerization of the ^{t}Bu derivative at 150 °C was subsequently carried out.[172] Two sequential first-order reactions were detected, and a radical mechanism was proposed (eq 121).



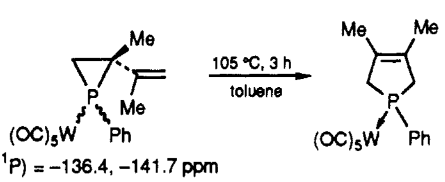
(120)

R = ^{t}Bu, hν, 25 °C, 80%, δ(^{31}P) = −7.2 ppm; Ni(COD)$_2$, overnight, 70%
R = c-C_6H_{11}, Pd(allyl)$_2$, 95%, δ(^{31}P) = −21.1 ppm
R = menthyl, mixture
R = Ph, Pd(methallyl)$_2$, 6 h, 25 °C, 91%, δ(^{31}P) = −26.3 ppm



(121)

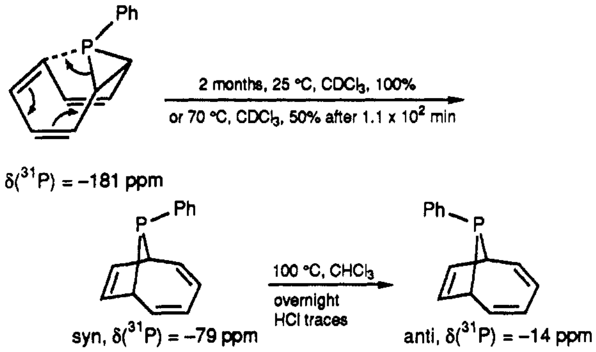
The same thermal rearrangement was found to proceed easily with 2-vinylphosphirane complexes[21] (eq 122).



(122)

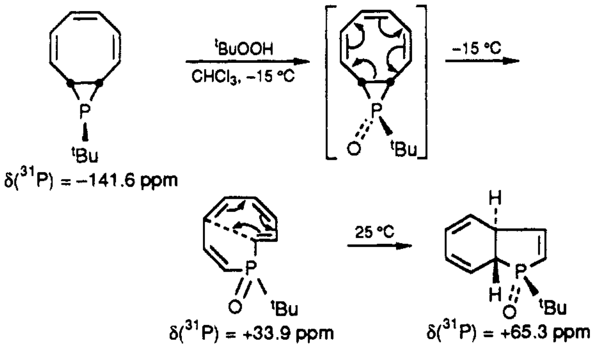
ca. 100% according to ^{31}P NMR; δ(^{31}P) = −5.2 ppm

Several intramolecular ring expansions have also been described with bicyclic phosphiranes. The first one was initially discovered by Katz[64] (eq 123). Quite logically, this [1,5] sigmatropic rearrangement is thermally much easier than the previous one. Much more recently, Quin[67] has performed a similar rearrangement with 2,4,6-^{t}Bu$_3C_6H_2$ as the P substituent (100% conversion after 7 h at 65 °C).



(123)

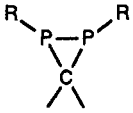
Another very interesting rearrangement of the same bicyclic system was discovered later by Quin.[173-175] Upon oxidation at phosphorus, the C–C bridge is weakened and an electrocyclic opening of the cyclooctatriene ring spontaneously takes place to give the first known C–H-substituted phosphonin oxides, which are stable only at low temperature (eq 124). According to the Woodward–Hoffmann rules this ring opening is conrotatory and leads to a phosphonin oxide with one trans C=C double bond. At room temperature, a subsequent disrotatory ring closure takes place, which gives a dihydrophosphindole oxide with a trans junction

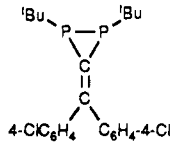
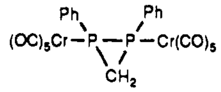
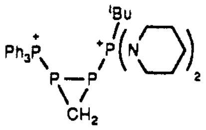
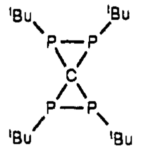
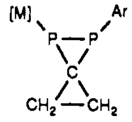
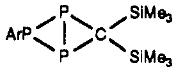
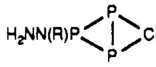
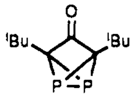
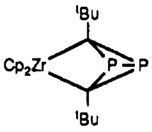
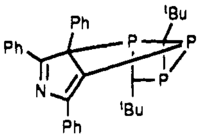
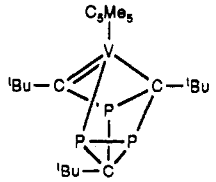


(124)

(also described with P–Ph derivatives)

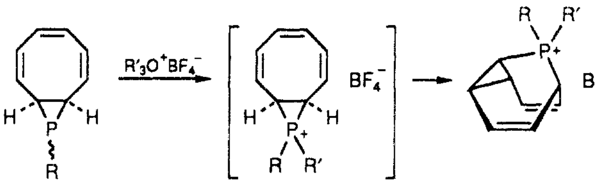
TABLE III. Structural Data for Diphosphiranes[a]



		bond angles, deg			bond lengths, Å			
compd	no.	P–C–P	P–P–C	C–P–R	P–P	P–C	P–R	ref
	**16**	75.2	52.2 52.6	107.7 108.2	2.195	1.794 1.804	1.861 1.883	107
	**17**	71.5	54.2 54.3		2.161	1.85		110
	**18**	73.2	52.9 53.9	96.7 98.5	2.210	1.84 1.87	2.243 (P–P) 2.212	117
	**19**	72.35	53.83		2.175		1.888	164
 [M] = $(\eta^5\text{-}C_5Me_5)Fe(CO)_2$; Ar = 2,4,6-$^tBu_3C_6H_2$	**20**	75.0	52.0 53.0	101.6 111.7	2.206	1.799 1.824	1.921 (P–C) 2.310 (P–Fe)	115
	**21a**				2.136	1.881 1.883	2.231 2.223	126a
 R = $SiMe_3$	**21b**	70.0	55.1		2.158	1.880 1.883	2.215 2.226	126b
	**22**				2.118	1.895 1.897		129
	**23**				2.147	1.900 1.891 1.912 1.886		127
	**24**	73.0	52.6 54.4	85.6 96.4	2.238	1.860 1.903	1.806 1.892	130
	**25**	71.8	52.6 55.6	85.9 87.3	2.206	1.845 1.915	1.937 (P–C) 2.382 (P–V)	128

[a] All the data are from X-ray crystal structure analyses.

(eq 124). Subsequently, Richter[66] found that tervalent 9-R-9-phosphabicyclo[6.1.0]nonatrienes with R = ^tBu or cyclohexyl followed the two preceding paths upon heating to give a mixture of the corresponding *syn*-9-phosphabicyclo[4.2.1]nonatrienes (eq 123) and tervalent *trans*-dihydrophosphindoles (eq 124). Finally, still another reorganization of these decidedly interesting bicyclic phosphiranes was found by Märkl[176] when quaternizing the phosphorus atom (eq 125). The final salts are degenerate Cope systems similar to barbara-

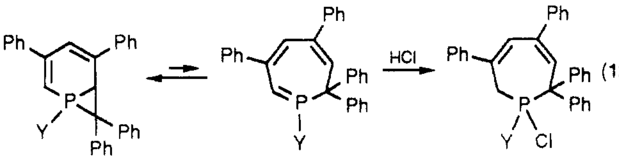


(125)

R, R' = Me; R = ${}^tBu$, R' = Me; R = ${}^tBu$, R' = Et; R = $PhCH_2$, R' = Me; R = Ph, R' = Et

lane. The proposed mechanism involves the initial formation of quaternary phosphonin salts. It must be noted here that 9-phenyl-9-phosphabarbaralane was previously obtained by Katz[177] via the photolysis of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene.

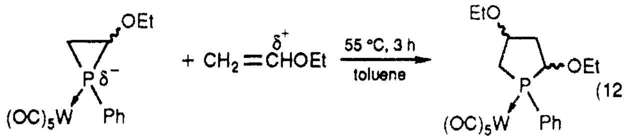
The last internal rearrangement of a bicyclic phosphirane described in the literature concerns 1-phosphanorcaradienes. Märkl[76] has shown the existence of an equilibrium between these species and the corresponding 2*H*-phosphepines (eq 126). The equilibrium is completely shifted to the left but can be displaced to the right by trapping 2*H*-phosphepines with HCl or diazocompounds.



(126)

Y = lone pair, $Mo(CO)_5$

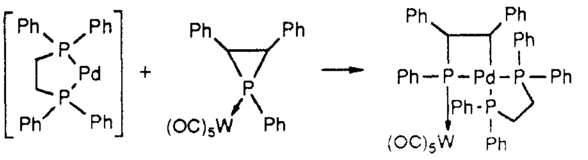
The insertion reactions within the phosphirane ring are far less numerous than its intramolecular rearrangements. At the moment, only two examples of such insertions are known. The first example was described by Marinetti.[21] An enol ether was inserted into a phosphirane complex with an activated P–C bond (eq 127). The second example was very recently described by Carmichael et al.[178] At room temperature, the 14-electron Pd(dppe) fragment inserts into the P–C bonds of phosphirane complexes with retention of the stereochemistry of the phosphirane ring (eq 128). The structures of the 4-membered rings were established by X-ray analysis. The retention of the stereochemistry suggests the intermediacy of an η^2-complex between palladium and the P–C bent bond of the phosphirane ring.



(127)

$\delta(^{31}P) = -168.3$ ppm

$\delta(^{31}P) = +19.5, +1.7$ ppm; 69%



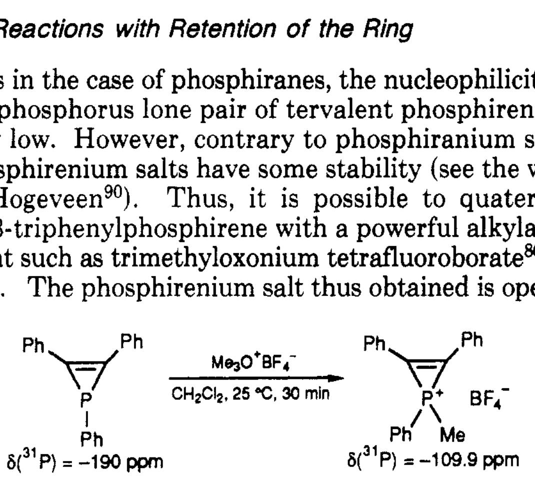
(128)

B. Phosphirenes

The chemistry of phosphirenes has already been studied in some depth in spite of their rather recent discovery. This undoubtedly results both from their theoretical interest (aromaticity and antiaromaticity) and from the ready availability of a series of stable derivatives. As a general statement, phosphirene derivatives indeed appear to be more stable than their saturated counterparts.

1. Reactions with Retention of the Ring

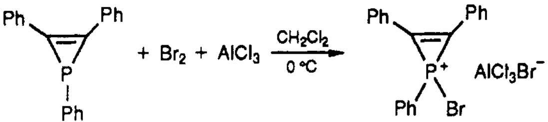
As in the case of phosphiranes, the nucleophilicity of the phosphorus lone pair of tervalent phosphirenes is very low. However, contrary to phosphiranium salts, phosphirenium salts have some stability (see the work of Hogeveen[90]). Thus, it is possible to quaternize 1,2,3-triphenylphosphirene with a powerful alkylating agent such as trimethyloxonium tetrafluoroborate[86] (eq 129). The phosphirenium salt thus obtained is opened by neutral water at room temperature (see eq 140). In the same vein, the reaction of bromine in the presence of $AlCl_3$ gives a bromophosphirenium salt[86] similar to the compounds of Hogeveen (eq 130).



(129)

$\delta(^{31}P) = -190$ ppm

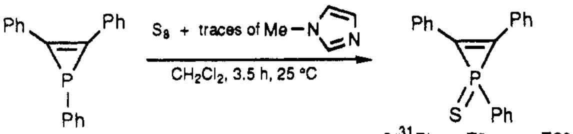
$\delta(^{31}P) = -109.9$ ppm



(130)

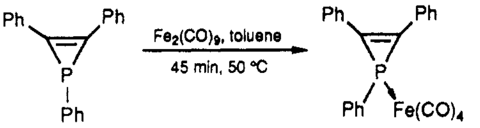
$\delta(^{31}P) = -66.8$ ppm

Whereas the oxidation of triphenylphosphirene by hydrogen peroxide has always led to ring-opened products (at the moment, no stable phosphirene oxide is known), the reaction of sulfur in the presence of *N*-methylimidazole as a catalyst gives a stable *P*-sulfide[86,77] (eq 131). Similarly, the reaction of tervalent phosphirenes with transition-metal derivatives in most cases leads to stable P complexes[87,159] (eqs 132 and 133).



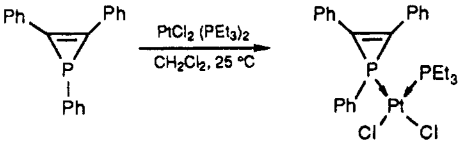
(131)

$\delta(^{31}P) = -79$ ppm; 76%



(132)

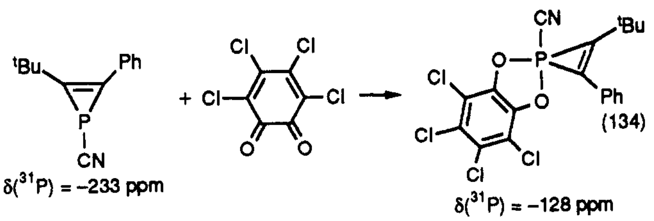
$\delta(^{31}P) = -92$ ppm



(133)

$\delta(^{31}P) = -124.9, -256.4$ ppm

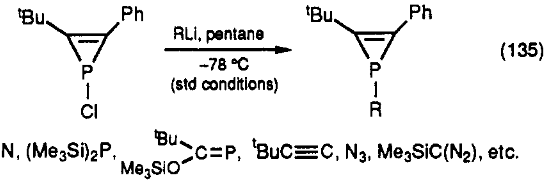
In some cases, however, an insertion of the transition metal into the ring is observed (see later text). Finally, a very recent work of Regitz and co-workers[160] has allowed the characterization of the first stable pentacoordinate phosphirene (eq 134). The structure of this peculiar phosphorane has already been discussed (see



(134)

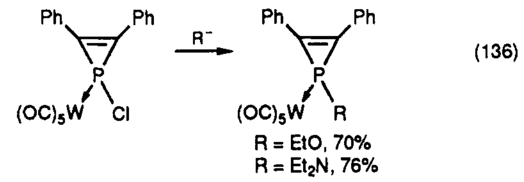
compound 14, Table II). Its stability is surprising to say the least!

Whereas the nucleophilicity of the phosphorus of tervalent phosphirenes is low, conversely, its electrophilicity appears to be quite normal. The recent availability of stable 1-chlorophosphirenes[100,101] has allowed numerous substitution reactions to be performed with ring retention. Examples are given in eq 135. The reaction of these 1-chlorophosphirenes with Lewis acids and silver salts has already been discussed in section III.B.2 and also leads to substitution products with ring retention (eq 89).

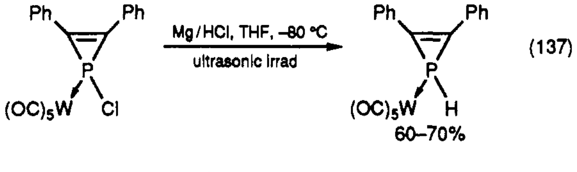


(135)

Nucleophilic substitutions can also be performed on 1-chlorophosphirene complexes[88] (eq 136), which are directly accessible via the desalkylation of 1-(β-chloroethyl)phosphirene complexes[83] (eq 90) or the reaction of 1-aminophosphirene complexes[89] (eq 47) with dry HCl. In that case, the opening of the ring is very easy and nucleophilic reduction by $LiAlH_4$ was unsuccessful. The corresponding P–H complex can be obtained via the reduction of the P–Cl complex in acidic medium[88] (eq 137). Since the corresponding anion is unstable (see section III.B.2), the substitution of the P–H bond by electrophiles must be carried out under phase-transfer conditions[88] (eq 138).



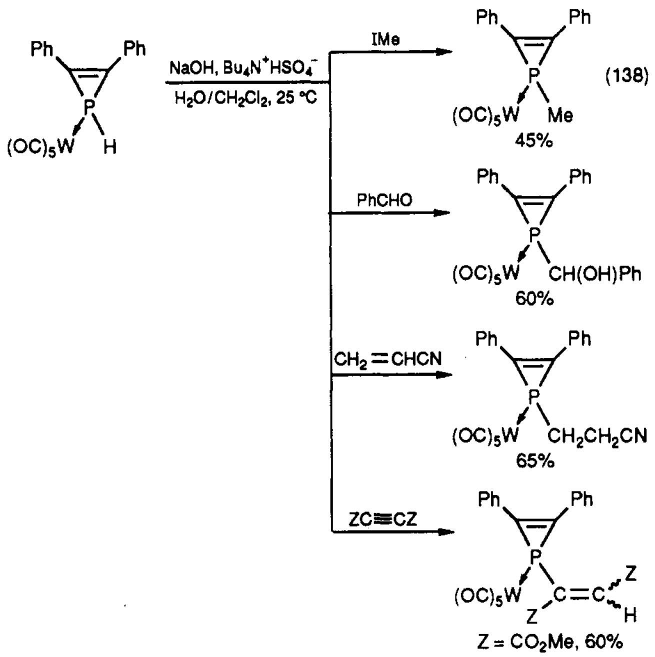
(136)



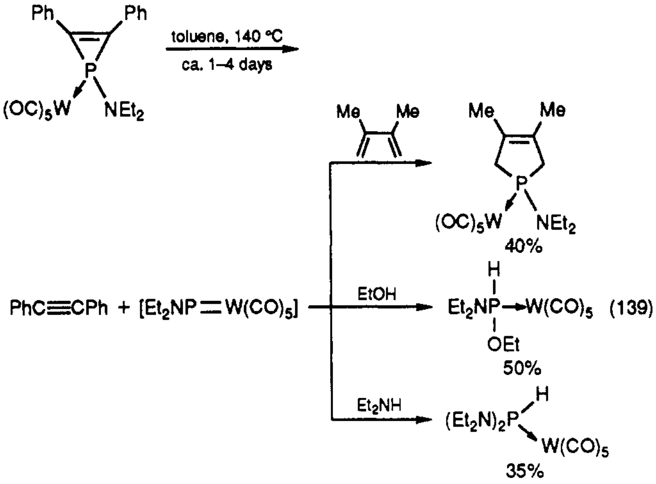
(137)

2. Reactions with Cleavage of the Two P–C Bonds of the Ring

This type of reaction is probably rather common in phosphirene chemistry, but at the moment, only one well-authenticated case has been described. It concerns the use of 1-aminophosphirene complexes as precursors of aminophosphinidene complexes[17] (eq 139). As such, phosphirene complexes are far less efficient than the corresponding phosphirane species; see eq 105.



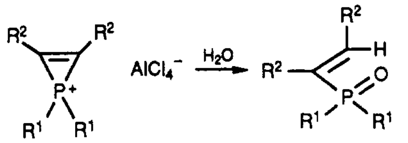
(138)



(139)

3. Reactions with Cleavage of One P–C Bond of the Ring

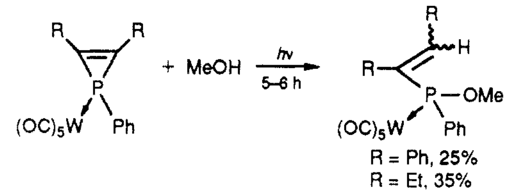
The cleavage of one P–C bond of the ring has been observed with protic reagents and nucleophiles. In fact, the failure of the first reported attempt to synthesize a phosphirene oxide[102] (eq 58) was due to the high sensitivity of such species to protic attack[103] (eq 59). This observation was again reported by Breslow for phosphirenium salts[91] (eq 140). The opening is instantaneous at room temperature.



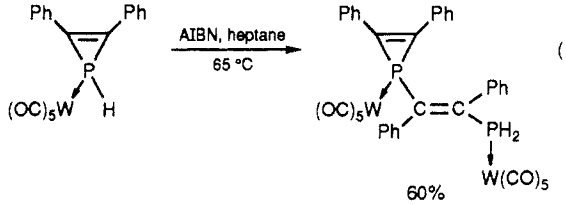
(140)

R^1, R^2 = Ph; R^1, R^2 = Et; R^1 = Et, R^2 = Ph

A somewhat related opening was reported for phosphirene complexes under irradiation in methanol[86] (eq 141). In that case, the precise mechanism of the cleavage is unknown. The UV irradiation may promote the homolytic cleavage of one of the P–C bonds of the ring followed by the trapping of the diradical thus formed by methanol. A related mechanism is perhaps involved in the dimerization of a P–H complex in the presence of AIBN[88] (eq 142). The attack of the

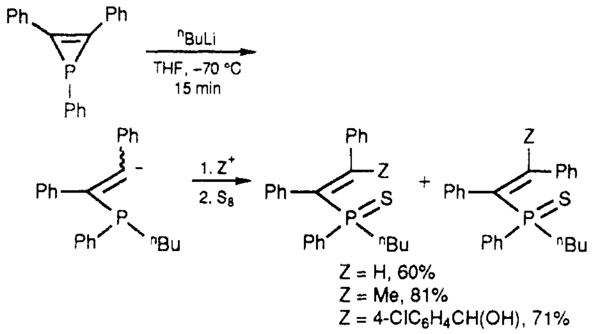


(141)

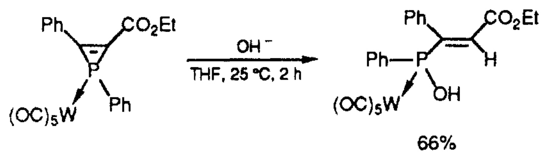


(142)

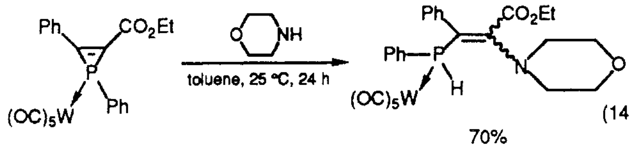
phosphirene ring by strong nucleophiles also leads to ring-opened products. For example, the reaction of triphenylphosphirene with butyllithium is almost instantaneous at low temperature and affords a vinylic carbanion[86] (eq 143). Nucleophilic attacks become very easy with activated phosphirene complexes. With unhindered oxygen nucleophiles, the attack takes place at phosphorus whereas with more hindered nitrogen nucleophiles the attack takes place at the C=C double bond[86] (eqs 144 and 145). Finally, triphenylphosphirene is also reductively cleaved by naphthalene-sodium in THF[86] (eq 146).



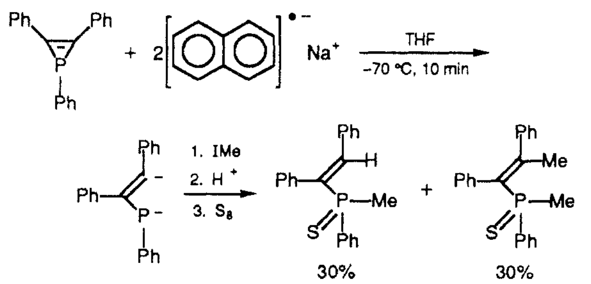
(143)



(144)



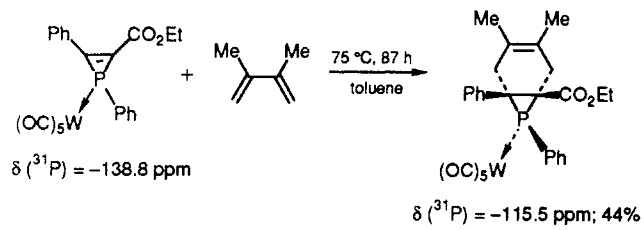
(145)



(146)

4. Reactions at the C=C Double Bond

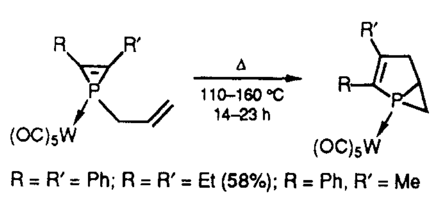
At least theoretically, it is possible to conceive a conversion of phosphirenes into phosphiranes via additions or cycloadditions onto the C=C double bond of phosphirenes. This type of conversion has been successfully carried out in one instance with an activated phosphirene complex[86] (eq 147). The cycloaddition selectively takes place on the tungsten side of the ring. The occurrence of such a reaction clearly demonstrates that there is no significant delocalization within the ring of phosphirene complexes.



(147)

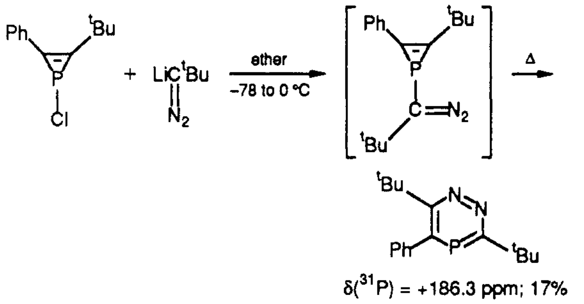
5. Ring Expansions

Contrary to the situation found in phosphirane chemistry (see section IV.A.4), at the moment, only a few ring expansions of phosphirenes occur via internal reorganizations. The first such reaction was found with 1-allylphosphirene complexes[23] (eq 148). The mechanism of this curious reaction is believed to involve a transient P–W–C_2 4-membered ring (see later text; eq 152). It is impossible to perform a similar reaction with an external olefin, and 1-allylphosphirane complexes do not ring-expand.

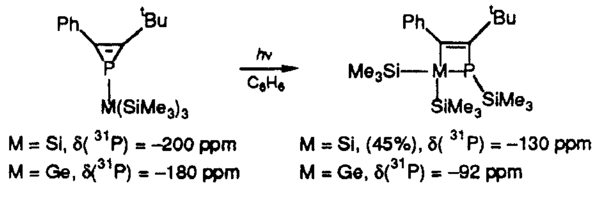


(148)

Another very peculiar intramolecular ring expansion of phosphirenes has been very recently reported by the group of Regitz[179] (eq 149). The intermediacy of the 1-diazoalkylphosphirene is established by previous experiments with $Me_3SiC(N_2)Li$; see eq 135. The precise mechanism of the ring expansion itself is speculative at the moment. 1,2,4-Diazaphosphinines were previously unknown. Still another item from the group of Regitz[180] is depicted in eq 150. Several insertions have also been described in the literature. At high temperature, it was found by Marinetti[181] that insertion of CO into the ring of phosphirene complexes becomes pos-

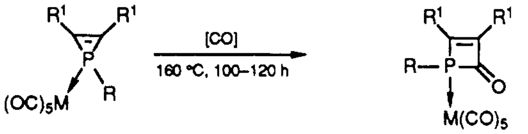


(149)



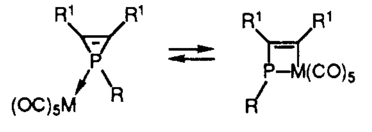
(150)

sible (eq 151). The X-ray crystal structure analysis of one of the resulting complexes was performed and showed a planar 4-membered ring with an extremely long P–CO bond (1.93 (1) Å). The key feature of the proposed mechanism was an equilibrium between the starting complex and a 4-membered metallacycle that would occur at high temperature (eq 152). A strong argument in favor of such a mechanism was later brought to light when Carmichael et al.[182,183] showed that phosphirene complexes readily insert 14-electron organometallic species (eq 153). The 4-membered nickelacycle inserts CO at 25 °C under 1 bar to give the previously described 1,2-dihydrophosphete complex[182] (see eq 151). The structure of the platinacycle was checked by X-ray analysis. Subsequently, it was shown that similar ring insertions also take place with tervalent phosphirenes[159] or phosphirene sulfides[182] (eqs 154 and 155).

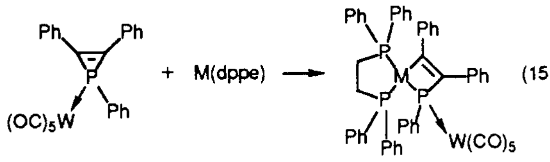


(151)

$R = R^1 = Ph, M = W, 34\%$
$R = Ph, R^1 = Et, M = W, 43\%$
$R = R^1 = Ph, M = Cr, 8\%$
$R = Ph, R^1 = Et, M = Cr, 21\%$
$R = R^1 = Ph, M = Mo, 24\%$

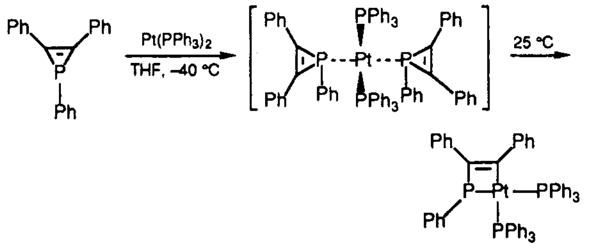


(152)

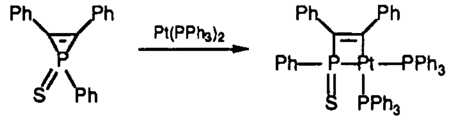


(153)

M = Ni, Pd, Pt

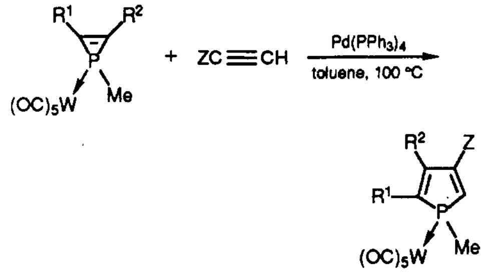


(154)



(155)

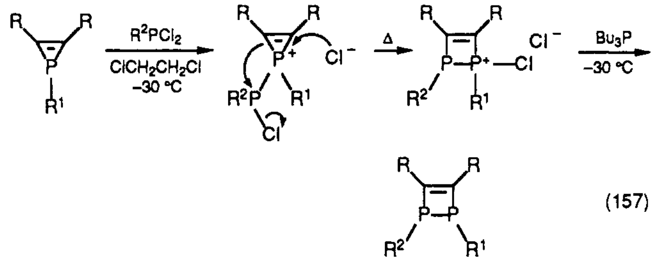
The contrasting behavior of tervalent phosphirenes toward Pt^{II} (η^1 P complexation; see eq 133) and Pt^0 species (η^2 P,C insertion; see eq 154) is especially noteworthy. Since it is known that the lone pair and the P–C ring bonds correspond to orbitals of comparable energies,[162] the observed results can be roughly rationalized on the basis of the HSAB principle: The hard center (lone pair) reacts with the hard $Pt^{(II)}$ species whereas the soft center (P–C bond) reacts with the soft Pt^0 species. Transition metals promote not only the insertion of CO but also the insertion of alkynes into the phosphirene ring[184] (eq 156). The reaction only works with terminal alkynes. An alkynylpalladium species is perhaps involved in the mechanism of this insertion.



(156)

$R^1 = R^2 = Z = Ph, 45\%$
$R^1 = R^2 = Ph, Z = EtO, 33\%$
$R^1 = R^2 = Ph, Z = EtOC(O), 85\%$
$R^1 = R^2 = Et, Z = EtOC(O), 50\%$
$R^1 = Ph, R^2 = Z = EtOC(O), 47(+31)\%$
$R^1 = Z = Ph, R^2 = EtOC(O), 61\%$

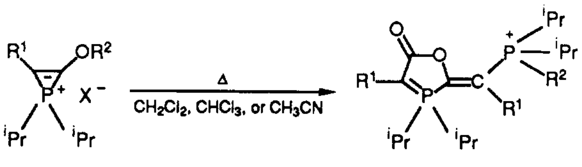
Another insertion not involving a transition metal as the catalyst has also been described in the literature. Its net overall result is the formal insertion of a phosphinidene into the phosphirene ring.[185] The actual mechanism is depicted in eq 157. The intermediate chlorophosphinophosphirenium salt is stable in the presence of $AlCl_3$, which traps Cl^- and prevents the ring expansion. This reaction represents the most general route to 1,2-dihydro-1,2-diphosphetes known at the present time.



(157)

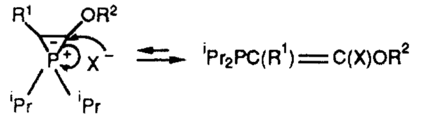
$R = R^1 = R^2 = Ph, 80\%$
$R = R^1 = Ph, R^2 = Me, 60\%$
$R = Ph, R^1 = {}^tBu, R^2 = Ph, 20\%$
$R = Ph, R^1 = R^2 = Me, 15\%$
$R = Et, R^1 = R^2 = Ph, 70\%$
$R = Et, R^1 = Ph, R^2 = Me, 50\%$
$R = Et, R^1 = Me, R^2 = Ph, 15\%$
$R = Et, R^1 = {}^tBu, R^2 = Me, 30\%$

Finally, a spontaneous dimerization upon dissolution in polar solvents has been observed with some peculiar phosphirenium salts[186] (eq 158). The structure of one such dimer has been checked by X-ray analysis. The key step of the proposed mechanism involves the opening of the ring by nucleophilic attack of X^- (eq 159).



(158)

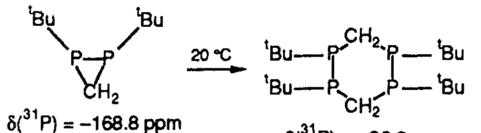
62–100%


(159)

C. Diphosphiranes

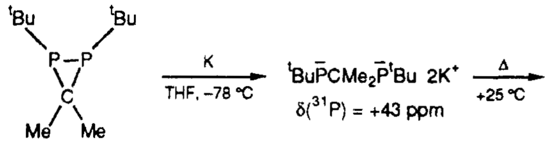
At the moment, the chemistry of diphosphiranes is deeply underdeveloped by comparison with the chemistry of phosphiranes or phosphirenes. Practically all the described reactions involve the cleavage of the strained P–P bond, which is obviously the weak point of the ring.

Reactions with Cleavage of the P–P Bond of the Ring. When discovering the first diphosphiranes, Baudler[5] immediately noticed the tendency of such species to dimerize when they are not kinetically stabilized by bulky substituents (eq 160). In the same vein, the cleavage of the P–P bond of diphosphiranes by potassium at low temperature easily affords the expected diphosphides, which display a limited thermal stability[187] (eq 161). The cleavage of 3-chloro-1,2-diphosphiranes by butyllithium also takes place at the P–P bond according to the work of Koenig[113] (eq 162).


(160)

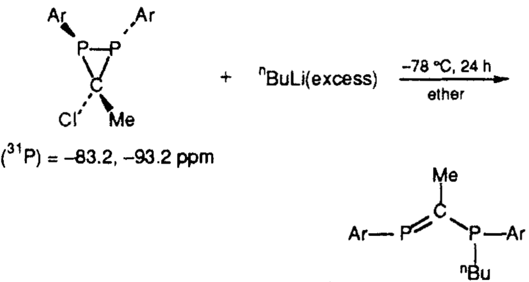
$\delta(^{31}P) = -168.8$ ppm

$\delta(^{31}P) = -26.2$ ppm


$\delta(^{31}P) = -91.7$ ppm

$^tBuPH^-K^+ + {}^tBu(^iPr)P^-K^+$ (161)

$\delta(^{31}P) = -60, +22$ ppm


$\delta(^{31}P) = -83.2, -93.2$ ppm

(162)

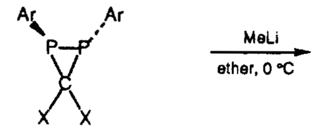
$\delta(^{31}P) = +230, +6.6$ ppm, 90%

Ar = 2, 4, 6-$^tBu_3C_6H_2$

Apparently, an intermediate η^3-1,3-diphosphaallyllithium species is transiently produced, and the opening of the ring is conrotatory. 3-Chloro-1,2-diphosphiranes are also opened by $AlCl_3$ to give 1,3-diphosphaallyl cations according to a very recent work of Koenig.[194]

The deshalogenation of 3,3-dihalodiphosphiranes produces the corresponding 1,3-diphosphaallenes[188-190] (eq 163). The deshalogenation is generally carried out by methyllithium. This reaction parallels a well-known synthesis of allenes from 1,1-dihalocyclopropanes.

Transition metals are also able to cleave the P–P bond of diphosphiranes as shown by a work of Seyferth[191] (eq 164). Finally, several original reactions of the zirconium complex of a bicyclic diphosphirane (see eq 81) have been described by the group of Regitz[192] (eqs 165–168).


Ar = 2, 4, 6-$^tBu_3C_6H_2$, X = Cl, $\delta(^{31}P) = -69.5$ ppm

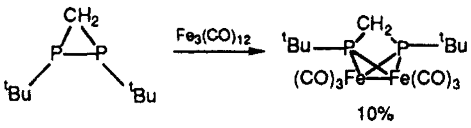
Ar = 2, 4, 6-$^tBu_3C_6H_2$, X = Br, $\delta(^{31}P) = -70.3$ ppm

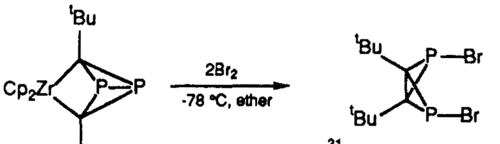
Ar = 2, 6-$^tBu_2C_6H_3$, X = Cl

$ArP{=}C{=}PAr$ (163)

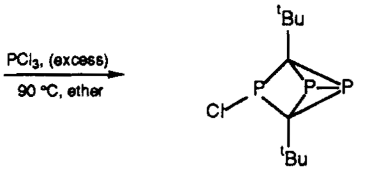
Ar = $^tBu_3C_6H_2$, X = Cl, 62%, $\delta(^{31}P) = +141.7$ ppm

Ar = $^tBu_2C_6H_3$, 40%

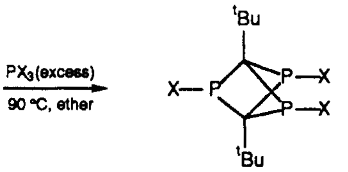

(164)


(165)

$\delta(^{31}P) = +92.8$ ppm, 73%

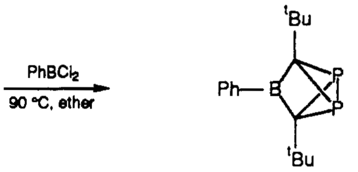

(166)

$\delta(^{31}P) = +234.4, -121.4, -302.0$ ppm, 75%


(167)

X = Br, 91%, $\delta(^{31}P) = +49.7$ ppm

X = I, 61%, $\delta(^{31}P) = +77.2$ ppm


(168)

$\delta(^{31}P) = -341.3$ ppm, 46%

V. Conclusion

As can be seen from the list of references, more than one-third of the bibliography on 3-membered carbon-phosphorus rings is less than 3-years old. The interconnection between their chemistry and the chemistry of low-coordinated species (phosphinidenes, phosphaalkenes, diphosphenes, phosphaalkynes, ...) is obvious. These observations suggest that this topic is on the eve of becoming a hot spot of organophosphorus chemistry. Many opportunities for discovering new syntheses and new reactions still exist in that field. My hope is to facilitate such developments with this review.

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