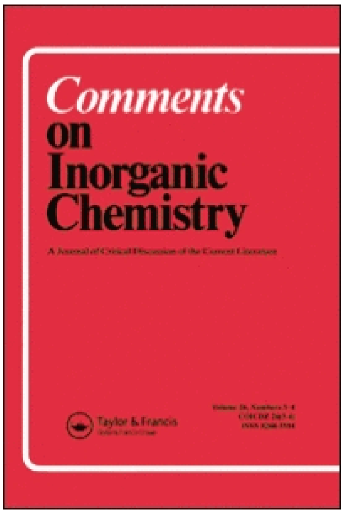
This article was downloaded by:
On: *15 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Unsaturated Four-Membered Phosphorus-Carbon Rings: From Organic to Coordination Chemistry

François Mathey[a]; Claude Charrier[a]; Nicole Maigrot[a]; Angela Marinetti[a]; Louis Ricard[a]; Ngoc Hoa HoaTran Huy[a]
[a] Laboratoire de Chimie du Phosphore et des Métaux de Transition, CNRS UM 13, Ecole Polytechnique, Palaiseau Cedex, France

To cite this Article Mathey, François , Charrier, Claude , Maigrot, Nicole , Marinetti, Angela , Ricard, Louis and Huy, Ngoc Hoa HoaTran(1992) 'Unsaturated Four-Membered Phosphorus-Carbon Rings: From Organic to Coordination Chemistry', Comments on Inorganic Chemistry, 13: 2, 61 — 90

To link to this Article: DOI: 10.1080/02603599208048459

URL: http://dx.doi.org/10.1080/02603599208048459

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Unsaturated Four-Membered Phosphorus–Carbon Rings: From Organic to Coordination Chemistry

FRANÇOIS MATHEY, CLAUDE CHARRIER,
NICOLE MAIGROT, ANGELA MARINETTI,
LOUIS RICARD and NGOC HOA TRAN HUY
Laboratoire de Chimie du Phosphore
et des Métaux de Transition,
CNRS UM 13, Ecole Polytechnique,
91128 Palaiseau Cedex, France

Received November 15, 1991

The chemistry of 1,2-dihydrophosphetes and 1,2-dihydro-1,2-diphosphetes is comprehensively reviewed. Several applications such as the synthesis of tetraphosphafulvalenes and 1,3-diphospholyl anions are mentioned. The interconversion with open-chain 1-phospha- and 1,4-diphosphadienes is emphasized. The various coordination modes are discussed.

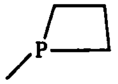
Key Words: *phosphorus–carbon heterocycles, 1,2-dihydrophosphetes, 1,2-dihydro-1,2-diphosphetes, 1-phosphadienes, 1,4-diphosphadienes, 1,3-diphospholyl anions, tetraphosphafulvalenes, insertion reactions, electrocyclisations*

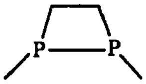
INTRODUCTION: THE PRESENT STATUS OF THE CHEMISTRY OF 4-MEMBERED PHOSPHORUS–CARBON HETEROCYCLES

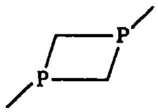
The 4-membered saturated PC_3 ring (phosphetane, I) has been known for many years. It was unambiguously characterized for the

Comments Inorg. Chem.
1992, Vol. 13, No. 2, pp. 61–90
Reprints available directly from the publisher
Photocopying permitted by license only

first time by Jungermann and McBride in 1961.[1] Since then, it has been the subject of considerable study and has served as a probe for mechanisms involving pentacoordinate phosphorus intermediates. On the other hand, the 1,2- and 1,3-diphosphetane rings (II, III) are by-products of the discovery of phosphaalkenes by Becker in 1976.[2] They result from the often reversible head to head or head to tail dimerization of phosphaalkenes.[2]

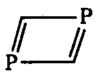

phosphetane (I)


1,2-diphosphetane (II)


1,3-diphosphetane (III)

If our knowledge is now reasonably complete on the saturated 4-membered rings containing carbon and phosphorus, the situation is still in a state of flux concerning the corresponding unsaturated rings. At the moment, the fully unsaturated phosphetes[3] (IV) and 1,3-diphosphetes[4] (V) are mainly known as η^4-complexes. They result from the [2 + 2] cycloaddition of alkynes and phosphaalkynes in the coordination sphere of transition metals. In the free state, IV and V apparently behave as anti-aromatic species and are highly unstable. On the contrary, stable tetracoordinate derivatives of V have been described.[5]

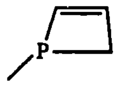

phosphete (IV)


1,3-diphosphete (V)

Similar limitations do not exist for the monounsaturated heterocycles. The first such species, i.e., the 1,2-dihydro-1,2-diphosphetes (VI), were discovered as early as 1964 by Mahler.[6] The corresponding monophosphorus ring (1,2-dihydrophosphete, VII) was first mentioned by Russian authors in 1983[7] but their results are questionable (see later). The first unambiguous characterization of VII as a complex came in 1985.[8] At the moment, the chemistry of these two rings (VI and VII) is developing rapidly. This review describes the present status of the field. Two other rings (2,3-dihydrophosphetes[9] VIII and 2,3-dihydro-1,2-

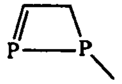
diphosphetes[10] IX) are also known but their chemistry has not been investigated.

1,2-dihydro-1,2-diphosphete
(VI)



1,2-dihydrophosphete
(VII)

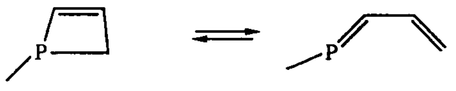
2,3-dihydrophosphete
(VIII)



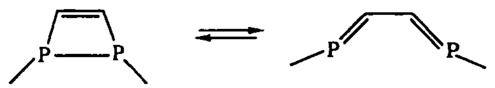
2,3-dihydro-1,2-diphosphete
(IX)

WHY DO 1,2-DIHYDRO-PHOSPHETES AND 1,2-DIPHOSPHETES DESERVE SPECIAL INTEREST?

A priori nothing pinpoints 1,2-dihydrophosphetes and 1,2-diphosphetes as deserving special attention among the nine 4-membered phosphorus–carbon heterocyles mentioned in the introduction. In fact, however, they are the only easily accessible unsaturated species in that group of rings. They can be obtained either as stable free phosphines or as stable derivatives (oxides, complexes, etc.). They can be considered as masked 1-phospha- and 1,4-diphosphabutadienes via ring opening (Eqs. (1) and (2)).



(1)



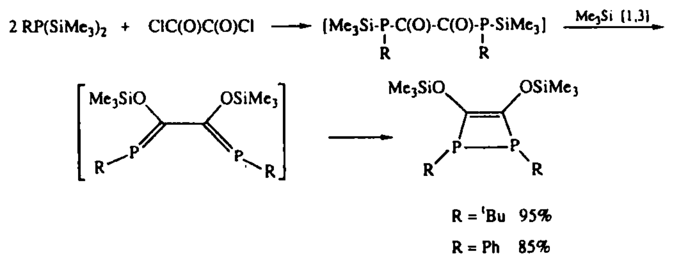
(2)

As such, they might play a crucial role in the development of a large phosphorus-based cycloaddition chemistry. Indeed stable *and* reactive phosphadienes are very difficult to obtain (see Ref. 2). In the case of VI, an additional factor must be considered. The presence of two lone pairs at phosphorus and one π-bond may induce some phenomena correlated with a 6-electron Hückel-type aromaticity. Together with the chemistry associated with the strain and the special geometry of these rings (intracyclic < CPC ca. 75°) which are common to all of this group, it seems clear that there is ample scope for their investigation.

SYNTHESIS OF 1,2-DIHYDRO-PHOSPHETES AND 1,2-DIPHOSPHETES

The strong parallelism which exists between the chemistry of VI and VII is immediately apparent when inspecting the various methods by which they may be prepared. In almost all cases, two versions of the same basic approach serve to obtain the two types of ring.

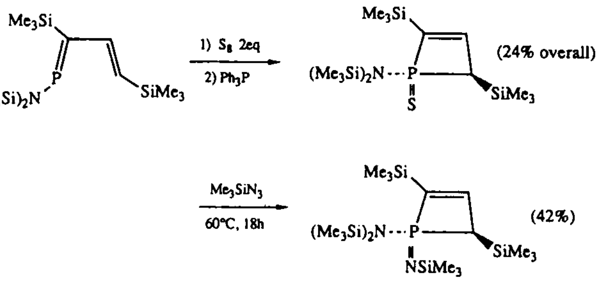
A first approach relies on the closure of transient 1-phospha- and 1,4-diphospha-butadienes as in Eqs. (1) and (2). Such a route was first proposed by Appel for the synthesis of 1,2-dihydro-1,2-diphosphetes.[11,12] (Eq. (3)).



(3)

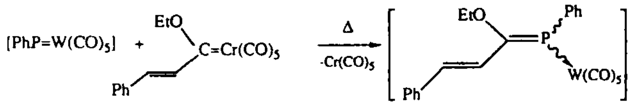
The main limitation of this scheme concerns the siloxy substitution of the ring carbons which is imposed by the choice of the Becker synthesis of P═C double bonds.[13] It is interesting to notice here that very bulky R-substituents at phosphorus such as 2,4,6-tris-tertbutylphenyl prevent the cyclisation of 1,4-diphosphadienes.[14]

The corresponding synthesis of 1,2-dihydrophosphetes by electrocyclisation of 1-phosphadienes was reported independently by the group of Neilson[15,16] and by ourselves.[17,18] In the first case, the electrocyclisation takes place upon reaction of the phosphorus lone pair of a stable 1-phosphadiene with sulfur or trimethylsilyl azide[15,16] (Eq. 4)). This route is limited by the availability of the reactive free phosphadiene.

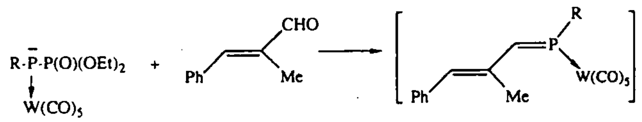


(4)

In the second case, a transient 1-phosphadiene P–W(CO)$_5$ complex is first formed via the coupling of a vinylcarbene complex with a phosphinidene complex[17], or from an α,β-unsaturated aldehyde[18] via the "phospha-Wittig" reaction[19] (Eqs. (5) and (6)).

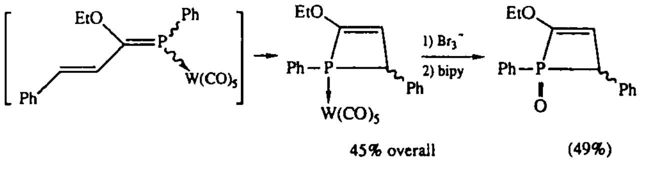


(5)

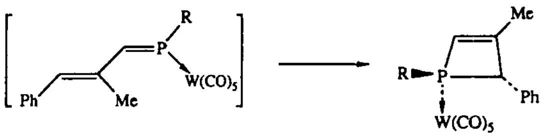


(6)

These 1-phosphadiene P–W(CO)$_5$ complexes spontaneously electrocyclise via a conrotatory process and the resulting 1,2-dihydrophosphete complexes can be transformed into the corresponding oxides via an oxidative displacement[17,18] (Eqs. (7) and (8)). A priori, this route has a reasonable generality.



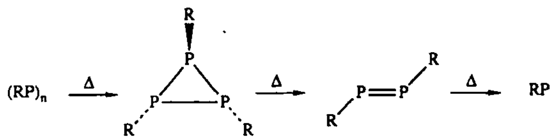
(7)



(8)

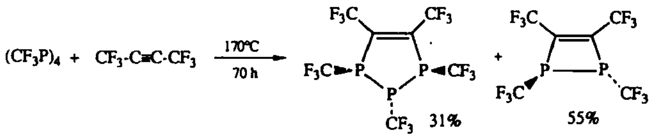
R = Ph (65% overall)
R = ᵗBu (69% overall)

The discovery of 1,2-dihydro-1,2-diphosphetes by Mahler[6] exemplifies another type of approach relying, at least formally, on the [2 + 2] cycloaddition of alkynes with phosphorus double-bonded species. At high temperature, it is known that cyclopolyphosphines decompose to give 3-membered P_3 rings, then diphosphenes, then phosphinidenes[20] (Eq. (9)).

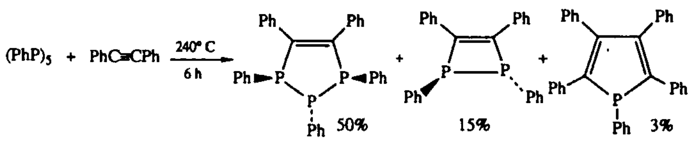


(9)

These reactive species can be trapped by alkynes[6,21–23] (Eqs. (10) and (11)).



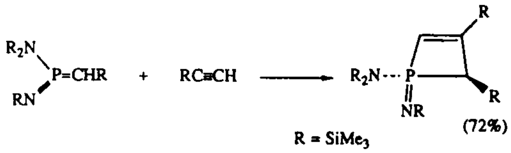
(10)[6]



(11)[22]

The formation of the 4-membered rings is promoted by bulky and electron-withdrawing substituents which both favor the depolymerisation of cyclopolyphosphines and stabilize the desired heterocycles. In spite of its simplicity, this route has several drawbacks: the yields are generally modest, the only accessible diphosphetes are those with a good thermal stability, and tedious separations must be carried out.

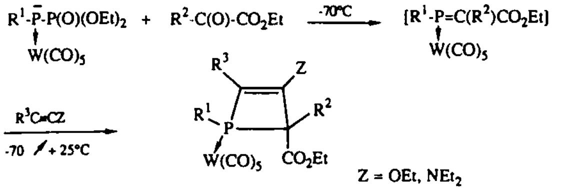
A first example of [2 + 2] cycloaddition leading to a 1,2-dihydrophosphete was mentioned by Neilson and colleagues in 1987[16] (Eq. (12)).



R = SiMe$_3$

(12)

A more general route was later proposed by two of us. Via the "phospha-Wittig" reaction, it is possible to synthesize very reactive electron-poor phosphaalkene complexes which are able to react at low temperature with electron-rich alkynes[24] (Eq. (13)).



(13)

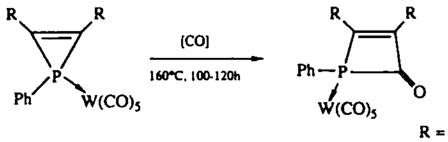
Z = OEt, NEt$_2$

R^1, R^2, R^3 = H, Me, Ph, CO$_2$Et

37 - 74% overall yields

A variety of functional derivatives are thus easily accessible. Decomplexation can be achieved by oxidative displacement as in Eq. (7).

The ring expansion of the easily available phosphirenes[25] represents a third approach for the synthesis of dihydro-phosphetes and diphosphetes. At high temperature, it was shown that insertion of carbon monoxide into the ring of phosphirene complexes becomes possible[8] (Eq. (14)).



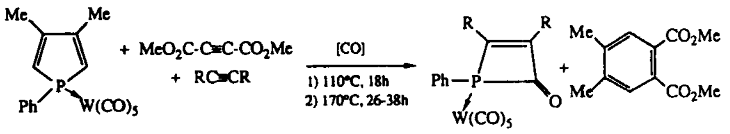
(14)

R = Ph 34%

R = Et 43%

(also works with Cr and Mo complexes)

The key feature of the proposed mechanism is an equilibrium between the starting complex and a 4-membered metallacyle. Subsequent results[26] showed that unsaturated metallic centers can insert into P–C bonds of phosphirene rings, thus giving some credibility to this proposal. Since phosphirene complexes are generally made from phosphole complexes via 7-phosphanorbornadiene complexes, it proved possible to combine the three steps in a one-pot reaction[27] (Eq. (15)).

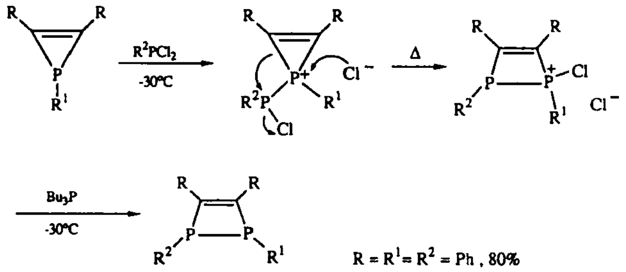


R = Ph 32%
R = Et 44%

(15)

Oxidative decomplexation (Eq. (7)) then allowed us to recover the 4-membered rings as their P-oxides.

In a related reaction, it was later shown that it is also possible to formally insert a phosphinidene unit into a phosphirene to yield a 1,2-dihydro-1,2-diphosphete[28] (Eq. (16)).

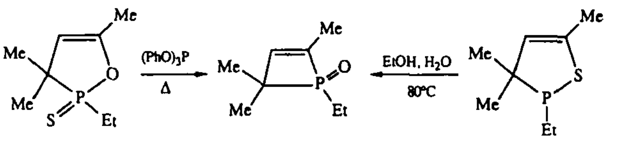


(16)

R = R1 = R2 = Ph, 80%
R = R1 = Ph, R2 = Me, 60%
R = Et, R1 = R2 = Ph, 70%
R = Et, R1 = Ph, R2 = Me, 50%
R = Et, R1 = tBu, R2 = Me, 30%
R = Me, R1 = R2 = Ph, 80%

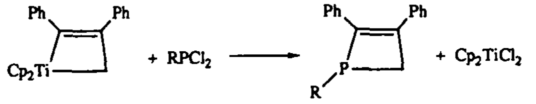
This low-temperature synthesis is versatile and often proceeds in reasonable yields. At the moment, this is the most frequently used preparation of 1,2-dihydro-1,2-diphosphetes. Its mechanism probably involves the nucleophilic attack of a chloride anion onto a phosphinophosphirenium salt with preferential cleavage of one of the intracyclic P–C bonds.

Several miscellaneous syntheses of the two rings under review have also been proposed in the literature. In 1983, Russian chemists reported the following reactions[7] (Eq. (17)).



(17)

The 4-membered ring is said to display a ${}^1J(Me_2\underline{C}-\underline{P})$ coupling constant of 18.3 Hz which is abnormally low for such a product (see Refs. 16, 17, 24 and 29). If the Russian work is questionable, such is not the case for the first reported synthesis of tervalent 1,2-dihydrophosphetes from titanacyclobutenes[29–31] (Eq. (18)).

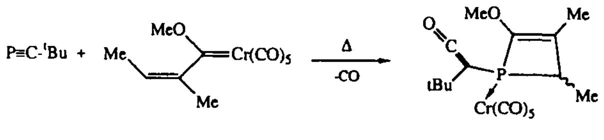


(18)

R = Ph : 66%; R = ᵗBu : 30-50%
R = EtO : 73%

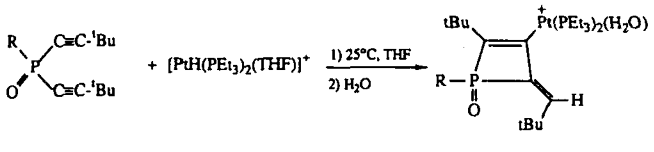
The starting titanium reagent is easily obtained from the so-called Tebbe reagent ($Cp_2TiCH_2.AlMe_2Cl$) and diphenylacetylene.[32] A large variety of R-substituents at phosphorus can be used. Changing the substitution at the carbons of the ring is more difficult.

Two other applications of transition metals in the synthesis of 1,2-dihydrophosphetes have been reported. In the first, Dötz and colleagues allowed a phosphaalkyne to react with a vinylcarbene complex[33] (Eq. (19)).



(19)

The first step is very likely to be an insertion of the phosphaalkyne unit into the Cr=C bond with formation of a 1-chroma-3-phosphahexatriene. According to the substitution scheme of the carbene complex, this kind of chemistry can also lead to several other products including some 1,3-oxaphospholes. The second route relies on the reaction of a platinum hydride with bis(alkynyl)phosphine oxides[34,35] (Eq. (20)).

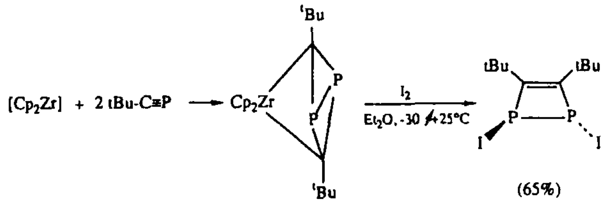


(20)

R = Ph : 26%
R = Me : 17%
R = ᵗBu-C≡C- : 74%

The mechanism first involves an addition of the platinum hydride onto one of the C≡C triple bonds. Then, probably, an alkynyl group migrates from phosphorus to platinum. An alternative mechanism is also proposed. The reaction still works with tris(alkynyl)phosphonium salts.

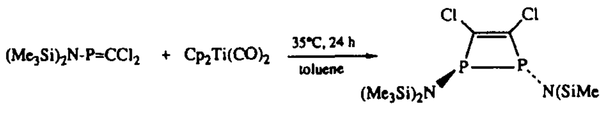
On the other hand, the group of Regitz[36] has described very recently a first synthesis of the 1,2-dihydro-1,2-diphosphete ring starting from a transition metal reagent (Eq. (21)).



(21)

(65%)

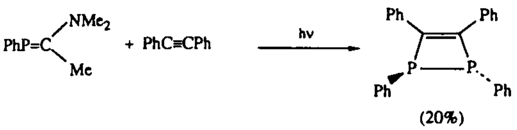
In the same vein, Majoral and Lavaud-Dufour[37] have obtained a 1,2-dihydro-1,2-diphosphete via a head to head dimerization of a C-chloro-phosphaalkene in the presence of $Cp_2Ti(CO)_2$ as a reducing agent (Eq. (22)).



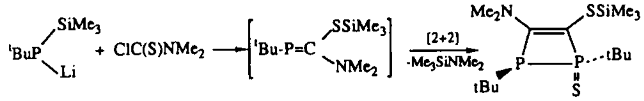
(22)

30%

Two other less general approaches were mentioned earlier (Eqs. (23a) and (23b)).



(23a)[38]



(23b)[39]

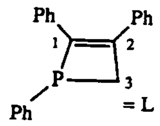
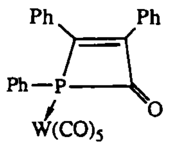
In the second case, the formation of the 4-membered ring was checked by X-ray crystal structure analysis.[40] Finally, it must be also mentioned here that the 1,2-dihydrophosphete ring is present in a recently synthesized 1-Dewar-phosphinine.[41] As can be seen, within a very short time, a large array of synthetic routes to these P,C 4-membered heterocycles has been developed.

SOME PHYSICOCHEMICAL DATA

The available structural data are collected in Tables I and II. Both types of ring are approximately planar, the 1,2-dihydro-1,2-diphosphetes being slightly more distorted than their monophosphorus counterparts. The strain at phosphorus as measured by the < CPC and < CPP intracyclic angles is approximately the same, as in both cases these angles are close to 75°. Large variations are observed for the intracyclic P–C sp^3 and P–P bond lengths between 1.766 and 1.93 Å in the first case and between 2.192 and 2.281 Å in the second case. Both rings are able to "breathe" as do phosphiranes and phosphirenes.[25] These bond lengths can be taken as an index measuring the tendency of the ring to open to give the corresponding phosphadiene. It is clear that the dicomplexation of **7** induces a lengthening of the P–P bond in **12**, thus explaining why **12** tends to equilibrate with the isomeric 1,4-diphosphadiene at high temperature.[42] On the contrary, the P–W(CO)$_5$ complexation tends to shorten the P–Csp^3 ring bond of **1**. The

TABLE I

Structural data for 1,2-dihydrophosphetes

Compound	n°	Bond lengths, Å			Bond angles, deg		Ref.
		$P-C_1$	$P-C_3$	$C_2=C_3$	$< C_1PC_3$	$P-C_1-C_2-C_3$	
	**1**	1.821	1.886	1.366	74.0	9.3	29
$[L.HgCl_2]_2$	**2**	1.80	1.82,1.80	1.34	76.8,77.9	5.2,1.0	29
$L.W(CO)_5$	**3**	1.82	1.81	1.36	75.4	2.3	29
	**4**	1.83	1.93	1.36	71.9	–	8

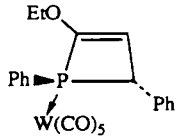
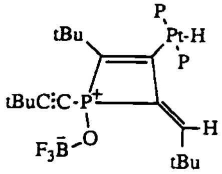
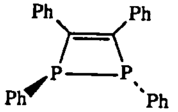
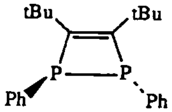
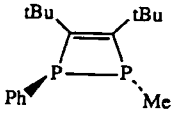
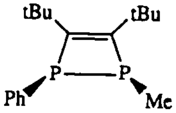
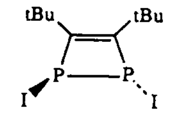
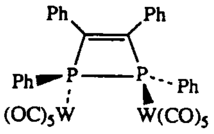
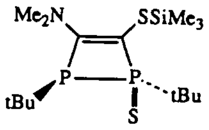
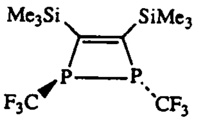
	**5**	1.815	1.902	1.331	74.0	3.9	17
 P = (^{n}Pr)$_3$P	**6**	1.754	1.766	1.365	77.9	2.8	34

TABLE II

Structural data for 1,2-dihydro-1,2-diphosphetes[a]

Compound	n°	Bond lengths, Å			Bond angles, deg		Ref.
		P–P	P–C_{ring}	C═C	< P–P–C_{ring}	< C–P–P–C	
	**7**	$2.248^{(1)}$	1.830	1.358	74.7	14.5	22[a]
	**8**	$2.214^{(4)}$	1.847	1.357	76.2	7.7	22[b]
	**9**	$2.202^{(1)}$	1.842	1.355	76.1	9.9	43
	**10**	$2.218^{(1)}$	1.848	1.360	76.5	1.6	43

	**11**	2.192$^{(4)}$	1.827	1.334	75.5	12.8	36
	**12**	2.281$^{(3)}$	1.843	1.36	75.5	0.4	42
	**13**	2.219$^{(1)}$	1.85 1.78	1.360	79 74	3.0	39
	**14**^{b}	2.223$^{(1)}$	1.841	1.356	75.8	9.7	23

---

[a] $[PW(CO)_5]_2$ complexes of **9** and **10** have also been structurally characterized.[43]

[b] As early as 1974, Cowley, Dewar and colleagues[47] had concluded that $(CF_3)_4C_2P_2$ has two *trans* lone pairs with a negligible coupling to the C═C π MO on the basis of PES data.

lengthening of the P–P bond in **12** is thus probably due to the steric repulsion between the two bulky complexing groups. Similarly, the steric repulsion between the substituents at the C═C double bond tends to shorten the P–P bond, as can be seen from a comparison of the data for **7** and **8**. On the other hand, the tendency of complex **5** to ring open (see later) is probably correlated with the ethoxy substitution at the double bond which can stabilize the phosphadienic isomer.

Another problem of interest is the potential 6π-electronic delocalization within *cis* 1,2-dihydro-1,2-diphosphetes. Indeed, in that case, a good overlap exists between the lone pair orbitals and Hückel aromaticity may result. The structural comparison between the *cis* and *trans* isomers **10** and **9** clearly shows, however, that no delocalization takes place in such systems.

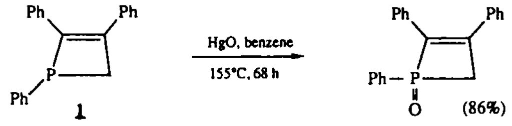
Generally speaking, the NMR characteristics of these 4-membered rings are normal and deserve no special comment. The only exception concerns the $^1J(P-P)$ coupling constants of 1,2-dihydro-1,2-diphosphetes. These coupling constants are abnormally small, as low as 29.3 Hz for the 1-phenyl-3,4-ditertiobutyl derivative,[44] but more frequently in the range 60–80 Hz.[22b] Higher couplings are observed upon oxidation at phosphorus, for example $^1J(P-P) = 120$ Hz for **13**.[39] These low couplings probably result from the superimposition of a $^1J(P-P)$ direct coupling with a $^3J(P \ldots P)$ indirect coupling of opposite sign.

Concerning now the theoretical aspects, as far as we know, only one ab initio study of the parent 1,2-dihydrophosphete ring has been carried out.[46] Using a calculated geometry which appears to be close to the geometry experimentally found for **1** (Table I), the author calculated a pyramidal inversion barrier at phosphorus of 46.6 kcal/mol (MP 2/6–31G* // HF /6–31G*) for the parent dihydrophosphete. This high value is explained in terms of geometric restrictions imposed by the cyclic structure.

Finally, an electrochemical study has been carried out on the tetrakis (trifluoromethyl)-1,2-dihydro-1,2-diphosphete.[46] At −130°C, the reduction produces an unstable radical anion. According to the observed ^{19}F and ^{31}P hyperfine coupling constants, the unpaired electron is mainly localized in the C═C double bond. This species decomposes above −130°C to give the hexakis (trifluoromethyl)benzene radical anion.

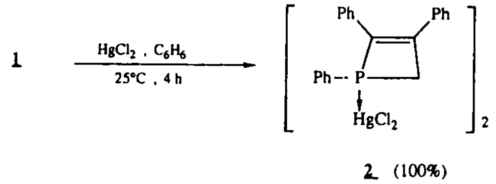
CHEMICAL PROPERTIES

What is known concerning the chemistry of dihydrophosphetes is scarce. At the time of writing, only six papers dealing with this topic have appeared. Doxsee and colleagues have carried out a preliminary chemical study of 1,3,4-triphenyl-1,2-dihydrophosphete **1**. The phosphorus lone pair appears to have a normal but rather sluggish reactivity. The oxidation is slow as shown in Eq. (24).[29]

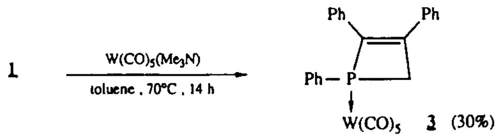


(24)

Complexation is sometimes easier[29] (Eqs. (25) and (26)).

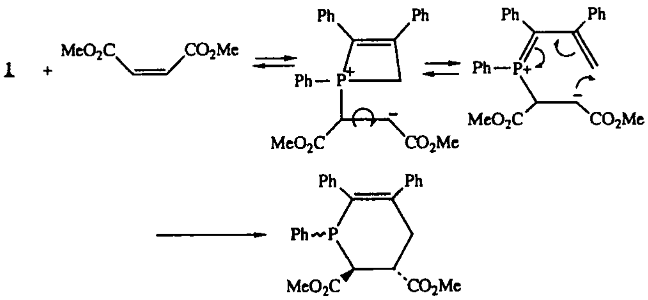


(25)



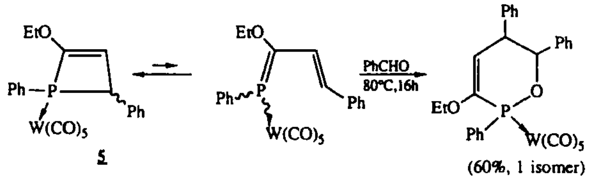
(26)

The relatively long P–Csp^3 bond within the ring (see Table I) suggested a rather easy concerted opening of **1** into the corresponding 1-phosphadiene. In fact, the reaction with dimethyl maleate gives the expected [4 + 2] cycloadduct but without retention of the *cis* stereochemistry of the olefin.[48] This result is interpreted by a nonconcerted mechanism as shown in Eq. (27).[48]



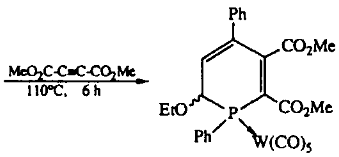
(27)

When blocking the phosphorus lone pair as in complex **5**, the electrophilic dienophile can no longer react at phosphorus and a classical Diels–Alder cycloaddition with retention of stereochemistry takes place with the open-chain phosphadienic isomer[49] (Eqs. (28)–(30)).



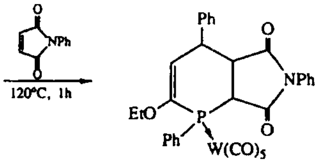
(60%, 1 isomer)

(28)



(70%, 2 isomers)

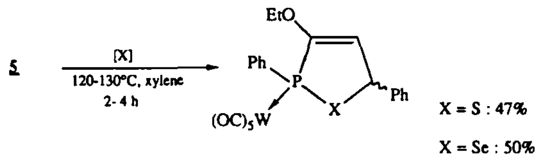
(29)



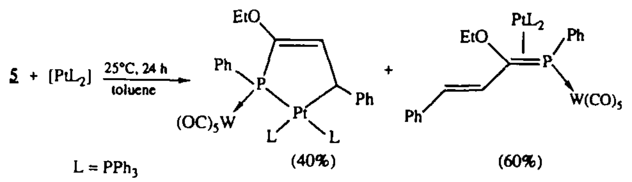
(70%, 1 isomer)

(30)

Some time later, we demonstrated that sulfur and selenium can insert into the P–Csp^3 ring bond of **5** probably via a similar mechanism involving a formal [4 + 1] cycloaddition with the phosphadienic isomer[50] (Eq. (31)).

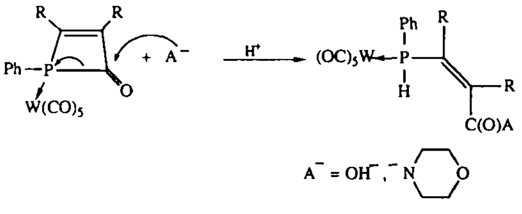
 (31)

The direct insertion of sulfur and selenium into a P–C σ-bond has no precedent in the literature as far as we know. Finally, with the group of John Nixon, we unambiguously established the existence of the equilibrium depicted in Eq. (28) by stabilizing the 1-phosphadiene as 1,2- or 1,4-complexes with platinum[51] (Eq. (32)).

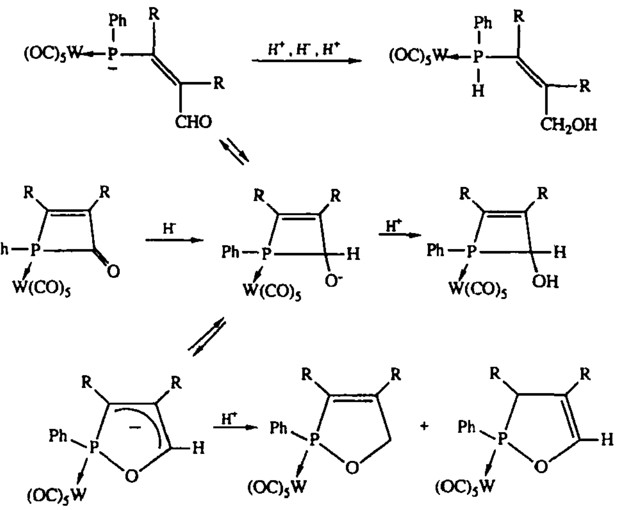
 (32)

The X-ray crystal structure analysis of the η^2-complex gave useful information on the stereochemistry of the phosphadiene. The platinacycle must be formulated as a Pt(II) complex with a pseudo-square planar geometry at Pt, well localized C=C double bond (1.33 Å) and long intracyclic P–C bond (1.83 Å). This means that the phosphadiene has accepted two electrons from the platinum (O) center thus suggesting a high electron affinity (low-lying LUMO).

The only other available study concerned the keto complex **4** (Table I) and its C_2Et_2 analogue.[27] The reactivity of the carbonyl group controls the chemistry of these species. Thus, the hydrolysis and aminolysis of these compounds lead to a cleavage of the P–C(O) bond via an initial attack at CO (Eq. (33)).

 (33)

Similarly, the reduction by $LiAlH_4$ or $NaBH_4$ leads to a variety of products according to the experimental conditions (reagent, solvent, temperature), but all of them result from an initial attack at CO (Eqs. (34)-(36)).

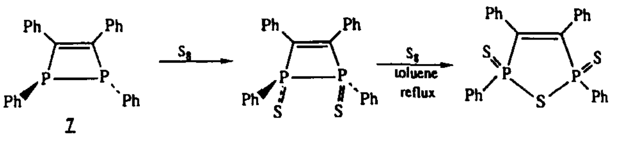


(34)

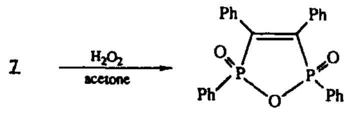
(35)

(36)

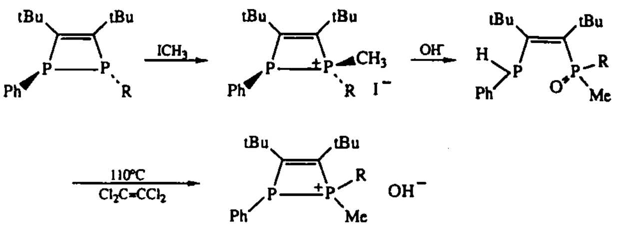
More information is available on the chemistry of 1,2-dihydro-1,2-diphosphetes. At first glance, the phosphorus lone pairs display a normal reactivity. The reaction with sulfur first gives the P,P disulfides, then a cleavage of the P-P bond is observed[21] (Eq. (37)). The oxidation by hydrogen peroxide directly gives the 5-membered rings[21] (Eq. (38)). Alkylation leads to monoquaternary salts[52] (Eq. (39)).



(37)

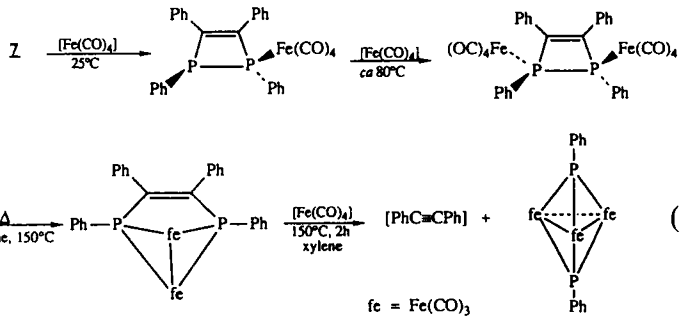


(38)



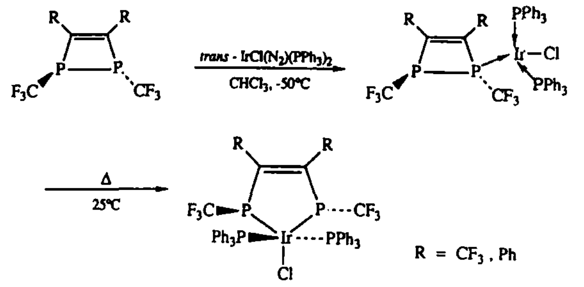
(39)

Cleavage of the P–P bond occurs upon hydrolysis of these salts as expected. More surprising is the reformation of the ring upon heating. The tertiobutyl substitution obviously stabilizes the 4-membered heterocycle to a great extent. Two studies have been carried out on the complexation of these cycles by iron carbonyls.[22a,53] The case of **7** is representative (Eq. (40)).



(40)

The $P_2[Fe(CO)_4]_2$ complex (numbered **10** in Ref. 22a) was later characterized by X-ray crystal structure analysis. The extrusion of tolane in the last step yields a μ^3-phosphinidene complex whose ^{31}P NMR resonance is very characteristic (δ^{31}P + 316 ppm vs. H_3PO_4). Huttner and colleagues subsequently showed that this last step is reversible.[54] In another study, Cavell and colleagues allowed a series of dihydrodiphosphetes to react with an Ir(I) complex.[23] In the first step, η^1-P complexes are formed at low temperature. At room temperature, these complexes slowly decompose to give iridadiphospholenes which were unambiguously characterized by NMR spectroscopy[23] (Eq. (41)).



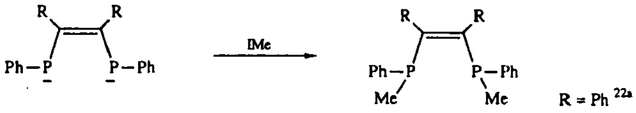
(41)

This reaction can be seen as an oxidative addition of the P–P bond onto the Ir(I) center to give an Ir(III) complex. Analogous reactions were observed in our group between dihydrodiphosphetes and NiL_2 and PtL_2 14 electron zero valent metallic centers.[55]

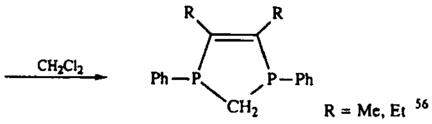
The most useful cleavage reactions are performed with lithium in THF. In most cases, the P–P bond is selectively broken[22] (Eq. (42)).

(42)

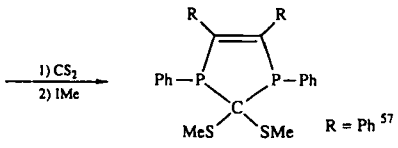
The resulting dianions are very powerful synthons. Several applications are underlined in Eqs. (43)–(49).



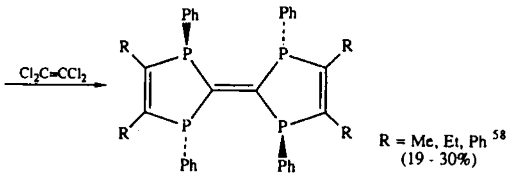
(43)



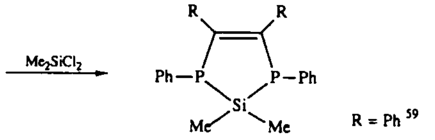
(44)



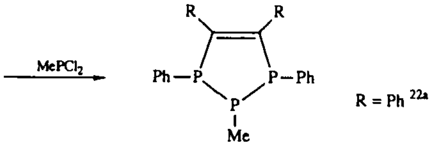
(45)



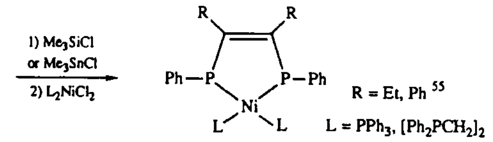
(46)



(47)

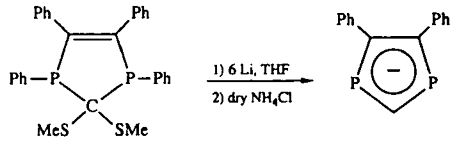


(48)

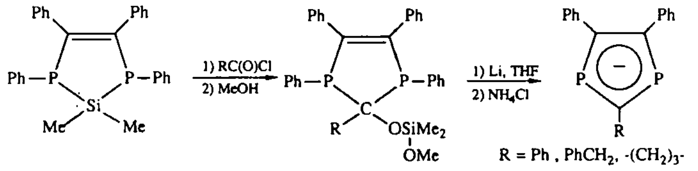


(49)

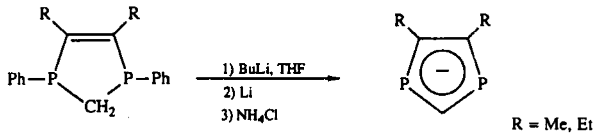
Three different syntheses of the newly discovered 1,3-diphospholyl anions were devised starting from some of the resulting 5-membered rings as shown in Eqs. (50)–(52).



(50)[57]



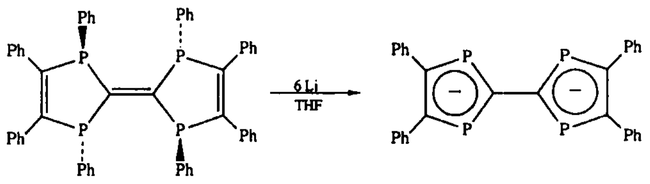
(51)[59]



R = Me, Et

(52)[56]

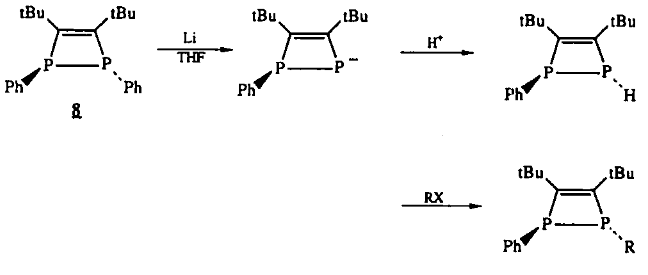
All these anions have been characterized by the X-ray crystal structure analyses of some of their η^5-complexes with iron (II). The tetraphosphafulvalenes (Eq. (46)) are the precursors of the corresponding planar dianions[60] (Eq. (53)).



(53)

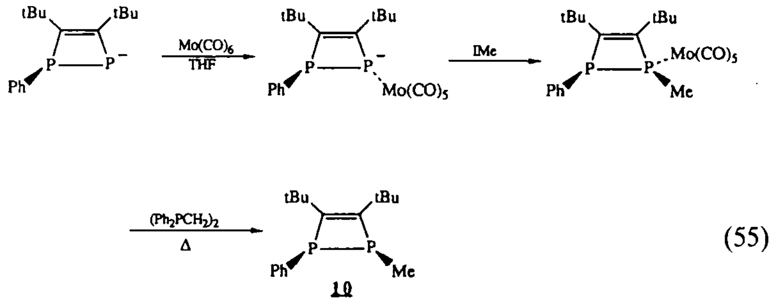
These species are isoelectronic with tetrathiafulvalene dications and could be useful for the preparation of new molecular materials of the TTF-TCNQ type. The dianion in Eq. (53) has been characterized by X-ray crystal structure analysis.[60]

We have seen in the preceding section that the length, and hence the strength, of the P–P bond of dihydrodiphosphetes is highly dependent on the substitution pattern of the ring. The 3,4-bis(tertiobutyl) substitution, for example, was shown to contract this P–P bond (Table II). In line with this observation, the reaction of lithium with dihydrodiphosphete **8** gave an unexpected result[22b,44] (Eq. (54)).



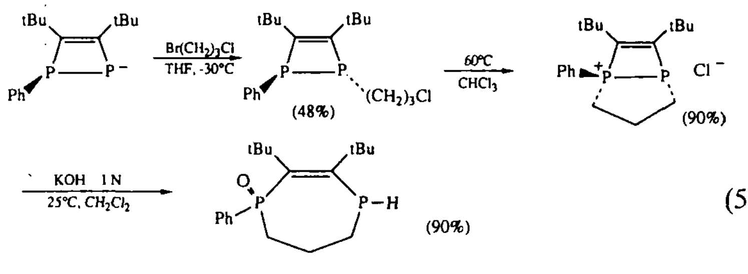
(54)

The resulting anion may benefit from some electronic delocalization explaining its formation when the P–P bond is somewhat strengthened. This anion proved to be an interesting synthon. For example, it allowed us to synthesize the first *cis*-1,2-dihydro-1,2-diphosphete[43] (Eq. (55)).



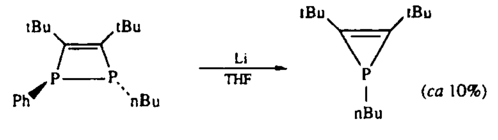
(55)

We have already seen that no delocalization appears to be at work in **10**. The preparation of an original diphosphorus macrocycle is another illustration of this synthetic potential[22b] (Eq. (56)).



(56)

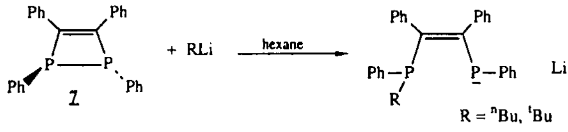
Finally, in one case, we have observed an even less conventional cleavage of the dihydrodiphosphate ring by lithium in THF[52] (Eq. (57)).



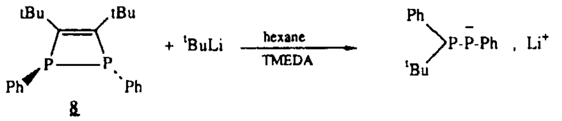
(57)

The 3-membered ring shows a characteristic ^{31}P NMR resonance at high field (δ-185 vs. H_3PO_4). This reaction has no practical application, however.

The outcome of the reaction of alkyllithiums with dihydrodiphosphetes also depends on the substitution pattern of the ring[22b] (Eqs. (58) and (59)).



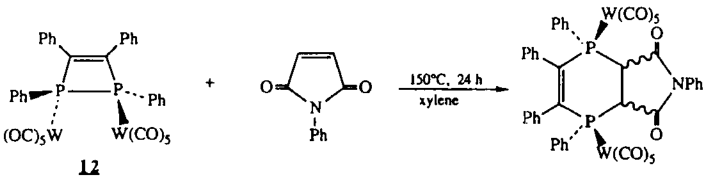
(58)



(59)

Compound **8** is far less reactive than compound **7**. Only the highly nucleophilic ^{t}BuLi-TMEDA complex is able to react and the result, retention of the P–P bond and cleavage of the two P–C ring bonds, is quite surprising.

We will close this section with a discussion on the 1,2-dihydro-1,2-diphosphete-1,4-diphosphabutadiene equilibrium. As in the dihydrophosphete case, it has been impossible to put this equilibrium in evidence with the tervalent dihydrodiphosphetes. For example, 7 does not cycloadd with *N*-phenylmaleimide at 150°C.[42] The complexation of the two lone pairs, however, weakens the P–P bond (see Table II) and stabilizes the 1,4-diphosphabutadiene isomer. The trapping of this isomer thus becomes possible at high temperature[42] (Eq. (60)).



2 isomers, 83%

(60)

Similar cycloadditions were observed with maleic anhydride, acrylonitrile and benzaldehyde. According to the structures of the cycloadducts, the opening of complex **12** is conrotatory and thus follows the Woodward–Hoffmann rules.

CONCLUSION

When looking at the first section of this review, the reader may have been sceptical concerning the interest of dihydrophosphetes and dihydrodiphosphetes. This comprehensive survey of what is known about these rings has probably convinced most of those who have been patient enough to read the whole review. The potential of these heterocycles is obviously enormous in coordination chemistry. Metalladiphospholenes such as those depicted in Eqs. (41) and (49) are analogous to the well-known dithiolene metal complexes whose applications as redox catalysts, dyes and organic conductors are being seriously investigated. Tetraphosphafulvalene dianions such as the one in Eq. (53) can be a source of new charge-transfer complexes with potential applications as organic conductors. 1,3-diphospholyl anions such as those of Eqs. (50)–(52) can serve as η^5-ligands for the synthesis of new phosphametallocenes.

As synthons in organic chemistry, these 4-membered rings can serve as precursors for open-chain compounds and larger rings via reductive, concerted, or homolytic cleavage of the P–Csp^3 or P–P ring bonds. Their electrocyclic opening into the corresponding phosphadienes offers a unique opportunity to study these elusive species from synthetic and theoretical standpoints. The high sensitivity of the structures and reactivities of these rings to the substitution patterns allows a finetuning of their chemistry according to the goals of synthetic chemists. Now that these rings are easily available, a broad range of applications become accessible.

Acknowledgments

Financial support for this work has been provided by CNRS, Ecole Polytechnique and SNPE over several years. We are grateful to several students and postdocs

who have carried out parts of this work, including Drs. S. Bauer, M. Sierra and G. Sillett.

References

1. E. Jungermann and J. J. McBride, Jr., J. Org. Chem. **26**, 4182 (1961); E. Jungermann, J. J. McBride, Jr., R. Clutter and A. Mais, J. Org. Chem. **27**, 606 (1962); E. Jungermann, J. J. McBride, Jr., J. V. Killheffer and R. J. Clutter, J. Org. Chem. **27**, 1833 (1962).
2. G. Becker, Z. Anorg. Allg. Chem. **423**, 242 (1976). For a review on phosphaalkenes and their dimers, see R. Appel, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, eds. M. Regitz and O. J. Scherer (Georg Thieme Verlag, Stuttgart, 1990), pp. 157–219.
3. P. Binger, R. Milczarek, R. Mynott and M. Regitz, J. Organomet. Chem. **323**, C35 (1987).
4. P. B. Hitchcock, M. J. Maah and J. F. Nixon, J. Chem. Soc., Chem. Commun. **1986**, 737; P. Binger, R. Milczarek, R. Mynott, M. Regitz and W. Rösch, Angew. Chem. Int. Ed. Engl. **25**, 644 (1986).
5. J. Svara, E. Fluck and H. Riffel, Z. Naturforsch **40b**, 1258 (1985); B. Neumüller and E. Fluck, Phosphorus Sulfur **29**, 23 (1986).
6. W. Mahler, J. Am. Chem. Soc. **86**, 2306 (1964).
7. S. Kh. Nurtdinov, N. M. Ismagilova, R. A. Fakhrutdinova and J. V. Zykova, Zh. Obshch. Khim. **53**, 1045 (1983); Chem. Abstr. **99**, 122548z (1983).
8. A. Marinetti, J. Fischer and F. Mathey, J. Am. Chem. Soc. **107**, 5001 (1985).
9. Ring VIII is present in a stable Dewar phosphinine: J. Fink, W. Rösch, U.-J. Vogelbacher and M. Regitz, Angew. Chem. Int. Ed. Engl. **25**, 280 (1986).
10. G. Becker, W. Becker, R. Knebl, H. Schmidt, U. Hildenbrand and M. Westerhausen, Phosphorus Sulfur **30**, 349 (1987); N. H. Tran Huy, L. Ricard and F. Mathey, Organometallics, in press.
11. R. Appel and V. Barth, Tetrahedron Lett. **21**, 1923 (1980).
12. R. Appel, V. Barth and F. Knoch, Chem. Ber. **116**, 938 (1983).
13. G. Becker, Z. Anorg. Allg. Chem. **423**, 242 (1976).
14. R. Appel, J. Hünerbein and N. Siabalis, Angew. Chem. Int. Ed. Engl. **26**, 779 (1987).
15. R. H. Neilson, B. A. Boyd, D. A. Dubois, R. Hani, G. M. Scheide, J. T. Shore and U. G. Wettermark, Phosphorus Sulfur **30**, 463 (1987).
16. B. A. Boyd, R. J. Thoma and R. H. Neilson, Tetrahedron Lett. **28**, 6121 (1987); B. A. Boyd, R. J. Thoma, W. H. Watson and R. H. Neilson, Organometallics **7**, 572 (1988).
17. N. H. Tran Huy, L. Ricard and F. Mathey, Organometallics **7**, 1791 (1988).
18. A. Marinetti, L. Ricard and F. Mathey, Organometallics **9**, 788 (1990); see also P. Le Floch and F. Mathey, Synlett, **1990**, 171.
19. A. Marinetti and F. Mathey, Angew. Chem. Int. Ed. Engl. **27**, 1382 (1988); A. Marinetti, S. Bauer, L. Ricard and F. Mathey, Organometallics **9**, 793 (1990).
20. This point is discussed in a review: U. Schmidt, Angew. Chem. Int. Ed. Engl. **14**, 523 (1975).
21. A. Ecker and U. Schmidt, Chem. Ber. **106**, 1453 (1973).
22. (a) C. Charrier, J. Guilhem and F. Mathey, J. Org. Chem. **46**, 3 (1981); (b) C. Charrier, N. Maigrot, F. Mathey, F. Robert and Y. Jeannin, Organometallics **5**, 623 (1986).

23. I. G. Phillips, R. G. Ball and R. G. Cavell, Inorg. Chem. **27**, 2269 (1988).
24. A. Marinetti and F. Mathey, J. Chem. Soc., Chem. Commun. **1990**, 153.
25. The chemistry of phosphirenes has been reviewed: F. Mathey, Chem. Rev. **90**, 997 (1990).
26. D. Carmichael, P. B. Hitchcock, J. F. Nixon, F. Mathey and A. Pidcock, J. Chem. Soc., Chem. Commun. **1986**, 762; S. S. Al Juaid, D. Carmichael, P. B. Hitchcock, A. Marinetti, F. Mathey and J. F. Nixon, J. Chem. Soc., Dalton Trans. **1991**, 905.
27. A. Marinetti and F. Mathey, Organometallics **7**, 633 (1988).
28. L. Ricard, N. Maigrot, C. Charrier and F. Mathey, Angew. Chem. Int. Ed. Engl. **26**, 548 (1987).
29. K. M. Doxsee, E. M. Hanawalt, G. S. Shen, T. J. R. Weakley, H. Hope and C. B. Knobler, Inorg. Chem. **30**, 3381 (1991).
30. K. M. Doxsee, G. S. Shen and C. B. Knobler, J. Am. Chem. Soc. **111**, 9129 (1989).
31. W. Tumas, J. A. Suriano and R. L. Harlow, Angew. Chem. Int. Ed. Engl. **29**, 75 (1990).
32. F. N. Tebbe and R. L. Harlow, J. Am. Chem. Soc. **102**, 6149 (1980).
33. K. H. Dötz, A. Tiriliomis and K. Harms, J. Chem. Soc., Chem. Commun. **1989**, 788.
34. C. M. Lukehart, A. T. McPhail, D. R. McPhail, J. B. Myers, Jr. and H. K. Soni, Organometallics **8**, 1007 (1989).
35. A. C. Dema, X. Li, C. M. Lukehart and M. D. Owen, Organometallics **10**, 1197 (1991).
36. P. Binger, T. Wettling, R. Schneider, F. Zurmühlen, U. Bergsträsser, J. Hoffmann, G. Maas and M. Regitz, Angew. Chem. Int. Ed. Engl. **30**, 207 (1991).
37. N. Lavaud-Dufour, Dissertation, Toulouse (1991).
38. A. Meriem, J. P. Majoral, M. Revel and J. Navech, Tetrahedron Lett. **24**, 1975 (1983).
39. G. Becker, W. Becker and G. Uhl, Z. Anorg. Allg. Chem. **518**, 21 (1984).
40. G. Becker, W. Becker and G. Uhl, Z. Anorg. Allg. Chem. **519**, 31 (1984).
41. K. Blatter, W. Rösch, U.-J. Vogelbacher, J. Fink and M. Regitz, Angew. Chem. Int. Ed. Engl. **26**, 85 (1987).
42. N. Maigrot, C. Charrier, L. Ricard and F. Mathey, Polyhedron **9**, 1363 (1990).
43. N. Maigrot, C. Charrier, L. Ricard, P. Le Goff and F. Mathey, Bull. Soc. Chim. Fr., in press.
44. C. Charrier, F. Mathey, F. Robert and Y. Jeannin, J. Chem. Soc., Chem. Commun. **1984**, 1707.
45. S. M. Bachrach, J. Org. Chem. **56**, 2205 (1991).
46. T. C. Wallace, R. West and A. H. Cowley, Inorg. Chem. **13**, 182 (1974).
47. A. H. Cowley, M. J. S. Dewar, D. W. Goodman and M. C. Padolina, J. Am. Chem. Soc. **96**, 3666 (1974).
48. K. M. Doxsee, G. S. Shen and C. B. Knobler, J. Chem. Soc., Chem. Commun. **1990**, 1649.
49. N. H. Tran Huy and F. Mathey, Tetrahedron Lett. **29**, 3077 (1988).
50. N. H. Tran Huy and F. Mathey, Heteroatom Chem. **1**, 33 (1990).
51. F. A. Ajulu, S. S. Al Juaid, D. Carmichael, P. B. Hitchcock, M. F. Meidine, J. F. Nixon, F. Mathey and N. H. Tran Huy, J. Organomet. Chem. **406**, C20 (1991).
52. C. Charrier and N. Maigrot, unpublished results.
53. A. H. Cowley and K. E. Hill, Inorg. Chem. **12**, 1446 (1974).
54. K. Knoll, G. Huttner and L. Zsolnai, J. Organomet. Chem. **307**, 237 (1986).
55. G. Sillett and L. Ricard, unpublished results.

56. N. Maigrot, M. L. Sierra, C. Charrier, L. Ricard and F. Mathey, Polyhedron, in press.
57. N. Maigrot, L. Ricard, C. Charrier and F. Mathey, Angew. Chem. Int. Ed. Engl. **29**, 534 (1990)
58. N. Maigrot, L. Ricard, C. Charrier and F. Mathey, Angew. Chem., Int. Ed. Engl. **27**, 950 (1988).
59. M. L. Sierra, N. Maigrot, C. Charrier, L. Ricard and F. Mathey, Organometallics, in press.
60. N. Maigrot, L. Ricard, C. Charrier and F. Mathey, to be published.