

Transient 2*H*-Phospholes as Powerful Synthetic Intermediates in Organophosphorus Chemistry

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ABSTRACT

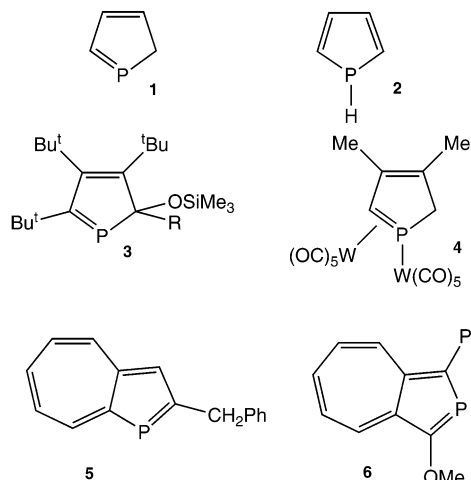
Transient 2*H*-phospholes are easily obtained from 1-*R*-1*H*-phospholes by a [1,5]-shift of the *R*-substituent from phosphorus to the α -carbons of the ring. They display cyclopentadiene-like chemistry: [4+2]-cycloaddition reactions with alkenes, alkynes, conjugated dienes and aldehydes, deprotonation to give the aromatic phospholide ions, and reaction with transition metal derivatives to give η^5 -phospholyl complexes. The resulting products have found some use in homogeneous and asymmetric catalysis and show some promise in the field of electroconducting polymers.

1. Introduction

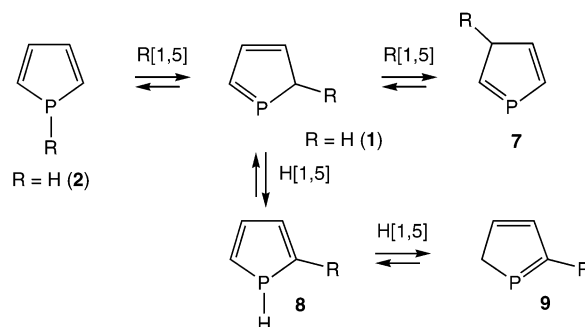
2*H*-Phosphole **1** is a tautomer of parent phosphole **2** (Scheme 1). Whereas 1*H*-phosphole **2** has been completely characterized at low temperature by ^1H , ^{13}C , and ^{31}P NMR spectroscopy,¹ 2*H*-phosphole **1** remains elusive and has never been observed as such. Its stabilization can be achieved by complete substitution with bulky groups as in derivative **3**,² complexation as in tungsten complex **4**,³ or inclusion into an aromatic system as in phosphazulenes **5**⁴ and **6**⁵ (Scheme 1). If the chemistry of 2*H*-phospholes was restricted to these few stable compounds, it would be of limited interest. Fortunately, transient 2*H*-phospholes are readily accessible with a huge variety of substitution patterns via the 1*H*-phosphole \rightleftharpoons 2*H*-phosphole equilibrium. They display a rich and versatile cyclopentadiene-like reactivity and served as precursors for the preparation of a variety of novel polycyclic P-containing structures, phospholide ions, phosphametalloenes, phosphinines, etc. Thus, they deserve special attention both from theoretical and practical standpoints. The data concerning 2*H*-phospholes are generally scattered throughout the papers devoted to 1*H*-phospholes. The only specific review of 2*H*-phospholes is already 7 years old and is poorly accessible.⁶ We present here an

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Scheme 1



Scheme 2



updated survey, which highlights the various possibilities offered by this chemistry in the fields of homogeneous catalysis and molecular materials.

2. The 1*H*-Phosphole \rightleftharpoons 2*H*-Phosphole Equilibrium

As a result of the pyramidal geometry of phosphorus,⁷ phospholes are poorly aromatic. The most recent evaluation of the aromatic stabilization energy of parent phosphole **2** is 3.2 kcal mol⁻¹.⁸ Conversely, the pyramidal geometry of phosphorus favors the [1,5]-sigmatropic shift of the phosphorus substituent from P to C as a result of the significant σ, π^* overlap between the exocyclic P–R bond and the dienic system. The most recent theoretical study of the 1*H*-phosphole \rightleftharpoons 2*H*-phosphole \rightleftharpoons 3*H*-phosphole equilibrium at the CCSD(T)/6-31G* level (Scheme 2, R = H)⁹ concludes that **1** is more stable than **2** by 6.0 kcal mol⁻¹ and more stable than **7** by 3.3 kcal mol⁻¹. The transition state (TS) between **2** and **1** is 19.6 kcal mol⁻¹ higher in energy than **2**. The transition state between **1** and **7** is 30.7 kcal mol⁻¹ higher in energy than **1**. These results confirm earlier calculations.¹⁰ They imply a facile transformation of **2** into **1** and a difficult transformation of **1** into **7**. These findings are in perfect agreement with the experimental observations.¹¹ 1*H*-Phospholes, as obtained by protonation of phospholide ions, readily equilibrate with 2*H*-phospholes below room

Table 1. Relative Energies (ΔE) for the Interconversion between 1-*R*-1*H*- and 2-*R*-2*H*-Phospholes (in kcal mol⁻¹)

R	$\Delta E((2\text{-}R\text{-}2\text{H}) - (1\text{-}R\text{-}1\text{H}))$	$\Delta E((\text{TS}) - (1\text{-}R\text{-}1\text{H}))$
H	-3.4	18.3
Me	2.1	37.7
vinyl	0.4	25.5
ethynyl	1.4	30.0
CN	0.2	28.7
CHO	-3.7	8.3
OH	16.1	46.7
SH	12.7	28.9
SiH ₃	2.5	14.2

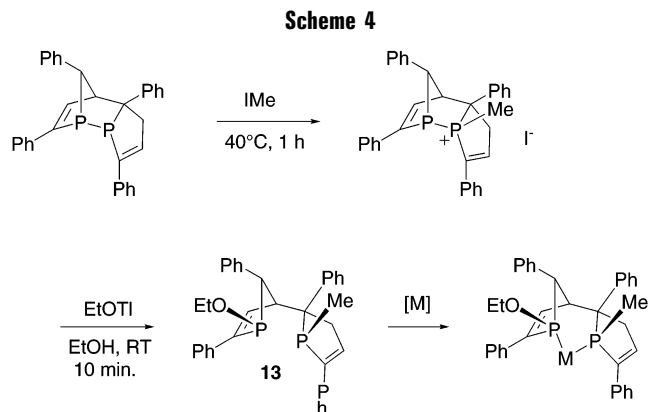
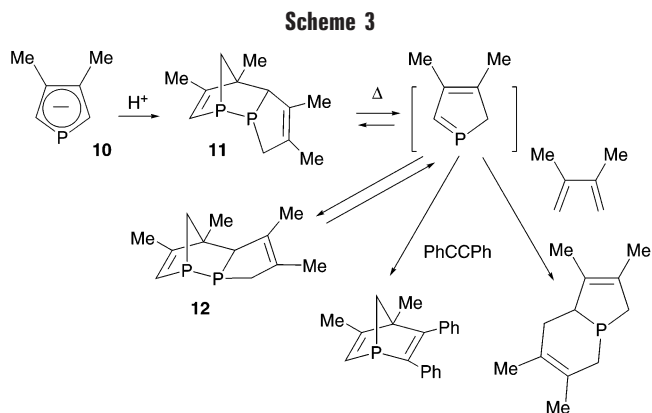
temperature. The formation of 3*H*-phospholes has never been observed.

Another set of experimental observations that has never been investigated from a theoretical standpoint is the ease with which sigmatropic shifts occur as a function of the nature of the migrating group. Whereas hydrogen migrates very easily below room temperature when no substituent is present on the α -positions of the ring, other groups require the application of heat (aryl,¹² alkynyl, CN, SR, etc.¹³), while some others do not migrate under conditions compatible with the intrinsic stability of the phosphole ring (alkyl, OR, etc.¹³). These variations in the migrating ability explain why the final result of the equilibration of a 1-*R*-1*H*-phosphole is always the 2-*R*-5*H*-phosphole **9** since H migrates more easily than R.

To gain a better insight into this phenomenon, we decided to carry out a series of calculations at the B3LYP/6-311+G(d,p) level.¹⁴ The results are summarized in Table 1. For R = H, our data are similar to those of Bachrach¹⁰ and Sastry.⁹ The observed trends fit nicely with the experimental observations. The substituents can be divided into three categories, those that do not migrate under practical conditions (OH, Me), those that migrate upon heating (vinyl, ethynyl, CN, SH), and those that migrate spontaneously at low temperature (H, CHO, SiH₃). It is clear that OH does not migrate because the high strength of the P–O bond heavily stabilizes the 1*H*-phosphole relative to the 2*H*-phosphole. A similar explanation is not valid in the case of R = Me. Here, it is the high-energy pentacoordinate geometry of the migrating carbon in the transition state that is responsible for the destabilization of the TS. The ease of migration of R = H and R = SiH₃ is well accounted for and does not come as a surprise. In contrast, the very low barrier to the migration of R = CHO comes as a shock. Here, it is the extreme weakness of the P–formyl bond (P–CHO = 1.932 Å) and the very high pyramidalicity of phosphorus in the 1*H*-phosphole that favors the shift, the out-of-plane angle between the phosphole plane and the substituent being as high as 85°.

3. Dimerization and Oligomerization of 2*H*-Phospholes

At low temperature, the normal dimerization products of 2*H*-phospholes are the P–P [4+2] endo dimers. The X-ray crystal structure of one of these dimers (**11**)¹⁵ shows long P–P and C–C bridging bonds (2.239 and 1.557 Å, respectively). The dimerization is reversible upon heating and



the monomer can be trapped by diphenylacetylene or 2,3-dimethylbutadiene at 110–130 °C (Scheme 3).

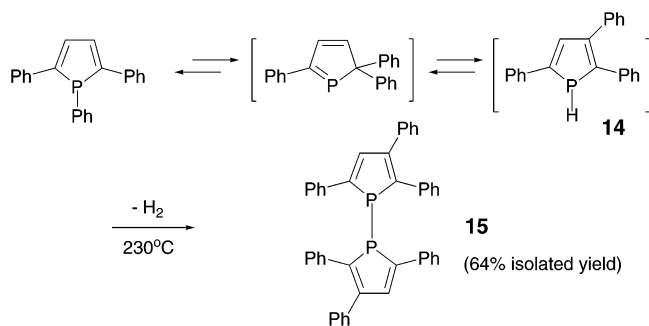
In the absence of a trapping reagent, the endo dimer **11** evolves toward the exo dimer **12**.¹¹ Under UV irradiation, dimers similar to **11** give the corresponding cage compounds by intramolecular [2+2] cycloaddition between the two double bonds.

The dimerization of parent 2*H*-phosphole **1** has been studied at the B3LYP/6-311+G(d,p) level.¹⁶ The TS for the endo dimer is 1.8 kcal mol⁻¹ lower in energy than the TS for the exo dimer. Conversely, the exo dimer is more stable than the endo dimer by 2.2 kcal mol⁻¹. The formation of the kinetic endo and thermodynamic exo [4+2] dimers is comparable to what is observed for cyclopentadiene.

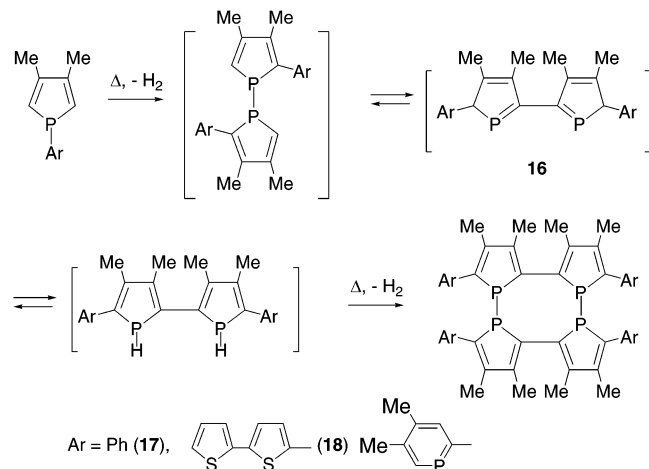
An interesting chemistry has been developed with the [4+2] endo dimers. Quaternization selectively takes place at the phosphorus of the former dienophile. The resulting monoquaternary salts are attacked by thallium ethylate with cleavage of the P–P bond (Scheme 4).¹⁷ The novel biphospholenes thus obtained readily chelate transition metals. The cationic rhodium(I) complex derived from **13** efficiently catalyzes the hydrogenation of (*Z*)-acetylcinnamic acid at room temperature in methanol.

The evolution of 2*H*-phospholes at high temperature is completely different. We shall take the case of the triphenyl derivative as an example. At 230 °C, 1,2,5-triphenylphosphole is transformed into the 1,1'-biphospholyl **15** (Scheme 5).¹⁸ The precursor of **15** is probably **14** resulting from a series of [1,5] shifts of Ph and H. Until now, the mechanism of the loss of H₂ remains mysterious, although this phenomenon appears to be quite general

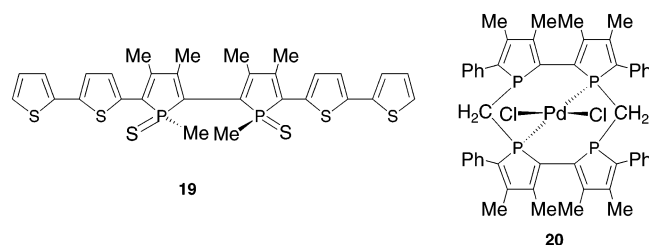
Scheme 5



Scheme 6

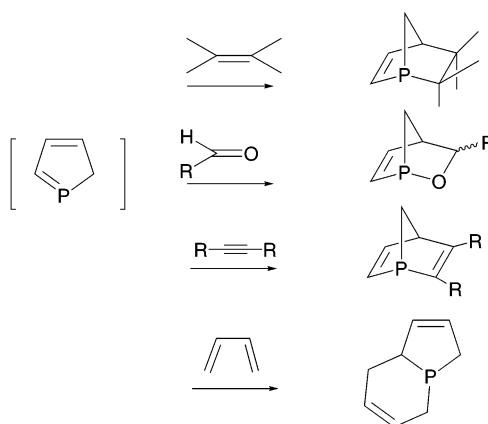


and has some interesting consequences. For example, the thermolysis of 1-aryl-3,4-dimethylphospholes yields a series of quite exciting tetramers (Scheme 6).^{19–21} The structures of these tetramers have been established by X-ray analysis. The formation of intermediates such as **16** has been demonstrated by trapping experiments.²² An electrochemical study has been performed on the derivatives of the hexanuclear chain **18**.²³ The bis-P(S)Me radical anion derived from the six-unit monomeric unit **19** should



present interesting electroconductive properties due to extensive delocalization along the chain. Recent work has shown the interest of using P–P dimers to reduce the HOMO–LUMO gap in a conjugated chain incorporating a phosphole unit.²⁴ In view of these data, **18** should also be an interesting starting point for the synthesis of electroconductive materials. From another standpoint, the phenylated tetramer **17** has served to synthesize a variety of novel tetraphosphorus macrocycles.²⁵ Since in these macrocycles each phosphorus atom is also incorporated in a phosphole ring, it readily inverts at around room temperature and thus, the macrocycle can adapt its

Scheme 7



stereochemistry to the requirements of any complexed metal. This property has been used to synthesize very stable palladium complexes such as **20**, which can be used as catalysts with very long half-lives for the Stille cross-coupling reaction, the allylation of malonate anions, and the Heck reaction.²⁶

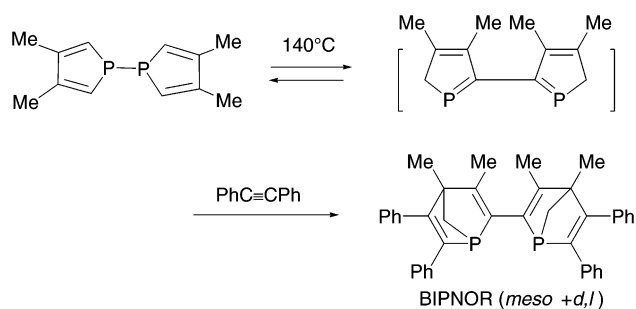
4. Cycloaddition of 2*H*-Phospholes with Alkenes and Alkynes

As already briefly shown in Scheme 3, 2*H*-phospholes can act as powerful dienes toward carbon–carbon double or triple bonds. A very recent addition to this type of reaction is [4+2] cycloaddition with the C=O double bond of aldehydes.²⁷ They also can act as dienophiles toward conjugated dienes via their P=C double bond (Scheme 7). This dual aspect of their reactivity has been studied from a theoretical standpoint. According to Bachrach,²⁸ the reaction of parent 2*H*-phosphole **1** with acetylene is concerted with an activation energy as low as 17.9 kcal mol⁻¹ (MP4 corrected for ZPE), which contrasts with the activation energy of the same reaction of cyclopentadiene with acetylene: 24.2 (experimental) and 27.9 kcal mol⁻¹ (MP4 corrected for ZPE). This clearly underlines the very high reactivity of **1** as a diene. Very low activation energies have also been computed by Sastry and co-workers⁹ in a more recent study of the reactions of **1** with ethylene and acetylene.

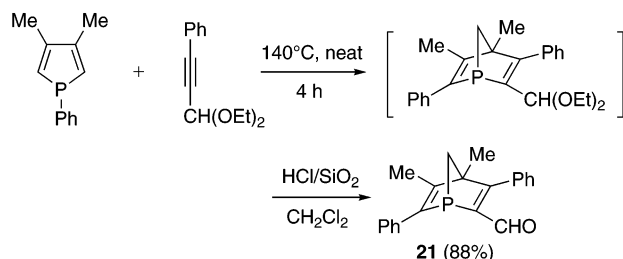
The reaction of **1** with 1,3-butadiene has also been investigated by Bachrach and Perriott.²⁹ The observed bicyclo[4.3.0]cyclononadiene appears to be the thermodynamic product, the kinetic product resulting from the 2*H*-phosphole (4π) + butadiene (2π) cycloaddition. The reaction leading to the favored *endo*-bicyclo[4.3.0]cyclononadiene proceeds through a stepwise biradical mechanism.

From a practical standpoint, this chemistry provides ready access to a wide range of novel bicyclic structures with phosphorus at the bridgehead. The phosphorus of such structures cannot racemize; thus their use as ligands in asymmetric catalysis is especially appealing. The work published to date has focused on the quite-stable 1-phosphanobornadienes. The so-called BIPNOR has been synthesized as shown in Scheme 8.³⁰ The two enantiomers

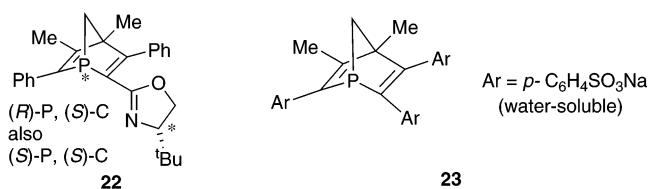
Scheme 8



Scheme 9



of the racemic mixture have been separated by complexation with an enantiopure palladium complex. BIPNOR is comparable to BINAP in the rhodium-catalyzed asymmetric hydrogenation of dehydroamino acids but superior in the asymmetric isomerization of a cyclic diene.³¹ A racemic 1-phosphanorbornadiene-2-carboxaldehyde has been efficiently synthesized as shown in Scheme 9.³² The resolution of **21** has been carried out through the formation of diastereomeric acetals with an enantiopure diol. The imine derivatives of **21** perform quite well in the palladium-catalyzed enantioselective allylic C- and N-alkylations of dimethyl malonate and benzylamine by 1,3-diphenylprop-2-enyl acetate.³³ In a similar vein, a 2-oxazolone derivative **22** is quite efficient as ligand for the

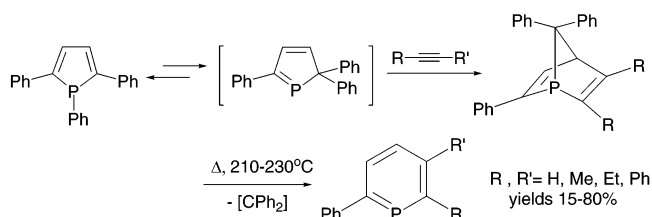


asymmetric Heck reaction.³⁴

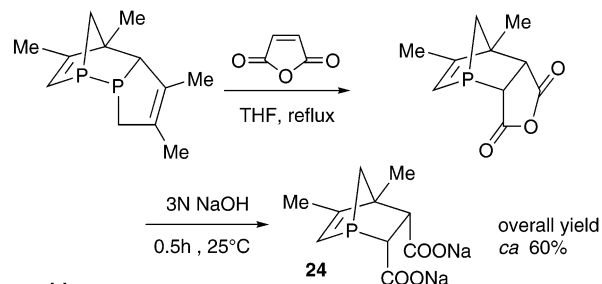
Racemic 1-phosphanorbornadienes have also been used as ligands in the rhodium-catalyzed hydroformylation of olefins.³⁵ A very efficient water-soluble version, **23**, has been proposed for the biphasic hydroformylation of propene.³⁶

In a completely different vein, the thermolysis of 7,7-diphenyl-substituted 1-phosphanorbornadienes provides an interesting entry into the chemistry of phosphinines (Scheme 10).¹⁸ The chemistry of 1-phosphanorbornenes is far less developed in part as a result of their relatively low thermal stability and of the possible formation of endo and exo isomers. An interesting water-soluble ligand, **24**, has nevertheless been synthesized (Scheme 11).³⁷

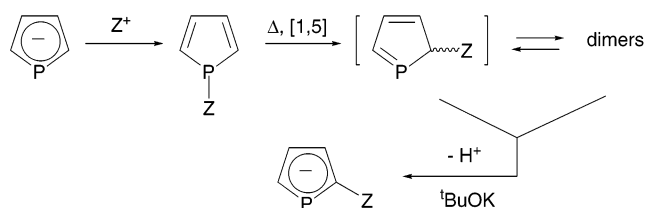
Scheme 10



Scheme 11



Scheme 12

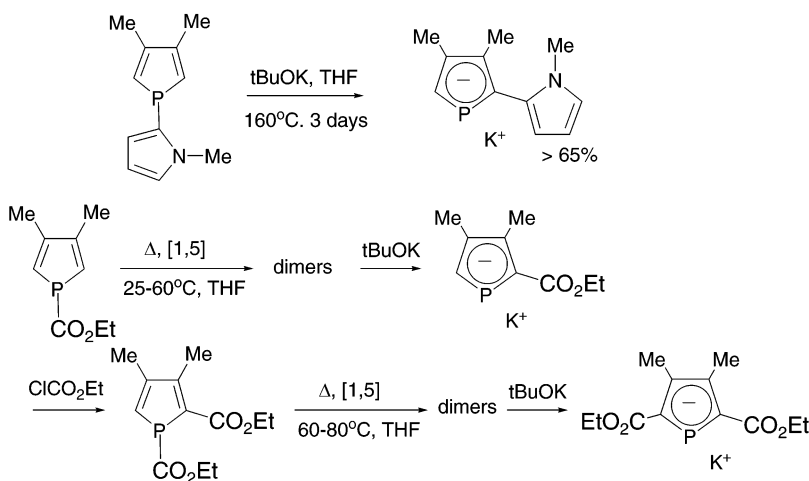


5. 2*H*-Phospholes as Sources of Phospholide Ions

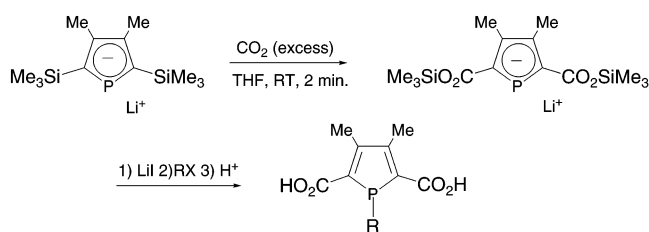
In terms of acid strength, 1*H*- and 2*H*-phospholes (**1** and **2**) are close to halogenated carboxylic acids. The gas-phase proton affinity of the parent phospholide ion has been measured by bracketing experiments to be 338 ± 3 kcal mol⁻¹.³⁸ Thus, 2*H*-phospholes are ideal sources of phospholide ions. In fact, they have served to devise the only simple method to functionalize a preformed phosphole ring (Scheme 12).³⁸ Two conditions are needed for the success of the reaction: (1) the group Z must be able to migrate, something that excludes alkyl and alkoxy substituents; (2) the Z substituent and, eventually, the P–Z bond must be compatible with the base. In practice, two techniques have been used to perform this transformation. With substituents resistant to heat and bases, the P–Z phosphole is heated in the presence of *t*-BuOK. This technique works for phenyl,³⁹ 2-(diphenylphosphino)phenyl,⁴⁰ 2-pyridyl,³⁹ *N*-methyl-2-pyrrolyl,⁴⁰ and 1,2,3,4-tetramethyl-cyclopentadienyl⁴¹ substituents. With reactive substituents, the [1,5]-shift is performed first, a variety of [4+2] dimers is thus obtained, and finally, the mixture is treated with *t*-BuOK. This technique has been applied to compounds where $\text{Z} = \text{CO}_2\text{Et}$,³⁹ $\text{C}(\text{O})\text{R}$,⁴² and SiR_3 .⁴³ Two typical examples are depicted in Scheme 13.

The example with the pyrrolyl substituent highlights the extraordinary thermal stability of phospholide ions. The example with the ethoxycarbonyl substituent shows how it is possible to use this chemistry to prepare 2,5-difunctional derivatives. This represents the only practical access to such species. A variant of this reaction provides

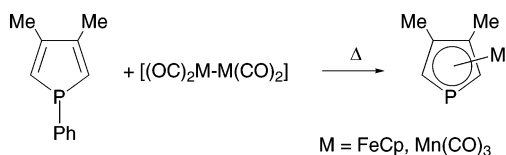
Scheme 13



Scheme 14



Scheme 15

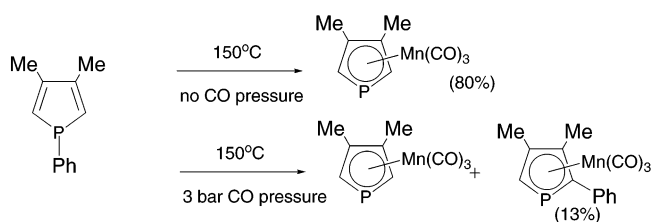


access to phosphole-2,5-dicarboxylic acids (Scheme 14).⁴⁴ Here, the [1,5]-shift of CO₂ is followed by a [1,3]-shift of the silicon substituent from the α -carbon of the ring to the carbonyl oxygen. The sodium salts of these phosphole-2,5-dicarboxylic acids are water-soluble. Also noteworthy is the preparation of a phospholide ion bearing a 2-(–)-menthoxycarbonyl substituent, which has been used for the synthesis and resolution of planar chiral phospharuthenocenes.⁴⁵

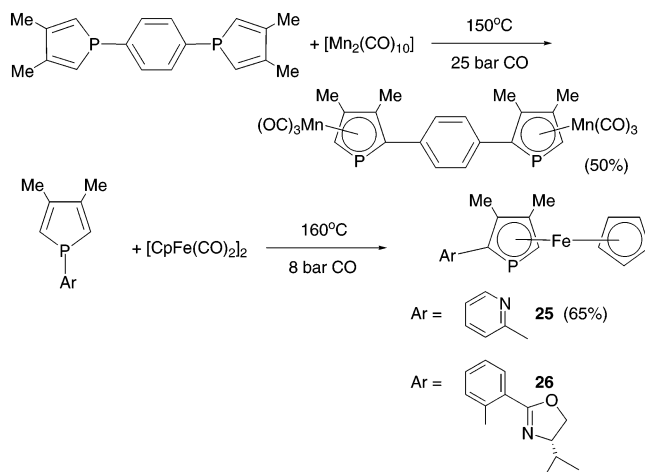
6. 2*H*-Phospholes in the Synthesis of Phosphametalloenes

It has been known for some time that dinuclear metal carbonyls react at high temperature with a substituted 1-phenylphosphole to give the corresponding phosphametalocene after splitting of the P–Ph bond (Scheme 15).⁴⁶ The mechanism probably involves the coordination of the phosphole lone pair onto the 15-electron [M(CO)][•] radical, followed by the loss of a phenyl radical in a manner similar to what occurs when alkali metals react with 1-phenylphospholes. Whatever the actual mechanism, a CO pressure disfavors the coordination of the phosphole onto the transition metal and prevents the formation of the phosphametalocene. If the temperature is high enough, then the [1,5]-shift of the phenyl substituent

Scheme 16



Scheme 17



ent becomes operative and the resulting 2*H*-phosphole reacts with the metal carbonyl to give the phenyl-substituted phosphametalocene. Scheme 16 compares the two reaction pathways for M = Mn(CO)₃.⁴⁷ This kind of chemistry has served to prepare some original phosphametalloenes. Some examples are shown in Scheme 17.^{48–50}

The two phosphoferrocenes **25** and **26** are both able to chelate transition metals between their sp² phosphorus and nitrogen centers. The oxazoline derivative might have some potential in asymmetric catalysis.

7. Conclusion

Like cyclopentadienes, 2*H*-phospholes can act both as dienes and dienophiles. In fact, they are very powerful

dienes as shown by their reaction with aldehydes. Like cyclopentadienes, 2*H*-phospholes give kinetic [4+2] endo dimers, which interconvert upon heating with the thermodynamic [4+2] exo dimers. Like cyclopentadienes, 2*H*-phospholes are readily deprotonated to give highly aromatic anions. Finally, like cyclopentadienes, 2*H*-phospholes readily react with transition metal derivatives to give η^5 -complexes. Thus, 2*H*-phospholes represent an almost perfect illustration of the diagonal phosphorus–carbon analogy.⁵¹ However, the phosphorus atom of 2*H*-phospholes adds a new dimension to their chemistry. The highly reactive P=C double bond of these species can easily give η^1 - and η^2 -complexes,³ it can also add alcohols¹² and water.² The [1,5] sigmatropic shifts of substituents, which are so characteristic of cyclopentadiene chemistry and allow a substituent to “dance” all around the ring, are in the case of 2*H*-phospholes practically restricted to migrations between phosphorus and the α -carbons of the ring. At high temperature, α -unsubstituted 2*H*-phospholes give, by loss of hydrogen, well-defined tetramers that have no equivalent in cyclopentadiene chemistry. Thus, in this respect, it can be stated that the chemistry of 2*H*-phospholes is even richer in possibilities than that of cyclopentadienes. Their ready availability, combined with a wide range of substitution patterns, means that they will find more and more synthetic uses in the future.

Most of the work described in this Account has been carried out in the laboratory of the author. The contribution of many dedicated co-workers, whose names are cited in the references, is gratefully acknowledged. Over the years, this research program has been supported by the CNRS, SNPE, Ecole Polytechnique, Rhodia, and more recently, the University of California, Riverside.

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