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From phosphorus heterocycles to phosphorus analogues of unsaturated hydrocarbon–transition metal π-complexes

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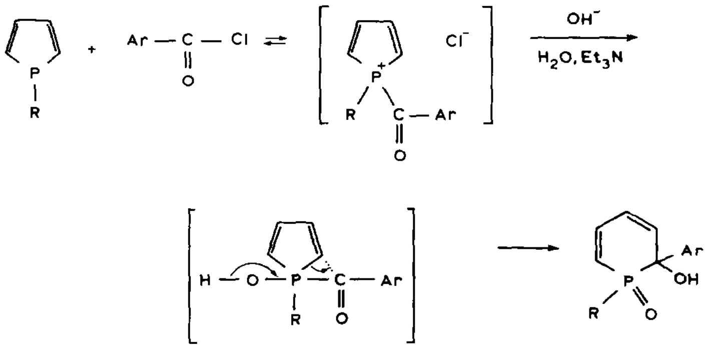
Unfortunately, phospholes are not aromatic...

At the beginning of the seventies, my research group was already deeply involved in the research on carbon-phosphorus heterocycles. One of the central questions being debated among phosphorus "heterocyclic" chemists at that time concerned the aromaticity of phosphole. In 1970, Coggon, Engel, McPhail and Quin [1] had demonstrated on the basis of an X-ray study that 1-benzylphosphole had a pyramidal phosphorus atom and rather long internal P–C bonds (1.783 Å). These two features suggested that phospholes were only weakly aromatic, in keeping with their rather high basicity: p*K*a ca. 0.5 for 1-methylphosphole [2]. These conclusions were supported by the results of a photoelectron spectroscopic study [3] which indicated that the energy of the phosphorus lone pair orbital remained almost unchanged upon saturation of the phosphole diene system. However, almost at the same time, a convincing argument in favor of phosphole aromaticity was advanced by Mislow and his group [4]. The phosphole pyramidal inversion barrier was shown to be ca. 20 kcal/mol lower than for saturated 5-membered cyclic phosphines. After some



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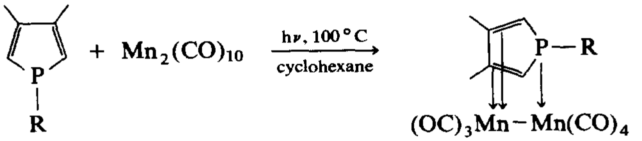
controversy, general agreement was reached on the following explanation [5]. In contrast to pyrroles, phospholes are pyramidal only because the aromatic stabilization of the planar transition state is insufficient to overcome the high inversion barrier for tervalent phosphorus. The pyramidal ground state displays a limited aromaticity owing to the reduced nπ overlap between the lone pair and the diene system.

This situation rendered almost hopeless any attempt to develop a classical aromatic chemistry for phospholes. However, things were not so clear at that time, and I decided to investigate in some depth the reaction of carboxylic acid chlorides with phospholes. The course of the reaction revealed by this study is depicted in eq. 1 [6].

Clearly, the nucleophilicity of the phosphole lone pair prevented any reaction of electrophiles on the diene system.

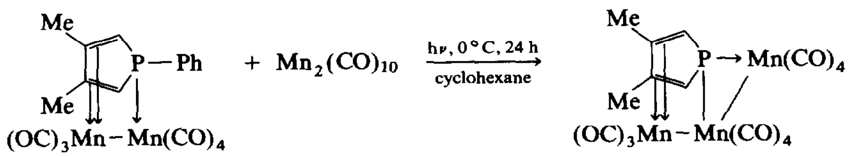
... but phosphacymantrenes are.

As an organic chemist, I was much concerned about the impossibility of functionalizing the phosphole diene system, since the absence of direct access to functional derivatives meant that there was no possibility of developing a substantial chemistry with phospholes. Some time later I read the account by Abel and his group of the first η^5-arsolyl transition metal complexes with manganese and rhenium tricarbonyls [7]. Since the analogous η^5-cyclopentadienyl complexes were known to have an extensive aromatic chemistry, it seemed logical to expect similar behaviour for η^5-arsolyl or η^5-phospholyl complexes. The electron-withdrawing complexing group seemed able to suppress the nucleophilicity of the remaining arsenic or phosphorus lone pairs in such complexes. At that time, there was no expertise on transition metal chemistry in my group, and so I decided to start cautiously and to investigate the reaction of phospholes with the commercially available $Mn_2(CO)_{10}$. It soon appeared that the main products of the reaction were dinuclear complexes involving both the lone pairs and the diene systems, as in eq. 2 [8].



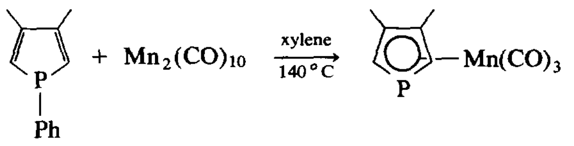
(2)

When R was phenyl or benzyl, however, a trinuclear complex was also formed that had resulted from the cleavage of the R–P bond Eq. 3.



(3)

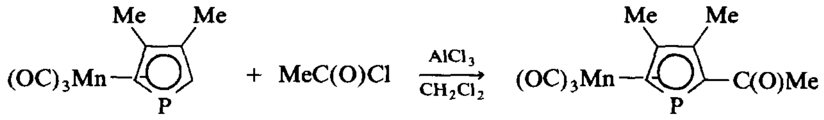
The correct formulation of that complex containing the two Mn–Mn bonds was only established later by an X-ray diffraction study [9]. But the key point was the formation of a phospholyl complex through cleavage of the P–Ph bond by $Mn_2(CO)_{10}$. It soon became apparent that this trinuclear complex decomposed upon heating to give the desired (η^5-phospholyl)manganesetricarbonyl or phosphacymantrene (phosphacyclopentadienyl-manganese-tricarbonyl). The next step was to find the appropriate experimental conditions to obtain directly phosphacymantrenes from 1-phenylphospholes by reaction with $Mn_2(CO)_{10}$. This was achieved one year later Eq. 4 [10].



(4)

(yields: 50–80%)

The similarity of the physical properties of these phosphacymantrenes to those of their all-carbon analogues was astonishing. For example, the unsubstituted compound had the same camphor-like odour as cymantrene itself. Solubility, colour, melting point, retention times, etc., were all quite similar. Obviously, the presence of phosphorus was masked in these compounds. More important, Friedel–Crafts acylations were readily performed, for the first time in phosphorus heterocyclic chemistry Eq. 5 [10].



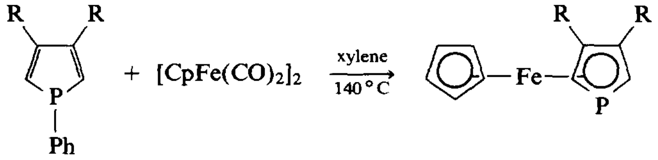
(5)

(80% yield)

Clearly, the nucleophilicity of the phosphorus lone pair had completely disappeared in these complexes. For example, no reaction was observed with iodine in boiling CCl_4, with pure methyl iodide, or pure trifluoroacetic acid at room temperature, or with benzyl bromide in refluxing toluene. Conversely, the compounds were very sensitive to nucleophilic attack; for example, they were destroyed by sodium cyanide in ethanol [11]. An X-ray diffraction study of one phosphacymantrene [11] definitively established the η^5-coordination of the phospholyl nucleus. The three intracyclic C–C bonds were almost equal, in keeping with a strong electronic delocalization within the ring. Comparison with the structure of cymantrene revealed that the only distorsions were in the vicinity of phosphorus. A theoretical study of phosphacymantrene [12] allowed rationalization of the chemical properties of these η^5-complexes. The LUMO is low-lying and highly localized on phosphorus. The lone pair orbital is only the fourth highest occupied orbital. Hence, phosphorus is electrophilic. With Anne Brèque, we developed some chemistry of these phosphacymantrenes, including chemical transformations of the acyl groups at the α carbons [13], and some replacements of carbon monoxide at manganese by other ligands [14].

The discovery of phosphaferrocenes

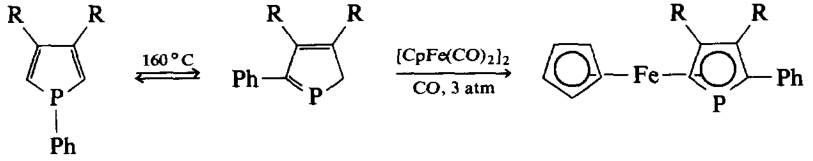
It soon became clear that phosphacymantrenes were not the definitive answer to our initial problem. Indeed, some very useful reactions, such as Vilsmeier formylation, did not work with these complexes. Obviously, the electron-withdrawing effect of the $Mn(CO)_3$ complexing group greatly lowered the susceptibility of the phospholyl nucleus towards attack by electrophiles. When we looked back again to the chemistry of η^5-cyclopentadienyl complexes, the logical next step seemed to be the synthesis of phosphaferrocenes. Ferrocenes are indeed, far more reactive towards electrophiles than cymantrenes. A simple extension of the synthesis of phosphacymantrenes allowed preparation of phosphaferrocenes, as in Eq. 6 [15].



(6)

(R = H, Me; Yields 20–30%)

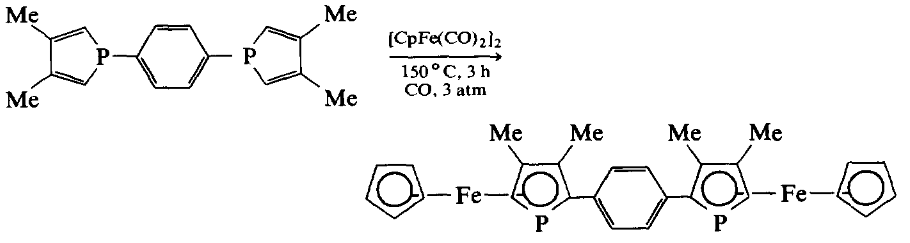
At that time, we had no routine access to ^{31}P NMR spectroscopy, and so were obliged to monitor the reactions by ^{1}H NMR spectroscopy. I vividly recall my excitement when I first looked at the ^{1}H NMR spectrum of the crude reaction product and saw the characteristic C*H*–P doublet at 3.71 ppm, with the 36 Hz *J*(H–P) coupling that indicated that the reaction had indeed produced the expected phosphaferrocene with R = Me. It immediately became apparent that these monophosphaferrocenes were extremely reactive. Both acylation and formylation were possible, but there were two drawbacks in the development of their chemistry. Firstly, other phosphaferrocenes bearing phenyl substituents were produced during the reaction [16]. It was unable to explain this until much later, when François Mercier discovered that the p-phenyl substituents were able to migrate around the phosphole nucleus [17]. These [1,5] sigmatropic shifts are a consequence of the pyramidality of phosphorus. There is a strong overlap between the σ-orbital of the P–Ph bond and the π-orbitals of the dienic system. This hyperconjugation, which is not present in pyrroles, favours the shift, which generally takes place above ca. 130–140 °C. The only way of slowing down such shifts is to substitute the two α-positions of the phosphole ring. As an alternative, we tried to slow down the cleavage of the P–Ph bond. Since a vacant site on iron is a prerequisite for the oxidative addition of the P–Ph bond, we decided to work under CO pressure. The course of the reaction was completely changed, as shown in Eq. 7 [18].



(7)

(R = H, Me; Yield ca. 50%)

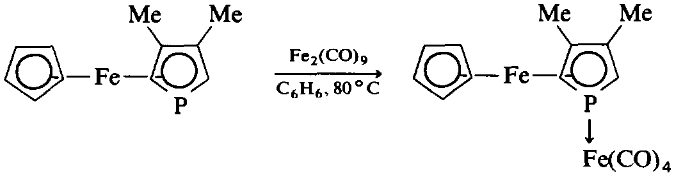
Very recently, we used this alternative technique to prepare a bis-phosphaferrocene with a paraphenylene bridge, Eq. 8 [19].



(8)

(25%)

The other drawback of monophosphaferrocenes was their high sensitivity toward oxidation, which meant that study of their chemistry was rather limited. The only notable result concerned the ability of the remaining phosphorus lone pair to coordinate with other metallic centers, as e.g. in Eq. 9 [20].

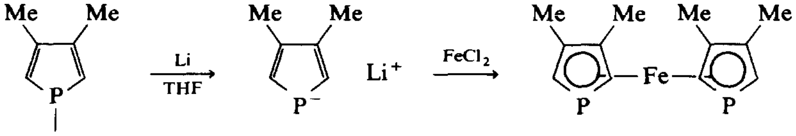


(75%)

(9)

This lone pair lies in the plane of the phospholyl nucleus, as directly demonstrated by a study of the electronic density map of 3,4-dimethylphosphaferrocene carried out in Strasbourg by Rees et al. [21]. The X-ray crystal structural study of the P–$Fe(CO)_4$ complex depicted in Eq. 9 confirmed this result [22]. As ligands, phosphaferrocenes behave as good π-acceptors, somewhat similar to phosphites. Apparently, the coordination of the phosphorus lone pair does not destroy the aromaticity of the phospholyl ring.

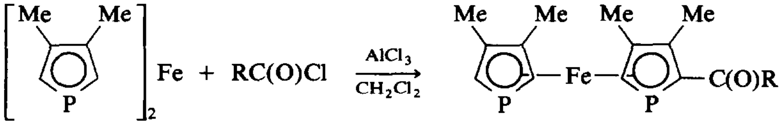
Still seeking a better compromise between reactivity, accessibility, and stability, I suggested to Guillaume de Lauzon that we should investigate the possible synthesis of 1,1′-diphosphaferrocenes. It should be remembered at this point that all the attempts up to that time to synthesize 1,1′-diazaferrocenes had failed. Such a species has been described only very recently [23]. Preliminary experiments, involving the direct reaction of a phospholyl anion with $FeCl_2$, gave the desired diphosphaferrocenes albeit in low yields, Eq. 10 [24].



(Yield ca. 15%)

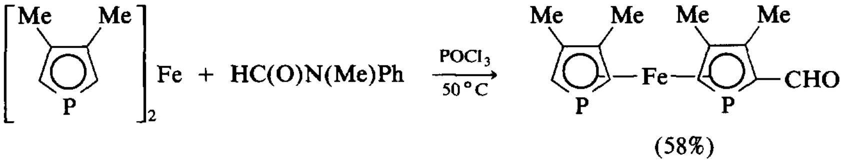
(10)

It immediately became clear that 1,1′-diphosphaferrocenes provided the compromise between stability and reactivity that we were looking for. Thus, we devoted a lot of effort to optimizing their synthesis. Since the nucleophiles (PhLi and similar species) involved in the preparation of diphosphaferrocenes tended to destroy the desired products, we added some Lewis acids to the solution of phospholyl anions before the condensation with iron chloride. Anhydrous aluminium chloride proved to have a very beneficial effect, and yields of up to 80% were obtained [25]. Having in hand sizable amounts of 1,1′-diphosphaferrocenes (quantities of up to 1 kg were prepared), we started an extensive study of their chemistry. Some electrophilic functionalization reactions are depicted in Eq. 11–13 [26,27].

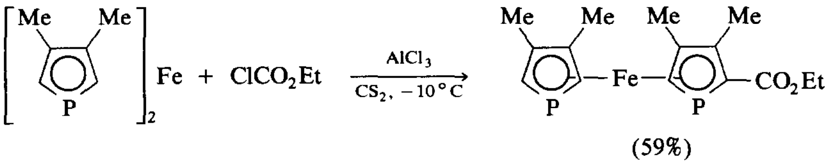


(R = Me 70%; R = Ph 50%)

(11)



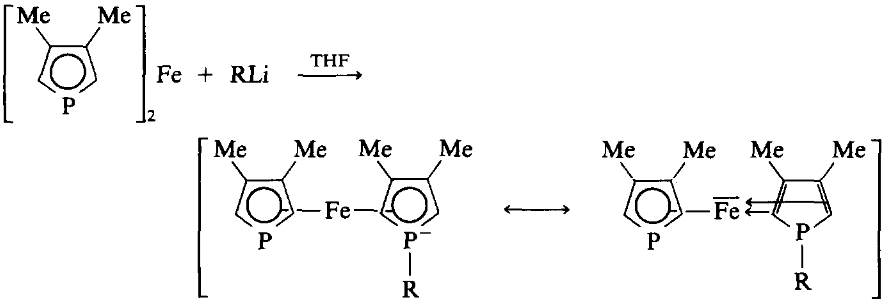
(12)



(13)

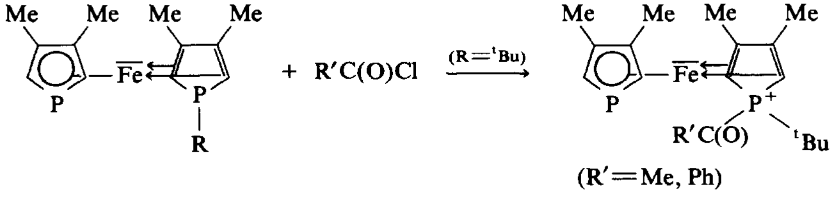
2,2′-Diacylations were also observed [26]. This series of reactions still remains as the only known aromatic chemistry in the field of carbon-phosphorus heterocycles.

The reactions with nucleophiles were also investigated in some depth by Bernard Deschamps. In each case, the initial attack takes place at phosphorus, as in e.g., Eq. 14 [28,29].



(14)

The anions thus obtained are better formulated with the negative charge at iron and one phosphorus outside the coordination sphere, as indicated by the ^{31}P NMR data. These anions were trapped by alkyl or acyl halides. The results are summarized in Eq. 15–17.



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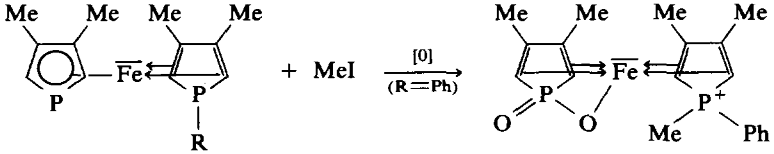
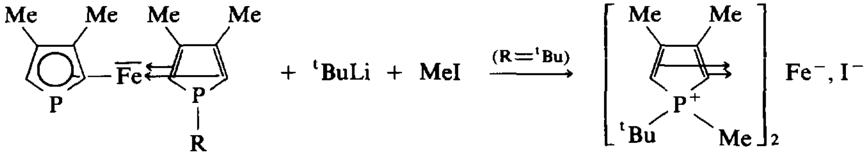


(16)

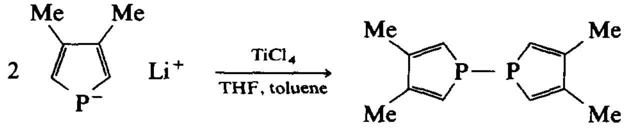


(17)

All the structures were established by X-ray diffraction studies in Strasbourg. Other investigations included the coordination of other metallic centres to the phosphorus lone pairs [30]. The electrochemistry of the parent diphosphaferrocenes and of their P-complexes [31] showed that the metal coordinated at the phosphorus lone pair did not interact with the iron atom sandwiched between the two rings.

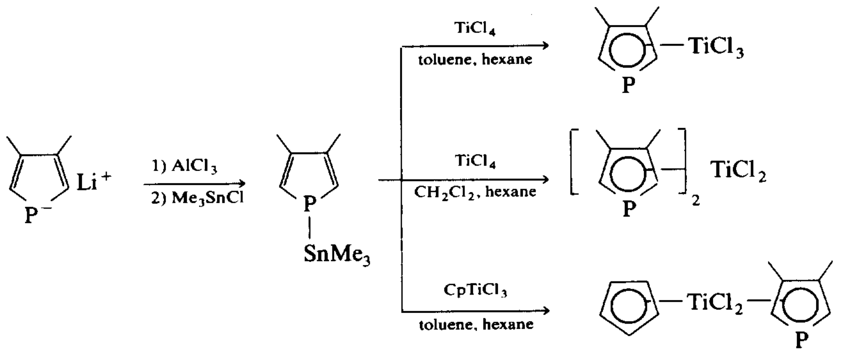
In search of other goals

For a while we remained almost alone in that new field. Then, in about 1986 numerous other groups began to study the chemistry of phosphaferrocenes. The most active in the area of mono- and di-phosphaferrocenes were Roberts, Silver and Wells. They devised a new synthesis of monophosphaferrocenes [32], and studied a series of reactions of mono- and di-phosphaferrocenes, including their protonation [33], their oxidation to phosphaferricinium cations [34], the η^5-phospholyl → η^6-arene exchange [35], the formation of α-phosphaferrocenylcarbenium ions [36], etc. At much the same time, the almost simultaneous discovery of a stable 1,2,3,4,5-pentaphosphaferrocene by Scherer [37] and of the stable pentaphospholyl anion by Baudler [38] came as a shock to both transition metal and phosphorus chemists. Then, Nixon started to study the η^5-complexes of 1,2,4-triphospholyl anions [39]. A reappraisal of our initial programme was obviously necessary. One possibility was to divert our studies from phosphorus to arsenic. (As early as 1979, Gérard Thiollet had prepared in our laboratory the first monoarsa- and diarsa-ferrocenes [40], and the X-ray crystal structural study of the diarsa species had been carried out in Toulouse [41].) I must confess that this idea did not meet with an enthusiastic response from my coworkers. Another possibility was to extend the range of η^5-phospholyl complexes to all the transition elements. Indeed, as long ago as 1979, Abel et al. had described a η^5-rhenium complex [42]. In our group, Claude Charrier [43] had prepared the first η^5-cobalt complex in 1982, and Serge Holand, the first η^5-tungsten complex in 1986 [44]. It was clearly possible to imagine a series of η^5-phospholyl complexes covering the whole range of transition metals. François Nief took charge of this programme. The first objective was to block the redox reactions which take place between phospholyl anions and reducible transition metal halides. One example of such a reaction is depicted in Eq. 18 [45].



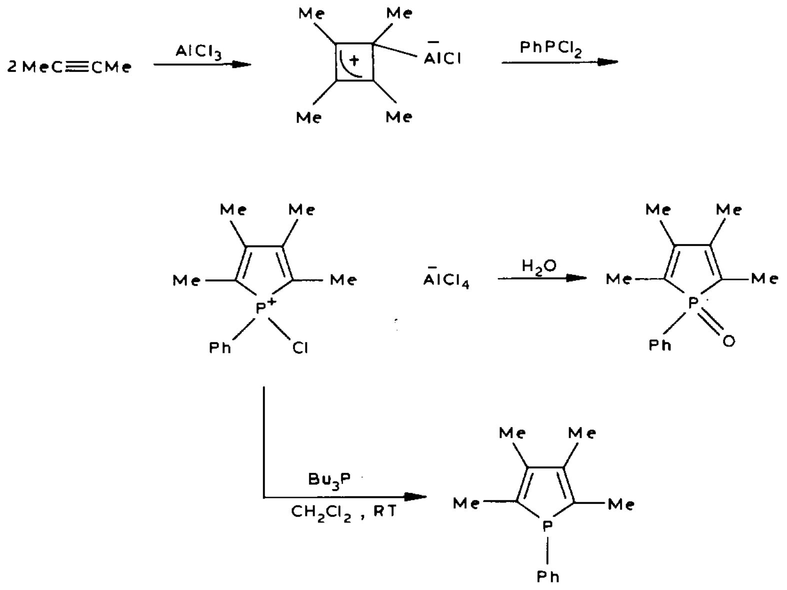
(18)

An obvious device was to replace the phospholyl anions by covalent phospholyl derivatives of electropositive main group elements. Silyl derivatives were ruled out because the silyl groups freely migrate around the phosphole nucleus [44]. In contrast, P-stannylphospholes proved to be stable at room temperature, and were used to synthesize the first η^5-phospholyltitanium complexes, as in Eq. 19 [45,46].



(19)

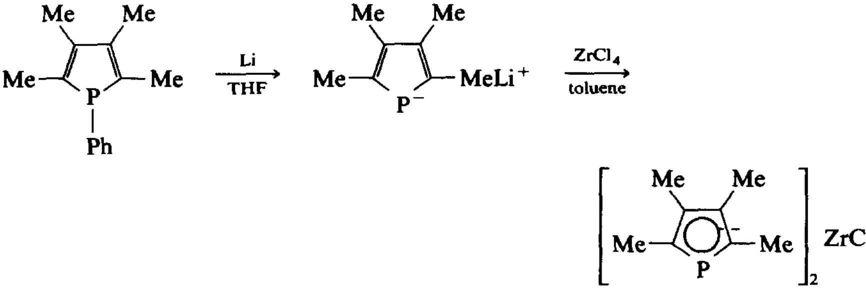
With other metals the redox reaction is not a problem, but the reactivity of the η^5-complexes is too high or the tractability too low. Such is the case with zirconium. Poorly characterized η^5-phospholylzirconium complexes were described as early as 1980 by Meunier and Gautheron [47]. In order to increase the tractability of these products, we chose to permethylate the phosphole nucleus (use of Cp* is well known to organometallic chemists). It was thus necessary to devise a synthesis of the still unknown 2,3,4,5-tetramethylphospholes. Some time earlier, Hogeveen and his colleagues had described the synthesis of 1-chloro-2,3,4,5-tetramethylphospholium chlorides, Eq. 20 [48].



(20)

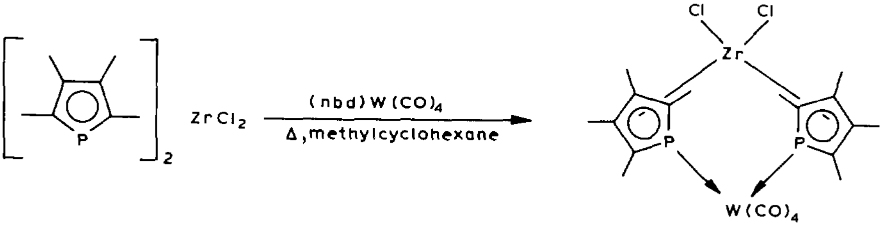
(21)

Reduction of these salts with tributylphosphine gave us a route to the desired 2,3,4,5-tetramethylphospholes Eq. 21 [49]. The same permethylated phospholes were independently obtained at the same time by Fagan et al. by reaction of the appropriate zirconacyclopentadiene with dichlorophosphines [50]. Classical chemistry then gave the bis (η^5-phospholyl)zirconium dichloride, which was obtained as crystals and fully characterized by X-ray methods, Eq. 22 [49].



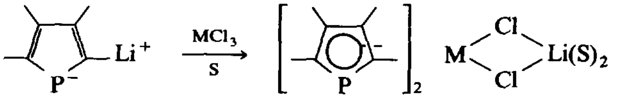
(22)

The structural study showed that the two phosphorus atoms are face to face. The interplane angle between the two rings is 48°. Thus, this diphosphazirconocene dichloride can chelate another transition metal. An example is given in Eq. 23 [51].



(23)

Use of the same tetramethylphospholyl anion also allowed preparation of the first heterocyclopentadienyl derivatives of the lanthanides, Eq. 24 [52].

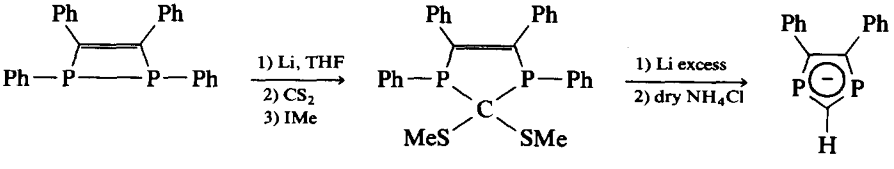


(24)

(M = Y, S = DME;
M = Lu, S = Et_2O)

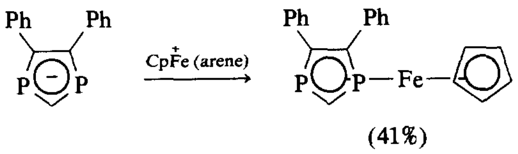
This programme still continues.

The third possibility was to participate in the investigations on the chemistry of polyphospholyl anions. Among these species, the 1,3-diphospholyl anions deserved special interest as the phosphorus analogues of imidazoles. The sole tris-tert-butyl derivative had previously been obtained as a by-product in the synthesis of the corresponding triphospholyl anion from t-Bu-C≡P [39,53]. To devise a versatile and general synthesis of these diphospholyl anions was thus a prerequisite. Very recently, Nicole Maigrot discovered a method of converting the readily available 1,2-dihydro-1,2-diphosphetes into diphospholyl anions, Eq. 25 [54].



(25)

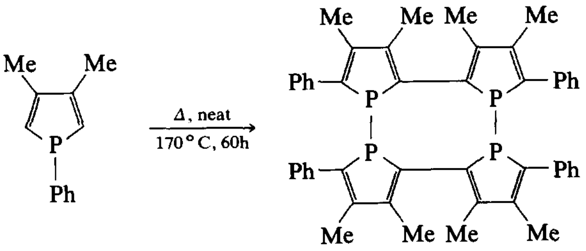
The precise mechanism of the second step of this conversion is unknown. The resulting anion was characterized as its 1,3-diphosphaferrocene derivative, Eq. 26.



(26)

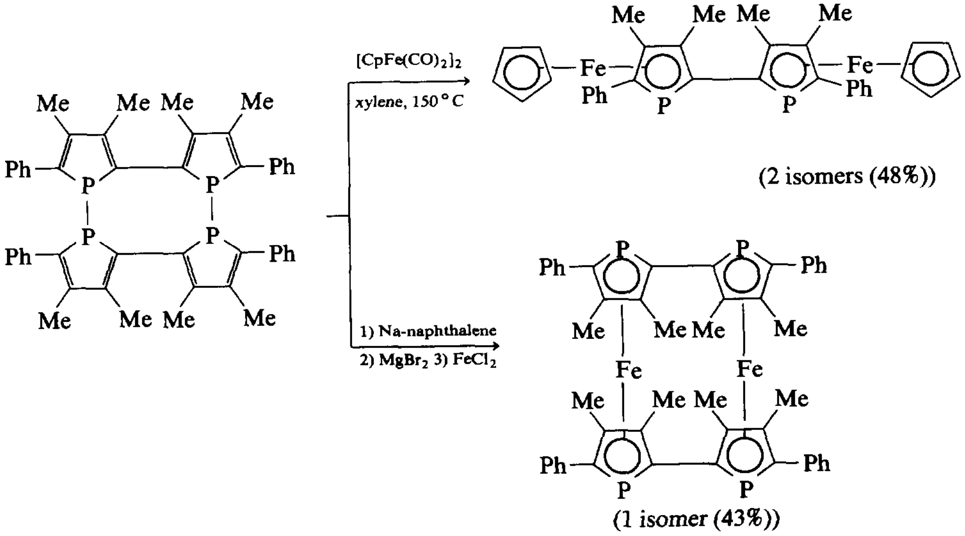
Numerous other reactions of these anions are currently being explored.

Still another possibility was to bridge the phospholyl anions to give the phosphorus analogues of η^5,η^5-fulvalene bimetallic complexes. These compounds are the precursors of interesting mixed valence species. François Mercier made the first 2,2′-biphospholyl, by thermolysis of 1-phenylyl-3,4-dimethylphospholes, Eq. 27 [55].



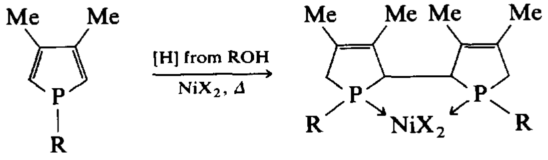
(27)

The mechanism of this conversion involves several H and Ph [1,5] shifts and the oxidative coupling of P–H units. The resulting tetramer could be converted into the corresponding ferrocene-like derivatives, Eq. 28.



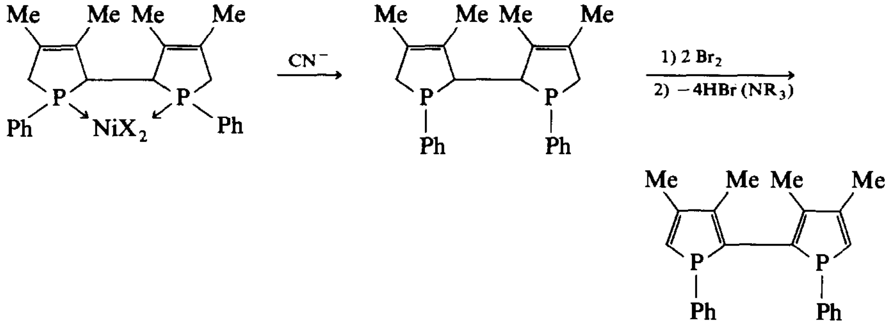
(28)

Another two-step route to 2,2′-biphospholyl dianions was subsequently found. It involved as a first step the reductive coupling of two phosphole units in the presence of nickel halides, Eq. 29 [56].



(29)

The resulting biphospholene was then converted into the corresponding biphosphole by a classical route, Eq. 30 [57].

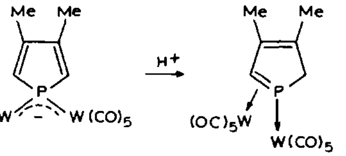


(30)

This biphosphole gave the corresponding dianion with lithium in THF. Some bis-η^5-complexes of manganese and iron were made.

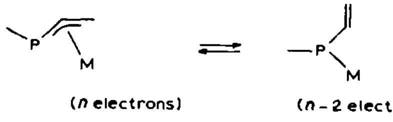
Extension towards other types of phosphorus analogues of π-complexes

In 1983, three independent groups prepared the first η^2-phosphaalkene complexes [58–60]. Then, in 1985, Appel prepared the first η^3-1,3-diphosphaallyl complex [61], and in 1986, Nixon and Binger the first η^4-1,3-diphosphete complexes [62,63]. Considered together with all the work on η^5-phosphacyclopentadienyl complexes, these achievements suggested that it would, in fact, be possible to prepare all the conceivable phosphorus analogues of the classical hydrocarbon π-complexes. We took our first step in that direction while studying the protonation of the 3,4-dimethylphospholyl anion in the coordination sphere of tungsten. Our objective was to stabilize a P–H phosphole by complexation. In fact, the H [1,5] shift took place as usual, and gave a 2*H*-phosphole stabilized as a η^1-P, η^2-PC complex, Eq. 31 [64].



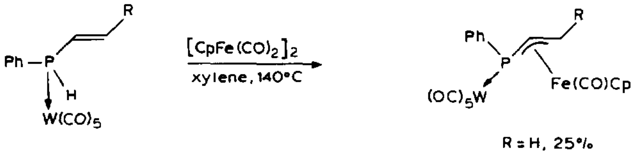
(31)

This complex was the first fully characterized species in which a phosphaalkene acted as a 4-electron η^1,η^2-donor (1984). We decided to go further, and selected the unknown η^3-1-phosphaallyl complexes as our next target. It is well known that η^3-allyl complexes have some potential in homogeneous catalysis. They mainly act as catalyst precursors by expulsion of the η^3-allyl from the coordination sphere of the metal. Two vacant sites are thus created. We thus expected that the η^3-1-phosphaallyl ligand could act as a reversible mask for one vacant site, Eq. 32.

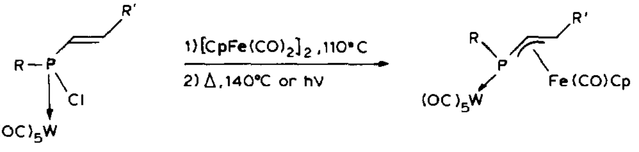


(32)

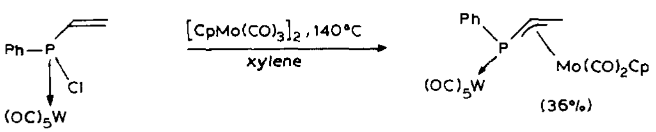
The synthesis of these new species proved to be surprisingly simple, as shown in Eq. 33–38 [65–69].



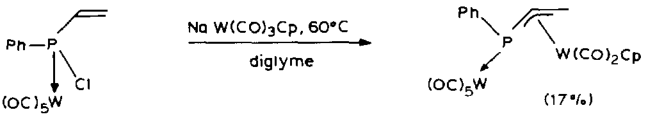
(33)[65]



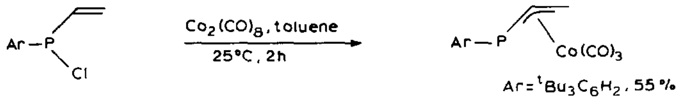
(34)[66]



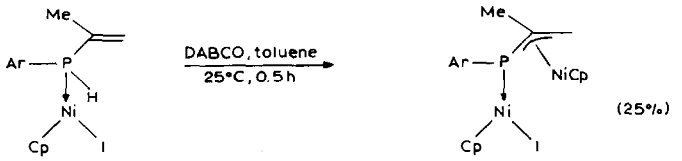
(35)[67]



(36)[67]

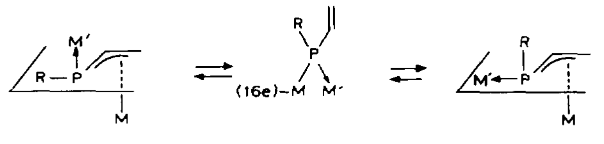


(37)[68]



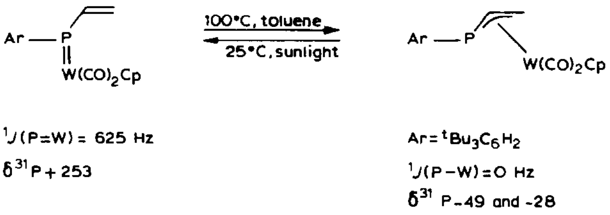
(38)[68]

Stable complexes were prepared with either bulky substituents at phosphorus (Eq. 37) or with ordinary substituents and additional η^1-coordination at the phosphorus lone pair. In almost all cases, two readily interconverting stereoisomers were obtained. Both structural types were characterized by X-ray diffraction studies. This isomerism originates as the phosphorus centre, as shown in Eq. 39, and probably involves transient 16-electron η^1-phosphaallyl complexes.



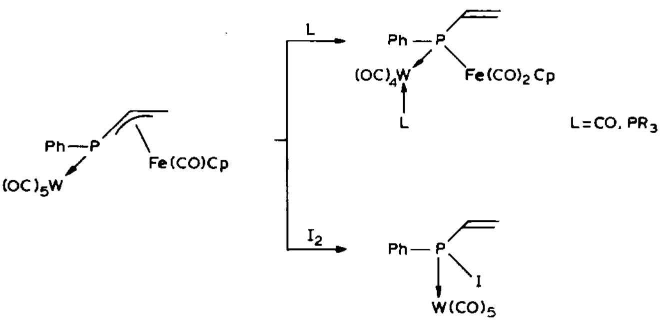
(39)

Very recently, François Mercier was able to establish the presence of this η^1–η^3-phosphaallyl equilibrium conclusively in a particular case, Eq. (40) [69].



(40)

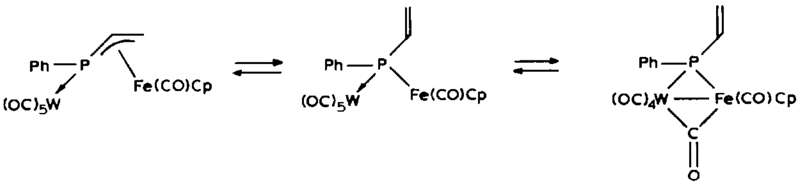
The interconversion was readily monitored by ^{31}P NMR spectroscopy. Some stoechiometric chemistry was also carried out in one case, shown in Eq. 41 and 42 [66].



(41)

(42)

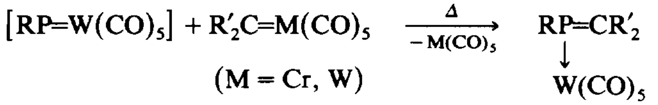
The process through which incoming ligand L becomes coordinated to tungsten was suggested to be that shown in Eq. 43.



(43)

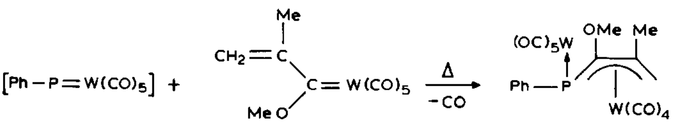
At this stage in our programme, catalytic applications of η^3-phosphaallyl complexes seem possible.

More recently, we also undertook some investigations of the synthesis and chemistry of the unknown η^4-1-phosphabutadiene complexes. Free 1-phosphabutadienes are unstable except when they are heavily substituted by bulky substituents [70]. Such species are unable to give η^4-complexes. Thus, the problem was to build the 1-phosphadiene moiety directly within the coordination sphere of a transition metal. For that purpose we decided to use two methods which had been devised in our laboratory for the synthesis of P=C double bonds in the coordination sphere of transition metals. The first one was studied by Ngoc Hoa Tran Huy, and involved the condensation of a transient phosphinidene complex with a carbene complex, Eq. 44 [71].



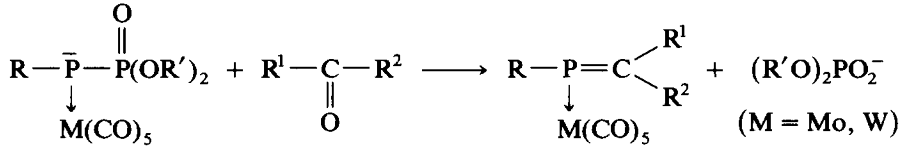
$$[\mathrm{RP{=}W(CO)_5}] + \mathrm{R'_2C{=}M(CO)_5} \xrightarrow[-\mathrm{M(CO)_5}]{\Delta} \underset{\substack{\downarrow\\ \mathrm{W(CO)_5}}}{\mathrm{RP{=}CR'_2}} \qquad (\mathrm{M} = \mathrm{Cr, W}) \tag{44}$$

When applied to a vinylcarbene complex, this technique gave the first known η^4-1-phosphabutadiene complex, Eq. 45 [72].



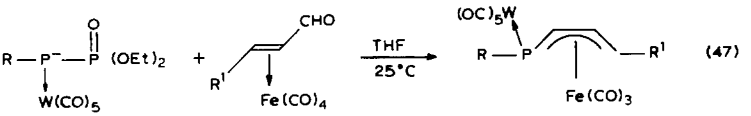
(45)

Another method, the so-called "phospha-Wittig" synthesis, was studied by Angela Marinetti. It involved the direct conversion of a carbonyl compound into a phosphaalkene complex, Eq. 46 [73,74].



$$\underset{\substack{\downarrow\\ \mathrm{M(CO)_5}}}{\mathrm{R{-}\bar{P}}}{-}\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{P}}\mathrm{(OR')_2} + \mathrm{R^1{-}}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{{-}R^2} \longrightarrow \underset{\substack{\downarrow\\ \mathrm{M(CO)_5}}}{\mathrm{R{-}P}}{=}\mathrm{C}\begin{smallmatrix}\mathrm{R^1}\\ \mathrm{R^2}\end{smallmatrix} + \mathrm{(R'O)_2PO_2^-} \qquad (\mathrm{M} = \mathrm{Mo, W}) \tag{46}$$

When applied to the η^2-complexes of α,β-unsaturated aldehydes, this approach provided a direct route to η^4-1-phosphabutadiene complexes, Eq. 47 [75].



(47)

The chemical study of these new η^4-complexes is still in the future. From a structural standpoint, we have already noticed that the same type of isomerism observed for η^3-1-phosphaallyl complexes takes place at phosphorus, but the interconversion between the stereoisomers appears to be more difficult with these new species.

Conclusion

In 1976, Becker [76] discovered the first stable phosphaalkenes. Since that time, it has been amply demonstrated that it is possible to mimic the chemistry of alkenes with phosphaalkenes. 1,2-Additions, inversion of polarity, $\mathrm{S_N2'}$ nucleophilic attack on allyl halides, [4 + 2], [3 + 2], [2 + 2] cycloadditions, 4π and 6π electrocyclisations, [1,5] and [3,3] sigmatropic shifts etc., can all be transposed from unsaturated hydrocarbons to their phosphorus analogues. In 1977, we discovered the first phosphaferrocene. Since that time, it has been amply demonstrated that almost all the conceivable phosphorus analogues of classical unsaturated hydrocarbon π-com-

π-complexes can be synthesized. At the moment, they include, among others, η^2-phosphaalkene, η^2-diphosphene, η^3-1-phosphaallyl, η^3-1,3-diphosphaallyl, η^4-1-phosphabutadiene, η^4-phosphacyclobutadiene, η^4-1,3-diphosphacyclobutadiene, η^5-mono-, di-, tri- and penta-phosphacyclopentadienyl, η^5-1-phosphacyclohexadienyl, and η^6-phosphabenzene complexes. Thus, it appears that phosphorus has an exceptional ability to mimic the chemistry of carbon. This diagonal relationship had been completely overlooked until very recently. It will probably have far-reaching consequences in organic synthesis, organometallic chemistry, homogeneous catalysis, and bioinorganic chemistry, and also in the production of new phosphorus-based molecular materials. In retrospect, our participation in the demonstration of this close relationship between phosphorus and carbon has been one of our most exciting scientific adventures.

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