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Account

Phosphametallocenes: from discovery to applications

François Mathey *

Laboratoire 'Hétéroéléments et Coordination', UMR 7653 CNRS, DCPH, Ecole Polytechnique, 91128 Palaiseau cedex, France

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Abstract

This account describes the development of phosphametallocene chemistry from the discovery of phosphacymantrenes in 1976 and phosphaferrocenes in 1977, to the preparation of paramagnetic and main group derivatives and to the development of catalytic applications starting in 1995. It does not intend to be comprehensive and is mainly focused on the work of the author's group. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phosphametallocene; Dicoordinate phosphorus; Homogeneous catalysis; Paramagnetic species

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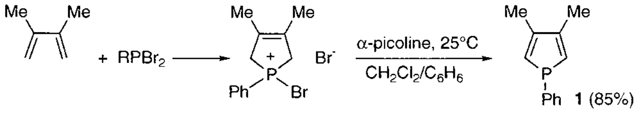
1. Introduction

In retrospect, if we try to highlight the key discoveries which progressively destroyed the so-called double-bond rule in organophosphorus chemistry, we would select the identification of the unstable phosphaacetylene $HC\equiv P$ by Gier in 1961 [1], the preparation of the first phosphinine 2,4,6-$Ph_3C_5H_2P$ by Märkl in 1966 [2], the first stable iminophosphine $(Me_3Si)_2N–P=N–SiMe_3$ by Niecke in 1973 [3], the first stable phosphaalkenes by Becker in 1976 [4], the discovery of phosphaferrocenes by us in 1977 [5], the first stable phosphaalkyne $^tBuC\equiv P$ by Becker [6] and the first stable diphosphene Mes*P=PMes* by Yoshifuji, both in 1981 [7]. Successively, these established the existence of the $C\equiv P$ triple bond, of 6π-aromatic rings containing phosphorus, of stable P=N, P=C, and P=P double bonds, and of phosphorus-containing transition metal π-complexes having a classical aromatic chemistry. In the 1970s and 1980s, this chemistry of low-coordinate phosphorus derivatives was clearly the 'new frontier' of our domain and, alongside many of our colleagues, we enthusiastically participated in its exploration. Our contribution was mainly focused on *2H*-phospholes, phosphinines, phosphaalkenes (via the phospha-Wittig reaction), and phosphametallocenes. This account aims to describe and explain the work of our group on phosphametallocenes. It will show how it has progressively evolved towards applied projects in homogeneous catalysis under the influence of specialists coming from other domains. Some preliminary results from other laboratories suggest a similar evolution for phosphinines and phosphaalkenes in the near future [8].

2. Discovery and initial exploration

The roots of our group are in industrial research and, for a long period, our work was influenced by industrial philosophy. A process had to be reliable, as simple and as economical as possible; a new product had to be easy to make on a large scale and, above all, useful; a research programme had to be versatile and self-coherent while exploiting to the fullest the expertise available on site. Our initial choice was to work in the poorly explored field of phosphorus heterocyclic chemistry where a lot of opportunities for new products, new reactions and new properties apparently existed. The starting point was the discovery of a very simple one-pot synthesis of phospholes from conjugated dienes and dihalophosphines via McCormack cycloadducts [9].



Scheme 1.

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* Tel.: +33-1-69334079; fax: +33-1-69333029.

E-mail address: mathey@poly.polytechnique.fr (F. Mathey).

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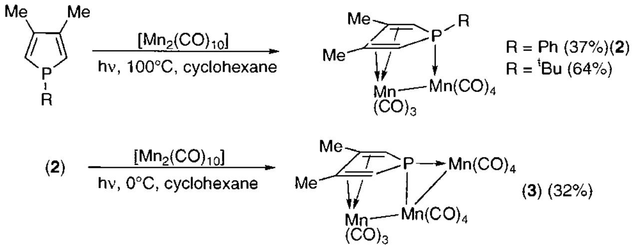

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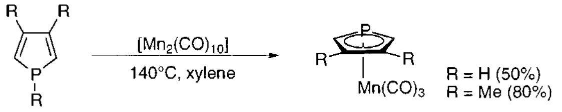

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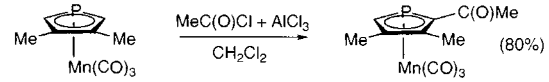

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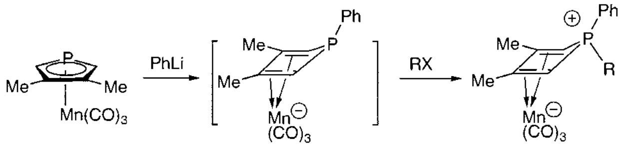

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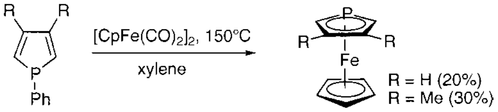

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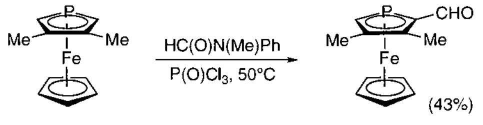

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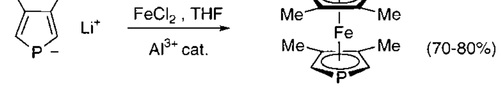


Scheme 8.

This synthesis was refined several times [10] and provided a reliable and simple access to a variety of weakly substituted phospholes (Scheme 1).

In 1975, we decided to undertake an exploration of the coordination chemistry of our phospholes. The initial attempts were made with manganese carbonyl [$Mn_2(CO)_{10}$] [11]. We obtained a series of well-characterized dinuclear σ,π complexes (**2**) and another type of trinuclear complex (**3**) whose correct structure was only established later [12], but where it was immediately clear that the exocyclic P-substituent had been cleaved off (Scheme 2).

This observation encouraged us to investigate other reaction conditions and finally, in 1976, we devised a very simple one-step synthesis of the so-called phosphacymantrenes [13] (Scheme 3).

Apart from their novelty, what immediately struck us was the extraordinary parallel which existed between the physico-chemical and chemical properties of cymantrenes and phosphacymantrenes: colours, odours, melting points, solubilities, elution rates, structural features, [14] reactivities with electrophiles, all were very similar in both cases. Apparently, the phosphorus atom of phosphacymantrenes was hidden or, if we adopted a different viewpoint, mimicked the behaviour of carbon. Of course, as synthetic chemists, what interested us most was the electrophilic acylation reaction [13–15] which represented the first clear-cut example of aromatic chemistry in the organophosphorus field (Scheme 4).

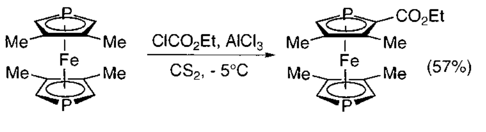
However two significant differences between the carbon and the phosphorus species were immediately apparent. Firstly, phosphacymantrenes are very sensitive toward nucleophiles: the attack takes place at phosphorus with cleavage of the P–Mn bond. This was definitively established only very recently [64] (Scheme 5).

Secondly, phosphacymantrenes can act as ligands toward transition metals: as such, they display strong π-acceptor properties [15]. This chemical behaviour was easily rationalized on the basis of a preliminary EHT study of these molecules [16]. The in-plane sp^2 phosphorus lone pair corresponds to the fourth highest occupied level and the low-lying LUMO is heavily localized at phosphorus and manganese. More sophisticated treatments may appear, but they will certainly not significantly modify this general picture.

In parallel, we started to develop the chemistry of phosphaferrocenes. The monophospha derivatives were initially prepared in 1977 using the same approach as that used for phosphacymantrenes [5,17] (Scheme 6).

As might be guessed, these phosphaferrocenes resembled ferrocenes very closely. They appeared to be more reactive toward electrophiles and less reactive toward nucleophiles than their manganese counterparts. From a synthetic standpoint, the Vilsmeier formylation [18] proved to be very useful (Scheme 7).

Phosphaferrocenes also displayed some capacity for coordination, albeit with lower π-acceptor ability than phosphacymantrenes [19]. The 1,1′-diphosphaferrocenes completed the picture; they were prepared through a straightforward approach [18] (Scheme 8).



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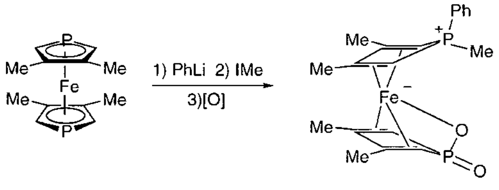

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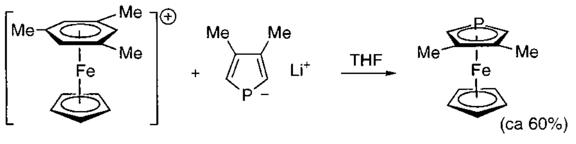

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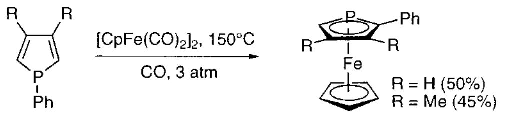

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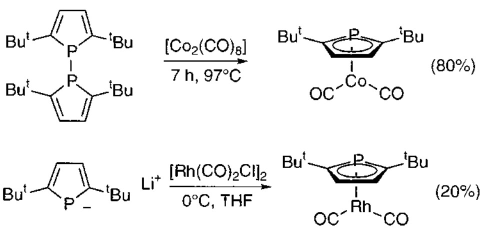

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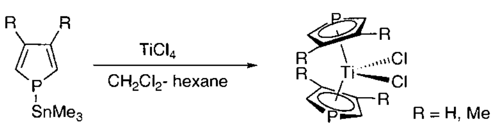


Scheme 14.

Electrophilic acylation, formylation, and even carboxylation [20] proved to be easily carried out (Scheme 9).

The reactivity toward nucleophiles appeared to be extremely varied as shown for one specific example in Scheme 10 [21].

Several complexes involving the two sp^2 lone pairs were made and structurally characterized, the most spectacular example being a ruthenium species in which a Ru(μ-Cl)$_2$Ru core is sandwiched between two molecules of diphosphaferrocene [22].

This abundant crop of results was followed by a period of lower activity. Roberts and Wells complemented our investigation of monophosphaferrocenes. In particular, they devised a high yield synthesis of these species by reaction of phospholide ions with a [CpFe]$^+$ precursor [23] (Scheme 11).

They also studied, inter alia, the protonation of phosphaferrocenes [24] and their derivatives [25], the preparation of phosphaferricinium salts [26], the phospholyl–arene exchange [27], the formation of phosphaferrocenylmethyl carbocations [28] and the complexation at iron [29].

For our part, we designed an alternate synthesis of phosphaferrocenes and cymantrenes under CO pressure [30]. Under these modified conditions, the transition metal complex traps a transient 2*H*-phosphole (Scheme 12).

We also investigated the electrochemistry of phosphaferrocenes [31]. They proved to be easier to reduce and more difficult to oxidize than the corresponding ferrocenes. We also prepared the η^5-phospholyl complexes of several other transition metals, including titanium [32], zirconium [33], tungsten [34], some lanthanides [35], uranium in collaboration with Ephritikhine [36], ruthenium, rhodium [37] and cobalt [38]. These studies emphasized that, in some cases, it is necessary to have two bulky substituents on the α-positions of the phospholyl ring in order to prevent η^1 or μ_2 coordination of phosphorus. Some examples are depicted in Scheme 13 [37,38].

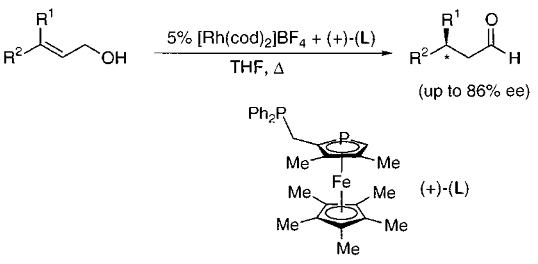
Sometimes, it proved necessary to replace the alkali metal phospholides by other sources of phospholides in order to prevent redox reactions, e.g. in the case of titanium(IV) [32] (Scheme 14).

3. Recent developments

At the beginning of the 1990s, the field was more or less dormant. In 1997, the groups of Fu [39] and Ganter [40] started to investigate the possible uses of chiral phosphaferrocenes in asymmetric catalysis. The most significant results concerned the rhodium-catalysed asymmetric hydrogenation of dehydroaminoacids [41] and asymmetric isomerization of non-protected allylic alcohols [42] (Scheme 15), and the palladium-catalysed asymmetric reaction of allyl acetates with sodium malonate [43,44] (Scheme 16).

Independently, several industrial chemists started to investigate the possible applications of phosphazirconocene and -titanocene derivatives as catalysts in the polymerization of ethylene and propylene [45–48]. We thus immediately decided to restart our research programme on phosphametallocenes in four directions, namely: (1) development of the aromatic chemistry of phosphaferrocenes and cymantrenes; (2) applications in catalysis; (3) synthesis and structural characterization of main group derivatives; and (4) synthesis and structural characterization of paramagnetic derivatives (16, 17, 19 and 20 electrons).

All these directions proved to be fruitful. For the first line, we mainly tried to enhance the reactivity of phosphacymantrenes toward electrophiles. An obvious idea was to replace one of the carbon monoxides of the strong electron-withdrawing [Mn(CO)$_3$] complexing group by a σ-donor such as triphenylphosphine. Such a trick makes the Vilsmeier formylation feasible (Scheme 17) [49].



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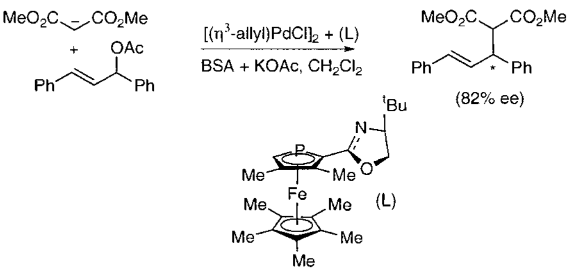

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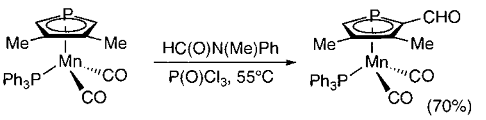

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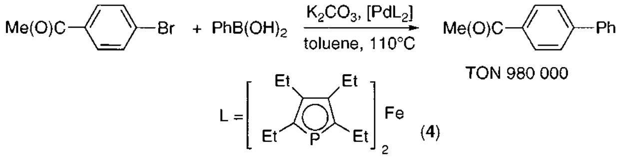

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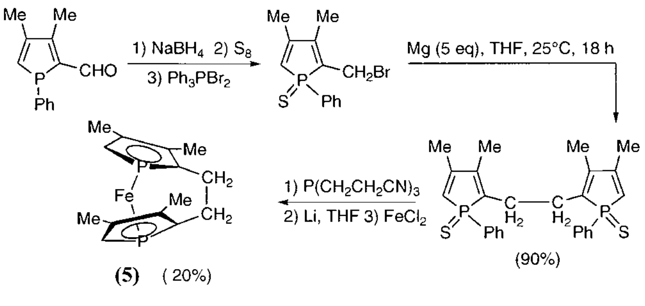


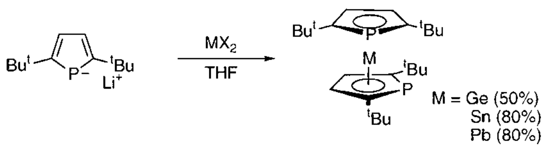
Scheme 19.

The second line gave less predictable results. An in-depth investigation of the reactivity of palladium(0) and (II) toward phospha- and diphosphaferrocenes led to the discovery of several stable and structurally characterizable complexes with the electron-enriched 2,2′,3,3′,4,4′,5,5′-octaethyl-1,1′-diphosphaferrocene (**4**) [50]. Among these species was a [Pd(**4**)$_2$] complex in which the palladium(0) appeared to be chelated between the phosphorus lone pairs of both diphosphaferrocenes. This type of chelates had been previously found by Cowley when studying the reaction of diphosphaferrocenes with silver(I) [51]. The electronic structure of phosphaferrocenes has been studied both from a theoretical standpoint [52] and by X–X mapping of the electronic density [53]. In addition to the low-lying sp^2 lone pair found on the x axis, there is also significant electron density lying outside of the Fe–P axis resulting from an overlap between the d_{xz} orbital of iron and the p_z orbital of phosphorus. On that basis, it is very likely that the empty d orbitals of palladium interact with both the lone pair at P and the $d_{xz} + p_z$ combination. Anyhow, this type of coordination is obviously labile and this [Pd(**4**)$_2$] complex can be considered as a masked form of the 14-electron [PdP$_2$] complex in which both molecules of **4** act as ordinary monodentate ligands through one of their sp^2 lone pairs. From a practical standpoint, [Pd(**4**)$_2$] was found to be an extraordinarily robust catalyst for the Suzuki cross-coupling reaction (Scheme 18) [50].

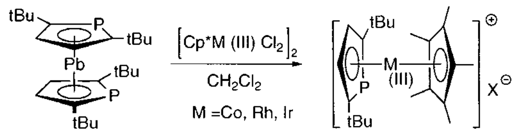
In a different vein, we were also interested in the synthesis of polymers containing the diphosphaferrocene unit with potential applications in catalysis. Manners [54] has shown that well-defined ferrocene polymers can be obtained by thermal polymerization of strained ferrocenophanes. Following the same approach, we have devised a route to a 1,1′-diphospha[2]ferrocenophane (**5**) [55] (Scheme 19).

In **5**, the tilt angle (ca. 20°) is almost identical to that found in its all-carbon analogues. Polymerization studies have not been undertaken yet.

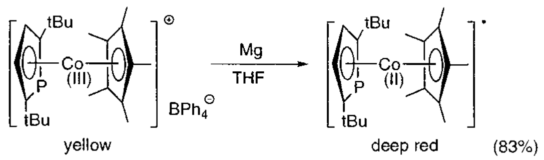
The third line has allowed us to prepare the first structurally characterized η^5-phospholyl complexes of gallium(I) in collaboration with Schnöckel [56], and those of germanium(II), tin(II) and lead(II) [57], using the 2,5-di-*tert*-butyl-substituted ring. The gallium(I) compound is viewed as a potential precursor for the vapour deposition of gallium phosphide. Our tin(II) derivative displays a genuine bis η^5-structure whereas another recently described phospholyl–tin compound is better represented by a bis η^3-structure [58]. This un-



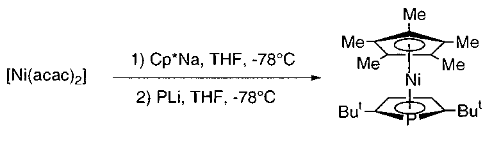
Scheme 20.



Scheme 21.



Scheme 22.



Scheme 23.

derlines the subtle balance which exists between η^1-, η^3-, and η^5-coordination in phospholyl chemistry. From a practical standpoint, the most interesting result was undoubtedly the isolation of a stable 1,1′-diphosphaplumbocene [57] (Scheme 20).

This yellow compound is soluble in saturated hydrocarbons and proved to be a highly valuable phospholyl transfer reagent. It displays a bis-η^5-sandwich structure with a tilt angle of 17.3°. We immediately used it to devise a reliable synthesis of the long sought after phospha-cobalticinium, -rhodicinium and -iridicinium salts [59] (Scheme 21).

The phosphacobalticinium salt is easily reduced at -0.74 (SCE) in THF versus -1.17 V for a similar all-carbon analogue. The corresponding stable deep red paramagnetic phosphacobaltocene can be prepared by magnesium reduction [60] (Scheme 22).

The ^{31}P resonance is shifted to high field (δ ^{31}P -126 ppm). The eclipsed sandwich structure shows no special feature. This first success encouraged us to investigate the synthesis of a stable phosphanickelocene. All the previous attempts described in the literature had led to alternative 18-electron η^3- or μ$_2$-structures [61–63]. Our own attempts were immediately successful. The synthesis is surprisingly straightforward [60] (Scheme 23).

The deep-green paramagnetic ($\mu_{\text{eff}} = 2.78$ BM at 293 K) phosphanickelocene displays a normal eclipsed sandwich structure with a plane of symmetry. Its ^{31}P resonance has not been detected.

4. Conclusions

Phosphametallocenes are readily accessible with a variety of metals and substitution patterns. In many cases, they are easily functionalized and thus, can be incorporated in complex structures. They display an original coordination chemistry typical of sp^2-phosphorus centres with a high π-acceptor combined with a tunable σ-donor ability. A series of preliminary results demonstrate their potential in homogeneous catalysis, especially in the field of asymmetry with planar chiral species. Thus, it is not an adventurous bet to forecast the development of catalytic applications. Additional possibilities can also be envisioned in the domain of molecular materials with paramagnetic species, although they remain to be demonstrated. It must be also pointed out that a very rich coordination chemistry is currently being developed around polyphospholide ions, mainly $[1,3\text{-}P_2C_3]^-$, $[1,2,4\text{-}P_3C_2]^-$ and $[P_5]^-$ by the groups of Nixon, Scherer, Zenneck and others. This chemistry has been recently reviewed [65] and has led to complex and fascinating structures. All together, it is quite certain that phosphametallocene chemistry will remain an active field of research in the years to come.

Acknowledgements

The results described in this account are due to many co-workers whose names are given in the list of references. In recent years, Bernard and Eliane Deschamps, and Patrick Toullec have developed novel functionalization reactions, Pascal Le Floch, Nicolas Mézailles, and Xavier Sava have worked on coordination chemistry and catalytic applications, Duncan Carmichael and Kareen Forissier on main group and paramagnetic derivatives, François Nief on lanthanide compounds. This work is theirs.

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