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The chemistry of phospha- and polyphosphacyclopentadienide anions

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CONTENTS

ABSTRACT

The synthesis, structural and spectroscopic features, organic and coordination chemistry of phospholide and polyphospholide anions are comprehensively reviewed.

1. INTRODUCTION

Apart from phosphinines, phospha- and polyphosphacyclopentadienide anions (also called phospholide anions) are the only known phosphorus–carbon heterocycles

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that show an extensive 6π-electronic delocalization. As such, they play a special role in phosphorus heterocyclic chemistry. Furthermore, their analogy with the ubiquitous cyclopentadienyl ligand implies a huge potential in transition metal chemistry.

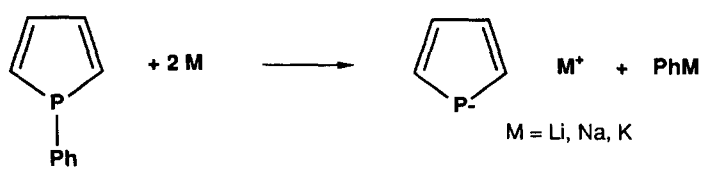
The first paper describing phospholide anions appeared in 1971 [1], although Braye had originally disclosed this pioneering work in a patent in 1967 [2]. The first η^5-phospholyl complexes were described by Mathey in 1976 [3], and further major steps came in 1987 when Scherer [4] and Baudler [5] discovered the first pentaphosphaferrocene and the free pentaphospholide anion, respectively. Almost simultaneously, several di- , tri- and tetraphospholide anions were reported, either as pure species or as mixtures with other phosphorus anions. Amongst all the possible analogues of $C_5H_5^-$, only the 1,2-diphospholide anion has so far escaped detection. However, its 1,2-diphosphaferrocene derivatives are known [6,7].

No review has previously described this fascinating field as a whole. The last comprehensive account on phospholes [8] included several sections dealing with phospholide anions, and their complexes have been the subject of two other reports [9,10]. More recently, Nixon [11] and Scherer [12] have published literature surveys including the first results concerning di-, tri- and pentaphospholyl coordination chemistry. The present paper, the first unified treatment of the subject, is all the more timely because numerous significant results have appeared very recently.

2. SYNTHESIS

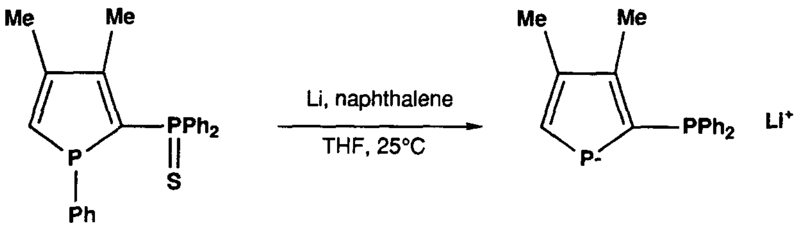
2.1. Phospholide anions

The classical Braye synthesis of phospholide anions [1,2] involves the alkali metal cleavage of the phosphorus–phenyl bond of 1-phenyl-substituted phospholes



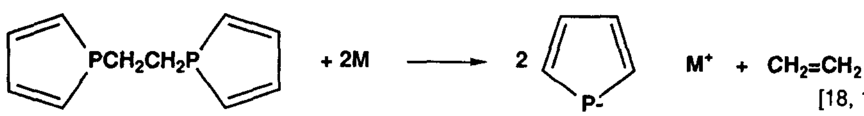
(1)

(eqn. 1). The reaction is driven by the aromaticity of the phospholide anion. According to electron spin resonance (ESR) studies [13,14], the mechanism involves a monoelectronic reduction which yields a phosphole radical anion. Above approx. −30°C, this radical decomposes and gives the phospholide anion and a phenyl radical. The main drawback of this method lies in the formation of phenylated by-products. The phenyl anion can sometimes be destroyed by an excess of *tert*-butyl chloride, but in some cases, this treatment leads to the formation of 1-*tert*-butylphospholes [15]. Alternatively, the crude solutions of phospholide anions are treated with a metal chloride. The metathesis of the phenyl anion reduces its nucleophilicity, thus avoiding side-reactions where it competes with the phospholide anion (for a typical example, see ref. 16). This point will be discussed later on. In spite of this kind of drawback, the Braye method is still widely used and a significant application of it has been described recently [17], concerning the synthesis of the first phospholide anion bearing a functional substituent (eqn. 2).

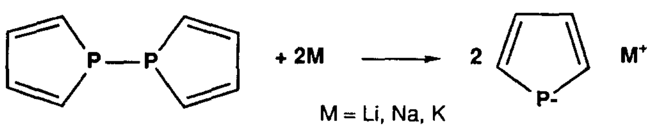


(2)

Several techniques avoiding the formation of phenyl by-products have been devised (eqns. 3, 4). They are especially useful when pure solutions of the anions are

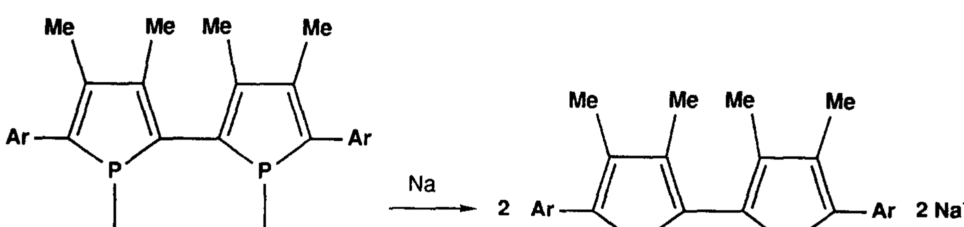


(3) [18, 19]



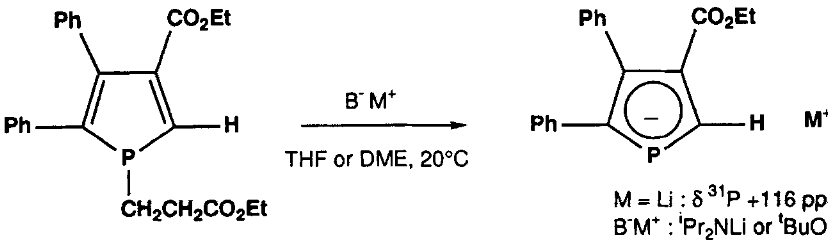
(4) [20, 21]

required for spectroscopic studies [18]. It is interesting to note here that the P–P bond can also be cleaved by non-alkali metals such as samarium and ytterbium [22]. Some non-conventional phospholide anions have also been made through alkali metal induced P–P bond cleavage, as exemplified by eqn. (5a).



(5a)

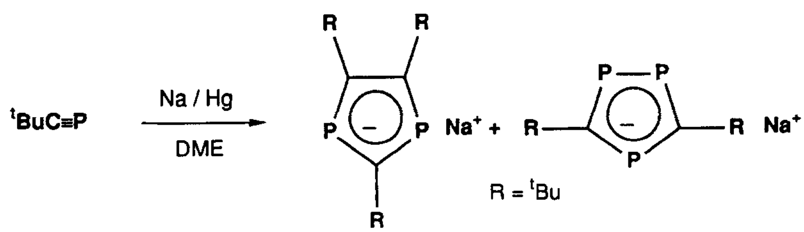
In order to prepare phospholide ions bearing reactive functionalities, it is clearly necessary to devise a route avoiding the use of alkali metals. Very recently, such a route has been found and applied to the synthesis of a 3-ethoxycarbonyl derivative (eqn. 5b) [153].



(5b)

2.2. Polyphospholide anions

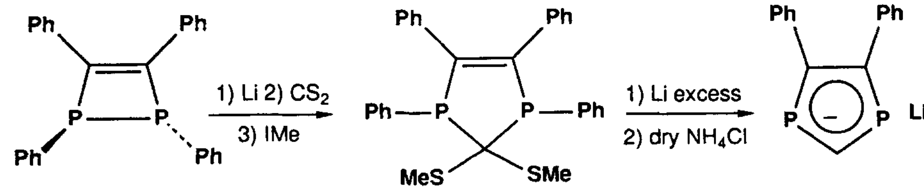
The 2,4,5-tris-(*tert*-butyl)-1,3-diphospholide anion was first detected by Nixon and co-workers [24]. It is formed as a by-product in the synthesis of the 2,5-bis-(*tert*-butyl)-1,3,4-triphospholide anion by the reaction of ^{t}BuC≡P with $LiP(SiMe_3)_2$, which was first described by Becker [25]. Later, Cowley [26] and Nixon [27] demonstrated that reduction of ^{t}BuC≡P leads to a 1:1 mixture of the di- and triphospholide anions mentioned above. Cowley used a low-valent tantalum species



(6)

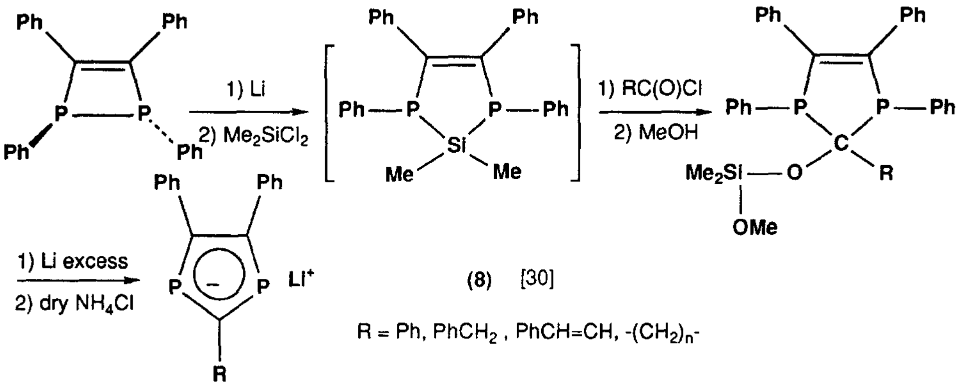
whilst Nixon used sodium amalgam as the reducing agent (eqn. 6). Fractional crystallization allows the separation of the two anions [26]. The mechanism of this reaction is unknown. The sodium procedure has also been used by Nixon to prepare a complex mixture of di- and triphospholide ions from a mixture of ^{t}BuC≡P and ^{i}PrC≡P [28].

Whereas no specific synthesis of the triphospholide ions has been described in the literature, several routes to 1,3-diphospholide ions free from their 1,3,4-triphosphorus counterparts have been devised by the group of Mathey. These routes start from the readily available 1,2-dihydro-1,2-diphosphetes, and are depicted

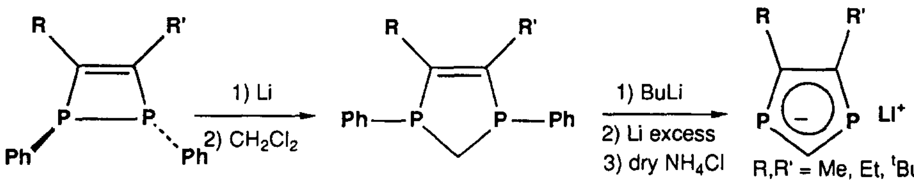


(7)
[29]

in eqns. (7)–(9). In each case, an intermediate dianion of unknown structure is monoprotonated by a weak acid (dry NH_4Cl) to give the desired monoanion. The

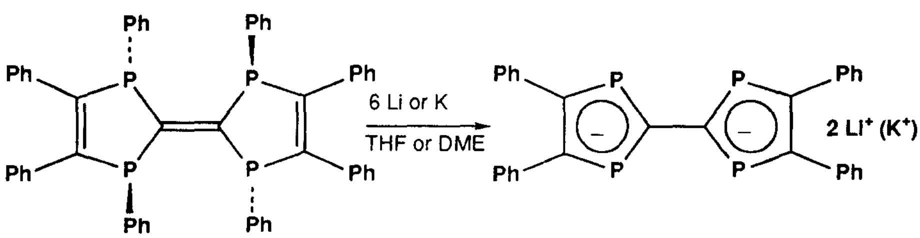


(8) [30]



(9) [31]

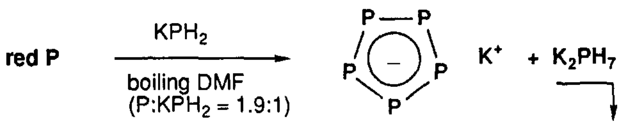
purest products are obtained via the third route (eqn. 9), which generates no sulfur- or silicon-containing by-products. In this latter case, the preliminary transformation of the weak P–CH_2–P into the stronger, delocalized $[P–CH–P]^-$ unit allows the selective cleavage of the exocyclic P–Ph bonds without breakdown of the ring. In a related reaction, the first tetraphosphafulvalene dianion has been obtained [32] via the selective cleavage of all four P–Ph bonds of a tetraphosphafulvalene (eqn. 10).



(10)

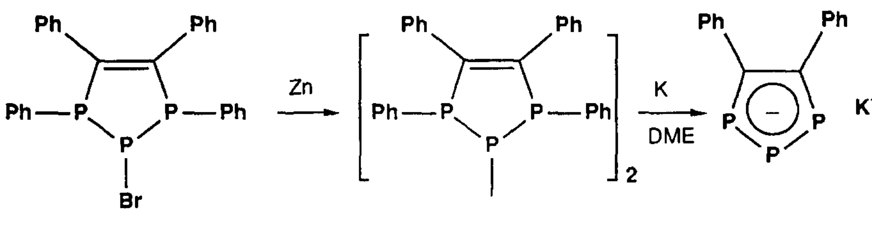
In their pioneering work of 1987, Baudler et al. [5] investigated the nucleophilic cleavage of P_4 by sodium in diglyme. In addition to several conventional polyphosphides (showing ^{31}P NMR resonances at high fields), this leads to three new species which resonate at low field ($472 > \delta^{31}P > 263$ ppm, ref. external H_3PO_4). The authors were immediately able to establish that the single resonance at +470 ppm corresponds to the pentaphospholide ion $(P_5)^-$ and that the multiplet centered at +359 ppm represents the tetraphospholide ion $(P_4CH)^-$. The third species was erroneously formulated as a triphosphacyclobutenide ion $(P_3CH_2)^-$, but subsequently a complete analysis of its proton-coupled ^{31}P NMR spectrum allowed the authors to reformulate it as the previously unknown parent 1,2,3-triphospholide ion

[33]. No more work has appeared on the tri- and tetraphosphorus species, but the synthesis of $(P_5)^-$ has been substantially improved. In the best procedure (eqn. 11) [34], the conventional polyphosphides tend to precipitate, and pure solutions of



(11)

KP_5 can be obtained. The yield of this synthesis is around 15%. Finally, very recently, the first specific synthesis of a 1,2,3-triphospholide ion has been devised by Maigrot et al. [35] (eqn. 12).



(12)

3. PHYSICOCHEMICAL DATA

3.1. Structural data

The only reported X-ray crystal structure analysis of a phospholide anion was published in 1989 [36]. $Li(TMEDA)PC_4Me_4$ displays a η^5-PC_4-bonded lithium atom chelated by tetramethylethylenediamine. A comparison of the average Li–C and P–C distances (2.39 and 2.53 Å, respectively) with the sums of the corresponding covalent radii (2.00 and 2.29 Å) shows that the lithium ion is displaced toward the phosphorus atom, suggesting a high electron density at P. The PC_4 ring is planar and aromatic. The comparison with the structure of 1-benzylphosphole [37] is illuminating. The formal C–C single bond is shorter in $(PC_4Me_4)^-$ than in the phosphole, 1.424 vs. 1.438 Å, and the formal C=C double bonds are longer, 1.396 vs. 1.343 Å. The P–C ring bonds are more contracted in the anion, 1.751 vs. 1.783 Å. In terms of differences between C–C and C=C bond lengths (a crude aromaticity criterion), the phospholide anion lies close to pyrrole, $\Delta = 0.028$ $(PC_4Me_4)^-$ vs. 0.035 Å (HNC_4H_4).

The only example of a 1,3-diphospholide ion that has been characterized by X-ray crystal structure analysis is the tetraphosphafulvalene dianion mentioned in eqn. (10) [32]. The two rings are strictly coplanar and the C–C bridge is rather long at 1.482(5) Å, indicating only a weak conjugative interaction between the two halves of the molecule. All four P–C bonds within each ring are very similar in length, between 1.748(3) and 1.761(3) Å. The intracyclic C–C separation 1.401(4) Å suggests a delocalized C=C double bond. These data support the description of the P_2C_3 ring as aromatic. The two potassium ions lie on opposite sides of the anionic plane at 2.82 Å, and are located in the plane of symmetry of the dianion. The K–K′ distance is 4.604(1) Å, and the P–K bond lengths at 3.267(1) and 3.393(1) Å are close to the sum of the covalent radii of P and K, 3.37 Å.

The only other available data concern the 1,3,4-triphospholide ion shown in eqn. (6). In a general account describing the work of his group on low-coordinated organophosphorus species [25], Becker gave some structural information on the lithium salt of the (2,5-$^t Bu_2C_2P_3$) anion. The P–C bond lengths are very similar to those recorded for the $(C_4P)^-$ and $(C_3P_2)^-$ anions at 1.75 Å. The P–P bond is substantially shortened with respect to a normal P–P single bond at 2.11 vs. 2.21 Å.

3.2. Spectroscopic data

Some representative data are collected in Table 1. The low field ^{31}P shifts of phospholides by comparison with classical phosphide ions was first noticed by Quin [38]. As a general rule, a downfield trend is observed as the number of phosphorus atoms in the ring increases, from approx. 50–100 ppm for one P to +470 ppm for five P. The nature of the counterion has only a limited influence on the ^{31}P shifts, as would be expected from the ionic nature of these compounds. The ^{31}P resonance of phospholide ions varies significantly with the substitution scheme; for example, whilst the 3,4-dimethyl-substituted phospholide ion resonates at +59 ppm, the tetraphenyl species appears at +97 ppm [39]. As intuitively expected, the influence of the substitution scheme seems to decrease as the number of phosphorus atoms within the ring increases (see ref. 28). In all these species, the ^1J(P–C) and ^1J(P–P) coupling constants are very high and lie close to those recorded for typical P=C and P=P double bonds. This magnitude probably reflects the aromatic nature of these rings. In addition to these NMR data, the UV spectrum of $(P_5)^-$ has also been recorded. It exhibits two π–π^* transitions of medium intensity at 260 and 320 nm (THF, 18-crown-6). The overall form of the spectrum is considered to be compatible with the aromatic character of $(P_5)^-$ [40].

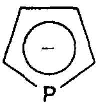
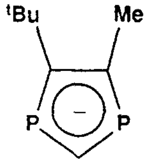
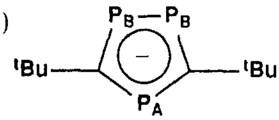
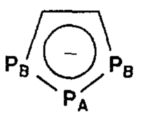
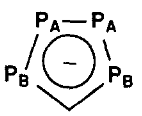
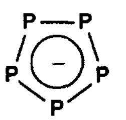
Before closing this section, an electrochemical study of 2,2′-biphospholide dianions [41] must be mentioned. It has been shown that the monoelectronic oxidation of the 5,5′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphospholide anion occurs at −0.69 V vs. SCE in diglyme, with total reversibility being achieved for scan rates above 50 V s^{-1}.

3.3. Aromaticity

The first theoretical calculations on the phospholide anion, which appeared in 1974 [42], used a classical CNDO/2 formalism and a geometry derived from that

TABLE 1

Representative NMR data for phospholide and polyphospholide ions[a]

Anion	$^{31}P\{^1H\}$ NMR	^1H NMR	^{13}C NMR	Ref.
(i) 	+77.2 (THF)	H_α 6.78, H_β 6.62, $^2J(H_\alpha–P)$ 40.76, $^3J(H_\beta–P)$ 6.42	C_α 129.71, C_β 119.74, $^1J(C_\alpha–P)$ 46.6, $^2J(C_\beta–P)$ 4.5	[18]
(ii) 	AB: δ_A +184.6, δ_B +192.6, $^2J_{AB}$ 19.5 (THF)			[31]
(iii) 	AB_2: δ_A +252.5, δ_B +245.5, $^2J_{AB}$ 47 (THF)			[26]
(iv) 	AB_2: δ_A +273.1, δ_B +262.9, $^1J_{AB}$ −485, $^2J_{BB'}$ +8.6 (diglyme)	$^3J(H–P_A)$ 4.6, $^2J(H–P_B)$ 47.9, $^3J(H–P_B)$ 17.8, $^3J(H–H)$ 7.0		[33]
(v) 	AA'BB': δ_A +355.1, δ_B +362.1, $^1J_{AA'}$ −505.8, $^1J_{AB}$ −483.8, $^2J_{AB'}$ −3.7, $^2J_{BB'}$ −53.5 (diglyme)	$^3J(H–P_A)$ 10.6, $^2J(H–P_B)$ 41.4		[33]
(vi) 	+468.8 Na^+ 18-crown-6 (THF)			[34]

[a] δ in ppm, ref. Me_4Si for ^1H and ^{13}C, external 85% H_3PO_4 for ^{31}P; J in Hz.

of 1-benzyl-phosphole. More recently, several ab initio treatments of this ion, using more accurate geometrical parameters derived from the structures of various η^5-phospholyl complexes (mainly phosphaferrocenes), have been reported [43–45]. In each case, the authors agree that a significant negative charge is localized at phosphorus and that the anion is highly aromatic. However, some discrepancies appear in the ordering of the most significant orbitals. The three highest occupied levels, the antisymmetric dienic orbital π_c and the two lone pair orbitals σ_p and π_p, appear to be very close in energy.

Only one publication deals specifically with the 1,3-diphospholide ion [46]. However, an old MNDO formalism was used and the computed geometry is not realistic: C$\overset{...}{-}$P, 1.64–1.67 Å vs. 1.74–1.76 Å observed in the related tetraphosphafulvalene dianion [32]. According to this work, the negative charge is spread over the whole P–C–P unit and the system is highly aromatic.

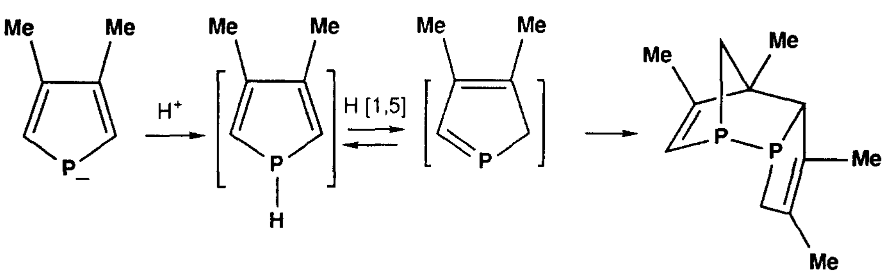
Several papers deal with the pentaphospholide anion [47–49]. According to the most accurate calculations, reported by Hamilton and Schaefer [49], the P–P distances in $(P_5)^-$ are 2.095 ± 0.02 Å; these may be compared with the experimental P–P bond length of 2.11 Å measured by Becker for a 1,2,4-triphospholide ion [25]. This perfect agreement underlines the reliability of these calculations. The same authors predict a P–P stretching frequency at 564 cm^{-1} in the IR spectrum of $(P_5)^-$, which casts some doubt upon an earlier assignment by Baudler [40].

The last work to be discussed under this heading compares the aromaticity of all the possible polyphospholide ions using the SINDO 1 method [50]. The computed geometries are rather realistic, with C┄C, C┄P and P┄P bond lengths in the ranges 1.37–1.42 Å, 1.74–1.77 Å and 2.17–2.20 Å, respectively. The relative aromaticities of the various ions, defined on the basis of the ring current criterion developed by Jug [51], are: $C_5H_5^-$, 100; $C_4H_4P^-$, 90.7; 1,3$-C_3H_3P_2^-$, 88.4; 1,2$-C_3H_3P_2^-$, 86.0; 1,2,3$-C_2H_2P_3^-$, 86.0; 1,3,4$-C_2H_2P_3^-$, 95.9; CHP_4^-, 94.8; P_5^-, 100.6.

4. ORGANIC REACTIVITY

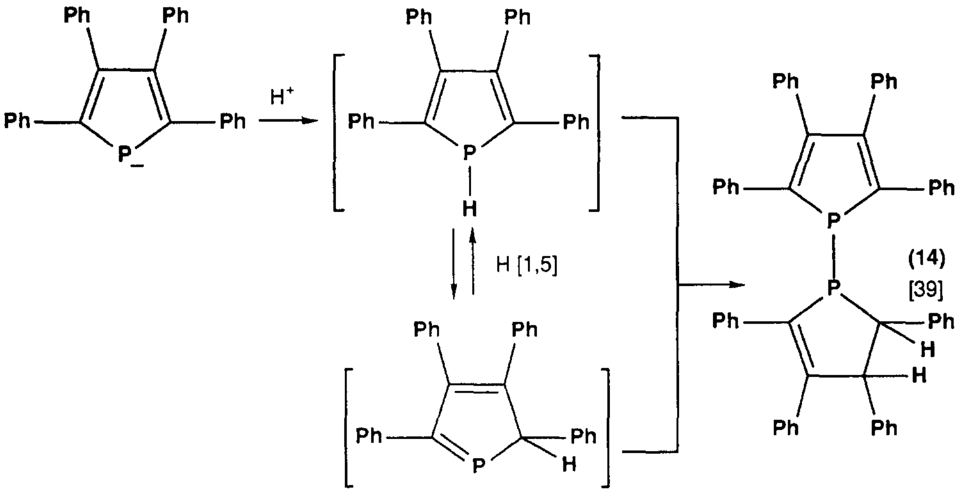
4.1. Phospholide anions

So far, all known reactions of phospholide anions take place at phosphorus. Thus, as demonstrated by low temperature ^{31}P NMR studies [39], the protonation of these ions yields unstable 1*H*-phospholes which easily rearrange via H [1,5] sigmatropic shifts to give 2*H*-phospholes. In turn, these 2*H*-phospholes instantly give dimers of various structures [39,52,53]. Two representative cases are depicted



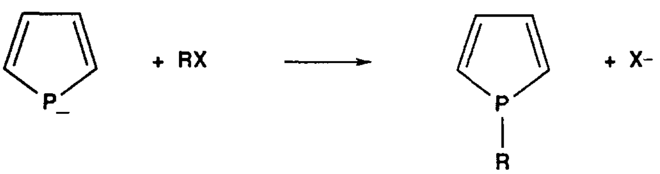
(13)
[53]

in eqns. (13) and (14). The unhindered 2*H*-phospholes tend to dimerize via a [4+2] pathway. However, steric hindrance tends to favour the P–H+P=C pathway. Qualitatively, it seems that the substitution pattern of the phospholide ions plays a significant role in their basicity. Polyphenyl-substituted ions do not react with neutral water, which means that their pK_a is lower than 14 [52]. The alkyl-substituted ions do react with water but are not decomposed by anhydrous ethanol [38].



(14)
[39]

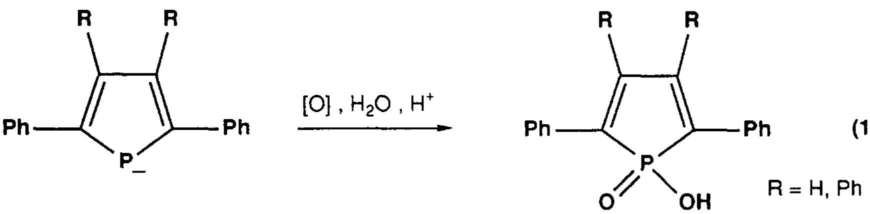
Alkylation at phosphorus by alkyl halides is by far the most useful reaction of



(15)

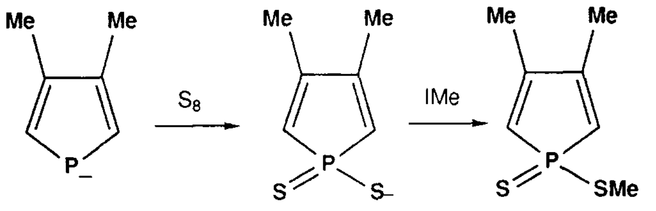
phospholide ions [1,19,54–56] (eqn. 15). The 1-alkylphospholes thus formed are able to quaternize with an excess of the more reactive alkyl halides (e.g. IMe, Br–CH_2Ph ...). Addition of $AlCl_3$ catalyzes the reaction in some cases [57]. This procedure is compatible with a number of functional groups such as esters, nitriles and ketones [16] which do not interfere with the alkylation reaction.

In two cases, the oxidative hydrolysis of phospholide ions has been shown to



(16)

give monomeric phospholic acids [1,58] (eqn. 16). Similarly, in one case, sulfur has yielded a dithiophospholate [59] (eqn. 17). The reaction of phospholide ions with halogens under mild conditions generally gives the 1,1′-biphospholyls [60,61] (eqn. 18). An excess of halogen may cleave the P–P bond. In a related reaction, cyanogen bromide has been shown to give the very useful 1-cyanophospholes [62] (eqn. 19). These compounds display a much higher stability than the corresponding



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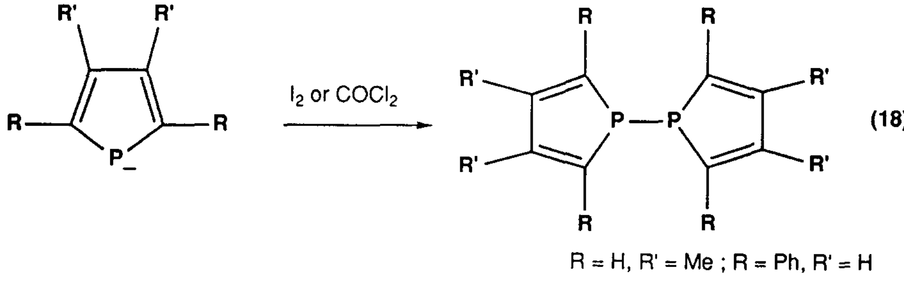
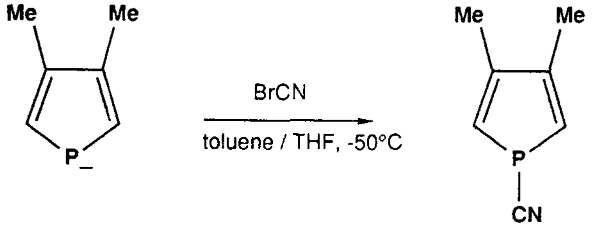


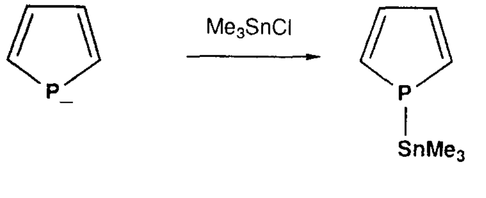
(18)

halophospholes and are also much better substrates for reactions towards nucleo-



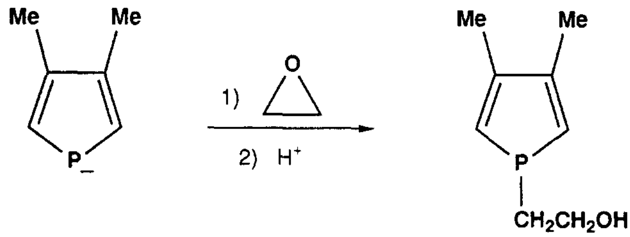
(19)

philes. 1-Silylphospholes are generally unstable and tend to give P–P bonded dimers because the silyl groups easily shift around the phosphole ring [59]. However, 1-stannylphospholes are stable under ordinary conditions and are easily prepared



(20)

via the reaction of phospholide ions with stannyl chlorides [63] (eqn. 20). These tin derivatives are good equivalents of phospholide ions for reactions with transition metal halides, because alkali metal phospholides often have a tendency to reduce the metallic centers. Finally, the reaction of a phospholide anion with ethylene oxide has been reported in one case [16] (eqn. 21).

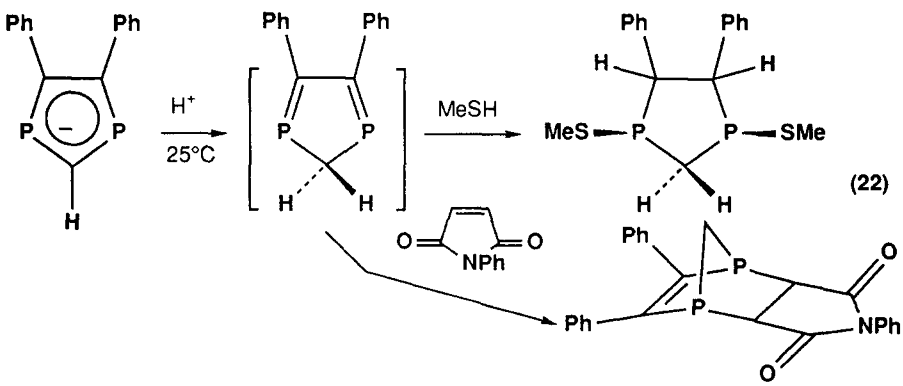


(21)

4.2. Polyphospholide anions

The reaction of any electrophile with a polyphospholide anion necessarily leads to initial products containing very reactive two-coordinate phosphorus centers. Generally, these products either decompose, dimerize or polymerize. Thus, the study of the organic reactivity of polyphospholide ions is very difficult and little work has been devoted to the topic.

Apparently, protonation of the 4,5-diphenyl-1,3-diphospholide ion takes place at the P–C–P carbon [64]. The resulting product can be trapped by MeSH or *N*-

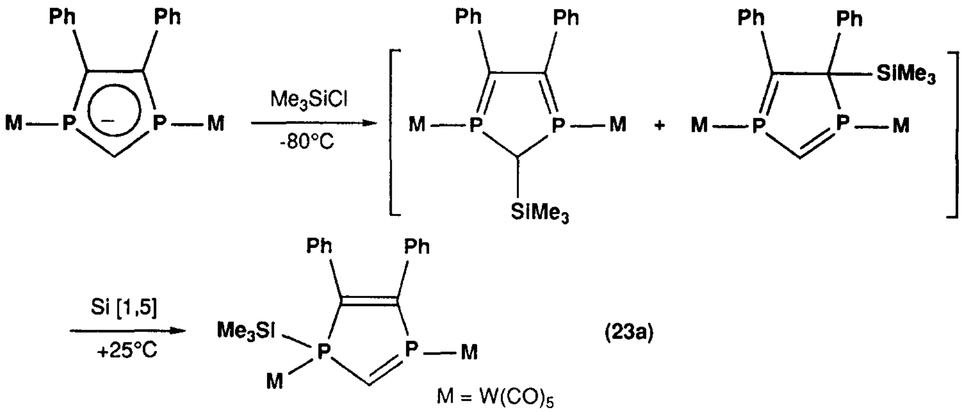


(22)

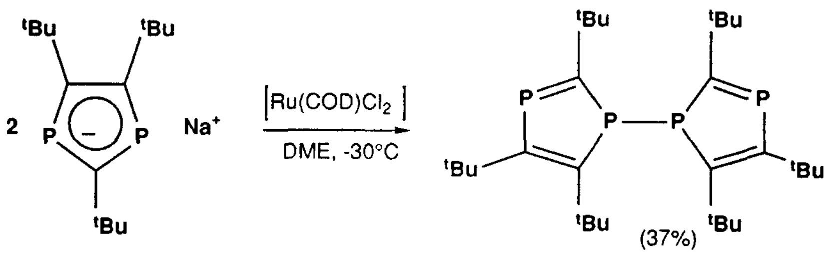
phenylmaleimide (eqn. 22). At low temperature the silylation of the *bis* (tungsten-complexed) anion occurs at both types of carbon center, but at room temperature the resulting products are converted into the more stable P–silyl derivative via [1,5] silyl shifts (eqn. 23a). Dimethyl acetylenedicarboxylate selectively traps the more reactive C–silyl isomers [64].

Very recently, the oxidative coupling of two 1,3-diphospholide ions has been successfully carried out (eqn. 23b) [154]. The resulting dimer has been characterized by ^{31}P NMR spectroscopy and X-ray crystal structure analysis: $\delta\ ^{31}P = +303.3$ and $+24.6$, $^{2}J_{(P-P)} = 24.4$ Hz, $^{1}J_{(P-P)} = 470$ Hz. The P–P bond length is normal at 2.244(2) Å, and the two rings are not parallel, inter-ring angle 46°.

The protonation of the 2,5-bis(*tert*-butyl)-1,3,4-triphospholide ion also takes place at carbon. The resulting species dimerizes via successive [4+2] and [2+2] cycloadditions which ultimately give a cage compound [65] (eqn. 24) whose crystal

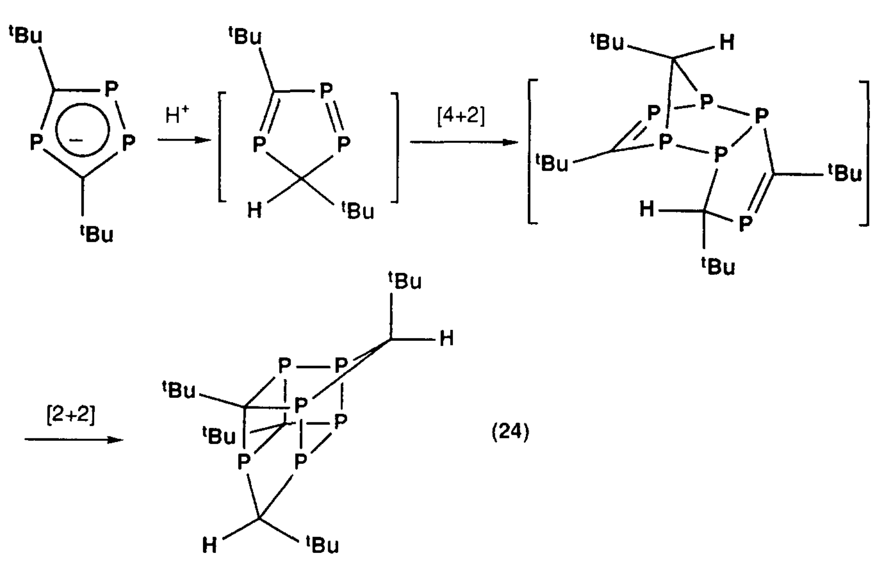


(23a)



(23b)

structure has been established by X-ray analysis. A similar protonation, when carried out with a mixture of 1,3-diphospholide and 1,3,4-triphospholide ions, leads to a [4+2] cycloadduct whose *exo* junction precludes the subsequent cage formation [66] (eqn. 25). The P=C double bond of this [4+2] dimer gives an ethanol adduct



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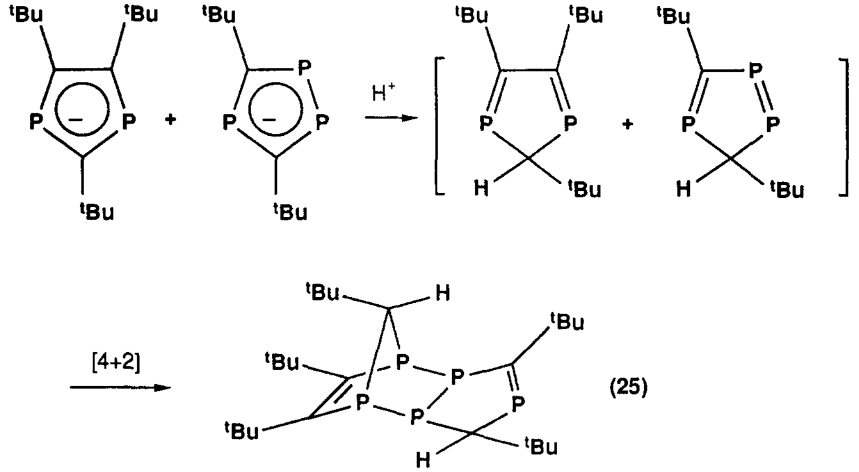
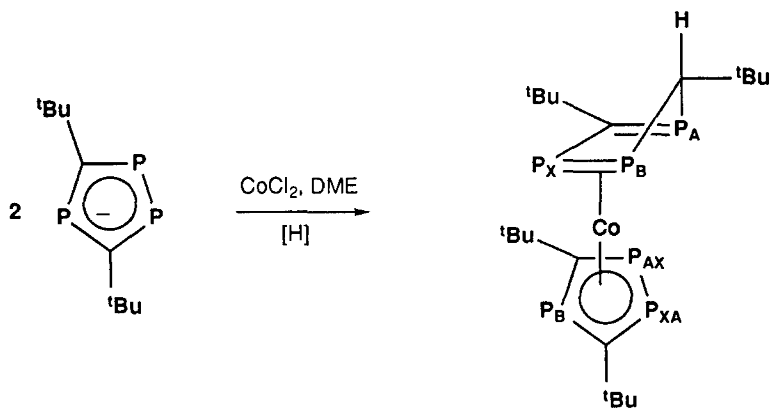


(25)

whose structure has been confirmed by X-ray analysis. It is interesting to note that only one [4+2] adduct is formed, and that the diphosphorus and triphosphorus units selectively act as the diene and dienophile, respectively.

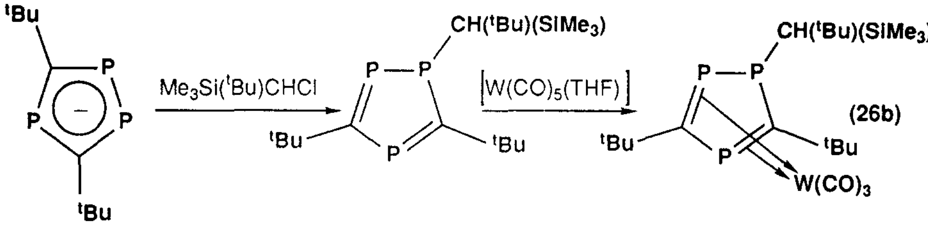
The intermediate C-protonation product of the triphospholide ion has been characterized as a stable η^4-cobalt complex. This was obtained, in 5% yield, by allowing the triphospholide ion to react with cobalt chloride in dimethoxyethane



(26a)

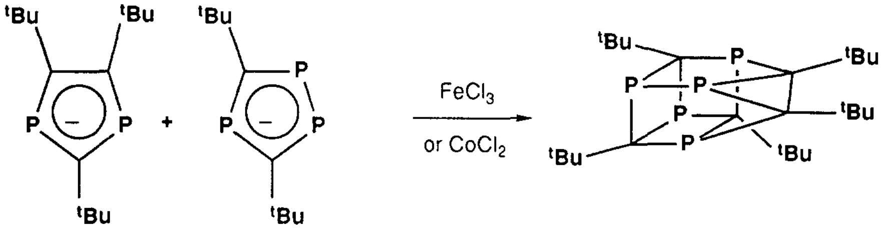
[67] (eqn. 26a).The product is probably formed via [H] abstraction from the solvent by an intermediate hexaphosphacobaltocene. The X-ray crystal structure shows two P$\overset{...}{-}$C bonds at 1.78 and 1.79(1) Å and a P$\overset{...}{-}$P bond at 2.136(4) Å, all in the expected ranges for a η^4-complexed unit. Interestingly, the $^{31}P\{^1H\}$ NMR spectrum exhibits two widely spaced ABX patterns: η^4, $\delta_x = +131.2$, $\delta_B = +109.5$, $\delta_A = +93.1$, $^1J_{BX} =$ 419.7 Hz; η^5, $\delta_x = +0.2$, $\delta_B = -20.1$, $\delta_x = -64.7$, $^1J_{AX} = 360.6$ Hz.

By contrast with protonation, alkylation of 1,3,4-triphospholide ions takes place at phosphorus, according to a very recent report [155]. The 1,2,4-triphosphole thus formed has been stabilized as a η^4-W(CO)$_3$ complex (eqn. 26b). The final complex has been characterized by X-ray crystal structure analysis.



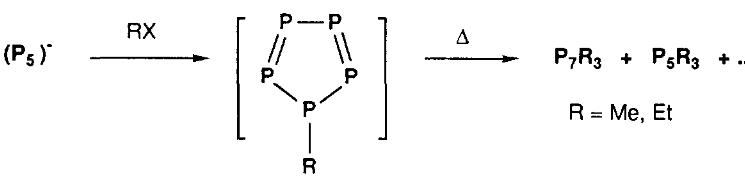
(26b)

On the other hand, the oxidative coupling of the diphospholide with the triphospholide ion by $FeCl_3$ or $CoBr_2$ affords a pentaphosphorus cage compound



(27)

via an unknown mechanism [68] (eqn. 27). The formation of the three-membered ring requires the cleavage of P–P and P–C bonds of the initial heterocycles. The structure has been established by X-ray analysis. Finally, it has been shown that the alkylation of $(P_5)^-$ leads to a mixture of polyphosphines [40] (eqn. 28).

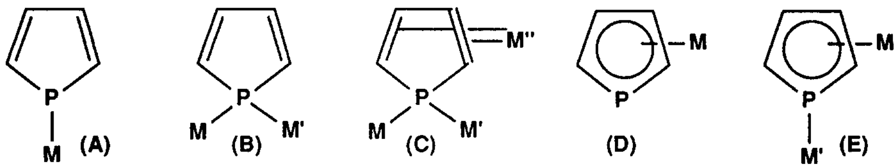


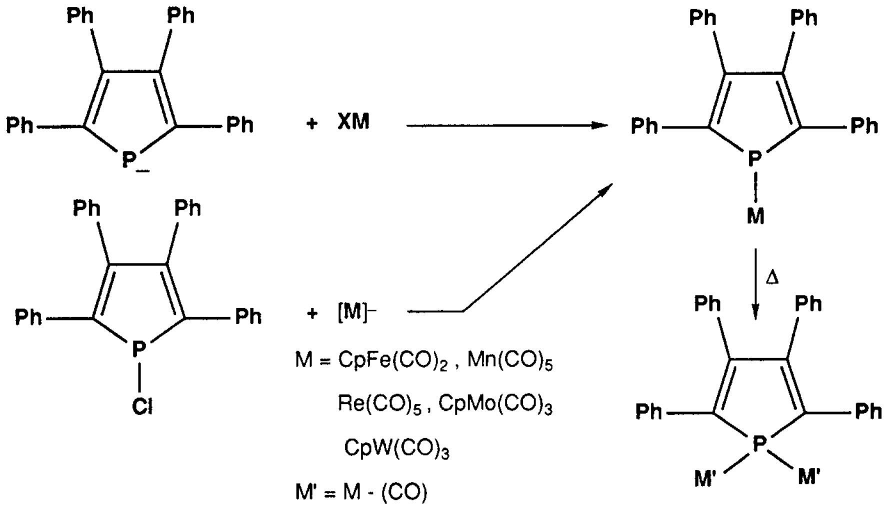
(28)

5. COORDINATION CHEMISTRY

5.1. Complexing modes of the phospholyl ligand

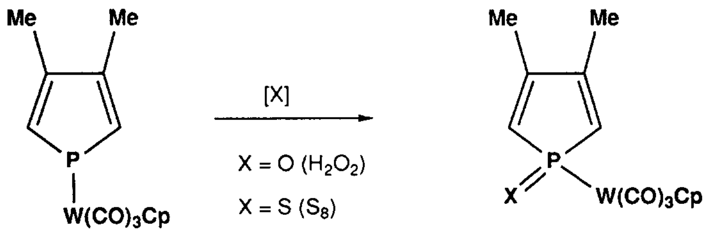
Five types of phospholyl complexes are known. The phospholide anion may act as a classical phosphide to give both η^1-P and μ^2-P complexes (types A and B). In the (B) type, no ring delocalization is possible, and the diene subunit may act as a η^4-ligand; this leads to trimetallic complexes of type (C). In the η^5-complexes of type (D), a lone pair at phosphorus is still available for complexation leading to type (E). Most studies have focused on type (D), although a few papers deal with types (A)–(C). For example, several η^1-P and μ^2-P phospholyl complexes have been





(29)

prepared from the easily accessible 1,2,3,4-tetraphenylphospholide [69,70] (eqn. 29). Apart from thermolysis, the only reported chemistry concerned P-oxidation and P–M bond cleavage by halogens. A thorough study of η^1-P phospholyl–tungsten complexes has been published recently [71]. These species are obtained via the reaction of 1-bromo- or 1-cyanophospholes with the appropriate tungsten anion. X-ray structure analysis of two such tungstaphospholes has revealed that the phosphorus atom is more planar and the ring more aromatic than in 1-alkyl- or 1-arylphospholes. From a structural standpoint, these compounds lie halfway between the pyramidal localized covalent phospholes and the planar delocalized phospholide ions. Three types of reactions which occur at the phosphorus lone pair, at the dienic system or at the tungsten coordination sphere have been observed. Representative examples are given in eqns. (30)–(35). Thermolysis of these η^1-P



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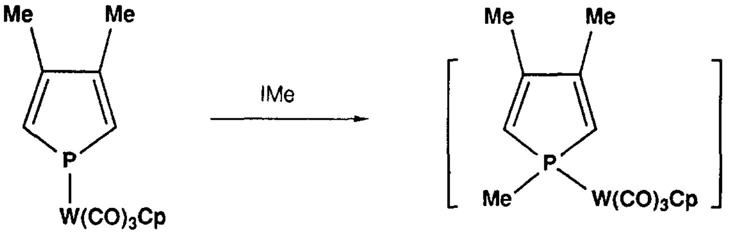

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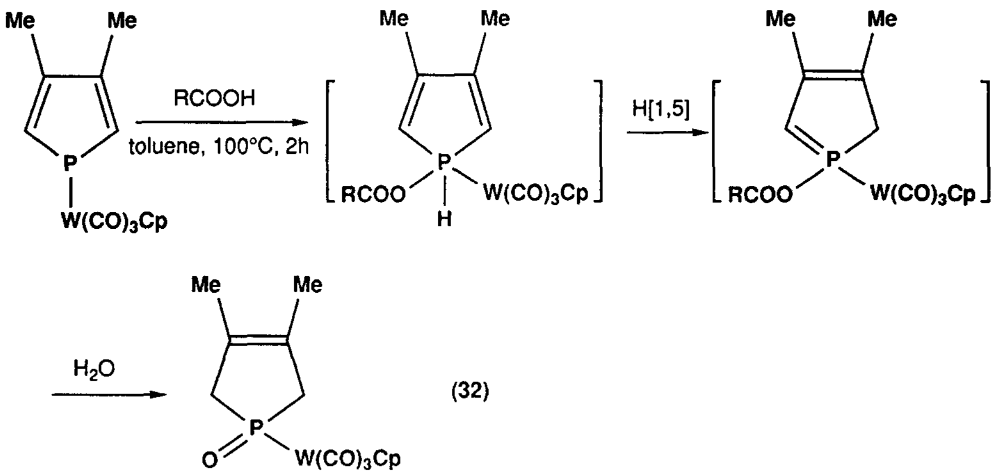

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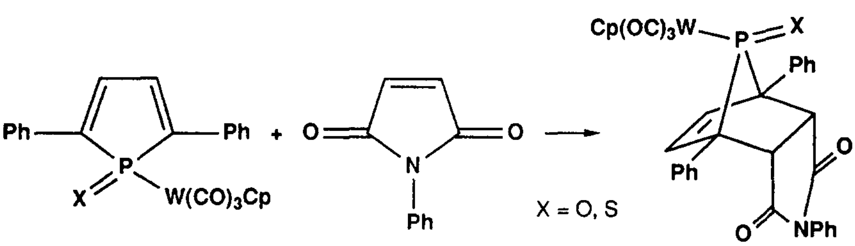

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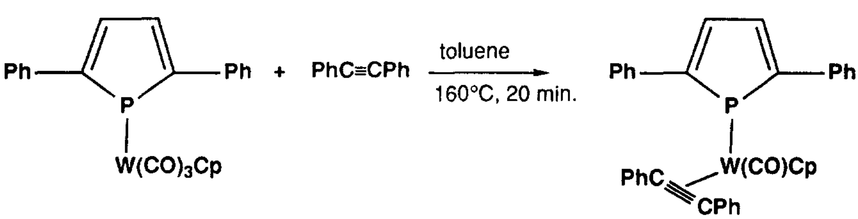
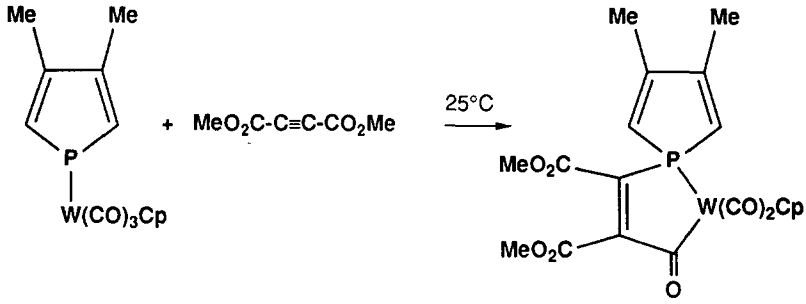


(34)

complexes leads to μ^2-P complexes of type (B) (eqns. 36, 37), as expected. In the second case, the low-field shift of the ^{31}P resonance reflects the presence of the W–W bond. The hydride resonance appears at -16.4 (C_6D_6) with a J(H–P) coupling of 24.7 Hz and a $J(^1H–^{183}W)$ coupling of 40 Hz. Toluene is probably the source of the



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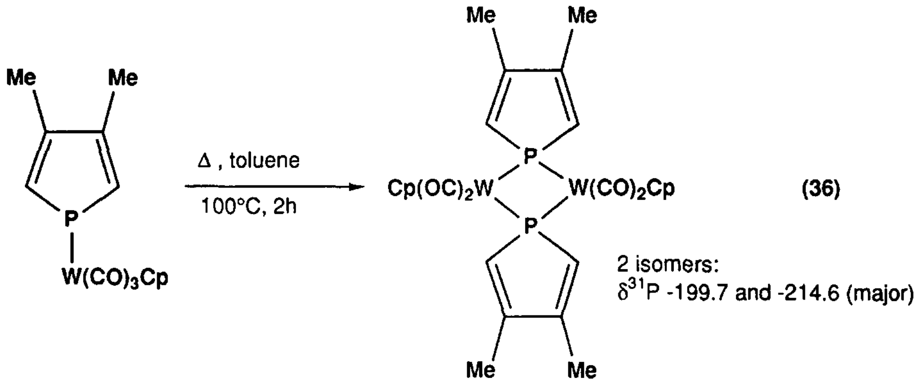

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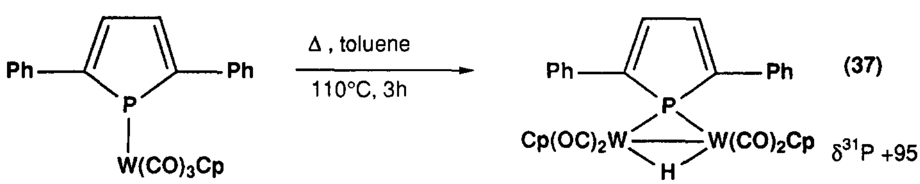
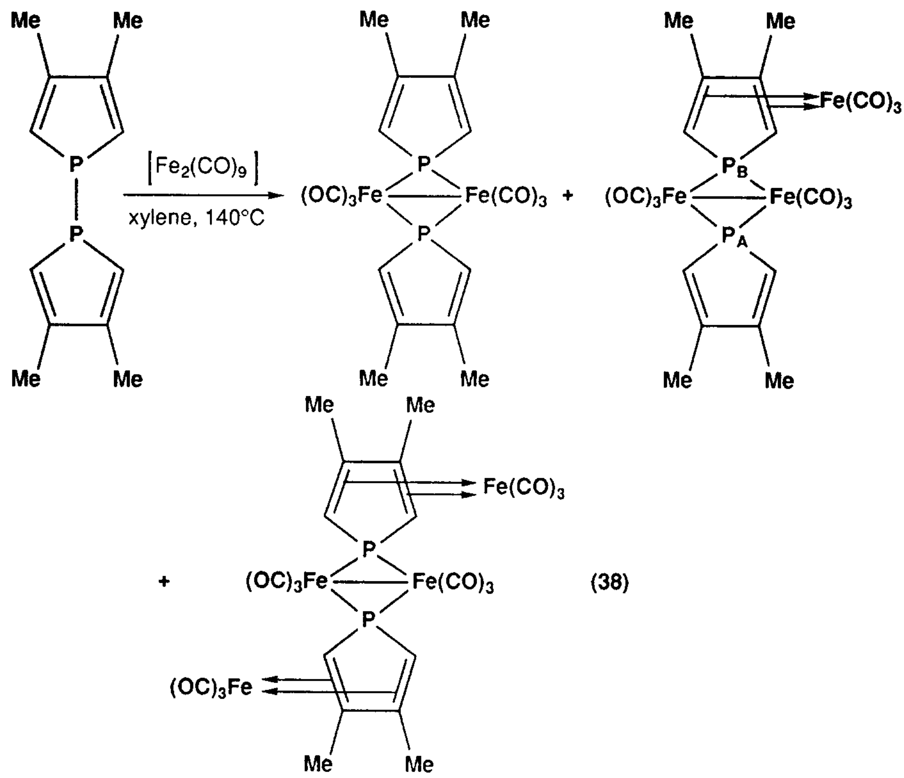


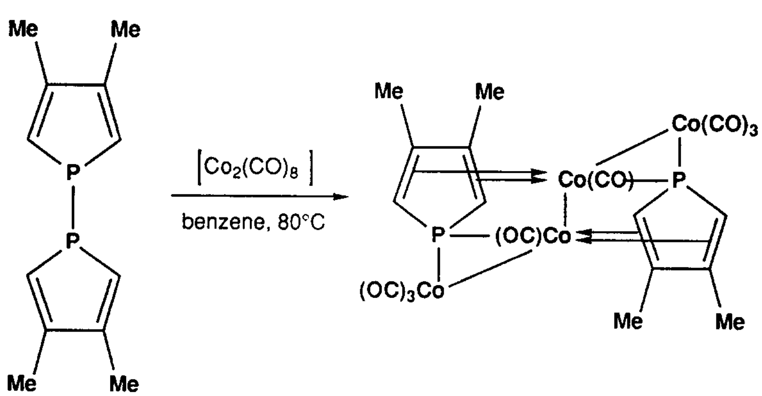
(37)

hydride ligand. A μ^2-P complex of type (B) was also obtained upon reaction of a 1,1′-biphospholyl with $[Fe_2(CO)_9]$ in refluxing xylene [61]. The π-complexation of the phosphole dienic systems of this complex by an excess of iron carbonyl then led to several other complexes of type (C) (eqn. 38). In the triiron complex, the two ^{31}P NMR resonances are very different: AB system, $\delta_A = +95$, $\delta_B = +202$, $J(A\text{–}B) = 132$ Hz. A similar reaction with $[Co_2(CO)_8]$ led to another complex of type (C) which was characterized by X-ray crystal structure analysis [61] (eqn. 39). Its structure incorporates an unprecedented chain of four cobalt atoms, whose central bond is weak: Co–Co, 2.635 and 2.787 Å.Only one other complex of type (C) has been structurally characterized in the literature [72]. It results from the reaction of a preformed phosphole–dimanganeseheptacarbonyl complex with an excess of manganese carbonyl under UV irradiation (eqn. 40). Its structure incorporates a rare trimanganese chain. Upon heating, it readily decomposes to give the corresponding phosphacymantrene (η^5-phosphacyclopentadienylmanganesetricarbonyl).



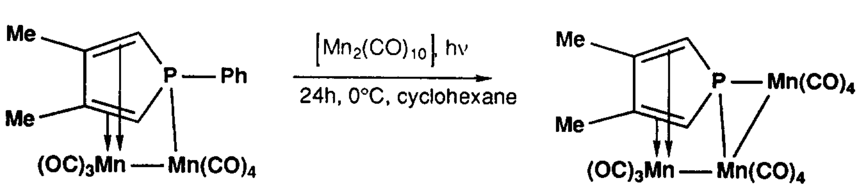
Me
$[Fe_2(CO)_9]$
xylene, 140°C
$(OC)_3Fe$
$Fe(CO)_3$
P
P_B
P_A

(38)



Me
$[Co_2(CO)_8]$
benzene, 80°C
$Co(CO)_3$
Co(CO)
(OC)Co
$(OC)_3Co$
P

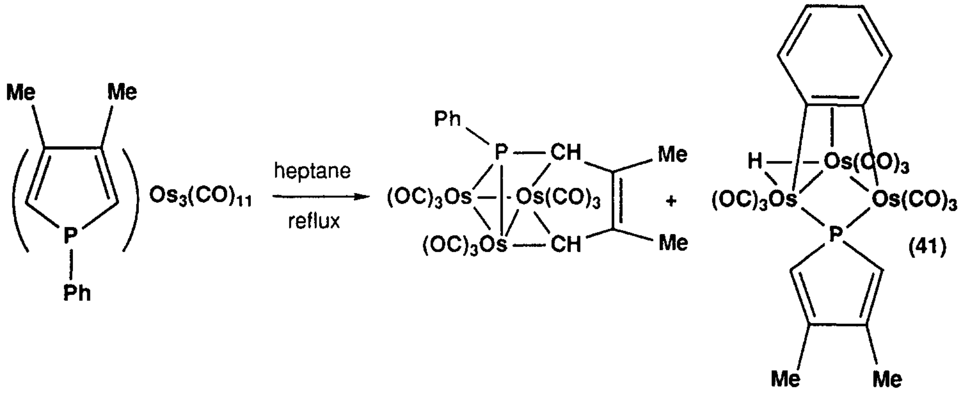
(39)



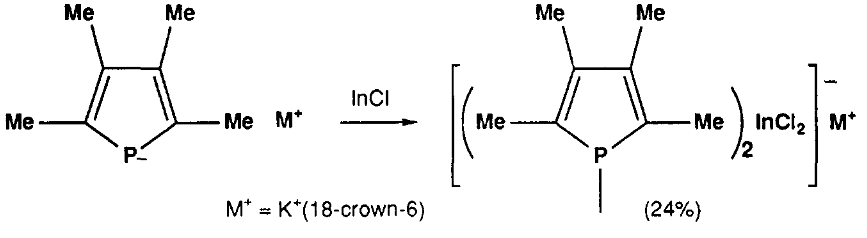
Me
P—Ph
$[Mn_2(CO)_{10}]$, hν
24h, 0°C, cyclohexane
$(OC)_3Mn$
$Mn(CO)_4$

(40)

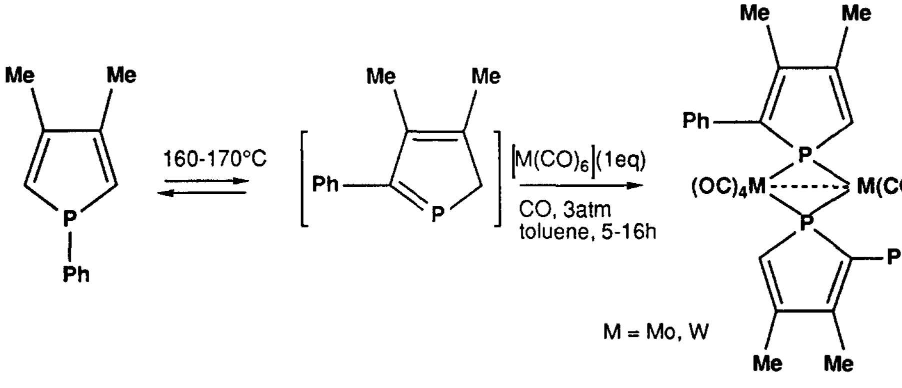
The thermal decomposition of $[Os_3(CO)_{11}L]$ (L = 1-phenyl-3,4-dimethylphosphole) has been shown to give mainly a ring-opened product together with a



very low yield of a μ^2-P phospholyl complex (eqn. 41) [73]. The phospholyl complex has been characterized by X-ray crystal structure analysis. The hydride resonance appears at -17.10 ppm. A first η^1-phospholyl complex of indium has been described



(42a)

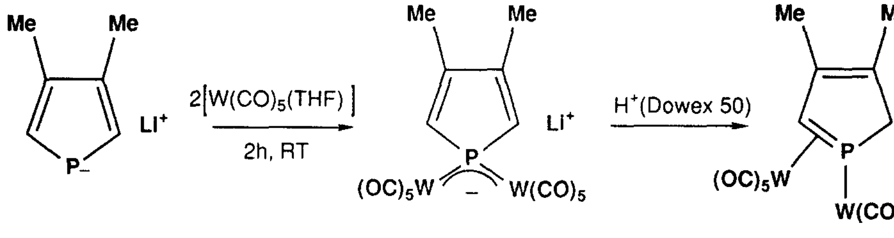


(42b)

recently (eqn. 42a) [74a]. The product has been characterized by X-ray diffraction. The indium–phosphorus bond lengths are close to the sum of the covalent radii at 2.481(3) and 2.491(3) Å, the phosphorus atoms are highly pyramidal (Σ angles = 291.4° and 289.3°), and the bond distances within the ring are normal for a covalent phosphole [8]. The ^{31}P resonance, which appears at -19.16 ppm in CD_2Cl_2, may be compared with $+74.16$ ppm for the starting anion in C_6D_6 [36].

It has been shown that it is possible to take advantage of the phenyl [1,5] sigmatropic shift that takes place above approx. 150°C in 1-phenyl-3,4-dimethylphosphole to prepare μ^2-P complexes of type (B) (eqn. 42b) [74b]. With $[Cr(CO)_6]$, partial hydrogenation of the phospholyl ring is observed under similar conditions.

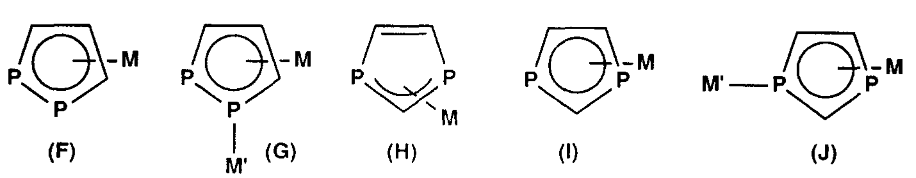
Finally, anionic η^1- and μ^2-P phospholyl complexes have been prepared by reaction of the 3,4-dimethylphospholide anion with $[M(CO)_5(THF)]$ (M = Cr, W) [59]. The tungsten μ^2-P complex is protonated to give an exceptional 2*H*-phosphole complex (eqn. 42c) which has been fully characterized by X-ray crystal structure analysis.



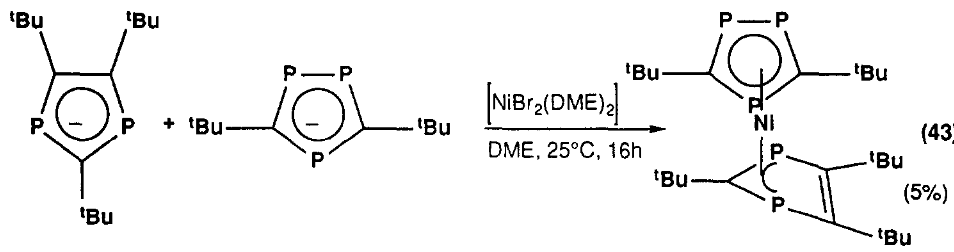
(42c)

5.2. *Complexing modes of the polyphospholyl ligands*

So far, the 1,2-diphospholide ion is known only as η^5-complexes of types (F) and (G) [6,7]. The coordination chemistry of the 1,3-diphospholide ion is far more developed. Besides the expected η^5- and η^5, η^1-complexes of types (I) and (J), Nixon has shown [75] that this ion is able to give η^3-complexes of type (H) which are

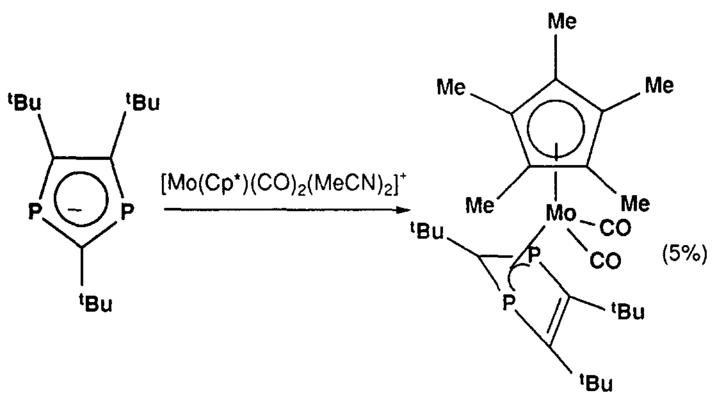


structurally related to the η^3-1,3-diphosphaallyl complexes discovered by Appel [76]. Thus, the treatment of a mixture of di- and triphospholide ions by $NiBr_2$ in dimethoxyethane affords a η^3,η^5-nickel complex (eqn. 43) [75]. X-ray crystal structure analysis reveals a substantial bending of the P_2C_3 ring around the P—P axis and away from nickel. In the mass spectrum, a strong peak at $m/z = 420$ corresponds to the loss of a $^tBu_2C_2$ fragment. The product is diamagnetic, as expected for an 18-electron complex. The $^{31}P\{^1H\}$ NMR spectrum was analysed as an A_2BC_2 spin system: $\delta_A = +115$, $\delta_B = +153.2$, $\delta_C = +111.4$, $J_{AB} = 51.2$ Hz, $J_{AC} = 10.9$ Hz, $J_{BC} = 2.9$ Hz (P_C in the P_2C_3 ring).



(43)

Another η^3-complex was obtained in the reaction of a source of $[Mo(Cp^*)(CO)_2]^+$ with the same diphospholide ion (eqn. 44) [77]. The C=C bond of the P_2C_3 ring is well localized at 1.346(4) Å vs. 1.31(6) Å in the η^3-nickel complex. The P$\overset{...}{-}$C bonds of the η^3-(P–C–P) unit lie around 1.77 Å, as expected for a delocalized system. When the (η^5-C_5Me_5) ring on molybdenum is replaced by a (η^5-C_9H_7) indenyl, a η^5–η^3 slippage of the indenyl ligand is observed and a (η^5-P_2C_3) complex is obtained (eqn. 45). This result suggests that the ease of ring slippage increases in the series cyclopentadienyl < diphospholyl < indenyl. Finally, it has also



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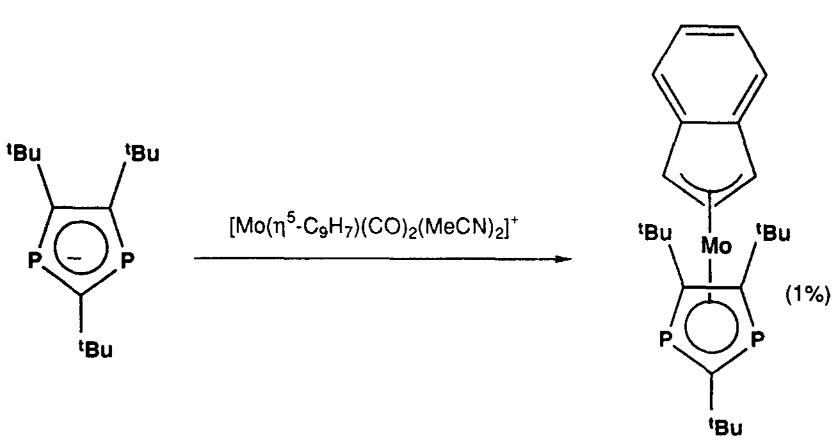
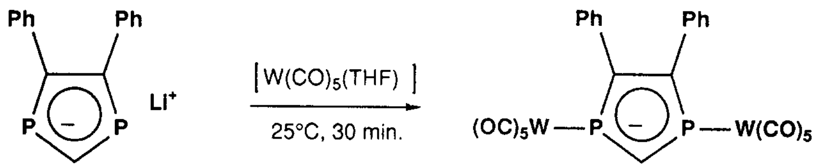


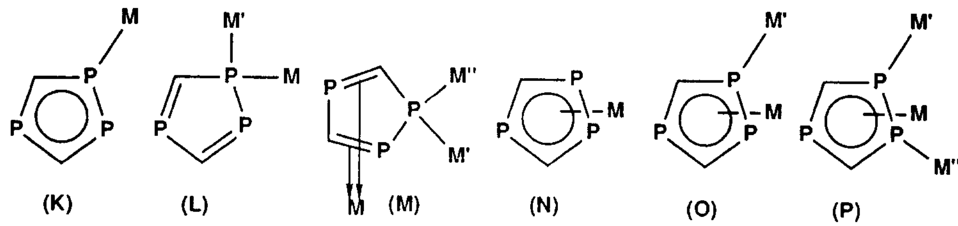
(45)



(46)

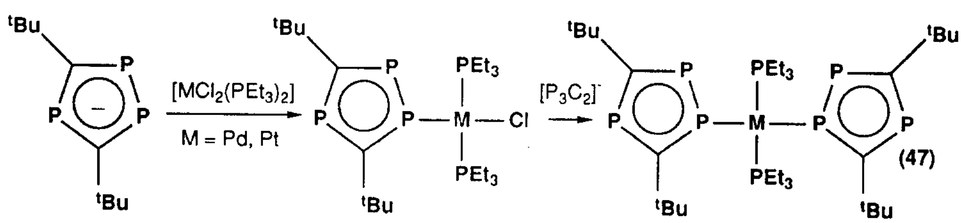
been demonstrated that a diphospholide can act as a bis-η^1-ligand (eqn. 46) [64]. A strong upfield shift of the ^{31}P resonance occurs upon complexation: $\Delta\delta = -96$ ppm.

The coordination chemistry of the 2,5-bis-(*tert*-butyl)-1,3,4-triphospholide ion has been studied in some depth by the group of Nixon. Six types of complexes,



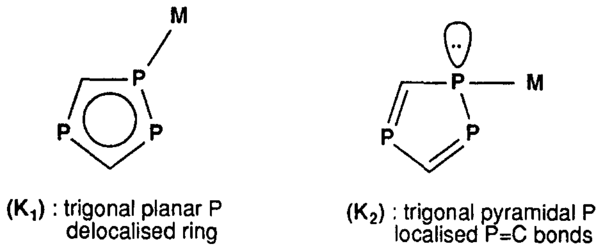
(K)–(P), are known. Apparently, only the lone pairs of the two connected phosphorus atoms are available for η^1 or μ^2 coordination, with or without additional η^4, η^5 coordination. This may reflect some steric hindrance around the isolated phosphorus centre, which presumably prevents complexation. The parallels between the coordination behaviour of the triphospholide and monophospholide ions are intriguing.

Type (K) was first described in 1988 [78]. Treatment of the triphospholide ion



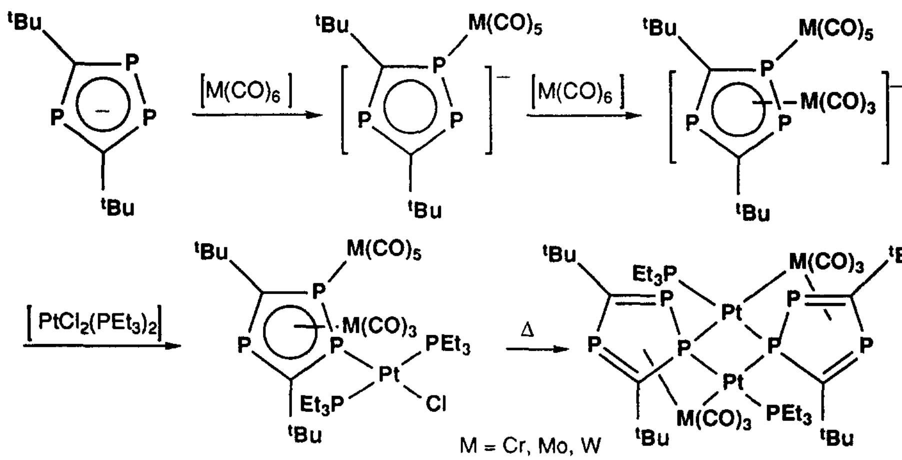
(47)

with *cis*-[$MCl_2(PEt_3)_2$] gives the corresponding η^1-complexes (eqn. 47) [78,79]. All of these complexes are fluxional in solution according to variable temperature $^{31}P\{^1H\}$ NMR studies. An intramolecular 1,2-shift of the metal atom takes place between the two connected phosphorus atoms of the ring. A strong upfield shift of their ^{31}P resonances is observed, as expected. The results of a structural study of these complexes are quite fascinating. Two models are possible, K_1 and K_2. Clearly, the halogeno complexes belong to the (K_1) type. In the [$Pt(Cl)(PEt_3)_2$] complex, the ring is strictly flat, with P$\cdots$C bonds at 1.711, 1.745, 1.726 and 1.740 Å and the P$\cdots$P bond at 2.068(3) Å. The sum of the angles around the complexed phosphorus is 360°, the Pt–P(ring) bond is short at 2.243(2) Å and the large ^1J(Pt–P) coupling constant (2833 Hz) implies a high s-character for the corresponding orbital.



The situation is more ambiguous in the complex *trans*-$[Pt(P_3C_2{}^tBu_2)_2(PEt_3)_2]$. The P⋯C bonds are still in the same range (1.72–1.75 Å) and the P⋯P bond seems only marginally longer at 2.098(8) Å. But the trigonal phosphorus is no longer planar: Σ angles = 348°, the ^1J(Pt–P) coupling constant decreases to 1860 Hz and the Pt–P(ring) bond elongates to 2.371(5) Å. Apparently, this complex lies halfway between the (K_1) and (K_2) bonding modes. It should be recalled here that the bonding mode of the η^1-phospholyl complexes corresponds to the (K_2) type. In the η^1-phospholyl–tungsten complex of eqn. (30), for example, the sum of the angles around phosphorus lies at approx. 320° [71]. In this light, it is interesting to note that calculations have shown the triphospholide to be more aromatic than the monophospholide ion [50]. Thus, we can expect that (K_1) lies lower in energy than the corresponding monophosphorus complex, whereas (K_2), with its localized P=C double bonds, is probably higher in energy than the corresponding phospholyl complex. Thus the trends toward planar η^1-triphospholide complexes and pyramidal η^1-phospholide complexes seem to be logical.

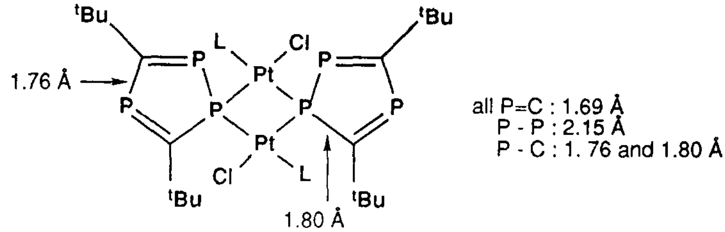
Other η^1-complexes of the triphospholide ion are also involved in a multistep



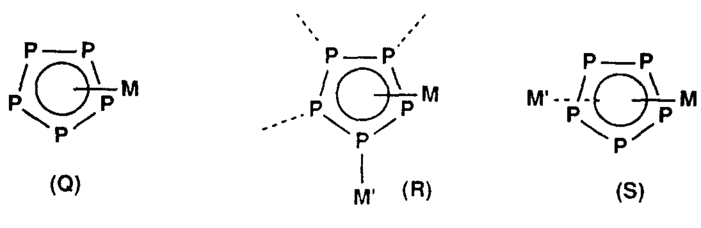
(48)

sequence described in eqn. (48) [80]. The neutral trimetallic complexes of type (P) lose $[M(CO)_5(PEt_3)]$ upon heating in toluene. This leads to dimers whose structures have been established by X-ray diffraction. Two features of these structures are noteworthy: one phosphorus of the ring bridges the two platinum atoms, and there is no platinum–platinum bond. The most likely formulation corresponds to type (M) as depicted in the scheme.

Very recently, the group of Nixon [155] has been able to prepare the first complex of type (L). X-ray crystal structure analysis clearly demonstrates the loss of aromaticity within the ring which acts as a classical μ^2-phosphido bridging ligand towards the two platinum centres.



Of all the other possible polyphospholide ions, the only one which has been subjected to any investigation as a ligand in coordination chemistry is the pentaphospholide anion. Most of the work comes from the group of Scherer. All the (P_5) complexes described in the literature so far display a η^5-bonded ring and, as such, will be discussed in the last section of the present review. In addition to the basic type (Q), the $(\eta^1)_n,\eta^5$ (R) and the $\eta^{5:5}$ (S) types also exist. Up to four metals have been connected to the phosphorus lone pairs of a central (η^5-P_5) unit to give (R) type complexes. This η^1,η^5-bonding mode is common to all phospholide ions, as we have already seen. By contrast, the triple-decker type (S) is specific for the $(P_5)^-$ ion, at least up to now.

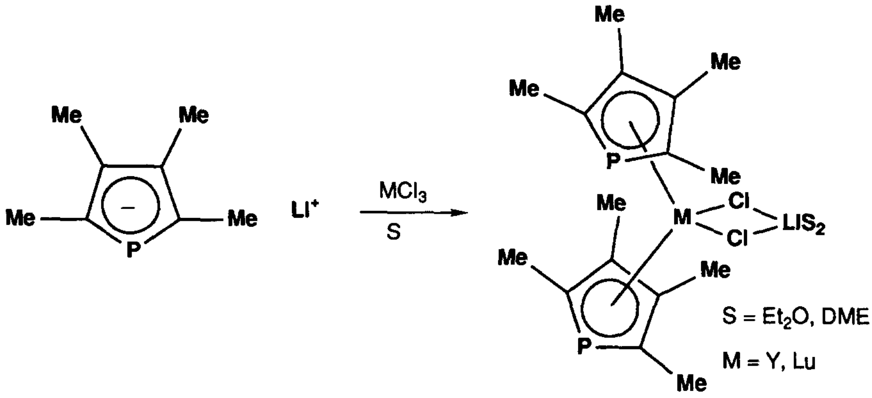


5.3. The chemistry of η^5-phospholyl complexes

Since the chemistry of η^5-phospholyl complexes has already been described in depth in a recent review [10], we will concentrate hereafter on the most significant and recent results. The material is organised according to the position of the complexed metal in the periodic table going from left to right.

Three recent papers have dealt with the η^5-phospholyl complexes of yttrium(III) [81], and some rare earths, including samarium(II), ytterbium (II) [22,82] and lutetium(III) [81]. The reaction of lithium tetramethylphospholide with MCl_3 (M =

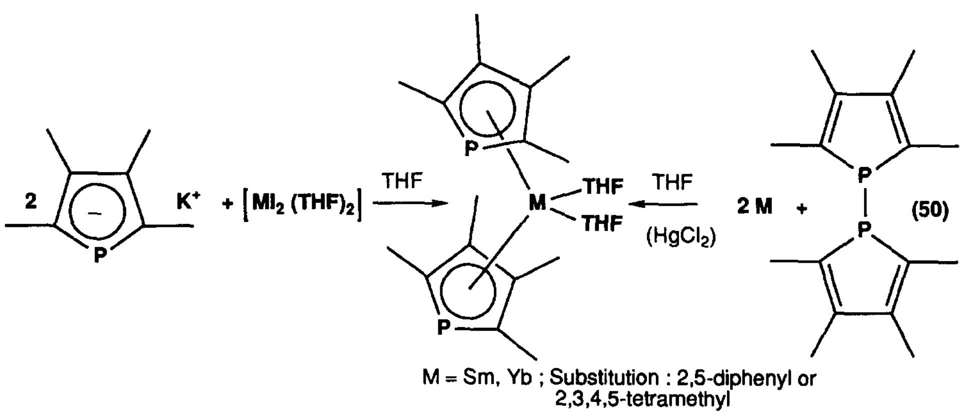
Y, Lu) yields the expected η^5-complexes (eqn. 49) [81]. These complexes have been



(49)

characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy. A very low ^1J(P–Y) coupling of 6.4 Hz was considered as characteristic of the η^5-bonding mode, since much higher values were recorded for σ (Y–P) complexes (approx. 50 Hz). An attempt to prepare the corresponding La(III) complex failed.

Samarium(II) and ytterbium(II) complexes have been obtained either by reaction of the appropriate phospholide ions with the metal diiodides or directly by cleavage of the P–P bond of 1,1′-biphospholyls with the activated metallic powders

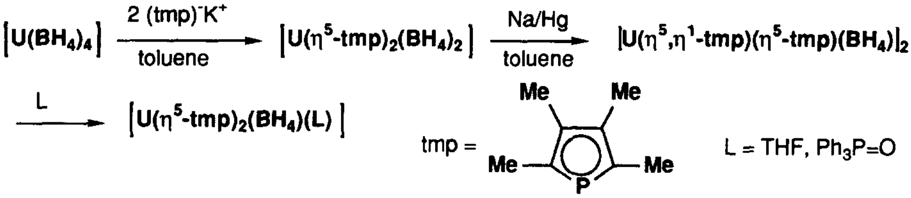


(50)

(eqn. 50) [22,82]. X-ray crystal structure analysis of the 2,5-diphenylphospholyl–ytterbium derivative shows centroid–Yb–centroid and O–Yb–O angles of 129° and 82°, respectively. The Yb–P bond lengths are normal at 2.959(1) and 2.986(1) Å. The geometry of the η^5-phospholyl rings is similar to that of the free ion, with slightly longer P–C bonds at 1.77–1.78 Å. The samarium complexes display impressive paramagnetic shifts of their ^{31}P resonances: $\delta^{31}P = -580$ and -417 ppm for the tetramethyl and 2,5-diphenylphospholyl derivatives, respectively.

Three papers have been devoted to the description of a series of

(η^5-2,3,4,5-tetramethylphospholyl)uranium complexes [83–85]. No other actinide–phospholyl complex has been investigated up to now. The reported chemistry is summarized in eqns. (51)–(53).



(51)

$$[\mathrm{U(Mes)(BH_4)_3}] \xrightarrow[\text{THF}]{2\,(\mathrm{tmp})^-\mathrm{K}^+} [\mathrm{U}(\eta^5\text{-tmp})_2(\mathrm{BH_4})_2]^-\mathrm{K}^+ \xrightarrow[\text{toluene}]{\Delta} [\mathrm{U}(\eta^5,\eta^1\text{-tmp})(\eta^5\text{-tmp})(\mathrm{BH_4})]_2 \tag{52}$$

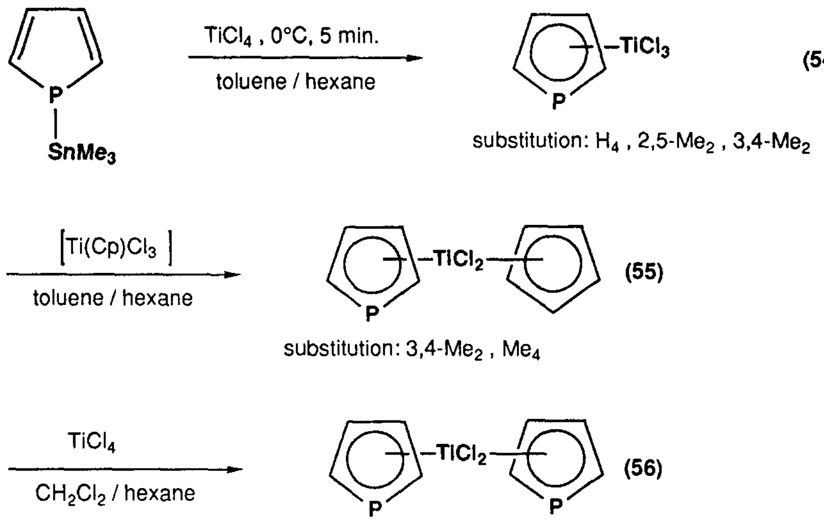
$$\mathrm{Mes} = \eta^6\text{-1,3,5-Me}_3\mathrm{C}_6\mathrm{H}_3$$

$$\mathrm{UCl_4} \xrightarrow[\text{toluene}]{3\,(\mathrm{tmp})^-\mathrm{K}^+} [\mathrm{U}(\eta^5\text{-tmp})_3\mathrm{Cl}] \xrightarrow{\mathrm{R}^-} [\mathrm{U}(\eta^5\text{-tmp})_3(\mathrm{R})] \tag{53}$$

$$\mathrm{R} = \mathrm{H},\ {}^i\mathrm{PrO},\ \mathrm{Me}$$

Both [$U(tmp)_2(BH_4)_2$] and [$U(tmp)_3Cl$] have been characterized by X-ray crystal structure analysis. In the first case, the average U–P and U–C bond lengths are 2.90(1) and 2.81(4) Å, respectively. In the second case, the corresponding data are 2.927(4) and 2.90(8) Å. It is clear that the uranium coordination sphere is more congested in the tris-phospholyl complex. This complex is all the more remarkable since it is the first tris (η^5-phospholyl)–metal complex ever reported. The phospholyl ring has a low electron-donating capacity as indicated by the reduction potentials of [$U(\eta^5\text{-tmp})_2(BH_4)_2$] and [$U(\eta^5\text{-}C_5Me_5)_2(BH_4)_2$], respectively -1.61 and -1.83 V vs. ferrocene–ferricinium. Another complex of interest is a dimeric species involving both η^5 and η^5,η^1-bonded phospholyl rings. This complex is fluxional above 50°C. At room temperature, it displays two ^{31}P NMR resonances at $+727$ and $+3471$ ppm (vs. H_3PO_4). The low-field signal corresponds to the η^1-U-bonded phosphorus. This astounding low-field shift is a consequence of the paramagnetism of uranium(III).

The synthesis of η^5-phospholyl complexes of titanium(IV) is plagued by the redox processes that take place when a phospholide ion is allowed to react with Ti(IV) chlorides. The formation of 1,1′-biphospholyls has been observed [63]. In order to avoid this reduction of Ti(IV), it suffices to replace the phospholide ion by its covalent 1-trimethylstannyl derivative (eqns. 54–56) [63,86]. The [$Ti(P)Cl_3$] and [$Ti(P)_2Cl_2$] complexes ($P = \eta^5$-3,4-dimethylphospholyl) have been characterized by X-ray crystal structure analysis. Their structures are closely related to those of the corresponding η^5-cyclopentadienyl complexes. A slight increase of the P–Ti bond lengths from 2.549(1) to 2.5871(8)–2.6040(8) Å is observed when comparing the first with the second complex. In the second case, the angles between the two phospholyl



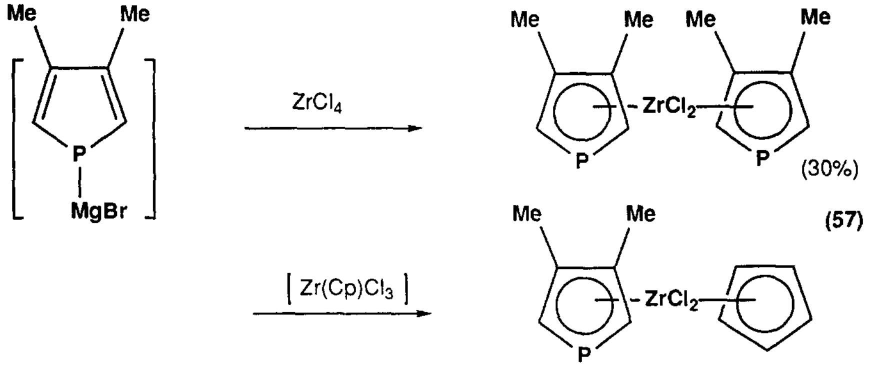
(54)

(55)

(56)

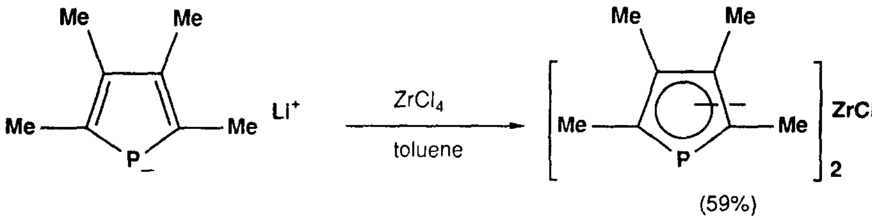
and the two P–centroid–Ti planes are 52° and 16.2°, respectively. The ^{31}P NMR resonances of these complexes are observed at low fields, for example $[Ti(C_4H_4P)Cl_3]$, $\delta = +182$ ppm. All these Ti(IV) complexes are sensitive to hydrolysis which destroys the ring–titanium bonds.

No redox reactions were encountered during the preparation of the first η^5-phospholyl–Zr(IV) complexes. The first such species were prepared as early as 1980, but their characterization was complicated by purification and solubility problems



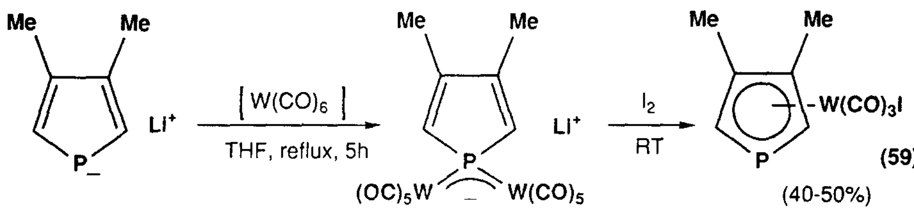
(57)

(eqn. 57) [87]. Duplicating this chemistry with the 2,3,4,5-tetramethylphospholide ion eliminated these problems and permitted the characterization of the resulting complex by X-ray crystal structure analysis (eqn. 58) [88]. The two rings are staggered, with a P....P distance of only 3.23 Å. The angle between the ring planes is 48.4° and the Zr–P bond lengths lie at approx. 2.73 Å. The staggered conformation of this complex allows chelation to an additional $[Fe(CO)_3]$ or $[W(CO)_4]$ transition metal centre via η^1-coordination at phosphorus. The $[Fe(CO)_3]$ chelate has been

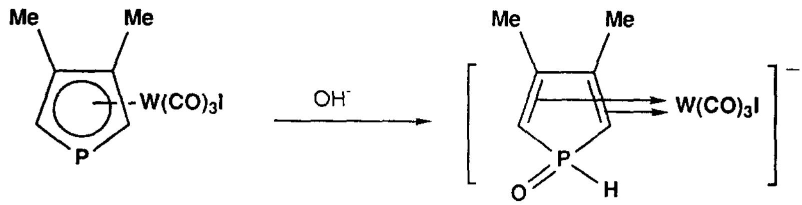

(58)

characterized by X-ray crystal structure analysis [89]. The inter-ring dihedral angle increases from 48.4° to 52.56° upon chelation of iron. The $ZrMe_2$ and $ZrPh_2$ derivatives have also been obtained by reaction of the appropriate lithium reagents, but an attempted synthesis of the dihydride failed.

In the chromium family, only tungsten has been incorporated into a η^5-phospholyl complex up to now. The reaction of iodine with the μ^2-P[W(CO)$_5$]$_2$ complex of a phospholide ion yields a η^5-phospholyl–tungsten complex via an unknown

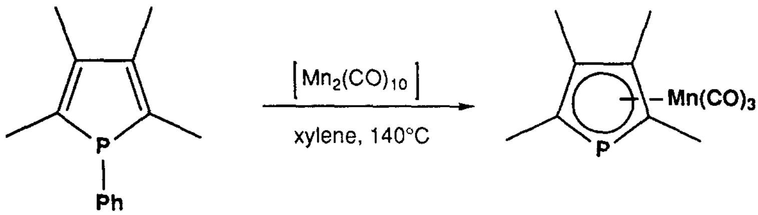

(59)

mechanism (eqn. 59) [59]. This η^5-complex displays a ^{31}P NMR resonance at −31.5 ppm, and no (^{31}P–^{183}W) coupling. This property seems to be characteristic of tungsten π-complexes involving P$\cdots$C delocalized multiple bonds. The X-ray crystal structure shows a tungsten–ring distance of 1.963 Å, with a W–P bond which is longer than a pure W–P σ bond at 2.516(2) Å. The folding of the ring around the C_α–C_α' axis and away from tungsten is not negligible at 6.8°. Otherwise, the geometry of the ring is normal. The hydroxide ion attacks this complex at phosphorus and


(60)

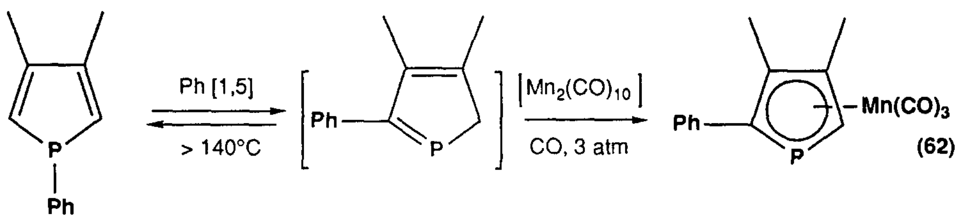
induces a breaking of the W–P bond (eqn. 60). The reaction with [W(CO)$_5$(THF)] gives a η^1-P–W(CO)$_5$ complex which shows a normal ^1J(^{31}P–^{183}W) coupling of 274 Hz.

Numerous investigations have been devoted to the (η^5-phospholyl)manganesetricarbonyls, the so-called phosphacymantrenes. By far the simplest technique for their preparation involves the thermal cleavage of the phosphorus–phenyl bond of



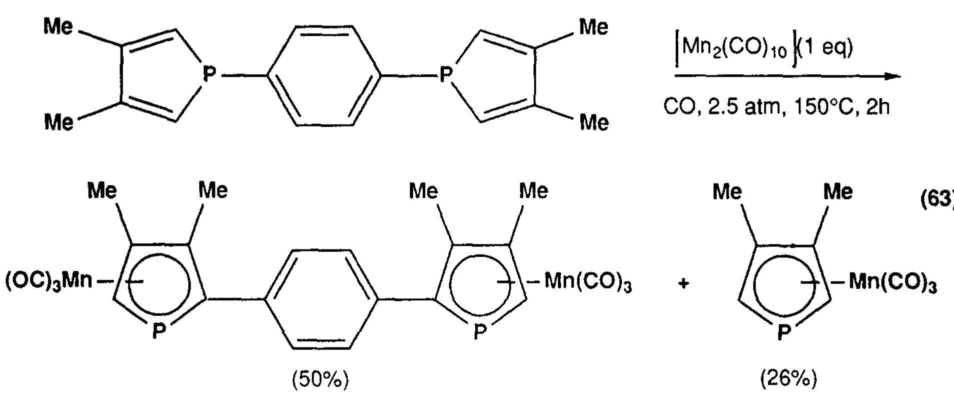
(61)

1-phenylphospholes by $[Mn_2(CO)_{10}]$ (eqn. 61) [3,90]. The yields can be as high as 80% and the method is quite general. For example, it has been successfully applied to 2,2′-biphospholes, which give the corresponding bis-complex [91]. By working under a modest CO pressure, it is possible to take advantage of the phenyl [1,5] shifts around the phosphole nucleus that occur above approx. 140°C. In these cases,



(62)

the manganese carbonyl traps the 2*H*-phosphole with H-abstraction (eqn. 62) [91]. A good illustration of the competition between P–aryl bond cleavage and aryl [1,5]



(63)

shifts is given in eqn. (63) [92]. Finally, it is possible to replace the cleavage of the P–aryl bond by the cleavage of the P–P bond of a 1,1′-biphospholyl [20,93].

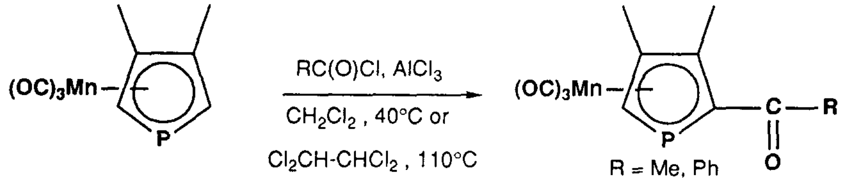
The ^{31}P NMR resonances of these phosphacymantrenes occur at high fields, e.g. δ (3,4-Me_2) = −46.6 ($CDCl_3$). The ^1J(C–P) couplings are huge, at approx. 65 Hz [90]. The CO stretching frequencies are higher than those of the corresponding cymantrenes, e.g. $[Mn(C_4H_4P)(CO)_3]$, υ(CO) 2032, 1958, 1954 cm^{-1}; $(C_5H_5)Mn(CO)_3$, υ(CO) 2025, 1938 cm^{-1}, suggesting a lower donor ability for C_4H_4P than C_5H_5 [90]. This result has been confirmed by a complete IR–Raman study of phosphacymantrene [94]. The Mn–phospholyl bond appears to be weaker than the corresponding Mn–Cp bond of cymantrene, force constants 2.6 and 3.2 mdyne Å^{-1}, respectively.

From a structural standpoint, X-ray crystal structure analysis of a 2-benzoyl derivative has demonstrated a remarkable structural analogy between cymantrene and phosphacymantrene [90]. The Mn–C ring bonds have the same lengths: Cp, 2.165(25) Å; PCp, 2.169(4) Å. The metal is slightly closer to the ring in the phosphacymantrene case because phosphorus expands the size of the ring: Cp, 1.80 Å; PCp, 1.757(1) Å. The Mn–P bond is rather long at 2.387(2) Å. As usual, the geometry of the ring is close to that found in a free phospholide ion.

A coupled UV–photoelectron spectroscopy and EHT study of phosphacymantrenes has given an interesting insight into the reactivity of these species [43]. The LUMO of phosphacymantrene has an important localization at phosphorus whereas it is mainly localized at manganese in cymantrene; hence, nucleophiles are expected to react at phosphorus. The σ lone pair at phosphorus corresponds to the fourth occupied level at 2.3 eV below the HOMOs; hence, a low reactivity of phosphorus toward electrophiles is expected. These results fit the experimental data.

Before closing this section, it is necessary to mention two proton NMR studies of phosphacymantrenes oriented in nematic solvents [95] and two investigations of the phase transitions that occur in solid phosphacymantrenes. An order–disorder transition takes place in phosphacymantrene and its 3,4-dimethyl derivative at 110 and 275 K, respectively, as revealed by calorimetry, Raman diffusion and X-ray diffraction [96].

The most striking chemical characteristic of phosphacymantrenes is the extraordinary resistance of phosphorus against electrophilic attack. 3,4-Dimethylphosphacymantrene is not protonated by pure trifluoroacetic acid, not oxidized by iodine in boiling CCl_4 and not quaternized by benzyl bromide in boiling toluene [90]. This inertness of the phosphorus lone pair combined with the electronic delocalization within the ring has a practical consequence: it becomes possible to carry

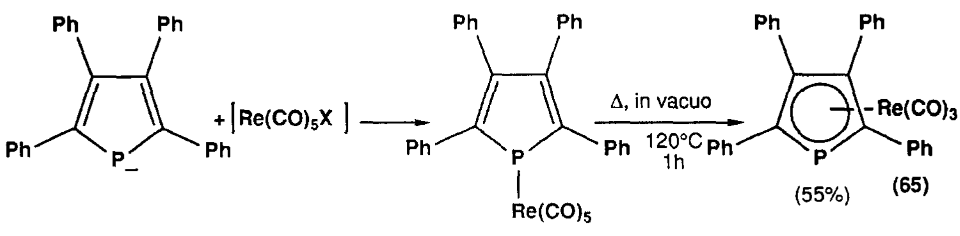


(64)

out Friedel–Crafts acylations at the α-carbons (eqn. 64) [3,90]. However, benzoylation takes place only at 110°C and neither formylation (Vilsmeier) nor carboxylation have been possible. Thus, the susceptibility of phosphacymantrenes towards electrophilic substitution remains limited. Nevertheless, when these acylations were described in 1976, they were the first successful electrophilic substitutions performed in phosphorus heterocyclic chemistry. Several chemical transformations were carried out on these acyl derivatives without destruction of the phosphacymantrene skeleton, i.e. CO–>CH_2 and CO–>CHOH [97].

In parallel with its high resistance toward electrophiles, the phosphorus of phosphacymantrenes displays a high sensitivity toward nucleophiles. Even the cyanide ion is able to destroy the P–Mn bond. Butyllithium leads to 1-butylphospholes [90]. Ligand substitution at manganese is difficult but possible. Carbonyl monosubstitution has been observed with phosphines [98,99]; phosphites are able to give disubstituted products [98]. The reactions are typically carried out in cyclohexane at 80°C under UV irradiation. In spite of its low electron-donor ability, the phosphorus of phosphacymantrenes is able to coordinate to another transition metal. As ligands, phosphacymantrenes behave as rather strong π-acceptors. η^1,η^5-Complexes have been described with [$Fe(CO)_4$] [97] and [$W(CO)_5$] [100]. In this last case, one η^1,η^5-complex has been characterized by X-ray crystal structure analysis. As expected, the overall structure of the phosphacymantrene unit is only weakly perturbed by complexation and the tungsten atom lies in the plane of the ring: d (P–W)=2.451(3) Å [100]. A strong downfield shift of the ^{31}P resonance is observed upon η^1-complexation, e.g. $\Delta\delta = +99$ ppm for the [$Fe(CO)_4$] complex [97].

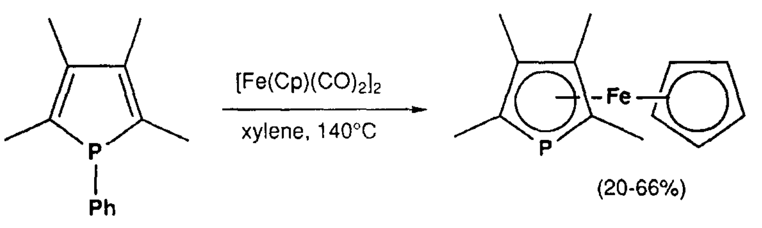
In contrast with the wealth of information on phosphacymantrenes, only one



(65)

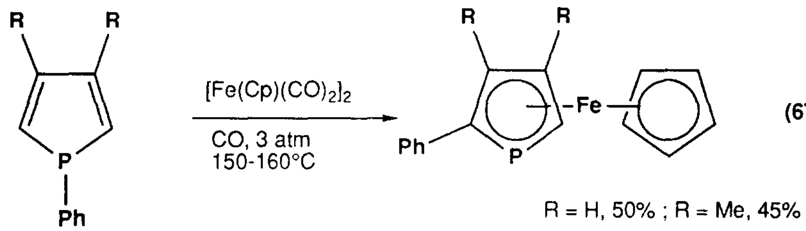
η^5-phospholyl complex of rhenium has been described up to now (eqn. 65) [93]. Similar routes have yielded the η^5-tetraphenylphospholyl [$Mn(CO)_3$] and [FeCp] complexes.

η^5-Phospholyl–iron complexes, more precisely phosphaferrocenes and 1,1′-diphosphaferrocenes, are by far the most studied of all η^5-phospholyl complexes. The first reported synthesis of phosphaferrocenes is a mere transposition of the



(66)

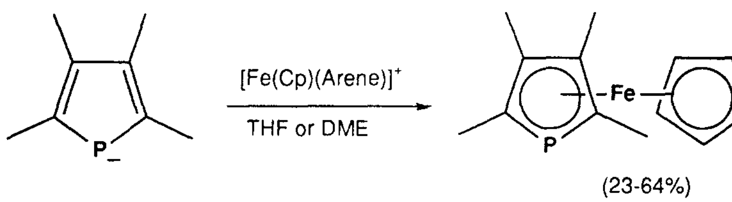
previously described synthesis of phosphacymantrenes (eqn. 66) [101,102]. As in the previous case, there is a competition between the P–Ph bond cleavage and the Ph [1,5] shift around the phosphole ring. The method described in eqn. (66) works better when α-substituents block the shift (see the case of 1,2,5-triphenylphosphole [102]). When the α-positions are free, the yield of phosphaferrocene becomes rather low. As previously, a modest CO pressure suffices to change the course of the



(67)

reaction, as shown in eqn. (67) [74b]. It is also possible to replace the cleavage of the P–Ph bond by the cleavage of the P–P bond of a 1,1′-biphospholyl. Such a technique has been used to prepare a 2,2′-biphosphaferrocene as a mixture of two diastereomers [21].

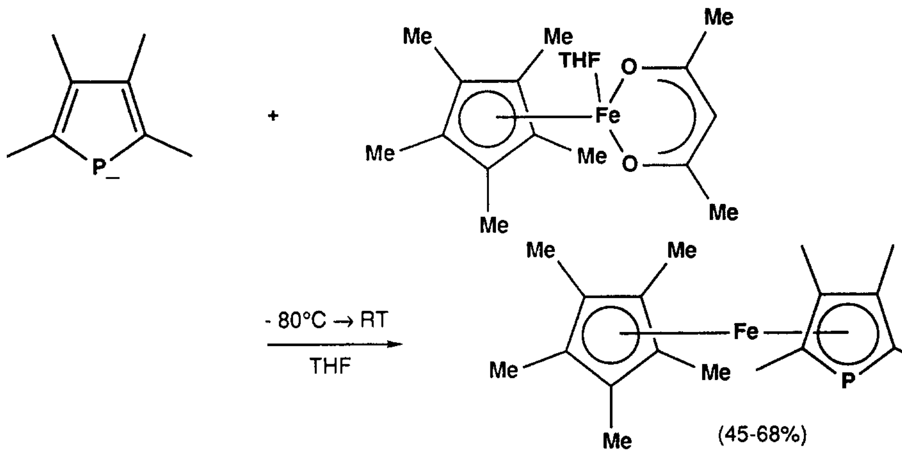
Two ionic routes to phosphaferrocenes have been described. The first involves the reaction of a phospholide ion with a (η^5-cyclopentadienyl)(η^6-arene)iron cation



(68)

(eqn. 68) [103]. Mesitylene and toluene appear to be the best arenes for this displacement reaction. This method can be adapted for the production of phosphaferrocenes with functional groups on the cyclopentadienyl ring [104]. The second route involves the reaction of a phospholide ion with a (η^5-pentamethylcyclopentadienyl)-iron acetylacetonate (eqn. 69) [105]. Finally, in one instance, the phospholyl ring has been constructed within the coordination sphere of iron (eqn. 70) [106].

In contrast to the numerous syntheses of phosphaferrocenes, there is only one basic scheme for the preparation of 1,1′-diphosphaferrocenes. It involves the reaction of phospholide ions with iron(II) chloride. The yield is generally low if no precautions are taken [15] to eliminate two fundamental problems. The first involves redox chemistry which can produce iron(0). The second is the presence of phenyllithium as a frequent by-product of the synthesis of phospholide ions from 1-phenylphospholes (eqn. 1). These problems are generally solved by replacing the ionic phospholides by more covalent metallic derivatives. As an illustration, we give some data concerning the synthesis of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (eqns. 71–73). The use of the tributyltin derivatives has also been proposed [109]. The syntheses of two bis(2,2′-diphosphafulvalene)diiron complexes using the same procedure are noteworthy [21,91].



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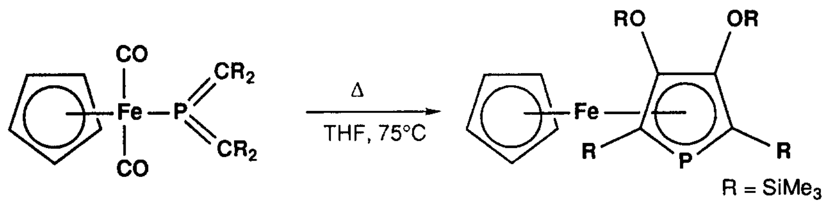

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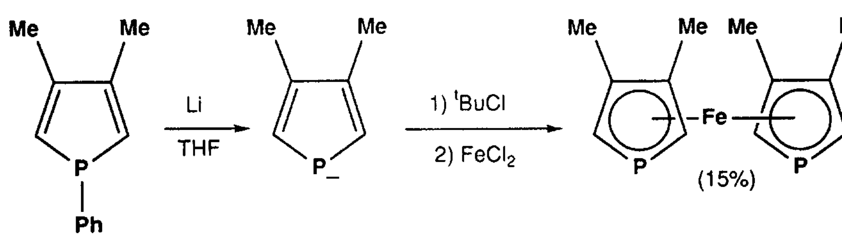

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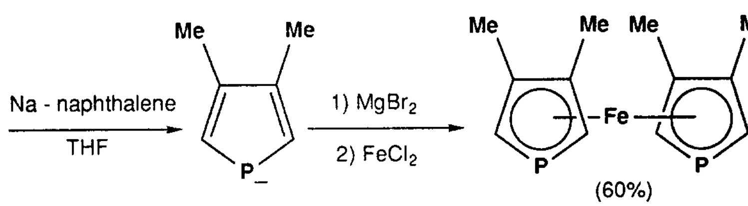

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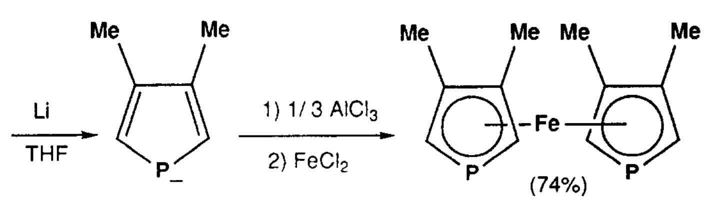
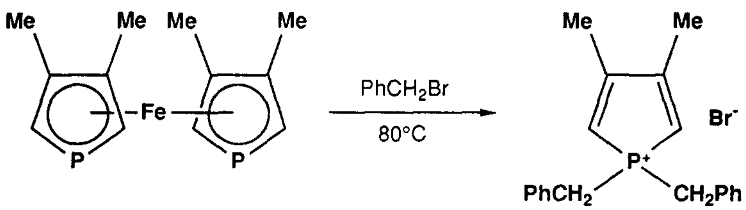
[107]



(73)
[108]

The ^1H, ^{13}C and ^{31}P NMR data for phosphaferrocenes show the same trends as those for phosphacymantrenes. The ^{31}P resonances are at high fields, e.g. −67.5 and −59 ppm for the parent mono- and diphosphaferrocenes (see ref. 10 for a collection of data). Both the mono- and the bis-(3,4-dimethylphospholyl) derivatives have been characterized by X-ray crystal structure analysis [107,110]. The overall structures are very similar to those of ferrocene. In the diphosphaferrocene, the greater radius of phosphorus than carbon means that the phospholyl rings are not parallel; the angle made by their mean planes lies between 2.57° and 4.39°. The angle between the planes which bisect each phospholyl ring is approx. 140°. EHT calculations have shown that this conformation is under the control of the d_{xz} and d_{yz} orbitals of the metal [45]. The rotation barrier is calculated to be 8.65 kcal mol^{-1} [45]. Two other theoretical studies on phospha- and diphosphaferrocene [44,111] have shown that the three highest occupied levels are practically pure d orbitals of iron. The next occupied level (σ_P) corresponds to the lone pair at phosphorus. The LUMO also has a strong localization at phosphorus. Among the other physical studies of phosphaferrocenes, we must mention the derivation of an experimental electronic density map for 3,4-dimethylphosphaferrocene by the X--X technique [112], a Mössbauer study of several mono- and diphosphaferrocenes [102] and a calorimetric study of the phase transitions in solid phosphaferrocene [113].

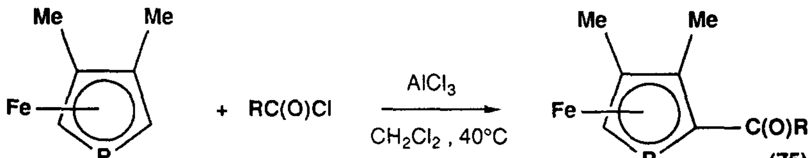
From a chemical standpoint, phosphorus displays a higher nucleophilicity in phosphaferrocenes than in phosphacymantrenes. For example, 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene reacts with pure benzyl bromide at 80°C (eqn. 74) [114].



(74)

The reactivity of the metal is also higher in phosphaferrocenes than in phosphacymantrenes. Both mono- and diphosphaferrocenes are protonated at iron by trifluoromethanesulfonic acid [109,115]. The protonation is accompanied by a strong upfield shift of the ^{31}P resonance (maximum −185 ppm). The hydride resonance in the product appears in the range −0.8 to −3 ppm with ^2J(H–P) couplings of between 48 and 71 Hz [115].

A complete set of electrophilic substitution reactions has been described with phosphaferrocenes. This series of reactions still stands today as the most extensive example of aromatic chemistry in the field of carbon–phosphorus heterocycles. Acylations, formylations and carboxylations have been described as shown in eqns. (75)–(77) [101,107,114]. Several additional studies on the acylation of monophosphaferrocenes include an improved procedure using catalytic amounts of CF_3SO_3H



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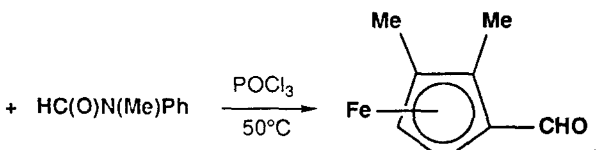

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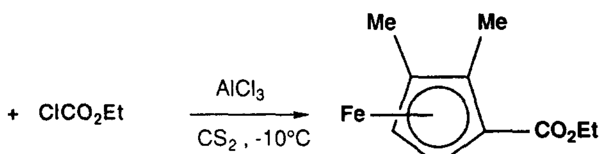
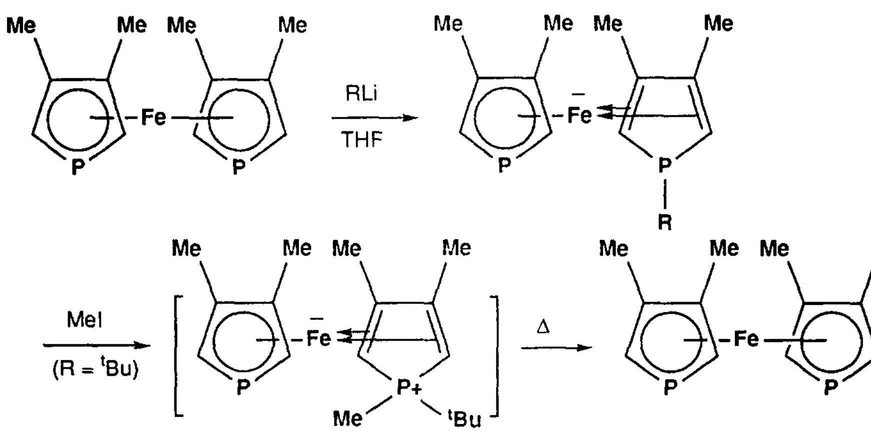


(77)

in lieu of $AlCl_3$ [116], an investigation of the directing effects of alkyl substitution [117], and the observation of competitive acylations at the phospholyl and phenyl rings in phenyl-substituted phosphaferrocenes [117]. Additional studies on functional diphosphaferrocenes include descriptions of 2,2′-diacylation [107] and several transformations on the functional groups [107,114]. It has also been shown that protonation takes place at the carbonyl oxygen in both acyl- monophospha- and diphosphaferrocenes [118,119].

Nucleophiles such as alkyl- or aryl-lithiums selectively attack phosphaferrocenes at phosphorus with cleavage of the phosphorus–metal bonds. The observed results are summarized in eqns. (78)–(81) [120,121]. Most of the species thus



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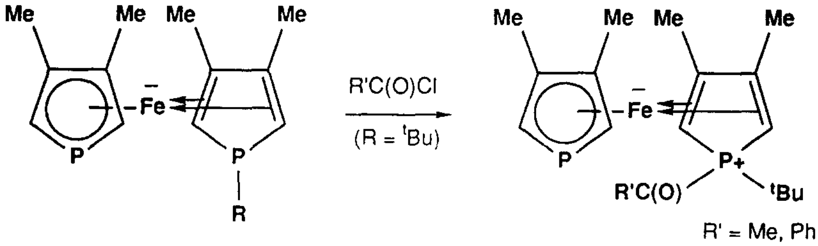

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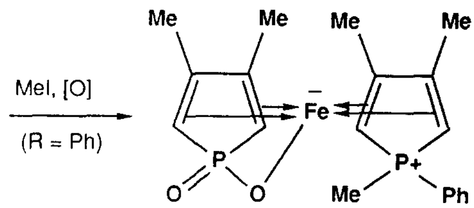

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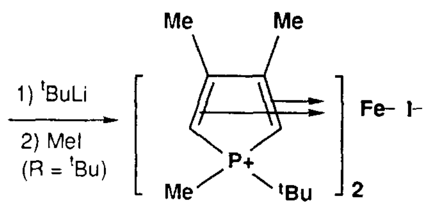
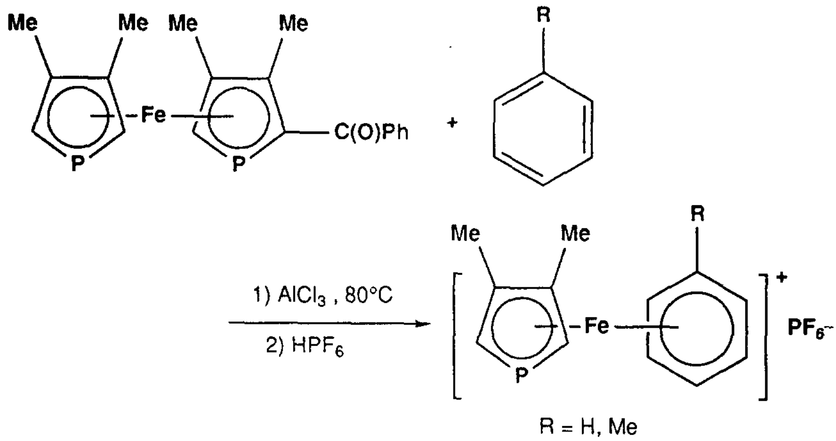


(81)

obtained have been characterized by X-ray crystal structure analysis. The 17 electron bis(diene)Fe^- anion is particularly noteworthy; its stability and solubility in water result from the presence of the two bulky phosphonium groups.

Several reactions of ferrocene have been transposed with phosphaferrocenes. Electrochemical studies [105,122,123] have shown that it is possible to oxidize mono- and diphosphaferrocenes to the corresponding phosphaferricinium salts. The oxidation can also be performed by tetracyanoethylene [124]. Broadly speaking, the oxidation of phosphaferrocenes is more difficult than the oxidation of ferrocene and the stability of phosphaferricinium salts is low. It has also been shown [125] that it is possible to perform a phospholyl- to-arene exchange in the presence of $AlCl_3$ (eqn. 82). In the same vein, the stabilizing effect of the phosphaferrocene moiety on α-carbocations has been investigated [126]. These phosphaferrocenyl carbocations are considerably less stable than the analogous ferrocenyl species.

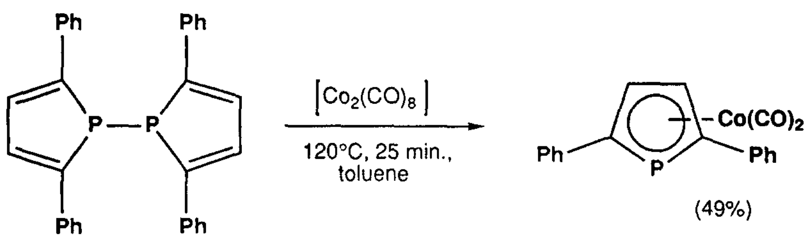
A last aspect of the chemistry of phosphaferrocenes must be discussed. It concerns the use of phosphaferrocenes as phosphorus ligands. Such complexes have been described with Fe(0) [114,127,128], Cr(0), Mo(0), W(0), Mn(I) and Ru(II) [129]. Upon complexation, a strong downfield shift of the ^{31}P resonance is observed, but the geometry of the sandwich does not change. As a general rule, the P–M bond is shorter than usual for similar [$M(PR_3)$] complexes. From an electronic standpoint, phosphaferrocenes can be considered as good π-acceptors, and have properties closer



(82)

to phosphites than to phosphines in that respect [128]. It should be noted here that Cu(I) and Ag(I) give complexes at iron [130]. In contrast to P-complexation, this coordination at the metal induces a strong upfield shift of the ^{31}P resonance. Also noteworthy is an electrochemical study which shows no cooperative effects between the sandwiched iron atom and the metal complexing the phosphorus lone pair [131]. Before leaving phosphaferrocenes, it must be added that a diphosphaferrocene has been used as a smoke-suppressant in polyvinyl chloride [132].

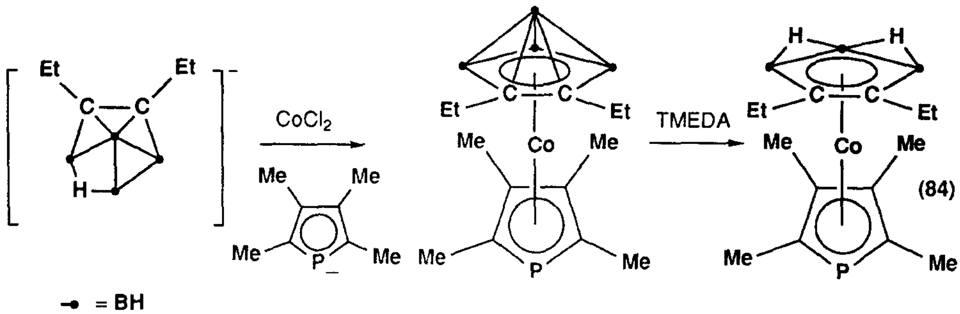
To the right of iron in the Periodic Table, only cobalt has been incorporated into η^5-phospholyl complexes. The first (η^5-phospholyl)dicarbonylcobalt complex was described as early as 1982 (eqn. 83) [60] and, much later, several triple-deckers containing (η^5-phospholyl)cobalt subunits were reported (eqns. 84–88) [133]. An (η^5-phospholyl) (η^5-pyrrolyl) complex has been characterized by X-ray crystal structure analysis.



(83)

5.4. *The chemistry of η^5-polyphospholyl complexes*

Two 1,2-diphosphaferrocenes have been described recently [6,7,134]. Their synthesis is depicted in eqns. (89) and (90). These η^5-complexes have been characterized by NMR and X-ray crystal structure analyses. They display ^{31}P resonances at high fields, and strong P–P couplings (i.e. in the second case: AB system, $\delta_A =$



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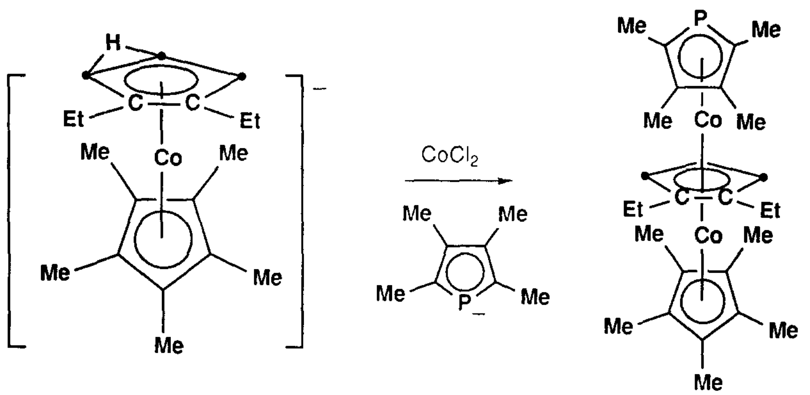

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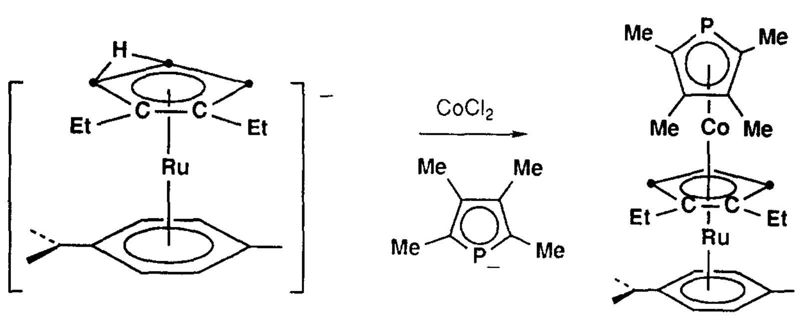
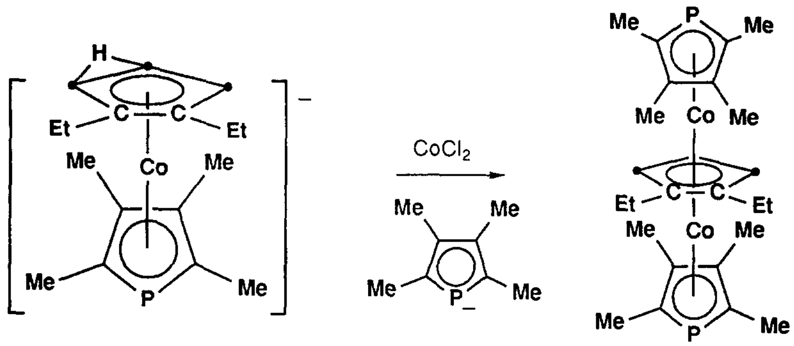


(86)

-66.2, $\delta_B = -67.2$, $^1J(P\text{–}P) = 379$ Hz). This type of synthesis is reminiscent of the preparation of monophosphaferrocene depicted in eqn. (70).

In addition to the η^5-1,3-diphospholyl complex already described in eqn. (45), several 1,3-diphospha- and 1,1′,3,3′-tetraphosphaferrocenes have been reported in the literature (eqns. 91,92) [29–31]. Some of these phosphaferrocenes have been characterized by X-ray crystal structure analysis. The ^{31}P resonances of the diphosphaferrocenes are in the range -2 to $+6$ ppm with a $^2J(P\text{–}P)$ coupling of about 30 Hz. Similar values are reported for the tetraphosphaferrocenes. Perhaps the most spectacular compound in this family is a [3]-tetraphosphaferrocenophane with a



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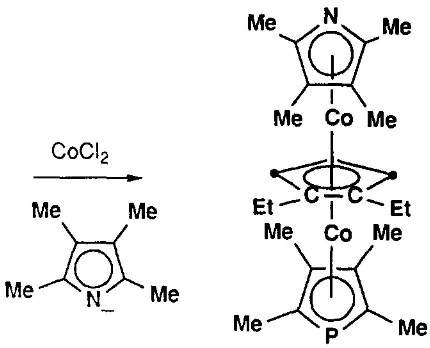

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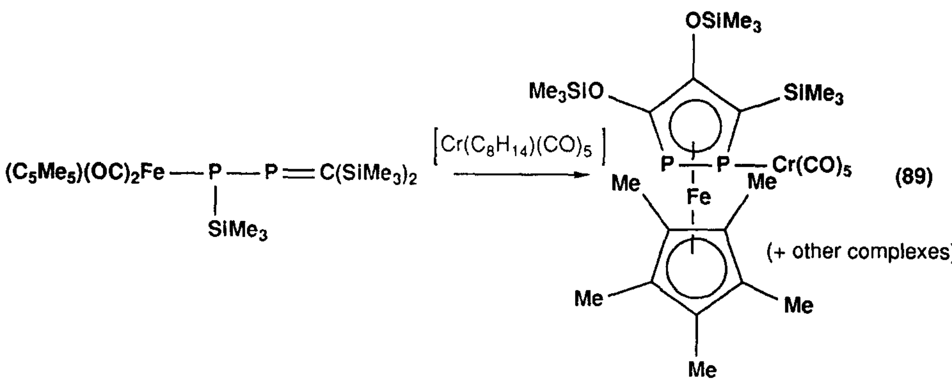
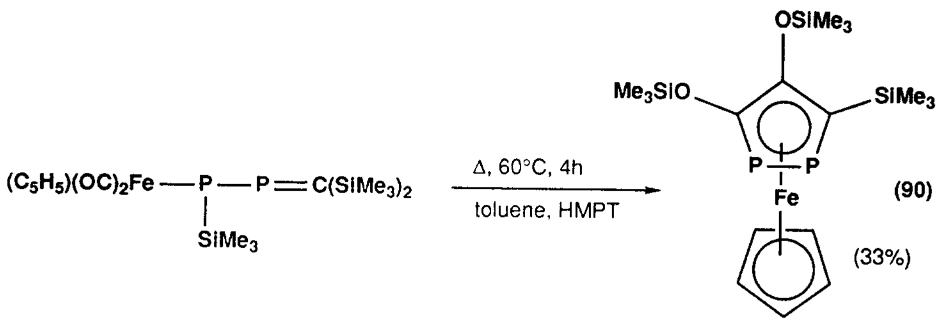


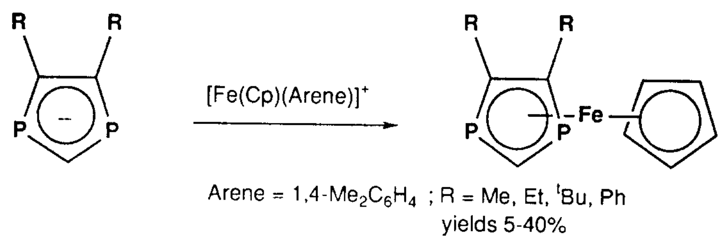
(89)

trimethylene bridge linking the two rings. As a result of this bridge, the angle between the two ring planes is 11° [30].

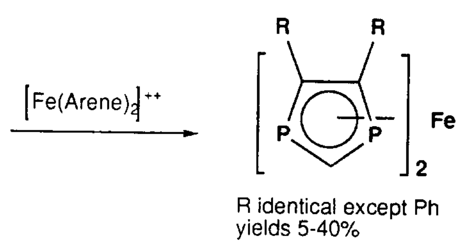
The first η^5-1,3-diphospholyl complexes ever reported were a series of pentaphosphaferrocenes obtained by the group of Nixon upon reaction of a mixture of 1,3-diphospholide and 1,3,4-triphospholide ions (see eqn. 6) with iron(II) chloride (eqn. 93) [24,28]. These pentaphosphaferrocenes are always mixed with the corresponding 1,1′,3,3′,4,4′-hexaphosphaferrocenes. It is interesting to note that, at least when $R = {}^tBu$, transition metals selectively coordinate to one of the P–P bonded


OSiMe3
Me3SiO
SiMe3
(C5H5)(OC)2Fe — P — P = C(SiMe3)2
SiMe3
Δ, 60°C, 4h
toluene, HMPT
P P
Fe
(33%)

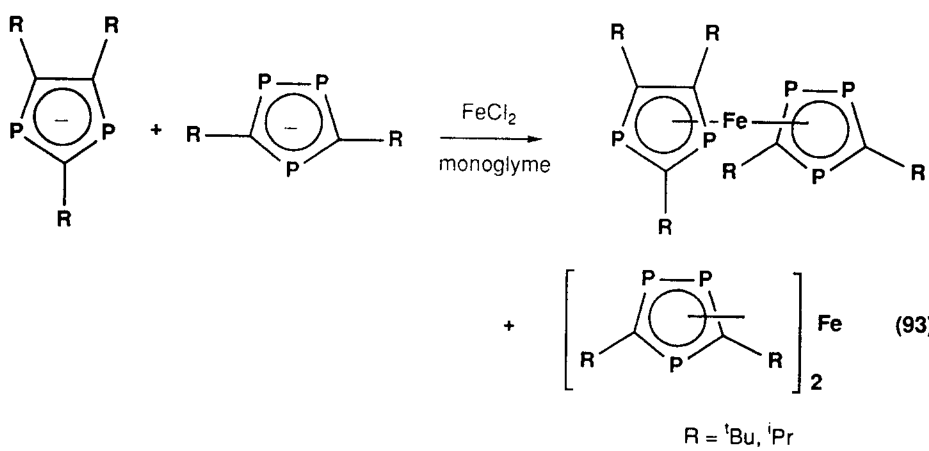
(90)


R R
P P
[Fe(Cp)(Arene)]+
Fe
Arene = 1,4-Me2C6H4 ; R = Me, Et, tBu, Ph
yields 5-40%

(91)

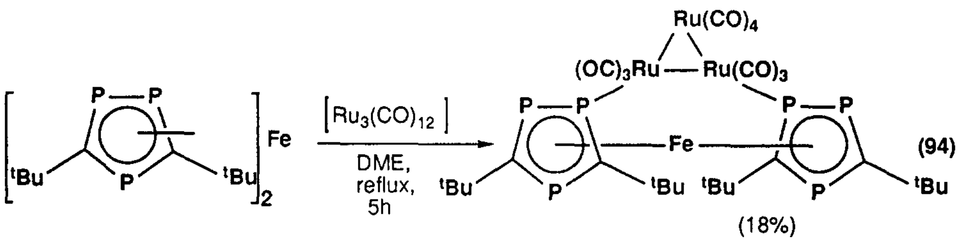

[Fe(Arene)2]++
R R
P P
Fe
2
R identical except Ph
yields 5-40%

(92)


R R
P P
R
+
P P
R R
P
FeCl2
monoglyme
Fe
+
Fe
2
R = tBu, iPr

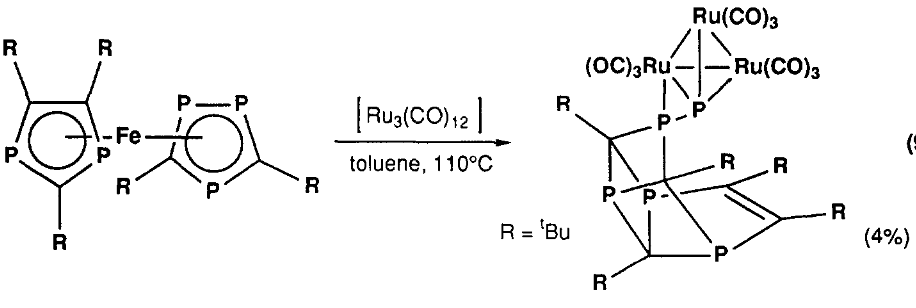
(93)

phosphorus of the 1,3,4-triphospholyl unit in these pentaphosphaferrocenes. With hexaphosphaferrocenes, a transition metal bridge can be created between the two



(94)

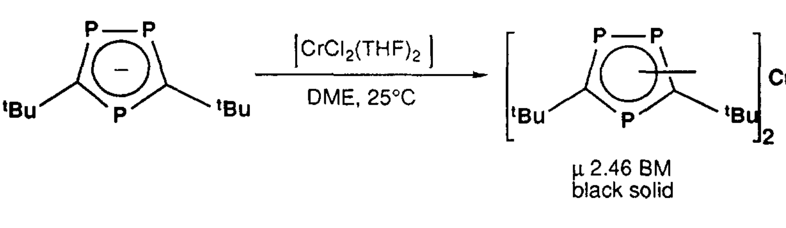
triphospholyl rings (eqn. 94) [135]. The same reaction leads to entirely different



(95)

results with pentaphosphaferrocenes (eqn. 95) [136]. The resulting phosphino-phosphinidene ruthenium cluster has been characterized by X-ray crystal structure analysis.

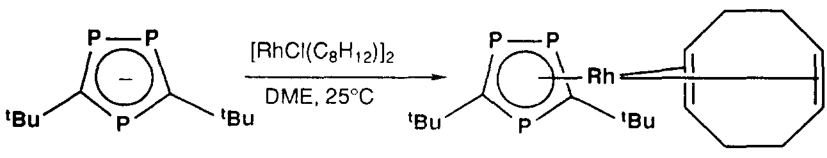
The study of η^5-triphospholyl complexes has encompassed not only nickel (eqn. 43), molybdenum, tungsten (eqn. 48) and iron (eqn. 93), but also chromium, rhodium and iridium derivatives. For example, a paramagnetic hexaphosphachromocene has been prepared and characterized by X-ray crystal structure analysis (eqn. 96)



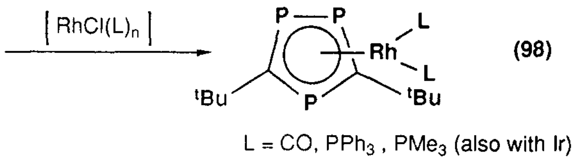
(96)

[137]. The compound is isomorphous with the corresponding iron sandwich but the metal-ring distances are significantly longer for the chromium complex. η^5-Rhodium and iridium complexes have also been prepared according to eqns. (97) and (98) [138]. No (^{31}P-^{103}Rh) couplings are observed between the phosphorus atoms of the ring and the rhodium atom. The ^{31}P spectra of the RhL_2 complexes also demonstrate that the [RhL_2] moiety lies in the plane of symmetry of the C_2P_3 ring.

Finally, a 1,3,4-triphosphaferrocene has been prepared in low yield and com-

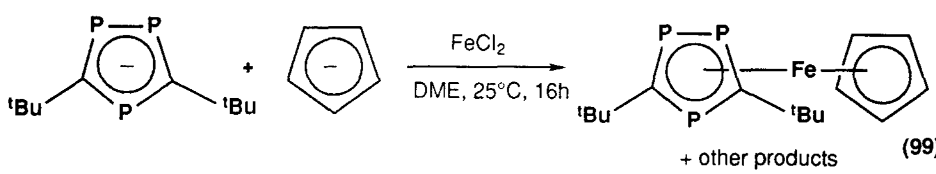


(97)



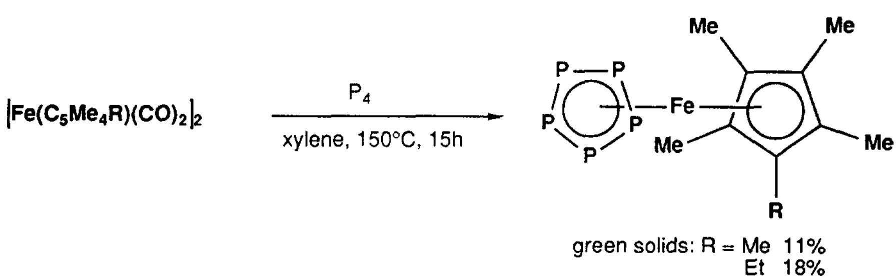
(98)

plexed at one of the P–P bonded phosphorus by [$W(CO)_5$] (eqn. 99) [139]. This study has been completed by a systematic investigation of the coordination chemistry of 2,5-bis-*tert*-butyl-1′,2′,3′,4′,5′-pentamethyl-1,3,4-triphosphaferrocene with Ni(0), Cr(0), W(0), Fe(0) [156] and Ru(0) [157]. Coordination takes place at the two adjacent phosphorus atoms and fluxionality is observed on the mono-complexes. As usual, the coordination at phosphorus does not alter the geometry of the phosphaferrocene.



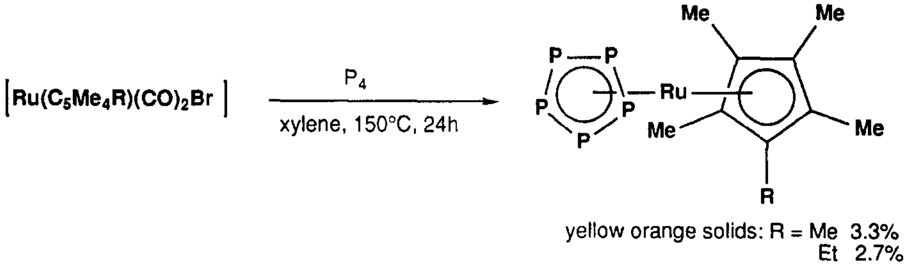
(99)

1,2,3,4,5-Pentaphosphaferrocenes and ruthenocenes have been prepared by a variety of methods. The first method, as described by Scherer in 1987, involves white

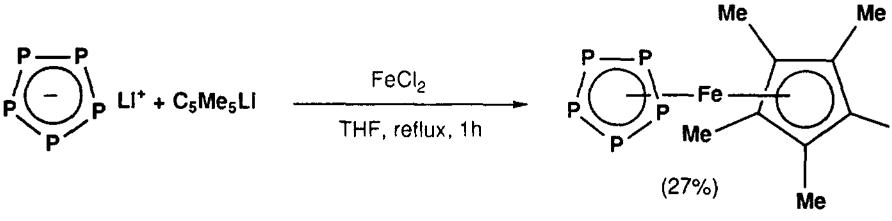


(100)

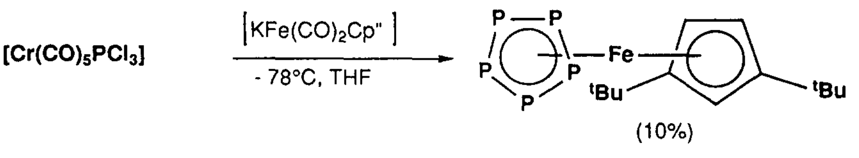
phosphorus as the source of the P_5 unit (eqns. 100 and 101) [4,140]. Subsequently, Baudler et al. [40] showed that it is possible to start from a preformed pentaphospholide ion (eqn. 102). Very recently, a third approach has been reported [141] involving a PCl_3 complex as the building block for the η^5-P_5 unit (eqn. 103). The pentaphosphaferrocenes and ruthenocenes shown in eqns. (100) and (101) display ^{31}P resonances at +153 and +84 ppm, respectively. X-ray crystal structure analysis of the iron and



(101)



(102)

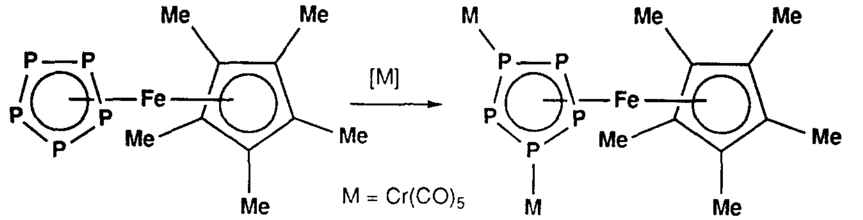


(103)

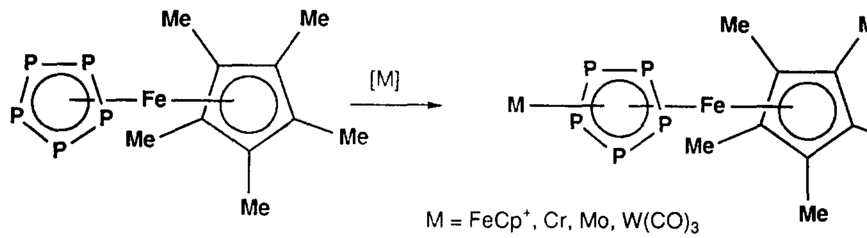
ruthenium derivatives with R = Et shows a staggered conformation in both cases, with P–P bond lengths in the range 2.08–2.12 Å. The M-P_5 ring distances are 1.526 and 1.652 Å for iron and ruthenium, respectively. The M-Cp′ distances are 1.707 and 1.850 Å. An electron-diffraction study of $(P_5)Fe(C_5Me_5)$ at 200°C in the gas phase produced similar results: P–P = 2.117(4) Å, Fe–P = 2.377(5) Å and Fe–C = 2.135(11) Å [142].

In her preliminary work on the chemistry of LiP_5, Baudler [40] mentioned its interaction with $FeCl_2$. This reaction yielded a black insoluble decaphosphaferrocene "FeP_{10}" which was not further characterized. This compound was studied from a theoretical standpoint at the extended Hückel level [143]. The conclusion was that the most stable isomer would be $(\eta^1\text{-}P_5)_2Fe$ with two Fe–P σ-bonds. Preliminary calculations at the same level have also been carried out on [Fe (Cp)(η^5-P_5)] [143,144]. This compound has also been studied by mass spectrometry using laser desorption ionization [145].

From a chemical standpoint, [Fe(η^5-C_5Me_5)(η^5-P_5)] has been shown to be able to coordinate to as many as four other transition metal moieties using the phosphorus lone pairs of the P_5 ring [146]. An example is shown in eqn. (104). Another aspect of the chemistry of pentaphosphaferrocenes and ruthenocenes concerns their use as building blocks for the synthesis of triple-decker sandwiches with P_5 middle decks



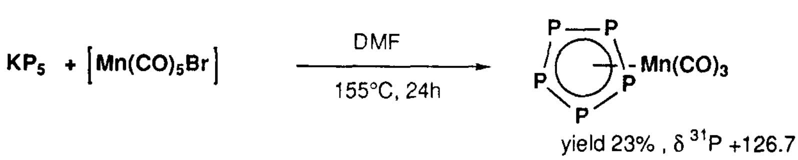
(104)



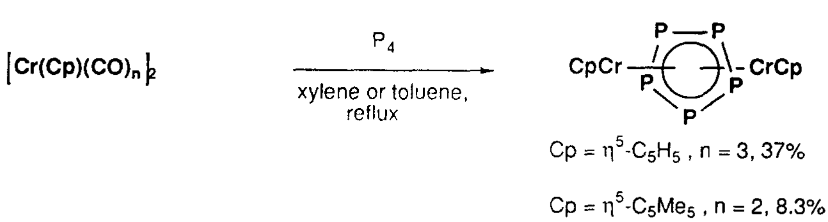
(105)

(eqn. 105) [146,147]. The additional η^5-coordination of the P_5 ring leads to a substantial shielding of the ^{31}P resonance, e.g. for $[CpFe(P_5)FeCp^*]^+$, δ $^{31}P = -15.8$ ppm [146]. Most of these triple-decker complexes have been characterized by X-ray crystal structure analysis. A series of (η^5-pentaphospholyl)tricarbonylmetal complexes of C_{3v} symmetry has been prepared by Baudler and Etzbach [148] directly from the pentaphospholide ion (eqns. 106 and 107).

$$KP_5 + [M(CO)_3(RCN)_3] \xrightarrow[155^\circ C]{DMF} [M(\eta^5\text{-}P_5)(CO)_3]^- \qquad M = Cr, Mo, W \tag{106}$$



(107)



(108)

Finally, dichromium triple-deckers have been directly prepared from white phosphorus (eqn. 108) [149,150]. Mechanistic studies [150] seem to indicate that the P_5 ring is formed by direct bimolecular interaction between initial (μ,η^2-P_2) and

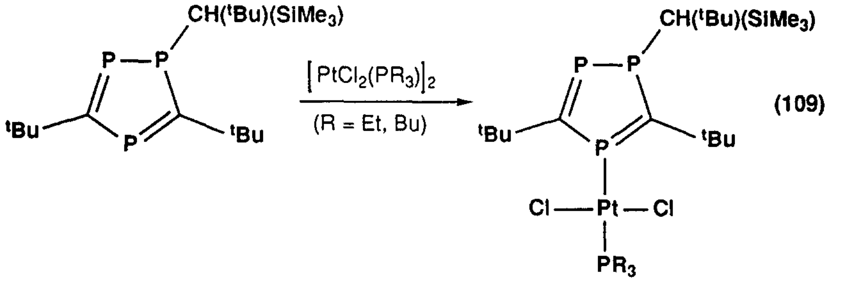
(η^3-P_3) complexes. The Cp complex gives rise to a sharp ^{31}P resonance at −100.5 ppm. Both Cp and Cp* complexes have been characterized by X-ray crystal structure analysis and display relatively short Cr–Cr distances of 2.738(1) and 2.727(5) Å, respectively. In both cases, all the P–P distances are equal. Some discrepancy exists between the two publications concerning the possible paramagnetism of these complexes. Several theoretical studies have attempted to rationalize the stability of these 27 valence-electron triple-deckers, because they do not obey the Wade–Mingos skeletal electron counting rules [151,152].

As a brief conclusion to this review, it is clear that the potential of the various phospholide ions in coordination chemistry is absolutely enormous. Its full development is limited mainly by the lack of satisfactory methods for the preparation of the ions. This is especially true for functional monophospholides and for polyphospholides. We hope that this review will catalyze further development of this exciting field.

6. ADDENDUM

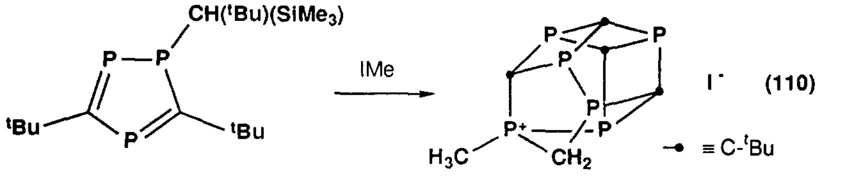
A more precise X-ray crystal structure analysis of the lithium salt of the (2,5-^{t}Bu$_2$- C_2P_3) anion has been performed by the group of Nixon [155]. At 2.078(6) Å, the P–P bond appears to be even shorter than previously reported by Becker [25]. The P$\overset{...}{-}$C bonds are found in the range 1.690(11)–1.752(13) Å.

The 1,2,4-triphosphole mentioned in eqn. (26b) gives a platinum complex at



(109)

the isolated phosphorus center [158] (eqn. 109). The complex with R=Et has been

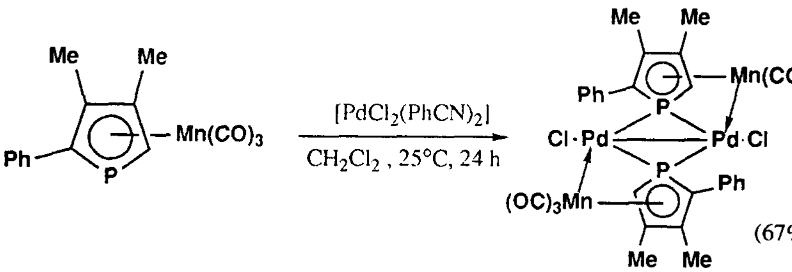


(110)

characterized by X-ray crystal structure analysis. The lengths of the intracyclic bonds are: P–P 2.086 Å, P=C 1.720(8) and 1.715(8) Å, P–C 1.719(8) and 1.740(8) Å. These data clearly indicate that the P=C double bonds are not precisely localized as shown in eqn. (109).

The same 1,2,4-triphosphole has been shown to react with methyl iodide to give a cage compound [155] (eqn. 110). The structure of the cage has been established by X-ray analysis. The postulated mechanism involves the transient formation of a dimethylphospholium salt at the sp^3 phosphorus center.

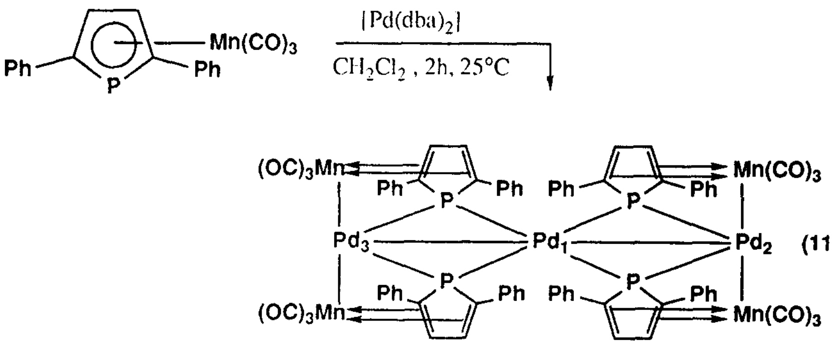
The coordination chemistry of phosphacymantrenes has been investigated further. The reaction with palladium(II) chloride gives a new type of complex where



(111)

both phosphorus and manganese act as two-electron donors [159] (eqn. 111). At 2.3712(9) Å, the P–Mn separation is shorter in the final complex than in the starting phosphacymantrene.

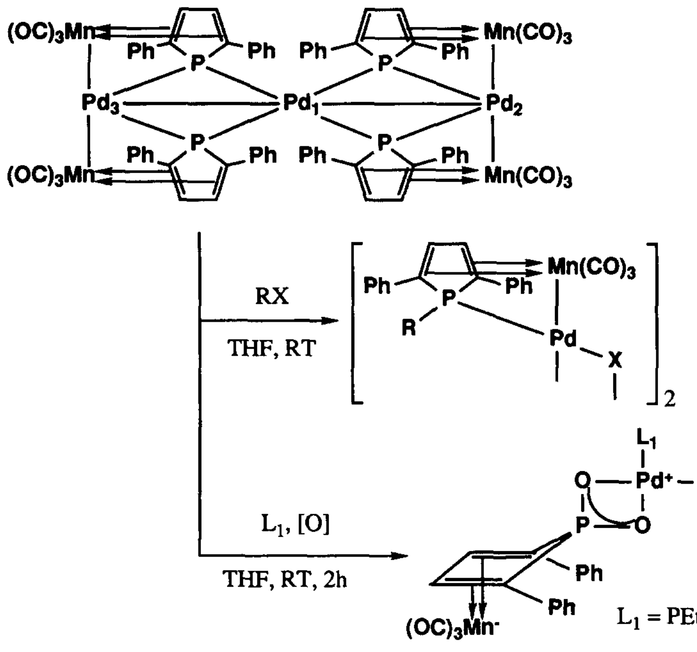
The reaction with palladium(0) follows a different course. An insertion into



(112)

the P–Mn bond is observed [159] (eqn. 112). As expected, the P....Mn separation is larger at 2.470(2)–2.489(1) Å. In this complex, the phosphacymantrene acts as a (3+1)-electron donor. The phosphido phosphorus is highly nucleophilic and can be arylated, alkylated and oxidized (eqns. 113 and 114). Obviously, this series of results significantly extends the potential use of η^5-phospholyl complexes in coordination chemistry. Octamethyl-1,1′-diphosphaferrocene [Fe(η^5-tmp)$_2$] has been shown to react with silver(I) to give (Ag[Fe(η^5-tmp$_2$]$_2$)$^+$ [160]. In this complex, both diphosphaferrocenes chelate AG$^+$ between their two phosphorus atoms.

Finally, several fluxional η^1-ligated 1,2,4-triphospholyl palladium(II) and



(113)

R = Me, Ph, PhCH$_2$

(114)

L$_1$ = PEt$_3$, PBu$_3$, PPh$_3$

platinum(II) complexes have been studied by ^{31}P and ^{195}Pt NMR, including variable temperature measurements [161].

ACKNOWLEDGEMENTS

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