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Transition-metal-functionalized homo- and heterocycles with phosphorus atoms[1]

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Contents

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[1] Dedicated to Professor Günter Schmid on the occasion of his 60th birthday.

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Abstract

Homo- and heterocycles containing transition-metal-functionalized phosphorus atoms are at the interface between organometallic and main group chemistry. In contrast to the familiar phosphane–metal complexes, where the organophosphane acts as good donor ligand with moderate acceptor properties, in metal-functionalized phosphanes the complex metal fragment transfers electron density onto the phosphane fragment enhancing its basicity. The compounds under discussion merit special interest, as they not only possess the features of either component but also exert unique properties. They are available by a number of synthetic approaches. Most prominent routes make use of the nucleophilic displacement of halide by carbonyl metalates and of cyclocondensation and cycloaddition processes. © 1997 Elsevier Science S.A.

Keywords: Heterocycle; Homocycle; Cycloaddition; Cyclocondensation; Phosphorus compounds

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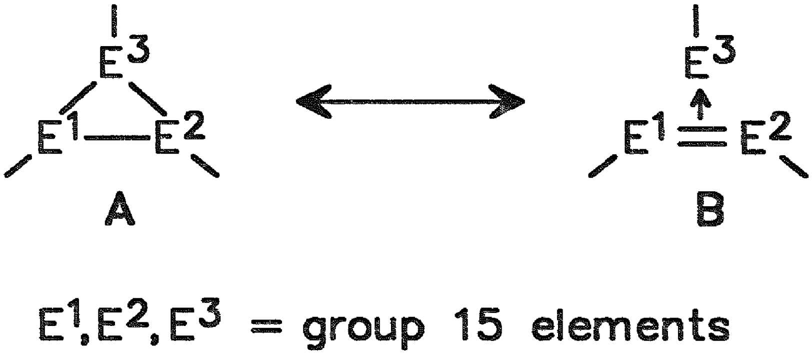
1. Introduction

Ring compounds containing phosphorus atoms play an important and fascinating role in main group chemistry. The concept of a diagonal relationship in the periodic table of carbon and phosphorus implies a close relationship of carbon and phosphorus chemistry. Indeed the array of phosphorus hydride chemistry is only surpassed by that of the hydrocarbons [1–3]. Needless to point to the structure of white phosphorus containing three-membered rings fused to a tetrahedron, and to that of Hittorf's phosphorus where a manifold combination of five-membered rings is encountered. Bonding and structures of three-membered heterocycles impose the interesting question as to whether a π-donor–acceptor interaction **B** between the building block E^3 and the $E^1=E^2$ fragment is a suitable description besides the more classical cyclopropane analog A [4] (Scheme 1).



Scheme 1.

The practical use of phosphorus-containing ring species is evident from the array of materials based upon the polymerization of functionalized cyclophosphazenes $(XYP{=}N)_n$ [5,6].

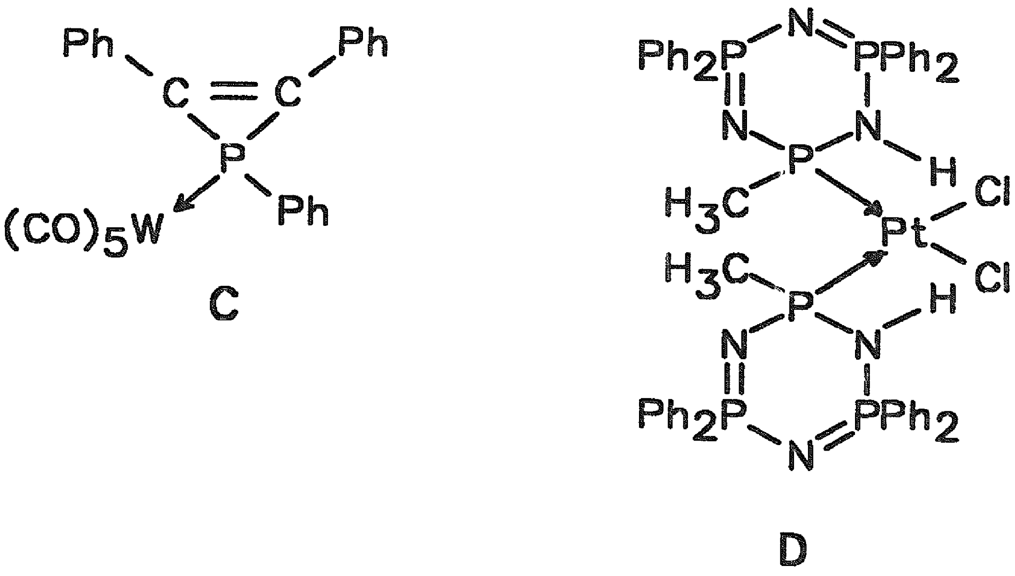
Unsaturated phosphorus ring systems, such as mono- and polyphosphacyclopentadienide anions $[P_n(CR)_{5-n}]^-$ ($n=1, 2, 3, 4, 5$; R = organic substituent) have attracted a considerable amount of interest as ligands in the coordination chemistry of transition metals [7–11]. Similar argumentation holds for λ^3- and λ^5-phosphinines [12,13] (where $\lambda=\sum$ of σ and π bonds; in phosphorus compounds, σ describes the number of σ bonds at the phosphorus atom and is usually identical with the coordination number at phosphorus), as well as cyclohexaphosphorus [11].

Among the first examples of phosphorus-containing rings were pentaphenylcyclopentaphosphane and hexaphenylcyclohexaphosphane obtained by reducing $PhPCl_2$ with magnesium metal, and erroneously presented as phosphobenzene Ph–P=P–Ph [14].

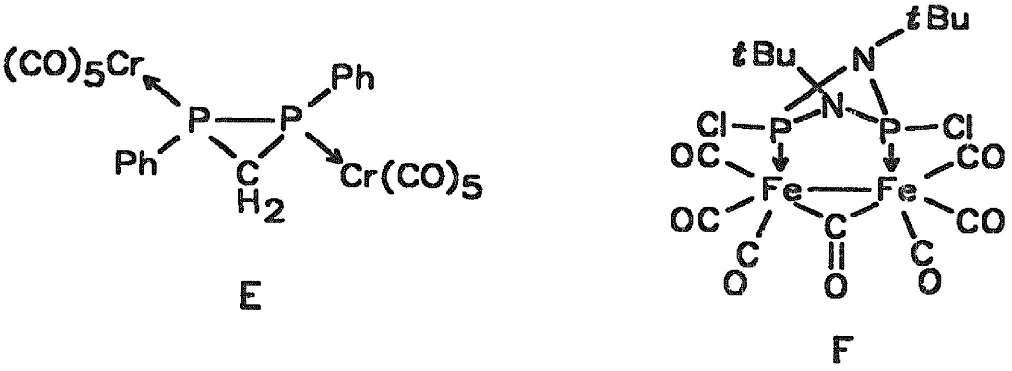
The first phosphorus-containing macrocycles $[PNCl_2]_n$ ($n=5, 6, 7$) were reported in 1897 [15], whereas phosphonitrilic chloride $(PNCl_2)_3$, as the earliest reported inorganic heterocycle, was described in 1834 [16,17].

Especially since the late 1950s, the chemistry of P-containing homo- and heterocycles has experienced a rapid development [18–22]. A large number of cyclic compounds with a varying number of ring atoms are described. They include species with skeletons such as P_3 [1], P_2B [1], P_2C [1,23], P_2Si [1], P_2Ge [1], P_2Sn [1], P_2N [24,25], P_2As [26], P_2S [1], P_2Se [1], PBN [27,28], PC_2 [23], PCSi [29], PCGe [30], PCN [31], PCAs [32], PCO [33], PCS [34], PSiS [35], PSiSe [35], PSiTe [36], PGeS [4], PGeSe [4], PN_2 [37,38], PAs_2 [39], PAsS [40,41], PAsSe [41] up to macrocycles containing these atoms [42]. Various reviews are concerned with this topic [1–3,5,7,8,11,12,23,35,42–45].

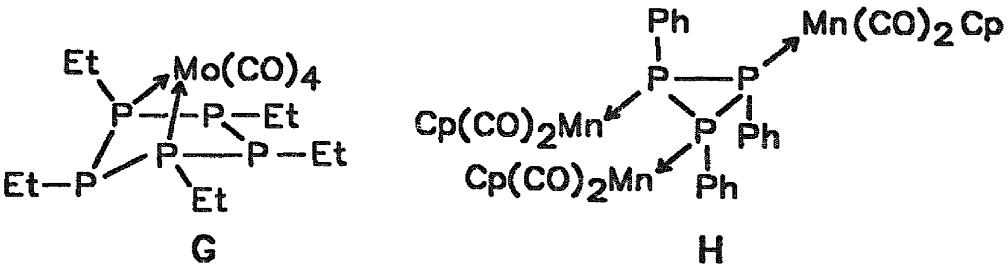
The dynamic development of this research area also includes numerous studies on the ligating properties of such species. Cycles with one or more P atoms may for example accommodate one metal center at one P atom, serving as terminal two-



Scheme 2.



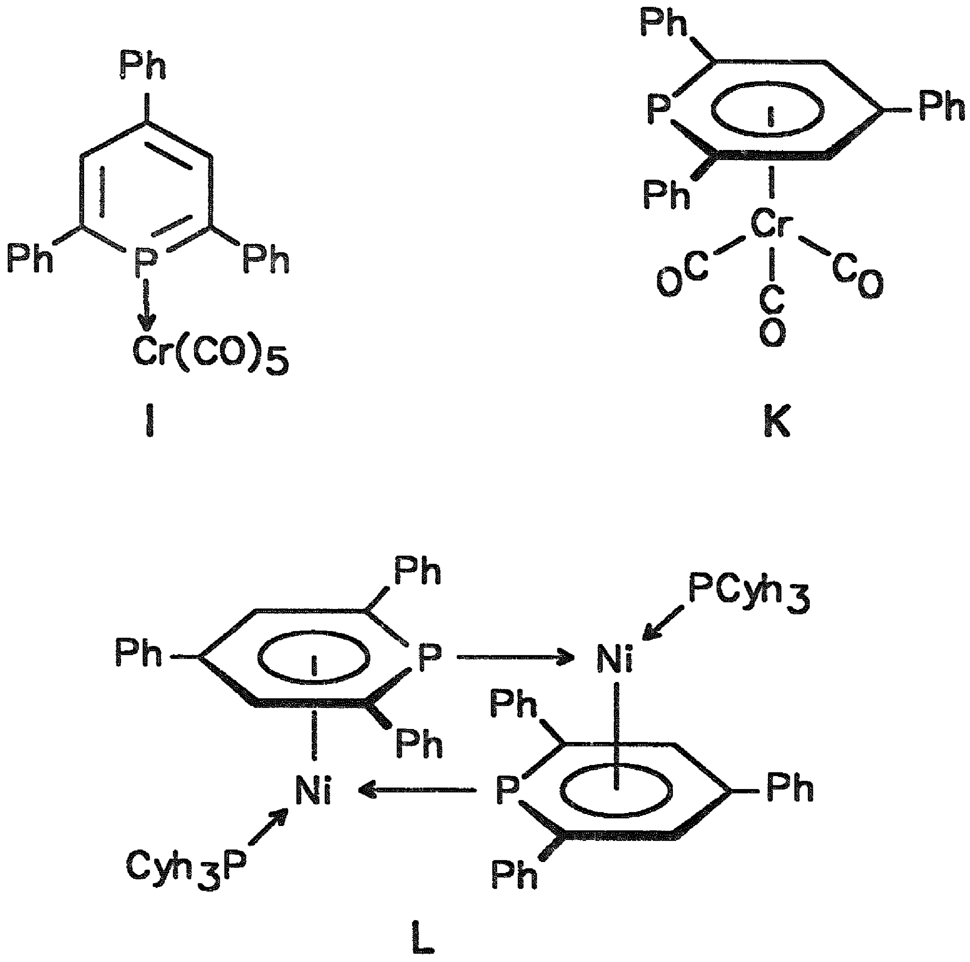
Scheme 3.



Scheme 4.

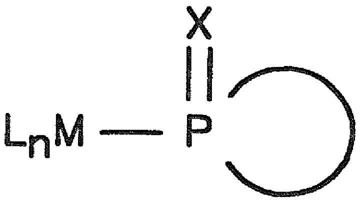
electron-donating ligands as given in **C** [23] and **D** [46] (Scheme 2; Ph = phenyl). Multifunctional cycles may also bridge two metal atoms, as shown in **E** [47] and **F** [48] (Scheme 3; Bu = butyl), or act as chelating ligands (**G**) [49] (Scheme 4; Et = ethyl; Cp = C_5H_5). In the trinuclear complex **H** all phosphorus atoms are involved in coordination [50].

Unsaturated systems such as λ^3-phosphinines may form η^1-(σ) complexes **I** [51,52] (Scheme 5; Cyh = cyclohexyl), η^6-(π) complexes of the type **K** [53,54] and dinuclear ($\eta^1 : \eta^6$) complexes **L** [55]. The chemistry of π complexes of various nuclearity of c-P_3 [56], c-P_4 [57], c-P_5 [11], c-P_6 ligands [11] and their phosphorus–carbon analogs [7–10] is described in the literature.



Scheme 5.

The structural integrity of the ring systems in compounds **C**, **D**, **E**, **F**, **G**, **H**, **I**, **J**, **K**, **L** usually remains unaffected by complexation to the metal. A different situation is encountered if one or more of the organic substituents at the ring skeleton are replaced by transition metal complex fragments. Whereas in compounds **C**, **D**, **E**, **F**, **G**, **H**, **I**, **J**, **K**, **L**, like in classical tertiary phosphane complexes, a net electron transfer from the ligand to the metal via the lone pair at the P atom occurs, in transition-metal-substituted phosphanes and cyclophosphanes electron density from the metal is released onto the main group element providing an increase of its basicity. Transition-metal-functionalized ring compounds **M** (Scheme 6) combine the structural features of an electron-releasing transition metal complex with those of the main group fragment, and are thus at the interface of organometallic and main group chemistry. As a consequence, these species should not only feature the chemistry of either parent fragment, but may also display unique characteristics.



M

Scheme 6. X = lone pair, O, S, NR, etc.; L = ligand; M = metal.

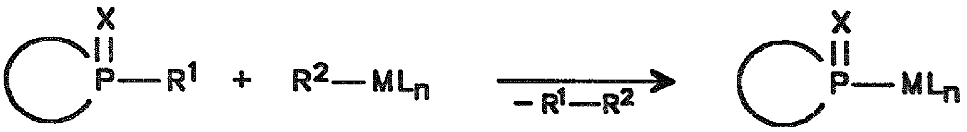
2. General comments

The content of the present account is restricted to the synthesis, structure and reactivity of ring compounds with at least one P atom. Via their phosphorus atom they act as one-electron-donor ligands towards transition metal complex fragments (M) with 15 or 17 valence electrons. This discrimination is not always unambiguous and straightforward, and we will see, especially in Section 5 and Section 6, that in some cases the differentiation between a pentavalent phosphorus center with two transition metal substituents and a trivalent phosphorus atom bridging two metal centers via its lone pair is more semantical than real. Nevertheless, we will follow the concept defined here. Fused systems are discussed with respect to the ring of concern (e.g. the metal-functionalized P cycle). Clusters and cage compounds will not be considered here.

The article is organized by:

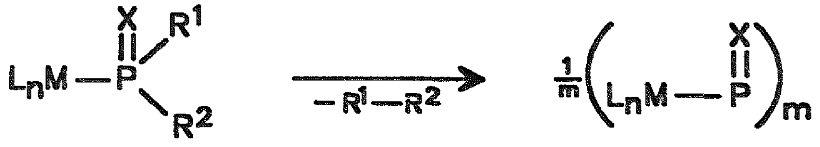
(1) increasing ring size;
(2) an increasing number of P atoms;
(3) an increasing number of metal functions.

In principle, two general synthetic approaches to the compounds under discussion may be discriminated. Firstly, the ring system is already preformed and attached to an appropriate transition metal complex fragment. This process may either proceed radically or in terms of nucleophilic substitution Eq. (1).



X = lone pair, O, S, NR etc. (1)

Secondly, the ring system is constructed in the coordination sphere of the transition metal provided that the M–P linkage is already present. This may be accomplished either by cycloadditions involving metallophosphaalkenes and metallodiphosphenes or by condensation processes of suitably functionalized metallophosphanes Eq. (3).



X = lone pair, O, S, NR etc. m > 2 (2)

3. Three-membered rings

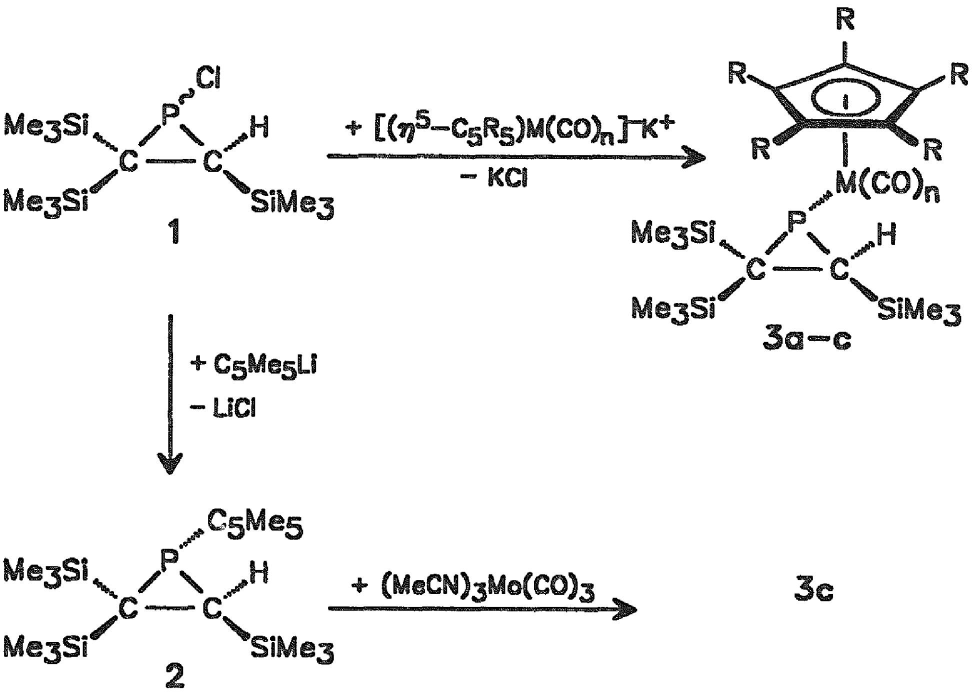
3.1. Three-membered rings containing one phosphorus atom

3.1.1. P-metallophosphiranes

The first P-metalated phosphiranes **3a**, **3b**, **3c** were obtained by heterogeneous metallation of $\mathrm{Cl\overline{P{-}CH(SiMe_3)C}(SiMe_3)_2}$ (**1**) (Me=methyl) or by reaction of phosphirane $\mathrm{C_5Me_5{-}\overline{P{-}CH(SiMe_3)C}(SiMe_3)_2}$ (**2**) with $\mathrm{(MeCN)_3Mo(CO)_3}$ (Eq. (3)) [58]. The latter reaction involved a $\mathrm{C_5Me_5}$ shift from phosphorus to the transition metal.

A complementary approach to such species made use of the formal [2+1] cycloaddition of aryl isocyanides to the P=C double bond of metallophosphaalkene **4** (Eq. (4)) [59].

The dinuclear complex **9** shows the structural features of a P-metallophosphirane serving as a two-electron donor to a second iron atom via the P lone pair. Compound **9** resulted from the formal dimerization of the transient metallophosphaalkene **8** at −30°C. **8** was obtained from metalate $\mathrm{K[Fe(\eta^3\text{-}C_3H_5)(CO)_3]}$ (**6**) and chlorophosphaalkene **7** in tetrahydrofuran (THF) at −70°C (Eq. (5)) [60].



3	M	R	n
a	Fe	H	2
b	Fe	Me	2
c	Mo	Me	3

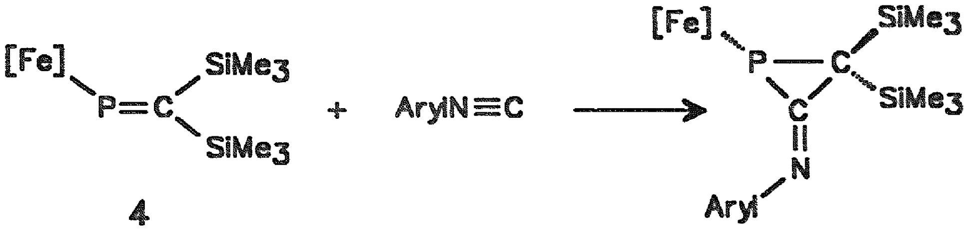
(3)

3.1.2. *P-metallophosphadiarsiranes*

The reaction of equimolar amounts of the metallodisilylphosphane **10a** and Mes*AsCl$_2$ (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) in THF at 0°C led to a dark green solution from which the orange P-metallophosphadiarsirane **11a** (5%) was crystallized in addition to red–violet [Cp*(CO)$_2$Fe–P]$_2$AsMes* (**12a**) (10%) (Cp* = C$_5$(CH$_3$)$_5$) and dark green [Cp*(CO)$_2$Fe–P–AsMes*]$_2$ (**13a**) (27%). Similarly, yellow Cp*(CO)$_2$Ru–P(AsMes*)$_2$ (**11b**) was synthesized from Cp*(CO)$_2$Ru–P(SiMe$_3$)$_2$ (**10b**) and the dichloroarsane. In this case, red [Cp*(CO)$_2$RuP]$_2$AsMes* (**12b**) was formed as the main product (45%). The unstable arsaphosphenes **14a**, **14b** were detected by ^{31}P NMR in the fresh reaction mixture (Eq. (6); [M] = metal–ligand fragment) [61,62].

3.1.3. *P-metallothiaphosphaarsiranes*

Treatment of a freshly prepared THF solution of **14a** with elemental sulfur afforded the P-metallothiaphosphaarsirane **15** in 38% yield as an orange crystalline

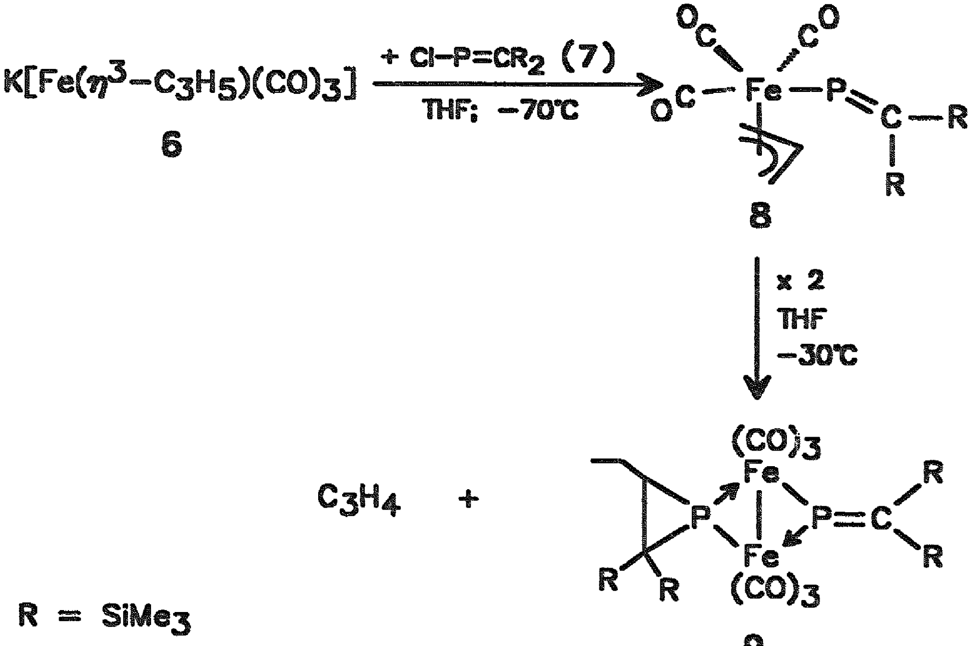


4

5a–c

5	Aryl
a	C_6H_5
b	$2\text{-}MeC_6H_4$
c	$2,6\text{-}Me_2C_6H_3$

(4)



6

8

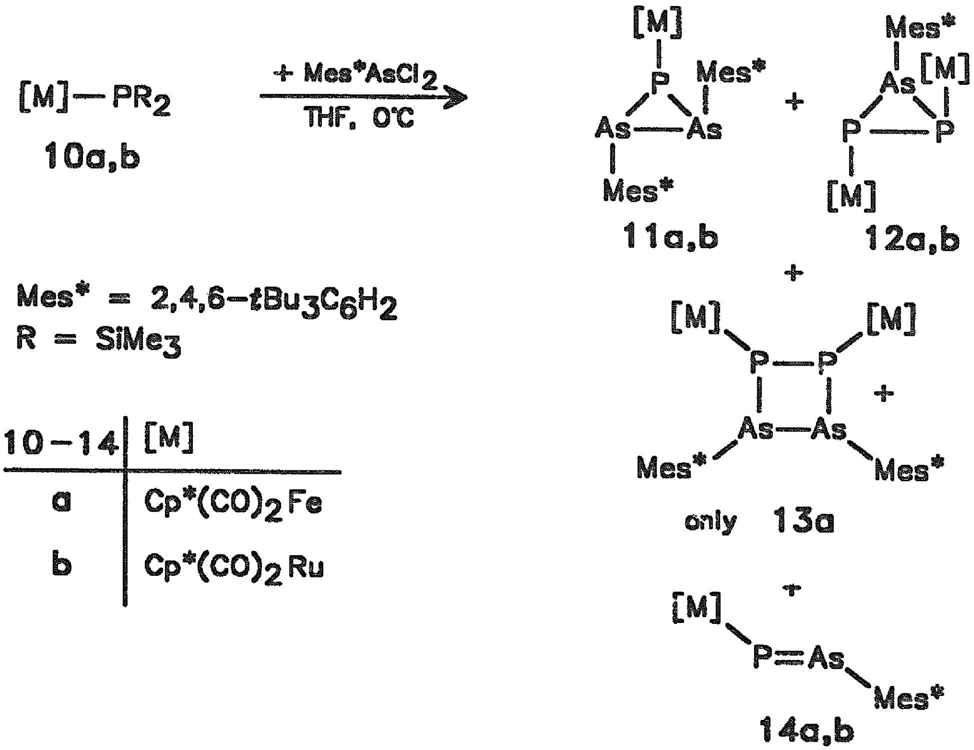
9

R = SiMe3

(5)

solid. The red complex **16** resulted from the subsequent sulfurization of **15** (Eq. (7)) [63].

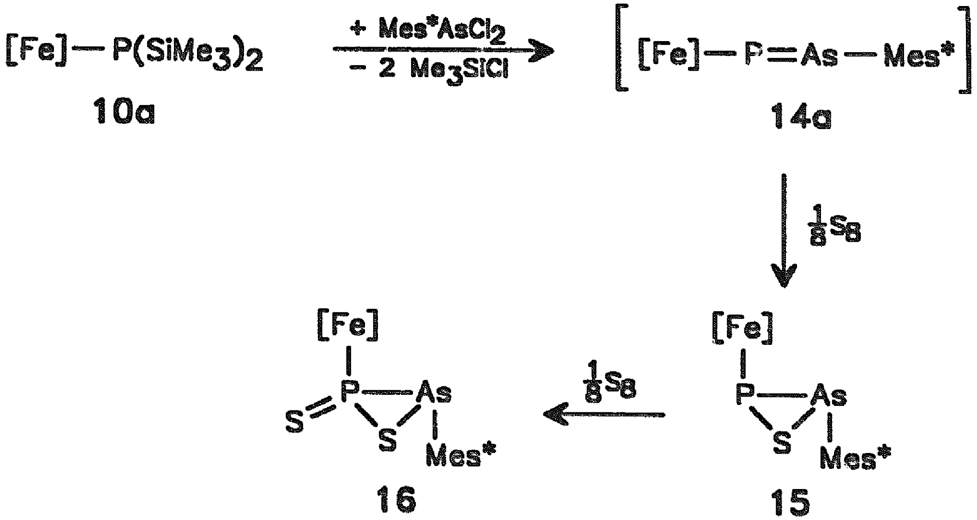
Here, compounds **18a**, **18b** are mentioned as structural isomers with metal–arsenic bonds. They were analogously synthesized from arsaphosphenes **17a**, **17b** Eq. (8) [63].



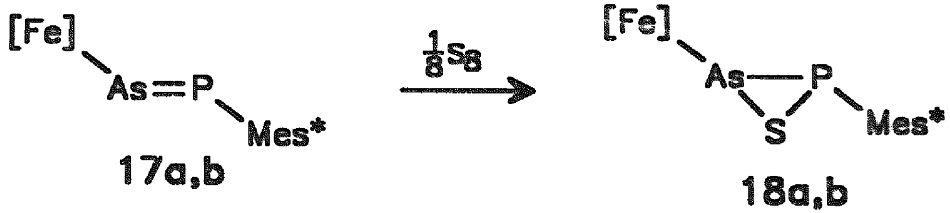
Mes* = 2,4,6-$tBu_3C_6H_2$
R = $SiMe_3$

10–14	[M]
a	$Cp^*(CO)_2Fe$
b	$Cp^*(CO)_2Ru$

(6)



(7)



17, 18	[Fe]
a	$Cp^*(CO)_2Fe$
b	$Cp(CO)(PPh_3)Fe$

(8)

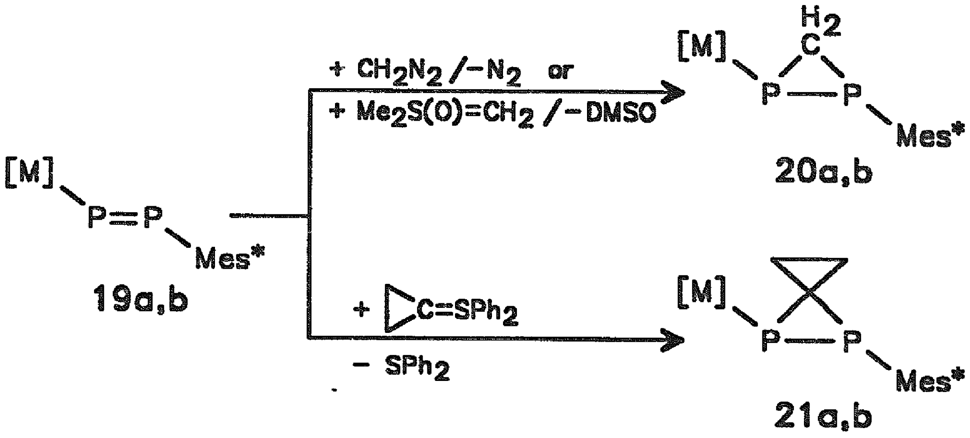
3.2. *Three-membered rings containing two phosphorus atoms*

3.2.1. *P-monometallodiphosphiranes*

The synthesis of monometalated diphosphiranes (Eq. (9)) was achieved by a formal methylene transfer of a carbene fragment to the P=P double bond of metallodiphosphenes. The ferrio- and rutheniodiphosphenes **19a,b** smoothly reacted with an excess of the sulfur ylide $Me_2S(O)=CH_2$ in THF to give the orange–yellow diphosphiranes **20a,b** in 45% and 32% yield respectively. Compounds **20a,b** were also accessible by treatment of **19a,b** with an excess of diazomethane, albeit in smaller yields. Similarly, **19a,b** were converted into the first 1,2-diphosphaspiro[2.2]pentanes **21a,b** by reaction with diphenylsulfonio cyclopropanide [64,65]. The availability of the respective metallodiphosphene and of the alkylidene transfer reagent pose a severe limitation to this approach.

Similarly, the addition of isocyanides to metallodiphosphenes afforded the 3-iminodiphosphiranes **23a,b**, **24a** (Eq. (10)) [66,67]. This reaction, however, also suffers from several limitations. The stability of the three-membered ring system is highly dependent on the steric bulk of the organic substituent in the metallodiphosphene. Thus the use of PhNC only furnished the metallodiphosphirane with the sterically very congested diphosphene **22**. The less bulky **19a** was converted by phenylisocyanide into a 2,4-diimino-1,3-diphosphetane (vide infra). The reaction of **19a** with CF_3NC may be stopped at diphosphirane **24a**, provided that an excess of the isocyanide is avoided [66,67].

A completely different route to metallodiphosphiranes started from 1-metallo-1,2-diphospha-2-propenes. Heating a methylcyclohexane solution of **25** to 80°C gave rise to a 1,2-$SiMe_3$ shift and the spontaneous cyclization of the transient phosphinidenemethylenephosphorane **26** to metallodiphosphirane **27**. Treatment of **27** with cyclooctene(pentacarbonyl)chromium afforded the $Cr(CO)_5$ adduct **28**, which was converted into the corresponding PH derivate **29** by hydrolysis on



19–21	[M]
a	$Cp^*(CO)_2Fe$
b	$Cp^*(CO)_2Ru$

(9)

alumina. **29** completely isomerized during the course of 3 days to compound **30** (Eq. (11); Δ = heat in equations) [68].

The base-induced condensation of $Cp^*(CO)_2Fe{-}PH_2$ (**31**) with chlorophosphaalkene **7** led to transient **32** which rapidly underwent rearrangement to complex **33**. The latter compound was intercepted as its stable $Cr(CO)_5$ adduct **34** (Eq. (12)) [69].

Thermolysis of 1-metallo-1,2-diphospha-2-propenes is no general method for the synthesis of metallodiphosphiranes, as is obvious from the thermally induced isomerizations depicted in Eq. (13) [68] and Eq. (14) [70].

3.2.2. P,P′-dimetallodiphosphiranes

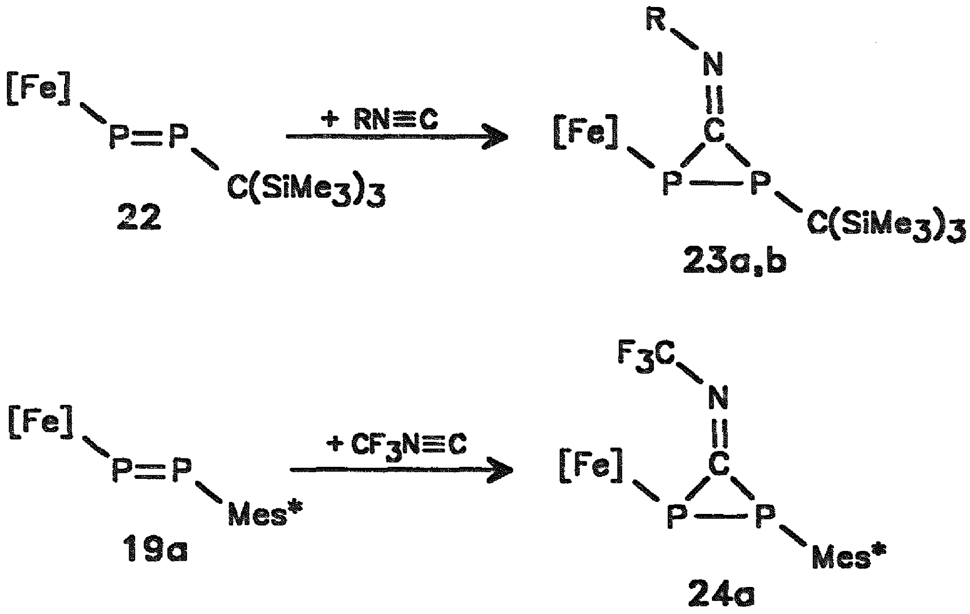
The synthesis of **35a** according to Eq. (15) was accompanied by the formation of small amounts of the crystalline P,P′-dimetallodiphosphirane **38** [71].

3.2.3. P,P′-dimetallodiphosphaarsiranes

As already indicated in Eq. (6) the P,P′-dimetallodiphosphaarsiranes **12a**, **12b** were isolated from the cyclocondensation of metallophosphanes $Cp^*(CO)_2M{-}P(SiMe_3)_2$ (M = Fe (**10a**) and M = Ru (**10b**)) with Mes^*AsCl_2 [61,62].

3.2.4. P-metallothia- and P-metalloselenadiphosphiranes

The reaction of equimolar amounts of $Cp^*(CO)_2Fe{-}P{=}P{-}Mes^*$ (**19a**) and sulfur in THF at 20°C gave rise to the formation of red thioxodiphosphenyl complex **39a**



23	R	[Fe]
a	CF_3	$Cp^*(CO)_2Fe$
b	Ph	$Cp^*(CO)_2Fe$

(10)

(66%), which upon heating to 80°C in benzene underwent rearrangement to the yellow thiadiphosphirane **40a** (Eq. (16)) [72].

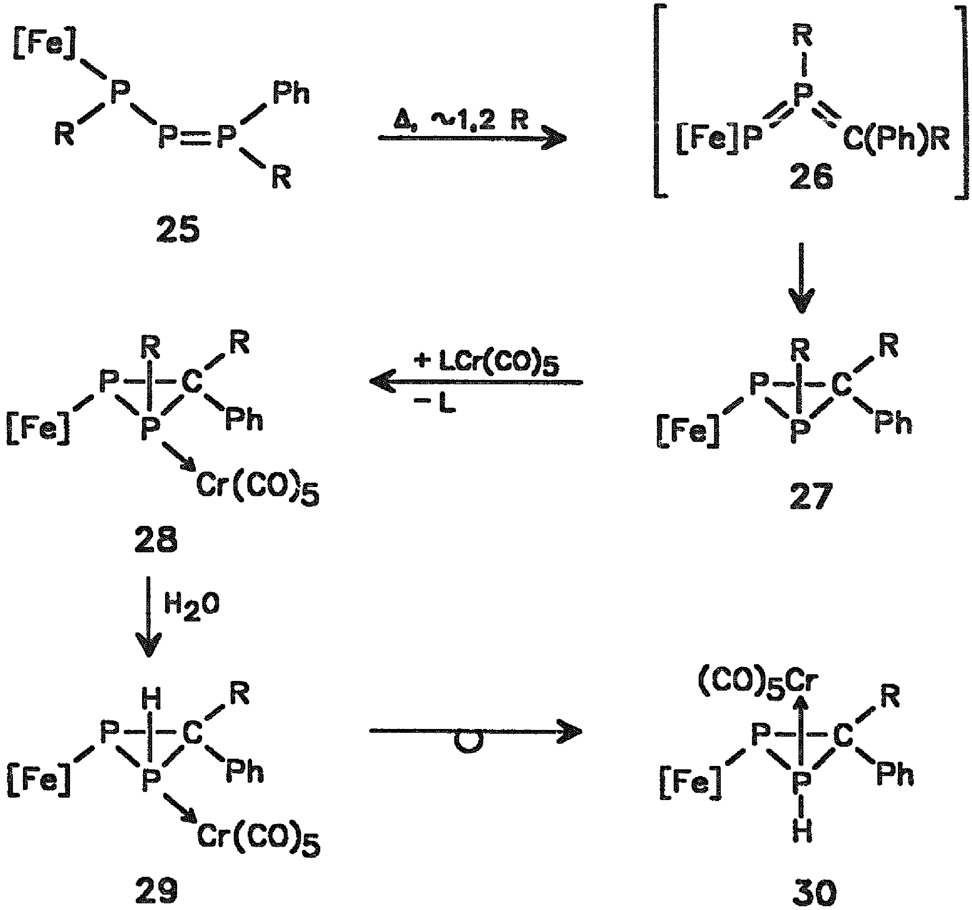
The corresponding selenoxodiphosphenyl complex **39b** was prepared from **19a** and gray selenium in benzene at ambient temperature. The compound rapidly rearranged to the yellow-green selenadiphosphirane **40b** (35%) [72].

3.3. Metalated cyclotriphosphanes

3.3.1. Monometallocyclotriphosphanes

The first monometallocyclotriphosphanes **41a–c** were synthesized in moderate yields by the action of the metallodisilylphosphanes **10a–c** with one equivalent of mesityldichlorophosphane. In the case of **10a,b**, metallocyclotetraphosphanes **42a,b**, and **43a,b** were also formed [73] (Eq. (17); Mes = 2,4,6-$(CH_3)_3C_6H_2$).

When **10a** was analogously treated with $^tBuPCl_2$, the corresponding cyclotri-



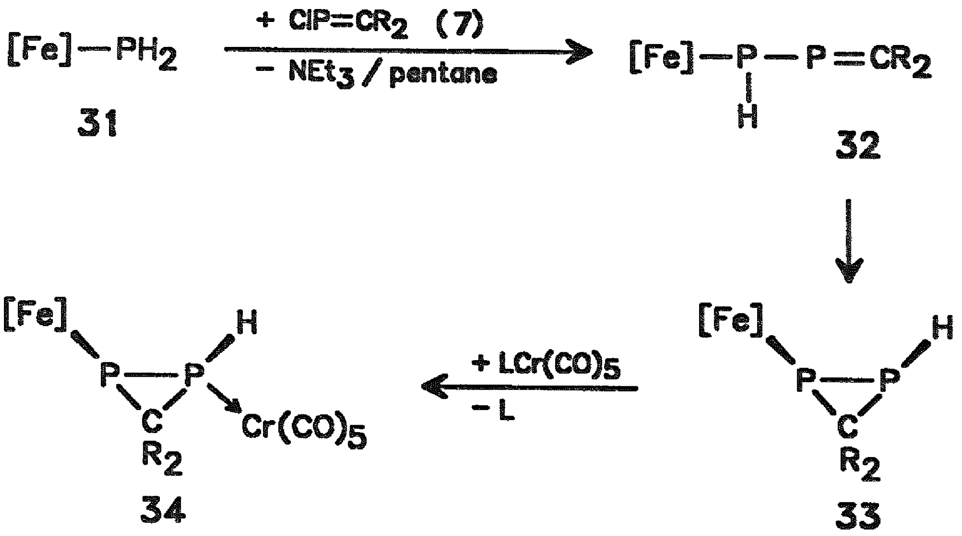
[Fe] = $Cp^*(CO)_2Fe$

R = $SiMe_3$ (11)

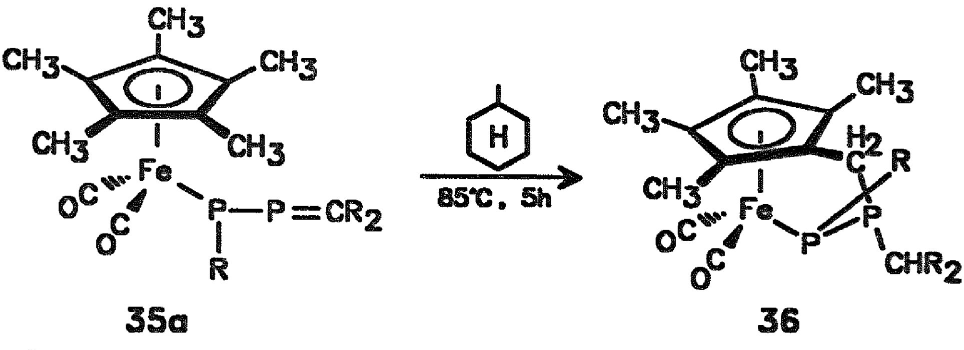
phosphane $Cp^*(CO)_2Fe\text{–}\overline{P\text{–}(P}\text{–}{}^tBu)_2$ was only detected as transient species by ^{31}P NMR spectroscopy [74]. On the contrary, the use of Mes^*PCl_2 [75] or 2,4,6-$(CF_3)_3C_6H_2PCl_2$ [76] essentially led to the formation of metallodiphosphenes instead of cyclic systems.

The reaction of $Cp^*(CO)_2Fe\text{–}PH_2$ (**31**) with **7**, as described in Eq. (12), was originally envisaged for the synthesis of diphosphenes of the type $[M]\text{–}P{=}P\text{–}CH(SiMe_3)_2$. If, however, **31** was reacted with two equivalents of **7** in a mixture of pentane and ether (1 : 1), and triethylamine was added after a period of 45 min, the two metalated cyclotriphosphanes **44** and **45** were generated (Eq. (18)) [69].

Whereas **45** could not be isolated without decomposition, the dimetalated species



[Fe] = Cp*(CO)$_2$Fe; L = Z-cyclooctene; R = SiMe$_3$ (12)

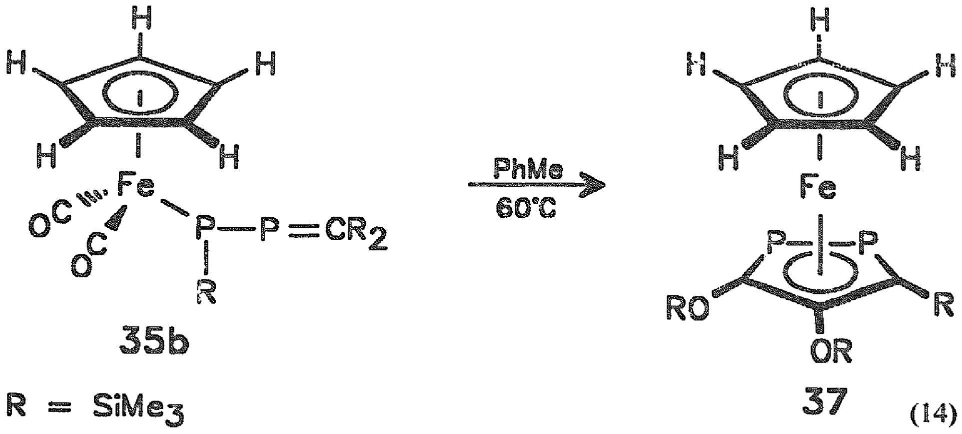


R = SiMe$_3$ (13)

44 was obtained as black–red crystals in 22% yield. It was assumed that both cyclotriphosphanes resulted from a sequence of cycloadditions of hypothetical metallodiphosphene Cp*(CO)$_2$Fe–P=P–CH(SiMe$_3$)$_2$ (**46**) which was derived from **32** by 1,3-H shift (Eq. (19)).

The reaction of **10a** with two equivalents of chlorophosphaalkene **7** took a different course. Instead of the expected coupling product **47**, the bicyclic compound **49** was isolated. Optimization of the yield of the latter species was achieved by using three molar equivalents of **7** (Eq. (20)) [77,78].

It is conceivable that intermediate **47** (not detectable by ^{31}P NMR) was rapidly attacked by a third molecule of **7** to give transient 2,4,5,6-tetraphosphahepta-1,3,6-triene **48**, which eventually cyclized to give **49**.



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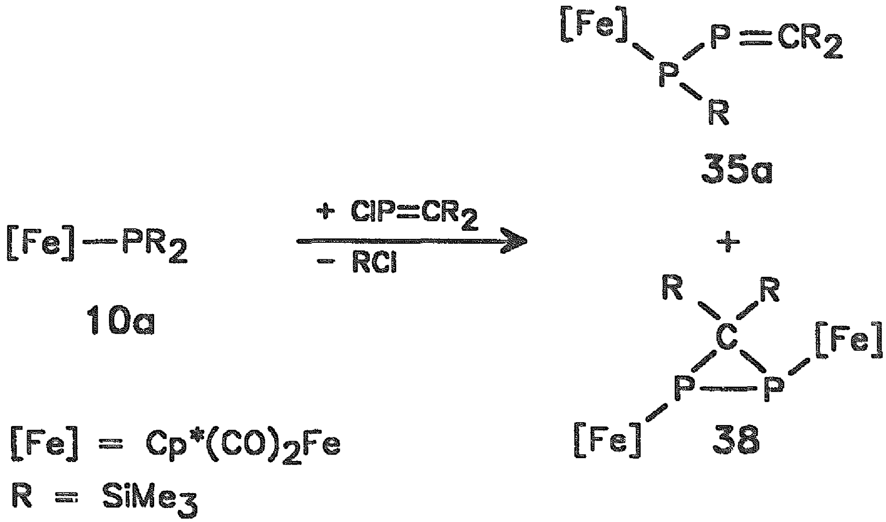
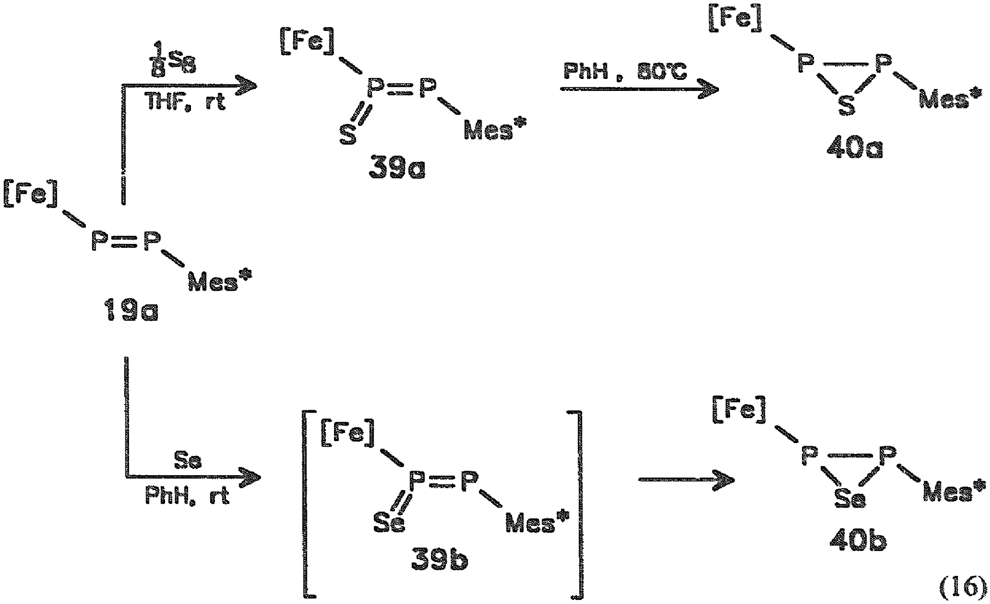


(15)

Opening of the P_4 tetrahedron was encountered, when $Cp_2Zr[P(SiMe_3)_2]_2$ was allowed to react with a five-fold excess of white phosphorus in toluene under ambient conditions. Red crystalline **50** was isolated in 42% yield (Eq. (21)) [79].

3.3.2. *Dimetallocyclotriphosphanes*

As later recognized, the preparation of metallodiphosphenes **19a,b** was accompanied by the formation of dimetallocyclotriphosphanes **51**, **52** (Eq. (22)). They were isolated in 15–20% yield from the mother liquors after precipitation of the diphosphenes (ca. 60% yield). Prolonged reaction times increased the yield of the cyclic compounds. Moreover, in a ^{31}P NMR experiment it was demonstrated that THF solutions of pure **19b** partially decomposed at ambient temperature to give **52** in addition to Mes^*PH_2 and $(Mes^*PH)_2$ [80,81].



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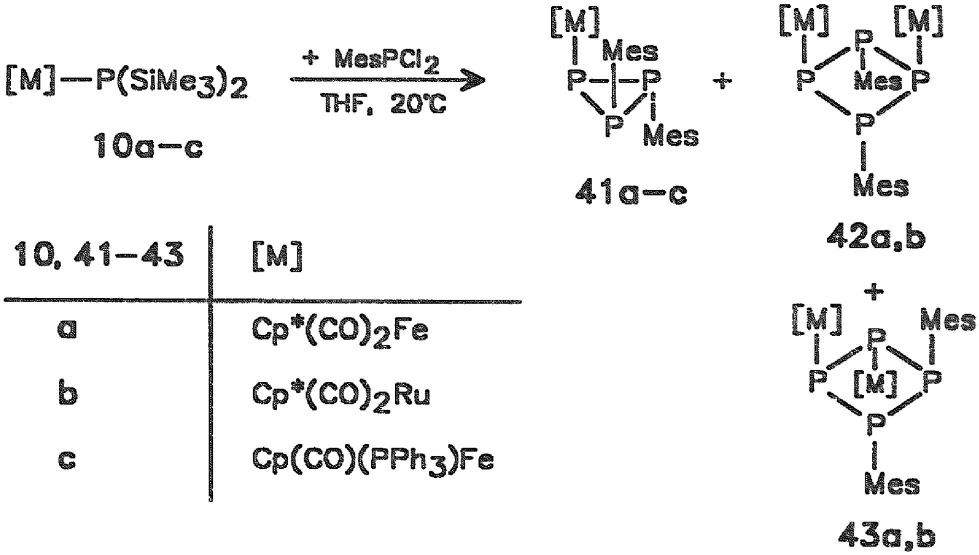
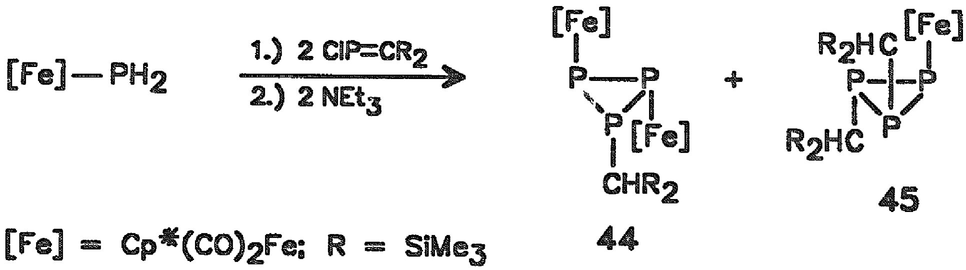


10, 41–43	[M]
a	Cp*(CO)$_2$Fe
b	Cp*(CO)$_2$Ru
c	Cp(CO)(PPh$_3$)Fe

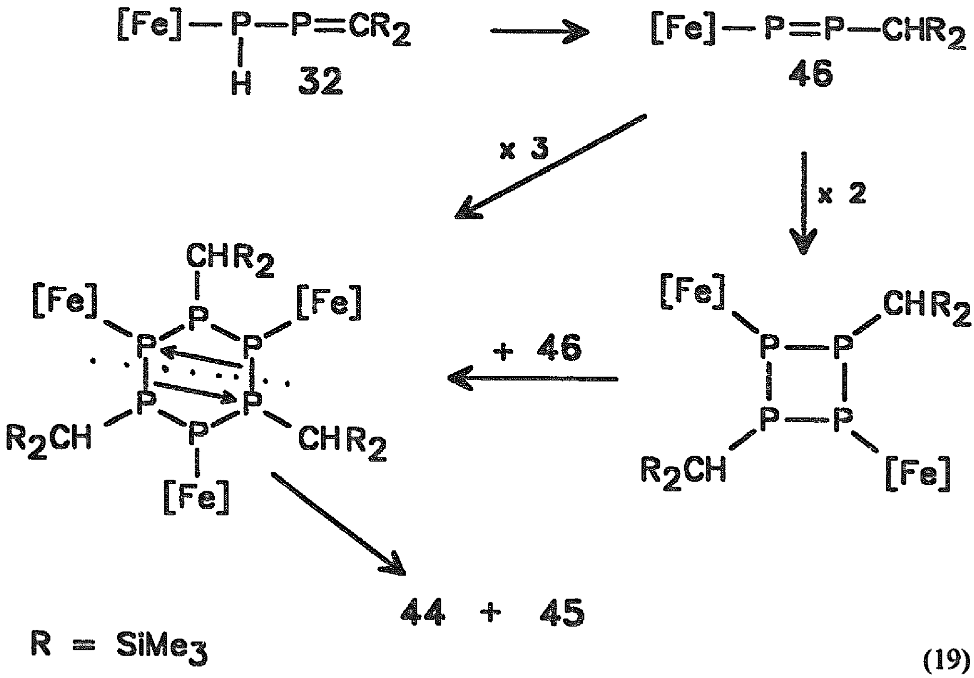
(17)

3.3.3. *Trimetallocyclotriphosphanes*

The triply metal-functionalized cyclotriphosphane **56** was generated as black crystals by the condensation of **10a** and metallodichlorophosphane **53** (58%). Dimetallotetraphospha[1.1.0]bicyclobutane **59** was detected as a thermolabile by product by its ^{31}P NMR resonances at $\delta_A = -46.5$; $\delta_B = -337.5$ ($^1J_{AB} = 185$ Hz). A



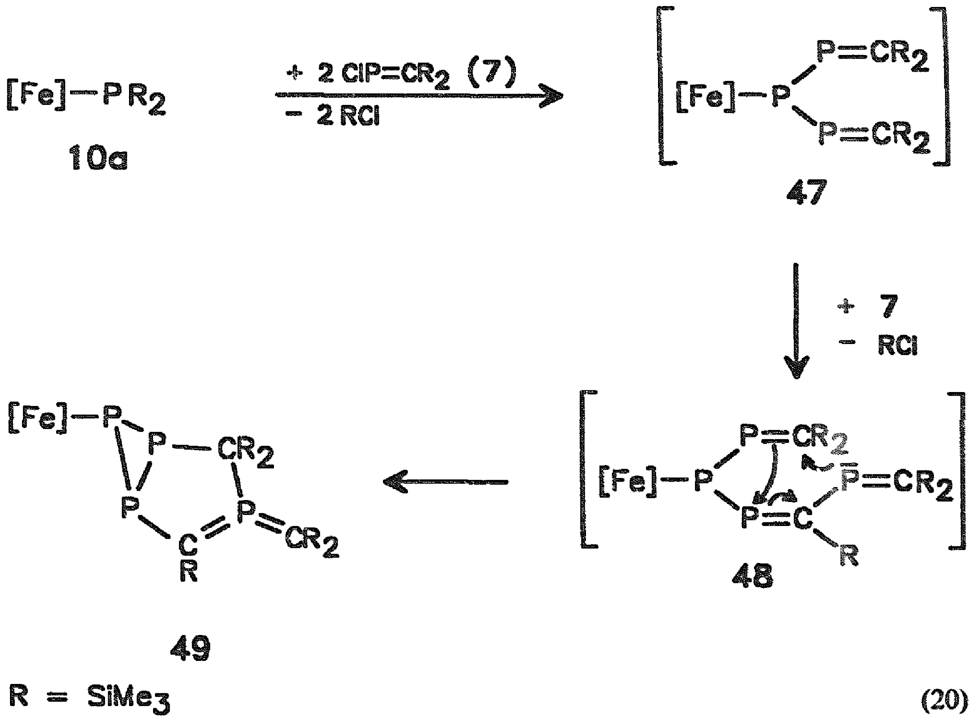
(18)



(19)

similar result was obtained, when **10a** was chlorinated with an equivalent amount of hexachloroethane, or alternatively by reduction of **53** with magnesium metal (Eq. (23)) [82].

A rationale for the observed product pattern invoked transient $Cp^*(CO)_2Fe–P(SiMe_3)(Cl)$ (**54**) ($\delta^{31}P = 299$ (s)), formed either by ligand exchange between **10a** and **53** or by partial chlorination of **10a** with hexachloroethane. Cyclocondensation of three molecules of **54** via diphosphane **55** furnished **56**. Cyclodimerization of **55** afforded cyclotetraphosphane **58** ($\delta^{31}P = 38$ (s)), which rapidly collapsed to **59** with extrusion of $[Cp^*(CO)_2Fe]_2$ (Eq. (24)). The orange–red ruthenium analog of **56** was similarly synthesized from **10b** and C_2Cl_6. Cyclotriphosphane **56** functions as a bidentate ligand in tetracarbonyl complexes of chromium (**60a**) and molybdenum (**60b**) (Eq. (25)) [83].



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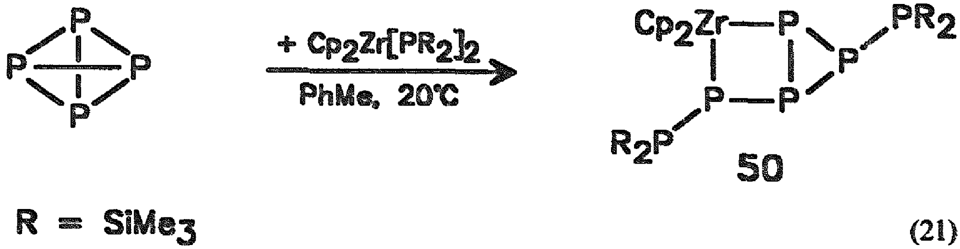


(21)

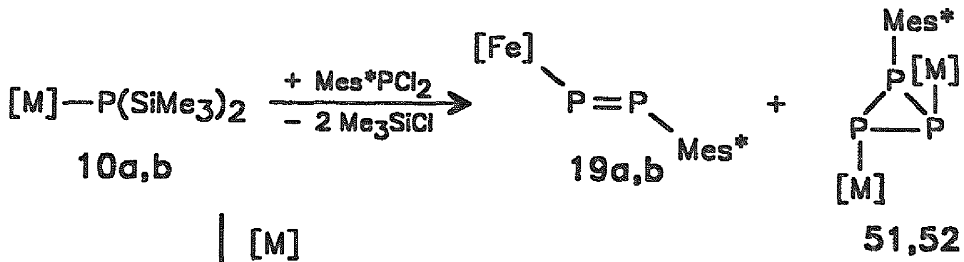
4. Four-membered rings

4.1. Four-membered rings with one phosphorus atom

4.1.1. P-metallo-1,2-dihydrophosphetes

There are essentially two synthetic approaches available to P-metallo-1,2-dihydrophosphetes, both employing metallophosphaalkenes such as $Cp^*(CO)_2M–P=C(NMe_2)_2$ (M= Fe (**61a**), Ru (**61b**)) as the starting materials. These routes imply the construction of the ring skeleton in the coordination sphere of the metal.

Compounds **61a,b** and electron-deficient alkenes, such as dimethyl fumarate, methyl acrylate, or fumarodinitrile, should undergo a [2+2] cycloaddition to yield



	[M]
10a,19a,51	$Cp^*(CO)_2Fe$
10b,19b,52	$Cp^*(CO)_2Ru$

(22)

metallophosphetanes **62**. Unexpectedly, the P-metallo-1,2-dihydrophosphetes **63** were formed in this process with violent effervescence of dimethylamine [84,85] (Eq. (26); EWG = electron-withdrawing group).

Metallophosphaalkene **61a**, when treated with methyl butynoate in ether, gave rise to the generation of 1,2-dihydrophosphete **66** [86]. If, however, this reaction was conducted in *n*-pentane the metallo-1-phosphabuta-1,3-diene **67a** precipitated from the reaction mixture (Eq. (27)).

In THF, ether or benzene solution compound **67a** was readily transformed into **66** with evolution of dimethylamine.

The synthesis of P-metallo-1,2-dihydrophosphetes from metallophosphaalkenes and alkynes, however, suffers from several restrictions. As metallophosphaalkenes are considered as electron-rich heteroalkenes, they only react with electron-deficient alkynes such as alkyne esters and 3-ketoalkynes. Moreover, the nature of the products from the reaction of **61a** with such alkynes is dependent upon the substitution pattern in both reactants. In keeping with this, rings such as **68**, and **69**, metallophosphabutadienes such as **67b** and other species may be obtained (Eq. (28)) [86,87].

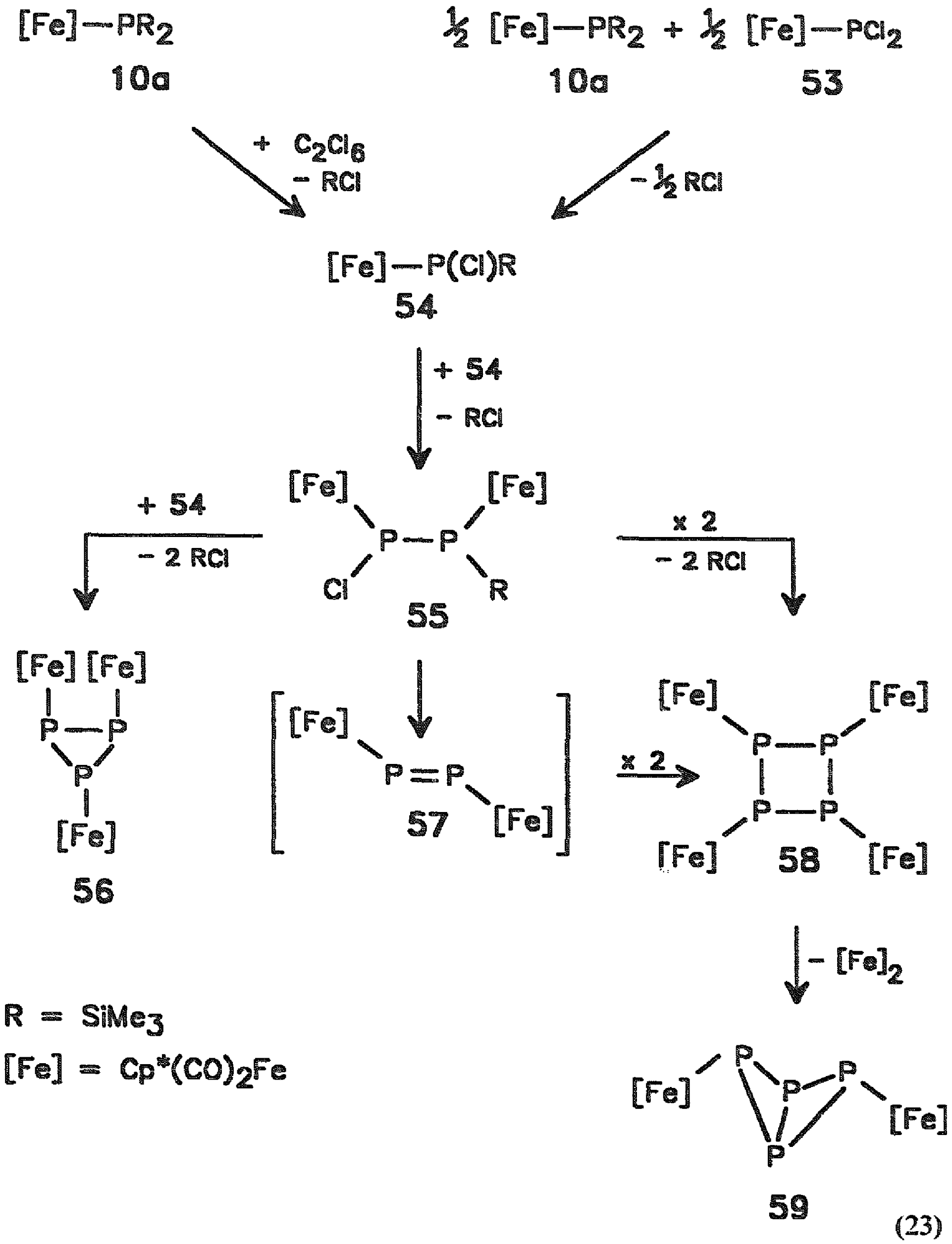
4.1.2. *P-metallo-1-aza-3-phosphetanes*

Diphosphene $Cp^*(CO)_2Fe–P{=}P–Mes^*$ (**19a**) combined with two equivalents of trifluoromethylisocyanide in *n*-pentane solution at −50°C to the P-metallo-1-aza-3-phosphetane **71**, which precipitated as yellow hexagonal platelets from the solution (47%).

A reasonable explanation for this process invoked the rearrangement of the initially formed **24a** into transient azaphosphirane **70**, which added a second molecule of the isocyanide to afford the observed product [66,67] Eq. (29).

4.1.3. *P-metallo-1,3-diaza-2-phosphetanes*

The nucleophilic cleavage of the P–Cl function in the spirobicyclic phosphoranes **72a**, **72b**, **73c** with $Na[Mn(CO)_5]$ led to the formation of transition-metal-substituted four-membered spirobicyclic phosphoranes **73a,b** as pale solids featuring the structural characteristics of 1,3-diaza-2-λ^5-phosphetanes [88] Eq. (30).



(23)

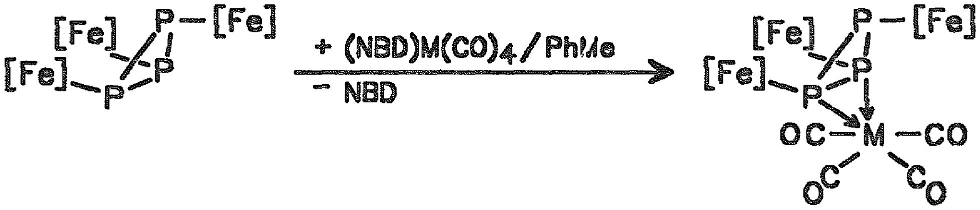
4.2. *Four-membered rings with two phosphorus atoms*

4.2.1. *P-metallo-1,2-diphosphetanes*

A reasonable approach to P-metallo-1,2-diphosphetanes involves a formal [2+2] cycloaddition between metallodiphosphenes and electron-deficient alkenes. In keep-

$$4\ [Fe]{-}PCl_2 \xrightarrow[-\,4\,MgCl_2]{+\,4\,Mg} \underset{\textbf{58}}{\big[[Fe]{-}P\big]_4} \longrightarrow \textbf{56} + \textbf{59}$$

(24)



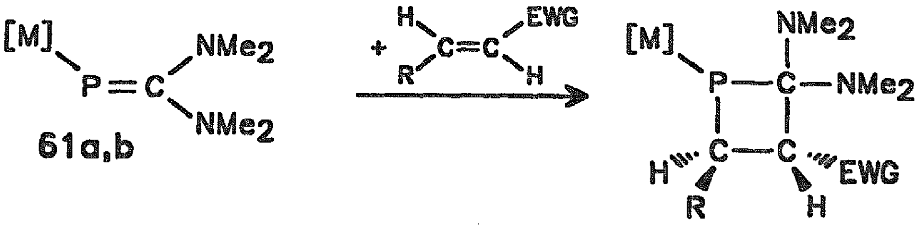
[Fe] = Cp*(CO)$_2$Fe

NBD = norbornadiene

60a: M = Cr

60b: M = Mo

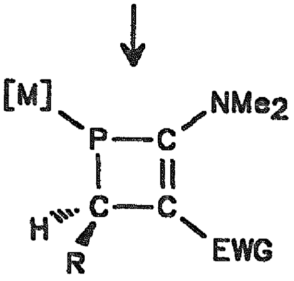
(25)



61a,b

62

	[M]	EWG	R
63	Cp*(CO)$_2$Fe	CO$_2$Me	H
64a	Cp*(CO)$_2$Fe	CO$_2$Me	CO$_2$Me
64b	Cp*(CO)$_2$Ru	CO$_2$Me	CO$_2$Me
65	Cp*(CO)$_2$Fe	CN	CN

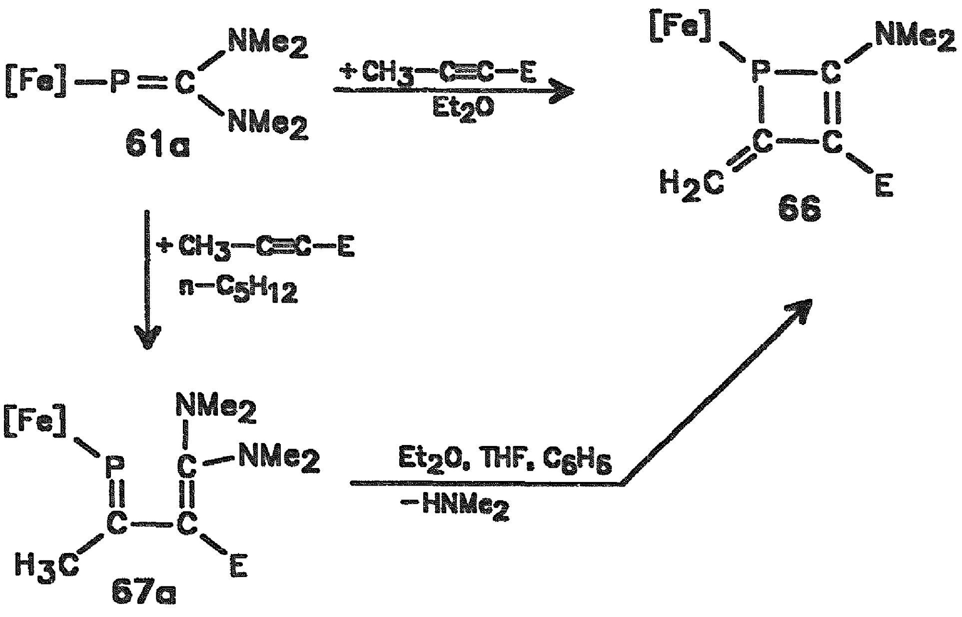


63–65

(26)

ing with this, heating a mixture of Cp*(CO)$_2$Fe–P=P–Mes* (**19a**) with an excess of fumarodinitrile in benzene led to the formation of compound **74** in 23% yield (Eq. (31)) [89].

Similarly, **19a** was converted into orange–yellow **76** by an excess of dimethyl fumarate. Compound **76** was also produced upon heating **19a** in the presence of an excess of dimethyl maleate in benzene at 75°C. It is remarkable that the excess of



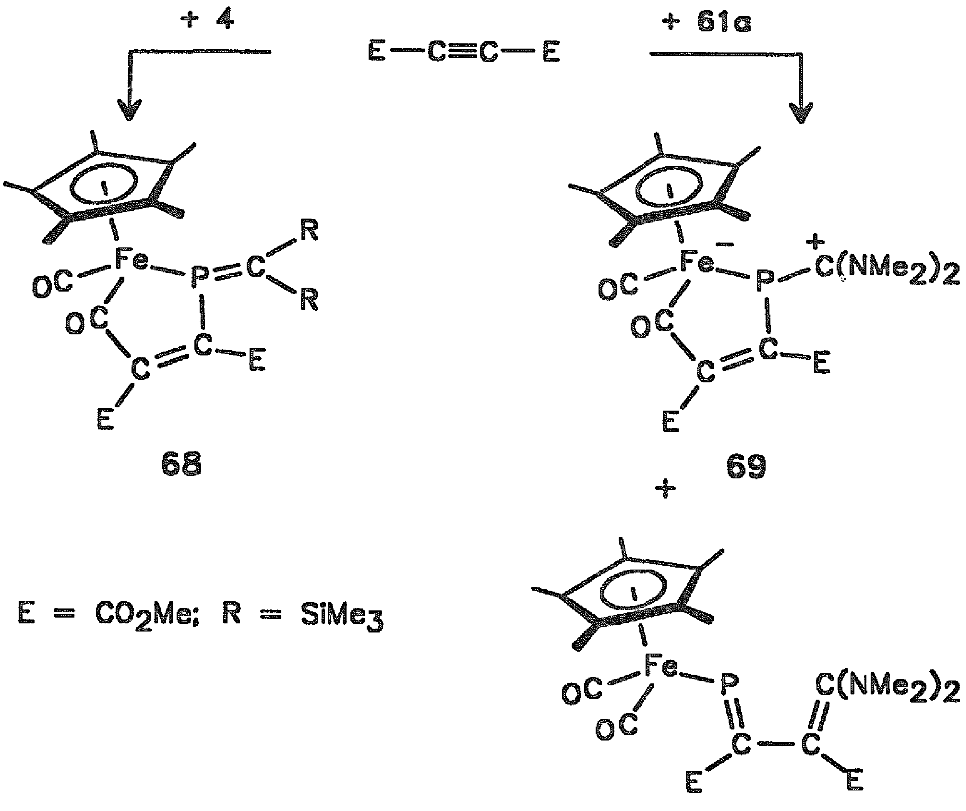
$E = CO_2Me$ (27)

dimethyl maleate was cleanly isomerized to dimethyl fumarate. Clearly this process was catalyzed by complex **19a**. Based upon these observations, and considering the fact that concerted [2+2] cycloadditions are thermally forbidden, the two-step mechanism of Eq. (32) was proposed [89]. The reaction is initiated by a nucleophilic attack of the metalated P atom of **19a** at the π^* orbital of the olefin to give zwitterion **75**. Rotation around the C–C single bond yielded conformer **75'**, which either cyclized to **76** or dissociated into **19a** and the fumarate. The latter recombined with **19a** to give **76**.

Reaction of **19a** with maleimide and N-methylmaleimide in benzene at 75°C afforded the transition-metal-functionalized orange–red 1,2-diphosphetanes **77** (R=H) and **78** ($R=CH_3$) as a 1 : 2 mixture of diastereoisomers. They resulted from an exo and/or endo [2+2] cycloaddition of the P=P double bond of the metallodiphosphene to the C=C functionality of the imides (Eq. (33)).
Separation of the diastereoisomers on a preparative scale failed. It was, however, possible to grow single crystals of the major isomer **78b**, in which, according to an X-ray study, the metal is oriented to the concave (endo) face of the bicyclic system [90].

4.2.2. *P-metallo-2,4-bisimino-1,3-diphosphetanes*

In contrast to the situation with CF_3NC described in Section 4.1.2 (Eq. (29)), metallodiphosphene **19a** smoothly reacted with two molecules of the isocyanides PhNC (**79a**), *o*-TolNC (**79b**) (Tol=)tolyl, C_6F_5NC (**79c**) to give the crystalline

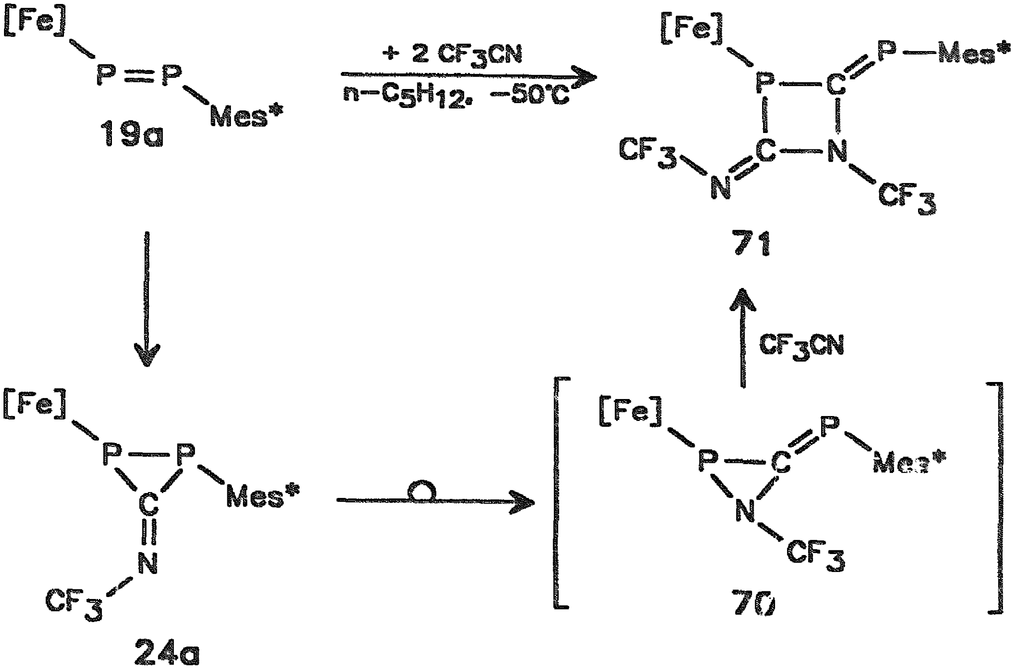


67 (28)

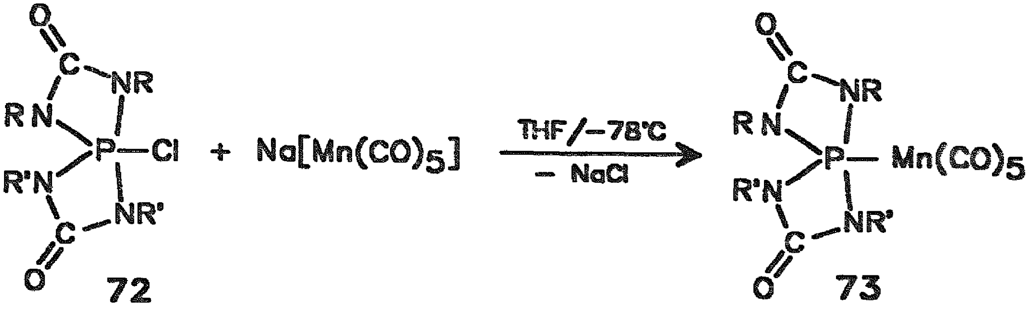
2,4-diimino-1,3-diphosphetanes **81a–c**. At the beginning of the reaction the iminodiphosphiranes **80a–c** were observed by ^{31}P NMR spectroscopy. From ^{31}P NMR data it was evident that the four-membered rings **81a,b** were formed as 2 : 1 mixtures of isomers, whereas for **81c** a 6 : 1 ratio was determined (Eq. (34)). In the major isomers, **A**, the substituents at the nitrogen atoms were present in an anti-orientation. For the minor products, **B**, two possible syn configurations (**B-1**; **B-2**) were discussed [66,67].

4.2.3. *P,P'-dimetallo-1,3-diphosphetane-2,4-diones*

On the quest for P-metallophosphaketenes [M]–P=C=O, such as **83**, bromocarbonyliron complexes **82a–c** were submitted to reaction with equimolar amounts of Li(DME)$_2$(OCP) (DME = 1,2-dimethoxyethane) [91] in DME. The red solid products were identified as the dimetalated 1,3-diphosphetane-2,4-diones **84a–c** which presumably resulted from a head-to-tail dimerization of the P=C bond in transient **83**. No intermediates were detected by ^{31}P NMR [92] (Eq. (35)). When treated with equimolar amounts of (cyclooctene)Cr(CO)$_5$ or nickel tetracarbonyl compound **84** was transformed into the adducts **85a** and **b** (Eq. (36)).

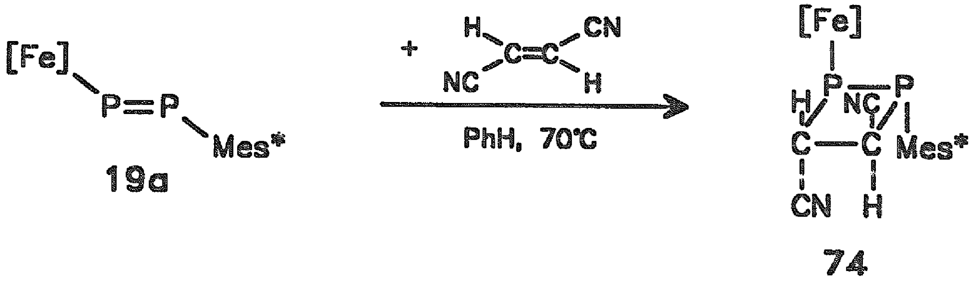


$[Fe] = Cp^*(CO)_2Fe$ (29)

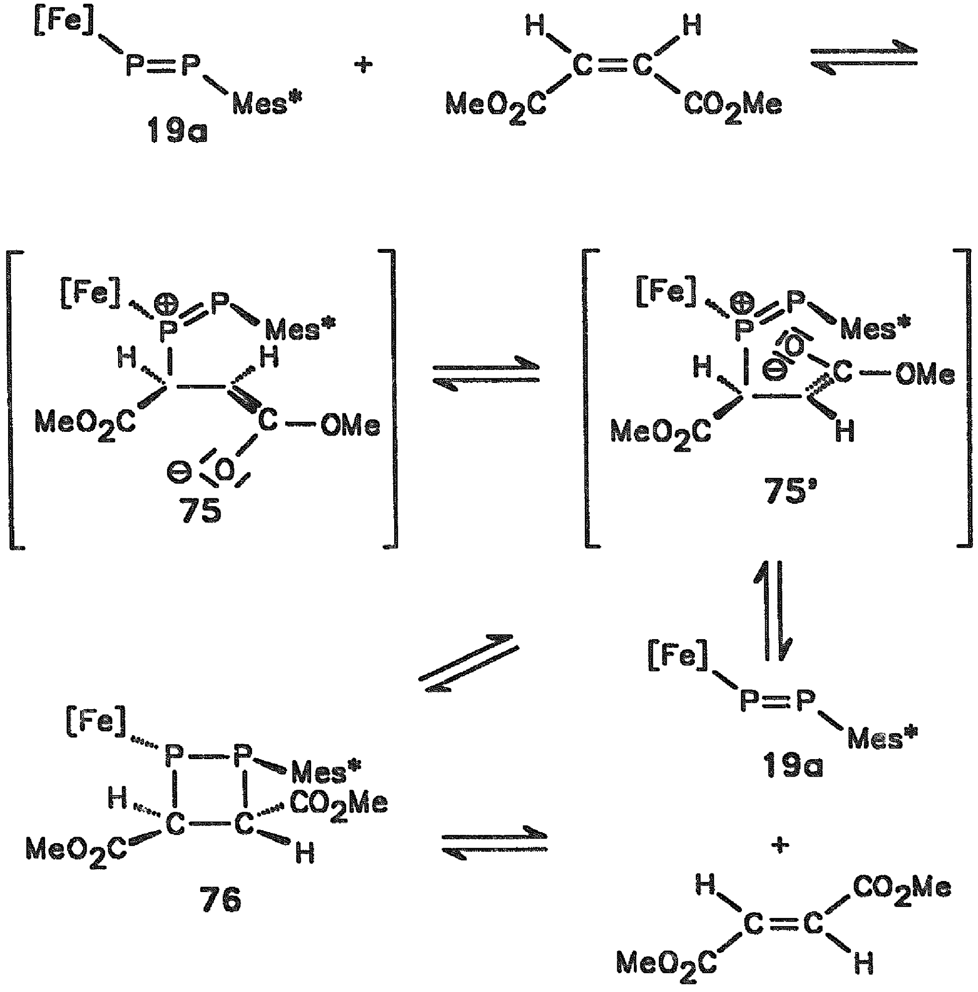


72, 73	R	R'
a	Me	Me
b	Ph	Ph
c	Me	Ph

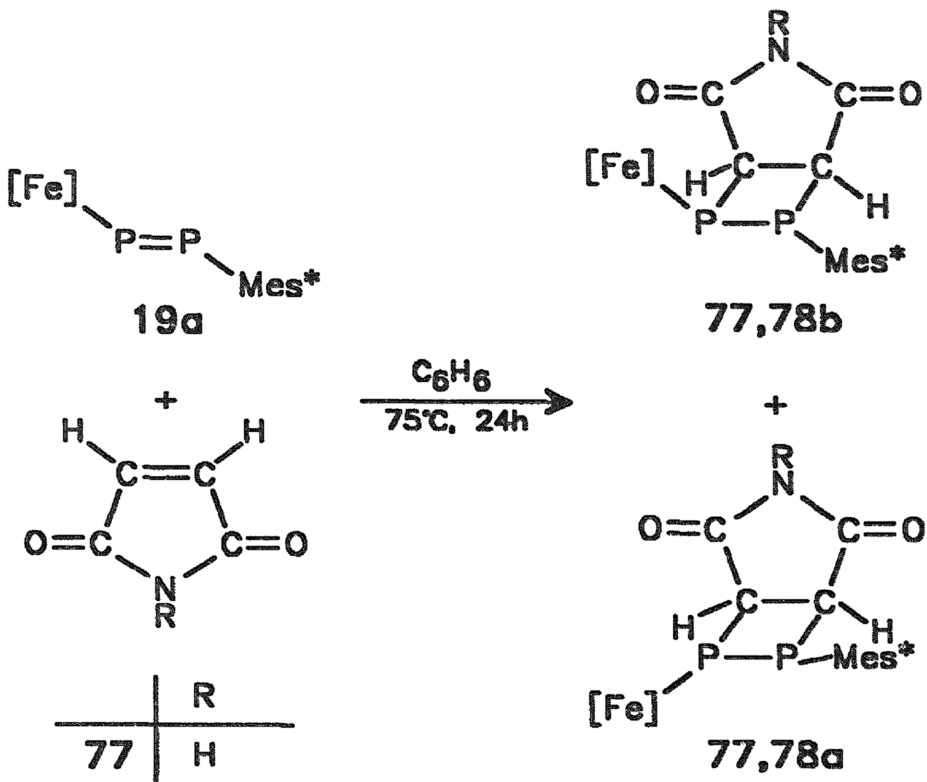
(30)


[Fe]
P=P
Mes*
19a
H
CN
NC
H
PhH, 70°C
74

(31)


[Fe]
P=P
Mes*
19a
MeO2C
CO2Me
75
75'
OMe
76
+

(32)



	R
77	H
78	Me

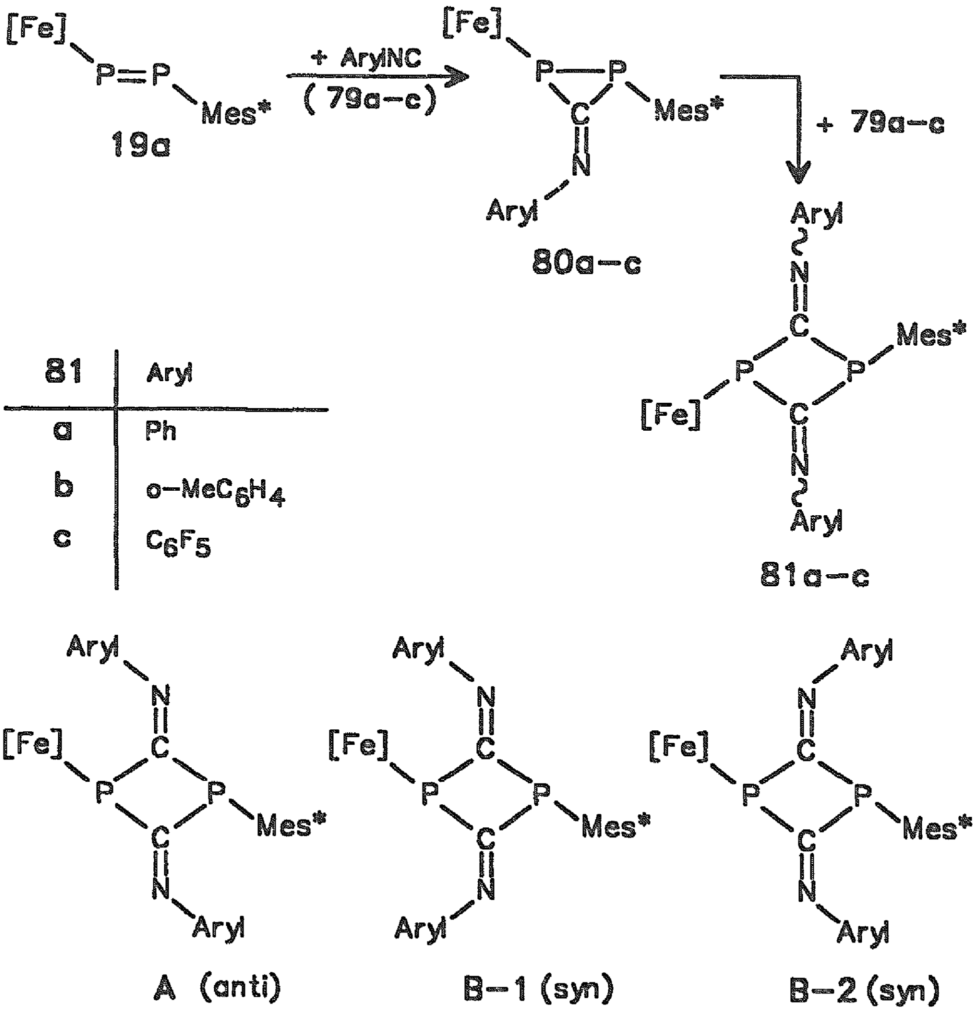
(33)

4.2.4. *P-metallo-1-oxa-2,3-diphosphetanes*

Metallodiphosphenes $(\eta^5\text{-}C_5R_5)(CO)_2M\text{–}P{=}P\text{–}Mes^*$ (**19a–g**) underwent reaction with anhydrous hexafluoroacetone (HFA) in *n*-pentane to afford either the five-membered metalloheterocycles $(\eta^5\text{-}C_5R_5)(CO)\overline{M\text{–}P({=}PMes^*)OC(CF_3)_2C}(O)$ (**86**) or metalated 1-oxa-2,3-diphosphetanes $(\eta^5\text{-}C_5R_5)(CO)_2M\text{–}\overline{P\text{–}P\text{–}(Mes^*)OC}(CF_3)_2$ (**87**) (Eqs. (37)). The course of the reaction and the nature of the products were largely influenced by the basicity of the cyclopentadienylmetal fragment. Thus, the increased metal basicity of the ruthenium rendered the derivatives (**86b,c,e,g**) markedly more stable than the corresponding iron analogs (**86a,d,f**). Cross experiments between **86e** and **19c** evidenced that the rearrangement **86**→**87** proceeds intramolecularly without the liberation of HFA. Thus, only **87e** and unreacted **19c** were obtained [93–95].

4.2.5. *P-metallo-1-thia-2,3-diphosphetanes*

Metalated 1-thia-2,3-diphosphetanes **88a,b** were available as red microcrystalline solids by treatment of metallodiphosphenes **19a,b** with equimolar amounts of carbon



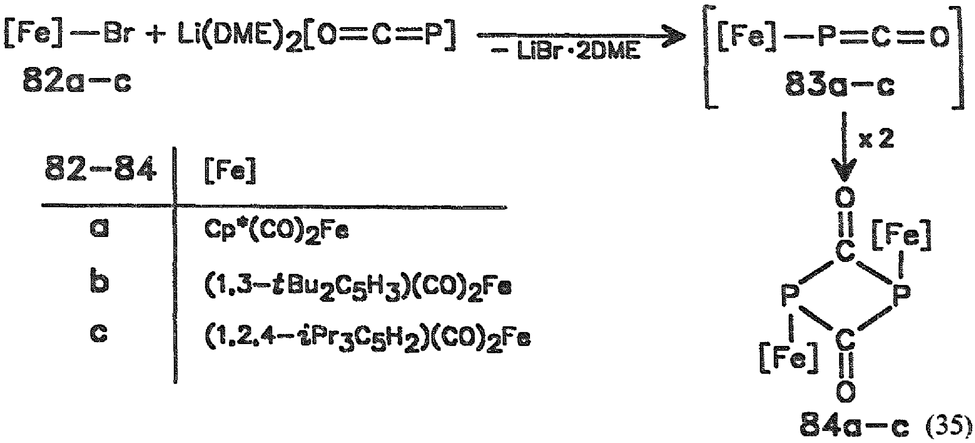
81	Aryl
a	Ph
b	o-MeC_6H_4
c	C_6F_5

(34)

disulfide in toluene solution (Eq. (38)) [67]. The use of a large excess of CS_2 favored the formation of brown 1 : 2 adducts of unknown structure.

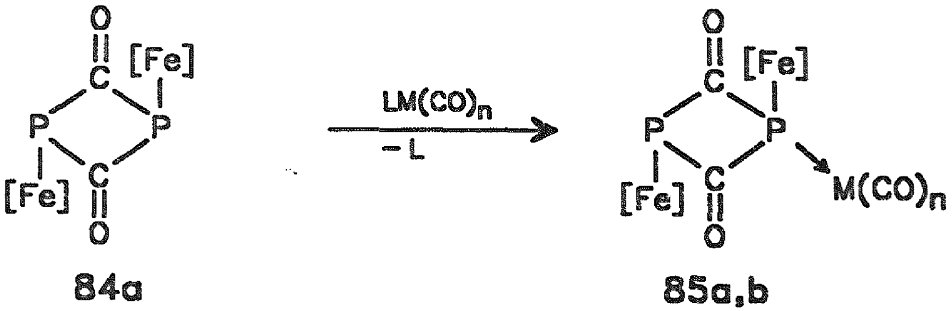
4.2.6. *P-metallo-1,2-diaza-3,4-diphosphetidines*

Metallodiphosphene **19a** was transformed into the bicyclic 1,2-diaza-3,4-diphosphetidines **90a,b** upon reaction with Δ^1-1,2,4-triazoline-3,5-diones (Δ in unsaturated rings describes the position of the double bond) in benzene solution. The nature of the substitutent R at the tricoordinate nitrogen atom in the triazoline-3,5-dione seemed to be crucial for the success of this transformation. All attempts to synthesize **90** with R = CH_2Ph, 4-ClC_6H_4 or 3,5-$Cl_2C_6H_3$ failed (Eq. (39)) [96,97]. At the beginning of the reaction, two doublets in the ^{31}P NMR spectrum



82–84	[Fe]
a	$Cp^*(CO)_2Fe$
b	$(1,3\text{-}tBu_2C_5H_3)(CO)_2Fe$
c	$(1,2,4\text{-}iPr_3C_5H_2)(CO)_2Fe$

(35)



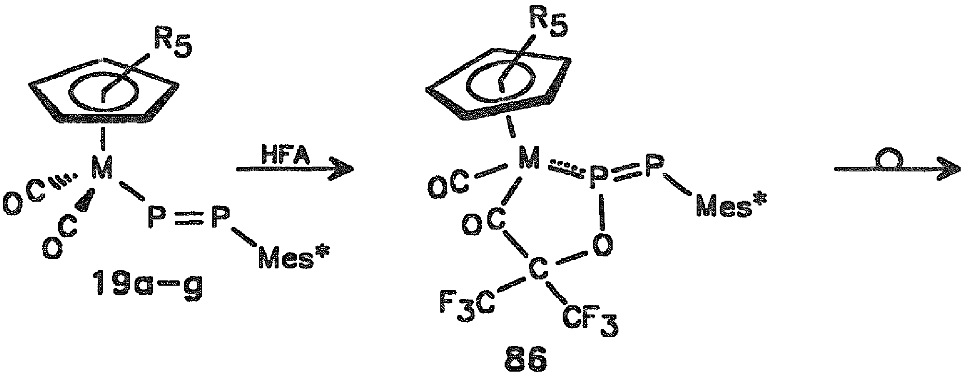
85a: $LM(CO)_n$ = (z-cyclooctene)$Cr(CO)_5$; **85b**: $Ni(CO)_4$

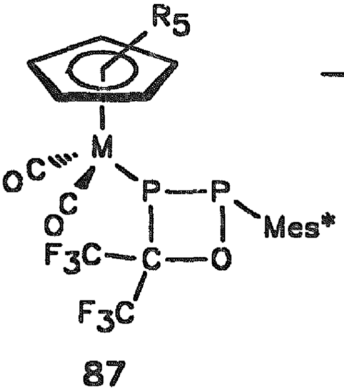
(36)

at $\delta = 341.3$ and 146.2 ($^1J_{PP} = 637.8$ Hz) were in agreement with an intermediate (**89a,b** or **89'a,b**), which rapidly decomposed to the final products.

4.2.7. P,P'-dimetallo-1,3-diaza-2,4-diphosphetidines

Heterolytic cleavage of the phosphorus–halogen bond in cyclic halophosphanes by carbonyl metalates was expected to be a general method for the formation of a metal–phosphorus linkages at the periphery of these ring systems. Indeed, such a process was observed when 2,4-dichloro-1,3-diaza-2,4-diphosphetidine **91** was allowed to react with $Na[Fe(CO)_2Cp^*]$ or $Na[Mn(CO)_5]$. Whereas in the case of the carbonylferrate compound **92** was cleanly generated, the treatment of **91** with $Na[Mn(CO)_5]$ in boiling THF furnished dinuclear **93** (Eq. (40)). Here, obviously, the halide displacement was accompanied by the reductive coupling of two rings and chelation to both metal centers [98].





87

19, 86, 87	(Ring)M
a	Cp^*Fe
b	Cp^*Ru
c	$(1,2,4\text{-}^iPr_3C_5H_2)Ru$
d	$(1,3\text{-}^tBu_2C_5H_3)Fe$
e	$(1,3\text{-}^tBu_2C_5H_3)Ru$
f	$[1,3\text{-}(Me_3Si)_2C_5H_3]Fe$
g	$[1,3\text{-}(Me_3Si)_2C_5H_3]Ru$

$$\mathrm{HFA} = (CF_3)_2C{=}O \qquad (37)$$

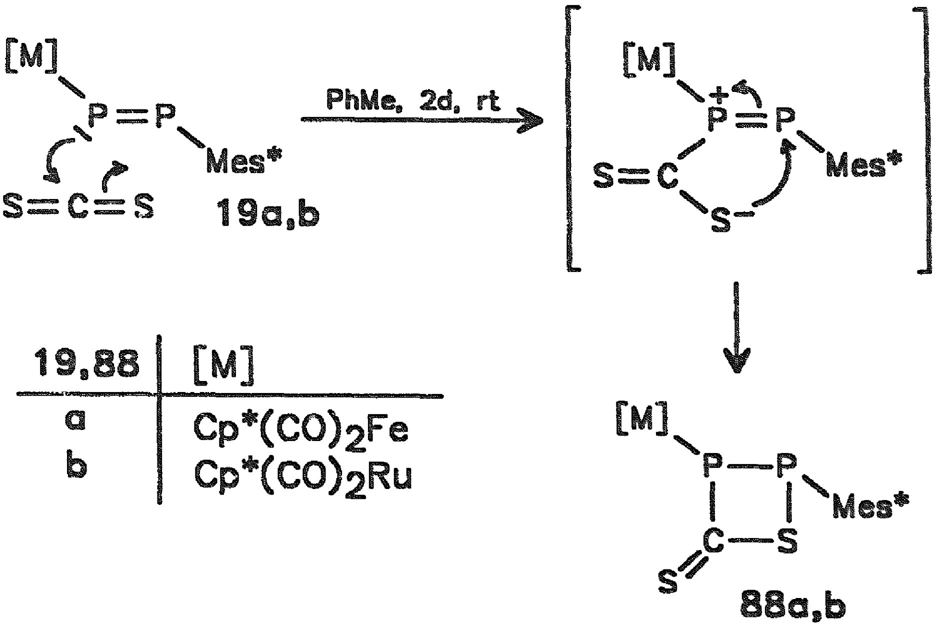
The lone pairs at the phosphorus atoms in metal-functionalized diazadiphosphetidines may also be involved in intramolecular CO extrusion with the generation of M=P double bonds, as observed in reaction of **91** with $Na[Mo(CO)_3Cp^*]$ to afford dinuclear **94** [99] (Eq. (40)).

The nucleophilic displacement of chloride from heterocycle **91** by carbonyl metalates is not always straightforward, as evidenced by the formation of $[(CO)_4Fe]\overline{P(H)N(^tBu)\text{-}P(H)[Fe(CO)_4]N}{}^tBu$ from $Na_2Fe(CO)_4 \cdot 1.5$ dioxane and **91** [100].

4.2.8. *Dimetallodiphosphadiarsetanes*

As already pointed out in Section 3.1.2 (Eq. (6)), dark green P,P′-dimetallo-1,2-diphospha-3,4-diarsetane **13a** was produced in 27% yield from reaction of $Cp^*(CO)_2Fe\text{–}P(SiMe_3)_2$ with supermesityldichloroarsane [61].

The formation of the isomeric As,As′-dimetallo-1,3-diphospha-2,4-diarsetane **95** was achieved upon combination of $Cp^*(CO)_2Fe\text{–}As(SiMe_3)_2$ with mesityldichlorophosphane (34%) (Eq. (41)) [101].



19,88	[M]
a	$Cp^*(CO)_2Fe$
b	$Cp^*(CO)_2Ru$

(38)

4.2.9. *Dimetallocyclotetraphosphanes*

In Section 3.1 it was reported that reaction of mesityldichlorophosphane with metallodisilylphosphanes $Cp^*(CO)_2M{-}P(SiMe_3)_2$ (M = Fe (**10a**), Ru (**10b**)) afforded mixtures of cyclotriphosphanes **41a,b** and the two isomeric cyclotetraphosphanes **42a,b**, and **43a,b** [73] (Eq. (17)). The three-membered rings were formed as main products in 25–30% yield, and they were easily removed from the product mixture by ether extraction. From the extracts, **43a,b** were obtained by fractional crystallization (11–17% yield), whereas the isomers **42a,b** remained in the mother liquor.

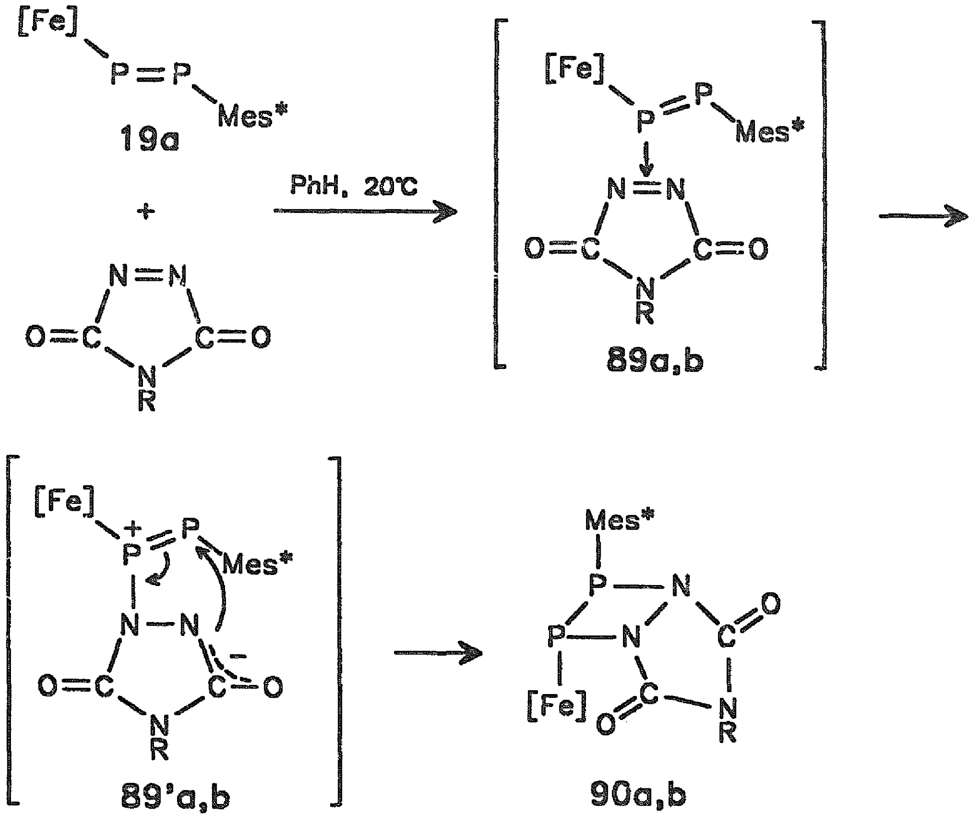
The condensation of $Cp^*(CO)_2Fe{-}P(SiMe_3)_2$ (**10a**) with an equivalent amount of *tert*-butyldichlorophosphane in THF furnished red microcrystalline **96** which was smoothly converted into tetrahedrane **97** or 1,3-diphospha-2-propanone **98** by action with 1.5 or 2.0 equivalents of $Fe_2(CO)_9$ respectively (Eq. (42)) [74].

5. Five-membered rings

5.1. *Five-membered rings with one phosphorus atom*

5.1.1. *P-metallophospholes*

Although in the vast majority of its transition metal complexes the phospholyl system $[C_4R_4P]^-$ functions as η^5 ligand, there exist a few examples of



89,90	R
a	Ph
b	4–EtOC$_6$H$_4$

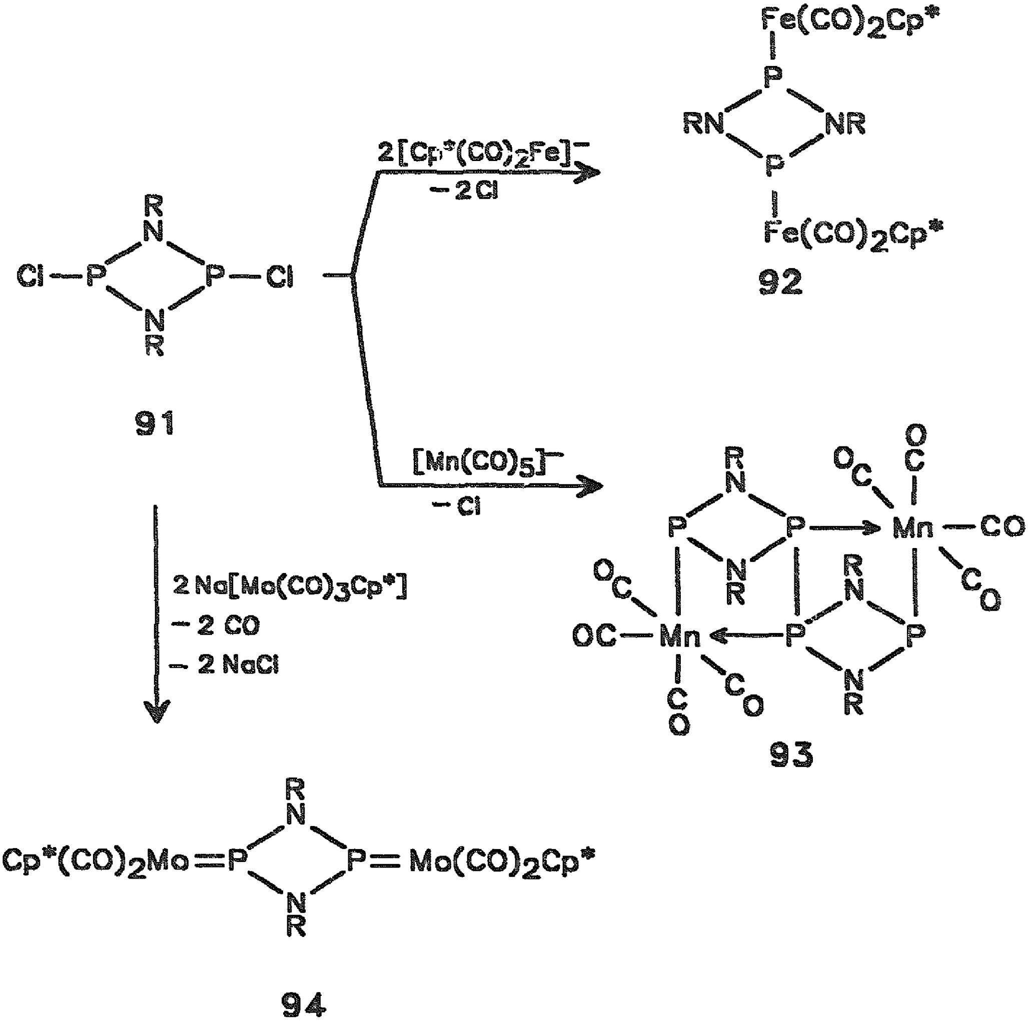
(39)

η^1-phospholyl complexes as well. Here, heterolytic P–X cleavage by carbonyl metalates seems to be a viable approach to this target. Consistently, 1-chlorotetraphenylphosphole reacted with pentacarbonylmanganate and -rhenate to give complexes **99a,b** in good yields (65% and 69% respectively) (Eq. (43)) [102].

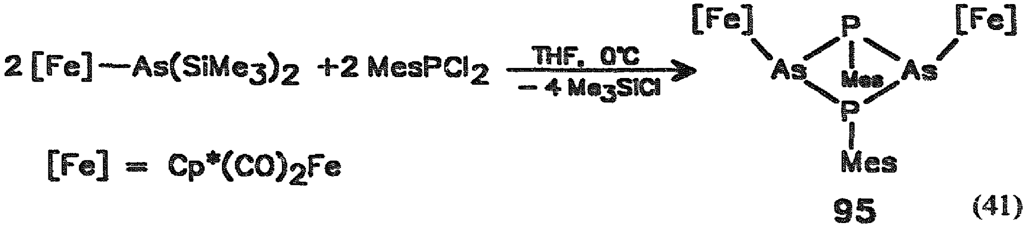
In an alternative, but less efficient, route to produce compound **99a**, phospholide **100a** and pentacarbonylmanganese were employed (Eq. (44)) [102].

Similar heterolytic P–Cl and M–Cl bond fissions furnished the iron derivative **101**, as well as the molybdenum and tungsten complexes **102a,b** (Eq. (45)) [102].

The conversion of **99a,b** into dinuclear complexes **103a,b** with bridging three-electron-donating phospholyl ligands was achieved by gentle heating (70°C) in hexane for 24 h [102], whereas brief thermolysis of **99a,b** in refluxing xylene, or

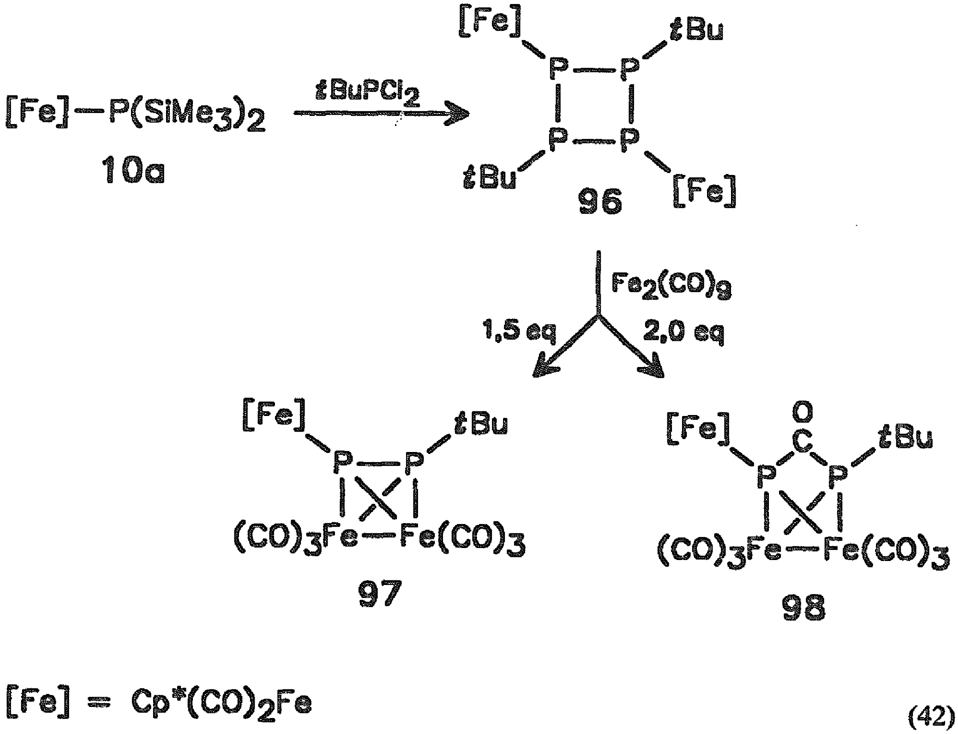


R = *t*Bu (40)



[Fe] = Cp*(CO)$_2$Fe

(41)



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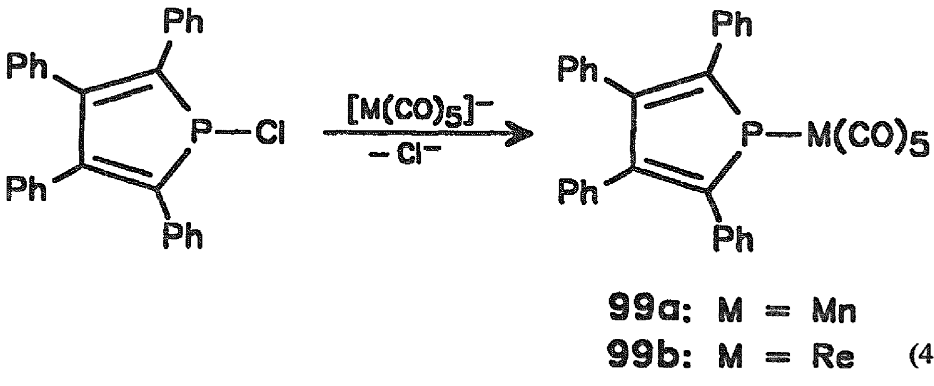


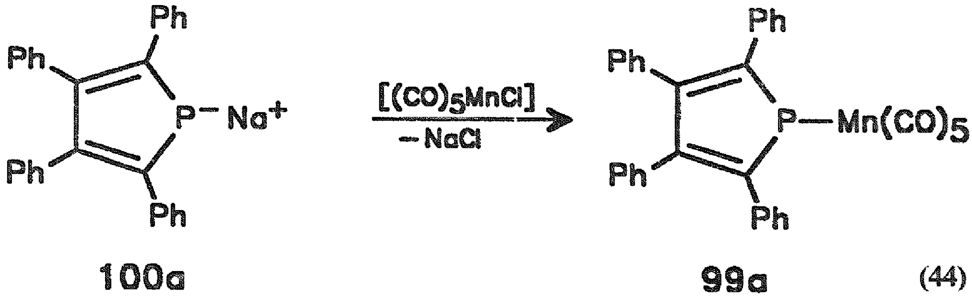
(43)

alternatively in vacuo at 120°C, produced the more common η^5-phospholyl complexes **104a,b** in moderate yields (Eq. (46)) [103].

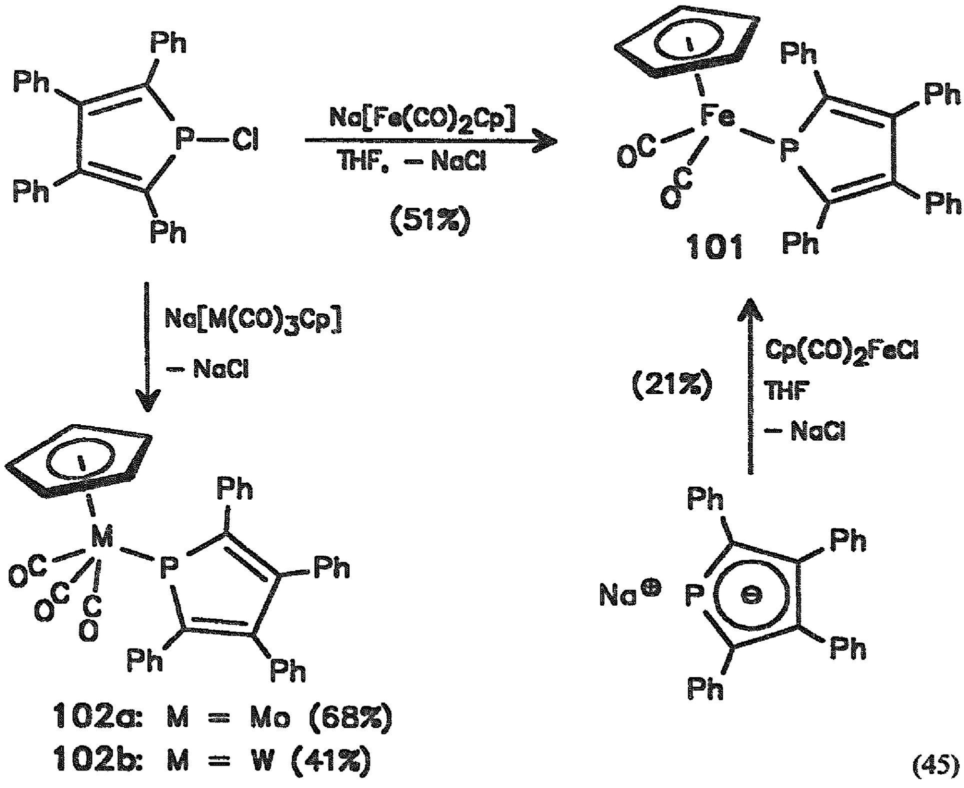
During the thermal transformation of the iron derivative **101** into phosphaferrocene **105** no intermediates analogous to **103** were detected (Eq. (47)) [103].

The metal–phosphorus bond in complexes **99a,b**, **101**, **102a,b** was easily cleaved by chlorine and bromine to give the corresponding 1-halogenophospholes and the complex transition metal halides [102].

The very interesting compound **107**, having the $(CO)_5Mn{-}PC_4H_2Me_2$ system as



(44)

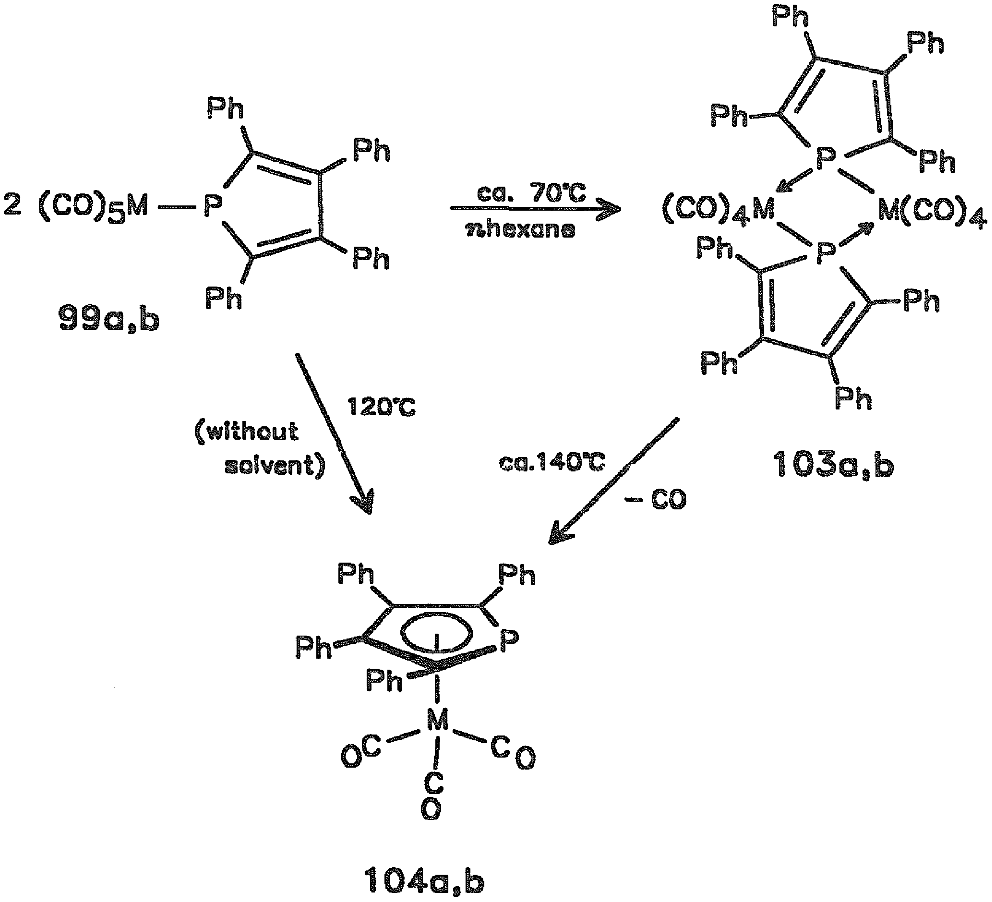


(45)

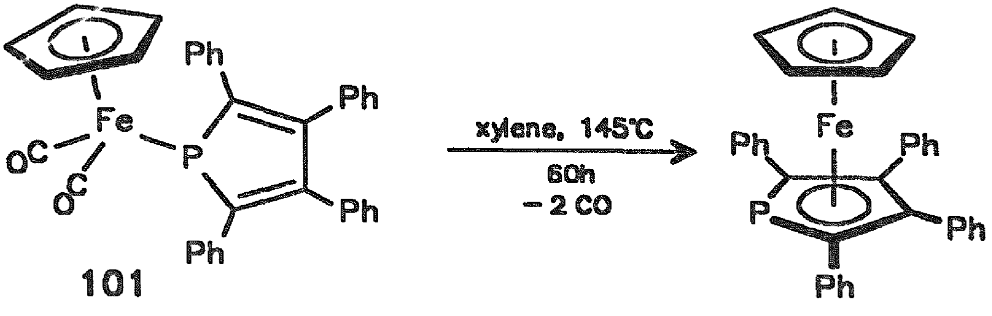
a six-electron donor towards a $Mn_2(CO)_7$ fragment, was obtained by irradiation of the dinuclear phosphole complex **106** in the presence of an excess of $Mn_2(CO)_{10}$ (Eq. (48)) [104].

Another account on the synthesis and reactivity of metal-functionalized phospholes appeared more recently [105]. The tungsten derivatives **109a,b** were easily obtained by reaction of the appropriate tungstate with 1-cyano-3,4-dimethylphosphole **108a** or 1-bromo-2,5-diphenylphosphole **108b** respectively (Eq. (49); diglyme = diglycol dimethylether).

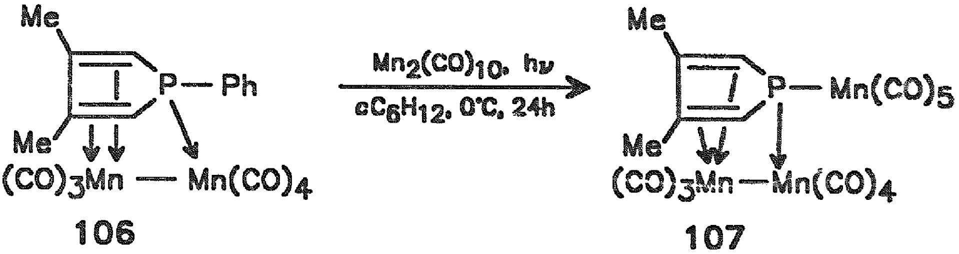
According to X-ray diffraction data, the phosphorus atom in **109a** (sum of angles



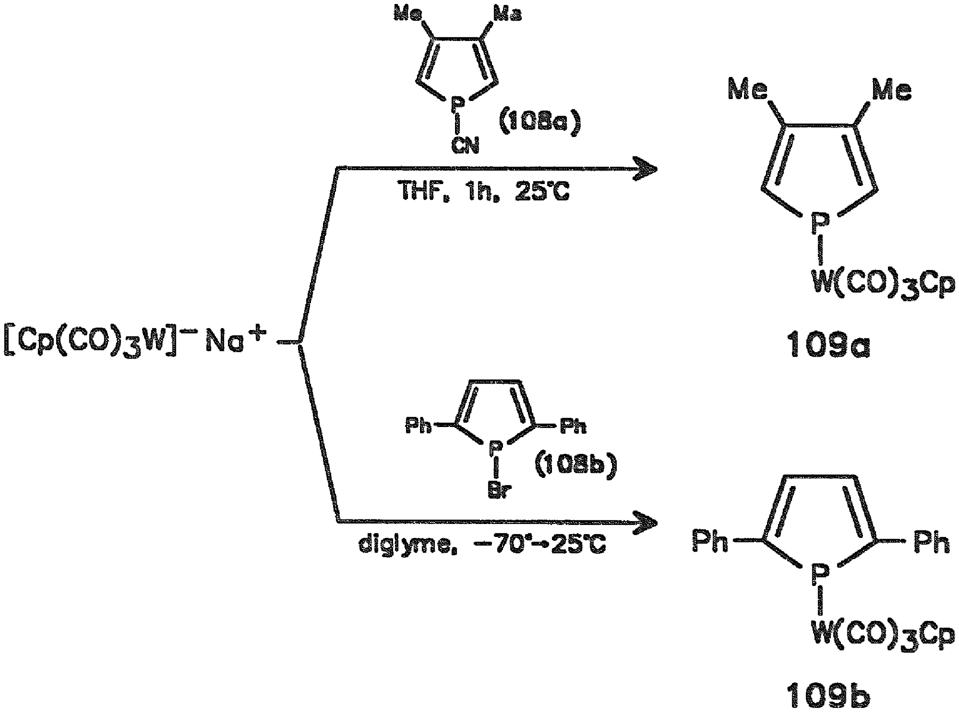
M = Mn, Re (46)



105 (47)



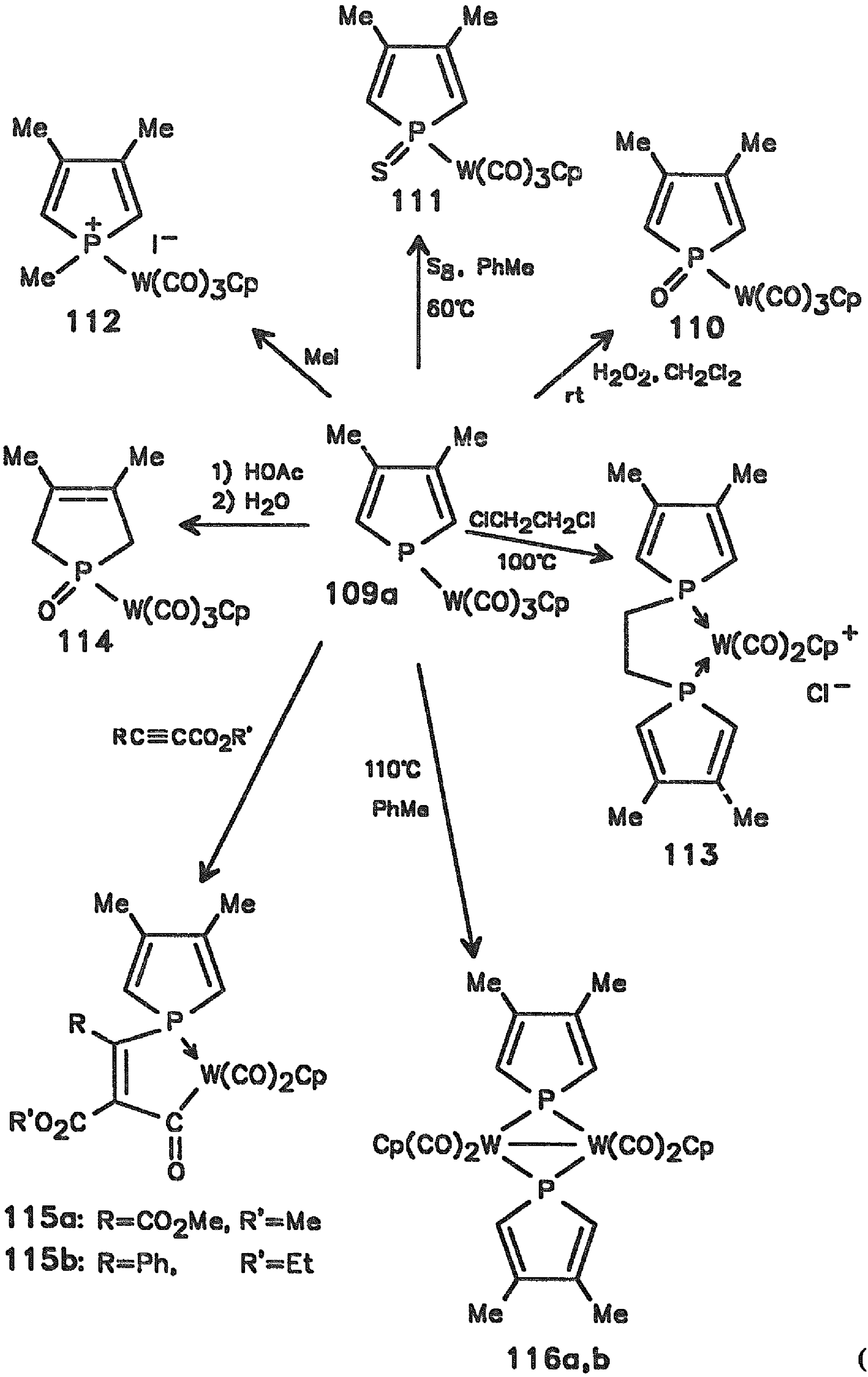
(48)



(49)

319.6°) is flattened in comparison with that in 1-benzylphosphole (sum of angles 302.7°), which indicates an increased degree of aromaticity in the metalated derivative. In contrast, the metalated ring in **109a** is less aromatic than the planar phospholide ion in Li[PC_4Me_4] [105].

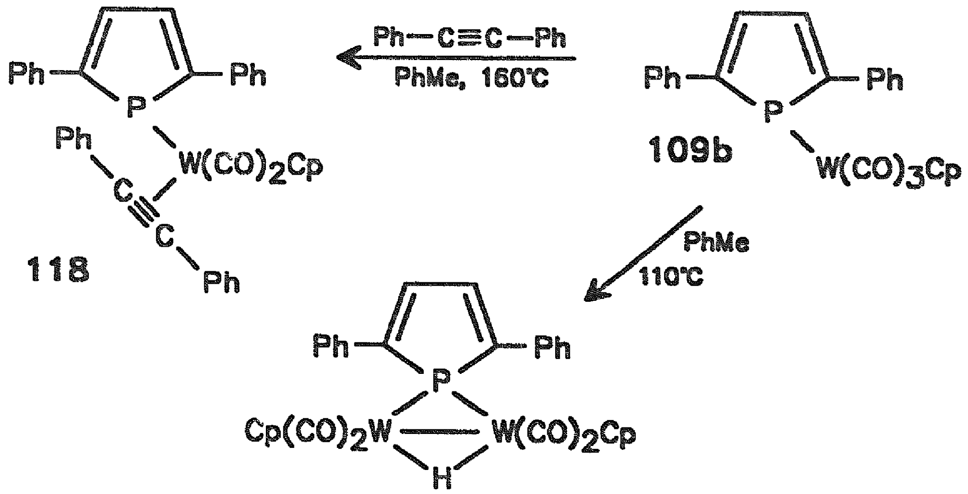
Metallophospholes **109a,b** display a rich chemistry (Eq. (50)). Oxidation and sulfurization proceeded with the toleration of the phosphorus–tungsten bond. Alkylation at phosphorus to give **112** and chelate **113** was effected by treatment with methyl iodide or 1,2-dichloroethane respectively. Protonation with acetic acid and subsequent chromatography afforded 2,5-dihydrophosphole-1-oxide **114**. A formal [2+3] cycloaddition to yield **115a,b** took place, when **109** was reacted with



111
S_8, PhMe
80°C
112
MeI
110
H_2O_2, CH_2Cl_2
rt
109a
1) HOAc
2) H_2O
114
$ClCH_2CH_2Cl$
100°C
113
$RC{\equiv}CCO_2R'$
110°C
PhMe
115a: R=CO_2Me, R'=Me
115b: R=Ph, R'=Et
116a,b

(50)

electron-deficient alkynes. In contrast to this, **109b** and tolane gave rise to displacement of two carbonyl ligands and the formation of **118** (Eq. (51)).

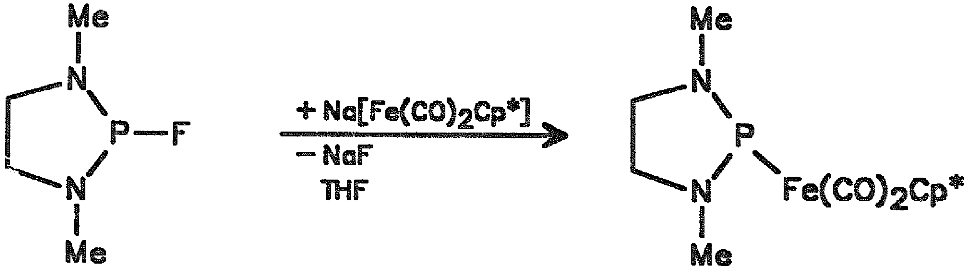


117 (51)

Different types of product were encountered when **109a** or **109b** were thermolyzed: the former metallophosphole gave an isomeric mixture of the dinuclear species **116** with two bridging phosphole ligands; **109b** was decomposed to the μ-phosphole (μ-hydrido) complex **117** featuring a W–W bond (Eq. (51)) [105].

5.1.2. P-metalated rings containing C, N and O atoms

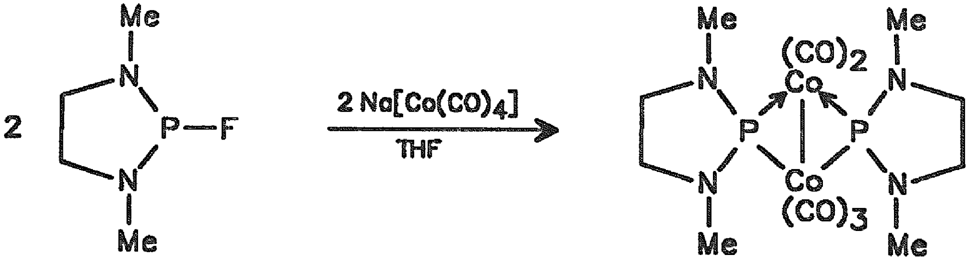
The synthesis of the red crystalline P-metallo-1,3-diaza-2-phospholanes **119** was achieved by combination of equal amounts of $\text{Me}{-}\overline{\text{NCH}_2\text{CH}_2\text{N(Me)P}}\text{F}$ and $\text{Na[Fe(CO)}_2\text{Cp*]}$ in THF (Eq. (52)).



119 (52)

According to an X-ray diffraction study, **119** features a puckered ring ligand with a pyramidal phosphorus atom and a typical Fe–P single bond [106].

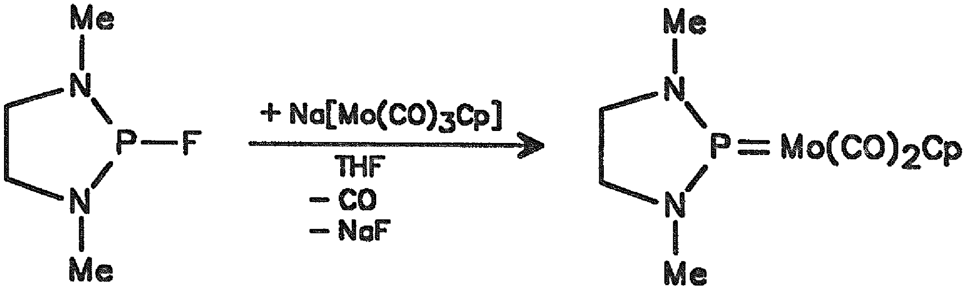
The synthetic strategy utilized in the preparation of **119** was extended into cobalt chemistry. Reaction of Me–$\overline{\text{N–CH}_2\text{CH}_2\text{–N(Me)P}}$F with Na[Co(CO)$_4$] in THF at 25°C resulted in the dinuclear complex **120**, where the bridging 1,3-diaza-2-phospholanyl ligand formally donates three electrons to the carbonylmetal skeleton (Eq. (53)) [107].



120

(53)

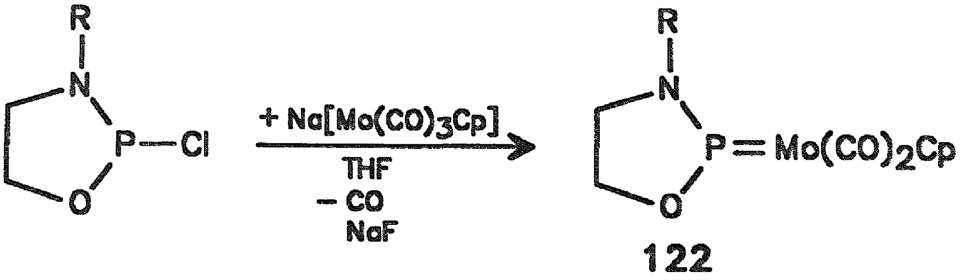
Complications were also encountered in molybdenum chemistry. The phosphorus atom of the $\overline{\text{P–N(Me)CH}_2\text{CH}_2\text{–N}}$Me ligand in **121**, which was obtained from Me–$\overline{\text{N–CH}_2\text{CH}_2\text{–N(Me)P}}$F and Na[Mo(CO)$_3$Cp], donates three electrons to the metal center (Eq. (54)). A hypothetical tricarbonylmolybdenum intermediate Cp(CO)$_3$ Mo–$\overline{\text{P–N(Me)CH}_2\text{CH}_2\text{–N}}$Me was not observed during the course of the reaction.



121 (54)

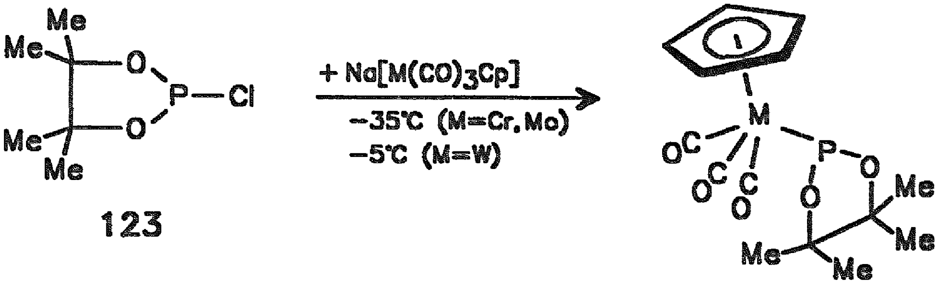
The X-ray determination of **121** showed the planar disposition of the molybdenum and all of the non-hydrogen atoms of the heterocycle, as well as metal phosphorus multiple bonding [108].

Analogously, azoxaphospholanes R–$\overline{\text{NCH}_2\text{CH}_2\text{OP}}$–Cl (R = Me, Et, ^{t}Bu, Ph) underwent heterolytic fission of the phosphorus–chlorine bond by Na[Mo(CO)$_3$Cp] to afford the cyclic phosphenium complexes **122** (Eq. (55)). No evidence for complexes of the type Cp(CO)$_3$Mo[$\overline{\text{POCH}_2\text{CH}_2\text{N}}$R] was obtained [109].



R = Me, Et, *t*Bu, Ph (55)

Metallodioxaphospholanes $Cp(CO)_3M{-}\overline{POCMe_2CMe_2{-}O}$ (M=Cr, Mo, W) (**124a–c**) with the σ-bonded metal atom in a pseudoaxial position at the pyramidally configured P atom were synthesized from 2-chloro-1,2,3-dioxaphospholane **123** and the salts $Na[M(CO)_3Cp]$ (M=Cr, Mo, W) (Eq. (56)) [109].



124(a: M=Cr; b: M=Mo; c: M=W)

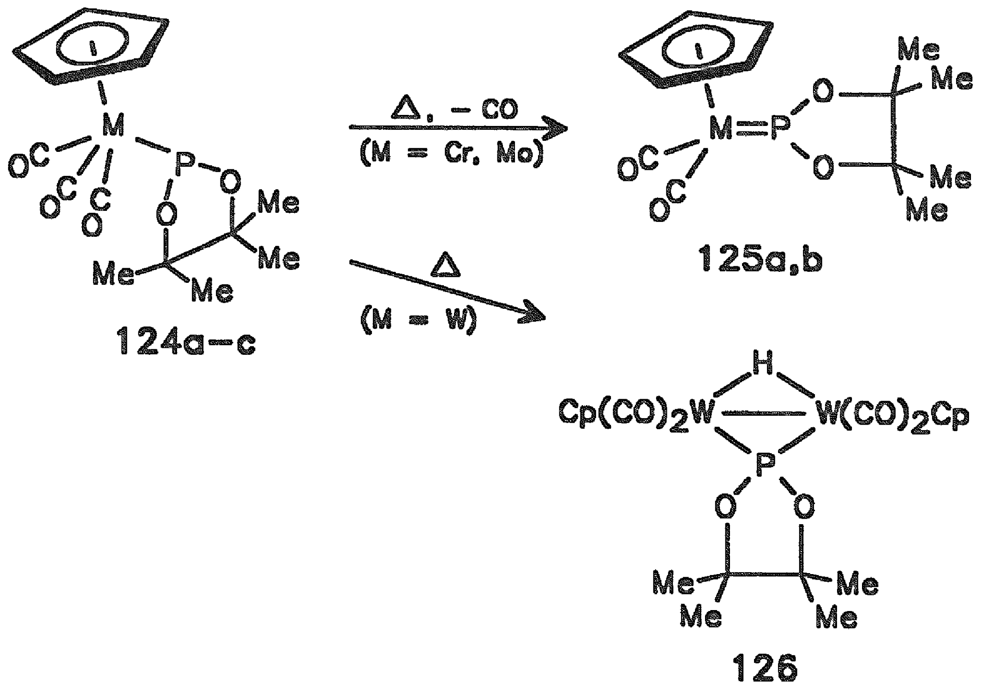
(56)

Decarbonylation of **124a,b** to the phosphenium complexes **125a,b** started at −5°C, whereas the transformation of **124c** into the dinuclear species **126** required temperatures of about 60°C (Eq. (57)) [110,111].

Compound **124c** was easily alkylated with methyl iodide or oxidized by sulfur, yielding **127** and **128** respectively. The replacement of CO by trimethyl phosphite afforded **129**, which rapidly rearranged to **130** (Eq. (58)) [112].

Five-membered heterocycles with metal-functionalized λ^5-phosphorus atoms, were also available by the [1+4] cheletropic cycloaddition of α,β-unsaturated aldehydes, ketones [113,114] or dialkyl azodicarboxylates [115,116] to metallodiphosphenes.

P-metallodihydro-1,2-λ^5-oxaphospholes **133a–e** (Eq. (59)) were generated by reaction of $Cp^*(CO)_2Fe{-}P{=}P{-}Mes^*$ and $Cp^*(CO)_2Ru{-}P{=}P{-}Mes^*$ with a slight excess of acrolein (**132a**), methacrolein (**132b**) or buten-3-one-2 (**132c**) in benzene at 20°C



(57)

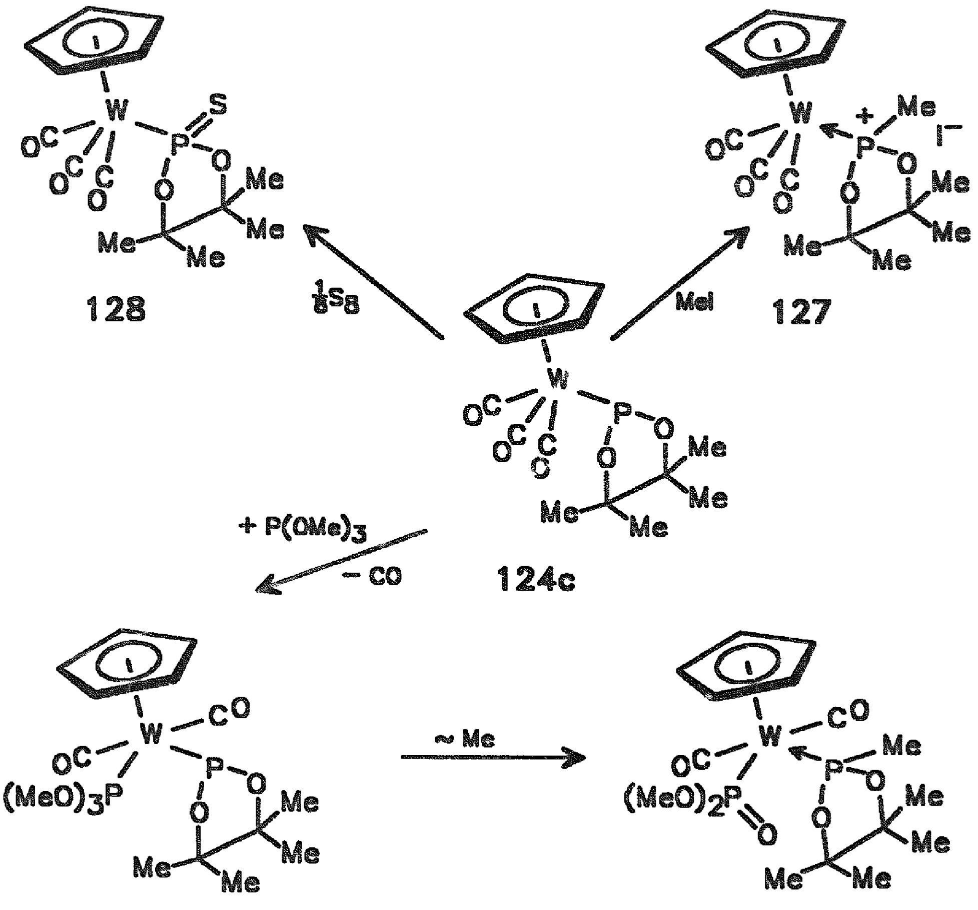
within 2 h. The reaction of **19a** with crotonaldehyde to give cycloadduct **133d**, however, required a temperature of about 50°C and a reaction time of about 10 days.

The [1+4] cheletropic cycloaddition between metallodiphosphene **19a** and the azodicarboxylates $RO_2C{-}N{=}N{-}CO_2R$ **134a–c** or the diamide $H_{10}C_5N{-}C(O){-}N{=}N{-}C(O)NC_5H_{10}$ (**134d**) afforded the first metallo-1,2-dihydro-λ^5-oxadiazaphospholes **135a–d** as brown solids in 45–80% yield (Eq. (60)) [115,116].

Very interesting P-metallo-λ^5,σ^5-phosphoranes were synthesized from phosphoranide anions and suitable complex metal halides.

Deprotonation of hydridophosphorane **136** was effected by KH in THF (Eq. (61)). Replacement of the halide in the complexes $Cp(CO)_2FeI$, $(Et_3P)AuBr$ or $Re(CO)_5Br$ by anion **137** afforded the P-metallo-λ^5,σ^5-phosphoranes **138**, **139**, **140** in high yields [117,118]. The stability of these hypervalent species was markedly enhanced by equatorial groups, which are able to stabilize the positive charge at the phosphorus atom. Electronegative substituents in the axial positions effectively stabilized the negative charge at these positions of the three-center four-electron bond.

Compared with the situation in hydridophosphorane **136**, the P–O bonds in **139** were markedly lengthened, which was rationalized by an overlap of filled metal orbitals with the vacant antibonding orbital of the three-center four-electron bond [117].

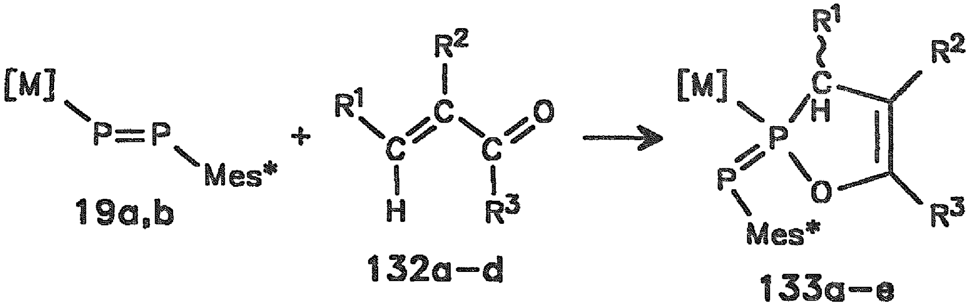


(58)

Metallo-λ^5,σ^5-phosphorane **143** was available by treatment of anion **142** with $Cp(CO)_2FeCl$ in THF at −78°C (76% yield). This process involved a hydrogen transfer in anion **142** from phosphorus to nitrogen (Eq. (62)) [119]. The hypervalent product was also formed, when the cationic complex $[Cp(CO)_2Fe\{P(OPh)_3\}]PF_6$ (**144**) was added to the reaction mixture obtained from two equivalents of *o*-$HOC_6H_4NH_2$ and one equivalent of *n*-butyllithium in THF at −78°C [119].

The Fe–P bond was already present in precursor **144**. The transformation of **144** into product **143** was made plausible by a series of association, dissociation and deprotonation steps [119].

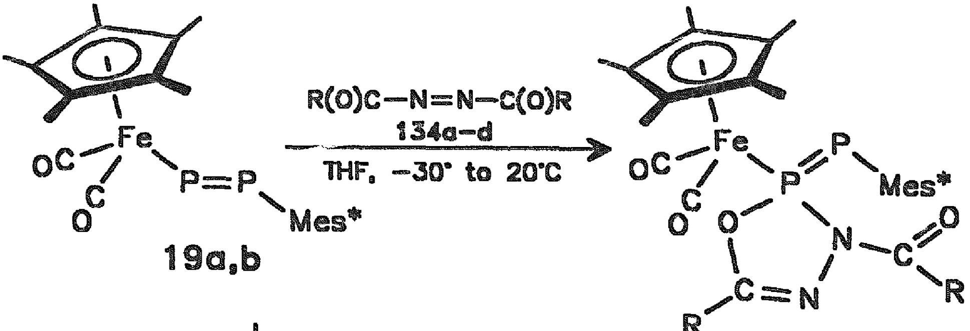
An inverse strategy was followed in the preparation of the 2-metallo-2,2-spirobi(1,3,2-benzodioxaphospholes) **146a,b**, which resulted as yellow–orange solids from 2-chloro-2,2′-spiro(1,3,2-benzodioxaphosphole) **145** and $Na[Mn(CO)_5]$ [120] or $Na[Co(CO)_3(PPh_3)]$ respectively (Eq. (63)) [121].



[M] = Cp*$(CO)_2$M

132,133	M	R^1	R^2	R^3
a	Fe	H	H	H
b	Fe	H	Me	H
c	Fe	H	H	Me
d	Fe	Me	H	H
e	Ru	H	H	H

(59)



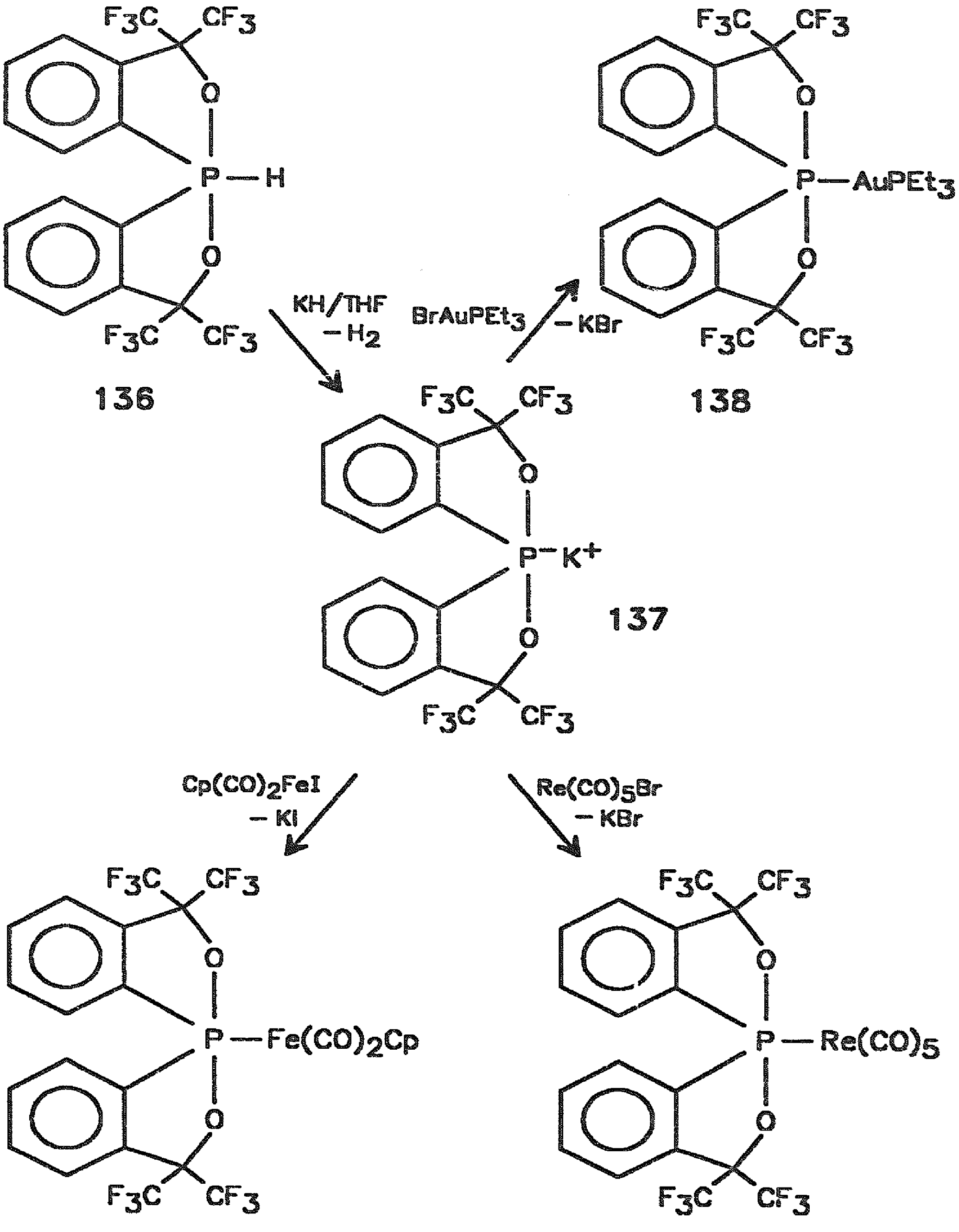
134,135	R
a	OEt
b	O*t*Bu
c	OCH_2Ph
d	NC_5H_{10}

135a–d

(60)

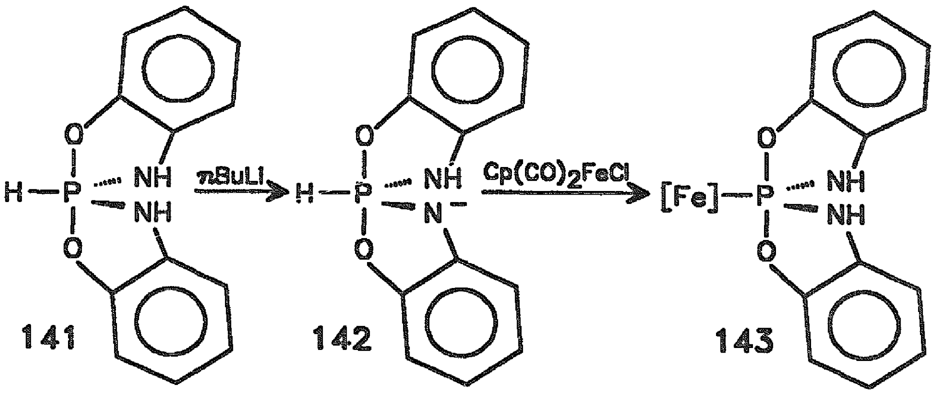
Molecule **146b** is composed of two trigonal-bipyramids which are fused at an axial position of the cobalt atom and an equatorial position about the pentacoordinate phosphorus center [121].

The bicyclic structure of **146a** was degraded by hydrolysis in THF or ether to

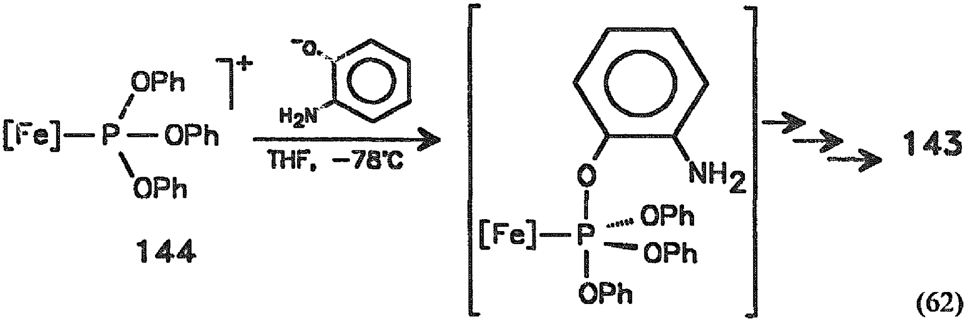


F3C
CF3
O
P — H
O
F3C
CF3
136
KH/THF
− H2
BrAuPEt3
− KBr
F3C
CF3
O
P — AuPEt3
O
F3C
CF3
138
F3C
CF3
O
P⁻K⁺
O
F3C
CF3
137
Cp(CO)2FeI
− KI
Re(CO)5Br
− KBr
F3C
CF3
O
P — Fe(CO)2Cp
O
F3C
CF3
F3C
CF3
O
P — Re(CO)5
O
F3C
CF3

139 **140** (61)



[Fe] = $Cp(CO)_2Fe$



(62)

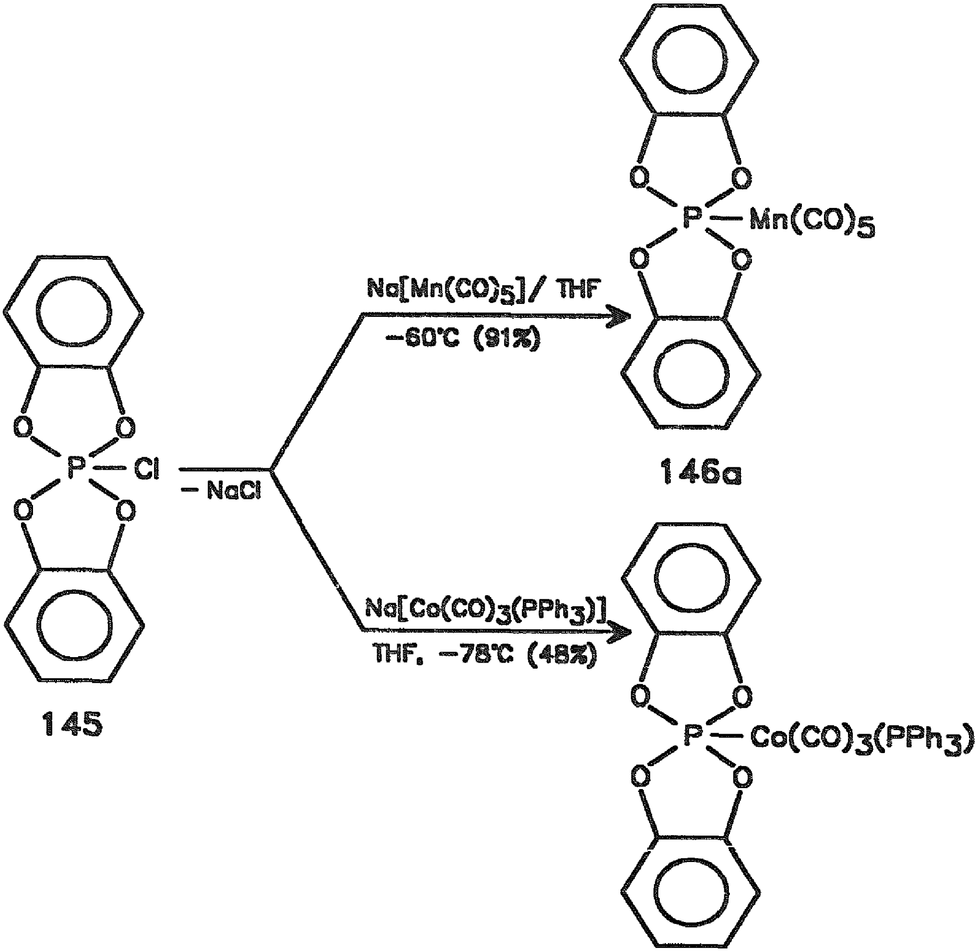
give catechole, metallophosphonate **147** and the 2-metallo-1,3,2-benzodioxaphosphole-2-oxide **148** [122,123]. It was further demonstrated that a THF solution of **147** was quantitatively converted into **148** and catechole (Eq. (64)).

Hydrolysis of **146b** also occurred in the solid state when the compound was exposed to air for a period of 7–10 days.

In contrast to compounds **138**, **139**, **140**, **143**, **146a,b**, where spiro-phosphoranes were functioning as monodentate ligands toward transition metal fragments, the phosphorane ligands in compounds **150** and **151** displayed a bidentate mode of coordination.

Complex **150** was obtained as a yellow crystalline solid upon deprotonation of cation **149a** with methyl lithium at −20°C. The compound rearranged to deep red **151** upon heating for 4 h in THF at 60°C (Eq. (65)) [124]. The latter species was also accessible by deprotonation of salt **149b** with methyl lithium in THF at 60°C [125].

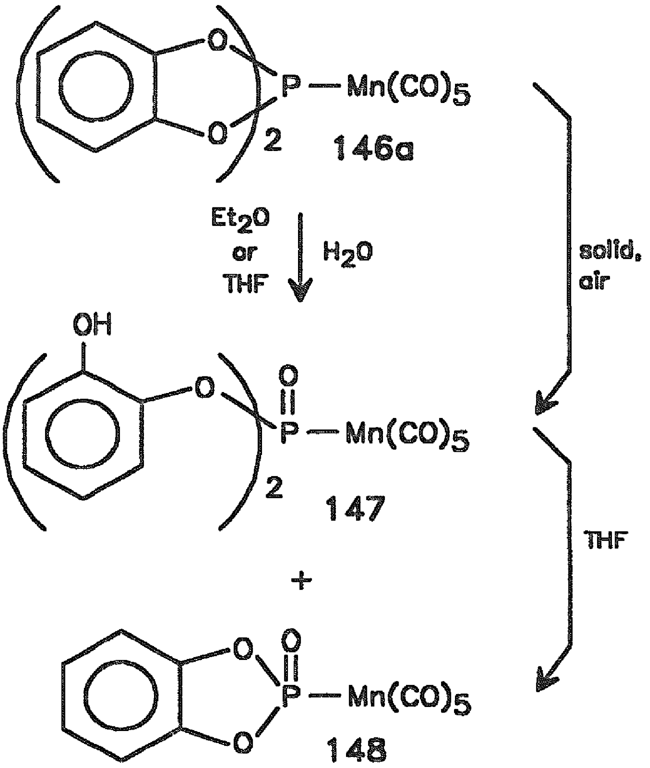
In line with X-ray structure determinations, both isomers **150** and **151** were described as λ^5,σ^5-phosphoranes containing the $Cp(CO)_2Mo$ functionality in an equatorial position of the trigonal bipyramid. In **150**, further coordination to an apical nitrogen atom completes the 18 valence electron shell of the metal. It is unusual that the more electronegative oxygen atoms are located at equatorial posi-



146b (63)

tions of the trigonal bipyramid, whereas a phenyl substituent is axially bound. These peculiarities were absent in the high-temperature isomer **151** with both oxygen atoms in apical positions of the bipyramid, providing an additional oxygen to molybdenum donation.

In some cases, metallophosphoranes were also obtained from tetracyclic cyclenphosphorane (the heterocycle 1,4,7,10-tetraazacyclododecane has been termed 'cyclen') and dinuclear metal carbonyl derivatives [126]. When cyclenPH was allowed to react with $Co_2(CO)_8$ in a 2 : 1 molar ratio, covalent **152** and ionic **153** were produced at low temperature (−78°C to 20°C). Upon heating to 55°C in THF solution **153** spontaneously lost H_2 and CO to give **152**. The corresponding reaction



(64)

of cyclenPH with $[MoCp(CO)_3]_2$ yielded analogous products **154** and **155**, although refluxing THF was required (Eq. (66)).

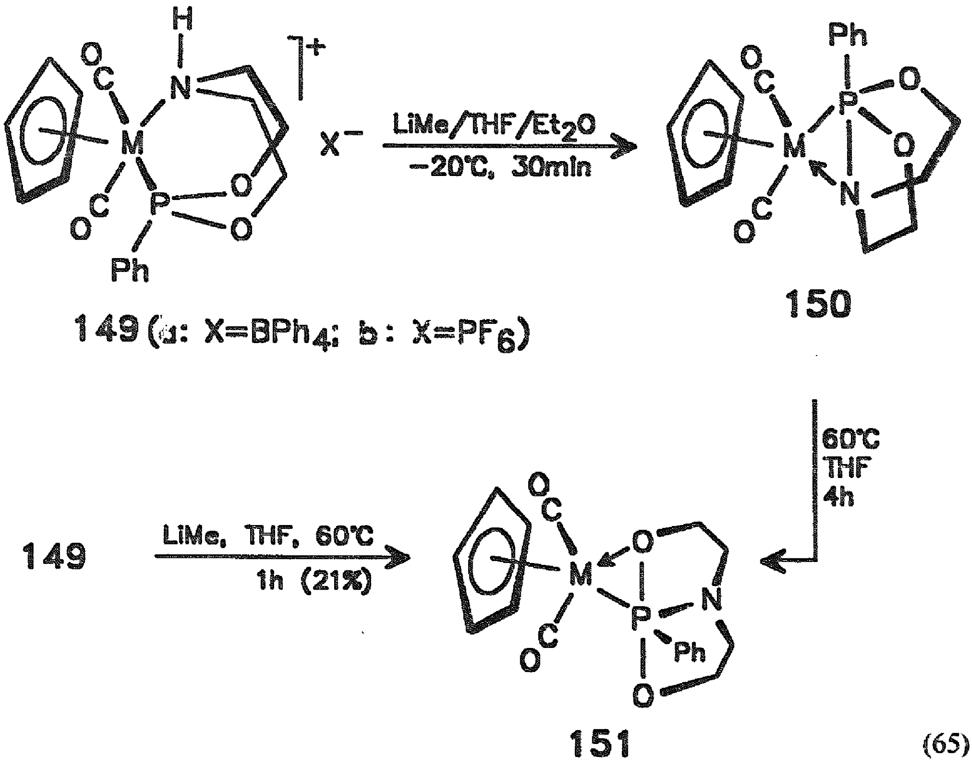
However, the attempted thermolysis of salt **155** to give covalent **154** failed [126]. No complexes comparable with **152** or **154** were available from the reactions of cyclenPH with $Mn_2(CO)_{10}$ or $[Cp(CO)_2Fe]_2$ [126]. The reaction of cyclenPH with *cis*-$Cl_2Pt(PPh_3)_2$ in a 1 : 1 molar ratio in THF afforded high yields of the two platinum complexes **156** and **157** (Eq. (67)) [127].

The very interesting Rh(III) phosphoranide complex **159** resulted from a formal three-fragment oxidative addition of dichloromethane to the rhodium(I) complex **158**. Precursor **158** was synthesized by treating $(Ph_3P)_3RhCl$ with cyclenPH in THF (Eq. (68)) [128].

More chemistry of metal derivatives of cyclenPH is described in a series of papers by Lattman and coworkers [129–131].

5.2. *Five-membered rings with three phosphorus atoms*

In addition to a series of η^5-1,2,4-triphospholyl complexes, a few representatives with the heterocyclic ligand in an η^1 fashion are known. Treatment of *cis*-$(PEt_3)_2MCl_2$ (M = Pd, Pt) with $[Li(DME)_3][P_3C_2R_2]$ (R = ^{t}Bu, ad; ad =



(65)

1-adamantyl) afforded the yellow platinum derivatives **160b,c** and the red palladium complex **160a**. Similarly, *cis*-$(Ph_3P)_2PtI_2$ was transformed into *trans*-$(Ph_3P)_2(I)Pt[P_3C_2(^tBu)_2]$ (**161**) [132,133].

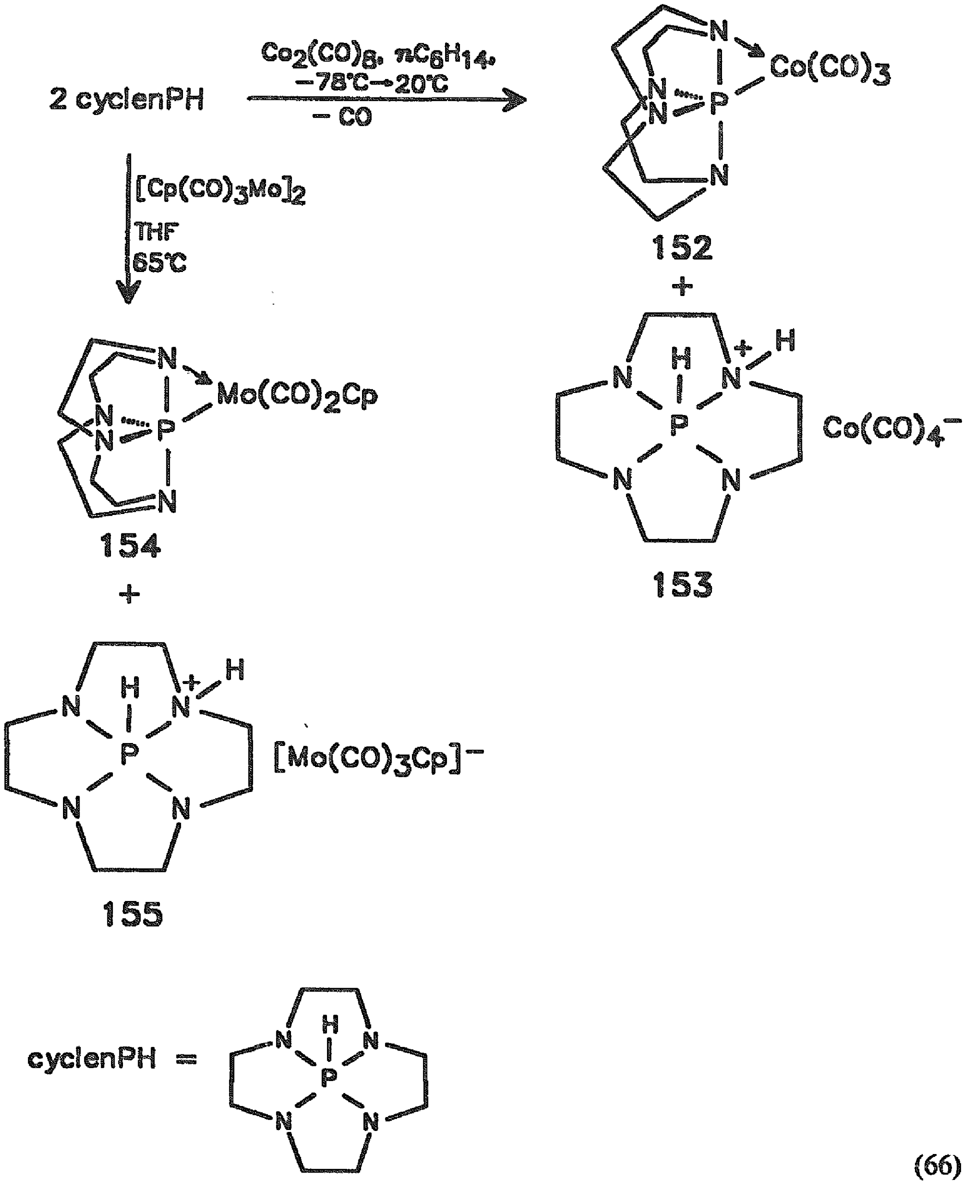
The molecular structures of **160b** and **161** showed that in each case the heterocycle was attached to the metal atom by one of the two adjacent phosphorus atoms. The ring ligand was perfectly flat and the Pt and halogen atoms were located in the same plane.

When a 1 : 2 molar ratio of *cis*-$(PEt_3)_2MCl_2$ and $[Li(DME)_3][P_3C_2(^tBu)_2]$ was employed in the reaction, the orange platinum complex **162a** and the deep red palladium analog **162b**, exhibiting two η^1-1,2,4-triphospholyl ligands, were obtained (Eq. (69)).

In contrast to the situation in **161**, the molecular structure of **162a** revealed a tetrahedral distortion of the metalated phosphorus atoms (sum of angles around P equal to 348°). The planarity of the ring ligands, however, was preserved [133].

The unprecedented rhodium(III) hydride **163**, exhibiting an η^1-ligated 1,2,4-triphospholyl ring, was synthesized by treatment of a mixture of $Na[P_3C_2(^tBu)_2]$ and $Na[P_2C_3(^tBu)_3]$ with $Cp^*Rh(PPh_3)Cl_2$ in dimethoxyethane at room temperature (Eq. (70)) [134].

In **163** the Rh atom deviates by 0.564 Å from the best plane containing the heterocycle. The sum of bond angles about the metalated P atom was determined to be 357.1° [134].



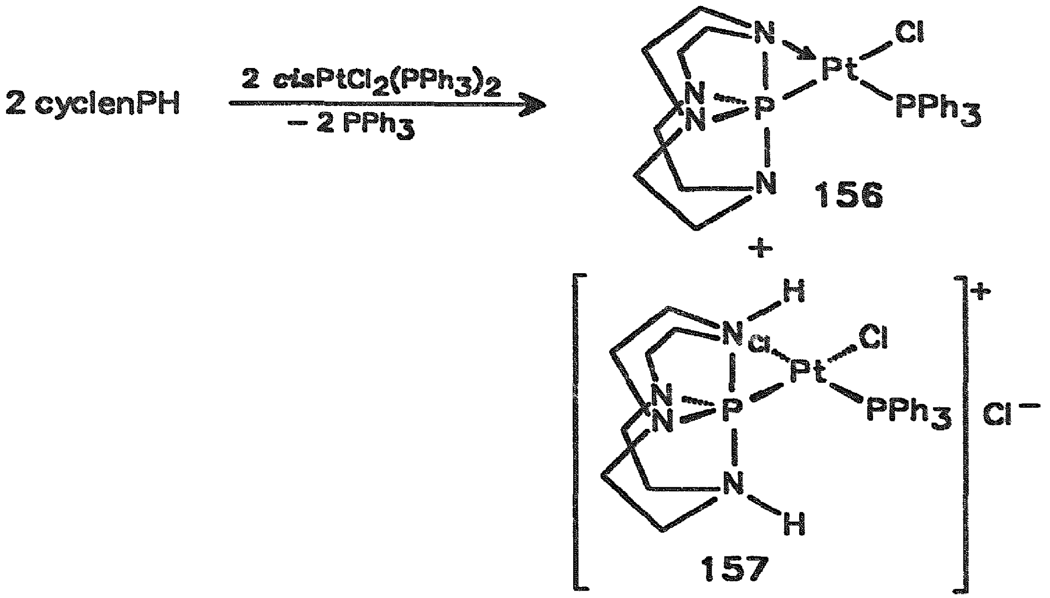
(66)

6. Six-membered rings

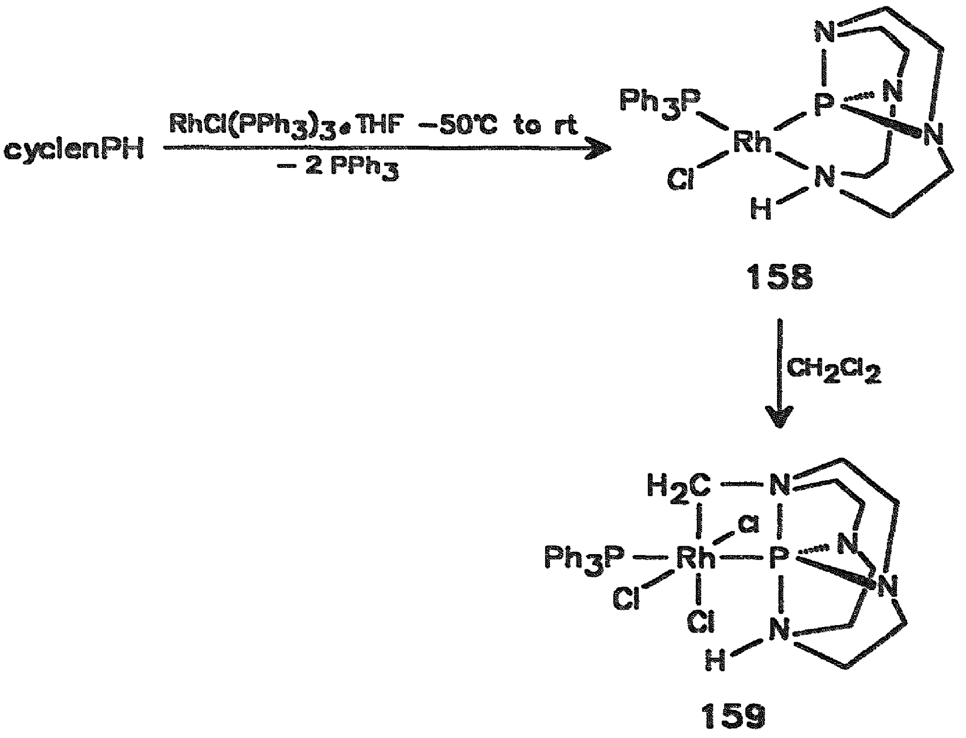
6.1. Six membered rings with one phosphorus atom

6.1.1. P-metallo-λ^5-phosphinines

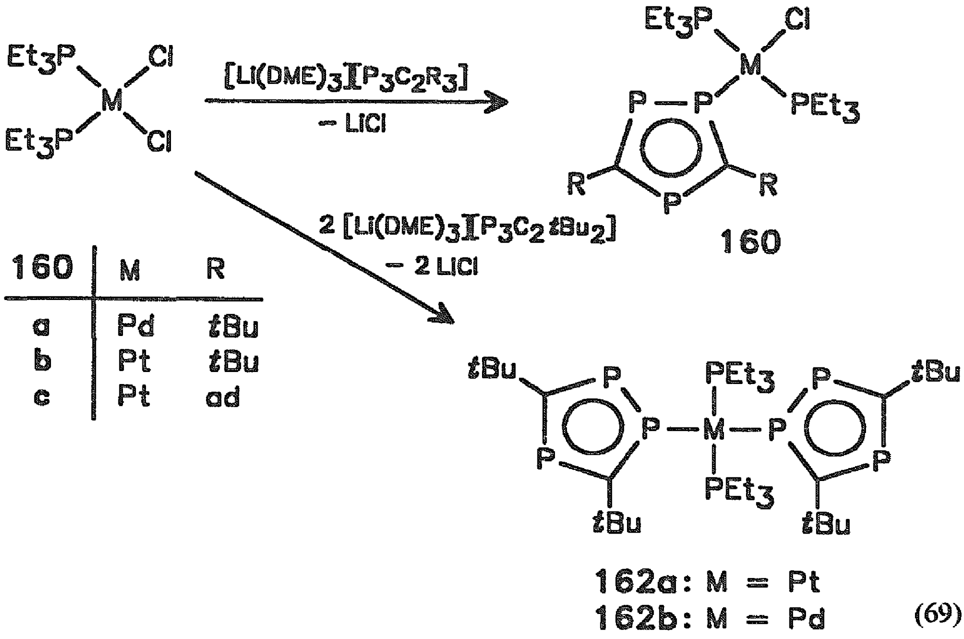
λ^4-Phosphinine anions are highly ambident species. Whereas their treatment with anhydrous $FeCl_2$ gave 'open-sandwich' complexes of the type **164**, reaction of lithium


2 cyclenPH
2 cisPtCl2(PPh3)2
– 2 PPh3
N
Pt
Cl
PPh3
N
N
P
N
156
+
H
N
Cl
Pt
Cl
N
N
P
PPh3
Cl–
N
H
157
+

(67)


cyclenPH
RhCl(PPh3)3•THF –50°C to rt
– 2 PPh3
Ph3P
Rh
Cl
N
P
N
N
N
H
158
CH2Cl2
H2C
N
Cl
Ph3P
Rh
P
N
N
Cl
Cl
N
H
159

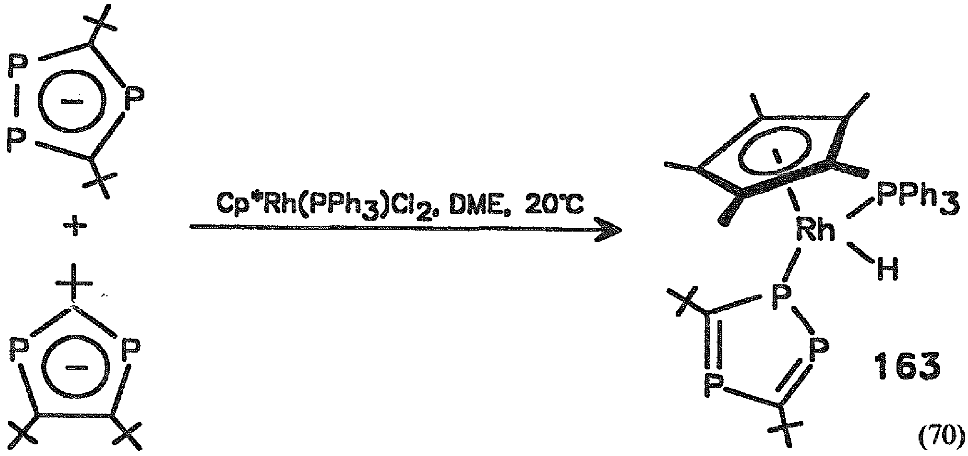
(68)



160	M	R
a	Pd	tBu
b	Pt	tBu
c	Pt	ad

160

162a: M = Pt
162b: M = Pd (69)

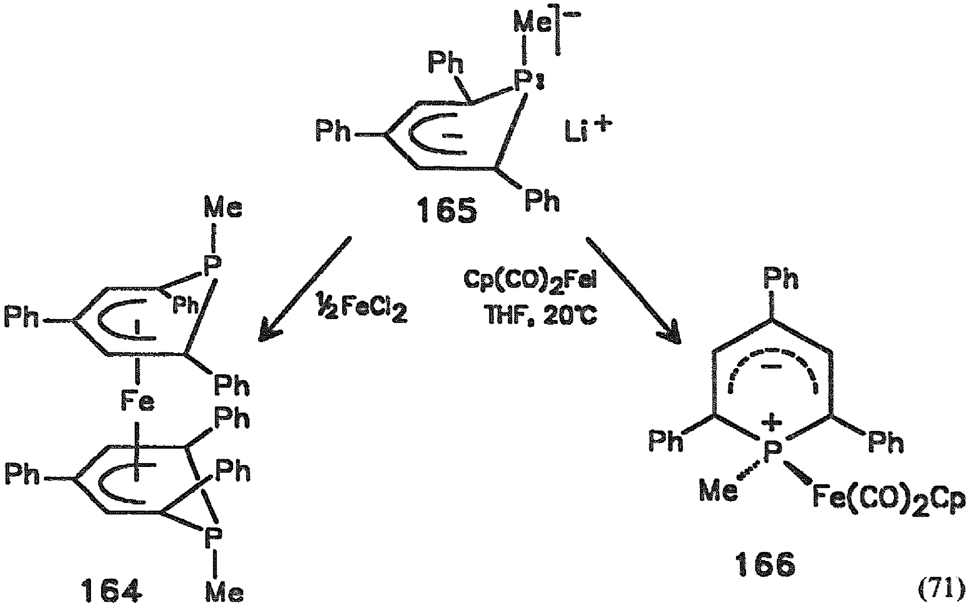


163

(70)

derivative **165** with $Cp(CO)_2FeI$ cleanly led to the formation of the P-metallo-λ^5-phosphinine **166** (Eq. (71)) [135].

Small amounts of the P-metallo-λ^5-phosphinines **169a,b** were isolated from the reaction of equimolar amounts of $Cp^*(CO)_2Fe{-}P{=}C(NMe_2)_2$ (**61a**) and methyl propiolate. An excess of propiolate did not improve the yield of **169a,b**. It was assumed, that the formation of **169a,b** was initiated by [2+2] cycloaddition, which was followed by a [2+2] cycloreversion to give 1-phosphabutadiene **167**. Similar



(71)

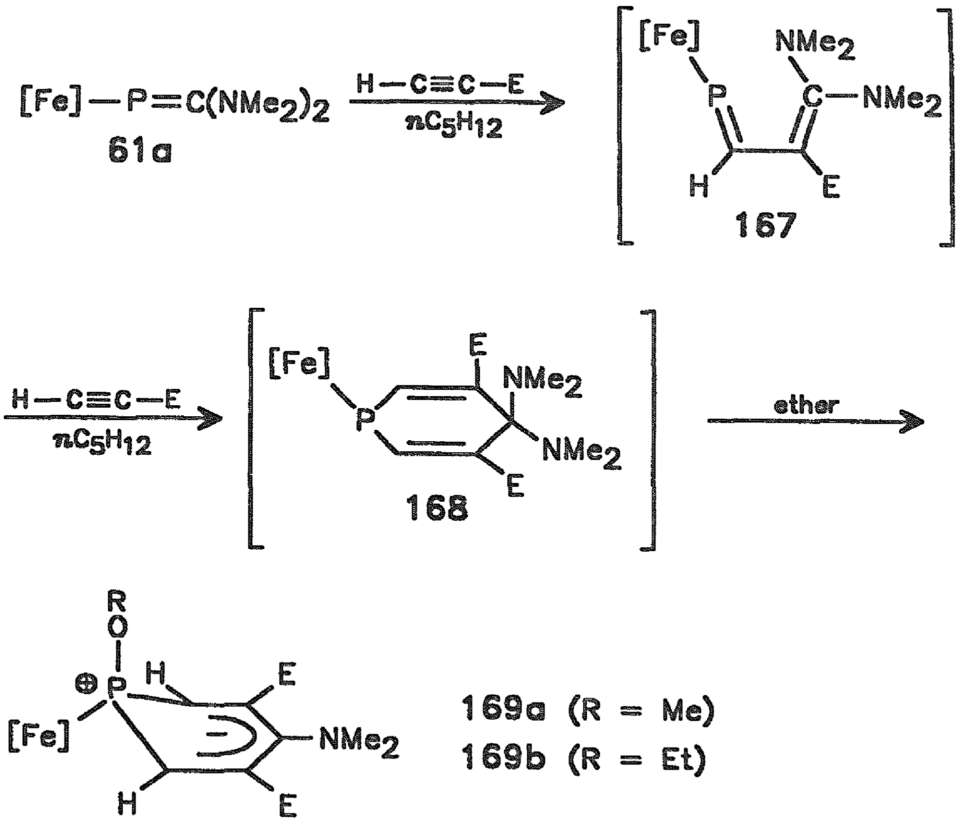
observations were made in the reactions of **61a** with dimethyl acetylene-dicarboxylate (Eq. (28)) and methyl butynoate (Eq. (27)). The subsequent [2+4] cycloaddition between **167** and the alkyne afforded P-metallo-1,4-dihydrophosphinine **168**, which in ethereal solution was converted to **169a,b** (Eq. (72)). The mechanism of the final step and the sources of the alkoxy groups are still unclear. An X-ray study confirmed the identity of **169a** as 1-metallo-λ^5-phosphinine with the bulky transition metal complex fragment in an equatorial position of the ring ligand. The phosphorus atom is displaced by 0.176 Å from the best plane defined by the five ring carbon atoms [84,136].

6.1.2. P-metallo-1,2-dihydrophosphinines

Reaction of $Os_3H_2(CO)_{10}$ with phosphinine in refluxing cyclohexane gave a yellow mixture of clusters **170** (20%) and **171** (30%). The generation of **171** implied the coupling of two molecules of phosphinine in the coordination sphere of the osmium atoms. The resulting ligand may be considered as a 1-metallo-6-phosphino-1,2-dihydrophosphinine. Only its metalated phosphorus atom donates to a second osmium center (Eq. (73)) [137].

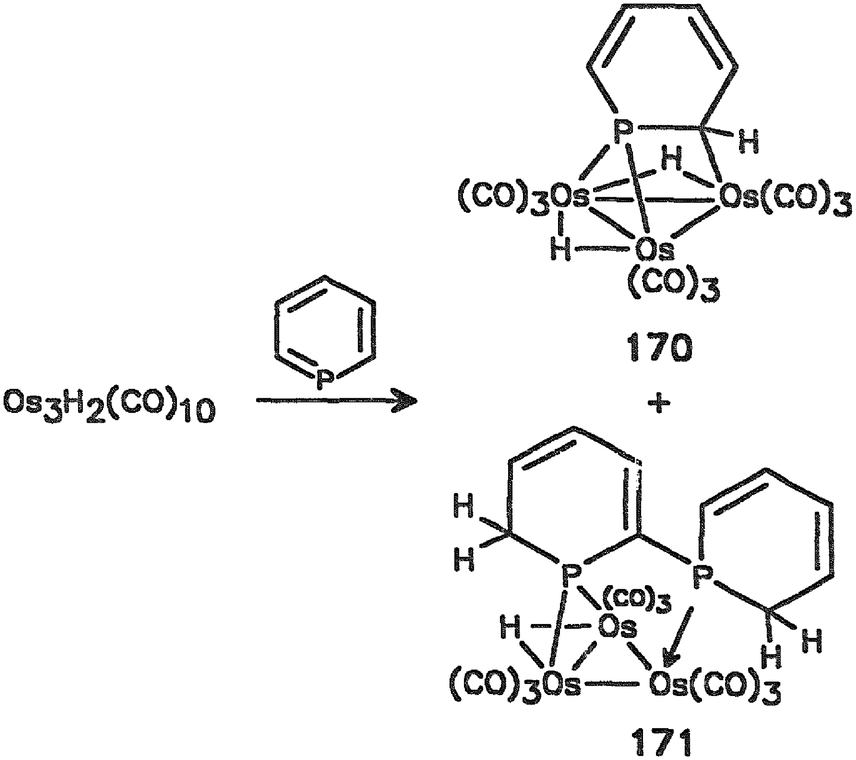
6.1.3. P-metalated rings containing C, N and O atoms

Two-fold dehydrochlorination of the dinuclear complex **172**, which was accessible by action of $CpMo(CO)_3H$ with 3,9-dichloro-2,4,8,10,3,9-tetraoxadiphosphaspiro[5.5]undecane, gave compound **173**. The two six-membered rings were metalated at phosphorus in a phosphenium-type fashion (Eq. (74)) [111].



[Fe] = Cp*(CO)$_2$Fe, E = CO$_2$Me (72)

In solution, cyclamphosphorane **174a** (cyclam = 1,5,8,12-tetraazacyclotetradecane) constitutes an equilibrium with its open tautomer **174b** in a ratio of 80 : 20 (Eq. (75)). One equivalent of carbon monoxide was evolved when a THF solution of CpMo(CO)$_3$Cl and **174** was stirred at 20°C, and a 3 : 1 mixture of complexes **175a** and **175b** was obtained. These complexes contain the mono- or bidentate organophosphorus ligand in the open form. The same reaction, when carried out with CpW(CO)$_3$Cl, only afforded **176** as the neutral analog of **175a**. The cationic complexes **177** and **178** were quantitatively synthesized from **175** and **176** respectively, by treatment with NaBPh$_4$. Phosphoranide complexes **179** and **180** resulted when cations **177** and **178** were deprotonated by means of methyl lithium (Eq. (76)) [138].



(73)

6.2. *Six-membered rings with three phosphorus atoms*

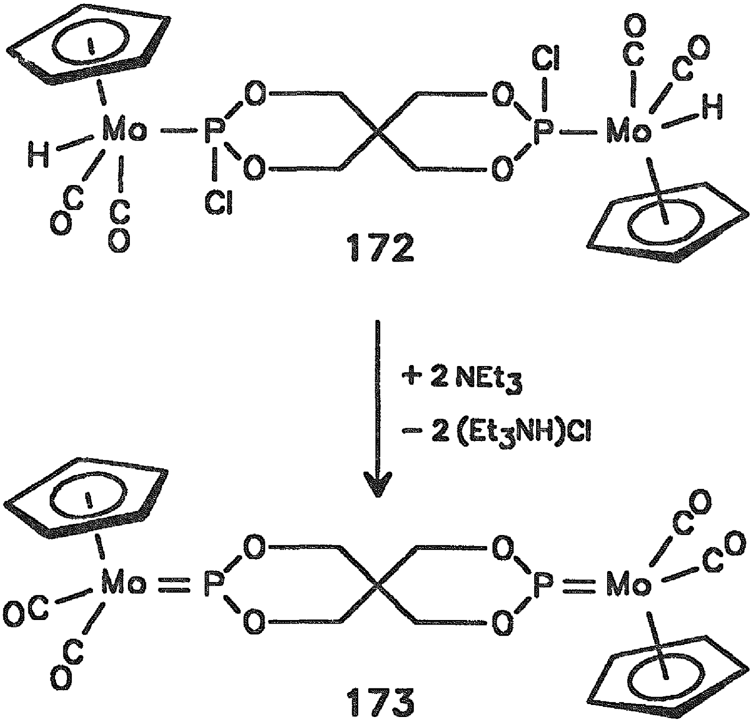
6.2.1. *P-metallocyclotriphosphazenes*

P-metallocyclotriphosphazenes were studied as potential precursors of new materials, which combine the properties of polyphosphazenes with those of organometallic complexes. Reactions of transition-metal-based nucleophiles with halogenated cyclotriphophazenes seemed to be a viable route to this target.

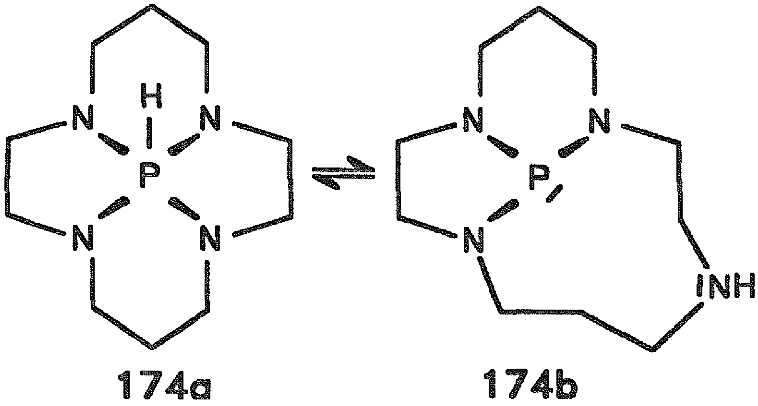
The first examples of this kind of transformation involved the interactions of $K[Fe(CO)_2Cp]$ and $K[Ru(CO)_2Cp]$ with $(NPF_2)_3$ to give the monometalated species **181** and **182** respectively [139–141]. Further reaction of ferriocyclotriphosphazene **181** with an excess of the ferrate resulted in the substitution of the geminal fluorine atom with formation of **183** [140]. Treatment of rutheniocyclotriphosphazene **182** with the ferrate afforded the mixed geminally dimetalated compound **184**. Both compounds **183** and **184** were photolabile and, when irradiated, gave rise to the generation of dinuclear complexes **185** and **186** (Eq. (77)).

Upon exposure to an excess of K[Ru(CO)Cp] rutheniocyclotriphosphazene **182** was directly converted into the analogous complex **187** [141] (Eq. (78)).

The mode of coordination in **185**, **186**, **187** may be rationalized as that of a 1-λ^3-, 3-λ^5-, 5-λ^5-cyclotriphosphazene containing a trivalent, dicoordinate phos-



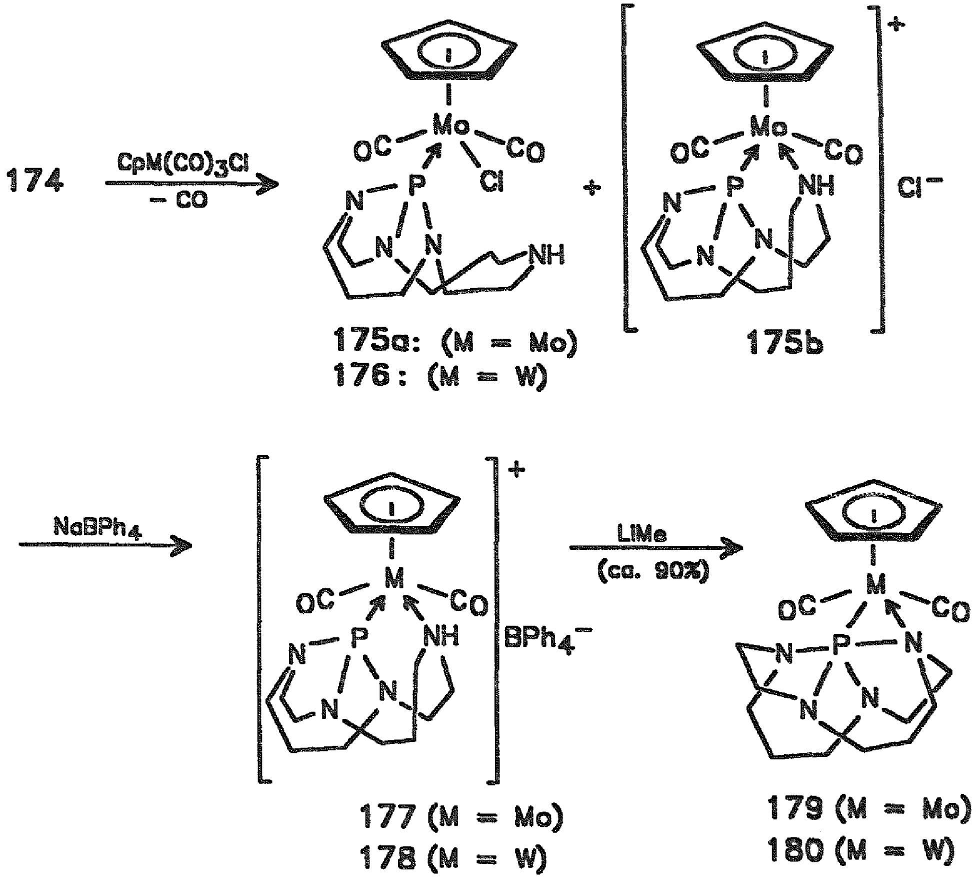
(74)



(75)

phorus atom bridging two metal centers in $[Cp_2M_2(CO)_3]$ by virtue of its lone pair of electrons. Formally, it replaces a bridging carbonyl ligand in the parent molecules $[Cp_2M_2(CO)_4]$.

Complexes **183**, **184**, **185**, **186**, **187** are structurally closely related, and the discrimination between doubly metalated pentavalent phosphorus atoms and trivalent phosphorus atoms in a μ_2-bridging situation is rather 'semantical' than real. Here,

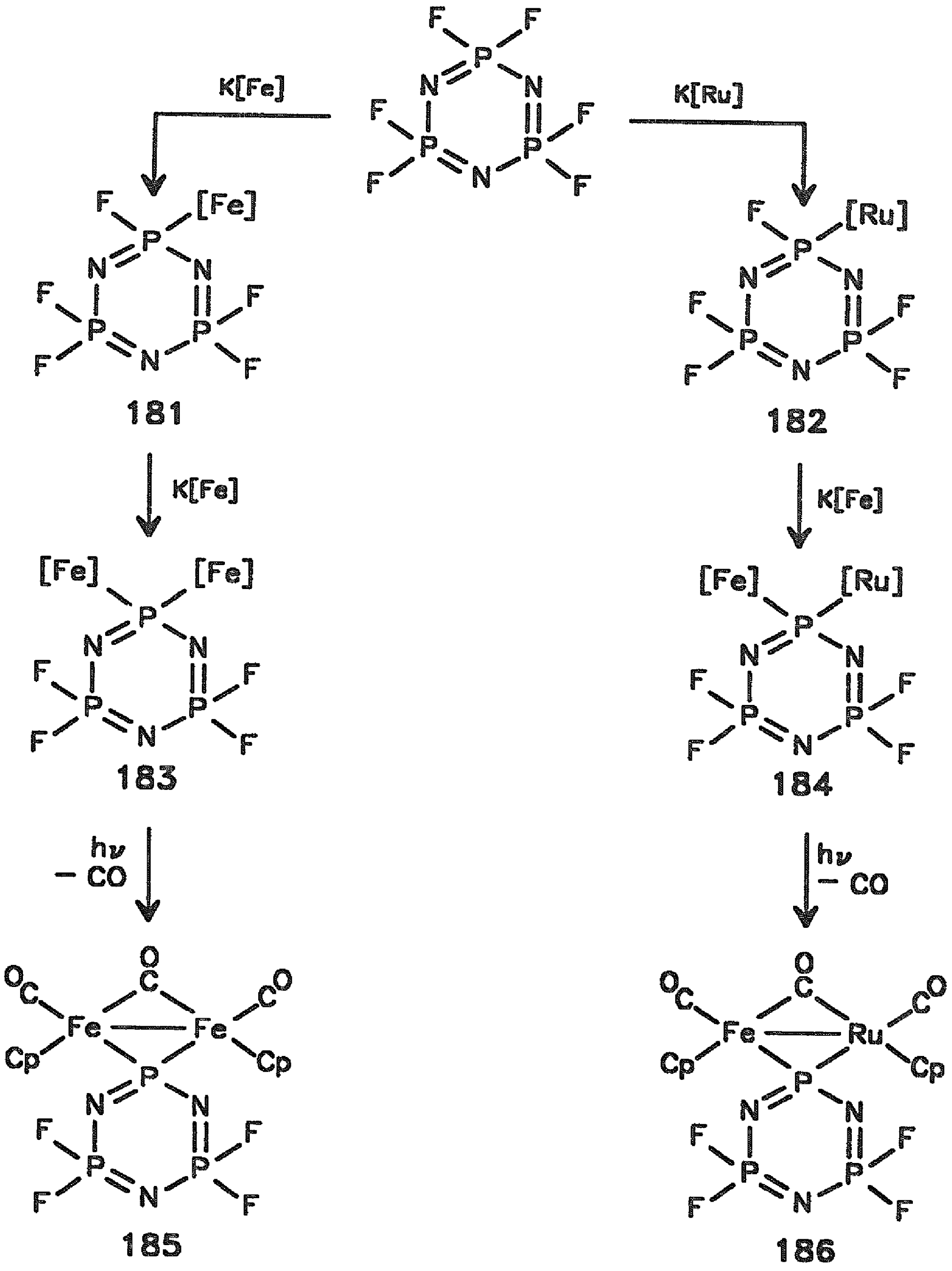


(76)

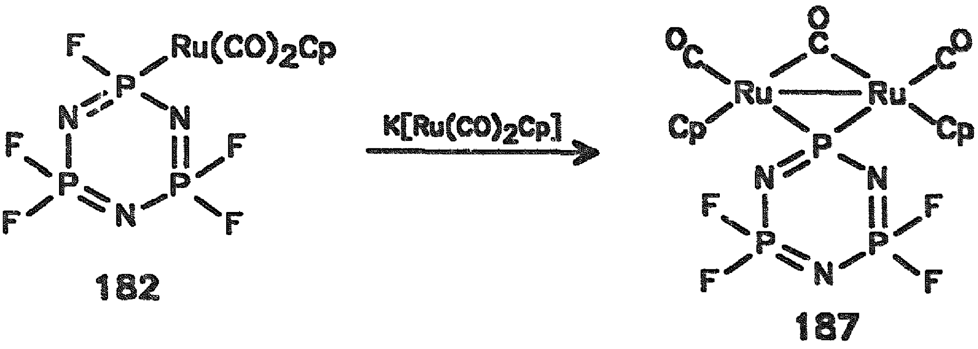
obviously, the validity of our concept of transition-metal-functionalized ring compounds with covalent phosphorus–metal bonds is fading.

The chlorinated cyclotriphosphazene $[NPCl_2]_3$ displayed a more complex reactivity toward cyclopentadienyl carbonyl metalates than its fluorinated analog. Treatment of $[NPCl_2]_3$ with $Na[Fe(CO)_2Cp]$ caused complete decomposition of the reactants [142].

Whereas treatment of $(^nBu_4N)[Cr(CO)_3Cp]$ with hexachlorocyclotriphosphazene led, as expected, to the chromiopentachlorocyclotriphosphazene **188**, the corresponding reactions of the molybdenum and tungsten analogs furnished metallocyclotriphosphazenes **190a,b**, in which a cyclopentadiene group and the complex fragment were covalently attached to one phosphorus atom of the ring. It was argued that in the case of the heavier metals cation–halogen exchange accounted for the formation of the transient anion **189**, which could be trapped, for example by methyl iodide, to give **191** (Eq. (79)). The mechanism concerning the Cp transfer onto this intermediate, however, remained unclear [143].



[Fe] = $Cp(CO)_2Fe$; [Ru] = $Cp(CO)_2Ru$ (77)



182 **187**

(78)

A converse synthetic strategy has been utilized for the preparation of 1-organo-1-(dicarbonylcyclopentadienylferrio)-3,3,5,5-tetra-chlorocyclotriphosphazenes **193a,b** from lithium derivatives **192a,b** and Cp(CO)$_2$FeI (Eq. (80)) [144].

This approach was successively extended to chromium-, molybdenum-, tungsten-, and ruthenium-substituted tetrachlorocyclophosphazenes [145]. The preparation of **194a** by reacting lithium species **192b** with Cp(CO)$_3$CrI was accompanied by the formation of considerable amounts of ionic **195a**, which resulted from a competitive CO displacement by anion **192**. Only poor yields of the molybdenum-, tungsten-, and ruthenium analogs **194b–d** were produced when **192b** was allowed to interact with the respective iodo complexes in boiling THF (Eq. (81)). The yields of **194** were improved by running the reactions under a high pressure of CO [145].

The conversion of the lithiated cyclotriphosphazenes **196a,b** to the corresponding ferriocyclotriphosphazenes **197a,b** was accomplished by treatment with Cp(CO)$_2$FeI (Eq. (82)).

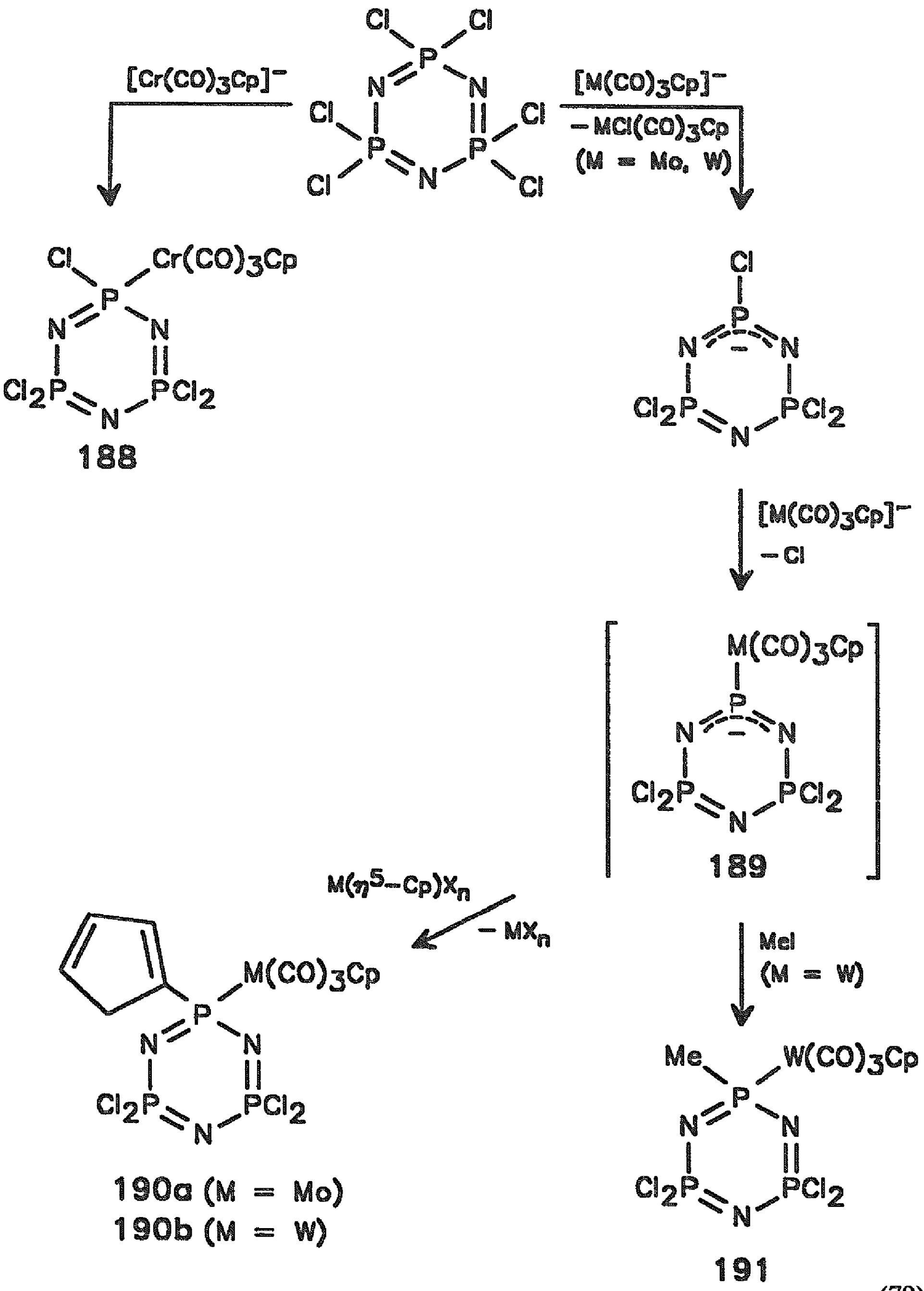
Complexes **197a,b** serve as important model compounds for polyphosphazenes, in which Cp(CO)$_2$Fe units are directly bonded to alternating phosphorus atoms of the (PN)$_n$ backbone [146].

According to the crystal structure analysis of **197a**, the metalated phosphorus atom is displaced by 0.23 Å from the plane defined by the remaining ring atoms. By the way, it is a general finding that transition metal complex fragments at one phosphorus atom strongly influence the geometry of the cyclotriphosphazene skeleton [146].

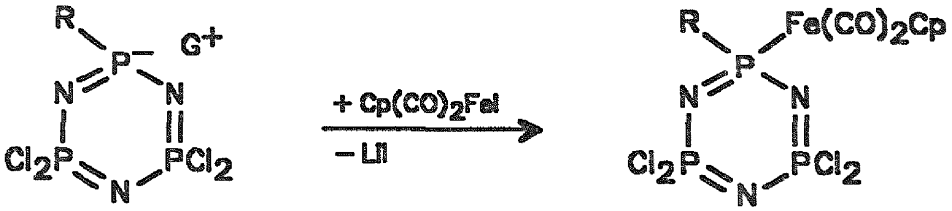
More information on the organometallic chemistry of cyclophosphazenes is given in a review by Allcock et al. [147].

7. Others

The first representatives of *E,E*-1,7-dioxa-4,5,10,11-tetraaza-3,4,8,9-tetraphosphadodeca-5,11-dienes **198a,b** resulted when metallodiphosphene **19a** and


[Cr(CO)3Cp]⁻
[M(CO)3Cp]⁻
− MCl(CO)3Cp
(M = Mo, W)
188
[M(CO)3Cp]⁻
− Cl
189
M(η5−Cp)Xn
− MXn
MeI
(M = W)
190a (M = Mo)
190b (M = W)
191

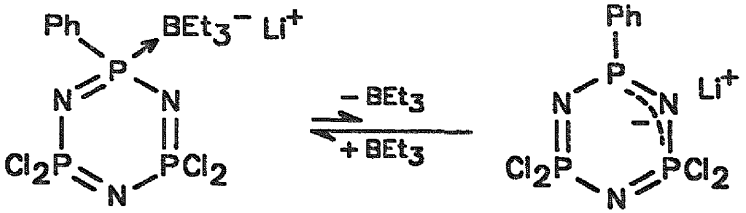
(79)



192	R	G
a	Me	Li
b	Ph	BEt$_3$Li

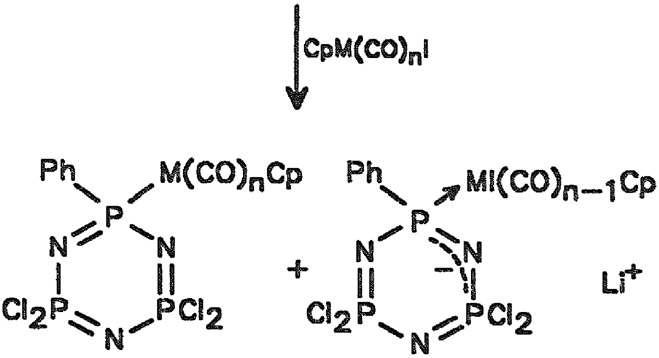
193	R
a	Me
b	Ph

(80)



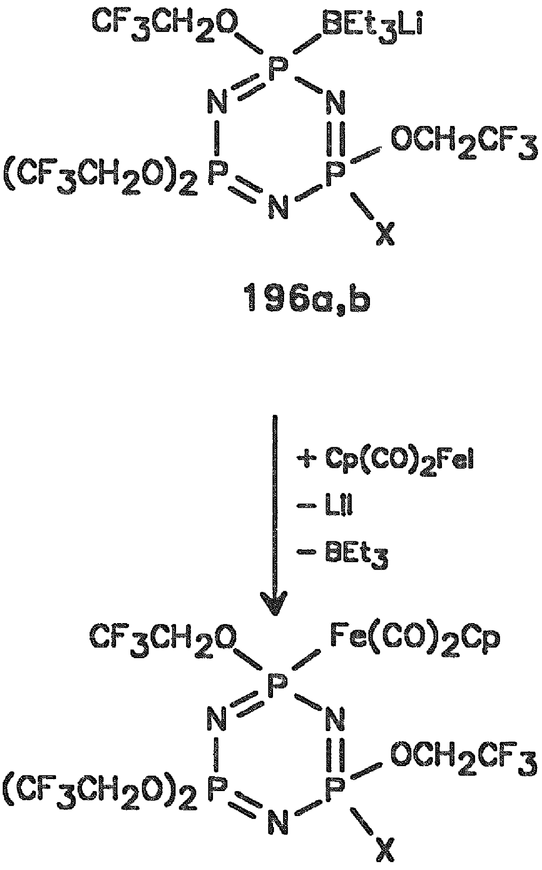
192b **192b'**

194,195	M	n
a	Cr	3
b	Mo	3
c	W	3
d	Ru	2



194a–d **195a,b** (81)

Δ^1-1,2,4-triazoline-3,5-diones were reacted in diethyl ether (Eq. (83)). Obviously the reactivity of **19a** towards the electrophilic azo species is highly dependent on the solvent, as the same reaction in benzene led to 1,2-diaza-3,4-diphosphetidine **90a,b**



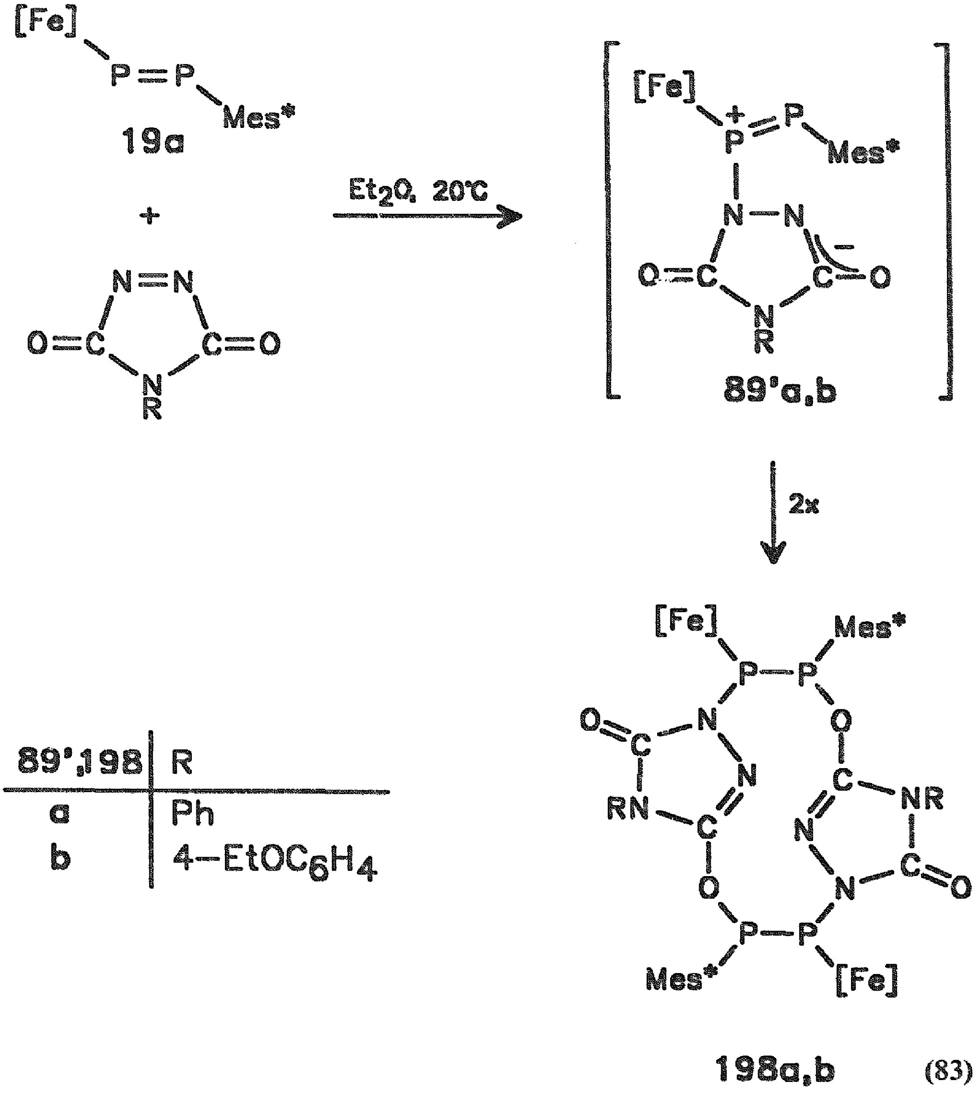
196,197	X
a	OCH_2CF_3
b	Cl

197a,b (82)

(Eq. (39)). An explanation for this invoked the dimerization of intermediate **89′a**, **89′b** in the dipolar solvent [96,97].

8. Conclusions

It is obvious that the organometallic chemistry of inorganic ring systems at the interface of several actual research areas is more than just a hybrid of two classes of compound. The combination of main group chemistry, organometallic chemistry and coordination chemistry in many cases creates new species with altered and sometimes unique properties. First perspectives in application, that exceed more fundamental research interests, are convincingly given in the field of metalated phosphazenes.



89',198	R
a	Ph
b	$4\text{-EtOC}_6\text{H}_4$

(83)

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