

# Functionalization of white phosphorus in the coordination sphere of transition metal complexes

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## Abstract

This review highlights the stoichiometric functionalization of both white phosphorus and naked  $P_n$  fragments derived from the metal-mediated demolition of the  $P_4$  tetrahedron. In a first section, the alkylation of  $P_n$  ligands is discussed giving specific examples such as: (i) the electrophilic alkylation of  $\eta^3-P_3$  or  $\mu, \eta^3-P_3$  ligands; (ii) the transfer of a methyl group from molybdenum to  $\eta^5-P_5$  ligands to yield a norbornadiene-like  $\mu_3, \eta^4: \eta^1: \eta^1-MeP_7$  ligand; (iii) the formation of P–C or P–H bonds mediated by rhodium and iron complexes; (iv) the use of ammonium salts to transfer an alkyl to polyphosphido clusters. Different methods to functionalise white phosphorus or other  $P_n$  ligands, including the cyclization of acrolein with diphosphenes and the insertion of CO or carbenes across P–P, P–M bonds, and P–E bonds (E = S, Se), are illustrated in appropriate sections. Finally, the last part of the article, reports on the astounding coupling of alkynes and phosphalkynes with  $P_n$  ligands which is a versatile, not yet completely explored, method to form an unprecedented variety of carbon–phosphorus heterocycles.

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## 1. Introduction

The chemistry of phosphorus currently has an enormous importance in many distinct sectors of industry and human life and practically parallels the chemistry of carbon in terms of complexity and importance [1,2].

The starting material for the industrial production of organophosphorus compounds is white phosphorus,  $P_4$ , which is readily available, inexpensive and a highly reac-

tive material. In manufacturing plants, white phosphorus is reacted with chlorine gas and the resulting  $PCl_3$  is further transformed into desired organophosphorus compounds by reaction with appropriate organic substrates.

All reagents involved in the currently adopted industrial method to produce organophosphorus compounds are very poisonous and dangerous compounds, thus the industrial process is expensive, very prone towards accidents [3] and utterly remote from being environmentally acceptable which is one of the most important challenges for modern industrial society. Furthermore, the vulnerability to terrorist attacks of chemical plants with large quantities of toxic materials has been pointed out

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recently [4]. Therefore, with growing commercial interest, with increasingly stringent environmental directives and safety considerations, the search for ecologically benign chemical ways to manufacture organophosphorus compounds is greatly encouraged [5].

A successful answer to this problem could be the development of a homogeneous catalytic process combining directly both white phosphorus and organic molecules in the coordination sphere of a transition metal complex [6]. From a perusal of the many excellent reviews dealing with the coordination chemistry of white phosphorus and derived  $P_n$  ligands [7–13], it is evident that elemental phosphorus displays a rich chemistry with transition metals.  $\eta^1$ - $P$ -coordination [14],  $\eta^2$ - $P,P$ -activation with a myriad of metal promoted degradation and reaggregation processes of the  $P_4$  cage have been documented [7], but no review has been published addressing the functionalization of these ligands [15]. Although the use of transition metal complexes to assist and promote the functionalization of white phosphorus must certainly be catalytic in order to be of practical use for future applications of industrial interest, the basic understanding of stoichiometric processes taking place in the coordination sphere of transition metals and involving phosphorus atoms derived from the metal activation of  $P_4$  is a necessary prerequisite for the design and the development of such highly attractive catalytic processes.

This article intends to cover this area providing a comprehensive overview of those processes, mediated by transition metal complexes, which result in the formation of a P–C bond starting from both white phosphorus or metal-coordinated  $P_n$  fragments originating from  $P_4$  activation reactions. A few reactions requiring the use of red phosphorus and some P–C coupling reactions of transition metal species obtained from P atom sources other than white phosphorus have also been included, but only when these complexes are related to those originating from elemental phosphorus. Since these reaction mechanisms are generally unknown, in a few cases possible mechanisms are suggested and unanswered questions critically addressed.

## 2. Metal-mediated stoichiometric functionalization of white phosphorus and naked $P_n$ units

### 2.1. Alkylation reactions

#### 2.1.1. Alkylation of metal-supported $P_n$ ligands

The mononuclear complexes  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{M}(\eta^3\text{-P}_3)]^{n+}$  ( $n=0$ ,  $\text{M}=\text{Co}$ ,  $\text{Rh}$ ,  $\text{Ir}$ ;  $n=1$ ,  $\text{M}=\text{Ni}$ ,  $\text{Pt}$ ) represent the most well defined family of transition-metal derivatives bearing the *cyclo*- $P_3$  ligand [8,16]. These exceedingly air stable complexes were prepared by Sacconi and co-workers [17a,b] about 20 years ago through a va-

riety of synthetic methods involving not only the use of white phosphorus ( $\text{M}=\text{Co}$ ,  $\text{Rh}$ ,  $\text{Ir}$ ,  $\text{Pt}$ ), but also with other less common and even unexpected and exotic sources of “ $P_3$ ” including  $\text{P}_4\text{S}_3$  ( $\text{M}=\text{Ni}$ ), red phosphorus,  $\text{P}_2\text{Te}_3$ , *cyclo*- $\text{P}_5\text{Me}_5$  and  $\text{P}_7(\text{SiMe}_3)_3$  ( $\text{M}=\text{Co}$ ) [c]. Homo- and heterodinuclear double sandwich complexes bearing the *cyclo*- $P_3$  ligand as internal layer  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{M}(\mu,\eta^3:\eta^3\text{-P}_3)\text{M}'\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}]^{n+}$  ( $\text{M}$ ,  $\text{M}'=\text{Fe}$ ,  $\text{Co}$ ,  $\text{Rh}$ ,  $\text{Ir}$ ,  $\text{Ni}$ ,  $\text{Pd}$  [8],  $\text{Ru}$ ,  $\text{Os}$ ) [18] were also described. The reactivity of these complexes has been largely studied [8,16,19], but reactions affording P–C bonds from *cyclo*- $P_3$  derivatives remain still limited, to the best of our knowledge, only two examples are known. In 1986, Stoppioni and co-workers [20] demonstrated that both trimethyloxonium tetrafluoroborate or methyl triflate readily react with the cyclotriphosphorus ligand in the triphos complexes  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{M}(\eta^3\text{-P}_3)]$  (**1a–c**) ( $\text{M}=\text{Co}$ ,  $\text{Rh}$ ,  $\text{Ir}$ ) to form the cationic  $\eta^3$ -methyltriphosphirene complexes  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{M}(\eta^3\text{-P}_3\text{Me})]\text{X}$  ( $\text{X}=\text{BF}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ) (**2a–c**) (Fig. 1). An X-ray analysis of the tetrafluoroborate salt (Fig. 2) confirmed the formation of the all-phosphorus analogue of azidomethane,  $\text{P}_3\text{Me}$ , whose existence as a free molecule

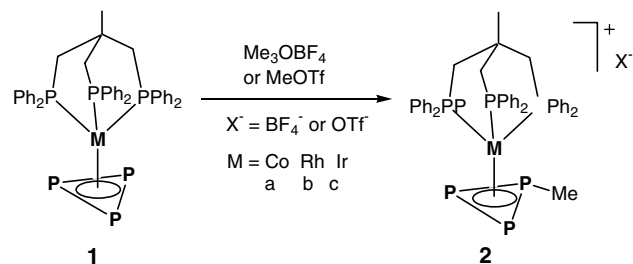


Fig. 1. Methylation of the *cyclo*- $P_3$  complexes  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{M}(\eta^3\text{-P}_3)]$  (**1**).

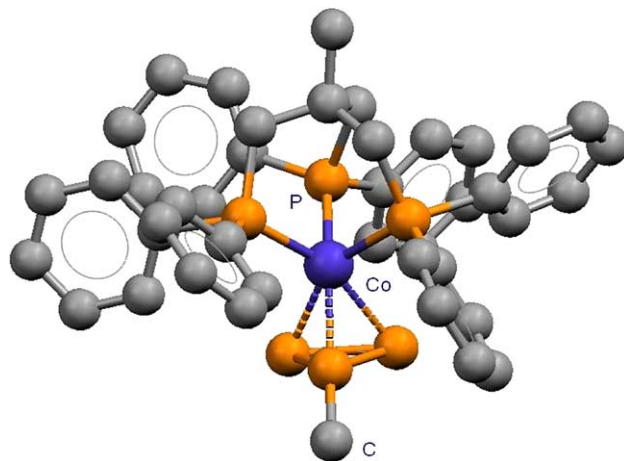


Fig. 2. Crystal structure of the cation  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Co}(\eta^3\text{-P}_3\text{Me})]^+$  (**2a**).

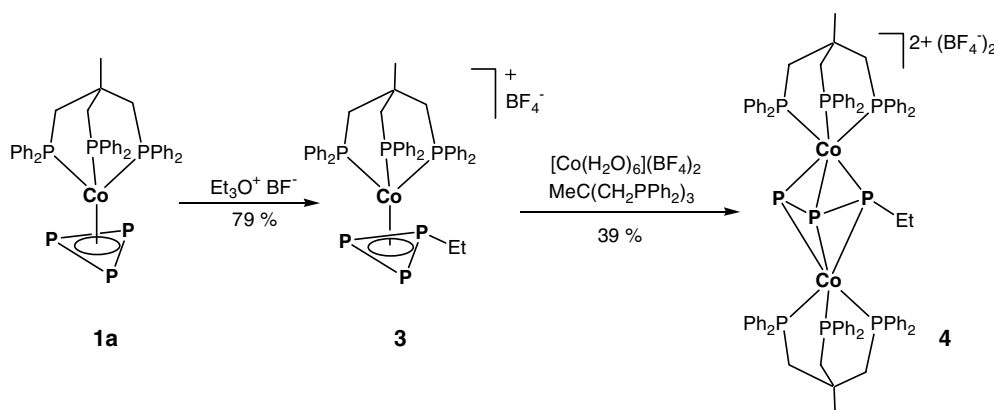


Fig. 3. Synthesis of ethyltriphosphirene complexes  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Co}(\eta^3\text{-P}_3\text{Et})\text{BF}_4$  (**3**)  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Co}(\eta^3\text{-P}_3\text{Et})\text{Co}\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}]$   $(\text{BF}_4)_2$  (**4**).

has never been reported. Noticeably, a severe deformation of the *cyclo*-P<sub>3</sub> ligand occurred upon alkylation with elongation of the P–P bond opposed to the alkylated P-atom (2.17 vs 2.08 Å).

Soon thereafter, Huttner and co-workers [21] reported a similar reaction with triethyloxonium tetrafluoroborate (Fig. 3). This latter transformation gave the cobalt complex  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Co}(\eta^3\text{-P}_3\text{Et})\text{BF}_4$  (**3**) with an ethyltriphosphirene ligand. Compound **3** transforms into the dinuclear dication  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Co}(\eta^3\text{-P}_3\text{Et})\text{Co}\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}]^{2+}$  (**4**) in the presence of one equivalent of  $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  and triphos. The structure of the dicobalt derivative displays an open  $\text{EtP}_3$  ligand in the solid state and in solution at low temperature. A slow exchange between the two unsubstituted P positions at room temperature in solution was also confirmed by  $^{31}\text{P}$  NMR spectroscopy.

### 2.1.2. Metal-mediated transfer of alkyl groups to naked phosphorus atoms

Pentaphosphaferrocenes (**5**) are readily available in a single step starting from P<sub>4</sub> and the dicarbonyl(pentamethylcyclopentadienyl)iron dimer  $[\{(\text{C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\}_2]$  (or similar derivatives with different Cp substituent pattern) [22] and have been shown to be versatile starting compounds for a variety of oligonuclear P<sub>n</sub> complexes [23]. The reaction of  $[(\text{C}_5\text{H}_2'\text{Bu}_3\text{-1,2,4})\text{Mo}(\text{CO})_3\text{CH}_3]$  (**6**) with  $[(\text{C}_5\text{Me}_5)\text{Fe}(\eta^5\text{-P}_5)]$  (**5a**) produced a complicated mixture of complexes including the 1:2 product  $[(\text{C}_5\text{Me}_5)\text{-Fe}(\mu^3, \eta^4: \eta^1: \eta^1\text{-P}_7\text{CH}_3)\{\text{Fe}(\text{CO})(\text{C}_5\text{Me}_5)\}(\mu, \eta^3: \eta^1\text{-P}_3)\{\text{Mo}(\text{CO})(\text{C}_5\text{H}_2'\text{Bu}_3\text{-1,2,4})\}]$  (**7**) with a norbornadiene-like P<sub>7</sub> cage containing a methyl group on the bridging P atom (Fig. 4). The three remaining P atoms form a *cyclo*-P<sub>3</sub> ring bridging molybdenum and one iron atom. One of the carbonyl ligands has migrated from the molybdenum to the iron atom [24]. The structural properties of the dinuclear iron complex  $[(\text{C}_5\text{Me}_5)\text{Fe}(\mu, \eta^4: \eta^1\text{-P}_5\text{CH}_3)\text{Fe}(\text{CO})_2(\text{C}_5\text{Me}_5)]$  (**8**), which has been isolated from the same reaction mixture [25], helped to clarify the ligand

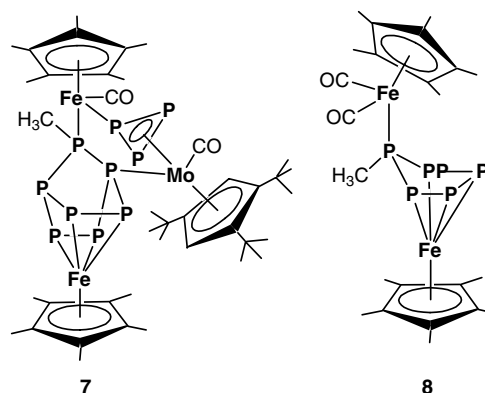


Fig. 4. Sketches of the diiron complexes (**7** and **8**) originating from pentaphosphaferrocene  $[(\text{C}_5\text{Me}_5)\text{Fe}(\eta^5\text{-P}_5)]$  and  $[(\text{C}_5\text{H}_2'\text{Bu}_3\text{-1,2,4})\text{Mo}(\text{CO})_3\text{CH}_3]$ .

transfer process. However, a complete mechanistic picture of this intriguing reaction has not been provided. In the dinuclear iron complex the two carbonyl ligands coordinated to one of the iron atoms and the methyl group bonded to one phosphorus atom of the five-membered ring originated from the molybdenum complex. In both complexes the iron centre connected to four phosphorus atoms bears a formal negative charge and the other iron atom, connected to three two-electron donors besides a cyclopentadienyl ligand, is formally positive (Fig. 5).

### 2.1.3. Metal-mediated alkylation of white phosphorus

The  $\sigma$ -alkyl or -aryl complexes  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{RhR}(\eta^2\text{-C}_2\text{H}_4)]$  (**9a,b**) (R = Me, Ph) rapidly react with white phosphorus, even at low temperature, to form the P<sub>4</sub>R complexes  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Rh}(\eta^3\text{-P}_4\text{R})]$  (**10a,b**) with ethene elimination [26] (Fig. 6). When the Rh-hydride complex  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{RhH}(\text{C}_2\text{H}_4)]$  (**9c**) is reacted with P<sub>4</sub>, the ethyl compound  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Rh}(\eta^3\text{-P}_4\text{Et})]$  (**10c**) is selectively obtained

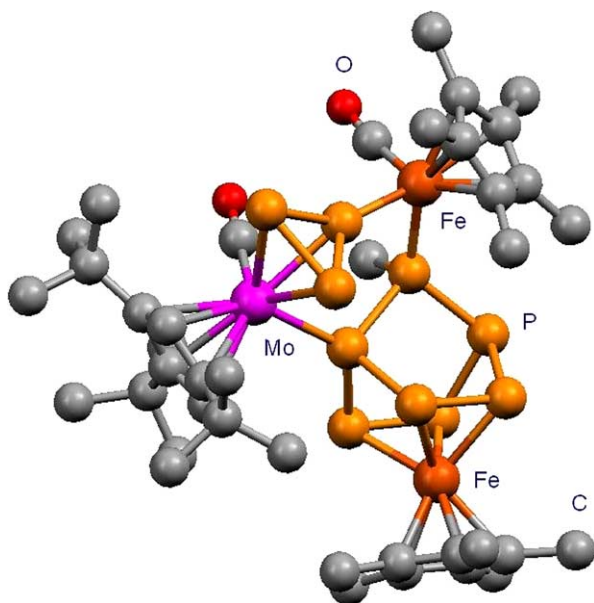


Fig. 5. Crystal structure of the trinuclear  $P_7Me$  complex  $[(C_5Me_5)Fe(\mu^3, \eta^4: \eta^1: \eta^1-P_7CH_3)\{Fe(CO)(C_5Me_5)\}(\mu, \eta^3: \eta^1-P_3)\{Mo(CO)-(C_5H_2'-Bu_3-1,2,4)\}]$  (7).

by insertion of coordinated ethene into the Rh–H bond with subsequent P–C bond formation. These reactions represent the first examples of transition metal-mediated P–C bond formation starting from white phosphorus and also the first examples of direct metal mediated transfer of an organyl fragment to the coordinated tetrahedral unit of elemental phosphorus [26]. Remarkably, these compounds react with  $H_2$  under pressure (20 atm) to yield, although in moderate yield, one equivalent of  $PH_2R$ , while the three remaining phosphorus at-

oms arranged forming the highly stable and generally unreactive *cyclo*- $P_3$  derivative  $[\{MeC(CH_2PPh_2)_3\}Rh(\eta^3-P_3)]$  (**1b**).

An analogous reaction occurs under highly forcing thermal conditions by reacting white phosphorus with the trihydride complex  $[\{MeC(CH_2PPh_2)_3\}RhH_3]$  (**11**) in refluxing THF. In contrast, the reaction results in orange microcrystals of  $[\{MeC(CH_2PPh_2)_3\}Rh(\eta^3-P_4H)]$  (**10d**) when **11** and white phosphorus were allowed to react at lower temperature under a nitrogen flow. Repeating the reaction under a hydrogen atmosphere afforded the *cyclo*- $P_3$  complex **1b** together with one equivalent of  $PH_3$  (Fig. 7). Noticeably, reaction of **10d** with dihydrogen in hot THF yielded **1b** and  $PH_3$  [27].

An insight into the mechanism accounting for the formation of the alkylated or hydrogenated tetraphosphorus complexes was obtained by studying the reaction of  $P_4$  with the dihydrido(ethyl) iridium complex  $[\{MeC(CH_2PPh_2)_3\}Ir(C_2H_5)_2H_2]$  (**5**). This latter complex readily eliminates  $C_2H_6$  rather than  $H_2$  in refluxing THF and reacts with white phosphorus to afford the pale yellow complex  $[\{MeC(CH_2PPh_2)_3\}IrH(\eta^2-P_4)]$  (**6**). This compound isomerizes to  $[\{MeC(CH_2PPh_2)_3\}Ir(\eta^3-P_4H)]$  (**7**) on standing at room temperature over a period of several days. Saturation with  $H_2$  and heating the solution at 70 °C provides one equivalent of  $PH_3$  and forms the *cyclo*- $P_3$  derivative  $[\{MeC(CH_2PPh_2)_3\}Ir(\eta^3-P_3)]$  (**1c**) [27]. Thus, in view of the experimental evidence, the mechanistic picture illustrated below (Fig. 8) may confidently be proposed to explain the reactivity of (triphos)M(R) fragments with white phosphorus and the hydrogenation reaction of the alkylated phosphorus atom in the family of  $[\{MeC(CH_2PPh_2)_3\}M(\eta^3-P_4R)]$  complexes.

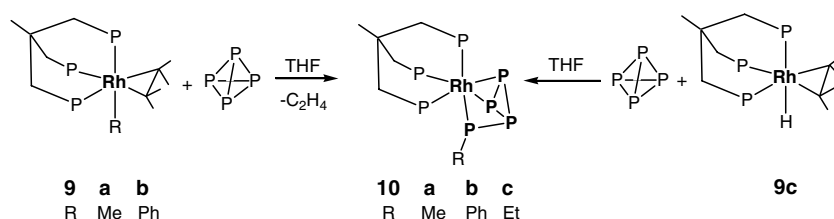


Fig. 6. Carbometalation of  $P_4$  with rhodium complexes **9a–c**.

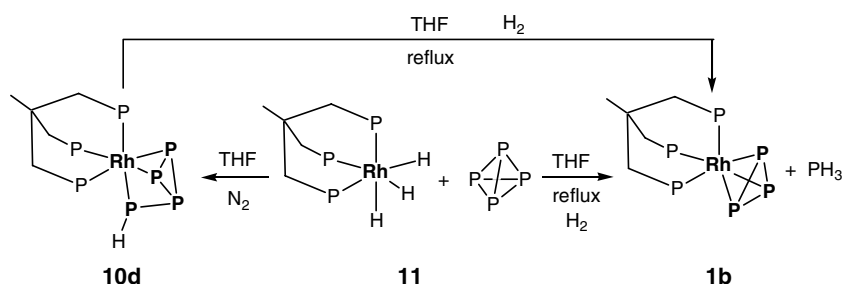


Fig. 7. Thermal reaction and hydrogenation of white phosphorus with the rhodium trihydride complex  $[\{MeC(CH_2PPh_2)_3\}RhH_3]$  (**11**).

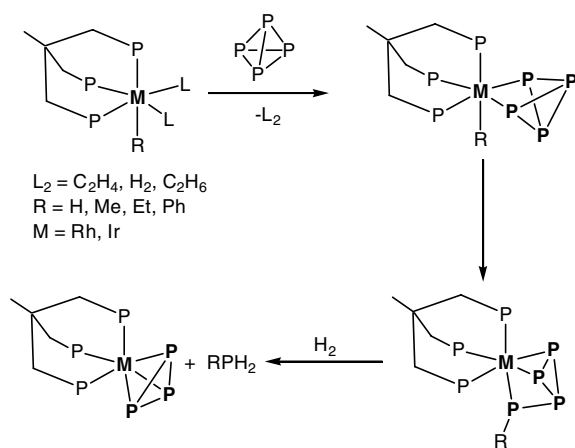


Fig. 8. The mechanism of white phosphorus carbometalation/hydrogenation by  $[\{MeC(CH_2PPh_2)_3\}MH_3]$  ( $M = Rh, Ir$ ).

Addition of electrophiles such as  $H^+$  and  $Me^+$  at  $-78^\circ C$  to the rhodium complexes  $[\{MeC(CH_2PPh_2)_3\}Rh(\eta^3-P_4R)]$  (**10**) affords bifunctionalised tetraphosphorus derivatives of the formula  $[\{MeC(CH_2PPh_2)_3\}Rh(\eta^1:\eta^2-P_4R(R'))]OSO_2CF_3$  (**16**). Remarkably, the electrophilic addition takes place with complete regioselectivity on the already functionalised P-atom. DFT calculations on a model compound confirmed that double substitution at the exocyclic P-position is energetically favoured [26b]. The methyl-phenyl derivative,  $[\{MeC(CH_2PPh_2)_3\}Rh(\eta^1:\eta^2-P_4Ph(Me))]OSO_2CF_3$  has been characterised by X-ray methods. A view of the complex cation is shown in Fig. 9.

The paramagnetic iron(II)  $\sigma$ -mesityl complex  $[(C_5-HR_4)Fe(C_6H_2Me_3-2,4,6)]$  ( $R = CHMe_2$ ) (**17**) reacts with

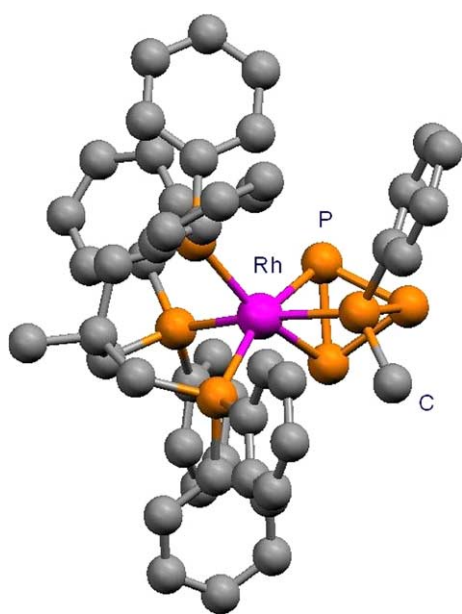


Fig. 9. X-ray crystal structure of the cation  $[(triphos)Rh(\eta^1:\eta^2-P_4Ph(Me))]^+$ .

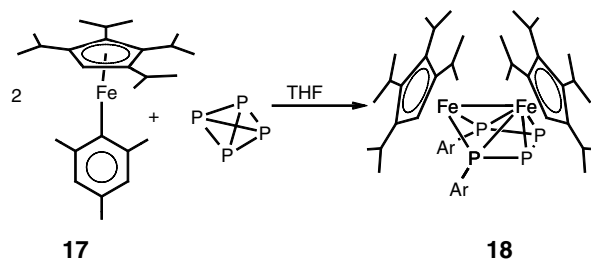


Fig. 10. Synthesis of the dimesityltetraphosphabutadiene complex **18**.

white phosphorus to give the dinuclear iron complex **18** featuring a dimesityltetraphosphabutadiene ligand originating from metal-promoted transfer of two mesityl groups to  $P_4$  (Fig. 10). The diamagnetic  $P_4Mes_2$  complex is formed as the only phosphorus compound observable by  $^{31}P$  NMR spectroscopy. The complex was isolated in ca. 90% yield [28].

#### 2.1.4. Alkylation of metalpolyphosphido clusters via tetraalkyl ammonium salts

The heptaphosphido  $[(P_7)M(CO)_3]^{3-}$  ions ( $M = Cr, Mo, W$ ) (**19a–c**) exhibit an all-phosphorus structure similar to the norbornadiene cage with one highly nucleophilic bridging P-atom. This unique two-coordinate phosphorus atom is highly reactive towards electrophiles which selectively attack this P-center [29]. In the course of an elegant study on this subject, Eichhorn and co-workers reported that the tungsten complex,  $[(P_7)W(CO)_3]^{3-}$  (**19c**), may be alkylated at the bridgehead P atom by tetraalkylammonium salts to form the monoalkylated dianions  $[(P_7R)W(CO)_3]^{2-}$  ( $R = Me, Et, n-Bu$ ) (**20a–c**) (Fig. 11). When an excess of ammonium salt was used, the isomerically pure dialkylated monoanions  $[P_7R_2]^-$  were obtained. The latter species could be further alkylated with alkyl halides to yield mixtures of symmetric and asymmetric  $P_7R_2R'$  isomers with no observable interconversion [30].

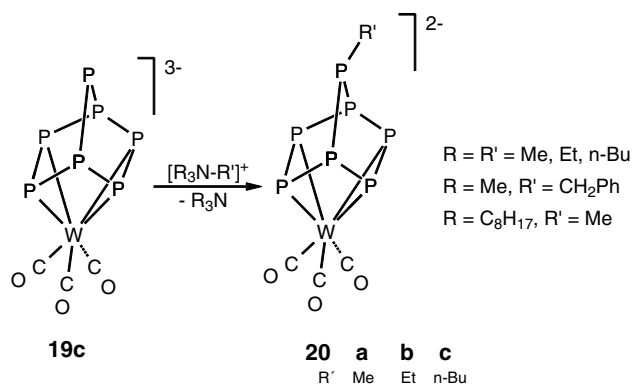


Fig. 11. Alkylation of a trianionic  $P_7$  complex with tetraalkylammonium salts.

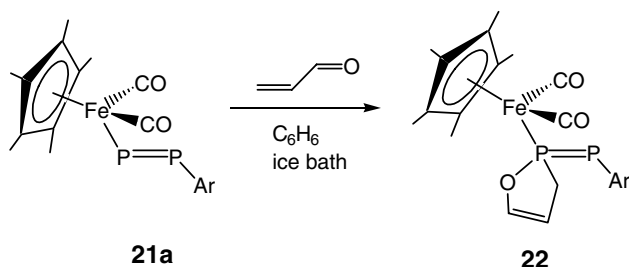


Fig. 12. Acrolein cycloaddition to the  $\eta^1$ -metallated diphosphene ligand in  $[\{\text{Cp}^*(\text{CO})_2\text{Fe}\}\text{P}=\text{PAr}]$ .

## 2.2. Cycloaddition reaction of metal-substituted diphosphenes

The chelotropic [1+4] cycloaddition of acrolein to Weber's diphosphene  $[\{\text{Cp}^*(\text{CO})_2\text{Fe}\}\text{P}=\text{PAr}]$  (**21a**) ( $\text{Ar} = 2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2$ ) occurs under mild conditions in benzene [31] (Fig. 12). Violet crystals of the air sensitive dihydro-1,2- $\lambda^5$ -oxaphosphole iron complex **22** could be isolated and were characterized by mass spectral analysis, spectroscopic methods and X-ray diffraction. A perusal of both  $^{31}\text{P}$  NMR data in solution and relevant metrical parameters in the solid state pointed to the formation of a metal-stabilised oxaphosphole ring with an exocyclic  $\text{P}=\text{P}$  double bond showing genuine ylide character.

## 2.3. Insertion of organic species across P–P bonds

### 2.3.1. Insertion of CO across P–P bonds

Insertion of carbon monoxide across P–P and P–M bonds mediated by transition metal complexes featuring naked  $\text{P}_n$  units is a relatively rare process which was firstly described by Weber et al. [32] for a family of diphosphene complexes containing the iron group elements. Thus, both P atoms of the diphosphene complexes, *trans*- $[\{\text{Cp}^*(\text{CO})_2\text{M}\}\text{P}=\text{PAr}]$  ( $\text{M} = \text{Fe, Ru, Os}$ ;  $\text{Ar} = \text{C}_6\text{H}_2\text{-}t\text{Bu}_3\text{-}2,4,6$ ) (**21a–c**), in the presence of

two equivalents of  $\text{Fe}_2(\text{CO})_9$  undergo addition of one  $\text{Fe}(\text{CO})_4$  fragment to form complexes **23** in addition to P–P bond cleavage and formal insertion of one CO molecule into the cleaved bond upon reaction with an excess of  $\text{Fe}_2(\text{CO})_9$ , formally generating complexes **24a–c** (Fig. 13). The formation of the unprecedented five-membered  $\text{Fe}_2\text{P}_2\text{C}$  system supporting a 1,3-diphospha-2-propanone ligand was corroborated by spectroscopic and X-ray diffraction methods and is mechanistically interpreted as originating from the concomitant addition of two  $\text{Fe}(\text{CO})_3$  fragments to the  $\text{P}=\text{P}$  ends of the diphosphene unit.

A second example of CO insertion into a metal coordinated P–P bond was reported by Scheer and co-workers in 1996 [33]. In that study, both the dimetalladiphosphatetrahydrene complex  $[\{(\text{C}_5\text{H}_4\text{-}t\text{Bu})\text{Mo}(\text{CO})_2\}_2(\mu_4, \eta^2: \eta^2: \eta^1: \eta^1\text{-P}_2)\{\text{Cr}(\text{CO})_5\}_2]$  (**25**) and the diphosphinmethanone species  $[\{(\text{C}_5\text{H}_4\text{-}t\text{Bu})\text{Mo}(\text{CO})_2\}_2(\mu_4, \eta^2: \eta^2: \eta^1: \eta^1\text{-PC(O)P})\{\text{Cr}(\text{CO})_5\}_2]$  (**26**), formally originating via CO insertion across both P atoms of the  $\text{Mo}_2\text{P}_2\text{Cr}_2$  cluster, were jointly formed during the reaction of  $[\{\text{Cr}(\text{CO})_5\}_2\text{PCl}]$  with  $[\{(\text{C}_5\text{H}_4\text{-}t\text{Bu})\text{Mo}(\text{CO})_3\}\text{K}]$  (Fig. 14). Remarkably, the CO insertion step could not be observed when the  $\text{P}_2$  product **25** was treated with carbon monoxide. The intermediacy of a highly reactive phosphido species,  $\{(\text{C}_5\text{H}_4\text{-}t\text{Bu})\text{Mo}(\text{CO})_2\text{-P}\{\text{Cr}(\text{CO})_5\}$ , along the reaction pathway leading to the two final products was postulated [34].

### 2.3.2. Insertion of CO across P–M bonds

Insertion of CO into an Ir–P bond was firstly reported by Scheer et al. from the reaction of  $[\text{Cp}^*\text{Ir}(\text{CO})_2]$  (**27**) with white phosphorus and  $[\text{Cr}(\text{THF})(\text{CO})_5]$  [35]. The presence of unsaturated Lewis-acid fragments in the reaction medium, such as  $\{\text{Cr}(\text{CO})_5\}$ , easily accessible via removal of the labile THF ligand from  $[\text{Cr}(\text{THF})(\text{CO})_5]$ , was the successful strategy used by Scheer to prevent the reaction products from uncontrolled  $\text{P}_4$  degradation. In the case at hand, the one-pot, three-component reaction

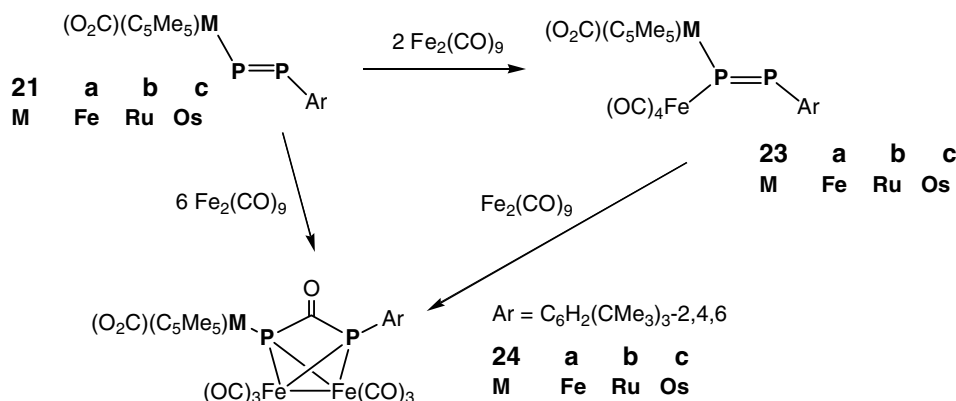


Fig. 13. Insertion of carbon monoxide into the  $\text{P}=\text{P}$  bond of the diphosphene complex *trans*- $[\{\text{Cp}^*(\text{CO})_2\text{M}\}\text{P}=\text{PAr}]$ .

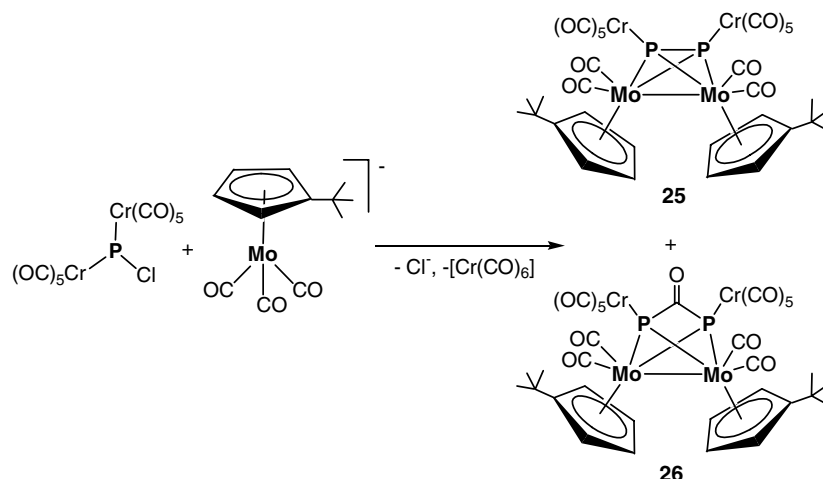


Fig. 14. Insertion of carbon monoxide into the P–P bond of a dimetalladiphosphatetrahedrane complex.

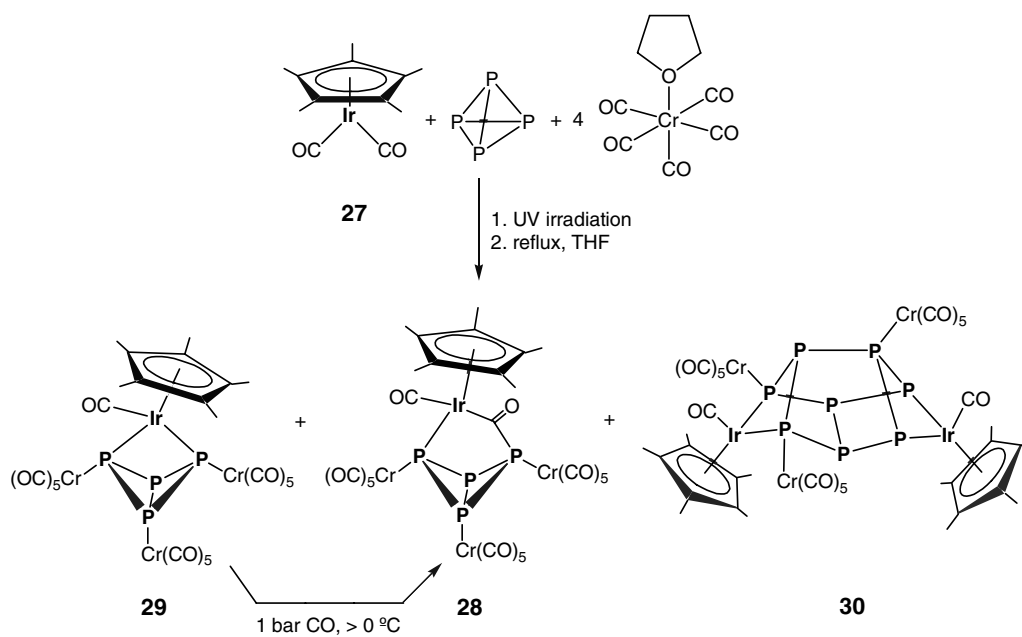


Fig. 15. Insertion of carbon monoxide into a Ir–P bond.

afforded inter alia, the tetranuclear complex  $[\text{Cp}^*\text{Ir}(\text{CO})\{\eta^1:\eta^1\text{-P,C-P}_4(\text{CO})\}\{\text{Cr}(\text{CO})_5\}_3]$  (**28**) with one CO molecule inserted into one of the Ir–P bonds of a  $\text{P}_4^{2-}$  ligand with a folded butterfly-like structure (Fig. 15). Three of the four P atoms exhibit additional terminal coordination to one  $\text{Cr}(\text{CO})_5$  unit each. Although the mechanism accounting for the formation of the CO insertion product was not specified, it is conceivable that the complex  $[\text{Cp}^*\text{Ir}(\text{CO})(\eta^2\text{-P}_4)\{\text{Cr}(\text{CO})_5\}_3]$  (**29**), containing a bicyclotetraphosphorus ligand chelating an iridium(III) fragment, is the actual species undergoing CO insertion. In keeping with this hypothesis, in a separate NMR tube experiment, a CO saturated THF- $\text{d}_8$  solution of the latter complex was shown to be capa-

ble of inserting CO between iridium and phosphorus centres above  $0^\circ\text{C}$  upon prolonged reaction with 1 bar of CO at room temperature. In a formal sense the third product originating from this reaction, i.e., the pentanuclear compound **30** with a  $\text{P}_8$  cuneane skeleton can be derived from two equivalents of **28** with elimination of three  $[\text{Cr}(\text{CO})_5]$  fragments. However, the reaction mechanism leading to **30** is not currently known [35].

### 2.3.3. Insertion of carbenes across P–P and P–E bonds

The complex  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Co}(\eta^3\text{-P}_2\text{S})]\text{BF}_4$  (**31**), which contains the thiadiphosphirane  $\text{P}_2\text{S}$  ring  $\eta^3$ -coordinated to the cobalt atom [36], readily

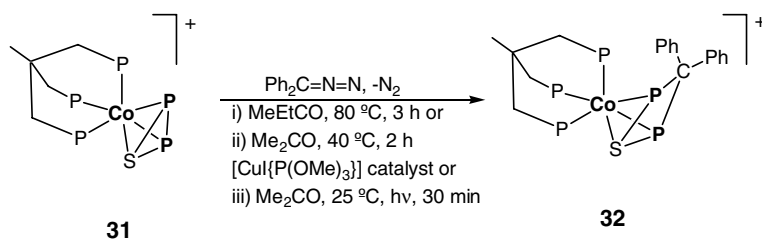


Fig. 16. Insertion of a carbene into the P–P bond of a thiadiphosphiranediy  $P_2S$  ligand.

undergoes P–P bond activation in refluxing methylethyl ketone when it is treated with a large excess of diphenyldiazomethane, yielding the insertion product  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Co}\{\eta^3\text{-SPC}(\text{Ph}_2)\text{P}\}]\text{BF}_4$  (**32**) in moderate yield [37] (Fig. 16). Compound **32** contains the unprecedented four-membered 3,3-diphenyl-1,2,4-thiadiphosphete moiety coordinated as a  $P,P,S$ -trihapto ligand to the  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Co}\}^+$  synthon.

The insertion reaction of the carbene fragment may also be accomplished, albeit with slightly reduced yield, at lower temperature (acetone 40 °C, 2 h) in the presence of a catalytic amount of the Moser–Arbuzov catalyst  $[\text{CuI}\{\text{P}(\text{OMe})_3\}]$  or through irradiating of a water-cooled acetone solution of the cobalt precursor with UV light for 30 min (mercury vapour lamp). Although crystals suitable for a diffraction analysis could not be obtained, the equivalence of the two phosphorus atoms in the final product, supporting a selective breakage of the P–P bond, was clearly indicated by the occurrence of a single resonance in the high field part of the spectrum where naked phosphorus atoms usually resonate [7,8,36].

In agreement with this proposition, the X-ray structure of the closely related complex  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Co}\{\eta^3\text{-SAsC}(\text{Ph}_2)\text{As}\}]\text{BF}_4$  (**33**) was determined by X-ray diffraction methods (Fig. 17) and confirmed the formation of the 3,3-diphenyl-1,2,4-thiadiarsete heterocyclic ring via formal insertion of the  $\text{CPh}_2$  carbene into the As–As bond. Upon insertion of the carbene, a significant elongation of the As–As bond from 2.34 Å in the parent compound  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Co}\{\eta^3\text{-As}_2\text{S}\}]\text{BF}_4$  (**34**) to 2.850 Å in **33** was observed [38].

Insertion of “genuine”,  $:\text{CR}_2$ , carbene fragments has never been observed for homocyclic  $P_3$  units or other polyphosphorus,  $P_n$ , ligands. Nonetheless, isolobal carbene-like fragments, such as  $\text{M}(\text{PR}_3)_2$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ), may easily insert across P–P bonds in a variety of polyphosphorus units and molecules. Selected examples comprise: (i) the vast family of complexes of formula  $L_n\text{M}(\eta^2\text{-P}_4)$  in which the metal–ligand fragment has been oxidatively added to a P–P bond of the white phosphorus tetrahedron forming a variety of bicyclo-tetraphosphine- $P_4$  complexes [25,39], (ii) the formation of the trinuclear platinum complex  $[\{\text{Pt}(\mu\text{-P}_4\text{S}_3)(\text{PPh}_3)_3\}_3]$  (**35**) via formal insertion of the  $\text{Pt}(\text{PPh}_3)_2$

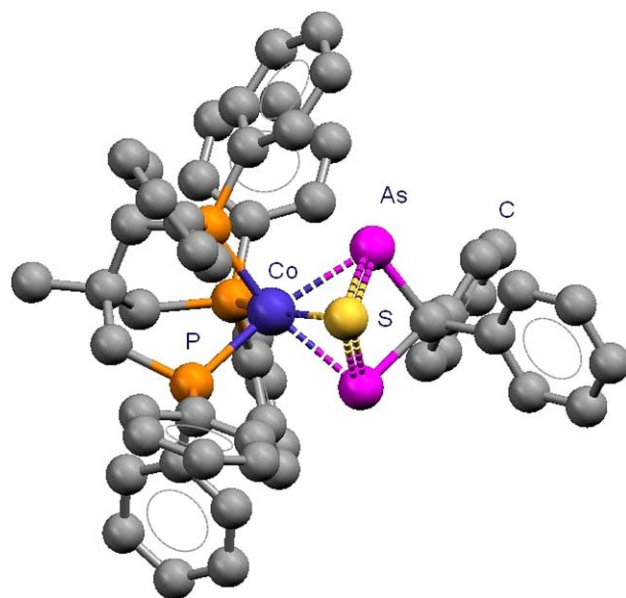


Fig. 17. Crystal structure of the thiadiarsete complex  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Co}\{\eta^3\text{-SAsC}(\text{Ph}_2)\text{As}\}]\text{BF}_4$  (**33**).

moiety into a basal P–P bond of the cage-like molecule  $P_4S_3$  [40], (iii) the asterane-like derivative  $[\{\text{SiMe}_3\}_2\text{P}_2\{\text{Pt}(\text{PPh}_3)_2\}]$  (**36**), prepared by West et al. from the reaction of a di-siladiphosphabicyclobutane with  $[(\text{C}_2\text{H}_4)\text{Pt}(\text{PPh}_3)_2]$  [41], and (iv) the structurally authenticated  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Ni}\{\text{P}_2\{\text{Pt}(\text{PPh}_3)_2\}\text{P}\}]\text{BPh}_4$  (**37**) obtained by insertion of the same platinum authenticated fragment in one of the P–P bonds of the cyclo- $P_3$  ring in the complex  $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Ni}\{\eta^3\text{-P}_3\}]\text{BF}_4$  (**1d**) after counteranion metathesis with  $\text{NaBPh}_4$  [42]. Non-disruptive P–P bond activation in  $\eta^1$ -tetrahedro-tetraphosphorus complexes  $[\text{Cp}^R\text{Ru}(\text{L-L})(\eta^1\text{-P}_4)]\text{PF}_6$  (**38**) ( $\text{Cp}^R = \text{C}_5\text{H}_5$ ,  $\text{L-L} = 1,1'$ -bis(diphenylphosphino)ferrocene;  $\text{Cp}^R = \text{C}_5\text{Me}_5$ ,  $\text{L-L} = 1,1'$ -bis(diphenylphosphino)ferrocene, 1,2-bis(diph enylphosphino)ethane) occurs upon reaction with  $[(\text{C}_2\text{H}_4)\text{Pt}(\text{PPh}_3)_2]$  at room temperature to afford dinuclear species of formula  $[\text{Cp}^R\text{Ru}(\text{L-L})(\eta^1:\eta^2\text{-P}_4\{\text{Pt}(\text{PPh}_3)_2\})]\text{PF}_6$  (**39**) [43]. Finally, it is worth mentioning that the pentaphosphaferrocene complex  $[(\text{C}_5\text{Me}_5)\text{Fe}(\eta^5\text{-P}_5)]$  (**5a**) adds to a  $[(\text{C}_5\text{Me}_5)\text{Ir}(\text{CO})]$  fragment generated during irradiation of the corresponding dicarbonyl complex  $[(\text{C}_5\text{Me}_5)\text{Ir}(\text{CO})_2]$  (**27**) forming the dinuclear compound  $[(\text{C}_5\text{Me}_5)\text{Fe}(\mu, \eta^5:\eta^2\text{-P}_5)\text{Ir}(\text{CO})-$



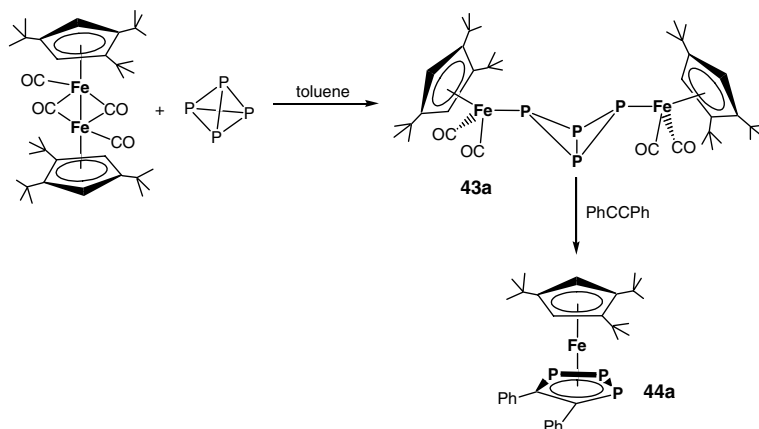


Fig. 18. Formation of the triphospholyl complex  $[\{(C_5H_2^tBu_3-1,2,4)(CO)_2Fe\}_2(\mu,\eta^1:\eta^1-P_4)]$  (**44a**) from a  $P_4$  butterfly complex and diphenylacetylene.

$(C_5Me_5)]$  (**40**) in which the cyclo- $P_5$  ring is additionally side-on coordinated to the 16 valence electron iridium fragment. The similar pentaarsacyclopentadienyl complex  $[(C_5Me_5)Fe(\mu,\eta^5:\eta^2-As_5)Rh(CO)(C_5Me_5)]$  (**41**) has been obtained at room temperature from the reaction between  $[(C_5Me_5)Fe(\eta^5-As_5)]$  (**5b**) and  $[\{(C_5Me_5)Rh(\mu-CO)\}_2]$  (**42**) [44].

#### 2.4. Coupling of alkynes and phosphalkynes with $P-P$ bonds

The  $P_4$  butterfly-type complex  $[\{(C_5H_2^tBu_3-1,2,4)(CO)_2Fe\}_2(\mu,\eta^1:\eta^1-P_4)]$  (**43a**) is generated in good yield from brief thermolysis of white phosphorus with the dinuclear iron complex  $[\{(C_5H_2^tBu_3-1,2,4)(CO)_2Fe\}_2]$  in toluene [45]. Complex **43a** reacts with diphenylacetylene in boiling toluene to form the triphosphaferrocene species  $[(C_5H_2^tBu_3-1,2,4)Fe(1,2,3-P_3C_2Ph_2)]$  (**44a**) featuring a 1,2,3-triphospholyl ligand [46] (Fig. 18). The product, isolated in 41% yield, exhibits a sandwich structure and contains a  $[(C_5H_2^tBu_3-1,2,4)FeP_3]$  fragment originating from the starting reagent (Fig. 19). Although the coupling of this fragment with one molecule of diphenylacetylene may well account for the formation of this interesting compound, the mechanism of the reaction remains obscure and the fate of the other  $[(C_5H_2^tBu_3-1,2,4)FeP]$  fragment is currently unknown.

Complex  $[\{(C_5R_5)(CO)_2Fe\}_2(\mu,\eta^1:\eta^1-P_4)]$  ( $R = CHMe_2$ ) (**43b**) [47], which is similar to **43a** apart from the presence of the sterically even more demanding pentaisopropylcyclopentadienyl ligand, reacts similarly with diphenylacetylene forming  $[(C_5R_5)Fe(1,2,3-P_3C_2Ph_2)]$  ( $R = CHMe_2$ ) (**44b**) [48] as a further example of a 1,2,3-triphosphaferrocene complex, 36% yield. However, the formation of **44b** in this latter reaction is accompanied by the unique  $P_{11}$  complex  $[\{(C_5R_5)Fe(CO)\}_2(\mu,\eta^2:\eta^2:\eta^1-P_{11})\{Fe(CO)_2(C_5R_5)\}]$  (**45**) as a side product obtained in low yield. The assemblage of the  $Fe_3P_{11}$  cluster **45** does not clarify the reaction mechanism, but suggested the occurrence

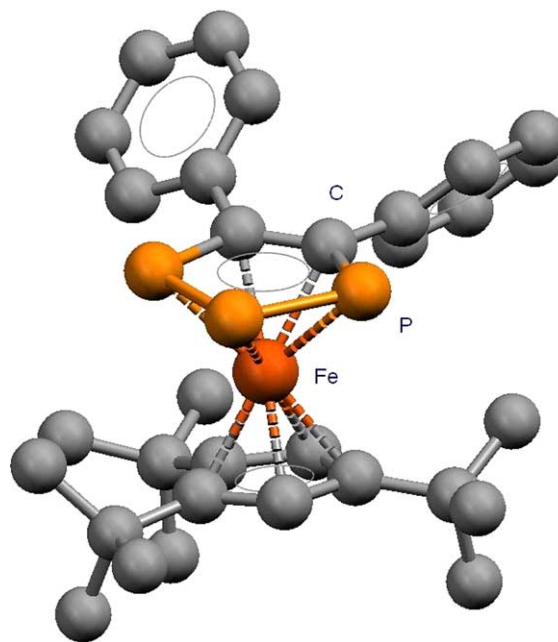


Fig. 19. Crystal structure of the triphosphaferrocene  $[(C_5H_2^tBu_3-1,2,4)Fe(1,2,3-P_3C_2Ph_2)]$  (**44a**).

of very complicated disaggregating and reaggregating processes involving naked polyphosphorus units which may take place under thermal conditions [7].

The scope of the reaction combining naked phosphorus atoms and alkyne  $C_2$  moieties was recently extended towards  $\pi$ -based ligand systems other than cyclopentadienyls and terminal alkynes (Table 1) [49]. When the di(*tert*-butyl)indenyl derivative of the  $P_4$  butterfly-complex  $[\{Ind^tBuFe(CO)_2\}_2(\mu,\eta^1:\eta^1-P_4)]$  (**43c**) is combined with either terminal or internal alkynes, the latter added to the  $[(ring)FeP_3]$  fragment to form the triphosphaferrocene derivatives  $[Ind^tBuFe(1,2,3-P_3C_2RR')]$  ( $R = R' = Me, Ph; R = Ph, ^tBu, SiMe_3, R' = H$ ) (**44c–g**) (complex type C in Fig. 20) with elimination of carbon monoxide and one  $[Ind^tBuFe]$  fragment. In addition, activated terminal

Table 1  
Product distribution from the reaction of  $[\{Cp^R(CO)_2Fe\}_2(\mu, \eta^1:\eta^1-P_4)]$  with alkynes

Cp ligand at Fe centre	Alkyne substituents	Product A	Product B	Product C	No.
$C_9H_5^tBu_2-1,3$	$R^1, R^2=Me$	–	–	30%	<b>44c</b>
$C_9H_5^tBu_2-1,3$	$R^1, R^2=Ph$	–	–	30%	<b>44d</b>
$C_9H_5^tBu_2-1,3$	$R^1=H, R^2=SiMe_3$	–	–	30%	<b>44e</b>
$C_9H_5^tBu_2-1,3$	$R^1=H, R^2=tBu$	–	–	30%	<b>44f</b>
$C_9H_5^tBu_2-1,3$	$R^1=H, R^2=Ph$	8%	8%	25–30%	<b>44g</b>
$C_9H_5^tBu_2-1,3$	$R^1=H, R^2=C(O)OMe$	–	25%	–	
$C_9H_5^tBu_2-1,3$	$R^1=H, R^2=C(O)OEt$	–	25%	–	
$C_5H_2^tBu_3-1,2,4$	$R^1=H, R^2=Ph$	–	–	37%	<b>44h</b>

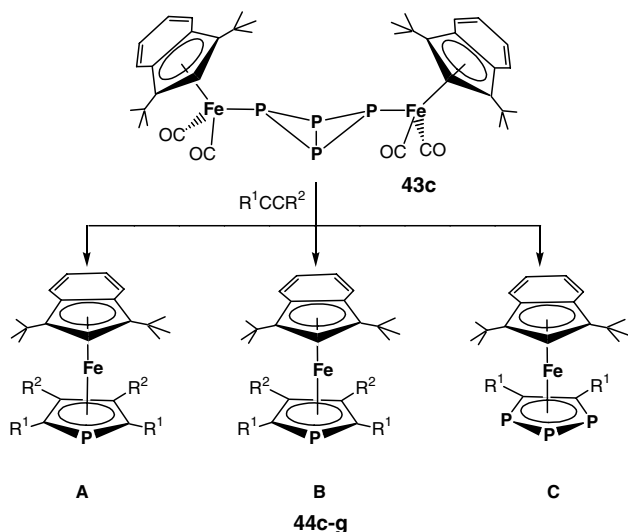


Fig. 20. Formation of iron complexes with phosphopoly or triphosphopoly units.

alkynes such as  $HC\equiv CPh$  and  $HC\equiv CCO_2R$  ( $R=Me, Et$ ) also provided clean access to monophosphoferrocenes (A or B, Fig. 20).

Remarkably, while ethyl- or methyl-propargylic esters gave only a single isomer, the reaction with phenylacetylene produced a mixture of two  $[Ind''Fe(R_2R^2_2C_4P)]$  regioisomers originating from tail-to-tail and tail-to-head coupling [47].

An obvious extension of this procedure encompasses the use of phosphalkynes as coupling reagents towards  $[(ring)FeP_3]$  synthons [50]. In agreement with these expectations, 1-methylcyclohexylphosphaacetylene,  $P\equiv C-C(CH_2)_5Me$ , was successfully reacted with the 1,3-di(*tert*-butyl)indenyl  $(Ind'')Fe_2P_4$  butterfly derivative **43c** giving a mixture of the triphosphoferrocene  $[(Ind'')Fe(R_2C_2P_3-1,2,4)]$  (**46**), the tetraphosphoferrocene  $[(Ind'')Fe(RCP_4)]$  (**47**) and the paramagnetic sandwich complex  $[(Ind'')Fe(R_2C_2P_2-1,3)]$  (**48**) ( $R=C(CH_2)_5Me$ ) (Fig. 21). The latter derivative includes a 1,3-diphosphacyclobutadiene ligand with a 17 valence electron count [49].

The heterodinuclear complex  $[\{(C_5H_2^tBu_3-1,2,4)(CO)Mo\}(\mu, \eta^2:\eta^2-P_2)_2\{Fe(C_5Me_4Et)\}]$  (**49a**), in which

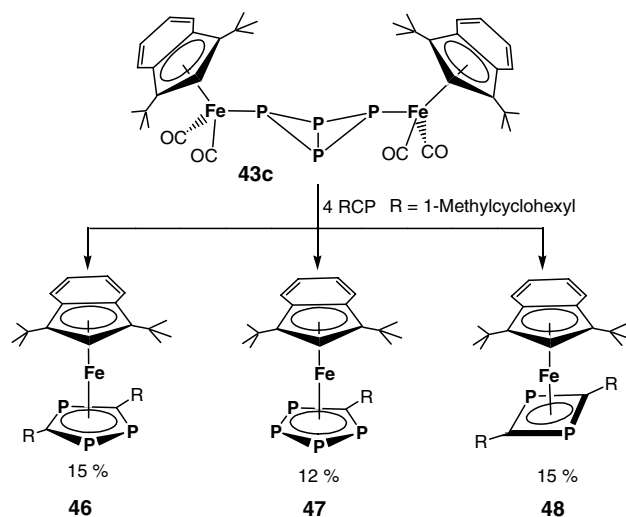


Fig. 21. Formation of iron complexes with di-, tri- or tetra-phosphaheterocyclic ligands.

two diphosphorus units bridge two different cyclopentadienyl metal moieties, undergoes addition with  $tBuC\equiv P$  to form  $[\{(C_5H_2^tBu_3-1,2,4)(CO)Mo\}(\mu, \eta^4:\eta^2-PPC(tBu)P)(\mu, \eta^2:\eta^2-P_2)\{Fe(C_5Me_4Et)\}]$  (**50**), in which a triphosphabutadiene ligand is assembled via coupling of a phosphalkyne with the coordinated  $P_2$  ligand. The other  $P_2$  ligand opposing the triphosphabutadiene unit remains unaffected (Fig. 22). The related compound  $[\{(C_5Me_3)(CO)Mo\}(\mu, \eta^2:\eta^2-P_2)_2\{Fe(C_5Me_3)\}]$  (**49b**) adds

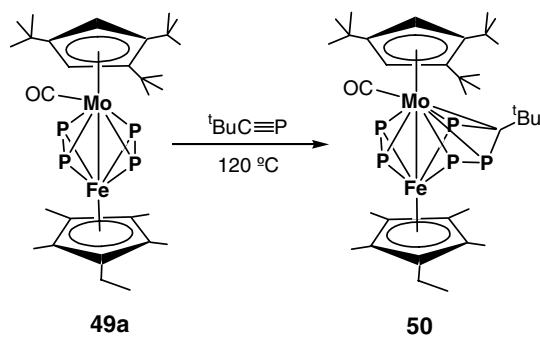


Fig. 22. Addition of *tert*-butylphosphaacetylene to a  $P_2$  ligand in  $[\{(C_5H_2^tBu_3-1,2,4)(CO)Mo\}(\mu, \eta^2:\eta^2-P_2)_2\{Fe(C_5Me_4Et)\}]$  (**49a**).

diphenylacetylene in a similar fashion forming  $[\{(\text{C}_5\text{Me}_5)(\text{CO})\text{Mo}\}(\mu, \eta^4:\eta^2\text{-PC}(\text{Ph})\text{C}(\text{Ph})\text{P})(\mu, \eta^2:\eta^2\text{-P}_2)\text{-}\{\text{Fe}(\text{C}_5\text{Me}_5)\}]$  (**51**) (Fig. 23). In this complex, in addition to an unmodified  $\text{P}_2$  unit, a diphosphabutadiene ligand arising from the [2+2] cycloaddition of phenylacetylene to the second  $\text{P}_2$  bridge, has been verified through X-ray diffraction methods [51]. All products mentioned in this section, resulting from the reactions of  $\text{P}_4$  butterfly complexes with alkynes or phosphalkynes can be postulated without the assumption of  $\text{C}\equiv\text{C}$  triple bond cleavage. This finding suggests a mechanism without alkyldiene intermediates and different from that governing the acetylene C–C cleavage upon co-condensation of alkynes with iron vapour [52,53].

Thermal isomerization of the  $\sigma$ -bonded pentamethylcyclopentadienylphosphinidene complex,  $[\{(\text{CO})_5\text{W}\}_2\text{-PC}_5\text{Me}_5]$  (**52**) produces the highly reactive intermediate  $[\{\eta^5\text{-}(\text{C}_5\text{Me}_5)\text{W}(\text{CO})_3\}\text{P}\{\text{W}(\text{CO})_5\}]$  [54]. There are two possible pathways to account for the degradation of this species. In the first process loss of CO affords the tungsten phosphido species,  $[\{\eta^5\text{-C}_5\text{Me}_5\text{W}(\text{CO})_2\}\text{-P}\{\text{W}(\text{CO})_5\}]$ , which spontaneously dimerizes to yield the  $\text{W}_2\text{P}_2$  tetrahedrane complex  $[\eta^5\text{-C}_5\text{Me}_5\text{W}(\text{CO})_2]_2(\mu^4, \eta^2:\eta^1:\eta^1)\text{P}_2\{\text{W}(\text{CO})_5\}_2$  (**53**) as the major product of the reaction. However, a side reaction results in the formation of a chiral metallaphosphine complex **54** with an unique phosphorus center exhibiting a  $\mu, \eta^1:\eta^1$  coordination mode (Fig. 24). The P–C bond in complex **54** is considered to have derived from C–H bond activation of one of the methyl groups of the cyclopentadienyl ligand.

When the thermolysis of  $[\{(\text{CO})_5\text{W}\}_2\text{PC}_5\text{Me}_5]$  **52** is carried out in the presence of alkynes different products may arise featuring spectacular geometries (Fig. 25) [55]. Relevant to this section is the thermal degradation of **52** in the presence of 4,4-dimethylpentyne-2 or tolane which affords compounds **55** and **56** or **57** and **58**, respectively,

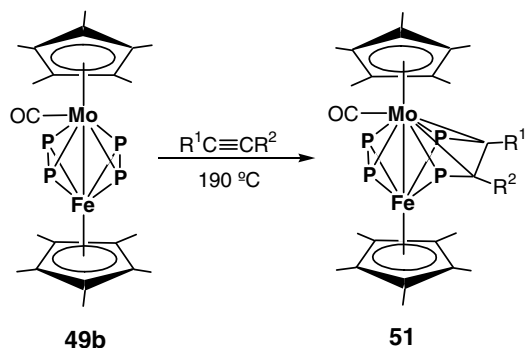


Fig. 23. Coupling of acetylenes with a  $\text{P}_2$  ligand in  $[\{(\text{C}_5\text{Me}_5)(\text{CO})\text{Mo}\}(\mu, \eta^2:\eta^2\text{-P}_2)_2\{\text{Fe}(\text{C}_5\text{Me}_5)\}]$  (**49b**).

where three of these species have incorporated P–C bonds.

With use of 4,4-dimethyl-2-pentyne two tetranuclear complexes are obtained, both of them containing two inequivalent phosphorus centres. In the unsymmetric complex **55** one of the two alkyne molecules forms a metallacyclopropene ring with a single tungsten centre and a second alkyne is linked to one phosphorus atom bridging three inequivalent tungsten fragments. Compound **56** has no P–C bonds, the only alkyne component forms a tetrahedrane structural motif with two different tungsten moieties. Compound **57** shows a  $\text{WPC}_2$  ring, which likely resulted from the [2+2] cycloaddition of the putative phosphido intermediate with the alkyne. Finally, complex **58** features a  $\text{W}_2\text{C}_2$  unit with the W–W bond bridged by a tetrahedral phosphorus atom embedded into a bicyclic unit. A formal coupling of the  $[\{(\text{CO})_5\text{W}\}_2\text{PC}_5\text{Me}_5]$  precursor with two molecules of alkyne may account for the formation of this product which does not share any common intermediate with the alternative reaction pathway leading to the  $\text{WPC}_2$  species.

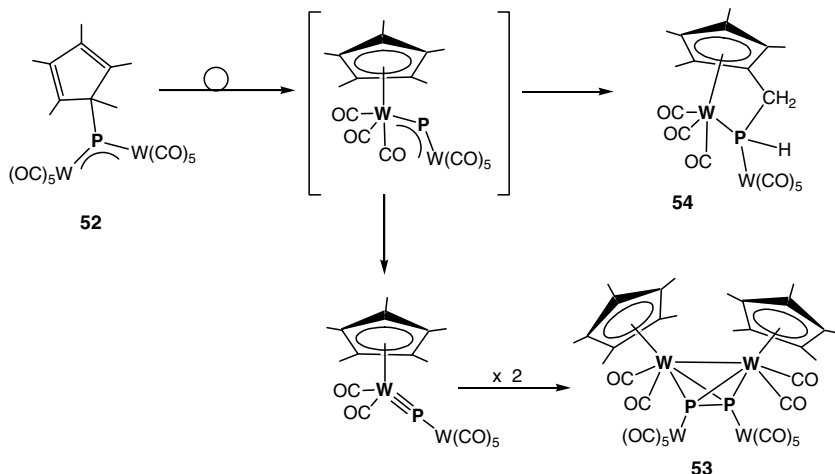


Fig. 24. Reactivity of the pentamethylcyclopentadienylphosphinidene complex **51**.

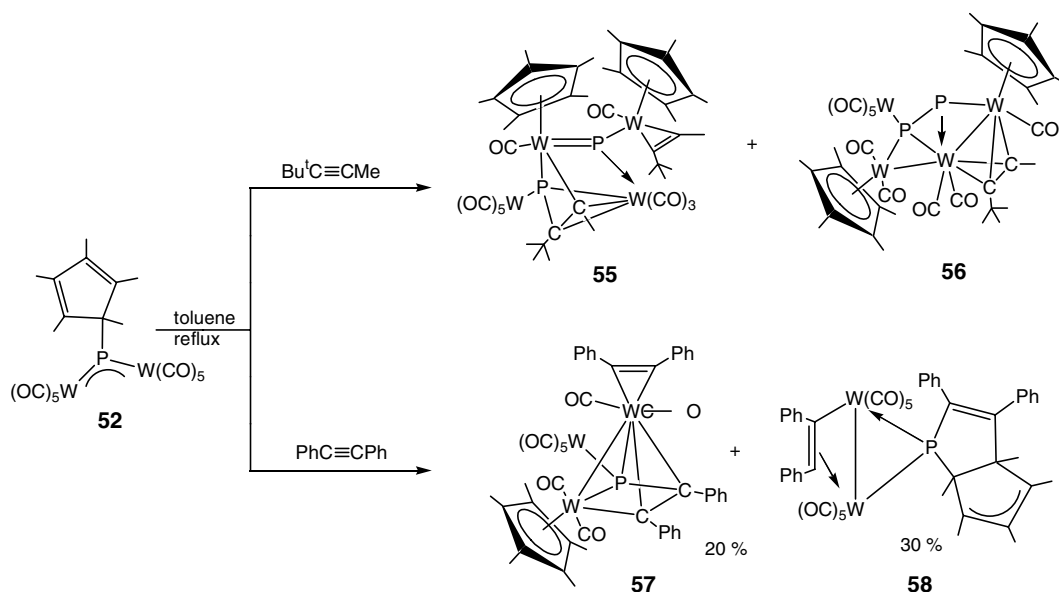


Fig. 25. Addition of acetylenes to the phosphinidene complex  $[(\text{CO})_5\text{W}]_2\text{PC}_5\text{Me}_5$  (**52**).

### 3. Conclusions

This article has highlighted novel organometallic compounds emerging from transition metal-mediated P–C bond formation reactions. Although the small number of reactions which have been gathered in this category does not allow us to draw a final conclusion, it is evident that no uniform reactivity pattern exists for P–C coupling reactions mediated by transition metal complexes, but instead display a vast diversity. Indeed, P–C bond formation by coupling reactions of  $\text{P}_n$  ligands may involve a wide variety of reactivity patterns encompassing the use of organic halides, carbocations and metal-bound hydrocarbyl ligands, or may employ unsaturated molecules like carbon monoxide, acetylenes or phosphaacetylenes as other P–C coupling reagents. Moreover, the organic ligands which have been used to construct a P–C bond with the assistance of a metal species may be attached to a phosphorus ligand of the same molecule or may originate from another complex molecule. Many of the known reactions leading to the formation of P–C bond from  $\text{P}_4$  within the coordination sphere of a transition metal–ligand system are mechanistically puzzling and the products formed are often unpredictable as they frequently contain phosphorus atoms in an odd or even number larger or less than four. For all these reasons, our knowledge in this field, in spite of the huge amounts of experimental information collected in the last three decades concerning the coordination chemistry of white phosphorus, is only in the preliminary stages, and requires further experimental and theoretical efforts before a systematic and rationale view of this topic may be achieved.

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