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Recent developments in the organometallic chemistry of phospha-alkynes, RC≡P

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Contents

Abstract

Recent developments in synthetic, structural and spectroscopic aspects Of novel organometallic compounds derived from phospha-alkynes are reviewed.

Keywords: Organometallic chemistry; Phospha-alkynes

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1. Introduction

The last decade has seen a rapid development in the synthetic, spectroscopic and structural aspects of main group element compounds containing multiple bonds. The so-called "double-bond rule", which originally suggested that multiple bonding involving the heavier elements would not occur because of weak $p\pi$–$p\pi$ bonding, has now been firmly laid to rest. Studies on compounds in which phosphorus is multiply bonded to itself, or to other elements, have played a central role in the rapid expansion of this area of chemistry.

In particular, phospha-alkynes, $RC{\equiv}P$, have been shown to have a rich organic and inorganic chemistry in which both the triple bond and the P lone pair electrons can participate. Several reviews have appeared in recent years [1–8] and the results have served to illustrate the strong inter-relationship between carbon and phosphorus chemistry. In the field of organometallic chemistry, it is now possible to synthesize a wide variety of stable phosphorus analogues of the better known unsaturated hydrocarbon π- complexes, which have been responsible for the rapid development of organotransition metal chemistry and its importance in homogeneous catalysis.

This review highlights some of the more important recent synthetic and structural developments in this rapidly growing area, concentrating on the interaction of phospha-alkynes and their derivatives with metals drawn from different parts of the Periodic Table.

2. Phospha-alkyne complexes

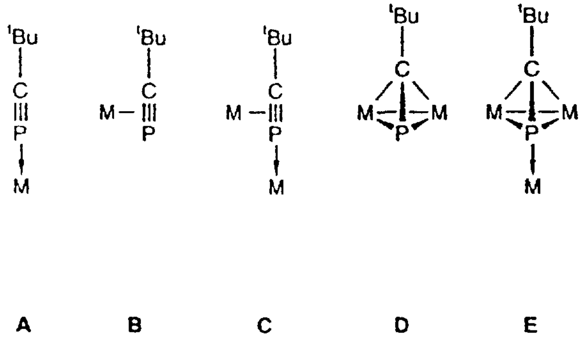


Fig. 1.

Just over a decade has passed since the first phospha-alkyne complex $[Pt(\eta^2\text{-}{}^tBuC{\equiv}P)(PPh_3)_2]$ was reported, in which the η^2-"side-on" interaction was noted between the $P{\equiv}C$ triple bond and the transition metal. Subsequently, types A–E have been synthesized using both the $RC{\equiv}P$ moiety as an η^2-bridging and/or P lone pair donor ligand (see Fig. 1) [9–11].

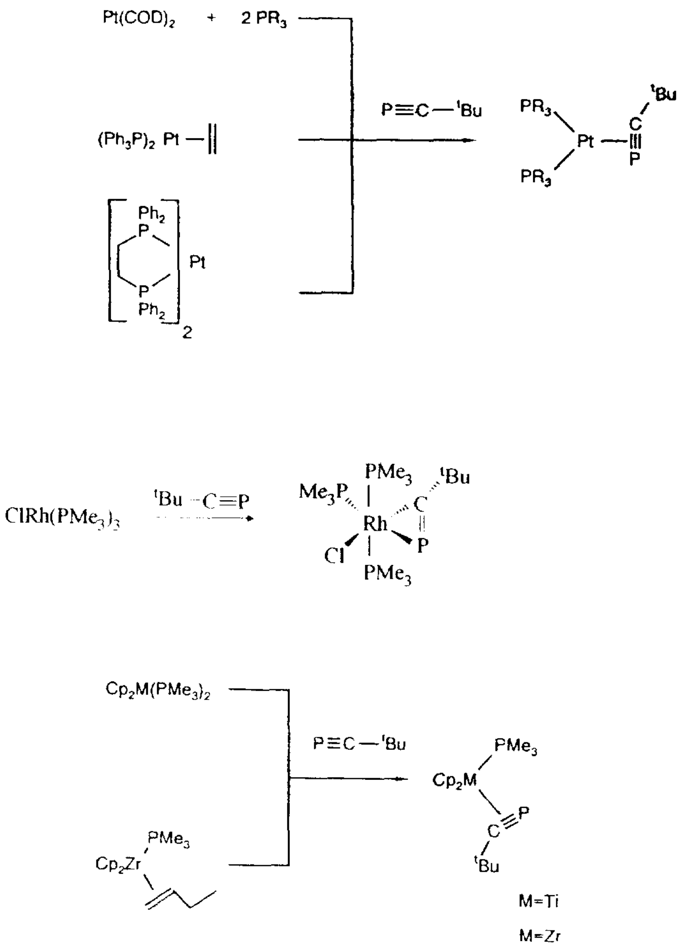


Fig. 2.

In recent years, a variety of other mononuclear complexes of type B containing η^2-ligated ^{t}BuCP have been reported for platinum, rhodium, titanium and zirconium (see Fig. 2) [12–14].

Photoelectron spectroscopic studies have previously established that the highest occupied molecular orbital (HOMO) in phospha-alkynes is the π-type P≡C triple bond, and so, not surprisingly, it is the η^2-ligating mode B–E that is preferred towards transition metals, and it is only possible to form preferentially η^1-complexes (type A) in suitably designed systems. To date, this has been achieved by creating a "pocket" into which the linear phospha-alkyne can coordinate to the metal specifically in an "end-on" η^1-fashion. Some typical examples of molybdenum(0) and tungsten(0) complexes, which are shown in Fig. 3, have been fully structurally and spectroscopically characterized and, in contrast with the η^2-ligated derivatives where

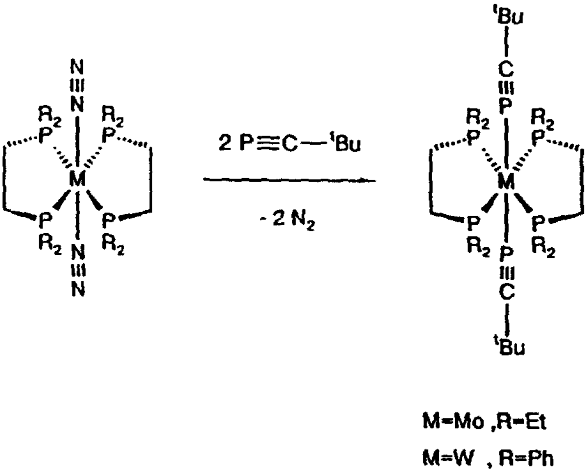


Fig. 3.

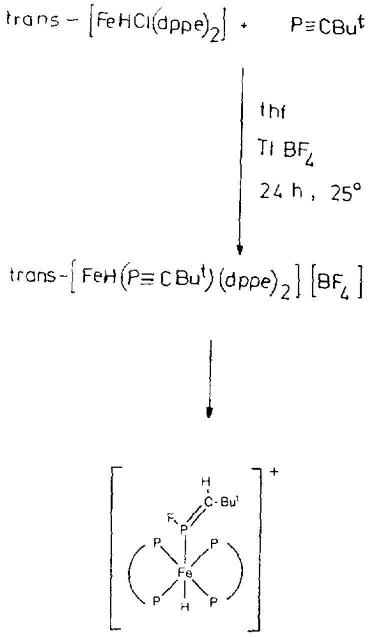


Fig. 4.

Fig. 5.

the P≡C bond is elongated, the P≡C bond length in the η^1-phospha-alkyne complexes remains close to the distance found in the "free" phospha-alkyne [15]. More recently, η^1-phospha-alkyne Fe(II) and Re(I) complexes have been synthesized. They

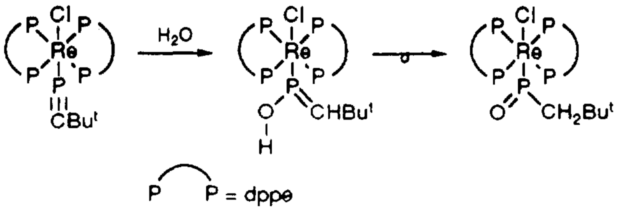


Fig. 6.

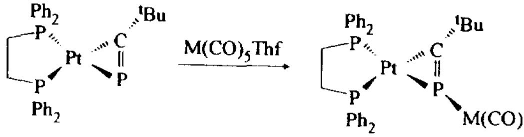


Fig. 7.

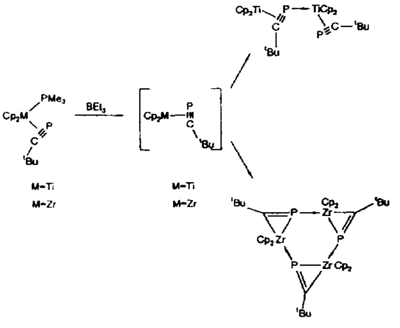


Fig. 8.

have been characterized by their ^{31}P nuclear magnetic resonance (NMR) spectra and, interestingly, they have been found to have considerably enhanced reactivity compared with the parent compound (see Fig. 4) [16,17].

Thus the phospha-alkyne complex $[Fe(dppe)_2(\eta^1\text{-}Bu^tCP)]^+BF_4^-$ rapidly undergoes a complex reaction in which HF is added across the P≡C triple bond of the coordinated phospha-alkyne to afford the $^{\eta}1$-ligated fluoro-phospha-alkene (Fig. 5) which has been fully structurally characterized. Likewise, the rhenium(I) phospha-alkyne complex rapidly reacts with water to afford the novel η^1-ligated phosphinidene oxide complex (Fig. 6).

Mixed metallic complexes of type C, in which both η^1- and η^2-bonding features of the phospha-alkyne are exploited, are typified by the chromium, molybdenum and tungsten pentacarbonyl derivatives of $[Pt(\eta^2\text{-}PC^tBu)L_2]$ ($L_2 \equiv$ diphos, $L \equiv PPh_3$) first obtained by Carmichael et al. [18] directly from the η^2-ligated mononuclear platinum(0) complexes (Fig. 7).

An alternative synthetic route to this class of compounds, reported by Binger et al. [13], is shown in Fig. 8 in which a vacant site in the preformed η^2-complex

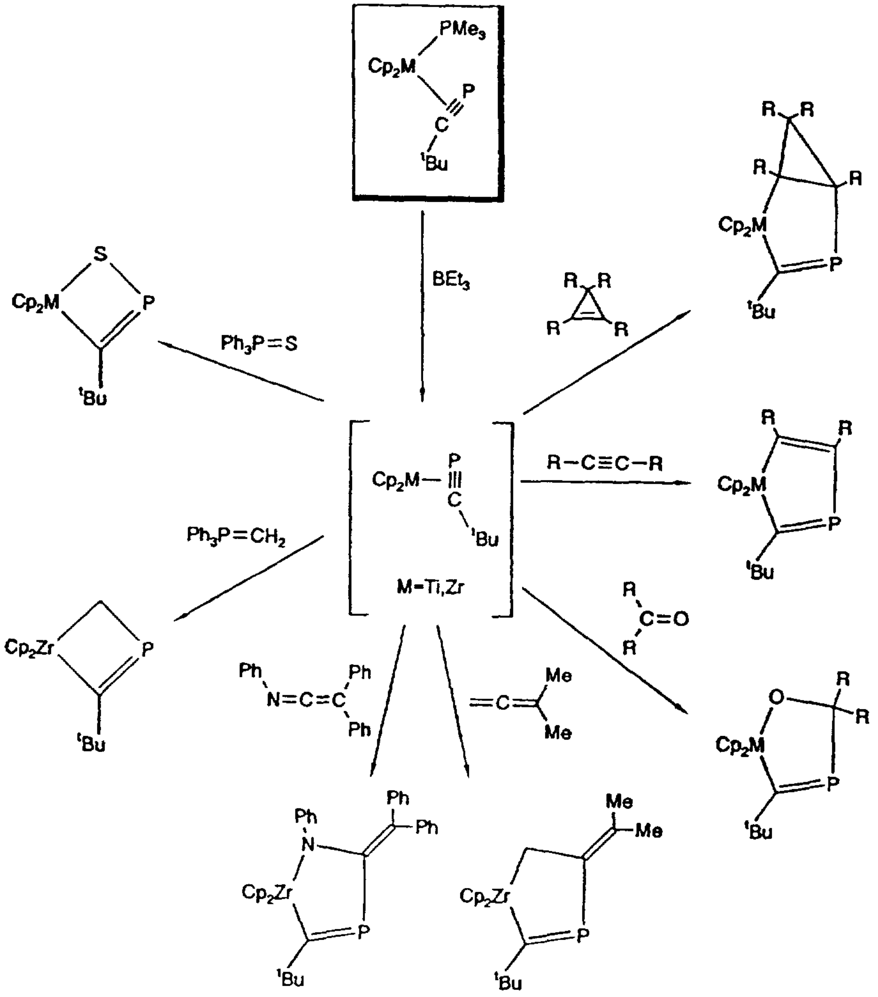
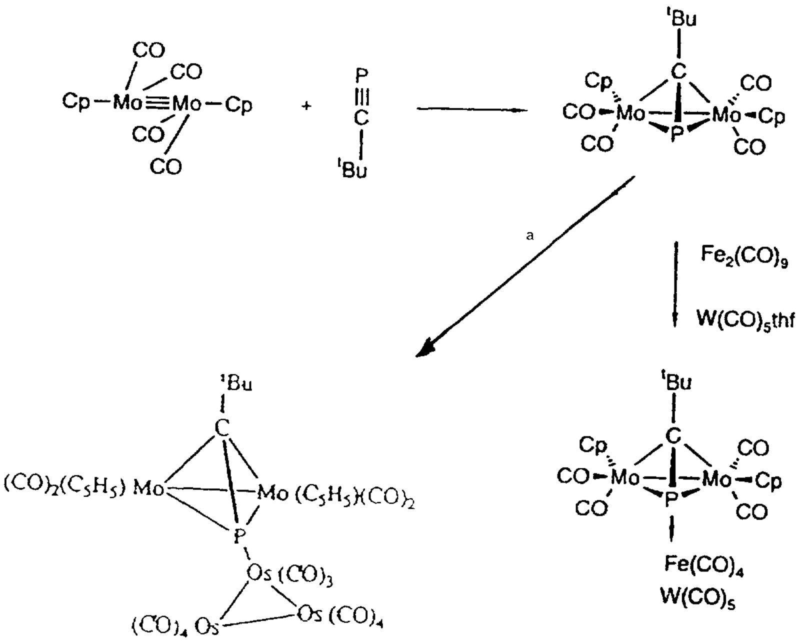


Fig. 9.

$[M(\eta^5\text{-}C_5H_5)_2(PC^tBu)(PMe_3)]$ ($M \equiv Ti$, Zr) is created by treatment with BEt_3 to remove the PMe_3. The resulting intermediate complex reacts with itself to give either the dimeric ($M \equiv Ti$) or trimeric ($M \equiv Zr$) compounds as stable products, or with a variety of substrates to produce compounds of the type shown in Fig. 9. Most of the metallacycles shown in Fig. 9 are stable only at temperatures below 0 °C and at room temperature they decompose back to the starting materials [13].

Complexes of type D and E, in which the phospha-alkyne can be considered to act as a four-electron or six-electron donor respectively, have been reported by a number of synthetic routes summarized in Fig. 10. Here, the behaviour mimics the better known dinuclear systems containing four- electron-bridging alkynes; however, the availability of the P lone pair electrons offers additional coordinating potential



a[$Os_3(CO)_{11}(MeCN)$]

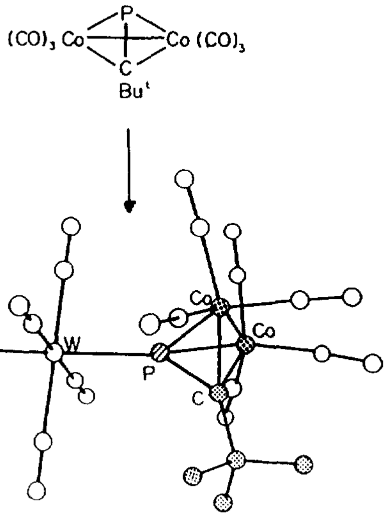


Fig. 10.

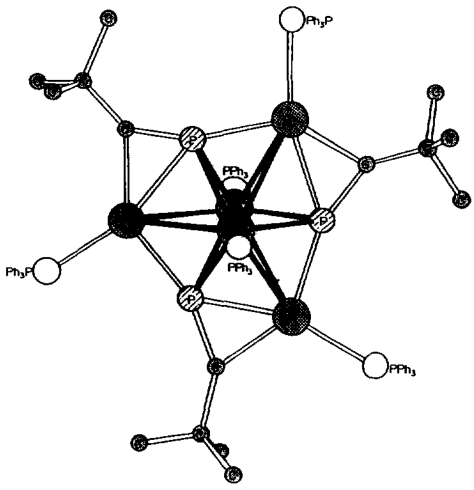


Fig. 11.

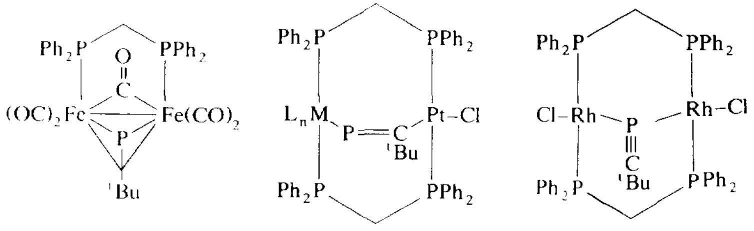


Fig. 12.

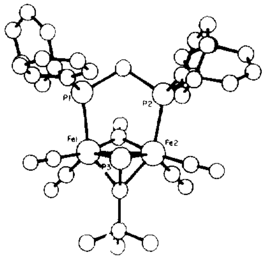


Fig. 13.

in the case of the phospha-alkyne [19–23], vividly illustrated by the pentametallic "star"-shaped complex [$Pt_3Pd_2(PPh_3)_5(^tBuCP)_3$] (Fig. 11) [24].

Very recently, new types of complex containing a μ-perpendicular-bridging phospha-alkyne in an "A"-frame setting have been reported [25,26], typified by the compounds shown in Fig. 12, and the first example [27] of a dinuclear metal complex containing a μ-parallel phospha-alkyne [$Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}^tBuCP)$] has been established by a detailed ^{31}P and ^{195}Pt NMR spectroscopic study. These latter results have links to the known behaviour of alkynes in dinuclear Pt and Pd "A"-frame-type complexes. The structure of the symmetrically bonded di-iron phospha-alkyne complex is shown in Fig. 13. A related, but clearly distinctly different, type of bonding to that established for several η^2-η^1-coordination complexes is the recent report by Binger et al. [28] of the novel orange titanium–boron complex $[Ti(\eta^5\text{-}C_5H_5)_2(^tBuCP)(BEt_2H)]$ shown in Fig. 14, which has been obtained in approximately 46% yield from the corresponding η^2-phospha-alkyne complex $[Ti(\eta^5\text{-}C_5H_5)_2(^tBuCP)(PMe_3)]$ with an equivalent amount of tetraethyldiborane $((Et_2BH)_2)$ at room temperature. A similar reaction product is obtained using the related tolane complex.

The remarkable feature of these reactions is the formation of the Et_2BH fragment which is bound exclusively, even though the starting diborane consists of an equilibrium mixture of the type (Et_xBH_{3-x}), (Et_yBH_{3-y}) $(x=1, 2; y=1, 2)$ and Et_3B. Detailed NMR studies were unable to unambiguously establish a structure for $[Ti(\eta^5\text{-}C_5H_5)_2(^tBuCP)(BEt_2H)]$. The strong shielding of the P atom in the phospha-alkyne comple,x revealed by ^{31}P NMR studies, suggests that the lone pair of electrons is not involved in the bonding, thus discriminating it from the η^2-η^1-ligation mode described previously. It appears from multinuclear NMR data that the boron atom is an electron donor to phosphorus, which may in turn transfer electron density to the plane which contains the σ-bonds to titanium. It has been suggested that the bonding is clearly different from that calculated for compounds containing a planar four-coordinate atom which cannot function as a donor centre [28].

Conclusive evidence for the planar environment at phosphorus has been obtained by a single crystal X-ray diffraction study, and the molecular structure is shown in Fig. 15, which may be regarded as consisting of a planar dimetalla-

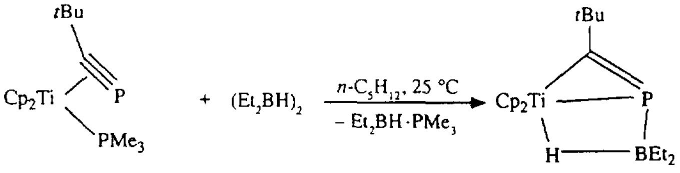


Fig. 14.

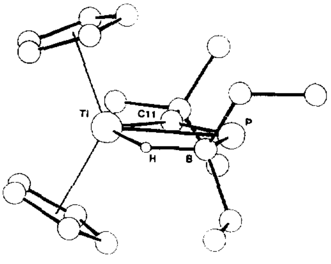


Fig. 15.

tricyclo[2.1.0]pentene unit containing the Ti(η^5-C_5H_5)$_2$ and Et_2B groups, the P and C atoms of the ligated phospha-alkyne and the bridging H atom. Thus the phospha-alkyne is η^2-ligated to the metal and η^1-bonded to boron, with the P atom acting as a bridgehead. The bond length data suggest that the short Ti–C (phospha-alkyne) bond (2.099(2) Å) has some partial double-bond character.

Interestingly, in spite of the high thermal stability of [Ti(η^5-C_5H_5)$_2$(^{t}BuCP)(BEt_2H)], it disintegrates readily with ethylene at room temperature to afford the known dinuclear complex [Ti(η^5-C_5H_5)$_2$(^{t}BuCP)]$_2$ referred to earlier in this section (Fig. 8). The tolane complex, on the other hand, reacts to afford the titanacyclopentene [Ti(η^5-C_5H_5)$_2$CPh=CPhCH$_2$CH$_2$].

3. Cyclodimerization reactions

3.1. 1,3-Diphosphacyclobutadiene complexes

In 1986, Hitchcock et al. [29] and Binger et al. [30] independently reported the first examples of phospha-alkyne cyclodimerization at cobalt, rhodium and iridium centres to afford complexes of the 1,3-diphosphacyclobutadiene ring (Fig. 16). Similar complexes containing zerovalent iron were reported soon afterwards [31,32], and subsequently treatment of [Ni(acac)$_2$] with BuLi at −78 °C in the presence of ^{t}BuCP

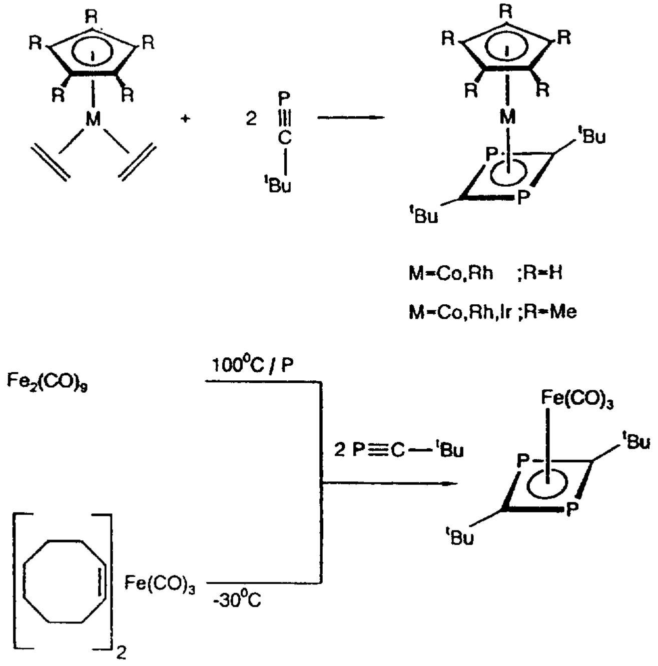
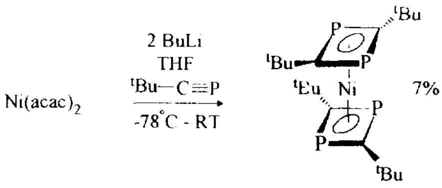


Fig. 16.

afforded the zerovalent nickel "sandwich" complex [$Ni(\eta^4-P_2C^t_2Bu_2)_2$] containing two 1,3-diphosphacyclobutadiene rings (Fig. 17) [33]. A single crystal analysis revealed that the 18- electron complex has C_2 symmetry and the ^{t}Bu substituents of the two rings are almost perfectly staggered. The four C–P bond lengths are identical (average 1.797 Å) and are comparable in length with those found in the complexes [$M(\eta^5-C_5H_5)(P_2C^t_2Bu_2)_2$] (M ≡ Co, Rh). "Sandwich" compounds containing both η^4-ligated $P_2C^t_2Bu_2$ rings and η^5-bonded 1,2-dicarbaboranes $B_2C_9H_{11}{}^{2-}$ are also known [34,35] (see Figs. 18 and 19). The rhodium complex forms a 1:1 adduct with [$AuPPh_3$].



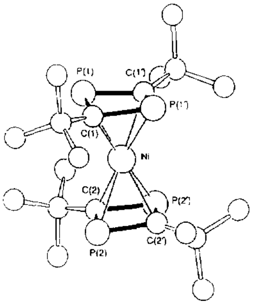


Fig. 17

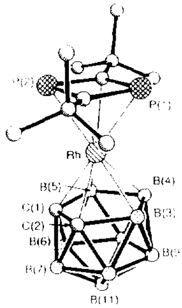


Fig. 18.

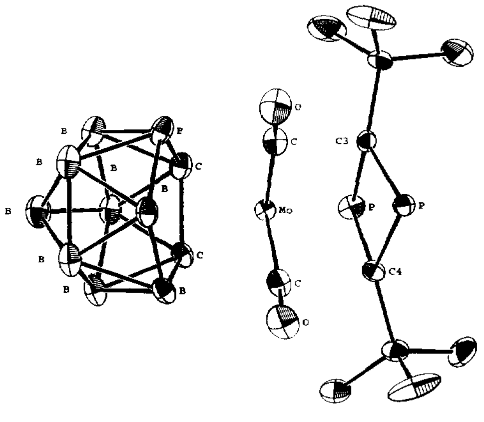


Fig. 19.

Interestingly, it has proved impossible to displace the η^4-ligated ($P_2C^t_2Bu_2$) rings from any of the above complexes, which contrasts with the behaviour of the analogous η^4-ligated cyclobutadiene ring complexes. Theoretical studies and photoelectron spectroscopic data on $[Fe(\eta^4\text{-}C_4H_4)(CO)_3]$ and $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ have been compared with their $[Fe(\eta^4\text{-}P_2C^t_2Bu_2)(CO)_3]$ and $[Co(\eta^5\text{-}C_5H_5)(P_2C^t_2Bu_2)]$ counterparts and the results have established that there is a significantly stronger π-interaction between the metal and the phosphorus-containing ring system [36]. Unlike their cyclobutadiene metal analogues, the η^4-ligated $P_2C^t_2Bu_2$ rings can themselves act as ligands towards other metal centres, typified by the examples shown in Figs. 20 and 21 [30,37–40].

Interesting differences are observed between alkynes and phospha-alkynes in their reactions at a molybdenum centre [41]. In the reaction of $[Mo(\eta^5\text{-}C_9H_7)(CO)_2(MeCN)_2][BF_4]$ with MeC≡CMe, the product is the bis-alkyne com-

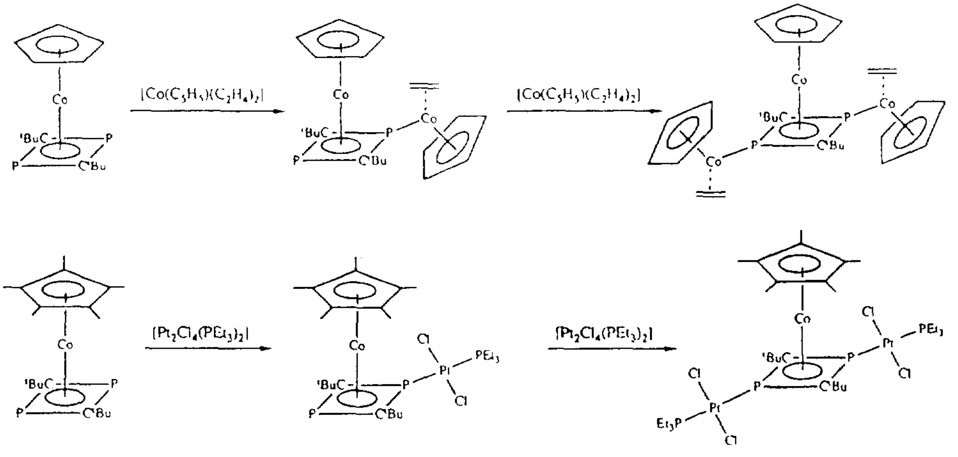


Fig. 20.

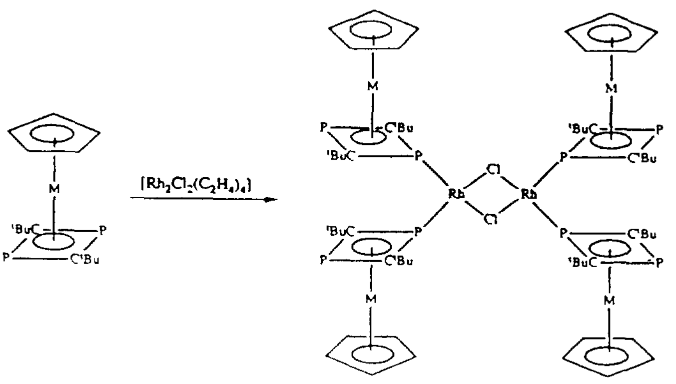


Fig. 21.

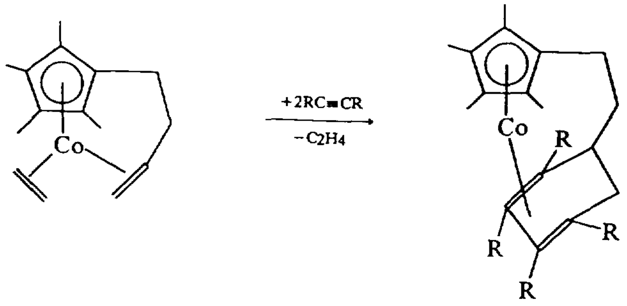


Fig. 23.

plex $[Mo(\eta^5\text{-}C_9H_7)(CO)(Me_2C_2)_2][BF_4]$, whereas, as shown in Fig. 22, the corresponding reaction with ^tBuCP affords the 1,3-diphosphacyclobutadiene complex in which the four-membered ring is unusually η^3-ligated to the metal in the solid state, but exhibits dynamic behaviour in solution. This difference between alkynes and phospha-alkynes is further illustrated in the reaction sequences at a cobalt(I) centre, shown in Figs. 23 and 24, where it can be seen that there is a preferential formation of the η^4-ligated 1,3-diphosphacyclobutadiene ring system [42].

Several polynuclear rhodium complexes which result from the reaction of the more reactive indenyl rhodium complex $[Rh(\eta^5\text{-}C_9H_7)(C_2H_4)_2]$ with ^tBuCP are illustrated

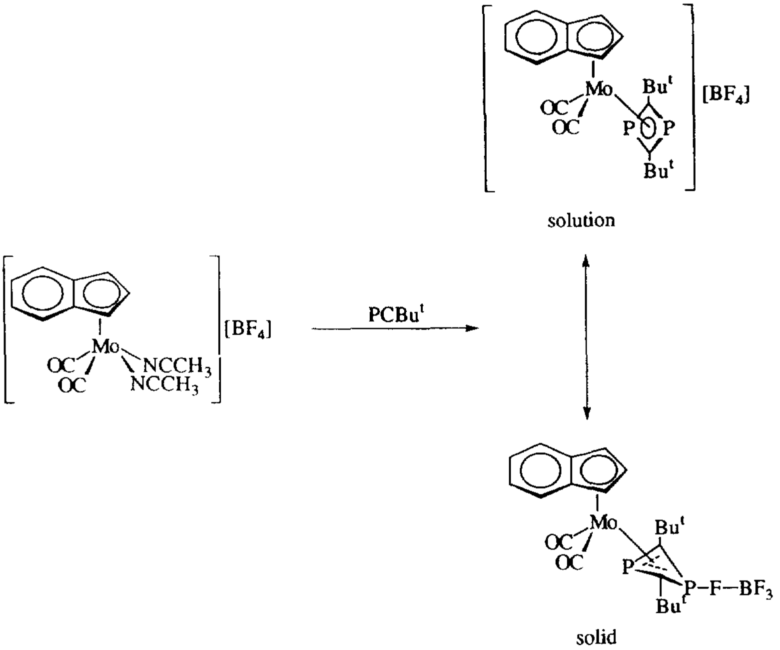


Fig. 22.

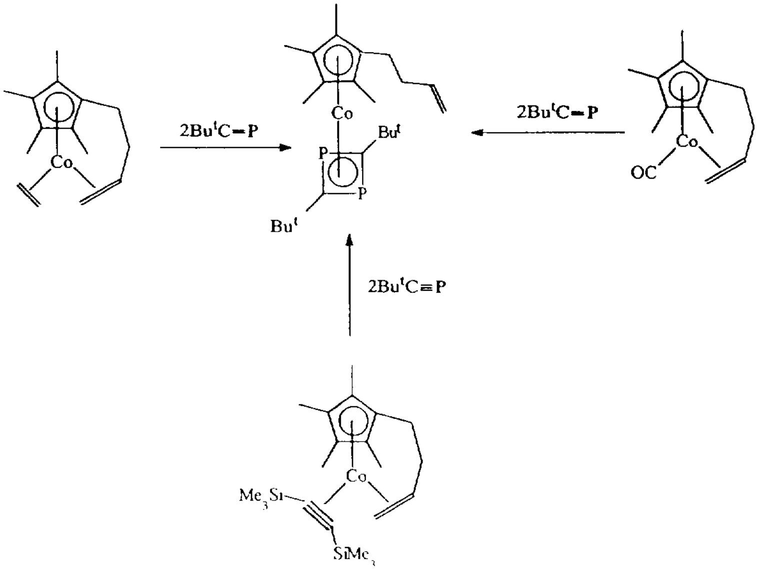


Fig. 24.

in Fig. 25 [40]. Detailed NMR and single crystal X-ray diffraction studies have confirmed the proposed structures, and a detailed reaction sequence has been established using [RhCl(PMe$_3$)$_3$] and ^{t}BuCP by isolation and full characterization of all the intermediates (Fig. 26) [43].

In an important paper, Wettling et al. [44] described a different type of cyclodimerization reaction which takes place when ^{t}BuCP reacts with [Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$] in the presence of magnesium in tetrahydrofuran (THF) at 0–25 °C. The diphosphabicyclo[1.1.0]butane complex shown in Fig. 27 is formed in good yield, which can be further improved if BuLi is used as the reducing agent instead of magnesium [44]. The [Zr(η^5-C$_5$H$_5$)$_2$] fragment can readily be substituted or eliminated by a series of reactions typified by those shown in Fig. 28 to afford a variety of interesting compounds. The analogous Hf complex can also be made by this route and exhibits a similar chemistry; however, the reaction of [Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$] with ^{t}BuCP and BuLi at −78–20 °C proceeds in a different fashion, as shown in Fig. 29 [45].

3.2. 1,2-Diphosphacyclobutadiene complexes

The first examples of these types of complex have only recently been described by Binger et al. [46]. Treatment of the bis(cyclo-octatetraene)titanium complex [Ti(η^4-COT)(η^8-COT)] with the phospha-alkynes RC≡P (R≡^{t}Bu, Ad) at 85 °C leads to displacement of the η^4-ligated ring and the formation of complexes containing both the η^4-ligated 1,3- and 1,2-diphosphacyclobutadiene ring systems (Fig. 30). Both compounds have been fully crystallographically characterized and their molecular structures are shown in Fig. 31. A mechanism has been proposed for their formation

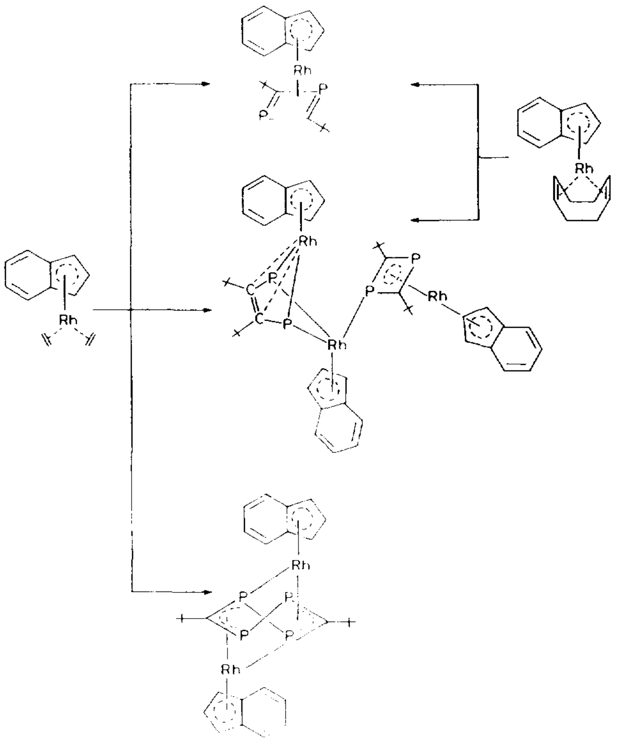

Rh
P
C
C-P

Fig. 25.

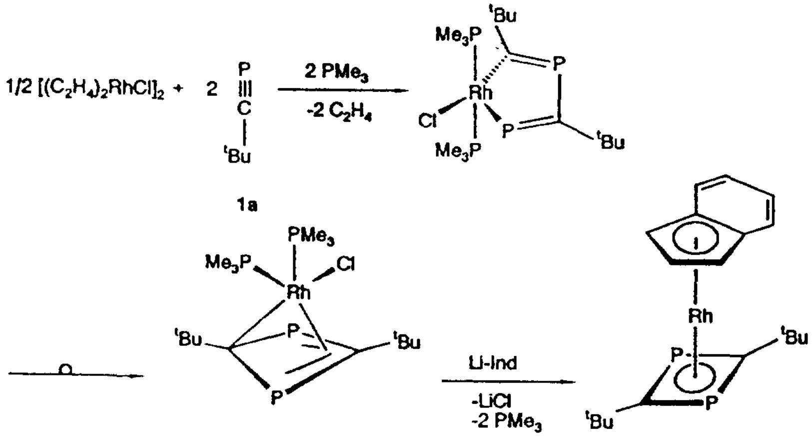

1/2 [(C$_2$H$_4$)$_2$RhCl]$_2$ + 2 P≡C–^{t}Bu
2 PMe$_3$
-2 C$_2$H$_4$
Me$_3$P
Rh
Cl
P
^{t}Bu
1a
PMe$_3$
Li-Ind
-LiCl
-2 PMe$_3$

Fig. 26.

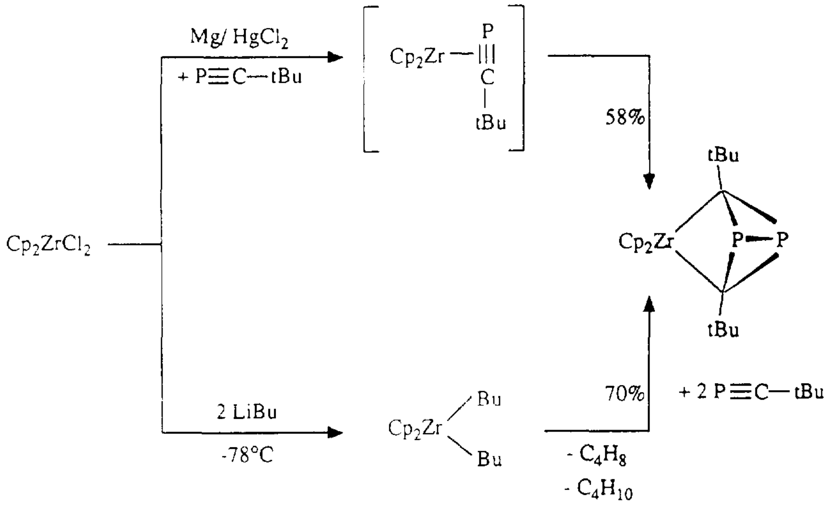


Fig. 27.

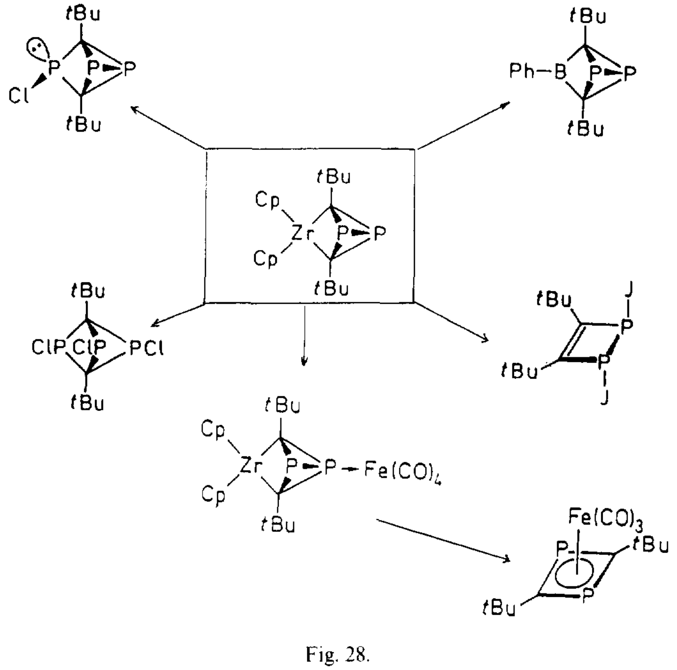


Fig. 28.

involving a reductive elimination step from two possible five-membered metallacycles (Fig. 32).

Use of the analogous Zr or Hf precursors leads instead to tetraphospha-barellene complexes (see section 6.2 and Fig. 70). The Ti complex containing the η^4-ligated

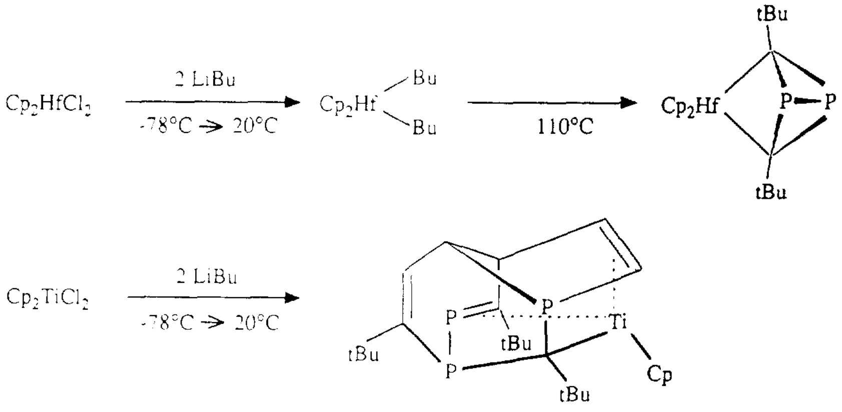


Fig. 29.

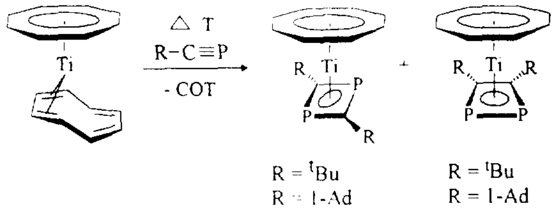


Fig. 30.

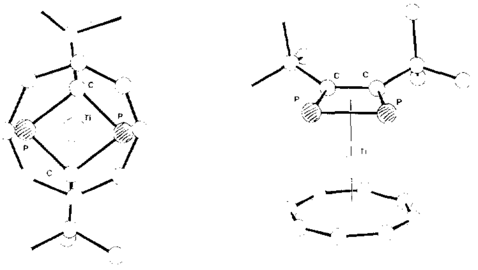


Fig. 31.

1,2-diphosphacyclobutadiene ring system is especially interesting since it is possible to remove the ring by treatment with hexachloroethane at room temperature to afford the novel tricyclic isomer of the ᵗBuCP tetramer, shown in Fig. 33 (see also Section 6).

3.3. Alkyne–phospha-alkyne coupling reactions

There are relatively few examples of monophosphacyclobutadiene metal complexes resulting from co-cyclodimerization reactions of alkynes and phospha-alkynes at

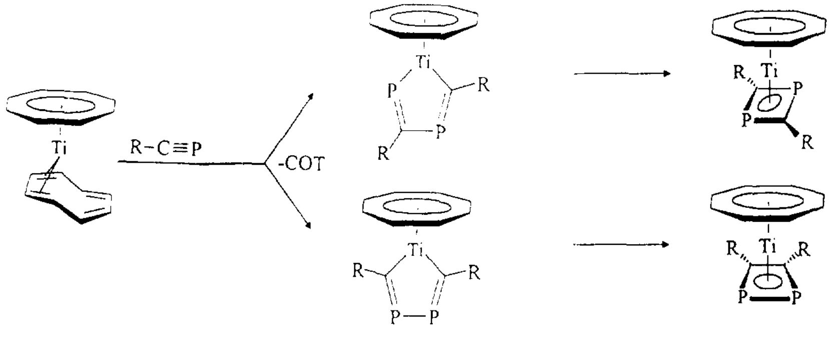


Fig. 32.

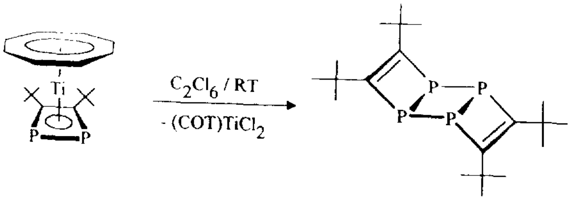


Fig. 33.

transition metal centres. Binger et al. [47] reported the first example using 1,2-bis(trimethylsilyl)acetylene and ^tBuCP at a cobalt centre (Fig. 34), and more recently they have extended the range of compounds in several rhodium(I) complexes, one of which is shown in Fig. 35. Full characterization, including single crystal X-ray diffraction studies, confirms the molecular geometry and, in the case of the P^iPr_3 rhodium complex, it is also possible to form a product in which two phospha-alkynes are coupled with PhC≡CPh (Fig. 35) [48].

3.4. Other coupling reactions

The first example of a 1-phospha-2-rhoda-cyclobutene was formed in 79% yield from the corresponding vinylidene rhodium complex (Fig. 36), which undergoes subsequent replacement of Cl by η^5-C_5H_5. The molecular structure of the chloro derivative reveals a planar heterocycle with the Rh atom being in a slightly distorted tetragonal bypyramid [48]. Other examples of these types of compound are illustrated in Fig. 37 [49,50].

There has been a single report of the linear coupling of two phospha-alkyne units at two samarium centres to give the dinuclear complex shown in Fig. 38, which has been fully structurally characterized [51].

Using the "isolobal" principle, it has been possible to relate the chemistry of metal carbyne compounds to phospha-alkynes, and Hill et al. [52] have isolated the bimetallic compound shown in Fig. 39 whose structure has been established by a single crystal X-ray diffraction study. The compound can be viewed as a 1-phospha-

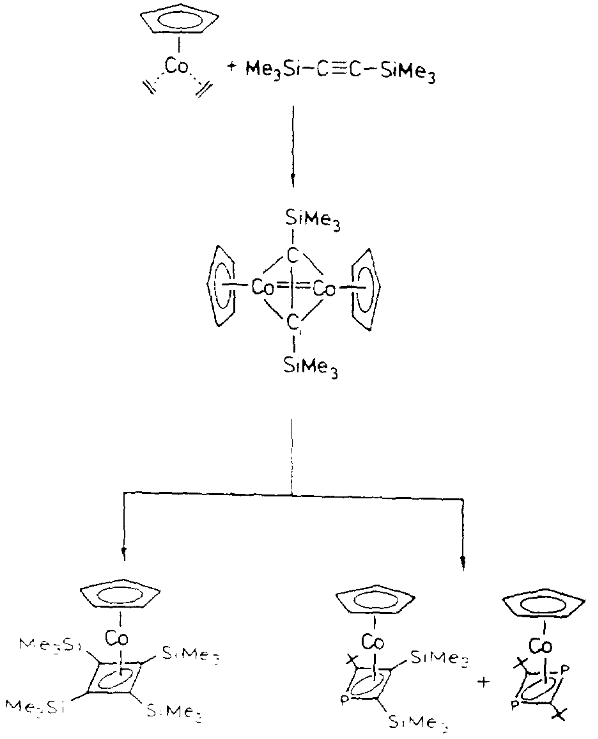
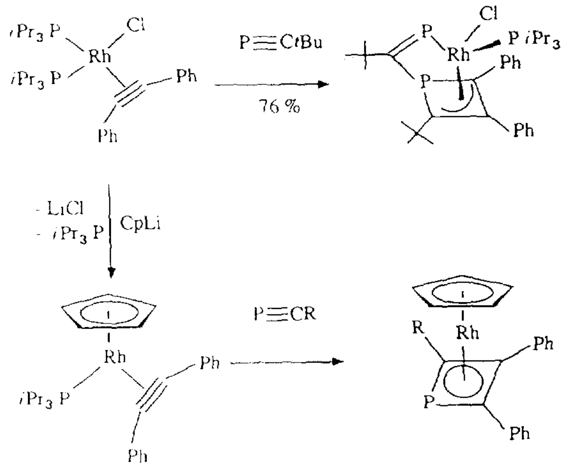


Fig. 34.



R = tBu; R = NiPr(SiMe$_3$)

Fig. 35.

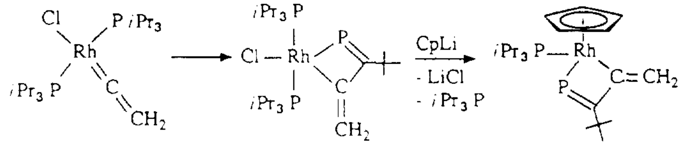


Fig. 36.

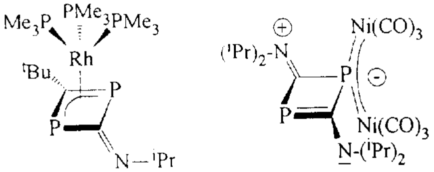


Fig. 37.

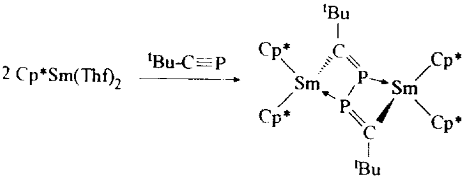


Fig. 38.

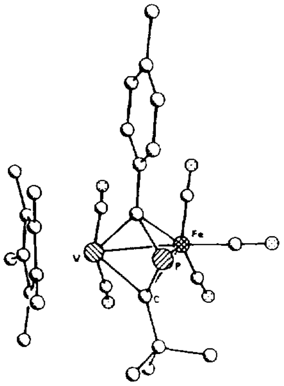
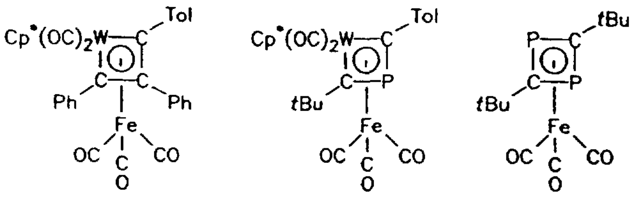


Fig. 39.

3-tungstacyclobutadiene moiety coordinated to an [$Fe(CO)_3$] unit, and the similarity of the structures of the three complexes shown in Fig. 40 underlines the importance of "isolobal" relationships throughout the Periodic Table.



Cp* = η^5-$C_5(CH_3)_5$; Tol = p-$H_3CC_6H_4$

Fig. 40.

4. Cycloaddition reactions

An extensive series of organic cycloaddition reactions of phospha-alkynes of the [2+2], [2+3] and [2+4] type have been widely studied by Regitz and coworkers [3,6,7,8]. Using the sterically hindered germene $(Me_3)_2Ge{=}CC_{12}H_8$, shown in

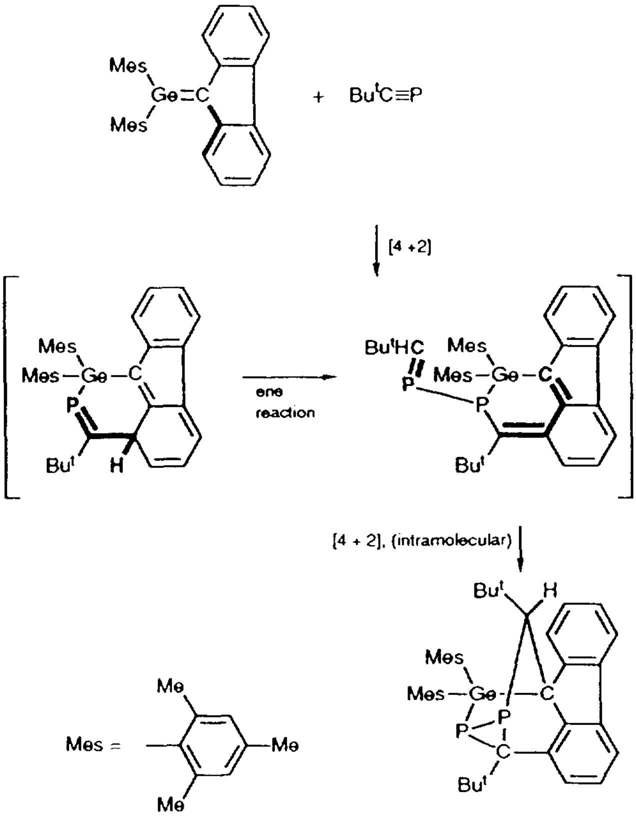


Fig. 41.

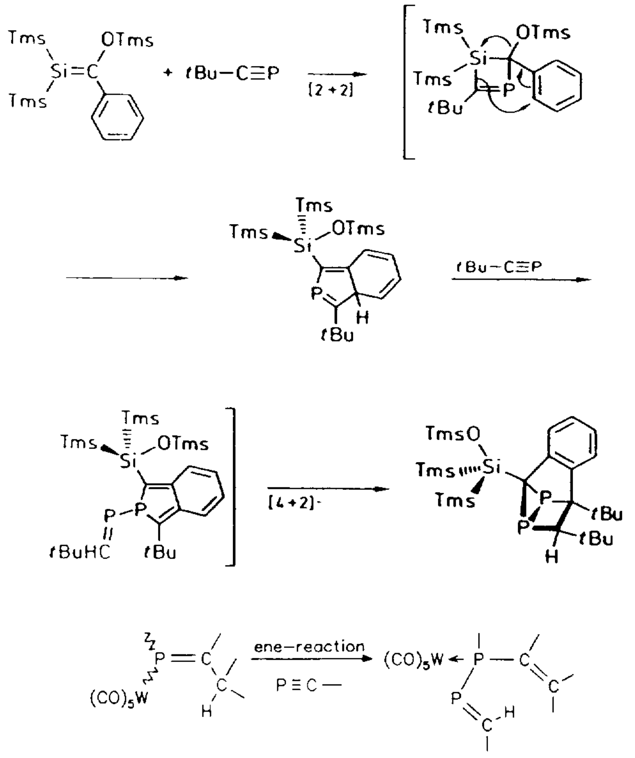


Fig. 42.

Fig. 41, an unexpected reaction ensued. Instead of the expected [2+2] cycloaddition to yield the germacyclobutene, a 1:2 stoichiometry of germene to phospha-alkyne gave the novel germadiphosphatricyclo-octene (Fig. 41) [53].

The process can be rationalized as arising from a [4+2] Diels- Alder reaction, followed by an "ene" reaction, followed by an intramolecular cycloaddition, and each step must proceed with high selectivity to result in a high yield (70%) of the polycyclic product. A similar reaction of buta-1,3-dienes with phospha-alkynes has been reported and, more recently, the analogous reaction has been carried out with ^{t}BuCP and the silene $(Me_3Si)_2{=}CPhOSiMe_3$ (generated thermally from the corresponding disilylacyclobutane) (Fig. 42). The resulting diphosphatricyclobenzoheptane has been fully characterized and its formation rationalized by cycloaddition steps and an "ene" reaction [54].

It was therefore of interest to see if "ene" products could be isolated directly from suitable phospha-alkenes and phospha-alkynes and, to this end, pentacarbonyl tungsten complexes of the former have been usefully employed to lead chemoselectively to diphosphanes having unsaturated units in 1,4-positions or, in certain cases, diphosphirane complexes (Fig. 43) [55].

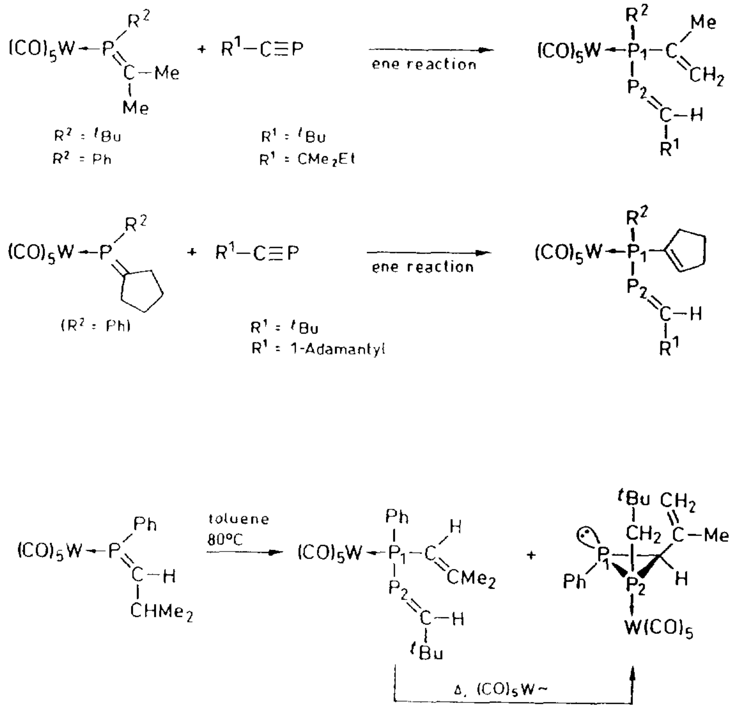


Fig. 43.

5. Cyclotrimerization reactions

5.1. *Cyclotrimerization of phospha-alkynes at metal centres*

By analogy with the known behaviour of alkynes, which readily cyclotrimerize to benzene derivatives in a large number of transition metal-catalysed processes, it might be expected that phospha-alkynes would readily form 1,3,5-tri-phosphabenzene derivatives or isomers thereof. However, to date, in spite of many attempts, there is no definitive evidence for the existence of these types of ring system. An early report of the molybdenum(0) complex shown in Fig. 44 could not be confirmed by independent investigation and therefore remains tentative [56], the main product formed

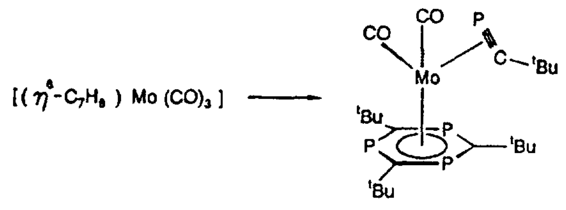


Fig. 44.

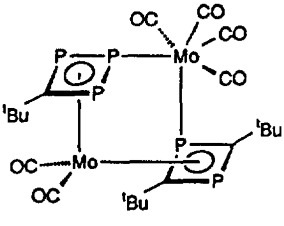


Fig. 45.

probably being the compound shown in Fig. 45 [57]. The 14-electron vanadium complex shown in Fig. 46 results when $[V(\eta^5\text{-}C_5Me_5)(\eta^6\text{-naphthalene})]$ reacts with three equivalents of ${}^tBuCP$; however, a single crystal X-ray diffraction study on the product showed it to be a derivative of 1,3,5-triphosphaprismane. In solution, it exhibits interesting fluxional behaviour indicative of a valence isomerization taking place [58].

The 14-electron vanadium complex reacts early with one mole of CO at room temperature to give a new complex in which the $P_3C_3^tBu_3$ ligand has rearranged to the complexed Dewar 1,3,5-benzene, which has also been fully characterized by a single crystal X-ray diffraction study (Fig. 47). A totally different cyclotrimerization of ${}^tBuCP$ occurs in its reaction with $TaCl_5$ to give the unusual products shown in Fig. 48. The origin of the oxygen atom is unknown [59].

The reaction of $[RhCl(P^iPr_3)_3]$ with ${}^tBuCP$, reported by Binger and Haas [60], differs from those discussed in Section 3 in that trimerization of the phospha-alkyne occurs and the interesting dimeric rhodium complex is formed in good yield. The structure (Fig. 49), which has been confirmed by a single crystal X-ray diffraction

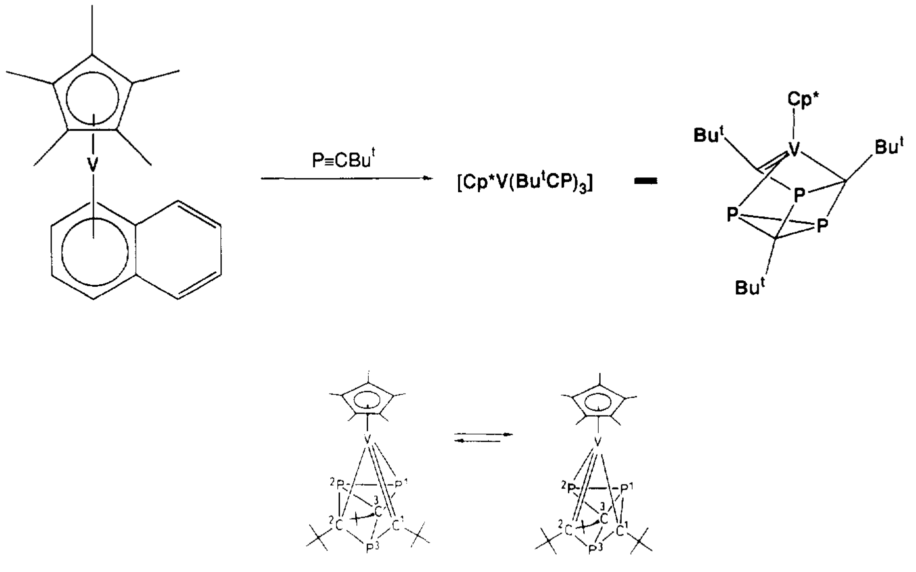


Fig. 46.

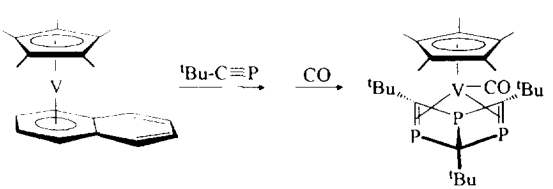


Fig. 47.

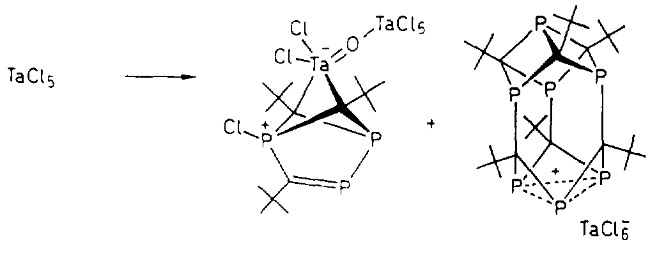


Fig. 48.

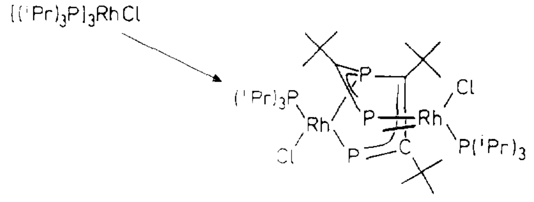


Fig. 49.

study, shows that the third phospha-alkyne is bonded to the preformed 1,4-diphospha-2-rhodacyclopentadiene via a C–C bond.

A closely structurally related complex containing three ^{t}BuCP units has recently been described by Hitchcock et al. [61] (see also Fig. 35). Treatment of the ionic ruthenium(II) complexes with either ^{t}BuCP or AdCP gives the yellow neutral complexes shown in Fig. 50, which can subsequently react with two equivalents of [W(CO)$_5$THF] to give the bis-[W(CO)$_5$] compounds (Fig. 51). Both have been fully structurally characterized. This behaviour of the three phospha-alkyne units contrasts with that of arenes which are normally strongly stabilized in the environment of an Ru(II) cation.

An important recent development was the report by Breit et al. [62] of the spirocyclotrimerization of the phospha-alkyne ^{t}BuCP with $AlCl_3$ in a 3:1 ratio with the incorporation of the Lewis acid (Fig. 52). When the metal halide is removed by

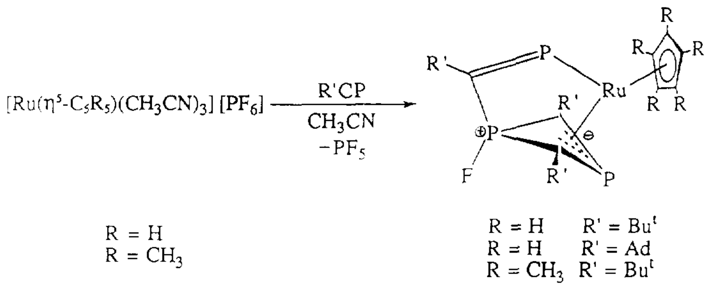


Fig. 50.

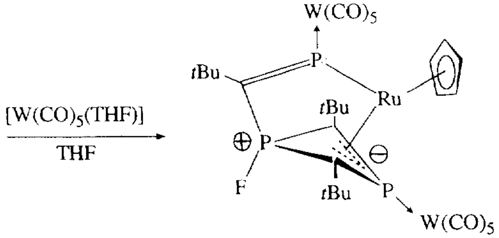


Fig. 51.

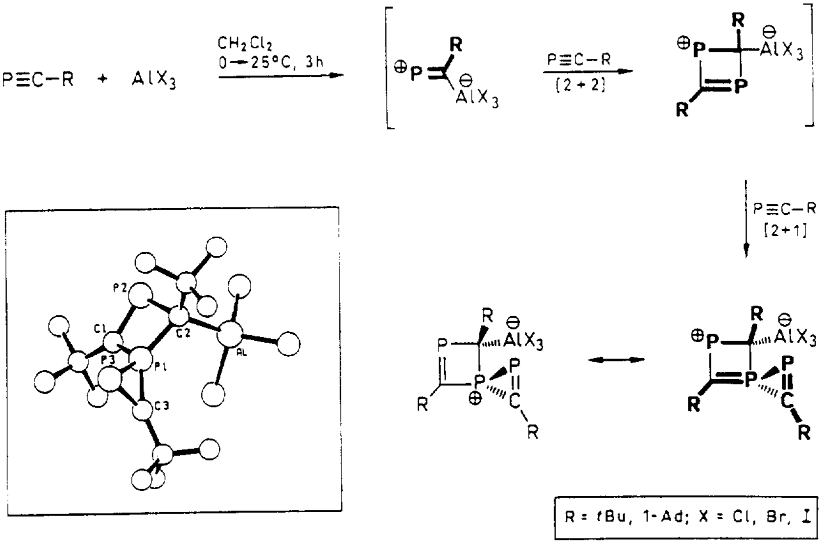


Fig. 52.

addition of Me_2SO in the presence of a further equivalent of ${}^tBuCP$, it gives a variety of novel products (Fig. 53) (see also Section 6).

A completely different reaction pathway occurs when cyclo-oligomerization reactions of ${}^tBuCP$ take place in the presence of Al_2Et_6, in which highly selective formation of phosphorus-containing polycycles with the incorporation of the Lewis acid occurs [63]. It appears that the composition of the complexes depends on the nature of the solvent in which the reaction takes place; for example, when ${}^tBuCP$ and $AlEt_3$ are reacted in a 3:2 ratio in *n*-hexane, the complex shown in Fig. 54, in which three Et groups have been transferred from Al to P, is obtained in 91% yield. This novel compound has been fully structurally characterized by multinuclear NMR spectroscopy and a single crystal X-ray diffraction study.

On the other hand, when ${}^tBuCP$ and $AlEt_3$ are allowed to react in the molar ratio 4:1 in diethyl ether, the carbon–phosphorus–aluminium polycycle shown in Fig. 55 is found in 74% yield, which has also been fully structurally characterized. Although a detailed mechanistic understanding is still incomplete, it is envisaged that the Lewis

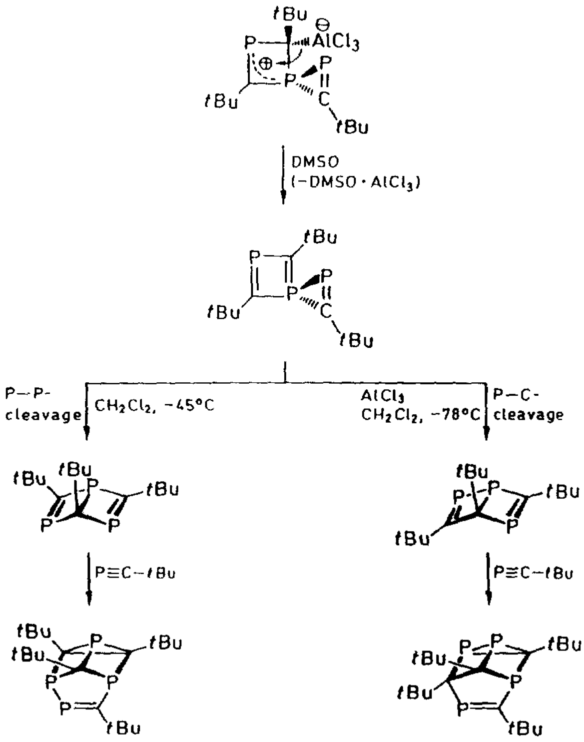


Fig. 53.

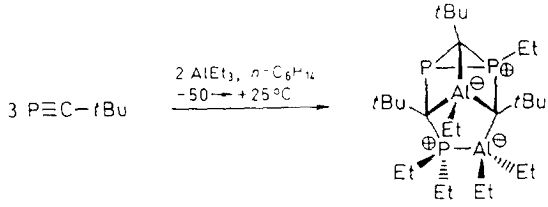


Fig. 54.

acid initially attaches at the C atom of the phospha-alkyne (note that the P≡C bond in phospha-alkynes is polarized in the sense $P^{\delta+}$-$C^{\delta-}$) and then $EtP{=}C({}^{t}Bu)(AlEt_2)$ is formed via a 1,2-ethyl shift. The reaction is believed to branch out at a stage no later than following the analogous 1,2-addition step involving a further equivalent of ${}^{t}BuCP$, and the role of the diethyl ether may be to block the Lewis acid.

5.2. *Cotrimerization of phospha-alkynes with other unsaturated systems*

Binger et al. [48,60] have developed several routes to complexes based on cotrimerization reactions involving two phospha-alkynes and one alkyne. These reactions,

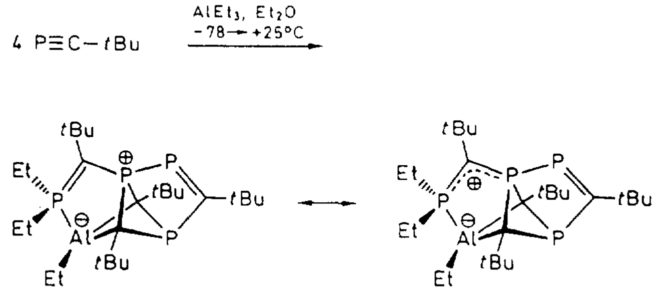


Fig. 55.

which are summarized in Figs. 56 and 57, reveal the interesting interplay of factors that affect the course of the reactions involved, and the most probable (^{13}C NMR) formation of the diphospha-Dewar benzene and 1,3-diphosphabenzene compounds is noteworthy. Both ^{t}BuCP and AdCP behave similarly. Very recent unpublished work by Bohm et al. [64] has led to the first example of a 1,3-diphosphabenzene derivative of the type shown in Fig. 58 which results from a synthetic route involving metal vapour synthesis.

Carbon monoxide can also be involved in a cyclotrimerization reaction with two moles of phospha-alkynes, for example in the reaction of $[Rh_2(CO)_2(\eta^5\text{-}C_5Me_5)_2]$ with ^{t}BuCP or AdCP (Fig. 59) to afford dinuclear complexes in which one Rh atom is η^2-ligated to each P=C double bond, while the other is bonded directly to two P

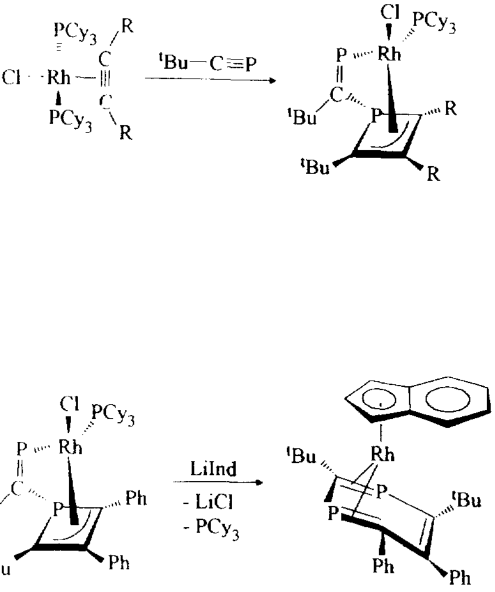


Fig. 56.

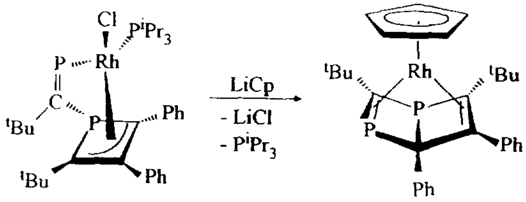


Fig. 57.

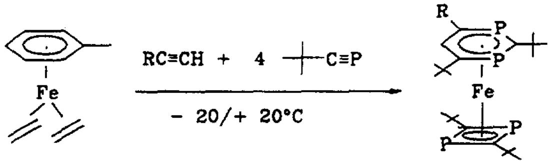


Fig. 58.

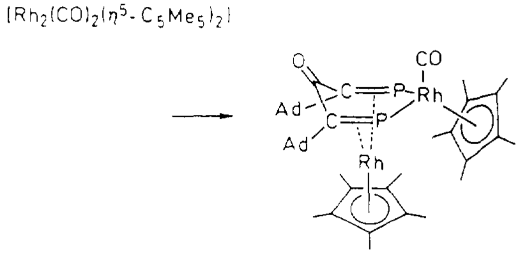


Fig. 59.

atoms. The compounds have been fully characterized by a single crystal X-ray diffraction study [65].

6. Phospha-alkyne tetramers and their coordination complexes

In the past 5 years, several tetramers of the phospha-alkyne ^{t}BuCP have been reported. The first studies by Wettling et al. [66] of the pyrolysis of ^{t}BuCP showed that, in the absence of solvent at 180 °C, the products were the tetraphosphacubane (10%) and the tetraphosphabis(homo)prismane (10%), together with similar amounts of the tetraphosphacubane in which one tertiary butyl group was lost via elimination of isobutylene (Fig. 60). Subsequently, Regitz and coworkers [44,64] developed a high yield (approximately 70%) synthesis of several tetraphosphacubanes, $P_4C_4R_4$, from the corresponding precursors $[Zr(\eta^5\text{-}C_5H_2)_2(P_2C_2R_2)]$ by treatment with C_2Cl_6 and proposed the mechanism shown in Fig. 61, and very recently Nixon et al. [67] showed that small quantities of the tricyclic tetramer

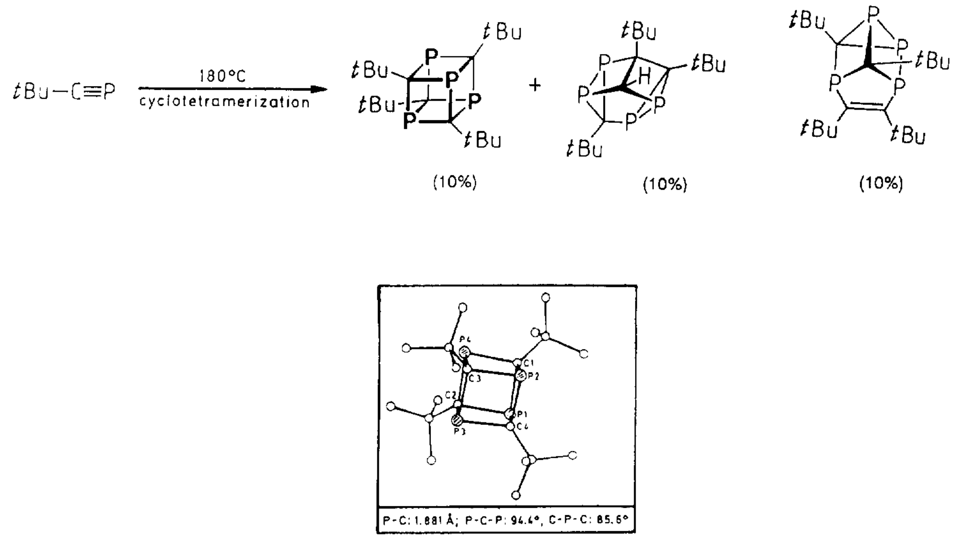


Fig. 60.

(R ≡ ^{t}Bu) are also formed in this reaction and the steric effect of adjacent ^{t}Bu groups prevents "cubane" formation via an internal [2+2] cycloaddition process (Fig. 61). Binger, Regitz et al. [67] also recently showed that treatment of [Zr(η^5-

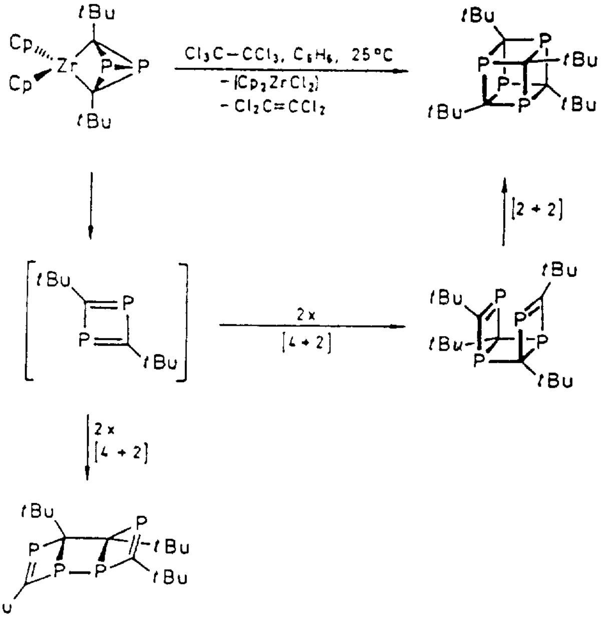


Fig. 61.

$C_5H_5)_2(P_2C_2^tBu_2)]$ with $[NiCl_2(PPh_3)_2]$ or using a mixture of $P_2I_2C_2^tBu_2$ and $[Pt(C_2H_4)(PPh_3)_2]$ gave yet another isomer, shown in Fig. 62, having a similar tricyclic structure and also not undergoing any further [2+2] cycloaddition step to form a "cubane" structure. Fig. 63 shows a possible reaction mechanism, and Fig. 64 illustrates its reaction with dioxygen and sulphur [67].

Full structural characterization of all the tetramers has been elucidated either by single crystal X-ray diffraction studies or proposed on the basis of NMR spectroscopic studies. The first full structural characterization of the bis-$[W(CO)_5]$ adduct shown in Fig. 65 has very recently been achieved by Hitchcock et al. [68], which fully confirms the earlier NMR spectroscopic results of Wettling et al. [66], and also indicates that it is the two P atoms in the strained P_2C three-membered ring that preferentially act as the donor centres.

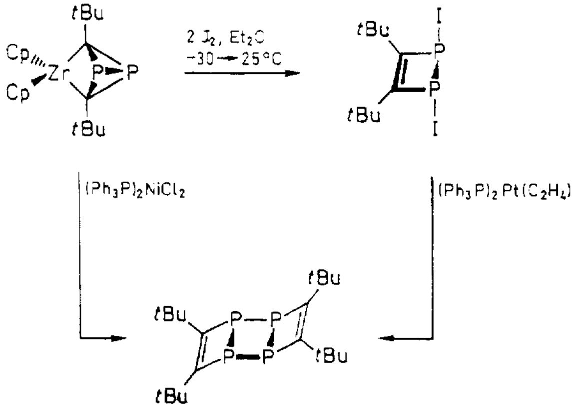


Fig. 62.

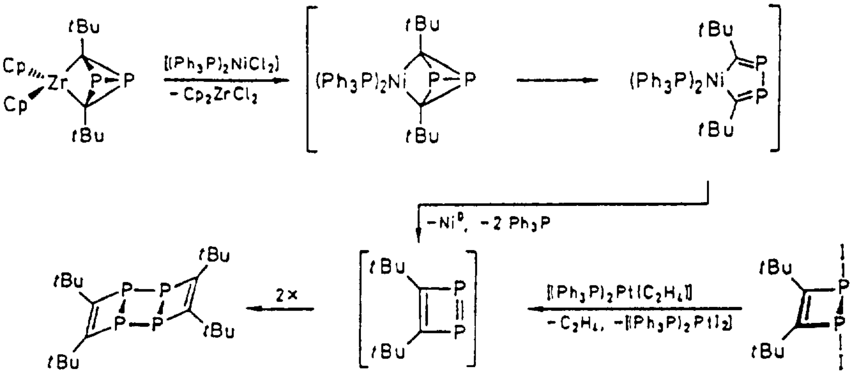


Fig. 63.

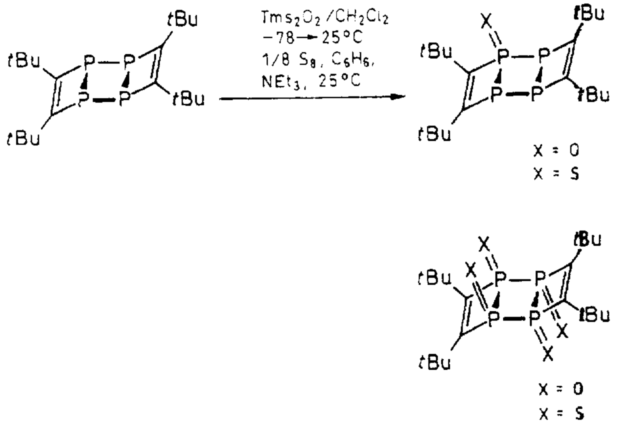


Fig. 64.

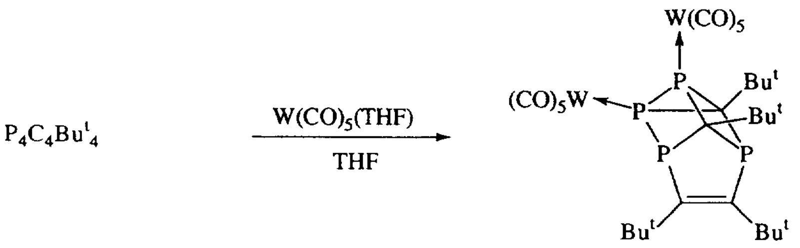


Fig. 65.

6.1. Coordination complexes of the tetraphosphacubane $P_4C^t_4Bu_4$

As mentioned above, the recent synthesis of the tetraphospha-"cubane" compound enabled a study of its ligating properties to be undertaken. Before discussing the progress to date in this area, it is necessary to comment firstly on the structural and bonding features of the $P_4C^t_4Bu_4$ "cube" [69]. As expected, the P–C bond lengths, determined by single crystal X-ray analysis, are all identical (d(P–C) = 1.881 Å), and are typical of single bonds. The angles at phosphorus are reduced from the idealized 90° to 85.6°, while those at carbon are widened to 94.4° (see Fig. 60).

The interesting features of the NMR spectroscopic studies are the high field shift of the skeletal C atoms and the low field signal for the P nuclei. It has also been established by both He(I) photoelectron and molecular orbital (MO) calculations [69] that the lone pair electrons on phosphorus participate significantly in the P–C σ-framework of the "cube" via electron transfer, thus causing the phosphorus atoms to have a formal positive charge. This affects the basicity of the phosphorus centres and strong electrophiles are required to quaternize the heteroatoms. Thus even an excess of "magic methyl" only affords the monomethylated phosphonium salt at −78 °C. Monoprotonation occurs with fluorosulphuric acid in liquid SO_2 at −78 °C and diprotonation is only achieved with "magic acid" FSO_3H/SbF_5 [70,71]. It is not surprising therefore that $P_4C^t_4Bu_4$ only forms the mono-tetracarbonyliron(0) complex shown in Fig. 66, even under forcing conditions [71].

Very recently, Caliman et al. [72] have shown that, by increasing the oxidation state of the transition metal, two P centres of the "cubane" can be made to coordinate to the metal centres even under mild conditions. Thus treatment of $P_4C^t_4Bu_4$ with $[PtCl_2(PR_3)]_2$ (R=Et, Bu) at room temperature gives the complexes *trans*-$[PtCl_2(PR_3)(P_4C^t_4Bu_4)]$ and *trans*-$[\{PtCl_2(PR_3)\}_2(P_4C^t_4Bu_4)]$ (Figs. 67 and 68) in a stepwise fashion. Both types of complex have been fully structurally characterized by ^{31}P NMR spectroscopy and by single crystal X-ray diffraction studies.

Mention should be made here of very new structural types of complex which are formally related by "isolobal" considerations to the dication of cubane $[C_8H_8]^{2+}$.

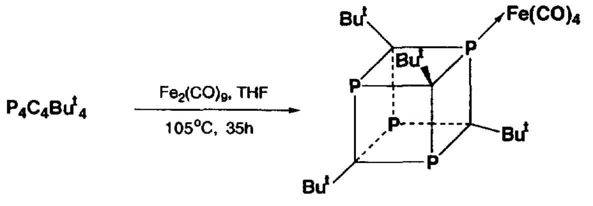


Fig. 66.

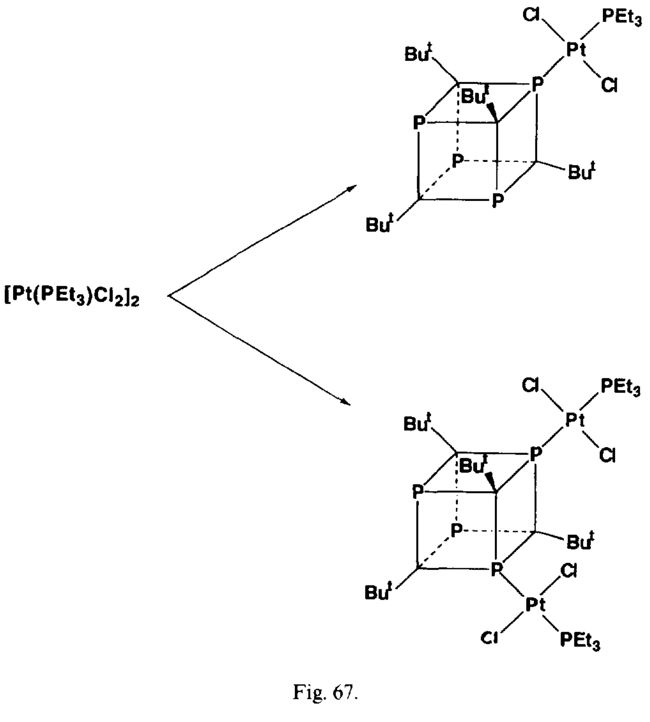


Fig. 67.

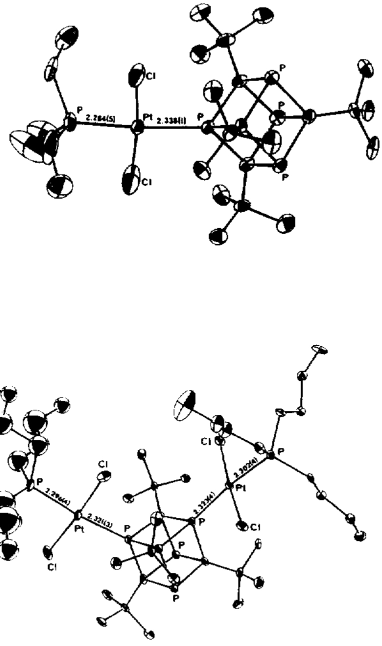


Fig. 68.

Thus reactions of the $P_3C_2^tBu_2$ anion (Section 7) with cobalt and rhodium metal halides give rise to the fully structurally characterized "pseudo"-cubane structures shown in Fig. 69 [73]. It is particularly noteworthy that the loss of two electrons from the ideal cubane structure appears to lead to a distortion of one face of the cube. This aspect is currently under theoretical consideration [74].

6.2. *1,3,5,7-Tetraphospha-barellene complexes*

Very recently, the first cyclotetramerization of a phospha-alkyne directly at a transition metal centre has been established by Binger et al. [75]. Interestingly, instead of the possible formation of an η^8-ligated 1,3,5,7-tetraphosphacyclooctatetraene derivative, or any of the tetramers of ^{t}BuCP described above, the product has been established by multinuclear NMR spectroscopic investigations to be the first example of a 1,3,5,7-tetraphospha-barellene derivative.

Thus treatment of the zirconium bis-cyclo-octatetraene complex $[Zr(\eta^8\text{-COT})(\eta^4\text{-COT})]$ with ^{t}BuCP in toluene for 2 days at 70 °C leads to the displacement of the η^4-ligated cyclo-octatetraene ligand and the formation of $[Zr(\eta^8\text{-COT})(\eta^4\text{-}P_4C_4^tBu_4)]$ (Fig. 70).

Of special interest in connection with the formation of the tetraphosphacubane discussed elsewhere is the observation that treatment of the zirconium tetraphospha-barellene complex with C_2Cl_6 results in the formation of the free 1,3,5,7-tetraphospha-barellene which has not been obtained by any other synthetic route. The mechanism

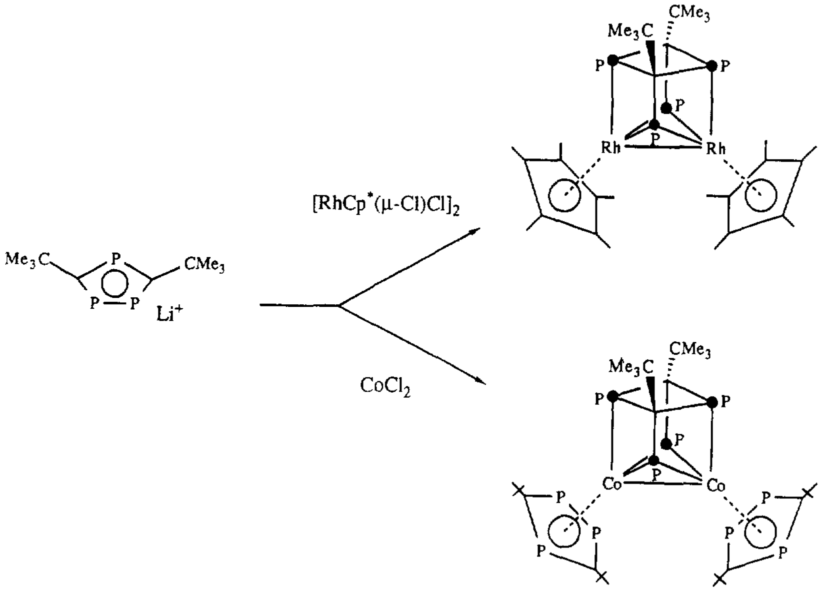


Fig. 69.

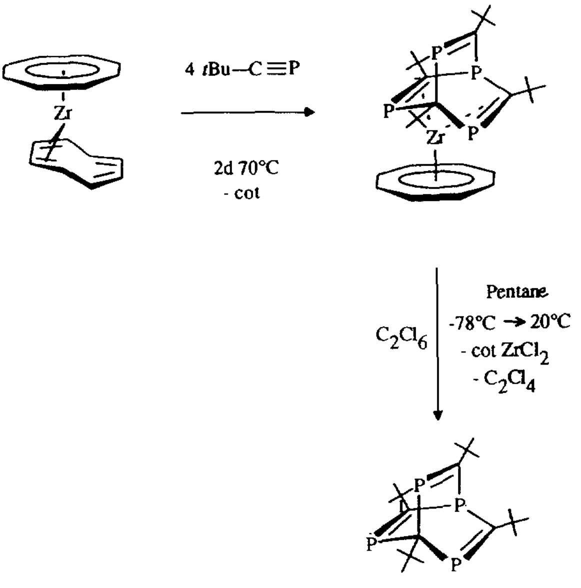


Fig. 70.

of formation of the tetraphospha-barellene zirconium complex shown in Fig. 71 assumes an initial step involving an oxidative coupling reaction of two phosphaalkynes with the concomitant displacement of one of the cyclo-octatetraene ligands.

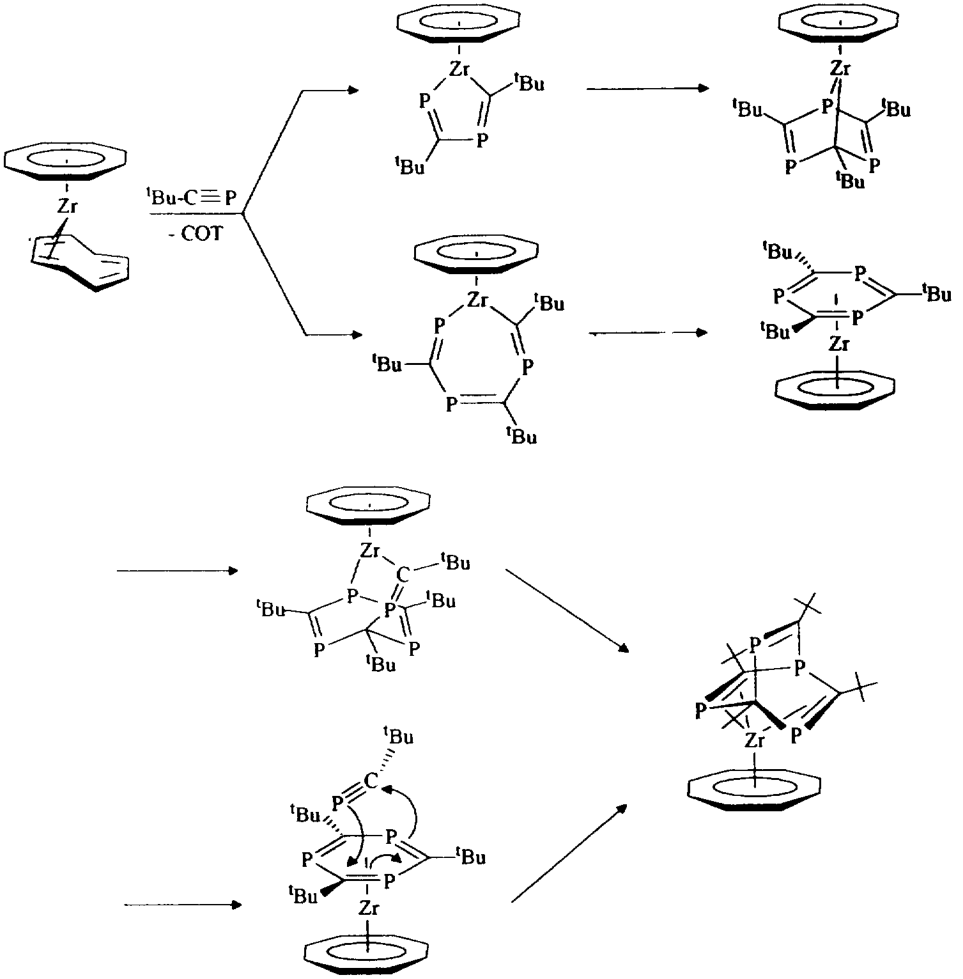


Fig. 71.

The resulting metallacycle can then react in two distinctly different ways: (1) a [4+2] cycloaddition process with ᵗBuCP, followed by a second step involving a 1,2-addition of ᵗBuCP to give the final product; (2) an initial 1,2-addition of ᵗBuCP to give the seven-membered metallacycle, followed by reductive elimination to give the as yet unknown 1,3,5-triphosphabenzene complex as an intermediate, which finally undergoes a [4+2] cycloaddition step to give the final product. Both possible reaction mechanisms are intriguing and should be the focus for further studies in this area.

In an attempt to obtain single crystals of the barellene complex, Cloke et al. [76] have recently utilized both the Zr and Hf complexes shown in Fig. 72 which contain two Me_3Si groups in each cyclo-octatetraene ring. Both complexes afford the corre-

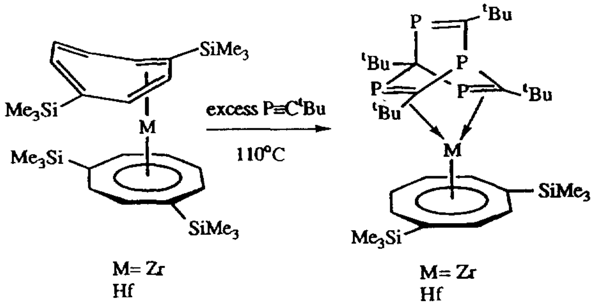


Fig. 72.

sponding green 1,3,5,7-tetraphospha-barellene metal complexes when treated with ${}^tBuCP$.

7. Di- and tri-phosphacyclopentadienyl anions and their metal complexes

The initial observation by Becker et al. [77] that the planar $P_3C^t_2Bu_2$ ion resulted from the reaction of ${}^tBuCP$ with $LiP(SiMe_3)_2$ was followed by the independent reports of Bartsch and Nixon [78] and Cowley and Hall [79] that mixtures of P_3C_2 ${}^tBu_2$ and $P_2C^t_3Bu_3$ anions resulted from the reduction of ${}^tBuCP$ with Na/Hg or low-valent tantalum species by a mechanism which is still unknown. Using the alkali metal/amalgam technique, a mixture of all possible di- and tri-phosphollide ions can be readily obtained from ${}^tBuCP$ and ${}^iPrCP$ [80].

The interesting structural and spectroscopic features of these aromatic polyphosphorus ring systems have been extensively discussed by Mathey [81] in an earlier review in this journal and will not be repeated here. Of special relevance to other sections of the present review is the coordination chemistry of the two ring systems and their recently obtained neutral derivatives.

Following the synthesis of the $P_3C^t_2Bu_2$ and $P_2C^t_3Bu_3$ anionic rings, Bartsch et al. [82] described their ready conversion by treatment with $FeCl_2$ in an ether solvent into the green, air-stable, sublimable penta- and hexa-phosphaferrocenes $[Fe(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^5\text{-}P_2C^t_3Bu_3)]$ and $[Fe(\eta^5\text{-}P_3C^t_2Bu_2)_2]$, which were both fully structurally characterized by single crystal X-ray diffraction studies (Fig. 73). Unpublished photoelectron spectroscopic data and cyclic voltammetry measurements [83] indicate that

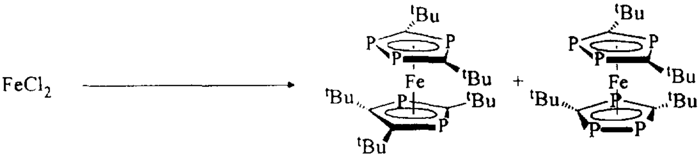


Fig. 73.

the P atoms in the rings exert an overall greater electron-withdrawing effect than the ring carbon atoms.

Low yields of $[\mathrm{Fe}(\eta^5\text{-}\mathrm{P_3C^t_2Bu_2})(\eta^5\text{-}\mathrm{P_2C^t_3Bu_3})]$ were reported by Driess et al. [84], together with $[\mathrm{Fe}(\eta^4\text{-}\mathrm{P_2C^t_2Bu_2})(\eta^6\text{-}\mathrm{C_6H_5Me})]$ and the paramagnetic complex $[\mathrm{Fe}(\eta^5\text{-}\mathrm{P_2C^t_3Bu_3})(\eta^4\text{-}\mathrm{P_2C^t_2Bu_2})]$ from the reaction of ^{t}BuCP with the highly reactive $[\mathrm{Fe}(\eta^6\text{-}\mathrm{C_6H_5Me})(\eta^4\text{-Me-naphthalene})]$ derivative, the latter being previously obtained from metal vapour synthesis (Fig. 74).

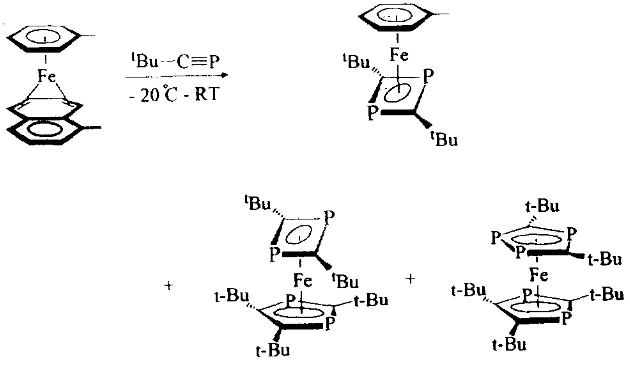


Fig. 74.

Very recently, Binger and Glaser [85] have obtained $[\mathrm{Fe}(\eta^5\text{-}\mathrm{P_3C_2R_2})(\eta^5\text{-}\mathrm{P_2C_3R_3})]$ (R ≡ ^{t}Bu, Ad) in 45% and 54% yields respectively in a very convenient synthesis in which the appropriate phospha-alkyne is treated with bis(cyclo-octatetraene)iron(0) at 80–100 °C (see Fig. 75).

Interestingly (see Section 8 on metal vapour syntheses), the pathway whereby five equivalents of the phospha-alkyne leads to the η^5-ligated di- and tri-phosphacyclopentadienyl ring system has not been elucidated, but it is known that pentamethylcyclopentadienyl chromium complexes can also result from the cyclo-oligomerization of five 2-butynes in the coordination chemistry of a chromium(I) species.

The analogous 16-electron hexaphosphachromocene derivative [Cr(η^5-

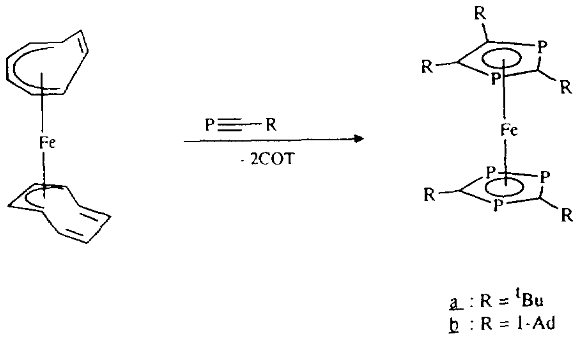


Fig. 75.

$P_3C^t_2Bu_2)_2]$, which is isostructural with its Fe analogue, could only be obtained in about 1% yield from the $P_3C^t_2Bu_2$ anion [86], and attempts to make the related 19-electron and 20-electron metallocenes containing Co and Ni by treatment of the $P_3C^t_2Bu_2$ anion with the appropriate metal halide in an ether solvent gave, instead, the diamagnetic 18-electron complexes shown in Fig. 76, which were both structurally characterized by single crystal X-ray diffraction studies [87,88].

Subsequently, it became clear that several types of ligation are possible for the di- and tri-phosphacyclopentadienyl ring system. In the case of the $P_2C^t_3Bu_3$ ring, it was found to ligate in either an η^5-fashion as in $[Fe(\eta^5\text{-}P_3C^t_2Bu_2)(\eta^5\text{-}P_2C^t_3Bu_3)]$ and $[Mo(\eta^3\text{-}C_9H_7)(\eta^5\text{-}P_2C^t_3Bu_3)(CO)_2]$ or in an η^3-mode as in $[Ni(\eta^5\text{-}P_3C^t_2Bu_2)(\eta^3\text{-}P_2C_3{}^tBu_3)]$ and $[Mo(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}P_2C^t_3Bu_3)(CO)_2]$ [88,89]. The $P_3C^t_2Bu_2$ ring, on the other hand, can exhibit η^5-ligation in a variety of complexes, but also a variety of additional modes of ligating behaviour shown in Fig. 77 [90,91].

Of special significance in the ligating properties of the $P_3C^t_2Bu_2$ anion is the utilization of the P lone pair electrons of the two connected P atoms in the ring. Then it is possible to attach a variety of further metal centres, for example in the complexes shown in Fig. 78 [90,91]. (For a more extensive review of these types of

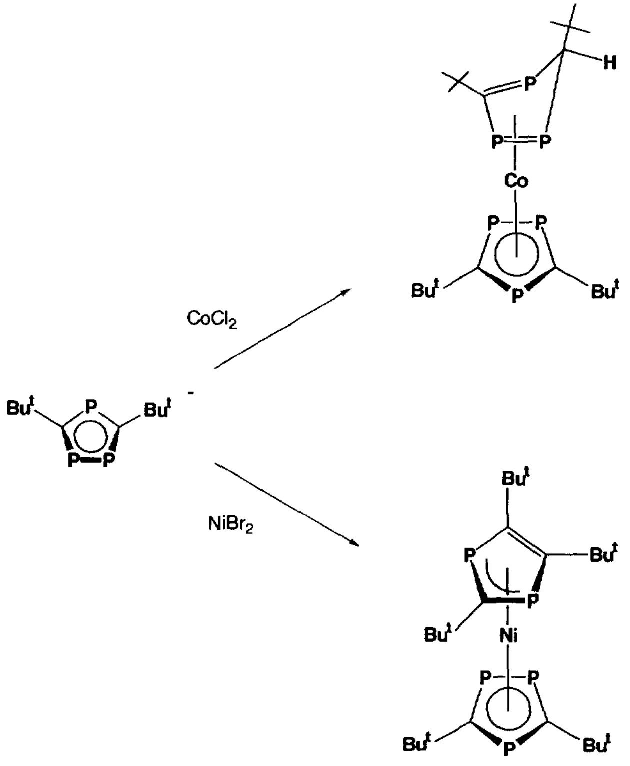


Fig. 76.

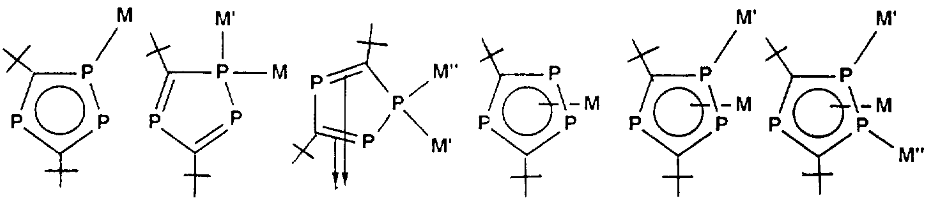
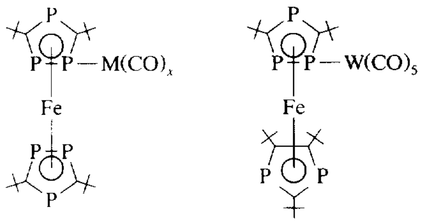


Fig. 77.



(M = Fe, $x = 4$)
(M = W, $x = 5$)

Fig. 78.

polyphospholyl-metal complex, the reader is referred to the Mathey review article in this journal [81].)

A particularly interesting example of the utilization of the P lone pair electrons is in the tetranuclear complex $[Fe(\eta^5\text{-}P_3C^t_2Bu_2)_2(Ru_3(CO)_{10})]$ in which the trinuclear ruthenium carbonyl complex links the two $P_3C^t_2Bu_2$ rings of the hexaphosphaferrocene (Fig. 79). A completely different reaction occurs when the pentaphosphaferrocene complex is reacted with $[Ru_3(CO)_{12}]$, because the $\eta^5\text{-}P_2C^t_3Bu_2$-ligated ring cannot undergo supplementary ligation via its P atoms, presumably because of the steric effect of the adjacent ^{t}Bu groups in the ring. Instead, a novel phosphinophosphinidene $P_5C^t_5Bu_5$ fragment results from the remarkable elimination of the Fe atom and coupling of the two ring systems, and this is subsequently trapped by the $[Ru_3(CO)_9]$ cluster. The novel molecular structure has been confirmed (Fig. 80) by a single crystal X-ray diffraction study [91,92].

Mixed ring "sandwich" compounds of the type $[Rh(\eta^5\text{-}P_3C^t_2Bu_2)(COD)]$, $[M(\eta^5\text{-}C_5R_5)(\eta^5\text{-}P_3C^t_2Bu_2)]$ and $[M(\eta^5\text{-}C_5R_5)(\eta^5\text{-}P_2C^t_3Bu_3)]$ (M = Fe; R = H, Me)

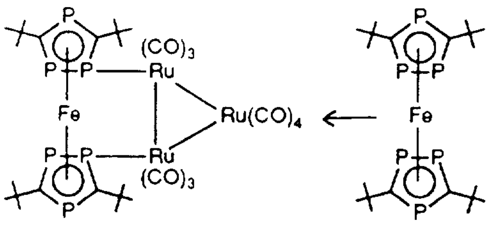


Fig. 79.

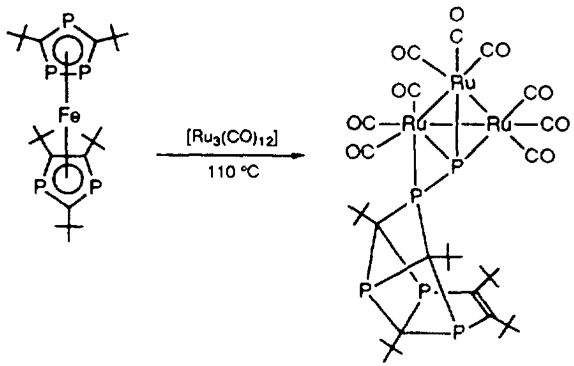


Fig. 80.

are also known [93], as well as an unusual hydride complex $[RhH(\eta^1\text{-}P_3C_2^tBu_2)(\eta^5\text{-}C_5Me_5)(PPh_3)]$, which does not undergo reductive elimination [93] (Fig. 81). Likewise, tri-, penta- and hexa-phospharuthenocenes have very recently been described [94]. These complexes, as expected, interact with other metal carbonyl centres via the $P_3C_2^tBu_2$ ring to give η^5-η^1-complexes typified by $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2^tBu_2)W(CO)_5]$ and many related compounds (Fig. 82).

Muller et al. [95] have succeeded in utilizing both lone pairs on the adjacent P atoms of the already η^5-ligated $P_3C_2^tBu_2$ ring systems in the nickel and ruthenium complexes shown in Fig. 83, which have been fully structurally characterized [95,96].

In unpublished work, Benvenutti et al. [97] have recently been able to attach the tetra-iridium undecacarbonyl complex to $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2^tBu_2)]$, as shown in Fig. 84. The molecular structure, which has been confirmed by single crystal X-ray analysis, is shown in Fig. 84(a), and of special interest is the further ligation of the η^5-$P_3C_2^tBu_2$ ring to an Ir atom of a second $[Ir_4(CO)_{11}]$ fragment with the subsequent loss of CO and a novel intramolecular C–H insertion reaction to give the novel complex shown in Fig. 84(b), which has been fully structurally characterized [97]. Likewise, the attachment of divalent platinum centres to this type of mixed ring metallocene has also been achieved (Fig. 85), clearly indicating the considerable potential of synthesizing a wide variety of mixed metal aggregates of novel structural types [98].

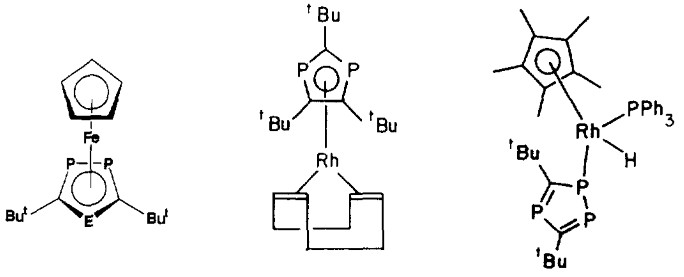
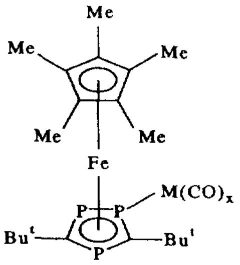


Fig. 81.



M = Cr, X = 5
M = W, X = 5
M = Fe, X = 4

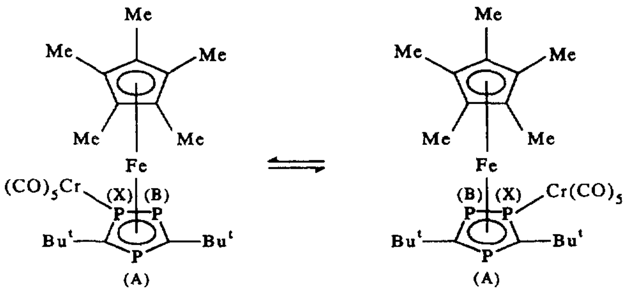


Fig. 82.

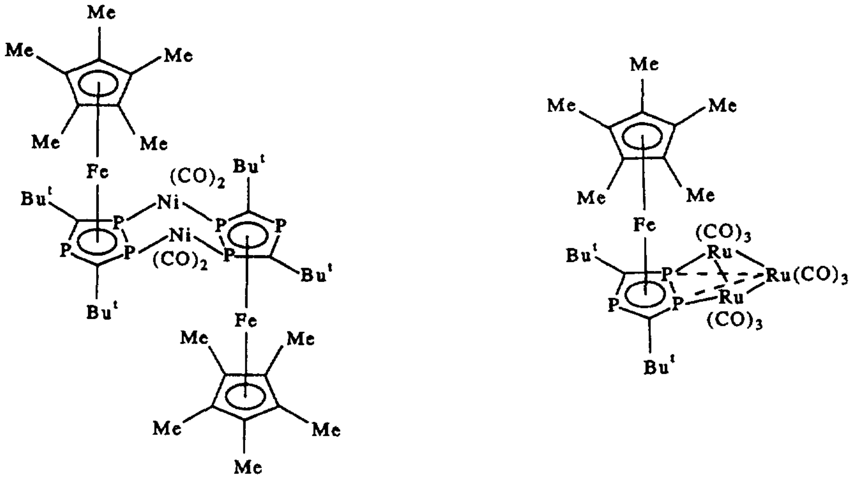


Fig. 83.

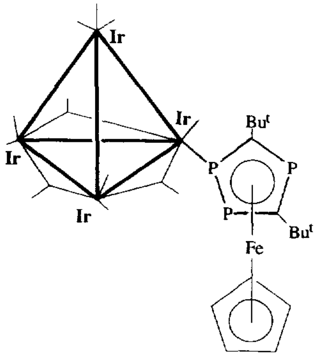


Fig. 84.

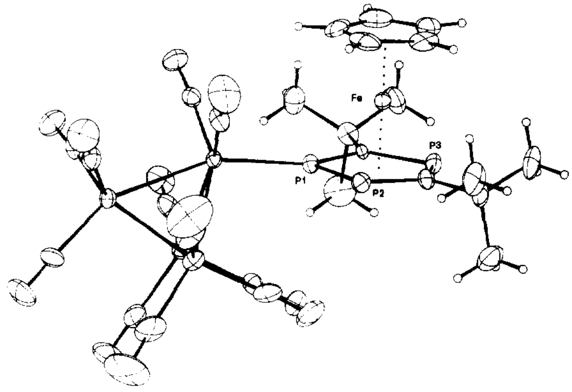


Fig. 84(a).

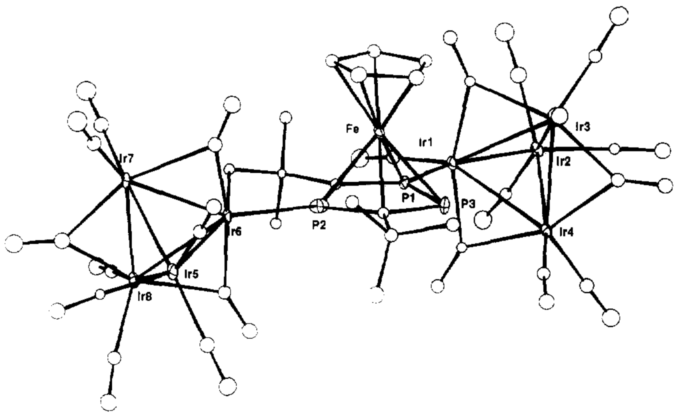


Fig. 84(b).

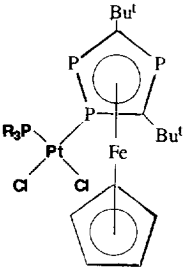


Fig. 85.

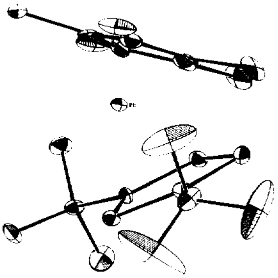


Fig. 86.

7.1. η^5-Ligated $P_3C^t_2Bu_2$ complexes of main group elements

The work described in this section represents a very new development, since until recently the only known compounds of the $(P_3C^t_2Bu_2)^-$ and $(P_2C^t_3Bu_3)^-$ ring anions were their alkali metal salts. Unpublished work by Nixon and Sillett [99] using Group 13 elements indicated that a compound of formula $(TlP_3C^t_2Bu_2)$ resulted from the reaction of TlCl and $NaP_3C^t_2Bu_2$, the compound being characterized by ^{31}P NMR studies and confirmed largely on the basis of its ready ring transfer reactions to form known η^1-$P_3C^t_2Bu_2$ Pt(II) or Pd(II) complexes.

The first examples of fully characterized main group element compounds containing the η^5-ligated $P_3C^t_2Bu_2$ ring system come from very recent unpublished work of Durkin et al. [100] on Group 14 elements. Treatment of the $P_3C^t_2Bu_2$ anion (as its lithium salt) with $PbCl_2$ in an ether solvent gave $[Pb(\eta^5\text{-}P_3C^t_2Bu_2)_2]$ as an orange oil which exhibited the characteristic pattern of lines in the $^{31}P\{^1H\}$ NMR spectrum and significant one-bond coupling between the two types of ring phosphorus atoms and the ^{207}Pb nucleus, $^1J_{PbP} = 366$, 252 Hz. Using $[Pb(\eta^5\text{-}C_5Me_5)Cl]$, it proved possible to obtain the crystalline complex $[Pb(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C^t_2Bu_2)]$ whose "bent" molecular structure, shown in Fig. 86, reveals that the η^5-ligated $P_3C^t_2Bu_2$ ring is significantly further from the Pb atom than the corresponding η^5-ligated C_5Me_5 ring. When the solvent is changed to TMEDA, the resulting new compound incorporates an LiCl molecule to afford an η^5-$P_3C^t_2Bu_2$ complex containing the interesting $LiCl_2Pb$ ring system. The Pb complexes also act as $P_3C^t_2Bu_2$ ring transfer reagents to afford compounds of a new structural type typified by $[PtCl(PEt_3)(P_3C_2{}^tBu_2)]_2$, which has been fully structurally characterized [100]. Very recently, the tin complex $[Sn(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C^t_2Bu_2)]$ has been synthesized and its structure determined by a single crystal X-ray crystallographic study [100] $Tl(\eta^5\text{-}P_3C^t_2Bu_2)$, Ref. [107].

7.2. *"Triple-decker" complexes containing $\mu\text{-}\eta^5\text{-}P_3C^t_2Bu_2$ rings*

Recently, it has proved possible to synthesize "triple-decker" compounds containing the $\eta^5\text{-}P_3C^t_2Bu_2$ ring system. Thus treatment of $[Fe(\eta^5\text{-}P_3C^t_2Bu_2)_2]$ with the cationic complex $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)_3]^+$ readily leads unexpectedly to the first example of a "triple-decker" complex $[Ru_2(\eta^5\text{-}C_5Me_5)_2(\eta^5\text{-}P_3C^t_2Bu_2)]$ containing the $P_3C^t_2Bu_2$ ring. Interestingly, it is the P-containing ring that acts as the bridging ring (see Fig. 87). The complex has been fully structurally characterized and intermediates and an alternative synthetic route have been established by NMR studies (Figs. 88 and 89) [101].

An interesting structurally related dipalladium(I) complex, shown in Fig. 90, has been recently synthesized from $[PdCl_2(dppe)]$ and the $P_3C^t_2Bu_2$ ring anion, in which the resulting "pseudo"-triple-decker "sandwich" compound contains a bridging $P_3C^t_2Bu_2$ ring that is revealed by single crystal X-ray diffraction to be tilted in the manner shown in Fig. 90. That this is not an artifact has been confirmed in a full structural study on a similar reaction product involving $[Pd(dppe)(CH_3CN)_2][BF_4]_2$ [102].

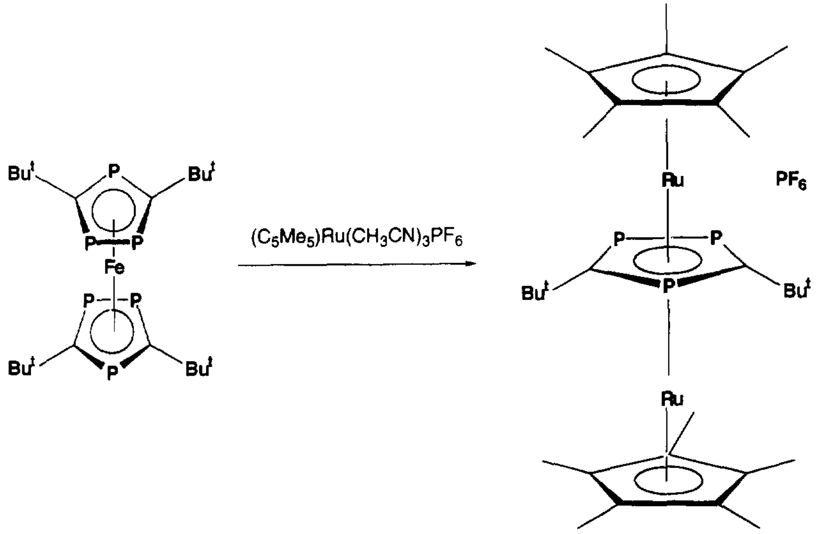


Fig. 87.

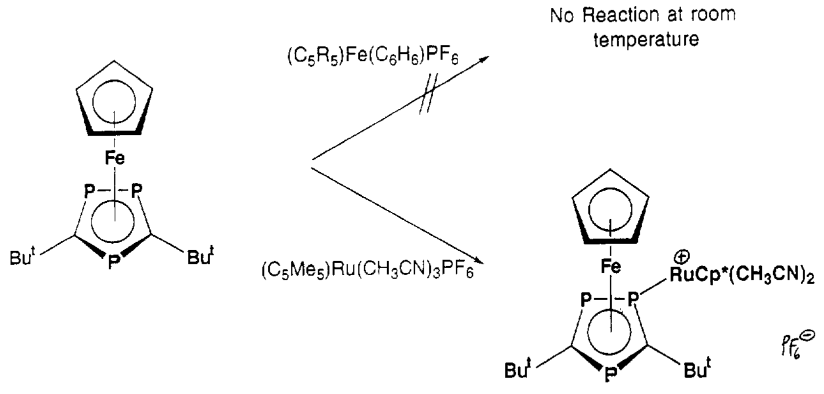


Fig. 88.

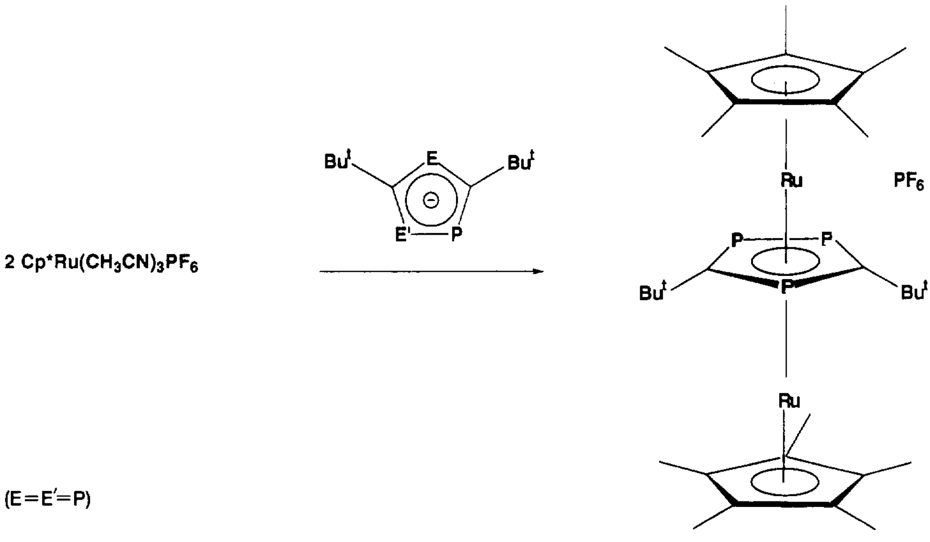


Fig. 89.

7.3. *Arsa-diphospholyl anions and their coordination complexes*

Following the brief report of the synthesis and NMR spectroscopic characterization of the 1-arsa-3,4-diphospholyl anion $(C^t_2BuAsP_2)^-$ from the reaction of ^tBuCP with $LiAs(SiMe_3)_2.DME$, its full characterization as the iron complex $[Fe(\eta^5-C_5H_5)(\eta^5-C^t_2BuAsP_2)]$ and the molecular structure of its $[W(CO)_5]$ adduct as determined by single crystal X-ray diffraction have very recently been described (Fig. 91) [103,104]. The new results also show evidence for the existence of the previously unknown 3-arsa-1,4-diphospholyl anion $(C^t_2Bu_2PAsP)^-$ (Fig. 92). The single crystal X-ray study shows that the iron is sandwiched between the two planar rings (dihedral

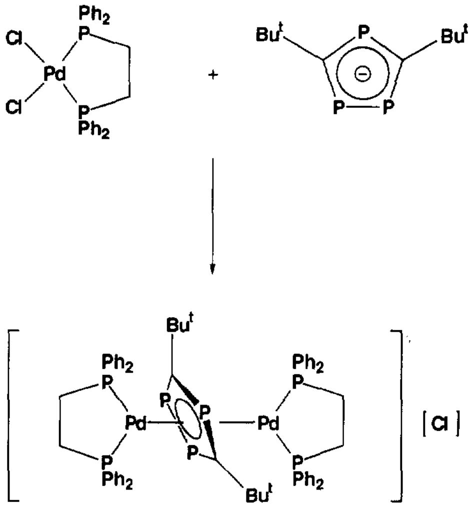


Fig. 90.

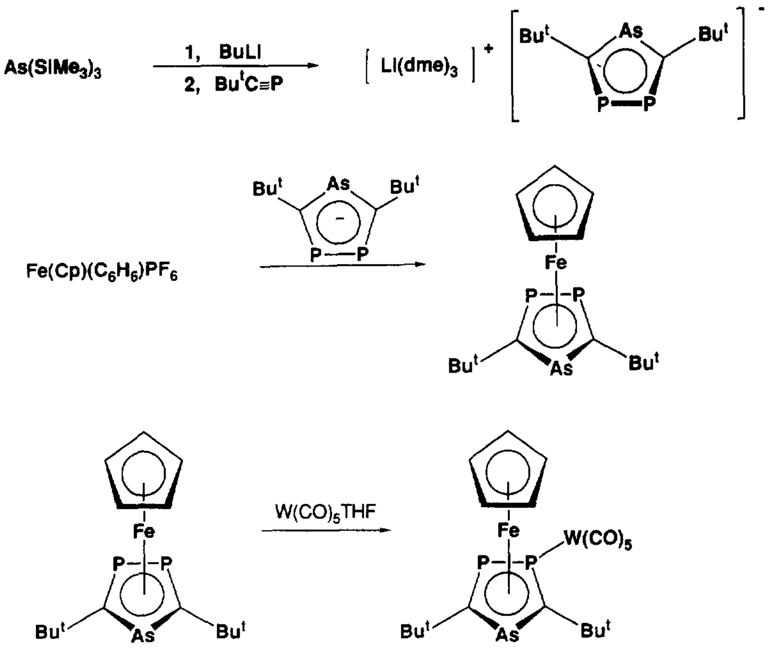


Fig. 91.

angle, 1°), with the W atom attached to one of the P atoms of the 1-arsa-3,4-diphospholyl ligand (Fig. 92) [105]. Of special interest is the observation of a high disorder of occupancy between the As atom and the uncoordinated P atom P(2). A

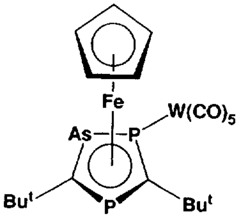


Fig. 92.

"triple-decker" diruthenium cationic complex containing the arsa-diphospholyl ring system, shown in Fig. 93, has also been obtained Ref. [105].

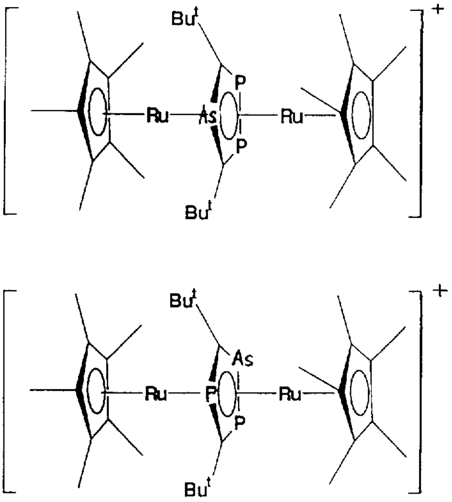


Fig. 93.

7.4. *1,2,4-Triphosphacyclopentadienes and their complexes*

An interesting new development is the recent observation that alkylation of the $P_3C_2^tBu_2$ anion affords the first examples of neutral 1,2,4-triphosphacyclopentadienes which exhibit a rich coordination chemistry (Fig. 94) exemplified by the selection of reactions shown. All products have been structurally characterized by single crystal X-ray diffraction studies [106].

8. Metal vapour syntheses

A major new development in phospha-alkyne–metal chemistry has resulted from the very recent studies of Cloke and coworkers [107–113] utilizing the technique of

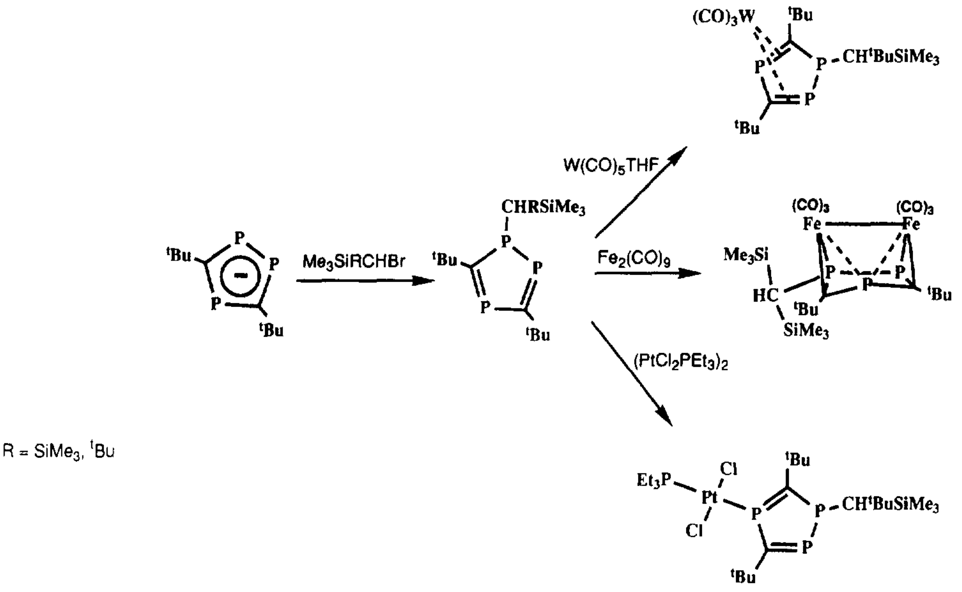


Fig. 94.

metal vapour synthesis (MVS) which has previously had wide application in conventional organometallic chemistry.

Co-condensation of metal atoms generated by MVS techniques with ^{t}BuCP has led to a variety of novel compounds (see below). The importance of the method is that, in principle, any metal may be used, i.e. main group metals, transition metals, lanthanides and/or actinides, products often result from P≡C bond cleavage and reassembly reactions and novel ring systems, e.g. complexes of the previously unknown phosphirenyl cation $PC^{t}_{2}Bu_{2}$, can be obtained by this synthetic route. The field is still in its infancy, but extensive developments can be expected in the future. Some highlights, [110,112] are detailed below.

Treatment of ^{t}BuCP with iron atoms using the MVS technique remarkably gives the known pentaphosphaferrocene $[Fe(\eta^{5}\text{-}P_{3}C^{t}_{2}Bu_{2})(\eta^{5}\text{-}P_{2}C^{t}_{3}Bu_{3})]$ [107]. Interestingly, the known hexaphosphaferrocene $[Fe(\eta^{5}\text{-}P_{3}C^{t}_{2}Bu_{2})_{2}]$ is not observed as a product and it thus appears that the metal has assembled five phospha-alkyne units distributed between the two five-membered rings. A similar reaction with vanadium atoms affords the orange–brown paramagnetic complex $[V(\eta^{5}\text{-}P_{3}C^{t}_{2}Bu_{2})(\eta^{5}\text{-}P_{2}C^{t}_{3}Bu_{3})]$ (Fig. 95) whose structure has been confirmed by a single crystal X-ray diffraction study [108]. Likewise, using Cr atoms, the resulting product is the new purple paramagnetic pentaphosphachromocene $[Cr(\eta^{5}\text{-}P_{3}C^{t}_{2}Bu_{2})(\eta^{5}\text{-}P_{2}C^{t}_{3}Bu_{3})]$, rather than the known hexaphospha derivative previously obtained by the conventional reaction of the $P_{3}C^{t}_{2}Bu_{2}$ anion with $CrCl_{3}$ (see Section 7).

Interesting differences are observed when either Mo or W atoms are treated with ^{t}BuCP, the products being the yellow–orange homoleptic tris-1,3-diphosphacyclobutadiene metal(0) complexes $[M(\eta^{4}\text{-}P_{2}C^{t}_{2}Bu_{2})_{3}]$ (M≡Mo, W) (Fig. 96). The struc-

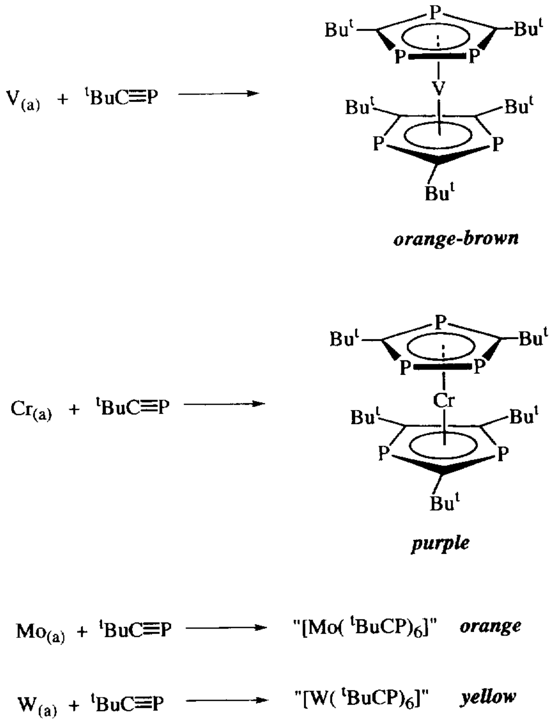


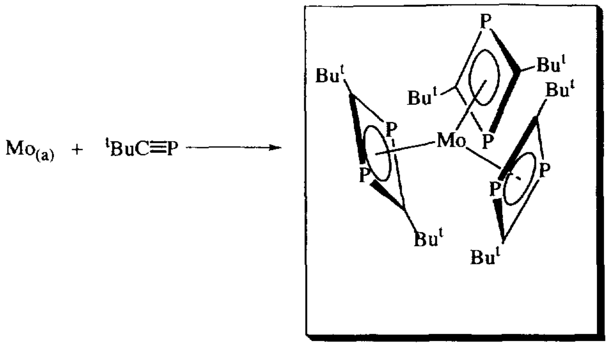
Fig. 95.

ture of the molybdenum complex has been determined by a single crystal X-ray diffraction study, and one of the four-membered rings is turned through 90° relative to the other two. Interestingly, no evidence has yet been obtained for the isoelectronic triphospha-arene complexes $[M(\eta^6\text{-}P_3C^t_3Bu_3)_2]$ [109].

A different type of behaviour is observed when Co atoms are treated with ᵗBuCP. Three products have been observed: a novel complex containing a protonated tetraphosphabarellene of uncertain composition, and the two diamagnetic "sandwich" complexes $[Co(\eta^4\text{-}P_2C^t_2Bu_2)(\eta^5\text{-}P_3C^t_2Bu_2)]$ and $[Co(\eta^4\text{-}P_2C^t_2Bu_2)(\eta^5\text{-}P_2C^t_3Bu_3)]$, one of which is shown in Fig. 97 [107]. Single crystal X-ray diffraction studies have been carried out to elucidate the structures of these novel compounds.

Perhaps the most interesting reactions of atoms of the first row transition series with ᵗBuCP are those involving Ti and Ni. In the former case, analysis of the product suggests a compound of formula $[Ti(P_6C^t_6Bu_6)]$; however, detailed ^{31}P NMR studies show that this does not contain two η^6-ligated 1,3,5-triphosphabenzene rings [108]. Studies are being carried out on Zr and Hf analogues to resolve the nature of this product.

The reaction of Ni atoms with ᵗBuCP is of special significance since it affords equal amounts of two orange–red compounds of molecular formula $[NiP_4C^t_4Bu_4]$. One is identical with the known "sandwich" complex $[Ni(\eta^4\text{-}P_2C^t_2Bu_2)_2]$ (see Section 3), but the second has been shown to be $[Ni(\eta^3\text{-}PC^t_2Bu_2)(\eta^5\text{-}P_3C^t_2Bu_2)]$



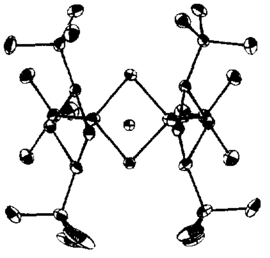


Fig. 96.

Co(a) + $Bu^tC{\equiv}P \rightarrow Co(\eta^5\text{-}P_2C_3Bu^t_3)(\eta^4\text{-}P_2C_2Bu^t_2)$

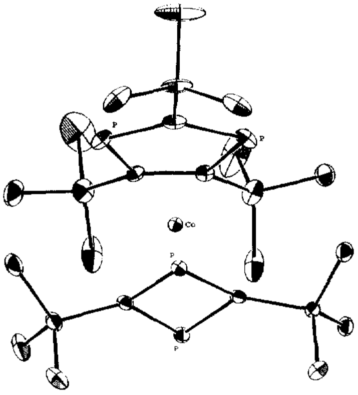


Fig. 97.

(Fig. 98), which contains the novel three-membered phosphirenyl ring system [111]. The free phosphirenyl cation, which is the simplest of all the aromatic 2π-ring systems containing phosphorus, had previously eluded synthesis, and its identity has been unambiguously established by a single crystal X-ray diffraction study on the [W(CO)$_5$] adduct (Fig. 99. The structural features of the three-membered ring indi-

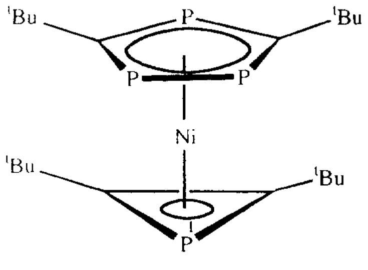


Fig. 98.

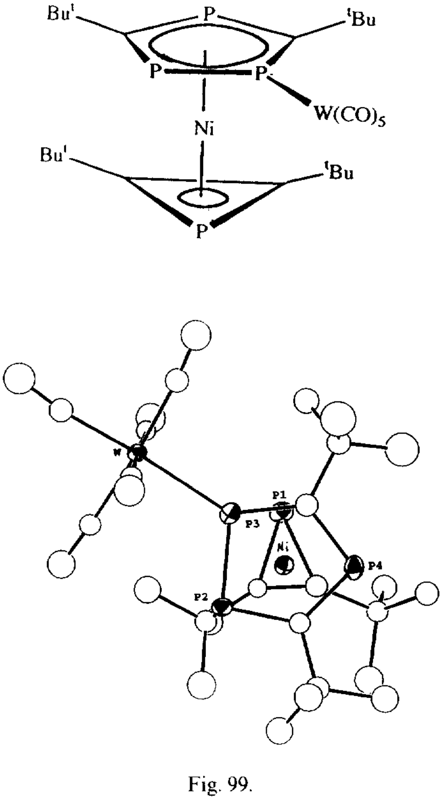


Fig. 99.

cate that the P–C bond lengths are average (1.80 Å), while the C–C bond length is 1.33 Å.

The first metal vapour synthetic studies have recently been carried out between lanthanide elements and ᵗBuCP. Treatment of Yb with ᵗBuCP leads to the deep green "bent-sandwich" complex $[Yb(\eta^5\text{-}P_2C^t_3Bu_3)_2]$, which can be made in approximately 40% yield and has been fully spectroscopically characterized (Fig. 100); the ^{171}Yb NMR spectrum exhibits a quintet pattern of lines [112].

The availability of an electropositive metal carrying only the η^5-ligated $P_2C^t_3Bu_3$

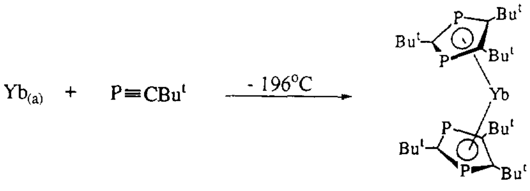


Fig. 100.

ring has enabled a ring transfer reaction to Ni to be carried out leading to the diamagnetic complex $[Ni(\eta^5\text{-}P_2C^t_3Bu_3)(\eta^3\text{-}P_2C^t_3Bu_3)]$ in which the two $P_2C^t_3Bu_3$ rings are differently ligated to the metal (Fig. 101). The complex can also be made conventionally from $NiBr_2$ and the $P_2C^t_3Bu_3$ anion [113]. This complex exhibits dynamic behaviour in solution, whereby the two rings become equivalently bonded, as evidenced by a variable temperature ^{31}P NMR study. The potential of the MVS method involving phospha-alkynes has recently been extended to include main group elements such as Sn [108].

9. Reactions of phospha-alkynes with metal hydrides

Although as yet there are no published examples for the simple insertion reactions of the type

$$L_nM\text{-}H + {}^tBuC{\equiv}P \rightarrow L_nM\text{-}P{=}CH{}^tBu$$

or

$$L_nM\text{-}H + {}^tBuC{\equiv}P \rightarrow L_nM\text{-}C{}^tBu{=}PH$$

there have been two recent reports of related reactions involving boron hydride clusters and transition metal hydrido carbonyl clusters. Meyer et al. [114] have shown that ^{t}BuCP reacts with the decaborane $[B_{10}H_{12}(SMe_2)_2]$ to give the remarkable product $[B_{10}H_{11}(SMe_2)][C^tBuPH][B_{10}H_{12}]$ shown in Fig. 102, in which two $[B_{10}]$ units are linked by an $HP{=}C^tBu$ bridge. The $[B_{10}H_{11}(SMe_2)]$ is bound to both P and C bridging atoms, by one B atom of the cluster and to P only by another B atom. The P–C bond distance (1.912 Å) in the bridging HPC^tBu moiety is typical for a single bond.

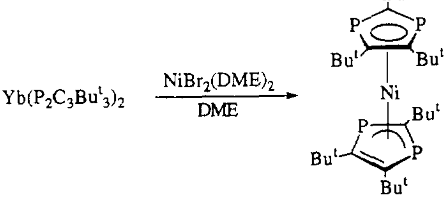


Fig. 101.

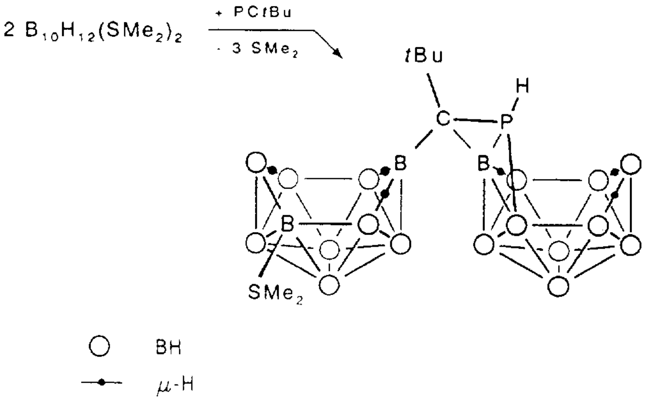
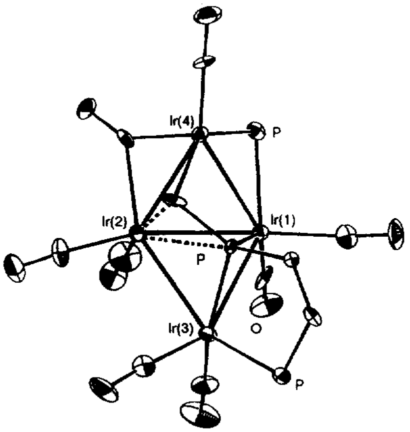


Fig. 102.



Simplified view — showing the 2-phosphabutadienylphosphine chain on the metallic framework; phenyl rings and the Bu^t group have been omitted for the sake of clarity

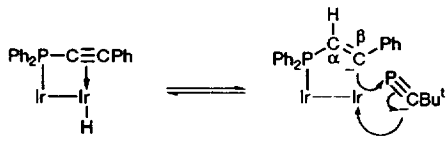


Fig. 103.

Very recent studies on the reaction of the tetranuclear cluster complex $[(\mu\text{-H})Ir_4(CO)_9(Ph_2PC_2Ph)(\mu\text{-PPh}_2)]$ reaction with ^tBuCP shows the product to be the unusual complex $[Ir_4(\mu\text{-CO})(CO)_7\{\mu_4\text{-}\eta^3\text{-Ph}_2PC(H)C(Ph)PC^t\ Bu\}(\mu\text{-PPh}_2)]$ which contains the novel 2-phosphabutadienyl fragment as a result of both the coupling of ^tBuCP with the alkyne ligand and incorporation of the original cluster-bonded H atom (Fig. 103). The compound has been fully characterized by both multinuclear NMR spectroscopy and a single crystal X-ray study. A detailed mechanistic understanding of the reaction pathway is still lacking; however, the intermediacy of an alkenyl species which undergoes nucleophilic attack of the β-carbon at the positive phosphorus centre of ^{t}BuCP would account for the observed product [115].

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