Phospha-alkynes, RC≡P: New Building Blocks in Inorganic and Organometallic Chemistry†

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1 Introduction

In the last decade, there has been a rapid development in synthetic, spectroscopic, and structural aspects of Main Group element compounds containing multiple bonds. All these compounds clearly violate the long-accepted 'double-bond rule', which stated that multiple bonding involving the heavier elements would not occur because of weak $p\pi-p\pi$ bonding. 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. Phospha-alkynes, RC≡P, in particular, 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. The results have served to illustrate the strong interrelationship between carbon and phosphorus chemistry.[1-8] 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.

2 Phospha-alkyne Complexes

Just over a decade has passed since we reported the first phospha-alkyne complex $[Pt(\eta^2\text{-}Bu^tC\equiv P)(PPh_3)_2]$, in which the η^2-'side-on' interaction was noted between the P≡C triple bond and the transition metal.[9] Subsequently, examples of types [A]—[E] have been synthesized using both the RC≡P moiety as an η^2-bridging and/or P lone-pair donor ligand (see Figure 1).[10,11]

In recent years, a variety of other mononuclear complexes of type [B] containing η^2-ligated Bu^tCP have been reported for platinum, rhodium, titanium, and zirconium (see Figure 2).[12-14]

Our early photoelectron spectroscopic studies established that the HOMO in phospha-alkynes is the π-type P≡C triple bond, and, as expected, it is the η^2-ligating mode [B]—[E] that is preferred towards transition metals, and it is only possible to form η^1-complexes [type A] preferentially by creating a suitable
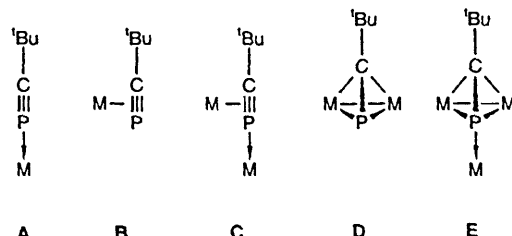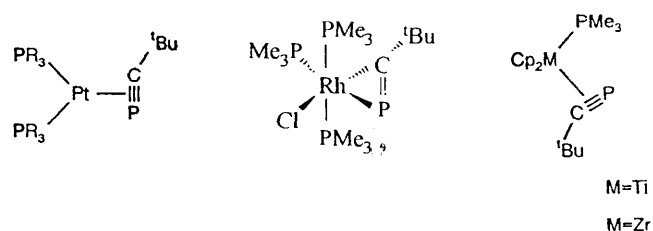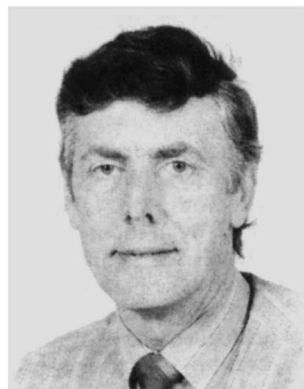

Figure 1

M=Ti

M=Zr

Figure 2

'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 reported by us are shown in Figure 3. In contrast to the η^2-ligated derivatives where 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 phospha-alkyne itself.[15] More recently, we have synthesized η^1-phospha-alkyne Fe^{II} and Re^I complexes, which interestingly have considerably enhanced reactivity compared with the parent compound.[16,17]

The rhenium(I)-phospha-alkyne complex, for example, rapidly reacts with water to afford the novel η^1-ligated phosphinidene oxide complex (Figure 4).

Several complexes of type [C] in which both η^1- and η^2-bonding features of the phospha-alkyne are exploited are exemplified by the chromium, molybdenum, and tungsten pentacar-

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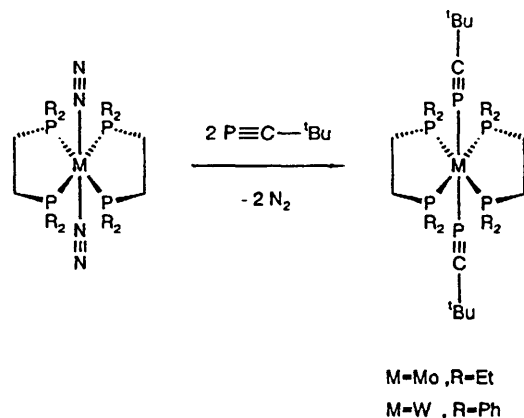
M=Mo ,R=Et

M=W , R=Ph
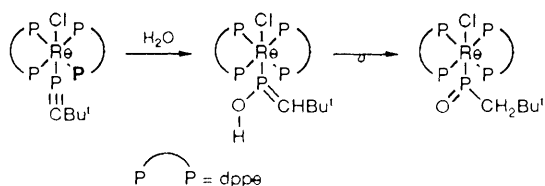
Figure 3

Figure 4

bonyl derivatives of [Pt(η^2-(PCBu^t)L$_2$] (L$_2$ = diphos. L = PPh$_3$)[18] (Figure 5). An alternative synthetic route[13] is shown in Figure 6 in which a vacant site is created in the preformed η^2-complex [M(η^5-C$_5$H$_5$)$_2$(PCBu^t)(PMe$_3$)] (M = Ti. Zr) by treatment with BEt$_3$ to remove the PMe$_3$. The resulting intermediate complex reacts with itself to give either the dimeric (M = Ti) or trimeric (M = Zr) compounds.

Figure 5

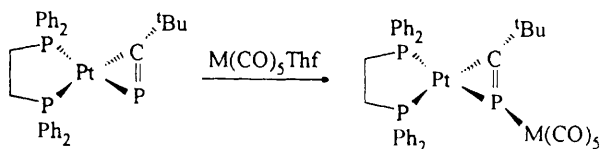Figure 6

Figure 7

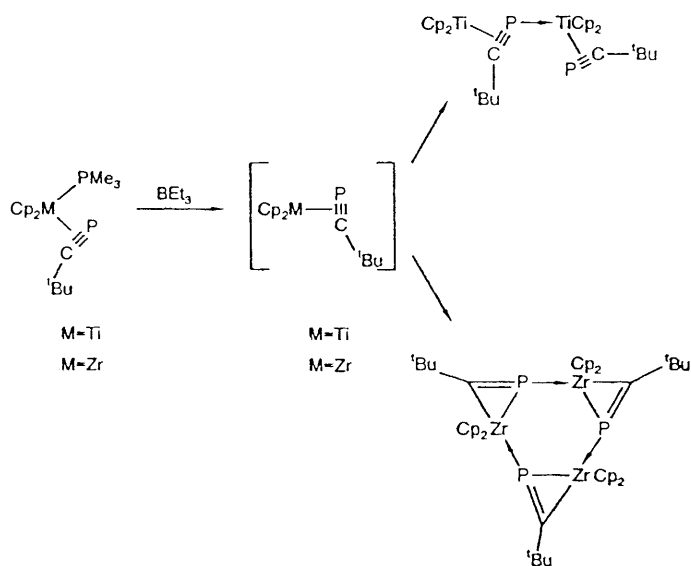
Figure 8

M=Co,Rh ;R=H

M=Co,Rh,Ir ;R=Me

Figure 9

Complexes of type [D] and [E] in which the phospha-alkyne is either a 4e or 6e donor respectively are available *via* a number of synthetic routes summarized in Figure 7. Here, the behaviour is very similar to the better known systems containing 4e-bridging alkynes. The availability of the P lone-pair electrons offers additional coordinating potential in the case of the ligated phospha-alkyne,[19] [23] beautifully illustrated by the spectacular pentametallic 'star'-shaped complex [Pt$_3$Pd$_2$(PPh$_3$)$_5$(Bu^{t}CP)$_3$] (Figure 8).[24]

3 Cyclodimerization of Phospha-alkynes at Metal Centres

3.1 Diphosphacyclobutadiene and Related Complexes

In 1986, Nixon and Binger and their co-workers independently reported the first examples of phospha-alkyne cyclodimerization at cobalt, rhodium, and iridium centres, to afford complexes of the 1,3-diphosphacyclobutadiene ring (Figure 9).[25-26]

Interestingly, it has proved impossible to displace the η^4-ligated (P$_2$C$_2$Bu$^t_2$) rings from the above complexes, which contrasts with the behaviour of the analogous η^4-ligated cyclo-

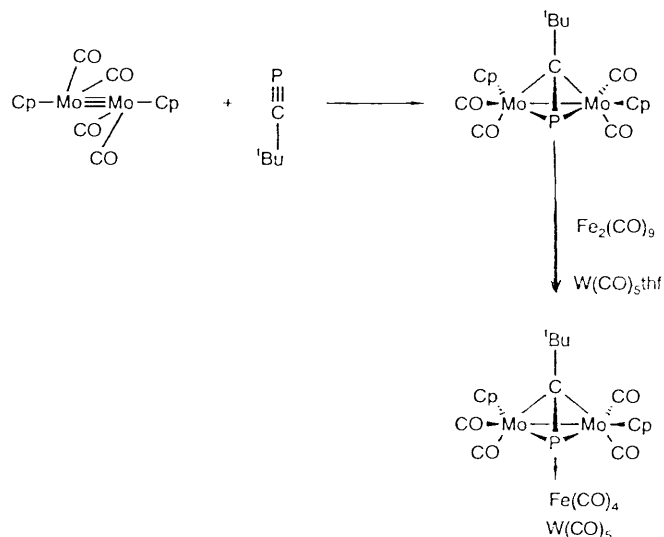butadiene ring complexes. Theoretical studies and photoelectron spectroscopic data on [Fe(η^4-C$_4$H$_4$)(CO)$_3$] and [Co(η^5-C$_5$H$_5$)(η^4-C$_4$H$_4$)] have been compared with their [Fe(η^4-P$_2$C$_2$Bu$^t_2$)(CO)$_3$] and [Co(η^5-C$_5$H$_5$)(η^4-P$_2$C$_2$Bu$^t_2$)] counterparts and the results have established that there is a significantly stronger π-interaction between the metal and the phosphorus-containing ring system.[27]
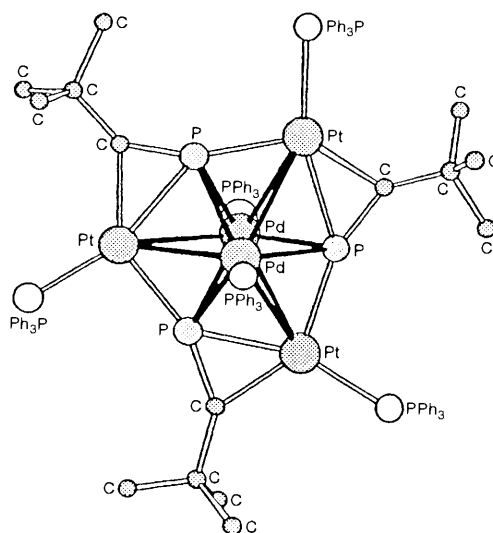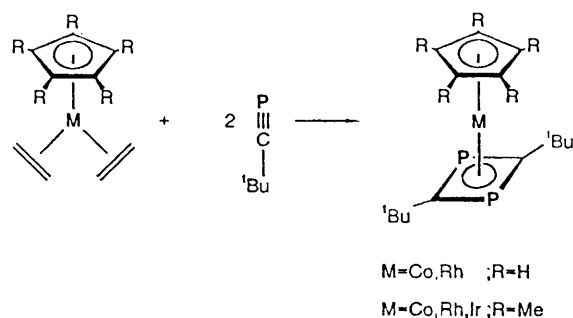
Unlike their cyclobutadiene metal analogues, the η^4-ligated P$_2$C$_2$Bu$^t_2$ rings can themselves act as ligands towards other metal centres, resulting in novel types of complexes typified by those shown in Figures 10 and 11.[26,28] [31]

In an important study, Regitz, Binger, and their co-workers[32] found a different type of cyclodimerization reaction when Bu'CP reacts with [Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$] in the presence of magnesium. The diphosphabicyclo[1.1.0]butane complex shown in Figure 12 is formed in good yield, and undergoes several interesting reactions (Figure 13). Very recently an η^4-1,2-diphosphacyclobutadiene titanium complex has been synthesized.[13a]
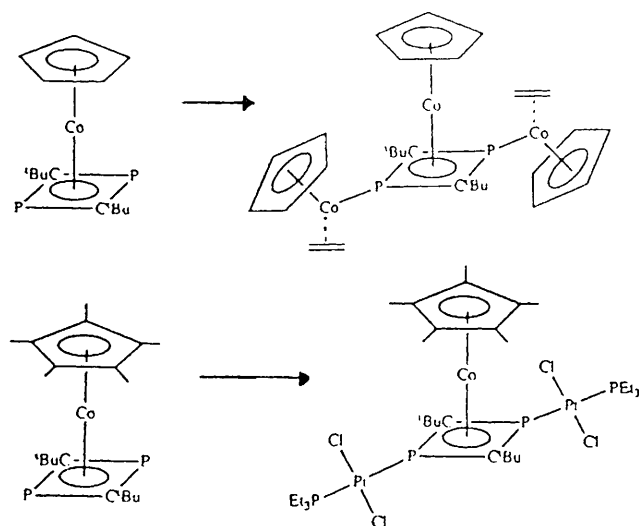
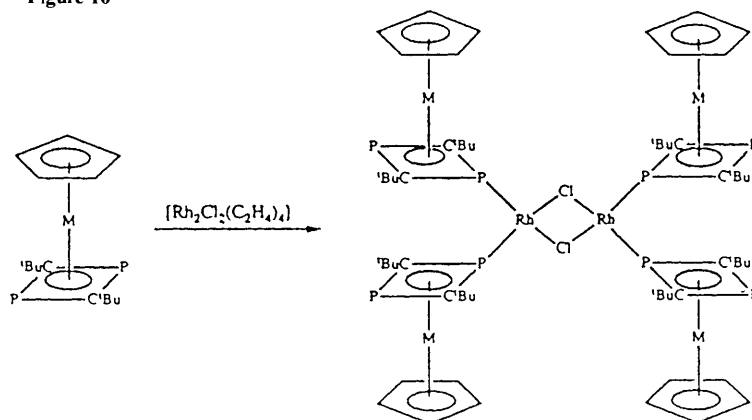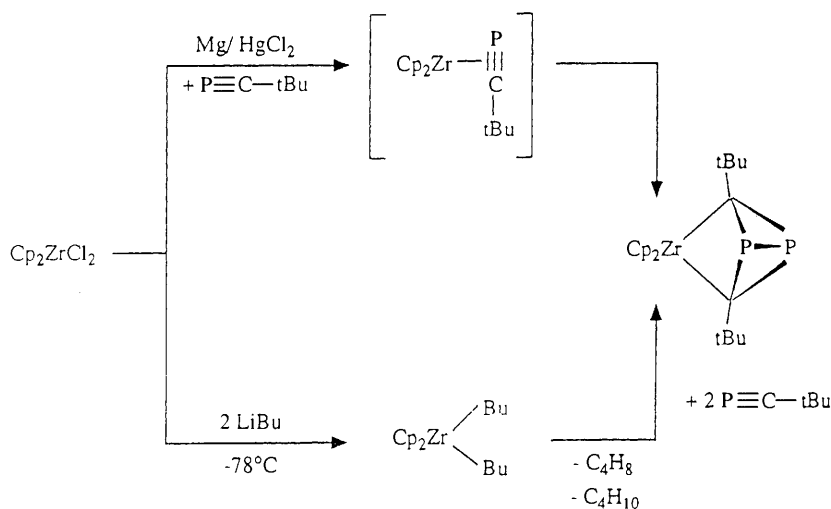## 3.2 Cyclotrimerization Reactions at Metal Centres

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.* An early report of the molybdenum(0) complex shown below (Figure 14) could not be confirmed by an independent investigation and therefore remains tentative.[33]

The 14e vanadium complex shown in Figure 15 results when [V(η^5-C$_5$Me$_5$)(η^6-naphthalene)] reacts with three equivalents of Bu'CP; however, a single crystal X-ray diffraction study on the product showed it to be a derivative of 1,3,5-triphosphaprismane.[34] It reacts with one mole of CO at room temperature to give a new complex in which the P$_3$C$_3$Bu'$_3$ ligand has rearranged to the complexed 1,3,5-Dewar benzene (Figure 16).

The reaction of [RhCl(Pr$_3^i$)$_3$] with Bu'CP reported by Binger et al.[35] differs from those discussed in that trimerization of the phospha-alkyne occurs and the interesting dimeric rhodium complex is formed in good yield. The structure (Figure 17), which has been confirmed by a single crystal X-ray diffraction 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 Bu'CP units has recently been described.[36] Treatment of the ionic ruthenium(II) complexes with either Bu'CP or AdCP gives yellow neutral complexes (shown in Figure 18), which can
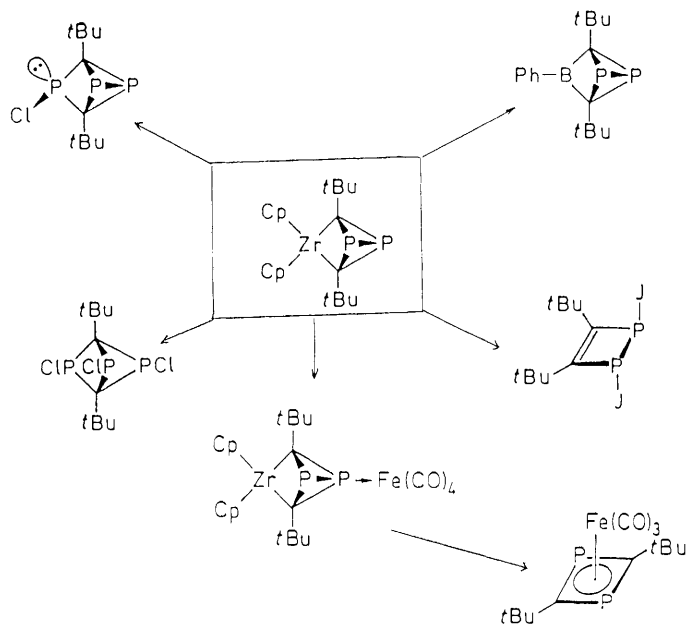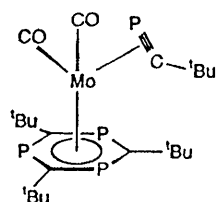
Figure 10

Figure 11

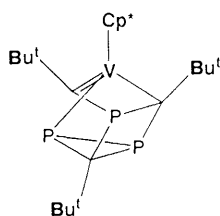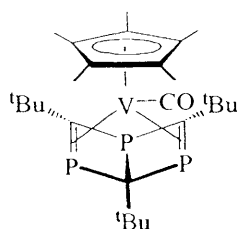Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

subsequently react with two equivalents of (W(CO)₅THF] to give the bis-[W(CO)₅] compounds. This behaviour of the three phospha-alkyne units contrasts with that of arenes which are normally strongly stabilized in the environment of a Ru^II cation.

An important recent development was the report by Regitz *et al.*[37] of the spirocyclotrimerization of the phospha-alkyne Bu'CP with AlCl₃ in a 3:1 ratio with incorporation of the Lewis Acid (Figure 19). When the metal halide is removed by addition of Me₂SO in the presence of a further equivalent of Bu'CP it gives a variety of novel products (Figure 20).
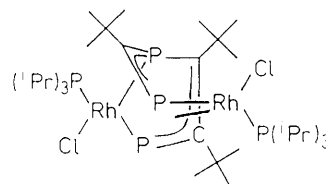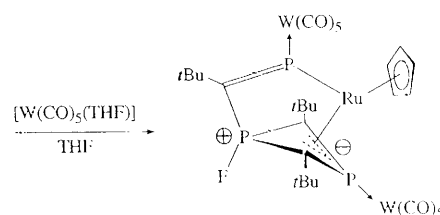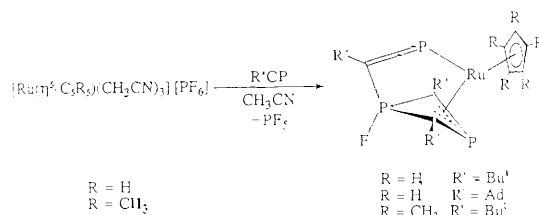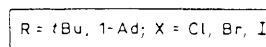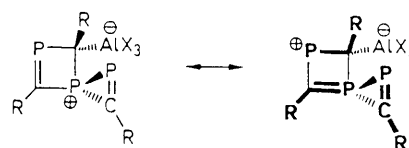

Figure 17

Figure 18
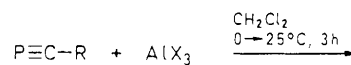
Figure 19

3.3 Metal-induced Reactions of Phospha-alkynes with other Unsaturated Systems

Binger and co-workers[35] have developed several routes to complexes based on co-trimerization reactions involving two phospha-alkynes and one alkyne (Figure 21).

Very recent work by Zenneck using a synthetic route involving metal vapour synthesis[38] has led to the first example of a 1,3-diphospha-benzene derivative of the type shown in Figure 22.

Carbon monoxide can also be involved in a cyclodimerization reaction with two moles of phospha-alkyne, for example in the reaction of [Rh₂(CO)₂(η⁵-C₅Me₅)₂] with Bu'CP or AdCP (Figure 23) to afford dinuclear complexes in which one Rh atom is η²-ligated to each P≡C double bond, while the other is bonded directly to two P atoms.[39]

4 Phospha-alkyne Tetramers and their Coordination Complexes

Several structurally different tetramers of the phospha-alkyne Bu'CP have been reported. Regitz *et al.*[40] showed that pyrolysis of Bu'CP in the absence of solvent at 180 °C gives the tetraphos-

Figure 20

Figure 21

Figure 22

$[Rh_2(CO)_2(\eta^5\text{-}C_5Me_5)_2]$

Figure 23

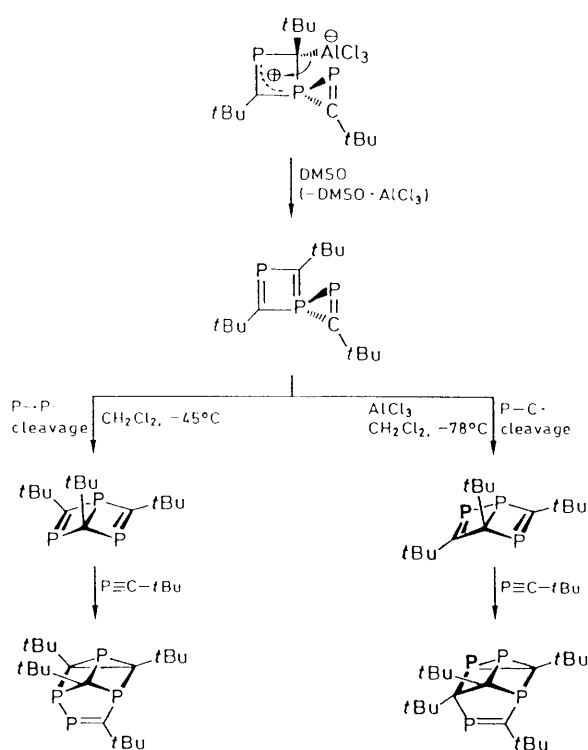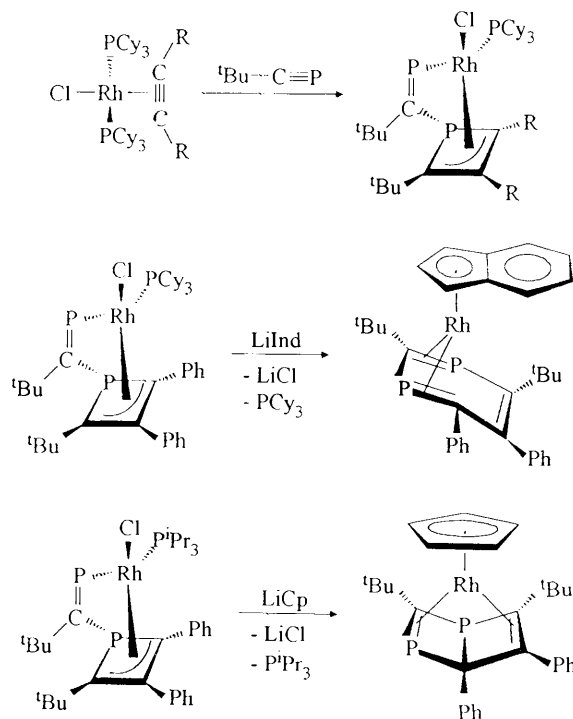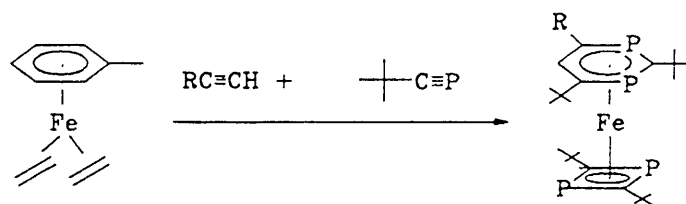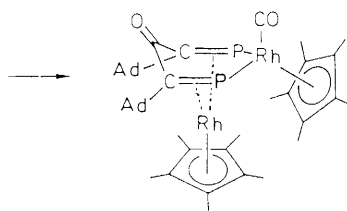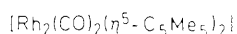phacubane (10%) and the tetraphosphabis(homo)prismane (10%) (Figure 24). Subsequently,[32,41] a high yield (ca. 70%) synthesis of several tetraphosphacubanes, $P_4C_4R_4$, was developed from the corresponding precursors [Zr(η^5-C_5H_2)$_2$($P_2C_2R_2$)] by treatment with C_2Cl_6, and very recently Nixon et al.[42] showed that small quantities of the new tricyclic tetramer (R = Bu^t) are also formed in this reaction (Figure 25).

Binger, Regitz and co-workers[42] also recently found that treatment of [Zr(η^5-C_5H_2)$_2$($P_2C_2Bu^t_2$)] with [NiCl$_2$(PPh$_3$)$_2$] or using a mixture of $P_2I_2C_2Bu^t_2$ and [Pt(C$_2H_4$)(PPh$_3$)$_2$] gave yet another isomer, shown in Figure 26, having a similar tricyclic structure.

Full structural characterization of all the tetramers have been elucidated either by single crystal X-ray diffraction studies or proposed on the basis of NMR spectroscopic studies and the first full structural characterization of the bis-[W(CO)$_5$] tetra-

phosphabis(homo)prismane complex shown below (Figure 27) has very recently been confirmed.[43]

4.1 Coordination Complexes of the Tetraphosphacubane $P_4C_4Bu^t_4$

As expected, the P—C bond lengths in the tetraphosphacubane as determined by a single crystal X-ray analysis, are all identical [d(P—C) = 1.881Å], and are typical for 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 Figures 24 and 25).[40]

It has been established by both He(I) photoelectron and MO calculations[44] 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 in turn reduces the basicity of the

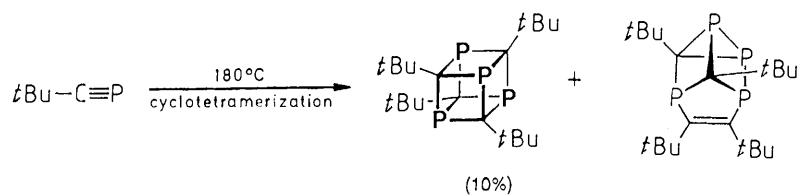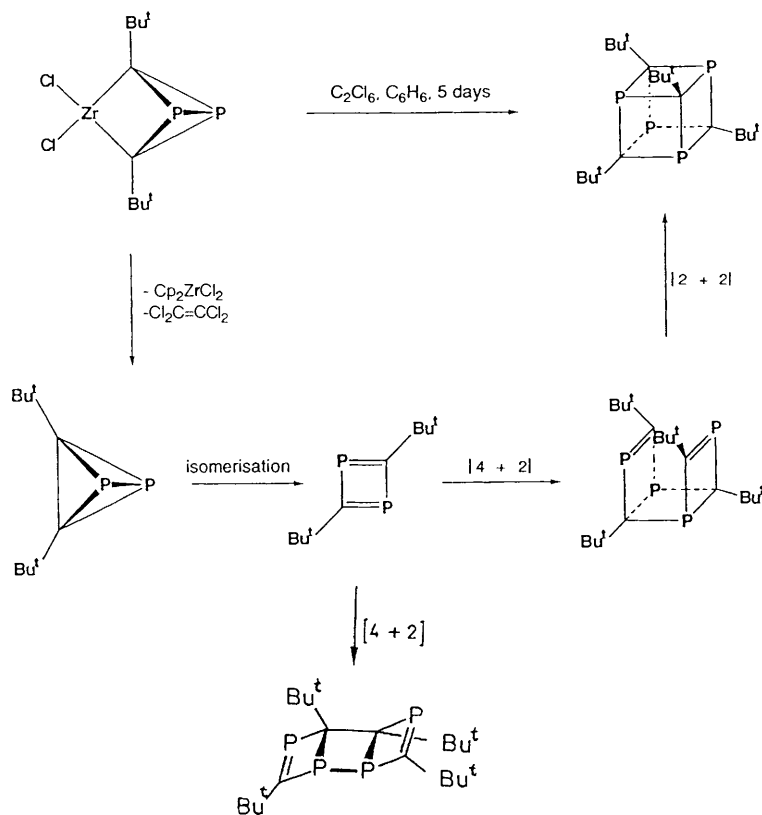tBu—C≡P $\xrightarrow[\text{cyclotetramerization}]{180°C}$

(10%)

Figure 24

C₂Cl₆, C₆H₆, 5 days

- Cp₂ZrCl₂
-Cl₂C=CCl₂

|2 + 2|

isomerisation

|4 + 2|

[4 + 2]

Figure 25

2 I₂, Et₂O
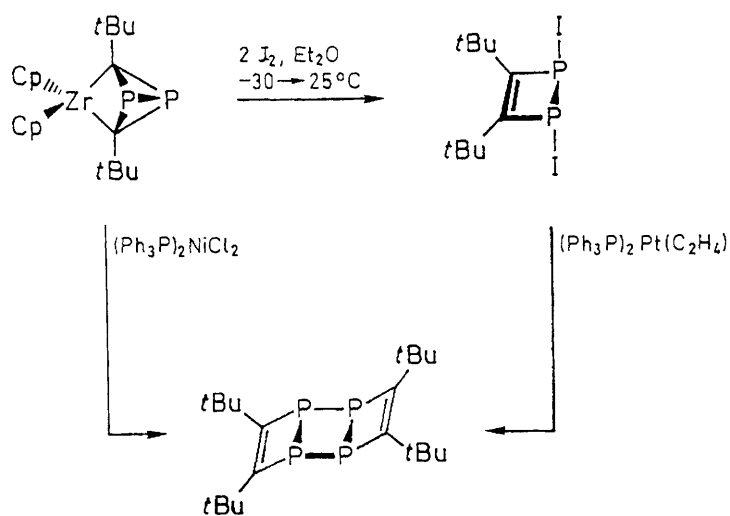-30 → 25°C

(Ph₃P)₂NiCl₂
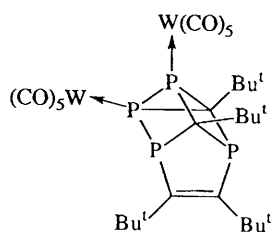
(Ph₃P)₂Pt(C₂H₄)

Figure 26

Figure 27

phosphorus centres and strong electrophiles are required to quaternize the heteroatoms.[45] It is not too surprising, therefore, that Regitz et al. found that $P_4C_4Bu_4^t$ only forms the mono-tetracarbonyliron(0) complex shown in Figure 28, even under forcing conditions. Nixon and co-workers[47] have very recently shown that by increasing the oxidation state of the transition metal, two P centres of the tetraphosphacubane can be made to coordinate to the metal centres under mild conditions. Thus treatment of $P_4C_4Bu_4^t$ with $[PtCl_2(PR_3)]_2$ (R = Et, Bu) at room temperature gives the complexes trans-$[PtCl_2(PR_3)(P_4C_4Bu_4^t)]$ and trans-$[\{PtCl_2(PR_3)\}_2(P_4C_4Bu_4^t)]$ (Figure 29) in a step-wise fashion. Both complexes have been fully structually characterized.
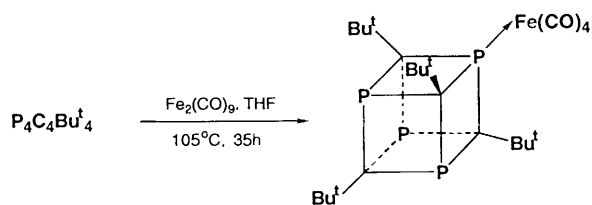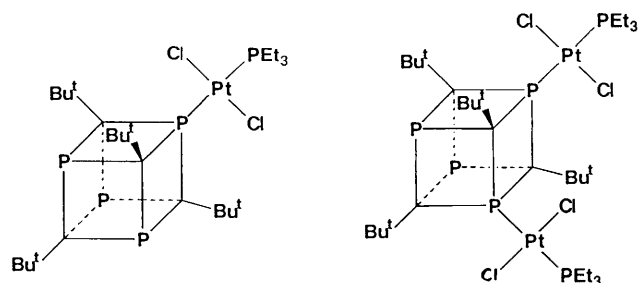

Figure 28

Figure 29

4.2 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 and co-workers.[48] Interestingly, instead of the possible formation of an η^8-ligated 1,3,5,7-tetraphosphacyclo-octatetraene derivative, or any of the tetramers of Bu'CP 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-octatraene complex $[Zr(\eta^8\text{-COT})(\eta^4\text{-COT})]$ (COT = cyclo-octatetraene) with Bu'CP in toluene for 2 days at 70 °C leads to the displacement of the η^4-ligated cyclo-octatetraene ligand and formation of $[Zr(\eta^8\text{-COT})(\eta^4\text{-}P_4C_4Bu_4^t)]$ (Figure 30).

5 Di- and Tri-phosphacyclopentadienyl Anions and their Metal Complexes

Becker et al.[49] showed that the planar $P_3C_2Bu_2^t$ ion resulted from the reaction of Bu'CP with $LiP(SiMe_3)_2$ and subsequently, it was shown that mixtures of $P_3C_2Bu_2^t$ and $P_2C_3Bu_3^t$ anions readily result from reduction of Bu'CP either with Na/Hg or
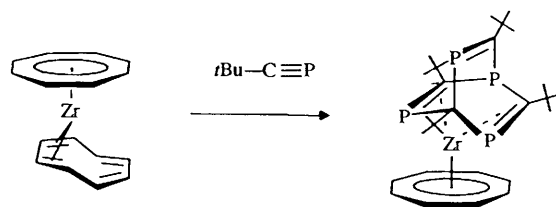

Figure 30

low-valent tantalum species, by a mechanism which is still unknown.[50,51]

Furthermore, these aromatic rings can be readily converted on treatment with $FeCl_2$ into the green air-stable sublimable penta- and hexa-phosphaferrocenes $[Fe(\eta^5\text{-}P_3C_2Bu_2^t)(\eta^5\text{-}P_2C_3Bu_3^t)]$, and $[Fe(\eta^5\text{-}P_3C_2Bu_2^t)_2]^{52}$ (Figure 31).
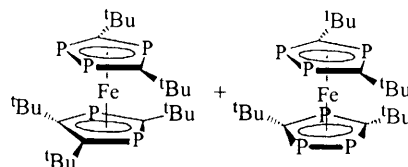
Figure 31

Low yields of $[Fe(\eta^5\text{-}P_3C_2Bu_2^t)(\eta^5\text{-}P_2C_3Bu_3^t)]$ were reported by Zenneck and Regitz, together with $[Fe(\eta^4\text{-}P_2C_2Bu_2^t)(\eta^6\text{-}C_6H_5Me)]$ and the paramagnetic complex $[Fe(\eta^5\text{-}P_2C_3Bu_3^t)(\eta^4\text{-}P_2C_2Bu_2^t)]$ from the reaction of Bu'CP with the highly reactive $[Fe(\eta^6\text{-}C_6H_5Me)(\eta^4\text{-Me-naphthalene})]$ derivative, the latter being previously obtained from metal vapour synthesis.[53] Very recently, Binger and Glaser have obtained good yields of $[Fe(\eta^5\text{-}P_3C_2R_2)(\eta^5\text{-}P_2C_3R_3)]$ (R = Bu', Ad) when the appropriate phospha-alkyne is treated with bis(cyclo-octatetraene)iron(0) at 80—100 °C.[54]

The analogous 16e hexaphospha-chromocene derivative $[Cr(\eta^5\text{-}P_3C_2Bu_2^t)_2]$, which is isostructural with its Fe analogue, could only be obtained in about 1% yield from the $P_3C_2Bu_2^t$ anion,[55] and attempts to make the related 19e and 20e metallocenes containing Co and Ni by treatment of the $P_3C_2Bu_2^t$ and $P_2C_3Bu_3^t$ anions with the appropriate metal halide in an ether solvent gave instead the diamagnetic 18e complexes shown in Figure 32.[56,57]

Figure 32

Figure 33

Several types of ligation are possible for the di- and tri-phosphacyclopentadienyl ring systems. In the case of the $P_2C_3Bu^t_3$ ring it was found to ligate in either an η^5-fashion as in [Fe(η^5-$P_3C_2Bu^t_2$)(η^5-$P_2C_3Bu^t_3$)] and [Mo(η^3-C_6H-)(η^5-$P_2C_3Bu^t_3$)(CO)$_2$)] or in an η^3-mode as in [Ni(η^5-$P_3C_2Bu^t_2$)(η^3-$P_2C_3Bu^t_3$)] and [Mo(η^5-C_5Me_5)(η^3-$P_2C_3Bu^t_3$)(CO)$_2$].[38]
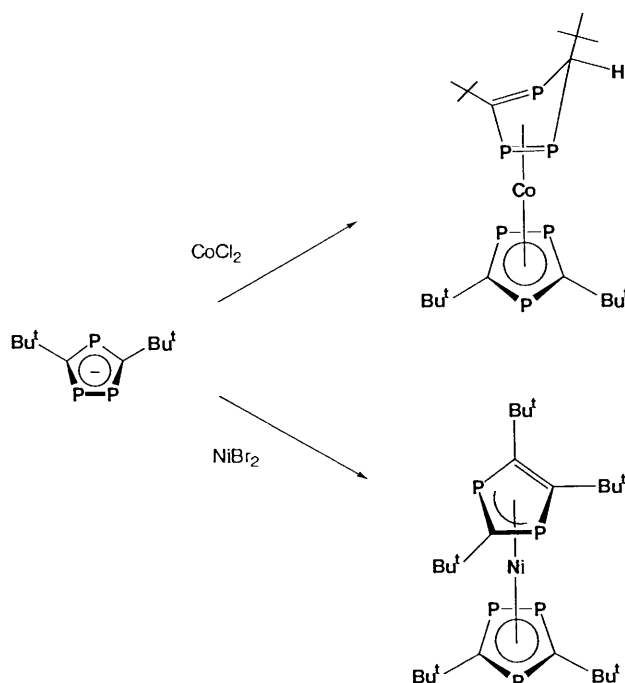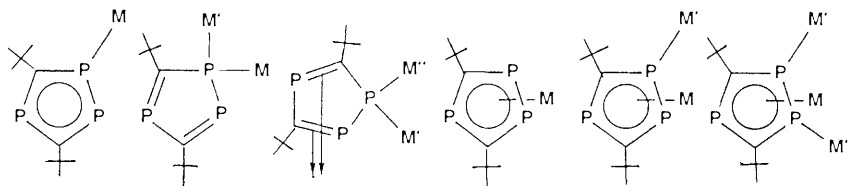
The $P_3C_2Bu^t_2$ ring, on the other hand, can exhibit η^5-ligation in a variety of complexes but also in a variety of additional modes of ligating behaviour, as shown in Figure 33.

Of special significance in the ligating properties of the $P_3C_2Bu^t_2$ 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 Figure 34.[56,60]
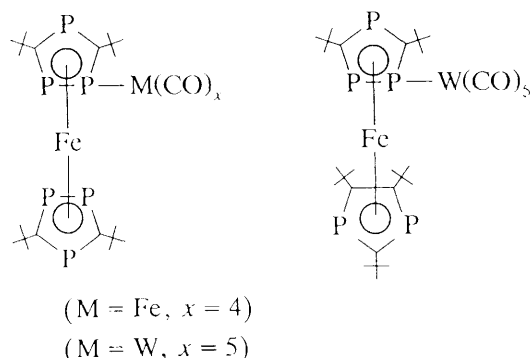

(M = Fe, x = 4)
(M = W, x = 5)

Figure 34

A particularly interesting example of the utilization of the P lone-pair electrons is in the tetrametallic complex [Fe(η^5-$P_3C_2Bu^t_2$)$_2$(Ru$_3$(CO)$_{10}$)] in which the trinuclear ruthenium carbonyl complex links the two $P_3C_2Bu^t_2$ rings of the hexaphospha-ferrocene (Figure 35).
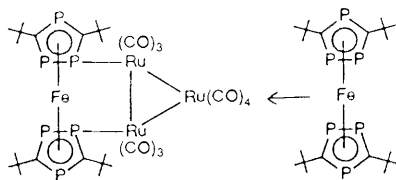

Figure 35

A completely different reaction occurs when the penta-phosphaferrocene complex is reacted with [Ru$_3$(CO)$_{12}$], because the η^5-$P_2C_3Bu^t_3$-ligated ring cannot undergo supplementary ligation via its P atoms, presumably because of the steric effect of the adjacent Bu^t-groups in the ring. Instead a novel phosphino-phosphinidene $P_5C_5Bu^t_5$ fragment results from the remarkable elision of the Fe atom and coupling of the two ring systems, and this is subsequently trapped by the [Ru$_3$(CO)$_9$] cluster (Figure 36).[61]

5.1 η^5-Ligated $P_3C_2Bu^t_2$ Complexes of Main Group Elements

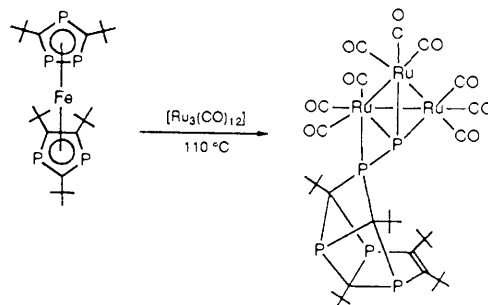The first examples of fully characterized Main Group element

Figure 36

compounds containing the η^5-ligated $P_3C_2Bu^t_2$ ring system come from very recent unpublished work of Durkin, Hitchcock, and Nixon on Group 14 elements.[62] Treatment of the $P_3C_2Bu^t_2$ anion (as its lithium salt) with PbCl$_2$ in an ether solvent gave [Pb(η^5-$P_3C_2Bu^t_2$)$_2$]. Using [Pb(η^5-C_5Me_5)Cl], it proved possible to obtain the crystalline complex [Pb(η^5-C_5Me_5)(η^5-$P_3C_2Bu^t_2$)] whose 'bent' molecular structure, shown in Figure 37, reveals that the η^5-ligated $P_3C_2Bu^t_2$ ring is significantly further away from the Pb atom than the corresponding η^5-ligated C_5Me_5 ring. Very recently, the structurally related tin complex [Sn(η^5-C_5Me_5)(η^5-$P_3C_2Bu^t_2$)] has also been synthesized, as the first η^5-($P_3C_2Bu^t_2$) ligated Group 13 element compound [In(η^5-$P_3C_2Bu^t_2$)].[64]

⬤ Pb
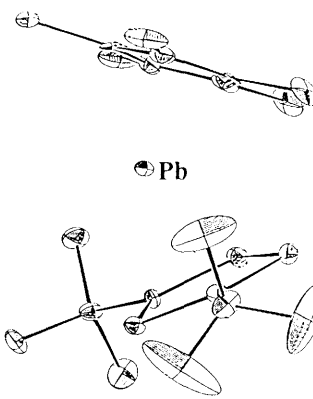
Figure 37

5.2 'Triple-decker' Complexes containing μ-η^5-$P_3C_2Bu^t_2$ Rings

The first 'triple-decker' compound containing the η^5-$P_3C_2Bu^t_2$ ring system has been obtained by treatment of [Fe(η^5-($P_3C_2Bu^t_2$)$_2$] with the cationic complex [Ru(η^5-C_5Me_5)(MeCN)$_3$]$^+$ but, unexpectedly, it was the diruthenium complex [Ru$_2$(η^5-C_5Me_5)$_2$(η^5-$P_3C_2Bu^t_2$)] that was formed.[63] Interestingly, it is the P-containing ring that acts as the bridging ring (see Figure 38).

6 Metal Vapour Synthesis involving Phospha-alkynes

A major new development in phospha-alkyne-metal chemistry has resulted from the very recent studies of Cloke, Nixon, and their co-workers at Sussex University utilizing the technique of
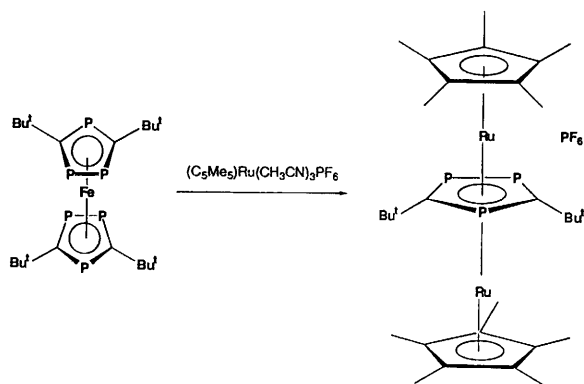
Figure 38

metal vapour synthesis which has previously had wide application in conventional organometallic chemistry. Co-condensation of metal atoms generated by MVS techniques with Bu^{t}CP has led to a variety of novel compounds (*vide infra*) and the importance of the method is that (i) in principle any metal may be used, *i.e.*, Main Group metals, transition metals, lanthanides, and/or actinides; (ii) products often result from P≡C bond cleavage and reassembly reactions; and (iii) novel ring systems, *e.g.*, complexes of the previously unknown phosphirenyl cation PC$_2$Bu$_2^t$ 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, including unpublished results, are detailed below.

Treatment of Bu^{t}CP with iron, chromium, or vanadium atoms using the MVS technique gave pentaphosphametallocenes [Fe(η^5-P$_3$C$_2$Bu$_2^t$)(η^5-P$_2$C$_3$Bu$_3^t$)], [Cr(η^5-P$_3$C$_2$Bu$_2^t$)(η^5-P$_2$C$_3$Bu$_3^t$)], and [V(η^5-P$_3$C$_2$Bu$_2^t$)(η^5-P$_2$C$_3$Bu$_3^t$)], respectively (Figure 39).[64] The latter two complexes are paramagnetic.
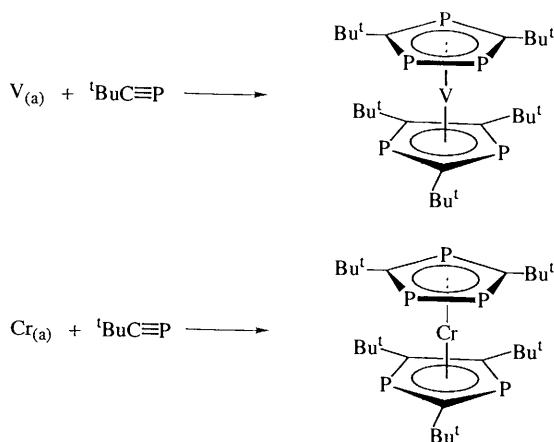

Figure 39

Interesting differences are observed when either Mo or W atoms are treated with Bu^{t}CP, the products being the yellow-orange homoleptic tris-1,3-diphosphacyclobutadiene metal(o) complexes [M(η^4-P$_2$C$_2$Bu$_2^t$)$_3$] (M = Mo, W) (Figure 40).

The structure of the molybdenum complex has been determined by a single crystal X-ray diffraction study, and one of the 4-membered rings is turned through 90° relative to the other two.[65]

The reaction of Ni atoms with Bu^{t}CP is of special significance since it affords equal amounts of two orange-red compounds of molecular formula [NiP$_4$C$_4$Bu$_4^t$]. One is identical with the known 'sandwich' complex [Ni(η^4-P$_2$C$_2$Bu$_2^t$)$_2$] containing two η^4-ligated 1,3-diphosphacyclobutadiene rings which has also been made by a different route, but the second has been shown to
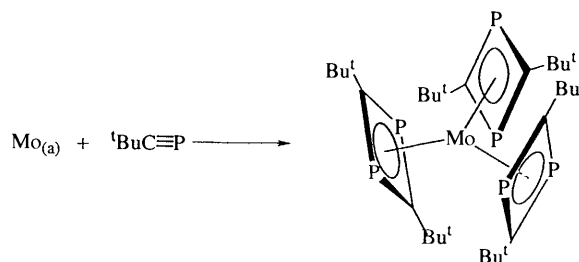

Figure 40

be [Ni(η^3-PC$_2$Bu$_2^t$)(η^5-P$_3$C$_2$Bu$_2^t$)$_2$] (Figure 41), which contains the novel 3-membered phosphirenyl ring system.[66]

The free phosphirenyl cation, which is the simplest of all the aromatic 2π-ring systems containing phosphorus, had previously eluded all attempts at its synthesis. Its identity has now been unambiguously established by a single crystal X-ray diffraction study on the [W(CO)$_5$] adduct. The structural features of the 3-membered ring indicate that the P—C bond lengths average 1.80 Å, while the C—C bond length is 1.33 Å (Figure 42).
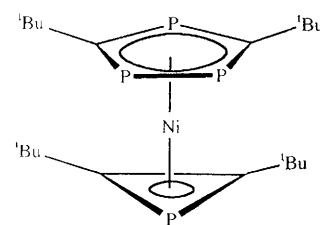
Figure 41
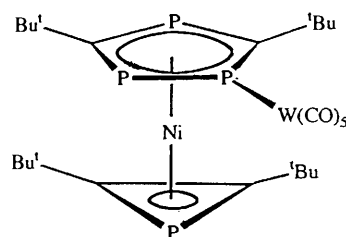
Figure 42

7 Conclusions

It is clearly evident, even from the very selective results detailed above, that phospha-alkynes offer enormous potential as building blocks for novel types of organometallic compounds. Further expansion of this rapidly growing area is expected both in Main Group and lanthanide element chemistry and in the generation of higher 'cage-like' oligomers.

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