The Coordination Chemistry of Compounds Containing Phosphorus–Carbon Multiple Bonds

JOHN F. NIXON

School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, Sussex, United Kingdom

Contents

John F. Nixon, Professor of Chemistry at the University of Sussex, England, received his B.Sc., M.Sc., and Ph.D. and D.Sc. doctorates from the University of Manchester and did postdoctoral work at Cambridge University and the University of Southern California. His first teaching experience was at St. Andrews University, and he has been Visiting Professor at the universities of Victoria and Simon Frazer, Canada. He was the recipient of the Royal Society of Chemistry Corday Morgan Medal and Prize in 1973 and the Main Group Chemistry Award in 1985. His research interests include synthetic and spectroscopic aspects of inorganic and organometallic chemistry. In recent years he has been a pioneer in the development of novel phosphorus compounds containing phosphorus–carbon multiple bonds and exploited their potential as ligands in transition-metal complexes.

I. Introduction

The past decade has seen a remarkable development in the chemistry of compounds containing phosphorus–carbon multiple bonds that violate the long-held view that compounds containing phosphorus–carbon $3p_\pi$–$2p_\pi$ bonds would be inherently unstable.

Progress has been so rapid that several major review articles have already appeared[1–12] detailing synthetic routes, structural studies, bonding considerations, and reactivity patterns of compounds typified by phosphaalkynes ($RC{\equiv}P$), phosphaalkenes ($R_2C{=}PR$), mono- and diphosphaallenes ($R_2C{=}C{=}PR$ and $RP{=}C{=}PR$), and related compounds.

In a major review of phosphaalkynes and phosphaalkenes written in 1981 Appel, Knoll, and Ruppert[1]
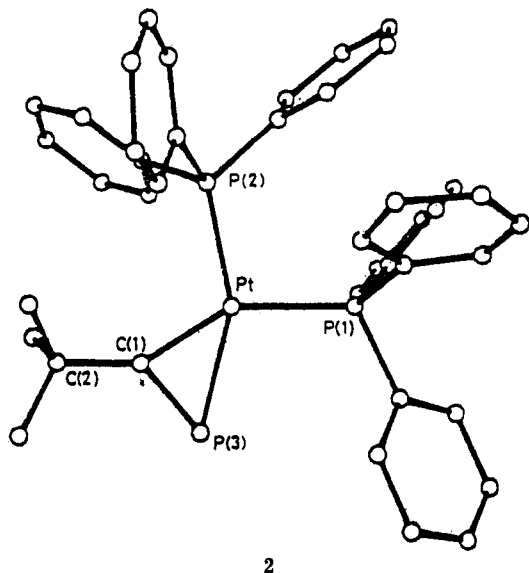
2

Figure 1. Molecular strucutre of 2. Some important bond lengths (Å) and angles (deg): Pt–P(1) = 2.292 (5), Pt–P(2) = 2.285 (5), Pt–P(3) = 2.320 (6), Pt–C(1) = 1.973 (21), P(3)–C(1) = 1.672 (17); P(1)–Pt–P(2) = 101.6 (2), P(2)–Pt–C(1) = 109.1 (5), P(1)Pt–P(3) = 104.6 (2), C(1)–Pt–P(3) = 45.0 (5), Pt–C(1)–P(3) = 78.6 (8), Pt–P(3)–C(1) = 56.5 (7), Pt–C(1)–C(2) = 149 (1), P(3)–C(1)–C(2) = 132 (2).

concluded with the comment "...only a small amount of information is available on the field of complex formation". The purpose of the present article is to indicate how rapidly this new chapter in transition-metal–organophosphorus chemistry has evolved. Structural types of unsaturated organophosphorus ligands that parallel their well-known organic counterparts such as alkynes, alkenes, dienes, cyclobutadiene, η^3-allyl, η^5-cyclopentadienyl, and η^6-arenes have now been developed. Some aspects have been described earlier,[4-7,14] especially by Scherer[13] in a more general review of metal complexes of multiply bonded systems containing phosphorus, arsenic, antimony, and bismuth, but the present review covers published work up to November 1987. An Appendix summarizes some important results reported up to August 1988. (η^5-Phosphacyclopentadienyl (or η^5-phospholyl) and η^6-phospharene metal complexes have recently been reviewed by Mathey[14] and are therefore excluded from this article.)

II. Phosphaalkynes

A. Phosphaalkyne Transition-Metal Complexes

Photoelectron spectroscopic studies[15] on a series of phosphaalkynes indicated that the HOMO is of the π-type and the π–n separation is greater than in the corresponding nitrile, indicating that side-on coordination of the RC≡P ligand might be preferred to P ligation. In mono- and dinuclear metal systems the following ligation modes are expected, and examples of all types A–D have subsequently been established (vide infra).
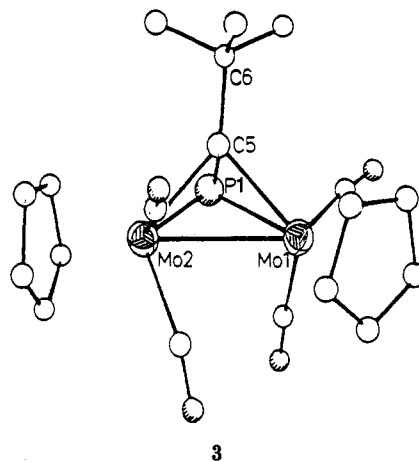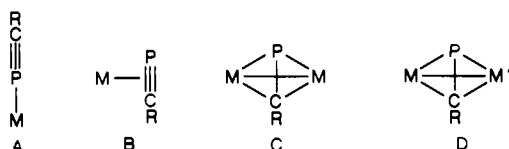

Figure 2. Molecular structure of 3. Selected bond lengths (Å) and angles (deg): Mo(1)–Mo(2) = 3.014 (0), Mo(1)–P(1) = 2.497 (1), Mo(2)–P(1) = 2.442 (1), Mo(1)–C(5) = 2.224 (4), Mo(2)–C(5) = 2.222 (4), P(1)–C(5) = 1.719 (3), C(5)–C(6) = 1.545 (6); Mo-(1)–P(1)–Mo(2) = 75.2 (0), Mo(1)–C(5)–Mo(2) = 85.3 (1), Mo-(1)–P(1)–C(5) = 60.4 (1), Mo(2)–P(1)–C(5) = 61.7 (1), Mo(1)–C-(5)–P(1) = 77.4 (1), Mo(2)–C(5)–P(1) = 75.4 (1), Mo(1)–Mo-(2)–C(5) = 47.7 (1), P(1)–C(5)–C(6) = 127.9 (3).

To date all complexes involve ligated Bu^tC≡P or AdC≡P except for a single report of complexes of type C that were not obtained directly from the phosphaalkyne but via in situ dehalogenation of RCCl₂PCl₂ by [Co₂(CO)₈].[16]

1, R = Ph, Me, Me₃Si
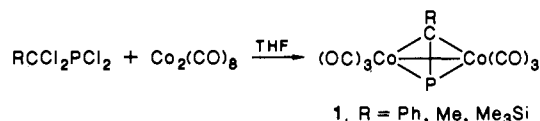
η^2-Complexes of type B were first reported by Nixon and co-workers[17-19] using the following synthetic routes:

R = Me, Ph
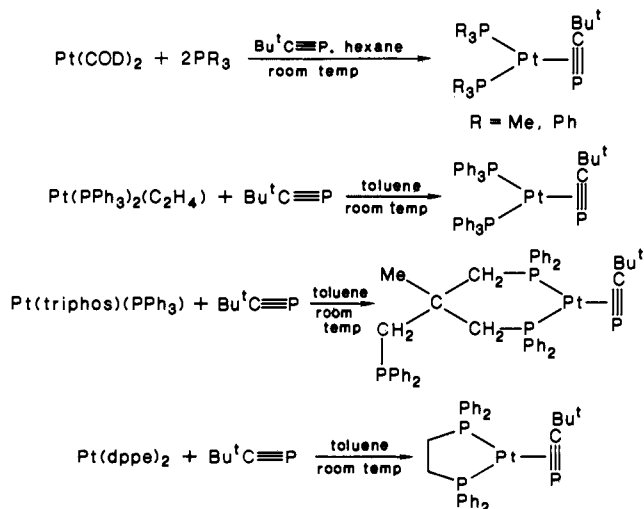
The molecular structure of [Pt(PPh₃)₂(Bu^tC≡P)] (2) shown in Figure 1 confirms the η^2-bonding mode and reveals that the P–C bond is considerably lengthened on coordination, consistent with the population of π^* orbitals. Complex 2 is also noteworthy in that the one-bond $J_{PtP(alkyne)}$ coupling constant (62 Hz) is the smallest so far recorded, reflecting the low s character of the Pt–P(alkyne) bond.[17]

Complexes of type C and D containing a tetrahedrane structure have been made by analogous reactions known
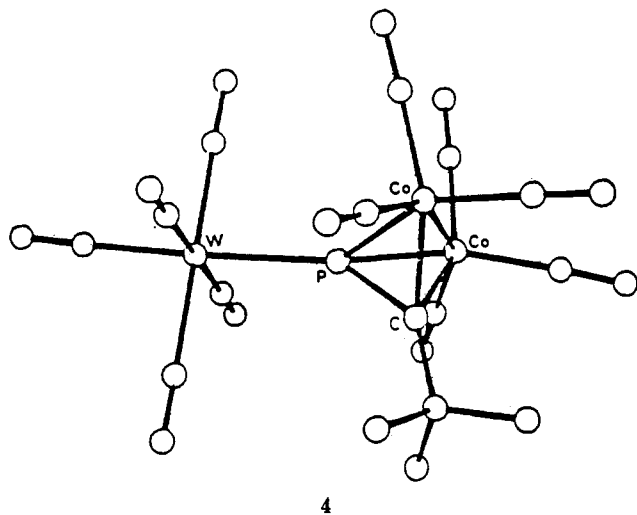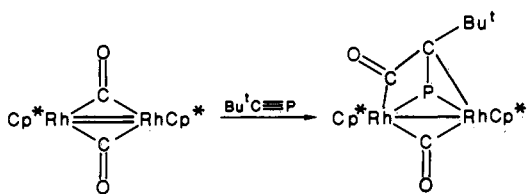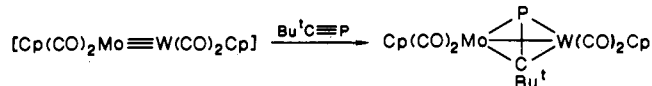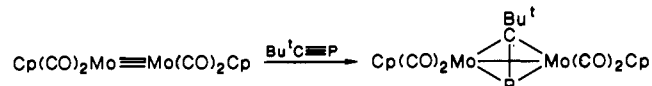
4

Figure 3. Molecular structure of $[Co_2(CO)_6(\mu\text{-}Bu^tCP)W(CO)_5]$[20] (**4**). Some important bond lengths (Å) and angles (deg): W–P = 2.465 (1), P–C = 1.695 (6); W–P–C = 148.1 (2), P–C–C = 139.4 (4)°.

for alkynes, namely by (i) treatment with $[Co_2(CO)_8]$ or $[CoNi(CO)_5(\eta^5\text{-}C_5H_5)]$ or (ii) via addition across metal–metal multiple bonds; e.g.[20,21]
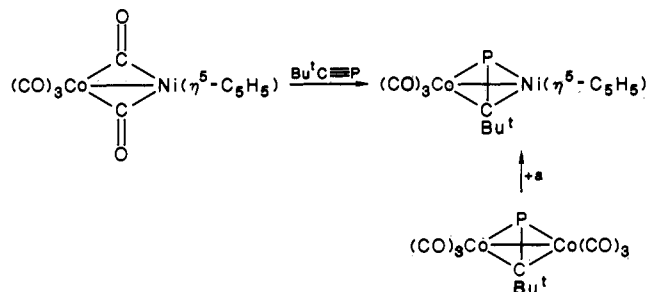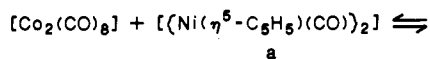
The molecular structure of **3** is shown in Figure 2.[22] Unlike the analogous alkyne derivatives complexes of type B–D have further ligating potential by virtue of the availability of the lone pair of electrons at phosphorus. Their complexes of type E and F result from
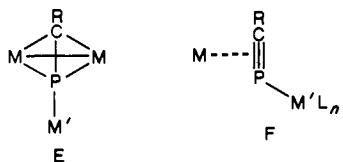
further interaction with other metal centers; viz.[23]

M = Cr, Mo, W

(a) $[W(CO)_5(THF)]$: $(ML_n = Co(CO)_3$, $Mo(CO)_2Cp$:
(b) $[M'_3(CO)_{11}(MeCN)]$. $(M' = Os$, Ru: $ML_n = Mo(CO)_2Cp)$:
(c) $[(PtCl_2(PR_3))_2]$. $(R = alkyl$, $aryl$: $ML_n = Mo(CO)_2Cp$:
(d) $[(RhCl[OC(NMePF_2)_2])_2]$. $(ML_n = Mo(CO)_2Cp$: $Cp = \eta^5\text{-}C_5H_5)$
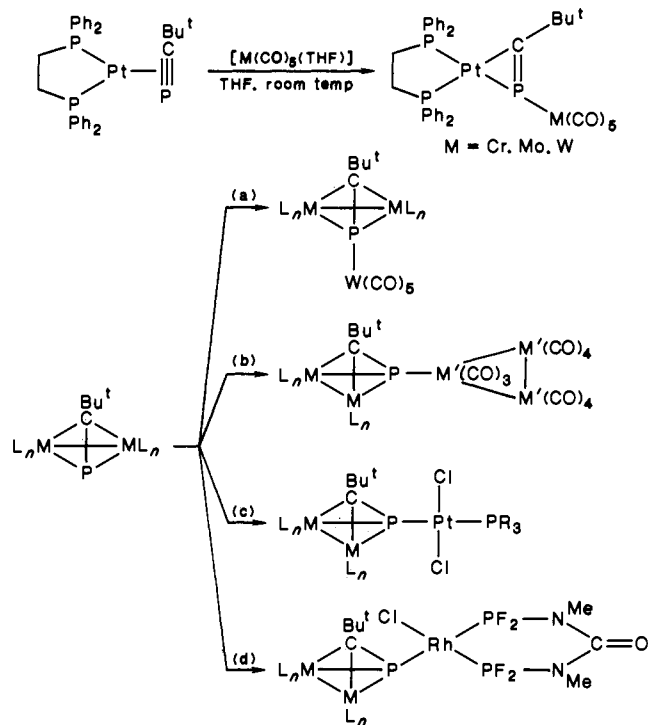
The method has been utilized to synthesize tri- and pentametallic derivatives.[24-26] The molecular structures of **4** (Figure 3), **5** (Figure 4), and **6** (Figure 5) have been confirmed by single-crystal X-ray diffraction studies. It is noteworthy that the analogous alkyne reaction with $[Mo(CO)_2(\eta^5\text{-}C_5H_5)]_2$ followed by treatment with $[Fe_2(CO)_9]$ leads to a cluster expansion reaction.

A further type of trimetallic phosphalkyne complex (type G) in which the RC≡P fragment transversely

G
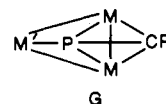
bridges an M–M bond to afford a $\mu_3\text{-}(\eta^2\text{-}\perp)$ ligating mode has been described.[27] The complex $[Fe_2Pt\text{-}(dppe)(CO)_6(Bu^tCP)]$ (**7**, Figure 6) is formed quantitatively from $[Pt(dppe)Bu^tCP]$ and either $[Fe_2(CO)_9]$ or $[Fe_3(CO)_{12}]$.

7
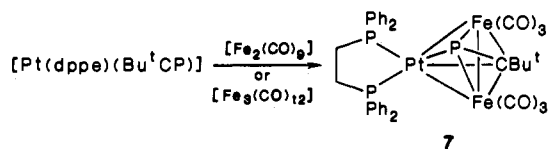
More recently, examples of anionic complexes containing $Bu^tC{\equiv}P$ in a $\mu_3\text{-}\eta^2$-bonding mode (**8**) have been described.[28]

8⁻
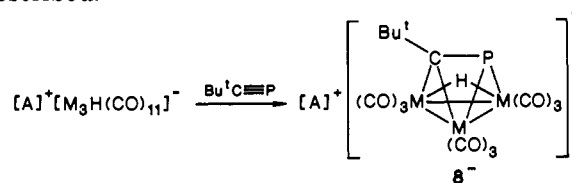
a. A = PPh_4, M = Fe
b. A = $N(PPh_3)_2$, M = Ru
c. A = Na, M = Ru
d. A = NEt_4, M = Ru

5
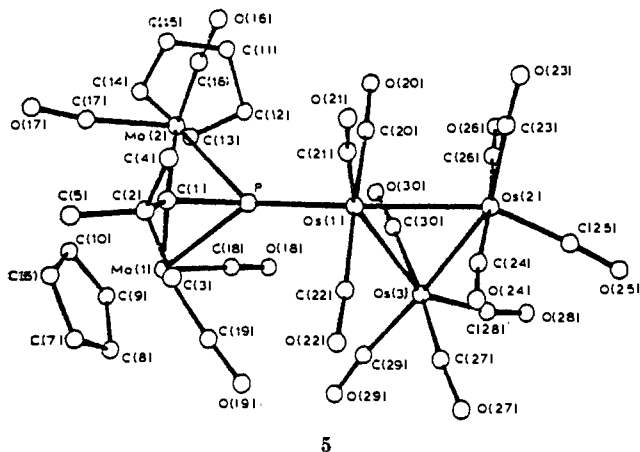
Figure 4. Molecular structure of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}^tBuCP)Os_3(CO)_{11}]^{24}$ (5). Selected dimensions: Os(1)–Os(2) = 2.860 (1), Os(1)–Os(3) = 2.892 (1), Os(2)–Os(3) = 2.860 (1), Os(1)–P = 2.360 (3), Mo(1)–P = 2.514 (3), Mo(2)–P = 2.397 (3), Mo(1)–C(1) = 2.36 (2), Mo(2)–C(1) = 2.33 (1), P–C(1) = 1.86 (1), C(1)–C(2) = 1.37 (2) Å; P–C(1)–C(2) = 132 (1)°.

6
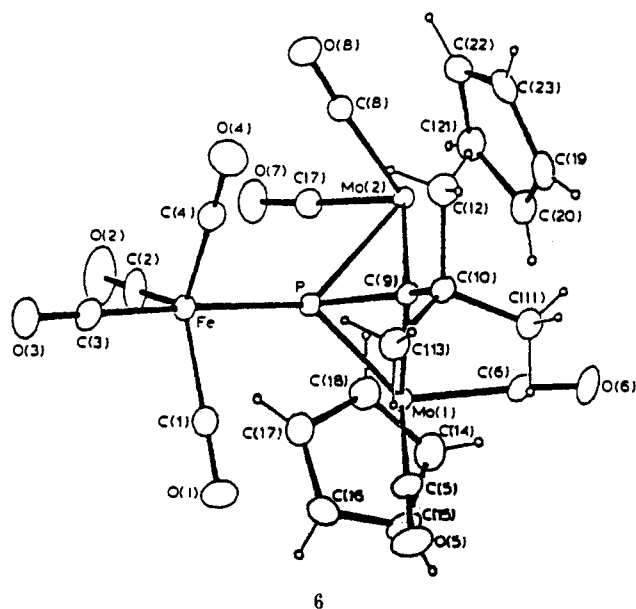
Figure 5. Molecular structure of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(Bu^tCP)Fe(CO)_4]^{26}$ (6).

The most remarkable examples of phosphaalkynes utilizing both their P≡C bonds and phosphorus lone-pair electrons to form cluster metal systems involve pentametallic complexes of the type $[Pd_2Pt_3(PPh_3)_5(Bu^tCP)_3]$ (9), whose molecular structure is shown in Figure 7. The analogous $[Pd_5(PPh_3)_5(Bu^tCP)_3]$ complex has also been prepared.[29]

$$[Pt(PPh_3)_2(Bu^tCP)] \xrightarrow{Pd(PPh_3)_4} [Pd_2Pt_3(PPh_3)_5(Bu^tCP)_3]$$

$$[Pd(PPh_3)_4] + Bu^tC{\equiv}P \xrightarrow[\text{room temp}]{\text{toluene}} [Pd_5(PPh_3)_5(Bu^tCP)_3]$$
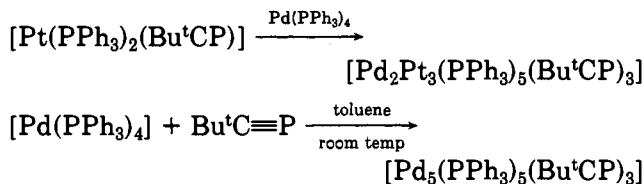
The molecular structure of 9 consists of a trigonal-bipyramidal arrangement of the metal atoms with the two Pd atoms (which are bonded) occupying axial positions and the three platinum stellated atoms in equatorial sites. The structure can be also considered as the first example of a hexagonal-bipyramidal *closo* cluster.

7
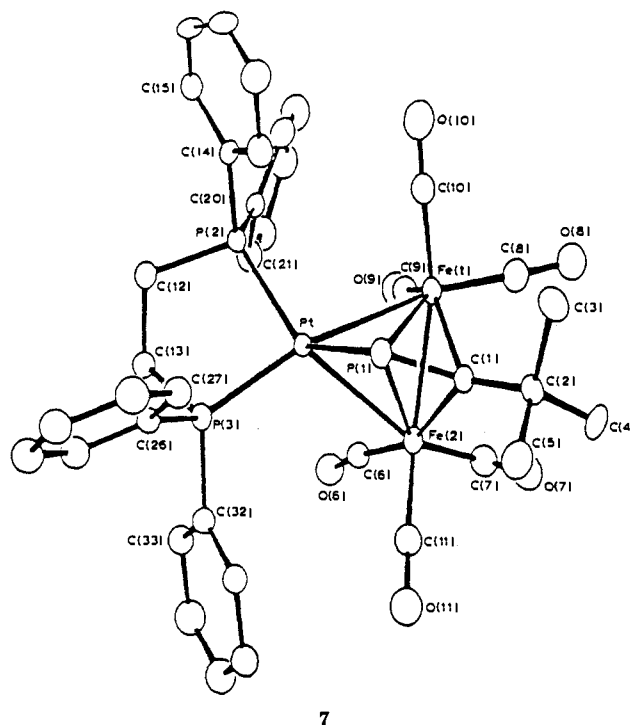
Figure 6. X-ray structure of $[Fe_2Pt(dppe)(CO)_6(Me_3CCP)]$ (7) showing the atomic numbering scheme. Selected bond lengths (Å) and bond angles (deg): Pt–Fe(1) = 2.671 (1), Pt–Fe(2) = 2.669 (1), Pt–P(1) = 2.343 (2), Pt–P(2) = 2.263 (2), Pt–P(3) = 2.270 (2), Fe(1)–Fe(2) = 2.518 (1), Fe(1)–P(1) = 2.343 (2), Fe(2)–P(1) = 2.446 (2), Fe(1)–C(1) = 2.080 (6), Fe(2)–C(1) = 1.974 (6), P(1)–C(1) = 1.703 (6); Pt–P(1)–C(1) = 113.6 (2), P(1)–C(1)–C(2) = 128.1 (5), Fe(1)–P(1)–Fe(2) = 63.40 (5).

9
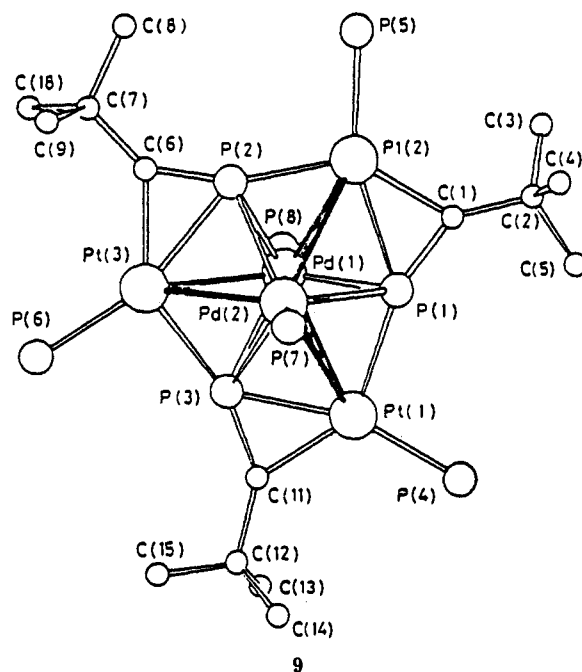
Figure 7. Molecular structure of $[Pd_2Pt_3(PPh_3)_5(Bu^tCP)_3]$ (9). Phenyl groups of PPh$_3$ are omitted for clarity.

B. η^1-Phosphaalkyne Transition-Metal Complexes

Although the "alkyne-like" behavior of phosphaalkynes dominates their coordination chemistry, the first example of η^1-bonded phosphaalkyne metal complexes (type A) has been reported recently by Nixon et al.[30]

10
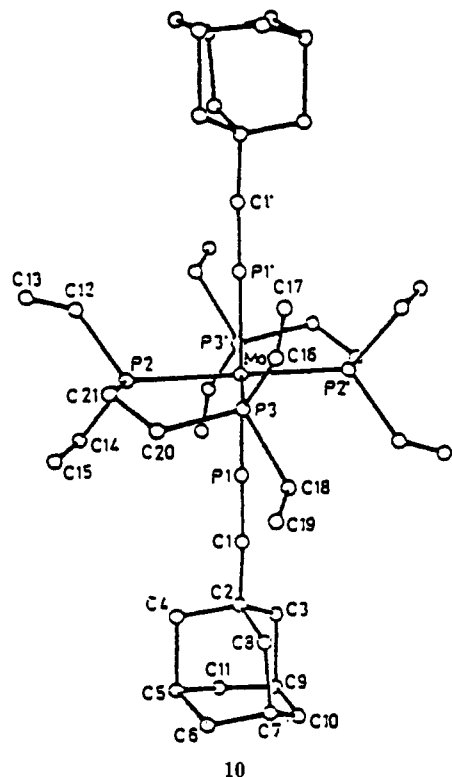
Figure 8. Molecular structure of **10**. Important bond lengths (Å) and angles (deg): Mo–P1 = 2.305 (3), Mo–P2 = 2.431 (4), Mo–P3 = 2.436 (4), P1–C1 = 1.520 (12), C1–C2 = 1.46 (2); P1–Mo–P2 = 89.9 (1), P1–Mo–P3 = 92.0 (1), P2–Mo–P3 = 81.2 (1), Mo–P1–C1 = 176.3 (5), P1–C1–C2 = 177.9 (8).

A series of complexes have been obtained by displacement of dinitrogen from $trans$-[$M(N_2)_2$-$(R'_2PCH_2CH_2PR'_2)_2$] (M = Mo, W) complexes as shown below. The metal–phosphorus network exploited is such that only ligands that are long and thin can approach the metal and bind in the axial positions.

M	R	R'
Mo	^tBu	p-ClC_6H_4
Mo	^tBu	Et
Mo	^tBu	Ph
Mo	^tBu	p-tolyl
Mo	Ad	Et
W	^tBu	Ph

A single-crystal X-ray study on $trans$-[$Mo(AdCP)_2$-$(Et_2PCH_2CH_2PEt_2)_2$] (**10**, Figure 8) reveals (a) the linear seven-atom CCPMoPCC framework, (b) a short Mo–P(alkyne) bond distance, and (c) a short P≡C bond distance that is comparable with that found in the free phosphaalkyne.[30] (See Table 1.)

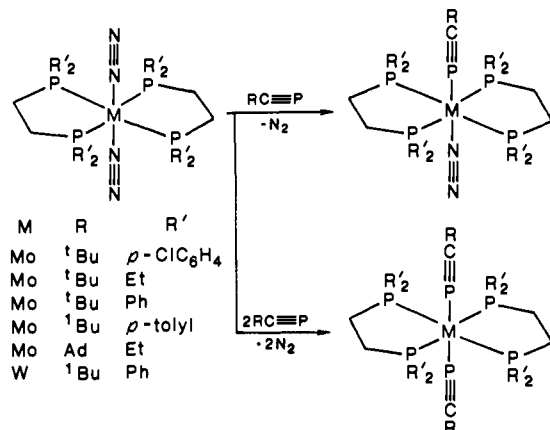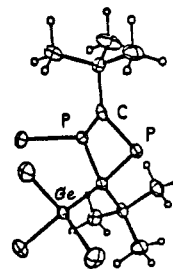## C. Reaction of Bu^{t}C≡P with Metal Halides

Volatile halides of main-group elements readily add across the triple bond of Bu^{t}C≡P to afford substituted phosphaalkenes, XP=C(Bu^t)MY$_n$, (M = Ge, Sn, X = Y = Cl, n = 3; M = B, n = 2, X = Y = Br, Cl). In the

TABLE 1. P–C Bond Lengths in Some Phosphaalkyne Transition-Metal Complexes^a

complex	d(P–C), Å	ref
[Pt(PPh$_3$)$_2$(Bu^{t}CP)]	1.672 (17)	17
[Mo(dppe)$_2$(AdCP)$_2$]	1.520 (12)	30
[Mo$_2$(η^5-C$_5$H$_5$)$_2$(CO)$_2$Bu^{t}CP)]	1.719 (3)	22
[Mo$_2$(η^5-C$_5$H$_5$)$_2$(CO)$_2$(Bu^{t}CP)W(CO)$_5$]	1.733 (12)	26
[Mo$_2$(η^5-C$_5$H$_5$)$_2$(CO)$_2$(Bu^{t}CP)Fe(CO)$_4$]	1.719 (5)	26
[Mo$_2$(η^5-C$_5$H$_5$)$_2$(CO)$_2$(Bu^{t}CP)Os$_3$(CO)$_{11}$]	1.86 (1)	24
[Co$_2$(CO)$_6$(Bu^{t}CP)W(CO)$_5$]	1.695 (6)	20
[Fe$_2$Pt(dppe)(CO)$_6$(Bu^{t}CP)]	1.703 (6)	27
[Pd$_2$Pt$_3$(PPh$_3$)$_5$(Bu^{t}CP)$_3$]	1.62 (2)	29

^{a} d(P–C) for free phosphaalkynes RC≡P = 1.540 (3) Å.

germanium system further addition of Bu^{t}C≡P gave the 1,2-diphosphete **11**, whose structure has been con-

11

firmed by a single-crystal X-ray diffraction study (see above). PBr$_3$ and Bu^{t}C≡P afford the novel cage **12**, which is formed via the **13** intermediate.[31-33]
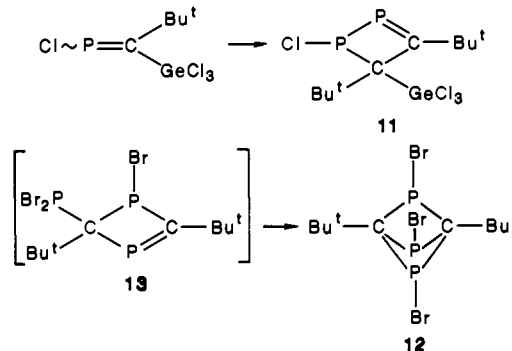
The reaction of Bu^{t}C≡P with high oxidation state transition-metal halides, on the other hand, gives remarkable products. WCl$_6$ or MoCl$_5$ reacts with Bu^{t}C≡P in POCl$_3$ to give PCl$_3$ and Bu^{t}C≡CBu^t complexes of tungsten (IV) and molybdenum(III).[34-35]
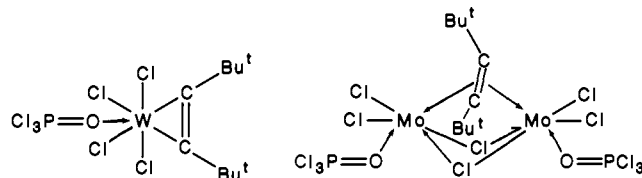
Surprisingly, the product from analogous reactions with TaCl$_5$ were mainly the yellow complex **14** and smaller amounts of the dark red **15**. Since both **14** and **15** are polycyclic, the possible oligomerization of phosphaalkynes in the presence of these transition-metal halides is suggested. Complex **15** represents an example of the previously unknown 1,3,5-triphosphatrishomocyclopropenylium cation, the bonding in which is best described as an overlapping of three p orbitals at the phosphorus atoms that are directed toward the center of the six-membered ring.

14   **15**
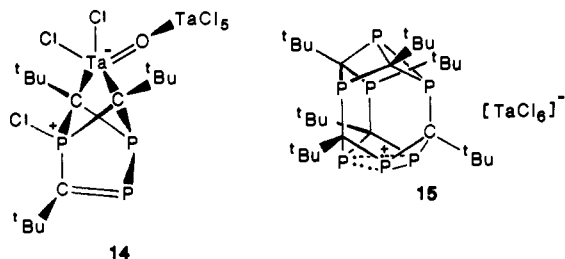
D. Phosphaalkyne Metathesis Reactions

Becker and co-workers[31,32] have extended the metathesis reactions of alkynes and nitriles with (hexa-*tert*-butoxy)ditungsten reported by Schrock, Chisholm, and co-workers to $Bu^tC\equiv P$. To date no intermediates of type 16 and 17 have been detected; however, by ad-

16   **17**

18   **19**
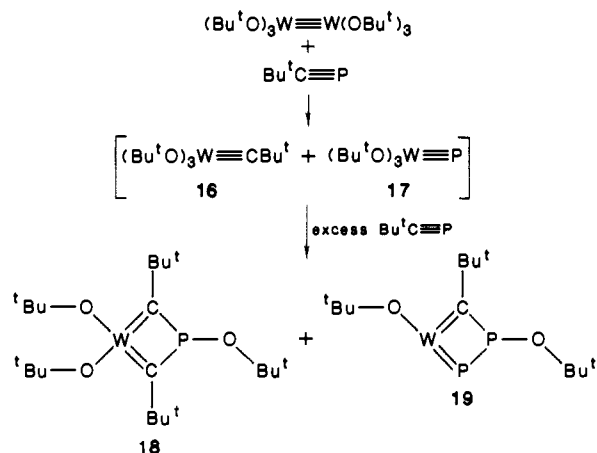
dition of an excess of $Bu^tC\equiv P$ and a 1,3 shift of a Bu^tO group from W to P, compounds of 1-phospha-3-tungstena- (18) and 1,4-diphospha-3-tungstena-2,3-cyclobutadiene (19) are formed. The former has been isolated and characterized and the latter formulated on the basis of NMR studies.

E. Metal Complexes Derived from Phosphaalkynes

(i) A P=CR(CO)CR=P Ligating Unit

Examples of novel ligands generated from phosphaalkyne metal complexes have recently been described. The coupling of two phosphaalkyne units via a carbonyl group to afford the novel ligating unit P=CR(CO)CR=P (R = adamantyl or Bu^t) occurs on treatment with $[Rh_2(CO)_2(\eta^5-C_5Me_5)_2]$.[36]

The solid-state structure of 20 (Figure 9) shows that

20

one Rh atom is attached in an η^2-fashion to each of the

20
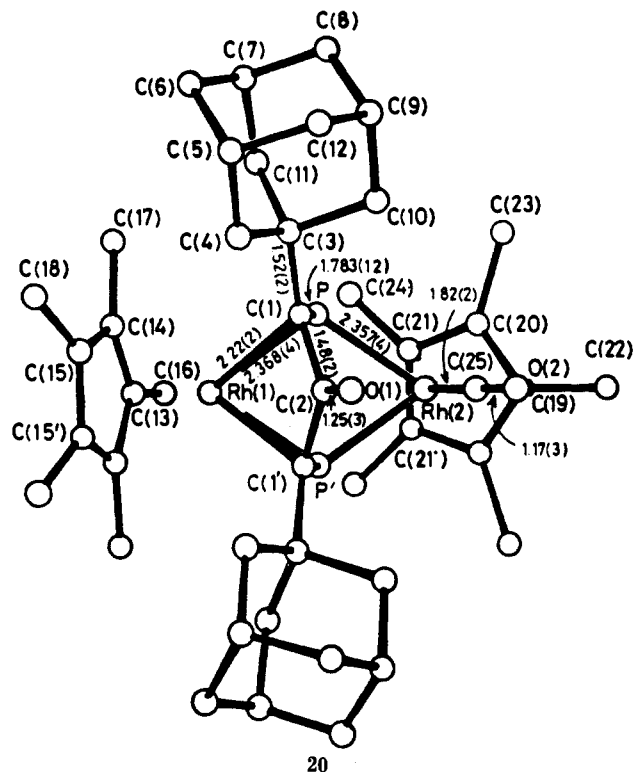
Figure 9. Molecular structure of $[Rh_2(CO)(\eta^5-C_5Me_5)_2\{PCRC-(O)CRP\}]$ (R = adamantyl) (20) with bond lengths in angstroms.

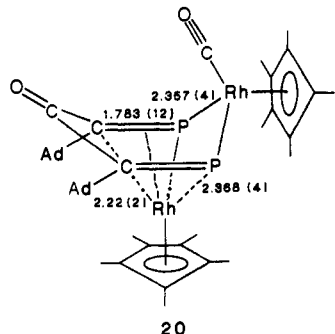P=C double bonds while the other Rh is directly bonded to both phosphorus atoms. The compound can be viewed as an example of a novel metallo diphosphaalkene that is ligated to a $[Rh(\eta^5-C_5Me_5)]$ unit (see also section VI).

(ii) An RCP(CO) Ligating Unit

The attack of carbon monoxide on the carbon of a single coordinated phosphaalkyne generates the novel phosphinidene ligand RC(CO)P (R = Bu^t), which has been trapped in the complex $[Re_2Pt(CO)_8(dppe)-(Bu^tCC(O)P)]$ (21)[37] (Figure 10), viz.

$[Pt(dppe)(Bu^tCP)] + [Re_2H_2(CO)_8] \longrightarrow$

21
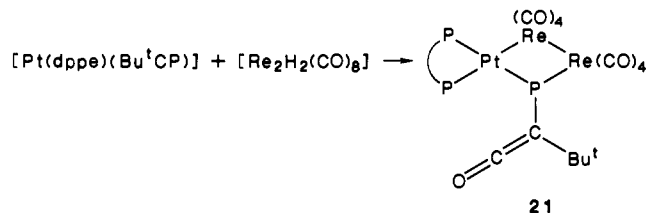
(iii) A 2H-Phosphirene Complex

The use of phosphaalkynes in the synthesis of other novel phosphorus compounds is underlined by the recent report of the synthesis of the first example of a 2H-phosphirene complex.[41]

Treatment of $Bu^tC\equiv P$ with a diazo*cyclo*hexane compound at -40 °C affords the spirocyclic compound 3H-1,1,4-diazaphosphole, which at 20 °C undergoes a [1,5]-sigmatropic rearrangement. However, photolysis at -40 °C gives a 5:1 mixture of the 1-phosphacyclopent-1-ene and the 2H-phosphirene. The latter has been complexed with [W(CO)_5] to afford (22) (Figure 11), whose structure has been fully established by a single-crystal X-ray diffraction study. The P=C bond length in 22 (1.634 (4) Å) is slightly shorter than that
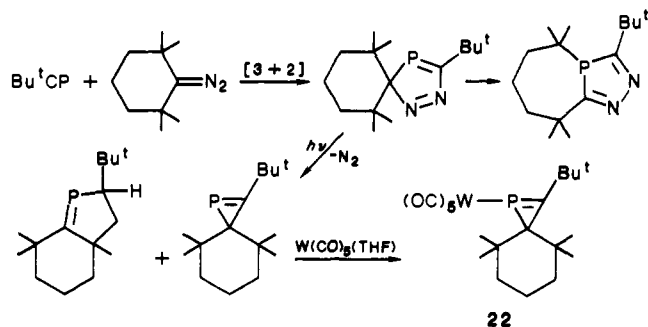
found in free or η^1-ligated phosphalkenes. (See section IV.)

(iv) A Ligated Bis(phosphavinyl) Ether

The remarkable bis(phosphavinyl) ether complex **23** (Figure 12) containing four [Mn(CO)$_2$(η^5-C$_5$H$_4$CH$_3$)] fragments has been synthesized unexpectedly by addition of water to 2 mol of Bu^{t}C≡P during its reaction with the manganese carbonyl precursor.[38]
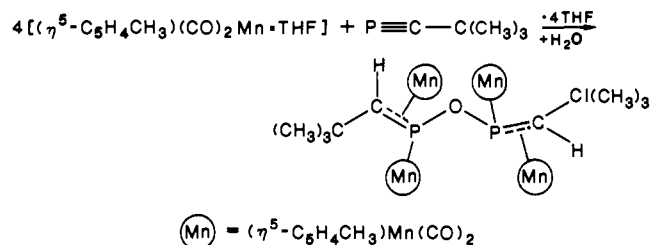
Of the four manganese complex fragments two are bonded to the phosphorus atoms and the other two to the P=C double bonds of the ligand.

(v) Phosphasilirene Metal Complexes

The first three-membered-ring compounds containing a P=C double bond reported recently by Weidenbruch et al.[39] by addition of a silylene to a phosphaalkyne form η^1-complexes with the [W(CO)$_5$] fragment. The X-ray structural analysis of the adamantyl analogue **24** (Figure 13) confirms the novel three-membered-ring system, and the P–C distance is typical of phosphaalkenes.

F. An η^2-λ^5-Phosphaalkyne Metal Complex

Only one example of this type of complex has been reported.[40] Sodium reduction of [TaCl$_4$(C$_5$Me$_5$)] in trimethylphosphine leads to double C–H activation and the formation of [TaH$_2$(C$_5$Me$_5$)(PMe$_3$)(η^2-CHPMe$_2$)] (**25**) (Figure 14).
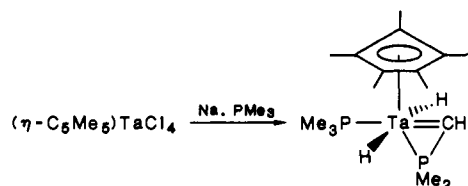
The tantalum–carbon distance lies within the range for a tantalum–carbon double bond; however, the P–C
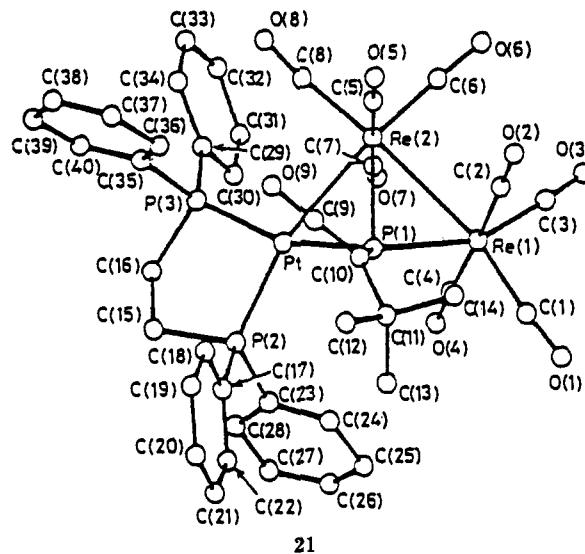
Figure 10. Molecular structure of 21.

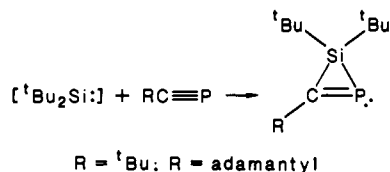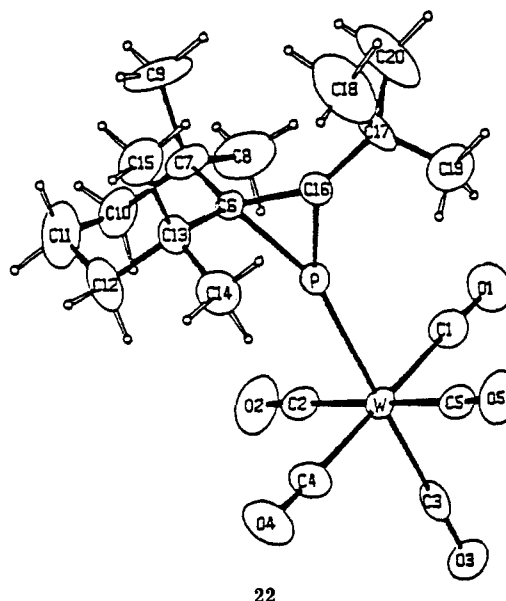**Figure 11.** Molecular structure of (**22**) (ORTEP). The thermal ellipsoids correspond to the 27% probability level. Selected bond lengths (Å) and angles (deg): W–P = 2.458 (1), W–C1 = 2.004 (6), W–C2 = 1.997 (6), W–C3 = 1.965 (5), W–C4 = 2.029 (6), W–C5 = 1.999 (5), P–C6 = 1.881 (4), P–C16 = 1.634 (4), C6–C16 = 1.482 (6); W–P–C6 = 157.7 (2), W–P–C16 = 153.1 (2), C6–P–C16 = 49.2 (2), P–C6–C16 = 56.7 (2), P–C16–C6 = 74.1 (3), C7–C6–C13 = 116.4 (4). The ^{t}Bu group is poorly defined owing to large thermal vibration amplitudes.

distance (1.714 (9) Å) is much shorter than that expected for a single bond, suggesting a significant contribution from structure II.
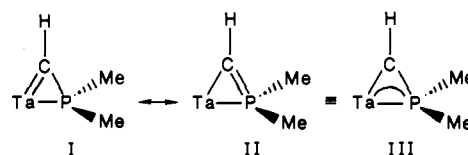
III. Use of Phosphaalkynes In Syntheses of Phosphorus Analogues of η^4-Cyclobutadiene, η^5-Cyclopentadienyl, and η^6-Arene Transition-Metal Complexes

A major recent development in the chemistry of

23
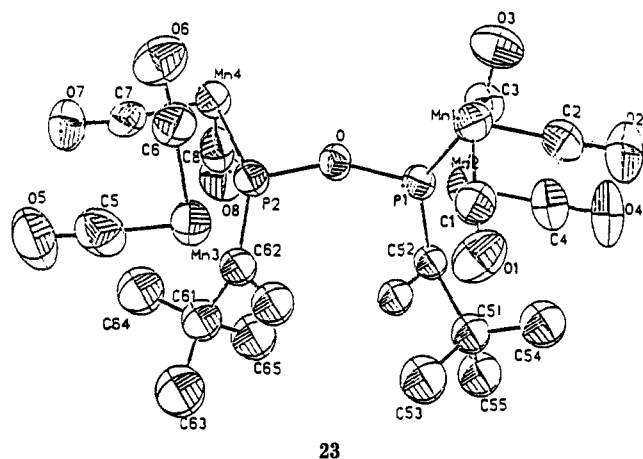
Figure 12. Molecular crystal structure of **23**. For clarity, the methylcyclopentadienyl moieties are omitted. Selected bond lengths (Å) and angles (deg): Mn1-P1 = 2.236 (4), Mn2-P1 = 2.402 (3), P1-C52 = 1.71 (1), Mn2-C52 = 2.157 (9), Mn4-P2 = 2.226 (3), Mn3-P2 = 2.438 (3), Mn3-C62 = 2.156 (10), P2-C62 = 1.70 (1), P1-O = 1.643 (7), P2-O = 1.665 (7); O-P1-C52 = 107.7 (7), O-P2-C62 = 107.2 (7), P1-O-P2 = 154.8 (7).

24
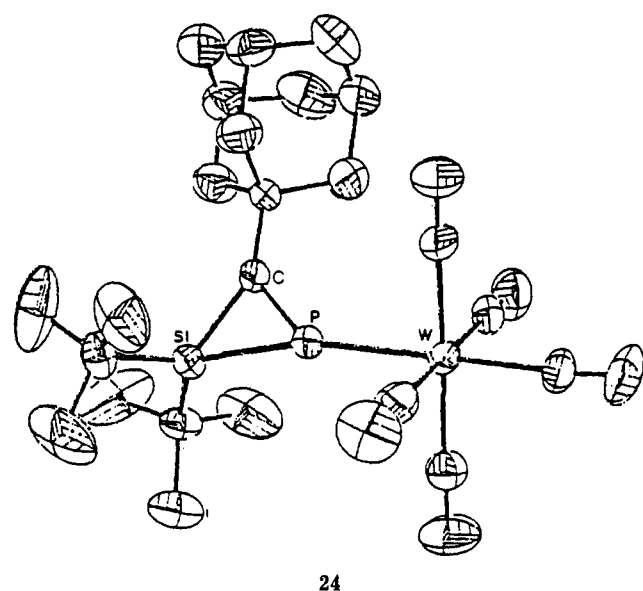
Figure 13. Crystal structure of **24** (H atoms omitted). Selected bond lengths (Å) and angles (deg): P-C1 = 1.686 (6), P-Si = 2.196 (2), C1-S1 = 1.842 (6), P-W = 2.475 (2), W-C24 = 1.992 (7), W-C = 2.036 (5), C1-C2 = 1.500 (9), Si-C12 = 1.895 (8), Si-C16 = 1.907 (8); Si-P-C1 = 54.8 (2), P-C1-Si = 76.9 (3), C1-Si-P = 48.4 (2), Si-P-W = 165.1 (11), C1-P-W = 139.9 (2). Dihedral angles (deg): W-P-Si-C1 = 171.1, W-P-C1-Si = 176.4.

phosphalkynes is their utility as building blocks for the synthesis of phosphorus analogues of the well-known η^4-cyclobutadiene, η^5-cyclopentadienyl, and η^6-arene transition-metal complexes.

A. 1,3-Diphosphacyclobutadiene Complexes

The first examples of this type of complex were reported by Nixon et al.[42] and independently by Binger, Regitz, and co-workers.[43] The similarity in chemical behavior of phosphaalkynes and alkynes is illustrated by the ready cyclodimerization of Bu^{t}CP by treatment with complexes of the type [M(η^5-C$_5$R$_5$)(C$_2$H$_4$)$_2$] (R =

25
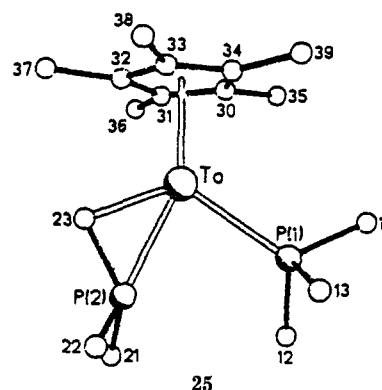
Figure 14. Molecular structure of (C$_5$Me$_5$)Ta(PMe$_3$)(H)$_2$(η^2-CHPMe$_2$) (**25**) (carbon atoms labeled by number only). Selected bond lengths (Å) and angles (deg): Ta-P(1) = 2.590 (3), Ta-P(2) = 2.480 (2), Ta-C(23) = 2.005 (10), Ta-ring centroid = 2.105 (8), P(1)-C(11) = 1.850 (14), P(1)-C(12) = 1.860 (15), P(1)-C(13) = 1.828 (16), P(2)-C(23) = 1.714 (9); P(1)-Ta-P(2) = 82.3 (1), P(1)-Ta-C(23) = 125.6 (3), P(2)-Ta-C(23) = 43.4 (3), P(1)-Ta-ring centroid = 124.6 (3), P(2)-Ta-ring centroid = 153.1 (3), C(23)-Ta-ring centroid = 109.7 (8).

26
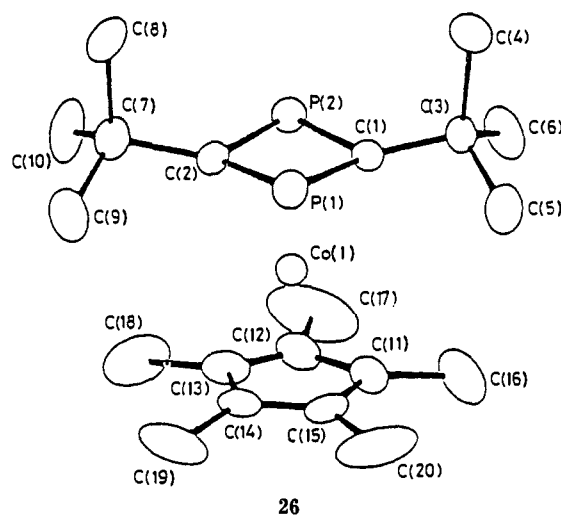
Figure 15. Molecular structure of [Co(η^5-C$_5$Me$_5$){η^4-(Bu^{t}CP)$_2$}] (**26**). Important dimensions: P(1)-C(1) = 1.80 (1), P(1)-C(2) = 1.79 (1), P(2)-C(1) = 1.82 (1), P(2)-C(2) = 1.80 (1), Co(1)-P(1) = 2.240 (3), Co(1)-P(2) = 2.244 (4), Co(1)-C(1) = 2.09 (1), Co-(1)-C(2) = 2.08 (1) Å; P(1)-C(1)-P(2) = 98.0 (5), P(1)-C(2)-P(2) = 98.7 (5), C(1)-P(1)-C(2) = 82.0 (5), C(1)-P(2)-C(2) = 81.0 (5)°. In the other independent molecule the comparable dimensions are as follows: P-C = 1.82 (1), 1.81 (1), 1.81 (7), 1.79 (1) Å, Co-P = 2.247 (3), 2.253 (4) Å, Co-C = 2.0. (1), 2.07 (1) Å; P-C-P = 98.8 (5), 97.5 (5), C-P-C = 81.2 (5), 82.0 (5)°.

H, M = Co, Rh; R = Me, M = Co, Rh, Ir) as shown below.
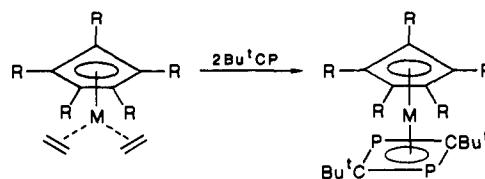
The formulation of the complexes was based on mass spectral and NMR data and was confirmed by single-crystal X-ray crystallographic studies.

In **26** (Figure 15) the η^4-1,3-diphosphacyclobutadiene ring is essentially planar and all the P-C bond lengths are equivalent, indicating that in the complexed form

the 1,3-diphosphacyclobutadiene ring is a square rather than a rectangle. This is of interest since it parallels the known behavior of coordinated cyclobutadienes (viz., structure A; cf. B). Interestingly, the phospho-

rus–carbon bond length (1.801 Å) is, as expected, much longer than that of free Bu^{t}CP (154 pm) and significantly logner than both the P=C double-bond length in phosphaalkenes R$_2$C=PR (169 pm) and phosphorus–carbon distances in phosphabenzenes (175 pm), in line with the anticipated bond orders.

An indenyl cobalt analogue is also known with that of **26**. (The structure of the indencyl complex has just been published by Binger, Regitz, Krüger, and their co-workers in *Chem. Ber.* **1988**, *121*, 637.) Analogous derivatives of Me$_2$CHC≡P are also known, and Maah and Nixon and Binger and co-workers have independently made AdC≡P analogues.[44,45] The former group has also cyclodimerized mixtures of Bu^{t}C≡P and AdC≡P (see below) but the mixed [AdCPBu^{t}CP] ring system is formed to a smaller extent than the parent [P$_2$(CR)$_2$] ring systems.

Most recently, Binger, Regitz, et al.[46] have reported that although attempts at cocyclodimerization of Bu^{t}C≡P and MeC≡CMe only gave ligated [PCBu^t]$_2$ and the arene Me$_6$C$_6$, the reaction between [Co(η^5-C$_5$H$_5$)(C$_2$H$_4$)$_2$] and Me$_3$SiC≡CSiMe$_3$ at −30 °C followed by treatment of the resulting intermediate with Bu^{t}C≡P gave a low yield of the previously unknown phosphacyclobutadiene complex **27**; viz.
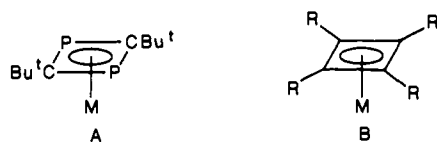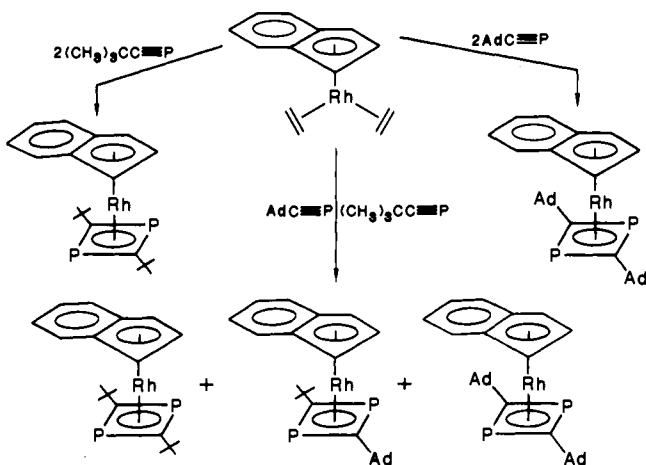

27
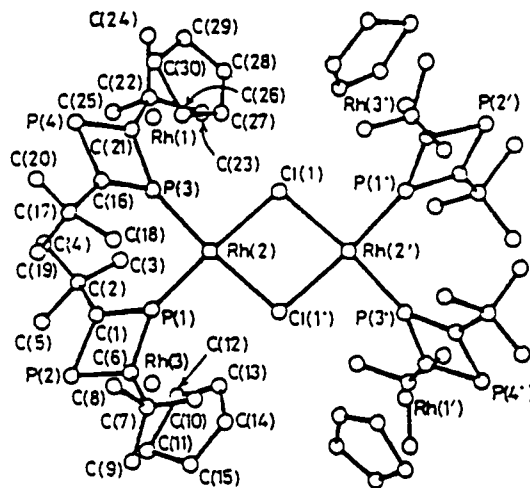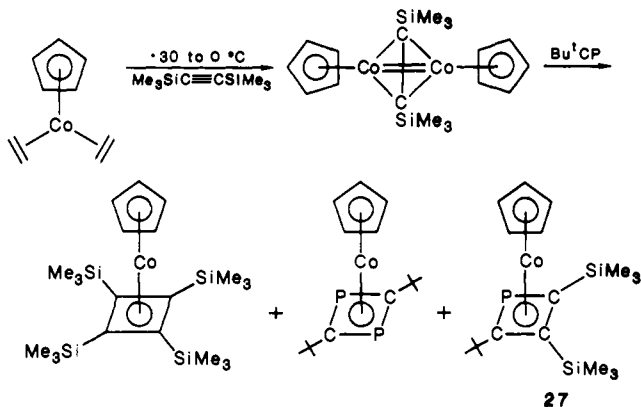
31

Figure 16. Molecular structure of complex **31**. Important dimensions: Rh(1)–P(3) = 2.317 (7), Rh(1)–P(4) = 2.333 (9), Rh(2)–P(1) = 2.174 (8), Rh(2)–P(3) = 2.178 (7), Rh(3)–P(1) = 2.339 (7), Rh(3)–P(2) = 2.351 (9), P(1)–C(6) = 1.84 (3), P(1)–C(1) = 1.79 (3), P(2)–C(1) = 1.84 (3), P(2)–C(6) = 1.83 (3) Å.

B. Metal Aggregates Containing Ligated 1,3-Diphosphacyclobutadienes

Treatment of **28** with [Co(η^5-C$_5$H$_5$)(C$_2$H$_4$)$_2$] gives successively the novel bi- and trimetallic complexes **29** and **30**, which have been characterized mainly by their

28   **29**

30
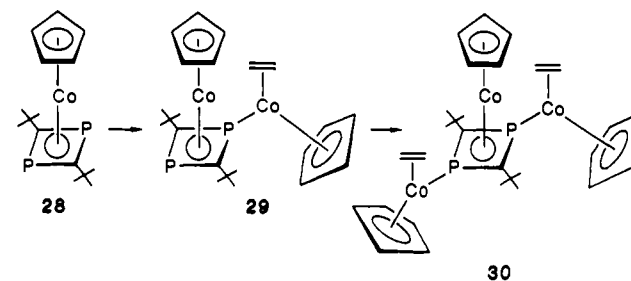
NMR spectra.[43] The method has been exploited by Nixon et al. in the syntheses of the remarkable hexametallic compounds **31** and **32**, the former being fully structurally characterized[47] (Figure 16).
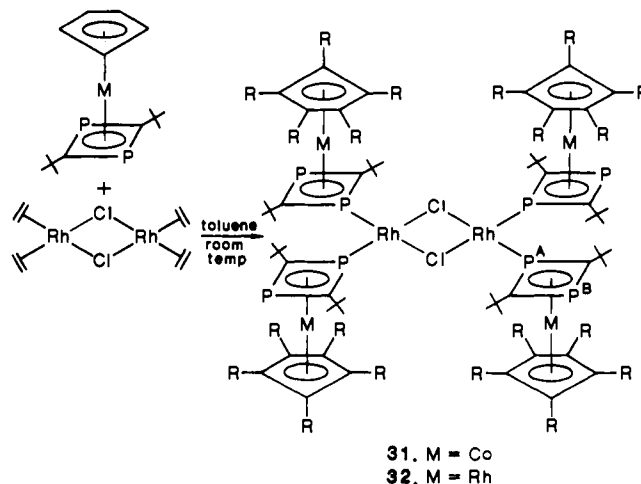
31. M = Co
32. M = Rh

More recently, other bi- and trimetallic compounds typified by **33** and **34** have been obtained.[44]

The 1,3-diphosphacyclobutadiene ring system can behave in an η^3-ligated fashion as evidenced by the recent report of the synthesis of the complex [Mo-
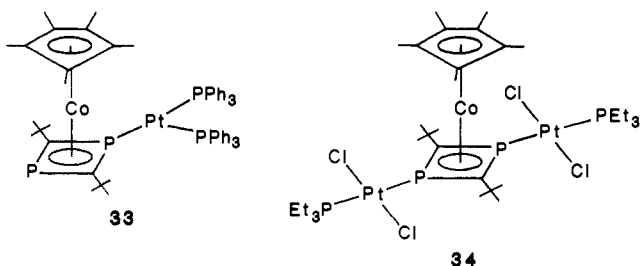
$(CO)_2(\eta^5\text{-}C_9H_7)(Bu^tCP)_2BF_4]$ (35), whose structure is shown in Figure 17.[48] The interesting features of the structure are the involvement of only a CPC fragment of the ring in bonding to molybdenum and the bridging fluorine in the P-F-B unit.

In a recent attempt to synthesize examples of 2-metalla-1,4-diphosphacyclopentadiene complexes of type 36, which are analogues of intermediates involved
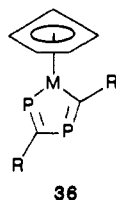
in numerous reported η^4-cyclobutadiene–metal complexes, Binger et al. treated $Bu^tC\equiv P$ with $[Zr(\eta^5\text{-}C_5H_5)_2]$ generated in situ.[49] However, the resulting compound was shown to be the unusual bis(η^5-cyclopentadienyl)(1,3-diphosphabicyclo[1.1.0]butane-2,4-diyl)zirconium compound 37.
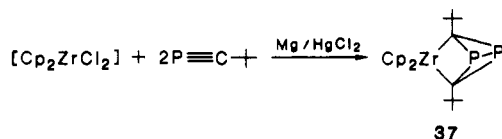
The single-crystal X-ray structural determination on 37 shown in Figure 18 indicates that the phosphaalkyne has undergone dimerization to form the folded bicyclic ring system bonded to the metal by two Zr–C bonds.

The ease of conversion of phosphaalkynes into ligated ring systems containing two or more phosphorus atoms is evidenced by the recent report of Zenneck and co-workers[50] in which reactive organometallic iron compounds form mixtures of complexes containing phosphorus heterocycles. The cleavage of the P≡C triple bond in these systems is noteworthy. (See also section IIIC.)
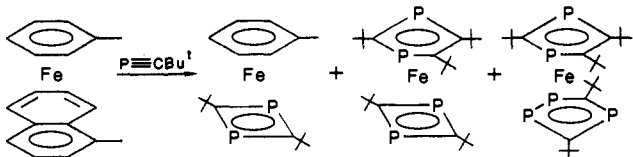
C. Tri-, Penta-, and Hexaphosphorus Analogues of Ferrocene

Becker et al.[51,52] reported the synthesis of the triphosphacyclopentadienyl anion $(C_2R_2P_3)^-$ (R = Bu^t) from the reaction of Bu^tCP and $Li[P(SiMe_3)_2]$. The

$$Bu^tCP \xrightarrow[\text{dme}]{\text{Li[P(SiMe}_3)_2]} [Li(dme)_3][C_2R_2P_3]$$
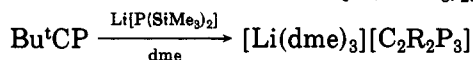
crystalline $[Li(dme)_3][C_2R_2P_3]$ (dme = 1,2-dimethoxyethane) has been fully characterized by ^{31}P NMR
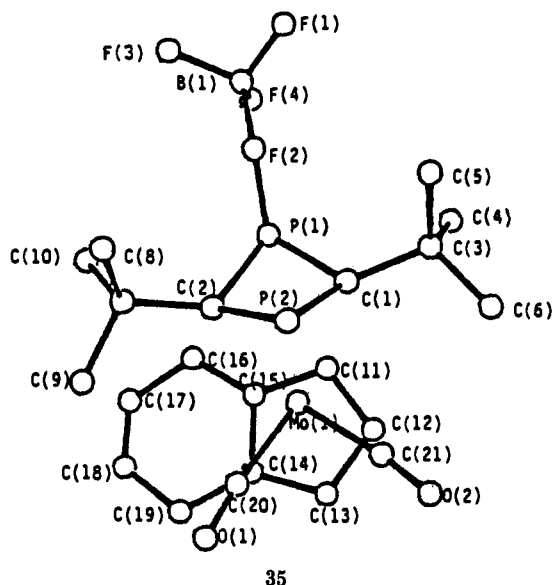
Figure 17. Molecular structure of 35. See Table 2 for bond lengths.
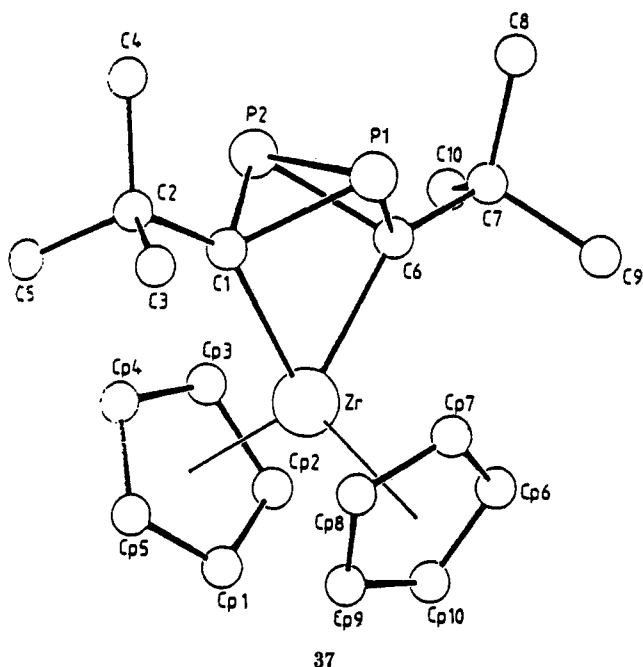
Figure 18. Crystal structure of 37. Important bond lengths (Å): Zr–C1 = 2.213 (3), Zr–C6 = 2.210 (3), C1–P1 = 1.900 (3), C1–P2 = 1.891 (3), C6–P1 = 1.912 (3), C6–P2 = 1.886 (3), P1–P2 = 2.147 (1).

TABLE 2. Selected Bond Lengths for 35

bond	length, Å	bond	length, Å
Mo(1)–P(2)	2.450 (2)	Mo(1)–C(1)	2.308 (7)
Mo(1)–C(2)	2.320 (6)		
P(1)–F(2)	1.536 (5)	P(1)–C(1)	1.739 (9)
P(1)–C(2)	1.766 (6)	P(2)–C(1)	1.823 (8)
P(2)–C(2)	1.824 (8)		

spectroscopy and an unpublished single-crystal X-ray study. Subsequent studies (vide infra) suggest that a second anion $[C_3R_3P_2]^-$ is also present in this reaction mixture.

Bartsch, Hitchcock, and Nixon reported the synthesis and structural characterization of penta- and hexaphosphorus analogues of ferrocene by treatment of the lithium salts of the $[C_2R_2P_3]^-$ and $[C_3R_3P_2]^-$ anions with $FeCl_2$ in monoglyme.[53]
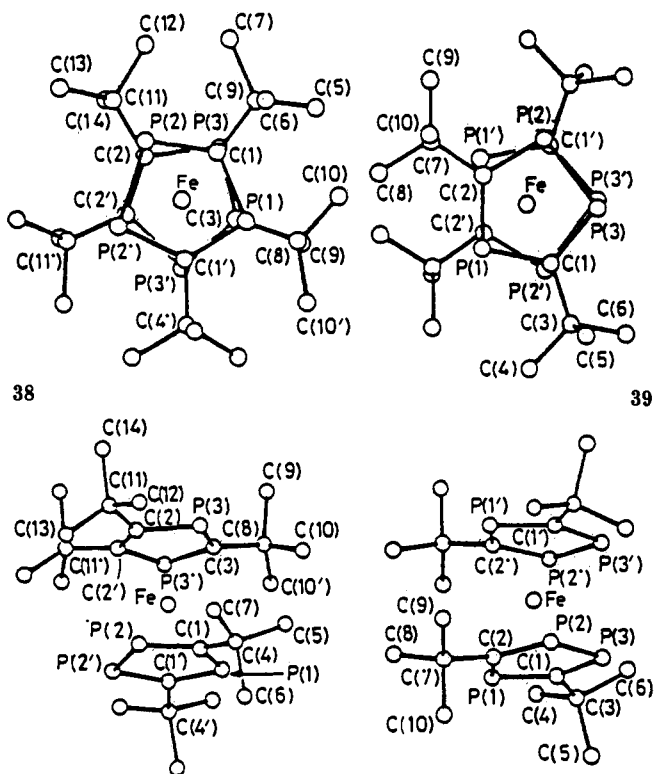
Figure 19. Two views of the molecular structures.
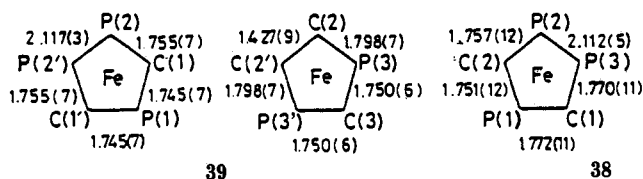
Figure 20. Bond lengths in **39** and **38** (Å). Bond lengths to iron in **39**: from P(1), 2.330 (3); P(2), 2.360 (2); P(3), 2.316 (2); C(1), 2.208 (7); C(2), 2.192 (7); C(3), 2.242 (9). Bond lengths to iron in **38**: from P(1), 2.330 (3); P(2), 2.358 (3); P(3), 2.359 (3); C(1), 2.197 (11); C(2), 2.222 (12).

The remarkable green, air-stable, sublimable complexes [Fe(η^5-C$_2$R$_2$P$_3$)$_2$] (**38**) and [Fe(η^5-C$_2$R$_2$P$_3$)(η^5-C$_3$R$_3$P$_2$)] (**39**) (R = Bu^t) have been fully structurally characterized by single-crystal X-ray diffraction studies. The sandwich structures are shown in Figure 19, and relevant bond length data are provided in Figure 20. Analogous adamantyl compounds have also been prepared. In both **38** and **39** the two η^5-bonded rings are eclipsed, and the disposition of the rings clearly minimizes inter-ring interaction of the Bu^t groups. Interestingly, in **38** the phosphorus atoms in the two rings that face each other (P(3), P(3′)) show a large coupling constant (53 Hz) in the ^{31}P NMR spectrum.

More recently, sandwich compounds containing both η^5-C$_5$H$_5$ and η^5-(C$_2$R$_2$P$_3$) or η^5-(C$_3$R$_3$P$_2$) ring systems have been obtained (**40** and **41**).[54] The former complex

interacts with [W(CO)$_5$(THF)] to give **42**, in which the

42
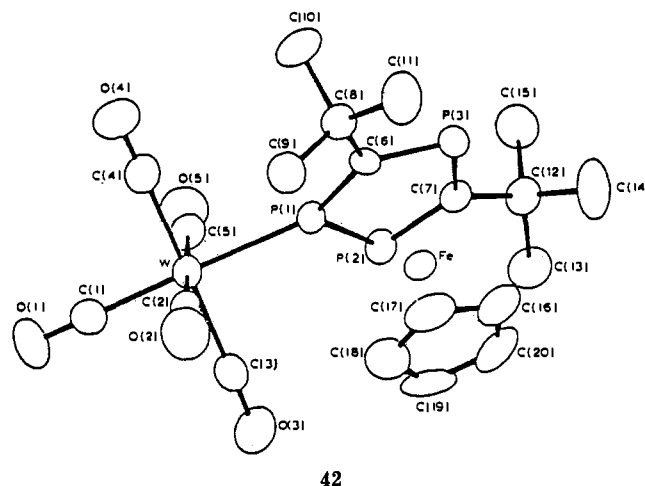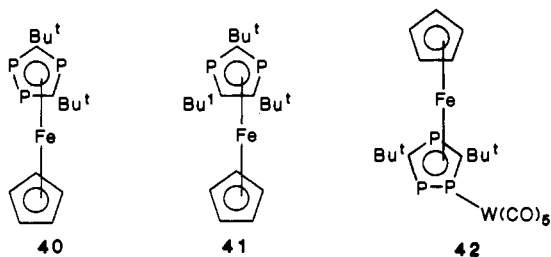
Figure 21. Molecular structure of [Fe(η^5-C$_5$H$_5$)(η^5-C$_2$R$_2$P$_3$)W-(CO)$_5$] (**42**). Selected bond lengths (Å): W–P = 2.510 (2), P-(1)–P(2) = 2.098 (2), P(1)–C(6) = 1.753 (7), P(2)—C(7) = 1.764 (8), P(3)–C(6) = 1.777 (7), P(3)–C(7) = 1.763 (6), Fe–P(1) = 2.299 (2), Fe–P(2) = 2.344 (3), Fe–P(3) = 2.294 (2), Fe–C(6) = 2.141 (4), Fe–C(7) = 2.133 (8).

tungsten is attached to one of the least sterically hindered phosphorus atoms of the η^5-(C$_2$R$_2$P$_3$) ring. The molecular structure is shown in Figure 21.[54] The easy formation of the carbonyl complex [Mn(CO)$_3$(η^5-C$_2$R$_2$P$_3$)] illustrates the ligating potential of this new class of organophosphorus transition-metal compounds.

It is now clear that the series of five-membered organophosphorus ring systems of the type (C$_n$R$_n$P$_{5-n}$) n = 0→5) can be stabilized in suitable sandwich metal complexes as shown below.
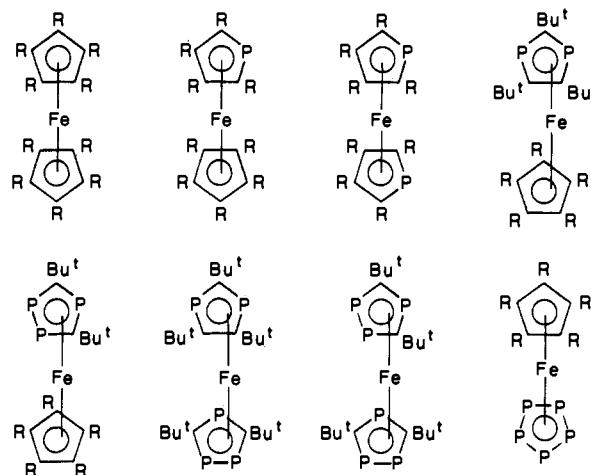
Preliminary electrochemistry, Mössbauer, and photoelectron spectroscopic studies on the above η^5-complexes indicate that the presence of phosphorus atoms in the rings exerts an overall electron-withdrawing effect on the transition-metal atom.[55] Complex **38** can be reversibly oxidized, and a wealth of interesting coordination chemistry can be expected in the future.

The C$_2$R$_2$P$_3$ ring system can also act in an η^1-ligated fashion, and the first examples of this class of compounds are trans-[PtX(PR′$_3$)$_2$(C$_2$R$_2$P$_3$)], **43a** and **43b** (R = Bu^t; a, R′ = Ph, X = I; (b) R′ = Et, X = Cl). The structures shown in Figure 22 reveal that one of the least sterically hindered phosphorus atoms is the donor site.[56]

A feature of interest is the perfectly planar η^1-C$_2$R$_2$P$_3$ ring in both complexes, indicating that the nature of
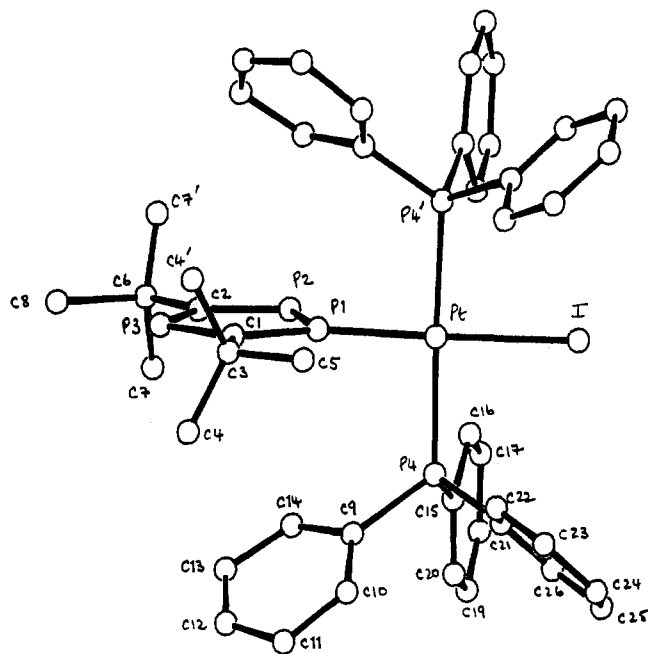
43a

P(1)–P(2) = 2.010 (11) Å
P(2)–C(2) = 1.73 (4) Å
C(2)–P(3) = 1.81 (4) Å
C(1)–P(3) = 1.69 (2) Å
C(1)–P(1) = 1.76 (4) Å
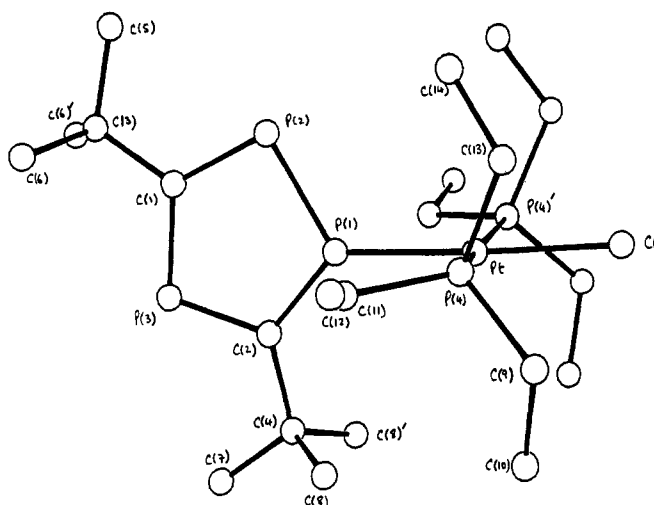
43b

P(1)–P(2) = 2.068 (3) Å
P(1)–C(2) = 1.711 (7) Å
P(2)–C(1) = 1.745 (7) Å
C(1)–P(3) = 1.726 (7) Å
C(2)–P(3) = 1.740 (8) Å

Figure 22. Molecular structures of **43a** and **43b**.

the bond between the ring phosphorus and the metal is of type A rather than B, and this is supported by the

A   B
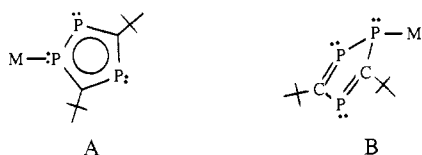
magnitude of $^1J_{PtP}$ in **43b**, which is 2920 Hz. The complexes are also fluxional, the metal undergoing 1,2 shifts between the two adjacent P atoms of the ring.[56]

D. 1,3,5-Triphosphabenzene Metal Complexes

The first reports of metal-promoted cyclo-trimerization of phosphaalkynes to give complexes containing 1,3,5-triphosphabenzene and its valence isomers have appeared recently. Treatment of *tert*-butylphosphalkyne with a source of the [V(C₅Me₅)] fragment results in the formation of the dark brown crystalline complex **44**, whose structure is shown below.[57]
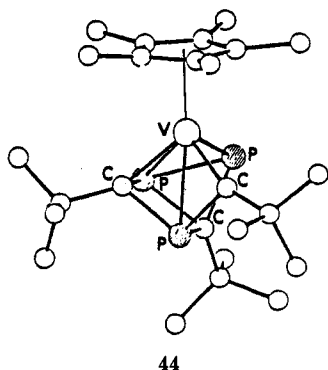
44

The ring system in **44** is derived from a 1,3,5-tri-phosphaprismane, and the complex exhibits dynamic behavior in solution involving a rapid valence isomer-ization between **44a** and **44b**. At room temperature **44**

44a   **44b**
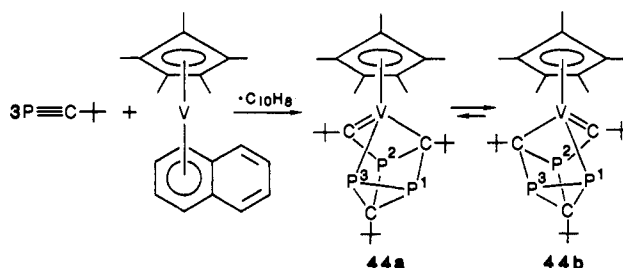
reacts readily with 1 mol of carbon monoxide to give the dark green complex **45**, which contains a ligated 1,3,5-triphospha-dewar benzene which has been fully structurally characterized by a single-crystal X-ray analysis.[57]
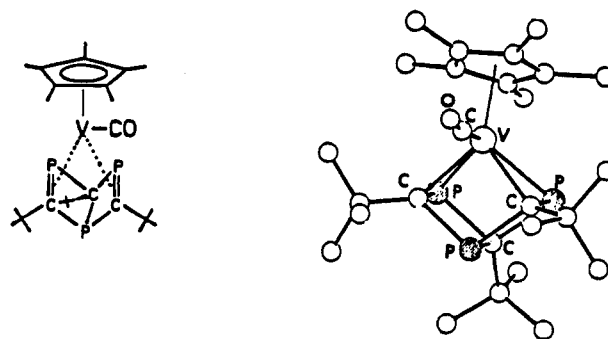
45

Treatment of (cycloheptatriene)molybdenum tri-carbonyl with Bu^{t}C≡P afforded the orange complex **46**, which has been formulated as a 1,3,5-triphosphabenzene

derivative on the basis of spectroscopic data.[58] This formulation may be incorrect (see Appendix).

46
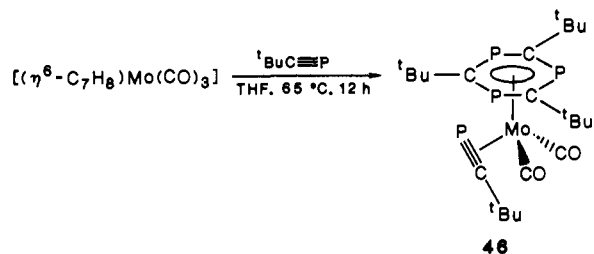
IV. Phosphaalkenes

A. Phosphaalkene Complexes

Ab initio STO/3G calculations and[59-62] limited photoelectron spectroscopic results on phosphaalkenes both indicate that the σ phosphorus lone pair and π-orbitals are very close in energy, with the π-orbital probably as the HOMO in the parent compound $CH_2=PH$ (see, however, ref 61) and with the π^*-orbital as the LUMO. Clearly the quasi-degeneracy of the σ- and π-type orbitals is likely to be affected in substituted phosphaalkenes. Likewise the energy differences between η^1- and η^2-ligating modes in transition-metal phosphaalkene complexes might be expected to be rather small, and in favorable cases $\eta^1 \leftrightarrow \eta^2$ interconversion will be possible (vide infra).

The five types of possible coordination modes for a phosphaalkene are illustrated in A–E, and although examples of all are known, complexes involving the η-coordination mode via the phosphorus lone-pair electrons (A) have been the most extensively reported to date.
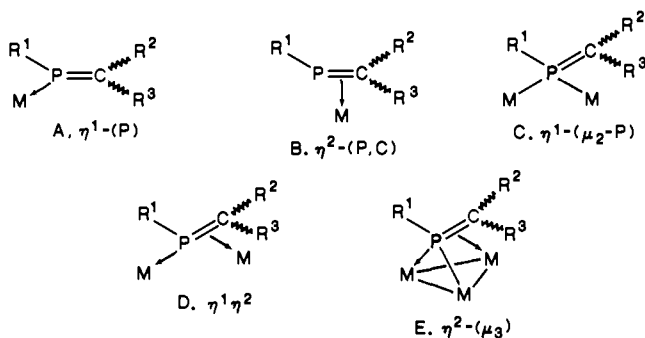
(i) Bonding Type η^1-(P) (Type A)

These were the first types of phosphaalkene complexes to be reported by Kroto and Nixon[63] and Bickelhaupt[64] and their co-workers utilizing the stable all-carbon-substituted phosphaalkene $Ph_2C=P(Mes)$ (Mes = mesityl).

NMR studies on complexes of the type cis-[W-$(CO)_4L_2$], trans-[RhCl(PPh_3)_2L], trans-[RhCl(CO)L_2], [Rh(η^5-C_9H_7)L_2], cis-[PtX_2L_2] (X = Cl, I, Me), and cis- and trans-[PtCl_2(PEt_3)L] (L = $Ph_2C=P(Mes)$) made by ligand displacement or bridge cleavage reactions provided strong evidence for the η^1-type of bonding in these phosphaalkene complexes since the magnitude of the coupling constants $^1J_{PM}$ (M = ^{183}W, ^{103}Rh, ^{195}Pt) in all these systems was comparable with those of analogous typical phosphine metal complexes.[63,65] Confirmation of the structural type was obtained for [cis-$PtCl_2(Ph_2C=P(Mes))(PEt_3)$] (**47**) and [Cr(CO)_5-
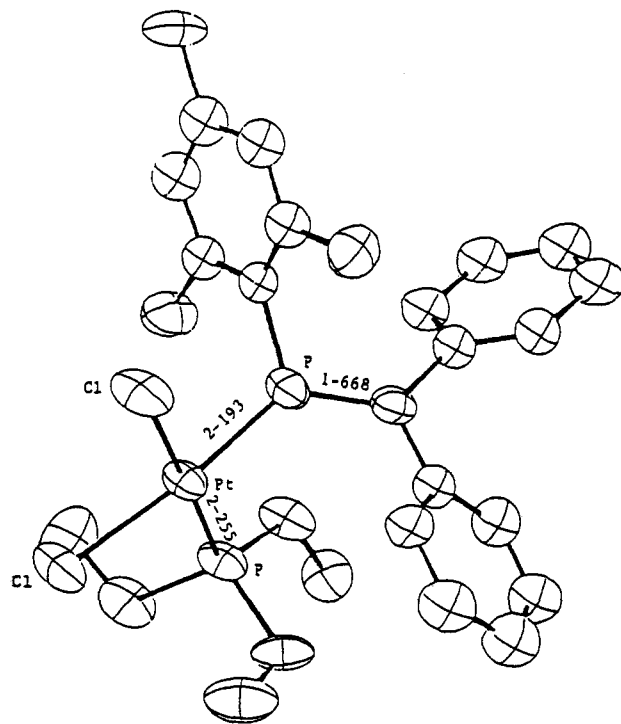
47

Figure 23. Structure of cis-$PtCl_2(PEt_3)(P(mes)=CPh_2)$ (**47**). (Bond lengths in Å.)
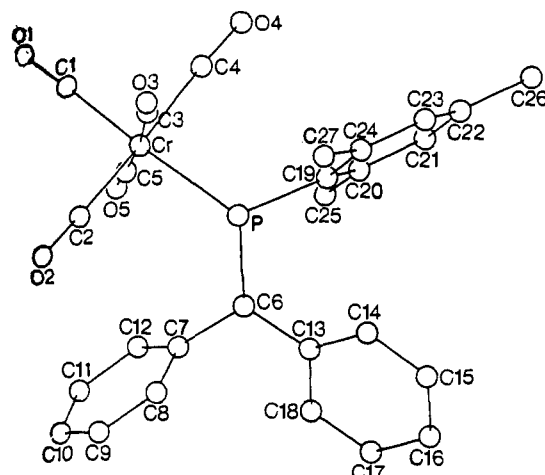
48

Figure 24. Structure of [Cr(CO)_5(Ph_2C=P(mes))] (**48**). See Table 3 for bond lengths and angles.

TABLE 3. Selected Bond Lengths and Bond Angles for 48

| bond lengths (Å)		bond angles (deg)	
P–Cr	2.356 (1)	CrPC(6)	130.8 (2)
P–C(6)	1.679 (4)	CrPC(19)	118.8 (2)
P–C(19)	1.822 (5)	C(6)PC(19)	109.8 (2)
Cr–C(1)	1.874 (5)	PCrC(1)	175.5 (2)
Cr–C(2)	1.893 (7)	PCrC(2)	93.5 (2)
Cr–C(3)	1.895 (6)	PCrC(3)	94.6 (2)
Cr–C(4)	1.896 (7)	PCrC(4)	86.9 (2)
Cr–C(5)	1.891 (4)	PCrC(5)	89.3 (1)

$(Ph_2C=P(Mes))$] (**48**) by single-crystal X-ray diffraction studies,[64-66] and the molecular structures are shown in Figures 23 and 24. In both complexes the phosphaalkene moiety is nearly planar and the P=C bond length is typically short and little different from that of free phosphaalkene.
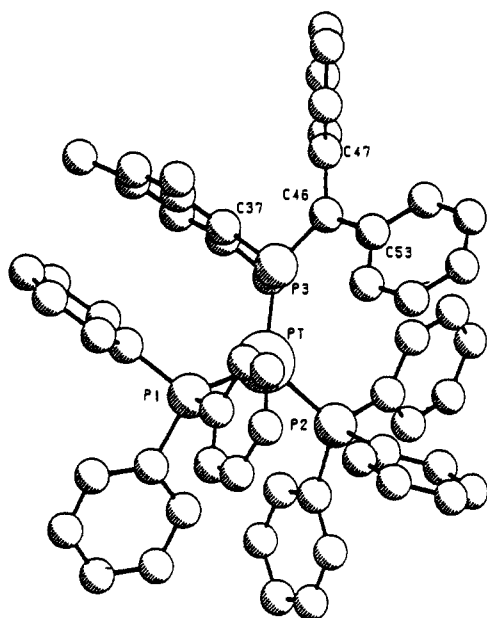
Figure 25. Structure of (mesityl(diphenylmethylene)phosphine)bis(triphenylphosphine)platinum(0) (54). Relevant bond distances (Å): Pt-P1, 2.288 (3); Pt-P2, 2.294 (3); Pt-P3, 2.218 (3); P3-C46, 1.65 (1); P3-C37, 1.982 (1); C46-C47, 1.56 (2); C46-C53, 1.51 (2); P1-C1, 1.87 (1); P1-C7, 1.83 (1); P1-C13, 1.85 (1); P2-C19, 1.82 (1); P2-C25, 1.82 (1); P2-C31, 1.80 (1). Relevant bond angles (deg): P1-Pt-P3, 120.6 (1); P2-Pt-P1, 121.9 (1); P2-Pt-P3, 117.3 (1); Pt-P3-C46, 133.3 (5); Pt-P3-C37, 118.2 (3); C46-P3-C37, 108.5 (5); C53-C46-P3, 122.6 (8); C53-C46-C47, 133.3 (8); C47-C46-P3, 124.0 (8).

Complex 48 is best made from [Cr(CO)$_5$THF] as is its W analogue. The latter, however, has also been obtained in low yield by dehydrochlorination of [W-(CO)$_5$(PCl(Mes)CHPh$_2$)] with DBU.[67]

The E isomer of benzylidene-P-(2,4,6-tri-$tert$-butylphenyl)phosphine (49) reacts with [Cr(CO)$_5$THF] at room temperature to give the η^1-complex 50 with retention of configuration,[68] whereas UV irradiation in the presence of [Cr(CO)$_6$] gives the Z isomer (51); viz.
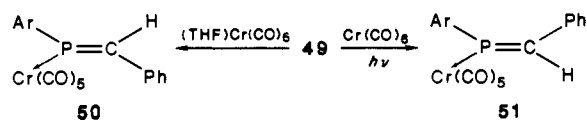
Recently, Niecke et al.[69] obtained NMR spectroscopic evidence for the silver(I) phosphaalkene complexes below, which were obtained by treatment of AgSO$_3$CF$_3$ with Me$_5$C$_5$P=C(SiMe$_3$)$_2$ at low temperature.
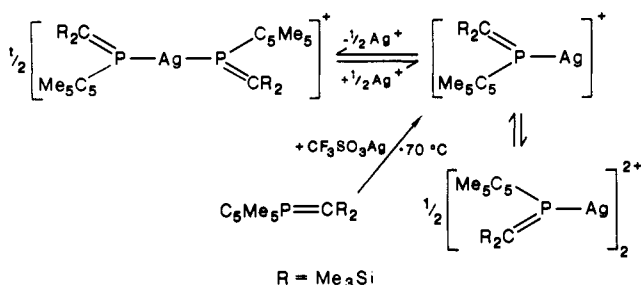
R = Me$_3$Si

The η^1-bonding mode is established by the characteristically large value of the ^{107}Ag-^{31}P and ^{109}Ag-^{31}P coupling constants, which lie in the range 418–912 Hz.

Pt(0) complexes of phosphaalkenes can be η^1- or η^2-ligated, depending on the other ligands present.

TABLE 4. Some Bond Lengths and Bond Angles for 56

A. Bond Lengths (Å)			
Rh-Cl(1)	2.364 (1)	Rh-P(1)	2.136 (1)
Rh-P(2)	2.310 (1)	Rh-P(3)	2.315 (1)
Cl(2)-P(1)	2.086 (2)	P(1)-C(1)	1.644 (5)
P(2)-C(8)	1.829 (5)	P(2)-C(1)	1.831 (4)

| B. Bond Angles (Deg)			
Cl(1)-Rh-P(1)	178.19 (5)	Cl(1)-Rh-P(2)	85.13 (4)
Cl(1)-Rh-P(3)	87.15 (4)	P(1)-Rh-P(2)	93.34 (4)
P(1)-Rh-P(3)	94.24 (4)	P(2)-Rh-P(3)	169.30 (4)
Rh-P(1)-Cl(2)	109.97 (7)	Rh-P(1)-C(1)	142.6 (2)
Cl(2)-P(1)-C(1)	107.4 (2)	Rh-P(2)-C(8)	107.5 (1)

Treatment of [Pt(COD)$_2$] (COD = 1,5-cyclooctadiene) with P(Mes)=CPh$_2$ gave the η^1-complex 52; likewise when a 2:1 mixture of P(Mes)=CPh$_2$ and Bu^{t}C≡P reacted with [Pt(COD)$_2$], the resulting complex 53 has η^1-ligated phosphaalkene ligands and an η^2-ligated phosphaalkyne.[70]
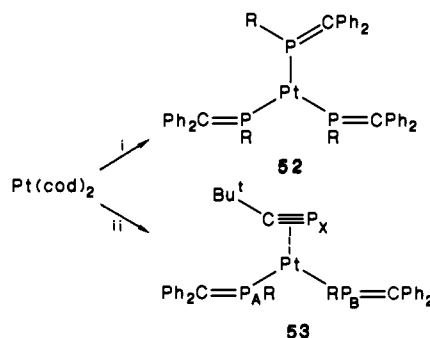
A particularly interesting example is [Pt(PPh$_3$)$_2$P-(Mes)=CPh$_2$)] (54, Figure 25), which is η^1 in the solid state as evidenced by a single-crystal X-ray structural determination but η^2 in solution (vide infra).[71] The system has been examined by NMR spectroscopy both in the solid state and in solution, and the equilibrium[72,73] has been established. When [Pt(PPh$_3$)$_2$] in 54
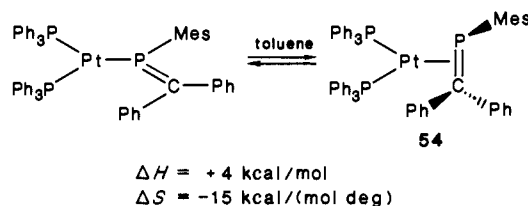
ΔH = + 4 kcal/mol
ΔS = –15 kcal/(mol deg)

is replaced by the sterically much more demanding [Pt(PCy$_3$)$_2$] group, the exclusive occurrence of η^1-coordination is observed in 55 (Xyl = 2,6-dimethylphenyl).[72,74] The influence of the other ligands is also
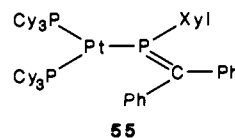
apparent in the nickel complexes [Ni(bpy)((Xyl)P=CPh$_2$)] and [Ni(CO)$_n$((Xyl)P=CPh$_2$)$_m$] (n = 3, 2, m = 1, 2) where the former contains an η^2-ligated phosphaalkene and the latter η^1-phosphaalkenes (vide infra).[74,75]

The first crystallographically proved example of an η^1-ligated chlorophosphaalkene complex is $trans$-[RhCl(PPh$_3$)$_2$(PCl=C(SiMe$_3$)$_2$)] (56, Figure 26). The P=C bond length in 56 (1.644 (5) Å) is, as expected, shorter than that found in the η^2-complex 64 (1.714 (2) Å (av)[76] (vide infra).

56
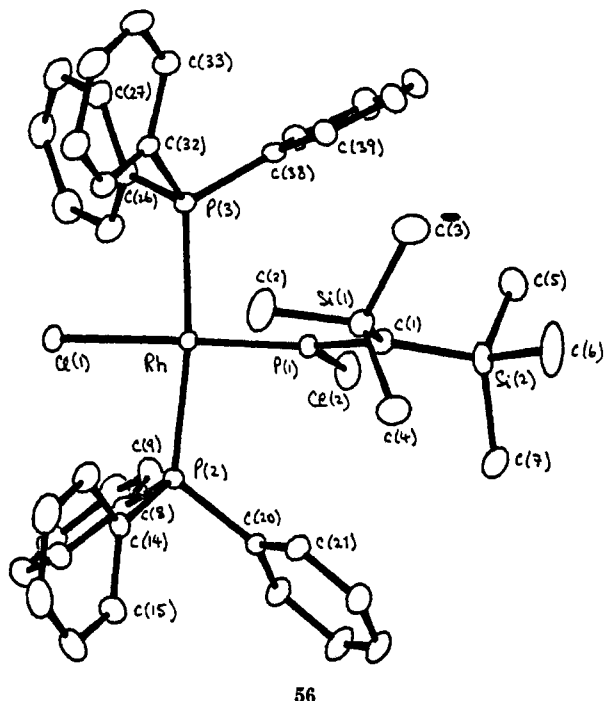
Figure 26. Molecular structure of trans-[RhCl(PPh₃)₂(PCl=C-(SiMe₃)₂)] (56). See Table 4 for bond distances and angles.

57
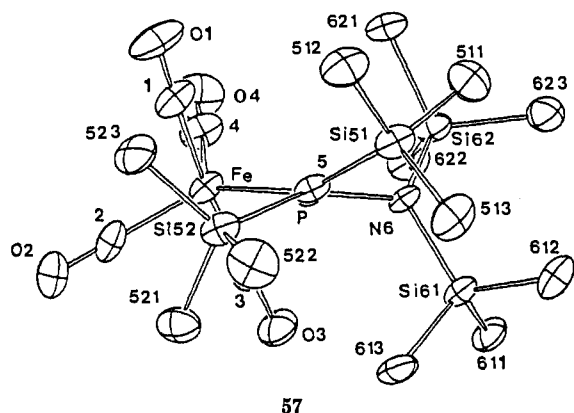
Figure 27. ORTEP drawing of 57 viewed down the C(5)=P bond. Thermal ellipsoids are drawn at the 35% probability level. Selected bond lengths (Å) and angles (deg): P–Fe = 2.208 (2), Fe–C(1) = 1.795 (4), Fe–C(2) = 1.794 (2), Fe–C(3) = 1.787 (4), Fe–C(4) = 1.768 (7), P=C = 1.657 (5), P–N = 1.681 (4), N–Si = 1.788 (4), 1.790 (4), C(5)–Si = 1.884 (7), 1.890 (6); Fe–P–C(5) = 128.0 (2), Fe–P–N = 116.8 (2), N–P–C(5) = 115.2 (8), P–C(5)–Si(51) = 135.0 (7), P–C(5)–Si(52) = 118.7 (3).

In the η¹-phosphaalkene complex [Fe(CO)₄-(Me₃Si)₂C=PN(SiMe₃)₂] (57, Figure 27) the phosphaalkene ligand is coordinated at an equatorial site in a slightly distorted trigonal-bipyramid structure, in contrast to most simple phosphine iron tetracarbonyl complexes.[77] A significant feature of the structure is the severe twist (ca. 30°) of the P=C bond. The corresponding complex of the (Me₃Si)CH=PN(SiMe₃)₂ ligand, on the other hand, appears to involve axial coordination[78,79] and has been established[80] in the η¹-complex [Fe(CO)₄RP=CPh(SiMe₃)] (R = 2,4,6-tri-tert-butylphenyl).

An interesting phosphinidene–carbene coupling reaction to generate an η¹-phosphaalkene complex has been described recently.[81] The reaction of the carbene complex [W(CO)₅C(OEt)Ph] with the transient phosphinidene complex [W(CO)₅PPh] gives the phosphaalkene complex [W(CO)₅(PPh=C(OEt)Ph] (58).
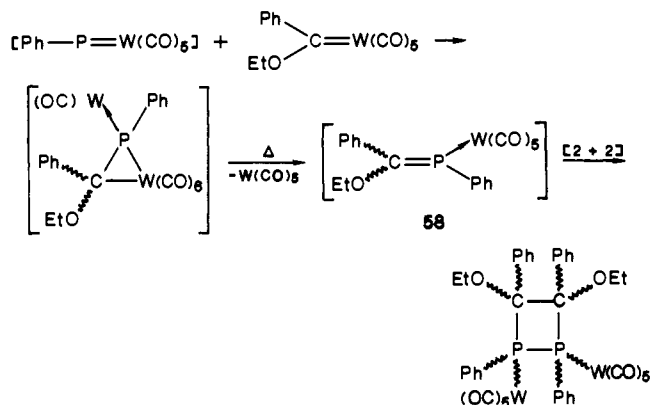

58

Although this compound spontaneously dimerizes to form the corresponding 1,2-diphosphetane complex, the reaction is reversible on heating, and the phosphaalkene complex can be trapped as [4 + 2] cycloadducts with either 2,3-dimethylbutadiene or cyclopentadiene.

The η¹-phosphaalkene complex [Cr(CO)₅(CF₃P=CF₂)] reported recently by Grobe and co-workers undergoes at least three types of reaction at room temperature: (a) rearrangement to the η²-derivative, (b) dimerization to the 1,3-diphosphetane complex, and (c) formation of a binuclear compound in which the CF₃-P=CF₂ unit acts as a 4e (σ + π) bridging ligand. A related complex containing CF₃P=CFNMe₂ has also been briefly described.[82]

First reports of phosphaalkene complexes of main-group compounds have only appeared in the literature recently. Treatment of BuᵗP=CHBuᵗ with BCl₃, AlCl₃, or GaCl₃ leads to the formation of 1:1 adducts.[83]

A = B. Al, Ga
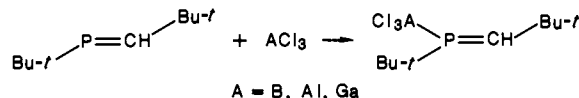
The boron compound is stable in solution only below −10 °C; however, the structure of the GaCl₃ adduct has been determined and is shown below (59). The expected coordination via phosphorus is confirmed, and the P=C bond (1.651 (3) Å) lies in the expected range for phosphaalkenes coordinated via the phosphorus lone-pair electrons.

59
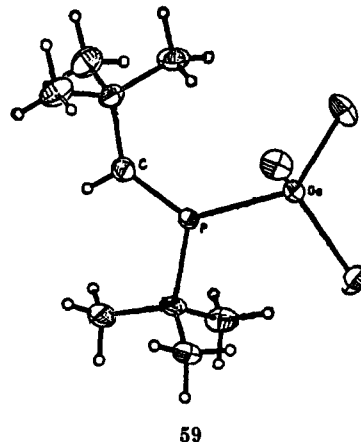
(ii) Bonding Type η²(P,C) (Type B)

As mentioned earlier, the first example of this type of complex was [Pt(PPh₃)₂((Mes)P=CPh₂)] *in solution*, where the characteristically low value of $^1J_{PtP(alkene)}$ (505 Hz) was diagnostic of the side-bonded phosphaalkene.

TABLE 5. Selected Bond Distances (Å) and Bond Angles (Deg) of 60

Bond Distances

Pt(1)–C(37)	2.141 (3)
Pt(1)–P(1)	2.3175 (9)
Pt(1)–P(2)	2.3017 (8)
Pt(1)–P(3)	2.3557 (10)
C(37)–P(3)	1.814 (4)

Bond Angles

C(37)–Pt(1)–P(1)	100.51 (14)
C(37)–Pt(1)–P(2)	160.54 (12)
C(37)–Pt(1)–P(3)	47.28 (14)
P(1)–Pt(1)–P(2)	98.92 (5)
P(1)–Pt(1)–P(3)	146.67 (4)
P(2)–Pt(1)–P(3)	113.36 (5)
Pt(1)–C(37)–C(38)	114.4 (3)
Pt(1)–C(37)–C(49)	117.8 (3)
Pt(1)–C(37)–P(3)	72.58 (20)

TABLE 6. P–C Bond Lengths in η^1- and η^2-Ligated Phosphaalkenes

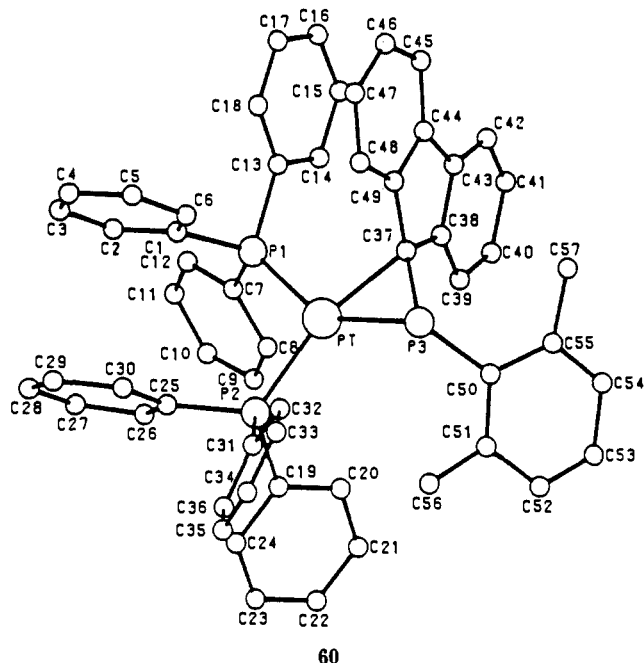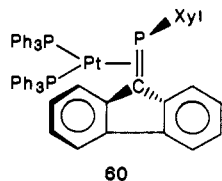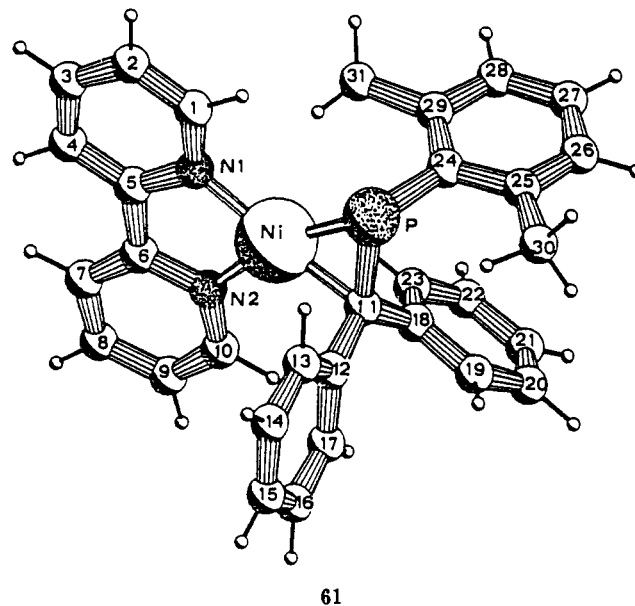|	d(P–C), Å
MesP=CPh$_2$	1.692 (3)
[Pt(PPh$_3$)$_2$(η^1-MesP=CPh$_2$)]	1.65 (1)
[Cr(CO)$_5$(η^1-MesP=CPh$_2$)]	1.679 (4)
[Pt(PPh$_3$)$_2$(η^1-C$_{12}$H$_8$C=PXyl)]	1.814 (4)
[Ni(bpy)(η^2-XylP=CPh$_2$)]	1.832 (6)
[Ni(PMe$_3$)$_2$[η^2-(Me$_3$Si)$_2$CHP=C(SiMe$_3$)$_2$]	1.773 (8)
[Ni(CO)(η^2-PCl=C(SiMe$_3$)$_2$)$_2$]	1.715 (6)
[Fe(CO)$_4$(η^1-RP=CPh(SiMe$_3$))$_4$]	1.670 (4)
[Fe(CO)$_4$(η^1-(Me$_3$Si)$_2$NP=C(SiMe$_3$))$_2$]	1.657 (5)
[RhCl(PPh$_3$)$_2$(η^1-PCl=C(SiMe$_3$)$_2$)]	1.644 (5)
[Ni(CO)(η^2-Ph$_2$PP=CPh(SiMe$_3$))]$_2$	1.766 (8)

61

Figure 29. PLUTO III drawing of (bpy)Ni(XylP=CPh$_2$) (61), including the adopted numbering scheme. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): NiP = 2.177 (2), NiC(11) = 1.987 (6), NiN(1) = 1.940 (5), NiN(2) = 1.951 (5), PC(11) = 1.832 (6), PC(24) = 1.845 (6), C(11)C(12) = 1.488 (8), C(11)C(18) = 1.491 (8); PNiC(11) = 52.0 (2), N(1)NiN(2) = 83.2 (2), NiPC(11) = 58.7 (2), NiC(11)P = 69.4 (2), C(11)PC(24) = 102.6 (3), NiPC(24) = 112.6 (2), PC(11)C(12) = 116.4 (4), PC(11)C(18) = 118.7 (4), C(12)C(11)C(18) = 118.7 (5); NiC(11)PC(24) = 108.9 (2), NiPC(11)C(18) = 113.7 (5), NiPC(11)C(12) = 94.3 (4).

60

Figure 28. PLUTO drawing and numbering scheme of [Pt^0-(PPh$_3$)$_2$(C$_{12}$H$_8$C=PC$_6$H$_3$Me$_2$-o,o')] (60). See Table 5 for bond distances and angles.

η^2-Ligation can be favored by both electronic or steric effects; thus a complete change from the η^1- to the η^2-coordination mode has been achieved by coordinating [Pt(PPh$_3$)$_2$] to (2,6-dimethylphenyl)(9-fluoren-ylidene)phosphine as in 60 (Figure 28).

60

In this complex the two C-aryl rings are forced into one plane, with the P=C bond making it much more accessible for η^2-ligation, and an X-ray structure determination and multinuclear NMR studies reveal that the η^2-P=C coordination exists *both* in the solid state and in solution. It is interesting to note that the P–C bond is substantially lengthened by the η^2-coordination (from ca. 1.69 to 1.83 Å) (see Table 6) whereas in η^1-complexes the P=C bond is comparable (very slightly shorter) with that of the free phosphaalkene (e.g., 1.65 (1) Å in

[Pt(PPh$_3$)$_2$((Mes)P=CPh$_2$)], 1.660 (9) Å in *cis*-[PtCl$_2$-(PEt$_3$)((Mes)P=CPh$_2$)], and 1.679 (4) Å in [Cr(CO)$_5$-((Mes)P=CPh$_2$)].

A theoretical analysis by Hartree–Fock–Slater (LCAO-Xα) calculations on the model compound [Pt(PH$_3$)$_2$(PH=CH$_2$)] agrees with the experimental results and shows that the η^2-coordination mode corresponds to the Dewar–Chatt–Duncansen model for alkene–transition-metal systems and is energetically favored over η^1-coordination due to the stronger d→π* back-donation even though σ-donation is weaker. However, it is important to note that the differences are not large and may be overruled by nonbonded interactions when larger ligands are involved.[84]

In the nickel complex [Ni(bpy)(η^2-(Xyl)P=CPh$_2$)] (61) the weaker π-accepting bipyridyl ligand enhances the η^2-ligation mode of the phosphaalkene compared with the η^1-behavior in the analogous complexes containing stronger π-accepting CO ligands;[75] (see Figure 29).

The η^2-ligated phosphaalkene nickel complex [Ni-(PMe$_3$)$_2$(Me$_3$Si)$_2$(CPC(H)SiMe$_3$)] (62), which was the first to be structurally characterized, was formed

unexpectedly by treatment of $[NiCl_2(PMe_3)_2]$ with $NaP[(Me_3Si)_2CH]_2$.[85] Other examples made directly from the phosphaalkene include $[Pt(triphos)((Mes)-P=CPh_2)]$ (63), where the η^2-ligation of the phosphaalkene forces the triphos ligand to act as a bidentate rather than a tridentate ligand.[19]
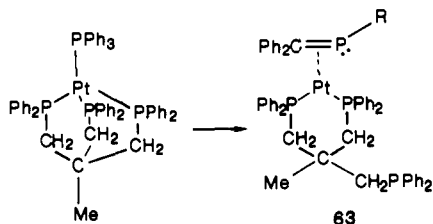
Werner and co-workers have obtained the phosphaalkene complex $[Rh(\eta^5-C_5Me_5)CO(PPh=CH_2)]$ by the route shown below.[86]

The complex is formulated as involving η^2-type bonding; however, the reported $^1J_{RhP}$ coupling constant (172.7 Hz) is more typical of that expected for an η^1-complex.

Functionalized phosphaalkenes, e.g., the chloro derivative $R_2C=PCl$, also can act in either an η^1- or η^2-fashion toward metal centers. Mathey et al.[87] report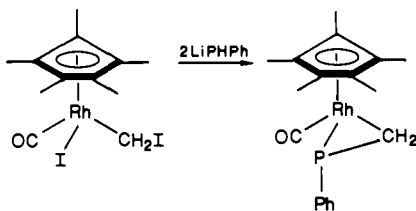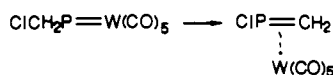ed spectroscopic evidence for the first example of an η^2-chlorophosphaalkene complex via the rearrangement of a transient phosphinidene compound $[ClCH_2P=W(CO)_5]$, viz.

$$ClCH_2P=W(CO)_5 \longrightarrow \underset{\underset{W(CO)_5}{|}}{ClP=CH_2}$$

Subsequently, Appel et al. obtained $[Ni(CO)\{PCl=C(SiMe_3)_2\}_2]$ (64, Figure 30), in which both chlorophosphaalkene ligands are η^2-ligated to the metal.[88] Other η^2-halogenophosphaalkene complexes include $[Pt(PPh_3)_2(PCl=C(SiMe_3)_2)]$ and $[Pt(PPh_3)_2(PF=C(SiMe_3)_2)]$.[89]

Interesting examples of $(\eta^2$-phosphaalkene)nickel complexes have been obtained from the unstable $(\eta^1$-(diphenylphosphino)phosphaalkene)nickel tricarbonyl precursors, which readily dimerize at room temperature to cyclic complexes whose structure has been established (for R = Me_3Si) by X-ray diffraction studies.[88]
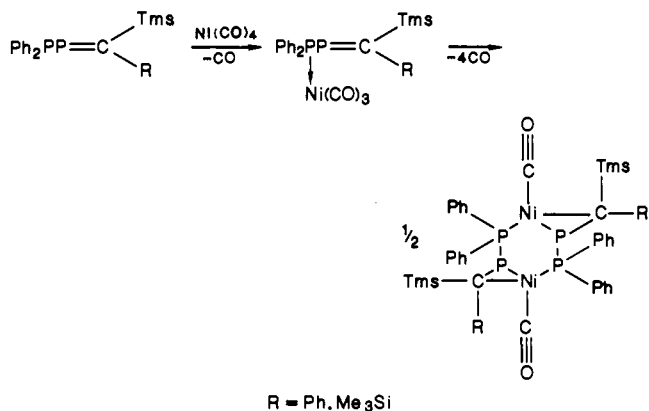
R = Ph, Me₃Si
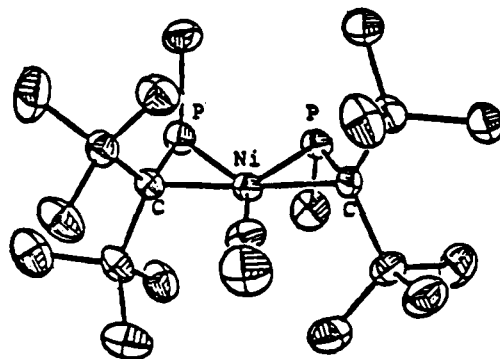
64

Figure 30. Structure of 64. Important distances (Å) and angles (deg): P(1)C(1) = 1.716 (6), P(1)Ni = 2.297 (2), C(1)Ni = 2.064 (6), P(2)C(2) = 1.713 (6), P(2)Ni = 2.281 (2), C(2)Ni = 2.054 (6), CNi = 1.770 (7), OC = 1.139 (9), C1P(1) = 2.104 (2), C1P(2) = 2.111 (2); P(1)C(1)Ni = 74.2 (2), C(1)NiP(1) = 46.0 (2), NiP(1)C(1) = 59.8 (2), P(2)NiC(2) = 46.2 (2), P(2)C(2)Ni = 73.9 (2), C(2)P(2)Ni = 59.9 (2), CNiP(1) = 141.9 (2), C(1)NiC(2) = 170.8 (2), P(2)NiC = 139.2 (2), C1P(1)Ni = 102.4 (1)8 C1P(1)C(1) = 107.8 (2), C1P(2)Ni = 101.6 (1), C1P(2)C(2) = 107.8 (2).

(iii) Bonding Type η^1-(μ_2-P) (Type C)

Coordination mode type C has been established by Mathey et al.[90] only in the 2H-phosphole complex 65 obtained in the reaction sequence shown below.

65
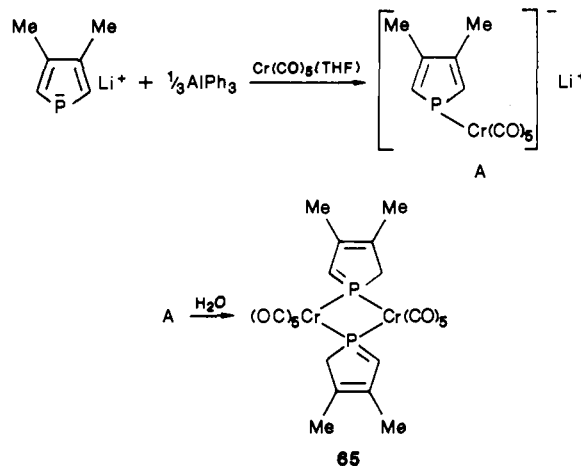
(iv) Bonding Type $\eta^1 \eta^2$ (Type D)

The same authors also described the first example of type D coordination in complex 66 synthesized by the following route.[90]

66
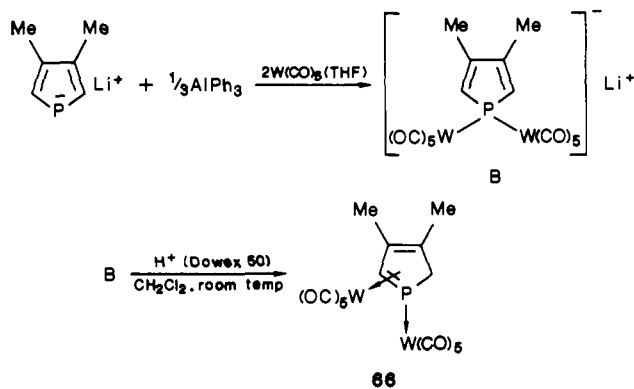
Confirmation of the $\eta^1 \eta^2$-type bonding comes from a single-crystal X-ray diffraction study (Figure 31), where the P–C bond length lies between that of a single bond (1.85 Å) and a double bond (1.67 Å).
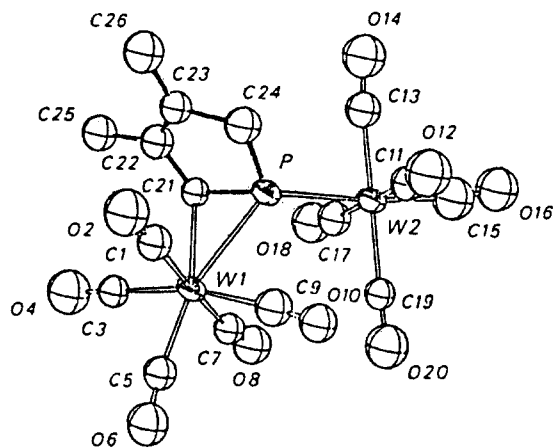
66

Figure 31. Structure of complex **66**. The heavy-atom ellipsoids are scaled to enclose 50% of the electron density; hydrogen atoms are omitted. Principal bond distances (Å): W_1-C_{21}, 246 (1); W_1-P, 2.607 (4); $P-C_{21}$, 1.78 (1); $P-C_{24}$, 1.81 (2); $C_{21}-C_{22}$, 1.49 (2); $C_{22}-C_{23}$, 1.21 (2); $C_{23}-C_{24}$, 1.54 (2); $P-W_2$, 2.490 (4). Selected bond angles (deg): W_1-P-W_2, 125.3 (1); W_1-P-C_{21}, 65.2 (4); $W_1-C_{21}-P$, 73.8 (5); $C_{21}-P-C_{24}$, 93.2 (8); $P-C_{21}-C_{22}$, 105 (1); $C_{21}-C_{22}-C_{23}$, 121 (2); $C_{22}-C_{23}-C_{24}$, 113 (1); $P-C_{24}-C_{23}$, 106 (1); W_2-P-C_{21}, 128.3 (5); W_2-P-C_{24}, 108.6 (6).
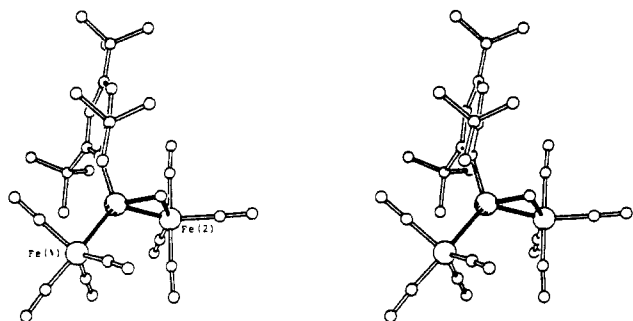
67

Figure 32. Structure of **67**. Bond lengths (Å): $P=C$ = 1.737 (6), $Fe(1)P$ = 2.305 (2), $Fe(2)P$ = 2.357 (2), $PC(1)-Ar$ = 1.861 (5), $Fe(2)CH_2$ = 2.081 (7). Bond angles (deg): $Fe(1)P=C$ = 120.4 (2), $PFe(2)=Cl$ = 45.6 (2), $P=CFe(2)$ = 75.6 (2), $Fe(2)P=C$ = 58.8 (3), $Fe(1)PFe(2)$ = 120.3 (1), $Fe(1)PC(1)-Ar$ = 125.3 (2), $C(1)Ar-P=C$ = 102.5 (3), $C_{ax}(Fe(2)C_{ax}$ = 179.8 (6), $C_{ax}Fe(1)P$ = 175.9 (5).

More recently, Appel and co-workers[91] have obtained the novel $\eta^1\eta^2$-complex $[[Fe(CO)_4]_2(RP=CH_2)]$ (R = 2,4,6-tri-*tert*-butylphenyl) (**67**), whose structure is shown in Figure 32.
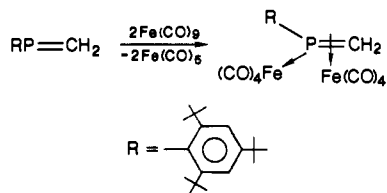
Interestingly, treatment of $[Fe_2(CO)_9]$ with 1 equiv of $RP=CH_2$ gives a mixture of the η^1 and η^2 $[Fe(CO)_4]$ complexes.
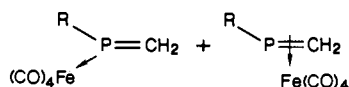
Both η^1- and η^2-forms of the analogous $[Fe(CO)_4$-$(Bu^tP=CHBu^t)]$ have recently been characterized in solution by NMR spectroscopy,[92] and treatment with
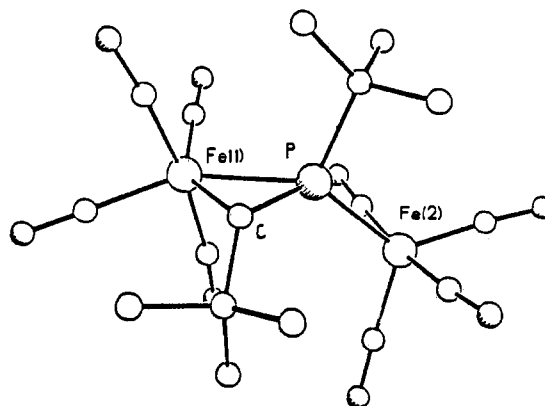
Figure 33. Molecular structure of **68**.

68

a further equivalent of $[Fe_2(CO)_9]$ affords the $\eta^1\eta^2$-complex $[[Fe(CO)_4]_2(Bu^tP=CHBu^t)]$ (**68**, Figure 33), which has been fully characterized by a single-crystal X-ray structure determination.

(v) η^2-(μ_3) Metal-Cluster-Stabilized Phosphaalkenes (Type E)

Huttner and co-workers[93] have reported the stabilization of the phosphaalkene $RP=CH_2$ as an η^2-(μ_3) bridging ligand. Thus twofold deprotonation of the triiron cluster $[Fe_3(CO)_9(\mu_3-RP)(\mu_2-H)_2]$ followed by treatment with CH_2I_2 gave the neutral phosphaalkene complex (**69**), in which one of the P–Fe bonds is bridged
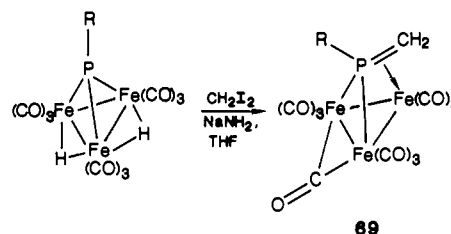
69

by a CH_2 group. The loss of the μ_2-H bridges of the starting cluster complex is electronically compensated by a μ_2-CO group, and the relatively short P–C distance (1.76 (1) Å) in **69** is typical for a coordinated phosphaalkene.

Modest yields of the phosphaalkene complex **70** result from an unusual reaction involving coupling of carbene and phosphinidene ligands.[94] Treatment of the phosphinidene complex C with PhLi generates the benzoyl complex D, which on treatment with $EtOSO_2CF_3$ at 22
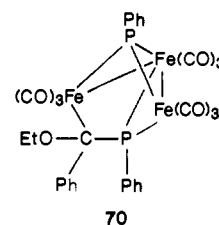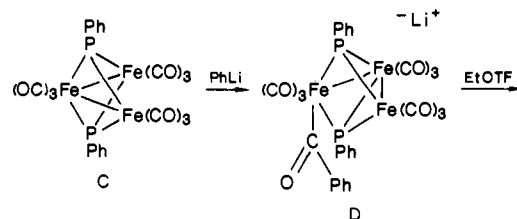
70
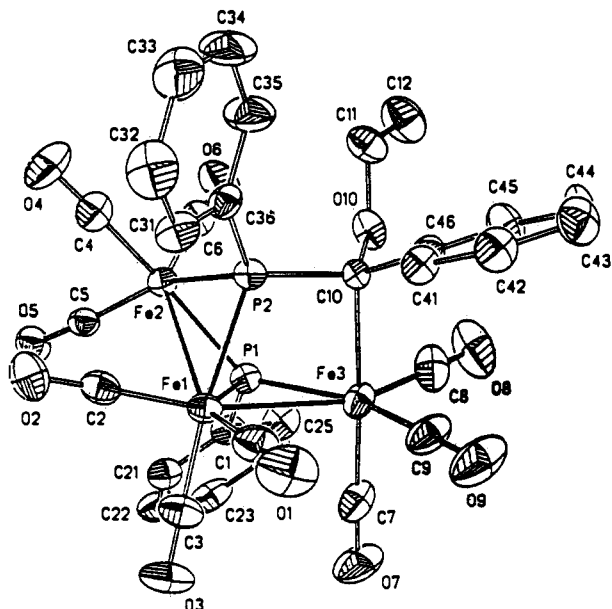
70

Figure 34. ORTEP drawing of $Fe_3(\mu_3\text{-PPh})\{\mu\text{-PhPC(OEt)Ph}\}(CO)_9$ (**70**). Relevant bond distances (Å) and angles (deg): Fe(1)–Fe(2), 2.671 (2); Fe(1)–Fe(3), 2.750 (1); Fe(1)–P(1), 2.256 (2); Fe(1)–P(2), 2.240 (2); Fe(2)–P(1), 2.198 (2); Fe(2)–P(2), 2.211 (2); Fe(3)–P(1), 2.192 (2); Fe(3)–C(10), 2.139 (6); P(2)–C(10), 1.800 (6); Fe(2)–Fe(1)–Fe(3), 90.31 (8); Fe(1)–P(2)–Fe(2), 73.7 (1); Fe(1)–P(1)–Fe(3), 76.4 (1); Fe(1)–P(2)–C(10), 107.9 (2); Fe(2)–P(2)–C(10), 115.6 (2); Fe(3)–C(10)–P(2), 96.5 (3); Fe(3)–C(10)–O(10), 104.7 (4); P(2)–C(10)–O(10), 114.7 (5); [Fe(1)–Fe(2)–P(1)]–[Fe(1)–Fe(3)–P(1)], 130.1.

°C in an attempt to obtain a phosphinidene–carbene complex (analogous to a fully characterized nitrene–carbene complex) gave instead the complex containing a coordinated PhP=C(OEt)Ph ligand.

The structure of **70** when the remaining μ_3-PPh ligand is included is best described as a "butterfly" structure, with the phosphaalkene ligand bridging the open face of the butterfly. The P–C bond length (1.800 (6) Å) is longer than in other coordination complexes of phosphaalkenes.

In solution two diastereoisomers of **70** that differ according to whether or not the OEt substituent lies on the same side of the molecule as P(1) (see Figure 34) exist in equal amounts.

B. A Metallaphosphirene Complex

As mentioned elsewhere, an η^1-phosphaalkene metal complex resulted from condensation of a terminal phosphinidene complex with a carbene complex (see section IVA(i)). The analogous reaction with a tungsten carbyne complex afforded the stable tungstaphosphirene compound **71**.[95]
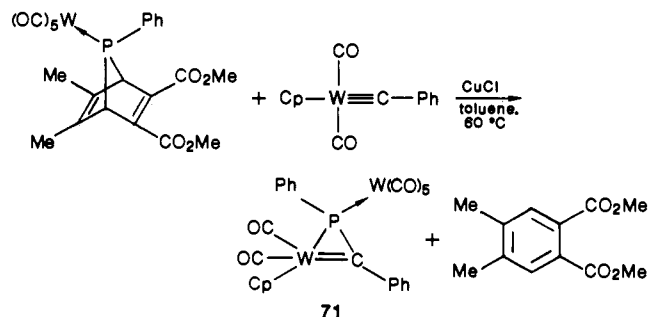
71
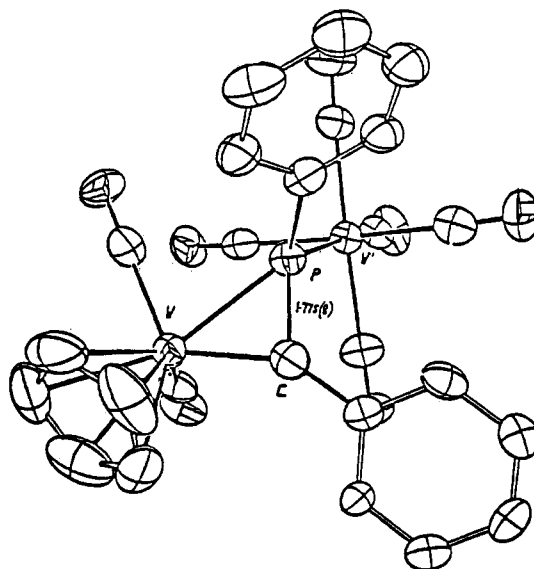
71

Figure 35. Molecular structure of **71**. (P–C bond length in Å.)

The molecular structure of the complex shown in Figure 35 suggests some double-bond character in the P–C (ring) bond (1.775 (8) Å), supporting the formulation **71b**, in which the P=C unit acts as a four-electron donor.

71a   **71b**
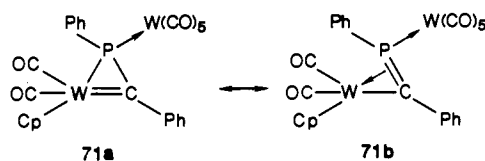
C. An η^4-1-Phosphabutadiene Complex

The first known η^4-1-phosphabutadiene metal complex (**72**), which was recently reported, was obtained by the condensation of a transient terminal phosphinidene complex and a vinylcarbene complex; viz.[96]
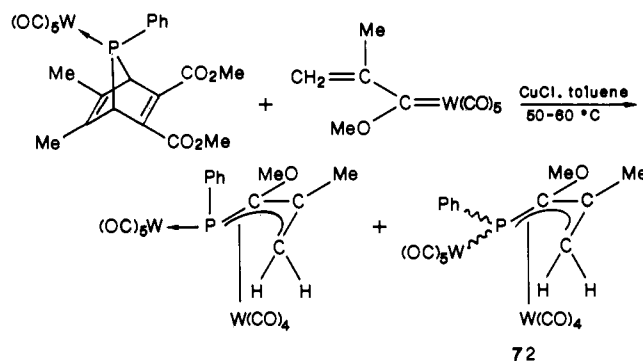
72

A single-crystal X-ray diffraction study of **72** (Figure 36) reveals that the phosphabutadiene unit is planar and fully delocalized (P=C = 1.782 (8) Å), with the PC_3 being η^4-bonded to the [W(CO)$_4$] unit.

D. An η^4-1,2,4-Triphosphabuta-1,3-diene Complex

The formal replacement of a CH fragment by P or a CH_2 fragment by PR in organic compounds leading to novel unsaturated organophosphorus ligands is evidenced by the recent report[140] of the first example of

72
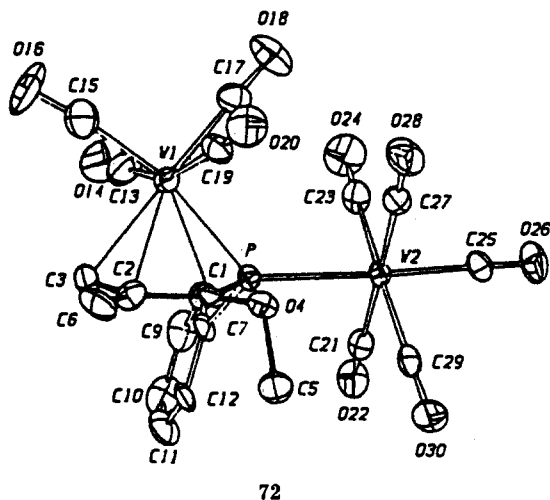
Figure 36. ORTEP drawing of one molecule of **72**. Vibrational ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted. Principal bond distances (Å): W1–P, 2.551 (2); W1–C1, 2.327 (3); W1–C2, 2.334 (8); W1–C3, 2.366 (8); P–W2, 2.512 (2); P–C1, 1.783 (8); P–C7, 1.826 (8); C1–C2, 1.44 (2); C2–C3, 1.41 (1); C1–O4, 1.387 (9); C2–C6, 1.51 (1). Selected bond angles (deg): W1–P–C1, 62.0 (2); W1–P–C7, 112.3 (3); W1–P–W2, 128.81 (8); C1–P–C7, 110.9 (4); C1–P–W2, 121.9 (3); C7–P–W2, 111.7 (3); P–C1–C2, 124.7 (6); P–C1–O4, 116.9 (5); C2–C1–O4, 117.8 (7); C1–C2–C3, 118.0 (7); C1–C2–C6, 120.5 (8); C3–C2–C6, 121.3 (8); P–W1C1, 42.6 (2); P–W1–C2, 71.6 (2); P–W1–C3, 79.1 (2); C1–W1–C2, 36.0 (3); C1–W1–C3, 62.9 (3); C2–W1–C3, 35.0 (4).

72a
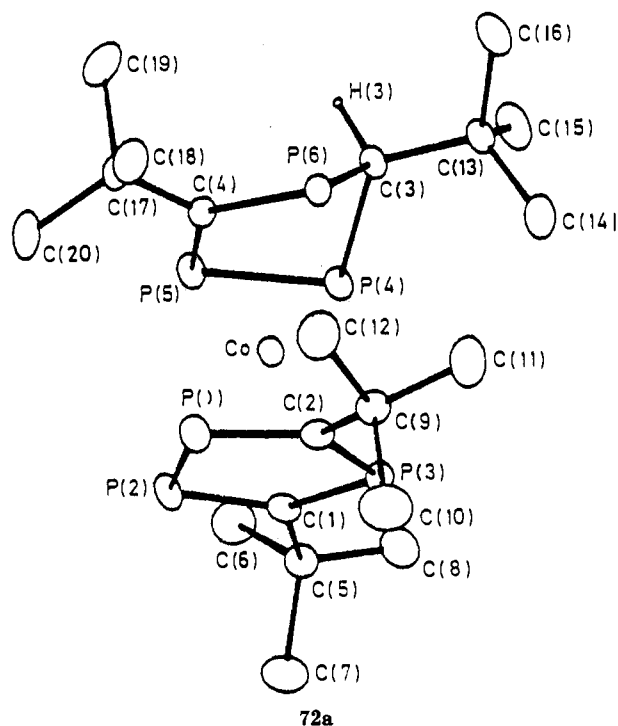
Figure 37. Molecular structure of **72a**.

a complex containing a 1,2,4-triphosphabuta-1,3-diene fragment. Thus treatment of $Li(dme)_3(C_2R_2P_3)$ (R = Bu^t) with $CoCl_2$ in monoglyme gives a low yield of the red diamagnetic cobalt complex $[Co(\eta^5\text{-}C_2R_2P_3)(\eta^4\text{-}C_2R_2HP_3)]$ (**72a**, Figure 37) containing a ligated η^4-1,2,4-triphosphacyclopentadiene. A single-crystal X-ray diffraction study shows that, as expected, the PPCP framework of the η^4-ligated unit is planar, and the C–P and P–P bond lengths lie in the range expected for this unsaturated system.

74
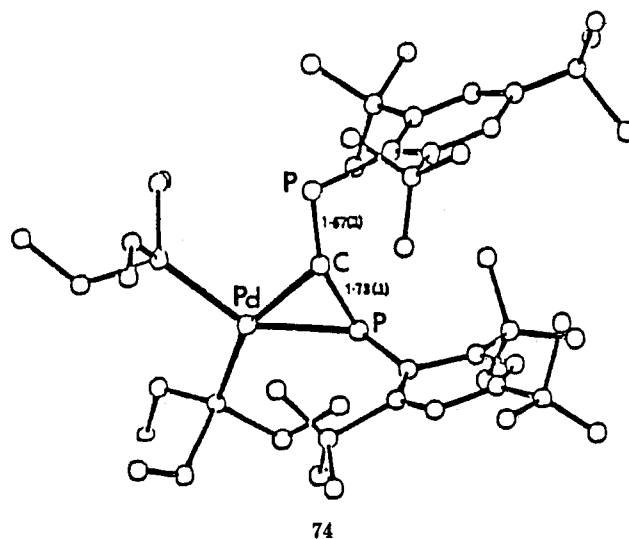
Figure 38. Molecular structure of **74**. (P–C bond lengths in Å.)

V. Phosphaallenes

A. Mono- and Diphosphaallene Metal Complexes

By analogy with phosphaalkenes discussed earlier, the more recently synthesized monophosphaallenes RP=C=CR$_2$ and diphosphaallenes RP=C=PR offer considerable potential as ligands. The bonding modes for the diphosphaallenes shown below are all feasible but so far examples have been established only for a, b, and c.
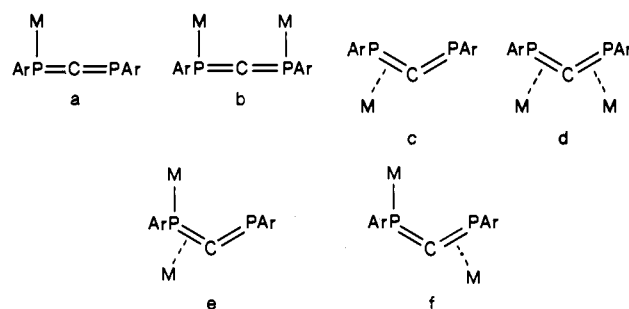
Recently ab initio calculations on HP=C=PH and HP=C=CH$_2$ indicate that the two sets of n,π-orbitals in the former are the quasi-degenerate HOMOs, whereas the P=C π-orbital is the HOMO in the latter.[97,98]

The first reports of complexes of RP=C=PR transition-metal complexes were of the η^2-type,[99] in [Pt-(PPh$_3$)$_2$(ArP=C=PAr)] (**73**) the structure in solution

73

Ar = 2,4,6-Bu$^t_3$C$_6$H$_2$
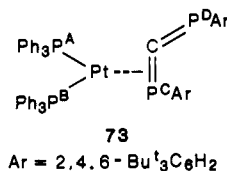
established by ^{31}P NMR studies being the same as in the isoelectronic CO$_2$ and CS$_2$ complexes. More recently, a wider series of η^2-mono- and -diphosphaallene metal complexes of Ni(0) and Pd(0) have been obtained, and a single-crystal X-ray strucutre on [Pd(PEt$_3$)$_2$-(RP=C=PR)] (R = 2,4,6-Bu$^t_3$C$_6$H$_2$) (**74**, Figure 38) confirms the structure.[100] However, the complexes exhibit dynamic behavior in solution.[101] As expected, the
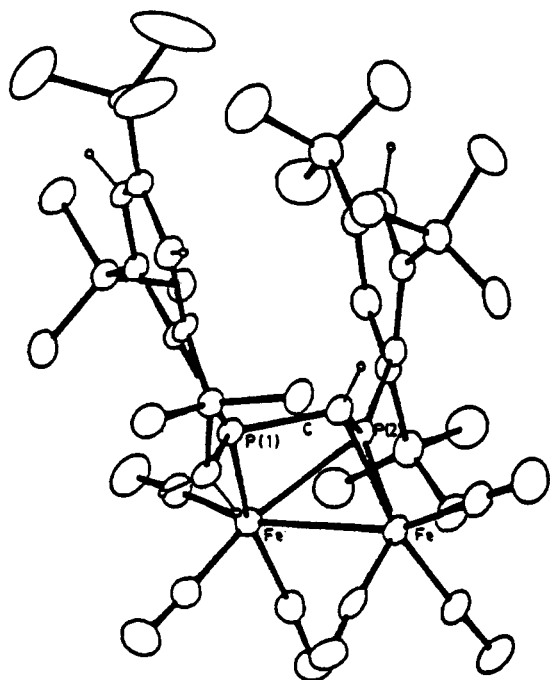
77

Figure 39. Molecular structure of [Fe₂(CO)₆-
{ArP=CHPCH₂C(Me₂)C₆H₂ᵗBu₂}] (77). Selected bond lengths
(Å): Fe(1)–Fe(2) = 2.738 (1), P(1)–C = 1.771 (7), P(2)–C = 1.783
(6), Fe(1)–P(1) = 2.295 (2), Fe(2)–P(2) = 2.171 (2), Fe(1)–P(2)
= 2.313 (2).

P=C bond that is η^2-ligated to the metal is lengthened.
Interestingly, in the η^2-monophosphaallene Pt(0) com-
plexes, e.g., [Pt(PR₃)₂(RP=C=CR'₂)] (R' = Ph), it is
the P=C bond and not the C=C bond that interacts
with the metal.

The monophosphaallene also can act as an η^1-ligand
as evidenced by the report of Appel et al. on the com-
plex [Ni(CO)₃(RP=C=CR₂)] (75), whose molecular

75
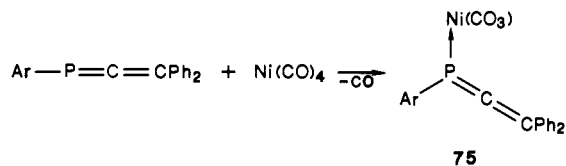
Ar = 2,4,6-tri-*tert*-butylphenyl

structure has been established by an X-ray study.[102]
Yoshifuji et al. have spectroscopically established η^1-
ligation of type a and b in complexes of the type [(M-
(CO)₅)ₙ(RP=C=PR)] (n = 1, 2) (M = W).[103]

B. Novel Complexes Derived from Diphosphaallenes

Interesting examples have recently appeared of facile
hydrogen migration reactions in ligated diphosphaallene
metal carbonyl complexes. Heating [W(CO)₅(THF)]
with RP=C=PR leads to a hydrogen migration from
carbon to phosphorus to give the carbon–carbon cou-
pled tetrahydro-1-phosphanaphthalene complex **76**
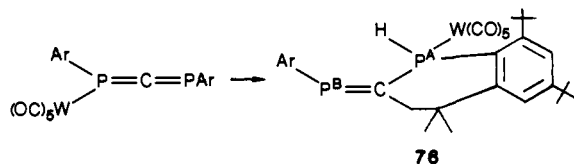
76

On the other hand, RP=C=PR reacts with [Fe₃
(CO)₁₂] to give two products in roughly equal amounts.
One of the products has been fully characterized by
X-ray diffraction methods and shown to contain a new
unsaturated ligand arising from an unexpected hydro-
gen migration from carbon to carbon within the di-
phosphaallene framework (77).[104]
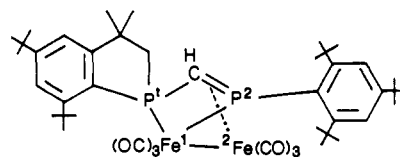
77

The full molecular structure is shown in Figure 39.
The importance of these H-migration reactions in
sterically crowded diphosphaallene metal complexes is
underlined by the novel *double*-hydrogen migration
from carbon to carbon to afford the ligated diphosphane
ligand Butᵗ₂C₆H₂(CMe₂CH₂PCH₂PCH₂)(CMe₂)C₆H₂Butᵗ₂
as its [W(CO)₄] complex **78**.
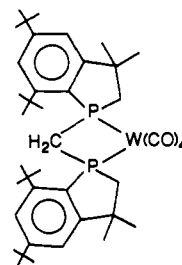
78

The molecular structure of **78** is shown in Figure 40.[101]

C. Novel Cluster-Stabilized Phosphaallenes

A recent report[105] describes the synthesis and struc-
tural characterization of the first cluster-stabilized
phosphaallene, ButᵗP=C=CHPh in the complex
[FeCo₂(CO)₉(μ_3-η^2-ButᵗP=C=CHPh)] (79). The com-
pound was obtained in very low yield (ca. 3%) by the
following sequence of reactions, the major product being
the phosphinidene cluster complex [FeCo₂(CO)₉(ButᵗP)]:
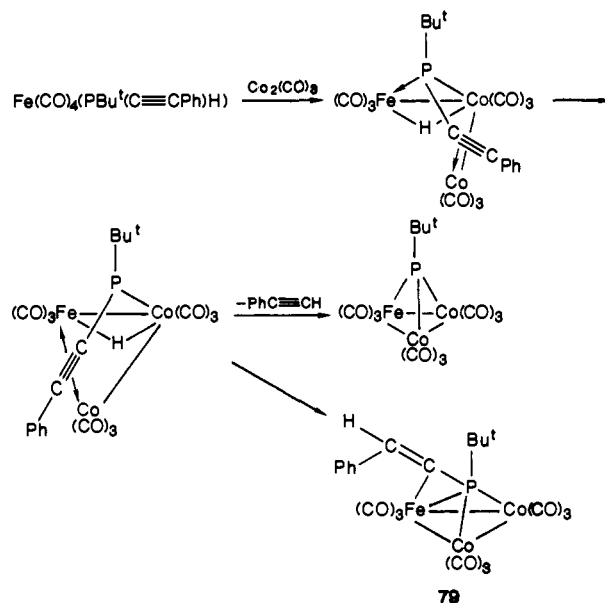
79

Although phenylacetylene is detected in the reaction
media, it has been established that **79**, results from an
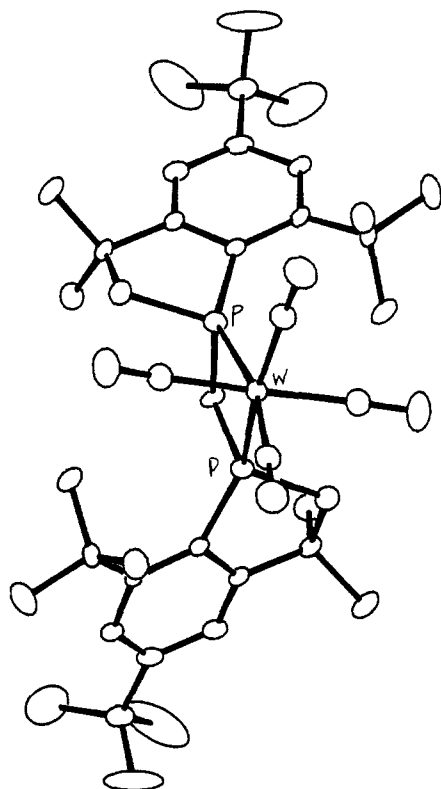
78

Figure 40. Molecular structure of **78**.

*intra*molecular rearrangement involving the migration of hydrogen from phosphorus to the β-carbon of the alkynyl group.

A single-crystal X-ray diffraction study on **79** (Figure 41) confirms that the phosphaallenyl ligand is bonded by the phosphorus to the two cobalt atoms of the metallic triangle and by the α-C atom to the iron. The P–C distance (1.753 (9) Å) in the phosphaallene is relatively short and comparable with the value for RP=CH_2 in complex **69**.

D. A Metallaphosphaallene Complex (Metalla-λ^5-σ^3-phosphorane)

The first example of this type of complex has been reported recently by Barron and Cowley.[106] The three-coordinate complex shown below was obtained by treatment of $K[Fe(\eta^5$-$C_5H_5)(CO)_2]$ with ClP(= $CSiMe_3)_2$. No structural data on **80** are yet available but NMR studies suggest the existence of R and S isomers.
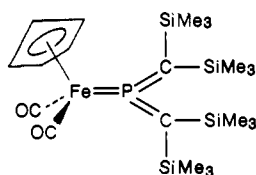
80

VI. Phosphaalkenyl and Phosphaallenyl Metal Complexes (Metallaphosphaalkenes and Metallaphosphaallenes)

By analogy with the variety of possible coordination modes exhibited by phosphaalkenes in their coordination complexes mentioned earlier, five types of metal-
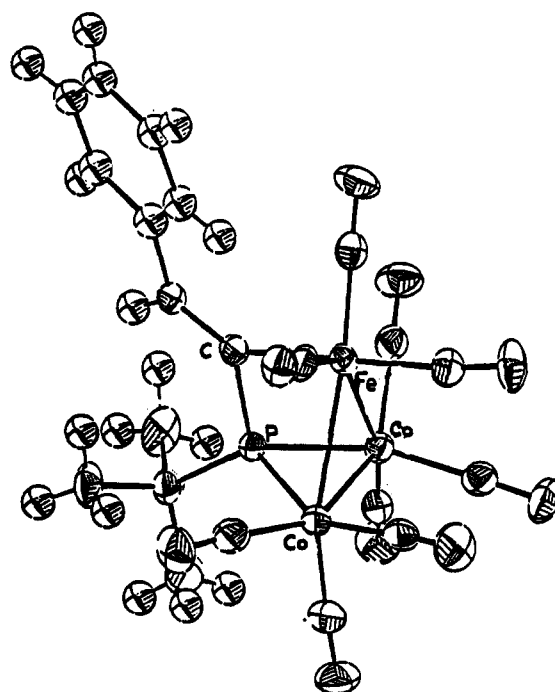
79

Figure 41. Molecular structure of **79**.

laphosphaalkenes (phosphaalkenyl metal compounds) I–V are possible.
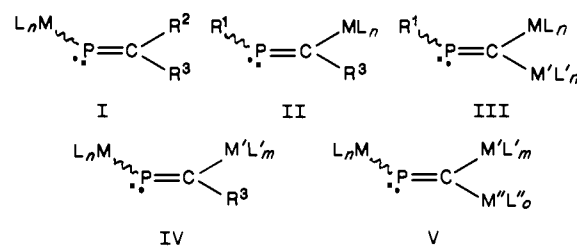
Phosphaalkenes are potentially ambidentate ligands because they possess two energetically high-lying but closely spaced molecular orbitals of the π and n(P) type.

A change in reactivity from "olefinic" toward "carbenic" character might be expected in certain cases[107] and in this context metallaphosphaalkenes (phosphaalkenyl metal complexes) $[ML_n(P=CR_2)]$ (L_n = other ligands) of type I are of interest since the σ-donating effect of the transition metal may destabilize the n(P) orbital and enhance the carbene character of the phosphaalkene.[108]

Several complexes of this structural type are now known;[108,109] for example, treatment of the chlorophosphaalkene $(Me_3Si)_2C$=PCl with sodium carbonyl metalates of Mo and W yield compounds **81–83**. The structures of **82** and **83** (Figure 42) indicate that the transition metal causes a significant opening of the M–P–C angle compared with the free phosphaalkenes,[1] but the P–C bond lengths (ca. 1.67 Å) are typical for uncoordinated phosphaalkenes. The $MPCSi_2$ fragment is planar and the destabilization of the n(P) orbital is suggested by the large bathochromic shift of the n–π^* optical transition of the P=C chromophore and the deshielding of the ^{31}P nucleus in the NMR spectrum.

The enhanced nucleophilicity of the phosphorus atom is evidenced by its ready reactivity toward trifluoromethanesulfonic acid to afford complexes that contain the unknown phosphaalkene $(Me_3Si)_2C$=PH. Treat-

81. M = Mo. R = H
82. M = Mo. R = Me
83. M = W. R = H
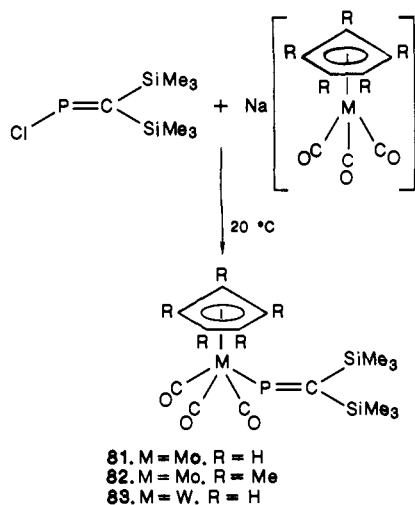
ment of **83** with sulfur yields a metallothio-phosphaalkene complex [W(η^5-C$_5$H$_5$)(SP=C-(SiMe$_3$)$_2$)(CO)$_3$] whose formulation is suggested by the very low value of the ^{31}P–^{183}W coupling constant (14 Hz).

Of special interest is the *intra*molecular substitution of a carbonyl ligand from the metallaphosphaalkene complex on heating with formation of the metal-laphosphaallene complex **84**. This type of complex had previously been reported by Cowley et al.[109] by direct treatment of K[Mo(CO)$_3$(η^5-C$_5$H$_5$)] with (Me$_3$Si)$_2$C=PCl in tetrahydrofuran, and the conditions for the extrusion of CO have been found to be strongly dependent on the transition metal.

As expected, the decrease in p character at the phosphorus atom in the tungsten phosphaallene complex (**84a**) is strikingly indicated by the magnitude of $^1J_{PW}$ (617 Hz). The single-crystal structure of the molybdenum complex (**84**) shown in Figure 43 confirms the η^1-PC(SiMe$_3$)$_2$ bonding mode and reveals a Mo–P bond length of 2.174 Å, which is significantly shorter than those found in typical molybdenum–tertiary phosphane complexes (2.40–2.57 Å) and also slightly shorter than values (2.21 Å) in complexes of the type [Mo(CO)$_2$(η^1-PR$_2$)(η^5-C$_5$H$_5$)], where multiple Mo–P bonding has been implied. Likewise, the P–C bond length (1.649 (4) Å) is shorter but similar to those found in uncoordinated phosphaalkenes.

Since the ligand configuration is such that the Mo–P–C angle is almost linear and the methylene C is trigonal planar and since this plane is orthogonal to the symmetry plane of the Mo(CO)$_2$(η^5-C$_5$H$_5$) unit, then canonical forms a and b can be envisaged. Structure

a   b

a is isovalent with known vinylidene complexes, e.g., [M=C=CR$_2$(CO)$_2$(η^5-C$_5$H$_5$)] (M = Mn, Re), and this conformation maximizes the interaction between the HOMO of the [M(CO)$_2$(η^5-C$_5$H$_5$)] fragment and a P(3p) orbital. In structure b the Mo–P bonding resembles that found in terminal alkylidyne complexes of the type

82

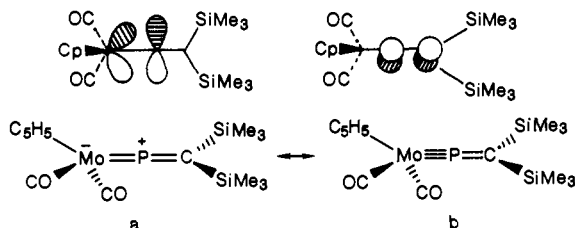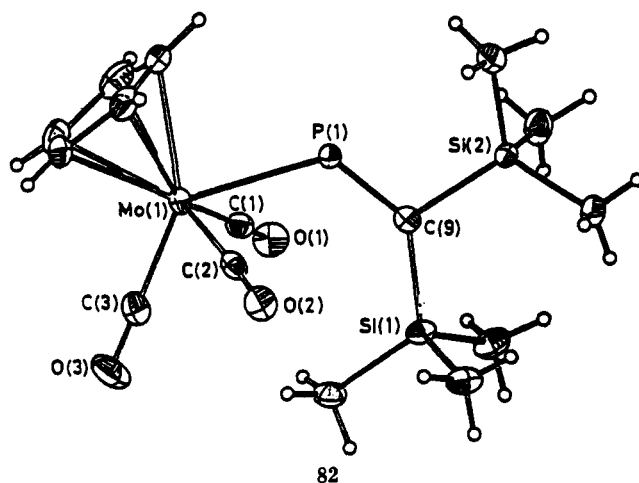**Figure 42.** ORTEP view of the strucuture of **82**. Important bond lengths (Å) and angles (deg) are as follows [the corresponding values for (**83**) are given in brackets]: P(1)–C(9) = 1.665 (3) [1.66 (2)], Mo(1)[W(1)]–P(1) = 2.568 (1) [2.569 (5)], Mo(1)[W(1)]–C(1) = 1.980 (3) [2.03 (2)], Mo(1)[W(1)]–C(2) = 1.967 (3) [2.02 (2)], Mo(1)[W(1)]–C(3) = 1.973 (3) [2.03 (2)]; Mo(1)[W(1)]–P(1)–C(9) = 123.45 (11) [125.0 (6)], P(1)–C(9)–Si(1) = 135.8 (2) [135.0 (10)], P(1)–C(9)–Si(2) = 107.4 (2) [108.3 (9)].

84
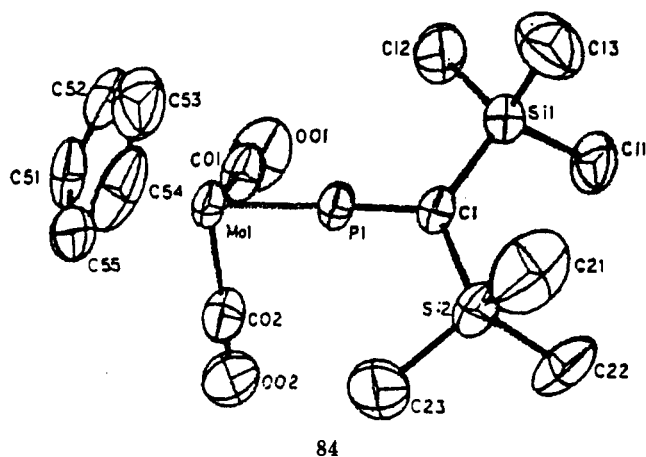
Figure 43. ORTEP view of [Mo(CO)$_2$(η^1-P=C(SiMe$_3$)$_2$)(η-C$_5$H$_5$)] (**84**). Pertinent metric parameters: Mo(1)–C(1) = 2.174 (1), P(1)–C(1) = 1.649 (4) Å; Mo(1)–P(1)–C(1) = 178.3 (2), P(1)–C-(1)–Si(1) = 116.7 (3), P(1)–C(1)–Si(2) = 116.9 (3), Si(1)–C(1)–Si(2) = 126.3 (2)°.

[M≡CR(CO)$_2$(η^5-C$_5$H$_5$)] (M = Cr, Mo, W).

Complex **84** reacts with both electrophilic and nucleophilic reagents;[110] thus with 1 equiv of EtOH **84** affords a high yield of [Mo(CO)$_2$(η^1-PR^{1}R^2)(η^5-C$_5$H$_5$)] (R^1 = (Me$_3$Si)$_2$CH, R^2 = OEt), whose single-crystal X-ray structure confirms that it is a three-electron donor phosphido (neutral phosphenium) complex having a trigonal-planar phosphorus atom and a relatively short metal–phosphorus distance.

Other electrophiles react virtually quantitatively (see scheme), and deuterium labels can be easily introduced by this route.

X = EtO, Pr$^i_2$N, C$_6$F$_5$S, Y = H; X = CD$_3$O, Y = D

88

Figure 45. ORTEP drawing of [Fe{η^1-P=C(SiMe$_3$)$_2$}(η^5-Me$_5$C$_5$)-(CO)$_2$] (88) showing the atom numbering scheme. Important structural parameters: P–Fe = 2.256 (2), P–C(13) = 1.680 (9) Å; Fe–P–C(13) = 126.2 (3), P–C(13)–Si(1) = 107.1 (5), P–C(13)–Si(2) = 134.4 (5), Si(1)–C(13)–Si(2) = 118.4 (5)°.

phasizing the parallel between **86** and bridging vinylidene complexes.

86
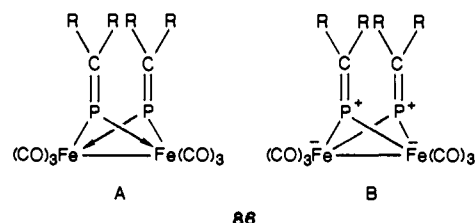
A novel synthetic route to phosphaalkenyl and phosphaallenyl complexes of (η^5-pentamethylcyclopentadienyl)metal carbonyls has recently been developed by Niecke et al.[111] in which the P–C single bond of the (pentamethylcyclopentadienyl)phosphaalkene Me$_5$C$_5$P=C(SiMe$_3$)$_2$ is cleaved on treatment with transition-metal complexes of the type [M(CO)$_3$-(MeCN)$_3$] (M = Mo, W); viz.
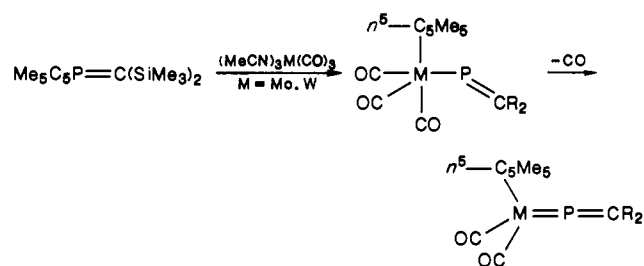
Transfer of the η^5-C$_5$Me$_5$ group of C$_5$Me$_5$P=C-(SiMe$_3$)$_2$ from phosphorus to iron and nickel has also been reported recently. Thus treatment with [Fe$_2$-(CO)$_9$] affords the η^1-complex [Fe(η^1-C$_5$Me$_5$)(P=C-(SiMe$_3$)$_2$)(CO)$_4$] (**87**), which on photolysis produces [Fe(η^1-P=C(SiMe$_3$)$_2$)(η^5-C$_5$Me$_5$)(CO)$_2$] (**88**).[113]

87   **88**
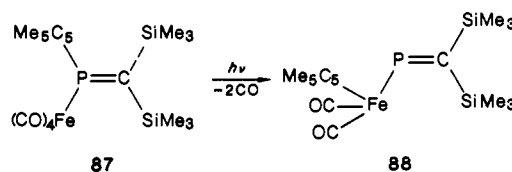
The structure of the latter, which can also be prepared by the metathetical reaction of (Me$_3$,Si)$_2$C=PCl with K[Fe(η^5-C$_5$Me$_5$)(CO)$_2$], is shown in Figure 45.

Likewise, [Ni(η^5-C$_5$Me$_5$)(P=C(SiMe$_3$)$_2$)(PR$_3$)] is obtained from Me$_5$C$_5$P=C(SiMe$_3$)$_2$ and an equimolar

86

Figure 44. Molecular structure of **86** showing the atom numbering scheme. Principal bond lengths (Å) and angles (deg): Fe(1)–Fe(1') = 2.666 (1), Fe(1)–P(1) = 2.184 (1), P(1)–C(4) = 1.650 (4); Fe(1)–P(1)–Fe(1') = 75.0 (1), Fe(1)–P(1)–C(4) = 142.5 (1), P(1)–C(4)–Si(1) = 121.6 (2), P(1)–C(4)–Si(2) = 116.0 (2), Si-(1)–C(4)–Si(2) = 122.0 (2).

In contrast to the related phosphaalkenyl complexes, proton attachment occurs at carbon rather than phosphorus.
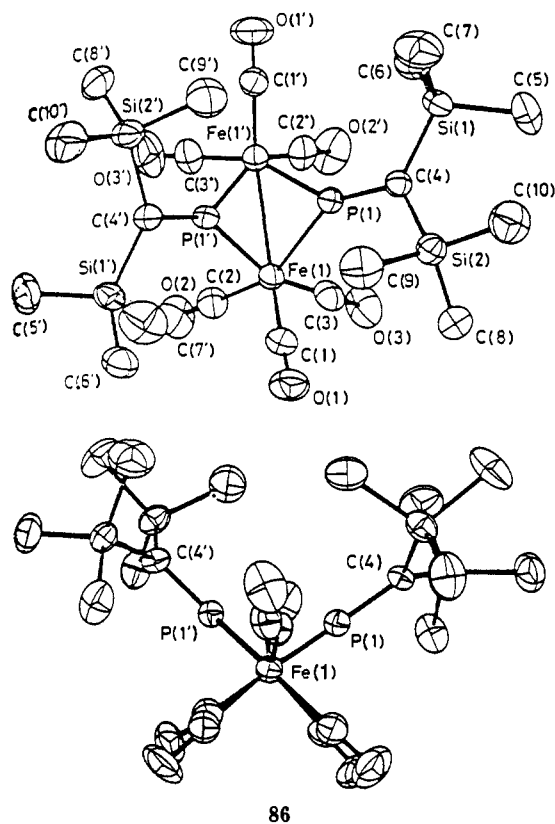

Complex **84** is also reactive toward nucleophiles; for example, with NaOMe the anion **85** is obtained as evidenced by NMR spectroscopy.

85

The first example of a complex involving bridging phosphaalkenyl ligands was reported by Cowley et al.[112] via treatment of (Me$_3$Si)$_2$C=PCl with Na$_2$[Fe(CO)$_4$]/dioxane at room temperature. The structure of [Fe$_2$-(CO)$_6$((Me$_3$Si)$_2$CP)$_2$] (**86**) shown in Figure 44 exhibits a P$_2$Fe$_2$ core of the "butterfly" type found for bis-(phosphido)diiron complexes. The phosphorus and carbon atoms both adopt trigonal-planar geometries, and the P–C bond length (1.650 (4) Å) corresponds to a bond order of 2, which is similar to that observed in both η^1-coordinated and free phosphaalkenes.

The electronic structure of **86** can be discussed in terms of the canonical forms A and B, the latter em-

90

Figure 46. Molecular structure of [Os(P=C[O]CF$_3$)(CO)$_2$-(PPh$_3$)$_2$] (**90**) (phenyl rings are omitted for clarity). Bond lengths are given in angstroms. 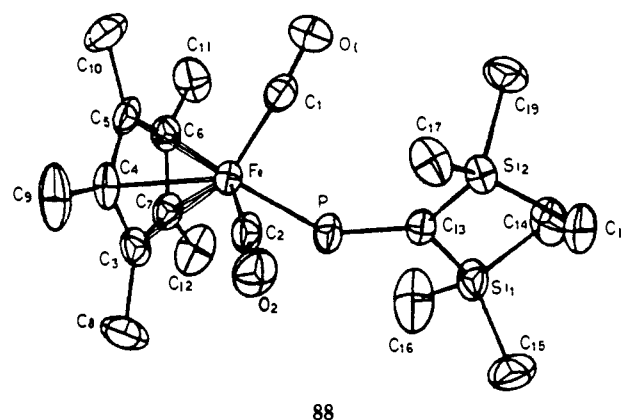Important angles are P(1)–Os–O(1) = 67.3 (4), Os–P(1)–C(1) = 73.6 (8), P(1)–C(1)–O(1) = 128.2 (1.6), and Os–O(1)–C(1) = 90.8 (1.2)°.

mixture of R$_3$P/Ni(COD)$_2$ in the presence of ethylene.[114]

The previously mentioned complex **84a** (M = W) has also been obtained by the following interesting synthetic route:
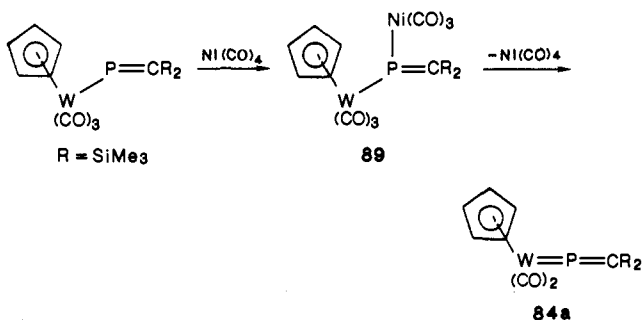
Complex **89** is only stable in the presence of an excess of [Ni(CO)$_4$] and readily forms the phosphaallenyl complex **84a** at room temperature.

An interesting synthesis of a metallaphosphaalkene complex of type I has recently been described by Roper et al.[115] Treatment of the terminal PH$_2$-metal complex [Os(PH$_2$)Cl(CO)$_2$(PPh$_3$)$_2$] with (CF$_3$CO)$_2$O gives [Os-{PH(C(O)CF$_3$)}Cl(CO)$_2$(PPh$_3$)$_2$], which is dehydrochlorinated by NaH to yield [Os(P=C(O)CF$_3$)(CO)$_2$-(PPh$_3$)$_2$] (**90**, Figure 46), whose structure has been proved by X-ray crystallography.

L = PPh$_3$
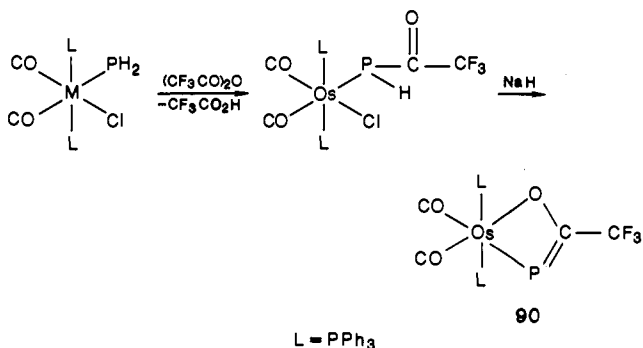
Weber and co-workers[116–125] in a series of papers have devised alternative synthetic routes to a variety of

92

94
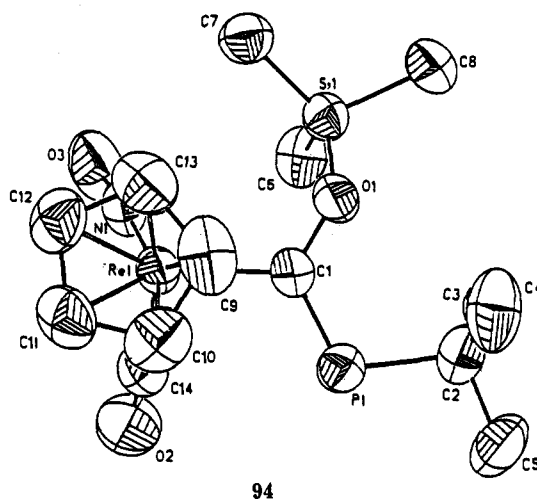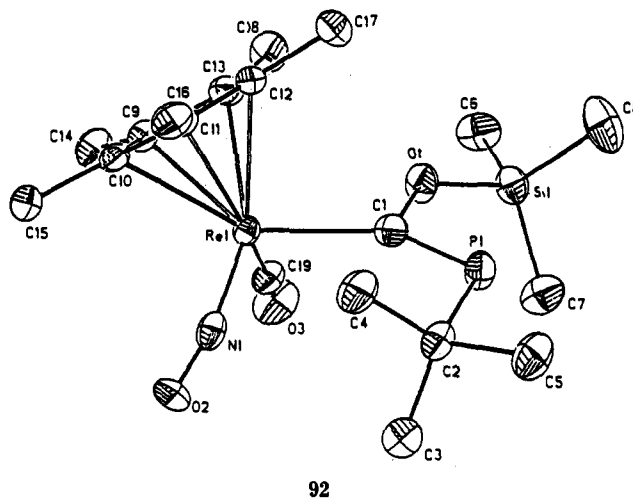
Figure 47. Molecular structures of (η^5-C$_5$Me$_5$)(CO)(NO)ReC-(OSiMe$_3$)=Pr^{t}Bu (**92**) and (η^5-C$_5$H$_5$)(CO)(NO)ReC(OSiMe$_3$)=P^{t}Bu (**94**).

metallaphosphaalkene complexes of different structural types.

Complexes of type II have been synthesized by using transition-metal carbonyl cations and silylated lithium phosphides. Thus treatment of [Re(CO)$_2$(NO)(η^5-C$_5$Me$_5$)]BF$_4$ with LiPR(SiMe$_3$) (R = SiMe$_3$, Bu^t, Ph) gives the phosphaalkenyl complexes [Re(C(OSiMe$_3$)=PR)(η^5-C$_5$Me$_5$)(CO)(NO)] (**91**, R = SiMe$_3$; **92**, R = Bu^t; **93**, R = Ph). A C$_5$H$_5$ analogue, [Re(C(OSiMe$_3$)=PBu^t)(η^5-C$_5$H$_5$)(CO)(NO)] (**94**), is also known.

^{31}P NMR studies indicate that the course of the reaction involves formation of phosphino–carbonyl complexes of the type [Re(C(O)P(R)SiMe$_3$)(CO)(NO)(η^5-C$_5$Me$_5$)] via nucleophilic addition of phosphide to a CO ligand prior to the 1,3-silyl migration from phosphorus to oxygen (see Scheme 1).

The molecular structures of **92** and **94** (Figure 47) have been established by single-crystal X-ray studies and differ in the configuration at the P=C double bond, presumably resulting from the steric bulk of the C$_5$Me$_5$ ring, which forces the Me$_3$Si group toward the phosphorus atom (see Figure 47). Both complexes have typical P–C bond lengths expected for phosphaalkenes (ca. 1.69 Å).

Analogous reactions have been carried out with cationic Fe and Ru complexes of the type [M(η^5-

SCHEME 1
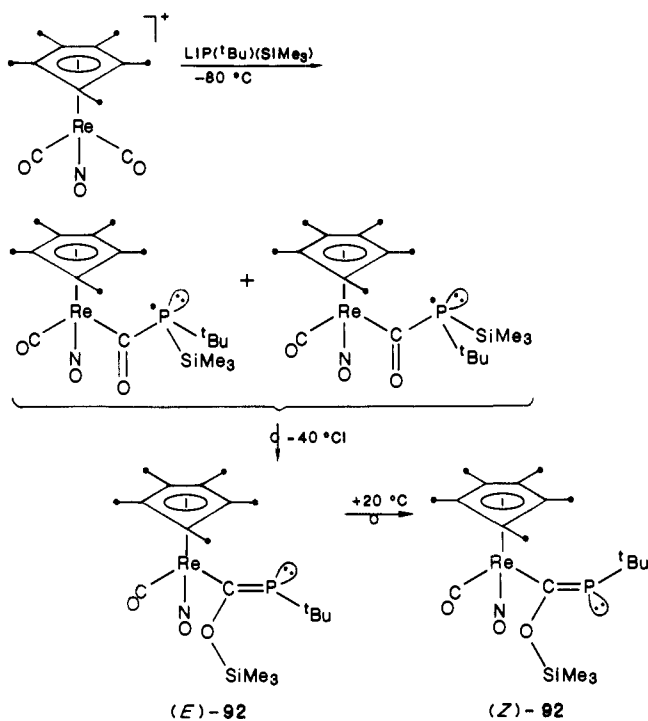
$C_5Me_5)(CO)_3]^+$ with the bulky $LiP(Ar)(SiMe_3)$ (Ar = 2,4,6-tri-*tert*-butylphenyl), viz.
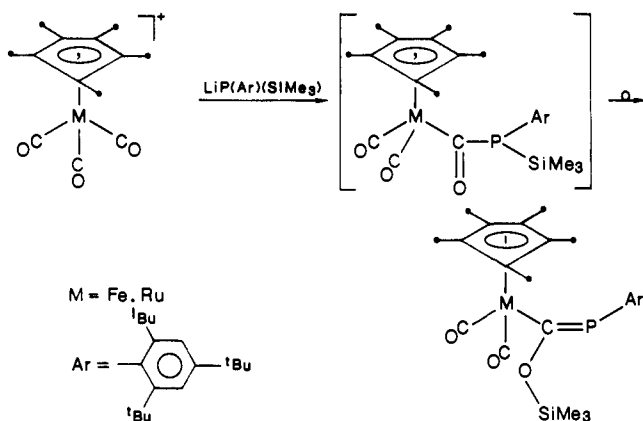
This contrasts with related reactions with $LiP(R)$-$(SiMe_3)$ (R = Ph, Bu^t, Me$_3$Si) where the intermediate phosphino–carbonyl complex eliminates CO to afford the phosphido complex rather than a phosphaalkenyl compound.
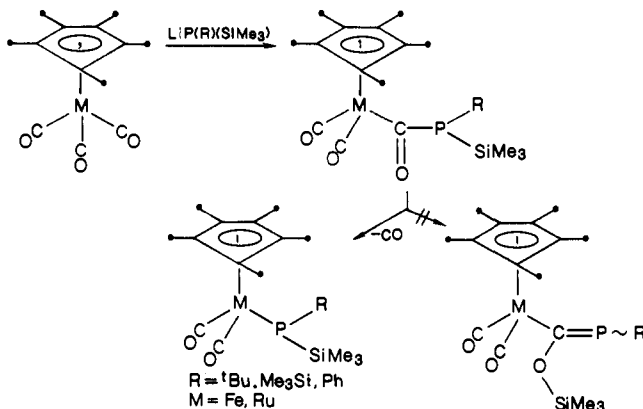
Phosphaalkenyl complexes of type I containing metal–phosphorus bonds can be obtained from [Fe(P-

Figure 48. Crystal structure of **95**. Selected bond lengths (Å) and angles (deg): Fe–P = 2.291 (1), P–Cl = 1.701 (4), Cl–O1 = 1.365 (5), C1–C4 = 1.529 (6), Fe–C2 = 1.753 (5), Fe–C3 = 1.783 (5), C2–O2 = 1.151 (6), C3–O3 = 1.108 (7), Fe–C(ring) = 2.112 (3)–2.119 (3); C2–Fe–P = 86.2 (1), P–Fe–C3 = 88.8 (2), C2–Fe–C3 = 96.5 (2), Fe–P–Cl = 113.8 (2), P–Cl–O1 = 123.9 (3), P–Cl–C4 = 120.5 (3), O1–C1–C4 = 115.3 (4), Cl–O1–Si = 144.7 (3).

$(SiMe_3)_2)(CO)_2(\eta^5\text{-}C_5H_5)]$ and acid chlorides $RCOCl$ (R = Ph, Bu^t, 2,4,6-Me$_3$C$_6$H$_2$). The structure of (Z)-[Fe-$(P=C)(OSiMe_3)Bu^t)(CO)_2(\eta^5\text{-}C_5H_5)]$ (**95**), shown in Figure 48, has been established by X-ray analysis.

R = 2,4,6-Me$_3$C$_6$H$_2$, Ph, ^{t}Bu
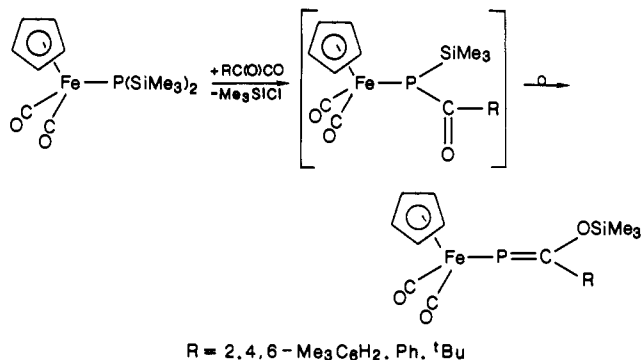
Steric effects appear to be important in these reactions; thus whereas treatment of [Fe(P(SiMe$_3$)$_2$)-$(CO)_2(\eta^5\text{-}C_5Me_5)]$ with 2,4,6-trimethylbenzoyl chloride yields the phosphaalkenyl complex [Fe(P=C-$(OSiMe_3)(Mes))(CO)_2(\eta^5\text{-}C_5Me_5)]$ (**96**), benzoyl chloride itself produces both the phosphaalkenyl complex **97** and the diacylphosphido complex [Fe(P(COPh)$_2$)(CO)$_2$-$(\eta^5\text{-}C_5H_5)]$ (**98**). Pivaloyl chloride forms only the diacylphosphido complex **99** (see Scheme 2). A similar situation is found in the analogous ruthenium and osmium systems.

Monoacylphosphido complexes **100** are generated with acid chlorides in the presence of ethanol and lithation with LiMe followed by treatment with Me$_3$SiCl, which converts them into the phosphaalkene complexes (Scheme 3).

VII. Phosphaallyl Metal Complexes

A. η^3-1-Phosphaallyl Metal Complexes

This type of complex is so far only known with additional coordination of a second metal at phosphorus.

SCHEME 2

96   **97**   **98**   **99**

103
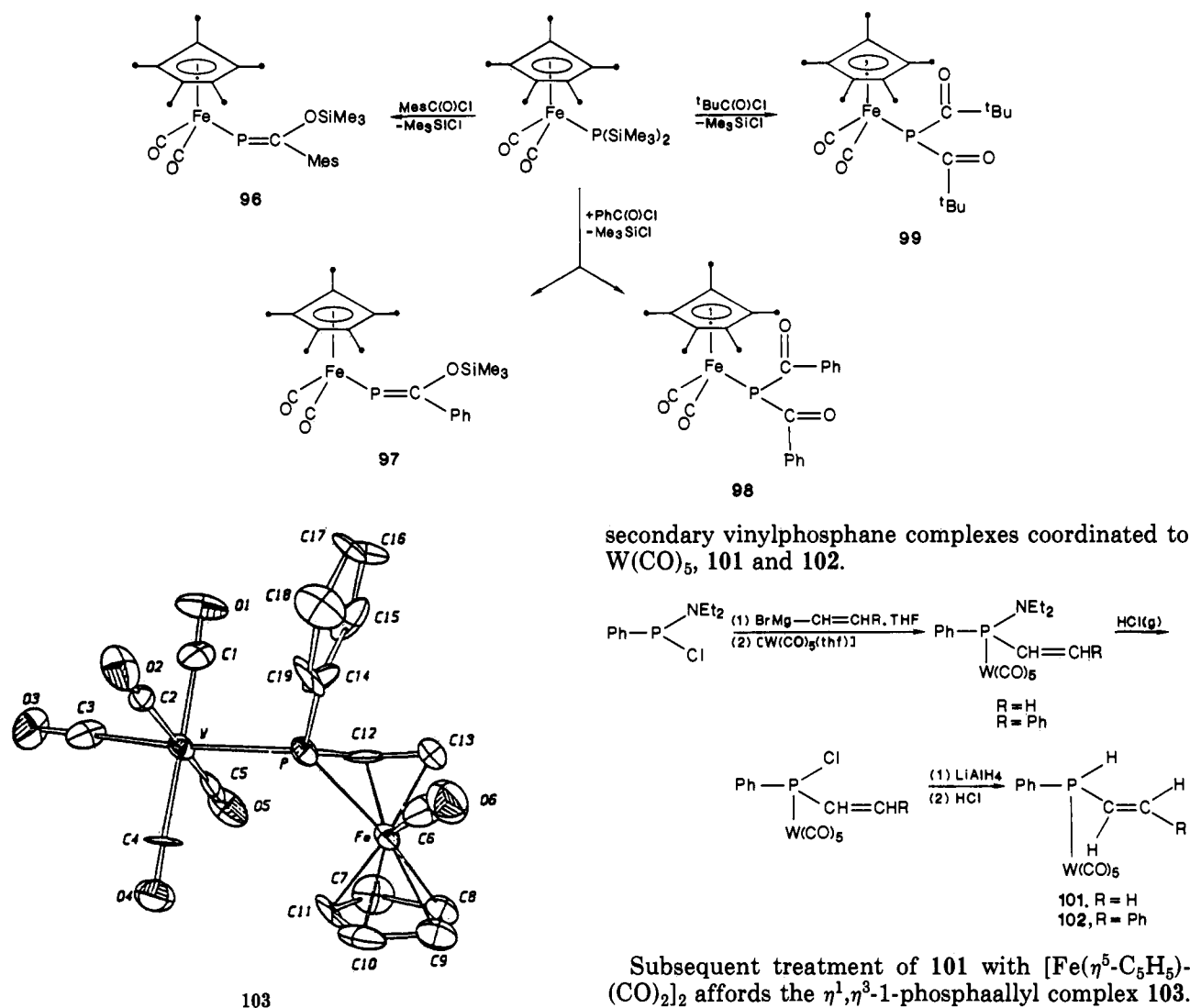
Figure 49. Structure of 103 in the crystal. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity.

SCHEME 3

100

R = Mes. Ph. ^{t}Bu
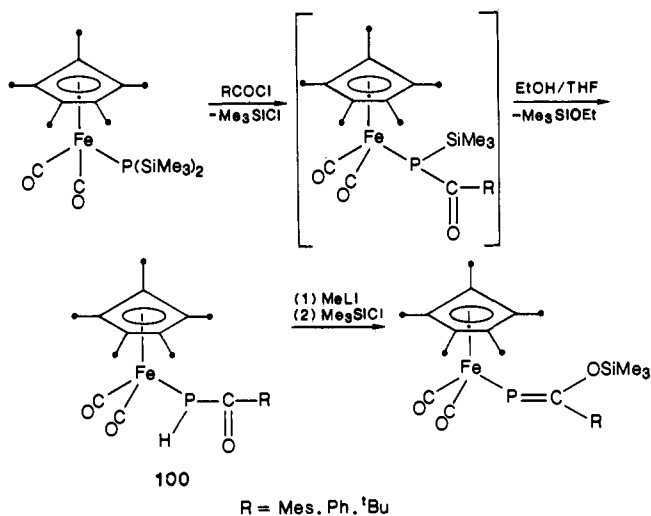
The 1-phosphaallyl ligand therefore acts as a bridging η^1,η^3 five-electron donor.

The elegant synthetic route devised by Mathey et al.[126,127] outlined below involves preparation of the stable

secondary vinylphosphane complexes coordinated to $W(CO)_5$, 101 and 102.

R = H
R = Ph

101. R = H
102. R = Ph

Subsequent treatment of 101 with $[Fe(\eta^5\text{-}C_5H_5)\text{-}(CO)_2]_2$ affords the η^1,η^3-1-phosphaallyl complex 103.

101 + [CpFe(CO)₂]₂ ⟶

103

Although sufficiently good crystals were not obtained for a full X-ray crystal structure analysis, nevertheless the data obtained furnished information about the stereochemistry of the complex (see Figure 49). The W–P–CH=CH$_2$ unit is approximately coplanar, the W and H^c are in cis positions, and the Fe–CO unit points in the opposite direction to C–H^c.
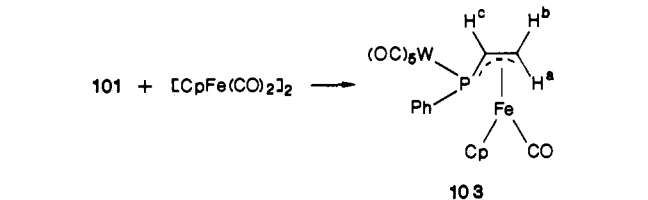
An analogous reaction with 102 led to the formation of three complexes, 104, 105, and 105a, which were

104
25%

105
10%

105a
3%

105
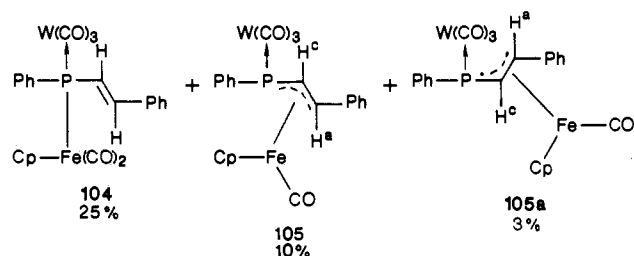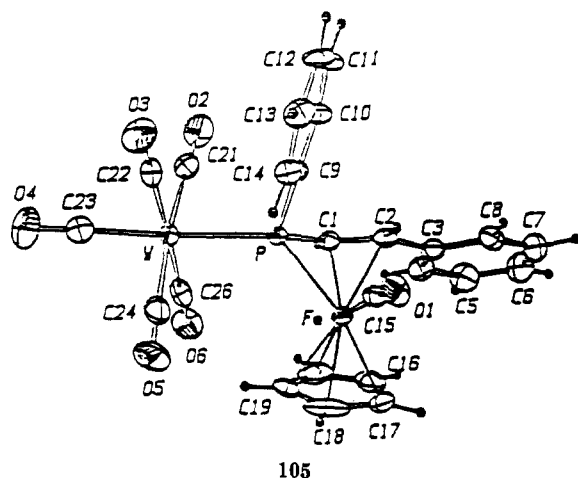
Figure 50. Molecular structure of 105. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity. Important bond distances (Å) and angles (deg): W–P = 2.511 (1), Fe–P = 2.270 (1), P–C(1) = 1.761 (5), P–C(9) = 1.819 (4), C(1)–C(2) = 1.380 (7), C(2)–C(3) = 1.489 (7), (W–C$_{eq}$) = 2.020 (3), W–C$_{ax}$ = 1.992 (6), (C–O)$_w$ = 1.158 (3), Fe–C(15) = 1.777 (6), C(15)–O(1) = 1.116 (6), (C–C)$_{Phe}$ = 1.385 (2), (C–C)$_{Cp}$ = 1.393 (4), Fe–C(Cp) = 2.056 (6)–2.098 (6); W–P–C(1) = 124.6 (2), W–P–C(9) = 111.7 (1), W–Pe–Fe = 130.11 (6), C(1)–P–C(9) = 106.5 (2), C(9)–P–Fe = 113.0 (1), P–C(1)–C(2) = 119.6 (4), C(1)–C(2)–C(3) = 126.4 (4), (C–C–C)$_{Phe}$ = 120.0 (1), (C–C–C)$_{Cp}$ = 108.0 (3).

separated by chromatography. Two of these, **105** and **105a**, are η^1,η^3-phosphaallyl complexes while the third complex, **104**, is a ferrio-substituted vinylphosphane. Brief irradiation of **104** gives further amounts of **105** and **105a**, which are in equilibrium at room temperature, possibly interconverting via a decoordination of the C=C double bond and subsequent 180° rotation of the vinyl unit around the P–C(vinyl) bond. The rate of equilibration is very slow, and **105** and **105a** can be separated by chromatography.

Complex **105** has the same stereochemistry as **103** as evidenced by a single-crystal X-ray diffraction study (Figure 50).

The short P–C(vinyl) bond (1.761 (5) Å) is similar to those found in η^5-phospholyl complexes and in the (1,3-diphosphaallyl)cobalt tricarbonyl complex referred to below.

B. η^3-1,3-Diphosphaallyl Metal Complexes

To date only few examples of this class of complexes have been described. Appel et al.[128] reported that the chlorophosphino-substituted methylenephosphane RP=CHPClR (R = 2,4,6-tri-*tert*-butylphenyl) reacts smoothly with [Na(Co(CO)$_4$)] in tetrahydrofuran to give the orange-brown (η^3-1,3-diphosphaallyl)cobalt tricarbonyl complex **106**, analogous to the long known η^3-allyl derivative.

106

R = 2,4,6-tri-*tert*-butylphenyl
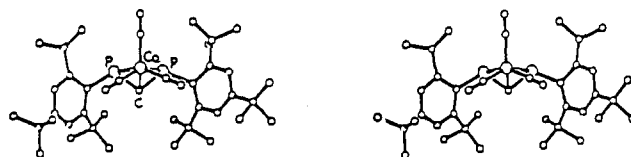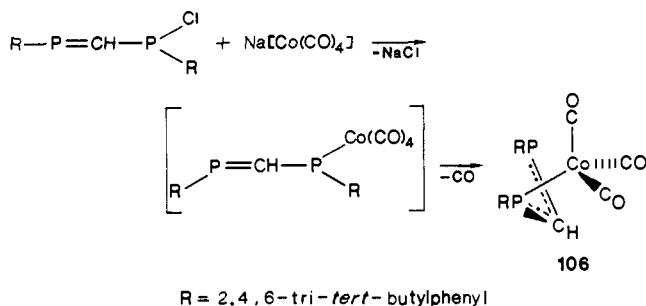
Figure 51. Stereograph of the crystal structure of **106**. Important bond distances (Å) and bond angles (deg) (standard deviations in parentheses): Co–P = 2.382 (2)–2.395 (2), P–C(allyl) = 1.769 (7)/1.791 (7), Co–C(allyl) = 2.034 (7), Co–C (carbonyl, basal) = 1.79 (1)–1.81 (1), Co–C (carbonyl, apical) = 184 (1); PCP = 1.018 (4), PCH = 129.
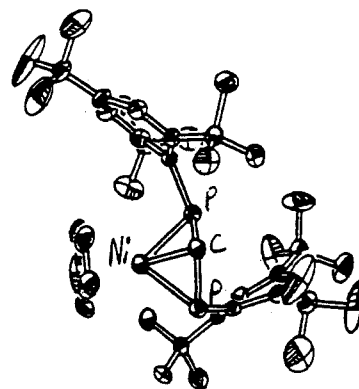
107

Figure 52. Molecular structure of **107**. Important distances (Å) and angles (deg): NiP(1) = 2.258 (2), NiP(2) = 2.303 (2), NiC(1) = 1.935 (5), NiC(2) = 2.162 (9), NiC(3) = 2.101 (8), NiC(4) = 2.087 (10), NiC(5) = 2.072 (8), NiC(6) = 2.144 (8), P(1)C(1) = 1.768 (6), P(2)C(1) = 1.750 (6); P(1)C(1)P(2) = 115.1 (3).

According to the X-ray structural analysis, complex **106** (Figure 51) is best described as a square pyramid having two P atoms and two CO ligands at the base and a third carbonyl group at the apex, with the allyl carbon atom below the basal plane pointing toward the cobalt center. Supporting information regarding the classification of the compound as involving a 1,3-diphosphaallyl ligand comes from the observations that (a) all three atoms of the PCP fragment are bonded to cobalt, (b) the C(1) atoms of the aryl moieties and the PCHP skeleton form a plane, and (c) the P–C distances (1.769 (7) and 1.791 (7) Å) are the same and lie between those of a P–C single bond and a P=C double bond.

Complex **106** has also been obtained independently by Nixon et al.[129] and Karsch et al.[130] from the reaction of the diphosphaallene RP=C=PR (R = 2,4,6-tri-*tert*-butylphenyl) with [CoH(CO)$_4$], e.g.
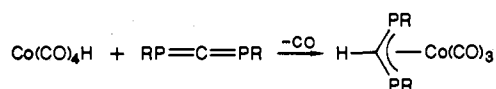
once again underlining the analogous behavior of allenes and diphosphaallenes.

Recently, two new nickel complexes containing the 1,3-diphosphaallyl ligand RPCHPR (R = 2,4,6-tri-*tert*-butylphenyl) have been described by Appel and co-workers.[131]

The complexes [Ni(η^5-C$_5$H$_5$)(η^3-RPCHPR)] (**107**) and [Ni(CO)$_2$(RPCHPR)]$_2$ (**108**) were obtained from RP=

108
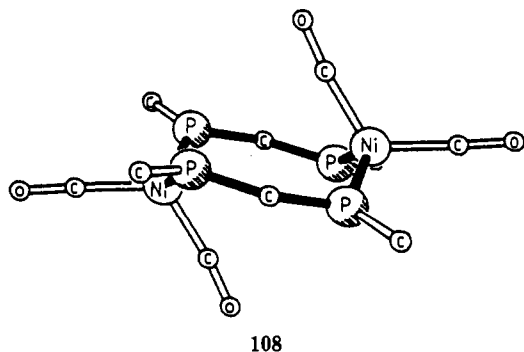
Figure 53. Molecular structure of 108. Important distances (Å) and angles (deg): Ni(1)P(1) = 2.214 (3), Ni(1)P(2a) = 2.212 (3), Ni(1a)P(2) = 2.212 (3), P(1)C(1) = 1.713 (9), C(1)P(2) = 1.722 (10); P(1)C(1)P(2) = 132.1 (6), Ni(1)P(1)C(1) = 121.5 (4), C(1)-P(2)Ni(1a) = 120.8 (3), Ni(1)P(1)C(10) = 133.5 (3), Ni(1a)P(2)-C(20) = 134.5 (3).

CHPClR by treatment with $K[Ni(\eta^5\text{-}C_5H_5)(CO)]$ and $[Ni(CO)_4]$, respectively
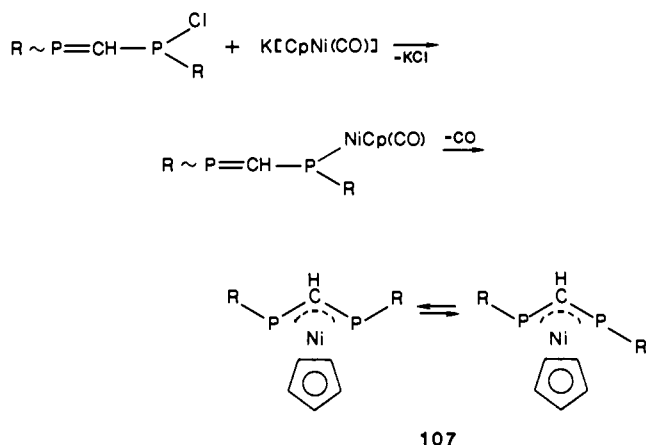
107
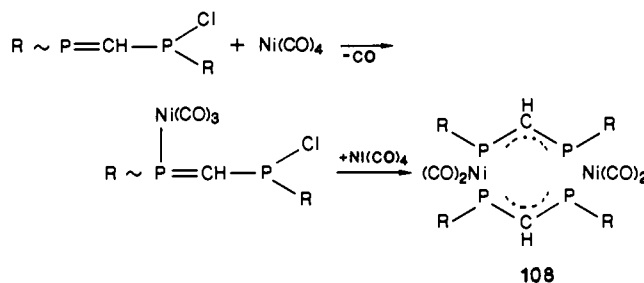
108

In the former case an unstable η^1-diphosphaallyl complex has been proposed on spectroscopic grounds. The structures of **107** and **108** elucidated by X-ray diffraction are shown in Figures 52 and 53.

The reaction of ArP=CHPClAr (Ar = 2,4,6-tri-*tert*-butylphenyl) with $[Na_2Fe(CO)_4]$ or treatment of its lithium salt with $[Fe(CO)_5]$ affords the (1,3-diphosph-aallyl)ferrate(1-)[133] **(109)** Condensation of **109** with
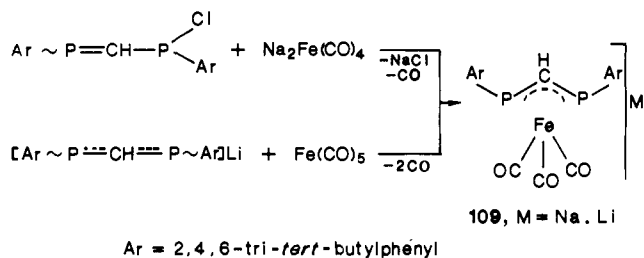
109, M = Na . Li

Ar = 2,4,6-tri-*tert*-butylphenyl

alkyl halides or chlorophosphanes gives either η^3,η^1- or
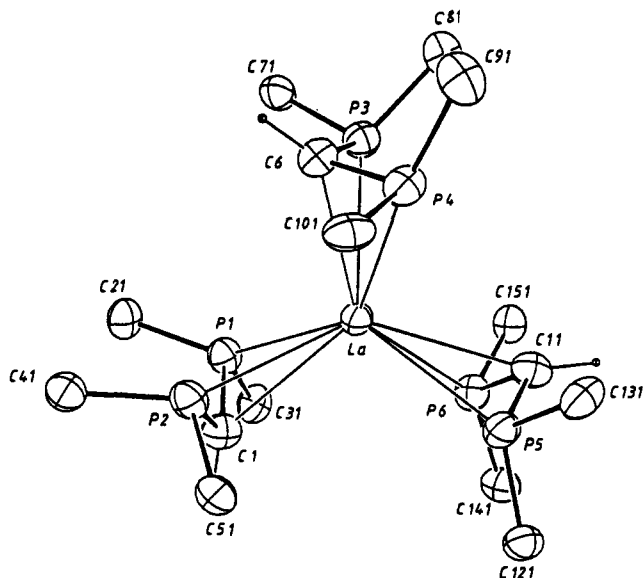
110

Figure 54. Molecular structure of 110 (ORTEP). Thermal ellipsoids are at the 50% probability level. H atoms have arbitary radii, and only the ipso-C atoms of the phenyl rings are shown. Selected bond lengths (Å) and angles (deg): La–P1 = 2.955 (1), La–P2 = 2.999 (1), La–P3 = 2.965 (1), La–P4 = 3.035 (1), La–P5 = 2.940 (1), La–P6 = 3.013 (1), La–C1 = 2.890 (5), La–C6 = 2.790 (4), La–C11 = 2.908 (5), C1–P1 = 1.771 (5), C1–P2 = 1.768 (5), C6–P3 = 1.778 (5), C6P4 = 1.764 (5), C11–P5 = 1.769 (5), C11–P6 = 1.780 (5); P1–C1–P2 = 115.9 (3), P3–C6–P4 = 111.2 (3), P5–C11–P6 = 113.9 (3).
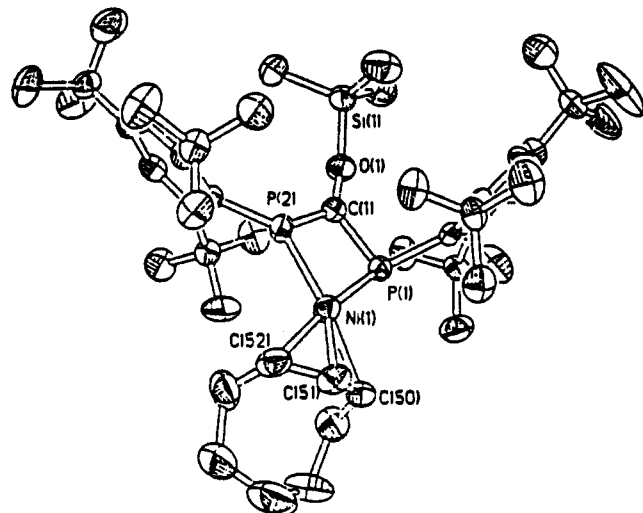
112

Figure 55. Molecular structure of 112. Important distances (Å): P(1)–C(1) = 1.78, P(2)–C(11) = 1.71, P(1)–Ni = 2.27, P(2)–Ni = 2.21, C(50)–Ni = 2.05, C(51)–Ni = 1.98, C(52)–Ni = 2.11, C-(50)–C(51) = 1.39, C(51)–C(52) = 1.39. Important angles (deg): P(1)–Ni–P(2) = 74.6, P(1)–Ni–C(52) = 170.8, P(2)–Ni–C(51) = 148.7, P(2)–Ni–C(50) = 164.1, P(1)–Ni–C(50) = 101.0, P(1)–Ni–C(51) = 136.1, P(2)–Ni–C(52) = 111.1, C(50)–C(51)–C(52) = 122.1.

η^2,η^1-1,3-diphosphapropene iron complexes. Protolysis with HCl gives a stable 1,3-diphosphapropene iron complex via a hydrido iron species.

Karsch et al.[132] have recently described the first example of a homoleptic lanthanum complex [La-{(Ph₂P)₂CH}₃] **(110)** in which the three diphosphino-methanide ligands are coordinated to the metal as η^3-heteroallyl analogues. Complex **110** is made from $LaCl_3$ and $K[(PPh_2)_2CH]$ in tetrahydrofuran. A sin-

SCHEME 4[a]

113   114

R = p -CH$_3$OC$_6$H$_4$
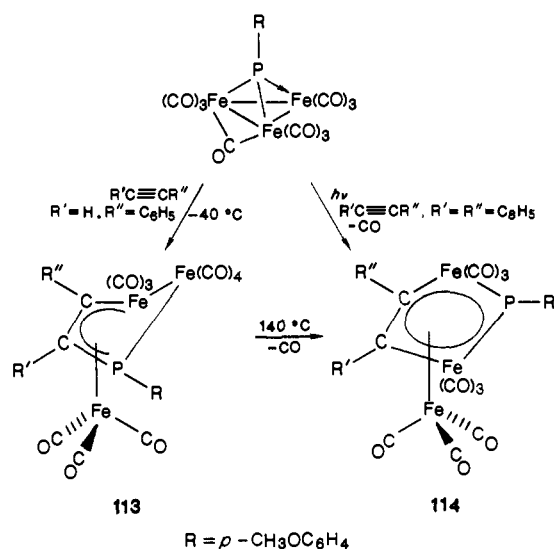
[a] Distances in the cyclic ligands (Å): (113) CC = 1.38 (1), CFe = 2.005 (6), FeFe = 2.833 (3), FeP = 2.240 (3), PC = 1.758 (7); (114) CC = 1.419 (5), CFe = 1.989 (3), FeP = 2.170 (2), PFe = 2.167 (2), FeC = 1.993 (4).

gle-crystal X-ray structure analysis of the toluene solvate (Figure 54) reveals that the La atom is trigonally planar coordinated by the Ph$_2$PCHPPh$_2$ ligands, and the overall structure suggests ionic character in the bonds between the metal and the diphosphino-methanide ligands.

Reaction of [Ni(COD)$_2$] with the 1,3-diphospha-propene 111 affords a catalyst that in situ polymerizes ethene at 70–100 °C/30 bar to give linear polyethylene ($M_r \approx 0.8 \times 10^6$) at activities of >1000 mol of ethene per mol of nickel per hour.[134]

The stoichiometric reaction gives 112, which also acts as a catalyst. The X-ray structure determination

111

112
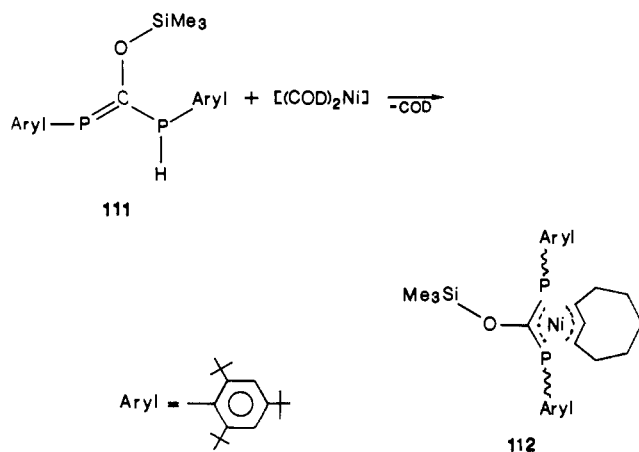
(Figure 55) reveals that the ligand is $\eta^1\eta^2$-coordinated to the nickel; however, in solution the complex contains an η^3-1,3-diphosphaallyl ligand, indicating that the following equilibrium exists

117

Figure 56. Structure of 117. ORTEP thermal ellipsoids are drawn at the 50% probability level. Methyl groups (and isotropic atoms) are drawn with arbitrary radii without H atoms. Important bond lengths (Å) and bond angles (deg): Mo–P1 = 2.268 (2), P1–C1 = 1.766 (6), P2–C1 = 1.685 (6), P1–C2 = 1.867 (6), P2–C8 = 1.867 (6); Mo–P1–C1 = 120.8 (2), Mo–P1–C2 = 138.9 (2), C2–P1–C1 = 100.3 (3), P1–C1–P2 = 125.1 (3), C1–P2–C8 = 103.4 (3).

VIII. Heterobutadiene Complexes

A. 1-Phospha-4-ferrabutadiene Complexes

Insertion of an alkyne into one of the P–Fe bonds of the phosphinidene complex [Fe$_3$(CO)$_{10}$PR] (R = p-MeOC$_6$H$_4$) proceeds remarkably smoothly and regios-electively to yield the first example of this class of compounds.[135] The reaction mechanism presumably involves scission of a P–Fe bond followed by addition of the nucleophilic Fe$_2$PR group to the alkyne.

The distances and angles in 113 suggest that the essentially planar FeCCP fragment can be described as a heterobutadiene ligand (see Scheme IV). Interestingly, 113 can be viewed as an arachno system that can be decarbonylated to the nido cluster 114, and this skeletal transformation has been likened to the behavior of carboranes.

B. 1,3-Diphospha-4-metallabutadiene Complexes

The analogy between free 1,3-diphospha-4-metal-labutadienes (115) and their metal complexes (116) on

115

116
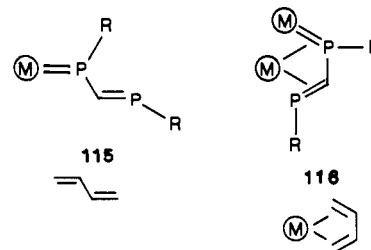
the one hand and free butadiene and its metal complexes on the other (see Scheme 4) has been dramatically confirmed by recent studies of Karsch et al.[136]

The green air-stable crystalline complex 117 was obtained from the 2-chlorophosphino-substituted phosphaalkene as shown below, and its structure was established as an s-trans-heterobutadiene by a single-

crystal X-ray structure analysis (Figure 56).

117. M = Mo; R = 2,4,6-ᵗBu₃C₆H₂
118. M = W; R = 2,4,6-ᵗBu₃C₆H₂
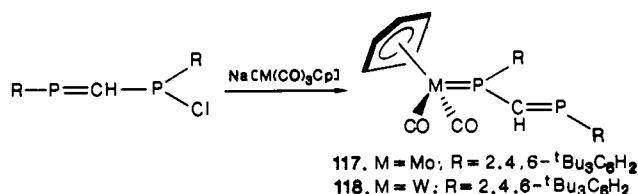
The 1,3-diphosphaallyl fragment is bonded to the metal "end on" through the planar coordinated phosphorus P(1) while a (noncrystallographic) mirror plane passes through Mo, P(1), C(1), and P(2).

The P–C bond lengths differ significantly, with P-(1)–C(1) corresponding to a slightly shortened single bond and P(2)–C(1) to a double bond. As expected, the Mo–P bond length is similar to other Mo–P double bonds and is much shorter than Mo–P single bonds. The tungsten analogue reveals the expectedly large $^1J_{WP}$ coupling constant (638 Hz) reflecting the high s character of the W–P bond.

Of special interest is the interaction of 118 (M = W) with [Fe₂(CO)₉] to afford 119, which is clearly structurally related to the well-known [Fe(CO)₃(η⁴-butadiene)] complex.

118

119

R = 2,4,6-ᵗBu₃C₆H₂
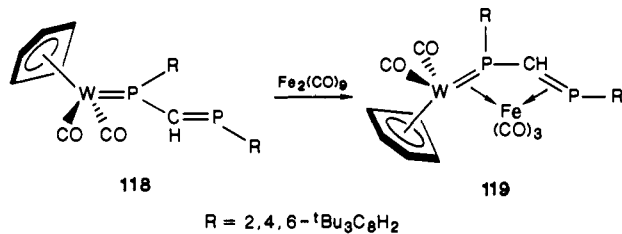
The single-crystal X-ray structural analysis reveals the almost planar arrangement of the framework WP-(1)C(1)P(2) and the near equivalence of the two P–C bond lengths, supporting the view that 119 is a heterobutadiene complex (Figure 57).

C. η⁴-1-Phospha-2-ferracyclobutadiene Complexes

These unusual complexes have been reported recently by Huttner and co-workers[137] via dehalogenation of μ-(tert-butylchlorophosphido)hexacarbonyl-μ-chlorodiiron(Fe–Fe) by Zn/Mg in the presence of alkynes.

121

120

R	R'
H	ᵗC₄H₉ (120)
H	SiMe₃
H	(CH₂)₄CH₃
C₂H₅	C₂H₅
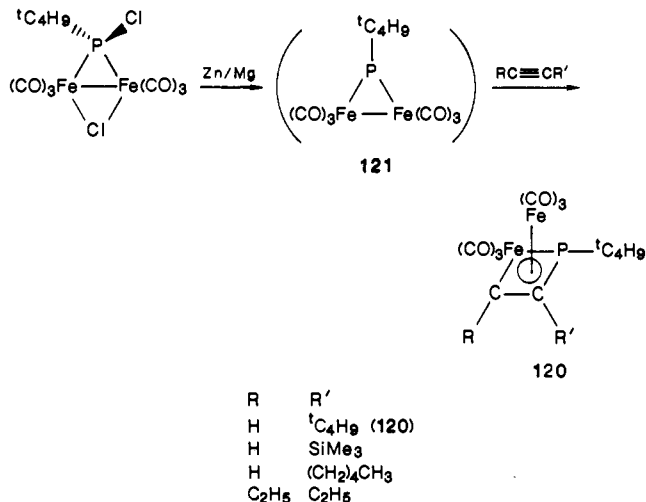
The cluster complexes 120 can be formulated as Fe-(CO)₃ derivatives of an organometallic 4π-ligand of the
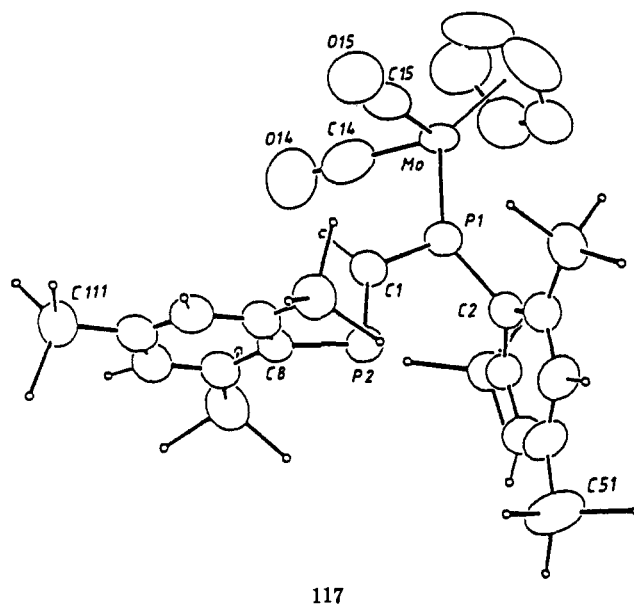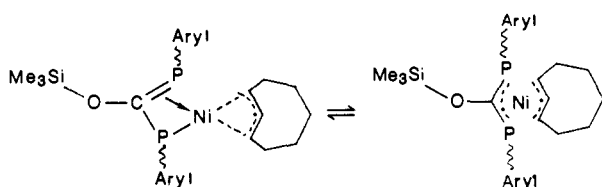

119
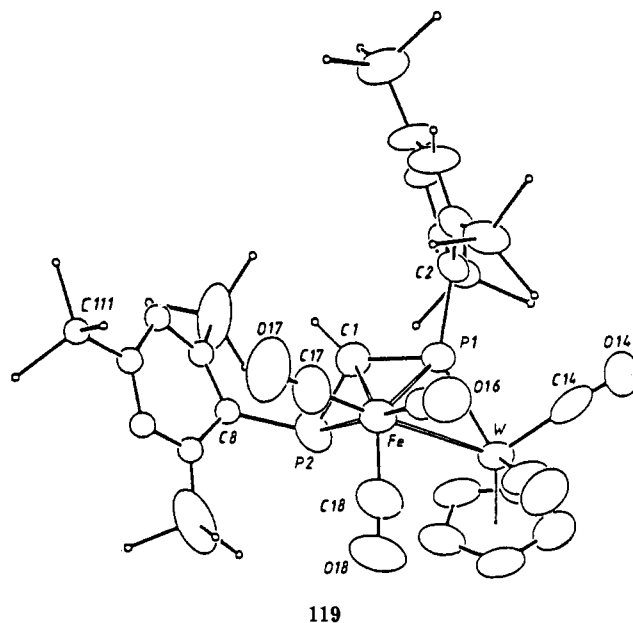
Figure 57. Structure of 119. ORTEP thermal ellipsoids are drawn at the 50% probability level. Methyl groups (and isotropic atoms) are drawn with arbitrary radii without H atoms. Important bond lengths (Å) and bond angles (deg): W–P1 = 2.365 (3), P1–C1 = 1.74 (1), P2–C1 = 1.76 (1), P1–C2 = 1.88 (1), P2–C8 = 1.86 (2), Fe–W = 2.980 (2), Fe–P1 = 2.295 (3), Fe–C1 = 2.11 (1), Fe–P2 = 2.441 (4); W–P1–C1 = 117., (4), W–P1–C2 = 140.4 (4), C2-P1–C1 = 100.5 (5), P1–C1–P2 = 120.3 (6), C1–P2–C8 = 101.3 (6).

1-phospha-2-ferracyclobutadiene type. A proposed intermediate in this reaction is the metal–organic 2π-system (OC)₃Fe-PR-Fe(CO)₃ (121).

The structure of 120 has been confirmed by a single-crystal X-ray diffraction study (Figure 58), and the C–P (1.750 (6) Å) and C–C (1.40 (1) Å) bond lengths within the ring are in good agreement with expectations based on bond orders. It is particularly interesting to see the analogy between 120 and the (cyclobutadiene)iron tricarbonyl analogue, particularly in view of the isolobal relationships

RC ⟷ P ⟷ Fe(CO)₃⁻ ⟷ PR⁺

Similarly, the cluster compound [(μ₃-(Mes)P)Fe₃-(CO)₁₀] reacts photochemically with diphenylacetylene to yield to [η⁵-[(Mes)PC(Ph)C(Ph)Fe(CO)₃Fe(CO)₃]-Fe(CO)₃] (122), which on thermal activation rearranges to [η⁵-[(Mes)PFe(CO)₃C(Ph)C(Ph)Fe(CO)₃]Fe(CO)₃] (123). The structure of 123 is shown in Figure 59.[138]

123
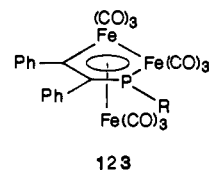
These types of reactions seem to be general, and recently Carty and co-workers[139] reported that [Ru₄-(CO)₁₃(PPh)], in which the phosphinidine group is coordinated between the wings of a Ru₄ butterfly, undergoes a similar skeletal expansion with Ph₂C₂ (see Scheme 5) to afford 124 (Figure 60).

IX. Appendix (Added in Proof)

Since submission of this manuscript several important studies have been carried out involving unsaturated

120

C–C	1.40 (1) Å
C–Fe	1.958 (7) Å
Fe–P	2.183 (3) Å
P–C	1.750 (6) Å
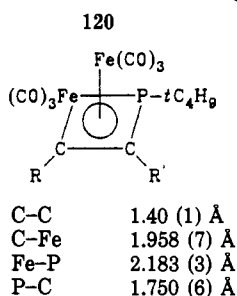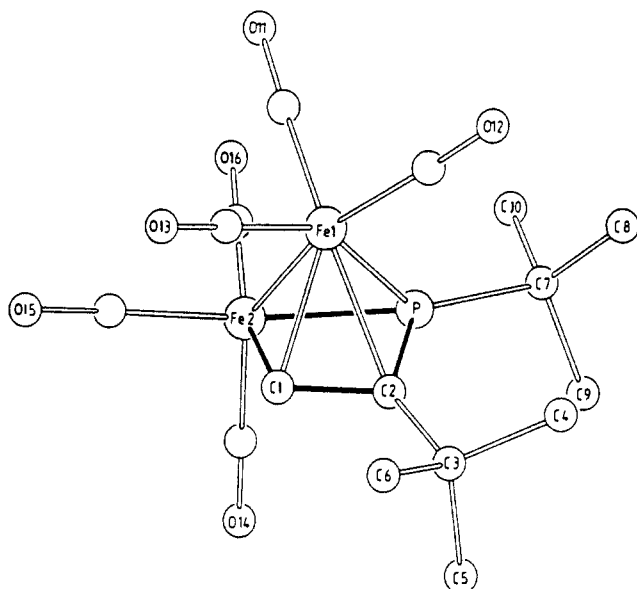
Figure 58. Structure of 120.

123
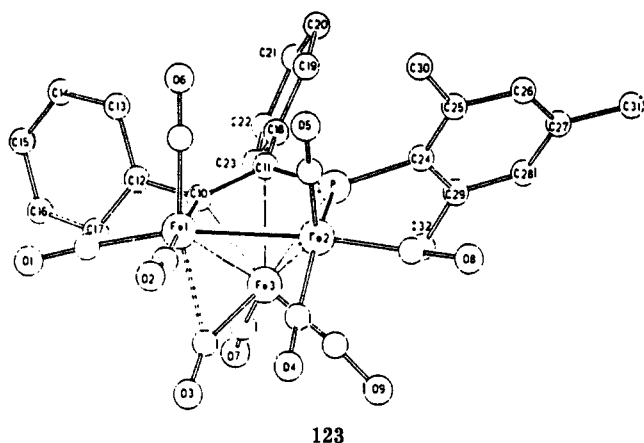
Figure 59. Structure of 123. Distances within the ring (Å): PC = 1.77 (2), CC = 1.44 (2), CFe = 2.02 (2), FeFe = 2.681 (5), FeP = 2.116 (6).

SCHEME 5

124
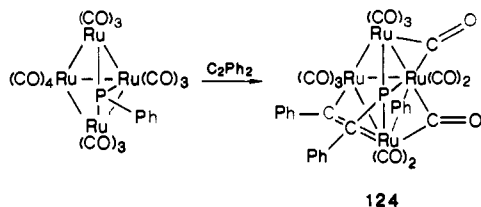
organophosphorus compounds and their interaction with transition metals. An important Euchem-sponsored international meeting PSIBLOCS (1st International Conference on Phosphorus, Silicon, Boron and Related Elements in Low Coordinated States) held in Palaiseau, Paris, in August 1988 clearly confirmed the

124
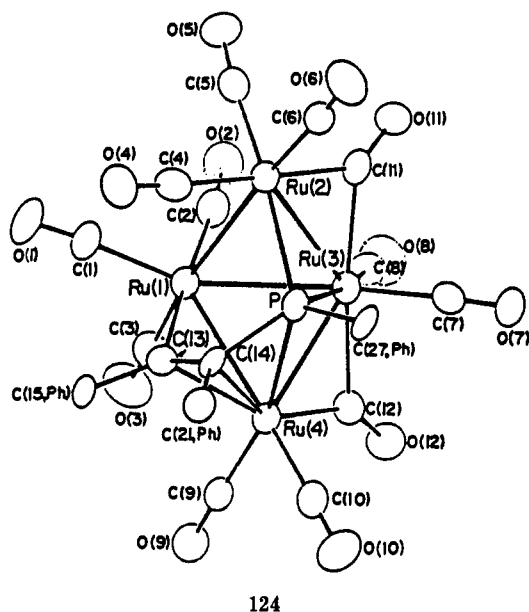
Figure 60. Perspective view of the structure of one independent molecule of $Ru_4(CO)_{10}(\mu\text{-}CO)_2[P(Ph)C(Ph)C(Ph)]$ (124) showing the atomic numbering. Structural parameters for molecules A and B are virtually identical. Important bond lengths (Å) and angles (deg) are as follows: Ru(1)–Ru(2) = 2.890 (1), Ru(1)–Ru(3) = 2.879 (1), Ru(1)–Ru(4) = 2.881 (1), Ru(2)–Ru(3) = 2.878 (1), Ru(3)–Ru(4) = 2.762 (1), Ru(2)···Ru(4) = 4.926 (1), C(13)–C(14) = 1.385 (12), Ru(1)–C(13) = 2.168 (8), Ru(4)–C(13) = 2.270 (8), Ru(4)–C(14) = 2.311 (9) Å; C(14)–C(13)–C(15) = 119.7 (5), C-(13)–C(14)–C(21) = 125.3 (5).

continuing rapid development of the topic of this review article. This appendix highlights some important results which have appeared during 1988.

As mentioned in sections IIIB and IIIC cyclodimerization of $Bu^tC\equiv P$ in the coordination sphere of a metal atom affords either 1,3-diphosphacyclobutadiene complexes (M = Co, Rh) or 1,3-diphosphabicyclo[1.1.0]butanediyl complex (M = Zr). Oxidative coupling of two phosphaalkynes at the metal center to form 1,4-diphospha-2-metallacyclopentadienes as intermediates was postulated.[43] Such species have now been isolated and characterized by Binger and co-workers.[141]

Treatment of $[RhCl(C_2H_4)_2]_2$ with Me_3P and Bu^tCP in a molar ratio of 1:4:4 at 0 °C resulted in a 1:2 mixture of the two rhodium complexes (124 and 125), both of which have been fully characterized by single crystal X-ray studies as a chlorobis(trimethylphosphane)-1,4-diphospha-2-rhodacyclopentadiene and the corresponding 1,3-diphosphacyclobutadiene derivative, respectively.

124

125
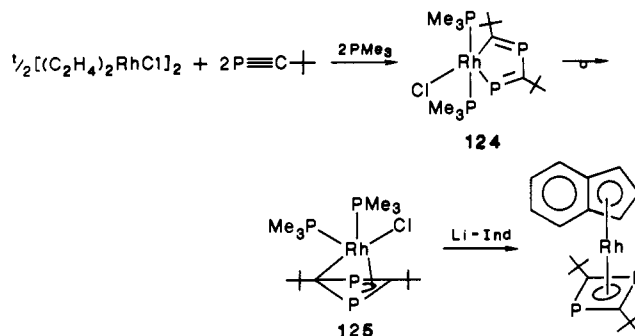
The molecular structures of 124 and 125 are given in Figure 61.
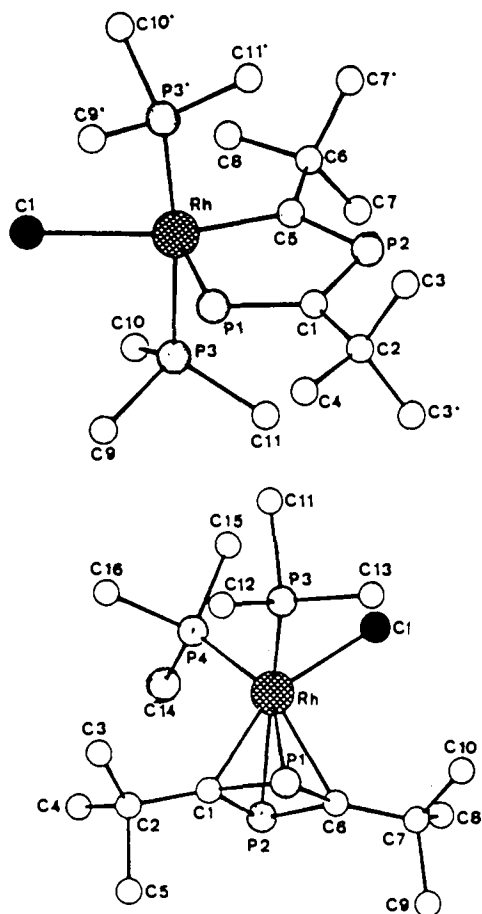
Figure 61. (Top) Molecular structure of **124**. Selected bond lengths (Å) and bond angles (deg): Rh–P1 2.235 (1), Rh–P3 2.345 (1), Rh–C1 2.456 (1), Rh–C5 1.980 (3), P1–C1 1.685 (4), P2–C1 1.802 (3), P2–C5 1.710 (4) C1–C2, 1.532 (5), C5–C6 1.549 (5); P3–Rh–P3* 171.6 (1). (Bottom) Molecular structure of **125**. Selected bond lengths (Å) and angles (deg): Rh–C1 2.473 (1), Rh–P1 2.381 (1), Rh–P2 2.397 (1), Rh–P3 2.325 (1), Rh–P4 2.334 (1), Rh–C1 2.179 (3), Rh–C6 2.307 (3), P1–C1 1.802 (3), P1–C6 1.766 (3), P2–C1 1.819 (3), P2–C6 1.792 (3); P1–Rh–P2 69.2 (1), P1–Rh–C1 46.3 (1), P1–Rh–C6 44.2 (1), C1–Rh–P2 46.5 (1), C6–Rh–P2 44.7 (1), C1–Rh–C6 63.0 (1), P1–C1–P2 97.1 (1), C1–P2–C6 81.1 (1), P2–C6–P1 99.3 (1), C6–P1–C1 82.3 (1).

Of special importance is the observation that **124** slowly rearranges to **125** in solution at room temperature (40% conversion in 24 h). Treatment of **125** with indenyllithium leads to the known complex [Rh(η^5-C$_9$H$_7$)(η^4-P$_2$C$_2$Bu$^t_2$)], and methyl- and allylmetal complexes are obtained from **125** by reaction with RMgBr (R = Me, allyl).[141b]

The reported formation by Barron and Cowley[58] of the first example of a 1,3,5-triphosphabenzene metal complex has not been confirmed in a reinvestigation by Binger and co-workers.[141b] Instead a low yield (ca. 5%) of the dimolybdenum complex (**126**) containing η^4-1,3-diphosphacyclobutadiene rings was obtained among other products, and its structure which was established by a single crystal X-ray diffraction study is

126
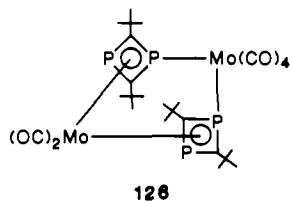
In related work, Binger et al.[142] have obtained the first examples of bis(cyclopentadienyl)-1-metalla-3-phosphaindene (**127**), (M = Ti, Zr), by heating the corresponding bis(cyclopentadienyl)diphenylmetal complexes with an excess of Bu^{t}C≡P at 80 °C.
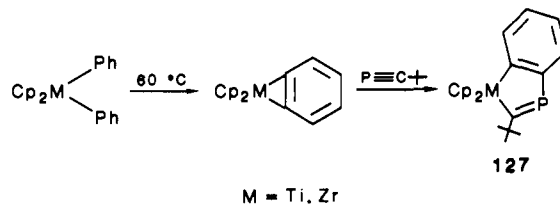
M = Ti, Zr

The same authors synthesized the η^2-phosphaalkyne complexes **128** (M = Ti, Zr), and a single crystal X-ray diffraction study has been carried out on the titanium complex (d(P=C) = 1.636 Å).[141b] Complex **128** readily reacts with unsaturated organic compounds as shown

M = Ti, Zr

128
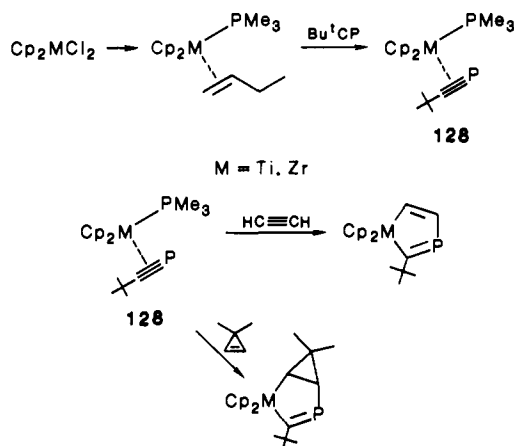
The first diphosphaallyl system coordinated to two metal centers has recently been described by Appel et al.,[143] and the molecular structure of [FeNi(η^5-

R = 2.4.6-Bu$^t_3$C$_6$H$_2$. Cp = η-C$_5$H$_5$
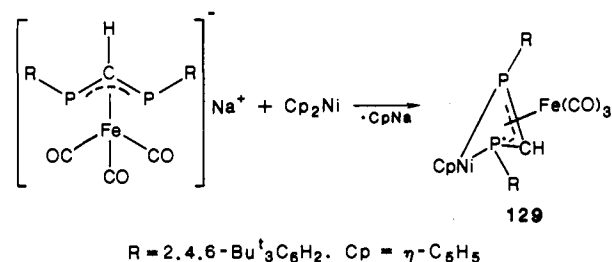
C$_5$H$_5$)(η^3-RPCHPR)(CO)$_3$] (**129**) (R=Bu$^t_3$C$_6$H$_2$) is shown in Figure 62.

Mathey et al. have extended their original syntheses[81] of the phosphorus–carbon double bond by cocondensing carbene complexes [M(CO)$_5$(CR^{1}R^2)] with a transient terminal phosphinidene complex [M(CO)$_5$PR], (M = Cr, W).[144] The phosphaalkene complex [Cr(CO)$_5$-(Ph$_2$C=PPh)W(CO)$_5$] is stable as a monomer. The (1,2-dihydrophosphete)(P–W)(pentacarbonyltungsten) complex (**130**) made by a similar route has an unusually long bond between the sp^3 ring carbon and phosphorus (ca. 1.90 Å) and behaves as a masked 1-phosphadiene complex
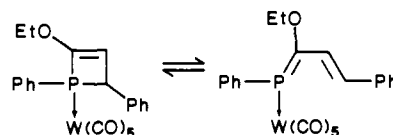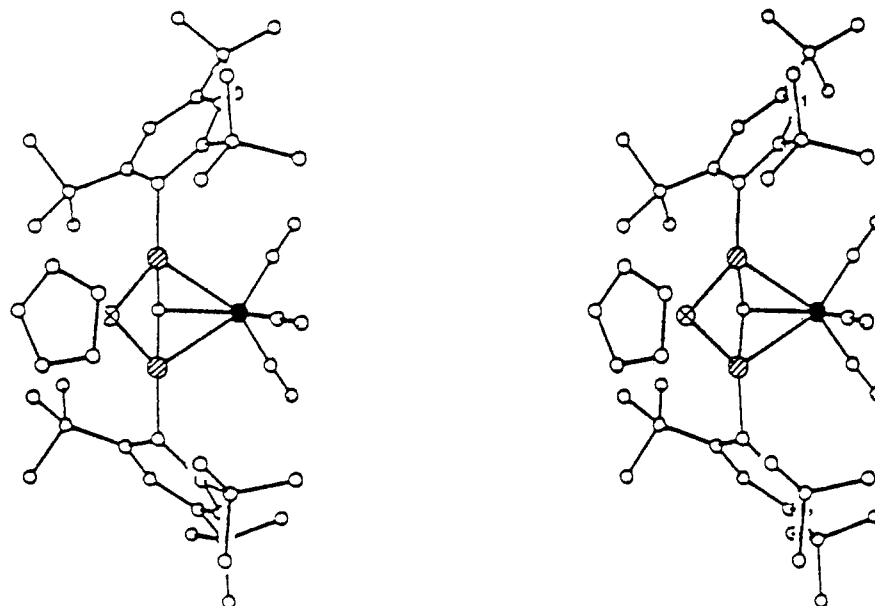
Figure 62. Stereoprojection of the molecular structure of **129.** ● Fe, ⊗ Ni, ○ P. Important distances (Å) and angles (deg) (standard deviations in parentheses): Fe-P 2.310 (2)/2.307 (2), Fe-C(allyl) 2.025 (7), P-C(allyl) 1.760 (7)/1.768 (7), Ni-P 2.194 (2)/2.201 (2), PCP 91.1 (3), PFeP 66.1 (1), PNiP 69.9 (1); dihedral angle PCP/PNiP 35.1.
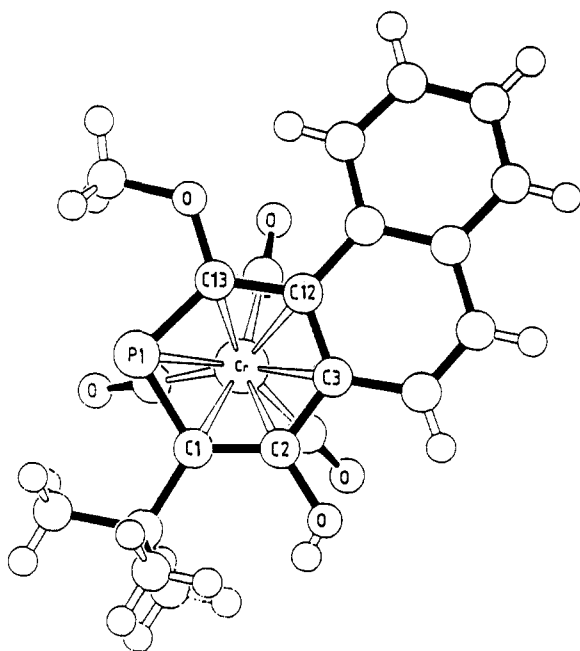
Figure 63. Structure of **131** (R = Me). Projection onto the plane of the phosphinine ring. Important bond lengths (Å): Cr-P1 2.4591 (4), Cr-C$_{heterocycle}$ 2.290 (1) (mean value), Cr-C$_{carbonyl}$ 1.836 (2) (mean value), C1-P1 1.768 (1), C13-P1 1.759 (1), C1-C2 1.400 (2), C2-C3 1.438 (2), C3-C12 1.428 (2).

At 100 °C the expected [4+2] cycloadducts with N-phenylmaleimide, dimethyl acetylenedicarboxylate, and benzaldehyde are obtained.[145]

An interesting example of the annelation of carbene ligands by Bu^{t}C≡P to afford a functionalized phosphaarene–metal complex (Figure 63, **131**) (subsequently the free phosphaarene) has been recently described by Dötz, Regitz, and co-workers.[146]

131. R = Me; Et
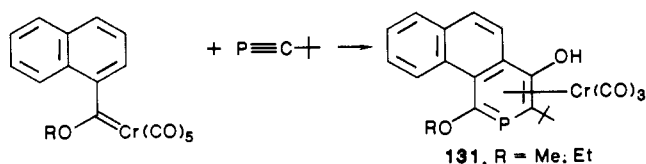
The paramagnetic 16-electron sandwich complex [Cr(η^5-C$_2$R$_2$P$_3$)$_2$] (**132,** R = Bu^t) has been recently synthesized by Bartsch, Hitchcock, and Nixon.[147] The structure is isomorphous with the iron analogue (**39**), however the Cr–ring distances are significantly longer.

A series of half-sandwich compounds of the type [Rh(η^5-C$_2$R$_2$P$_3$)L$_2$] (R = Bu^t, L = PR$_3$, 1,5-cyclooctadiene) have been reported[148] and structurally characterized by NMR and single crystal X-ray crystallographic studies.

X. Acknowledgments

XI. References

(1) Appel, R.; Knoll, F.; Ruppert, I. Angew. Chem., Int. Ed. Engl. 1981, 20, 731.
(2) Fluck, E. Top. Chem. 1980, 10, 193.
(3) Becker, G.; Becker, W.; Mundt, O. Phosphorus Sulfur 1983, 14, 267.
(4) Ishmaeva, E. A.; Patsanovskii, I. I. Russ. Chem. Rev. (Engl. Transl.) 1985, 54, 243.
(5) Markovskii, L. N.; Romanenko, V. D. J. Gen. Chem. USSR (Engl. Transl.) 1986, 56, 221.
(6) Markovskii, L. N.; Romanenko, V. D. J. Gen. Chem. USSR (Engl. Transl.) 1986, 56, 2153.
(7) Markovskii, L. N.; Romanenko, V. D. J. Gen. Chem. USSR (Engl. Transl.) 1987, 57, 1.
(8) Weber, B.; Regitz, M. In Methoden Org. Chem. (Houben-Weyl) 1982, 1, 28.
(9) Lutsenko, I. E. Z. Chem. 1984, 345.
(10) Schmidt, H.; Issleib, K.; Wiss, Z. M. Naturwiss. Rundsch. 1983, 32, 41.
(11) Markovskii, L. N.; Romanenko, V. D.; Ruban, A. V. Sov. Sci. Rev. Sect. B 1984, 6, 270.
(12) Kroto, H. W. Chem. Soc. Rev. 1982, 11, 435.

(13) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* 1985, *24*, 924.
(14) Mathey, F. *Nouv. J. Chim.* 1987, *11*, 585.
(15) Burckett-St. Laurent, J. C. T. R.; King, M. A.; Kroto, H. W.; Nixon, J. F.; Suffolk, R. J. *J. Chem. Soc., Dalton Trans.* 1983, 755.
(16) Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* 1978, *162*, C35. Seyferth, D.; Merola, J. S.; Henderson, R. S. *Organometallics* 1982, *1*, 859.
(17) Burckett-St. Laurent, J. C. T. R.; Hitchcock, P. B.; Kroto, H. W.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* 1981, 1141.
(18) Meidine, M. F.; Nixon, J. F., unpublished results.
(19) Al-Resayes, S. I.; Klein, S. I.; Kroto, H. W.; Meidine, M. F.; Nixon, J. F. *J. Chem. Soc., Chem. Comun.* 1983, 930.
(20) Burckett-St. Laurent, J. C. T. R.; Hitchcock, P. B.; Kroto, H. W.; Meidine, M. F.; Nixon, J. F. *J. Organomet. Chem.* 1982, *288*, C82.
(21) Bartsch, R.; Nixon, J. F.; Sarjudeen, N. *J. Organomet. Chem.* 1985, *294*, 267.
(22) Becker, G.; Herrmann, W. A.; Kalcher, W.; Kriechbaum, G. W.; Pahl, C.; Wagner, C. J.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* 1983, *22*, 413; *Suppl.*, 501.
(23) Al-Resayes, S. I.; Nixon, J. F., unpublished. Al-Resayes, S. I. D.Phil. Thesis, University of Sussex, 1986.
(24) Bartsch, R.; Hitchcock, P. B.; Meidine, M. F.; Nixon, J. F. *J. Organomet. Chem.* 1984, *266*, C41.
(25) Meidine, M. F.; Meir, C. J.; Morton, S.; Nixon, J. F. *J. Organomet. Chem.* 1985, *297*, 255.
(26) Hitchcock, P. B.; Meidine, M. F.; Nixon, J. F. *J. Organomet. Chem.* 1987, *333*, 337.
(27) Al-Resayes, S. I.; Hitchcock, P. B.; Meidine, M. F.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* 1984, 1080. *J. Organomet. Chem.* 1988, *341*, 457.
(28) Meidine, M. F.; Nixon, J. F.; Mathieu, R. *J. Organomet. Chem.* 1986, *314*, 307.
(29) Al-Resayes, S. I.; Hitchcock, P. B.; Nixon, J. F.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* 1985, 365.
(30) Hitchcock, P. B.; Maah, M. J.; Nixon, J. F.; Zora, J. A.; Leigh, G. J.; Bakar, M. A. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 474.
(31) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Weber, U.; Westerhausen, M. *Nova. Acta Leopold.* 1985, *59*, 55.
(32) Becker, G., personal communication.
(33) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Hillenbrand, U.; Westerhausen, M. *Phosphorus Sulfur* 1987, *30*, 349.
(34) Uhl, G.; Hey, E.; Becker, G.; Weller, F.; Dehnicke, K.; *Z. Anorg. Allg. Chem.* 1983, *497*, 213.
(35) Becker, G.; Becker, W.; Mundt, O. *Phosphorus Sulfur* 1983, *14*, 267.
(36) Hitchcock, P. B.; Maah, M. J.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* 1987, 658.
(37) Al-Resayes, S. I.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* 1987, 928.
(38) Ziegler, M. L.; Balles, R.; Nuber, B.; Becker, G.; Schmidt, H.; Kanellakopulos, B.; Powietzka, B. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 900.
(39) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 776.
(40) Kee, T. P.; Gibson, V. C.; Clegg, W. *J. Organomet. Chem.* 1987, *325*, C14.
(41) Wagner, O.; Maas, G.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 1257 (personal communication, Sept 1987.)
(42) Hitchcock, P. B.; Maah, M. J.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* 1986, 737.
(43) Binger, P.; Milczarek, R.; Mynott, R.; Regitz, M.; Rösch, W. *Angew. Chem., Intl. Ed. Engl.* 1986, *25*, 644. Binger, P.; Milczarek, R.; Mynott, R.; Kruger, C.; Tsay, Y. H.; Raabe, E.; Regitz, M. *Chem. Ber.* 1988, *121*, 637.
(44) Maah, M. J.; Nixon, J. F., unpublished results. Maah, M. J. D.Phil. Thesis, University of Sussex, 1987.
(45) Binger, P., personal communication, 1987.
(46) Binger, P.; Milczarek, R.; Mynott, R.; Regitz, M. *J. Organomet. Chem.* 1987, *323*, C35.
(47) Hitchcock, P. B.; Maah, M. J.; Nixon, J. F.; Woodward, C. *J. Chem. Soc., Chem. Commun.* 1987, 844.
(48) Green, M.; Hitchcock, P. B.; Maah, M. J.; Nixon, J. F., to be published.
(49) Binger, P.; Biedenbach, B.; Kruger, C.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 764.
(50) Zenneck, U., personal communication, Sept 1987. Driess, M.; Hu, H.; Pritzkow, H.; Regitz, M.; Rösch, W.; Schäufele, H.; Zenneck, U. *J. Organomet. Chem.* 1987, *334*, C35.
(51) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Weeber, U.; Westerhausen, M. *Nova Acta Leopold.* 1985, *59*, 55.
(52) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Hildebrand, V.; Westerhausen, M. *Phosphorus Sulfur* 1987, *30*, 349.
(53) Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* 1987, 1146.
(54) Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Organomet. Chem.* 1988, *340*, C37.
(55) Bartsch, R.; Pickett, C. J.; Nixon, J. F.; Parish, R. V.; Suffolk, R. J., unpublished results.
(56) Bartsch, R.; Hitchcock, P. B.; Meidine, M. F.; Nixon, J. F.; Sillett, G. J. D. *J. Chem. Soc., Chem. Commun.*, in press.
(57) Milczarek, R.; Rüsseler, W.; Binger, P.; Jonas, K.; Angermund, K.; Krüger, C.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 908.
(58) Barron, A. R.; Cowley, A. H. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 907.
(59) Schoeller, W. W.; Niecke, E. *J. Chem. Soc., Chem. Commun.* 1982, 569.
(60) Thomson, C. *J. Chem. Soc., Chem. Commun.* 1977, 322.
(61) Van der Knaap, T. A.; Klebach, T. C.; Visser, F.; Bickelhaupt, F.; Ros, P.; Baerends, E. J.; Stam, C. H.; Konijn, M. *Tetrahedron* 1984, *40*, 765.
(62) Gudat, D.; Niecke, E.; Sachs, W.; Rademacher, P. *Phosphorus Sulfur* 1987, *30*, 796; *Z. Anorg. Allg. Chem.*, in press.
(63) Hosseini, H. E.; Kroto, H. W.; Nixon, J. F.; Maah, M. J.; Taylor, M. J. *J. Chem. Soc., Chem Commun.* 1981, 199.
(64) Klebach, T. C.; Lourens, R.; Bickelhaupt, F.; Stam, C. H.; van Herk, A. *J. Organomet. Chem.* 1981, *210*, 211.
(65) Kroto, H. W.; Nixon, J. F.; Taylor, M. J.; Frew, A.; Muir, K. W. *Polyhedron* 1982, *1*, 89.
(66) Kroto, H. W.; Nixon, J. F. *ACS Symp. Ser.* 1981, *No. 171*, 383.
(67) Burckett-St. Laurent, J. C. T. R.; Hitchcock, P. B.; King, M. A.; Kroto, H. W.; Meidine, M. F.; Klein, S. I.; Al-Resayes, S. I.; Suffolk, R. J.; Nixon, J. F. *Phosphorus Sulfur* 1983 *18*, 259.
(68) Yoshifuji, M.; Toyota, K.; Inamoto, N. *Tetrahedron Lett.* 1985, *26*, 1727.
(69) Gudat, D.; Niecke, E.; Krebs, B.; Dartmann, M. *Chimia* 1985, *39*, 277.
(70) Al-Resayes, S. I.; Klein, S. I.; Kroto, H. W.; Meidine, M. F.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* 1983, 930.
(71) Van der Knaap, T. A.; Bickelhaupt, F.; van der Poel, H.; van Koten, G.; Stam, C. H. *J. Am. Chem. Soc.* 1982, *104*, 1756.
(72) Van der Knaap, T. A.; Bickelhaupt, F.; Kraaykamp, J. G.; van Koten, G.; Bernards, J. P. C.; Edzes, H. T.; Veeman, W. S.; de Boer, E.; Baerends, E. J. *Organometallics* 1984, *3*, 1804.
(73) Kroto, H. W.; Klein, S. I.; Meidine, M. F.; Nixon, J. F.; Harris, R. K.; Packer, K. J.; Reams, P. *J. Organomet. Chem.* 1985, *280*, 281.
(74) Van der Knaap, T. A.; Bickelhaupt, F. *Phosphorus Sulfur* 1983, *18*, 47.
(75) Van der Knaap, T. A.; Jenneskens, L. W.; Meeuwissen, H. J.; Bickelhaupt, F.; Walther, D.; Dinjus, E.; Uhlig, E.; Spek, A. L. *J. Organomet. Chem.* 1983, *254*, C33.
(76) Gudat, D.; Meidine, M. F.; Hitchcock, P. B.; Nixon, J. F.; Wang, H., unpublished results.
(77) Neilson, R. H.; Thoma, R. J.; Vickovic, I.; Watson, W. H. *Organometallics* 1984, *3*, 1132.
(78) Ford, R. R.; Li, B. L.; Nielson, R. H.; Thoma, R. J. *Inorg. Chem.* 1985, *24*, 1993.
(79) Neilson, R. H. *Phosphorus Sulfur* 1983, *18*, 43.
(80) Appel, R.; Cassar, C.; Immenkeppel, M.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 895.
(81) Huy, N. H. T.; Mathey, F. *Organometallics* 1987, *6*, 207.
(82) Grobe, J.; Le Van, D.; Nientiedt, J.; Szameitat, J. *Phosphorus Sulfur* 1987, *30*, 401.
(83) Niecke, E., personal communication.
(84) Kraaykamp, J. G.; van Koten, G.; van der Knaap, T. A.; Bickelhaupt, F.; Stam, C. H. *Organometallics* 1986, *5*, 2014.
(85) Cowley, A. H.; Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H. M. *J. Am. Chem. Soc.* 1984, *106*, 7015.
(86) Werner, H.; Paul, W.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 626.
(87) Deschamps, B.; Mathey, F. *J. Chem. Soc., Chem. Commun.* 1985, 1010.
(88) Appel, R.; Casser, C.; Knoch, F. *J. Organomet. Chem.* 1985, *297*, 21.
(89) Akpan, C. A.; Gudat, D.; Meidine, M. F.; Niecke, E.; Nixon, J. F., unpublished results.
(90) Holand, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* 1984, *106*, 826.
(91) Appel, R.; Casser, C.; Knoch, F. *J. Organomet. Chem.* 1985, *293*, 213.
(92) Niecke, E., personal communication.
(93) Knoll, K.; Huttner, G.; Wasiucionek, M.; Zsolnai, L. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 739.
(94) Williams, G. D.; Geoffroy, G. L.; Whittle, R. R.; Rheingold, A. L. *J. Am. Chem. Soc.* 1985, *107*, 729.
(95) Huy, N. H. T.; Fischer, J.; Mathey, F., personal communication.
(96) Huy, N. H. T.; Fischer, J.; Mathey, F. *J. Am. Chem. Soc.* 1987, *109*, 3475.
(97) Nguyen, M. T.; Hegarty, A. F.; McGinn, M. A.; Ruelle, P. *J. Chem. Soc., Perkin Trans. 2* 1985, 1991.
(98) Nguyen, M. T.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* 1985, 1999, 2005.

(99) Akpan, C. A.; Meidine, M. F.; Nixon, J. F.; Yoshifuji, M.; Toyota, K.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* 1985, 946.
(100) Nixon, J. F. *Phosphorus Sulfur* 1987, 30, 471.
(101) Akpan, C. A.; Hitchcock, P. B.; Nixon, J. F., to be published. Akpan, C. A. D.Phil. Thesis, University of Sussex, 1986.
(102) Appel, R.; Knoch, F.; Winkhaus, V. *J. Organomet. Chem.* 1986, 307, 93.
(103) Yoshifuji, M.; Shibayama, K.; Hashida, T.; Toyota, K.; Niitsu, T.; Matsuda, I.; Sato, T.; Inamoto, N. *J. Organomet. Chem.* 1986, 311, C63.
(104) Akpan, C. A.; Hitchcock, P. B.; Nixon, J. F.; Yoshifuji, M.; Niitsu, T.; Inamoto, N. *J. Organomet. Chem.* 1988, 338, C35.
(105) Mathieu, R.; Caminade, A. M.; Majoral, J. P.; Daran, J. C. *J. Am. Chem. Soc.* 1986, 108, 8007.
(106) Barron, A. R.; Cowley, A. H. *J. Chem. Soc., Chem. Commun.* 1987, 1272.
(107) Niecke, E.; Gudat, D.; Schoeller, W. W.; Rademacher, P. *J. Chem. Soc., Chem. Commun.* 1985, 1050.
(108) Gudat, E.; Niecke, E.; Malisch, W.; Hofmockel, U.; Quashie, S.; Cowley, A. H.; Arif, A. M.; Krebs, B.; Dartmann, M. *J. Chem. Soc., Chem. Commun.* 1985, 1687.
(109) Cowley, A. H.; Norman, N. C.; Quashie, S. *J. Am. Chem. Soc.* 1984, 106, 5007.
(110) Arif, A. M.; Cowley, A. H.; Quashie, S. *J. Chem. Soc., Chem. Commun.* 1986, 1437.
(111) Gudat, D.; Niecke, E.; Krebs, B.; Dartmann, M. *Chimia* 1985, 39, 237.
(112) Arif, A. M.; Cowley, A. H.; Quashie, S. *J. Chem. Soc., Chem. Commun.* 1985, 428.
(113) Gudat, D.; Niecke, E.; Arif, A. M.; Cowley, A. H.; Quashie, S. *Organometallics* 1986, 5, 593.
(114) Gudat, D.; Niecke, E., personal communication.
(115) Bohle, D. S.; Rickard, C. E. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* 1985, 1594.
(116) Weber, L.; Reizig, K. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 53.
(117) Weber, L.; Reizig, K.; Boese, R.; Polk, M. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 604.
(118) Weber, L.; Reizig, K.; Boese, R. *Organometallics* 1985, 4, 1890.
(119) Weber, L.; Reizig, K.; Meine, G. *Z. Naturforsch., B* 1985, 40b, 1698.
(120) Weber, L.; Reizig, K.; Polk, M. *Organometallics* 1986, 5, 1098.
(121) Weber, L.; Reizig, K.; Frebel, M.; Boese, R.; Polk, M. *J. Organomet. Chem.* 1986, 306, 105.
(122) Weber, L.; Reizig, K.; Frebel, M. *Chem. Ber.* 1986, 119, 1857.
(123) Weber, L.; Bungardt, D.; Reizig, K.; Boese, R. *Z. Naturforsch., B* 1986, 41b, 1096.
(124) Weber, L.; Bungardt, D. *J. Organomet. Chem.*, in press.
(125) Weber, L.; Reizig, K.; Boese, R. *Organometallics* 1985, 4, 2097.
(126) Mercier, F.; Fischer, J.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 357.
(127) Mercier, F.; Mathey, F. *Phosphorus Sulfur* 1987, 37, 217.
(128) Appel, R.; Schuhn, W.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 420.
(129) Akpan, C. A.; Nixon, J. F., unpublished results. Akpan, C. A. D.Phil. Thesis, University of Sussex, 1986.
(130) Karsch, H. H., personal communication, Sept 1986.
(131) Appel, R.; Schuhn, W.; Knoch, F. *J. Organomet. Chem.* 1987, 319, 345.
(132) Karsch, H. H.; Appelt, A.; Müller, G. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 823.
(133) Appel, R.; Schuhn, W. *J. Organomet. Chem.* 1987, 329, 179.
(134) Keim, W.; Appel, R.; Gruppe, S.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 1012.
(135) Knoll, K.; Orama, O.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 976.
(136) Karsch, H. H.; Reisacher, H. U.; Huber, B.; Müller, G.; Malisch, W.; Jörg, K. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 455.
(137) Lang, H.; Zsolnai, L.; Huttner, G. *Chem. Ber.* 1985, 118, 4426.
(138) Knoll, K.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* 1986, 312, C57; 1987, 332, 175.
(139) Lunniss, J.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J.; Sappa, E. *Organometallics* 1985, 4, 2066.
(140) Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* 1988, 819.
(141) (a) Binger, P.; Biedenbach, B.; Mynott, R.; Kruger, C.; Betz, P.; Regitz, M. *Angew. Chem., Int. Ed. Engl.*, in press. (b) Binger, P., paper presented to PSIBLOCS meeting, Paris, August 1988.
(142) Binger, P.; Biedenbach, B.; Mynott, R.; Regitz, M. *Chem. Ber.* 1988, 121, 1455.
(143) Appel, R.; Schuhn, W.; Nieger, M. *Angew. Chem., Intl. Ed. Engl.* 1988, 27, 416.
(144) Huy, N. H. T.; Ricard, L.; Mathey, F. *Organometallics* 1988, 7, 1791.
(145) Huy, N. H. T.; Mathey, F. *Tetrahedron Lett.* 1988, 29, 3077.
(146) Dotz, K. H.; Tiriliomis, K. H.; Regitz, M.; Annen, U. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 713. Dotz, K. H., paper presented to PSIBLOCS meeting, Paris, August 1988.
(147) Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Organometal. Chem.*, in press. Nixon, J. F., paper presented to PSIBLOCS meeting, Paris, August 1988.
(148) Bartsch, R.; Hitchcock, P. B.; Madden, T. J.; Meidine, M. F.; Nixon, J. F.; Wang, H. *J. Chem. Soc., Chem. Commun.*, in press. Nixon, J. F., paper presented to PSIBLOCS meeting, Paris, August 1988.