

# Synthesis of Di-, Tri-, and Polyphosphane and Phosphene Transition-Metal Complexes

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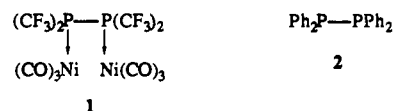
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## I. Introduction

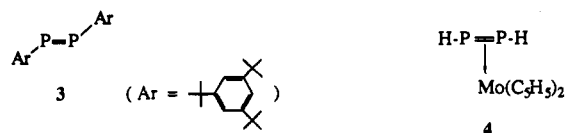
This review concerns complexes with one or more phosphorus-phosphorus bonds, whatever the coordination of phosphorus atoms and the type of bonds between phosphorus and metal or phosphorus and phosphorus ( $\sigma$  or  $\pi$  bonds,  $\eta^1$  or  $\eta^2$  complexation). It covers extensively the literature on diphosphane (P—P) and diphosphene (P=P) complexes up to the middle of 1989. Only compounds obtained by complexation of white phosphorus (P<sub>4</sub>)<sup>1</sup> or phosphorus pentasulfide (P<sub>4</sub>S<sub>10</sub>) are excluded from the scope of this review.

Diphosphene complexes have been reviewed in 1984<sup>2,3</sup> and 1986<sup>4</sup> by Cowley and 1985 by Scherer,<sup>5</sup> but there have been several developments since that time. Furthermore no review has ever been published about diphosphane complexes.

From an historical point of view, the starting point of the present review dates back to 1958, when Burg and Mahler<sup>6</sup> synthesized the first diphosphane complex, 1, 70 years after the synthesis of the first free diphosphane, 2, by Dörken.<sup>7</sup>



Since then, more than 250 articles have been published in this field, mainly in the last 10 years. This is partly due to the dramatic spread of the chemistry of low-coordinated phosphorus compounds, which started in 1981 with the synthesis of the first diphosphene, 3, by Yoshifuji,<sup>8</sup> 7 years after that of the first diphosphene complex, 4, by Green and Morris.<sup>9</sup>



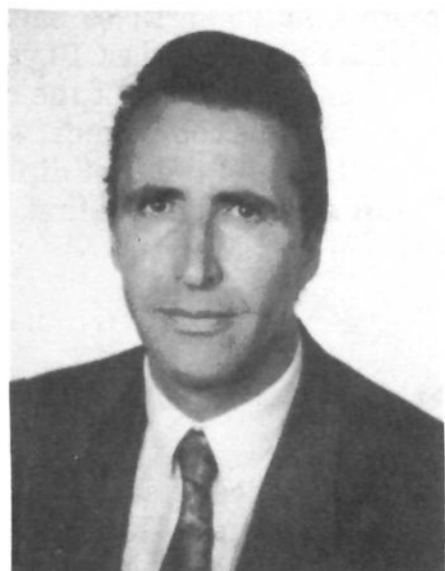
The numerical importance of each type of complex is very different; approximately 475 diphosphane complexes and 125 diphosphene complexes have been synthesized. This important difference expresses both the anteriority of researches and the easier synthesis of diphosphane complexes.

The first part of this review consists of a presentation of the different types of compounds and their structural and spectroscopic characteristics. The second part is a survey of methods used for the preparation of all those complexes. The hundreds of compounds thus synthesized are listed at the end of the review together with their methods of synthesis and the yield of the reactions.

The following abbreviations will be used all along this review: Ac (acetyl), An (anisyl), Ar (2,4,6-tri-*tert*-butylphenyl), Bipy (2,2'-bipyridine), *i*Bu (isobutyl), *n*Bu (butyl), *t*Bu (*tert*-butyl), COD (cyclooctadiene), Cp (cyclopentadienyl), Cp\* (1,2,3,4,5-pentamethylcyclopentadienyl), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), Et (ethyl), *c*Hex (cyclohexyl), Me (methyl), (-)-Ment ((-)-menthyl), Mes (mesityl), Nor (norbornadiene), Ph (phenyl), Phen (1,10-phenanthroline), Pip (piperidine), Pyr (pyridine), *i*Pr (isopropyl), TMEDA (*N,N,N',N'*-tetramethylenediamine), *Tmp* (2,2,6,6-tetramethylpiperidyl), *Tms* (trimethylsilyl), *Tol* (toluidyl), *Trisyl* (tris(trimethylsilyl)methyl).



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Jean Pierre Majoral received his Doctorat d'État in 1972 from the Université Paul Sabatier of Toulouse. In 1973, he carried out postdoctoral studies with Prof. A. R. Katritzky at the University of East Anglia, England. He became Directeur de Recherche at the Centre National de la Recherche Scientifique in 1978 in Toulouse where he is currently at the head of a research group. His research interest includes synthetic and mechanistic aspects of low-coordinated heavier main group elements' chemistry and photochemical and thermal behavior of organometallic azides. A further field of interest consists of the preparations of organometallic precursors of ceramics. Emphasis is also made on the synthesis and the complexation properties of phosphorus macrocyclic multidentate compounds.

## II. Structure of Diphosphane and Diphosphene Complexes

Three types of phosphorus-metal bonds can be distinguished and will be noted as follows: (i) P-M for  $\sigma$  bonds, (ii) P $\rightarrow$ M for  $\sigma$ -donor bonds ( $\eta^1$  complexation of a phosphorus lone pair), and (iii)

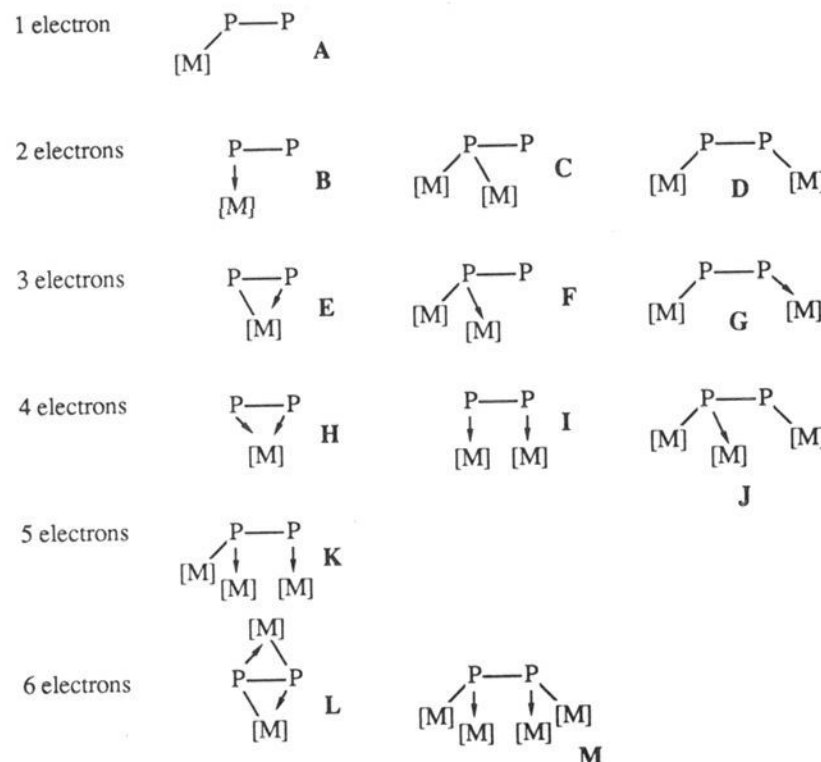


for  $\pi$  complexation ( $\eta^2$  complexation of a double bond). These three types of bonds are found in diphosphene



René Mathieu received his Doctorat d'Etat from the Université Paul Sabatier, Toulouse, in 1973 in Prof. R. Poilblanc group. In 1982 he became Directeur de Recherche in the C.N.R.S. at the Laboratoire de Chimie de Coordination, Toulouse. His current research interests include the study of carbon-carbon bond formation on polynuclear metal complexes, the synthesis and study of the reactivity of heterobimetallic compounds, and the synthesis and the use of new ligands in transition-metal chemistry.

### SCHEME 1<sup>a</sup>



<sup>a</sup> For the sake of clarity, all organic substituents are omitted.

complexes, whereas only the first two occur in diphosphane complexes.

### A. Diphosphane Complexes

Diphosphanes can act as one to six electron-donor ligands. Of the following coordination types (A-M) which have so far been described (Scheme 1), only type H has never been structurally characterized by X-ray crystallography (see Tables 6 and 7).

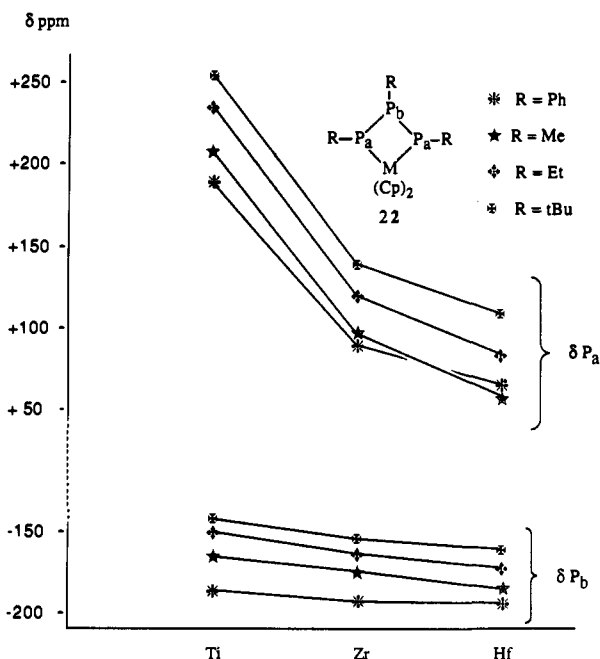
The number of compounds of each type is very different. Only one example is known for types E, J, and L, two for types C and G, less than 10 for types D, H, and M, between 15 and 35 for types A, F, and K, around 180 for type B, and around 250 for type I. Thus, types B and I are the preferred coordination modes of diphosphane ligands.

#### 1. $\eta^1$ Diphosphane Complexes

As noted previously, a type A compound, 1, was the first reported diphosphane complex.<sup>6</sup> The first one



## SCHEME 2



of homogeneous series preclude a comprehensive analysis of  $\delta^{31}\text{P}$  for transition metal substituted diphosphanes. However, selected data for compounds 22<sup>34</sup> allow emphasis of important trends and correlations (Scheme 2).

First of all, a comparison of  $^{31}\text{P}$  NMR data between  $\delta P_a$  (phosphorus linked to the metal) and  $\delta P_b$  (phosphorus linked to organic substituents) shows in all cases a dramatic deshielding of  $\delta P_a$ :  $\Delta\delta = 242\text{--}377$  ppm, depending on metal and R substituents. Furthermore, it is well-documented for complexed phosphanes that the  $^{31}\text{P}$  shift decreases as the atomic number increases from top to bottom in a triad.<sup>36,38</sup> A similar trend is observed for 22: changing the early transition metal from Ti to Zr leads in each case to an upfield shift in  $\delta^{31}\text{P}$ . On the other hand, the coupling constant  $J_{ab}$  is little sensitive to the metal and to the organic substituent:  $294.4 < J_{ab} < 349.5$  Hz. Few X-ray data are available for this type of complexes, but the P–P distances are in the same range as those for  $\eta^1$  diphosphane complexes: 2.18 and 2.21 Å for R = Ph and M = Hf.<sup>37</sup>

The general applicability of these tendencies to most of the transition metal substituted diphosphanes and polyphosphanes is not demonstrated but seems to be quite reasonable. However, the problem becomes intricate when a R–P–P–R unit is linked to two or more metals. Are these molecules diphosphane complexes or diphosphene complexes?

It is difficult to give an answer because the P–P bond lengths are highly variable: for 25 and 26, it is typical of that for diphosphanes, whereas for 24 it is close to that of  $\eta^2$  diphosphene complexes and for 23 close to that of  $\eta^1$  diphosphane complexes, as we will see in the next paragraph.

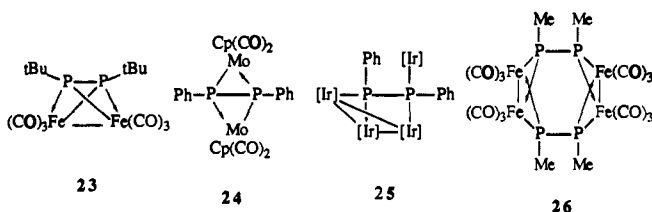
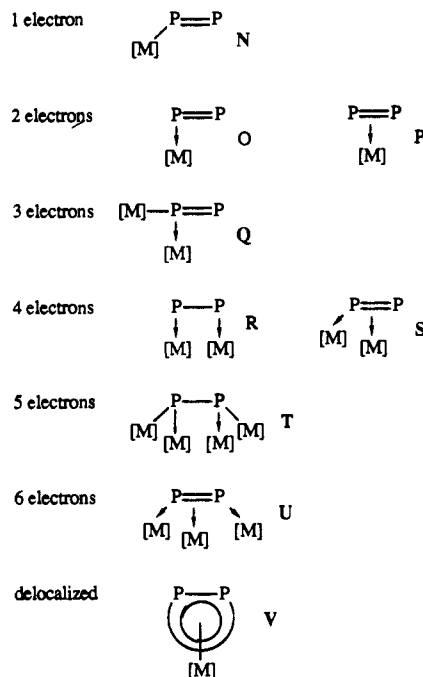


TABLE 2. X-ray Data for 23–26

	23	24	25	26
$d_{\text{P-P}}$ , Å	2.059 (3)	2.136 (3)	2.186 (13)	2.226 (4)
ref	38, 39	40	41	42

SCHEME 3<sup>a</sup>

<sup>a</sup> For the sake of clarity, all organic substituents are omitted.

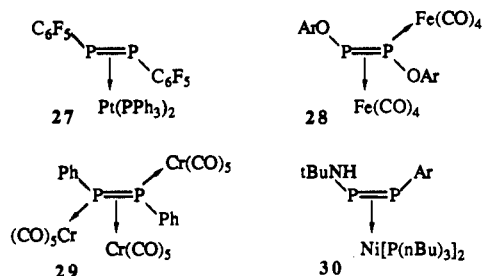
## B. Diphosphene Complexes

A classification analogous to the one depicted in Scheme 1 for diphosphane complexes is also appropriate for diphosphene complexes, since they can act as one to six electron-donor ligands (Scheme 3). Of the many possible coordination types, structures N–V have so far been characterized.

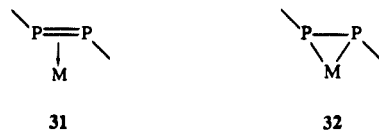
The structures of all the above-mentioned types of diphosphene complexes have been ascertained by X-ray diffraction studies. About 10–20 compounds are known for each type of complexes; the only exceptions are type P (about 40) and type T (only one).

1.  $\eta^2$  Diphosphene Complexes

$\eta^2$  complexes are both the oldest and the most abundant type of diphosphene complexes; they were synthesized far before free diphosphenes.<sup>8</sup> The main reason is that the complexation of the double bond brings a strong stabilization to the structure, even when the phosphorus substituents are as small as hydrogen.<sup>9</sup> As seen previously, the first one, 4, was described in 1974<sup>9</sup> and its structure was ascertained further by X-ray crystallography in 1977.<sup>43</sup> However, this was not the first X-ray study of a diphosphene complex, since the structure of 27 had been determined 1 year before.<sup>44</sup> Later, in 1983, the first examples of types S and U complexes, 28<sup>45</sup> and 29,<sup>46</sup> respectively, were also fully characterized. In all cases, the organic substituents of the diphosphenes are in the trans position. The only exception is the unstable compound 30, recently reported.<sup>47</sup>

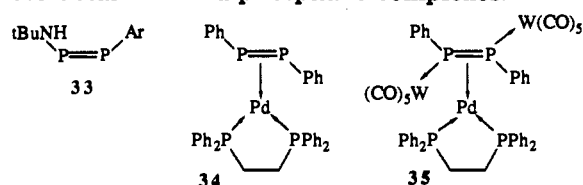


The nature of the bond which links the P=P double bond to the metal remains a problem; is it the complexation of a  $\pi$  bond (31) analogous to the complexation of ethylene, or is it a three-membered metallacycle formed by two metal-phosphorus  $\sigma$  bonds (32) analogous for instance to a cyclotriphosphane?



Answering this question is not simple, since no *ab initio* calculation has ever been worked out for this type of complexation of diphosphenes. Nevertheless, calculations about the complexation of ethylene in  $\text{Ni}(\text{P-H}_3)_2(\text{C}_2\text{H}_4)$  show an important electron back-bonding from nickel into the unoccupied  $\pi^*$  molecular orbital of the olefin.<sup>48</sup> Furthermore calculations about  $\text{HP}=\text{P}^{\text{H}}$ <sup>49-52</sup> show that the  $\pi^*$  (P—P) molecular orbital is the LUMO. This orbital is easily accessible, therefore it seems reasonable to suggest that the model of complexation of ethylene might be used to describe the  $\eta^2$  complexation of diphosphenes:<sup>2</sup> there would be first formation of a  $\pi$ -donor bond from the double bond toward the unoccupied orbitals of the metal, then electrons back-bonding from the metal toward the unoccupied  $\pi^*$  orbital of the double bond. However, since ethylene and diphosphenes are substantially different, such an interpretation is highly speculative.

Table 3 depicts selected data for some diphosphene complexes. The main feature is the dramatic variation of the  $^{31}\text{P}$  NMR chemical shift values between complexes 30 and 33, which differ only by the complexation of the double bond ( $\Delta\delta \approx 280$  ppm). Whether this phenomenon could be partly related to an electron back-bonding from metal to phosphorus remains questionable. On the other hand, the lone pair complexation seems to play a minor part in the variation of the  $^{31}\text{P}$  NMR chemical shift, as shown by 34 and 35. These values are in the middle of the range observed for  $\eta^2$  diphosphene complexes, between +250 and -200 ppm, depending on the organic substituents and the metal. The second point noticeable in Table 3 is the length of the complexed P=P double bond, between 2.12 and 2.18 Å: these values are somewhat shorter than those obtained for diphosphane complexes.



## 2. $\eta^1$ Diphosphene Complexes

The first diphosphene complexes of type O, 36<sup>55,56</sup> and 37,<sup>45</sup> and type R, 38,<sup>46</sup> 39,<sup>57</sup> and 40,<sup>58</sup> were syn-

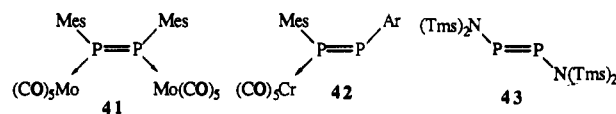
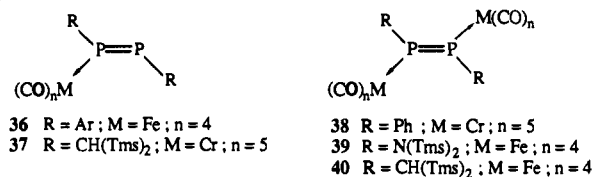
TABLE 3.  $^{31}\text{P}$  NMR and X-ray Data for 30, 33-35

compd	$^{31}\text{P}$ NMR		X-ray $d_{\text{P=P}}$ , Å	ref
	$\delta$ , ppm	$J_{\text{PP}}$ , Hz		
30	377 214	526	2.038 (2)	47
33	85.2 -55.1	427		47
34	34.3		2.121 (4)	53, 54
35	17		2.186 (6)	53

TABLE 4.  $^{31}\text{P}$  NMR and X-ray Data for 3 and 36-43

compd	$^{31}\text{P}$ NMR		X-ray $d_{\text{P=P}}$ , Å	ref
	$\delta$ , ppm	$J_{\text{PP}}$ , Hz		
36	423.6 and 396.4	578	2.050 (1)	55, 56, 61
37	477.2 and 446.2	510	2.027 (3)	45, 59, 62, 63
38	927		2.021	46
39	403.9		2.053 (1)	57, 64
40	384.5		2.039 (1)	58, 64
41	367.7		2.026 (2)	59
42	393.9 and 384.9	603	2.039 (3)	60a,b
3	492		2.034 (2)	8, 65
43	572			66

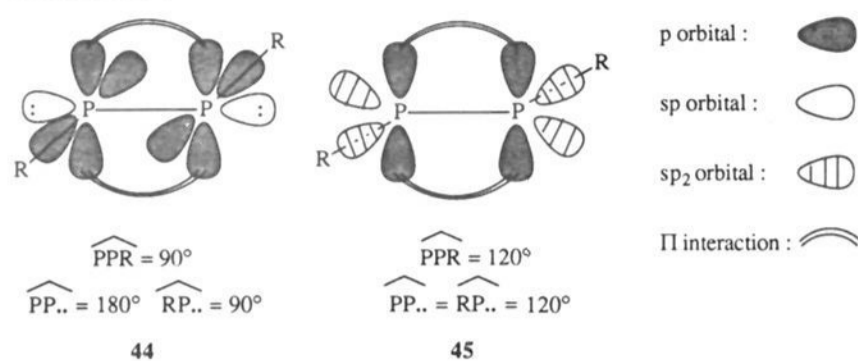
thesized independently in three laboratories in 1983. All of these are *trans* compounds. The first X-ray studies of *cis* complexes were performed in 1985 for 41<sup>59</sup> and 42.<sup>60</sup>



Selected data of these complexes are given in Table 4, along with data of the free diphosphenes 3 and 43. As a result of the  $\eta^1$  complexation, the  $\delta$   $^{31}\text{P}$  values for 36 and 39 are shifted upfield, compared to that of the corresponding free diphosphenes 3 and 43, respectively. This is opposite to what is usually observed for  $\eta^1$  diphosphane complexes. However, as seen previously for diphosphane complexes, a decrease in the  $^{31}\text{P}$  NMR chemical shift of homogeneous series of  $\eta^1$  diphosphene complexes is observed as the atomic number of the metal increases in a triad, for instance from chromium to tungsten.<sup>60b</sup> Most of the compounds of types O and R have  $^{31}\text{P}$  NMR shifts in the range 600–200 ppm. The only noticeable exception comes from the value of 927 ppm obtained for 38,<sup>46</sup> which is rather surprising.

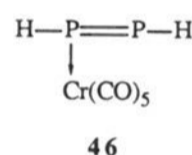
X-ray data for all these complexes show that the P=P bond length remains essentially unchanged compared to that of free diphosphenes, around 2.02–2.05 Å. It means that the  $\eta^1$  complexation has no influence on the PP bond order. On the other hand, the RPP angles are increased by complexation: 102.8 (1)° for 3, 109.3 (1)° and 108.4 (1)° for 36. From steric reasons, this increase of the PPR angles intuitively seems to be wrong. An explanation of this phenomenon might be a modification in the hybridization of the phosphorus orbitals. For an idealized free diphosphene, it seems that the most suitable orbital description consists in forming the  $\pi$  (P—P) and  $\sigma$  (P—R) bonds by overlaps using pure P(3p) atomic orbitals, whereas the  $\sigma$  (P—P) bond could be formed via pure P(3p) overlap or by use

SCHEME 4



of sp hybrid orbitals.<sup>61</sup> Such an arrangement would lead to a PPR bond angle of 90° (44, Scheme 4), closer to the experimental value (102.8°) than the theoretical value obtained for a sp<sup>2</sup> hybridization (120°) (45, Scheme 4).<sup>67</sup>

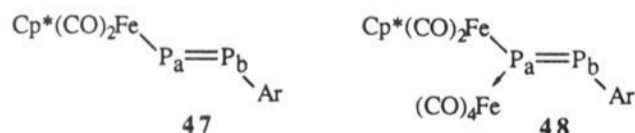
It is easily understandable from this scheme that the complexation of the lone pair will not occur by keeping an sp hybridization, which would lead to two interactions of 90°, between R and P=P on the one hand M and R on the other hand. The hybridization will then approximate sp<sup>2</sup>, creating three interactions of 120°, by far more suitable. This may explain the increase of the PPR bond angles experimentally observed by complexation. This tendency to go from an sp hybridization to an sp<sup>2</sup>, then to decrease the s character of the lone pair orbital, is in agreement with NMR results: indeed, a decrease of the s character is usually associated with an increase of the screening constant  $\sigma$  and therefore a shielding of the <sup>31</sup>P NMR signal. Another phenomenon could be added: according to Hückel type calculations worked out for 46, it seems that the simple idea of  $\eta^1$  complexation of diphosphenes by means of a phosphorus metal  $\sigma$ -donor bond does not fit in with reality.



These calculations<sup>68</sup> display that the coordination of diphosphenes not only occurs via a  $\sigma$ -donor bond but also via an important back-bonding (0.3 electron) of  $\pi$  electrons from metal to phosphorus. This is also in agreement with experimental results obtained for diphosphane complexes, as we have already seen.<sup>15</sup>

### 3. Transition Metal Substituted Diphosphenes

These are the most recent types of diphosphene complexes. The first one, 47,<sup>69</sup> was described in 1985 and characterized by X-ray crystallography<sup>70</sup> in 1987, as well as its corresponding  $\eta^1$  complex 48.<sup>71</sup>



Diphosphenes which are substituted by transition metals instead of organic groups should be substantially different in character, but the metallic part often behaves like an organic substituent: most of the spectroscopic data of metalladiphosphenes are close to those of "organic" diphosphenes. However, a comparison of <sup>31</sup>P NMR data of 47 and 3 shows an important deshielding of the signal corresponding to the phosphorus atom linked to the metal (see Table 5). It is likely to be an indication of the high attractive power of the

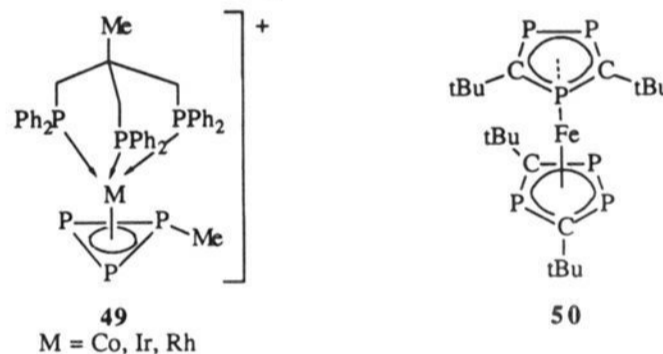
TABLE 5. <sup>31</sup>P NMR and X-ray Data for 3, 47, and 48

compd	<sup>31</sup> P NMR		X-ray <i>d</i> <sub>P=P</sub> , Å	ref
	$\delta$ P <sub>a</sub> , ppm	$\delta$ P <sub>b</sub> , ppm		
3		492	2.034 (2)	8, 65
47	715.2	553.5	2.027 (3)	70
48	546.3	514.6	2.032 (5)	71

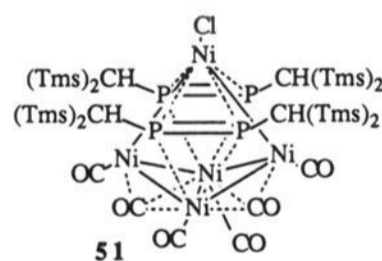
metal for the phosphorus electrons. On the other hand, the  $\eta^1$  complexation of P<sub>a</sub> in 48 comes to an upfield shift in <sup>31</sup>P NMR, as shown previously for organic diphosphenes. Furthermore, the presence of the  $\sigma$  M-P bonds does not lead to noticeable modifications of the phosphorus-phosphorus bond: the P=P double bond length in 47 and 48 is essentially unchanged when compared to that of 3.

### 4. Miscellaneous Diphosphene Complexes

In addition to compounds of type M described at the end of section II-A, other complexes could be related to diphosphenes. This concern mainly compounds of type V, in which the P=P double bond is delocalized. The first compound reported and characterized by X-ray crystallography is the cationic three-membered ring 49,<sup>72</sup> but most of the compounds of type V are five-membered heterocycles such as 50.<sup>73</sup> The PP bond length reflects the delocalization: 2.08 (2) and 2.17 (2) Å for 49 and 2.112 (5) Å for 50.



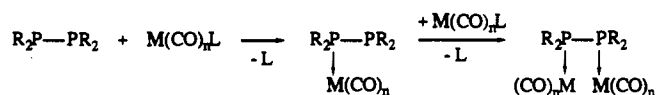
Finally, the original cluster 51<sup>74</sup> is also difficult to file. In spite of the presence of five nickel atoms, X-ray data show that the two P=P double bonds are essentially unsupported (*d*<sub>P=P</sub> = 2.085 (4) Å<sup>74</sup>). The cis arrangement of the organic substituents of diphosphenes is also noticeable.



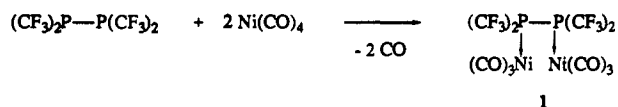
### III. Synthetic Methods

Three general synthetic methods are applied to prepare diphosphane or diphosphene complexes, as well as metalladiphosphanes or diphosphenes: (i) complexation of a ligand which already possesses the phosphorus-phosphorus bond, (ii) simultaneous formation of the phosphorus-phosphorus bond and complexation, and (iii) modification of a complex which already possesses the phosphorus-phosphorus bond. However, these three methods have not the same importance for diphosphanes and diphosphenes. Thus, it is more convenient to consider the syntheses of diphosphane complexes and diphosphene complexes one after the other in each case.

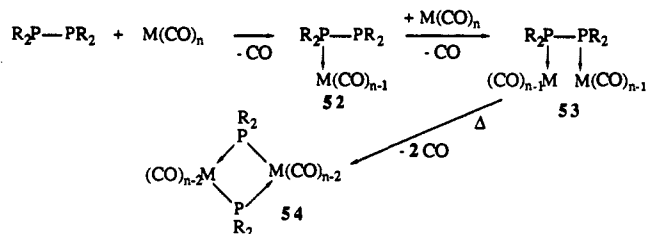
## SCHEME 5



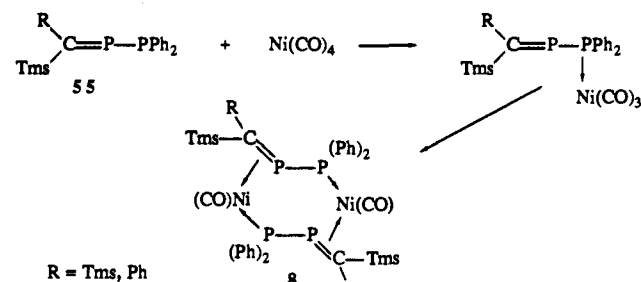
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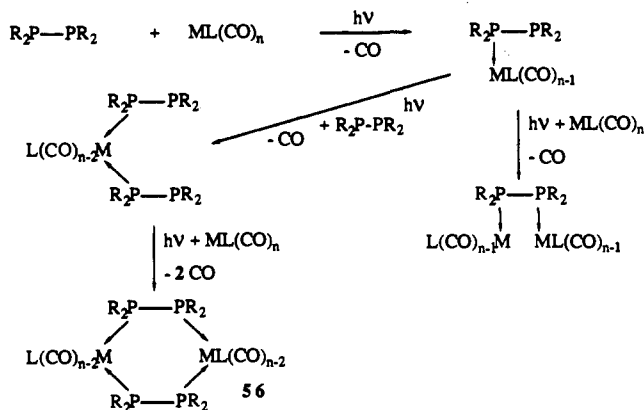
## SCHEME 7



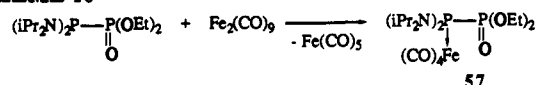
## SCHEME 8



## SCHEME 9



## SCHEME 10

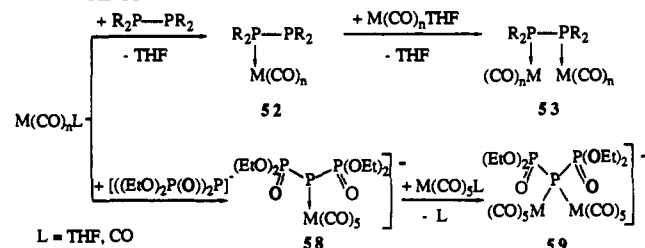


## A. Direct Complexation of a P—P or P=P Ligand

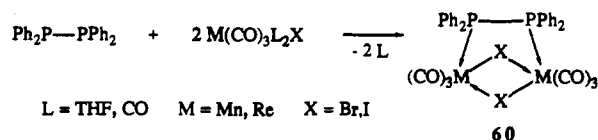
## 1. Complexation of Diphosphanes

a. Substitution of a Ligand. It is both the oldest and the most useful method for most of the transition

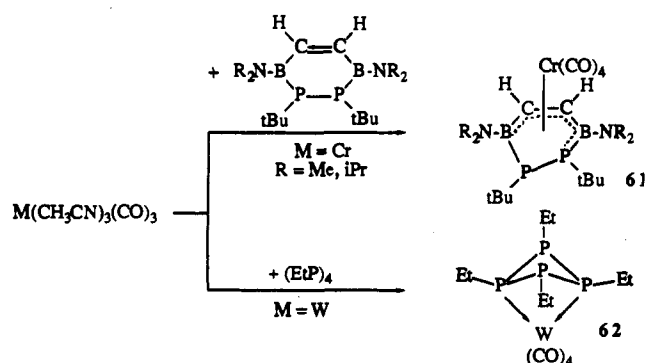
## SCHEME 11



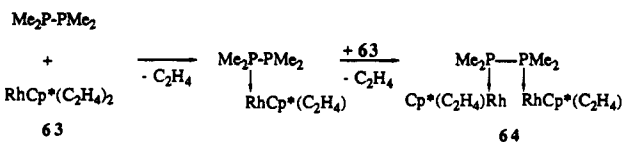
## SCHEME 12



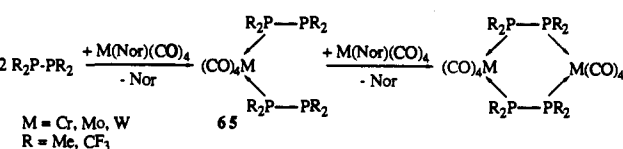
## SCHEME 13



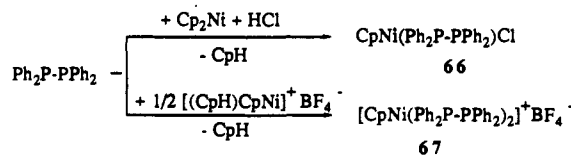
## SCHEME 14



## SCHEME 15



## SCHEME 16



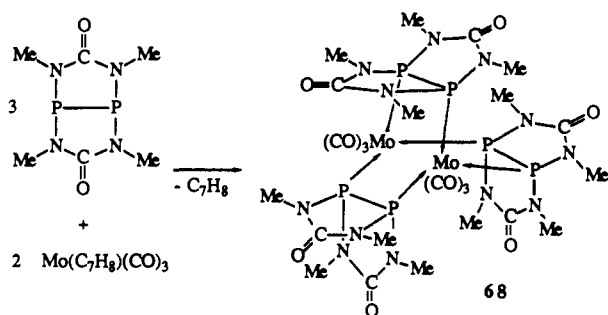
metals. It allows the synthesis of numerous  $\eta^1$  complexes of type B and I, in accordance with the well-known reaction of phosphanes with carbonyl metals (Scheme 5).

Burg and Mahler synthesized in this way the first diphosphane complex 1<sup>6</sup> (Scheme 6).

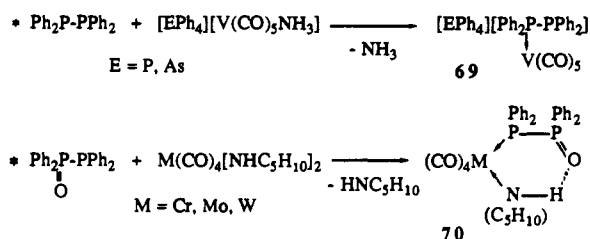
For most of these reactions, the leaving ligand L is either carbon monoxide or basic solvents or unsaturated hydrocarbons.

*α. Carbon Monoxide.* Only one CO group is removed and only one phosphorus atom is complexed when a

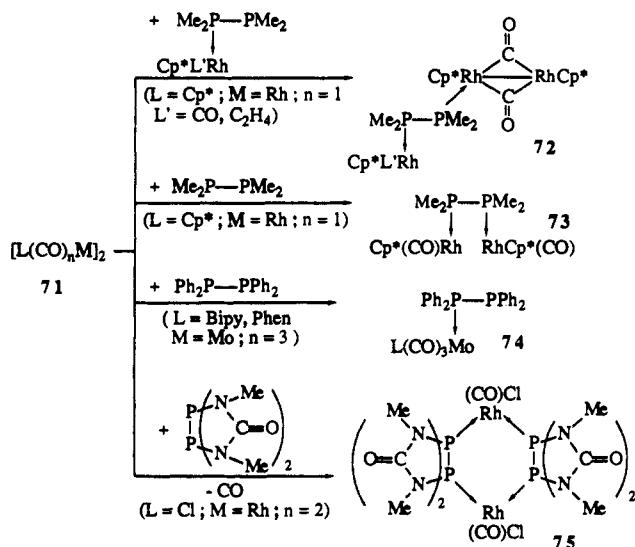
SCHEME 17



SCHEME 18



SCHEME 19



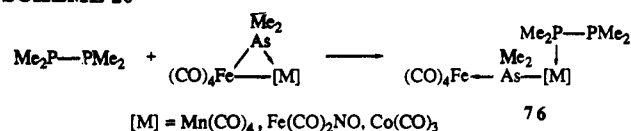
reaction between a diphosphane and a carbonyl metal is carried out under mild conditions.<sup>75-84</sup> However, in many cases, this reaction proceeds by thermal activation; it is difficult to stop at the first step,<sup>52</sup> and the isolated compounds are often the  $\eta^1\eta^1$  complexes **53**<sup>10,86-88</sup> (Scheme 7).

This is also the case with the phosphalkene derivative **55**, which reacts with nickel carbonyl to produce heterocycle **8**<sup>18</sup> (Scheme 8).

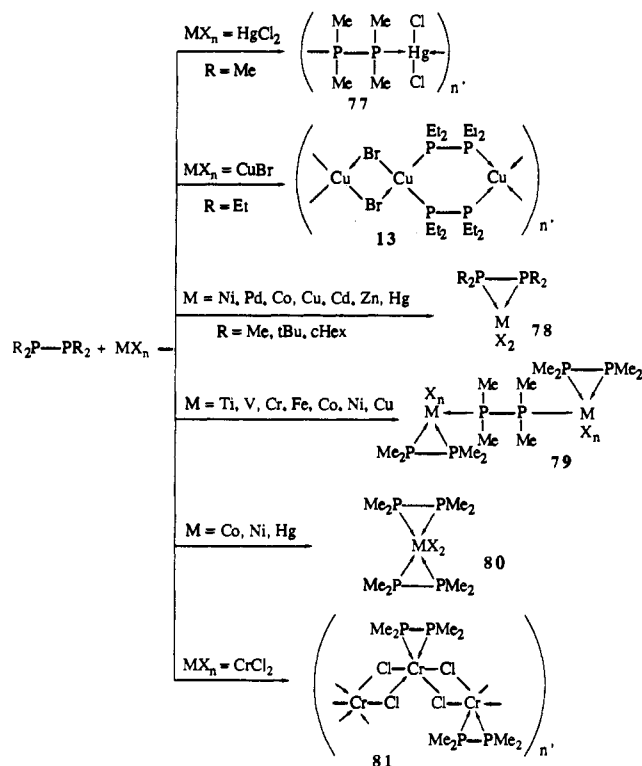
If drastic conditions are used a phosphorus-phosphorus bond cleavage occurs to give the phosphido bridged complexes **54**.<sup>89-93</sup> Such a P-P bond cleavage considerably lowers the yield of diphosphane complex.<sup>91,94</sup> That is the reason why complexation reactions induced by thermal activation are often forsaken on behalf of milder reactions, like irradiation.<sup>15,92,95,96</sup> Depending on the length of irradiation, different types of complexes are obtained<sup>15,87,96-98</sup> (Scheme 9).

However, in this case also, it is difficult to stop the reaction at the first step, and a mixture of products is often obtained, especially, if the metallic center pos-

SCHEME 20



SCHEME 21



sesses more than one leaving group. For instance, six-membered heterocycles **56** are synthesized either in this way or by thermal reactions.<sup>99-102</sup> More reactive complexes, which can be used without activation, are needed for a best selectivity. Some reactions are carried out with  $\text{Fe}_2(\text{CO})_9$ ,<sup>21,91,103-106</sup> in these cases, the leaving group is  $\text{Fe}(\text{CO})_5$  (Scheme 10).<sup>106</sup> However, we will see later that more complicated reactions often occur with iron (Schemes 27 and 28).

In most cases, reactivity and selectivity are increased by use of ligands more labile than carbon monoxide, such as basic solvents and unsaturated hydrocarbons.

$\beta$ . *Basic Solvents.* Tetrahydrofuran is often used as leaving ligand in chromium, molybdenum, or tungsten pentacarbonyl, or more rarely in iron tetracarbonyl. Many diphosphane complexes of type B (**52**) and I (**53**) are thus obtained in good yield,<sup>25,26,105,107-126</sup> as well as the anionic complexes **58** and **59**<sup>125-127</sup> (Scheme 11).

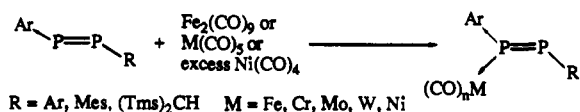
Among the numerous compounds prepared in this way, let us also mention the five-membered heterocycles **60** which are likewise obtained by exchange with carbon monoxide<sup>117,123,124,128,129</sup> (Scheme 12).

Acetonitrile complexes are not as widely used as THF complexes. Some reactions are analogous to the one described in Scheme 11.<sup>130,131</sup> However, unexpected reactions are sometimes observed with chromium<sup>132</sup> or tungsten<sup>133</sup> complexes, such as an increase of the number of CO ligands linked to the metallic center (Scheme 13).

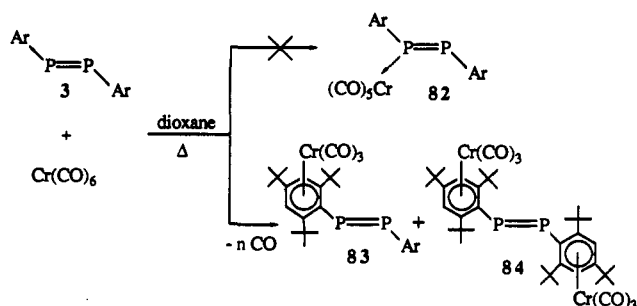
$\gamma$ . *Unsaturated Hydrocarbons.* Two-, four-, five-, and six-electron-donor hydrocarbons are sometimes



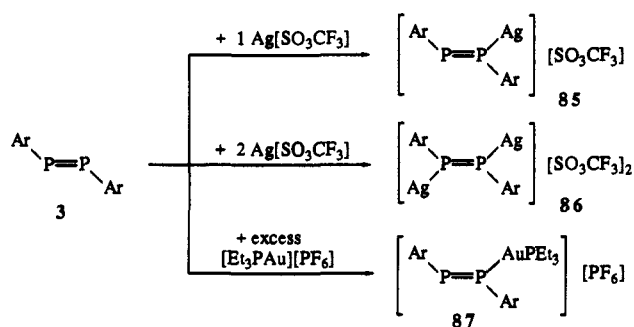
SCHEME 22



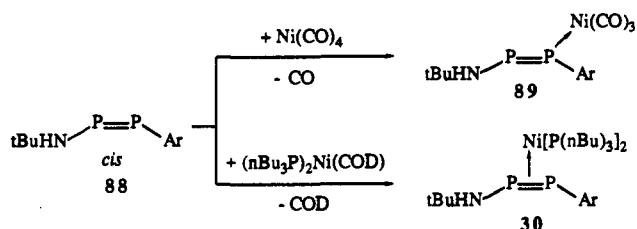
SCHEME 23



SCHEME 24



SCHEME 25



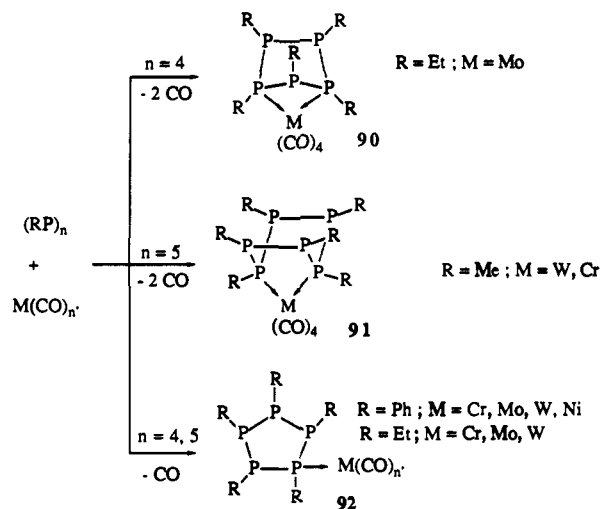
used as exchangeable ligands in the synthesis of diphosphane complexes. This is the case with ethylene,<sup>134,136</sup> however, this two-electron-donor hydrocarbon is rarely used (Scheme 14).

On the other hand, many reactions are carried out with four-electron-donor hydrocarbons such as cyclooctadiene<sup>22</sup> and above all norbornadiene.<sup>26,108,136-141</sup> This allows the synthesis of bis(diphosphane) complexes **65**<sup>26,140</sup> (Scheme 15). Let us note that here, diphosphanes act as two-electron-donor ligands and not as four. Thus, two diphosphanes are needed to replace norbornadiene.

The reaction is slightly different when a cyclopentadiene ligand is used: as expected, the anionic bis(diphosphane) complex **67** is obtained when 2 equiv of diphosphane is used, whereas the mono(diphosphane) complex **66** is isolated when 1 equiv is used<sup>142</sup> (Scheme 16).

Six-electron-donor hydrocarbons such as benzene<sup>27</sup> or cycloheptatriene<sup>27,143,144</sup> allow for instance the synthesis of polycyclic compounds such as **68** (Scheme 17).<sup>143,144</sup> In these cases, three phosphorus lone pairs

SCHEME 26



are needed to fill the hole created by elimination of cycloheptatriene.

**δ. Nitrogen Derivatives.** Few reactions are done with nitrogen derivatives. They concern dinitrogen itself,<sup>83</sup> piperidine,<sup>20</sup> or ammonia<sup>145</sup> (Scheme 18). In all cases, only one phosphorus atom is complexed, even when two leaving ligands are linked to the metallic center as in  $(\text{CO})_4\text{M}[\text{NHC}_5\text{H}_9]_2$ .<sup>20</sup>

**b. Complexation without Elimination of Ligand.** Dimeric complexes of type **71** react sometimes without elimination of ligands. The dimeric structure is either retained to give **72**,<sup>134</sup> or cleaved to give **73** or **74**.<sup>146,147</sup> However, this cleavage may also result from elimination of carbon monoxide<sup>141</sup> as for **75** (Scheme 19).

The complexation may also occur by cleavage of a metal-metal bond of strained three-membered metallacycles **76**<sup>148</sup> (Scheme 20).

Group 4 to 12 metallic halides in which the metallic center shows a deficit of electrons react with phosphorus compounds bearing no good leaving groups, allowing the metallic center to fill its electronic shell. In most cases the metal is acceptor of two lone pairs which come from either two diphosphanes or the same diphosphane, with formation of three-membered rings. In the former case, the first complexes were claimed to be monomeric,<sup>149,150</sup> whereas X-ray diffraction structural determinations show that **77**<sup>151,152</sup> and **13**<sup>23,153</sup> are in fact polymeric. Most of the three-membered metallacycles such as **78**,<sup>154-157</sup> **79**,<sup>156</sup> and **80**<sup>158</sup> are also supposed to be monomeric, except **81**<sup>158</sup> (Scheme 21). However, the existence of all those three-membered heterocycles remains questionable since no X-ray structure determination has ever been done. Polymeric structures should be suspected in many cases.

## 2. Complexation of Diphosphanes

Section III-A-1 and Tables 6 and 7 point out that the substitution of a ligand is the most widely used method to synthesize diphosphane complexes from free diphosphanes. The same reaction is applicable to diphosphenes, but is limited by the difficulty to obtain stable free diphosphenes. Furthermore, in all cases only one metal carbonyl group is bonded,<sup>3,55,56,80,81,159</sup> even when excess of metal is used.<sup>55,61</sup> This is probably due to the steric hindrance of organic substituents needed

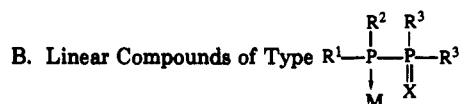
TABLE 6.  $\eta^1$  Di-, Tri- and Tetraphosphane Complexes

A. Linear Compounds of Type  $\begin{array}{c} R^2 \quad R^3 \\ | \quad | \\ R^1 - P - P - R^4 \\ | \\ M \end{array}$

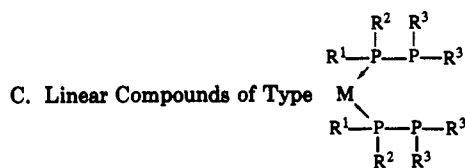
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	M	method	yield (ref)
Me	Me	Me	Me	Co(CO) <sub>2</sub> (NO)	7	75 (140)
Me	Me	Me	Me	Co(CO) <sub>2</sub> AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	20	80 (148)
Me	Me	Me	Me	Cr(CO) <sub>5</sub>	9	83 (92)
					as 95	(98)
					38	(98, 184)
Me	Me	Me	Me	Fe(CO) <sub>4</sub>	68	(224)
Me	Me	Me	Me	Fe(CO) <sub>2</sub> (NO)AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	20	59 (148)
Me	Me	Me	Me	Mn(CO) <sub>4</sub> Br	7	82 (140)
Me	Me	Me	Me	MnCp(CO) <sub>2</sub>	7	55 (140)
Me	Me	Me	Me	Mn(CO) <sub>4</sub> AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	20	91 (148)
Me	Me	Me	Me	Mo(CO) <sub>5</sub>	9	27 (92)
Me	Me	Me	Me	MoCp(CO) <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	49	(196)
Me	Me	Me	Me	Ni(CO) <sub>3</sub>	7	(140)
Me	Me	Me	Me	Rh(Cp*)Me(CO) <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	111	(147)
Me	Me	Me	Me	Rh(Cp*)Me(CO) <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	111	(147)
Me	Me	Me	Me	RhCp*(C(O)Me)I	111	76 (147)
Me	Me	Me	Me	RhCp*I <sub>2</sub>	as 111	94 (135)
Me	Me	Me	Me	RhCp*MeI	111	72 (135)
Me	Me	Me	Me	RhCp*(CO)	7	89 (147)
Me	Me	Me	Me	RhCp*(C <sub>2</sub> H <sub>4</sub> )	14	69 (135)
Me	Me	Me	Me	VCp(CO) <sub>3</sub>	9	(96, 97)
Me	Me	Me	Me	V(CO) <sub>5</sub> -NEt <sub>4</sub> <sup>+</sup>	9	(96)
Me	Me	Me	Me	W(CO) <sub>5</sub>	9	80 (92)
					38	(184)
Me	Me	Me	Me	WCp(CO) <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	49	(196)
Me	Me	CF <sub>3</sub>	CF <sub>3</sub>	Co(CO) <sub>3</sub> Mn(CO) <sub>5</sub>	7	(82)
Me	Me	CF <sub>3</sub>	CF <sub>3</sub>	Cr(CO) <sub>5</sub>	11	38 (115)
Me	Me	CF <sub>3</sub>	CF <sub>3</sub>	Mo(CO) <sub>5</sub>	11	32 (25)
Me	Me	CF <sub>3</sub>	CF <sub>3</sub>	W(CO) <sub>5</sub>	11	56 (258)
					95	(258)
Me	Ph	Me	Ph	VCp(CO) <sub>3</sub>	9	(96)
Me	Cl	Me	Cl	Fe(CO) <sub>4</sub>	89	30 (244) (245)
Me <sub>2</sub> P	Ph	Me	Me	W(CO) <sub>5</sub>	51	64 (198)
Tms	Tms	Tms	Tms	Ni(PMe <sub>3</sub> )	88	(179)
Tms	Tms	Tms	Tms	Ni(PEt <sub>3</sub> )	88	(179)
Tms	Tms	Tms	Tms	Ni(P(iPr) <sub>3</sub> )	88	(179)
Tms	Tms	Tms	Tms	Ni(P(nBu) <sub>3</sub> )	88	(179)
Tms	Tms	Tms	Tms	Ni(P(iBu) <sub>3</sub> )	88	(179)
Tms	Tms	Tms	Tms	Ni(PPh <sub>3</sub> )	88	(179)
Tms	Tms	Tms	Tms	Ni(P(cHex) <sub>3</sub> )	88	(179)
Tms	tBu	Tms	tBu	Ni(PEt <sub>3</sub> )	88	47 (179)
Tms	tBu	Tms	tBu	Ni(Et <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PEt <sub>2</sub> )	88	(180)
Ph	Ph	Ph	Ph	Fe(CO) <sub>4</sub>	38	(186)
Ph	Ph	Ph	Ph	Mo(Phen)(CO) <sub>3</sub>	19	(146)
Ph	Ph	Ph	Ph	Mo(Bipy)(CO) <sub>3</sub>	19	(146)
Ph	Ph	Ph	Ph	NbCp(CO) <sub>3</sub>	9	(97)
Ph	Ph	Ph	Ph	NiCpCl	16	57 (142)
Ph	Ph	Ph	Ph	NiCpI	101	(142)
					109	(268)
Ph	Ph	Ph	Ph	Re(CO) <sub>4</sub> I	7	(78)
Ph	Ph	Ph	Ph	Ru(CO) <sub>5</sub> -Co(CO) <sub>3</sub> PPh <sub>2</sub>	40	60 (187)
Ph	Ph	Ph	Ph	VCp(CO) <sub>3</sub>	9	18 (79) (15, 96)
Ph	Ph	Ph	Ph	V(CO) <sub>5</sub> -AsPh <sub>4</sub> <sup>+</sup>	18	35 (145)
Ph	Ph	Ph	Ph	V(CO) <sub>5</sub> -PPh <sub>4</sub> <sup>+</sup>	18	44 (145)
Ph	Ph	Ph	Ph <sub>2</sub> P	Fe(CO) <sub>4</sub>	99	(157, 185)
Ph	Ph	Ph	Ph <sub>2</sub> P	Mo(CO) <sub>5</sub>	99	(185)
Ph	Ph	Ph <sub>2</sub> P	Ph <sub>2</sub> P	Cr(CO) <sub>5</sub>	53	(199)
Ph	Ph	Ph <sub>2</sub> P	Ph <sub>2</sub> P	Mo(CO) <sub>5</sub>	53	(199)
Ph	Ph	Ph <sub>2</sub> P	Ph <sub>2</sub> P	W(CO) <sub>5</sub>	53	(199)
Ph	Ph <sub>2</sub> P	Ph	Ph	Fe(CO) <sub>4</sub>	112	71 (185) (157*)
Ph	Ph <sub>2</sub> P	Ph	Ph	Mo(CO) <sub>5</sub>	112	83 (185)
Ph	Br	Ph	Br	Cr(CO) <sub>5</sub>	11	(113)
Ph	Br	Ph	Br	W(CO) <sub>5</sub>	11	(113)
Ph	Cl	Ph	Cl	Fe(CO) <sub>4</sub>	89	80 (244) (245)
Ph	H	tBu	tBu	Mo(CO) <sub>5</sub>	38	92 (185)
Ph	H	Ph	Ph	Fe(CO) <sub>4</sub>	38	43 (185)
					99	(157)
Ph	H	Ph	Ph	Mo(CO) <sub>5</sub>	38	94 (185)
Ph	I	Ph	I	Cr(CO) <sub>5</sub>	11	(113)
cHex	cHex	cHex	cHex	VCp(CO) <sub>3</sub>	9	(96)
cHex	cHex	cHex	cHex	V(CO) <sub>5</sub> -NEt <sub>4</sub> <sup>+</sup>	9	(96)
iPr <sub>2</sub> N	H	iPr <sub>2</sub> N	Cl	W(CO) <sub>5</sub>	31	14 (177*)

TABLE 6 (Continued)

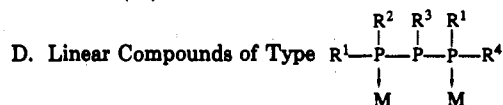
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	M	method	yield (ref)
C <sub>6</sub> F <sub>5</sub>	C <sub>6</sub> F <sub>5</sub>	C <sub>6</sub> F <sub>5</sub>	C <sub>6</sub> F <sub>5</sub>	Cr(CO) <sub>5</sub>	68	31 (223)
					38	15 (223)
C <sub>6</sub> F <sub>5</sub>	C <sub>6</sub> F <sub>5</sub>	C <sub>6</sub> F <sub>5</sub>	C <sub>6</sub> F <sub>5</sub>	Mo(CO) <sub>5</sub>	68	17 (223)
					38	16 (223)
An	Br	An	Br	Cr(CO) <sub>5</sub>	11	(113)
Cl	H	iPr <sub>2</sub> N	iPr <sub>2</sub> N	W(CO) <sub>5</sub>	31	(177)



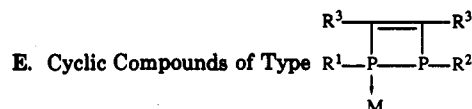
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	X	M	method	yield (ref)
Me	Me	Me	S	Fe(CO) <sub>4</sub>	117	(224)
Me	Me	Me	S	RhCp*(C <sub>2</sub> H <sub>4</sub> )	117	30 (135)
Me	Me	Me	Se	RhCp*(C <sub>2</sub> H <sub>4</sub> )	117	50 (135)
Me	H	OEt	O	W(CO) <sub>5</sub>	58	(209)
NEt <sub>2</sub>	NEt <sub>2</sub>	OEt	O	Mo(CO) <sub>5</sub>	7	34 (106)
P(O)(OEt) <sub>2</sub>	P(O)(OEt) <sub>2</sub>	OEt	O	Mo(CO) <sub>5</sub>	7	23 (106)
P(O)(OEt) <sub>2</sub>	P(O)(OEt) <sub>2</sub>	OEt	O	W(CH <sub>3</sub> CN)(CO) <sub>4</sub>	5(CH <sub>3</sub> CN)	48 (130)
P(O)(OEt) <sub>2</sub>	Ph	OEt	O	Mo(CO) <sub>5</sub>	7	93 (106)
Ph	Ph	OEt	O	Mo(CO) <sub>5</sub>	7	87 (106*)
Ph	Ph	OEt	O	Mo(Pip)(CO) <sub>4</sub>	18	(106)
Ph	Ph	OEt	O	Mo(PPh <sub>3</sub> )(CO) <sub>4</sub>		(106)
Ph	Ph	Ph	O	Cr(CO) <sub>5</sub>	5(CH <sub>3</sub> CN)	50-60 (20)
Ph	Ph	Ph	O	Mo(CO) <sub>5</sub>	7	53 (20*)
Ph	Ph	Ph	O	W(CO) <sub>5</sub>	5(CH <sub>3</sub> CN)	50-60 (20)
Ph	Ph	Ph	O	Cr(Pip)(CO) <sub>4</sub>	18	60-70 (20)
Ph	Ph	Ph	O	Mo(Pip)(CO) <sub>4</sub>	18	60-70 (20)
Ph	Ph	Ph	O	W(Pip)(CO) <sub>4</sub>	18	60-70 (20)
Ph	H	OEt	O	W(CO) <sub>5</sub>	58	(209)
iPr <sub>2</sub> N	iPr <sub>2</sub> N	OEt	O	Fe(CO) <sub>4</sub>	10	83 (106)



R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	M	method	yield (ref)	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	M	method	yield (ref)
Me	Me	Me	Cr(CO) <sub>4</sub>	15	80 (106)	Ph	Ph	Ph	NiCp <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	16	89 (142)
Me	Me	Me	Mo(CO) <sub>4</sub>	15	48 (106)	Ph	Ph	Ph	NiCp <sup>+</sup> Cl <sup>-</sup>	16	57 (142)
Me	Me	Me	W(CO) <sub>4</sub>	15	49 (106)	Ph	Ph	Ph	NiBr <sub>2</sub>	21	(150)
Me	Me	CF <sub>3</sub>	Cr(CO) <sub>4</sub>	15	91 (26)	Ph	Ph	Ph	PdCl <sub>2</sub>	21	(150)
Me	Me	CF <sub>3</sub>	Mo(CO) <sub>4</sub>	15	82 (26)	Ph	Ph	Ph	Rh(CO)Cl	7	(77)
Me	Me	CF <sub>3</sub>	W(CO) <sub>4</sub>	15	63 (26)	Ph	Ph	Ph	VCp(CO) <sub>2</sub>	9	(15)
Ph	Ph	Ph	CoBr <sub>2</sub>	21	(150)	Ph	H	Ph	Mo(CO) <sub>4</sub>	38	78 (185)
Ph	Ph	Ph	CoI <sub>2</sub>	21	(150)	H	H	Ph	Mo(CO) <sub>4</sub>	38	(185)
Ph	Ph	Ph	NbCp(CO) <sub>2</sub>	9	(97)						

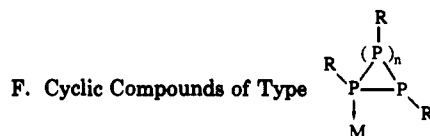


R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	M	method	yield (ref)
Me	Me	Ph	Me	W(CO) <sub>5</sub>	97	13 (198)
Ph	PPh <sub>2</sub>	Ph	PPh <sub>2</sub>	Fe(CO) <sub>4</sub>	112	63 (185)
Ph	PPh <sub>2</sub>	Ph	H	Mo(CO) <sub>5</sub>	113	16 (185)
Ph	H	Ph	H	Fe(CO) <sub>4</sub>	52	(185)
Ph	H	Ph	H	Mo(CO) <sub>5</sub>	52	47 (185)

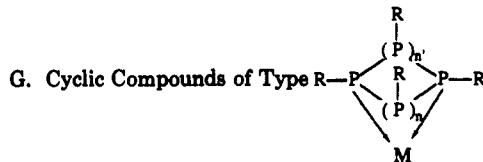


R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	M	method	yield (ref)	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	M	method	yield (ref)
Me	Tms	CF <sub>3</sub>	Ir(PPh <sub>3</sub> ) <sub>2</sub> Cl	as 18 (N <sub>2</sub> )	(83)	Ph	Ph	CF <sub>3</sub>	Ir(PPh <sub>3</sub> ) <sub>2</sub> Cl	as 18 (N <sub>2</sub> )	(83)
CF <sub>3</sub>	CF <sub>3</sub>	CF <sub>3</sub>	Fe(CO) <sub>4</sub>	5 (Fe(CO) <sub>5</sub> )	45 (169)	Ph	Ph	Ph	Fe(CO) <sub>4</sub>	as 11	(105)
CF <sub>3</sub>	CF <sub>3</sub>	CF <sub>3</sub>	Ir(PPh <sub>3</sub> ) <sub>2</sub> Cl	as 18 (N <sub>2</sub> )	(83)						

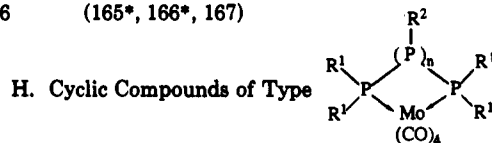
TABLE 6 (Continued)



<i>n</i>	R	M	method	yield (ref)	<i>n</i>	R	M	method	yield (ref)
1	iPr	Cr(CO) <sub>5</sub>	as 11	98 (116) (107)	2	Ph	Fe(CO) <sub>4</sub>	as 7	(75, 164)
			63	(217)	2	Ph	Ni(CO) <sub>3</sub>	as 7	(164)
1	iPr	Mo(CO) <sub>5</sub>		(107)	3	Et	Cr(CO) <sub>5</sub>	as 7	(75)
1	iPr	W(CO) <sub>5</sub>	as 11	95 (116) (107, 109*)				26	(92)
1	tBu	Cr(CO) <sub>5</sub>	as 11	98 (116) (107*, 108*)	3	Et	Mo(CO) <sub>5</sub>	as 7	(75)
			63	51 (217)				26	(92)
1	tBu	W(CO) <sub>5</sub>	as 11	98 (116) (107)	3	Et	W(CO) <sub>5</sub>	as 7	(75)
1	Ph	Cr(CO) <sub>5</sub>	63	(217)				26	(92)
1	cHex	Cr(CO) <sub>5</sub>	100	62 (217)	3	Ph	Cr(CO) <sub>5</sub>	as 7	(75)
1	Mes	Cr(CO) <sub>5</sub>	81	15 (62*)				26	(92)
1	(-)-Ment	Cr(CO) <sub>5</sub>	63	(217)	3	Ph	Mo(CO) <sub>5</sub>	as 7	(75)
								26	(92, 164)
					3	Ph	Ni(CO) <sub>3</sub>	26	(168)
					3	Ph	W(CO) <sub>5</sub>	as 7	(75)
								26	(92, 164)



<i>n</i>	<i>n'</i>	R	M	method	yield (ref)	<i>n</i>	<i>n'</i>	R	M	method	yield (ref)
1	1	Et	Mo(CO) <sub>4</sub>	13	10 (133) (167)	2	2	Me	Cr(CO) <sub>4</sub>	26	(19)
1	1	Et	W(CO) <sub>4</sub>	13	23 (133)	2	2	Me	W(CO) <sub>4</sub>	26	(19*)
2	1	Et	Mo(CO) <sub>4</sub>	26	(165*, 166*, 167)						



<i>n</i>	R <sup>1</sup>	R <sup>2</sup>	method	yield (ref)	<i>n</i>	R <sup>1</sup>	R <sup>2</sup>	method	yield (ref)
1	Me	tBu	55	61 (203) 4 (201) (16*)	2	Me	Me	55	26 (203) 20 (204) (201, 202, 205*)
1	Me	Ph	55	(203)	2	Me	tBu	55	3 (203)
1	Ph	Me	55	49 (203)	2	Me	Ph	55	13.7 (203)
1	Ph	Ph	55	3 (203)	2	Ph	Ph	55	(203)

## I. Miscellaneous Linear Compounds

compound	R	method	yield (ref)	compound	R	method	yield (ref)	
			118	27 (147)	(CO) <sub>4</sub> Mo		15	61 (106)
			118	80 (147)	(CO) <sub>2</sub> CpMo		as 7	(84)
	Tms	8	(18)					
	Ph	8	(18)					

## J. Miscellaneous Cyclic Compounds (M outside the cycle)

compound	R	M	method	yield (ref)
		Cr(CO) <sub>5</sub>	as 11	70 (120) 68 (103) (141*)
		Fe(CO) <sub>4</sub>	as 5 (Fe(CO) <sub>5</sub> )	22 (103)
		Mo(Bipy)(CO) <sub>3</sub>	as 5 (CH <sub>3</sub> CN)	(131)
		Mo(Phen)(CO) <sub>3</sub>	as 5 (CH <sub>3</sub> CN)	78 (131)
			68	80 (29)
			as 5 (Fe(CO) <sub>5</sub> )	(21*)

TABLE 6 (Continued)

## J. Miscellaneous Cyclic Compounds (M outside the cycle)

compound	R	M	method	yield (ref)
	Me iPr		13 13	88 (132) 87 (132)
			74	(232)
	Me Et		as 7 as 7	(81*) (80*)
			79	70 (236)
			as 11	67 (118)
		Cr W	as 11 as 11	32 (110) (112) (111)
			28	45 (171) 14 (170) (172)
			as 15	60 (103)
		Cr(CO)5 Mn(CO)2Cp Mo(CO)5	as 11 as 11 as 9	(101*, 136) (136) (136)
			81	30 (62*)
			as 11	70 (119*)
			17	53 (143)

## K. Miscellaneous Cyclic Compounds (M inside a cycle)

compound	R	M	method	yield (ref)	compound	R	M	method	yield (ref)
			75	8-10 (233)		P=C-Tms Ph HC=CHPh tBu		41 as 41	56 (188) 73 (188)
		Cr Mo W	57 57 57	(28) 60-70 (28*) (28)			Cr(CO)3 Mo(CO)3 W(CO)3	as 26 as 26 as 26	(19) (19) (19)

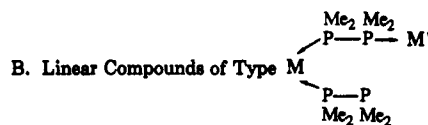
TABLE 7.  $\eta^3\eta^1$  Di- and Triphosphane Complexes

A. Linear Compounds of Type  $\begin{array}{c} R^2 \quad R^3 \\ | \quad | \\ R^1 - P - P - R^4 \\ | \quad | \\ M \quad M' \end{array}$

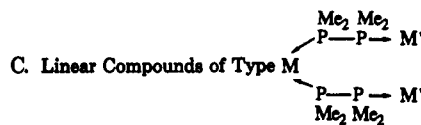
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	M	M'	method	yield (ref)
Br	Br	Br	Br	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	116	90 (210, 269)
						59	33 (212) 21 (211)
Br	Br	Br	Br	W(CO) <sub>5</sub>	W(CO) <sub>5</sub>	59	23 (211)
Br	Ph	Br	Ph	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	11	18-57 (113)
						121	40 (287)
Br	Ph	Br	Ph	W(CO) <sub>5</sub>	W(CO) <sub>5</sub>	11	34 (113)
Br	MeOC <sub>6</sub> H <sub>4</sub>	Br	MeOC <sub>6</sub> H <sub>4</sub>	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	11	45 (113)
Me	Me	Me	Me	Co(CO) <sub>2</sub> NO	Co(CO) <sub>2</sub> NO		(260)
Me	Me	Me	Me	Co(CO) <sub>2</sub> NO	Cr(CO) <sub>5</sub>	96	68 (98) (260)
Me	Me	Me	Me	Co(CO) <sub>2</sub> NO	Fe(CO) <sub>4</sub>	96	(224, 260)
Me	Me	Me	Me	CoCp(CO)	CoCp(CO)	as 7	42 (87) (260)
Me	Me	Me	Me	CoCp(CO)	Cr(CO) <sub>5</sub>	96	22 (98) (260)
Me	Me	Me	Me	CoCp(CO)	Fe(CO) <sub>4</sub>	96	(224, 260)
Me	Me	Me	Me	CoCp(CO)	RhCp*(CO)	96	80-90 (134)
Me	Me	Me	Me	Co(CO) <sub>3</sub> AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	Co(CO) <sub>3</sub> AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	20	97 (148)
						96	85 (148)
Me	Me	Me	Me	Co(CO) <sub>3</sub> AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	Fe(CO) <sub>2</sub> (NO)AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	96	84-95 (148)
Me	Me	Me	Me	Co(CO) <sub>3</sub> AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	Mn(CO) <sub>4</sub> AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	96	72-88 (148)
Me	Me	Me	Me	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	7	47 (90) 12 (91)
						98	1-68 (137)
						96	(92, 260)
Me	Me	Me	Me	Cr(CO) <sub>5</sub>	Fe(CO)(NO) <sub>2</sub>		(260)
Me	Me	Me	Me	Cr(CO) <sub>5</sub>	Fe(CO) <sub>4</sub>	96	18 (98) (91, 224, 260)
Me	Me	Me	Me	Cr(CO) <sub>5</sub>	Mn(CO) <sub>4</sub> Br	96	33 (98) (260)
Me	Me	Me	Me	Cr(CO) <sub>5</sub>	MnCp(CO) <sub>2</sub>	96	21 (98) (260)
Me	Me	Me	Me	Cr(CO) <sub>5</sub>	Mo(CO) <sub>5</sub>	96	38 (92) (260)
						98	11 (137)
Me	Me	Me	Me	Cr(CO) <sub>5</sub>	Ni(CO) <sub>3</sub>	96	52 (98)
						98	11 (137)
Me	Me	Me	Me	Cr(CO) <sub>5</sub>	W(CO) <sub>5</sub>	96	33-49 (92) (91, 260)
						98	18-27 (137)
Me	Me	Me	Me	Fe(CO)(NO) <sub>2</sub>	Fe(CO)(NO) <sub>2</sub>	as 7	34 (99) (260)
Me	Me	Me	Me	Fe(CO)(NO) <sub>2</sub>	Fe(CO) <sub>4</sub>	96	(224, 260)
Me	Me	Me	Me	Fe(CO) <sub>4</sub>	Fe(CO) <sub>4</sub>	as 5	33 (91)
						7	(85*, 89)
						96	(224, 260)
Me	Me	Me	Me	Fe(CO) <sub>4</sub>	Mn(CO) <sub>4</sub> Br	96	(224, 260)
Me	Me	Me	Me	Fe(CO) <sub>4</sub>	MnCp(CO) <sub>2</sub>	96	(224, 260)
Me	Me	Me	Me	Fe(CO) <sub>4</sub>	Mo(CO) <sub>5</sub>	96	(224, 260)
Me	Me	Me	Me	Fe(CO) <sub>4</sub>	Ni(CO) <sub>3</sub>	96	(224, 260)
Me	Me	Me	Me	Fe(CO) <sub>4</sub>	W(CO) <sub>5</sub>	96	(224, 260)
Me	Me	Me	Me	Fe(CO) <sub>2</sub> (NO)AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	Fe(CO) <sub>2</sub> (NO)AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	96	85 (148)
						20	84 (148)
Me	Me	Me	Me	Fe(CO) <sub>2</sub> (NO)AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	Mn(CO) <sub>4</sub> AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	96	81-89 (148)
Me	Me	Me	Me	Mn(CO) <sub>4</sub> Br	Mn(CO) <sub>4</sub> Br		(260)
Me	Me	Me	Me	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	98	32 (137) 17 (140)
						9	21 (87) (260)
Me	Me	Me	Me	MnCp(CO) <sub>2</sub>	RhCp*(CO)	96	70 (134)
Me	Me	Me	Me	Mn(C <sub>6</sub> H <sub>4</sub> Me)(CO) <sub>2</sub>	RhCp*(CO)	96	70 (134)
Me	Me	Me	Me	Mn(CO) <sub>4</sub> AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	Mn(CO) <sub>4</sub> AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	20	88 (148)
						96	83 (148)
Me	Me	Me	Me	Mo(CO) <sub>5</sub>	Mo(CO) <sub>5</sub>	7	34 (90) 26 (91) (89)
						96	(92, 260)
						98	13 (137)
Me	Me	Me	Me	Mo(CO) <sub>5</sub>	W(CO) <sub>5</sub>	96	56 (92)
Me	Me	Me	Me	Ni(CO) <sub>3</sub>	Ni(CO) <sub>3</sub>	98	2-20 (137)
						7	(91, 260)
Me	Me	Me	Me	RhCp(CO)	RhCp*(CO)	96	80-90 (134)
Me	Me	Me	Me	RhCp*(CO)	RhCp*(CO)	19	69 (147)
						as 7	5 (147)
Me	Me	Me	Me	RhCp*(CO)	[RhCp*(CO)] <sub>2</sub>	19	80-85 (134)
Me	Me	Me	Me	RhCp*(C <sub>2</sub> H <sub>4</sub> )	RhCp*(C <sub>2</sub> H <sub>4</sub> )	14	5 (135)
Me	Me	Me	Me	RhCp*(C <sub>2</sub> H <sub>4</sub> )	[RhCp*(CO)] <sub>2</sub>	19	80-85 (134)
Me	Me	Me	Me	V(CO) <sub>5</sub> -NEt <sub>4</sub> <sup>+</sup>	V(CO) <sub>5</sub> -NEt <sub>4</sub> <sup>+</sup>	as 9	(96)
Me	Me	Me	Me	W(CO) <sub>5</sub>	W(CO) <sub>5</sub>	7	48 (90) 9 (91) (89)
						98	17-38 (137)
Me	Me	CF <sub>3</sub>	CF <sub>3</sub>	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	96	17 (28)
Me	Me	CF <sub>3</sub>	CF <sub>3</sub>	Mo(CO) <sub>5</sub>	Mo(CO) <sub>5</sub>	96	23 (28)
Me	tBu	Me	tBu	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	113	42 (24*)
Me	iBu	iBu	H	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	60	45 (24)
Me	tBu	tBu	H	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	113	74 (24)
						60	37 (24)
Me	Ph	Me	Ph	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	113	5 (24)
Me	Ph	Me	Ph	VCp(CO) <sub>3</sub>	VCp(CO) <sub>3</sub>	9	(96)
Me	cHex	cHex	H	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	60	30 (24)
Me	Cl	Me	H	Fe(CO) <sub>4</sub>	Fe(CO) <sub>4</sub>	89	(244)
MeO	Et	Et	H	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	121	67 (240)
MeO	Ph	Ph	H	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	121	73 (287)
MeO	An	An	H	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	121	67 (240)
CF <sub>3</sub>	CF <sub>3</sub>	CF <sub>3</sub>	CF <sub>3</sub>	Ni(CO) <sub>3</sub>	Ni(CO) <sub>3</sub>	6	(6)
Ac	Ph	Ph	H	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	121	58 (240)

TABLE 7 (Continued)

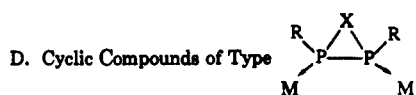
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	M	M'	method	yield (ref)
Et	Et	Et	Et	Mo(CO) <sub>5</sub>	Mo(CO) <sub>5</sub>	7	(88*, 89)
Et	Et	Et	Et	W(CO) <sub>5</sub>	W(CO) <sub>5</sub>	7	(89)
Et	Cl	Et	Cl	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	82	19 (240)
iPr	H	iPr	H	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	60	15 (24)
Tms	cHex	cHex	H	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	60	15 (24)
nBu	Ph	nBu	Ph	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	114	45 (113)
nBu	Cl	nBu	Cl	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	82	14 (240)
tBu	D	tBu	D	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	113	84 (24)
tBu	H	tBu	H	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	60	48 (24)
						as 64	32 (24)
Et <sub>2</sub> N	Et <sub>2</sub> N	Et <sub>2</sub> N	Et <sub>2</sub> N	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	11	20 (289) (210)
BuNH	Ph	Ph	H	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	121	88 (287*)
TmsCH <sub>2</sub>	H	TmsCH <sub>2</sub>	H	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	60	35 (24)
Ph	Ph	Ph	Ph	Ag(pyr) <sub>3</sub> <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>	Ag(pyr) <sub>3</sub> <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>	78	(235*)
Ph	Ph	Ph	Ph	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	9	30 (87)
Ph	Ph	Ph	Ph	Mo(CO) <sub>5</sub>	Mo(CO) <sub>5</sub>	46	12 (93)
Ph	Ph	Ph	Ph	NbCp(CO) <sub>3</sub>	NbCp(CO) <sub>3</sub>	9	(97)
Ph	Ph	Ph	Ph	Ni(CO) <sub>5</sub>	Ni(CO) <sub>5</sub>	7	82 (91) (10*)
Ph	Ph	Ph	Ph	Ni(CH <sub>2</sub> CHCH <sub>2</sub> )Br	Ni(CH <sub>2</sub> CHCH <sub>2</sub> )Br	110	(91)
Ph	Ph	Ph	Ph	V(CO) <sub>5</sub> <sup>-</sup> NEt <sub>4</sub> <sup>+</sup>	V(CO) <sub>5</sub> <sup>-</sup> NEt <sub>4</sub> <sup>+</sup>	as 9	(15, 96)
Ph	Ph	Ph	H	Ni(CO) <sub>5</sub>	Mo(CO) <sub>5</sub>	96	91 (185)
Ph	Cl	Ph	Cl	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>		(114*)
Ph	Cl	Ph	H	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	121	48 (287)
Ph	Cl	Ph	H	Fe(CO) <sub>4</sub>	Fe(CO) <sub>4</sub>	89	(244)
Ph	H	Ph	H	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	114	71.5 (113)
						82	14 (240)
Ph	H	Ph	H	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	61	(213*)
Ph	H	Ph	OH	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	121	50 (287*)
Ph	I	Ph	I	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	11	37 (113)
cHex	cHex	cHex	cHex	V(CO) <sub>5</sub> <sup>-</sup> NEt <sub>4</sub> <sup>+</sup>	V(CO) <sub>5</sub> <sup>-</sup> NEt <sub>4</sub> <sup>+</sup>	as 9	(96)
cHex	H	cHex	H	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	60	15 (24)
Mes	H	Mes	H	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	88	2 (82*)
Mes	H	Mes	H	Mn(C <sub>2</sub> H <sub>4</sub> Me)(CO) <sub>2</sub>	Mn(C <sub>2</sub> H <sub>4</sub> Me)(CO) <sub>2</sub>	64	10 (24)
3,5-(Me) <sub>2</sub> (C <sub>6</sub> H <sub>3</sub> )CH <sub>2</sub>	H	3,5-(Me) <sub>2</sub> (C <sub>6</sub> H <sub>3</sub> )CH <sub>2</sub>	H	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	60	10 (24)
(-)-Ment	H	(-)-Ment	H	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	121	59 (218)
Cl	Cl	Cl	Cl	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	59	14 (212)
H	H	H	H	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	11	(121)
H	H	H	H	MnCp(CO) <sub>2</sub>	MnCp(CO) <sub>2</sub>	11	(121)



M	M'	method	yield (ref)	M	M'	method	yield (ref)
Cr(CO) <sub>4</sub>	Co(CO) <sub>2</sub> (NO)	as 96	98 (140)	Mo(CO) <sub>4</sub>	Fe(CO)(NO) <sub>2</sub>	as 96	88 (140)
Cr(CO) <sub>4</sub>	Cr(CO) <sub>5</sub>	as 96	(98)	Mo(CO) <sub>4</sub>	W(CO) <sub>5</sub>	as 96	62 (140)
Cr(CO) <sub>4</sub>	Fe(CO)(NO) <sub>2</sub>	as 96	83 (140)	W(CO) <sub>4</sub>	Co(CO) <sub>2</sub> (NO)	as 96	53 (140)
Mo(CO) <sub>4</sub>	Co(CO) <sub>2</sub> (NO)	as 96	99 (140)	W(CO) <sub>4</sub>	Fe(CO)(NO) <sub>2</sub>	as 96	72 (98)
Mo(CO) <sub>4</sub>	Cr(CO) <sub>5</sub>	as 96	100 (140)				

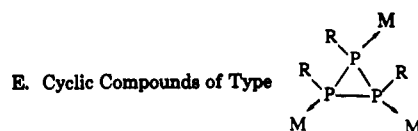


M	M'	method	yield (ref)	M	M'	method	yield (ref)
Co(CO)(NO)	Cr(CO) <sub>5</sub>	as 96	20 (137)	Cr(CO) <sub>4</sub>	Mo(CO) <sub>5</sub>	as 96	38 (137)
Cr(CO) <sub>4</sub>	Co(CO) <sub>2</sub> (NO)	as 96	59 (137)	Cr(CO) <sub>4</sub>	Ni(CO) <sub>5</sub>	as 96	69 (137)
Cr(CO) <sub>4</sub>	CoCp(CO)	as 96	27 (137)	Cr(CO) <sub>4</sub>	W(CO) <sub>5</sub>	as 96	41 (137)
Cr(CO) <sub>4</sub>	Cr(CO) <sub>5</sub>	as 96	50 (137)	Fe(CO) <sub>3</sub>	Cr(CO) <sub>5</sub>	as 96	(98)
Cr(CO) <sub>4</sub>	Fe(CO)(NO) <sub>2</sub>	as 96	45 (137)	Fe(NO) <sub>2</sub>	Cr(CO) <sub>5</sub>	as 96	55 (137)
Cr(CO) <sub>4</sub>	Fe(CO) <sub>4</sub>	as 96	45 (137)	Fe(NO) <sub>2</sub>	Mn(CO) <sub>4</sub> AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	as 96	79 (138)
Cr(CO) <sub>4</sub>	Mn(CO) <sub>4</sub> Br	as 96	68 (137)	Mn(CO) <sub>3</sub> Br	Cr(CO) <sub>5</sub>	as 96	72 (137)
Cr(CO) <sub>4</sub>	MnCp(CO) <sub>2</sub>	as 96	64 (137)	Ni(CO) <sub>2</sub>	Cr(CO) <sub>5</sub>	as 96	66 (137) 19 (98)
Cr(CO) <sub>4</sub>	Mn(CO) <sub>4</sub> AsMe <sub>2</sub> Fe(CO) <sub>4</sub>	as 96	95 (138)				

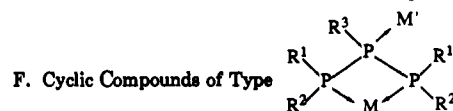


R	X	M	method	yield (ref)	R	X	M	method	yield (ref)
iPr	P(iPr)	Cr(CO) <sub>5</sub>	63	60 (217)	cHex	P(cHex)	Cr(CO) <sub>5</sub>	63	44 (217)
			as 11	28 (116) (107)				85	23 (237*)
iPr	P(iPr)	W(CO) <sub>5</sub>		(107)	Ph	C(OEt)(Ph)	W(CO) <sub>5</sub>	94	7.6 (256)
Ph	CH <sub>2</sub>	Cr(CO) <sub>5</sub>	123	64 (287*)	Ph	S	Cr(CO) <sub>5</sub>	123	48 (287*)
Ph	NPh	Cr(CO) <sub>5</sub>	123	69 (237)	An	S	Cr(CO) <sub>5</sub>	123	38 (237)
Ph	P(Ph)	Cr(CO) <sub>5</sub>	63	28 (217)					

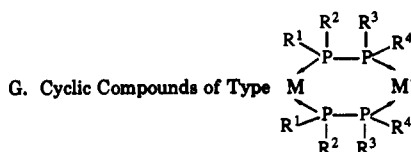
TABLE 7 (Continued)



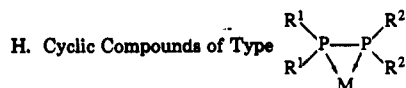
R	M	method	yield (ref)	R	M	method	yield (ref)
Me	Cr(CO) <sub>5</sub>	63	36 (217)	nBu	Cr(CO) <sub>5</sub>	as 85	8 (237)
Et	Cr(CO) <sub>5</sub>	63	39 (217)	Ph	MnCp(CO) <sub>2</sub>	61	14 (214*) (215)



R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	M	M'	method	yield (ref)
Me	Me	tBu	Mo(CO) <sub>4</sub>	Ni(CO) <sub>3</sub>	as 96	61 (203)
Me	Cl	Me	Fe(CO) <sub>3</sub>	Fe(CO) <sub>4</sub>	89	50 (244) (245)
Ph	Ph	Me	Mo(CO) <sub>4</sub>	Ni(CO) <sub>3</sub>	as 96	91 (203)
Ph	Ph	Ph	PtCl <sub>2</sub>	Fe(CO) <sub>4</sub>	as 96	(157)



R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	M	M'	method	yield (ref)
Me	Me	Me	Me	Co(CO)(NO)	Co(CO)(NO)	98	27 (140) 1-11 (137)
Me	Me	Me	Me	Co(CO)(NO)	Cr(CO) <sub>4</sub>	98	0.5-32 (137) 28 (140)
Me	Me	Me	Me	Co(CO)(NO)	Mo(CO) <sub>4</sub>	98	62 (140)
Me	Me	Me	Me	Co(CO)(NO)	W(CO) <sub>4</sub>	98	58 (140)
Me	Me	Me	Me	Cr(CO) <sub>4</sub>	Cr(CO) <sub>4</sub>	98	1-76 (137) 72 (140)
						9	23 (98)
Me	Me	Me	Me	Cr(CO) <sub>4</sub>	Fe(NO) <sub>2</sub>	98	30 (140) 4-28 (122)
Me	Me	Me	Me	Cr(CO) <sub>4</sub>	Mn(CO) <sub>3</sub> Br	96	17 (140)
						98	5 (137)
Me	Me	Me	Me	Cr(CO) <sub>4</sub>	Ni(CO) <sub>2</sub>	98	4-26 (137)
						96	9 (140)
Me	Me	Me	Me	Cr(CO) <sub>4</sub>	Mo(CO) <sub>4</sub>	96	42 (140)
Me	Me	Me	Me	Cr(CO) <sub>4</sub>	W(CO) <sub>4</sub>	98	16 (137)
						96	15 (140)
Me	Me	Me	Me	Fe(NO) <sub>2</sub>	Fe(NO) <sub>2</sub>	as 7	27 (99)
						98	1-12 (137)
Me	Me	Me	Me	Fe(NO) <sub>2</sub>	Mo(CO) <sub>4</sub>	98	55 (140)
Me	Me	Me	Me	Fe(NO) <sub>2</sub>	Ni(CO) <sub>2</sub>	96	15 (140)
Me	Me	Me	Me	Fe(NO) <sub>2</sub>	W(CO) <sub>4</sub>	98	41 (140)
Me	Me	Me	Me	Mn(CO) <sub>3</sub> Br	Mn(CO) <sub>3</sub> Br	98	34 (140)
Me	Me	Me	Me	Mn(CO) <sub>3</sub> Br	W(CO) <sub>4</sub>	96	58 (140)
Me	Me	Me	Me	Mo(CO) <sub>4</sub>	Mo(CO) <sub>4</sub>	98	79 (140) 28 (137)
Me	Me	Me	Me	Mo(CO) <sub>4</sub>	Mn(CO) <sub>3</sub> Br	96	53 (140)
Me	Me	Me	Me	Mo(CO) <sub>4</sub>	Ni(CO) <sub>2</sub>	96	34 (140)
Me	Me	Me	Me	Mo(CO) <sub>4</sub>	W(CO) <sub>4</sub>	96	16 (140)
Me	Me	Me	Me	Ni(CO) <sub>2</sub>	Ni(CO) <sub>2</sub>	98	14 (140) 2-7 (137)
Me	Me	Me	Me	Ni(CO) <sub>2</sub>	W(CO) <sub>4</sub>	96	19 (140)
Me	Me	Me	Me	VCp(CO) <sub>2</sub>	VCp(CO) <sub>2</sub>	9	(96)
Me	Me	Me	Me	W(CO) <sub>4</sub>	W(CO) <sub>4</sub>	98	37 (140) 17-27 (137)
Me	Me	CF <sub>3</sub>	CF <sub>3</sub>	Cr(CO) <sub>4</sub>	Cr(CO) <sub>4</sub>	as 96	38 (26)
Me	Me	CF <sub>3</sub>	CF <sub>3</sub>	Mo(CO) <sub>4</sub>	Mo(CO) <sub>4</sub>	as 96	60 (26)
Me	Me	CF <sub>3</sub>	CF <sub>3</sub>	W(CO) <sub>4</sub>	W(CO) <sub>4</sub>	as 96	10 (26)
Me	Ph	Me	Ph	VCp(CO) <sub>2</sub>	VCp(CO) <sub>2</sub>	as 9	(96)
Ph	Ph	Ph	Ph	Fe(Cp)(PPh <sub>2</sub> H) <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	Fe(Cp)(PPh <sub>2</sub> H) <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	48	(195)
Ph	Ph	Ph	Ph	NbCp(CO) <sub>2</sub>	NbCp(CO) <sub>2</sub>	9	(97)
Ph	Ph	Ph	Ph	V(CO) <sub>4</sub> -NEt <sub>4</sub> <sup>+</sup>	V(CO) <sub>4</sub> -NEt <sub>4</sub> <sup>+</sup>	9	(15, 96)
Ph	H	Ph	H	Ag(PPhH <sub>2</sub> ) <sup>+</sup> AsF <sub>6</sub> <sup>-</sup>	Ag(PPhH <sub>2</sub> ) <sup>+</sup> AsF <sub>6</sub> <sup>-</sup>	77	(234)
Ph	H	Ph	H	Cu(PPhH <sub>2</sub> ) <sup>+</sup> AsF <sub>6</sub> <sup>-</sup>	Cu(PPhH <sub>2</sub> ) <sup>+</sup> AsF <sub>6</sub> <sup>-</sup>	77	(234)
cHex	cHex	cHex	cHex	VCp(CO) <sub>2</sub>	VCp(CO) <sub>2</sub>	9	(96)



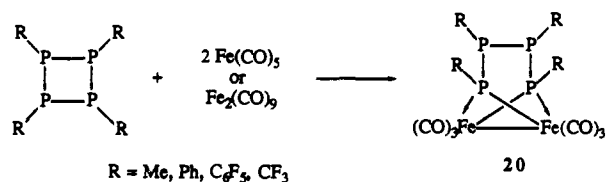
R <sup>1</sup>	R <sup>2</sup>	M	method	yield (ref)	R <sup>1</sup>	R <sup>2</sup>	M	method	yield (ref)
Me	tBu	WCp(CO) <sub>2</sub> <sup>+</sup> Cl <sup>-</sup>	50	84 (197)	cHex	cHex	CoI <sub>2</sub>	21	(154)
iPr	iPr	WCp(CO) <sub>2</sub> <sup>+</sup> Cl <sup>-</sup>	50	76 (197)	cHex	cHex	NiBr <sub>2</sub>	21	54 (154)
tBu	tBu	NiBr <sub>2</sub>	21	51 (155)	cHex	cHex	NiCl <sub>2</sub>	21	62 (154)
cHex	cHex	CoBr <sub>2</sub>	21	56 (154)	cHex	cHex	PdCl <sub>2</sub>	21	(154)
cHex	cHex	CoCl <sub>2</sub>	21	(154)					



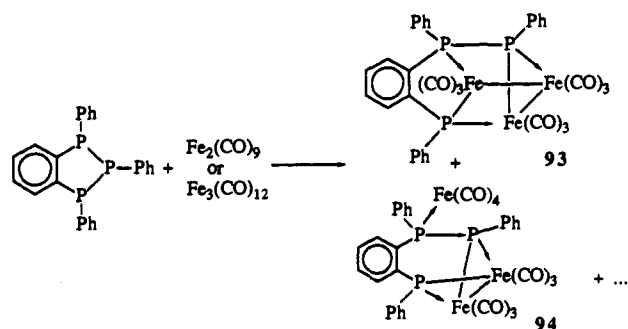
TABLE 7 (Continued)

I. Miscellaneous Compounds (M outside a cycle)										
compound	R	M	method	yield (ref)	compound	R	M	method	yield (ref)	
			as 11	72 (141)				94	56 (254) 31 (255)	
			42	55 (189)				as 97	14 (185) (262*)	
			47	85 (189) 65 (194)			Cr	as 11	(111)	
							W	as 11	(111)	
	nBu		122	36 (240)			Cr	as 11	(111, 112*)	
	Ph		122	56 (267*)			W	as 11	(111)	
			122	58 (267)				as 11	(138)	
J. Miscellaneous Cyclic Compounds (M inside a cycle)										
compound	X	M	method	yield (ref)	compound	X	M	method	yield (ref)	
			as 9	(95)				as 15 (COD)	47 (22*)	
	Me		44	34 (193)				as 7	(94)	
	H		44	35 (192*, 193*)						
	Br	Mn	12	(128*)						
	Br	Re	12	48-75 (124*)						
	I	Re	12	(123*) 57 (117)		Tms		8	43 (18*)	
			98	15 (137)		Ph		8	52 (18)	
			98	1 (137)				as 98	59 (102)	
		Cr(CO) <sub>4</sub>	as 15	43 (141*)				17	29 (143*) 28 (144)	
		Mo(CO) <sub>4</sub>	as 15	73 (141)						
		Rh(CO)Cl	19	59 (141)				15	(101*, 138)	
			69	40 (225*)						
								as 17	(27*)	

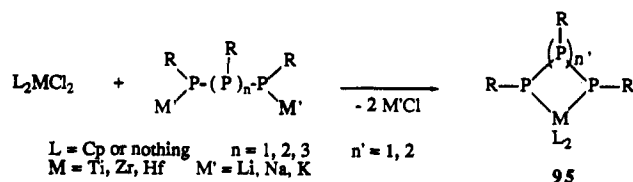
## SCHEME 27



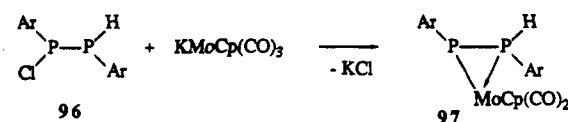
## SCHEME 28



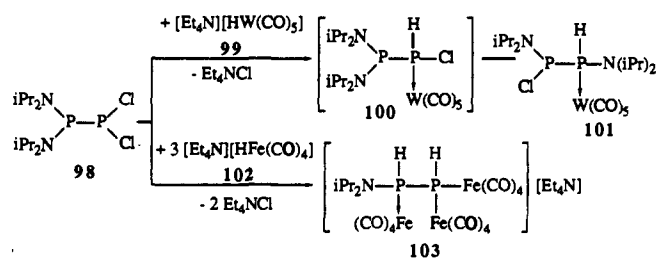
## SCHEME 29



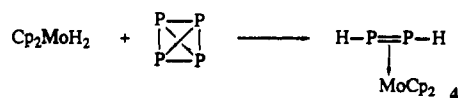
## SCHEME 30



## SCHEME 31



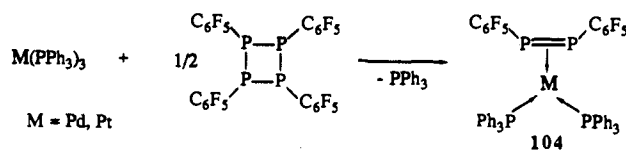
## SCHEME 32



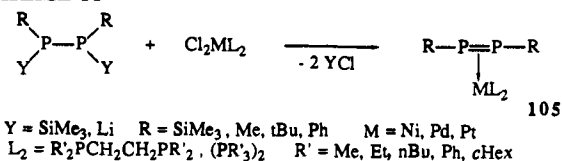
to stabilize free diphosphenes (Scheme 22). Moreover, the diphosphene  $\text{Tris}-\text{P}=\text{P}-\text{Tris}$ , which bears the bulky substituent  $\text{tris}(\text{trimethylsilyl})\text{methyl}$ , has never been complexed.

Unsymmetrical trans diphosphenes illustrate also this phenomenon: the reaction always takes place on the less crowded phosphorus atom.<sup>55,56,60,61,156</sup> The steric hindrance of metallic groups is also an influential factor for this reaction, since diphosphene 3 does react with  $\text{Cr}(\text{CO})_6$ , which is bulkier than  $\text{Ni}(\text{CO})_4$  or  $\text{Fe}(\text{CO})_5$ , but in this case, the reaction gives the  $\pi$  (arene) tri-

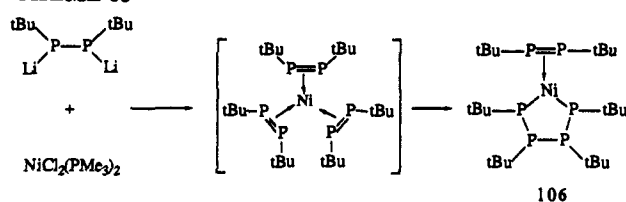
## SCHEME 33



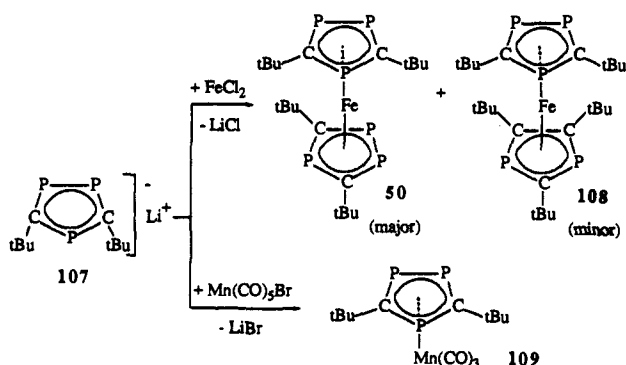
## SCHEME 34



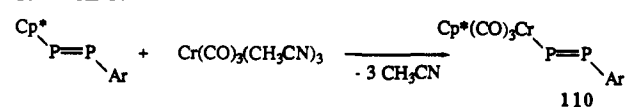
## SCHEME 35



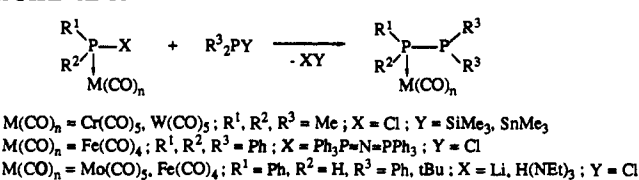
## SCHEME 36



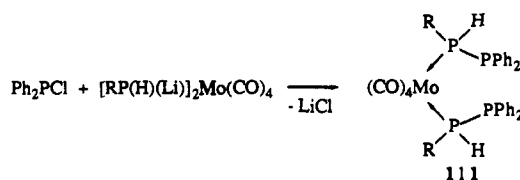
## SCHEME 37



## SCHEME 38



## SCHEME 39

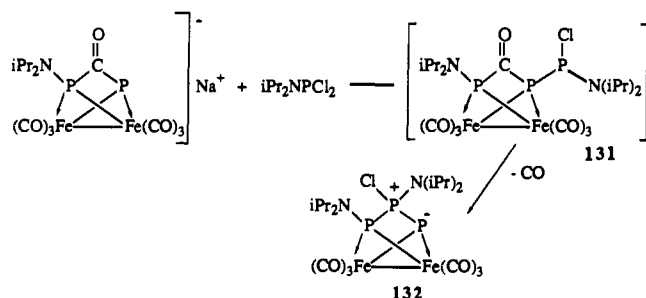


carbonylchromium complexes 83 and 84 instead of the  $\eta^1$  complex 82 (Scheme 23).<sup>160,161</sup>

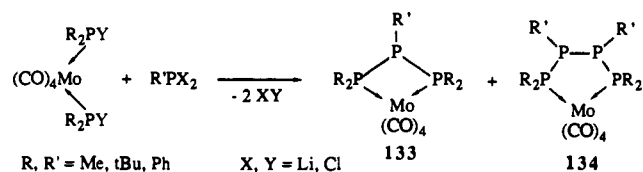
The influence of steric factors is also illustrated when silver or gold salts are involved. A cationic diphosphene complex is obtained with Ag, while only the mono cation 87 is formed with [Et<sub>3</sub>PAu][PF<sub>6</sub>], presumably as



SCHEME 54



SCHEME 55



## B. Complexation with Modification of a P—P or P=P Ligand

Modifications of a free ligand may occur by cleavage either of the phosphorus–phosphorus bond or of a phosphorus–substituent bond, during the course of the complexation. Most of the metalladiphosphanes are obtained in this way.

### 1. Synthesis of Diphosphane Complexes

**a. Phosphorus–Phosphorus Bond Cleavage.** A P–P bond cleavage frequently happens when drastic conditions are used to carry out a complexation reaction (see Scheme 7). The consequence with cyclopolphosphines is a ring extension, formally induced by insertion reaction of phosphinidene<sup>19,75,133,164–168</sup> (Scheme 26). Compounds of types 90 and 91 were claimed to be 1,2 complexes in first reports.<sup>75,76</sup> Later this assertion has been refuted<sup>19,133,141</sup> and the proposed structures of 1,3 and 1,4 complexes, depicted in Scheme 26, seems to be more reasonable.

With iron, a ring extension occurs by insertion of the metal into a phosphorus–phosphorus bond.<sup>30,32,94,169</sup> The reaction is clean with iron pentacarbonyl and gives phosphido-bridged metallacycles 20 (Scheme 27).

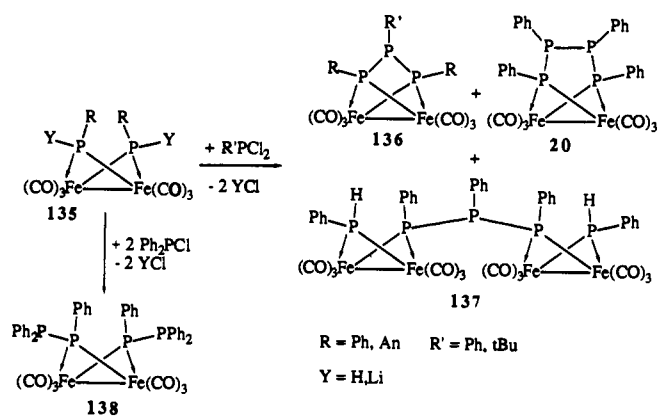
However, some reactions carried out with  $\text{Fe}_2(\text{CO})_9$  or  $\text{Fe}_3(\text{CO})_{12}$  produce a mixture of products sprung from insertion and complexation reactions<sup>170–172</sup> (Scheme 28).

**b. Phosphorus–Substituent Bond Cleavage.** Free di- or polyphosphanes which bear good leaving groups such as alkali or halides react with metal halides or hydrides. Formation of  $\sigma$  metallacycles 95<sup>31,34,173,174</sup> occurs with linear polyphosphane salts, but the length of the phosphorus chain is not always kept ( $n$  may be different from  $n'$ ) (Scheme 29).

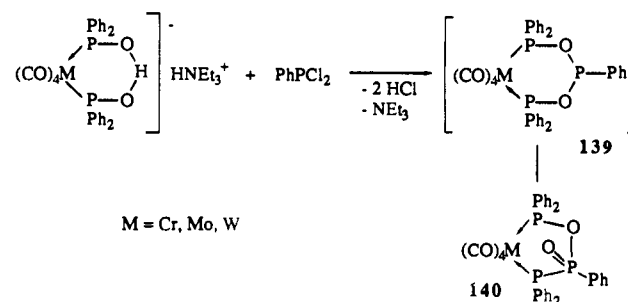
The reaction of a metal salt with monochlorodiphosphane 96, giving rise to the original three-membered metallacycle 97, is to be related to this series<sup>175</sup> (Scheme 30). Complex 97 is the only stable compound of type E. Earlier, formation of analogous complexes was postulated in mass spectrometry.<sup>176</sup>

For our part, we have studied the reactivity of two anionic hydrides 99 and 102 with a gem dihalogenated diphosphane 98. The compound isolated with tungsten

SCHEME 56



SCHEME 57



is diphosphane complex 101, which arises from a rearrangement of the intermediate compound 100.<sup>177</sup> We have also isolated an original anionic metalladiphosphane 103, obtained by addition of 3 equiv of iron hydride 102 on diphosphane 98<sup>177</sup> (Scheme 31).

### 2. Synthesis of Diphosphane Complexes

Most of  $\eta^2$  diphosphane complexes are obtained starting with compounds in which a phosphorus–phosphorus bond already exists. This is the case for the first reports in this field. One concerns the reaction of white phosphorus with a neutral molybdenum hydride<sup>9,43</sup> (Scheme 32).

The second reports a P–P bond double cleavage of a cyclotetraphosphane induced by a platinum or palladium complex, which allows the synthesis of diphosphane complex 104<sup>44,53</sup> (Scheme 33).

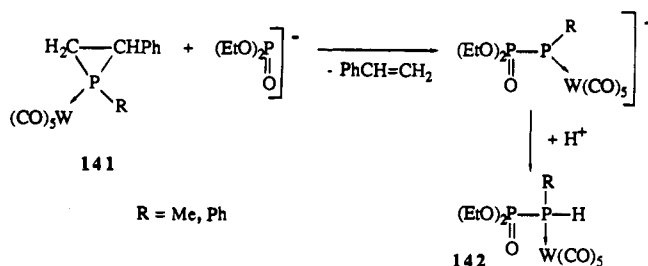
However, from a practical point of view, the reaction of linear diphosphane lithium salts or silylated diphosphanes with metallic halides is the most widely used to produce  $\eta^2$  diphosphane complexes of type P in good yield (70–90%)<sup>53,54,178–182</sup> (Scheme 34). Some of these compounds are palladium<sup>53,54</sup> or platinum<sup>53,54,181</sup> complexes, but most of them are nickel complexes.<sup>178–180,182</sup>

In one case, the reaction is more surprising: isolated compound 106 presumably arises from a coupling reaction between two diphosphane units in the coordination sphere of nickel,<sup>33</sup> with formation of a  $\sigma$  metallacycle (Scheme 35).

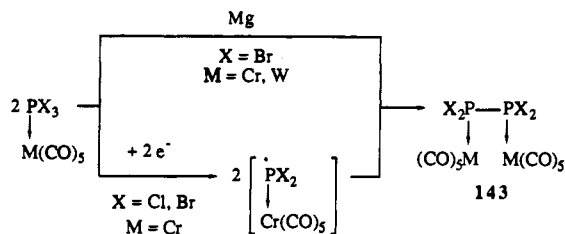
Some phosphorus analogues of ferrocene, 50 and 108, or cyclopentadienylmanganese tricarbonyl, 109, are also obtained starting from the phosphorus lithium salt 107 and metallic halides<sup>73</sup> (Scheme 36).

The last reaction related to a phosphorus–substituent bond cleavage implies the migration of a penta-

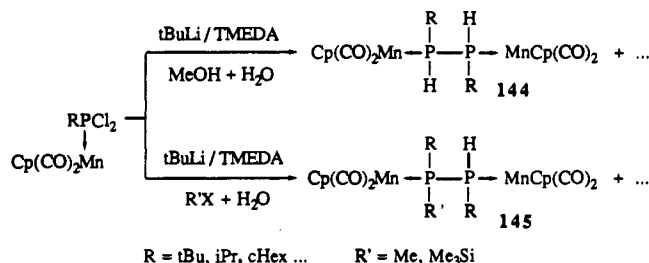
SCHEME 58



SCHEME 59



SCHEME 60



methylcyclopentadienyl group  $\eta^1$  bonded to phosphorus toward a metallic center, where it becomes  $\eta^5$  bonded and gives metalladiphosphane 110<sup>183</sup> (Scheme 37).

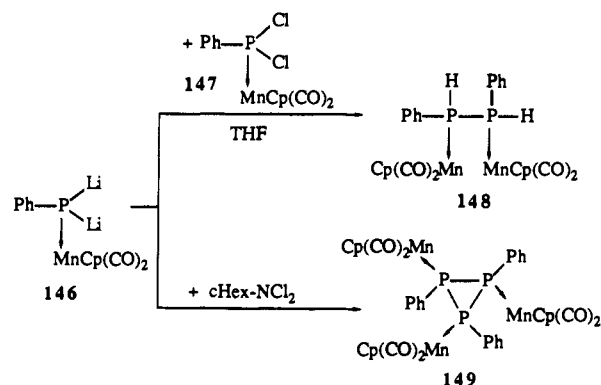
### C. Formation of a Phosphorus-Phosphorus Bond

The synthesis of diphosphane and diphosphene complexes by creating phosphorus-phosphorus bonds offers a wide range of possibilities. Generally, the phosphorus-phosphorus bond is formed by elimination reactions. Some reactions give univocally diphosphane complexes, other give either diphosphane or diphosphene complexes. The main factors directing the reaction are the number of leaving groups on the starting phosphane, the bulk of the organic substituent R, and sometimes the steric demand of the metallic group. Most of these reactions concern eliminations between a cationic group (Li, Na, H,  $\text{Me}_3\text{Si}$ ,  $\text{Me}_3\text{Sn}$ , etc.) of one of the starting phosphanes and a chloride anion of another phosphane. If at least one of the starting phosphorus compound possesses only one leaving group, the products are obviously diphosphane complexes, whereas with two leaving groups on each phosphorus compound, the reaction may result in the formation of diphosphene complexes.

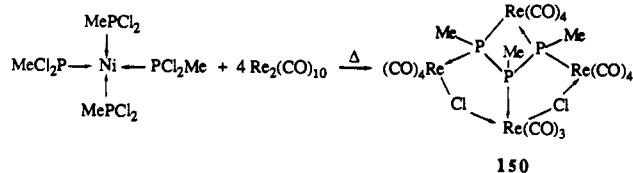
#### 1. Reactions of Complexed Phosphanes

**a. Monofunctionalized Phosphanes.** Complexed phosphanes may react with free phosphanes when each compound possesses a labile group. Elimination of  $\text{Me}_3\text{SiCl}$ ,<sup>98</sup>  $\text{Me}_3\text{SnCl}$ ,<sup>184</sup>  $\text{LiCl}$ ,<sup>185</sup> and  $[\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3]\text{Cl}$ <sup>186</sup> occurs spontaneously (Scheme 38). Bis( $\eta^1$

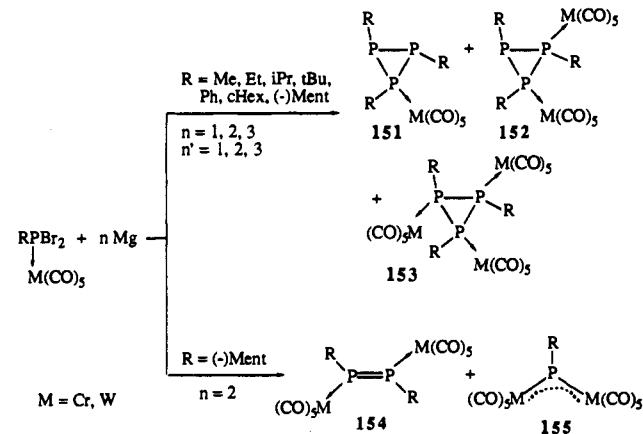
SCHEME 61



SCHEME 62



SCHEME 63



diphosphane) complexes 111<sup>185</sup> are also obtained in good yield (Scheme 39).

Analogous reactions are observed with delocalized anions. Intermediate 112, with both bridging and terminal  $\text{PPh}_2$  groups, prepared in situ from  $\text{LiPPh}_2$ , reacts with electrophiles such as chlorodiphenylphosphane<sup>187</sup> (Scheme 40).

The original low-coordinated diphosphadiene compound 114 is synthesized in an analogous way<sup>188</sup> (Scheme 41).

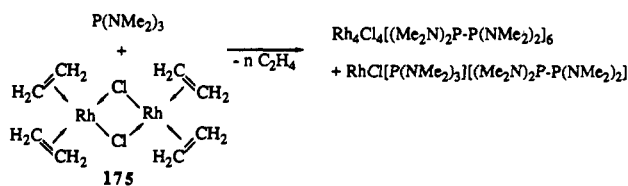
Two complexed phosphanes bearing labile substituents (mainly Li) can also associate under the influence of a third reactive to give  $\eta^1\eta^1$  diphosphane complexes. For instance, demetallation reactions of lithiated phosphane complexes occur with oxidants such as iodine<sup>189</sup> (Scheme 42).

In the case of halogenoalkanes, the reaction of the diphosphido complex 116 is mainly intermolecular,<sup>42,190,191</sup> side reactions with dibromoethane (117) or the solvent (118) also occur (Scheme 43). An intramolecular reaction leading to 23 is observed only when the organic substituent of phosphorus is a tert-butyl group.<sup>38</sup>

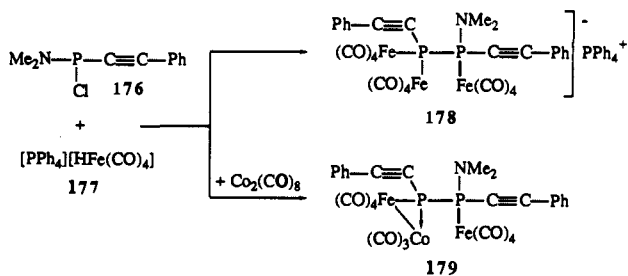
Some couplings of two  $\text{PPh}_n$  groups are observed by oxidation of monoanions with  $\text{RCHI}_2$ .<sup>192,193</sup> (Scheme 44)



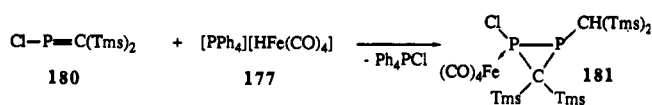
## SCHEME 72



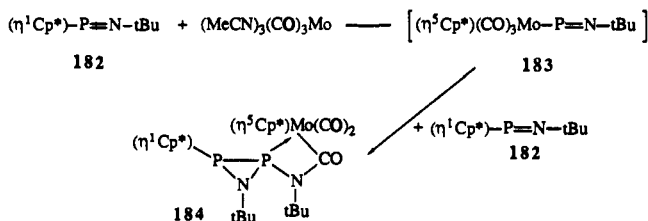
## SCHEME 73



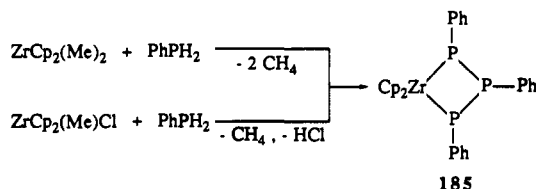
## SCHEME 74



## SCHEME 75



## SCHEME 76



131 on the phosphorus atom to which it is not directly bonded and subsequent evolution of carbon monoxide led to 132<sup>200</sup> (Scheme 54).

Dichlorophosphanes react also with diphosphane complexes of type  $M(R_2PY)_2$  and give, besides the expected product 133, five-membered ring 134<sup>16,201-205</sup> (Scheme 55).

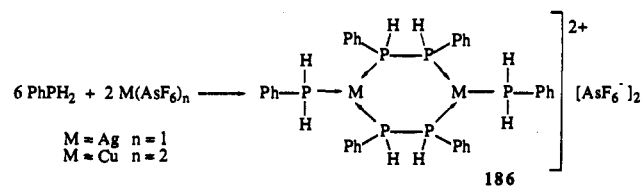
An analogous ring extension is observed with phosphido-type complexes 135<sup>206-208</sup> (Scheme 56).

On the other hand, a ring contraction has been noticed in a particular case<sup>28</sup> (Scheme 57). The driving force for the tautomerization of intermediate 139 may be the formation of the  $P=O$  bond or of the five-membered ring structure.

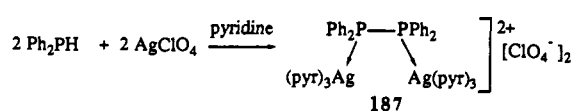
Another type of phosphorylphosphane complex, 142, is obtained via elimination of styrene from phosphirane complex 141<sup>209</sup> (Scheme 58).

Di- or polyphosphane complexes are also obtained when some of the so-called labile substituents do not react. For instance, this is the case for trihalophosphane complexes: their reaction with magnesium<sup>210,211</sup> or their irreversible cathodic reduction<sup>212</sup> gives tetrahalide diphosphane complexes 143 (Scheme 59).

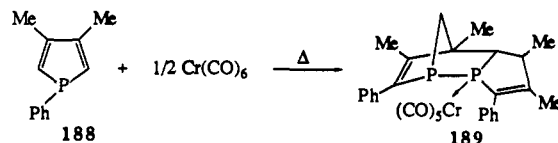
## SCHEME 77



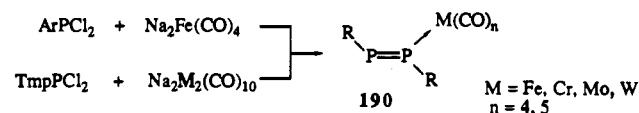
## SCHEME 78



## SCHEME 79



## SCHEME 80



Hydrolysis of lithium salts of complexed phosphanes results in the formation of other diphosphane complexes 144 and 145<sup>24</sup> (Scheme 60).

The analogous secondary diphosphane complex 148 is obtained by reacting dichlorophosphane complex 146 with its lithium salt 147 in THF,<sup>213</sup> whereas the reaction of the same lithium salt with a dichloroamine gives cyclotriphosphane complex 149<sup>214,215</sup> (Scheme 61).

An unexpected reaction leading to cyclometallatriphosphane 150 is observed with a rhenium carbonyl complex<sup>216</sup> (Scheme 62).

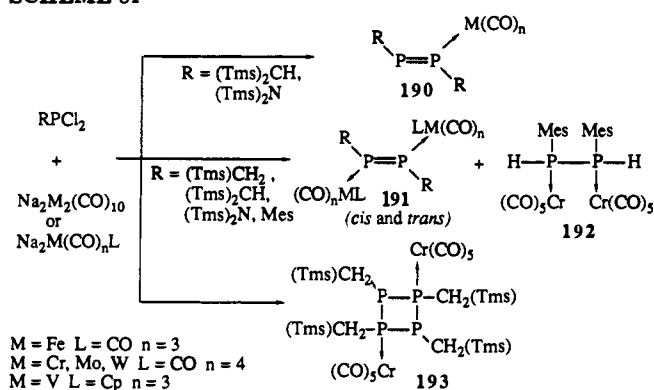
*β. Synthesis of Diphosphene Complexes.* Most of the reactions of difunctionalized phosphane complexes give a mixture of diphosphane and diphosphene complexes. This is for instance what happens when dibromophosphane complexes are allowed to react with magnesium. The main products of the reaction are cyclotriphosphane complexes 151, 152, and 153, which are respectively linked to one, two, and three metallic groups.<sup>217</sup> However, the (*−*)-menthyl substituent gives, besides cyclotriphosphane and phosphinidene complexes,  $\eta^1\eta^1$  diphosphene complex 154<sup>218</sup> (Scheme 63).

Dichlorophosphane complexes behave essentially like dibromophosphane complexes. Their reduction with zinc/magnesium amalgam leads to a mixture of compounds, including diphosphane 156 and diphosphene 157 complexes<sup>24</sup> (Scheme 64).

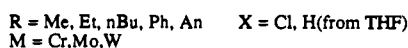
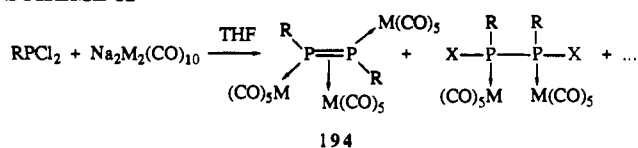
Elimination reactions with a chromium salt give either phosphido complex 158 or  $\eta^1\eta^2\eta^1$  diphosphene complex 159, depending mainly on the metal of the starting phosphane complex and also on the substituent  $R$ <sup>208</sup> (Scheme 65).

The reactivity of free dichlorophosphanes toward difunctionalized phosphane complexes and metallophosphanes depends on the steric hindrance of the substituents; with bulky substituents, diphosphene complexes are obtained. However, the base-induced deshydrochlorination depicted in Scheme 66 does not

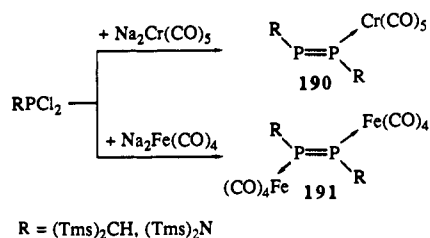
## SCHEME 81



## SCHEME 82



## SCHEME 83



lead to the expected compound 160; the isolated one is 161, arising from a migration of the metal toward the less hindered phosphorus atom.<sup>159</sup>

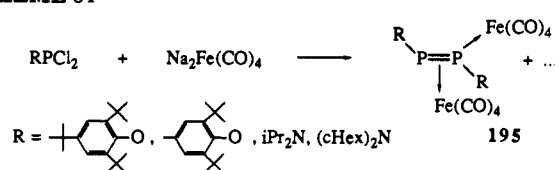
The nature of the product isolated with metal-phosphanes depends on the substituent of the "organic" phosphane. Metalladiphosphenes 163 are obtained starting from the bulky (2,4,6-tri-*tert*-butylphenyl)dichlorophosphane and metalladiphosphane 162.<sup>69,70,219-221</sup> Metallacyclo tri- or tetraphosphanes 164 and 165 are isolated with less bulky dichlorophosphines, even with mesityldichlorophosphine.<sup>222</sup> However, analogous compounds are also obtained with the bulky (tri-*tert*-butylphenyl)dichloroarsine<sup>221</sup> (Scheme 67).

## 2. Reactions of Free Phosphanes with Metallic Groups

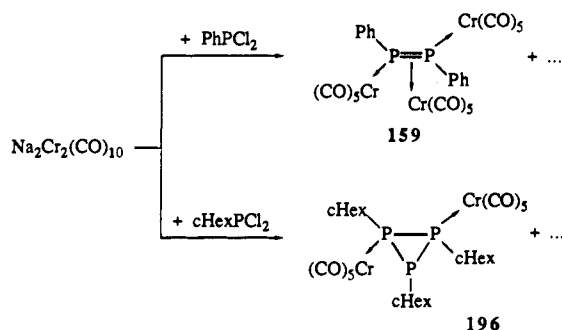
**a. Synthesis of Diphosphane Complexes.** Few diphosphane complexes are synthesized starting from free phosphanes. Most of these reactions are carried out between free monohalophosphanes and metal carbonyl sodium salts. The first step of the reaction generally gives salts of phosphane complexes 166, which react further with free halophosphanes. The second step of the reaction is analogous to the one described in Scheme 38 and  $\eta^1$  diphosphane complexes are isolated<sup>29,186,223,224</sup> (Scheme 68).

However, some unexpected reactions occur, mainly with aminochlorophosphanes. The surprising cage structure 169 is obtained starting from dichlorodiazadiphosphetidine 168<sup>225</sup> (Scheme 69).

## SCHEME 84



## SCHEME 85



The influence of the solvent on the reaction is to be noticed: conducting the reaction of dichloro(diisopropylamino)phosphane with iron tetracarbonyl sodium salt in tetrahydrofuran rather than diethyl ether leads to the phosphido derivatives 171 and 172 as major products instead of phosphorus-bridging carbonyl compound 170<sup>226,227,228</sup> (Scheme 70).

A migration of an amino substituent may also occur. The unexpected products 173 and 174, obtained with dichloro(diethylamino)phosphane come from the migration of amino groups from one phosphorus to another and from one phosphorus to a carbon atom.<sup>226,229</sup> Derivative 173 is the only compound of type J fully characterized so far (Scheme 71).

Elimination of amino groups also leads to the synthesis of diphosphane complexes. A mixture of compounds is obtained from hexamethylphosphorus triamide and rhodium complex 175<sup>230</sup> (Scheme 72).

Addition of the anionic iron hydride 177 to the acetylenic (dimethylamino)chlorophosphane 176 allowed us to isolate the anionic diphosphane complex 178 and the related neutral compound 179<sup>231</sup> (Scheme 73).

Unexpectedly, we have obtained the functionalized diphosphirane complex 181 from chlorophosphaalkene 180 and the same hydride<sup>232</sup> (Scheme 74).

Another spirocyclic complex, 184, is formed via the shift of a Cp\* ligand, in an attempt to synthesize metallaminophosphane 183. Compound 184 is presumably generated by addition of the phosphorus lone pair of intermediate 183 on the phosphorus nitrogen double bond of the starting iminophosphane 184<sup>233</sup> (Scheme 75).

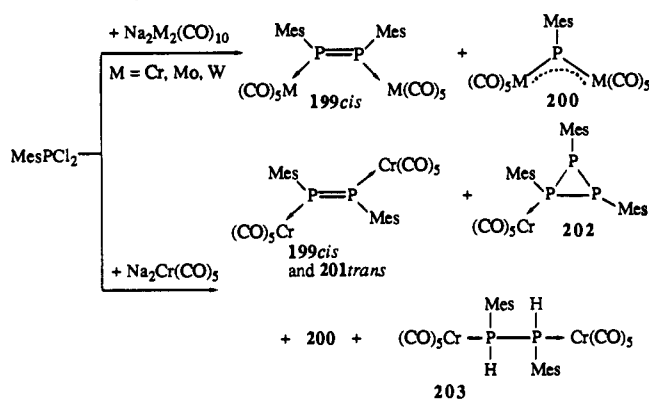
Primary and secondary phenyl phosphanes are also suitable materials for the synthesis of diphosphane complexes. For instance, metallacycle 185, in which the phosphorus atoms are  $\sigma$ -bonded to zirconium, is obtained from phenylphosphane and zirconocene derivatives with elimination of methane<sup>37</sup> (Scheme 76).

Phenyl phosphane gives also cationic secondary diphosphane complexes 186 when it reacts with silver or copper salts<sup>234</sup> (Scheme 77).

An analogous coupling is observed with diphenylphosphane; however, the reaction stops at the first step and gives the linear diphosphane complex 187 instead of a cyclic one<sup>235</sup> (Scheme 78).



SCHEME 86



The last reaction used to synthesize a diphosphane complex from a free diphosphane concerns the thermal dimerization of phosphole 188. This dimerization, induced by chromium hexacarbonyl, involves evolution of carbon monoxide and shift of phenyl groups from phosphorus to carbon<sup>236</sup> (Scheme 79).

**b. Synthesis of Diphosphene Complexes.** *α. Sodium Salts of Carbonyl Metals.* Reactions of dichlorophosphanes are often unforeseeable; the nature of the products depends on the organic substituent of the phosphorus atom, the metal (Fe, Cr, Mo, W, etc.), the nature of the complex (mono or dinuclear), and the solvent. Formally, most of the products arise from combinations of metal carbonyl fragments  $\text{M}(\text{CO})_n$  and phosphinidene fragments P-R in variable proportions. The main factor directing the reaction seems to be the steric hindrance: generally, with bulky substituents such as tri-*tert*-butylphenyl<sup>65</sup> or tetramethylpiperidyl, only one product is obtained,  $\eta^1$  diphosphene complex **190**<sup>237,238</sup> (Scheme 80).

On the other hand, with less bulky substituents, reactions are less specific.<sup>63</sup> A mixture of  $\eta^1$  (**190**) and  $\eta^1\eta^1$  (**191**) diphosphene complexes is obtained when  $(\text{Tms})_2\text{CH}$ <sup>45,58,59,62,64</sup> and  $(\text{Tms})_2\text{N}$ <sup>57,62,64</sup> substituents are involved.  $\eta^1\eta^1$  diphosphene complexes are the preferred reaction products<sup>59,62,64,239</sup> with mesityl groups: diphosphenes *cis*-**191** and *trans*-**191** are obtained in 38% and 21% yield, respectively, whereas diphosphane **192** is isolated in only 13% yield. A mixture of *trans*-diphosphene **191** and diphosphane **193** is obtained with  $(\text{Tms})\text{CH}_2$  groups (12% and 30% yield, respectively)<sup>62</sup> (Scheme 81).

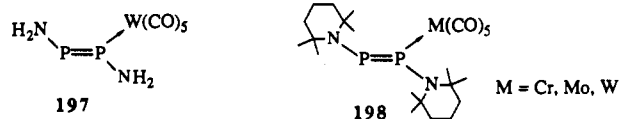
When smaller substituents are used, the only diphosphene complex isolated from the reaction mixture is  $\eta^1\eta^2\eta^1$  complex **194**<sup>240</sup> (Scheme 82).

These examples show that the more the steric hindrance of the substituents diminishes, the more the number of metallic centers needed to stabilize the diphosphene increases. However, the part played by the steric hindrance of the metallic center itself can be exemplified: a same diphosphene ligand is stabilized either by one  $\text{Cr}(\text{CO})_5$  group<sup>45,62,63</sup> or by two  $\text{Fe}(\text{CO})_4$  groups<sup>57,58,64</sup> (Scheme 83).

Electronic effects of the organic substituent on phosphorus probably add to steric effects, but elements of comparison are not sufficient to draw a conclusion. For instance, it is difficult to know why, among the 15 or so substituents used (aryl, alkyl, amino, alkoxy groups), only crowded alkoxy and amino substituents give  $\eta^1\eta^2$  diphosphene complexes **195**<sup>45,64,226</sup> (Scheme 84).

However, conjugation seems to play a part, by promoting the formation of a double bond. Indeed, diphosphene complex **159**<sup>240</sup> is obtained from phenyldichlorophosphane, whereas the same reaction carried out with the corresponding saturated derivative (cyclohexyldichlorophosphane) gives only a mixture of polyphosphane complexes (Scheme 85).

On the other hand, calculations worked out with **197**, as a model of **198**, show that the lone pair of the nitrogen atoms does not contribute to the conjugation with the P=P double bond.<sup>238</sup>



These reactions point out the influence of the organic substituent of the dichlorophosphane on the reaction. However, the nature of the sodium salt itself must also be taken into account. This has been shown with chromium carbonyl salts.<sup>59,62</sup> In this case, the dinuclear complex seems to give a more selective reaction than the mononuclear one (Scheme 86).

All those examples (Schemes 80–86) show that the reaction of dichlorophosphanes with sodium salts of carbonyl metals allows the synthesis of numerous diphosphane and diphosphene complexes, often inaccessible by other ways. Cluster **51**, built around two diphosphene units, exemplifies the originality of complexes obtained in this way<sup>74</sup> (Scheme 87).

*β. Other Metal Complexes.* The preceding reaction is the only one carried out with a sodium salt of nickel; nickel chloride complexes are most often used. They react with silylated phosphanes to produce  $\eta^2$  diphosphene complexes, generally in low yield<sup>178–182,241–243</sup> (Scheme 88).

For our part, we have studied the reactivity of the anionic iron hydride **177** toward dichlorophosphanes. The first step of the reaction is always the reduction and the complexation of the phosphane. The secondary chlorophosphane complex **205** thus obtained reacts with the starting dichlorophosphane to give  $\eta^1$  diphosphane complex **206**, which reacts further with hydride **177** to give  $\eta^1\eta^1$  diphosphane complex **207**<sup>244,245</sup> (Scheme 89). These  $\eta^1\eta^1$  diphosphane complexes are unstable; their behavior depends on the R substituent.  $\eta^1\eta^2$  diphosphene complexes **208** and **209** are obtained when R is a phenyl group<sup>244–246</sup> or a cyclic phosphalkene,<sup>247</sup> whereas four-membered heterocycle **210** is isolated when R is a methyl group<sup>244,245</sup> (Scheme 89).

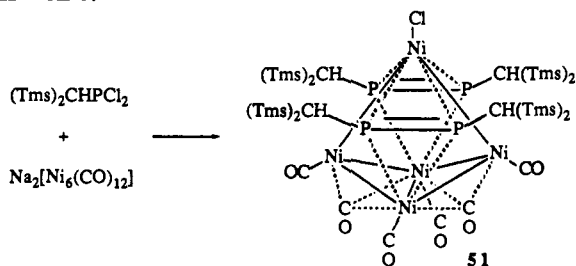
A primary phosphane is also used for the synthesis of a diphosphene complex:  $\eta^2$  complex **211** is obtained by reacting phenylphosphane with a magnesium derivative<sup>248</sup> (Scheme 90).

### 3. Miscellaneous Syntheses of Diphosphene Complexes

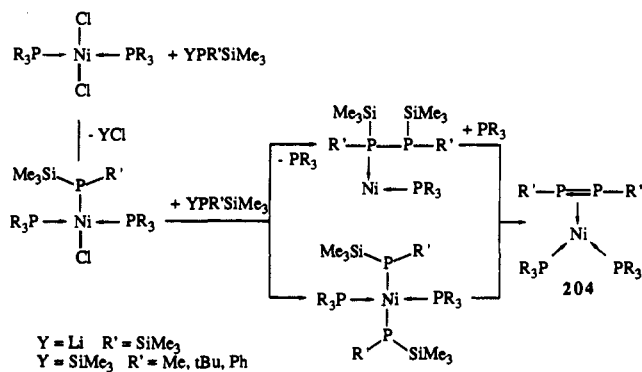
Some reactions cannot be connected to the main types described previously. This is the case for reactions which involve phosphalkyne **212**. Thus, phosphoferrocene-type complexes **108** and **214** are obtained in low yield among other compounds<sup>249</sup> when **212** is reacted with iron derivative **213** (Scheme 91).

However, the analogous reaction carried out with vanadium leads to polycyclic complex **215** instead of phosphavanadocene<sup>250</sup> (Scheme 92).

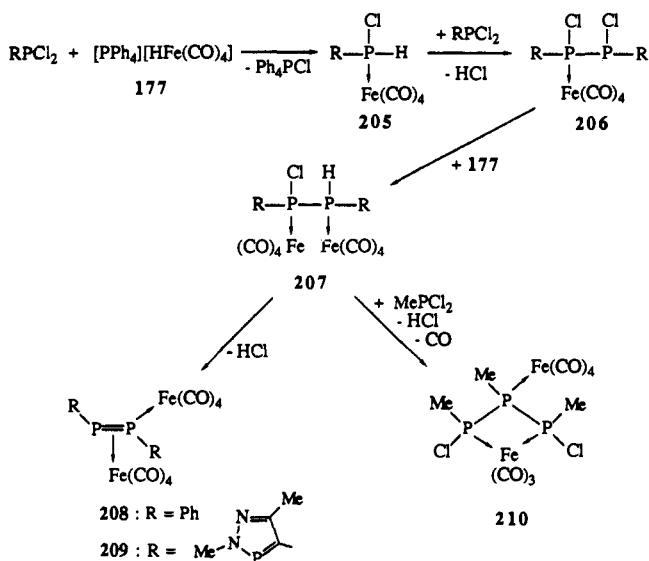
## SCHEME 87



## SCHEME 88



## SCHEME 89



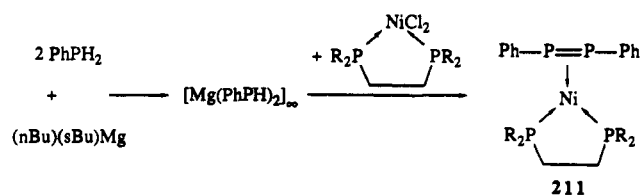
Thermolysis reactions of phosphorus complexes also lead in some cases to diphosphene complexes. Phosphinidene complexes of type 216<sup>63</sup> give  $\eta^1\eta^2\eta^1$  diphosphene complexes 29<sup>46</sup> and 217,<sup>251</sup> for R = Ph and R = tBu, respectively (Scheme 93).

Some thermolysis are also catalyzed by copper(I) chloride. Complexes of diphosphene (219), 1,2-diphosphetane (220), and diphosphirane (221) formally arise from the generation of terminal phosphinidene complexes 218<sup>252-257</sup> (Scheme 94).

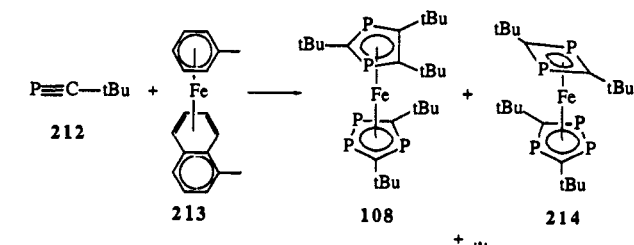
#### D. Reactivity of Diphosphane and Diphosphene Complexes

Reactions which lead to the cleavage of the phosphorus-phosphorus bond will not be presented here, except the dismutation of a diphosphane complex in

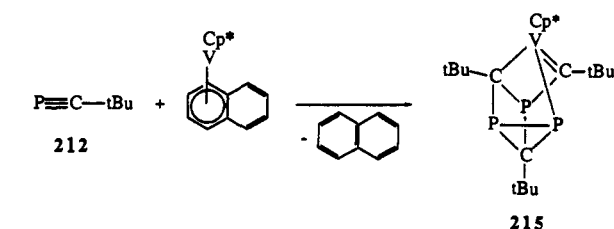
## SCHEME 90



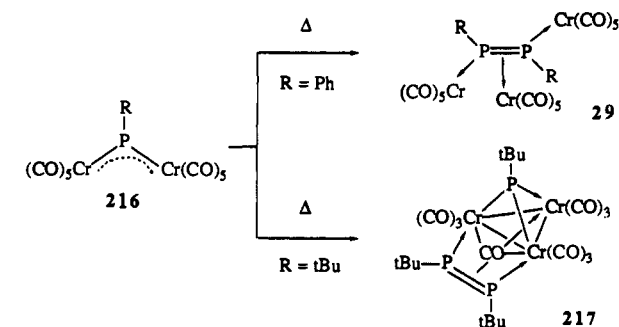
## SCHEME 91



## SCHEME 92



## SCHEME 93



presence of a free diphosphane,<sup>258,259</sup> which produces the unsymmetrical diphosphane complex 16 (Scheme 95).

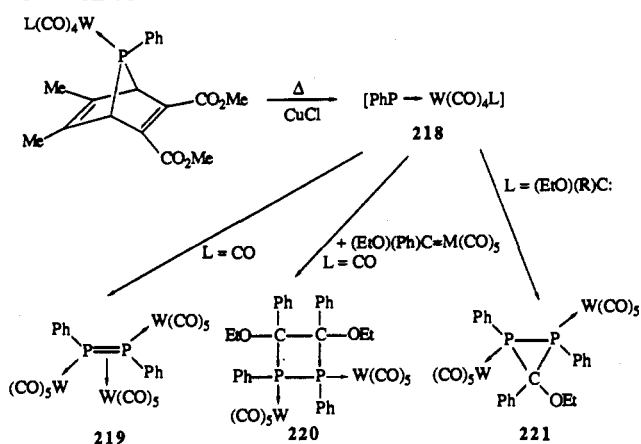
Two series of reactions keeping the phosphorus-phosphorus bond occur with diphosphane and diphosphene complexes: some could be named "organometallic" reactions, i.e. mainly complexations and decomplexations. Others could be named "organic" reactions, i.e. mainly additions and substitutions.

#### 1. Complexation, Decomplexation Reactions

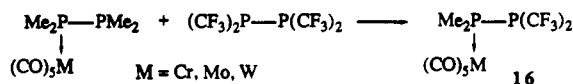
**a. Diphosphane Complexes.** We have already seen, in part III-A-1 of this review, some examples of additional complexation of  $\eta^1$  diphosphane complexes (Schemes 6, 7, and 9). These reactions are rather frequent.<sup>92,98,137,138,140,148,224,260,261</sup> They can be schematized as follows, for the two main types of  $\eta^1$  diphosphane complexes 222 and 223 (Scheme 96).

The M'L<sub>n</sub> reagents are analogous to those described in part III-A; the L' ligands are mainly CO, THF, and nornorbornadiene. Additional complexation on polyphosphane complexes occurs first on the  $\beta$  phosphorus

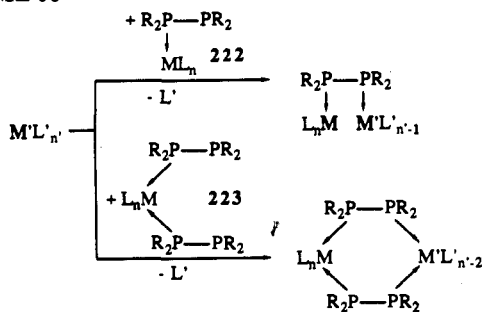
SCHEME 94



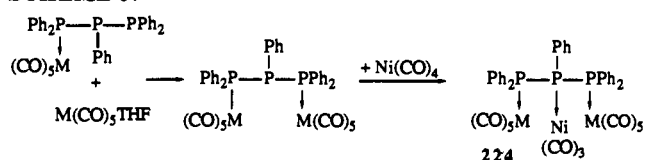
SCHEME 95



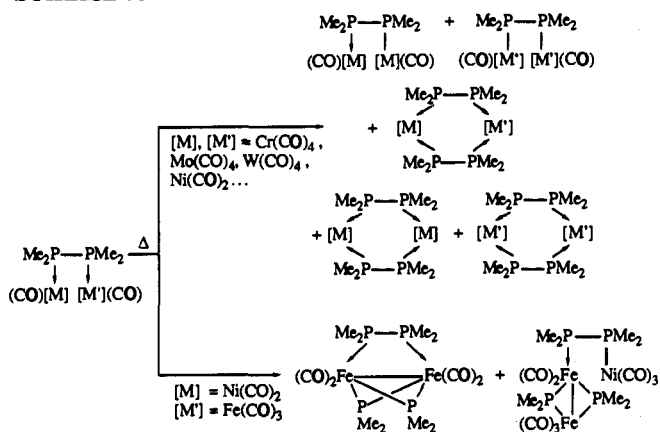
SCHEME 96



SCHEME 97



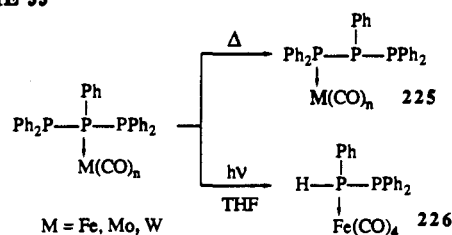
SCHEME 98



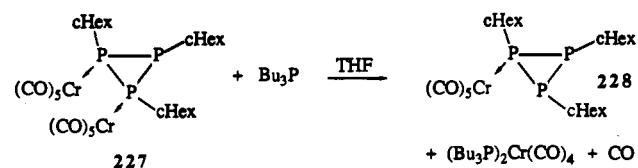
atom relative to the complexed phosphorus atom,<sup>198</sup> but a third complexation may occur<sup>185,282</sup> (Scheme 97).

Other transformations are induced by thermal or photochemical activation. A mixture of numerous complexes in variable proportions is obtained starting from  $\eta^1\eta^1$  diphosphane complexes<sup>18,98,137,140</sup> (Scheme 98). Most of the compounds seem to result from exchange

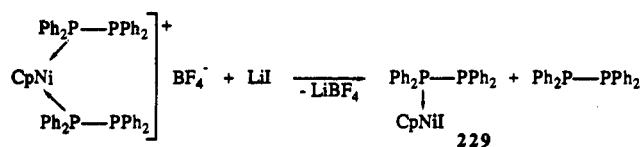
SCHEME 99



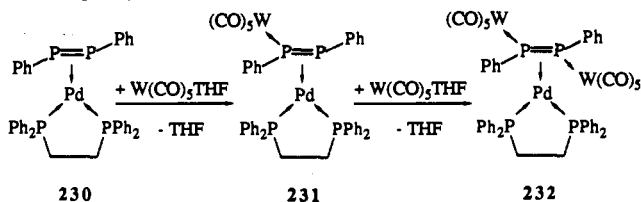
SCHEME 100



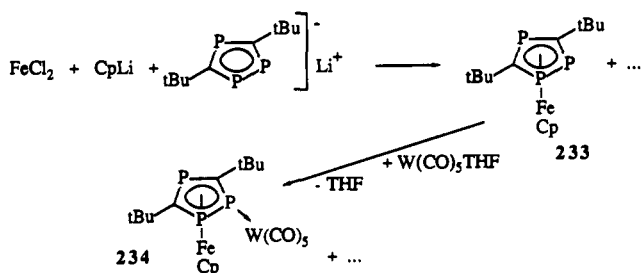
SCHEME 101



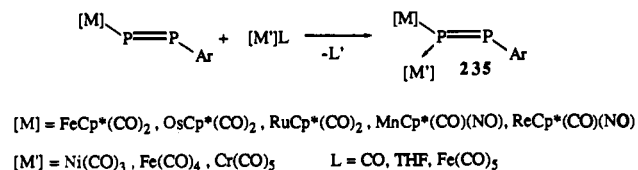
SCHEME 102



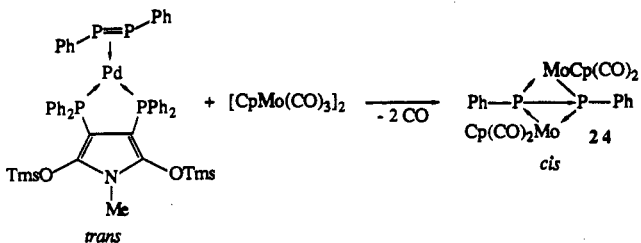
SCHEME 103



SCHEME 104



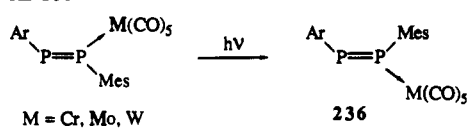
SCHEME 105



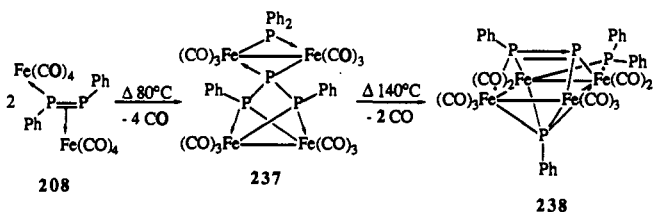
reactions of ligands, either carbon monoxide or the diphosphane itself.

A migration of the metal from the central phosphorus atom to an external one may occur upon heating tri-

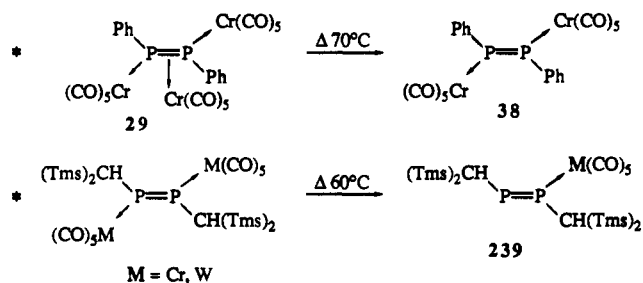
## SCHEME 106



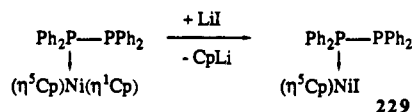
## SCHEME 107



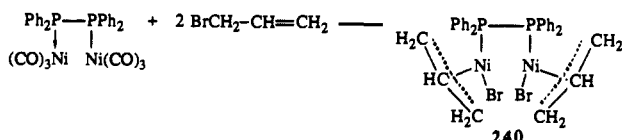
## SCHEME 108



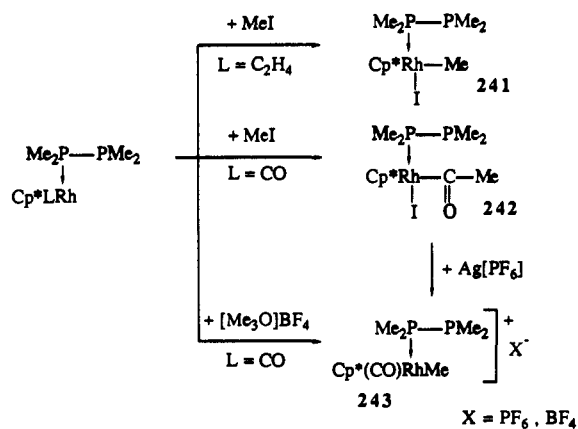
## SCHEME 109



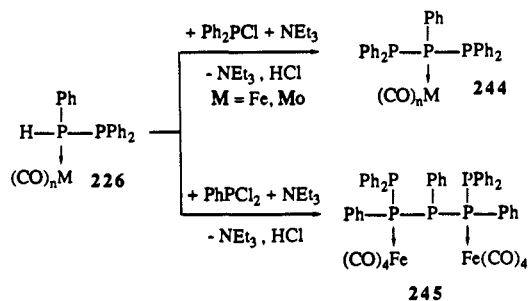
## SCHEME 110



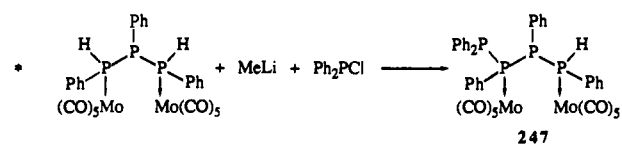
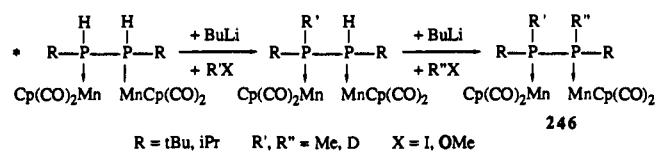
## SCHEME 111



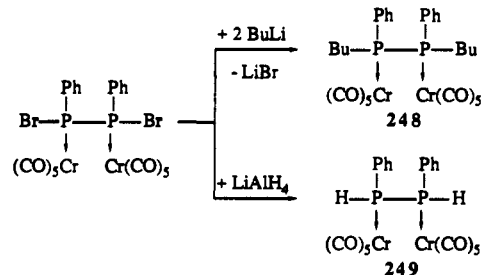
## SCHEME 112



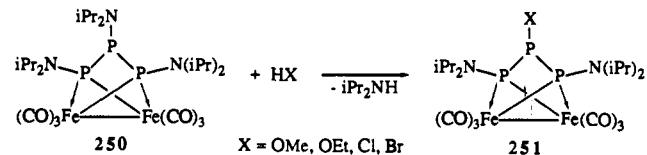
## SCHEME 113



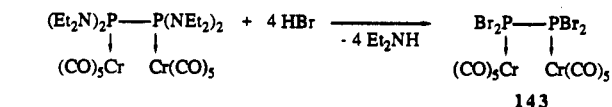
## SCHEME 114



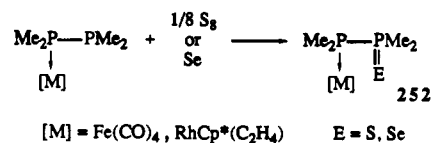
## SCHEME 115



## SCHEME 116



## SCHEME 117



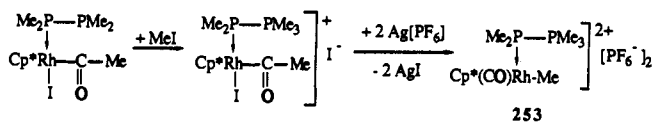
phosphane complexes,<sup>157,185,262</sup> whereas irradiation in THF medium induces a phosphorus-phosphorus bond cleavage<sup>157</sup> (Scheme 99).

Some decomplexation reactions are also reported. An exchange of ligand occurs between cyclotriphosphane

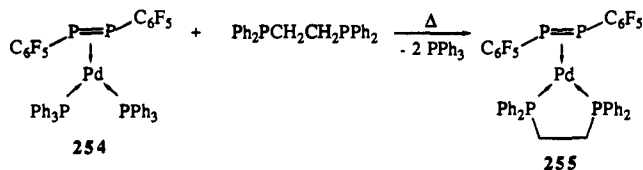
227 and tributylphosphane<sup>217</sup> (Scheme 100).

Lastly, the neutralization of a cationic complex by

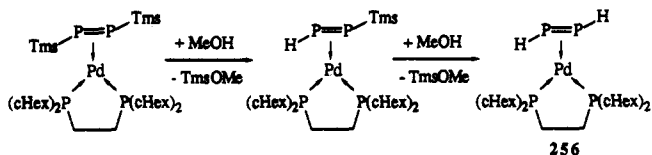
SCHEME 118



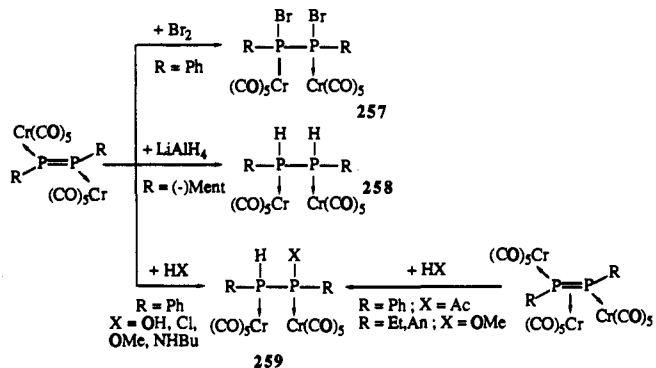
SCHEME 119



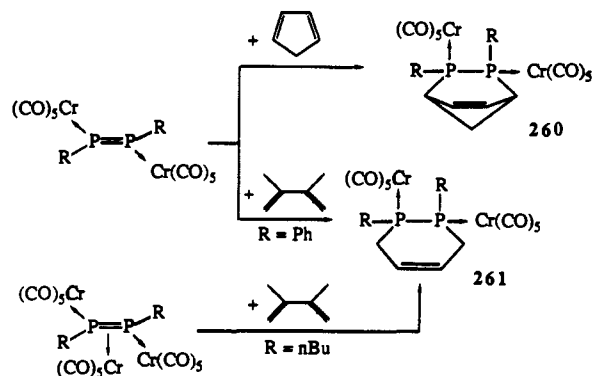
SCHEME 120



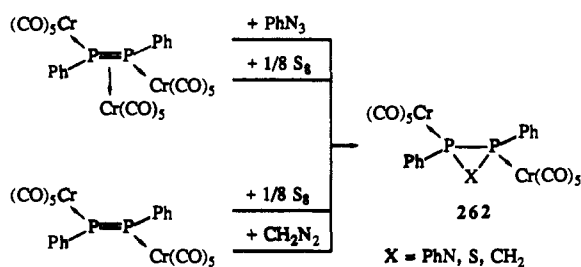
SCHEME 121



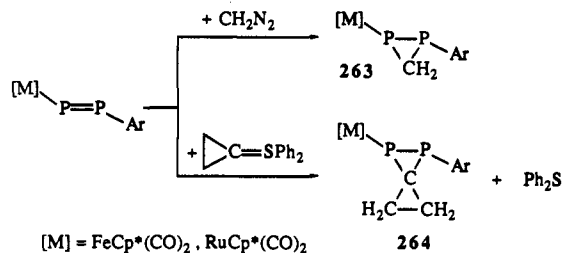
SCHEME 122



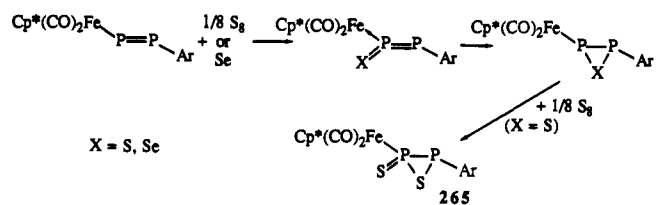
SCHEME 123



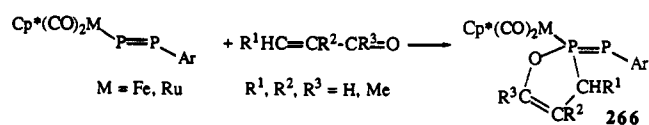
SCHEME 124



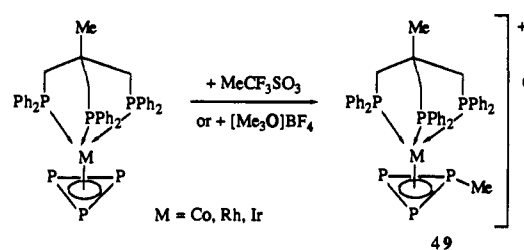
SCHEME 125



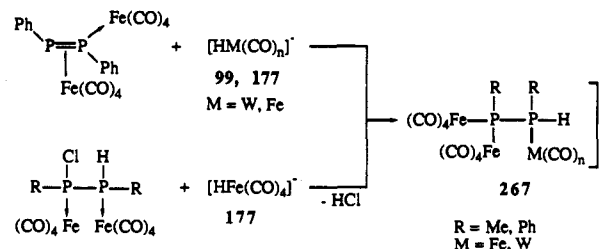
SCHEME 126



SCHEME 127



SCHEME 128



lithium iodide also induces a decomplexation<sup>142</sup> (Scheme 101).

**b. Diphosphene Complexes.** The complexation of diphosphene complexes mainly occurs on the phosphorus lone pair. For instance, the two lone pairs of  $\eta^2$  diphosphene complex **230** react one after the other

TABLE 8. Metalladiphosphanes

A. Linear Compounds of Type  $(\text{CO})_4\text{Fe}-\text{P}(\text{R}^1)_2-\text{P}(\text{R}^2)_2-\text{M} \left[ \text{X}^+ \right]^-$

R <sup>1</sup>	R <sup>2</sup>	X	M	method	yield (ref)	R <sup>1</sup>	R <sup>2</sup>	X	M	method	yield (ref)
Me	H	PPh <sub>4</sub>	Fe(CO) <sub>4</sub>	128	20 (244)	PhC≡C	Me <sub>2</sub> N	PPh <sub>4</sub>	Fe(CO) <sub>4</sub>	73	37 (231)
Ph	H	PPh <sub>4</sub>	Fe(CO) <sub>4</sub>	128	55 (244) (245, 246)	H	iPr <sub>2</sub> N	NEt <sub>4</sub>	Fe(CO) <sub>4</sub>	31	19 (177*)
Ph	H	NEt <sub>4</sub>	W(CO) <sub>5</sub>	128	62 (244) (246)						

B. Cyclic Compounds of Type  $\text{M}-\text{P}(\text{R})_2-\text{P}(\text{R})_2-\text{X}$

R	X	M	method	yield (ref)	R	X	M	method	yield (ref)
FeCp*(CO) <sub>2</sub>	AsAr	FeCp*(CO) <sub>2</sub>	67	10 (221*)	Ar	CH <sub>2</sub>	RuCp*(CO) <sub>2</sub>	124	9-33 (270, 271)
Mes	PMes	FeCp*(CO) <sub>2</sub>	67	25 (222)	Ar	CCH <sub>2</sub> CH <sub>2</sub>	FeCp*(CO) <sub>2</sub>	124	37 (271*)
Mes	PMes	Fe(PPh <sub>3</sub> )Cp(CO)	67	13 (222)	Ar	CCH <sub>2</sub> CH <sub>2</sub>	RuCp*(CO) <sub>2</sub>	124	21 (271)
Mes	PMes	RuCp*(CO) <sub>2</sub>	67	30 (222)	Ar	S	FeCp*(CO) <sub>2</sub>	125	60 (272, 273)
Ar	CH <sub>2</sub>	FeCp*(CO) <sub>2</sub>	124	38-45 (270, 271)	Ar	Se	FeCp*(CO) <sub>2</sub>	125	35 (272, 273)

C. Cyclic Compounds of Type  $\text{R}-\text{P}(\text{R})_2-\text{M}-\text{P}(\text{R})_2-\text{R}$

n	R	M	method	yield (ref)	n	R	M	method	yield (ref)
1	Me	HfCp <sub>2</sub>	29	71 (34)	1	tBu	ZrCp <sub>2</sub>	29	34 (34)
1	Me	TiCp <sub>2</sub>	29	(34)	1	Ph	HfCp <sub>2</sub>	29	57 (34) (37*)
1	Me	ZrCp <sub>2</sub>	29	75 (34)	1	Ph	TiCp <sub>2</sub>	29	57 (34) (174)
1	Et	HfCp <sub>2</sub>	29	63 (34)	1	Ph	ZrCp <sub>2</sub>	29	84 (34) (37)
1	Et	TiCp <sub>2</sub>	29	40 (34)	2	tBu	Ni(tBu-P=P-tBu)	35	30 (33*)
1	Et	ZrCp <sub>2</sub>	29	70 (34)	2	Ph	MoCp <sub>2</sub>	29	(31)
1	tBu	HfCp <sub>2</sub>	29	28 (34)	3	Ph	TiCp <sub>2</sub>	29	(31)
1	tBu	TiCp <sub>2</sub>	29	(34)	3	Ph	ZrCp <sub>2</sub>	29	(31)

D. Phosphido Compounds of Type  $(\text{CO})_3\text{Fe}-\text{P}(\text{R}^1)_2-\text{P}(\text{R}^2)_2-\text{Fe}(\text{CO})_3$

n	R <sup>1</sup>	R <sup>2</sup>	method	yield (ref)	n	R <sup>1</sup>	R <sup>2</sup>	method	yield (ref)
0	tBu		43	11 (38*, 39*)	1	An	tBu	56	95 (208*)
1	Ph	Ph	56	(206, 207)	1	An	Ph	56	84 (208)
1	iPr <sub>2</sub> N	MeO	115	(227, 228, 261)	1	(cHex) <sub>2</sub> N	(cHex) <sub>2</sub> N	as 70	30 (226)
1	iPr <sub>2</sub> N	EtO	115	70 (261) (227, 228)	2	Me	Me	27	(32*)
1	iPr <sub>2</sub> N	iPr <sub>2</sub> N	70	35 (226*) 30 (227*) (228)	2	CF <sub>3</sub>	CF <sub>3</sub>	27	67 (169)
1	iPr <sub>2</sub> N	Mn(CO) <sub>5</sub>	as 115	82 (261*)	2	Ph	Ph	56	35 (206)
1	iPr <sub>2</sub> N	Br	115	97 (261) (227)	2			27	(32*)
1	iPr <sub>2</sub> N	Cl	115	100 (261) (227)	2	C <sub>6</sub> F <sub>5</sub>	C <sub>6</sub> F <sub>5</sub>	27	(30)
1	iPr <sub>2</sub> N	H	115	78 (261) (227)					

E. Phosphido Compounds of Type  $(\text{CO})_3\text{Fe}-\text{P}(\text{R}^1)_2-\text{P}(\text{R}^2)_2-\text{M}-\text{P}(\text{R}^1)_2-\text{Fe}(\text{CO})_3$

R <sup>1</sup>	R <sup>2</sup>	M	method	yield (ref)	R <sup>1</sup>	R <sup>2</sup>	M	method	yield (ref)
iPr <sub>2</sub> N	Cl	Cr(CO) <sub>5</sub>	as 96 (THF)	45 (261*)	iPr <sub>2</sub> N	H	Fe(CO) <sub>4</sub>	as 96 (Fe(CO) <sub>5</sub> )	77 (261)
iPr <sub>2</sub> N	H	Cr(CO) <sub>5</sub>	as 96 (CO)	55 (261)	cHex	cHex	Cr(CO) <sub>5</sub>	65	28 (208*)

F. Miscellaneous Linear Compounds

compound	M	method	yield (ref)	compound	M	method	yield (ref)
$\left[ \text{M}-\text{P}(\text{P}(\text{OEt})_2)_2 \right]^- \text{pipH}^+$	Cr(CO) <sub>5</sub>	11	55 (126*)	$\left[ \text{M}-\text{P}(\text{P}(\text{OEt})_2)_2 \right]^- \text{pipH}^+$	Cr(CO) <sub>5</sub>	11	68 (126*)
	Mo(CO) <sub>5</sub>	11	35 (125) (127)		Mo(CO) <sub>5</sub>	11	(127*)
	W(CO) <sub>5</sub>	11	80 (127*)				

G. Miscellaneous Cyclic Metalladiphosphanes

compound	M	method	yield (ref)	compound	M	method	yield (ref)
		30	90 (175*)	$\text{Cp}^*(\text{CO})_2\text{Fe}-\text{P}-\text{As}-\text{Ar}$		67	27 (221)
$\text{Cp}^*(\text{CO})_2\text{Fe}-\text{P}(\text{S})_2-\text{P}(\text{S})_2-\text{Ar}$		125	(273)	$\text{Cp}^*(\text{CO})_2\text{Fe}-\text{P}-\text{As}-\text{Ar}$			
						92	(250*)

TABLE 8 (Continued)

G. Miscellaneous Cyclic Metalladiphosphanes							
compound	M	method	yield (ref)	compound	M	method	yield (ref)
$M-P-P-Mes$	$FeCp^*(CO)_2$	67	11 (222)	$M-P-P-Mes$	$FeCp^*(CO)_2$	67	(222)
$M-P-P-Mes$	$RuCp^*(CO)_2$	67	17 (222)	$Mes-P-P-M$	$RuCp^*(CO)_2$	67	(222*)
H. Miscellaneous Phosphido Compounds							
compound	R	method	yield (ref)	compound	R	method	yield (ref)
		105	30 (40*)			28	5 (171*, 172*)
		73	(231)			62	30 (216*)
		54	20 (200*)			Me	43
		71	35 (226*) (229*) (228)		Ph	43	10 (190*) 8 (42*)
		71	37 (226*) (228, 229*)		Tol	43	12 (190)
	$iPr_2N$	70	3 (226*) (228, 229*)			43	9 (190)
	$(cHex)_2N$	70	5 (226)		Ph	43	37 (191)
		as 56	(171)		Tol	43	13 (190)
		28	9 (170)			107	70 (266*)
		28	2 (170)			45	31 (41*)
		28	8 (172*) 4 (171*)			56	45 (206)
		28	(172)			56	60 (207) 35 (206)

TABLE 9.  $\eta^1$  Diphosphene Complexes
$$\begin{array}{c} \text{R}^1-\text{P}=\text{P}-\text{R}^2 \\ | \\ \text{M} \end{array}$$

R <sup>1</sup>	R <sup>2</sup>	M	method	yield (ref)
Ph	Ar	Cr(CO) <sub>5</sub>	66	(159)
Ph	Ar	Mo(CO) <sub>5</sub>	66	(159)
Ph	Ar	W(CO) <sub>5</sub>	66	(159)
(Tms) <sub>2</sub> N	(Tms) <sub>2</sub> N	Cr(CO) <sub>5</sub>	83	18 (62) (57)
(Tms) <sub>2</sub> CH	(Tms) <sub>2</sub> CH	Cr(CO) <sub>5</sub>	108	80 (59)
(Tms) <sub>2</sub> CH	(Tms) <sub>2</sub> CH	Mo(CO) <sub>5</sub>	83	60 (59) 45 (45*, 62*, 63)
(Tms) <sub>2</sub> CH	(Tms) <sub>2</sub> CH	Mo(CO) <sub>5</sub>	81	76 (59*)
(Tms) <sub>2</sub> CH	(Tms) <sub>2</sub> CH	W(CO) <sub>5</sub>	108	73 (59)
(Tms) <sub>2</sub> CH	Ar	Fe(CO) <sub>4</sub>	81	69 (59)
Mes	Ar	Cr(CO) <sub>5</sub>	22	63 (55, 61) (56)
Mes	Ar	Cr(CO) <sub>5</sub>	66	70 (159)
Mes	Ar	Cr(CO) <sub>5</sub> (cis)	22	48 (159) (60)
Mes	Ar	Cr(CO) <sub>5</sub> (cis)	106	(60*)
Mes	Ar	Mo(CO) <sub>5</sub>	22	60 (159) (60)
Mes	Ar	Mo(CO) <sub>5</sub> (cis)	66	(159)
Mes	Ar	Mo(CO) <sub>5</sub> (cis)	106	(60)
Mes	Ar	W(CO) <sub>5</sub>	22	68 (159) (60)
Mes	Ar	W(CO) <sub>5</sub> (cis)	66	(159)
Mes	Ar	W(CO) <sub>5</sub> (cis)	106	(60)
Tmp	Tmp	Cr(CO) <sub>5</sub>	80	25 (238)
Tmp	Tmp	Mo(CO) <sub>5</sub>	80	22 (238) (237)
Tmp	Tmp	W(CO) <sub>5</sub>	80	13 (238*) (237)
Ar	tBuNH	Ni(CO) <sub>5</sub> (cis)	25	80 (47)
Ar	Ar	Ag <sup>+</sup> SO <sub>3</sub> CF <sub>3</sub> <sup>-</sup>	24	(162, 163)
Ar	Ar	Au(PEt <sub>3</sub> ) <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	24	(162, 163)
Ar	Ar	Fe(CO) <sub>4</sub>	22	70 (61*) 65 (55*) (56*)
Ar	Ar	Fe(CO) <sub>4</sub>	80	(56)
Ar	Ar	Ni(CO) <sub>5</sub>	22	(56, 61)

TABLE 10.  $\eta^1\eta^1$  Diphosphene Complexes
$$\begin{array}{c} \text{R} \quad \text{M} \\ \diagdown \quad / \\ \text{P}=\text{P} \\ / \quad \diagdown \\ \text{M} \quad \text{R} \end{array} \quad \text{or} \quad \begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad / \\ \text{P}=\text{P} \\ / \quad \diagdown \\ \text{M} \quad \text{M} \end{array}$$

R	M	method	yield (ref)
TmsCH <sub>2</sub>	Cr(CO) <sub>5</sub>	81	12 (62*)
Ph	Cr(CO) <sub>5</sub>	108	80 (46*)
(Tms) <sub>2</sub> N	Fe(CO) <sub>4</sub>	83	45 (57*, 64)
(Tms) <sub>2</sub> CH	Cr(CO) <sub>5</sub>	81	28 (59)
(Tms) <sub>2</sub> CH	Fe(CO) <sub>4</sub>	83	50 (58*, 64)
(Tms) <sub>2</sub> CH	W(CO) <sub>5</sub>	81	14 (59)
Mes	Cr(CO) <sub>5</sub>	86	21-30 (62*)
Mes (cis)	Cr(CO) <sub>5</sub>	86	23-38 (62*) 44 (59)
Mes	Fe(CO) <sub>4</sub>	81	35 (64*)
Mes	Mn(MeC <sub>5</sub> H <sub>4</sub> )(CO) <sub>2</sub>	64	(24)
Mes (cis)	Mo(CO) <sub>5</sub>	86	56 (59*)
Mes	V(Cp)(CO) <sub>3</sub>	81	34 (239*)
Mes (cis)	W(CO) <sub>5</sub>	86	20 (59)
(-)-Ment	Cr(CO) <sub>5</sub>	63	44 (218*)
(-)-Ment	W(CO) <sub>5</sub>	63	51 (218)
Ar	Ag <sup>+</sup> CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	24	(162, 163)

to give  $\eta^1\eta^2$  complex **231** and  $\eta^1\eta^2\eta^1$  diphosphene complex **232**<sup>53</sup> (Scheme 102).

The complexation of triphosphaferrocene **233** (obtained as a mixture with other phosphoferrocene derivatives) occurs on one phosphorus atom of the "cis-diphosphene" unit<sup>263</sup> (Scheme 103).

Metalladiphosphenes are always complexed on the phosphorus atom  $\sigma$ -bonded to a metal<sup>170,71,220,264</sup> (Scheme 104). No example of additional complexation on the second phosphorus atom is known.

A diphosphene unit can also be transferred from a metal to another<sup>40</sup> (Scheme 105). Two points are noticeable in this reaction: **24** is the only complex of type L, and the transfer induces a trans-cis isomerization of the diphosphene.

Irradiation of  $\eta^1$  diphosphene complexes also induces

a trans-cis isomerization<sup>60a,b,159</sup> (Scheme 106), which is analogous to the one observed for free diphosphenes.<sup>265</sup> Both cis and trans complexes are stable.

A complicated "dimerizationlike" reaction<sup>266</sup> leading first to phosphorus spiranic species **237** is observed by heating  $\eta^1\eta^2$  diphosphene complex **208**. Heating further phosphido complex **237**, we have obtained the original cluster **238**<sup>266</sup> in which a metallaphosphoranylidene-phosphane unit serves as a building block. Up to now, complex **238** is the only one of type T (Scheme 107).

Thermal activation may also induce a selective decomplexation either of the double bond<sup>46,267</sup> or of one phosphorus atom<sup>241</sup> (Scheme 108).

## 2. Substitution, Addition Reactions

**a. Diphosphene Complexes.** Few substitution or addition reactions concern the metallic center. Diphosphene complex **229** shown in Scheme 101 is also obtainable by replacement of the  $\eta^1$  cyclopentadienyl group by iodine<sup>268</sup> (Scheme 109).

Carbon monoxide can also be replaced by allyl bromide<sup>91</sup> (Scheme 110). However, the extreme sensitivity of complex **240** prevented its full characterization.

Addition reactions occur with methyl iodide either directly on the metal, with evolution of ligand such as ethylene,<sup>135</sup> or on a metal-ligand bond.<sup>147</sup> The addition of Me<sup>+</sup> on rhodium gives a cationic diphosphene complex when trimethylxonium tetrafluoroborate is involved (Scheme 111).

However, many reactions concern the diphosphene ligand itself; these are mainly substitution reactions. For instance, base-induced eliminations of proton are observed for secondary diphosphene complexes and polyphosphane complexes are thus synthesized<sup>157,185,269</sup> (Scheme 112).

Hydrogen atoms of secondary di- or triphosphane complexes are selectively substituted, using first butyllithium or methyllithium and then halocompounds such as methyl iodide<sup>24</sup> or chlorodiphenylphosphane<sup>185</sup> (Scheme 113).

Halide-substituted diphosphane complexes react also with butyllithium and are reduced by lithium aluminum hydride<sup>113</sup> (Scheme 114).

Amino groups are suitable leaving groups. They react with compounds of type HX, with X = halide or alkoxy groups.<sup>227,228,261</sup> The reaction always takes place on the free phosphorus atom of complex **250** and does not concern the complexed phosphorus atoms (Scheme 115).

However, in another example, all amino groups of complexed phosphorus atoms are substituted by bromine<sup>210,269</sup> (Scheme 116).

Addition reactions on diphosphane complexes are rare and concern only compounds of type B. They obviously occur on the lone pair of the uncomplexed phosphorus atom. This is the case with sulfur and selenium<sup>134,135,224</sup> (Scheme 117).

Methyl iodide adds also to the uncomplexed phosphorus atom, leading to phosphonium salts.<sup>135,147</sup> The cationic acetyl complex thus obtained reacts further with AgPF<sub>6</sub> to form the dication **253** (Scheme 118).

**b. Diphosphene Complexes.** Only one reaction concerning the metallic center is known: a ligand exchange occurs when diphosphene complex **254** is treated



TABLE 11.  $\eta^2$  Diphosphene Complexes
$$\begin{array}{c} \text{R}^1-\text{P}=\text{P}-\text{R}^2 \\ | \\ \text{M} \end{array}$$

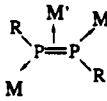
R <sup>1</sup>	R <sup>2</sup>	M	method	yield (ref)
Me	Me	Ni[(cHex) <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> P(cHex) <sub>2</sub> ]	88	23 (180)
Tms	Tms	Ni(PMe <sub>3</sub> ) <sub>2</sub>	34	24 (179)
			88	5 (179) (243)
Tms	Tms	Ni[Et <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PEt <sub>2</sub> ]	88	37 (178, 180)
Tms	Tms	Ni(PEt <sub>3</sub> ) <sub>2</sub>	88	38 (243) 16 (179) (242*)
			34	32 (179)
Tms	Tms	Ni[P(nBu) <sub>3</sub> ] <sub>2</sub>	88	10 (179) (243)
			34	9 (179)
Tms	Tms	Ni[P(iBu) <sub>3</sub> ] <sub>2</sub>	88	(179)
Tms	Tms	Ni[Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ]	88	(180)
Tms	Tms	Ni[(cHex) <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> P(cHex) <sub>2</sub> ]	88	28 (178, 180)
Tms	Tms	Ni(PPh <sub>3</sub> ) <sub>2</sub>	88	(179)
Tms	Tms	Pt(PEt <sub>3</sub> ) <sub>2</sub>	34	31 (181)
			88	7 (181)
Tms	Tms	Pt(PPh <sub>3</sub> ) <sub>2</sub>	34	(181)
			88	(181)
Tms	tBu	Ni[Et <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PEt <sub>2</sub> ]	34	32 (182)
Tms	tBu	Ni(PEt <sub>3</sub> ) <sub>2</sub>	88	(179)
Tms	tBu	Ni[Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ]	34	(182)
Tms	tBu	Ni[(cHex) <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> P(cHex) <sub>2</sub> ]	34	77 (182)
Tms	tBu	Pt[PEt <sub>3</sub> ] <sub>2</sub>	34	(181)
Tms	H	Ni[(cHex) <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> P(cHex) <sub>2</sub> ]	120	(182)
tBu	tBu	Ni[Et <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PEt <sub>2</sub> ]	34	61 (180)
tBu	tBu	Ni(PEt <sub>3</sub> ) <sub>2</sub>	34	84 (179)
			88	11-14 (179)
tBu	tBu	Ni[tBuP(P(tBu)) <sub>2</sub> P(tBu)]	34	30 (33*)
tBu	tBu	Ni[Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ]	34	74 (180) 60 (178)
tBu	tBu	Ni[(cHex) <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> P(cHex) <sub>2</sub> ]	34	92 (180)
tBu	tBu	Pt[PEt <sub>3</sub> ] <sub>2</sub>	34	79 (181)
tBu	tBu	Pt[PPh <sub>3</sub> ] <sub>2</sub>	34	(181)
tBu	H	Ni[(cHex) <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> P(cHex) <sub>2</sub> ]	120	83 (182)
tBuNH	Ar	Ni[P(nBu) <sub>3</sub> ] <sub>2</sub>	25	(47)
Ph	Ph	Ni[Et <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PEt <sub>2</sub> ]	88	17 (180)
Ph	Ph	Ni(PEt <sub>3</sub> ) <sub>2</sub>	88	11 (179)
Ph	Ph	Ni[Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ]	88	5 (180)
Ph	Ph	Ni[(cHex) <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> P(cHex) <sub>2</sub> ]	90	53 (248)
			88	44 (178, 180)
Ph	Ph	Pd(Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> )	34	(53*, 54*)
Ph	Ph	Pt(PMe <sub>2</sub> Ph) <sub>2</sub>	34	(53)
Ph	Ph	Pt(Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> )	34	(53, 54)
Ph	Ph	Pt(PPh <sub>3</sub> ) <sub>2</sub>	34	(53, 54)
C <sub>6</sub> F <sub>5</sub>	C <sub>6</sub> F <sub>5</sub>	Pd(Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> )	119	(53)
C <sub>6</sub> F <sub>5</sub>	C <sub>6</sub> F <sub>5</sub>	Pd(PPh <sub>3</sub> ) <sub>2</sub>	33	(53)
C <sub>6</sub> F <sub>5</sub>	C <sub>6</sub> F <sub>5</sub>	Pt(PPh <sub>3</sub> ) <sub>2</sub>	33	(44*, 53)
H	H	Mo(Cp) <sub>2</sub>	32	(9, 43*)
H	H	Ni[(cHex) <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> P(cHex) <sub>2</sub> ]	88	39 (182)

TABLE 12.  $\eta^1\eta^2$  Diphosphene Complexes
$$\begin{array}{c} \text{M}' \\ | \\ \text{R}-\text{P}=\text{P}-\text{R} \\ | \\ \text{M} \end{array}$$

R	M	M'	method	yield (ref)
MeC≡N(Me)NP=C	Fe(CO) <sub>4</sub>	Fe(CO) <sub>4</sub>	89	31 (247*)
Ph	Fe(CO) <sub>4</sub>	Fe(CO) <sub>4</sub>	89	65 (246*) (244, 245)
Ph	W(CO) <sub>5</sub>	Pd(Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> )	102	(53)
iPr <sub>2</sub> N	Fe(CO) <sub>4</sub>	Fe(CO) <sub>4</sub>	84	(226)
(cHex) <sub>2</sub> N	Fe(CO) <sub>4</sub>	Fe(CO) <sub>4</sub>	84	(226)
2,6-tBu-4-Me(C <sub>6</sub> H <sub>3</sub> )O	Fe(CO) <sub>4</sub>	Fe(CO) <sub>4</sub>	84	(64)
ArO	Fe(CO) <sub>4</sub>	Fe(CO) <sub>4</sub>	84	40 (45*, 64*)

with 1,2-bis(diphenylphosphino)ethane upon heating<sup>53</sup> (Scheme 119).

Substitution reactions on phosphorus are also very rare: the only one known for a diphosphene complex

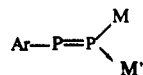
TABLE 13.  $\eta^1\eta^1$  Diphosphene Complexes


R	M	M'	method	yield (ref)
Me	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	82	56 (240)
Me	Mo(CO) <sub>5</sub>	Mo(CO) <sub>5</sub>	82	12 (240)
Et	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	82	35 (240)
nBu	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	82	40 (240)
Ph	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	65	(46*)
			82	(240)
Ph	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	Pd(Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> )	as 102	(53)
Ph	W(CO) <sub>5</sub>	Pd(Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> )	102	(53*)
Ph	W(CO) <sub>5</sub>	W(CO) <sub>5</sub>	94	20 (252*) (253)
			82	9 (240*)
An	Cr(CO) <sub>5</sub>	Cr(CO) <sub>5</sub>	82	41 (240)

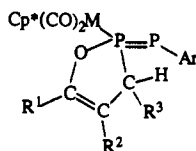
TABLE 14. Metalladiphosphenes

Ar—P=P—M

M	method	yield (ref)
CrCp*(CO) <sub>3</sub>	37	61 (183)
FeCp*(CO) <sub>2</sub>	67	59 (69, 70*)
Fe(PPh <sub>3</sub> )Cp(CO)	67	57 (70)
MnCp*(CO) <sub>2</sub>	67	39 (219)
OsCp*(CO) <sub>2</sub>	67	(70)
ReCp*(CO)(NO)	67	(220)
RuCp*(CO) <sub>2</sub>	67	67.5 (69, 70)

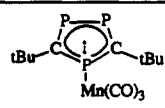
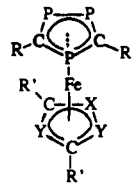

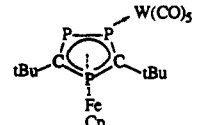


M	M'	method	yield (ref)
FeCp*(CO) <sub>2</sub>	Cr(CO) <sub>5</sub>	104 (THF)	57 (220*)
FeCp*(CO) <sub>2</sub>	Fe(CO) <sub>4</sub>	104 (Fe(CO) <sub>5</sub> )	55 (71*)
FeCp*(CO) <sub>2</sub>	Ni(CO) <sub>3</sub>	104 (CO)	31 (264)
MnCp*(CO)(NO)	Cr(CO) <sub>5</sub>	104 (THF)	51 (220)
OsCp*(CO) <sub>2</sub>	Fe(CO) <sub>4</sub>	104 (Fe(CO) <sub>5</sub> )	38 (71)
OsCp*(CO) <sub>2</sub>	Ni(CO) <sub>3</sub>	104 (CO)	22 (70) (264)
ReCp*(CO)(NO)	Cr(CO) <sub>5</sub>	104 (THF)	31 (220)
ReCp*(CO)(NO)	Ni(CO) <sub>3</sub>	104 (CO)	(220)
RuCp*(CO) <sub>2</sub>	Fe(CO) <sub>4</sub>	104 (Fe(CO) <sub>5</sub> )	24 (71)
RuCp*(CO) <sub>2</sub>	Ni(CO) <sub>3</sub>	104 (CO)	63 (264)



R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	M	method	yield (ref)
Me	H	H	Fe	126	49 (277)
H	Me	H	Fe	126	35 (277)
H	H	Me	Fe	126	12 (277)
H	H	H	Fe	126	47 (276*, 277*)
H	H	H	Ru	126	42 (277)

TABLE 15.  $\pi$  Complexes of Diphosphenes

compound	R	R'	X	Y	method	yield (ref)
						36 (73)
	tBu	H	CH	CH	103	(263*)
	tBu	tBu	P	P	36	30 (73*)
	tBu	tBu	C-tBu	P	36	(73*)
					91	(249)
	Ad	Ad	P	P	36	(73)
	Ad	Ad	C-Ad	P	36	(73)
					103	(263)

concerns the reaction of trimethylsilyl groups with methanol, owing to the oxophilicity of silicon<sup>182</sup> (Scheme 120).

On the other hand, addition reactions on diphosphene are more usual. They mainly take place on the double bond, which can also be reduced by lithium aluminum hydride.<sup>218</sup> [1,2] additions are observed with compounds of type HX. Interestingly, the same diphosphene complexes are obtained starting either from  $\eta^1\eta^1$  diphosphene complexes<sup>267</sup> or from  $\eta^1\eta^2\eta^1$  diphosphene complexes<sup>240</sup> (Scheme 121). Thus in the later case, the addition also induces a decomplexation of the double bond.

1,3 dienes react also with free<sup>267</sup> or complexed<sup>240</sup> phosphorus-phosphorus double bonds to give heterocycles (Scheme 122).

Analogous reactions occur with sulfur,<sup>237,267</sup> diazomethane,<sup>267</sup> and phenyl azide,<sup>237</sup> leading to phosphirane complexes 262 (Scheme 123).

Metalladiphosphene react also with diazomethane<sup>270</sup> and diphenylsulfonium cyclopropanide<sup>271</sup> and give metalladiphosphirane (Scheme 124).

The products isolated with sulfur and selenium are also three-membered heterocycles, but the first step of the reaction is an addition on the lone pair of the phosphorus atom linked to the metal<sup>272,273</sup> (Scheme 125). This reaction is analogous to the one observed for organic diphosphenes.<sup>274,275</sup>

$\alpha,\beta$  unsaturated compounds also add on the phosphorus lone pair by a [1 + 4] cycloaddition reaction, giving rise to an oxaphosphole complex with an exocyclic P=P double bond<sup>276,277</sup> (Scheme 126).

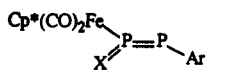
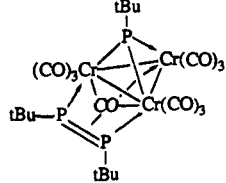
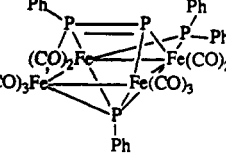
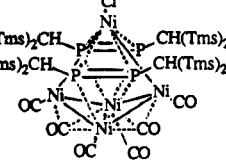
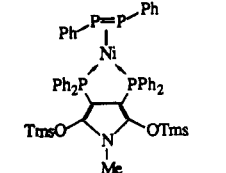
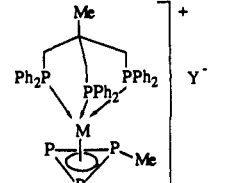
Methylation reactions on triphosphirene complexes occurs also on a phosphorus lone pair<sup>72</sup> (Scheme 127).

Finally, we have shown that the anionic hydrides 99 and 177 add on the lone pair of the uncomplexed phosphorus atom of  $\eta^1\eta^2$  diphosphene complexes. The anionic diphosphane complexes 267 thus synthesized are also obtainable starting from diphosphane complexes<sup>244</sup> (Scheme 128).

#### IV. Organization of Tables

Tables 6–16 give listings of  $\eta^1$  diphosphane complexes (Table 6),  $\eta^1\eta^1$  diphosphane complexes (Table 7), metalladiphosphanes (Table 8),  $\eta^1$  diphosphene complexes (Table 9),  $\eta^1\eta^1$  diphosphene complexes (Table 10),  $\eta^2$

TABLE 16. Miscellaneous Diphosphene Complexes

compound	X	method	yield (ref)
	S Se	125 125	66 (272*, 273*) (272, 273)
		93	20 (251*)
		107	30 (266*)
		87	15 (74*)
		as 88	60 (241)
	M = Co*, Ir, Rh Y = BF4*, CF3SO3	127	80 (72*)

diphosphene complexes (Table 11),  $\eta^1\eta^2$  diphosphene complexes (Table 12),  $\eta^1\eta^2\eta^1$  diphosphene complexes (Table 13), metalladiphosphenes (Table 14), and miscellaneous diphosphene complexes (Tables 15 and 16). Polymeric compounds are excluded. The following remarks are pertinent to the tables.

### Organization of Listings

Each table is organized with organic substituents listed first, then metallic groups. Organic substituents are filed according to their empirical formula; the Chemical Abstracts classification is used, i.e. for instance, Br, Me, CF<sub>3</sub>, Ph, cHex, Cl, H. The metallic groups are filed, first according to the alphabetical order of the metal, then according to the empirical formula of the sum of all ligands, excepted the diphosphene or diphosphane unit. Miscellaneous compounds are filed according to the number of phosphorus atoms. Abbreviations mentioned in the introduction of the review are used in the tables. The number of the method given in the tables refers to the number of the corresponding scheme in part III. For general reactions, the leaving ligand L is specified in brackets. The term "as 12" indicates that the method used is similar to that in Scheme 12. In the column "yield (ref)", the term "63 (30\*, 31) (53)" means that a 63% yield is given in refs

30 and 31, whereas no yield is given in ref 53. The asterisk indicates that the structure of the compound has been determined by X-ray crystallography in ref 30.

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