Coordination Chemistry Reviews, 48 (1983) 1–58
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

THE COORDINATION CHEMISTRY OF YLIDES

WILLIAM C. KASKA

Department of Chemistry, University of California, Santa Barbara, CA 93106 (U.S.A.)

(Received 8 February 1982; in revised form 15 April 1982)

CONTENTS

A. INTRODUCTION

Traditionally the term ylide denotes a compound with a negatively charged carbon atom adjacent to a heteroatom which bears a formal positive charge. This prompts some to call ylides carbanions, but this is not always the case because many ylides can be prepared salt-free. Therefore, the carbanionic term should specifically refer to species shown in Fig. 1.

The most commonly studied examples of ylides include phosphorus [1], sulfur [2], nitrogen [3], and arsenic [4] as the heteroatoms, although transition metals like tantalum and iridium form "metallic ylides" [5]. A typical

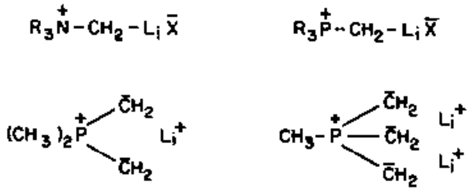


Fig. 1. Examples of carbanionic ylides.

example is triphenylphosphonium methylide, methylenetriphenylphosphorane or alkylidenetriphenylphosphorane for the generalized case where the hydrogen atoms are replaced by a variety of substituents.

$$Ph_3\overset{+}{P}-\overline{C}H_2$$

1

The ubiquitous 1,2-dipolar nature of most ylides suggests a more general proposal that these compounds be considered as onium stabilized complexes of low valent atoms. In this sense phosphorus ylides are little different from nitrogen, sulfur, or phosphorus stabilized complexes of various transition metal atoms. Thus, methylenetriphenylphosphorane is a complex of divalent carbon just as the triphenylphosphine compound

$$(Ph_3P)_2 \rightarrow NiCl_2$$

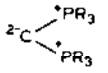
2

is a complex of divalent nickel chloride. Support for this analogy comes from the observation that ylides can be prepared by generation of a carbene and trapping in situ [1c,6]

$$Ph_3P + :CCl_2 \rightarrow Ph_3\overset{+}{P}-\overline{C}Cl_2$$

Of course, the analogy can be extended to triphenylphosphine complexes of oxygen ($Ph_3\overset{+}{P}-\overline{O}$) and the broad class of phosphineimines ($Ph_3\overset{+}{P}-\overline{N}R$) which are simply complexes of nitrenes. All of these compounds are rather stable thermally whereas the corresponding sulfur and nitrogen analogs often have marginal thermal stabilities and sometimes cannot be isolated.

The bis-ylides of phosphorus [7]

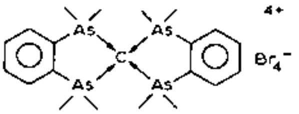


R = Me, Ph

3

can be considered as phosphine complexes of carbon in much the same way that $(R_3P)_2Ni^0$ $R = C_6H_{11}$ and $(R_3P)_2$ Pt^0 $R = C_6H_{11}$ are commonly viewed as complexes of zerovalent metals even though the oxidation state of the metal atom is perhaps meaningless [8] (cf. vide infra).

This analogy is elegantly expressed in the often poorly recognized complex described by Nyholm and co-workers [9]

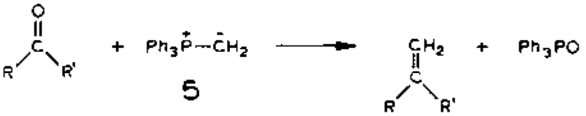


4

which is an alkyl, aryl arsine complex of carbon, albeit the carbon is in a high oxidation state.

Modern physical techniques seem to support the dipolar nature of ylides and thus to a certain extent the analogies described above [10]. This is an intriguing possibility because it helps to generalize two fields of chemistry i.e. the chemistry of non-metal complexes with those of metal complexes. Such an aspect is even more exciting because it offers the possibility of studying a new way of carbon—metal bond formation which is one of the primogenetors of organometallic chemistry itself.

The serious investigations of ylide chemistry were initiated by Staudinger and Mayer [11] and later by Wittig and co-workers [12] who uncovered and popularized their synthetic usefulness as in the Wittig olefin synthesis



(1)

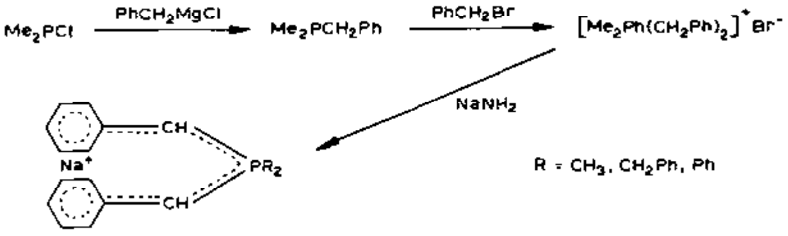
Even though there have been recent examples of methylenation [13] reactions, the Wittig synthesis still stands as a mark of generality and simplicity.

Except for a flurry of activity in the organometallic chemistry of ylides by Seyferth and co-workers in the late 1950s [14] organometallic chemists seem to have neglected the potential of ylides for studying the formation of the carbon—metal bond. The recent resurgence of interest in the σ-carbon—metal bond [15] and the realization that ylides can be used as negative or neutral ligands to a wide variety of metals has attracted many investigators to this field.

B. YLIDE COMPLEXES OF NON-TRANSITION METALS

(i) *Complexes of alkali and alkaline earth metals*

Alkali metal salts form stable adducts with ylides. Lithium salts are so strongly bound to ylides that they present a major problem in isolation of salt-free compounds [16,17]. Spectroscopic studies such as ^{1}H, ^{13}C, ^{31}P and



6

Scheme 1

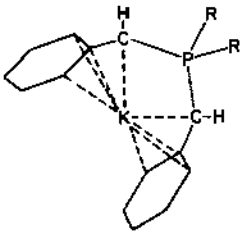
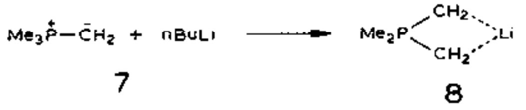


Fig. 2. X-ray structure of a potassium benzylide.

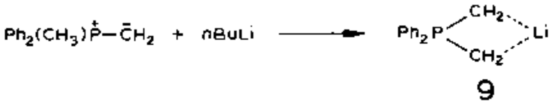
photoelectron spectroscopy [18—20] suggest that there is a strong interaction between the metal and the carbanionic center. Recent X-ray results seem to confirm this interpretation.

Spectroscopic data show coordinative interaction of the metal with two equivalent benzylide groups. A crystal structure of the potassium derivative shows a preferred coordination of the metal towards the ylidic carbon and *ortho* carbon atoms of the benzylide group [26].

A rather exciting and unusual example is side-chain metalation with alkylithium compounds [18,21,22]



(2)



(3)

These carbanionic derivatives with equivalent anionic centers are often insoluble in ether solvents. They are versatile reagents for organometallic synthesis (see above). Other less well known systems are the triphenylborane adduct of a lithiated phosphonium ylide, $\text{Ph}_3\overset{+}{\text{P}}-\text{CHLi}\overset{-}{\text{B}}\text{Ph}_3$ * [23] and the LiBr adduct of the nitrogen ylide, $[\text{Me}_3\overset{+}{\text{N}}\text{CH}_2\text{Li}]\text{Br}$ [24]. Interestingly enough, multi-lithiated ylides have not been successfully isolated, where the onium center is a triphenylphosphine group.

Ordinarily the heat of formation per equivalent for an ionic salt increases when the positive ion is replaced by another ion of equal charge but greater radius [25]. Hence, one might expect the heavier alkali metal cations to form stable adducts with ylides. Instead, sodium and potassium halides do not form complexes, although a cesium adduct $\text{Cs}^+[\text{Me}_2\text{P}(\text{CH}_2)]^-$ can be isolated [26]. Unfortunately, the structures of alkali metal ylide salts are not

---

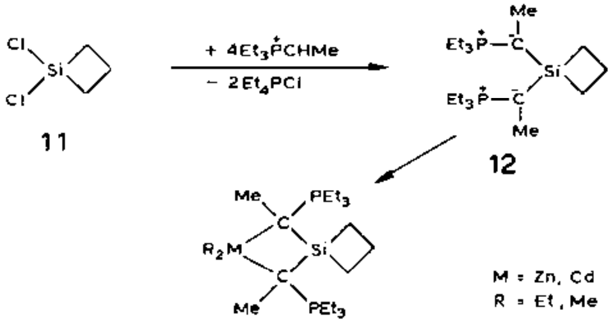
* Note added in proof: the parent lithiated ylide has been synthesized by E.J. Corey and J. Kang, J. Am. Chem. Soc., 104 (1982) 4724.

known, hence the apparent reasons for instability are not clear [26]. Nevertheless, this instability is used to some advantage in the synthesis of salt free phosphonium ylides by using sodamide or alkali-metal hydride reagents. The reaction with sodamide is not without its problems, however. Experiments have shown that $NaNH_2$ and Me_4PCl at room temperature (not reflux) in THF do not give the expected ylide $Me_3\overset{+}{P}-\overline{C}H_2$, but the imino complex [27]

$$2\,Me_4PCl + 2\,NaNH_2 \longrightarrow Me_3\overset{+}{P}-\overset{-}{N}-\overset{+}{P}(CH_3)_2-\overset{-}{C}H_2 \qquad (4)$$

10

Complexes of the alkaline earth metals have been most adequately described by a series of double ylide compounds,



11

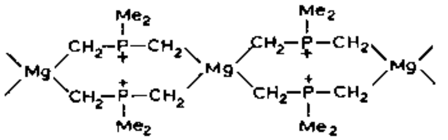
12

13

M = Zn, Cd
R = Et, Me

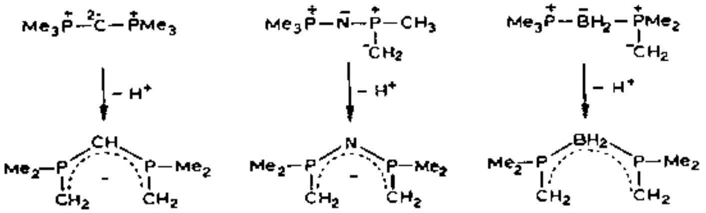
(5)

Some coordination polymers of magnesium are formed with simple ylides

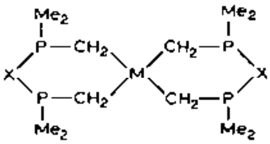


14

or



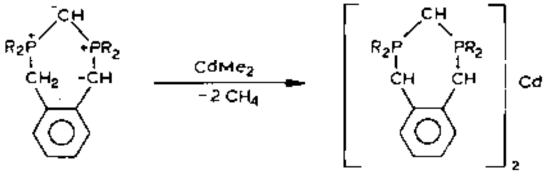
15



16

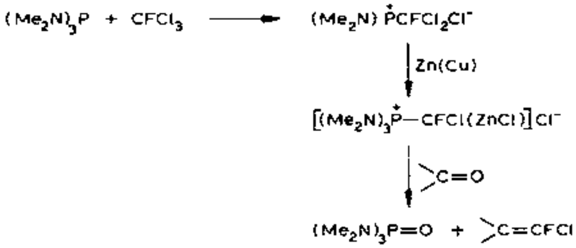
M = Zn, Cd, Be
X = CH, N, BH2

or with the cyclic ylides [28]



17 18 (6)

Zinc ylide complexes have been used in the synthesis of halogenated ylides as illustrated below [27]



(7)

(ii) Complexes of group III metals

Most tricovalent boron compounds form Lewis acid—base adducts with ylides. In all instances zwitterionic products are formed with $Ph_3\overset{+}{P}-\overline{C}H_2$ [14,29,30], $Me_3\overset{+}{P}-\overline{C}H_2$ [31], $Ph_3As^+-\overline{C}H_2$ [32] and Me_3N-CH_2LiBr [33] so that a σ-carbon—boron bond is formed:

$$R_3\overset{+}{P}-\overline{C}H_2 + MR'_3 \rightarrow R_3\overset{+}{P}-CH_2-\overline{M}R'_3 \qquad (8)$$

7 19 M = B, Al, Ga, In, Tl

Polyhedral boron compounds behave a little differently in that $Ph_3\overset{+}{P}-\overline{C}H_2$ and $(Ph_3P)_2C$ with $B_{10}H_{14}$ give salt like products, $[Ph_3PCH_3]^+[B_{10}H_{13}]^-$ [29] and $[(Ph_3P)_2CH]^+[B_{10}H_{13}]^-$ [34], respectively. The acidity of $B_{10}H_{14}$ apparently renders insertion of the ylidic carbon into the polyhedral cage very difficult. In spite of this lack of success with boron clusters, similar attempts with transition metal clusters have been partially successful (see above).

Zwitterionic boron phosphorus ylide adducts give interesting thermal rearrangement products

$$\mathrm{Ph_3\overset{+}{P}CH_2\overset{-}{B}R_3} \rightarrow 1/3\ \mathrm{Ph_3P} + 1/3\ \mathrm{B(CH_2R)_3}\ (\text{ref. } 35) + 2/3\ \mathrm{Ph_3\overset{+}{P}{-}\overset{-}{B}Ph_3}$$

20 R = Ph, H

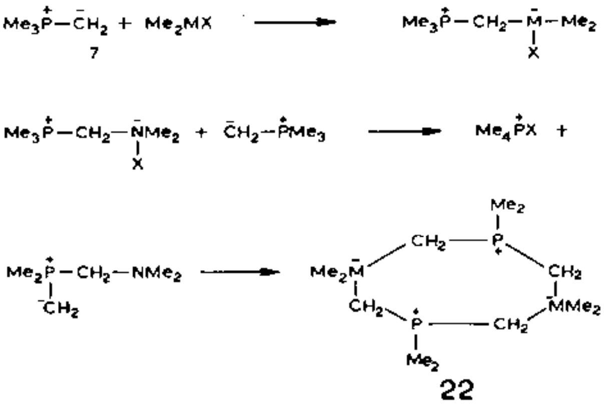
(9)

$$\mathrm{R_3B + Me_2\overset{+}{S}(O){-}CH_2 \rightarrow Me_2\overset{+}{S}(O){-}CH_2{-}\overset{-}{B}R_3 \rightarrow Me_2SO + R_2BCH_2R}$$

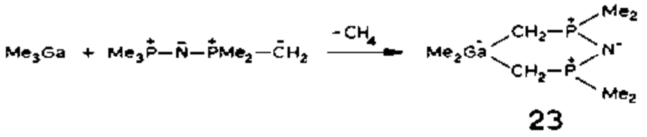
(9a)

The chemistry of aluminum, gallium, indium and thallium compounds with ylides is similar to boron ylide chemistry, although more complex structures can be formed. Although the tri-alkyls give 1 : 1 betaine adducts, treatment of $\mathrm{Et_2AlCl}$, $\mathrm{Me_2GaCl}$, $\mathrm{Me_2InCl}$, and $\mathrm{Me_2TlBr}$ with $\mathrm{Me_3\overset{+}{P}{-}\overset{-}{C}H_2}$ in a 1 : 2 molar ratio respectively, gives heterocyclic systems [36].

(10)



(11)



(12)

(iii) Complexes of silicon

The major body of information on organometallic ylides revolves around the Group IV elements, silicon, germanium, and tin [37—43]. This is

especially true because silicon has an exceptional stabilizing effect on the ylidic carbon atom [44]. The effects of silicon on the ylidic carbon atom can be summarized as follows:
(a) the stabilizing influence of Group IV atoms on ylidic carbon atoms;
(b) the role of silicon in transylidation;
(c) the role of silicon ylides in synthesis.

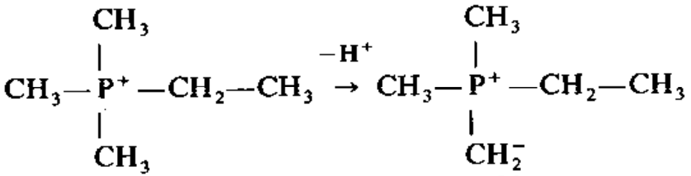
The silicon effect

The introduction of a silicon substituent on a carbon atom α to an onium atom appears to promote an increase of acidity for the protons on the α-carbon atom [45,46]. Hence, treatment of such phosphonium, arsonium [47] or sulfonium salts [48] with organometallic bases gives the ylide with the silicon substituent directly attached to the ylidic carbon atom

$$\underset{\mathbf{24}}{Me_3P^+{-}CH_2{-}\overline{Si}H_3} \xrightarrow{-H^+} \underset{\mathbf{25}}{Me_3\overset{+}{P}{-}\overline{C}HSiH_3} \tag{13}$$

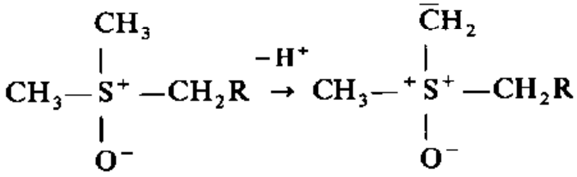
$$\underset{\mathbf{26}}{Me_2\overset{+}{S}(O){-}CH_2SiR_3Cl^-} \xrightarrow{-HCl} \underset{\mathbf{27}}{Me_2\overset{+}{S}(O){-}C\overline{H}SiR_3} \tag{14}$$

In contrast to this, the deprotonation of onium salts that do not have Group IV substituents gives ylides where the proton loss comes from the least alkylated carbon atom



$$CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{P^+}}{-}CH_2{-}CH_3 \xrightarrow{-H^+} CH_3{-}\underset{\underset{CH_2^-}{|}}{\overset{\overset{CH_3}{|}}{P^+}}{-}CH_2{-}CH_3 \tag{15}$$

28 **29**



$$CH_3{-}\underset{\underset{O^-}{|}}{\overset{\overset{CH_3}{|}}{S^+}}{-}CH_2R \xrightarrow{-H^+} CH_3{-}{}^+\underset{\underset{O^-}{|}}{\overset{\overset{\overline{C}H_2}{|}}{S^+}}{-}CH_2R \tag{16}$$

30 **31**

One obvious explanation for these effects is enhanced *d*-orbital participation by the heavier Group IV atoms which could account for the delocalization of the ylidic electron pair [43,45]. Yet another possibility is based on an electrostatic effect where the longer ylidic carbon—silicon bond extends the electrostatic sphere of the carbonionic carbon atom with a corresponding reduction of repulsive forces [44].

Neither of these explanations is totally satisfying although photoelectron [49] and ^{13}C NMR [50] spectroscopy seem to support these suggestions with silicon, germanium, tin and lead substituents of phosphorus and arsenic ylides.

Transylidation

Transylidation is the acid/base reaction between onium salts and ylide pairs of significantly different acidity, or basicity and lattice energy differences of the onium salts. This is a consequence of the carbanionic stabilization of silyl substituted ylides and their homologs [51,52].

In the following example

$$\begin{aligned} &\underset{\mathbf{32}}{Et_3\overset{+}{P}-\overline{C}HCH_3} + [Et_3\overset{+}{P}-CH_2-SiH_3]\overline{Cl} \rightarrow Et_3\overset{+}{P}-\overline{C}HSiH_3 + \\ &\qquad\qquad\qquad\qquad\qquad\qquad\qquad Et_4\overset{+}{P}Cl^- \quad \mathbf{33} \end{aligned} \tag{17}$$

the silylated ylide forms easily because the silylated onium salt has a much higher acidity than the alkylated onium salt (Et_4PCl), and the product silylated ylide has a reduced basicity compared to the alkylated ylide (starting material) [46,53].

Synthesis

Initially it appeared that pure salt-free ylides could be prepared only by desilylation of silylated ylides [36,48].

$$R_3\overset{+}{P}-\overline{C}HSiR'_3 + R''OH \rightarrow R_3\overset{+}{P}-\overline{C}H_2 + R'_3SiOR'' \tag{18}$$

$$R_3\overset{+}{As}-\overline{C}HSiR'_3 + R''OH \rightarrow R_3\overset{+}{As}-\overline{C}H_2 + R'_3SiOR'' \tag{19}$$

$$R = CH_3, C_2H_5, i\text{-}C_3H_7, n\text{-}C_3H_7, n\text{-}C_4H_9, C_6H_5$$

However, more traditional methods have been developed so that a wide variety of salt free ylides can be easily made and systematically studied.

Nevertheless, the silylated precursors are readily available in good yield with an extensive variety of substituents, which can even be exchanged by transilylation of a complete silyl group [36,41,45,46,53,54]

$$\begin{aligned} &R_3\overset{+}{P}-\overline{C}(SiMe_3)SiMe_3 + 2\ Me_{(4-n)}SiCl_n \xrightarrow{-Me_3SiCl} \\ &R_3\overset{+}{P}-\overline{C}[SiMe_{3-m}Cl_{m-2}] \qquad n = 2,3,4(m = n-1) \end{aligned} \tag{20}$$

$$R_3\overset{+}{P}-\overline{C}(SiMe_3)SiMe_3 + 2\ PCl_3 \xrightarrow{-2\ Me_3SiCl} R_3\overset{+}{P}-\overline{C}[PCl_2]_2 \tag{21}$$

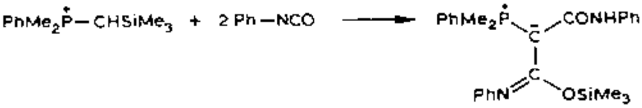
$$R_3\overset{+}{P}-\overline{C}HSiMe_3 + R_3AsOSiMe_3 \rightarrow R_3\overset{+}{P}-\overline{C}HAsR_2 + R_3SiOSiR_3 \tag{22}$$

This reaction unites the principles of desilylation with that of substituent exchange by transilylation [55—69]. With more complex reactants in the silicon series, cyclic or branched systems can be made [70—72].

The interactions of silyl ylides with simple organic compounds have not been completely investigated. Indeed, carbonyl compounds when treated with silyl ylides often do not give normal Wittig products with silylated olefins. Instead, one observes desilylation [39,69]

$$3\,Ph_2CO + 2\,Me_3\overset{+}{P}-CHSiMe_3 \rightarrow Me_3PO + Me_3SiOMe_3 + 2\,Ph_2C{=}CH_2 + Me_2P(\overline{O})CH{=}CPh_2 \qquad (23)$$

Insertion products are formed with isocyanates, isothiocyanates and carbon disulfide [73]


(24)

On the other hand ylide derivatives of germanium, tin and lead disproportionate to give disubstituted products [37,45]

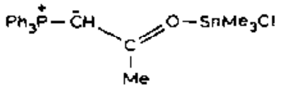
$$2\,Me_3\overset{+}{P}-\overline{C}HMMe_3 \rightarrow Me_3\overset{+}{P}-CH_2 + Me_3\overset{+}{P}-\overline{C}(MMe_3)_2 \qquad (25)$$

$M = Ge, Sn, Pb$

Similar reactions occur with diazo alkanes [74]

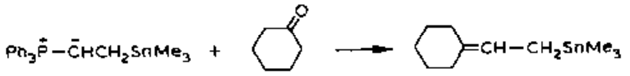
$$Me_3M-CHN_2 \rightarrow CH_2N_2 + (Me_3M)_2CN_2 \qquad (26)$$

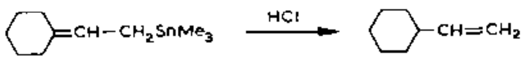
Carbonyl stabilized ylides also form compounds with organotin and organolead halides. The 1 : 1 adducts have a completely different structure in which the components are linked by the carbonyl substituents [75,76]



The addition of trimethyltinlithium to triphenylvinyl phosphonium bromide gives the metallo-ylide [77]

$$Ph_3\overset{+}{P}-CH{=}CH_2Br^- + Me_3SnLi \longrightarrow Ph_3\overset{+}{P}-\overline{C}HCH_2SnMe_3 \qquad (27)$$


(28)


(29)

The relative ease of desilylation has been used effectively in the synthesis of a bis ylide [78]

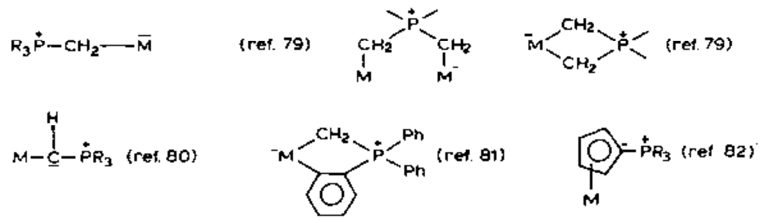
$$Me_3\overset{+}{P}—\overset{-}{C}HSiMe_3 + Me_3PF_2 \rightarrow [Me_3P—CH\overset{+}{P}Me_3]F^- + Me_3SiF \qquad (30)$$

$$[Me_3P—CHPMe_3]^+F^- + CH_2Cl_2 \rightarrow [Me_3P—CHPMe_3]^+Cl^- \xrightarrow{NaH} (Me_3P)_2C \qquad (31)$$

C. YLIDE COMPLEXES OF TRANSITION METALS

(i) Introduction

Perhaps the most exciting aspect of ylide chemistry is their use as ligands in transition metal complexes. In a sense, ylides complement the extensive literature of organophosphine complexes because a variety of complexation modes are now possible



Such diversity is possible because the ylide can be a neutral and an anionic ligand. Moreover, the formation of the carbon—metal bond is apparently compatible with both low valent transition metal complexes and cationic complexes in higher oxidation states. This diversity makes ylide ligand complexes versatile candidates for use in transition metal combinations for catalysis [83].

(ii) Reaction pathways in ylide transition metal complexes

Displacement of coordinated ligands by an ylide with formation of a direct carbon—metal bond

The alkylidenephosphoranes are among the most powerful bases known [84], hence the displacement of coordinated ligands is not totally surprising. Perhaps the most common ligand subject to displacement is the carbon monoxide group. This group seems to be most easily displaced from low valent transition metal complexes, especially from Group VIII transition metals such as tetracarbonylnickel. Angelici [85] and Darensbourg and Darensbourg [85] have proposed that CO ligands with carbon—oxygen force constants near 18 mdyn Å^{-1} or CO stretching frequencies at 2000 cm^{-1} or above will be subject to addition rather than substitution reactions. Likewise, complexes with carbonyl stretching modes below 2000 cm^{-1} like some nickel and cobalt species appear to give substitution products when treated with alkylidene phosphoranes. This is not a hard and fast rule, of course, and the generalities with respect to kinetic factors must still be explored.

Interestingly enough $Ni(CO)_4$ with alkylidene phosphoranes gives only a mono-substitution product [86]

$$Ni(CO)_4 + R_3\overset{+}{P}—\overline{C}R'R'' \rightarrow (CO)_3\overline{Ni}—CR'R''\overset{+}{P}R_3 \tag{32}$$

34

The structure of one such product is shown in Fig. 3 and clearly indicates carbon—metal bond formation [87]. Here the σ-nickel carbon bond of 2.09 Å is longer than other metal—carbon bonds and the phosphorus—carbon distance of 1.83 Å is longer than the same distance in the free ylide, $Ph_3\overset{+}{P}—\overline{C}H_2$ (1.66 Å) [88]. Perhaps the reluctance of these ylides to further substitution is because the metal—carbonyl bonds are extremely non-labile. This can be explained if electron density from the ylide-carbon bond is delocalized by the carbonyl groups in such a way that the nickel carbonyl groups are more strongly held to the metal atom because of excessive back-bonding [87].

Another instance of carbonyl group substitution occurs in the cobalt group with triphenylphosphonio-cyclopentadienide [89]

35 36 (33)

The π-bonded ylide dicarbonyl complex is an effective cyclotrimerization catalyst. Similar carbonyl substitutions can be observed with triphenylphosphoniocyclopentadienide, and the following metals [90], $Ph_3\overset{+}{P}—C_5H_4\overline{M}(CO)_3$, M = Cr, Mo, W; $Ph_3P—C_5H_4M(CO)_3^+ PF_6^-$, M = Re, Mn.

Interestingly enough, $Fe(CO)_5$ [91] and triphenylphosphonio-cyclopenta-

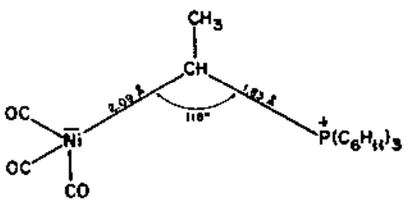


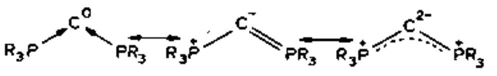
Fig. 3. X-ray molecular structure of a nickel carbonyl ylide complex.

dienide, do not give isolable products, and isolation of other metal carbonyl adducts has not been reported. The success of this ylide as an effective agent for carbonyl displacement probably comes from the 6π electrons in the cyclopentadienide ring. This makes the system isoelectronic with benzene and the numerous arene metal complexes [92] are only a prelude to the possibilities envisioned with these aromatic ylides.

An unusual instance of carbonyl substitution occurs with $Ph_3\overset{+}{P}—\bar{C}HR$, R = Ph, $CH{=}CH_2$, $CH{=}CHCH_3$, $CH{=}CHPh$ [93]. These complexes give pentacarbonyl and tetracarbonyl adducts of Group VI metal carbonyls (Cr, Mo, W) by refluxing the ylide and $M(CO)_6$. Again, these ylides act as donor ligands by changing the hybridization of the ylide carbon atom from $sp^2 \rightarrow sp^3$. There must be a strong dependence on steric factors, because $\bar{C}H_2—\overset{+}{P}Ph_3$ gives no substitution of CO with $M(CO)_6$, M = Cr, Mo, W; only addition to the carbonyl group is observed (cf. data above).

The interaction of bis ylides [94] with metal carbonyl compounds has been investigated only briefly, although recent innovations in the synthesis of these materials offer a better opportunity to study the chemical and physical properties of these interesting molecules [95,96].

Actually, the molecules are unusual [97] but classical examples of phosphine complexes of "low-valent carbon". This makes them excellent σ- and π-electron donor molecules (a rarity with ligands in organometallic chemistry) which can be best described by the following resonance forms

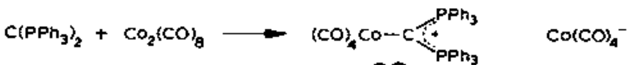


R = Me, Ph

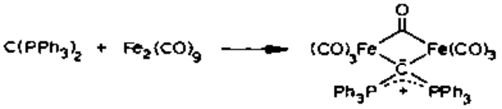
37

The organometallic reaction chemistry of the bis-ylides seems to favor substitution of CO with metal carbonyl compounds such as $Co_2(CO)_8$, $Ni(CO)_4$, and $Fe_2(CO)_9$ with the formation of direct carbon—metal bonds [98]; this is at least true for R = Ph, (cf. data for R = Me)

38 (34)

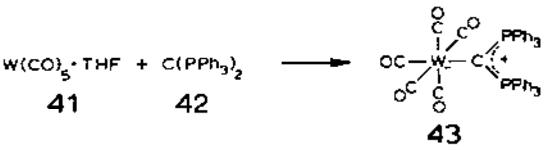


39 (35)



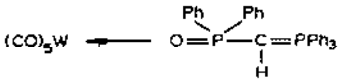
40 (36)

There are additional examples of carbon—metal bond formation with bis-ylides when olefins, phosphines and other weakly coordinated ligands are removed from the metal atom. Thus the interaction of $W(CO)_5 \cdot THF$ with $C(PPh_3)_2$ gives

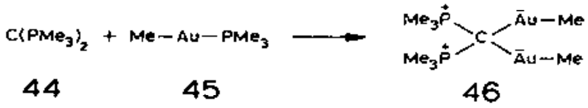


(37)

which rapidly absorbs moisture to give the isolable complex [99]

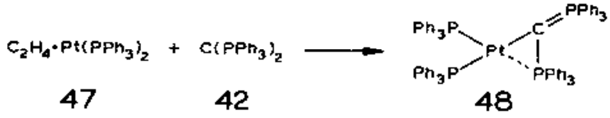


Clearly, two coordination sites are available on the central carbon atom, but only one metal carbonyl moiety coordinates to the carbodiphosphorane, probably because of steric constraints on the system. This does not mean that such double coordination is impossible since interaction of $C(PMe_3)_2$ with Me—Au—PMe_3 gives [100]



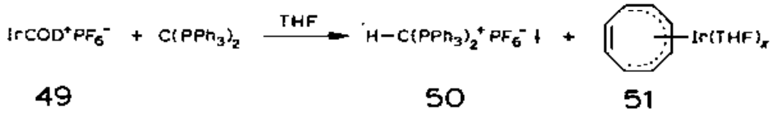
(38)

Facile substitution of ethylene occurs with $C_2H_4 \cdot Pt(PPh_3)_2$ and $C(PPh_3)_2$ to give a complex with partial triphenylphosphine transfer [101]



(39)

The easy displacement of ethylene from platinum complexes suggests the possibility of a similar displacement from other olefin complexes such as $Ir(COD)^+PF_6^-$. Instead a facile intramolecular metalation occurs to give a π-allylic complex [102]

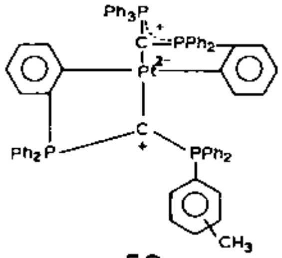


(40)

A similar effect is observed with $Ir(cyclooctene)_2^+ PF_6^-$. Extensions of this idea to the interaction of $C(PPh_3)_2$ with $Pt(Me_3)_3 \cdot 3\,THF^+PF_6^-$ gives a series of *o*-metalated products and loss of methane in a complicated set of reactions [103]

$$Pt(Me_3)_3^{+}\cdot 3\,THF\,PF_6^- \;+\; 3\,C(PPh_3)_2 \longrightarrow H{-}C(PPh_3)_2^+\,PF_6^-$$

52



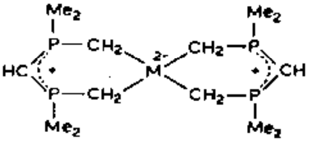
53

(41)

Both examples of platinum and iridium complex interaction with $C(PPh_3)_2$ seem to be promoted by the σ—π electron donor properties of the bis-ylide.

The bis-ylides $(CH_3)_n(C_6H_5)_{3-n}\overset{+}{P}—\overset{2-}{C}—\overset{+}{P}(C_6H_5)_{3-n}(CH_3)_n$ exhibit an ambident ligand behavior with organometallic compounds. Thus the type of complex formed is dependent to a great extent on the central metal atom and its ligands. For example, if $n = 3$ in the bis-ylide described above, the product of the reaction with most metal complexes is a chelate complex [104]

$$4\,C(PMe_3)_2 \;+\; MCl_2 \longrightarrow 2\,H{-}C(PMe_3)_2^+Cl$$

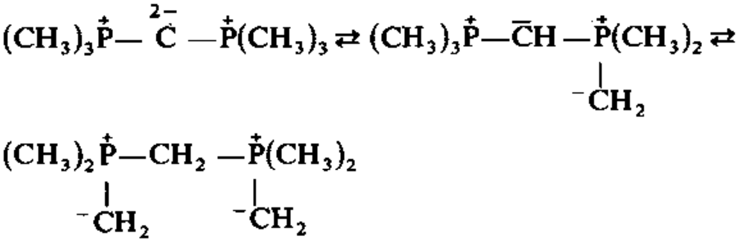


M = Ni, Pd, Pt, Hg

54

(42)

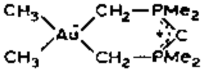
because the chemistry of $C(PMe_3)_2$ is governed by the prototropy [105]



$$(CH_3)_3\overset{+}{P}—\overset{2-}{C}—\overset{+}{P}(CH_3)_3 \rightleftarrows (CH_3)_3\overset{+}{P}—\overline{C}H—\underset{^-CH_2}{\underset{|}{\overset{+}{P}}}(CH_3)_2 \rightleftarrows$$

$$(CH_3)_2\underset{^-CH_2}{\underset{|}{\overset{+}{P}}}—CH_2—\underset{^-CH_2}{\underset{|}{\overset{+}{P}}}(CH_3)_2$$

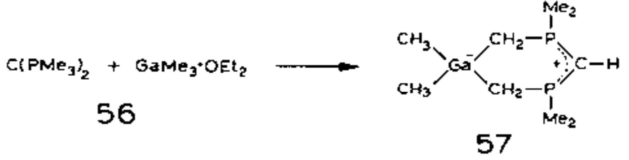
$$4\,C(PMe_3)_2 \;+\; AuClMe_2 \longrightarrow 2\,H{-}C(PMe_3)_2^+Cl^- \;+$$



55

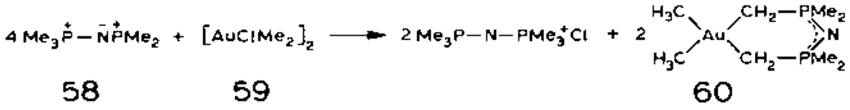
(43)

Sometimes methane can be eliminated from the coordination spheres of the complex particularly when the metal—carbon bond is very polar as with $GaMe_3$ or $AlMe_3$ [106]



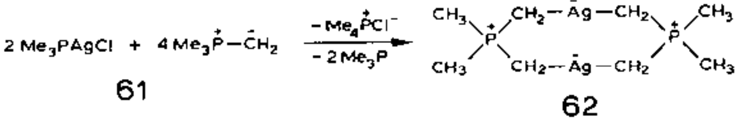
(44)

Similar complexes can be formed if the central carbon atom of the bis-ylide is replaced with a nitrogen atom as in [107]

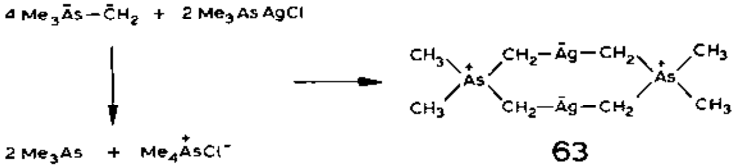


(45)

Perhaps the most studied reaction of ylides and transition metal compounds is the displacement of olefins, phosphines and their coordinated ligands for the formation of carbon—metal bonds. This type of displacement is often followed by transylidation, or reaction of the initially formed ylide metal complex with a second equivalent of ylide. This is illustrated for the following set of transition metals, which emphasize the bond formation.



(46)



(47)

In this case the ligand Me_3P is displaced by the stronger donor $Me_3\overset{+}{P}{-}\overline{C}H_2$, then the intermediate adduct $Me_3\overset{+}{P}{-}CH_2{-}\overline{A}g{-}Cl$ (**64**) is deprotonated by additional equivalents of ylide to give the observed product [108].

The chemistry of gold has been expanded with this set of reactions to form compounds with many gold—carbon σ-bonds [109]

$$Me{-}Au{-}PMe_3 + Me_3\overset{+}{P}{-}\overline{C}H_2 \xrightarrow{-Me_3P} Me\overline{Au}{-}CH_2{-}\overset{+}{P}Me_3 \qquad (48)$$

65

$$Me_3P{-}Au{-}Cl + Me_3\overset{+}{P}{-}\overline{C}H_2 \rightarrow Me_3P{-}Au{-}CH_2{-}\overset{+}{P}Me_3Cl^-$$

$$-Me_3P\Big\downarrow \overline{C}H_2{-}\overset{+}{P}Me_3$$

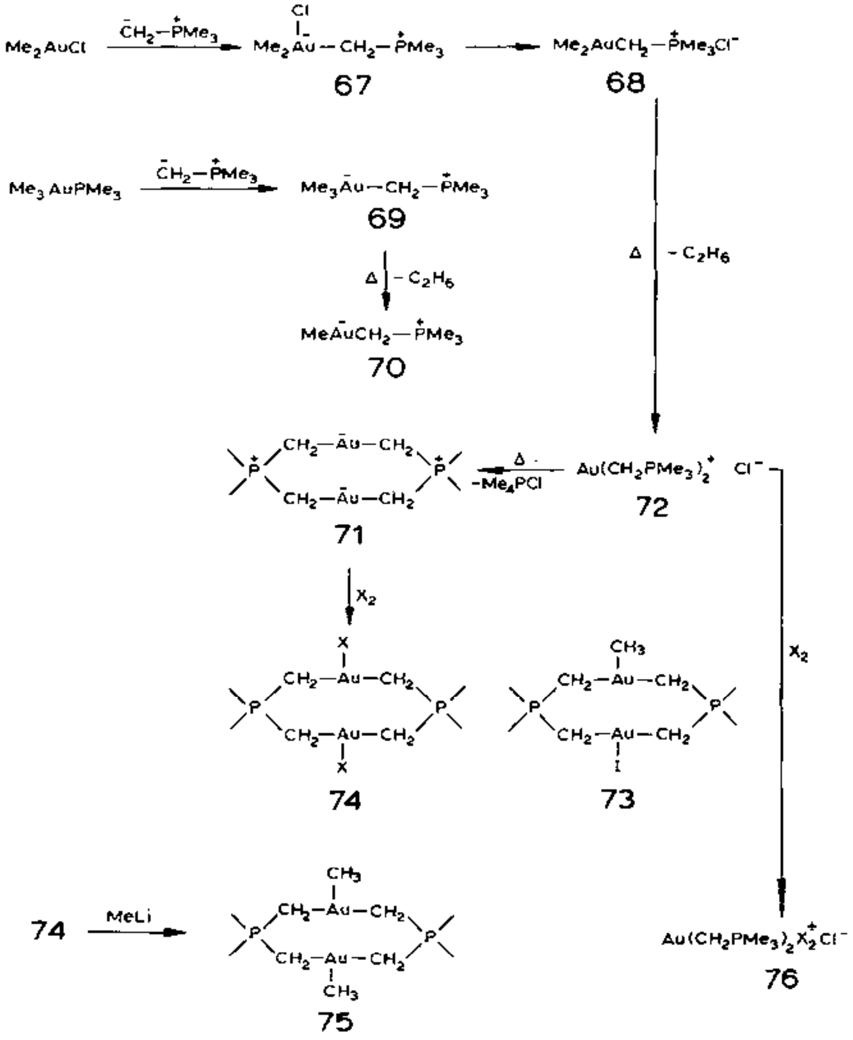
$$(Me_3P{-}CH_2)_2Au^+Cl^- \qquad (49)$$

66

Yamamoto has shown that this type of ligand displacement can be observed for the ylide $(Me_2N)_3\overset{+}{P}-\overline{C}H_2$,

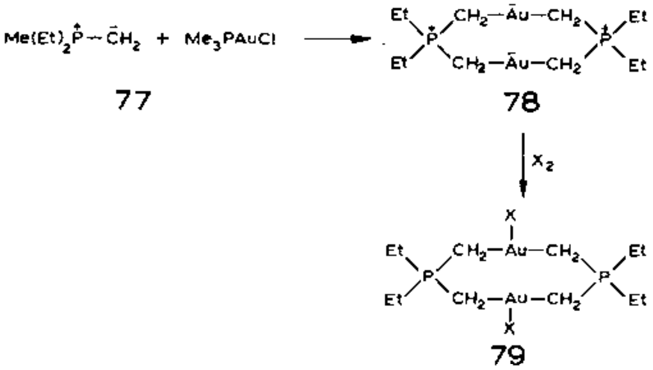
$$3(Me_2N)_3\overset{+}{P}-\overline{C}H_2 + Ph_3P-Au-Cl \rightarrow \left[(Me_2N)_3P-CH_2-Au-CH_2-P(NMe_2)_3\right]^+Cl^- \qquad (50)$$

Often displacement of a coordinated ligand is not necessary to form a carbon–metal bond. This is best illustrated by the following sequence of reactions [109]



Scheme 2

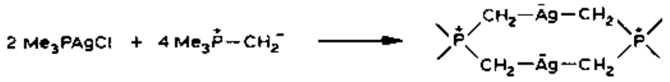
An unusual complex with gold in a formal oxidation state II can be synthesized with ylide ligands [110]



77 78 79

(51)

Silver(I) forms some similar complexes with ylides as illustrated by the following equations [108]



80

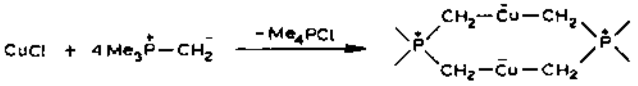
(52)

Again these are substitution or displacement reactions which give compounds of unusual thermal stability. Such stability far exceeds that of silver alkyls.

Similarly copper ylide complexes of exceptional stability are formed by a displacement reaction. Secondary reactions of transylidation give the final product [111]

$$Me_3\overset{+}{P}-\overset{-}{C}H_2 + Me_3PCuCl \longrightarrow (Me_3\overset{+}{P}-CH_2)_2\overset{-}{Cu}\quad Cl^- \qquad (53)$$

81

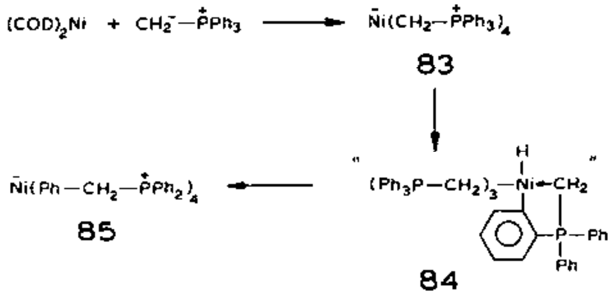


82

(54)

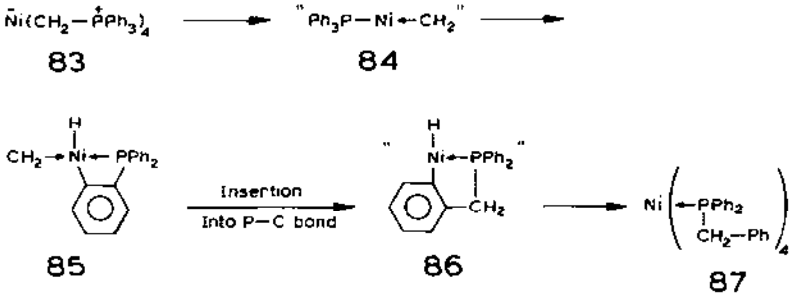
Among the Group VIII transition metal compounds, displacement of coordinated phosphines and olefins is the most prominent reaction. Nowhere is this more evident than in the case of nickel chemistry. Treatment of bis(1,5-cyclooctadiene) nickel with $Ph_3\overset{+}{P}-\overset{-}{C}H_2$ gives $Ni(PhCH_2PPh_2)_4$ [87].

Presumably the cyclooctadiene is displaced to give $Ni^-(CH_2-\overset{+}{P}Ph_3)_4$ which then undergoes a Stevens-type rearrangement to give the observed product



(55)

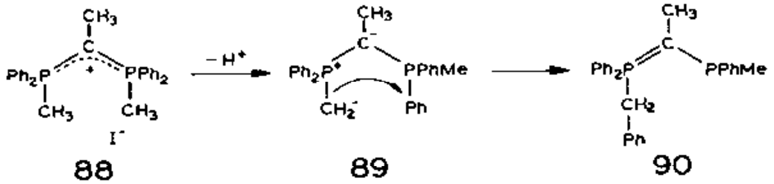
Perhaps the reaction involves oxidative addition or *o*-metalation of the phosphonium aromatic ring. Such a sequence is possible because of similar observations in the platinum series (see above). The recent observations of alkylidene transfer [112] (see above) to metals like zirconium [150], tantalum [112] and iron [112] suggest that this might also occur with low-valent nickel compounds



(56)

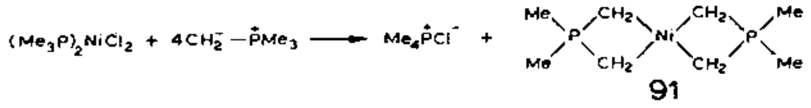
In this respect it is interesting that the interaction of Ni(COD)$_2$ with $\bar{C}H_2-\overset{+}{P}Me_3$ gives only Ni(PMe$_3$)$_4$ as the isolated product [86,113].

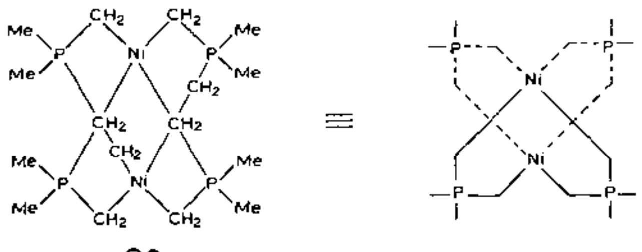
Perhaps this type of rearrangement is not too different from the migration observed in new bis-ylides [114]



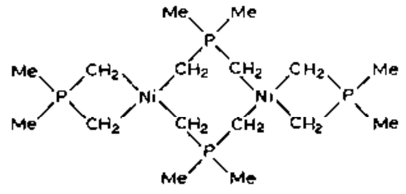
(57)

Nickel, palladium and platinum(II) halides with their phosphine adducts offer the best examples of novel ylide one-center and two-center chelate structures. Almost all of these reactions involve multiple transylidation steps [115]

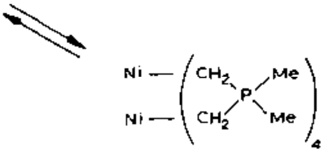




92

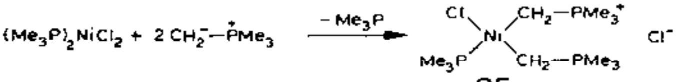


93



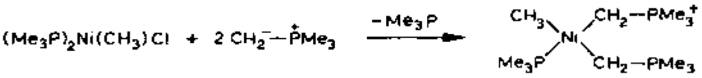
94

Frequently the coordinated phosphine is displaced along with concurrent transylidation [116]



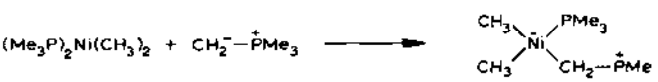
$$(Me_3P)_2NiCl_2 + 2\,CH_2^{-}\!-\!\overset{+}{P}Me_3 \xrightarrow{-Me_3P} (Cl)(Me_3P)Ni(CH_2-PMe_3^{+})(CH_2-PMe_3)\ Cl^{-} \qquad (58)$$

95



$$(Me_3P)_2Ni(CH_3)Cl + 2\,CH_2^{-}\!-\!\overset{+}{P}Me_3 \xrightarrow{-Me_3P} (CH_3)(Me_3P)Ni(CH_2-PMe_3^{+})(CH_2-PMe_3)\ Cl^{-} \qquad (59)$$

96

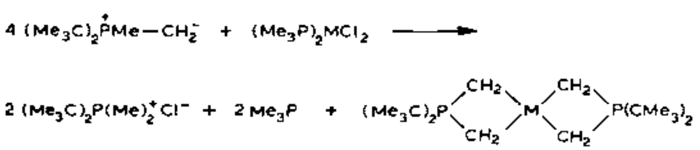


$$(Me_3P)_2Ni(CH_3)_2 + CH_2^{-}\!-\!\overset{+}{P}Me_3 \longrightarrow (CH_3)_2\overset{-}{Ni}(PMe_3)(CH_2-\overset{+}{P}Me) \qquad (60)$$

97

Some interesting aspects of ylide coordination arise when the phosphorus atom has sterically demanding groups. The principal ylide capable of illustrating these steric effects is $(CH_3)_n[(CH_3)_3C]_{3-n}\overset{+}{P}-\overline{C}H_2$ where $n = 0, 1, 2$ [117].

Whereas the less bulky ylide $Me_3\overset{+}{P}-\overline{C}H_2$ forms a complex variety of isomeric complexes (see above), this bis-t-butyl ylide $n = 1$ gives a single product, by transylidation



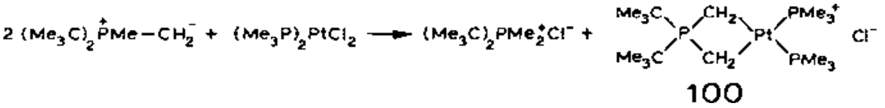
$$4\,(Me_3C)_2\overset{+}{P}Me-CH_2^{-} + (Me_3P)_2MCl_2 \longrightarrow 2\,(Me_3C)_2P(Me)_2^{+}Cl^{-} + 2\,Me_3P + (Me_3C)_2P(CH_2)_2M(CH_2)_2P(CMe_3)_2 \qquad (61)$$

98

M = Ni, Pd

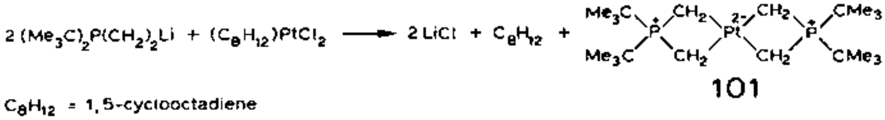
99

With platinum, however, the salt half-complex is obtained [118]



100 (62)

unless the lithiated ylide is treated with bis(1,5-cyclooctadiene) platinum(II) chloride [118,119]

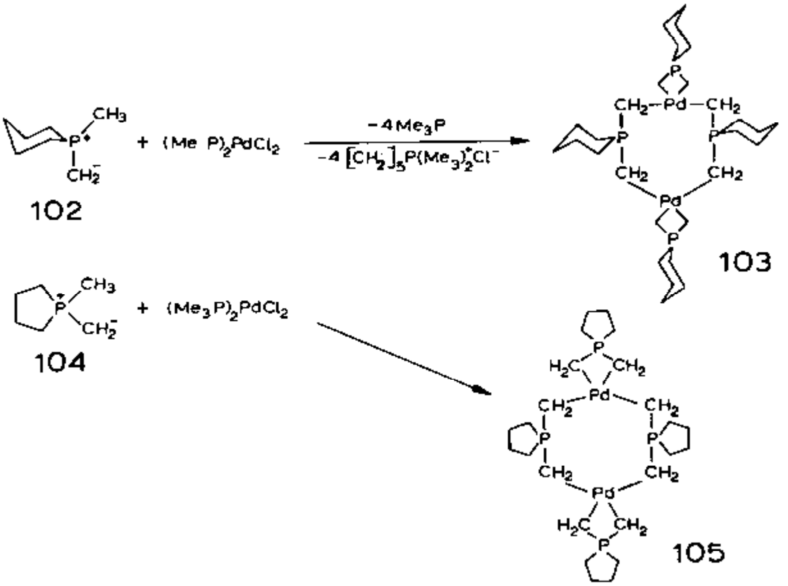


101 (63)

C_8H_{12} = 1,5-cyclooctadiene

Olefins are often much easier to displace from metal atoms and there is no re-association with the metal as there often is with phosphine complexes.

Some additional examples of steric control of transylidation can be observed when the phosphorus atom is part of a heterocyclic ring system. Here the interaction of $[CH_2]_4\overset{+}{P}(Me)—\overset{-}{C}H_2$ or $[CH_2]_5\overset{+}{P}(CH_3)—\overset{-}{C}H_2$ gives multiple chelates with palladium(II) chloride but monomeric [117] complexes with nickel



(64)

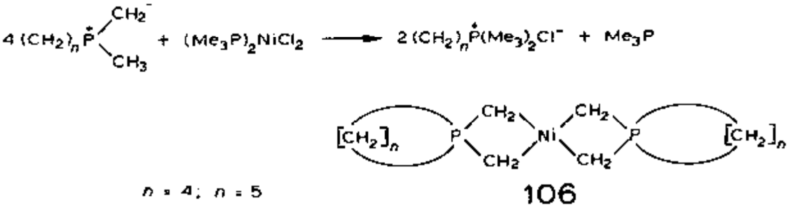
102

103

104

(65)

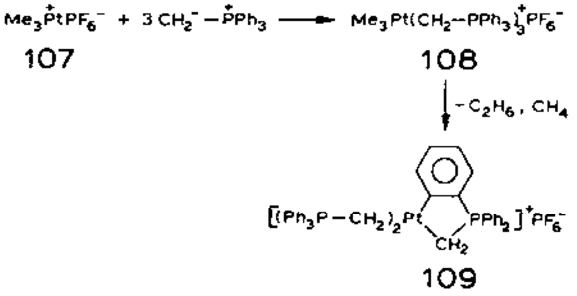
105



(66)

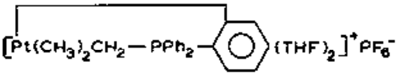
106

Transylidation does not seem to occur when $Me_3Pt^+PF_6^-$ is treated with three equivalents of $\bar{C}H_2{-}\overset{+}{P}Ph_3$. Ethane and methane are the gases evolved with formation of a cyclometalated complex



(67)

Treatment with $Ph_3\overset{+}{P}{-}\bar{C}D_2$ and mass spectral analysis of the evolved gases shows no deuterium incorporation. Treatment of $Me_3Pt^+PF_6^-$ with one equivalent of $\bar{C}H_2{-}\overset{+}{P}Ph_3$ gives only methane as the evolved gas and



Although the presence of methane can be explained by *o*-metalation of the arylphosphine system, the processes of ethane formation are less clear. This is especially true because the steric influence of $Ph_3\overset{+}{P}{-}\bar{C}H_2$ has not been assessed [119].

At this point some mention must be made about the thermal stability of ylide complexes. Most of the complexes previously cited are very stable thermally. For example, $Me_3\overset{+}{P}CH_2\overset{-}{Tl}Me_3$ decomposes above 100°C whereas $TlMe_4^-$ is very unstable thermally. In another example $Me\overset{-}{Au}CH_2\overset{+}{P}Me_3$ and $Me_3\overset{-}{Au}CH_2\overset{+}{P}Me_3$ are very stable thermally, but $Li[Me_2Au]$ and $Li[Me_4Au]$ are very unstable thermally.

Since one of the most important pathways for σ-carbon—metal bond decomposition is β-hydride elimination [15], ylides are an ideal ligand for carbon—metal bond formation because the onium group is in the β-position to prevent β-hydride elimination. The high thermal stability of $(Me_3\overset{+}{P}CH_2)_2\overset{-}{Pt}Me_3$ compared to $Li_2[PtMe_4]$ and $Li_2[PtMe_6]$ is probably related to the presence of the onium group instead of the highly charged metal cation. The onium group prevents β-elimination from the ylide ligand which in turn would generate coordination sites on the metal for ligand decomposition. In all the peralkylate compounds the charged metal cation can assist the removal of alkyl ligands electrostatically. This can promote decomposition because coordination sites on the metal are open for further ligand reactions.

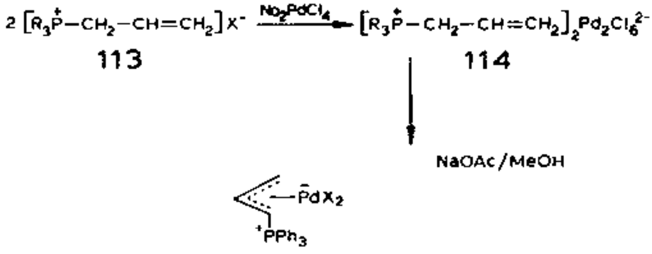
The ylide ligand, on the other hand, is such a good electron donor [84] that it effectively reduces the charge on the metal atom and the onium group is so far removed from the other ligands on the metal that no effective generation of free coordination sites on the metal surface is possible.

In reality the ease of olefin and/or phosphine displacement from transition metal halides makes many ylide complexes available for synthesis. For example, the oligomeric tetrakis(methoxycarbonyl)palladiacyclopentadiene readily reacts with triphenylphosphonium cyclopentadienylide [120]

110 111 112

(68)

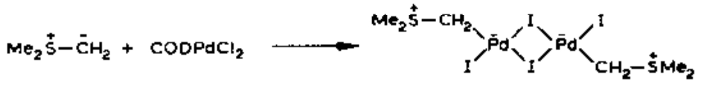
Bis(alkylphosphonium) ylides can be obtained by the following series of reactions [121]



113 114 115

(69)

Sulfur ylides of marginal thermal stability can be treated with complexes to form stable ylide derivatives

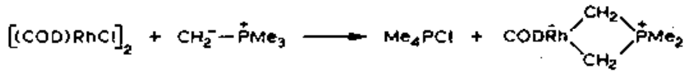


116 117

(70)

and a wide variety of complexes can be generated with keto stabilized ylides [122].

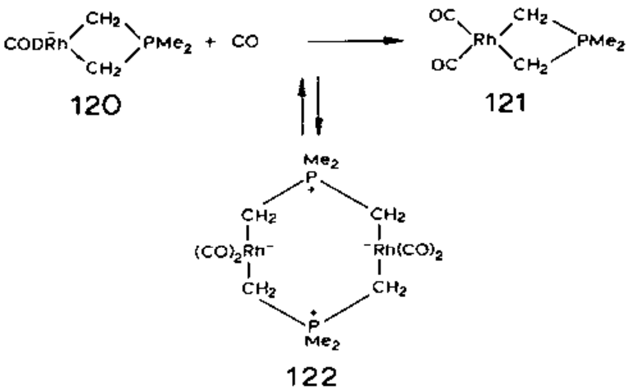
The generalities of the neutral ligand displacement by ylides to give new complexes with carbon—metal bonds can be easily extended to other transition metal systems. Grey and Anderson [123] have shown that the neutral olefin complex need not be displaced by basic ylides with a minimal steric requirement



118 119

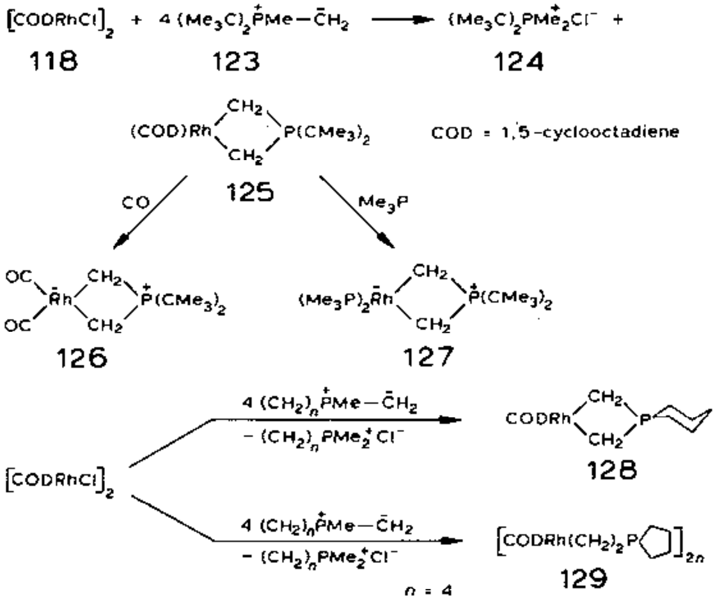
(71)

However, treatment of the cyclooctadiene complex with CO gives a mixture of materials [123].



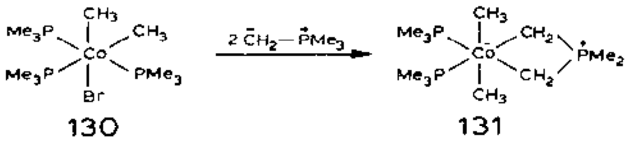
(72)

Sterically demanding ylides also give similar complexes, as shown in Scheme 3. However, there is no oligomerization of the ylide ring system except for the phospholane homologue [124].



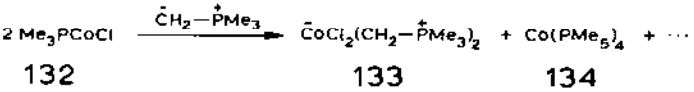
Scheme 3

While these examples show the potential for making low valent ylide complexes of the cobalt group by substitution of neutral ligands, high valent complexes of cobalt are particularly stable and can be prepared by transylidation methods [125]



(73)

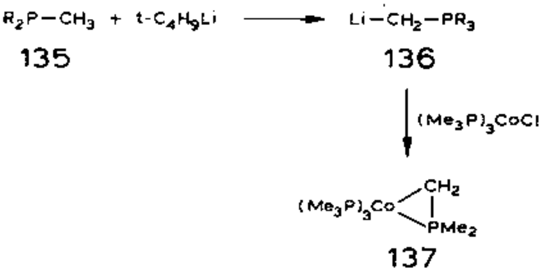
Interestingly enough methyltetrakis(trimethylphosphine)cobalt(I), $CH_3Co(PMe_3)_4$, gives no substitution of Me_3P with $\bar{C}H_2—\overset{+}{P}Me_3$, $CoCl(PMe_3)_3$ gives the following products



$$2\ Me_3PCoCl \xrightarrow{\bar{C}H_2-\overset{+}{P}Me_3} \bar{C}oCl_2(CH_2-\overset{+}{P}Me_3)_2 + Co(PMe_3)_4 + \cdots \quad (74)$$

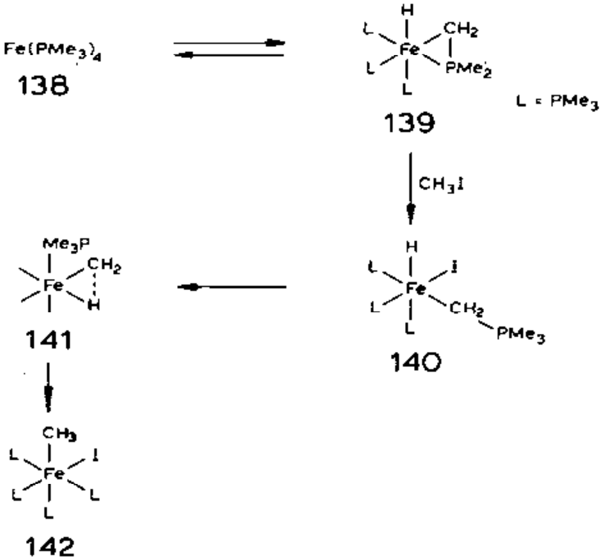
(74)

The dichloride complex can also be synthesized from anhydrous $CoCl_2$ and $\bar{C}H_2—\overset{+}{P}Me_3$. Since Me_3P can be metalated with alkyllithium compounds, some new approaches to ylide complexes exist [126]



(75)

In a series of papers Karsch [126] has shown that the synthesis of $Fe(PMe_3)_4$ gives an equilibrium mixture which can react via ylide type products. In the following example, alkylidene transfer is possible but the iron—alkylidene moiety is too unstable and picks up a hydrogen atom to form a methyl group (cf. Sharp and Schrock [143]).



(76)

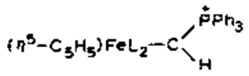
In other instances iron ylide adducts can be prepared as shown in the equation

$$C_5H_5L_2(THF)^+PF_6^- + \bar{C}H_2-\overset{+}{P}Ph_3 \rightarrow \left[C_5H_5L_2CH_2-\overset{+}{P}Ph_3\right]PF_6^- \qquad (77)$$

143 **144**

There is no displacement of ligands except the weakly coordinated tetrahydrofuran (THF) molecules. Two aspects are significant about this reaction [127]:
(a) the THF adduct is critical to the success of the reaction because the ylide will not react directly with $(h^5\text{-}C_5H_5)FeL_2I$; (b) there is no evidence for transylidation of the ylide adducts.

The most probable reason for non reaction in part (a) is the mode of ylide synthesis via $[CH_3PPh_3]Br$ and n-butyllithium. This gives the adduct $Ph_3\overset{+}{P}-\bar{C}H_2 \cdot LiBr$ which reacts differently from pure $\bar{C}H_2-\overset{+}{P}Ph_3$. In contrast, Knoll [128] observed that $\eta^5\text{-}C_5H_5Fe(CO)_2I$ reacts readily with lithium halide free $\bar{C}H_2-\overset{+}{P}Ph_3$ to give non-transylidated adducts which can be converted to BF_4^- or PF_6^- salts. Transylidation of ylide adducts with aryl ligands on phosphorus is rare. There seems to be no basic reason why complexes such as

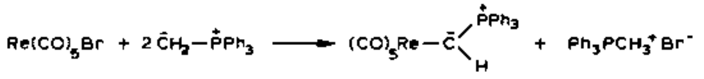


$(\eta^5\text{-}C_5H_5)FeL_2-C\genfrac{}{}{0pt}{}{\diagup\,\overset{+}{P}Ph_3}{\diagdown\,H}$

145

could not be isolated provided proper conditions and choice of L are used.

When ylides are used to synthesize organometallic complexes with carbon—metal bonds there must be some concern about interactions with the coordinated ligands on the transition metal atom. This is particularly true when transition metal complexes to the left of the cobalt group are being used. If particular care is exercised, the interaction of $Re(CO)_5Br$ with $\bar{C}H_2-\overset{+}{P}Ph_3$ gives a transylidated product and no CO addition (cf. ref. 101)



$$Re(CO)_5Br + 2\,\bar{C}H_2-\overset{+}{P}Ph_3 \longrightarrow (CO)_5Re-\bar{C}\genfrac{}{}{0pt}{}{\diagup\,\overset{+}{P}Ph_3}{\diagdown\,H} + Ph_3PCH_3^+Br^- \qquad (78)$$

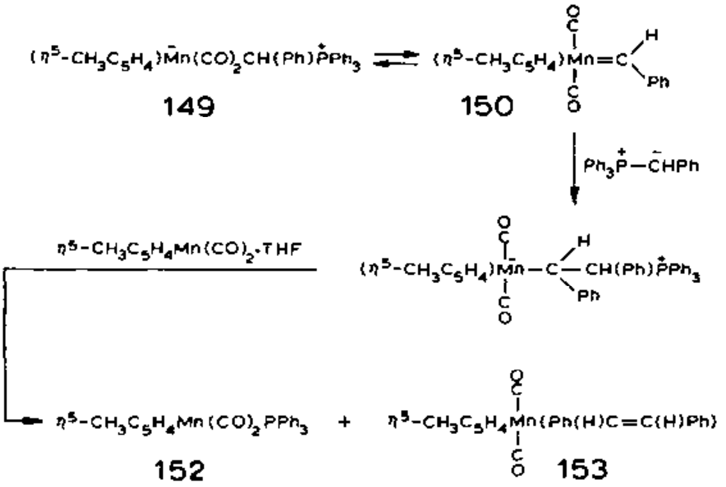
146 147

Furthermore, treatment of $(\eta^5\text{-}C_5H_5)Mn(CO)_2THF$ with $\bar{C}H_2-\overset{+}{P}Me_3$ gives displacement of THF and formation of the ylide adduct [129]

$$\left(\eta^5\text{-}C_5H_5\right)-Mn^-(CO)_2CH_2-\overset{+}{P}Me_3$$

148

More recent work by Knoll [128] shows that alkylidene transfer can occur with (η^5-$CH_3C_5H_4$)Mn(CO)$_2$ · THF and certain ylides. Thus, the isolable complex, (η^5-$CH_3C_5H_4$)$\bar{M}$n(CO)$_2$CH(Ph)$\overset{+}{P}$Ph$_3$ loses triphenylphosphine to give a nonisolable alkylidene intermediate which eventually forms a



(79)

manganese stilbene compound. The triphenylphosphine lability of (η^5-$CH_3C_5H_4$)Mn$^-$(CO)$_2$CH(Ph)$\overset{+}{P}$Ph$_3$ can be demonstrated by treating it with PMe$_3$. Here the triphenylphosphine group is readily substituted by trimethylphosphine,

$$\begin{array}{l}\left(\eta^5\text{-}CH_3C_5H_4\right)Mn^-(CO)_2CH(Ph)PPh_3 + PMe_3 \\ \qquad\qquad\quad \mathbf{154} \\ \rightarrow \left(\eta^5\text{-}CH_3C_5H_4\right)Mn^-(CO)_2CH(Ph)\overset{+}{P}Me_3 \\ \qquad\qquad\qquad\quad \mathbf{155}\end{array} \tag{80}$$

The lability of the C(ylide)—P bond is more likely affected by greater electron density on the incipient carbene carbon atom i.e. (η^5-$CH_3C_5H_4$)Mn$^+$(CO)$_2$—$\bar{C}$H—Ph rather than (η^5-$CH_3C_5H_4$)Mn$^-$(CO)$_2$—$\overset{+}{C}$H—Ph. Greater electron density on the ylide carbon would promote loss of nucleophilic PPh$_3$. A similar reason can be proposed for the non-lability of C(ylide)—P bonds in other metal carbonyl adducts i.e. (CO)$_5$M$^-$—CH$_2$—$\overset{+}{P}$Ph$_3$ (M = Cr, Mo, W). Here the predominant resonance form of the incipient carbene is (CO)$_5$M$^-$—$\overset{+}{C}$H$_2$. The carbonyl groups can remove excess electron density on the metal atom by back-bond formation. Therefore, the nucleophilic phosphine will remain coordinated to the ylide carbon atom.

By far the most studied examples of transition metal ylide complexes are those with chromium, molybdenum and tungsten. The facile displacement of cycloheptatriene from cycloheptatrienemolybdenum tricarbonyl gives a stable ylide complex [130]

$$C_7H_8Mo(CO)_3 + 3\,CH_3\overline{C}H-\overset{+}{P}Ph_3 \rightarrow (Ph_3\overset{+}{P}-CHCH_3)_3\overline{Mo}(CO)_3 + C_7H_8$$

156 **157**

C_7H_8 = cycloheptatriene (81)

Under certain conditions with specific ylides, displacement of carbon monoxide can be observed with multisubstituted metal carbonyls [131]

$$\overline{C}HR-\overset{+}{P}Ph_3 + M(CO)_6 \rightarrow M(CO)_5\overline{C}HR-\overset{+}{P}Ph_3 + CO \qquad (82)$$

158 **159** **160**

M = Cr, Mo, W
R = C_6H_5, CH=H_2,
CH=$CHCH_3$, CH=CHPh

$$\overline{C}HPh-\overset{+}{P}Ph_3 + M(CO)_6 \rightarrow M(CO)_4(\overline{C}HPh-\overset{+}{P}Ph_3)_2 + 2\,CO \qquad (83)$$

161 **159** **162**

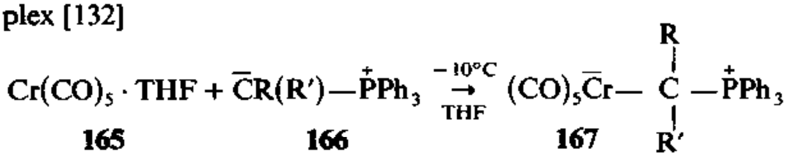
$$CH_2{=}CR-\overline{C}H-\overset{+}{P}Ph_3 + M(CO)_6$$

163 **159**

$$\rightarrow M(CO)_4(CH_2{=}CR-\overline{C}H-\overset{+}{P}Ph_3)M(CO)_4 \qquad (84)$$

164

The easily displaced THF molecule in $Cr(CO)_5 \cdot THF$ gives the ylide complex [132]



$$Cr(CO)_5 \cdot THF + \overline{C}R(R')-\overset{+}{P}Ph_3 \xrightarrow[THF]{-10°C} (CO)_5\overline{Cr}-\underset{R'}{\overset{R}{C}}-\overset{+}{P}Ph_3 \qquad (85)$$

165 **166** **167**

R, R' = H
R = H, R' = C_6H_5
R, R' = CH_3

A variation of this theme has been reported by Knoll in which halogenated metal carbonyl compounds give substitution products [133]

$$[Br\overline{Cr}(CO)_5]NEt_4 + \overline{C}H_2-\overset{+}{P}Ph_{3-x}(CH_3)_x \rightarrow NEt_4Br$$

168

$$+ (CO)_5Cr^- -CH_2-\overset{+}{P}Ph_{3-x}(CH_3)_x \qquad x = 0, 1, 2, 3 \qquad (86)$$

169

$$\underset{\textbf{168}}{[\mathrm{BrCr(CO)_5}][\mathrm{N(C_2H_5)_4}]} + \underset{\textbf{170}}{\mathrm{C_6H_5\bar{C}H{-}\overset{+}{P}(C_6H_5)_{3-x}(CH_3)_x}}$$

$$\rightarrow [\mathrm{N(C_2H_5)_4}]\mathrm{Br} + \underset{\textbf{171}}{\mathrm{(CO)_5\bar{C}r{-}CH(C_6H_5){-}\overset{+}{P}(C_6H_5)_{3-x}(CH_3)_x}}$$

$$+ \underset{\textbf{172}}{\mathrm{(CO)_5Cr^-{-}CH_2{-}\overset{+}{P}CH_2C_6H_5(C_6H_5)_{2-y}(CH_3)_y}} \qquad y = 1, 2 \quad (87)$$

The ylide is strongly bound to the metal complex since further substitution of CO is possible

$$\underset{\textbf{173}}{\mathrm{(CO)_5\bar{C}r{-}CH_2{-}\overset{+}{P}(C_6H_5)_{2-x}(CH_3)_{1+x}}} + \underset{\textbf{174}}{\mathrm{P(C_6H_5)_{2-y}(CH_3)_{1+y}}}$$

$$\rightarrow \mathrm{CO} + \underset{\textbf{175}}{cis\mathrm{(CO)_4Cr[P(C_6H_5)_{2-y}(CH_3)_{1+y}] - CH_2P(C_6H_5)_{2-x}(CH_3)_{1+x}}} \quad (88)$$

$x = 2, 1, 0 \qquad y = 0, 1, 2$

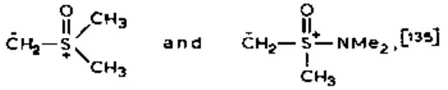
In some cases where an ylide function is adjacent to a phosphine, the phosphine displaces the THF [134]

$$\mathrm{Cr(CO)_5THF} + \underset{\textbf{176}}{\mathrm{Ph_3\overset{+}{P}{-}\bar{C}R{-}PPh_2}} \rightarrow \underset{\textbf{177}}{\mathrm{Cr(CO)_5P(Ph_2){-}\bar{C}R{-}\overset{+}{P}Ph_3}} \quad (89)$$

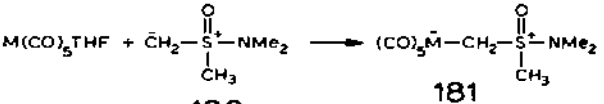
Very few examples of this are known and the generalities are not certain. When methylenetriphenylphosphorane is treated with $\mathrm{Cr(CO)_5PPh_3}$, the triphenylphosphine group is displaced [101]

$$\underset{\textbf{178}}{\mathrm{Cr(CO)_5PPh_3}} + \mathrm{\bar{C}H_2{-}PPh_3} \rightarrow \underset{\textbf{179}}{\mathrm{\bar{C}r(CO)_5CH_2{-}\overset{+}{P}Ph_3}} + \mathrm{PPh_3} \quad (90)$$

The displacement of such weakly coordinated ligands can be also extended by using other ylides like



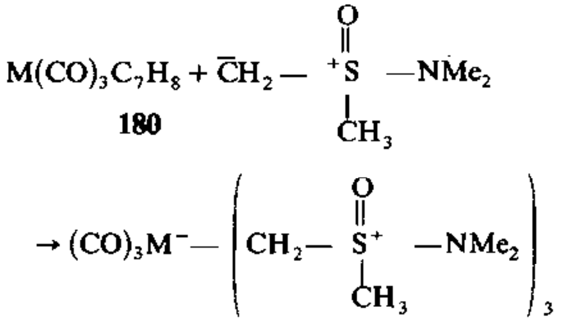
$\mathrm{\bar{C}H_2{-}\overset{+}{S}(=O)(CH_3)_2}$ and $\mathrm{\bar{C}H_2{-}\overset{+}{S}(=O)(CH_3){-}NMe_2}$, [135]



$$\mathrm{M(CO)_5THF} + \mathrm{\bar{C}H_2{-}\overset{+}{S}(=O)(CH_3){-}NMe_2} \longrightarrow \mathrm{(CO)_5\bar{M}{-}CH_2{-}\overset{+}{S}(=O)(CH_3){-}NMe_2} \quad (91)$$

180 181

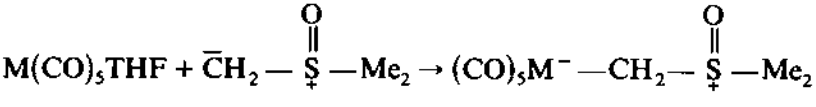
M = Cr, Mo, W



$$M(CO)_3C_7H_8 + \bar{C}H_2-\underset{\underset{CH_3}{|}}{\overset{\overset{O}{\|}}{{}^{+}S}}-NMe_2 \rightarrow (CO)_3M^{-}-\left(CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{O}{\|}}{S^{+}}}-NMe_2\right)_3 \qquad (92)$$

180 **182**

C_7H_8 = cycloheptatriene



$$M(CO)_5THF + \bar{C}H_2-\underset{+}{\overset{\overset{O}{\|}}{S}}-Me_2 \rightarrow (CO)_5M^{-}-CH_2-\underset{+}{\overset{\overset{O}{\|}}{S}}-Me_2 \qquad (93)$$

180 **183**

M = Cr, Mo, W

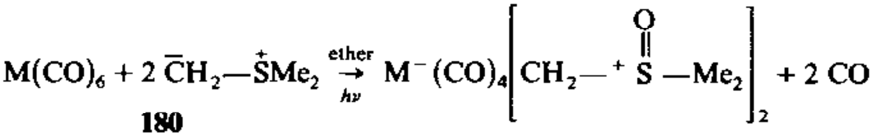
In some of these complexes, however, the sulfoxonium ylide can be displaced by a phosphine as described in the following set of reactions [136]

$$(CO)_5C\bar{r}CH_2-\overset{+}{S}(O)Me_2 + PR_3 \rightleftarrows (CO)_5CrPR_3 + \bar{C}H_2-\overset{+}{S}(O)Me_2 \qquad (94)$$

$$\bar{C}H_2-\overset{+}{S}(O)Me_2 + PR_3 \rightleftarrows \bar{C}H_2-\overset{+}{P}R_3 + Me_2S{=}O \qquad (95)$$

$$(CO)_5CrPR_3 + \bar{C}H_2-\overset{+}{P}R_3 \rightarrow (CO)_5\bar{C}r-CH_2-\overset{+}{P}R_3 + PR_3 \qquad (96)$$

Displacement of CO is the only reaction observed when $\bar{C}H_2-\overset{\overset{O}{\|}}{S}(Me)_2$ is treated with Cr, Mo, W carbonyls in the presence of UV light [137]



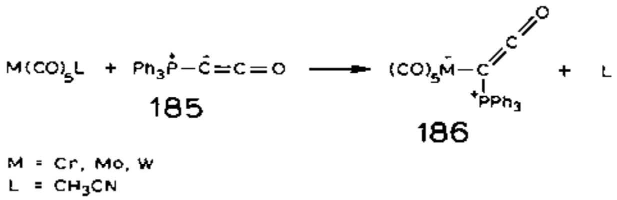
$$M(CO)_6 + 2\,\bar{C}H_2-\overset{+}{S}Me_2 \underset{h\nu}{\overset{\text{ether}}{\rightarrow}} M^{-}(CO)_4\left[CH_2-{}^{+}\overset{\overset{O}{\|}}{S}-Me_2\right]_2 + 2\,CO \qquad (97)$$

180 **184**

M = Cr, Mo, W

Apparently the sulfoxonium ylide is not sufficiently basic to interact with the coordinated carbonyl, or if it does the adduct is unstable and CO is eliminated (cf. data above).

There are some additional examples of neutral ligand displacement in the Group VI transition metal series. One such case involves treatment of the cumulated ylide, $Ph_3\underset{+}{P}-\bar{C}{=}C{=}O$ with metal carbonyls [138].



185 186 (98)

Here the ylide displaces a weakly coordinated ligand to give the C-bonded ylide complex. In some instances this complex can lose triphenylphosphine and the ketene moiety in the presence of suitable trapping agents. Thus, cumulated organic compounds can be prepared.

Knoll [128] has also shown that $(\eta^6\text{-}C_6H_6)Cr(CO)_2 \cdot THF$ readily forms an ylide complex by displacing the weakly coordinated THF

$$\eta^6\text{-}C_6H_6Cr(CO)_2THF + Ph_{3-x}(CH_3)_x\overset{+}{P}-\overline{C}HR$$

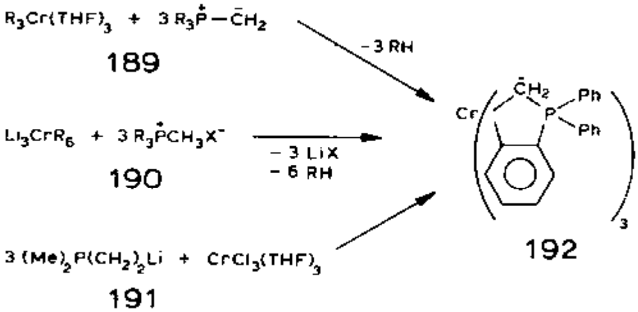
187

$$\rightarrow \eta^6\text{-}C_6H_6\overset{+}{C}r(CO)_2CHR\overline{P}(Ph)_{3-x}(CH_3)_x \qquad (99)$$

188

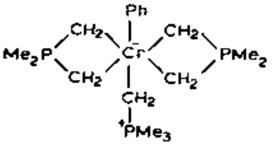
$R = H, x = 0, 1, 2, 3$
$R = Ph, x = 1, 2, 3$

Perhaps some of the most interesting chemistry in this group comes from the treatment of $R_3Cr(THF)_3$ and Li_3CrR_6 with phosphorus ylides. These reactions can be described in the equations below [139]



189 190 191 192 (100)

The dissociation of phenyllithium from Li_3CrPh_6 allows one to isolate an intermediate product [139] from the interaction of Li_3CrPh_6 and $[(CH_3)_4P]^+ Cl^-$.

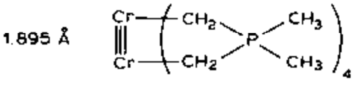


193

A similar molybdenum product can be obtained in the same manner [139].

$$\underset{\mathbf{194}}{Li_4Mo_2(CH_3)_8} + 4\ Me_4PCl \rightarrow \underset{\mathbf{195}}{Mo_2[(CH_2)_2PMe_2]_4} + 8\ CH_4 + 4\ LiCl \qquad (101)$$

A recent X-ray molecular structure of the chromium complex shows it to have the shortest chromium–chromium bond thus far observed [140]. By comparison $[Cr_2(CH_3)_4]^{4-}$ is 1.980 Å, $[Cr_2(O_2CCH_3)_4](H_2O)_2$ is 2.385 Å, $[Cr_2(allyl)_4]$ is 1.97 Å.



196

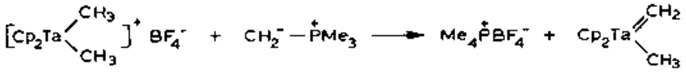
One additional example of ligand displacement is noted here because it illustrates the strong donor characteristic of the ylide system to transition metal atoms.

$$\underset{\mathbf{197}}{W(CH_2{=}CH{-}C(O)CH_3)_3} + 3\ Ph_3\overset{+}{P}{-}\overline{C}H_2$$

$$\rightarrow \underset{\mathbf{198}}{W(\overline{C}H_2{-}PPh_3)_3} + 3\ CH_2{=}CHCOCH_3 \qquad (102)$$

The methylvinylketone ligand is completely displaced by the alkylidene phosphorane in such a way that the displaced ketone does not react with the ylide [141].

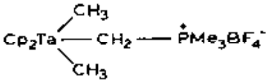
The Group V transition metal complexes offer intriguing examples of ylide reactivity. Initial attempts to form carbon–metal bonds with for example, $[TaCp_2Me_2]^+BF_4^-$ gave instead deprotonation of the primary alkyl α-carbon atom [142]



$$[Cp_2Ta(CH_3)_2]^+ BF_4^- + CH_2^-{-}\overset{+}{P}Me_3 \longrightarrow Me_4\overset{+}{P}BF_4^- + Cp_2Ta({=}CH_2)(CH_3) \qquad (103)$$

199 200

One might imagine that the ylide would form a bond to the tantalum so that transylidation might occur



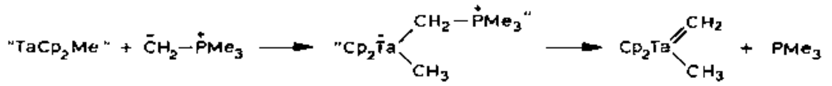
$$Cp_2Ta(CH_3)_2{-}CH_2{-}\overset{+}{P}Me_3BF_4^-$$

201

because the central methylene protons would then be between a cationic phosphorus atom and a high valent metal atom. This should make the methylene groups very acidic. This apparently does not happen because of steric crowding around the metal atom. In any case, the interaction of $TaCp_2(CD_3)_2^+ BF_4^-$ with $Me_3\overset{+}{P}{-}\overline{C}H_2$ to give $TaCp_2(CD_2)(CD_3)$ and the preparation of $TaCp_2(CH_2)(CH_3)$ with the hindered base $LiN(SiMe_3)_2$

suggest that the metal atom is not attacked [142].

The 16 electron complex "$TaCp_2Me$" can be readily generated from the 18 electron complex $TaCp_2(L)Me$ ($L = C_2H_4$ or PMe_3) photochemically and thermally. Treatment of this complex with Me_3P generates the alkylidene complex by transfer of the alkylidene moiety to tantalum [143]


(104)

202 203 204

This is the first concrete example of alkylidene transfer [143]. Other examples are shown below

$$TaCp_2(PMe_2Ph)Me + \bar{C}HPh{-}\overset{+}{P}Me_3$$

205

$$\rightarrow TaCp_2(CHPh)Me + PMe_3 + PMe_2Ph \qquad (105a)$$

206

$$TaCp_2(PMe_3)Me + \bar{C}HMe{-}\bar{P}Et_3 \rightarrow TaCp_2(CHMe) + PMe_3 + PEt_3 \qquad (105b)$$

207 **208** **209**

Interestingly enough these tantalum alkylidene complexes are the only derivatives where the alkylidene carbon atom has enough electron density so that it behaves as a Lewis base. Most of the other examples in the Group VIa series for instance are electrophilic. Indeed, the ready alkylidene transfer from phosphorus to tantalum may depend on the fact that the phosphorus alkylidene species bear a much higher negative charge than the tantalum alkylidene moieties (cf. section C(ii), reaction of ylides with coordinated ligands).

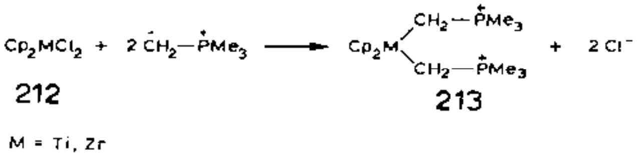
Alkylidene transfer does not occur with some tantalum carbene complexes, but α-hydrogen atom abstraction can readily occur to give carbyne compounds [144]

$$TaCp(CHCMe_3)Cl_2 \xrightarrow[\bar{C}H_2{-}\overset{+}{P}Ph_3]{PMe_3} Cp(Me_3P)_2ClTa \equiv C{-}CMe_3 \qquad (106)$$

210 **211**

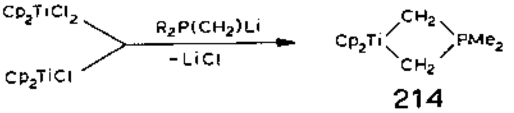
Although some alkyls of the early transition metal series are notably unstable to thermal decomposition, the ylide derivatives of titanium, zirconium, and hafnium are relatively easy to prepare and have good thermal properties [145].

For instance, $TiCp_2Cl_2$ and $ZrCp_2Cl_2$ form complexes



(107)

On the other hand, treatment of either $TiCp_2Cl_2$ or $TiCp_2Cl$ with $R_2P(CH_2)Li$, ($R = Me$ or Ph) gives a chelate complex [146]



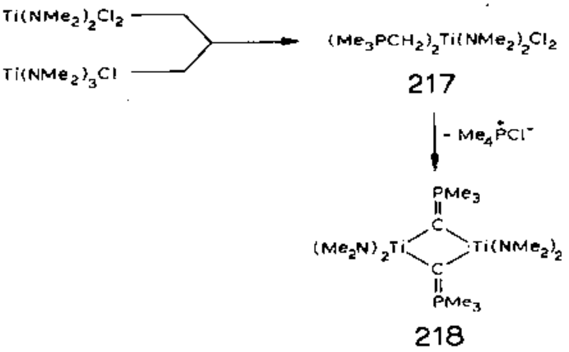
(108)

A nitrogen ylide gives a similar chelate

(109)

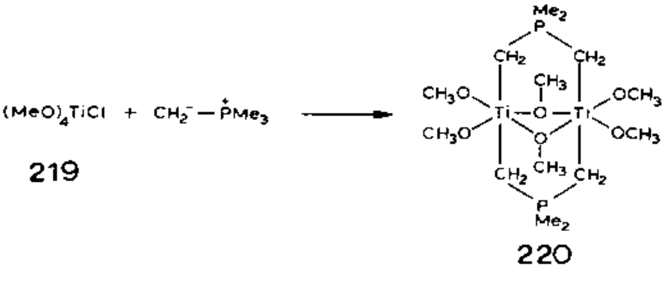
Scandium and vanadium chelate ylides are similarly obtained, $ScCp_2(CH_2)PR_2$ ($R = Ph$, Me) [146,147]; $VCp_2(CH_2)PR_2$ ($R = Ph$, Me).

In contrast to these results, treatment of $CH_2—PMe_3$ with $Ti(NMe_2)_3Cl$, Ti(NM[illegible]l_2 or $Ti(NMe_2)_4$ gives cyclic structures which have a counterpart in the [illegible]try of silicon and tin ylides [148]



(110)

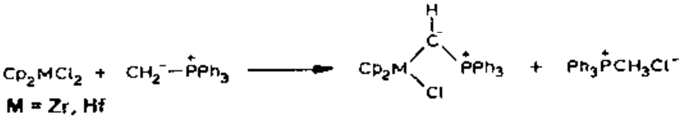
Another multibridged titanium complex is formed with $\bar{C}H_2—\overset{+}{P}Me_3$



(111)

The X-ray molecular structure shows this to have bridging ylide and methoxy ligands instead of metal—metal bonds like the chromium and molybdenum compounds with bridging ylide ligands.

When $ZrCp_2Cl_2$ and $HfCp_2Cl_2$ are treated with excess $\overset{-}{C}H_2—\overset{+}{P}Ph_3$ at room temperature, ready transylidation occurs to give the complex [149]



221

(112)

The X-ray molecular structure of the complex shows an approximately tetrahedral arrangement of ligands about the zirconium atom, with the shortest Zr—C bond length thus far reported. The hydrogen atom H(50) is not significantly out of the Zr—C(50)—P plane which means there is probably some overlap of the 2*pz* orbital on the alkylidene carbon atom with zirconium *d*-orbitals. This could explain the observed hindered rotation about the Zr—C(50) bond.

Reactions of this ylide zirconium complex have been limited to treatment with CO. This readily occurs across the metal—carbon rather than carbon—phosphorus bond

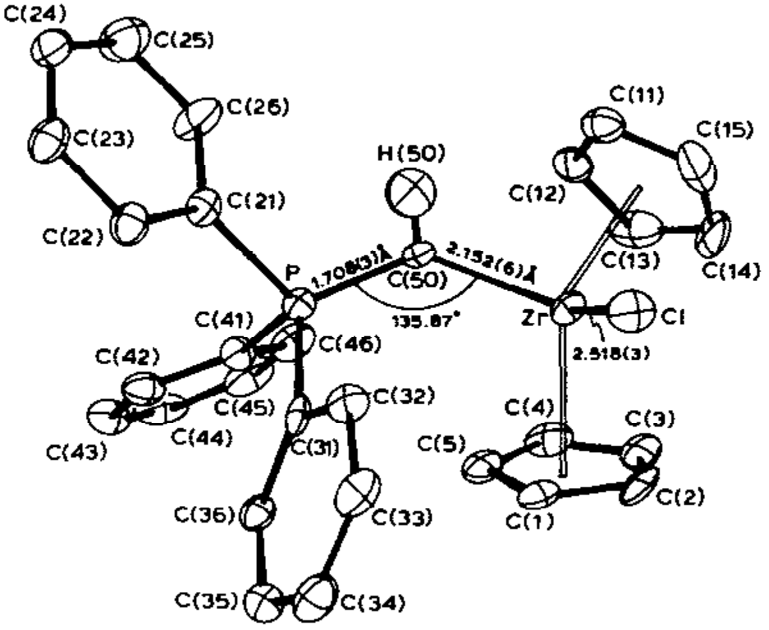
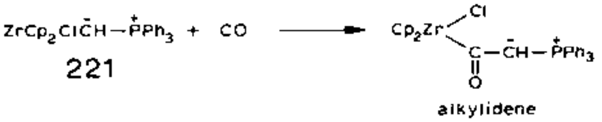


Fig. 4. X-ray molecular structure of ${}^5\eta$-biscyclopentadienylzirconiumalkylidenephosphorane.



221 **222** (113)

The displacement of neutral ligands from zirconium has also been observed [150]

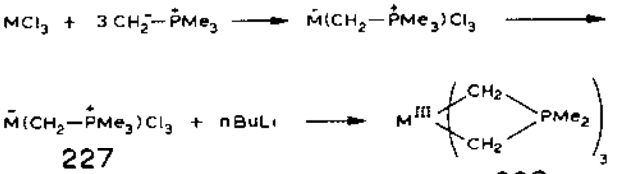
$$\mathrm{ZrCp_2(PMe_3)_2 + \bar{C}H_2{-}\overset{+}{P}Me_3 \rightarrow Cp_2Zr(CH_2)PMe_3 + 2\;PMe_3} \qquad (114)$$

223 **224**

$$\mathrm{ZrCp_2(PPh_2Me)_2 + \bar{C}H_2{-}\overset{+}{P}Ph_3 \rightarrow Cp_2Zr(CH_2)PPh_2Me + PPh_2Me + PPh_3} \qquad (115)$$

225 **226**

Carbon σ-bond lanthanide chemistry has been advanced in recent years with the synthesis of ylide complexes. Schumann has shown that the anhydrous lanthanide chlorides give tris ylide complexes according to the following equation [151]



227 **228** (116)

In addition, treatment of $\mathrm{Cp_3UCl}$ and $\mathrm{Li(CH_2)_2PPh_3}$ gives a series of complexes [152]

$$\mathrm{Cp_3UCl + Li(CH_2)_2PPh_2 \rightarrow Cp_3\bar{U}{-}CH{-}\overset{+}{P}(CH_3)Ph_2} \qquad (117)$$

229 **230** **231** green complex

$$\mathrm{Cp_3UCl + 2\;Li(CH_2)_2PPh_2 \rightarrow red\ complex} \qquad (118)$$

232

The green complex is easily converted to the red complex by treatment

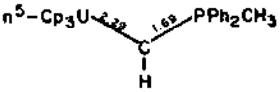
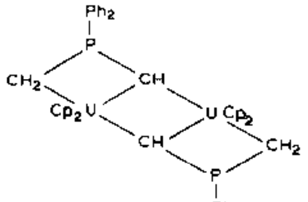


Fig. 5. X-ray molecular structure of ${}^5\eta$-tricyclopentadienyluraniumalkylidenephosphorane.

with $Li(CH_2)_2PPh_2$

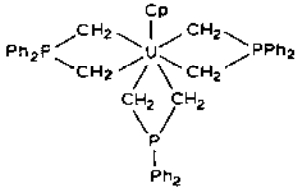
$$\underset{231}{Cp_3\bar{U}\text{-}CH{-}\overset{+}{P}(CH_3)Ph_2} + Li(CH_2)_2PPh_2 \longrightarrow \underset{232\ \text{red complex}}{Cp_2U(CHPPh_2CH_2)_2UCp_2} \qquad (119)$$



232

The green complex like the ylide zirconium complex in Fig. 4 has the shortest uranium—carbon bond length known, 2.29 Å. Like the zirconium complex, **231** forms an acyl complex when treated with carbon monoxide. A third gold colored complex can be formed by treating Cp_3UCl with $Li(CH_2)_2PPh_2$

$$Cp_3UCl + 3\,Li(CH_2)_2PPh_2 \rightarrow \underset{\mathbf{233}}{CpU[CH_2CH_2PPh_2]_3} + LiCl + 2\,LiCp \qquad (120)$$

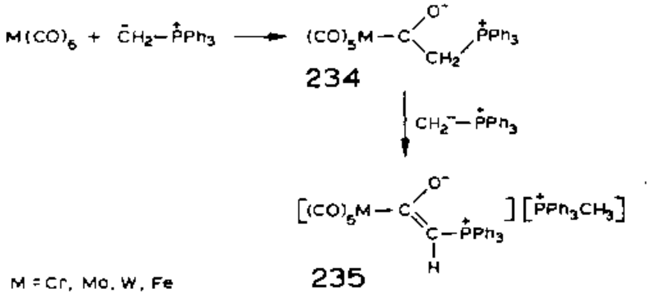


233

Reactions of ylides with transition metal coordinated ligands

Although most ylide transition metal complexes are noted for their thermal stability, the interaction of these compounds and the interaction of ylides with coordinated transition metal ligands offer exciting possibilities.

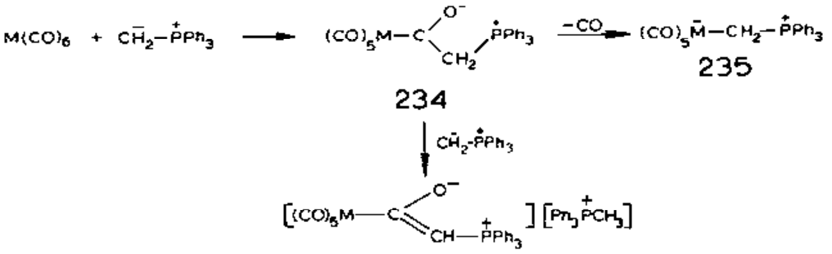
One of the first examples of ylide reactivity with a coordinated ligand is with metal carbonyls. The metal carbonyls of Group VI give a facile addition across the C═O bond, followed by transylidation to give the salt [98,153]



(121)

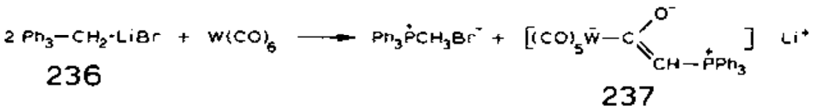
M = Cr, Mo, W, Fe

The addition of ylides to the carbonyl group of transition metal carbonyls can be related to the force constant of the CO ligand. Angelici [85] and Darensbourg and Darensbourg [85] have proposed that CO ligands with force constants near 18 mdyn $Å^{-1}$ or CO stretching frequencies at 2000 cm^{-1} or above will be subject to addition. This seems to be the case for metal carbonyls of chromium, molybdenum, tungsten and iron, whereas other carbonyls in the manganese, cobalt and nickel groups give substitution products. In reality, all of the metal carbonyls may interact to give addition products but kinetic factors will decide whether metal—carbon or carbon—carbon bonds are formed



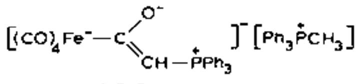
(122)

The LiBr adducts of $\bar{C}H_2—\overset{+}{P}Ph_3$ give precipitates of $Ph_3\overset{+}{P}CH_3Br^-$ and the ylide carbonyl adduct is isolated as the lithium salt. This is probably due to the greater insolubility of $Ph_3\overset{+}{P}CH_3Br^-$ in THF [98]

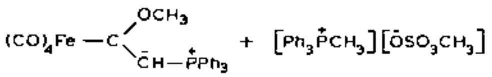


(123)

The phosphonium salts of the metal carbonyl ylide adducts can be easily alkylated to give carbene-adducts [98]



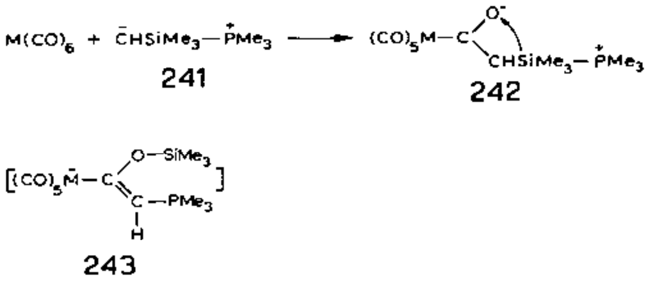
238



239 240

(124)

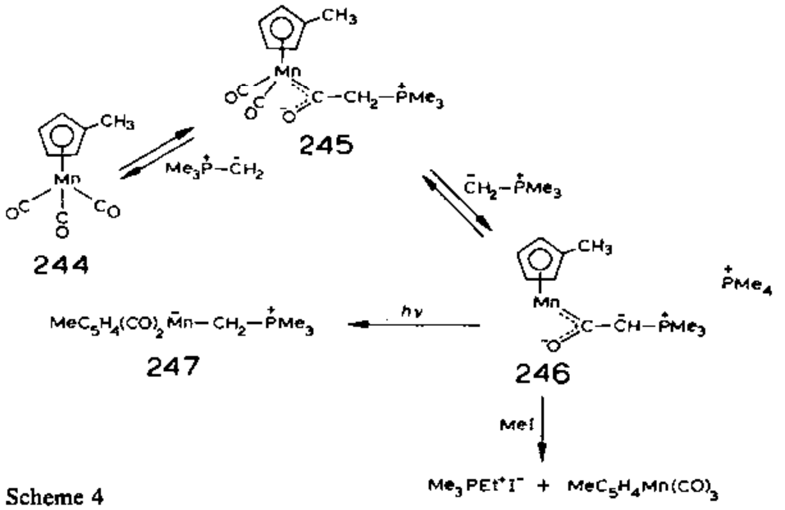
A more recent and intriguing example of intra-molecular alkylation involves the interaction of metal carbonyls with $\bar{C}HSiMe_3—\overset{+}{P}Me_3$ [154]



(125)

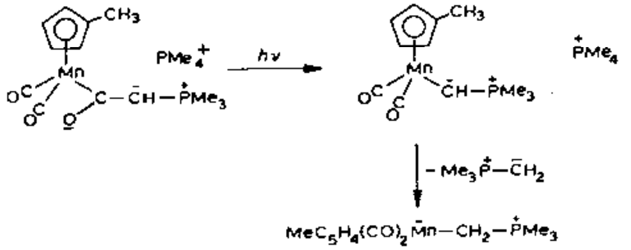
Nickel tetracarbonyl only forms on the complex, $(CO)_3\bar{Ni}$—CHSiMe$_3$—$\overset{+}{P}$Me$_3$ + CO.

Blau and Malisch [155] have recently shown that ylides will add to the carbonyl group of methylcyclopentadienylmanganesetricarbonyl. Interestingly enough, the acyl ylide complex is in equilibrium with the starting material



Scheme 4

Photolysis of the acyl ylide phosphonium salt includes carbon monoxide elimination to presumably give the manganese substituted phosphorane [156]



(126)

which deprotonates the tetramethylphosphonium cation to give $\bar{C}H_2$—$\overset{+}{P}Me_3$

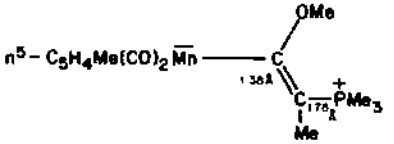


Fig. 6. X-ray molecular structure of $^5\eta$-cyclopentadienylmanganesecarbonylylideacyl complex.

and the ylide coordinated manganese complex. Treatment of the acyl complex with $MeOSO_2F$ is shown in the following equations where both ylide carbon and acyl oxygen atoms are alkylated,

$$\left[C_5H_4Me(CO)_2Mn{-}C(O)\bar{C}H{-}\overset{+}{P}Me_3\right]PMe_4 \xrightarrow[-4\,Me_4PSO_3F]{MeSO_3F}$$

248

$$C_5H_4Me(CO)_2Mn{-}C(OMe)\bar{C}H{-}\overset{+}{P}Me_3 \xrightarrow{MeSO_3F}$$

249

$$\left[C_5H_4Me(CO)_2Mn{-}C(OMe)\bar{C}HMe{-}\overset{+}{P}Me_3\right]SO_3F^- \xrightarrow{C\bar{H}_2{-}\overset{+}{P}Me_3}$$

250

$$\left[C_5H_4Me(CO)_2Mn{-}C(OMe)\bar{C}Me{-}\overset{+}{P}Me_3 + Me_4PSO_3F\right] \qquad (127)$$

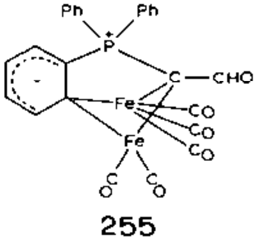
251

An X-ray molecular structure analysis of the alkylated acyl ylide complex shows the predominant resonance form to have substantial carbon–carbon double bond character [157]; presumably this also holds true for the previously described addition adducts of chromium and tungsten [98]

The scission of other groups from substituted ylides shows the versatility of the ylide reagent with metal carbonyl compounds. Such novel structures suggest possible uses of ylide reactivity in organic synthesis [158]

$$(Me_3Sn)_2\bar{C}{-}\overset{+}{P}Ph_3 + Fe_3(CO)_{12} \longrightarrow (Me_3Sn)_2Fe(CO)_4 + Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)] + CO$$

252 253 254 255



255

(128)

Some preliminary attempts have been made to use ylide—metal carbonyl chemistry in organic synthesis. Alper and Partis [159] treated $Fe(CO)_5$ with $p\text{-}XC_6H_4\overline{C}H\text{—}\overset{+}{P}Ph_3$ ($X = H$, CH_3, OCH_3) in THF. The products of the reaction are *cis*- and *trans*-stilbenes, $Ph_3PFe(CO)_4$ and Ph_3PO.

When $X = H$ only *trans*-stilbene is obtained but when $X = CH_3$, OCH_3, the major product is *cis*-stilbene. The nature of this reaction is not yet clear, but it does suggest that a variety of ylides can be useful in the preparation of selected small organic molecules.

Substituted metal carbonyls are also subject to carbonyl attack to give acyl complexes [160]

$$\left[(\eta^5\text{-}C_5H_5)Fe(CO)_3\right]PF_6^- + 2\,\underset{\textbf{256}}{\overline{C}HR\text{—}\overset{+}{P}Ph_3}$$

$$\rightarrow \underset{\textbf{257}}{(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{—}C(O)\text{—}\overline{C}R\text{—}\overset{+}{P}Ph_3} + \left[Ph_3\overset{+}{P}CH_2R\right]PF_6^- \qquad (129)$$

$R = H, CH_3, Ph$

Even with the varied examples of carbonyl addition by ylides, there are other instances where this does not occur as for example [161]

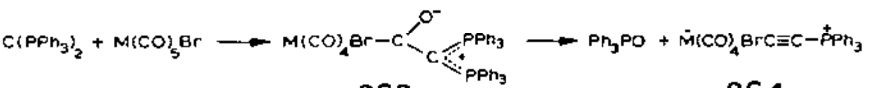
$$\eta^5\text{-}C_5H_5Mo(CO)_3SnMe_3 + 2\,\underset{\textbf{258}}{\overline{C}H_2\text{—}\overset{+}{P}Me_3}$$

$$\rightarrow \underset{\textbf{259}}{\left[\eta^5\text{-}C_5H_5Mo(CO)_3H\right]} + \underset{\textbf{260}}{Me_3\overset{+}{P}\text{—}\overline{C}HSnMe_3} \qquad (130)$$

$$\underset{\textbf{261}}{\eta^5\text{-}C_5H_5M(CO)_3H} + \overline{C}H_2\text{—}\overset{+}{P}R_3 \rightarrow \underset{\textbf{262}}{\left[R_3\overset{+}{P}CH_3\right]\left[\eta^5\text{-}C_5H_5\overline{M}(CO)_3\right]} \qquad (131)$$

In the last example the ylide behaves like a base and removes a hydrogen atom as a proton to give a salt.

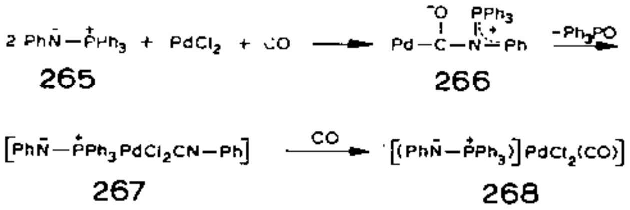
The first example of a Wittig reaction with a coordinated carbonyl group is the product isolated following treatment of $C(PPh_3)_2$ with $M(CO)_5Br$ ($M = Mn$ and Re). Presumably the reaction proceeds according to the following pathway [98,162]



263 264

M = Mn, Re (132)

Another more recent example is shown by the following equation [163]


265 266 267 268 (133)

Here a coordinated isocyanide is formed.

Another recent development has been addition to coordinated nitriles [164]

$$(CO)_5Cr{-}\overset{+}{N} \equiv C{-}R + \overline{C}H_2{-}\overset{+}{P}Ph_3 \rightarrow (CO)_5Cr\ NH{=}CR{-}\overline{C}H{-}\overset{+}{P}Ph_3 \qquad (134)$$

269 **270**

The ylide adds to the nitrile carbon atom which is electrophilic because of the positively charged, coordinated nitrogen atom. Hydrogen transfer occurs to give the imine coordinated ylide.

Other coordinated ligands interact equally well with ylides [165]

$$(CO)_5CrP(C_6H_5)_2Cl + \overline{C}HR{-}\overset{+}{P}Ph_3$$

271

$$\rightarrow (CO)_5CrP(C_6H_5)_2\overline{C}R{-}\overset{+}{P}Ph_3 + Ph_3\overset{+}{P}CH_3Cl^- \qquad (135)$$

272

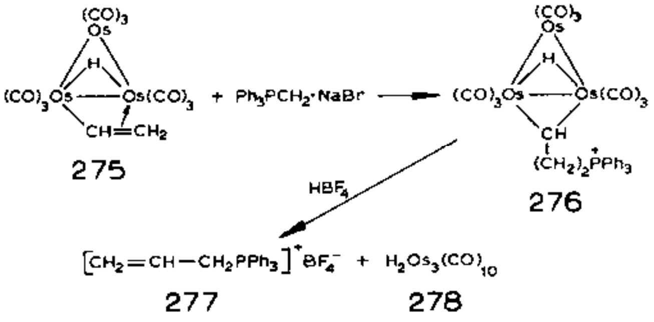
$$(CO)_4FeP(C_6H_5)_2Cl + \overline{C}H_2{-}\overset{+}{P}Ph_3$$

273

$$\rightarrow (CO)_4FeP(C_6H_5)_2\overline{C}H{-}\overset{+}{P}Ph_3 + Ph_3PCH_3^+Cl^- \qquad (136)$$

274

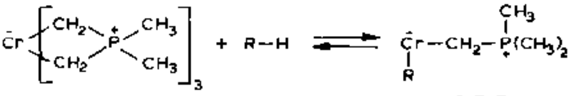
The interaction of ylides with transition metal olefin complexes usually results in the displacement of the olefin by the ylide. This is not the case, however, when $HOs_3(CO)_{10}(\mu\text{-}CH{=}CH_2)$ is treated with $Ph_3PCH_2 \cdot NaBr$ [177]



275 276 277 278

Scheme 5

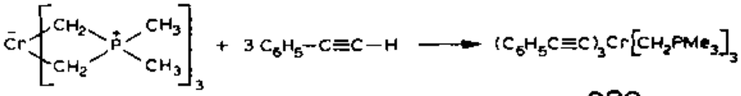
Perhaps one of the most intriguing recent applications of ylide complexes has been the treatment of $Cr[(CH_2)_2P(CH_3)_2]_3$ with acidic hydrocarbons. This can be described in the following way [139]



279 280

(137)

The reaction is very specific with phenylacetylene



281 282

(138)

and suggests that suitable ylide complexes can be important in carbon–hydrogen bond activation.

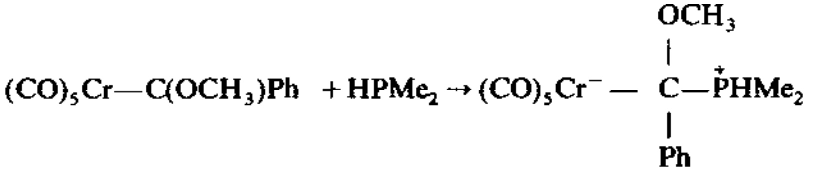
The displacement of a cyclopentadienyl ring in the reaction of nickelocene and methylenetriphenylphosphorane is an additional example of strong carbon–metal bond formation with ylides

$$NiCp_2 + \overset{-}{C}H_2{-}\overset{+}{P}Ph_3 \xrightarrow[THF]{NH_4PF_6} [Ni(CH_2PPh_3)_2Cp]PF_6 \qquad (139)$$

283 **284**

NMR results suggest an increased electron density at the nickel atom of the ylide complexes, compared to phosphine complexes [166].

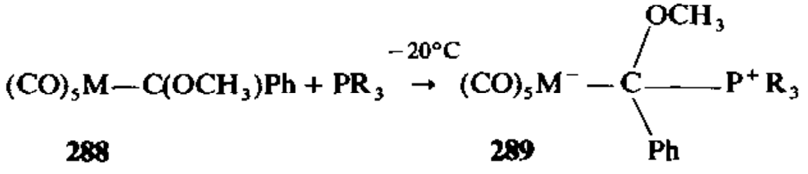
Ordinarily organophosphines will interact with carbene complexes at elevated temperatures to substitute a carbonyl ligand or even a carbene, but secondary phosphines will form ylide complexes instead [167]



$$(CO)_5Cr{-}C(OCH_3)Ph + HPMe_2 \rightarrow (CO)_5Cr^{-}{-}\underset{Ph}{\overset{OCH_3}{C}}{-}\overset{+}{P}HMe_2 \qquad (140)$$

285 **286** **287**

Subsequent experiments showed that the ylide complexes with tertiary phosphines could be prepared at low temperatures and that these would rearrange to carbonyl substituted derivatives at higher temperatures [168]



$$(CO)_5M{-}C(OCH_3)Ph + PR_3 \xrightarrow{-20^\circ C} (CO)_5M^{-}{-}\underset{Ph}{\overset{OCH_3}{C}}{-}P^{+}R_3$$

288 **289**

M = Cr, W

↓60–80°(cont' next page)

$cis(CO)_4Cr—C(OCH_3)PhPR_3$

290

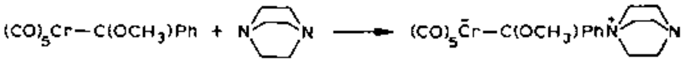
$trans(CO)_4Cr—C(OCH_3)PhPR_3$

291

$trans(CO)_4Cr(PR_3)_2$ (141)

292

Even selected alkylamines will coordinate to the carbene carbon to form nitrogen ylide complexes [169]

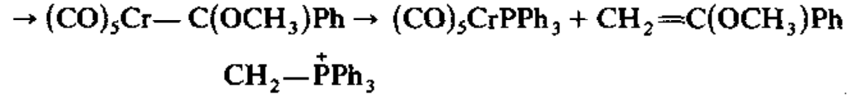


293 294 295 (142)

Ylides such as $\bar{C}H_2—\overset{+}{P}Ph_3$ will form complexes with carbenes; these complexes can be decomposed thermally to give vinyl ethers

$(CO)_5Cr—C(OCH_3)Ph + \bar{C}H_2—\overset{+}{P}Ph_3$

296



$$\rightarrow (CO)_5Cr—\underset{CH_2—\overset{+}{P}Ph_3}{C}(OCH_3)Ph \rightarrow (CO)_5CrPPh_3 + CH_2{=}C(OCH_3)Ph \quad (143)$$

297

Since $(CO)_5CrPPh_3$ can be recycled with CO to give $Cr(CO)_6$ and thence to form more carbene complex, this reaction represents a useful synthesis of vinyl ethers [170].

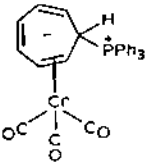
D. NOVEL APPROACHES TO YLIDE COMPLEXES

A recent approach to ylide complexes has been the nucleophilic attack of phosphines on coordinated olefinic or methylenic complexes. For instance, stopped flow measurements of R_3P to the ethylene ligand in $[CpFe(CO)_2\eta^2\text{-}C_2H_4]^+$ show second order kinetics [171]

298 299 (144)

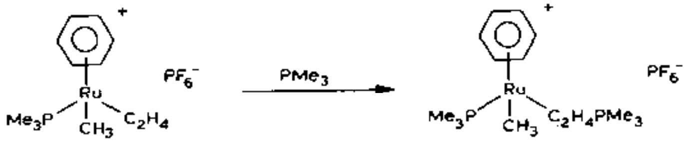
Other examples include the interaction of phosphines with $[C_7H_7Cr(CO)_3$

$]BF_4$. Here there is direct attack on the ring rather than the metal atom to give a phosphonium salt [172,173]



300

Ruthenium and rhodium complexes also can interact with phosphine to generate ylide phosphonium complexes [174]



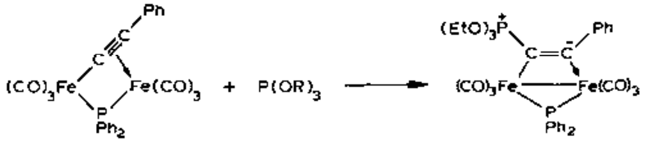
301 302

(145)

$$[CpRh(PMe_3)_2C_2H_4]^+[PF_6]_2 + N \longrightarrow [CpRh(PMe_3)_2C_2H_4N][PF_6]_2 \quad (146)$$

303 304

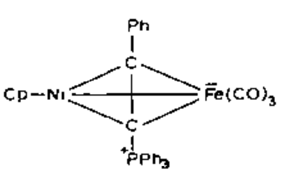
Nucleophilic attack at the carbon atom of complexed acetylides can also give ylide complexes as shown in the following equations [175]



305 306

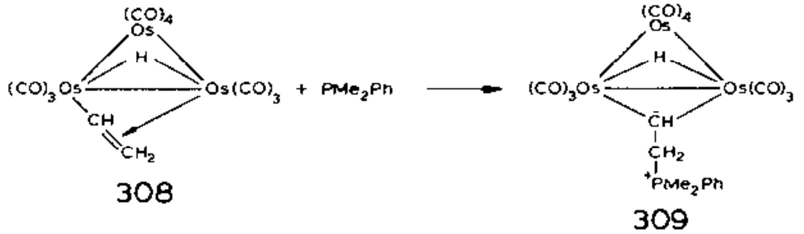
(147)

Direct interaction of the phosphonium salt $[Ph_3\overset{+}{P}—C \equiv C—H]\overset{-}{Br}$ with Cp_2Ni and $Fe_2(CO)_9$ gives the ylide complex as a tetrahedral cluster [176]



307

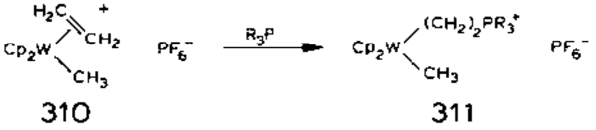
Similar cluster ylide complexes are observed with osmium [177]



308 309 (148)

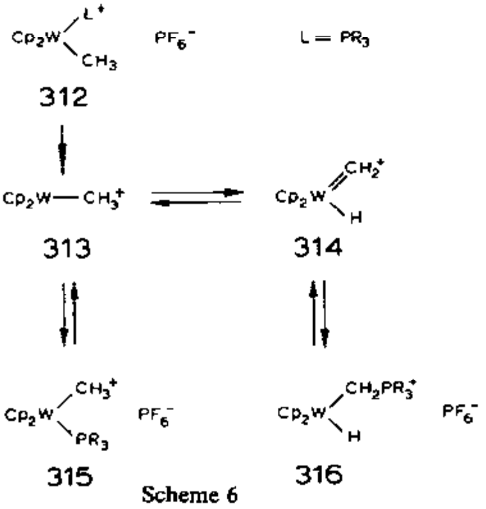
Here, an ylide forms the basis for modification of carbon bonding in a cluster compound; surely ylides can be valuable reagents to introduce carbon atoms in transition metal cluster compounds.

Some of the most novel syntheses of ylide transition metal complexes have been observed with bis(η-cyclopentadienyl)tungsten compounds. The synthesis of $[W(\eta^5\text{-}C_5H_5)_2MeL]PF_6 L = C_2H_4$, Et_2S or Ph_3P compounds and treatment with PMe_2Ph or PMe_3 gives the ylide complex $[W(\eta^5\text{-}C_5H_5)_2H(CH_2PMe_3]^+PF_6^-$. If L is ethylene a longer chain ylide can be formed.



310 311 (149)

Elimination of ethylene can give a 16 electron complex [178] which can give different ylide compounds.



312 313 314 315 316

Scheme 6

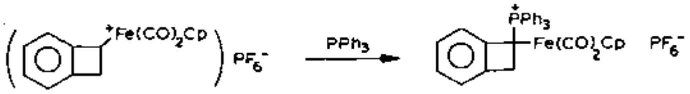
Attempts to prepare ylide complexes by treating Cp_2MCl_2 (M = Mo, W) with $\bar{C}H_2—\overset{+}{P}Ph_3$ gives intractable products often with loss of a cyclopentadienyl ring [179].

A similar lack of identifiable products is observed when $Cp_2W(SMe_2)Br^+PF_6^-$; $Cp_2W(SMe_2)CH_3^+OSO_2CF_3^-$ or $Cp_2WH^+OSO_2CF_3^-$ is treated with $\bar{C}H_2—\overset{+}{P}Ph_3$ [179].

The cationic carbenes of rhenium offer synthetic approaches to onium ylide complexes [180]

$$\begin{tikzcd} \underset{\mathbf{317}}{CpReNOPPh_3CH_2^+PF_6^-} \arrow[r, "Py"] \arrow[d, "PPh_3"] & \underset{\mathbf{318}}{CpReNOPPh_3CH_2—\overset{+}{P}yPF_6^-} \\ \underset{\mathbf{319}}{CpReNOPPh_3CH_2—\overset{+}{P}Ph_3PF_6^-} & \end{tikzcd} \qquad (150)$$

and an iron cationic carbene complex also forms an ylide complex with triphenylphosphine [181]



320 321 (151)

A rather unusual approach to some ylide complexes of cobalt has been reported by Klein et al. [182]

324 (152)

Treatment of $Pt(PPh_3)_4$ with chloroiodomethane gives an ylide complex directly [183]

$$\underset{\mathbf{325}}{Pt(PPh_3)_4} \rightleftarrows \underset{\mathbf{326}}{Pt(PPh_3)_3} + PPh_3$$

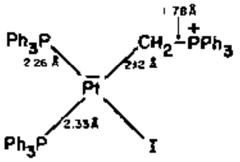


Fig. 7. X-ray molecular structure of iodobis(triphenylphosphine)methylenetriphenylphosphoraneplatinum(II).

$$PPh_3 + CH_2ClI \rightarrow [Ph_3PCH_2Cl]I$$

327 **328**

$$Pt(PPh_3)_3 + [Ph_3PCH_2Cl]I \rightarrow cis[Pt(PPh_3)_2(CH_2PPh_3)Cl]I \qquad (153)$$

329 **330**

This type of reaction simplifies the preparation of ylide complexes because the intermediate alkylidene phosphoranes do not have to be used in the synthesis.

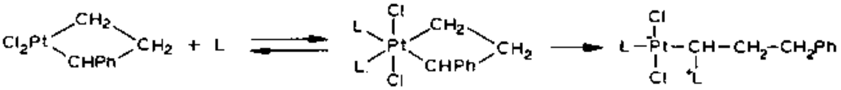
This idea has been extended to include other compounds

$$Pt(PEt_3)_3 + CH_2I_2 \rightarrow trans\text{-}[Pt(CH_2PEt_3)I(PEt_3)_2] \qquad (154)$$

331 **332** **333**

Apparently an intermediate halogenoalkylmetal is formed which is then converted to the ylide complex [183].

Another facet of ylide chemistry must include the compounds formed by treating platinacyclobutanes with Lewis bases [184]

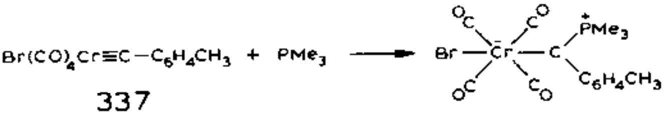


334 335 336 (155)

Here, loss of L is promoted by α-elimination from the platinacycle.

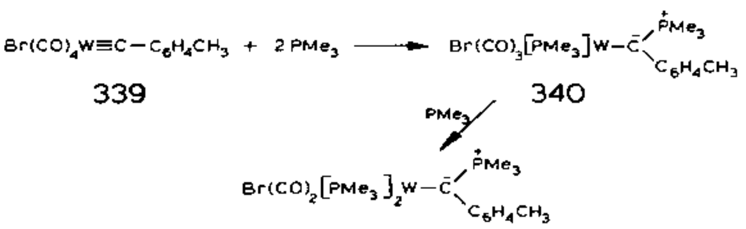
E. SYNTHESIS OF YLIDE COMPLEXES VIA TRANSITION METAL CARBYNES

Whereas the treatment of carbenes with organophosphines will give ylide complexes that have tetra-coordinate carbon, carbyne complexes give tricoordinated ylide compounds [185]



337 338 (156)

but the corresponding tungsten complex gives carbonyl substituted products.

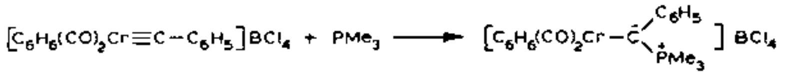


339 340 341 (157)

A wide variety of Lewis base ligands can give various substitution products; for example, triphenylphosphite with a chromium carbyne gives carbon monoxide substitution instead of ylide formation [186]

$$\underset{\mathbf{342}}{Br(CO)_4Cr \equiv C{-}C_6H_5} + \underset{\mathbf{343}}{2\,P(OPh)_3} \rightarrow \underset{\mathbf{344}}{Br(CO)_2P(OPh)_3Cr \equiv CC_6H_5} \quad (158)$$

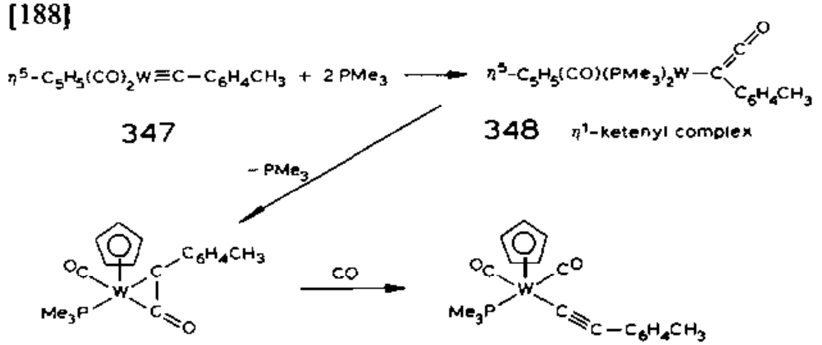
Cationic carbyne complexes interact by forming ylide derivatives with phosphines instead of phosphine coordinated to the metal atom [187]



$$[C_6H_6(CO)_2Cr{\equiv}C{-}C_6H_5]BCl_4 + PMe_3 \longrightarrow [C_6H_6(CO)_2Cr{-}\bar{C}(C_6H_5)(\overset{+}{P}Me_3)]\,BCl_4 \quad (159)$$

345 346

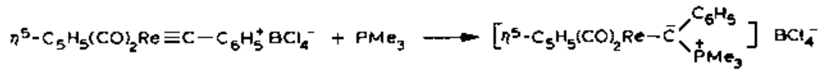
Thus the ligand in the *trans* position to the carbyne ligand will often determine whether η^1 or η^2 ketenyl complexes, dinuclear complexes with ylide bridges or metal substituted phosphorus ylides will form. For example [188]



347 348 (160)

349 350

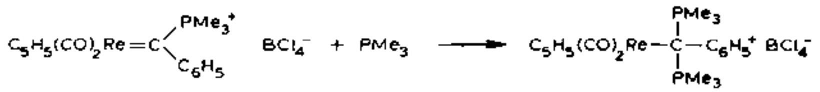
However, the cationic complex η^5-$C_5H_5(CO)_2Re \equiv C{-}C_6\overset{+}{H}_5$ gives a metal substituted ylide compound [189]



$$\eta^5\text{-}C_5H_5(CO)_2Re{\equiv}C{-}C_6H_5^+\,BCl_4^- + PMe_3 \longrightarrow [\eta^5\text{-}C_5H_5(CO)_2Re{-}\bar{C}(C_6H_5)(\overset{+}{P}Me_3)]\,BCl_4^- \quad (161)$$

351 352

This cationic complex can add more phosphine ligand to form the bis-ylide adduct

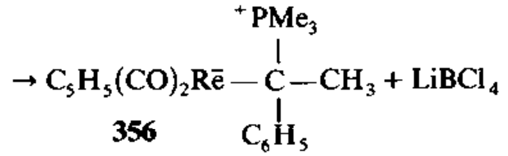


$$C_5H_5(CO)_2Re{=}C(PMe_3^+)(C_6H_5)\;BCl_4^- + PMe_3 \longrightarrow C_5H_5(CO)_2Re{-}C(PMe_3)_2{-}C_6H_5^+\,BCl_4^- \quad (162)$$

353 354

or treatment with MeLi will give a complex that has the methyl group on the ylide carbon

$$\underset{\mathbf{355}}{C_5H_5(CO)_2Re{=}C(C_6H_5)P\overset{+}{M}e_3BCl_4^-} + MeLi$$

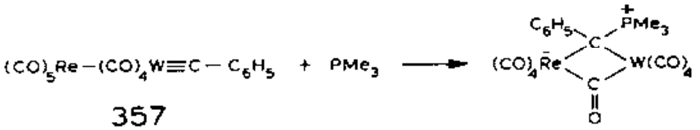


$$\rightarrow C_5H_5(CO)_2R\bar{e}-\underset{C_6H_5}{\overset{+PMe_3}{C}}-CH_3+LiBCl_4 \qquad (163)$$

356

Again this supports the X-ray diffraction results which suggest extensive delocalization of the ylide negative charge to the rhenium atom (see above) [189].

When the *trans* ligand is another metal atom, a bridged structure forms [190]

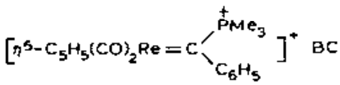


357

358

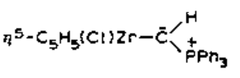
(164)

At this juncture it is interesting to compare the carbon–metal distances in the metal substituted ylide complex of



359

with those of



221

The rhenium complex (**359**) shows a carbon–metal bond length of 1.97 Å and a carbon–phosphorus bond length of 1.79 Å. The corresponding zirconium complex (**221**) shows instead a much longer carbon–zirconium bond of 2.15 Å and a carbon–phosphorus bond of 1.71 Å. The considerable shortening of the rhenium–carbon bond can be ascribed to overlap of the filled *p*-orbital on the ylide carbon atom with unfilled orbitals on the rhenium atom and the positive charge of the rhenium atom. Thus, the ylide carbon atom although traditionally negative, is converted into an electrophilic center by the rhenium atom. Hence a completely different set of reaction chemistry can be expected from such a system. Indeed such examples illustrate a potential variety of synthetic possibilities by substitution of the ylide hydrogen atoms with transition metal atoms.

F. BONDING IN YLIDES

In conjunction with the versatile reactivity of ylides, their structure and bonding have evoked considerable interest. X-ray molecular structures of stabilized ylides, $Ph_3\overset{+}{P}-\bar{C}H_2$ have been discussed by Bart [191] and these confirm the planarity of the methylene hydrogenatoms, or approximately sp^2

hybridization on the ylide carbon atom. The ^{13}C NMR spectrum and $^{1}J(^{13}C-^{1}H)(Me_3\overset{+}{P}-\overline{C}H_2)$ (149 Hz) also support the hypothesis concerning the highly negatively charged phosphonium substituted carbon atom [192].

Of course this leaves open the delicate question of which resonance structure $R_3P{=}CH_2$ (A) or $R_3\overset{+}{P}-\overline{C}H_2$ (B), best describes the bonding in these compounds. The P—C bond length in $Ph_3\overset{+}{P}-\overline{C}H_2$ is 1.661 Å and the sum of the Pauling double bond radii is 1.665 Å suggesting that there is considerable $d\pi-p\pi$ double bond character to the P—C bonds. Nevertheless recent calculations show that the P—C rotational barrier is very small (3—16 kcal $mole^{-1}$) and the ionic bond order is very high. The electron density maps of $H_3P{=}CH_2$ for example show only minor changes with *d*-orbital participation. Hence, the preferred electronic picture of phosphorus ylides is most likely the polar resonance form described in (B) [193].

G. CONCLUSIONS

The Wittig ylide is a reagent which after thirty-three years still remains one of the tried and true compounds used to make olefins from carbonyl compounds. As just recognition for the manifold application of the Wittig reaction and recognition of its usefulness in chemical synthesis, Prof. Wittig received the Nobel Prize (1979) in Chemistry. Now a new vista has been established for alkylidene phosphoranes and hopefully new avenues of synthesis with transition metal organometallic compounds will be discovered.

ACKNOWLEDGMENTS

W.C. Kaska is grateful to his graduate and postdoctoral students whose contributions are presented in many of the references. The research support in the form of grants from the Army Research Office and the Petroleum Research Fund, administered by The American Chemical Society is deeply appreciated, as is the correspondence and encouragement of Professor H. Schmidbaur during this project.

REFERENCES

1 (a) G. Wittig, Accounts Chem. Res., 7 (1974) 6.
(b) H.J. Bestmann, Angew. Chem. Int. Ed. Engl., 16 (1977) 349; H.J. Bestmann and R. Zimmermann, Fortschr. Chem. Forsch., 20 (1971) 1.
(c) A.W. Johnson, Ylid Chemistry, Academic Press, New York, 1966.
2 B.M. Trost and L.S. Melvin, Jr., Sulfur Ylides, Academic Press, New York, 1975.
3 W.K. Musker, J. Chem. Educ., 45 (1968) 200; W.K. Musker, Fortschr. Chem. Forsch., 14 (1970) 295; I. Zugravescu and M. Petrovanu, N-Ylid Chemistry, McGraw-Hill, New York, 1976.

4 H. Schmidbaur, Adv. Organometallic Chem., 14 (1976) 205.
5 R.R. Schrock and P.R. Sharp, J. Am. Chem. Soc., 100 (1978) 2389; C. Crocker, R.J. Errington, R. Markham, C.J. Moulton, K.J. Odell and B.L. Shaw, J. Am. Chem. Soc., 102 (1980) 4373.
6 G. Trinquier and J.P. Malrieu, J. Am. Chem. Soc., 101 (1979) 7169.
7 F. Ramirez, N.B. Desai, B. Hansen and N. McKelvie, J. Am. Chem. Soc., 83 (1961) 3539; C.N. Matthews and G.H. Birum, Accounts Chem. Res., 2 (1969) 373.
8 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 2nd Edn. Interscience, New York, p. 761.
9 R.N. Collinge, R.S. Nyholm and M.L. Tobe, Nature (London), 201 (1964) 1322.
10 H. Bock, Pure Appl. Chem., 44 (1975) 343; K.A.O. Starzewski and H. Tom Dieck, Phosphorus, 6 (1976) 177.
11 H. Staudinger and J. Mayer, Helv. Chim. Acta, 2 (1919) 635.
12 G. Wittig and G. Geissler, Justus Liebigs Ann. Chem., 580 (1953) 44; G. Wittig and H. Laib, Justus Liebigs Ann. Chem., 580 (1953) 51; D.D. Coffmann and C.S. Marvel, J. Am. Chem. Soc., 51 (1929) 3496.
13 Y. Hata and M. Watanabe, J. Am. Chem. Soc., 95 (1973) 8450; K. Takai, Y. Hotta, K. Oshima and H. Nozaki, Tetrahedron Lett., (1978) 2417; S.H. Pine, R. Zahler, D.A. Evans and R.H. Grubbs, J. Am. Chem. Soc., 102 (1980) 3271.
14 D. Seyferth and S.O. Grim, J. Am. Chem. Soc., 83 (1961) 1613; D. Seyferth, S.O. Grim and T.O. Read, J. Am. Chem. Soc., 82 (1960) 1510; D. Seyferth, Angew. Chem., 72 (1960) 36.
15 G. Wilkinson, Science, 185 (1974) 109; P.S. Braterman and R.J. Cross, J. Chem. Soc. Dalton Trans., (1972) 657.
16 T.A. Albright and E.E. Schweizer, J. Org. Chem., 41 (1976) 1168.
17 H. Daniel and J. Paetsch, Chem. Ber., 98 (1965) 1915.
18 H. Schmidblaur and W. Tronick, Chem. Ber., 101 (1968) 3556.
19 K.A.O. Starzewski and H. Tom Dieck, Phosphorus, 6 (1976) 177 and references therein.
20 A. Piskala, M. Zimmerman, G. Fouquet and M. Schlosser, Collect. Czech. Chem. Commun., 36 (1972) 1482.
21 R.E. Cramer, R.B. Maynard and J.W. Gilje, J. Am. Chem. Soc., 100 (1978) 5562.
22 L.E. Manzer, Inorg. Chem., 15 (1976) 2567.
23 D. Seyferth and S.O. Grim, J. Am. Chem. Soc., 83 (1613) 1961.
24 W.K. Musker and R.R. Stevens, Tetrahedron Lett., 11 (1967) 995; Inorg. Chem., 8 (1969) 255.
25 A.E. VanArkel, Molecules and Crystals, Interscience, New York, 1956, p. 73.
26 H. Schmidbaur, U. Deschler, B. Zimmer-Gasser, D. Neugebauer and U. Schubert, Chem. Ber., 113 (1980) 902; H. Schmidbaur, U. Deschler, B. Milewski-Mahrle and B. Zimmer-Gasser, Chem. Ber., 114 (1981) 608.
27 H. Schmidbaur and H.J. Fuller, Angew. Chem. Int. Ed. Engl., 15 (1976) 501.
28 H. Schmidbaur and W. Walt, Chem. Ber., 108 (1975) 2851; H. Schmidbaur, J. Organometal. Chem., 200 (1980) 287 and references therein; M.J. van Hamme and D.J. Burton, J. Organometal. Chem., 169 (1979) 123.
29 M.F. Hawthorne, J. Am. Chem. Soc., 80 (1958) 3480; 83 (1961) 367.
30 S.O. Grim and D. Seyferth, Chem. Ind. (London), (1959) 849.
31 N.E. Miller, Inorg. Chem., 4 (1965) 1458; D.R. Mathiason and N.E. Miller, Inorg. Chem., 7 (1968) 709.
32 D. Seyferth and H.M. Cohen, J. Inorg. Nucl. Chem., 20 (1961) 73.
33 F. Bickelhaupt and J.W.F.R. Barnick, Rec. Trav. Chim. Pays-Bas, 87 (1968) 188.

34 W.C. Kaska, unpublished observations, 1973.

35 J.J. Tufariello and L.T.C. Lee, J. Am. Chem. Soc., 88 (1966) 4757; R. Koster and B. Rickborn, J. Am. Chem. Soc., 89 (1967) 2782; P.I. Paetzold and H. Grundke, Synthesis, (1973) 635.

36 H. Schmidbaur and W. Tronick, Angew. Chem. Int. Ed. Engl., 6 (1967) 448; Chem. Ber., 101 (1968) 595; H. Schmidbaur and H.J. Fuller, Chem. Ber., 107 (1974) 3674.

37 H. Schmidbaur, J. Eberlein and W. Richter, Chem. Ber., 110 (1977) 677.

38 D.R. Mathiason and N.E. Miller, Inorg. Chem., 7 (1968) 709.

39 H. Gilman and R. Tamasi, J. Org. Chem., 27 (1962) 3647.

40 D. Seyferth, G. Singh and R. Surzuki, Pure Appl. Chem., 13 (1966) 159.

41 H. Schmidbaur, Adv. Organometal. Chem., 9 (1970) 260.

42 H. Schmidbaur, Third Int. Symp. Organosilicon Chem., Madison, Wisconsin, 1972; Internat. Conference on Ylide Chem., Leicester, 1970.

43 N.E. Miller, J. Am. Chem. Soc., 87 (1965) 390.

44 E.A.V. Ebsworth, D.W.H. Rankin, B.Z. Gasser and H. Schmidbaur, Chem. Ber., 113 (1980) 1637.

45 H. Schmidbaur and W. Tronick, Chem. Ber., 100 (1967) 1032.

46 H. Schmidbaur and W. Malisch, Chem. Ber., 103 (1970) 3007.

47 H. Schmidbaur and G. Kammel, Chem. Ber., 104 (1971) 3252; H. Schmidbaur and W. Kapp, Chem. Ber., 105 (1972) 1203.

48 H. Schmidbaur and W. Tronick, Inorg. Chem., 7 (1968) 168.

49 K.A.O. Starzewski, H. Tom Dieck and H. Bock, J. Organometal. Chem., 65 (1974) 311.

50 H. Schmidbaur and F.H. Kohler, unpublished results, 1976.

51 H.J. Bestmann, Chem. Ber., 95 (1962) 58.

52 H.J. Bestmann, Neuere Methoden Prep. Org. Chem., Teil V, Verlag Chemie, Neinheim/Bergstrasse, 1967.

53 H. Schmidbaur, H. Stuhler and W. Vornberger, Chem. Ber., 105 (1972) 1084.

54 H. Schmidbaur and W. Malisch, Chem. Ber., 102 (1969) 83.

55 H. Schmidbaur and W. Malisch, Chem. Ber., 103 (1970) 3448.

56 H. Schmidbaur and T. Tronick, Chem. Ber., 101 (1968) 604.

57 H. Schmidbaur, W. Buchner and D. Scheutzow, Chem. Ber., 106 (1973) 1251.

58 K. Hildenbrand and H. Dreskamp, Z. Naturforsch. Teil B, 28 (1973) 226.

59 W. Sawodny, Z. Anorg. Allg. Chem., 368 (1969) 284.

60 H. Schmidbaur, unpublished dipole moment studies, 1976.

61 E.A.C. Lucken and C. Mazeline, J. Chem. Soc. A, (1966) 1074; (1967) 439.

62 K. Issleib and R. Lindner, Justus Liebigs Ann. Chem., 699 (1966) 40; 707 (1967) 112; K. Issleib and M. Lischenski, J. Prakt. Chem., 311 (1969) 857.

63 H. Schmidbaur and H. Stuhler, Angew. Chem. Int. Ed. Engl., 11 (1972) 145.

64 H. Schmidbaur, K.H. Mitschke and J. Weidlein, Angew. Chem. Int. Ed. Engl., 11 (1972) 144.

65 H. Schmidbaur, H. Stuhler and W. Buchner, Chem. Ber., 106 (1973) 1238.

66 H. Schmidbaur, K.H. Mitschke, W. Buchner, H. Stuhler and J. Weidlein, Chem. Ber., 106 (1973) 1226.

67 H. Schmidbaur, W. Buchner and F.H. Kohler, J. Am. Chem. Soc., 96 (1974) 6208.

68 H. Schmidbaur and H. Stuhler, Chem. Ber., 107 (1974) 1420.

69 H. Schmidbaur and H. Stuhler, Angew. Chem. Int. Ed. Engl., 12 (1973) 320.

70 H. Schmidbaur and W. Vornberger, Angew. Chem. Int. Ed. Engl., 9 (1970) 737.

71 H. Schmidbaur and W. Vornberger, Chem. Ber., 105 (1972) 3173, 3187.

72 H. Schmidbaur and W. Malisch, Chem. Ber., 103 (1970) 97.

73 K. Itoh, H. Hayashi, M. Fukui and Y. Ishii, J. Organometal. Chem., 78 (1974) 339.

74 M.F. Lappert, J. Lorberth and J.S. Poland, J. Chem. Soc. A, (1970) 2954.

75 J. Buckle and P.G. Harrison, J. Organometal. Chem., 77 (1974) C22.

76 J. Buckle, P.G. Harrison, T.J. King and J.A. Richards, J. Chem. Soc. Chem. Commun., (1972) 1104.

77 S.J. Hannon and T.G. Traylor, J. Chem. Soc. Chem. Commun., (1975) 630.

78 O. Gasser and H. Schmidbaur, J. Am. Chem. Soc., 97 (1975) 6281.

79 H. Schmidbaur, Accounts Chem. Res., 8 (1975) 62.

80 J.C. Baldwin, N.L. Keder, C.E. Strouse and W.C. Kaska, Z. Naturforsch. Teil B, 35 (1980) 1289.

81 J.C. Baldwin, Ph.D. Thesis, University of California, Santa Barbara, 1978.

82 N.L. Holly, N.C. Baenziger and R.M. Flynn, Angew. Chem. Int. Ed. Engl., 17 (1978) 686, and references therein.

83 N. Petragnani and M. de Moura Campos, Chem. Ind., (1964) 1461, U.S. Patent 3,686,159; R. Bauer, H. Chung, K.W. Barnett, P.W. Glockner and W. Keim, Shell Oil Co., U.S. Patent 2,998,416; A. Mendel, Cities Service R&D, New York; W. Keim, F.H. Kowaldt, R. Goddard and C. Kruger, Angew. Chem. Int. Ed. Engl., 17 (1978) 466.

84 J.P. Fackler, Jr., Am. Chem. Soc. Meeting, Miami, Florida, 1978, paper no. Inor 53; J. Stein, J.P. Fackler, Jr., C. Paparizos and H.W. Chen, J. Am. Chem. Soc., 103 (1981) 2192.

85 R.J. Angelici, Accounts Chem. Res., 5 (1972) 335; D. Darensbourg and M. Darensbourg, Inorg. Chem., 43 (1972) 351.

86 F. Heydenreich, A. Mollbach, G. Wilke, H. Dreeskamp, E.G. Hoffmann, G. Schroth, K. Seevogel and W. Stempfle, Israel J. Chem., 10 (1972) 293.

87 P.W. Jolly and G. Wilke, The Organic Chemistry of Nickel, Vol. I, Academic Press, New York, 1974, p. 38.

88 J.C.J. Bart, Angew. Chem. Int. Ed. Engl., 7 (1968) 730.

89 N.L. Holly, N.C. Baenziger and R.M. Flynn, Angew. Chem. Int. Ed. Engl., 17 (1978) 686.

90 E.W. Abel, A. Singh and G. Wilkinson, Chem. and Ind. (London), (1959) 1067; V.I. Zdanovitch, N.E. Kdobova, N.I. Vasyukova, Yu.S. Nekrasov, G.A. Panosyan, P.V. Petrovskil and A.Zh. Zhakaeva, J. Organometal. Chem., 148 (1978) 63.

91 D. Cashman and F.J. Lalor, J. Organometal. Chem., 32 (1971) 357.

92 H. Zeiss, P.J. Wheatley and H.J.S. Winkler, Benzenoid Metal Complexes, The Ronald Press, New York, 1966.

93 K.A. Ostoja Starzewski, H. Tom Dieck, K.D. Franz and F. Hoffmann, J. Organometal. Chem., 42 (1972) C35.

94 F. Ramirez, N.B. Desai, B. Hansen and N. McKelvie, J. Am. Chem. Soc., 83 (1961) 3539; C.N. Matthews and G.H. Birum, Accounts Chem. Res., 2 (1969) 373.

95 O. Gasser and H. Schmidbaur, J. Am. Chem. Soc., 97 (1975) 6281; R. Appel, F. Knoll, H. Scholer and H.D. Wihler, Angew. Chem. Int. Ed. Engl., 15 (702) 1976.

96 H. Bestmann, Angew. Chem. Int. Ed. Engl., 16 (1977) 349; E.A.V. Ebsworth, T.E. Fraser and D.W.H. Rankin, Chem. Ber., 110 (1977) 3508; H.P. Oechsner, Diplomarbeit Institut für Organische Chemie II, Fredrick-Alexander-Universität, Erlangen-Nurnburg, 1979.

97 G.E. Hardy, J.C. Baldwin, J.I. Zink, W.C. Kaska, P.H. Liu and L. Dubois, J. Am. Chem. Soc., 99 (1977) 3552.

98 W.C. Kaska, D.K. Mitchell, R.F. Reichelderfer and W.D. Korte, J. Am. Chem. Soc., 96 (1974) 2847.

99 S.Z. Goldberg and K.N. Raymond, Inorg. Chem., 12 (1973) 2923.

100 H. Schmidbaur and O. Gasser, Angew. Chem., 88 (1976) 542.

101 W.C. Kaska, D.K. Mitchell and R.F. Reichelderfer, J. Organometal. Chem., 47 (1973) 391.

102 W.C. Kaska and R.F. Reichelderfer, J. Organometal. Chem., 78 (1974) C47.

103 J.C. Baldwin and W.C. Kaska, Inorg. Chem., 18 (1979) 686.

104 H. Schmidbaur, O. Gasser, C. Krüger and J.C. Sekutowski, Chem. Ber., 110 (1977) 3517; C. Krüger, J.C. Sekutowski, R. Goddard, H.J. Fuller, O. Gasser and H. Schmidbaur, Israel J. Chem., 15 (1976/77) 149.

105 H. Schmidbaur, O. Gasser and M.S. Hussain, Chem. Ber., 110 (1977) 3501; H. Schmidbaur, O. Gasser, T.E. Fraser and E.A.V. Ebsworth, Chem. Commun., (1977) 334.

106 H. Schmidbaur, H.J. Fuller, V. Bejenki, A. Frank and G. Huttner, Chem. Ber., 110 (1977) 3536.

107 H. Schmidbaur and H.J. Fuller, Chem. Ber., 110 (1977) 3528.

108 H. Schmidbaur, J. Adlkofer and M. Heinmann, Angew. Chem. Int. Ed. Engl., 12 (1973) 415; H. Schmidbaur, J. Adlkofer and M. Heinman, Chem. Ber., 107 (1974) 3697; Y. Yamamoto and H. Schmidbaur, J. Organometal. Chem., 96 (1975) 133; 97 (1975) 479; H. Schmidbaur and W. Richter, unpublished results.

109 H. Schmidbaur and R. Franke, Angew. Chem. Int. Ed. Engl., 12 (1973) 416; Chem. Ber., 108 (1975) 1321; Inorg. Chim. Acta, 13 (1975) 79, 84; Y. Yamamoto, Chem. Lett., (1980) 311.

110 G. Huttner and A. Frank, Diplomarbeit, Tech. Univ. Munich, 1975.

111 Y. Yamamoto and H. Schmidbaur, J. Organometal. Chem., 96 (1975) 133; H. Schmidbaur, J. Adlkofer and M. Heinmann, Chem. Ber., 107 (1974) 3697; G. Nardin, L. Randaccio and E. Zangrando, J. Organometal. Chem., 72 (1974) C23.

112 R.R. Schrock, Accounts Chem. Res., 12 (1979) 98.

113 The interaction of Ni (atoms) and $Me_3\overline{P}-\overline{C}H_2$ also gives $Ni(PMe_3)_4$; P.S. Skell and H.F. Klein, Angew. Chem. Int. Ed. Engl., 19 (1980) 362; ref. 79.

114 A. Wohlleben and H. Schmidbaur, Angew. Chem. Int. Ed. Engl., 16 (1977) 417; H. Schmidbaur and A. Wohlleben-Hammer, Chem. Ber., 112 (1979) 510.

115 H.H. Karsch and H. Schmidbaur, Chem. Ber., 107 (1974) 3684; D.J. Brauer, C. Krüger, P.J. Roberts and Y.H. Tsay, Chem. Ber., 107 (1974) 3706.

116 H.H. Karsch, H.F. Klein and H. Schmidbaur, Chem. Ber., 107 (1974) 93.

117 H. Schmidbaur, Pure Appl. Chem., 50 (1978) 19; H. Schmidbaur and H.P. Scherm, Chem. Ber., 111 (1978) 797; H. Schmidbaur, G. Blaschke and H.P. Schern, Chem. Ber., 112 (1979) 3311; H. Schmidbaur, H.P. Scherm and U. Schubert, Chem. Ber., 111 (1978) 764.

118 H. Schmidbaur, Pure Appl. Chem., 52 (1980) 1057.

119 G. Blaschke, W.C. Kaska and H. Schmidbaur, J. Organometal. Chem., 182 (1979) 251; J.C. Baldwin, Ph.D. Thesis, Univ. California, Santa Barbara, 1978; see the following refs. for studies on elimination of alkanes from platinum; M.P. Brown, R.J. Puddephatt, C.E.E. Upton and S.W. Lavington, J. Chem. Soc. Dalton Trans., (1974) 1613, (1974) 2547; P.S. Braterman, J. Chem. Soc. Chem. Commun., (1979) 70; K. Tasumi, R. Hoffmann, A. Yamamoto and J.K. Stille, Bull. Chem. Soc. Jpn., 54 (1981) 1857; G.W. Rice and R.S. Tobias, Inorg. Chem., 15 (1976) 489.

120 C.G. Pierpont, H.H. Downs, K. Itoh, H. Nishiyama and Y. Ishii, J. Organometal. Chem., 124 (1976) 93.

121 P. Bravo, F. Fronza, G. Gaudiano and C. Ticozzi, Gazz Chim. Ital., 103 (1973) 623; P. Gravo, G. Fronza, C. Ticozzi and G. Gaudiano, J. Organometal. Chem., 74 (1974) 143.

122 E.T. Weleski, Jr., J.L. Silver, M.D. Jansson and J.L. Burmeister, J. Organometal. Chem., 102 (1975) 365; H. Nishiyama, K. Itoh and Y. Ishii, J. Organometal. Chem., 87 (1975)

129; P. Bravo, G. Fronza and C. Ticozzi, J. Organometal. Chem., 111 (1976) 361; G. Fronza, P. Bravo and C. Ticozzi, J. Organometal. Chem., 157 (1978) 299.

123 R.A. Grey and L.R. Anderson, Inorg. Chem., 16 (1977) 3187; R.L. Lapinski, H. Yue and R.A. Grey, J. Organometal. Chem., 174 (1979) 213.

124 H. Schmidbaur, G. Blaschke, H.J. Fuller and H.P. Scherm, J. Organometal. Chem., 160 (1978) 41; T.E. Fraser, H.J. Fuller and H. Schmidbaur, Z. Naturforsch., 346 (1979) 1218.

125 H.F. Klein, Angew. Chem. Int. Ed. Engl., 19 (1980) 362 and references therein.

126 H.H. Karsch and H. Schmidbaur, Z. Naturforsch., 326 (1977) 762; H.H. Karsch, Chem. Ber., 111 (1978) 1650 and references therein.

127 D.K. Reger and E.C. Culbertson, J. Organometal. Chem., 131 (1977) 297.

128 L. Knoll, Z. Naturforsch. Teil B, 32 (1977) 1268.

129 L. Knoll, J. Organometal. Chem., 193 (1980) 47, see also ref. 155.

130 H. Bock and H. Tom Dieck, Z. Naturforsch. Teil B, 21 (1966) 739.

131 K.A. Ostoja Starzewski, H. Tom Dieck, K.D. Franz and F. Hohmann, J. Organometal. Chem., 42 (1972) C35.

132 L. Knoll, J. Organometal. Chem., 148 (1978) C25.

133 L. Knoll, J. Organometal. Chem., 182 (1979) 77.

134 K. Knoll, Z. Naturforsch. Teil B, 33 (1978) 396.

135 L. Weber, J. Organometal. Chem., 142 (1977) 309.

136 L. Weber, J. Organometal. Chem., 131 (1977) 49.

137 L. Weber, Z. Naturforsch. Teil B, 31 (1976) 780.

138 E. Lindner and H. Berke, Chem. Ber., 107 (1974) 1360.

139 E. Kurras, U. Rosenthal, H. Mennenga and G. Olhme, Angew. Chem. Int. Ed. Engl., 12 (1973) 854; E. Kurras, H. Mennenga, G. Oehme, U. Rosenthall and G. Engelhardt, J. Organometal. Chem., 84 (1975) C13; E. Kurras and U. Rosenthal, J. Organometal. Chem., 160 (1978) 35.

140 F.A. Cotton, B.E. Hanson, W.H. Isley and G.W. Rice, Inorg. Chem., 18 (1979) 2713; F.A. Cotton, B.E. Hanson and G.W. Rice, Angew. Chem. Int. Ed. Engl., 17 (1978) 953; F.A. Cotton and P.E. Fanwick, J. Am. Chem. Soc., 101 (1979) 5252.

141 W.C. Kaska, R.F. Reichelderfer and L. Prizant, J. Organometal. Chem., 129 (1977) 97.

142 R.R. Schrock and P.R. Sharp, J. Am. Chem. Soc., 100 (1978) 2389; R.R. Schrock, Accounts Chem. Res., 12 (1979) 98.

143 P.R. Sharp and R.R. Schrock, J. Organometal. Chem., 171 (1979) 43.

144 S.J. McLain, C.D. Wood, L.W. Messerle, R.R. Schrock, F.J. Hollander, W.J. Youngs and M.C. Churchill, J. Am. Chem. Soc., 100 (1978) 5692.

145 H. Schmidbaur, W. Scharf and H.J. Fuller, Z. Naturforsch. Teil B, 32 (1977) 858.

146 L.E. Manzer, J. Organometal. Chem., 110 (1976) 291; L.E. Manzer, Inorg. Chem., 15 (1976) 2567.

147 W. Heiber, E. Winter and E. Schubert, Chem. Ber., 95 (1962) 3070.

148 W. Scharf, D.N. Neubauer, W. Schubert and H. Schmidbaur, Angew. Chem. Int. Ed. Engl., 17 (1978) 601.

149 J.C. Baldwin, N.L. Keder, C.E. Strouse and W.C. Kaska, Z. Naturforsch. Teil B, 35 (1980) 1289.

150 J. Schwartz and K.I. Gell, J. Organometal. Chem., 189 (1980) C1; J. Schwartz, Pure Appl. Chem., 52 (1980) 733.

151 H. Schumann, Chem. Ztg. Chem. App., 100 (1976) 336.

152 R.E. Cramer, R.B. Maynard and J.W. Gilje, J. Am. Chem. Soc., 100 (1978) 5562; R.E. Cramer, R.B. Maynard and J.W. Gilje, Inorg. Chem., 20 (1981) 2466; R.E. Cramer, R.B. Maynard, J.C. Paw and J.W. Gilje, J. Am. Chem. Soc., 103 (1981) 3589.

153 C. Creaser and W.C. Kaska, Transition Met. Chem., 3 (1978) 360.
154 W. Malisch, H. Blau and S. Voran, Angew. Chem. Int. Ed. Engl., 17 (1978) 780.
155 H. Blau and W. Malisch, Angew. Chem. Int. Ed. Engl., 19 (1980) 1019.
156 H. Blau and W. Malisch and U. Schubert, Angew. Chem. Int. Ed. Engl., 19 (1980) 1020 .
157 W. Malisch, H. Blau and U. Schubert, Angew. Chem. Int. Ed. Engl., 20 (1981) 216.
158 M.R. Churchill, F.J. Rotella, E.W. Abel and S.A. Mucklejohn, J. Am. Chem. Soc., 99 (1977) 5820; M.R. Churchill and F.J. Rotella, Inorg. Chem., 17 (1978) 2614.
159 H. Alper and R.A. Partis, J. Organometal. Chem., 44 (1972) 371.
160 L. Knoll, J. Organometal. Chem., 152 (1978) 311.
161 W. Malisch, Angew. Chem. Int. Ed. Engl., 12 (1973) 235.
162 S.Z. Goldberg, E.N. Duesler and K. Raymond, Inorg. Chem., 11 (1972) 1397.
163 J. Kiki, A. Matsumura, S.O. Kazaki, T. Haishi and J. Furukawa, J. Chem. Soc. Chem. Commun., (1975) 751.
164 L. Knoll, J. Organometal. Chem., 155 (1978) C63.
165 L. Knoll, Z. Naturforsch. Teil B, 33 (1978) 396.
166 B.L. Booth and K.G. Smith, J. Organometal. Chem., 178 (1979) 361.
167 H. Werner and H. Rascher, Inorg. Chim. Acta, 2 (1968) 181; F.R. Kreissl, C.G. Kreiter and E.O. Fischer, Chem. Ber., 106 (1973) 1262; U. Schubert and E.O. Fischer, J. Organometal. Chem., 51 (1973) C11; F.R. Kreissl and W. Held, Chem. Ber., 110 (1977) 799.
168 H. Fischer, E.O. Fischer and F.R. Kreissl, J. Organometal. Chem., 64 (1974) C41.
169 F.R. Kreissl and E.O. Fischer, Chem. Ber., 107 (1974) 183.
170 T.J. Burkhardt and C.P. Casey, J. Am. Chem. Soc., 94 (1972) 6543.
171 L. Cosslett and L.A.P. Kane-Maguire, J. Organometal. Chem., 178 (1979) C17.
172 P. Hackett and G. Jaoven, Inorg. Chim. Acta, 12 (1975) L19.
173 M. Gower, G.R. John, L.A.P. Kane-Maguire, T.I. Odiaka and A. Salzer, J. Chem. Soc. Dalton Trans., (1979) 2003.
174 H. Werner and R. Werner, J. Organometal. Chem., 174 (1979) C63.
175 Y.S. Wong, H.N. Paik, P.C. Chieh and A.J. Carty, J. Chem. Soc. Chem. Commun., (1975) 309; A.J. Carty, N.J. Taylor, W.F. Smith, M.F. Lappert and P.L. Pye, J. Chem. Soc. Chem. Commun., (1978) 1017; A.J. Carty, G.N. Mott, N.J. Taylor and J.E. Yule, J. Am. Chem. Soc., 100 (1978) 3051.
176 K. Yasufuku, K. Aoki and H. Yamazaki, J. Organometal. Chem., 84 (1975) C48.
177 M.R. Churchill, B.G. DeBoer, J.R. Shapley and J.B. Keister, J. Am. Chem. Soc., 98 (1976) 2357; A.J. Deeming and S. Hasso, J. Organometal. Chem., 112 (1976) C39; J.R. Shapley, private communication, 1981.
178 N.J. Cooper and M.L.H. Green, J. Chem. Soc. Dalton Trans., (1979) 1121; M. Canestrari and M.L.H. Green, J. Chem. Soc. Chem. Commun., (1979) 913.
179 R.F. Reichelderfer, J.C. Baldwin and W.C. Kaska, unpublished results, 1978.
180 W.K. Wong, W. Tam and J.A. Gladysz, J. Am. Chem. Soc., 101 (1979) 5440.
181 A. Sanders, T. Bauch, C.V. Magatti, C. Lorenc and W.P. Giering, J. Organometal. Chem., 107 (1976) 359.
182 H.F. Klein, J. Wenninger and U. Schubert, Z. Naturforsch. Teil B, 34 (1979) 1391.
183 J.R. Moss and J.C. Spiers, J. Organometal. Chem., 182 (1979) C20; O.J. Scherer and H.J. Jungmann, J. Organometal. Chem., 208 (1981) 153; N.J. Kermode, M.F. Lappert, B.W. Skelton and A.H. White, Chem. Commun., (1981) 698; C. Engelter, J.R. Moss, M. Nivan, L.R. Massimbeni and J.C. Spiers, Int. Conf. Platinum Group Metals, Royal Society of Chemistry Dalton Division, C48, Bristol, England, 1981.
184 R.J. Al-essa and R.J. Puddephatt, J. Chem. Soc. Chem. Commun., (1980) 45.

185 F.R. Kreissl, J. Organometal. Chem., 99 (1975) 305; F.R. Kreissl, W. Uedelhoven and A. Ruhs, J. Organometal. Chem., 113 (1976) C55.

186 E.O. Fischer, A. Ruhs and F.R. Kreissl, Chem. Ber., 110 (1977) 805.

187 F.R. Kreissl, P. Stuckler and E. Meinke, Chem. Ber., 110 (1977) 3040.

188 F.R. Kreissl, K. Eberl and W. Uedelhoven, Angew. Chem. Int. Ed. Engl., 17 (1978) 860; F.R. Kreissl, W. Uedelhoven and K. Eberl, Angew. Chem. Int. Ed. Engl., 17 (1978) 859.

189 F.R. Kreissl, A. Frank, U. Schubert, T.L. Lindner and G. Huttner, Angew. Chem. Int. Ed. Engl., 15 (1976) 632.

190 F.R. Kreissl, P. Friedrich, T.L. Lindner and G. Huttner, Angew. Chem. Int. Ed. Engl., 16 (1977) 314.

191 J.C.J. Bart, J. Chem. Soc. B, (1969) 350.

192 K.A.O. Starzewski and M. Feigel, J. Organometal. Chem., 93 (1975) C20.

193 Papers which have a bearing on the nature of the P—C bond are: H. Kwart and K. King, in K. Hafner, C.W. Rees, B.M. Trost, J.M. Lehn, P. von R. Schlayer and R. Zahradnik, α-orbitals in the chemistry of silicon, phosphorus and sulfur, Reactivity and Structure Concepts in Organic Chemistry, Vol. 3, Springer Verlag, New York, 1977; H. Bock, Pure Appl. Chem., 44 (1975) 343; K.A.O. Starzewski and H. Tom Dieck, Inorg. Chem., 18 (1979) 3307; G. Trinquier and J.P. Malrieu, J. Am. Chem. Soc., 101 (1979) 7169; H. Lischka, J. Am. Chem. Soc., 99 (1977) 353; F. Bernard, H.B. Schlegel, M.H. Whangbo and S. Wolfe, J. Am. Chem. Soc., 99 (1977) 5633; R. Hoffmann, D.B. Boyd and S.Z. Goldberg, J. Am. Chem. Soc., 92 (1970) 3929; A. Stritch, Nouveau J. Chem., 3 (1979) 105; T.A. Albright, P. Hoffmann and A. Rossi, Z. Naturforsch. Teil B, 35 (1980) 343 and references therein.