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Review

Overview of the Synthesis and Catalytic Reactivity of Transition Metal Complexes Based on C=P Bond Systems

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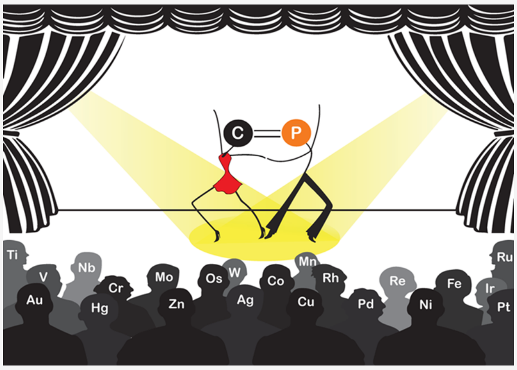
ABSTRACT: This report provides an overview of the use of phosphaalkenes (C=P) in syntheses of various complexes. Going through successive complexes containing the d-block metals, we sought how this area of chemistry was formed over the years. Additionally, this work contains information on the possible coordination types and means of constructing the complexes. In addition, this review reveals the reactivities of phosphaalkene complexes with a strong emphasis on catalytic properties.

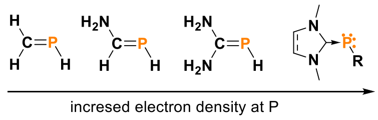


1. INTRODUCTION

Many reactions in organic or inorganic chemistry as well as in industry require the use of a catalyst. The search for selective and economically advantageous catalysts is high on the list of contemporary research.[1] It is well-known that transition metal complexes are widely applied in catalysis, and the selection of appropriate ligands plays an important role. A weighted group, namely, phosphaalkenes provides a good collection of such ligands. Generally, phosphaalkenes form a group containing unsaturated carbon−phosphorus $\sigma^2\lambda^3$-bonds (sp^2), which show lower strength, approximately 22 kcal/mol, than the C=C bond and makes the phosphaalkenes more reactive species.[2] Commonly known phosphaalkenes are polarized with a distribution of $P^{\delta+}{=}C^{\delta-}$ electrons in the P−C bond and this is due to the different electronegativity of the carbon (2.5) and phosphorus (2.1) atoms. NBO calculations performed for $HP{=}CH_2$ showed that the $\sigma+\pi$ charge is +0.387 e at the P atom and −0.810 e at the C atom, while the π P−C bond is essentially nonpolar (+0.030 e at P and −0.039 e at C).[3] Calculations for simple $HP{=}CH_2$ revealed that the lone pair of P atom has a higher s character (66% 3s) then sp^2 hybridization (34% s, 66% p). Additionally, the C=P−R angle of phosphaalkene results from the high s-character of a lone pair, and the low s-character of the σ bonds.[4] The experimentally determined and calculated energies for $HP{=}CH_2$ of the HOMO orbital are the π-bond and the lone pair of P atom being HOMO−1.[5] LUMO orbital is π*-character.[6] The literature also contains a whole range of phosphaalkenes with reverse polarity of the P=C bond.[7] Quantum chemical calculations indicate a strong reverse polarity of the π-bond when two amine groups are present on the carbon atom (NBO charge for $HP{=}CH(NH_2)$: −0.285 e at the P atom and +0.013 e at the C atom; for $HP{=}C(NH_2)_2$: −0.504 e at the P atom and +0.059 e at the C atom).[8] In recent years, carbene-phosphinidene adducts have generated interesting combinations.[9−11] Some of these compounds can be classified phosphaalkenes which have inversely polarized π-bond and polarized covalent δ-bond.[8,12−14] It is also conducive to donation of the lone electron pair from phosphorus to the free carbene p-orbital center, thus increasing the contribution of resonance (Scheme 1).[15]

The first reports of stable phosphaalkenes appeared over 40 years ago,[16] and since then, several methods have been developed to synthesize and isolate these compounds. To the method of synthesis we can include, reactions of dichlorophosphines or primary phosphines (Scheme 2, Reactions 1

Scheme 1. Differences in the Polarity of the C−P Bond



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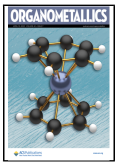

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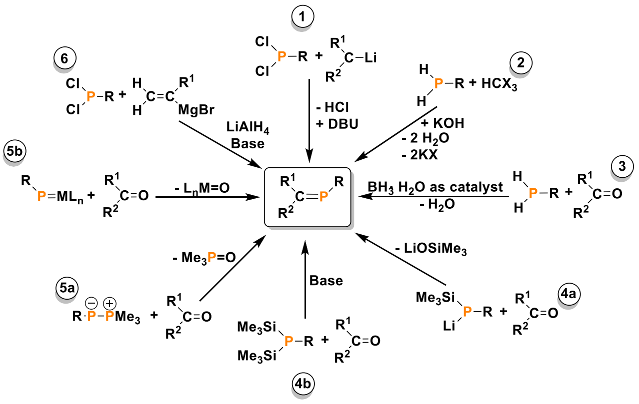
Scheme 2. Methods of Phosphaalkenes Synthesis

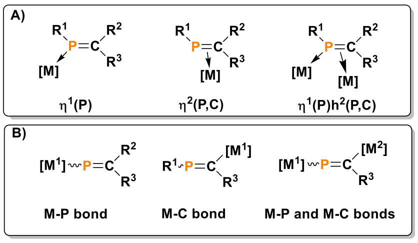


and 2)[17,18] Primary phosphines have also enabled the development of a different route for reactions with aldehydes or ketones (Scheme 2, Reaction 3).[19] Phosphorus analogous of two popular methods for alkene synthesis are the phospha-Peterson and phospha-Wittig reactions involving the use of an aldehyde or ketone. The first method may be implemented in two ways: reaction with a lithiated silylphosphine or with silylphosphine (Scheme 2, Reactions 4a and 4b).[20]

In the case of the second method, low-valent P species are employed (Scheme 2, Reaction 5a), including phosphoranylidenephosphines.[21,22] A variant of this method is metal-phospha-Wittig reaction, in which phosphinidene metal complexes are sources of phosphorus atoms (Scheme 2, Reaction 5b).[23−26] The reaction of a phosphaalkyne with a Grignard reagent is also method used for phosphaalkene synthesis (Scheme 2, Reaction 6).[27,28] These P═C compounds can take various forms.[29,30]

Phosphaalkene complexes are rather poor δ-donors and strong π-acceptors which is particularly important in the selection of these complexes in catalytic reactions. The donation of electrons to the metal occurs from the nonbonding lone pair of phosphorus, while the back bonding from the metal center occurs in the antibonding empty orbit $\pi^*_{P=C}$.[4] Complexes based on phosphaalkene ligands can be formed in two main ways, first, via coordination of the P lone pair and/or the P═C π-bond (Scheme 3, Part A). Second, formation of complexes may proceed by replacing substituents on the phosphaalkene with a transition metal. In these metal-functionalized phosphaalkenes (in some cases called metallophosphaalkenes), the P atom and P═C bond may act as donors and interact further as ligands (Scheme 3, Part B).[31]

Scheme 3. Examples of Phosphaalkene Transition Metal Complexes (A) and Metallophosphaalkenes (B)



The first type of complexes (A) is dominated by two types of η^1 and η^2 coordination (and less often η^1-η^2-fashion), while the synthesis of the second type of complexes is much less frequent (B). The reactivity and the use of phosphaalkenes in further synthesis are influenced by the substituents on the phosphorus atom. It seems that such compounds are not sufficiently stable, but the situation changes if they are electronically delocalized or sterically protected with appropriate substituents.[32] It is necessary to use sterically demanding substituents while still providing a large Tolmann angle. The calculations showed that the value of the cone angle decreases with increasing steric congestion around the central metal.[33] The literature is dominated primarily by the supermesityl group,[31,34,35] which ensures kinetic stabilization via steric protection.[36] The stabilization of phosphaalkenes with a small substituent on phosphorus atom requires assistance from the substituents on the carbon.[37] An alternative that has been used for a long time is employment of transition metal carbonyl compounds (especially Mo, Cr, and W).[22,38]

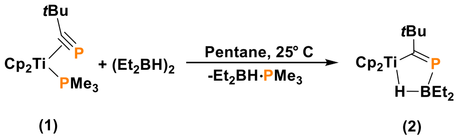
In the work presented here, there are many examples in which phosphaalkene ligands are used for formation of transition metal complexes. The work contains numerous synthetic routes and characterization data for phosphaalkene complexes, mainly those formed via lone pair (or via the π-bond) but also metallophosphaalkenes, as well as in-depth analyses of catalytic properties.

2. SYNTHESIS OF D-BLOCK ELEMENT PHOSPHAALKENE COMPLEXES

2.1. Group 4 Elements. It is well-known that titanium compounds and complexes exhibit catalytic properties.[39−47] However, the number of reports on phosphaalkene derivatives of titanium and zirconium is rather small.

2.1.1. Titanium. In 1990, Binger et al. described phosphaalkene formation resulted from coordinatively unsaturated phosphaalkyne by fast and spontaneous dimerization in the case of titanium and trimerization in the case of zirconium.[48] The next report appeared a few years later and was focused on the synthesis of boron−titanium-type phosphaalkene complexes. Dinuclear phosphaalkene complex **2** with a titanium and boron center was obtained in a reaction between phosphaalkyne complex **1** and with tetraethyldiborane (Scheme 4).[49]

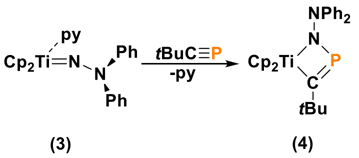
Scheme 4. Synthesis of Titanium Phosphaalkene Complex 2



Nixon and Cloke et al. reported the reactions of $[TiCl_2(NtBu)(py)_3]$ with excess of $tBuC{\equiv}P$ to give $[TiCl_2(P_2C_2tBu_2NtBu)(py)]$. Additionally, authors extended investigation with sterically encumbered titanium imide complex $[Ti\{(SiMe_3)N[CH_2CH_2N(SiMe_3)_2]\}(NtBu)(py)]$ to yield $[Ti\{N(Si\text{-}Me_3)[CH_2CH_2N(SiMe_3)]_2\}(P{=}CtBuNt\text{-}Bu)]$.[50] Mountford et al. presented very interesting [2 + 2] cycloaddition reaction between the diamidopyridine-supported titanium imide $[Ti(NtBu)(L)(py)]$ ($L = MeC(2\text{-}C_5H_4N)(CH_2{-}NSiMe_3)_2$) and phosphaalkyne $tBuC{\equiv}P$. As a result of the reaction, the mononuclear product $[Ti\{N(tBu)P{=}C(tBu)\}(L)]$ was obtained.[51] In 2003 Mindiola et al. reported reaction of $(Nacnac)Ti{=}PMes^*(CH_2tBu)$ with 3 equiv of

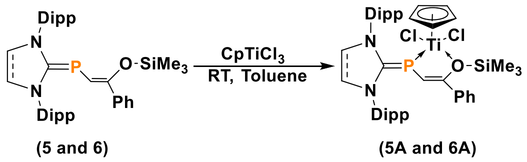
CN*t*Bu and afforded azaallene titanium complex [(η^1-Nacnac)-Ti(CN*t*Bu)(η^2-(N,C)-*t*BuN═CCH$_2$*t*Bu)(η^2-(N,C)-*t*BuN═C═PMes*)].[52] Several years later, another example of cycloaddition reactions was demonstrated. In reaction of titanium complex **3** with *t*BuC≡P crystals of **4** were isolated (Scheme 5).

Scheme 5. Synthesis of Titanium Complex with C═P–N Ligand



Performed DFT calculation revealed that the compound with Ti–P bond is thermodynamically competitive to the compound with Ti–C bond, however, the energies of transition state predicted that experimentally observed complex (Ti–C–P–N) is certainly kinetically favored ($\Delta\Delta E$ = 11.4 kJ·mol^{-1}).[53] In 2020, Lavoie et al. reported the first titanium complexes (**5A** and **6A**; Scheme 6) with monoanionic bidentate ligands containing an *N*-heterocyclic carbene-phosphinidene adduct (**5** and **6**).[54]

Scheme 6. Syntheses of Titanium Complexes with Inversely Polarized P═C Ligand[a]



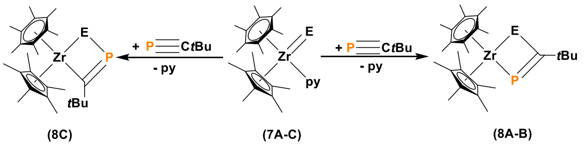
[a] **5** and **5A**: imidazole derivative; **6** and **6A**: imidazoline derivative; Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$.

2.1.3. *Zirconium.* Nixon et al. presented [2 + 2] cycloaddition reaction of **7A-B** with *t*BuC≡P led to phosphaalkene products **8A-B**. The authors concluded that the use of **7C** as substrate in reaction with *t*BuC≡P gave complex **8C** with P atom coordinated to Te atom instead to Zr atom (Scheme 7). As main reason for this behavior authors assumed formation of longer Zr–Te bond compared to the Zr–S or Zr–Se.[55]

2.2. Group 5 Elements.

Publications on Group 5 elements are exclusively focused on the syntheses and characterization of V and Nb phosphaalkene complexes. There are no reports of analogous Ta complexes.

Scheme 7. Synthesis of Zirconium Phosphaalkene Complexes through [2 + 2] Cycloaddition Reaction[a]

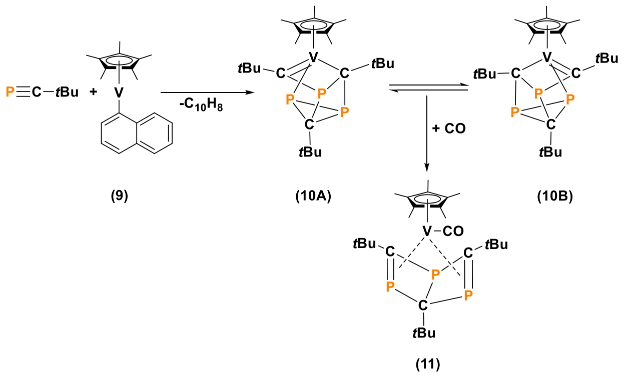


[a] A: E = S; B: E = Se; C: E = Te.

2.2.1. *Vanadium.* Binger et al. presented the formation of a vanadium phosphaalkene complex with three phosphorus atoms that were bonded to the vanadium center.

The reaction between *t*BuC≡P and naphthalene vanadium complex **9** gave **10A** and **10B**. Obtained compound **10** was reacted with CO, which led to formation of V complex **11** with 1,3,5-triphospha-Dewar-benzene ligand (Scheme 8).[56]

Scheme 8. Synthesis of V Diphosphaalkene Complex 11



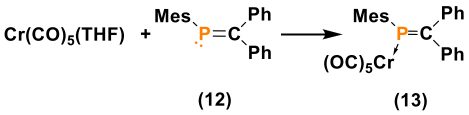
2.2.2. *Niobium.* The report concerning Nb phosphaalkene complex was published by Glueck et al., and it detailed the syntheses and reactivates of niobium complexes. The reaction of Mes*P═C-NPh with Cp′$_2$NbCl led to the desired complex [Cp′$_2$Nb(Cl){η^2-(*N*,*C*)-PhNC═PMes*}]. Treatment of the product with HBF$_4$·Me$_2$ gave the phosphaimino acyl complex {Cp′$_2$Nb(Cl)[η^2-(*N*,*C*)-PhN═CPHMes*]}BF$_4$. On the other hand, photolysis (Hg lamp) of the phosphaalkene led to the complex Cp′$_2$NbCl(CNPh) and phosphaindan.[57]

2.3. Group 6 Elements.

In the literature there are over a dozen interesting reports about phosphaalkene complexes involving elements of Group 6. A large proportion in this group constitute complexes with the [M(CO)$_5$] fragments.

2.3.1. *Chromium.* In 1981, Bickelhaupt et al. reported a synthetic route to a stable all-carbon substituted phosphaalkene involving a photochemical reaction of Cr(CO)$_5$(THF) with **12** in THF solution (Scheme 9).

Scheme 9. Synthesis of Pentacarbonylchromium(0) Phosphaalkene Complex 13



Complex **13** was more stable than free phosphaalkene **12** and was unreactive toward H$_2$O and oxygen; however, slow oxidation was observed in THF solution.[58] Scheer et al. reported the reactions of [W$_2$(O*t*Bu)$_6$] with Mes*C≡P in the presence of [M(CO)$_5$(THF)] (M = W, Cr) and formation the complexes [M(CO)$_4$P(R′)C(Mes*)P-{M(CO)$_5$}] (M = Cr; W; R′ = 2,4-*t*Bu$_2$-7-Me$_2$-indanyl) with a spirocyclic compound.[59] Weber et al. described the reactions of RP═C(NMe$_2$)$_2$ (R = *t*Bu, Me$_3$Si, H) with Cr or W arylcarbene complexes. Complexes **14A-B** reacted with the two phosphaalkenes RP═C(NMe$_2$)$_2$ (Scheme 10). Phosphaalkene complexes **15A-B** and **17A-B** were isolated, while complexes

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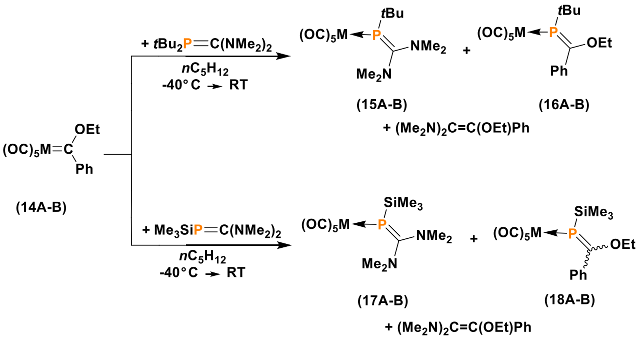
16A-B and **18A-B** were also formed. Isolation attempts ended in decomposition.[60]

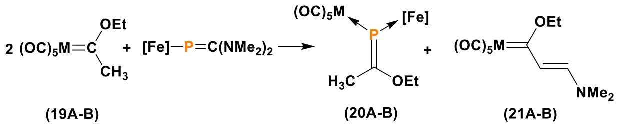
Scheme 10. Synthesis of Chromium and Tungsten Complexes[a]



[a]A: M = W; B: M = Cr.

In 2003, the Weber research group also presented a series of ferriophosphaalkene complexes **20A-B**. Described products were formed via reactions between a ferriophosphaalkene and complexes **19A-B** (Scheme 11). As a second product, *β*-aminoalkenyl carbene complexes **21A-B** were created.

Scheme 11. Formation of Ferriophosphaalkene Complexes 20A-B with Chromium and Tungsten[a]



[a]A: M = Cr; B: M = W; [Fe] = Cp*(CO)$_2$Fe.

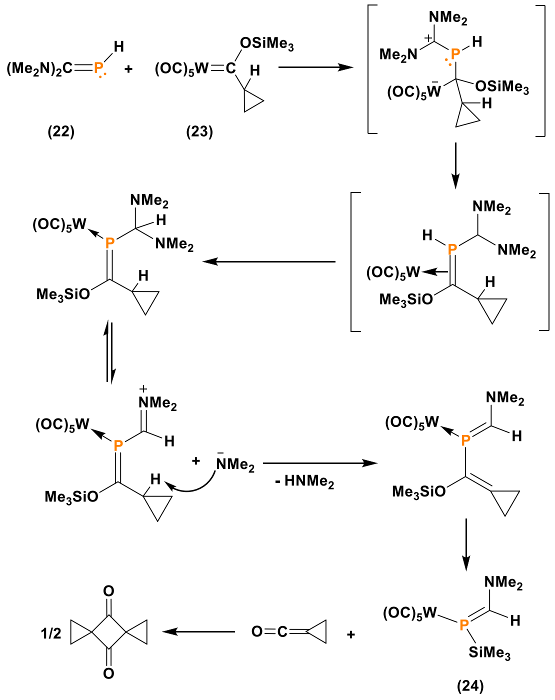
As a continuation of the work, they isolated complex **24** with a silyl-substituted P atom, which was formed in the reaction of complex **23** with an equimolar amount of phosphaalkene HP=C(NMe$_2$)$_2$ (**22**; Scheme 12). An analysis of complex **24** confirmed the *E*-configuration for the C=P ligand exhibiting η^1-coordination to a [W(CO)$_5$] fragment.[61]

2.3.2. Molybdenum. in 1992, Yoshifuji et al. synthesized chelate-type tetracarbonyl-molybdenum(0) complex **29** (Scheme 13). The synthetic method was based on a reaction of diphosphinidenecyclobutene ligand **28** from phosphaallenyl compound **27**. Diphosphane **26** was afforded after lithiation of **25** with 2 equiv of *t*BuLi but was unstable and immediately isomerized after heating to yield compound **28**. Importantly, all procedures were carried out in the dark because of the facile photoisomerization. Finally, complex **29** was prepared via the reactions with Mo(CO)$_6$, Mo(CO)$_5$(THF), and (bicycle[2.2.1]hepta-2,5-diene)Mo(CO)$_4$.[62]

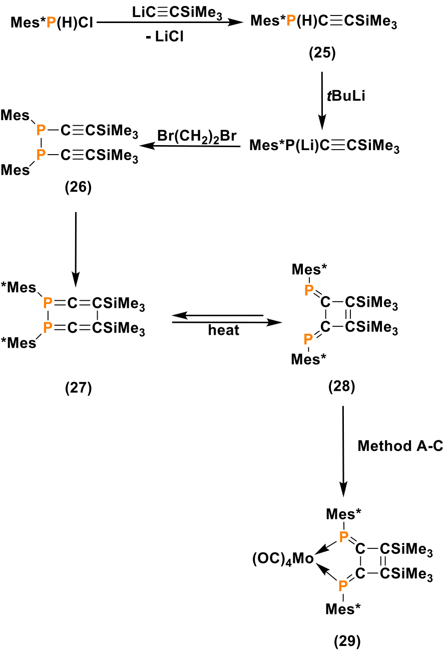
Mays et al. presented another type of Mo species, with a *trans*-bismolybdenum complex coordinated via an η^1-η^2 bonding mode to a phosphaalkene. They demonstrated a possible reaction pathway for the formation of *trans*-**34**, in which acryloyl chloride attacked deprotonated compound **30** to give **31**. Next, elimination of the CO molecule from **31** led to **32**. After this, reductive elimination formed **33**, followed by a 1,3-hydrogen shift leading to *trans* isomer **34** (Scheme 14).[63]

The same research group reported a wide range of examples relating to the reactivity of the *cis*/*trans*-[Cp$_2$(CO)$_4$Mo$_2$(η^1-η^2-PhP-CHMe)] (**34**) complexes.[64] In these reactions, electrophilic addition occurred at the P atom[65] or resulted at the phosphaalkene carbon atom.[66,67] In this case, the reaction between **23** and HBF$_4$ in acetonitrile resulted in [{Cp-(MeCN)$_4$Mo}$_2$(μ-O)][BF$_4$].[64] Yoshifuji et al. published phosphaalkene complexes including all three metals of Group 6 (Cr, Mo, and W). They presented tetracarbonyl complexes, in which the metal center was Cr (A), Mo (B), or W (C). The four-step synthesis stared with conversion of the phenyl-

Scheme 12. Synthesis of Pentacarbonyltungsten Complex 24

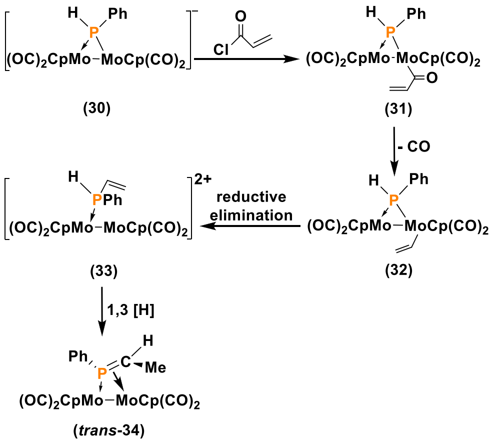


Scheme 13. Synthesis of Tetracarbonylmolybdenum Complex 29[a]



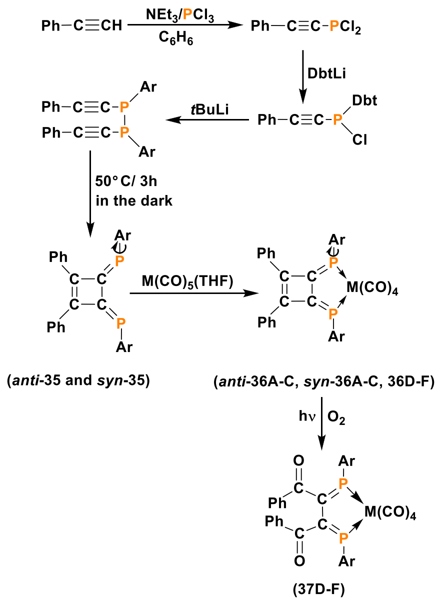
[a]Mes* = 2,4,6-*t*Bu$_3$C$_6$H$_2$.

Scheme 14. Possible Reaction Pathway for the Formation of *trans*-34



acetylene into diphosphinidenecyclobutene ligand **35** (Scheme 15). Interestingly, resulting ligand **35** occurred in the form of two isomers, *syn*-**35** and *anti*-**35**. Compounds **36A-F** were obtained after addition of $M(CO)_5(THF)$.[68] Additionally, Yoshifuji et al. reported that the previously presented tetracarbonyl complexes were oxidized upon exposure to light, resulting in complexes **37D-F**.

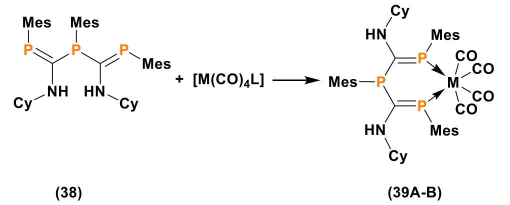
Scheme 15. Synthesis of Ligand 35 and Formation of Cr, Mo, and W Complexes 36 and Oxidation Process[a]



[a]A: M = Cr; Ar = 2,4-tBu_2-6-MeC_6H_2; B: M = Mo; Ar = 2,4-tBu_2-6-MeC_6H_2; C: M = W; Ar = 2,4-tBu_2-6-MeC_6H_2; D: M = Cr; Ar = 2,4,6-$tBu_3C_6H_2$; E: M = Cr; Ar = 2,4,6-$tBu_3C_6H_2$; F: M = Cr; Ar = 2,4,6-$tBu_3C_6H_2$.

Complexes **36D-F** were irradiated with a 500 W Xe lamp in the presence of oxygen to prepare complexes **37D-F** (Scheme 15). The free diphosphinidenecyclobutene ligand did not react with oxygen even in the presence of a triplet sensitizer.[69] Recently, Hey-Hawkins et al. synthesized Mo(0) **39A** and W(0) **39B** from diphosphaalkene ligand **38** (Scheme 16). In this reaction, only the terminal P atoms were coordinated to the M center and exhibited a *cis* relationship.[70]

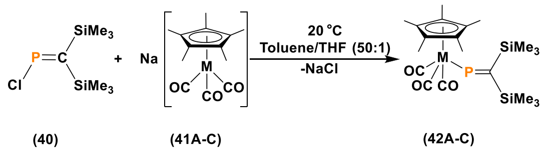
Scheme 16. Synthesis of Carbonyl Mo and W Complexes with Phosphaalkene Ligands 39A-B[a]



[a]**39A**: M = Mo, L = norbornadiene; **39B**: M = W, L = $(MeCN)_2$; Mes = 2,4,6-$Me_3C_6H_2$.

2.3.3. Tungsten. The first examples of tungsten- and molybdenum-substituted phosphaalkenes were complexes (**42A-B**) reported by Niecke et al. in 1985. The syntheses were based on the heterogeneous metalation, and **40** was reacted with **41A-C** (Scheme 17).[71]

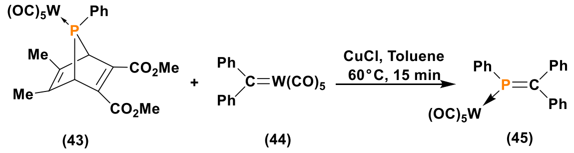
Scheme 17. Syntheses of Mo and W Phosphaalkene Complexes 42A-C[a]



[a]A: M = Mo, R = H; B: M = Mo, R = Me; C: M = W, R = H.

Mathey et al. published a report of tungsten phosphaalkene complexes stabilized with the carbonyl units. A reaction occurred between phosphinidene precursor **43** and complex **44** in the presence of copper(I) chloride, which was a catalyst that promoted the decomposition of compound **43** (Scheme 18).[72,73]

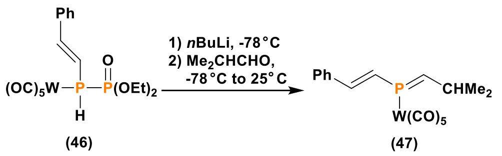
Scheme 18. Synthesis of Tungsten Phosphaalkene Complex 45



The same research group presented the synthesis of complex **47** via a phospha-Wittig approach, using compound **46** (Scheme 19). Isolated **47** reacted as a normal phosphaalkene with various reagents.[74]

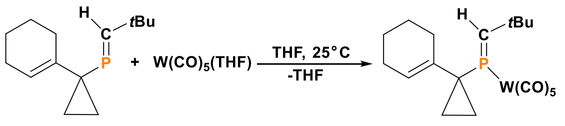
Another example of a tungsten C═P-type complex stabilized by a $[W(CO)_5]$ unit was reported by Regitz et al. with phosphaalkene prepared via an ene reaction. Alkylidene-

Scheme 19. Synthesis of W-Diene Phosphaalkene Complex 47



phosphane **48** was used as the initial material and treated with a $W(CO)_5$ fragment. The reaction of **48** with *in situ* generated pentacarbonyltungsten resulted in complex **49** (Scheme 20).[75]

Scheme 20. Synthesis of Tungsten Phosphaalkene Complex 49



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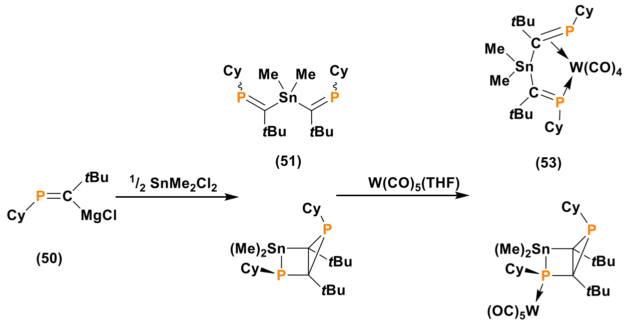
The Bertrand research group presented a method for synthesis of a dinuclear diphosphirene tungsten complexes. 1*H*-Diphosphirene was mixed with 1 equiv of $[W(CO)_4(THF)_2]$ in THF to give [1,3-bis(diisopropylamino)-1*H*-diphosphirene]$\{W(CO)_4\}_2$.[76] Jones and Richards presented the synthesis of bis(phosphaalkene) tungsten complexes involving tin compounds. First, $SnMe_2Cl_2$ was reacted with 2 equiv of **50**, and then the mixture (**51** and **52**) was treated with an excess of $W(CO)_5(THF)$ (Scheme 21). The molecular structure of major product, **53**, confirmed that the bis(phosphavinyl) ligand was coordinated to a $W(CO)_4$ fragment in an η^1-fashion through P(1) and in an η^2-fashion through the P−C double bond.[77]

Scheme 21. Two-Step Synthesis of Tungsten Phosphaalkene-Tin Complex 53



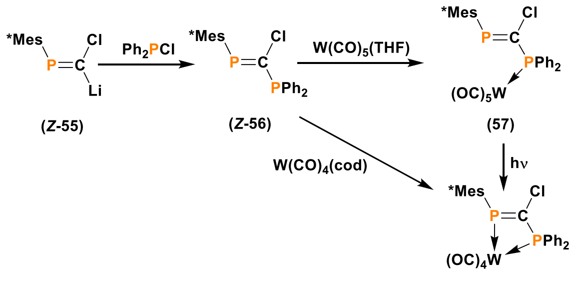
(50) (51) (52) (53) (54)

Yoshifuji et al. reported a method for synthesizing of phosphaalkene carbonyl W(0) complexes and investigated the coordination properties of **Z-56** with W(0). Compound **Z-56**, obtained after reaction of **Z-55** with Ph_2PCl, was reacted with $W(CO)_5(THF)$ and allowed to obtain corresponding complex **57**, in moderate yield, together with trace amounts of **58** (Scheme 22).

Complex **58** was synthesized from **Z-56** and $W(CO)_5(cod)$. Interestingly, complex **58** was also quantitatively obtained by photoirradiation of **57**.[78] Another example of synthesis of the W phosphaalkene compound was air-stable **60** with fluorenylidene unit. The desired compound was synthesized by the reaction of **59** with $W(CO)_5(THF)$ (Scheme 23).[79−81]

Yoshifuji et al. also investigated a chelated W(0) complex containing a P=C−P=S ligand, and the two resulting complexes differed in the coordination mode of the P-substituent (**Z-62A**: P=C 319.0 ppm, $^1J_{PW}$ = 290 Hz, P(S)Ph_2 48.4 ppm, or **Z-62B**: P=C 306.4 ppm, $^1J_{PW}$ = 280 Hz, P(S)Ph_2 77.3 ppm, $^2J_{PP}$ = 145 Hz) (Scheme 24).[82,83] A synthesis resulting in platinum complexes is described in section 2.7.2[82]

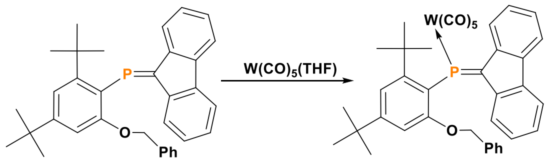
Scheme 22. Synthesis of Phosphaalkene Carbonyltungsten(0) Complexes 57 and 58[a]



(Z-55) (Z-56) (57) (58)

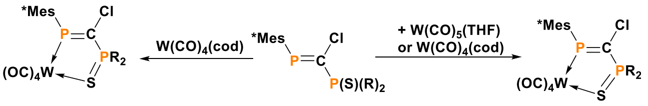
[a]Mes* = 2,4,6-$tBu_3C_6H_2$; cod = cycloocta-1,5-diene.

Scheme 23. Synthesis of Fluorenylidenephosphine Tungsten Complex 60



(59) (60)

Scheme 24. Reactions of Z-61A-B with Tungsten(0) Carbonyls[a]

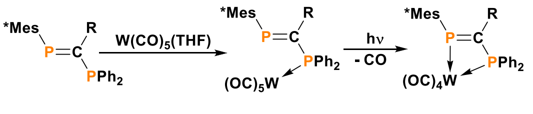


(Z-62A) (Z-61A-B) (Z-62B)

[a]A: Ph; B: $NiPr_2$ Mes* = 2,4,6-$tBu_3C_6H_2$; cod = cycloocta-1,5-diene.

Another example of preparation of W(0) complexes involved the reactions of compound ***E*-63A-B** with $W(CO)_5(THF)$. Bulky substituent (Mes*) direct carbonyl compound to coordinate phosphorus with smaller substituents (PPh_2). After irradiation of complexes **64A-B**, compounds **65A-B** were afforded by release of one CO unit (Scheme 25).[88,89]

Scheme 25. Preparation of Tungsten(0) Complexes 64A-B and 65A-B[a]



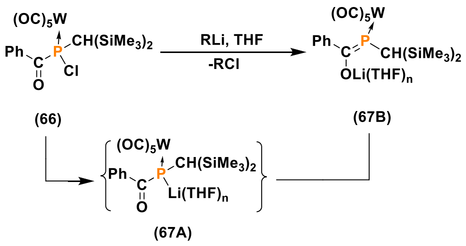
(E-63A-B) (64A-B) (65A-B)

[a]A: R = Me; B: R = $SiMe_3$; Mes* = 2,4,6-$tBu_3C_6H_2$.

After over 25 years, Streubel et al. reported the reactions of compound **66** with organolithium compounds RLi (R = Me, *n*Bu, or *t*Bu) led to selective preparation of phospha-enolate complex **67B** (Scheme 26). The probable mechanism of the reaction involved transient species **67A**, which rapidly rearranged to thermodynamically more favored isomer **67B**.

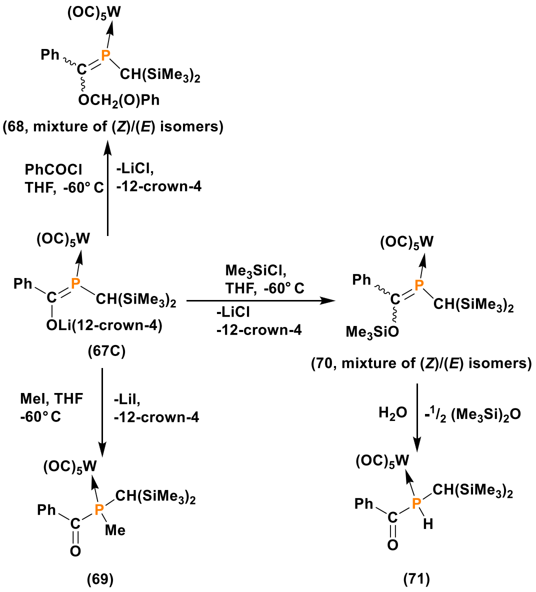
https://doi.org/10.1021/acs.organomet.2c00379

Scheme 26. Synthesis of Phosphaalkene Tungsten Complex 67B



Interestingly, if the reactions were carried out in the presence of 12-crown-4, then complex **67C** was obtained with the lithium ion coordinated to the crown ether. Both complexes **67B** and **67C**, can be considered as P analogous of metal enolates.[84,85] For confirmation, the reaction of complex **67C** with various electrophiles was examined (Scheme 27).

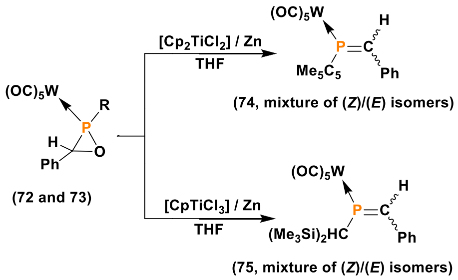
Scheme 27. Reactivity of 67C towards PhCOCl, MeI, and Me_3SiCl



The reaction of compound **67C** with benzoyl chloride led to selective formation of a mixture of *Z*/*E*-phosphaalkene complexes **68**. Complex **67C** was also treated with methyl iodide to provide *P*-methyl-substituted complex **69**. To examine the effect of the transition metal on the reactivity, compound **67C** was reacted with trimethylsilyl chloride. The main product was complex **70**, which was formed as two isomers (*Z* and *E*), and after treatment with small amounts of water, selective formation of complex **71** was observed.[86]

Streubel's research group also presented a synthetic route to similar phosphaalkene tungsten complexes by deoxygenation of coordinated oxaphosphiranes. Oxaphosphirane complexes **72** and **73** were reacted with $[TiCp_2Cl]$ or $[TiCpCl_2]$, which were prepared *in situ* and allowed to form two major products, **74** and **75**, as mixtures of *E*/*Z* isomers in ratios of 56:44 and 29:71, respectively (Scheme 28).[87]

Scheme 28. Synthesis of *E*/*Z* Phosphaalkene Complexes 74 and 75[a]

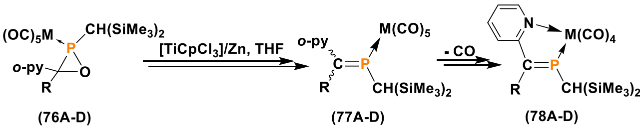


[a] **74**: R = C_5Me_5; **75**: R = $CH(SiMe_3)_2$.

A preliminary study revealed a tendency for CO elimination in the absence of an intramolecular nitrogen donor center.[88] First, isomeric phosphaalkene complexes **77A-D** were obtained from **76A-D**, using a standard methodology described previously.[87]

Surprisingly, CO substitution occurred rapidly in most cases to yield chelate complexes **78A-D** (Scheme 29).[88] The carbonyl tungsten phosphaalkene complexes were described by Gates et al. as resulting from a phosphaalkene in equilibrium with a 1,2-diphosphetane.

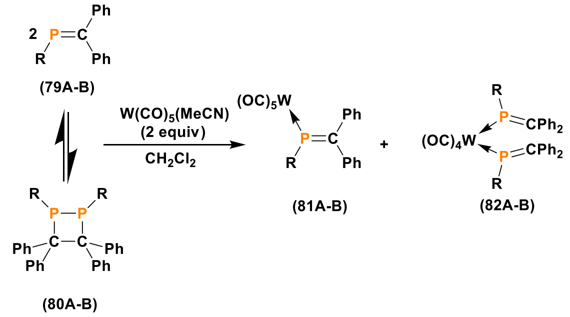
Scheme 29. Synthesis of Diastereomeric Mixtures of 77A-D and their Reactions[a]



[a] A: M = W, R = Me; B: M = W, R = H; C: M = Mo, R = H; D: M = Cr, R = H.

A solution of **79** and **80** was reacted with $W(CO)_5(MeCN)$ and form complexes **81** and **82** (Scheme 30).[89] Boeré and Masuda reported a synthetic protocol for Mo phosphaalkene complexes **84A-B**, using phosphaamidines (**83**) and $Mo(CO)_6$. The same reactions of $Cr(CO)_6$ and $W(CO)_6$ led to decomposition. However, complexes **85A** and **86A** were formed in a reaction with photochemically produced $M(CO)_5(THF)$ (Scheme 31).[90]

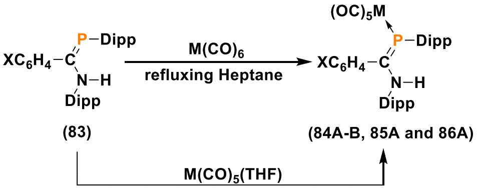
Scheme 30. Synthesis of Carbonyltungsten Mono- and Diphosphaalkene Complexes[a]



[a] A: R = Ph; B: R = *o*-Tol.

2.4. Group 7 Elements. The literature describes complexes of rhenium with a C═P bond or complexes supported by a diphosphine ligand[91−94] and a few examples of complexes with a phosphaalkene ligand. In the case of manganese, there are several interesting reports that present

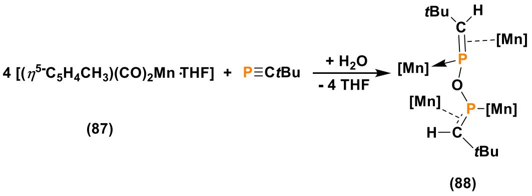
Scheme 31. Synthesis of Mo, W, and Cr Phosphaalkene Complexes 84A-B, 85A, and 86A[a]



[a] **84**: M = Mo; **85**: M = Cr; **86**: M = W; A: X = Me; B: X = OMe; Dipp = 2,6-iPr$_2$C$_6$H$_3$.

different types of metal-phosphaalkene ligand coordination. In 1986 Weber et al. reported metallophosphaalkene Re complex obtained in reaction of pivaloyl chloride and disilylated phosphines. From the series of planned complexes, two were isolated as single crystals (Z)-[(η^5-C$_6$Me$_5$)(CO)(NO)ReC(OSiMe$_3$)=PtBu] and (E)-[(η^5-C$_5$H$_5$)-(CO)(NO)Re−C(OSiMe$_3$)=PtBu]. Complexes differ in configuration (Z or E) at C=P bond, and this was probably due to the steric bulkiness of the ligand on the Re atom (C$_6$Me$_5$).[95] One year later, Ziegler et al. revealed the first mention of manganese phosphaalkene complex **88**, obtained in reaction of complex **87** with phosphaalkyne (Scheme 32).[34]

Scheme 32. Synthesis of the Mn Phosphaalkene Complex 88[a]

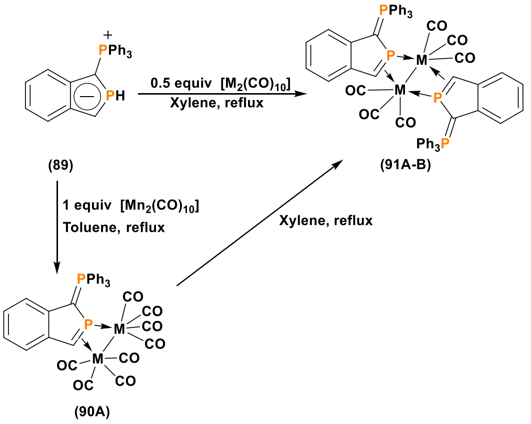


[a] [Mn]: (η^5-C$_5$H$_4$CH$_3$)Mn(CO)$_2$.

In 2003, Gudat et al. presented a synthetic route to rhenium and manganese phosphoniobenzophospholide complexes **90A** and **91A-B**. Dinuclear complexes **91A-B** were prepared by reacting **89** and carbonyl compound Mn (**91A**) and Re (**91B**). On the other hand, when the reaction was run in refluxing and with M$_2$(CO)$_{10}$, only single benzophospholide complex **90A** was observed (Scheme 33).[96]

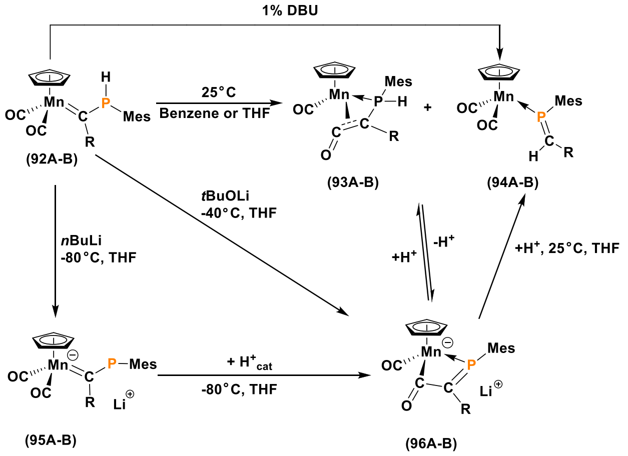
Lugan et al. reported a wide range of η^1-α-phosphinocarbene complexes of manganese. The rearrangement product from complexes **92A-B** were **94A-B** together with **93A-B**. Monocarbonyl acyl derivatives **96A-B** represent another interesting complex type, and several methods have been proposed to prepare these compounds. Addition of traces of water to a solution of **95A** in THF results in its immediate and quantitative isomerization (**96B**; for all reactions see Scheme 34). Additionally, monocarbonyl acyl anion **96A** reacted with iodine to afford a thermally unstable η^3-phosphinoketene complex [Cp(CO)$_2$Mn(η^3-C(O)C-(Ph)PIMes)], which upon warming to room temperature rearranged into the η^1-phosphaalkene complex [Cp(CO)$_2$Mn(η^1-P(Mes)=C(I)-Ph)].[97]

Scheme 33. Synthesis of Binuclear Phosphaalkene Mn and Re Complexes 91A-B[a]



[a] A: M = Mn; B: M = Re.

Scheme 34. Syntheses of η^1-α-Phosphinocarbene Complexes of Manganese[a]



[a] A: R = Ph; B: R = Me; Mes: 2,4,6-Me$_3$C$_6$H$_2$.

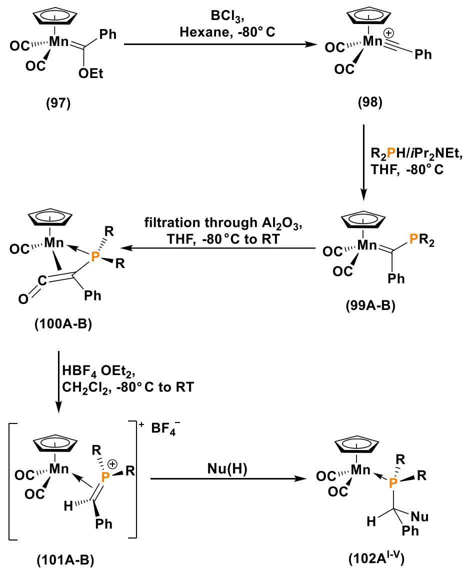
Lugan and Valyaev described the syntheses and reactivities of manganese methylene phosphonium complexes **101A-B**. Their precursor was obtained from Fischer carbene **97** and Hünig's base. In the first step, Mn carbyne compound **98** was formed, and its reaction with phosphine and DBU led to complexes **99A-B**. Next, CO insertion occurred to afford complexes **100A-B**. Finally, the protonation step led to complexes **101A-B** (Scheme 35).

These complexes were air stable and almost insensitive to moisture. On the other hand, in solution, they reacted with a wide range of nucleophiles and afforded manganese K^1-phosphine complexes **102A**$^{\text{I−V}}$. The reaction with anionic nucleophile (Cl$^-$) as well as neutral nucleophiles (2,4,6-trimethylaniline, PPh$_3$, tetramethylthiourea) formed the corresponding products in almost quantitative yields (90−99%).[98]

2.5. Group 8 Elements. The complexes of Group 8 of elements show good catalytic properties, and their application is widespread.[99−102] In the case of phosphaalkene complexes, the number of complexes with Fe or Os atoms is quite limited, but in the case of Ru, the properties are better known.

2.5.1. Iron. One example is the η^1-P complex with the formula (η^1-Me$_5$C$_5$)[(CO)$_4$Fe]P=C(SiMe$_3$)$_2$, which resulted from the reaction of (η^1-Me$_5$C$_5$)P=C(SiMe$_3$)$_2$ with Fe$_2$(CO)$_9$. In the next step, photolysis led to the complex [Fe-{η^1-P=C(SiMe$_3$)$_2$}{η^5-Me$_5$C$_5$}(CO)$_2$] which is metallophosphaalkene type. The metathetical reaction of (SiMe$_3$)$_2$C=PCl with K[Fe{η^5-Me$_5$C$_5$}(CO)$_2$] led to the

Scheme 35. Synthesis of Cationic Manganese Methylenephosphonium Complexes 101A-B and Reactivity of 101A toward Different Nucleophiles[a]

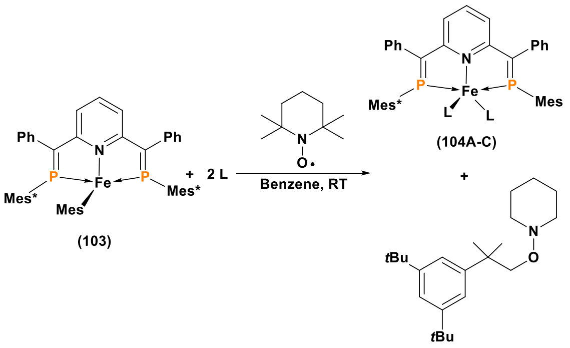


[a] A: R = Ph; B: R = Cy; I: Nu(H) = MeO(H); II: Cl ; III: MesNH(H); IV: PPh_3; V: $(Me_2N)_2CS$.

same complex.[103] In 1986, Weber et al. reported ferriophosphaalkene complex. Metallophosphaalkenes $[Cp(CO)_2Fe{-}P{=}C(OSiMe_3)R]$ (R = Mes, Ph, or *t*Bu) were obtained in reaction of iron disilylphosphane and with acid chlorides.[104] Next, the synthesis[105] and reactivity of another complex $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(NMe_2)_2]$ was demonstrated toward Me_3Al, Me_3In and Me_3Ga, and three corresponding complexes $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP\{MMe_3\}C(NMe_2)_2]$ (M = Al, In, Ga) were created.[106] An iron(I) complex was obtained after one-electron reduction of $[FeBr_2(BPEP)]$ by KC_8, MesMgBr, or $Mes_2Mg(THF)_2$.[107,108] Another example (**104A-C**) involved one-electron reductions of **103** in reactions with π-acid ligands (L = CO, RNC), TEMPO, and homolytic elimination of Mes* from a highly congested phosphorus atom. The released Mes* radical combined with TEMPO (Scheme 36).[109]

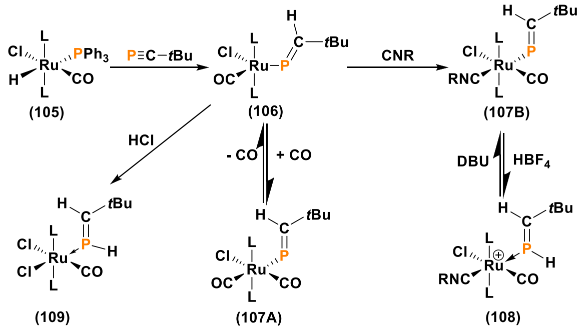
2.5.2. Ruthenium. Hill and Jones et al. reported method of stabilization of phosphaalkene using transition metals. In hydrometalation of phosphaalkynes, they obtained complex **106** from complex **105**. Reaction of **106** with CO led to complex **107A**, while reaction with CNR led to **107B**. Treating **107B** with $HBF_4{\cdot}Et_2O$ provided cationic **108**. The protonation of **107B** was reversed upon treatment with DBU. Addition of HCl to metallaphosphaalkene yielded a neutral phosphaalkene complex **109** (Scheme 37).[110]

Scheme 36. Reduction of 103 Using π-Acid Ligands and TEMPO[a]



[a] A: L= $Me_2C_6H_3NC$; B: L = *t*BuNC; C: L = Me_3SiNC; Mes*: 2,4,6-*t*$Bu_3C_6H_2$ Mes: 2,4,6-$Me_3C_6H_2$.

Scheme 37. Syntheses of Ruthenium Complexes with C═P Ligands[a]

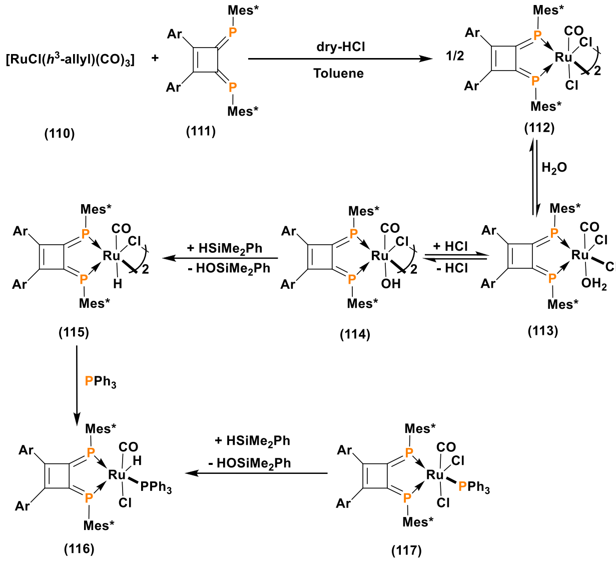


[a] R = 2,6-$Me_2C_6H_3$; L = PPh_3.

In next work they presented reaction of complex **106** with MeI and afforded $[Ru(MeP{=}CH\textit{t}Bu)Cl(I)(CO)(PPh_3)_2]$. Treatment of **106** with HCl or methylation of P atom caused significant shift in NMR spectrum from 450.4 to 187.9 ppm and 225.1 ppm, respectively.[111] Ozawa et al. reported the reduction of **112** in water with $HSiMe_2Ph$, and as a result, they achieved **115**. Complex **112** was obtained in reaction of **110** and DPCB-OMe ligand **111** and next was treated with dry-HCl.

Complex **112** was smoothly converted into **115** and then reacted with phenylacetylene. Compound **113** was aqua complex which served as an intermediate. Additionally, **115** reacted with PPh_3, and **116** was obtained, which was also directly synthesized from **117** (Scheme 38).[112] The reactions

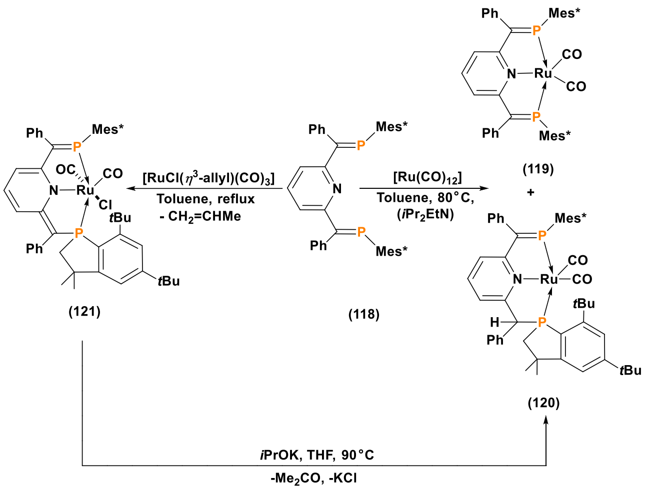
Scheme 38. Synthesis of Ruthenium Complexes with a DPCB Ligand[a]



[a] Mes*: 2,4,6-*t*$Bu_3C_6H_2$; Ar: *p*-MeO-Ph.

of diphosphaalkene ligand **118** with $[Ru_3(CO)_{12}]$ or $[RuCl(\eta^3\text{-allyl})(CO)_3]$ provided three complexes (**119−121**; Scheme 39). The addition of excess Pr_2EtN (100 equiv) prevented formation of **120**, and **119** was isolated separately.

Scheme 39. Syntheses of Ru-BPEP Complexes[a]

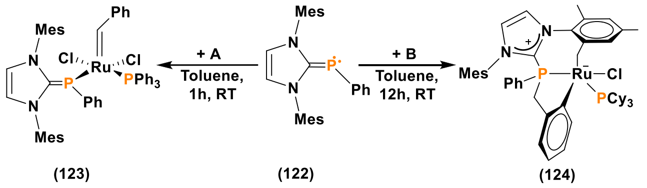


[a]Mes* = 2,4,6-$tBu_3C_6H_2$.

Additionally, the reaction of **121** with *i*PrOK led to formation of **120**.[113] An example of Ru complexes reactivities were shown by the work of Crossley et al. on the ambiphilic nature. Reactions leading to functionalization of P center used both electrophiles and nucleophiles. Reactions of a ruthenaphosphaalkenyl complex with Li(pz′) or $K[HB(pz')_3]$ (pz′ = pz, pz*) led to a rare example of an η^2-phosphaalkene complex of Ru(0) and the first example of a *P*-pyrazolylphosphaalkene. On the other hand, in a reaction with electrophile PhHgCl, the phosphorus atom was metallated, and the mercurio-phosphaalkene complex was formed.[114] Larocque and Lavoie reported the reaction of **122** with the Grubbs first-generation ruthenium benzylidene complexes $RuCl_2L_2(CHPh)$ (L = PPh_3 and PCy_3).

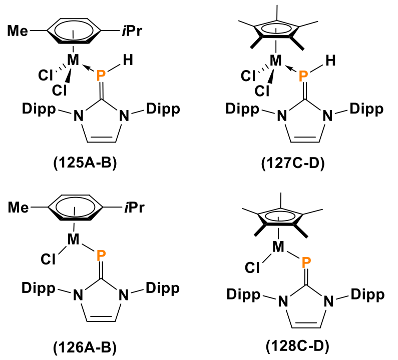
In the reaction with $RuCl_2(PPh_3)_2(CHPh)$, product **123** exhibited distorted square-pyramidal coordination, with a rare *cis* chloride arrangement without other chelating ligands. In the second case with $RuCl_2(PCy_3)_2(CHPh)$, the reaction led to an unusual decomposition product formed via sequential C−H activations **124** (Scheme 40).[14]

Scheme 40. Reactivity of IMes═PPh towards Ru Species



2.5.3. Osmium. In the 1980s, Roper reported a complex with a phosphaalkene moiety. Complex $[Os(P{=}C[O]CF_3)(CO)_2(PPh_3)_2]$ was obtained by dehydrochlorination of $[Os\{PH(C[O]CF_3)\}Cl(CO)_2(PPh_3)_2]$ with NaH.[115,116] Shortly after, Hill and Jones, described the reaction of $[OsHCl(CO)(PPh_3)_2(BTD)]$ (BTD = 2,1,3-benzothiadiazole) with $tBuC{\equiv}P$ and formation of the complex $[Os\{\kappa^1P,\kappa^1P'\text{-}P{=}CCMe_3P({=}CHCMe_3)\}Cl(CO)(PPh_3)_2]$. Formation of this complex presumably involved slow insertion of 1 equiv of $tBuC{\equiv}P$ into the osmium hydride bond, rapid insertion of a second equivalent into the Os−P bond, and subsequent metallacyclization.[117] The most recent report describes syntheses of *N*-heterocyclic complexes with the C═P moiety, which provided a series of compounds containing 4d and 5d metals (Group 8 and 9 of metals). Tamm et al. demonstrated a series of half-sandwich complexes containing, Os, Ru, Rh, and Ir. The presented Scheme 41 shows the obtained and compiled products of two main types of reactions. Complexes with phosphorus coordinated to metal center, including compounds **125** and **127**, were obtained from NHC-phosphinidene ligand and dimeric metal complexes. In the case of complexes with P-metalated complexes, also termed metallophosphaalkenes, **126** and **128**, the authors presented two reaction routes. However, reactions of $[LMCl_2\{HP(IPr)\}]$ (L = η^6-p-cymene, M = Ru, Os; L = η^5-C_5Me_5, M = Rh, Ir) with strong bases (DBU) were not selective enough. A more selective reaction was realized with $(IPr)PSiMe_3$ (NHC-phosphinidene ligand) and the dimeric metal chloride precursors underwent elimination of Me_3SiCl.

Scheme 41. NHC-Phosphinidene and NHC-Phosphinidenide Complexes[a]



[a]A: M = Ru; B: M = Os; C: M = Rh; D: M = Ir; Dipp = 2,6-$iPr_2C_6H_3$.

Osmium complexes displayed three-legged piano stool geometries around the metal atoms and included an osmium complex (**125B**). After conversion into the corresponding carbene-phosphinidenide, osmium (**126B**) and other the metals adopted two-legged piano stool geometries.[10]

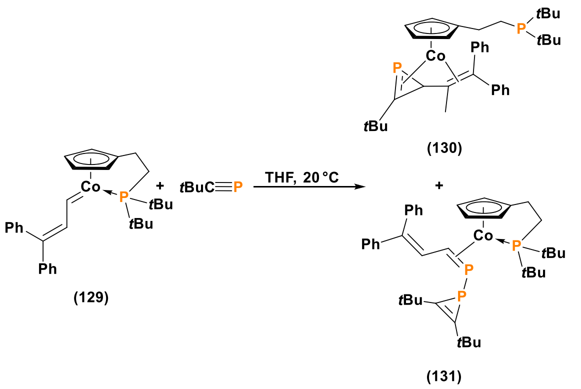
2.6. Group 9 Elements.

This group includes metals whose complexes often find many applications, including those involving catalytic[118−120] and biological[121,122] processes. Their phosphaalkene variants also exhibit many properties.

2.6.1. Cobalt. In the late 1980s, the first work was presented and described the formation of a Co(I) phosphaalkene complexes by cycloaddition of **129** and the P−C triple bond. Two products of this reaction were characterized: Complex **130** is a phosphaalkene species, while complex **131** contains a phosphaalkene ligand with additional P−P bond. In both cases, coordination of the metal to the C═P double bond involves η^2 bonding (Scheme 42).[123]

A year later, a complex with a similar coordination mode was reported by Gudat. The reaction of bis-phosphonio-benzo[*c*]-phospholide with $CpCo(C_2H_4)_2$ led to a chelate complex. Moreover, the resulting complex was reacted with dimethyl

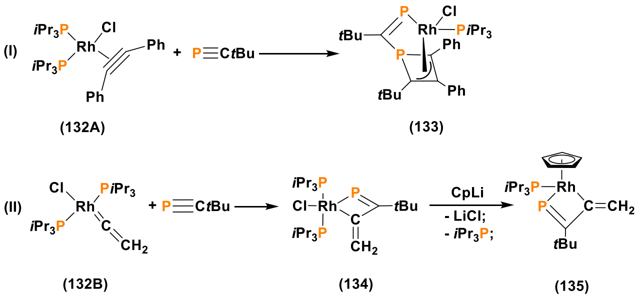
Scheme 42. Synthesis of η^2-Coordinated Cobalt(I) Complexes with Phosphaalkene Ligands



butadiene or benzaldehyde, but no Diels−Alder or phospha-Wittig product was observed.[124]

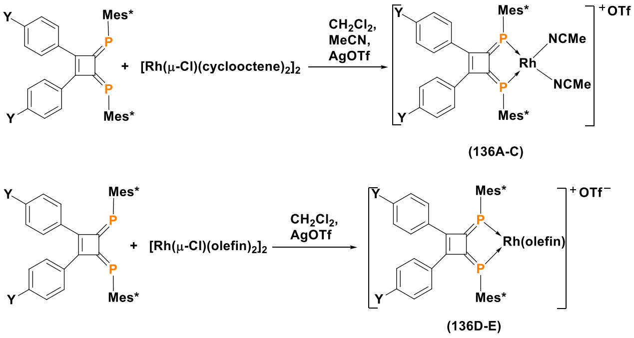
2.6.2. Rhodium. The first mention of rhodium complexes containing phosphaalkene *trans*-$RhCl(PPh_3)_2[P(Mes){=}CPh_2]$ and *trans*-$RhCl(CO)[P(Mes){=}CPh_2]_2$ was reported by Kroto and Nixon in 1981.[125] Six years later, Nixon et al. revealed a complex $[Rh_2(CO)(\eta^5\text{-}C_5Me_5\}_2\{P{=}CRC(O)C{=}P(\text{adamantly})\}]$ in which one rhodium atom (with a Cp ligand) attached in an η^2-fashion to the C=P bond, while a second rhodium (with a CO ligand) was directly bonded to both phosphorus atoms.[126] After two more years, Nixon demonstrated the first η^1-ligated halogenophosphaalkenes complexes: *trans*-$[RhCl(PPh_3)_2\{\eta^1\text{-}PCl{=}C(SiMe_3)_2\}]$ and *trans*-$[RhCl(PPh_3)_2\{\eta^1\text{-}PF{=}C(SiMe_3)_2\}]$.[127] Moreover, Binger et al. revealed the formation of the phosphaalkene complex resulting from cyclization of phosphaalkynes.[128,129] In reactions of Rh-unsaturated complexes **132A-B** with other unsaturated system (*t*BuC≡P) led to cooligomerization and formation of phosphaalkene complexes. After the reaction of **132A**, (alkyne complex) cotrimer complex **133** containing a η^3-monophosphacyclobutenyl ligand was obtained (Scheme 43, reaction (I)).

Scheme 43. Cooligomerisation of Unsaturated Rhodium(I) Complexes



Reaction of **132B** (vinylidene complex) with *t*BuC≡P underwent a [2 + 2] cycloaddition and yielded **134** complex. Replacement of the chloro ligand in **134** by a cyclopentadienyl ligand provided **135** (Scheme 43, reaction (II)).[128] Series of complexes **136A-C**, **136D**, and **136E** were reported. MeCN-substituted rhodium complexes (**136A-C**) were prepared in reaction of $[Rh(\mu\text{-}Cl)(\text{cyclooctene})_2]_2$ with DPCB−Y, and next were treated with AgOTf in the presence of MeCN (Scheme 44).

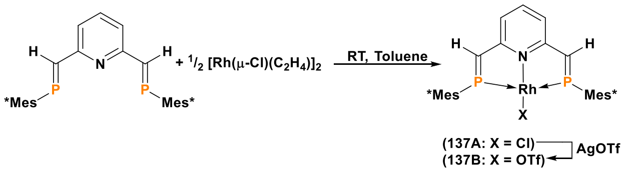
Scheme 44. Synthesis of DPCB-Y Rhodium Complexes[a]



[a] A: Y = H; B: Y = OMe; C: Y = CF_3; D: Y = H, olefin = 1,5-cyclooctadiene; E: Y = H, olefin = 2,5-norbornadiene.

Complexes **136D** and **136E** were prepared from reactions of $[Rh(\mu\text{-}Cl)(\text{olefin})_2]_2$ $[(\text{olefin})_2$ = 1,5-cyclooctadiene (cod), norbornadiene (nbd)] with DPCB−Y. Analogous complexes (**136_Pd**) showing catalytic properties were prepared for Pd species.[130] In addition to previous complexes reported by Ozawa et al., they examined Rh(I) complexes bearing PNP ligands in the reactions of *α*,*β*-unsaturated ketones. The reaction of PNP ligand with $[Rh(\mu\text{-}Cl)(C_2H_4)_2]_2$ gave **137A**. In the next step, **137A** was converted to cationic rhodium triflate **137B** by treatment with AgOTf (Scheme 45).[131]

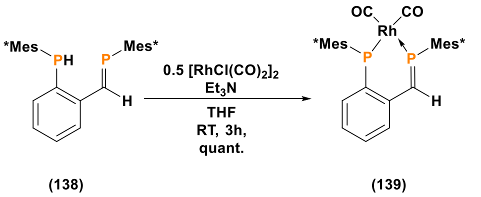
Scheme 45. Syntheses of PNP Rhodium Complexes 137A-B



Several years later, Tokitoh et al. presented a rhodium carbonyl complex with a bidentate phosphaalkene−phosphido ligand.[132] The obtained compound contained a ligand analogous to the P,N-chelating ligand reported earlier.[133] Complex **139** was afforded in a reaction of protonated phosphaalkene ligand **138** with 0.5 equiv of $[RhCl(CO)_2]_2$ in the presence of triethylamine. Product **139** was completely stable to air and moisture (Scheme 46).[132]

The newest face of Rh(I) phosphaalkene complexes was reported by Hering-Junghans et al. in 2022. They showed synthetic protocol for Rh(I) bisphosphaalkene complexes, using as initial source, the respective P,N-ligands. Compound **140** was combined with $[Rh(\mu\text{-}Cl)(cod)]_2$ and give complex **141**. The reaction between **142** and $[Rh(\mu\text{-}Cl)(cod)]_2$ had to

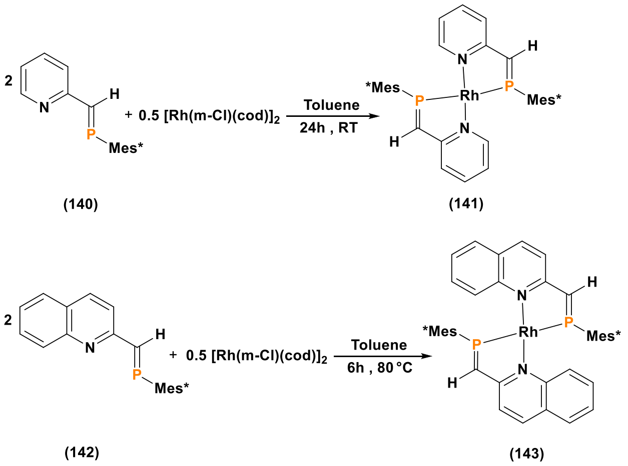
Scheme 46. Synthesis of Rh(I) with Phosphaalkene−Phosphido Ligand 139[a]



[a] Mes* = 2,4,6-$tBu_3C_6H_2$.

be heating, and after that provided complex **143** (Scheme 47).[134]

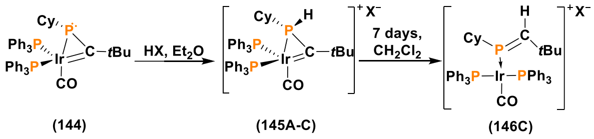
Scheme 47. Synthesis of Rh(I) Phosphaalkene Complexes 141 and 143[a]



[a]Mes* = 2,4,6-tBu$_3$C$_6$H$_2$; cod = cycloocta-1,5-diene.

2.6.3. Iridium. Similar to rhodium complexes, organoiridium compounds are of great interest and have a wide range of applications in catalysis and as anticancer agents.[135−138] Jones et al. presented one of the first syntheses of an iridium complex with a C═P-containing ligand, which resulted from a reactivity study of an iridaphosphirene complex.[139] The synthetic route began with the reaction of iridaphosphirene complex **144** and acids. Cationic phosphaalkene complex **146C** was formed from the **145C** by way of 1,2-hydrogen migration (Scheme 48).[140]

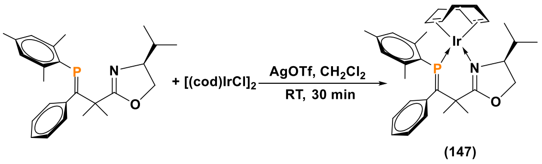
Scheme 48. Synthesis of Ionic Iridium-Phosphaalkene Complex 146C[a]



[a]A: X$^-$ = CF$_3$SO$_3$$^-$; B: X$^-$ = CF$_3$CO$_2$$^-$; C: X$^-$ = BF$_4$$^-$.

Another example of cationic species are Ozawa et al., iridium(III) complexes bearing phosphaalkene and 2-pyridylphenyl ligands. The DPCB-CF$_3$ ligand acted as a particularly effective π-acceptor to cause bluish-green luminescence at 492 nm.[141] Trio, Dugal-Tessier, Dake, and Gates reported the reaction of a phosphaalkene ligand with [(cod)IrCl]$_2$ and AgOTf (Scheme 49), and their main goal was to create a P(sp^2)-based compound that could be used in asymmetric catalysis. The first example of a new class of enantiomerically pure phosphaalkenes was presented, and it was applied as a bidentate ligand in iridium complex **147**.[142]

Scheme 49. Synthesis of Cationic Iridium Complex 147[a]

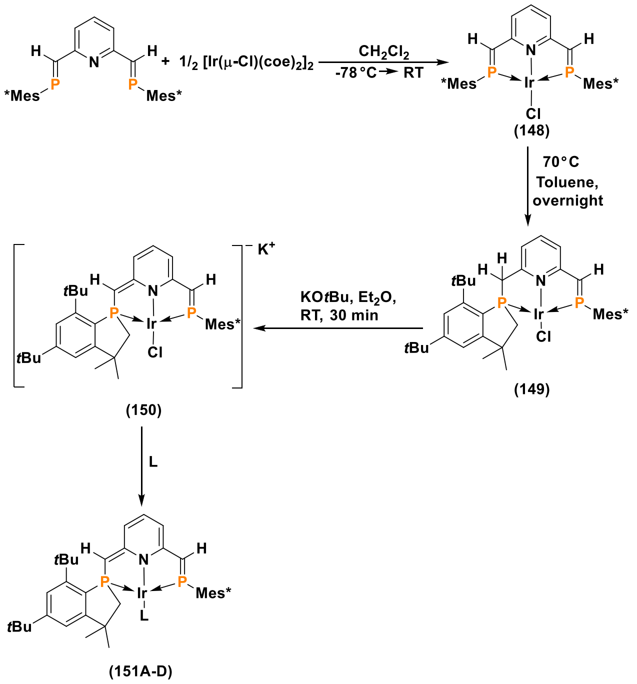


[a]cod = cycloocta-1,5-diene.

An equally interesting case was a novel PNP-phosphaalkene complex of iridium, which was employed to cleave of N−H bonds in ammonia via metal−ligand cooperation.[143] Additionally, cleavage of the N−H bond in aniline was subject of mechanistic investigations using kinetic and theoretical methods.[144] Iridium complexes were also used for cleavage of a C−H bond in acetonitrile.[145] Ozawa et al. reported the synthesis and catalytic use of the **148**. Heating of **148** led to selective formation of **149**.

The reaction of **149** with tBuOK proceeded via deprotonation at the benzylic position to afford **150** with a dearomatized PPEP* ligand. Additionally, deprotonation also occurred with other bases, such as tertiary amines. Finally, ligand displacement reactions of **150** with CO, tBuNC, PMe$_3$, and PPh$_3$, gave neutral complexes **151A-D** (Scheme 50).[143] Unfortunately isolation was difficult by removing the [K(18-crown-8)]Cl. Therefore, the synthesis of **151A-D** on a preparative scale was performed with K[IrCl(PPEP*)] in situ generated from **150**. This one-pot synthesis of **151A-D** was carried out from **149**.[146]

Scheme 50. Synthesis of Iridium Complexes with PPEP and PPEP* Ligands[a]



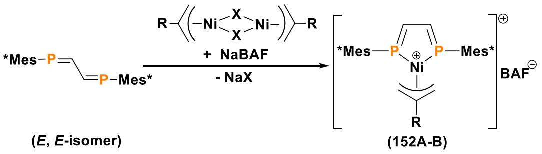
[a]A: L = CO; B: L = tBuNC; C: L = PMe$_3$; D: L = PPh$_3$; Mes* = 2,4,6-tBu$_3$C$_6$H$_2$; coe = cyclooctene.

2.7. Group 10 Elements.

In discussing Group 10, the metals from this group form a large series of complexes with catalytic properties.[147−150] After considering the material related to complexes with C═P ligands, it can be boldly stated that palladium complexes have attracted the most attention.

2.7.1. Nickel. Several papers have been published, particularly in the 1980s and 1990s.[151−153] One of the examples is that of Bickelhaupt et al., who reported two complexes of Ni(0) exhibiting η^1- and η^2-coordination modes for phosphaalkene ligands.[154] Cowley, Jones et al. demonstrated the η^2-phosphaalkene complex $(Me_3P)_2Ni$-$[(Me_3Si)_2C{=}PC(H)(SiMe_3)_2]$ a square-planar geometry for nickel.[155,156] Many years later, Ionkin et al. reported the catalytic properties of nickel catalysts (**152A-B**) bearing P,P-ligands with two sp^2-hybridized phosphorus atoms (Scheme 51).[157]

Scheme 51. Synthesis of Nickel Complex (152A-B) with Diphosphaalkene Ligand[a]

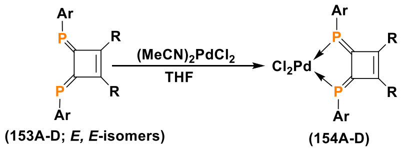


[a]A: R = H, X = Cl; B: R = CO_2Me, X = Br; BAF = B[3,5-$CF_3)_2C_6H_3]_4$; Mes* = 2,4,6-tBu$_3C_6H_2$.

Nakajima, Ozawa et al. shared research on the reactivity of nickel complexes with N,P-chelating phosphaalkene ligands. The mentioned complex $[Ni(Br)(\mu\text{-}Br)(PEP)]_2$ reacted with $R_2Mg(THF)_2$ and yielded three types of nickel complexes, depending on the magnesium substituents and temperature: a bridged Ni(I) dimer with two μ-Br $[Ni(\mu\text{-}Br)(PEP)]_2$, $[NiR_2(PEP)]$ (R = Me, Me_3SiCH_2), and [Ni(Mes*)(Br)-(PEP*)].[158]

2.7.2. Palladium. Syntheses of palladium complexes with P=C ligand have been of great interest for many years, and these complexes are often presented alongside those containing Pt.[159,160] Yoshifuji et al. presented four corresponding dichloropalladium complexes **154A-D** obtained from **143A-D** ligands and $(MeCN)_2PdCl_2$ (Scheme 52).[161]

Scheme 52. Synthesis of Palladium(II) Phosphaalkene Complexes with DPCB Ligand[a]

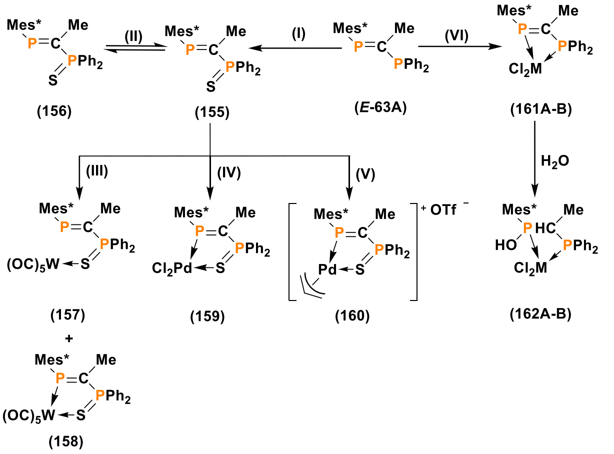


[a]A: R = H; B: R= $SiMe_3$; C: R = Ph; D: R = tBu; Mes* = 2,4,6-tBu$_3C_6H_2$.

Platinum complexes bearing four kinds of DPCB-Y ligands (Y = OMe, H, CF_3, $(CF_3)_2$) were prepared by ligand displacement from $[PtMe_2(\mu\text{-}SMe_2)]_2$ with DPCB-Y. On the other hand, Pd(II) phosphaalkene complexes were prepared in reactions between $PdMe_2$(tmeda) or $PdMe_2$(cod) with DPCB-Y.[162] In 2003, Yoshifuji et al. reported that a 3-methyl-3,3-diphenyl-1,3-diphosphapropene derivative afforded the corresponding chelate Pd(II) complex. Compound ***E*-63A** reacted with $PdCl_2(CH_3CN)_2$ or $PtCl_2$(cod) to afford Pd(II) or Pt(II) complexes **161A-B**. Next, their reactions with H_2O led to hydrolyzed products **162A-B**.[163]

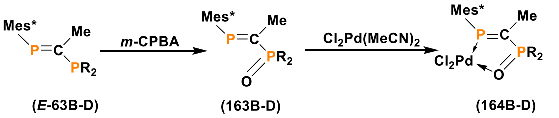
In the same year, Yoshifuji et al. a prepared the palladium(II) complex that contained the P=C–P=S system. After isomerization of **155** upon irradiation (Hg lamp) **156** was observed. Compound **155** was reacted with $PdCl_2(MeCN)_2$ and yielded complex **159**, which was not sensitive to air and moisture. The reaction of **155** with $[(\eta^3\text{-}allyl)PdCl]_2$ and silver(I) triflate afforded complex **160** (Scheme 53).[193] Additionally, two complexes **157** and **158** were obtained as a mixture.[164] Palladium(II) complexes **164A-C** with a P=C–P=O skeleton were also investigated (Scheme 54). The syntheses proceeded as follows: ***E*-63B-D** were reacted with an equimolar amount of m-chloroperbenzoic acid (m-CPBA), yielding **163B-D**. The corresponding dichloropalladium(II) complexes **164B-D** were formed in reactions of 3-oxo-1,3-diphosphapropenes with $(MeCN)_2PdCl_2$.[165]

Scheme 53. Synthesis of Pd(II), Pt(II), and W(0) Complexes[a]



[a]Mes* = 2,4,6-tBu$_3C_6H_2$. Reagents and conditions: (I) 1/8 S_8, toluene, reflux, 20 h; (II) medium-pressure Hg lamp (100 W), THF, 21 h; (III) $W(CO)_5THF$, THF, RT, 16 h; (IV) $PdCl_2(MeCN)_2$, CH_2Cl_2, RT, 0.5 h; (V) $[(allyl)PdCl]_2$, AgOTf, CH_2Cl_2, RT, 2 h; (VI) $PdCl_2(MeCN)_2$ (A) or $PtCl_2$(cod) (B); CH_2Cl_2, 12 h.

Scheme 54. Synthesis of Complexes Palladium Complexes (164B-D) with P=C–P=O Ligand[a]

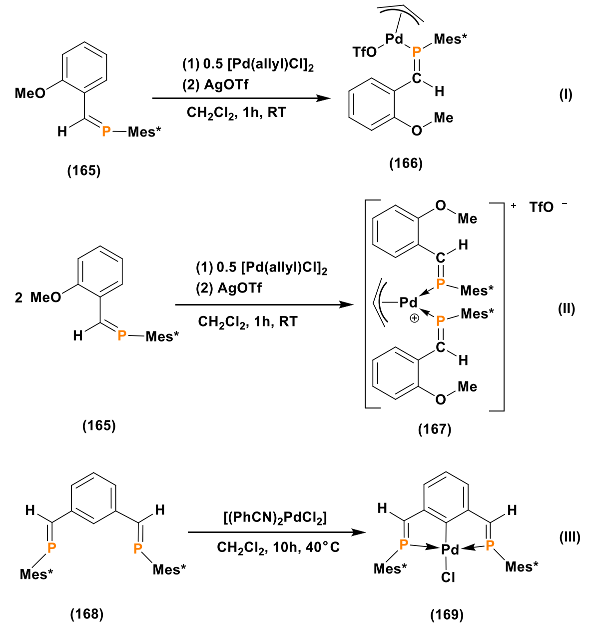


[a]Mes* = 2,4,6-tBu$_3C_6H_2$; B: R = p-MeC_6H_4; C: R = p-$MeOC_6H_4$; D: R = nBu; m-CPBA = m-chloroperbenzoic acid.

Le Floch et al. synthesized also palladium(II) phosphaalkene complexes. In synthesis of complex **166**, the starting ligand included a methoxy group at the α-position and was supposed to act as a hemilabile ligand. Reaction of ligand **165** with half equivalent of $[Pd(allyl)Cl]_2$ in the presence of AgOTf as a chloride abstractor led to formation of **166** (I). On the other hand, a reaction of two equivalents of this ligand **165** with half equivalent of $[Pd(allyl)Cl]_2$ afforded complex **167** (II).[166] Finally, complex **169**, which was previously reported,[167] was prepared by heating the **168** with $[(PhCN)_2PdCl_2]$ (III; Scheme 55).[166]

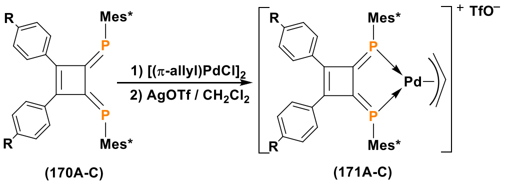
Palladium complexes with similar formulas were prepared from the DPCB ligand (**170A-C**), which provided C=P bonds and (allyl)palladium complexes.[168−170] One example is the reaction of DPCB ligand, $[(\pi\text{-}allyl)PdCl]_2$, and silver triflate, which gave (π-allyl)(DPCB)palladium complexes **171A-C** (Scheme 56).

Scheme 55. Three Syntheses of Phosphaalkene Palladium(II) Complexes with Different P═C Ligands[a]



[a]Mes* = 2,4,6-$t\mathrm{Bu}_3\mathrm{C}_6\mathrm{H}_2$.

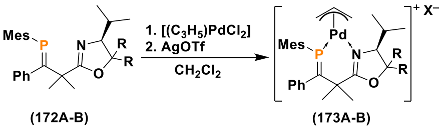
Scheme 56. Synthesis of a Cationic Pd(II) Complexes 171A-C[a]



[a]A: R = H; B: R = −OMe; C: R = $-\mathrm{CF}_3$; Mes* = 2,4,6-$t\mathrm{Bu}_3\mathrm{C}_6\mathrm{H}_2$.

Gates et al. reported the first application of phosphaalkene PhAk-Ox-palladium allyl complexes **173A-B**. These complexes were obtained in reaction of chiral P(sp^2),N(sp^2) ligands **172A-B** with [(C_3H_5)$PdCl_2$] and AgOTf (Scheme 57).[171]

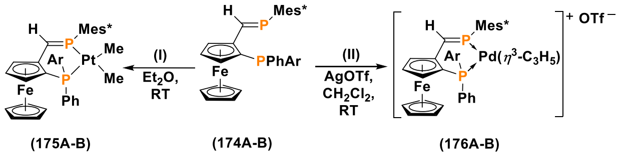
Scheme 57. Synthesis of Ionic Palladium(II) Complexes 173A-B[a]



[a]A: R = H, X = OTf; B: R = Me, X = BF_4.

Ozawa et al. demonstrated the reaction of [Fc(CH═PMes*)PAr_2] (PAr_2 = **174A** = PPh_2; **174B** = P(1-naphthyl)-Ph) with 0.5 equiv of [$PtMe_2$(μ-SMe_2)$]_2$, which yielded complexes **175A-B**. On the other hand, the reactions of **174A-B** with 0.5 equiv of [Pd(η^3-allyl)(μ-Cl)$]_2$ in the presence of AgOTf yielded corresponding π-allyl complexes **176A-B** (Scheme 58).[172]

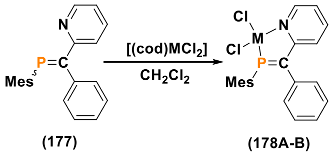
Scheme 58. Preparation of Palladium and Platinum Ferrocenes with Phosphaalkene Ligands[a]



[a]A: Ar = Ph; B: Ar = Np (1-naphthyl); (I): + 0.5[$PtMe_2$(μ-SMe_2)$]_2$; (II): + 0.5[Pd(η^3-allyl)(μ-Cl)$]_2$; Mes* = 2,4,6-$t\mathrm{Bu}_3\mathrm{C}_6\mathrm{H}_2$.

In 2007, Gates et al. reported another P,N-chelate-type ligand **177** used to form Pd(II) and Pt(II) complexes containing phosphaalkene moieties **178A-B**. Reactions of the phosphaalkene with (cod)$PdCl_2$ or (cod)$PtCl_2$ gave related complexes (Scheme 59).[173]

Scheme 59. Syntheses of Pd(II) and Pt(II) Complexes with P,N-Chelate Ligands[a]



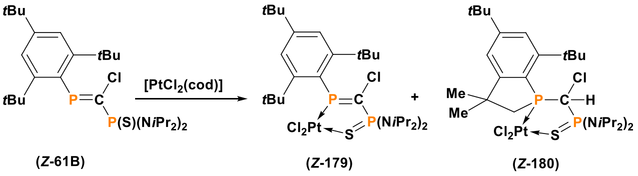
[a]A: M = Pt; B: M = Pd; Mes = 2,4,6-$\mathrm{Me}_3\mathrm{C}_6\mathrm{H}_2$; cod = cycloocta-1,5-diene.

2.7.3. Platinum. Despite their excellent catalytic properties,[174−177] platinum complexes of phosphaalkene are not as common as the analogous palladium complexes. The first reports of Pt-containing complexes appeared in 1982. Nixon et al. described syntheses of the Pt(II) phosphaalkene complexes *trans*-[$PtCl_2$(PEt_3)(Mes)P═CPh_2] and *cis*-[PtX_2{(Mes)P═CPh_2}$_2$] (X═Cl, I, Me).[178] Next, the platinum(0) complexes were obtained via reactions of phosphaalkenes with the corresponding Pt(PCy_3)$_2$ and Pt(PPh_3)$_2$ precursors. Two complexes were prepared, with η^1-P coordination and with η^2-P═C bonding.[179] Another example is the diplatinum complex obtained in a two-step process. First, Cl_2C═PMes* was reacted with Pt(PEt_3)$_4$, and the product [(Cl)(PEt_3)$_2$Pt(μ-C(Cl)═PMes*)] was isolated. Second, addition of another equivalent of Pt(PEt_3)$_4$ led to [(Cl)(PEt_3)Pt(μ-C═PMes*)-Pt(PEt_3)$_2$(Cl)].[180] Angelici et al. reported the synthesis and reactivity of the η^1-phosphavinyl complex *cis*-Cl(Et_3P)$_2$Pt[C-(Cl)═PN($SiMe_3$)$_2$]. This complex isomerized to the *trans* compound, and in reaction with Pt(PEt_3)$_2Cl_2$ and Na/benzophenone ketyl, it provided the η^1,η^2-bridged cyaphide complex Cl-(Et_3P)$_2$Pt(μ-η^1,η^2-C≡P)Pt(PEt_3)$_2$.[181] An interesting Pt(0) species [Pt(PPh_3)(Eind-BPEP)] was reported by Ozawa et al. This complex resulted from the reaction of [Pt(cod)$_2$] with ligand Eind_2-BPEP (pyridine-based) and PPh_3 (analogous complexes see Scheme 63). The authors compared the unique distorted tetrahedral geometry at Pt with homologoues complexes of Pd and Ni containing the same ligand.[182] As mentioned earlier, Yoshifuji et al. presented Pt phosphaalkene complexes with the P═C−P═S system.

Compound ***Z*-61B** reacted with $PtCl_2$(cod) to give corresponding platinum(II) complex ***Z*-179**. Additionally, another product, ***Z*-180** was also observed and isolated in very poor yield (Scheme 60). The 5-membered cycle (with phosphaindole fragment) was created with activation of C−H by intramolecular proton migration.[83] In 2008, Ozawa et al. presented Pt(0) phosphaalkene complexes **181A-D** with the DPCB ligand and proposed an interaction between the dπ

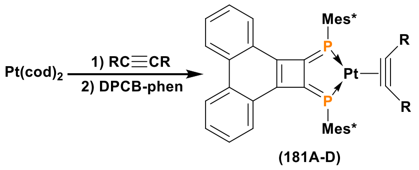
orbitals of platinum and the out-of-plane π orbitals from alkyne ligands. They obtained four Pt(0) complexes via stepwise displacement of the cod ligands (Scheme 61).[183]

Scheme 60. Reactions of Z-61B with Platinum(II) Chloride[a]



[a] cod = cycloocta-1,5-diene.

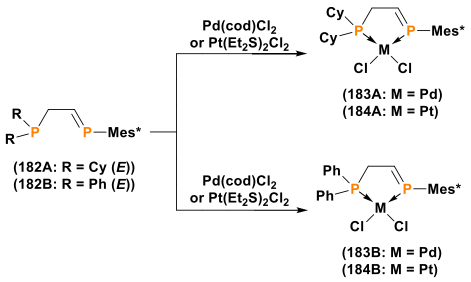
Scheme 61. Syntheses of DPCB-Pt Complexes with Alkyne Ligands[a]



[a] A: R = CO_2Me; B: R = Ph; C: R = C_6H_4-*p*-OMe; D: R = C_6H_4-*p*-NMe_2; cod = cycloocta-1,5-diene; Mes* = 2,4,6-*t*$Bu_3C_6H_2$; DPCB-phen = 1,2-bis[(2,4,6-tri-*tert*-butylphneyl)phosphinidene]cyclobuta[*l*]phenantrene.

Cain et al. published a short communication on hybrid phosphine-phosphaalkene ligands (**182A-B**) contained in Pt(II) and Pd(II) complexes. Ligands were prepared via the phospha-Wittig reaction and then reacted with Pd (**183**) and Pt (**184**) species such as M(cod)Cl_2 or M$(Et_2S)_2Cl_2$ (Scheme 62).[184]

Scheme 62. Syntheses of Pt and Pd Complexes with Hybrid Phosphine-Phosphaalkene Ligands[a]



[a] cod = cycloocta-1,5-diene; Mes* = 2,4,6-*t*$Bu_3C_6H_2$.

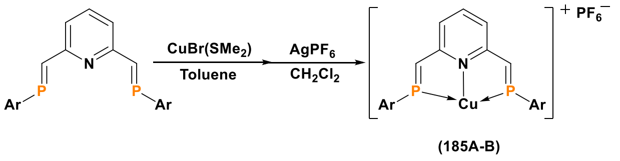
Another example came from a series of Pt(0) complexes with general formula [Pt(L)($Eind_2$-BPEP)] (L = 4-(*N,N*-dimethylamino)pyridine (DMAP); 3,5-lutidine; PMe_3; *t*BuNC; CO) these were reported by Ozawa et al., in which the synthetic method was based on the reaction of the $Eind_2$-BPEP ligand with $[Pt(cod)_2]$ and an L-ligand.[185]

2.8. Group 11 Elements.

Cu, Ag, and Au constitute an interesting group and their complexes are used in many areas. Copper complexes not only are widely used as catalysts[186] but also are of great biological and medical importance.[187−189] This also applies to complexes containing phosphorus ligands.[190,191] Similar statements can be made about the silver and gold complexes.[192−194]

2.8.1. Copper. Le Floch et al. reported syntheses of complexes with bis-phosphaalkene ligands. For all three metals, the structures of complexes with these bidentate ligands were determined for reactions of the bis-phosphaalkene ligand and $[Cu(CH_3CN)_4](BF_4)$, $AgBF_4$, and $(SMe_2)AuCl$.[195] Another series of complexes contained *N*-heterocyclic carbenes, and these were obtained from reactions with CuCl, AgCl, and $(SMe_2)AuCl$. The main products were monometallic complexes.[196] These pincer-type phosphaalkene ligands are of interest due to their stiffening properties.[197,198] Takeuchi and , Choi et al. revealed two three-coordinate Cu(I) complexes. The first complex, **185A**, was obtained from a reaction of the $Eind_2$-BPEP ligand with $CuBr(SMe_2)$ in the presence of $AgPF_6$. A second complex, **185B**, with the smaller ligand $Mes*_2$-BPEP was obtained analogously (Scheme 63).[198]

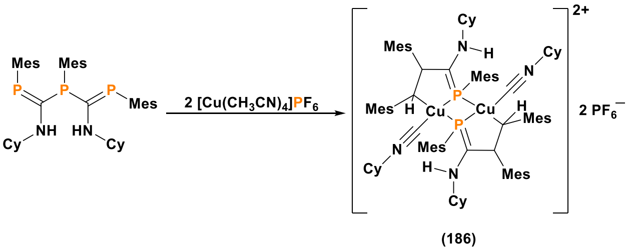
Scheme 63. Syntheses of Cu(I) Complexes with BPEP Ligand[a]



[a] A: Ar = Eind = 1,1,3,3,5,5,7,7-octaethyl-1,2,3,5,6,7-hexahydro-*s*-indacen-4-yl; B: Ar = 2,4,6-*t*$Bu_3C_6H_2$.

Hey-Hawkins et al. demonstrated the reactivity of bisphosphaalkene diamino compounds toward Mo, W and Cu complexes. The first two were described in the section on Group 6 elements (section 2.3). The reaction with copper as the $[Cu(CH_3CN)_4]PF_4$ salt led to intermolecular rearrangement with P−P bond formation and elimination of cyclohexyl isocyanide, and complex **186** was isolated (Scheme 64).[70]

Scheme 64. Synthesis of Copper(I) Complex 186[a]

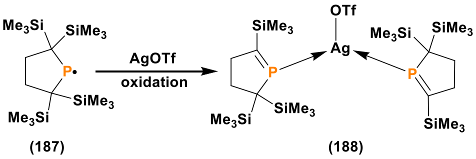


[a] Mes = 2,4,6-$Me_3C_6H_2$.

2.8.2. Silver. Among the complexes described are those with PNP-type ligands. Ozawa et al. reported complexes of Cu and Ag with C=P ligand. The Ag complex was obtained from the reaction of AgOTf with PNP, while the copper complex was obtained from the reaction of $[Cu(MeCN)_4]PF_6$ with PNP.[199] Another preparation of a Ag-containing complex used stable phosphinyl radical **187**, as reported by Ishida and Iwamoto. The oxidation of $R^H{}_2P\cdot$ with AgOTf led to a silver(I) phosphaalkene complex (**188**; Scheme 65).[200]

2.8.3. Gold. In 2006, Ito and Yoshifuji et al. reported syntheses of sterically protected digold(I)-diphosphaalkene complexes. Within a six-membered metallacycle, the P=C−

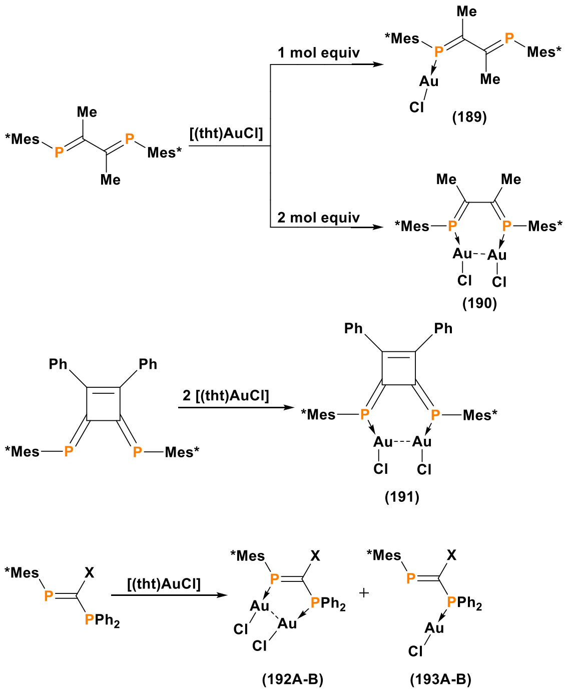
Scheme 65. Synthesis of a Phosphaalkene Silver(I) Complex 188



$C=P$ core was coordinated with two gold atoms. The results indicated on aurophilic interactions despite the steric hindrance of Mes* groups.[201] Two ligands, including diphosphabuta-1,3-diene and DPCB, were selected as source of two $P=C$ bonds, and two ligands, including 2,2-bis(methylsulfanyl)-1-phosphaethene and 1,3-diphosphapropene, were selected as single $P=C$ systems. In the reactions of (tht)AuCl (tht = tetrahydrothiophene) with different stoichiometry, these ligands were converted into complexes. The same complexes showed aurophilic interactions, depending on the ligand (Au−Au type). A number of gold phosphaalkene complexes were synthesized and isolated, including open-chain complex **189** and six-membered metallacycle **190**.

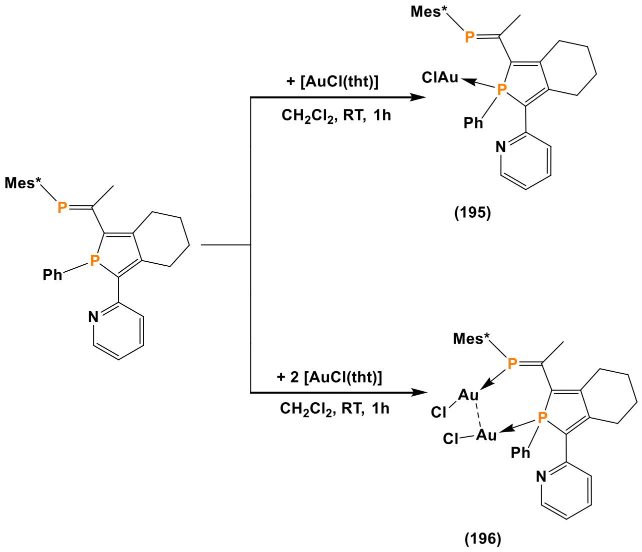
Moreover, complex **191** showed a distorted DPCB skeleton, as did mono- and digold(I) complexes **192A-B** and **193A-B** (Scheme 66). Additionally, they obtained complex [Mes*$P=C(SMe)_2$](AuCl) **194** (used in catalysis) in reaction of Mes*$P=C(SMe)_2$ with (tht)AuCl.[202] Du Mont et al. tested the reactivity of $[(i\text{PrMe}_2\text{Si})_2C=P]_2\text{NSiMe}_3$ in reactions with (tht)AuCl or $[\text{RhCl(cod)}]_2$. These reactions resulted in Au(I) and Rh(I) complexes containing the imidobis(phosphaalkene) anion $[(i\text{PrMe}_2\text{Si})_2C=P]_2N^-$.[203] Nemes et al. demonstrated an interesting approach to Au complexes with $C=P$ ligands in reaction with phosphaalkenyl(chloro)tin(II). The compound NHC−Sn(Cl)-[$C(SiMe_3)=P$Mes*] reacted with (SMe_2)-AuCl to yield the trinuclear gold complex [AuC-$(SiMe_3)=P$Mes*]$_3$.[204] The synthesis of gold complexes was presented by Ott et al. with the use of phosphole-substituted phosphaalkenes (PPAs). The presence of two phosphorus atoms with different types of hybridization ($\sigma^2\lambda^3$ and $\sigma^3\lambda^3$) may provide variable reactivity. PPAs selectively reacted with (tht)AuCl and provided coordination to phosphole phosphorus (complex **195**). Addition of another equivalent of (tht)AuCl resulted in dimetallic compound **196** with gold−gold interaction (Scheme 67).

Scheme 66. Syntheses of Gold(I) and Digold(I) Complexes[a]



[a]A: X = Me; B: X = Cl; Mes* = 2,4,6-$t\text{Bu}_3\text{C}_6\text{H}_2$; tht = tetrahydrothiophene.

Scheme 67. Coordination of AuCl to Phosphole-Phosphaalkene[a]

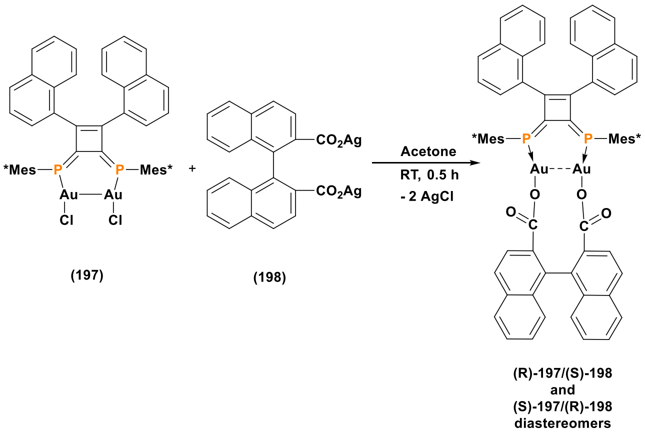


[a]tht = tetrahydrothiophene.

The authors highlighted that the Au−Au interaction causes a twist in the molecular structure which is responsible for a significant reduction in the path of conjugation.[35] In 2014, Ito and Yoshifuji et al. demonstrated various 1,2-diaryl-substituted DPCB complexes. Corresponding bis-gold(I) complexes $(\text{DPCB-Y})\text{Au}_2\text{Cl}_2$ (Y = Ph; 1-naphtyl; 2-naphthyl; *p*-biphenyl; *o*-biphenyl; *p*-MeO-Ph; cyclopropyl; cyclohexyl), and analogous to **191**, were afforded in reactions with 2 equiv of (tht)AuCl and DPCB ligands.[205] In 2016, Ito and Mikami et al. showed that bis-gold complex can be twisted into a C_2-type helical structure upon coordination of the two AuCl units. The enantiopure compound was afforded by exchanging the chloride ligands of **197** in a reaction with silver binaphthyl dicarboxylate **198** (Scheme 68).[206]

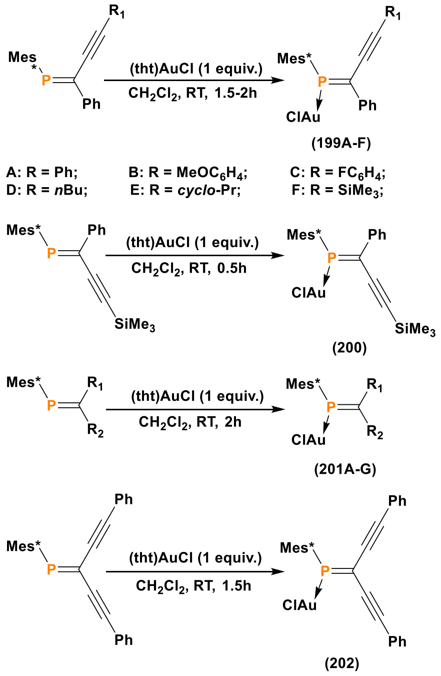
In subsequent work, Ito and Mikami et al. introduced a series of alkene-like phosphaethenes. Selected phosphaalkene compounds substituted with alkenes were prepared using palladium catalyst. Prepared 2-alkynyl-2-aryl-1-phosphaethene ligands were coordinated by chloro-Au(I) species and exhibited the π-accepting property. Complexes **199A-E**, **200**, **201A-B**, and **201D-F** were obtained in quantitative yields, while complexes **201C** and **202** were obtained in excellent yields. Complex **201G** was isolated in fair yield (Scheme 69).[207]

Scheme 68. Preparation of Digold Phosphaalkene Complexes[a]



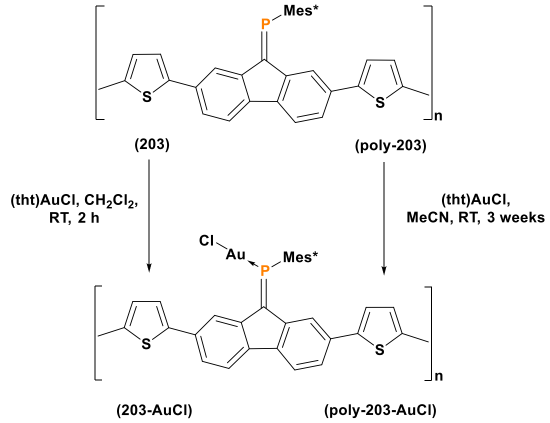
[a]Mes* = 2,4,6-$tBu_3C_6H_2$.

Scheme 69. Preparation of Mononuclear Chloro-Gold(I) Complexes 199–202[a]



[a]A: R_1 = R_2 = Ph; B: R_1 = Ph, R_2 = 4-$MeOC_6H_4$; C: R_1 = Ph, R_2 = 4-ClC_6H_4; D: R_1 = R_2 = 4-PhC_6H_4; E: R_1 = R_2 = 2-naphthyl; F: R_1 = R_2 = 2-thienyl; G: R_1 = Br, R_2 = Ph;. Mes* = 2,4,6-$tBu_3C_6H_2$; tht = tetrahydrothiophene.

Scheme 70. Preparation of a Poly-Gold Complex with a Phosphaalkene Ligand[a]



[a]tht = tetrahydrothiophene.

Orthaber et al. introduced functionalized phosphaalkene species with fluorene cores formed by the stable phospha- and arsaalkenes. These small molecules were used as substrates for electropolymerization reactions. Accessibility of a lone pair on the P atom in compounds **203** and **poly-203**, was confirmed in reactions with (tht)AuCl; this led to formation of **203-AuCl** and **poly-203-AuCl** (Scheme 70), which caused redshifts in the absorption spectrum.[208]

The next study was focused on a phosphaalkene with a heterofulvenoid core, cyclopentadithiophene, which is air- and moisture-stable. Spectroscopic studies showed low-energy transitions involving the exocyclic π*-MO of the P═C bond. Phosphaalkene complex **205** was formed via a reaction of cyclodithiophene-phosphaalkene **204** with (tht)AuCl.[209]

An expansion of this work resulted in tunable materials suitable for optoelectronic applications. Treatment of the gold complex (**206**) with $AgPF_5$ and 2,6-dimethylphenyl isocyanide or another equivalent of phosphaalkene led to formation of homoleptic complex **207** or cationic heteroleptic complex **208**. The initial Au complex slowly was decomposed by hydrolysis and formed hydrogen-bonded monometallic species **209** (Scheme 71).[210] Last interesting report described functionalization of fluorenyl phosphaalkenes with heteroaromatic substituents (bithiophene, benzothiophene, and pyridine) leading to varying reactivity and bathochromically shifted maxima and onset of low energy absorption.[80]

2.9. Group 12 Element. There are only a few examples of C═P-containing Group 12 complexes in literature, and they include Zn and Hg phosphaalkene complexes. Elements of this group are relatively soft and exhibit low melting point, and they are more electropositive than their near neighbors in the transition block.

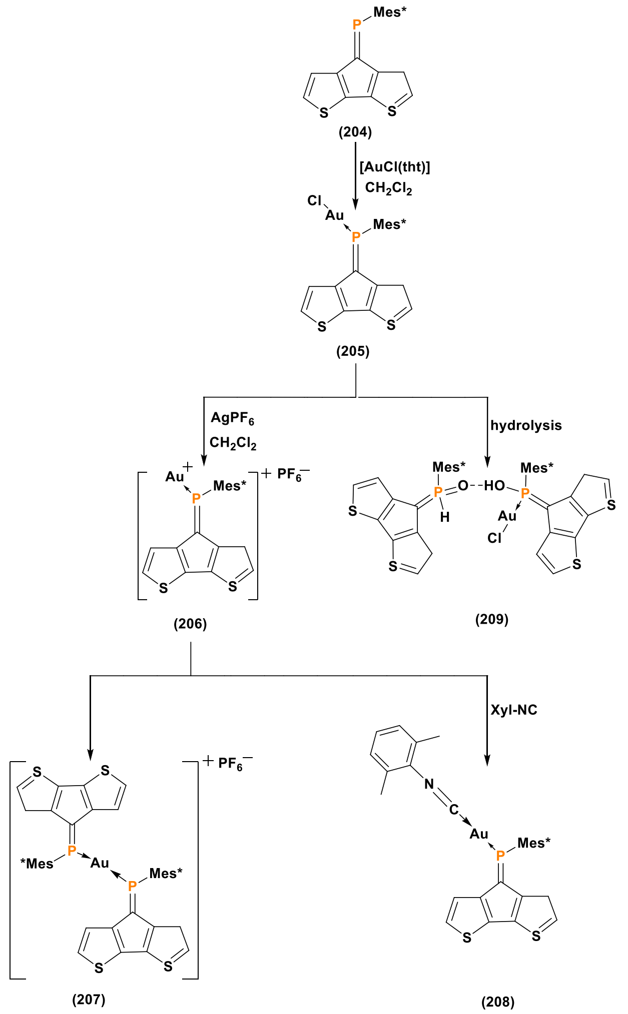
2.9.1. Zinc. Bollwein et al. reported a metathesis reaction between dilithium compound **210** and zinc dichloride. The reaction led to trinuclear zinc complex **211** (Scheme 72).

The six-membered CP_2N_2Zn ring showed a boat conformation with P–C–P angles of 120°. The reason for this conformation was probably coordination between the positively charged chloro-zinc units and the carbanions.[211]

2.9.2. Mercury. A route for synthesizing the diorganomercury phosphaalkene complexes was transmetalation of phosphaethenyllithium derivatives **212A-B** with mercury(II) chloride, which give the corresponding coupling product reported by Yoshifuji et al. Two organomercury compounds **213A** and **213B** were afforded (Scheme 73).

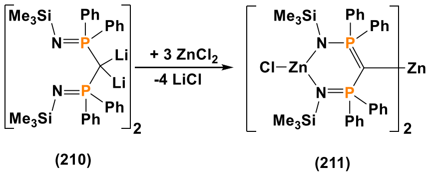
Molecular structure of **213A** revealed a straight skeleton (C–Hg–C) and perpendicularly positioned aryl groups.[212] In 2016, Grützmacher et al. described the synthesis of bis(carbenephosphinidenyl)mercury(II) complexes **215**. As a ligand, phosphinidene–carbene adduct **214** was employed. Formation of these complexes was achieved by slowly adding $HgCl_2$ to **214** (Scheme 74).[213]

Scheme 71. Reactivity of an Au Complex with a Heterofulvenoid Cyclopentadithiophene-Phosphaalkene Ligand[a]

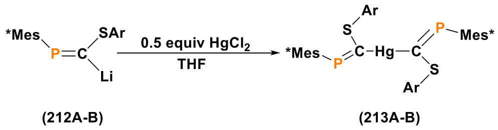


[a] Mes* = 2,4,6-tBu$_3$C$_6$H$_2$; tht = tetrahydrothiophene.

Scheme 72. Synthesis of Zinc Phosphaalkene Complex 211



Scheme 73. Transmetallation of Phosphaethenyllithium Derivatives[a]

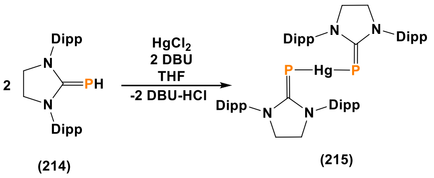


[a] A: Ar = Ph; B: Ar = Tol; Mes* = 2,4,6-tBu$_3$C$_6$H$_2$.

3. CATALYTIC PROPERTIES OF D-BLOCK ELEMENT PHOSPHAALKENE COMPLEXES

Some of the above-described complexes have been examined for their catalytic properties. Below we present those metal complexes with a phosphaalkene moieties that exhibit mentioned properties.

Scheme 74. Synthesis of a Mercury Phosphaalkene Complex 215[a]

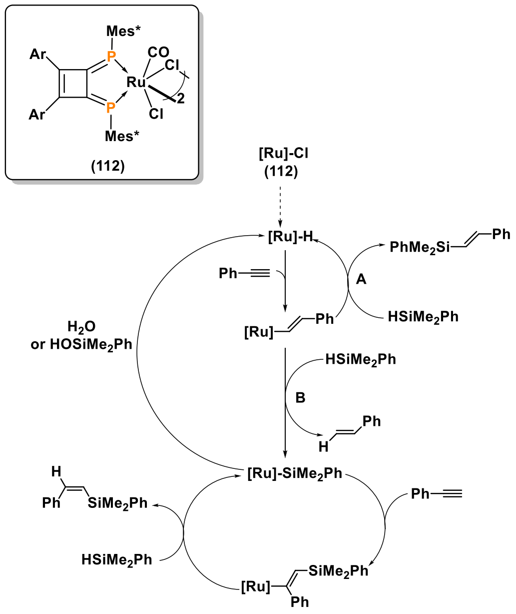


[a] Dipp = 2,6-iPr$_2$C$_6$H$_3$.

3.1. Titanium. Considering consecutively the metals of individual groups with phosphaalkene ligands, their catalytic properties start with titanium. Lavoie established that the recently obtained titanium complexes (**5A-6A**) catalyzed ethylene polymerization. This process was initiated (at room temperature and 1 atm) with the use of $CpTiCl_3$ as a benchmark catalyst. During the experiment, the titanium phosphaalkene complex converted over 165 mol of ethylene per mole of catalyst, which represented a rate of 9.3 kg PE/mol Ti/h. In summary, the titanium phosphaalkene complexes show promising activities in polymerizations of olefins under ambient and mild conditions.[54]

3.2. Ruthenium. Next in the literature reports is the use of ruthenium complex in the catalytic hydrosilylation reactions of terminal alkynes. It is known that the large majority of catalytic hydrosilylation reactions of terminal alkynes generally occur *via* *syn*-addition to afford (*E*)-alkenylsilanes.[214] The reaction of $PhC\equiv CH$ with $HSiMe_2Ph$ in the presence of ruthenium complex **112** exhibited an anti-addition to afford (*Z*)-$PhCH=CHSiMe_2Ph$ with 98% selectivity. Scheme 75 shows a proposed mechanism for catalytic hydrosilylation of phenylacetylene. Reaction A gave *E*-alkenylsilanes, and reaction B gave *Z*-alkenylsilanes, respectively. Process B gives silyl complex that is the precursor to the (*Z*)-hydrosilane. This is

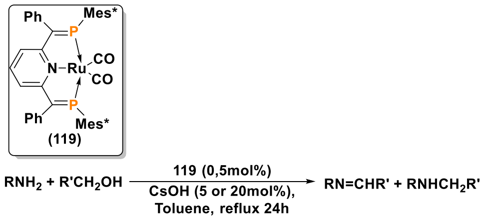
Scheme 75. Catalytic Cycle for Hydosilylation of Phenylacetylene Catalyzed by [Ru]-$SiMe_2Ph$



most likely because the DPCB ligand effectively stabilizes the electron-rich silyl complex.[112]

The *N*-alkylation of amines with alcohols has attracted much attention for synthesizing amine derivatives.[215−218] The catalytic properties of **119** were tested in this respect. The reaction proceeded via a hydrogen borrowing process, which consisted of three steps: dehydrogenation of an alcohol to aldehyde, dehydrative condensation of the aldehyde with an amine to give an imine, and hydrogenation of the imine. They described complex served as a good catalyst in forming imines as the major products with efficiencies of 60−100% (Scheme 76).[113]

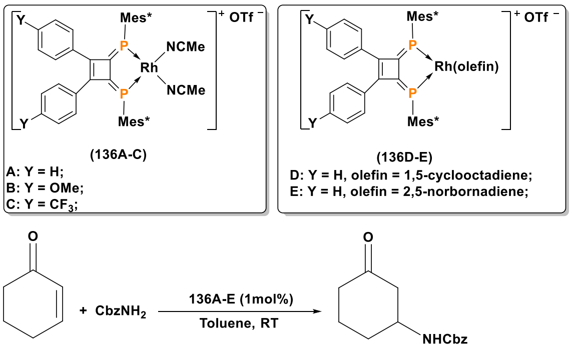
Scheme 76. *N*-Alkylation of an Amine Using Complex 119



3.3. Rhodium.

The catalytic properties were also tested toward rhodium complexes with phosphaalkene moieties. Their catalytic properties were investigated with reactions of α,β-unsaturated ketones (Scheme 77). The best catalytic results showed complex **136A** when the reaction was carried out for 18 h. A shorter reaction time (2 h) for **136A-E** produced α,β-unsaturated compounds in very poor yields (0−25%).

Scheme 77. Additions to α,β-Unsaturated Ketones Catalyzed by Rhodium(I) DPCB Complexes[a]

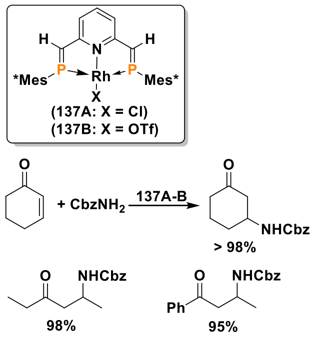


[a]CbzNH$_2$, benzyl carbamate.

In particular, complexes with dienes coordinated to rhodium(I), e.g., **136D-E** were absolutely inactive under these catalytic conditions. The low catalytic activity of reported rhodium(I) complexes and poor yields of obtained products were partly due to facile ligand displacement by rhodium complexes.[130]

Ozawa et al. demonstrated that catalysis with **137A** and a small amount of AgOTf successfully led to addition of benzyl carbamate (CBzNH$_2$) to enones. Illustrated reaction occurred between 2-cyclohexanone and benzyl carbamate with a catalytic amount of complexes **137A-B** in the presence of AgOTf (Scheme 78). The reaction proceeded smoothly for α,β-unsaturated compounds and showed very high yields >98%. Importantly, the reported reaction conditions were effective for addition of CbzNH$_2$ to 4-hexen-3-one and 1-phenyl-2-butenone in 95−99% yields.[131]

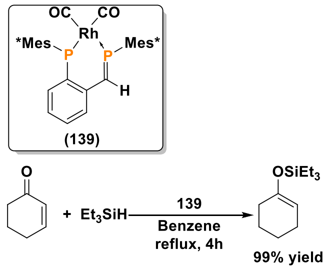
Scheme 78. Addition to α,β-Unsaturated Ketones Catalyzed by Rhodium(I) PNP Complexes[a]



[a]CbzNH$_2$, benzyl carbamate.

The next rhodium(I) complex with catalytic properties was complex **139** (0.5 mol %), which catalyzed 1,4-hydrosilylation in the reaction of 2-cyclohexen-1-one with triethylsilane. The reaction proceeded in benzene under reflux conditions and delivered the corresponding silylenolate in a very high yield (Scheme 79). The authors proposed that the initiation step could be the reaction of complex **139** with triethylsilane; unfortunately, the full mechanism is not well understood.[132]

Scheme 79. 1,4-Hydrosilylation Catalyzed by Complex 139

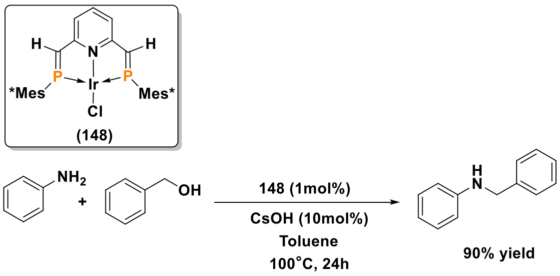


3.4. Iridium.

Iridium complex was used for *N*-alkylation of amines with alcohols. The catalytic activity of complex **148** was examined in a reaction between aniline and benzyl alcohol in the presence of a catalytic amount of base (Scheme 80).

The catalytic reaction proceeded successfully in the presence of strong bases and a catalytic amount of CsOH. Ozawa's research group presented a plausible catalytic cycle for *N*-alkylation. First, dehydrative condensation of PhCHO with

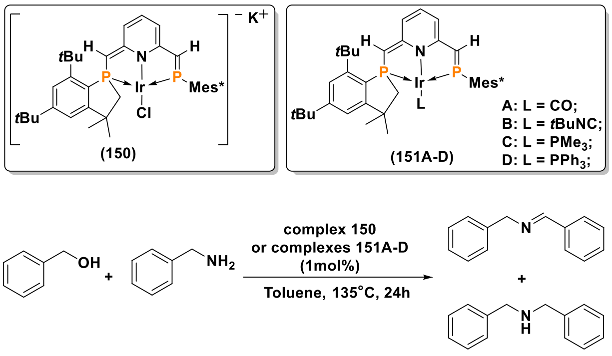
Scheme 80. *N*-Alkylation of Aniline with Benzyl Alcohol Catalyzed by Complex 148



aniline forms PhN═CHPh. Next, PhN═CHPh is inserted into the Ir−H bond. This is followed by alcoholysis of the (amido)iridium species, and $PhNHCH_2Ph$ was obtained as the main product.[219] The authors suggested that the unique BPEP-H ligand with strong π-accepting capability formed a highly electron-deficient Ir(I) complex that was reactive toward a variety of primary and secondary amines and alcohols. Complex **148** was activated in the presence of CsOH but unfortunately was poorly reactive in the absence of the base. On the other hand, when complex **148** was treated with a PPh_3, the selectivity was changed remarkably and produced the imine as a major product.[146]

The catalytic activity of iridium complexes was successfully examined in a dehydration/condensation reaction of amines with alcohols (Scheme 81). Different complexes were used for this purpose, ionic complex **150** and two complexes **151A** with CO and complex **151B** with the *t*BuNC ligand. Reactions with several combinations of amines and alcohols provided *N*-alkylated amines in high yields.[36,146]

Scheme 81. Dehydration/Condensation Catalyzed by PPEP* Complexes



Ozawa et al. presented these results in their next paper, in which they examined three aliphatic amines in reaction with $PhCH_2OH$. In all cases, the corresponding imines were obtained in 70−93% yields. Reaction with alcohol other than $PhCH_2OH$ did not give expected results, because expected products did not feature the thermodynamics stability of imines derived from $PhCH_2OH$. Moreover, the selectivity changed depending on the L group. Complexes **151A** and **151B** bearing π-accepting ligands (CO, *t*BuNC) led to *N*-alkylated amines as the major products with 92% yields, whereas complex **151D** with the PPh_3 ligand formed imines as the major products with yields of 93%.[146]

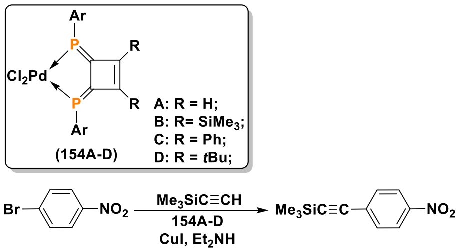
3.5. Nickel. Catalytic activity was also investigated for Ni complexes **152A-B** in ethylene polymerization process. The productivity of the polymerization was approximately 30 kg polymer/g Ni. The nickel catalyst was thermally stable up to 160 °C. Compared to the polyethylene resulting reported catalysts containing an α-diimine, the prepared polyethylene showed a low degree of branching. Ionkin's research group decided to increase the temperature of the polymerization from 60 to 160 °C. After this change, the polyethylene had properties similar to that from the catalyst based on the α-diimine: The productivity and molecular weight were decreased, but the degree of branching was increased.[157]

3.6. Palladium. Definitely more literature reports on the metal complex with phosphaalkene moiety and catalytic properties may found for the Group 10 and 11 elements.

The catalytic activity of palladium complexes with phosphaalkene moieties can be divided into several major reactions, as shown below:

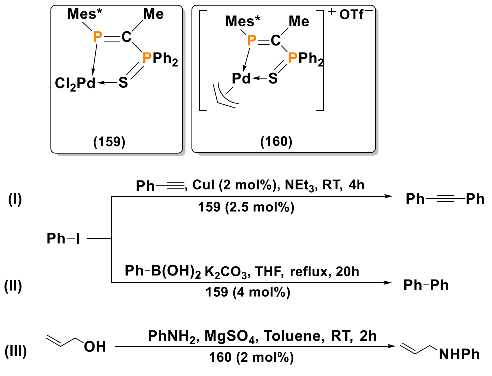
3.6.1. Sonogashira and Suzuki Cross Coupling Reactions. The catalytic activities of described palladium complexes **154A-D** were demonstrated for the coupling reaction of trimethylsilylacetylene with *p*-bromonitrobenzene (Scheme 82).

Scheme 82. Reaction between Trimethylsilylacetylene and *p*-Bromonitrobenzene Catalyzed by Palladium(II) Complexes 154A-D



In this case, catalytic activity depended on the R groups contained in the ligand and on reaction conditions. When the reactions were performed at room temperature, the yields were very low. On the other hand, when the reactions proceeded at reflux temperature, the reported yields were 69−77%. Furthermore, the best result was achieved for a complex with substituted phenyl groups (**154C**).[161] The Ozawa research group reported catalytic applications of phosphaalkene palladium complexes. They found that diphosphaalkene ligands on palladium produced compounds that selectively catalyzed ethylene polymerization. Notably, the reported catalyst exhibited high thermal stability under the reaction conditions and no decomposition even at 100 °C. The catalytic reactivity of complexes for ethylene polymerization strongly depended on the R groups of the diphosphinidenecyclobutene ligands. Catalysis involved compounds **154A-C** modified with two Me groups at the metal atom instead of Cl. Furthermore, higher activity was achieved by increasing the pressure, but unfortunately, this gave lower molecular weights.[162,220] As shown for the Sonogashira reaction (Reaction I, Scheme 83), iodobenzene reacted with phenylacetylene in the presence of catalyst **159** and formed diphenylacetylene with an 83% yield. On the other hand, in the Suzuki coupling reaction (Reaction

Scheme 83. Palladium(II) Phosphaalkene Complexes with the P═C−P═S Skeleton and their Catalytic Applications



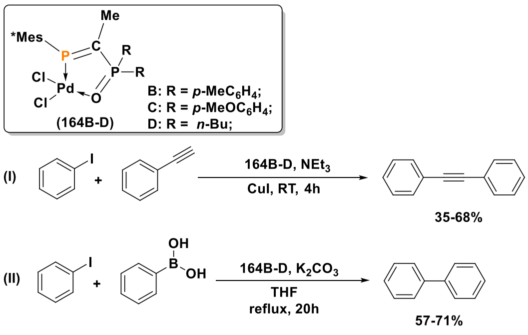
II, Scheme 83), iodobenzene reacted with phenylboronic acid in the presence of catalyst **159** to prepare biphenyl in almost quantitative yield. In the case of cation **160**, the palladium(II) phosphaalkene complex was used for the reaction of allyl alcohol with aniline.

Reagents were mixed in a 1:1 molar ratio to obtain *N*-(2-propenyl)aniline in 63% yield (reaction III, Scheme 83). In general, this reaction has been difficult to effect with the use common phosphine ligand because of ready cleavage of the C−O bond in allyl alcohol. This may have resulted because the low-coordinate sp^2 phosphorus atom enhance π-backbonding due to the low lying P═C π*orbital.[164]

The catalytic properties of palladium(II) complex **162A** in the Sonogashira coupling reaction under mild conditions were also studied. Using coupling reactions of iodobenzene and acetylenes at room temperature of the presence of obtained palladium(II) complex, the corresponding acetylenes were obtained in poor to excellent yields (from 4% to 99%).[163]

The next palladium(II) complex that have been investigated in the Sonogashira and Suzuki cross-coupling reactions are complexes **164B-D**. The best result was obtained with complex **164C**, indicating that the *p*-anisyl group might facilitate oxidative addition more than other substituents (Scheme 84). Reaction conditions used to determine the catalytic activities of palladium(II) complexes were described previously.[221−224]

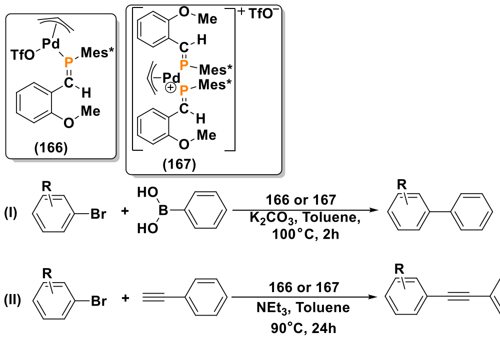
Scheme 84. Catalytic Activity of Palladium(II) Phosphaalkene Catalysts Containing a P═C−P═O Skeleton in Sonogashira (I) and Suzuki (II) Cross Coupling Reactions



The catalytic activities of complexes **164B-D** did not support formation of products from the Sonogashira and Suzuki cross coupling reactions in high yields. However, the results presented in this studies constituted a huge step in developing the unique activity of the P═C−P═O ligands.[165] The catalytic activities of Pd(II) phosphaalkene complexes in cross-coupling reactions were also investigated by the Floch research group. The catalytic reactivities of complexes **166** and **167** were presented, and two well-known transformations were evaluated that allowed formation of new C−C bonds (Scheme 85).

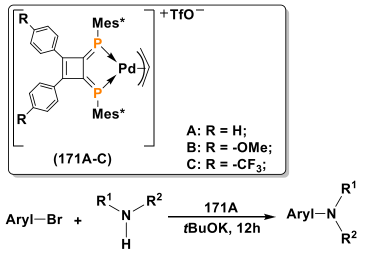
In general, complexes **166** and **167** exhibited the highest activities in both processes. The presented results indicated that in the Sonogashira reaction, the TON (TON, or turnover number, the number of molecules reacted per active sites of catalyst) fell within the range of 40 × 10^5−99 × 10^5. Interestingly, Sonogashira coupling could be carried out without the presence of copper(I) salts. In summary, in Suzuki coupling reactions, TONs ranging from 400 to 950.[166]

Scheme 85. Catalytic Activities of Phosphaalkene Palladium(II) Complexes in Suzuki (I) and Sonogashira (II) Couplings



3.6.2. Buchwald−Hartwig Reactions. The palladium phosphaalkene complexes were also used to catalyze Buchwald−Hartwig coupling. In this reaction, anilines were reacted with bromoarenes in the presence of a palladium catalyst (**171A**) and potassium *tert*-butoxide (Scheme 86). The reactions proceeded under mild conditions without solvent and at room temperature. The corresponding products also included alkylamines, not only aromatic amines. The best results were achieved for aniline derivative with electron-donating substituents. Reaction of morpholine and piperidine in reaction with bromobenzene under complex **171A** was significant because arylmorpholines and arylpiperidines are important classes of medicinal compounds.[170]

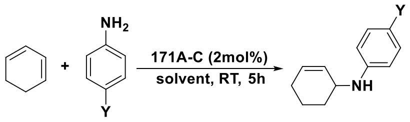
Scheme 86. Aminations Occurring at Room Temperature without Solvent and Catalyzed by the (π-Allyl)(DPCB) palladium Complex (171A)



3.6.3. Hydroamination/Hydroamidation. The addition of amines to alkenes or dienes is a rather difficult reaction and has been run at high temperature.[225−232] Hartwig et al. reported an improved catalyst generated *in situ* from [Pd(PPh$_3$)$_4$] and CF$_3$CO$_2$H, which added aniline to 1,3-dienes at room temperature.[233,234] Ozawa et al. reported efficient hydroamination of 1,3-dienes catalyzed by (η^3-allyl)palladium complexes bearing DPCB ligands with sp^2-hybridized phosphorus (**171A-C**; Scheme 87).

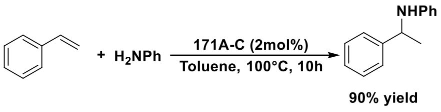
The high reactivity of complex **171A-C** was demonstrated in hydroamination of 1,3-cyclohexadiene with aniline. The

Scheme 87. Hydroamination of Dienes with Aniline Catalyzed by 171A-C



catalytic activity decreased with increasing solvent polarity, and toluene was the best solvent. On the other hand, the reaction did not proceed in dimethylformamide. Interestingly, catalysts **171A-C** were also effective in 1,2-addition of aniline to styrene at 100 °C (Scheme 88).[168]

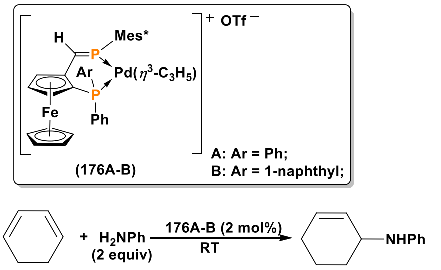
Scheme 88. Hydroamination of Styrene with Aniline Catalyzed by 171A-C



An interesting example of catalytic hydroamination is a reaction in which a phosphanylferrocene (bearing both phosphaalkene and phosphane moieties) complex of palladium was used. Palladium complex-catalyzed hydroamination of 1,3-cyclohexadiene with aniline led to *N*-cyclohexen-3-ylaniline.

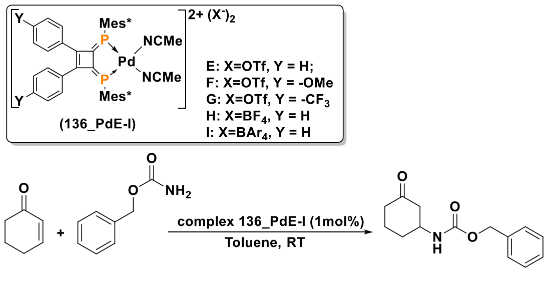
The reaction was performed with 1,3-cyclohexadiene, aniline, 2 mol % of palladium complex, and activated molecular sieves MS5A at room temperature, which clearly improved the catalytic system for hydroamination (Scheme 89).[172]

Scheme 89. Hydroamination of 1,3-Cyclohexadiene with Aniline Catalyzed by Complexes 176A-B



Dicationic palladium (containing $[Pd(MeCN)_2]^{2+}$) complexes bearing DPCB-Y ligands also showed high catalytic activity for addition of benzyl carbamate to enones. A 1:1 mixture of benzyl carbamate and 2-cyclohexenone in toluene was treated with 1 mol % of catalysts **136_PdE-I** (Scheme 90).

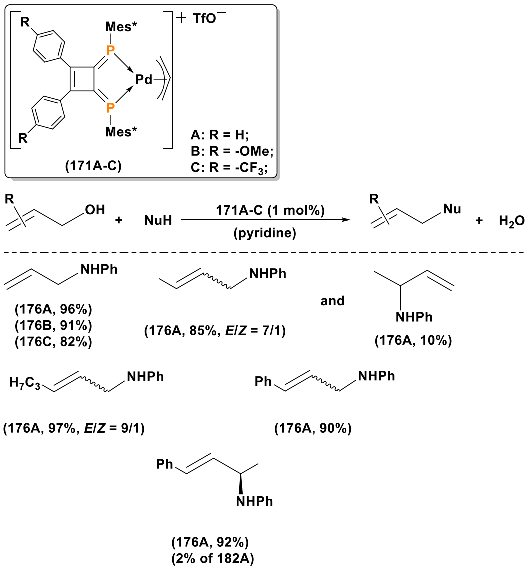
Scheme 90. Hydroamidation of Cyclohexenone Catalyzed by Palladium Complexes (136_PdE-I)



Complex **136_PdE**, with a DPCB ligand and OTf anions, gave a 65% yield. Complexes **136_PdG** (DPCB-CF_3/OTf) and **136_PdI** (DPCB/BAr_4 (Ar = 3,5-$(CF_3)_2C_6H_3$)) exhibited slightly higher activities than **136_PdE**. On the other hand, complexes **136_PdF** (DPCB-OMe/OTf) and **136_PdH** (DPCB/BF_4) were less reactive than **136_PdE**. The DCPB-Y ligands on the cationic palladium(II) centers were found to be fairly stable in this catalytic system.[130]

3.6.4. Nucleophilic Substitution. The palladium-catalyzed Buchwald−Hartwig reaction as well as the hydroamination reaction are reliable and widely used methods for constructing C−N bonds. Formation of C−N bonds is just as important as the formation of C−C bonds. Transition metal-catalyzed reactions that involve formation of C−C and C−heteroatom (N,O,S) bonds are most important for various syntheses of biologically active molecules.[235] Among various processes, allylic alkylations are some of the most studied reactions. In 2002, Ozawa et al. presented (π-allyl)palladium complexes bearing DPCB ligands as highly active catalysts for conversion of allylic alcohols. Catalytic conversions of allylic alcohols have been examined in most cases through *in situ* activation of the OH groups with the aid of Lewis acids (e.g., $Ti(OPr^i)_4$, BEt_3, BPh_3, $SnCl_2$),[236−242] and this is required by the poor leaving ability of the OH group. The Ozawa research group reported that (π-allyl)palladium complexes (**171A-C**) bearing sp^2-hybridized phosphorus ligands effectively catalyzed the conversions of allylic alcohols in the absence of activating compounds (Scheme 91).[169] The synthetic importance of this allylation process prompted investigation of the possible mechanistic pathways. Le Floch et al. used DFT calculations and proposed a mechanism (Scheme 92).

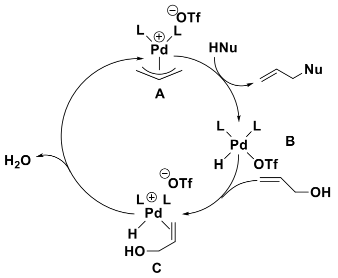
Scheme 91. Catalytic Allylation of Allylic Alcohol Catalyzed by Palladium(II) Complexes



However, the authors suggested that the strong π-accepting capacity of the DPCB ligand could expedite the elimination of water from palladium complex C to produce catalytic precursor A, and complex B could be assembled during the catalytic cycle.

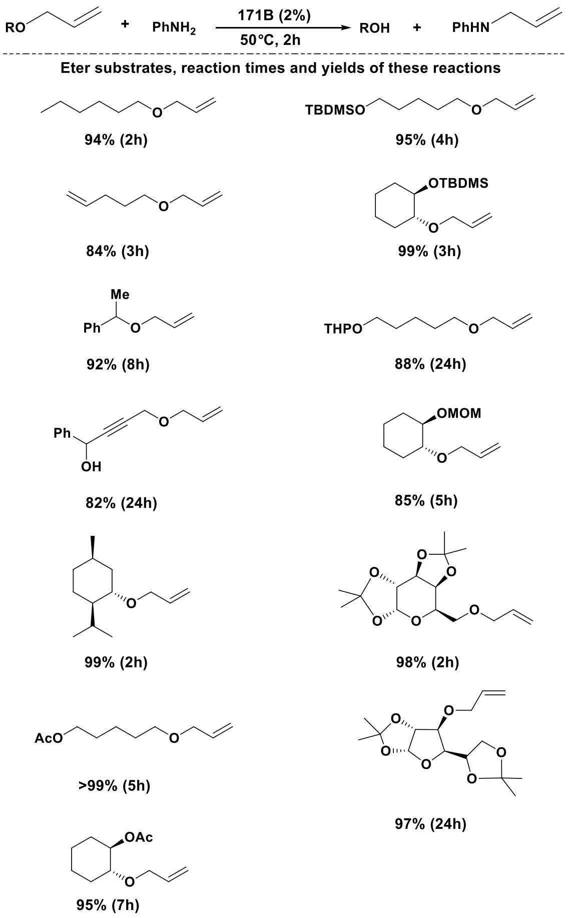
They found that strong π-acceptor ligands favored the dissociation step. Importantly, their calculations showed that the electronic nature of the ligands played a central role in the transformation. This justifies why strong π-accepting ligands are desirable for this reaction.[243,244] Alcohol allylation catalyzed by palladium phosphaalkene complexes generally employs allylic esters. On the other hand, there have been synthetic pathways used to deallylate allylic compounds. Ozawa et al. reported direct conversion of allylic alcohols

Scheme 92. Catalytic Cycle Proposed by Le Floch's Research Group for Nucleophilic Allylic Substitution



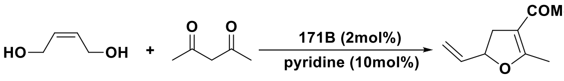
into allylation products. They found that a (π-allyl)palladium complex bearing the DPCB-OMe (**171B**) moiety catalyzes direct conversion of allylic alcohol to an N- or C-allylated compound (Scheme 93). A variety of aliphatic ethers were similarly deallylated. This catalytic process was successfully applied to substrates with vinyl, alkynyl, hydroxy, acetoxy, silyloxy, and acetal groups. Deallylation of aromatic ethers and deprotection of allyloxycarbonyls were also described, and these are known to be useful protecting groups for hydroxy groups in carbohydrates and in nucleoside bases and peptides.[245]

Scheme 93. Palladium-Catalyzed Deallylation



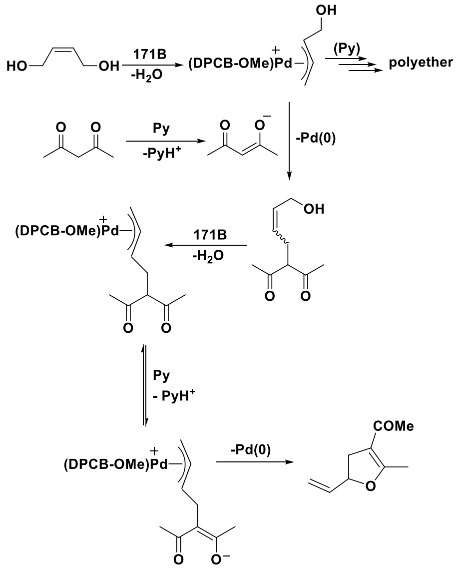
3.6.5. Cyclodehydration. Ozawa et al. also reported the catalytic properties of previously described complex **171B** in cyclodehydration of *cis*-2-butene-1,4-diol (Scheme 94).

Scheme 94. Cyclodehydration of *cis*-2-Butene-1,4-diol with Acetylacetone in the Presence of Complex 171B



Cis-2-Butene-1,4-diol successively reacted with acetylacetone in the presence of catalytic amounts of complex **171B** and pyridine to form 2-vinyl-4-acetyl-5-methyl-2,3-dihydrofuran. The catalytic reactions proceeded in toluene and THF (Scheme 95). Interestingly, in the same catalytic system, some of π-allyl complex **171B** dimerized to give diallyl ether as a byproduct.[246]

Scheme 95. Reaction Processes for Formation of 2-Vinyl-4-acetyl-5-methyl-2,3-dihydrofuran

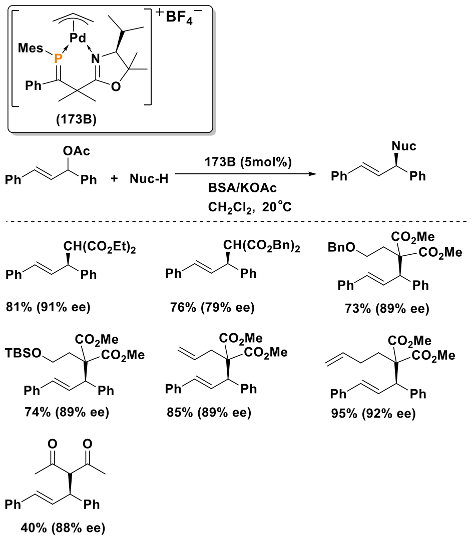


PhAk-Ox-palladium allyl complexes **173B** reported by Gates et al. were used and led to improved performance for allylic alkylation (Scheme 96). The reaction was carried out in CH_2Cl_2 at 20 °C, and BSA (1 equiv) and KOAc (0.01 equiv) were added. The presented application was quite convenient and efficient because it used a wide range of nucleophiles with different functional groups. These studies resulted in synthetically useful yields and high ee values (enantiomeric excess) with a range of functionalized dicarbonyl nucleophiles. Gates et al. also presented results using similar Pd complex to **173B** with the $[BF_4]^-$ counterion in asymmetric allylic alkylation. These change gave poorer results but these experiments contributed a lot efforts to optimize the performance of catalyst.[171]

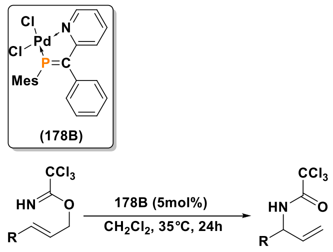
3.6.6. Overman–Claisen Reaction. Pd(II) complex **178B** was also successfully tested for catalytic activity in rearrangements of allyl trichloroacetimidates, namely, the Overman–Claisen rearrangement (Scheme 97).[247]

The Overman–Claisen rearrangement allows conversion of available allylic alcohols into allylic amines via a two-step synthesis involving rearrangement of an allylic trichloroacetimidate to an allylic trichloroacetamide with 1,3-transposition of the alkenyl moiety.[173] Allylic amines are useful precursors to a variety of nitrogen-containing molecules, such as alkaloids, antibiotics, and unnatural amino acids.[248]

Scheme 96. Scope of Enantioselective Allylic Alkylation Using PhAk-Ox Catalyst 173B Showing the Functional Group Tolerance



Scheme 97. Overman–Claisen Rearrangement with the Use of Complex 178B[a]

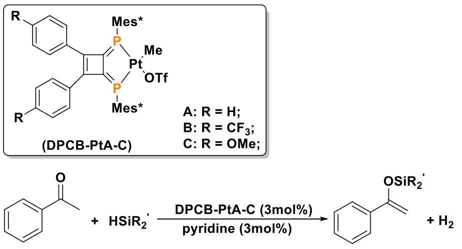


[a]R = Me, *n*-Pr, *n*-Hep, $PhCH_2CH_2$, *i*-Pr.

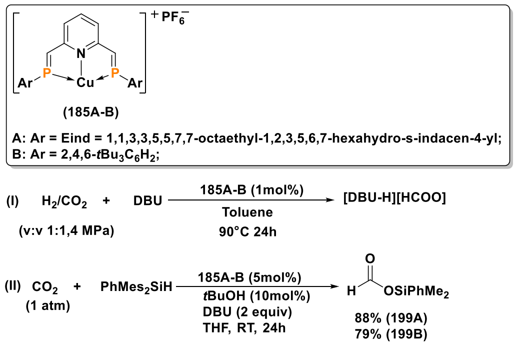
3.7. Platinum. As seen with palladium complexes, the DPCB ligand provided good support for platinum complexes.[182,249,250] Methylplatinum triflate coordinated with ligand showed a high catalytic activity in dehydrogenative silylations of ketones with $HSiMe_2Ph$. An early example of dehydrogenative silylation utilized a mixture of $Co_2(CO)_8$ and pyridine.[251] Complexes **DPCB-PtA-C** reported by Ozawa et al. seem to be highly selective catalysts for converting ketones into silyl enol ethers in high yield (Scheme 98). In general, the reactions can be run without solvent, and the only byproduct is dihydrogen gas.[250]

3.8. Copper. A reactivity study of **185A** led to FLP-type activity toward hydrogen and phenylacetylene. Despite the well-known catalytic properties of copper compounds, there are few reports in the literature of using copper phosphaalkene complexes in catalytic reactions. The catalytic activities of Cu(I) PNP-type complexes for CO_2 hydrogenation and hydrosilylation were presented.[198] The hydrogenation reaction of CO_2 was performed with the reaction conditions presented by Appel et al.[252] They used copper complexes as catalysts and DBU as the base. Catalysts **185A** and **185B** in Scheme 99 exhibited catalytic activity in hydrogenation of CO_2 with TONs of 11 (**185A**) and 20 (**185B**). After 48 h, the TON of catalyst **185B** increased to 39.

Scheme 98. Dehydrogenative Silylation of Ketones



Scheme 99. Hydrogenation (I) and Hydrosilylation (II) of CO_2 in the Presence of 185A and 185B

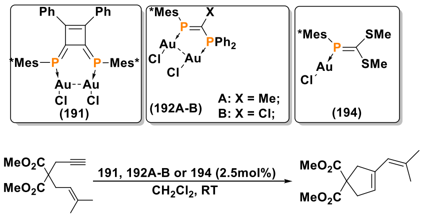


The catalytic activity of complex **185B** was higher than that of complex **185A**, which may be due to the higher reactivity of the intermediate hydride complex [CuH(Mes*$_2$-BPEP)]. This could also be attributed to the lower steric hindrance and lower acidity of complex **185B** compared to **185A**. On the other hand, hydrosilylation of CO_2 over **185A** and **185B** required presence of 10 mol % *t*BuOH and 2 equiv of DBU. The addition of *t*BuOH promoted formation of copper hydride. In contrast to the hydrogenation reaction, complex **185A** was more catalytically active in hydrosilylation than complex **185B**. This could be due to the chemical difference between the copper hydride intermediates. In general, complexes **185A** and **185B** catalyzed hydrogenation and hydrosilylation of CO_2 under mild conditions and with good yields.[198]

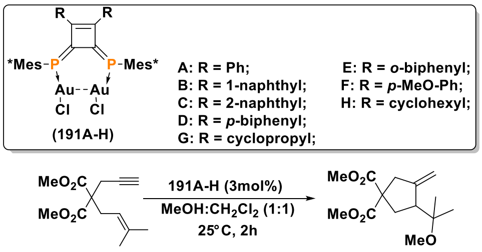
3.9. Gold. Three gold(I) complexes (**191**, **192**, and **194**) and their reactivities in 1,6-enyne cycloisomerization were investigated. This type of reaction, which usually, proceeds in the presence of a silver catalyst that generates the reactive Au intermediate, suffers from limitations. Complexes **191**, **192**, and **194** catalyzed the cycloisomerization reaction without a silver cocatalyst. Reactions were carried out in dichloromethane at room temperature to afford vinylcyclopentenes in quantitative yields (Scheme 100). Importantly, these complexes were recovered from solution after the cycloisomerization reaction and were suitable for reuse.[202]

Additionally, the catalytic properties of Au(I)-DPCB complexes were investigated. The catalytic activity of **191B** was determined for alkoxycyclization of a 1,6-enyne and acetyl-assisted hydration of terminal alkynes (Scheme 101). All of the catalysts exhibited high efficiencies; however, the best results were obtained with **191B**, which provided a 99% yield. Additionally, **191B** enabled the alkoxycyclization with catalyst loading of 0.5 mol % and simultaneous extension of the reaction time. Interestingly, **191B**-catalyzed reaction without solvent might be effective for practical homogeneous catalysis with Au.

Scheme 100. Au-Catalyzed 1,6-Enyne Cycloisomerization Reactions

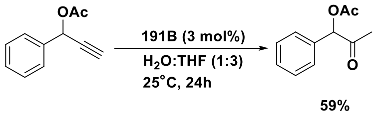


Scheme 101. Alkoxycyclizations of a 1,6-Enyne in the Presence of Gold(I) Complexes 191A-H



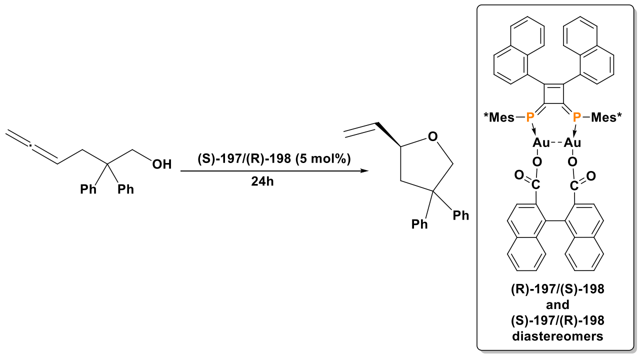
For the acetyl-assisted hydration reaction, **191B** successfully catalyzed acetyl-supported hydration of a terminal acetylene under mild conditions. The resulting methylketone derivative was formed in 59% yield (Scheme 102).[205] Complex **191B** was also used as catalyst in the acetyl-assisted hydration of a terminal acetylene.

Scheme 102. Acetyl-Assisted Hydration of a Terminal Acetylene Catalyzed by 191B



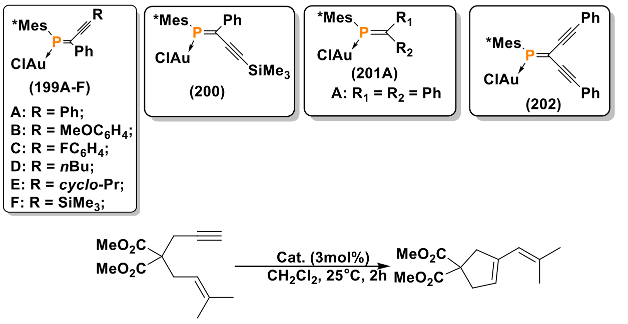
Asymmetric DPCB complexes were used as catalysts in the intramolecular alkoxycyclization of a hexa-4,5-dien-1-ol derivative. Two digold phosphaalkene complexes and their catalytic activities in asymmetric alkoxycyclization reactions were investigated (Scheme 103). The best result was realized in toluene solution, and the product was isolated in 37% yield. The combination, after adding the allene derivative gave decomposition. Additionally, cooling or heating the reaction did not improve the catalytic activity of the digold complexes.[206]

Scheme 103. Alkoxycyclization of Allene Derivative in the Presence of Digold Phosphaalkene Complexes



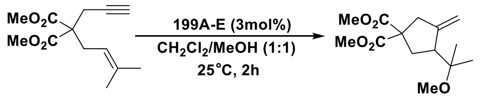
Complexes presented by Ito and Mikami et al. were used in such reaction as cycloisomerization of a 1,6-enyne, alkoxycyclization of a 1,6-enyne and hydration of propargyl acetate. The results of the cycloisomerization reactions carried out in the presence of **199A-F**, **200** and related complexes **201A** and **202** are summarized in Scheme 104. The π-donating methoxy and fluorine groups effectively increased the catalytic activity. Interestingly, the difference between **199F** and stereoisomer **200** was significant. In complex **199F**, the π-accepting silyl group increased the catalytic activity. On the other hand, stereoisomer **202** showed a remarkable reduction in catalytic activity. The authors claimed that the difference resulted from steric encumbrance in the structure.

Scheme 104. Au-Catalyzed Cycloisomerization of a 1,6-Enyne in the Presence of 199A-F, 200, 201A, and 202



As with the cycloisomerization reaction, **200** showed poor activity, whereas complex **199F** shows very promising results. With 6 mol % **199F**, the reaction proceeded almost quantitatively and gave the methylenecyclopentene derivative in good yield. Complexes **199A-E** were ineffective catalysts for the alkoxycyclization reaction (Scheme 105).

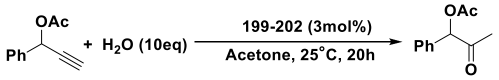
Scheme 105. Au-Catalyzed Alkoxycyclizations of a 1,6-Enyne



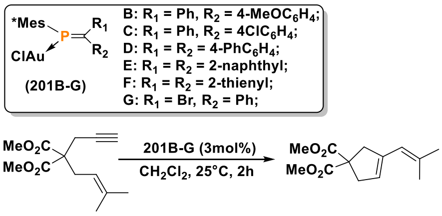
The catalytic activities of complexes **199**–**202** in hydration reaction of a propargyl acetate are shown in Scheme 106. As previously described, the derivative with the trimethylsilyl group, **199F**, gave the best result (88% yield).

Chloro-gold(I) complexes bearing 2,2-diaryl-1-phosphaethene ligands **201B-G** were also investigated for catalysis of cycloisomerization reactions (Scheme 107). All products were afforded in almost quantitative yields. Unfortunately, complexes **201B-G** were not effective catalysts for hydration

Scheme 106. Au-Catalyzed Hydration of a Propargyl Acetate



Scheme 107. Au-Catalyzed Cycloisomerizations of a 1,6-Enyne in the Presence of Catalysts 201B-G



reactions or alkoxycyclizations. Despite this, all chloro-gold(I) complexes showed promise for use in cocatalyst-free catalytic reactions.[207]

4. CONCLUSIONS

In conclusion, the chemistry of complexes containing phosphaalkene ligands is colorful and rich in applications. The review revealed that no complexes were obtained for a few metals, including Hf, Ta, Tc, and Cd. Methods for preparation of these complexes have been reported for the remaining metals. Interestingly, even the metals of Group 12 were among these that formed complexes with phosphaalkenes, albeit to a slight extent. The survey undertaken showed the different coordination modes these complexes demonstrate. The most common two modes for metal-phosphaalkene ligand bonding were η^1-P and η^2-P,C. In some cases, phosphaalkene ligands forced unusual coordination geometries for the central atom, such as square planar coordination of platinum. Important elements of this chemistry are also inversely polarized phosphaalkenes, which include those of the NHC type. Despite their monodentate nature, they well stabilize transition metal complexes. DPCB and BPEP are particularly important ligands that serve as sources of C═P binding, which may be related to the high stability these systems impart to transition metals. Although attention was paid to ligands containing C═P bonds, the N,P-chelating system were also considered here.

This review reveals the importance of complexes with phosphaalkene ligands in catalysis. They are used as catalysts for many organic reactions, and this is especially evident for late transition metals. It is particularly clear in the case of palladium complexes, which were widely developed by the Yoshifuji and Ozawa research groups. The great possibility of changing the properties of the ligands within the central atom and the properties of the ligands themselves make it possible to design many promising compounds. The collected works show how sufficiently reactive compounds bearing the phosphaalkene ligands are used now and can be applied in further transformations. Moreover, this report revealed possibilities for application of these compounds, especially in catalysis.

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Notes

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■ ABBREVIATIONS

Ar, aryl; BAr, tetrakis(3,5-bis(trifluoromethyl)phenyl)borate; Bipy, 2,2-bipyridine; BPEP, 2,6-bis(1-phenyl-2-phosphaethenyl)-pyridine; BSA, *N,O*-bis(trimethylsilyl)acetamide; BTD, 2,1,3-benzothiadiazole; COD, cycloocta-1,5-diene; Coe, cyclooctene; Cp, cyclopentadienyl; Cp′, $C_5H_4SiMe_3$; Cy, cyclohexyl; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DCI, 1,1′-carbonyldiimidazole; DCM, dichloromethane; DME, 1,2-dimethoxyethane; DMF, dimethylformamide; DPCB-Y, 1,2-diaryl-2,4-bis[(2,4,6-tri*tert*-butylphenyl)phosphinidene]-cyclobutene (diphosphinidenecyclobutene); DPPE, 1,2-bis-(diphenylphosphino)ethane; EE, enantiomeric excess; Eind, 1,1,3,3,5,5,7,7-octaethyl-1,2,3,5,6,7-hexahydro-s-indacen-4-yl; IPr, 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene; *i*Pr, *iso*-propyl; IR, infrared spectroscopy; Me, methyl; Mes, 1,3,5-*tri*-methylbenzene; Mes*, 1,3,5-*tri*-tertbutylbenzene; NacNac⁻, *β*-diketiminate ligand; NaHMDS, sodium hexamethyldisilazide; NBD, norbornadiene; NBO, natural bond orbital; NMR, nuclear magnetic resonance; OTf⁻, trifluoromethanesulfonate ion; PNP, N,N′-bis(diphenylphosphine)-2,6-diaminopyridine; PPEP, 2-(phospholanylmethyl)-6-(2-phosphaethenyl)pyridine; RNC, isocyanides (R = alkyl groups); RT, room temperature; *s*Bu, *sec*-butyl; *t*Bu, *tert*-butyl; THF, tetrahydrofuran; THT, tetrahydrothiophene; TON, turnover number; Tol, tolyl group ($CH_3C_6H_4$−); TMEDA, *N,N,N′,N′*-tetramethylethylenediamine; TMSCl, trimethylsilyl chloride; Xyl, 2,6-dimethylphenyl

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