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Phospha- and Arsaalkenes RE=C(NMe$_2$)$_2$ (E = P, As) as Novel Phosphinidene- and Arsinidene-Transfer Reagents

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Keywords: Phosphaalkenes / Arsaalkenes / Phosphinidene / Arsinidene

Phosphinidenes (phosphanylidenes) (RP) are electronically and coordinatively unsaturated phosphorus compounds, which, as six-electron species, are formally analogous to the more familiar carbenes and nitrenes. In contrast to carbenes (CR$_2$), the extremely reactive phosphinidenes cannot be isolated without decomposition. Thus, our knowledge on phosphinidenes is mainly limited to trapping reactions and quantum-chemical calculations. There are a number of synthetic methods for phosphinidenes available, for example photolysis or thermolysis of cyclic phosphanes and oligophosphanes, dehalogenation of organodihalophosphanes, liberation of dinitrogen from organodiazidophosphanes, or decomposition of phosphoranylidene-σ^4-phosphoranes (arylP=PMe$_3$). A plethora of information is available on the generation of highly reactive terminal phosphinidene complexes [RPW(CO)$_5$] and their chemistry. Many of these methods suffer from comparatively harsh conditions (strong base, heat, etc.) which limit their preparative use.

1. Introduction

Phosphinidenes R–P (phosphanylidenes) are elusive six-electron species, which can only be evidenced by interception reactions or by their oligomerization to oligocyclophosphanes.[1]

The chemistry of unsupported phosphinidenes is only poorly developed in comparison to the rich chemistry displayed by free carbenes. One reason might be sought in the limited number of suitable precursors for these electron-deficient molecules. Moreover, general difficulties in the unambiguous identification of phosphinidenes as key compounds in reactions have to be noted at this point. Often it has not been sufficient to draw a conclusion about their identity solely from an observed product pattern.

Phosphinidenes occur as singlet and triplet species, whereby, like in the case of methylene, the parent compound [PH] has a triplet ground state with an experimentally determined triplet–singlet separation of 22 kcal mol^{-1}. Quantum chemical calculations have evidenced that, with π-donor substituents at the phosphorus atom, the energy of the open-shell particles approach the singlet state.

2. Synthesis and Trapping Reactions of Phosphinidenes

Convincing arguments for the intermediacy of phosphinidenes where obtained from their photochemical generation. Photolysis of Mes*P(N$_3$)$_2$ (**1**) (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) with UV light (254 nm) afforded phosphaindane **3**, the formation of which was rationalized by the insertion of the P atom into a C–H bond of one *tert*-butyl group in the *ortho* position of the arene ring (Scheme 1).[2]

When the photolysis of **1** was conducted in deuterated solvents, *no* deuterium incorporation into product **3** was observed. Obviously, the intramolecular rearrangement of transient **2** into **3** occurred very rapidly. Photolyses of Mes*P=C=O and Mes*P=PMes* also gave compound **3** as the final product in high yields.[2]

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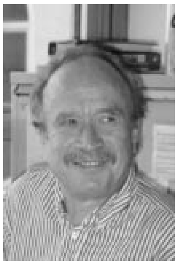
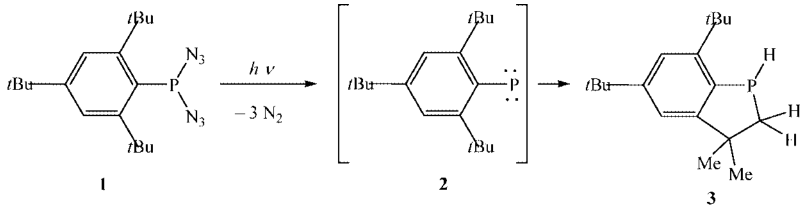
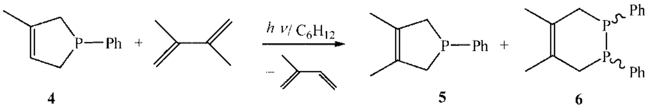


Lothar Weber was born in 1944 in Langenöls in Schlesien. He studied at the University of Marburg and received his doctorate there under the direction of Professor Günter Schmid in 1973. Afterwards, he carried out postdoctoral studies with Professor Barry M. Trost at the University of Wisconsin in Madison, USA. On his return to Marburg, he began the experimental work leading to his Habilitation, which was completed in 1982 at the University of Essen. His work focused on the coordination chemistry of sulfur ylides. In 1985, he became a C2 Professor and then joined the Fakultät für Chemie der Universität Bielefeld. His research interests include the chemistry of compounds with low-coordinate elements of the fifth main group, the synthesis of homo- and heterocycles with heavy elements, as well as new aspects in boron chemistry.



Scheme 1. Generation of phosphaindane **3** by photolysis of **1**.

The "retro-addition strategy" seemed to be particularly useful for the synthesis of phosphinidenes. Thus, photolysis of 3-methyl-1-phenyl-3-phospholene (**4**) in the presence of 2,3-dimethylbutadiene furnished phospholene **5** in addition to a *cis*/*trans* mixture of 4,5-dimethyl-1,2-diphenyl-1,2-diphosphacyclohexenes **6** (Scheme 2).



Scheme 2. Photolysis of **4** in the presence of 2,3-dimethylbutadiene.

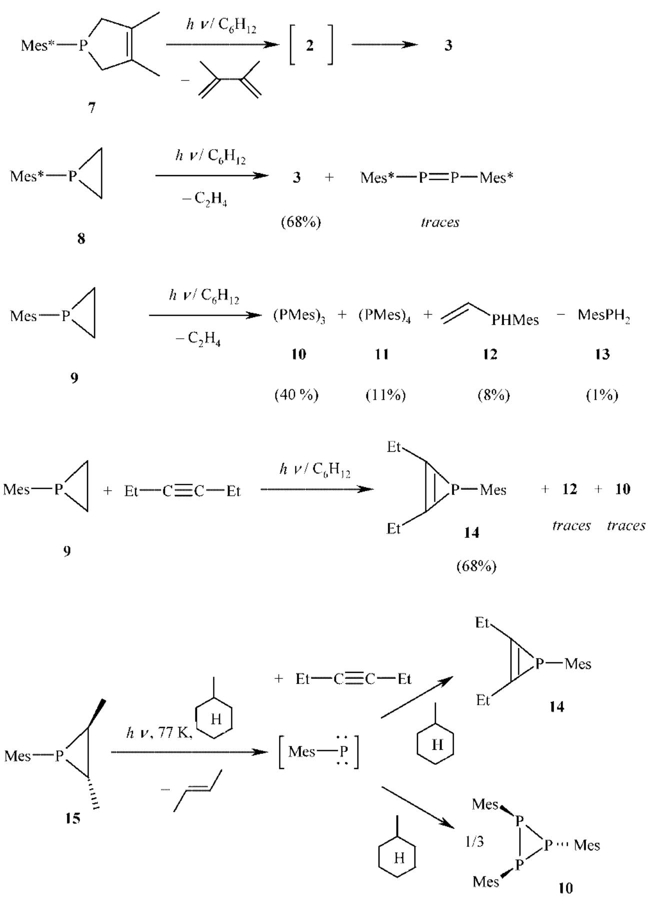
These observations were explained by invoking the photochemical extrusion of phenylphosphinidene from **4** and its subsequent cheletropic [1+4] cycloaddition to the diene. In a competing process, the phosphinidene dimerized to a diphosphene which underwent a Diels–Alder reaction to give isomers **6**.[3]

Irradiation of 3,4-dimethyl-1-supermesityl-3-phospholene (**7**) afforded phosphinidene **2**, which isomerized to **3**. Compound **3** was obtained in 68% yield upon photolysis of **8** even in the presence of potential trapping reagents such as alkenes, dienes, or alkynes. Only traces of diphosphene Mes*P=PMes* were observed (Scheme 3).

Photolysis of mesitylphosphirane **9** furnished a mixture of cyclophosphanes **10** (40%) and **11** (11%) in addition to mesitylvinylphosphane **12** (8%) and mesitylphosphane **13** (1%) (Scheme 3). In the presence of alkenes, dienes or alkynes, the yield of the oligocyclophosphanes decreased in favor of the formation of three-membered rings.

Frozen solutions of phosphirane **15** in methylcyclohexane at 77 K turned yellow upon irradiation with UV light (λ = 254 nm). Thawing the glass in the absence of trapping reagents gave cyclotriphosphane **10** in 30% yield. In the presence of 3-hexyne, phosphirene **14** was formed in yields up to 88%, which was rationalized by the initial liberation of mesitylphosphinidene. In an ESR experiment at 4 K, the yellow glass displayed a strong signal at 11492 Gauss, which was assigned to the free [Mes–P] in the triplet ground state.[4a] A recent careful theoretical analysis of the fragmentation reaction demonstrated that free [Mes–P] was probably not generated in the presence of alkenes.[4b]

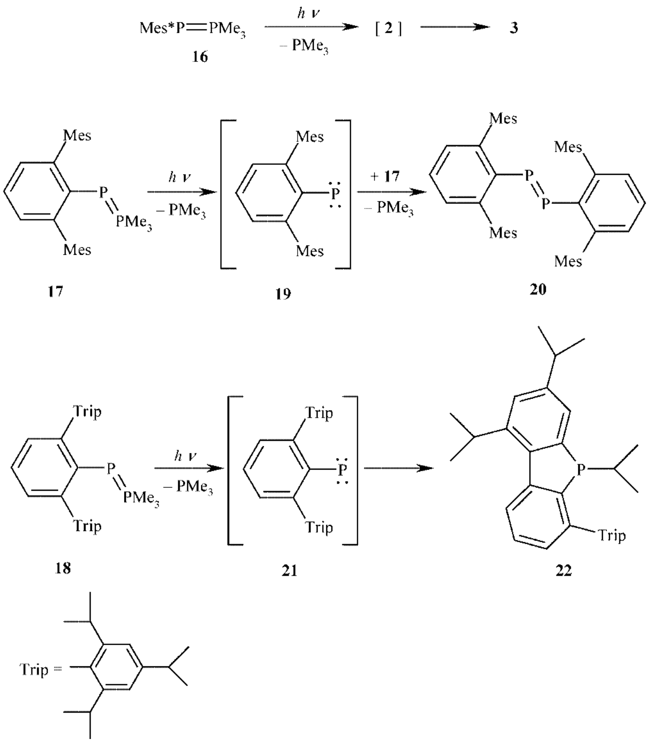
Phosphanylphosphinidene [tBu$_2$P–P] has been known for some time.[5a] Its chemistry as well as theoretical calculations[5b] on it agree with a singlet ground state of the molecule.



Scheme 3. Photolysis of phospholene **7** and phosphiranes **8**, **9**, and **15**.

Stimulated by the work of Burg and Mahler, who studied the decomposition of $CF_3P{=}PMe_3$,[6] Protasiewicz et al. photolyzed the phosphinidenephosphoranes **16**–**18** (Scheme 4).[7] Release of PMe_3 from derivative **16** gave phosphinidene **2**, which rearranged immediately to **3**.

In contrast, irradiation of **17** afforded diphosphene **20** in 90–95% yield, which was explained by an attack of phosphinidene **19** at the precursor. The photochemical treatment of phosphinidenephosphorane **18** led to phosphafluorene **22** as the product of the insertion of the P atom of transient **21** into the carbon–carbon bond of an *ortho*-isopropyl group. Interestingly, compound **22** was also formed in 68% yield during the magnesium reduction of 2,6-trip$_2$C$_6$H$_3$PCl$_2$.[7b,8] The reductive dechlorination of aryl-PCl$_2$, however, does not necessarily proceed via free phos-

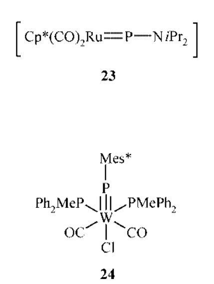


Scheme 4. Photolysis of phosphinidenephosphoranes **16**–**18**.

phinidenes as intermediates. It is equally conceivable that this process may involve radicals or species of the type arylP(Cl)MgCl.

3. Phosphinidene Complexes as Phosphinidene Transfer Reagents

A rich area of transition-metal complexes featuring terminal phosphinidene ligands contrasts with the scarcely developed chemistry of free phosphinidenes.[9] There was a considerable effort to develop a phosphinidene chemistry analogous to the well familiar carbene complex chemistry.[10] Here, however, it proved troublesome to employ synthetic methods that proved fruitful in carbene chemistry. In contrast, one had to face the task of individually modifying the reaction conditions according to the demands of the substituents at the P atoms. A useful approach was the stabilization and fixation of singlet phosphinidene in the coordination sphere of d-block metals. At this point, two different types of terminal phosphinidene complexes may be discriminated: coordination compounds with phosphinidenes as two electron donors with a nonlinear M–P–R arrangement (e.g. **23**)[11] or those with phosphinidenes that serve as four electron donors with a linear M–P–R skeleton (e.g. **24**).[12] It is obvious that complexes with sp^2-hybridized phosphorus atoms show ^{31}P NMR resonances at very low field, which is in sharp contrast to those with sp-hybridized phosphorus.

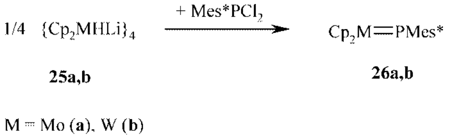


d(Ru=P)	2.2654(5) Å
∡ Ru–P–N	119.6°
$\delta(^{31}P)$	+ 932 ppm
d(W≡P)	2.169(1) Å
∡ W–P–C	168.2°
$\delta(^{31}P)$	+ 193.0 ppm

3.1 Nucleophilic Phosphinidene Complexes

The discrimination between nucleophilic and electrophilic phosphinidene complexes is mainly justified by their reactivity. Early transition metals with an electron-abundant coordination sphere favor a polarity $P^{\delta-}$–$M^{\delta+}$ of the metal–phosphorus bond. Thereby the gradual variation of the ancillary ligands to some extent allows tuning of the mode of reactivity of the PR ligand from nucleophilic to electrophilic. This aspect was analyzed in a theoretical study.[13]

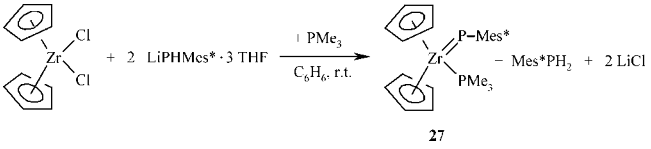
The first stable transition-metal complexes having nucleophilic phosphinidene ligands [$Cp_2M{=}PMes^*$] (**26a**,**b**) (M = Mo, W) were synthesized as red solids by the reaction of Mes*PCl_2 with the hydridolithium species **25a**,**b** (Scheme 5).



Scheme 5. Synthesis of **26a**,**b**.

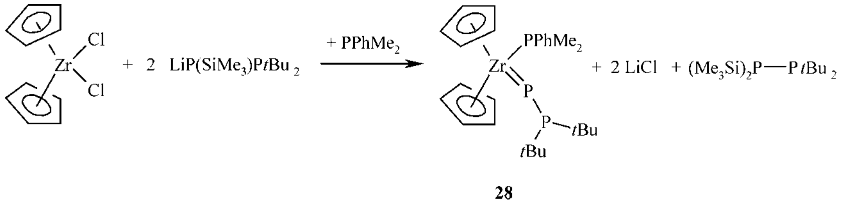
According to an X-ray structural analysis of the molybdenum complex **26a** the M–P–R skeleton is bent [115.8(2)°] with a MoP double bond of 2.370(2) Å.[14]

A bent terminal phosphinidene derivative, [$Cp_2Zr({=}PMes^*)(PMe_3)$] (**27**), was isolated from the reaction of [Cp_2ZrCl_2] with LiPHMes* in the presence of PMe_3 (Scheme 6).

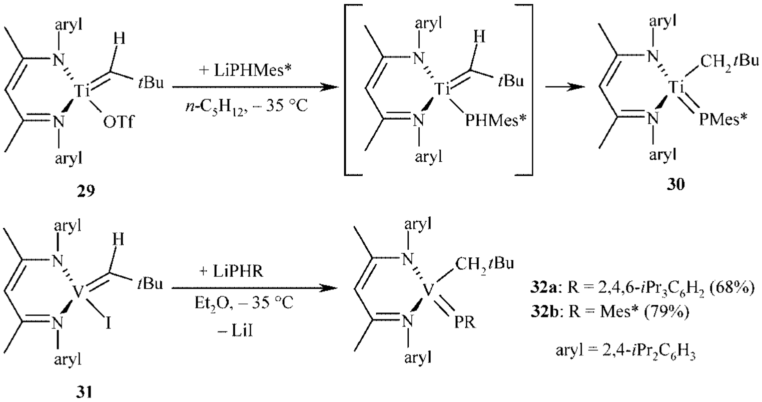


Scheme 6. Synthesis of **27**.

The outcome of such a protocol is crucially dependent on the steric requirements of the ligands at the metal and the phosphorus atom.[15] According to a comparable protocol, the synthesis of the first terminally bonded phosphanylphosphinidene complex [$Cp_2Zr\{{=}P{-}P(tBu)_2\}(PPhMe_2)$] (**28**) was achieved. The ZrP contact to the phosphinidene ligand was considerably shorter [2.488(3) Å] than that to the phosphane ligand [2.734(3) Å] (Scheme 7).[16]



Scheme 7. Synthesis of **28**.



Scheme 8. Titanium and vanadium complexes with nucleophilic terminal phosphinidene ligands.

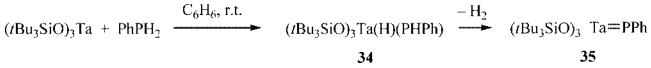
Until 2004, η^2-coordination was found to be essential to stabilize the tBu$_2$PP ligand, whose source is phosphanylphosphinidine-σ^4-phosphoranes.[5a,17]

A strategy for preparing a terminal titanium phosphinidene complex, **30**, involved treatment of the nucleophilic and four-coordinate titanium alkylidene complex [(Nacnac)-Ti=CHtBu(OTf)] (**29**) [Nacnac = 2,6-iPr$_2$C$_6$H$_3$NC(Me)-CHC(Me)N-C$_6$H$_3$-iPr$_2$-2,6] with LiPHMes* in pentane at –35 °C (Scheme 8). The structure of the molecule in the crystal displays a four-coordinate titanium–phosphinidene complex with an exceptionally short Ti=P bond [2.183(4) Å] and a nearly linear Ti=P–C$_{ipso}$ angle [164.44(5) Å].[18a]

Dark blocks of crystalline **32a** and **32b** were obtained in good yield from the layering of a cold ethereal solution (–35 °C) of the lithium phosphide onto a similarly cold ether solution of vanadium(IV) complex **31** (Scheme 8).[18b]

In contrast to a series of phosphinidene complexes, which owe their stability to very bulky substituents, Schrock developed a synthetic procedure for stable tantalum phosphinidenes **33**, which tolerate Ph, Cy, and tBu groups as substituents. This is due to the bulky tetradentate amido ligand $\{N(CH_2CH_2NSiMe_3)_3\}^{3-}$ (Scheme 9).

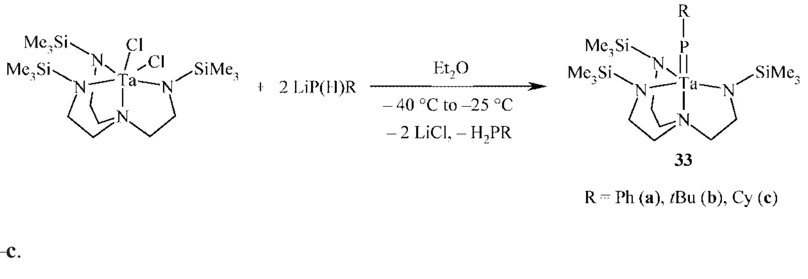
The X-ray diffraction study of **33c** displays a nearly linear Ta–P–C unit with a short Ta–P bond of 2.145(7) Å. The ^{31}P NMR resonances of the complexes range from 175.1 to 227.3 ppm.[19] Tantalum phosphinidene complex **35** (δ^{31}P = 334.6 ppm) resulted from a 1,2-H$_2$-elimination of phosphanido complex (tBu$_3$SiO)$_3$(H)Ta–P(H)Ph (**34**), (Scheme 10).[20] The angle Ta–P–C in **35** is 110.2(4)°, and the Ta=P bond length is 2.317(4) Å.



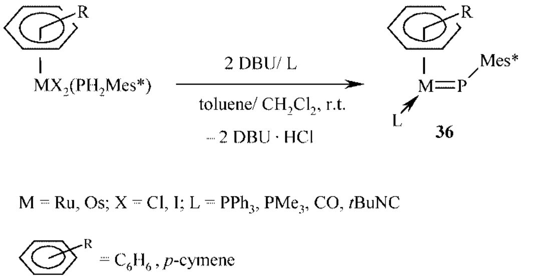
$$(tBu_3SiO)_3Ta + PhPH_2 \xrightarrow{C_6H_6,\ r.t.} \underset{\mathbf{34}}{(tBu_3SiO)_3Ta(H)(PHPh)} \xrightarrow{-H_2} \underset{\mathbf{35}}{(tBu_3SiO)_3\,Ta{=}PPh}$$

Scheme 10. Synthesis of **35**.

Terminal nucleophilic complexes of group 8 (**36**) and group 9 (**37**) transition metals were synthesized by Lammertsma et al. by the base-induced dehydrohalogenation of appropriate precursor complexes in the presence of stabilizing ligands. ^{31}P NMR resonances of the Ru complexes were observed between 801 and 846 ppm, and in the Os compounds they range from 668 to 744 ppm. The p-cymene(PPh$_3$)Os complex displays a bent Os–P–C backbone [106.56(9)°] with an Os–P bond of 2.2195(7) Å (Scheme 11).[21]

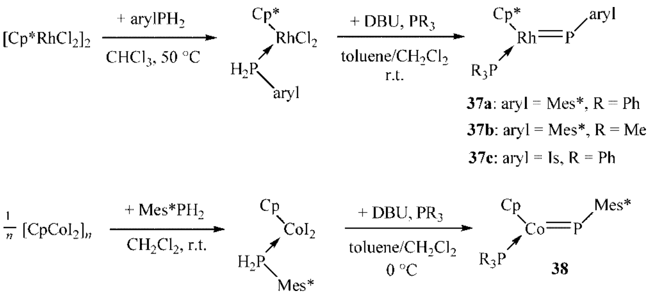


Scheme 9. Synthesis of **33a**–**c**.



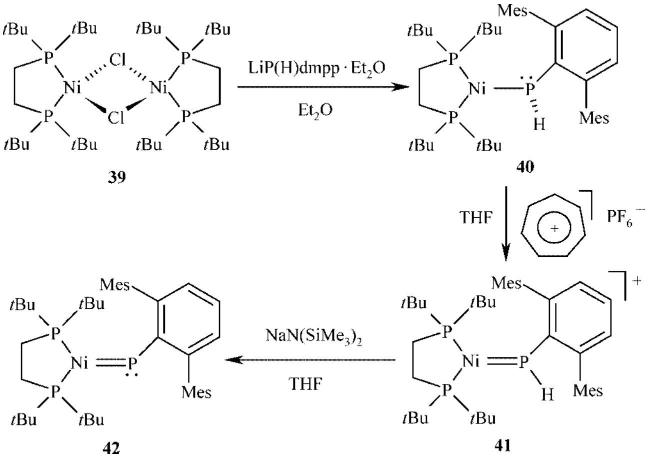
Scheme 11. Synthesis of phosphinidene complexes of Ru and Os.

Similarly, iridium complexes [Cp*(L)Ir=Paryl] (aryl = Mes, Is, Mes*), L = PR$_3$, P(OR)$_3$, AsR$_3$, dppe, RNC, and CO,[22] and the corresponding cobalt and rhodium complexes [Cp*(R$_3$P)Rh=Paryl] (**37**) [aryl = Mes*, Is (Is = 2,4,6-*i*Pr$_3$C$_6$H$_2$); R = Me, Ph], and [Cp*Co(PPh$_3$)=PMes*][23] were synthesized (Scheme 12).

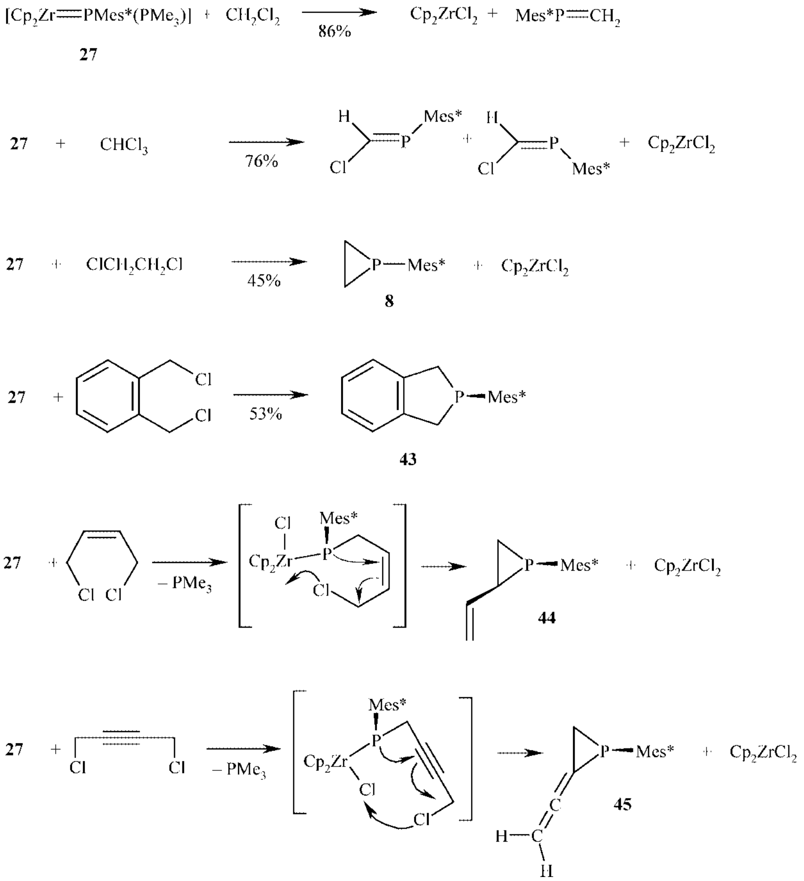


Scheme 12. Synthesis of phosphinidene complexes of Rh and Co.

Ether solutions of lithium-2,6-dimesitylphenylphosphanide [LiP(H)dmpp] reacted cleanly with **39** to give the paramagnetic primary phosphanido complex **40**, which, after oxidation to **41** by tropylium hexafluorophosphate and deprotonation, afforded the nickel–phosphinidene complex **42** as bright green crystals in 86% yield (Scheme 13).[24]



Scheme 13. Synthesis of Ni–phosphinidene complex **42**.



Scheme 14. Reactions of **27** with organic dichlorides.

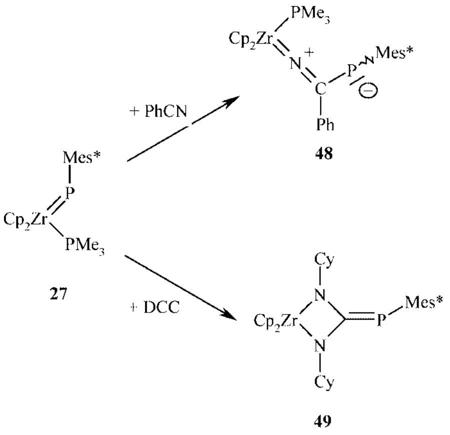
The terminal phosphinidene complex [$Cp_2Zr{=}PMes^*(PMe_3)$] (**27**) proved useful in delivering the phosphinidene [PMes*] to suitable acceptors. The high oxo- and chlorophilicity of the zirconium center in **27** allows exchange of its phosphinidene unit for two chlorine atoms or an oxygen atom of a substrate to form either [Cp_2ZrCl_2] or [Cp_2ZrO]$_n$, respectively. For example, reactions of **27** with dichloromethane or chloroform readily afforded the phosphaalkenes $Mes^*P{=}CH_2$ and (*E*/*Z*)-Mes*P=CHCl[25] (Scheme 14).

With 1,2-dichloroethane phosphirane **8** was formed in addition to [Cp_2ZrCl_2]. The use of *o*-dichloroxylene produced the new phospholane **43** in 53% yield. In contrast to these results, the reaction of **27** with 1,4-dichloro-2-butene did not produce the anticipated five-membered ring, but rather the *cis*-isomer of vinyl-substituted phosphirane **44** in 38% yield. Likewise, the reaction of **27** with 1,4-dichloro-2-butyne produced the vinylidenephosphirane **45** (53% yield). The reactions with alkyl halides were thought to involve phosphanide–halide intermediates of the form [$Cp_2Zr(PMes^*R)Cl$].

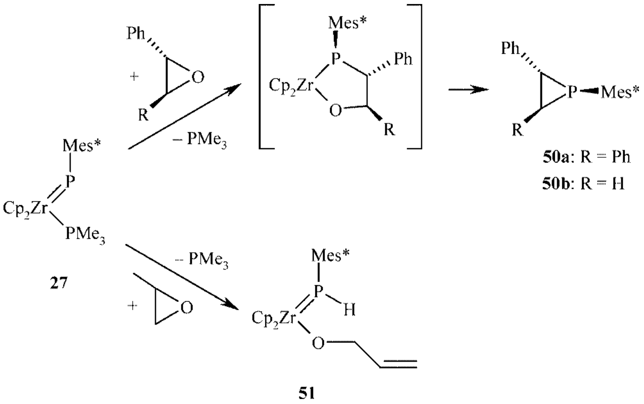
In a Wittig-type process, compound **27** reacted with benzaldehyde to give an insoluble colorless precipitate {presumably [(Cp_2ZrO)$_n$]}, free PMe_3 and (*E*)-Mes*P=CHPh. An analogous synthetic procedure using benzophenone provided an 82% yield of $Mes^*P{=}CPh_2$, and in the same manner the use of 2 equiv. of **27** and isophthalaldehyde furnished exclusively the *E*,*E* isomer of the bis(phosphaalkene) **46** in 86% yield. The related transformation of **27** with phenylisothiocyanate gave the heteroallene *trans*-PhN=C=P–Mes* **47** (81% yield) along with the crystalline blue byproduct [Cp_2ZrS]$_2$[25] (Scheme 15).

The reaction of **27** with benzonitrile afforded the red compounds **48** as a 55:45 isomeric mixture. The addition of **27** with dicyclohexyl carbodiimide (DCC) led to the phosphoguanidino complex **49**[23] (Scheme 16).

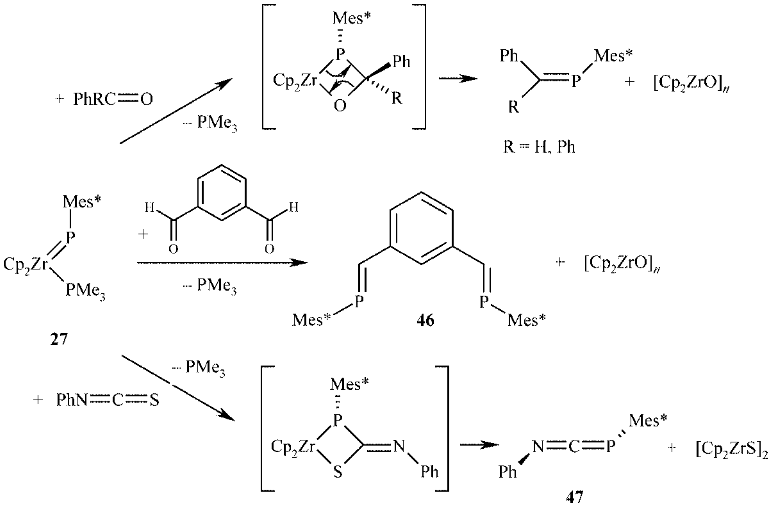
Phosphiranes **50a** and **50b** were derived from reactions of **27** with *trans*-stilbene oxide and styrene oxide, respectively. In the related reaction with propylene oxide, complex **51**, with a secondary phosphanido and a propenolato ligand, was obtained. This process probably involves precoordination of the epoxide to the zirconium center followed by abstraction of the enolizable proton and ring opening[25] (Scheme 17).



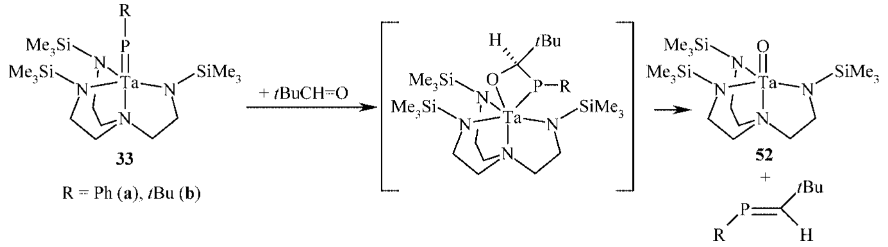
Scheme 16. Reaction of **27** with PhCN and DCC.



Scheme 17. Reaction of [$Cp_2Zr{=}PMes^*(PMe_3)$] (**27**) with epoxides.



Scheme 15. Reaction of **27** with carbonyl compounds and isothiocyanate.

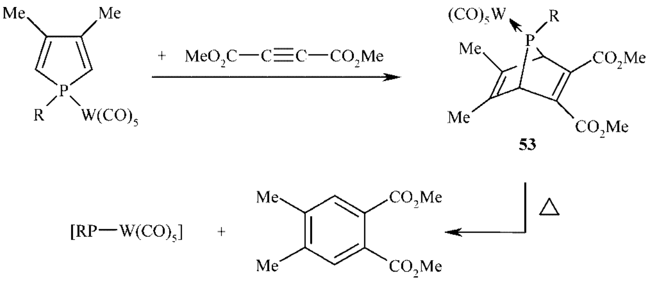


Scheme 18. Synthesis of phosphaalkenes from complex **33** and aldehydes.

Aldehydes react cleanly with tantalum–phosphinidene complexes **33**, providing the stable oxotantalum complex **52** in addition to the corresponding phosphaalkenes. The reaction of **33b** with pivaldehyde took 7 h at 95 °C to reach completion and furnished (*E*)-*t*BuP=CH*t*Bu. Phosphaalkene (*E*)-PhP=CH*t*Bu resulted as an oil in 83% yield from the treatment of **33a** with pivaldehyde[19a] (Scheme 18).

3.2 Electrophilic Phosphinidene Complexes

The synthetically most valuable phosphinidene complexes are unstable species exhibiting the [M(CO)$_5$] (M = Cr, Mo, W) fragment. In two recent reviews, is has been reported that these complexes almost always mirror the chemistry of singlet carbenes in Fischer-type complexes.[9,10] Thus, only a brief survey of this area with selected aspects is presented at this point. The most prominent access to these reagents involved the pyrolysis of [W(CO)$_5$] adducts of 7-phosphanorbornadienes **53** (Scheme 19).[9]



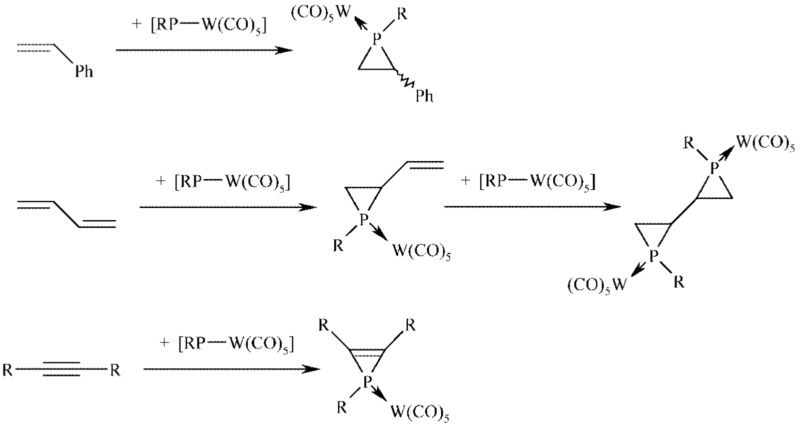
Scheme 19. Generation of [RP–W(CO)$_5$].

The concomitant interception of [RP–W(CO)$_5$] with alkenes proceeded with retention of stereochemistry (Scheme 20).[26] Reaction with alkynes preferentially afforded phosphirene complexes.[27] With 1,3-butadiene, vinyl phosphirane and 2,2′-bisphosphiranyl complexes were obtained.[26,28]

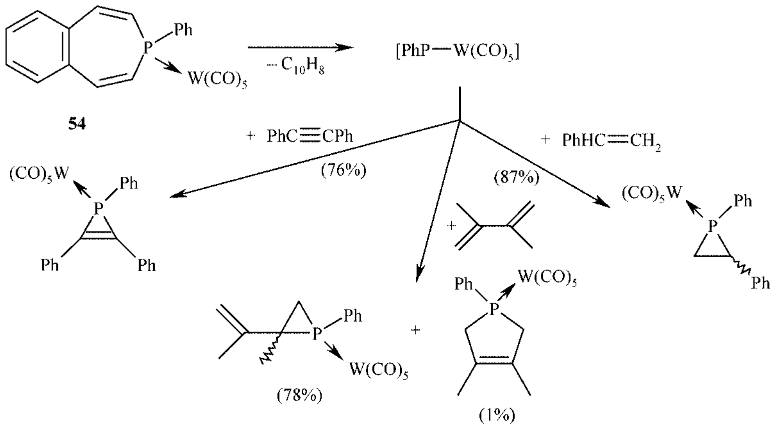
Recently, Lammertsma et al. used the thermolysis of benzophosphepine complexes **54** for the generation and trapping of [PhP–W(CO)$_5$] at 75–80 °C (Scheme 21). Apart from considerably milder reaction conditions, better yields were achieved than with other precursors.[29]

A striking difference between carbenes and electrophilic phosphinidene complexes became evident in their reactivity towards aromatic compounds. In contrast to the reaction of methylene [:CH$_2$] with benzene to afford mainly norcaradiene, which rearranges to cycloheptatriene and toluene, phosphinidene complexes are inert and may be generated in arenes such as toluene. Nevertheless, [RP–W(CO)$_5$] reacted with several selected aromatic compounds. The nucleophilic cyclopentadienyl ligand of ferrocene is an attractive target for the electrophilic phosphinidene, and the reaction results in C–H insertion.[30] Another rare example is the unique [1+4] cycloaddition to ansa compound **55** (Scheme 22) to afford **56**, because it describes the reverse of the cheletropic elimination of [RP–W(CO)$_5$].

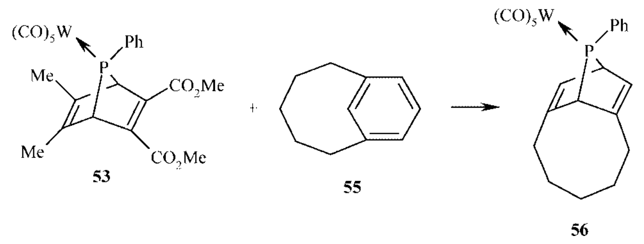
The reaction of [PhP–W(CO)$_5$] generated from **53** in the presence of CuCl at 60 °C leads to C–H-insertion product **57a** (55%) and the formal 1,4 adducts **58a** and **58b** (45%) (Scheme 23). The analogous transformation with guaiazulene favors the formation of the 1,4 adducts **58c** and **58d** (77%) (Scheme 23).[31a]



Scheme 20. Addition reactions of [RP–W(CO)$_5$].



Scheme 21. Thermolysis of **54** and selected trapping reactions of [PhP–W(CO)$_5$].



Scheme 22. Synthesis of **56**.

The reaction of electrophilic phosphinidene complex [MeP–W(CO)$_5$] with 1,6-methano[10]annulene (**59**) resulted in the exclusive formation of the isomeric C–C-insertion products **60a** (main) and **60b** (minor)[31b] (Scheme 24).

Treatment of [(CO)$_5$W–PPh] with 2,4,6-tri-*tert*-butyl-1,3,5-triphosphinine **61** in toluene at 110 °C unexpectedly afforded products **62** and **63a** in 25% and 39% isolated yields (Scheme 25).[32]

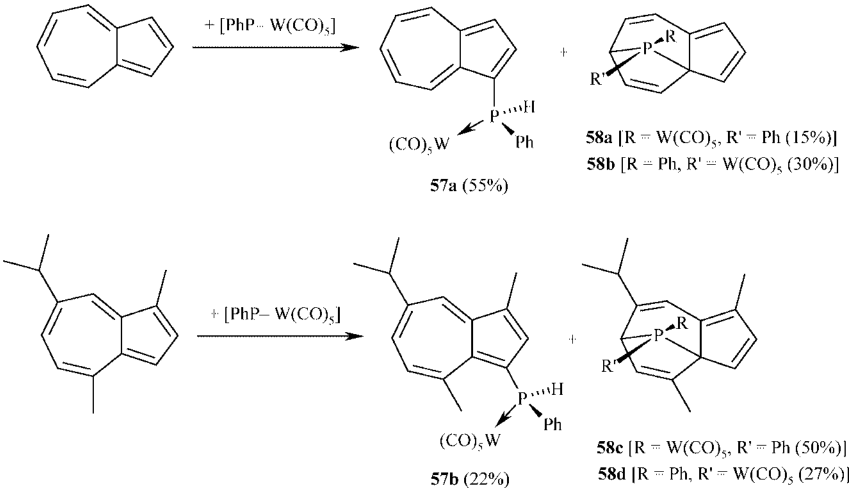
The reaction of [MeP–W(CO)$_5$] with **61**, however, resulted in a mixture of tetraphosphanorbornadiene **64**, a formal 1,4 adduct, and its corresponding quadricyclane **63b** as a 1:8 mixture.[32]

Interception of complexed phosphinidenes generated from **65** with 1-ethoxy-2-(triorganostannyl)acetylene afforded phosphaallene **66** in addition to the expected cycloadduct **67**, which was rationalized by the intermediacy of a zwitterion[33] (Scheme 26).

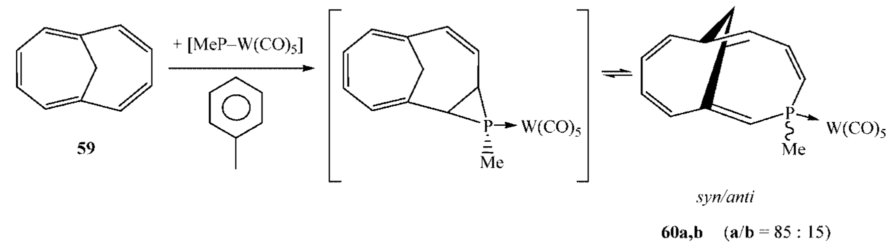
The reaction of tungsten–phosphinidene complexes with ketones and nitriles furnished zwitterionic 1,3-dipolar adducts whose structure depended on the substitution pattern at the P atom[34–36] (Scheme 27).

Functionalized phosphinidene complexes are frequently involved in interesting intramolecular rearrangement processes, which impressively underline the great versatility of the P-substituents[30,37–39] (Scheme 28).

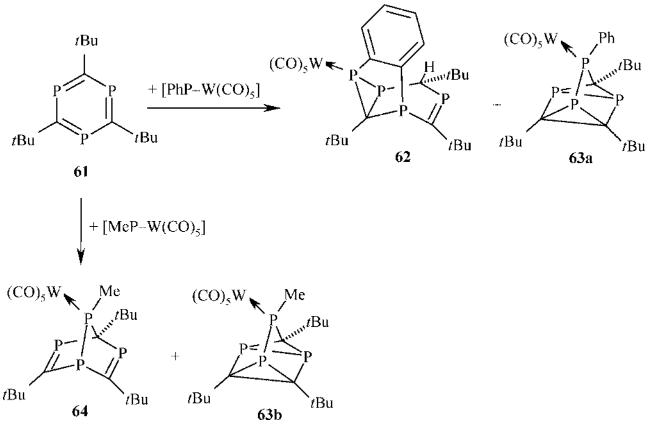
Another type of intramolecular addition of a coordinated phosphinidene was realized by heating complex **68a** in tolu-



Scheme 23. Reaction of [RP–W(CO)$_5$] with azulenes.

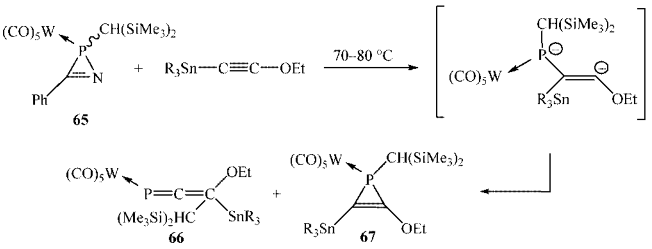


Scheme 24. Phosphinidene addition to **59**.

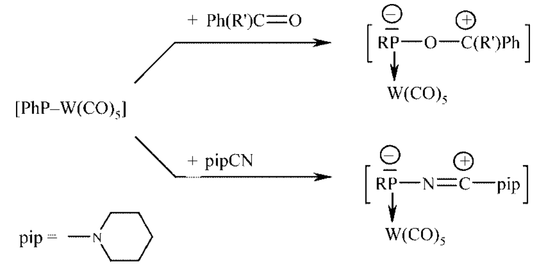


Scheme 25. Reaction of triphosphinine **61** with phosphinidene complexes.

ene at 80 °C to give the diphosphane basket **69a** as the sole isolable product in 66% yield. Similarly, the diphosphane baskets **69b**,**c** were obtained (Scheme 29).[40]

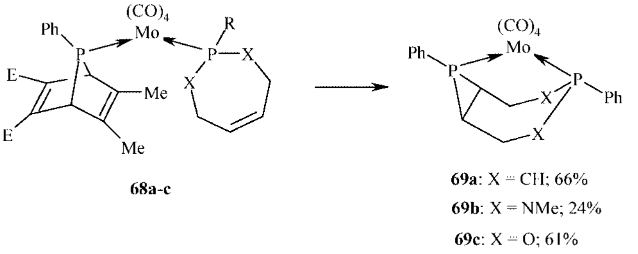


Scheme 26. Synthesis of **66** and **67**.

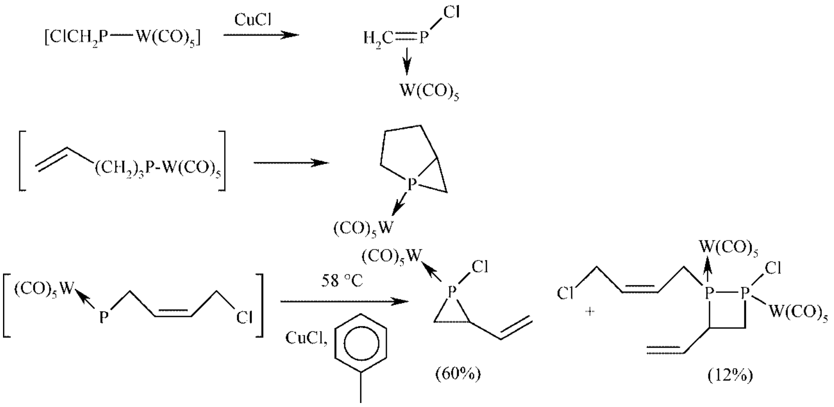


Scheme 27. Zwitterions from phosphinidene addition to ketones and nitriles.

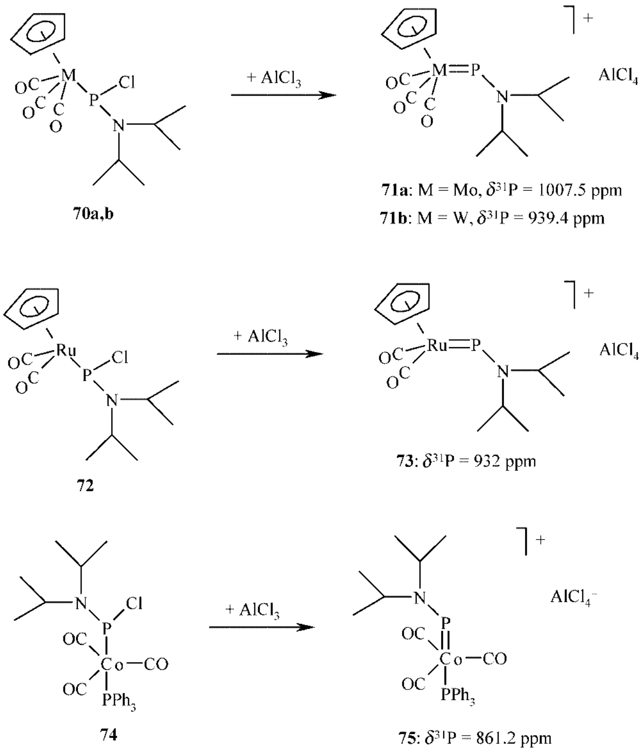
A different route to electrophilic "Fischer Type" phosphinidene complexes of molybdenum, tungsten, ruthenium and cobalt was devised by Carty et al.[11,41,42] Their approach was based on the chloride abstraction from preformed chloro(diisopropylamino)phosphanido complexes **70a**,**b**, **72**, and **74** by using the Lewis acid aluminum chloride (Scheme 30).



Scheme 29. Formation of **69a**–**c**.



Scheme 28. Rearrangement reactions of functionalized phosphinidene complexes.



Scheme 30. Formation of cationic phosphinidene complexes.

So far, the reactivity studies of these cations are limited to alkyne additions.

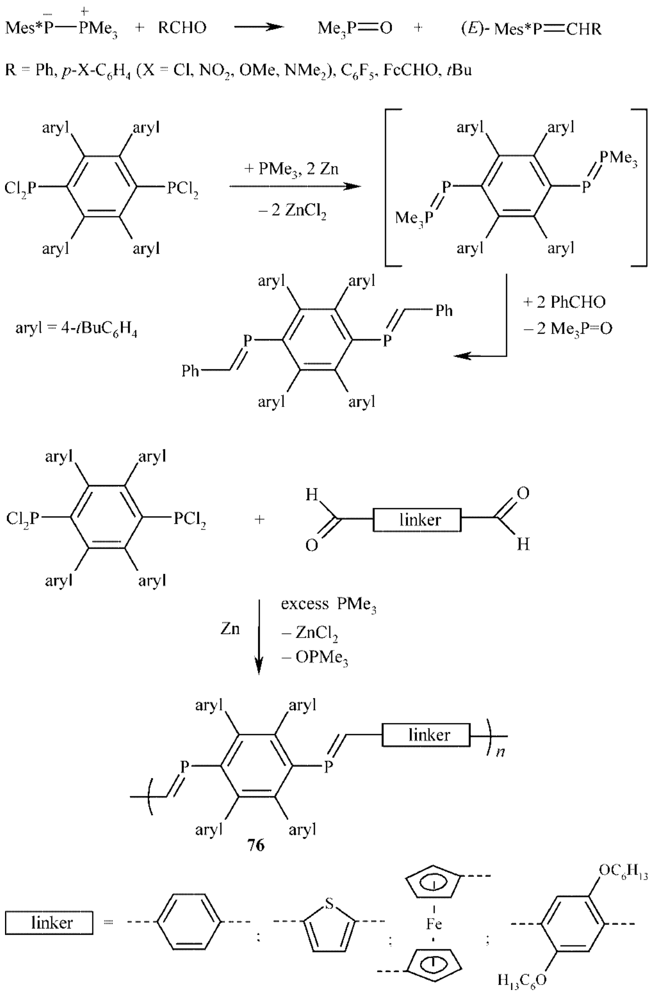
4. Phosphinidene Transfer from Phospha-Wittig Reagents

The Wittig reaction between phosphorus ylides $Ph_3P=CHR^1$ – these reagents may also be considered as carbanions with an α-phosphonium center – and aldehydes and ketones furnished alkenes. Particularly in the light of the diagonal relationship C/P in the periodic table, the quest for an analogous phospha-Wittig reaction was obvious. The required reagents $R^1_3P=PR^2$ are formed by a formal phosphinidene addition to a Lewis basic tertiary phosphane, and they are easily accessible by the reaction of dichlorophosphanes, trialkylphosphanes, and zinc metal. With aldehydes they form phosphaalkenes.[43–45]

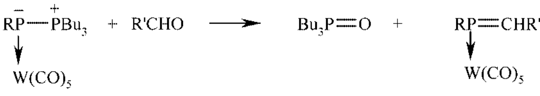
This approach was extended to the preparation of fluorescent (*E*)-poly-*p*-phenylenephosphaalkenes **76**[46] (Scheme 31).

A serious limitation of this protocol is the need of bulky substituents to provide the phospha-Wittig reagents with sufficient stability. This hurdle was circumvented by the coordination of the phosphinidene group to a transition-metal-complex fragment, preferentially to pentacarbonyltungsten, which stabilizes the organophosphorus precursor as well as the resulting phosphaalkene[47,48] (Scheme 32).

This type of reaction can only be performed with aldehydes and usually failed with ketones. This limitation can be overcome by the employment of anionic phosphorylphosphane complexes in a process analogous to the Horner–Wittig reaction[49,50] (Scheme 33).



Scheme 31. Phospha-Wittig reactions.



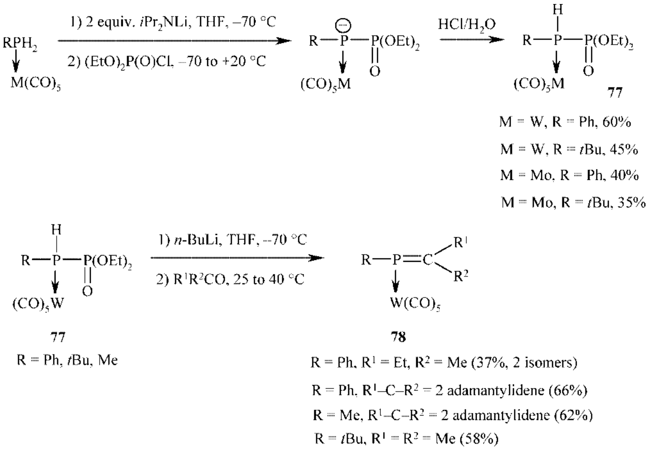
Scheme 32. Phospha-Wittig reactions with $[W(CO)_5]$-supported phosphinidenephosphoranes.

A different type of reaction was observed when phosphinidene-σ4-phosphoranes $arylP=PMe_3$ (aryl = $2,6\text{-}Mes_2C_6H_3$ or $2,4,6\text{-}tBu_3C_6H_2$) were combined with selected *o*-quinones. The formation of 1,3,2-dioxophospholanes **79** and **80** was observed[51] (Scheme 34).

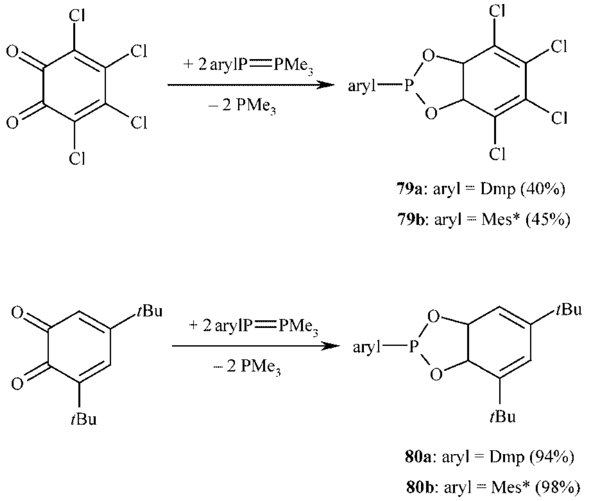
5. Phosphinidene Transfer from Inversely Polarized Phosphaalkenes

5.1 To Diphenylketene

The phosphorus atom of inversely polarized phosphaalkenes such as $R–P=C(NR'_2)_2$ (R = H, alkyl, aryl, $SiMe_3$; R′

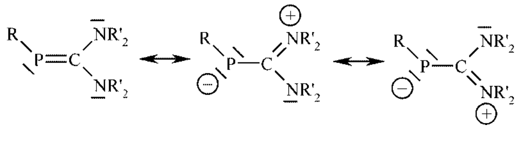


Scheme 33. Selected Phospha-Horner–Wittig reactions.



Scheme 34. Reaction of phosphinidenephosphorane with *o*-quinones.

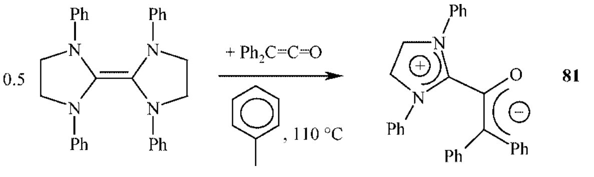
= Me, Et) is highly nucleophilic, which is rationalized by an effective π-electron delocalization of the lone pair of electrons at the trigonal-planar amino substituents into the P–C multiple bond[52] (Scheme 35).



Scheme 35. Limiting formulae of amino-substituted phosphaalkenes.

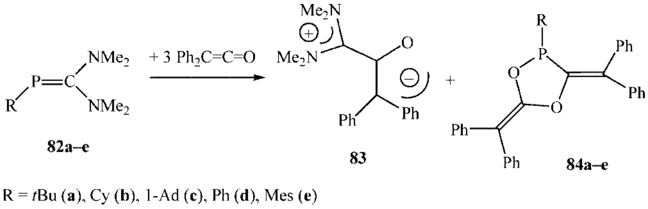
Quantum chemical calculations were performed on the parent methylenephosphane and its amino-substituted derivatives $(H_2N)(H)C=PH$ and $(H_2N)_2C=PH$ at the B3LYP/6-31g* level. The parent compound has a σ + π NBO charge of +0.387 *e* at the phosphorus atom and –0.810 *e* at the carbon atom, whereas its P–C π-bond is essentially nonpolar (+0.030 *e* at P; –0.039 *e* at C). The calculations on the C-amino-substituted phosphaalkenes predict a strong polarization of the π-bond. One, and to a greater extent, two amino groups at the carbon atom induce an inverse electron density distribution at the π-bond [for example, in $(H_2N)(H)C=PH$ a π NBO charge of –0.285 *e* at phosphorus and +0.013 *e* at carbon; in $(H_2N)_2C=PH$ values of –0.504 *e* at phosphorus and +0.059 *e* at carbon were determined].[52] This effect is mirrored in the P=C-double bond lengths, which in nonconjugated phosphaalkenes range from 1.65–1.67 Å, whereas in C-amino-functionalized phosphaalkenes P–C distances of 1.72–1.76 Å are frequently measured. ^{31}P NMR shifts in normally polarized phosphaalkenes $R^1P^{\delta+}=C^{\delta-}R^2R^3$ are mainly governed by a paramagnetic contribution, which is influenced by the HOMO–LUMO gaps in such molecules. Small HOMO–LUMO gaps are responsible for low field shifts in the range between δ = 740 ppm in $[Cp^*(PEt_3)Ni–P=C(SiMe_3)_2]$ and δ = 233 ppm in $MesP=CPh_2$. In inversely polarized phosphaalkenes, where π-conjugation of the nitrogen lone pair with the P=C-double bond operates, the P atom in β-position to the N atoms experiences additional negative charge, which causes a pronounced high-field shift [e.g. δ = –62.6 ppm in $HP=C(NMe_2)_2$].[52]

Protonation,[53] alkylation,[53,54] silylation,[54] and coordination to metal centers occur at the P atom with increase of the coordination number.[53,55,56] With regard to the diagonal relationship in the periodic table between the elements carbon and phosphorus, these electron-abundant C-amino phosphaalkenes are formally analogous to the tetraamino-substituted alkenes of the Wanzlick-type.[57] Accordingly, the homolytic cleavage of phosphaalkene should furnish a relatively stable bis(amino)carbene[58] and a highly reactive phosphinidene. Thus, the quest for Wanzlick-type reactions of the electron-rich bis(amino)phosphaalkenes was obvious. Thereby the reaction of 1,1′,3,3′-tetraphenyl-2,2′-bis(imidazolidinylidene) with diphenyl ketene to afford adduct **81**, performed previously by Regitz et al., served as a model reaction[59] (Scheme 36).



Scheme 36. Formation of a carbene/ketene adduct **81**.

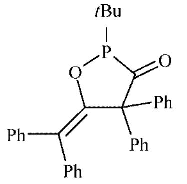
Combination of the phosphaalkenes $R–P=C(NMe_2)_2$ (**82**) [R = *t*Bu (**a**), Cy (**b**), 1-Ad (**c**), Ph (**d**), Mes (**e**)] with an excess of diphenyl ketene in *n*-pentane led to the precipitation of the light yellow zwitterionic compound **83** in about 85% yield. After removal of **83** and destruction of $Ph_2C=C=O$ with powdered NaOH, 3,5-dibenzhydrylidene-1,4,2-dioxophospholanes **84a–e** were isolated as colorless waxes in 45–53% yield[60] (Scheme 37).



R = *t*Bu (**a**), Cy (**b**), 1-Ad (**c**), Ph (**d**), Mes (**e**)

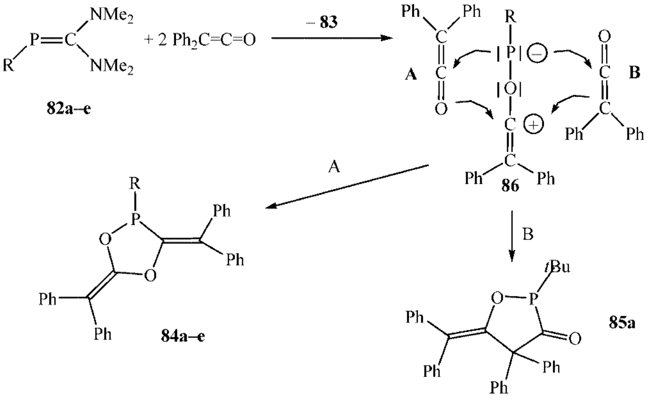
Scheme 37. Formation of compounds **83** and **84a**–**e**.

When the reaction of a concentrated solution **82a** was performed with neat $Ph_2C=C=O$, a dark-violet emulsion was formed, from which product **83** was obtained as previously from the pentane solution. Moreover, a few crystals of 5-benzhydrylidene-2-*tert*-butyl-4,4-diphenyl-1,2-oxaphospholan-3-one (**85a**) were isolated as a byproduct.



85a

According to a series of exchange experiments, transient, free electron-sextet species have to be excluded as intermediates. The following mechanism, invoking 1,3-dipolar species **86**, was proposed to explain the formation of **84a**–**c** and **85a** (Scheme 38).

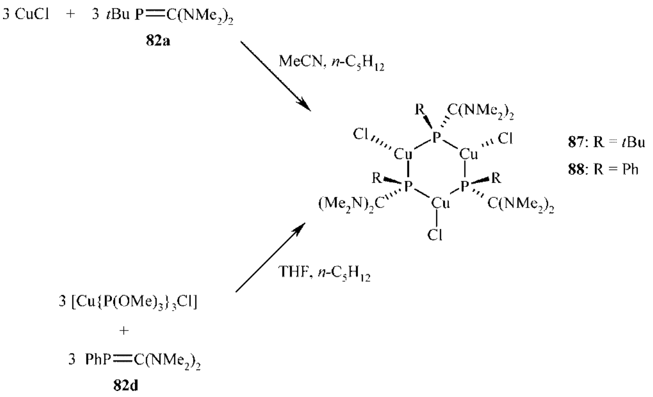


Scheme 38. Proposed mechanism for the formation of compounds **84a**–**e** and **85a**.

It is conceivable that zwitterion **86** and **83** were first formed from **82a**–**e** and two equiv. of ketene. Intermediate **86** then underwent a 1,3-dipolar addition to the C=O bond of another ketene molecule to yield major product **84** (path A). Alternatively, the 1,3-cycloaddition to the C=C double bond of the ketenes afforded **85a** (path B).[52] Reaction of inversely polarized phosphaalkenes with aldehydes did not succeed as yet.

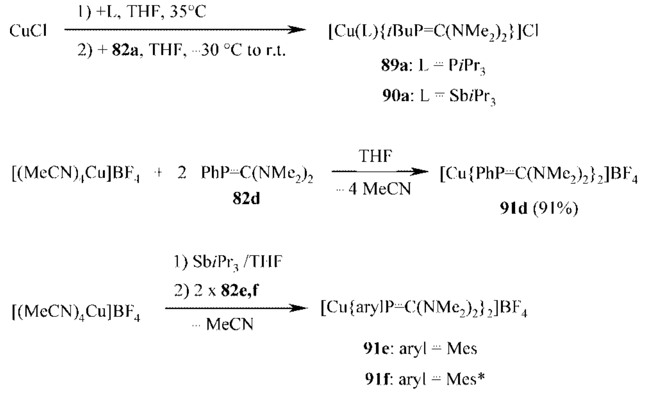
5.2 To Coinage Metal Complexes

In a recent study, the coordination behavior of inversely polarized phosphaalkenes towards copper and gold compounds were investigated. The reaction of equimolar amounts of tBuP=C(NMe$_2$)$_2$ (**82a**) and copper(I) chloride afforded the complex [Cu_3Cl_3\{μ_3-P(tBu)C(NMe$_2$)$_2$\}$_3$] (**87**) as the formal result of the cyclotrimerization of a 1:1 adduct (76% yield).[61] Analogously, complex **88** was synthesized in 66% yield from phosphaalkene PhP=C(NMe$_2$)$_2$ (**82d**) and [Cu\{P(OMe)$_3$\}$_3$Cl] [38] (Scheme 39). Similarly, the analogous complexes [Cu_3X_3\{μ-P(tBu)C(NMe$_2$)$_2$\}$_3$] (X = Br, I) were generated.[62]



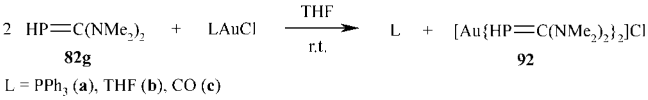
Scheme 39. Synthesis of complexes **87** and **88**.

Treatment of **82a** with [Cu(L)Cl] (L = PiPr$_3$; SbiPr$_3$) led to the formation of compounds [CuCl(L)\{P(tBu)C(NMe$_2$)$_2$\}] **89a** (L = PiPr$_3$) and **90** (L = SbiPr$_3$)[62] (Scheme 40). The reaction of [(MeCN)$_4$Cu]BF$_4$ with 2 equiv. of PhP=C(NMe$_2$)$_2$ (**82d**) yields compound [Cu\{P(Ph)C(NMe$_2$)$_2$\}$_2$]BF$_4$ (**91d**). Similarly, complexes [Cu\{P(aryl)C(NMe$_2$)$_2$\}$_2$]BF$_4$ (**91e**: aryl = Mes; **91f**: aryl = Mes*) are obtained from arylP=C(NMe$_2$)$_2$ [aryl = Mes (**82e**) and Mes* (**82f**)].



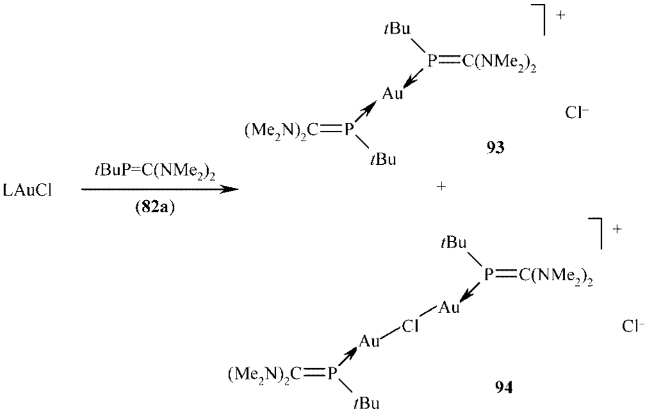
Scheme 40. Formation of the copper complexes **89a**, **90a**, and **91d**–**f**.

A different situation was observed with gold complexes. Combination of the gold complexes [Au(Cl)L] [**a**: L = PPh$_3$; **b**: L = tetrahydrothiophene(THF); **c**: L = CO] with two molar equivalents of phosphaalkene HP=C(NMe$_2$)$_2$ (**82g**) in THF at 20 °C led to the yellow mononuclear complex **92**[63] (Scheme 41).



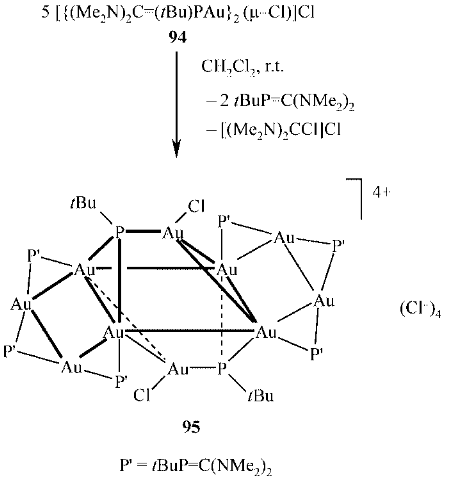
Scheme 41. Reaction of $HP=C(NMe_2)_2$ with [LAuCl].

The reaction of complexes [LAuCl] with the more bulky and more basic phosphaalkene tBuP=$C(NMe_2)_2$ (**82a**) under analogous conditions produced a mixture of cationic complexes **93** and **94** as an amorphous green-yellow precipitate (Scheme 42).



Scheme 42. Reaction of tBuP=$C(NMe_2)_2$ with [LAuCl].

Attempts to separate the compounds by crystallization from dichloromethane or acetonitrile led to the complete transformation of **93** and **94** into the yellow salt **95** with a decanuclear cluster cation (Scheme 43).



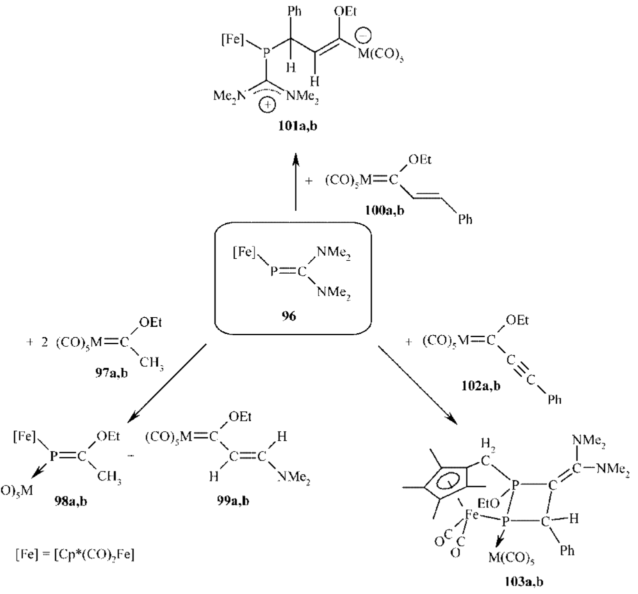
Scheme 43. Formation of **95** from **94** (idealized).

The cation $[(Me_2N)_2CCl]^+$ was formed from an unprecedented nucleophilic cleavage of a P=C double bond by a chloride. According to an X-ray structure analysis, eight gold atoms form a puckered ladder made up of three quadrangles. The central quadrangle is capped on both faces by a [tBu-PAuCl] entity. Three edges of each peripheral rectangle are bridged by phosphaalkene ligands.

5.3 To Fischer Carbene Complexes

Fischer carbene complexes are organometallic electrophiles with a carbene ligand highly susceptible to nucleophilic attack, which renders them extremely useful as reagents and catalysts in modern preparative chemistry. Thus, the question of the reactivity of inversely polarized phosphaalkenes towards these compounds became relevant.

Ferriophosphaalkene **96** was allowed to react with two molar equivalents of carbene complexes **97a** and **97b** in diethyl ether, forming the novel ferriophosphaalkene complexes **98a**,**b** and β-aminoalkenyl(ethoxy)carbene complexes **99a**,**b** (Scheme 44).

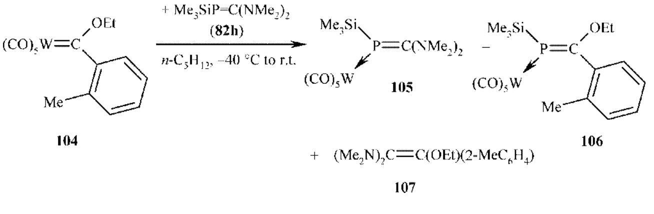


Scheme 44. Reaction of **96** with several Fischer carbene complexes.

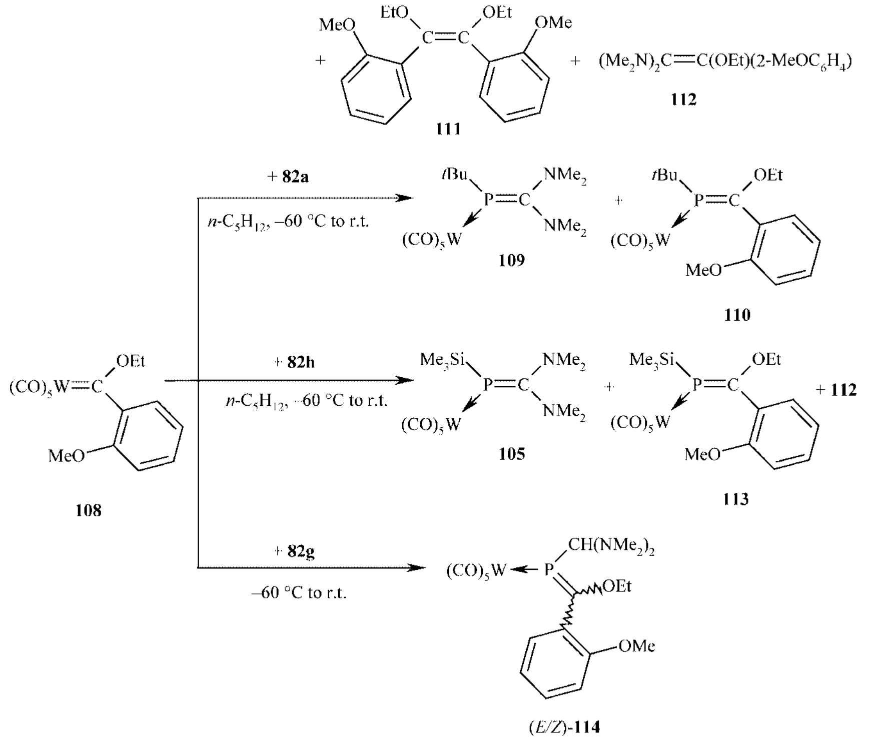
Combination of **96** and the alkenyl carbene complexes **100a**,**b** in a mixture of n-pentane and diethyl ether at –30 °C led to the precipitation of orange zwitterionic Michael-type adducts **101a**,**b** (Scheme 44).

In sharp contrast to the synthesis of **98a**,**b** and **101a**,**b**, treatment of **96** with an equimolar amount of ethynyl(phenyl) carbene complexes **102a**,**b** in n-pentane at –60 °C afforded the yellow pentacarbonylmetal adducts **103a**,**b** of a 1-ferriophosphetane as the only tractable phosphorus-containing products (ca. 20% yield)[64] (Scheme 44).

When the ethoxy(o-tolyl)carbene complex **104** was subjected to reaction with $Me_3SiP=C(NMe_2)_2$ (**82h**) in n-pentane at –40 °C, the yellow complex **105** (38%) was obtained in addition to the novel orange crystalline η^1-phosphaalkene complex **106** and alkene **107** (Scheme 45). No reaction oc-



Scheme 45. Reaction of **104** with phosphaalkene $Me_3SiP=C(NMe_2)_2$.



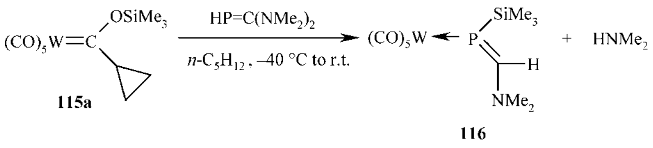
Scheme 46. Reaction of **108** with the phosphaalkenes $RP=C(NMe_2)_2$ (**82a**: R = *t*Bu; **82h**: R = Me_3Si; **82g**: R = H).

curred between **104** and tBuP=C$(NMe_2)_2$ (**82a**). Precursor **104** was decomposed by exposure to $HP=C(NMe_2)_2$ (**82g**).[65]

The reaction of *o*-methoxyphenyl carbene complex **108** with tBuP=C$(NMe_2)_2$ (**82a**) under comparable conditions yielded the yellow η^1-phosphaalkene complex **109** (29%) and the orange η^1-phosphaalkene complex **110** (39%), after fractioning crystallization from pentane. Small amounts of an oily 1:1 mixture of alkenes [(*E*/*Z*)-2-$MeOC_6H_4(EtO)C]_2$ (**111**) and $(Me_2N)_2C=C(OEt)(2-MeOC_6H_4)$ (**112**) were identified as byproducts[65] (Scheme 46).

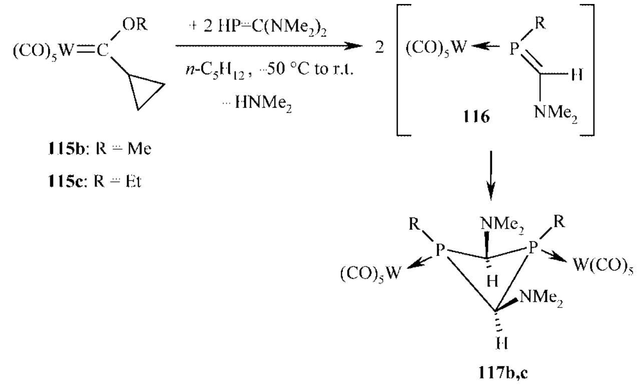
Similarly, combination of **108** with $Me_3SiP=C(NMe_2)_2$ (**82h**) gave rise to the formation of **105** (51%) and the metathesis product $[\{Me_3SiP=C(OEt)(2-MeOC_6H_4)\}W(CO)_5]$ (**113**), which was isolated as an orange solid in 21% yield. Alkene **112** was also identified in the reaction residue (Scheme 46). The course of the reaction of carbene complex **108** with $HP=C(NMe_2)_2$ (**82g**) was completely different. Here $[(CO)_5W]$ complexes of the two geometric isomers of the phosphaalkene $(Me_2N)_2CH–P=C(OEt)(2-MeOC_6H_4)$ (*E*/*Z*)-**114** were obtained as orange crystals in 80% yield. The *E*/*Z* ratio was 1:2[65] (Scheme 46).

As pointed out, the course of the reaction and the product pattern of the processes under discussion are sensitively governed by the nature of substituents at the carbene ligand as well as at the P atom of the organophosphorus reagent. In keeping with this, yet different, results were obtained in the reaction of inversely polarized phosphaalkenes **82** with Fischer carbene complexes having secondary alkyl or cycloalkyl substituents at the carbene carbon atom, which are less electron-withdrawing than aryl groups, but cannot be involved in condensations as primary alkyl substituents at the carbene center. When cyclopropyl carbene complex **115a** was treated with an equimolar amount of phosphaalkene $HP=C(NMe_2)_2$ (**82g**) in *n*-pentane in the range –40 °C to room temperature, phosphaalkene complex **116** separated from the filtered reaction mixture at –16 °C as orange crystals in 47% yield, and dimethylamine was identified as a byproduct. The fate of the cyclopropyl moiety remained unclear (Scheme 47).



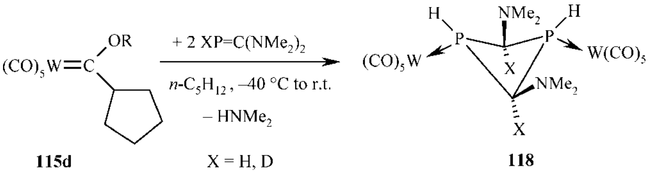
Scheme 47.

In contrast to this, cyclopropyl(methoxy)- and cyclopropyl(ethoxy)carbene complexes **115b** and **115c** were converted by $HP=C(NMe_2)_2$ (**82g**) into the 1,3-bis(pentacarbonyltungsten)-1,3-diphosphetane complexes **117b** and **117c**, which separated from pentane solutions at –16 °C as yellow-to-orange crystals in 60% and 72% yields, respectively.[66] In many cases 1,3-diphosphetanes result from a [2+2] head-to-tail dimerization of relatively unhindered phosphaalkenes. Accordingly, it is most likely that phosphaalkene complexes analogous to **116** were initially generated and subsequently suffered from self-dimerization[66] (Scheme 48).

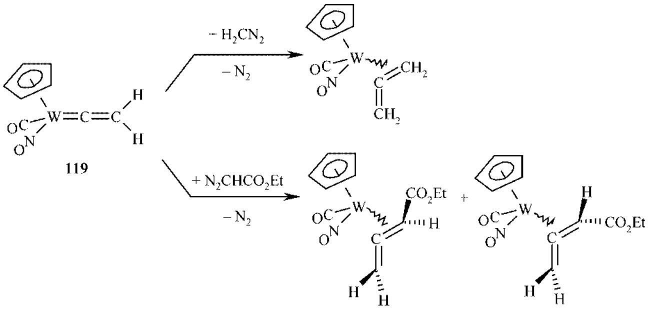


Scheme 48. Preparation of **117b,c**.

Cyclopentyl(ethoxy)carbene complex **115d** and XP=C(NMe$_2$)$_2$ (X = H, D) did not react to afford the expected 1,3-diphosphetane **117c**. Instead, the PH-functionalized 1,3-diphosphetane complex **118** was isolated from *n*-pentane at –16 °C as colorless crystals (42%) (Scheme 49). With DP=C(NMe$_2$)$_2$ product **[D$_2$]118** resulted, where the ring carbon atoms are deuterated. Thus the phosphaalkene cannot be the source of the hydrogen atom at phosphorus in the 1,3-diphosphetane.



Scheme 49. Synthesis of **118**.



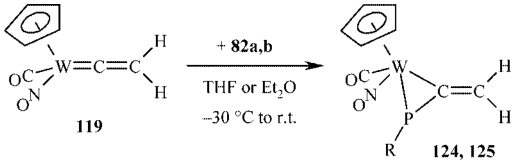
Scheme 50.

5.4 To Vinylidene Complexes

The obvious next step was to study the nucleophilic transfer of phosphinidenes from inversely polarized phosphaalkenes to the electrophilic ligand of vinylidene complexes, which are closely related to transition-metal carbenes. A motivation for this came from a recent paper of Ipaktschi et al. who succeeded in the transformation of vinylidene complex **119** into η^2-allene complexes by exposing it to diazomethane and ethyl diazoacetate[67] (Scheme 50).

Treatment of [Cp(CO)(NO)W=C=C(H)Ph] (**120**) with half a molar equivalent of phosphaalkenes RP=C(NMe$_2$)$_2$ **82** (**a**: R = *t*Bu; **b**: *c*-C$_6$H$_{11}$) in ethereal solvents at 0 °C to 20 °C afforded the crystalline η^2-1-phosphaallene complexes **121** (20% yield) and **122** (19%) after chromatography[68] (Scheme 51). Red crystalline carbene complex **123** was formed as a byproduct in these reactions.

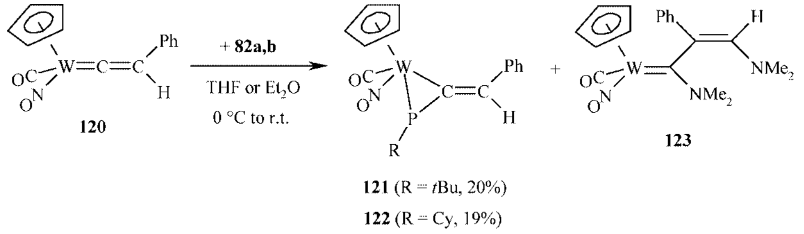
Similarly, yellow crystalline **124** (R = *t*Bu) resulted from the reaction of **82a** and vinylidene complex **119** in THF at 20 °C (30% yield). The synthesis of **125** (R = C$_6$H$_{11}$) from **119** and **82b** was accomplished in diethyl ether at –30 °C (12% yield) (Scheme 52).



Scheme 52. Preparation of the 1-phosphaallene complexes **124** and **125**.

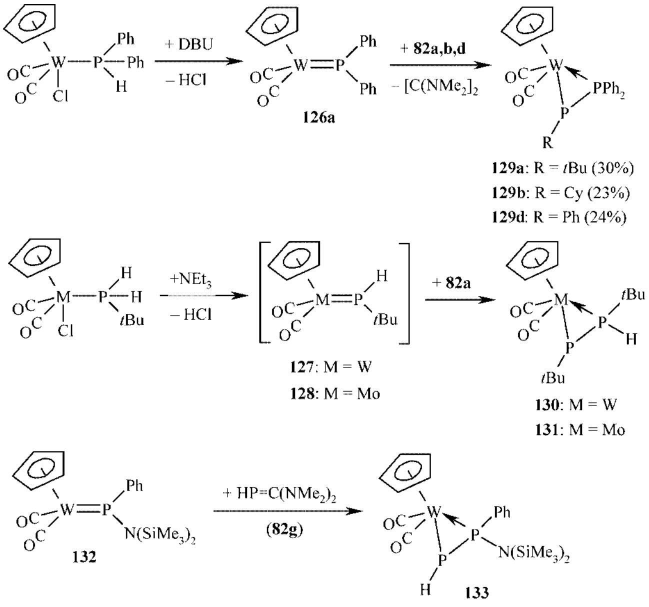
5.5 To Phosphenium Complexes

From a formal point of view, carbene CR$_2$- and phosphenium ligands [PR$_2$$^+$] are isolobal, both exhibiting pronounced electrophilic character. Thus it was obvious to also include transition-metal–phosphenium complexes in the investigations on the nucleophilicity and on the phosphinidene-transfer tendency of inversely polarized phosphaalkenes. Phosphenium complexes [Cp(CO)$_2$W=PPh$_2$] (**126**), [Cp(CO)$_2$-W=P(H)*t*Bu] (**127**), and [Cp(CO)$_2$MoP(H)*t*Bu] (**128**) were freshly prepared by the dehydrochlorination of the chlorophosphane complexes [Cp(CO)$_2$(Cl)W–P(H)Ph$_2$], [Cp(CO)$_2$-(Cl)W–P(H)$_2$*t*Bu], and [Cp(CO)$_2$(Cl)Mo–P(H)$_2$*t*Bu] with



Scheme 51. Preparation of η^2-1-phosphaallene complexes **121** and **122**.

DBU or triethylamine at –78 °C and subsequently combined with phosphaalkenes RP=C(NMe$_2$)$_2$ **82** (**a**: R = *t*Bu; **b**: R = Cy; **d**: R = Ph; **g**: R = H). Alternatively, the isolated compound [Cp(CO)$_2$W=P(Ph)N(SiMe$_3$)$_2$] (**132**) was directly subjected to reaction with HP=C(NMe$_2$)$_2$. Thereby η^2-diphosphanyl complexes **129a**,**b**,**d**, **130**, **131**, and **133** were generated and isolated as crystalline compounds after column chromatography in 24–30 % yield[69] (Scheme 53).



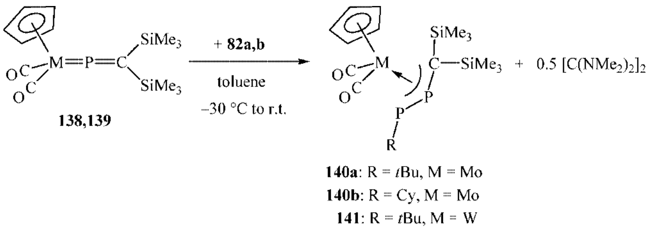
Scheme 53. Preparation of the η^2-diphosphanyl complexes **129a,b,d**, **130**, **131**, and **133**.

The reaction of **126a**,**b** was also conducted with an excess of carbonyl-stabilized phosphaalkenes arylC(O)P=C(NMe$_2$)$_2$ (**134**: aryl = Ph; **135**: aryl = 4-EtC$_6$H$_4$) in toluene in the range –30 °C to room temperature to afford metallophosphaalkenes **136a**,**b** and **137a**,**b** in modest yields (30–46 %)[70] (Scheme 54).

As a mechanism for the formation of the chelates, an initial attack of the phosphaalkene onto the phosphenium center with formation of transient **A** was postulated. Extrusion of carbene [C(NMe$_2$)$_2$] was accompanied by ring closure to give diphosphanyl complex **B**. Insertion of the C=O moiety of **B** into the P–P bond furnished the final products.

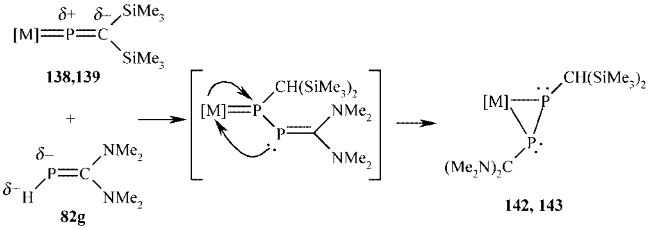
5.6 To Phosphavinylidene Complexes

Phosphavinylidene complexes [Cp(CO)$_2$M=P=C(SiMe$_3$)$_2$] (**138**: M = Mo; **139**: M =W) are organometallic electrophiles closely related to vinylidene as well as to phosphenium complexes. The reaction of phosphavinylidene complex **138** with an equimolar amount of phosphaalkene *t*BuP=C(NMe$_2$)$_2$ (**82a**) in toluene afforded the yellow η^3-1,2-diphosphaallyl complex **140a** by a phosphinidene transfer process from the phosphaalkene onto the ligand (31 % yield). Similarly, **138** was converted into orange product **140b** when allowed to react with CyP=C(NMe$_2$)$_2$ (**82b**) (49 % yield). The reaction of **139** with **82a** under comparable conditions led to the formation of complex **141** (Scheme 55).



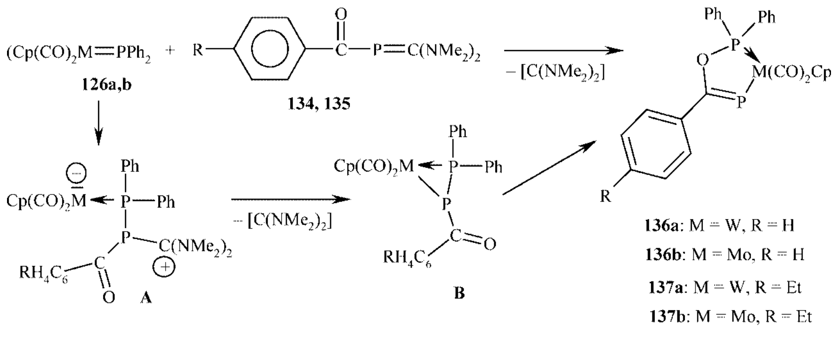
Scheme 55. Synthesis of 1,2-diphosphaallyl complexes.

The reaction of **138** and **139** with an equivalent amount of phosphaalkene HP=C(NMe$_2$)$_2$ (**82g**) in diethyl ether in the range –30 °C to room temperature took another course. Here, a proton transfer from the phosphorus atom on to the disilylmethylene unit of the precursor complex led to the formation of the unsymmetrical diphosphene complexes **142** and **143** as yellow-to-orange crystals[71] (Scheme 56).



[M]= [Cp(CO)$_2$Mo] (**138, 142**); [Cp(CO)$_2$W] (**139, 142**)

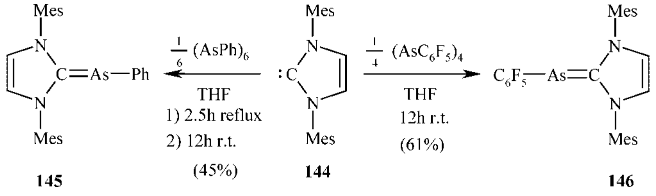
Scheme 56. Formation of complexes **142** and **143**.



Scheme 54. Formation of **136a**,**b** and **137a**,**b**.

6. Arsinidenes

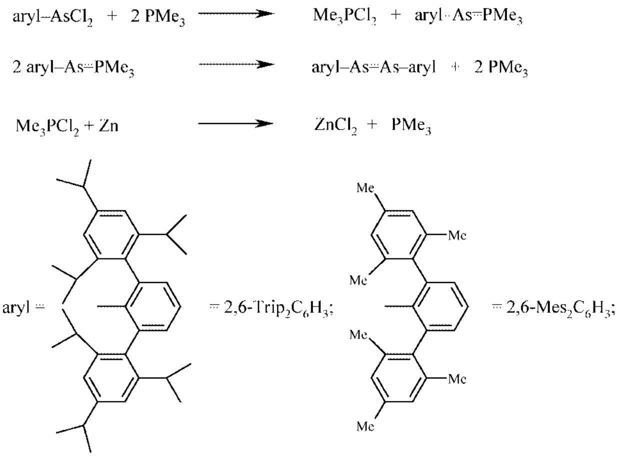
In comparison to the well-developed chemistry of phosphinidenes, little attention has been addressed to the homologous arsinidenes. A few adducts of arsinidenes to carbenes and trimethylphosphane have been prepared recently. Carbene **144** was treated with hexaphenylcyclohexaarsane to form the adduct **145** as a yellow crystalline solid melting at 148–152 °C with decomposition[72] (Scheme 57).



Scheme 57. Preparation of **145** and **146**.

Compound **146** was prepared similarly from **144** and tetrakis(pentafluorophenyl)cyclotetraarsane as a yellow solid in 61% yield.[72]

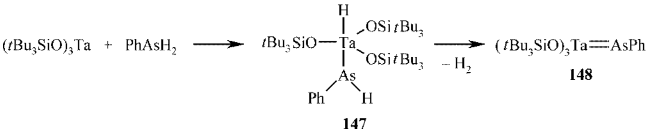
An arsa-Wittig reagent (arsanylidene-σ^4-phosphorane) was synthesized by the zinc reduction of 2,6-Trip$_2$C$_6$H$_3$AsCl$_2$ (Trip = 2,4,6-iPr$_3$C$_6$H$_2$) in the presence of excess of PMe$_3$. The labile product decomposed upon attempted purification to the diarsene 2,6-Trip$_2$C$_6$H$_3$As=AsC$_6$H$_3$Trip$_2$-2,6. Thus, when heated in THF for a few minutes, the arsa-Wittig reagent was quantitatively converted into the diarsene. Attempts to synthesize the arsa-Wittig reagent 2,6-Mes$_2$C$_6$H$_3$-As=PMe$_3$ by reduction of 2,6-Mes$_2$C$_6$H$_3$AsCl$_2$ with zinc and PMe$_3$ gave only the corresponding diarsene in quantitative yield[73] (Scheme 58).



Scheme 58. Synthesis of diarsenes by using arsa-Wittig reagents.

Huttner et al.,[74] conducted pioneering studies of μ_2-arsinidene complexes L$_n$M=As(R)=ML$_n$; however, only little information on complexes with terminal arsinidene ligands is available to date.

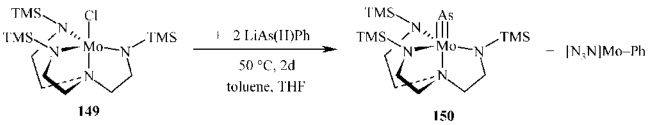
The need to employ bulky groups for the kinetic stabilization of the reactive metal–arsenic multiple bond was also fulfilled by the employment of sterically encumbering ancillary ligands at the metal. Thus, Wolczanski et al. have used the (tBu$_3$SiO)$_3$Ta fragment to support the terminal AsPh group. This first terminal arsinidene complex **148** was prepared by a two-step process, the first of which was an oxidative addition reaction of (tBu$_3$SiO)$_3$Ta with phenylarsane to afford the arsenido complex **147**[20] (Scheme 59).



Scheme 59. Synthesis of **148**.

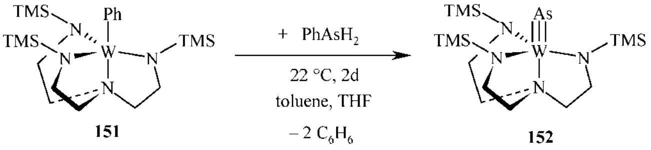
In benzene solution, the arsenido tantalum hydride **147** underwent loss of dihydrogen to yield the terminal arsinidene complex **148**.

The reaction between [N$_3$N]MoCl complex **149** and 2 equiv. of LiAsPhH in the absence of light afforded orange diamagnetic [N$_3$N]Mo≡As complex **150** in ca. 30% yield in addition to an equal amount of [N$_3$N]Mo–Ph, whereby no intermediates could be detected[75] (Scheme 60).



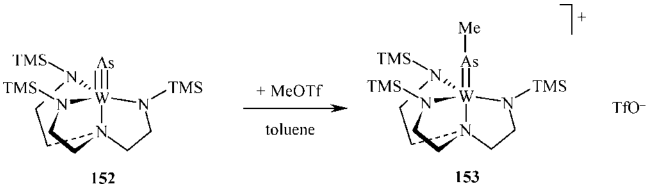
Scheme 60. Preparation of arsenido complex **150**.

The tungsten analogue **152** could not be prepared by a protocol analogous to Scheme 60. Instead, the treatment of phenyl tungsten complex **151** with phenylarsine led to the desired tungsten–arsenido complex[75] (Scheme 61).



Scheme 61. Synthesis of arsenido complex **152**.

This tungsten arsenido complex reacted readily with methyl triflate in toluene to give the cationic arsinidene complex **153**[75] (Scheme 62).



Scheme 62. Methylation of **152** to yield arsinidene complex **153**.

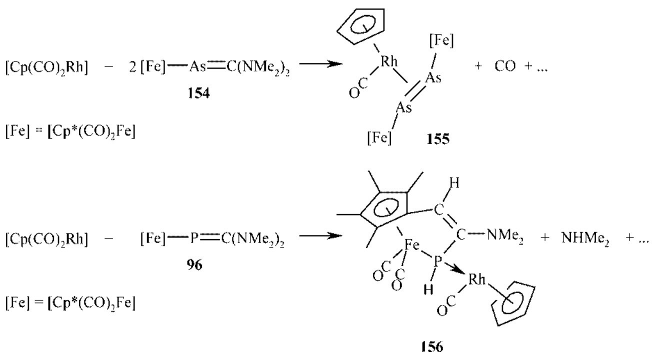
The most interesting features in the molecular structure of **153** are the essentially linear arsinidene ligand [W–As–C = 173.3(6)°] and a W=As bond length of 2.2494(14) Å, which is virtually the same as the Mo≡As bond length in [N$_3$N]Mo≡As. The linearity of the arsinidene ligand in **153** contrasts strongly with the dramatically bent phenylarsinidene ligand [107(4)°] and longer Ta=As bond length [2.428(2) Å] in [(tBu$_3$SiO)$_3$Ta=AsPh].[20]

7. Arsinidene Transfer from Inversely Polarized Arsaalkenes

7.1 With the Formation of (RAs)$_n$ (n = 2, 3)

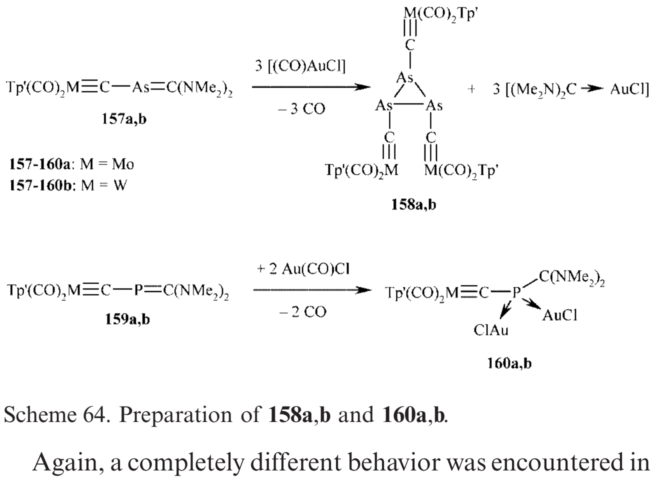
A first evidence for the facile cleavage of the As=C bond of arsaalkenes was observed in the reaction of [Cp*(CO)$_2$-Fe–As=C(NMe$_2$)$_2$] (**154**) with CpRh(CO)$_2$ to afford an η^2-diarsene rhodium complex **155** as dark-red crystals in 63% yield[76] (Scheme 63).

This is in sharp contrast to the behavior of the analogous ferriophosphaalkene **96**, which, upon reaction with the rhodium complex, furnished compound **156** as the result of a condensation process of one methyl group of the Cp* ligand and the tricoordinate C atom of the P=C double bond[76] (Scheme 63).



Scheme 63. Formation of **155** and **156**.

During the studies on [HB(3,5-Me$_2$HC$_3$N$_2$)$_3$(CO)$_2$-M≡C–As=C(NMe$_2$)$_2$] (**157a**: M = Mo; **157b**: M = W) a facile metal-assisted cleavage of the As=C multiple bond was observed in the reaction of the arsaalkene was allowed to react with [(CO)AuCl]. Cyclotriarsanes **158a**,**b** resulted from the formal trimerization of the respective arsinidenes [HB(3,5-Me$_2$HC$_3$N$_2$)$_3$(CO)$_2$M≡C–As]. Thereby the carbene fragment [C(NMe$_2$)$_2$] was intercepted as the known carbene complex [(Me$_2$N)$_2$C→AuCl][77] (Scheme 64).

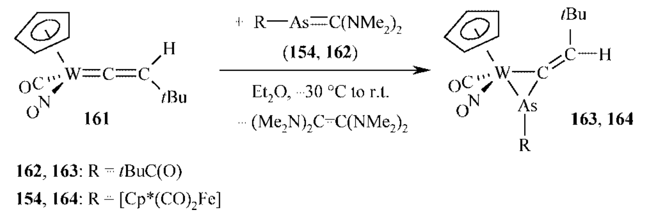


Scheme 64. Preparation of **158a**,**b** and **160a**,**b**.

Again, a completely different behavior was encountered in the reaction of phosphaalkenes **159a**,**b** with the gold compound, where simply a twofold addition of AuCl to the phosphorus atom occurred[77] (Scheme 64).

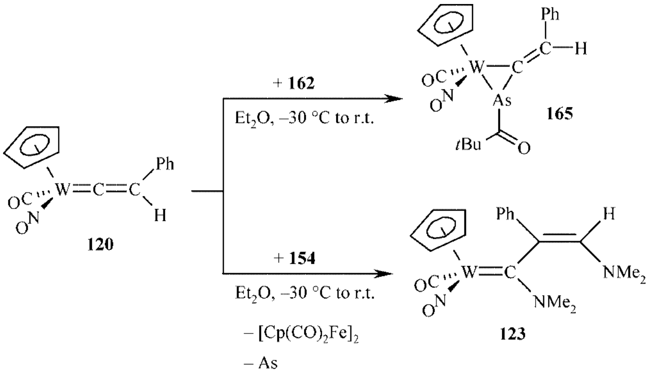
7.2 With Vinylidene Complexes

In order to explore the scope and limitations of inversely polarized arsaalkenes to formally act as a source for arsinidene species, the investigations were extended to vinylidene complexes. Treatment of complex [Cp(CO)(NO)-W=C=C(H)(tBu)] (**161**) with an equimolar amount of arsaalkenes R–As=C(NMe$_2$)$_2$ {**162**: R = tBuC(O); **154**: R = Cp*(CO)$_2$Fe} in diethyl ether solution in the range –30 °C to room temperature afforded the crystalline η^1-1-arsaallene complexes **163** (50% yield) and **164** (73% yield), respectively after chromatography. Compound **164** was obtained as a mixture of two isomers[78] (Scheme 65).



Scheme 65. Formation of the 1-arsaallene complexes **163** and **164**.

An analogous treatment of vinylidene complex **120** with the pivaloylarsaalkene **162** afforded the thermolabile complex **165** as orange crystals in 29% yield (Scheme 66).

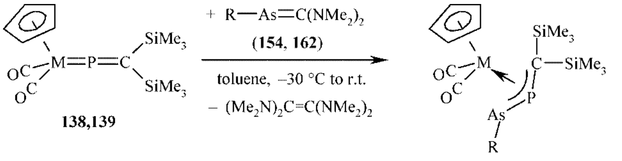


Scheme 66. Reaction of **120** with arsaalkenes **154** and **162**.

In sharp contrast to this, reaction of **120** with ferrioarsaalkene **154** did not lead to the anticipated arsaallene system. Instead, red crystalline carbene complex **123** was isolated in 69% yield. Elemental arsenic and complex [Cp*Fe(CO)$_2$]$_2$ were also obtained (82% yield).[78] The generation of carbene complex **123** was previously observed in the reaction of **120** with phosphaalkenes RP=C(NMe$_2$)$_2$ **82** (**a**: R = tBu; **b**: Cy).[68]

7.3 With Phosphavinylidene Complexes

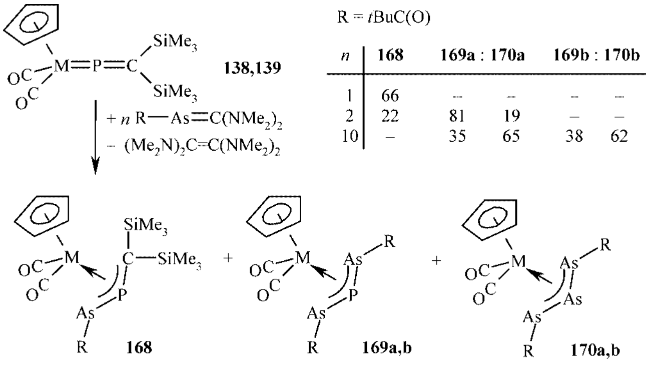
Combination of complexes [Cp(CO)$_2$M=P=C(SiMe$_3$)$_2$] (**138**: M = Mo; **139**: M = W) with an equimolar amount of ferrioarsaalkene [Cp*(CO)$_2$Fe–As=C(NMe$_2$)$_2$] (**154**) in toluene afforded the deep red crystalline η^3-2-phosphaarsaallyl complexes **166** and **167**. Analogously, reaction of compound **162** with an equimolar amount of **139** gave rise to the formation of heteroallyl complex **168** as an orange solid (63% yield). Tetrakis(dimethylamino)ethane was formed as a byproduct[79] (Scheme 67).



166: R = Cp*(CO)$_2$Fe, M = Mo (35%)
167: R = Cp*(CO)$_2$Fe, M = W (52%)
168: R = *t*BuC(O), M = W (63%)

Scheme 67. Formation of the 2-phospha-1-arsaallyl complexes **166**–**168**.

The outcome of the reaction between precursors **138**, **139** and *t*BuC(O)As=C(NMe$_2$)$_2$ proved to be crucially dependent on the respective stoichiometry employed.[80] Thus, when the reaction of [Cp(CO)$_2$W=P=C(SiMe$_3$)$_2$] (**139**) was conducted with twice the molar equivalent of arsaalkene under otherwise comparable conditions, complex **168** was isolated in only 22% yield from the first orange-red zone of the column. From the second deep-red zone, dark-red crystals were obtained, which, according to an X-ray analysis, were disclosed as an inseparable 81:19 mixture of the η^3-2-phospha-1,3-diarsaallyl complex **169a** and the η^3-1,2,3-triarsaallyl complex **170a**. The employment of a 10-fold amount of arsaalkene in this process afforded a 35:65 mixture of **169a** and **170a**[80] (Scheme 68).

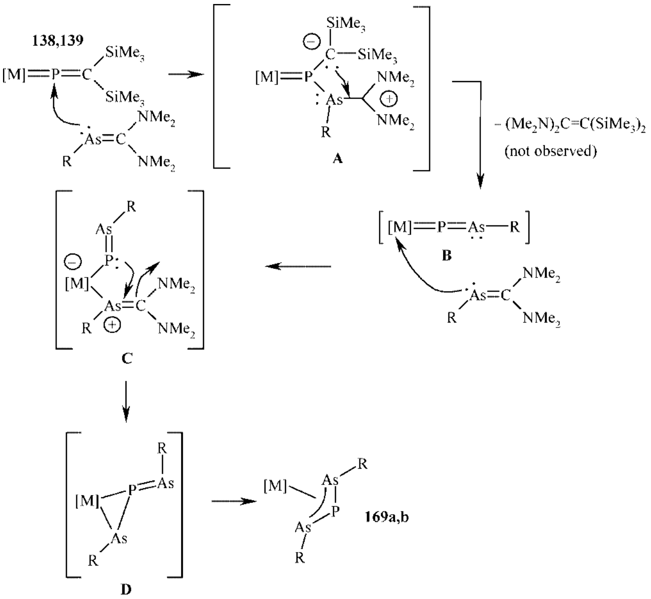


R = *t*BuC(O)

n	168	169a : 170a		169b : 170b	
1	66	–	–	–	–
2	22	81	19	–	–
10	–	35	65	38	62

Scheme 68. Reactions of **138** and **139** with *t*BuC(O)As=C(NMe$_2$)$_2$.

Analogously, the reaction of **138** (M = Mo) with a 10-fold excess of arsaalkene gave a 38:62 mixture of [Cp(CO)$_2$-Mo{η^3-*t*BuC(O)AsPAsC(O)*t*Bu}] (**169b**) and [Cp(CO)$_2$-Mo{η^3-*t*BuC(O)AsAsAsC(O)*t*Bu}] (**170b**). A proposal for the mechanism of the formation of **169a**,**b** involves the initial formation of adduct **A**, which extrudes the putative alkene (Me$_2$N)$_2$C=C(SiMe$_3$)$_2$ with the formation of [Cp(CO)$_2$-M=P=As–C(O)(*t*Bu)] (**B**). The latter arsaphosphene adds a second equivalent of arsaalkene to give intermediate **C**. Liberation of [C(NMe$_2$)$_2$] to form **D** and rearrangement furnish the final products **169a**,**b**. The mechanism of the formation of **170** remained unclear[80] (Scheme 69).

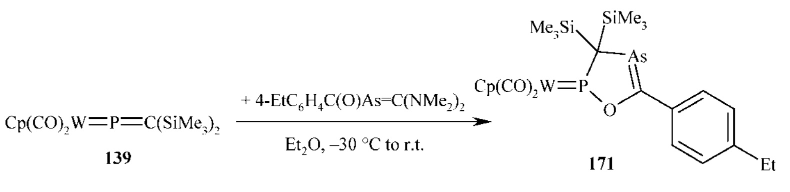


Scheme 69. Proposed mechanism for the formation of compounds **169a**,**b**.

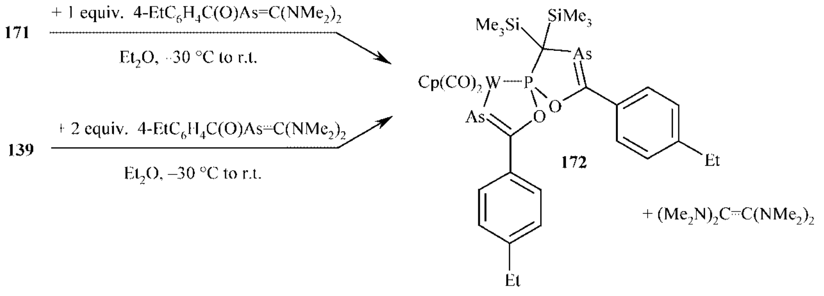
In contrast to this, the more reactive arsaalkene 4-EtC$_6$H$_4$C(O)As=C(NMe$_2$)$_2$ and the tungsten complex **139** underwent reaction to afford the cyclic phosphenium complex **171** as red crystals in 41% yield[79b] (Scheme 70).

The reaction of complex **171** with a second equivalent of 4-EtC$_6$H$_4$C(O)As=C(NMe$_2$)$_2$ or, alternatively, treatment with **139** with two molar equivalents of arsaalkene led to the formation of the bicyclic metalloarsaalkene **172** as yellow crystals in 71% yield (Scheme 71).

Similarly, treatment of complexes **138**, **139** with 2 equiv. of freshly prepared arsaalkene PhC(O)As=C(NMe$_2$)$_2$ in diethyl ether solution afforded the yellow microcrystalline metalloarsaalkenes **173** (80%) and **174** (75%). In the case of the reaction of the molybdenum complex **138** with PhC(O)-As=C(NMe$_2$)$_2$, a few crystals of a second product, **175**, were isolated from the mother liquor after chromatography and

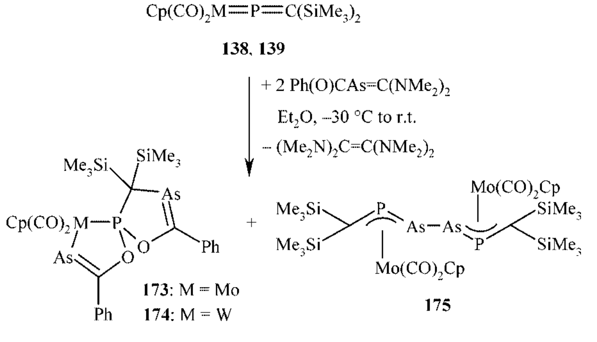


Scheme 70. Formation of phosphenium complex **171**.



Scheme 71. Formation of spiro compound **172**.

separation of **173**. According to an X-ray structural analysis, compound **175** has to be regarded as the yet unknown {Cp(CO)$_2$Mo}η^3(1–3):η^3(3–6)-2,5-diphospha-3,4-diarsadiallyl system[80] (Scheme 72).

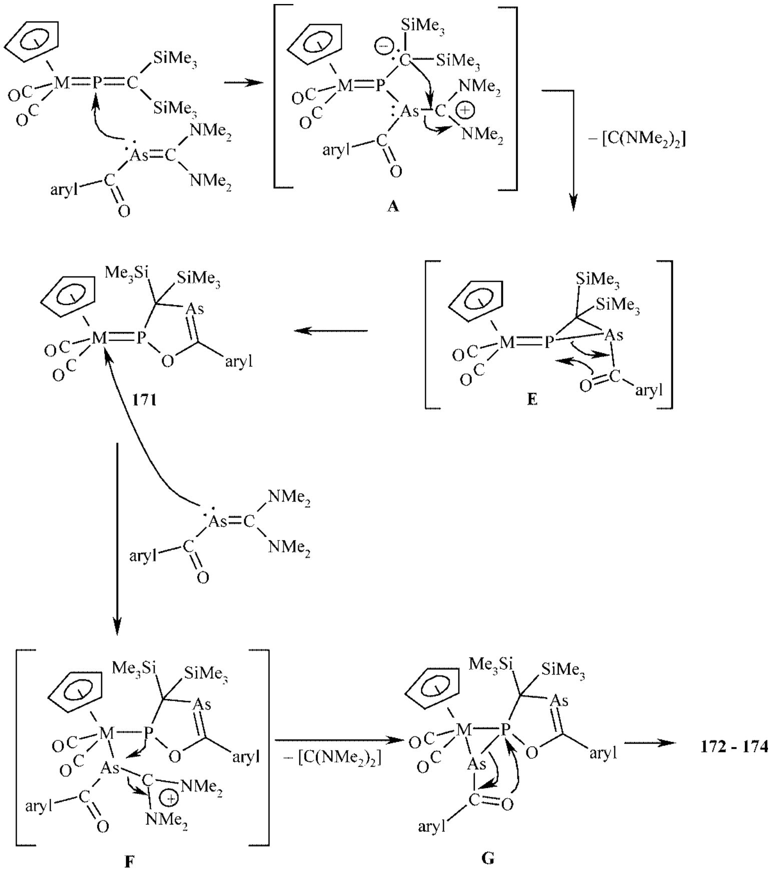


Scheme 72. Formation of **173**–**175**.

For a mechanism, it was suggested that adduct **A** is formed from the precursors, which lose [C(NMe$_2$)$_2$] with formation of intermediate **E**. Insertion of the carbonyl unit into the P–As bond of the three membered ring in **E** afforded the phosphenium complex **171**. Attack of the arsaalkene at the metal center of **171** would lead to intermediate **F**, which extrudes [C(NMe$_2$)$_2$] to give transient **G**.

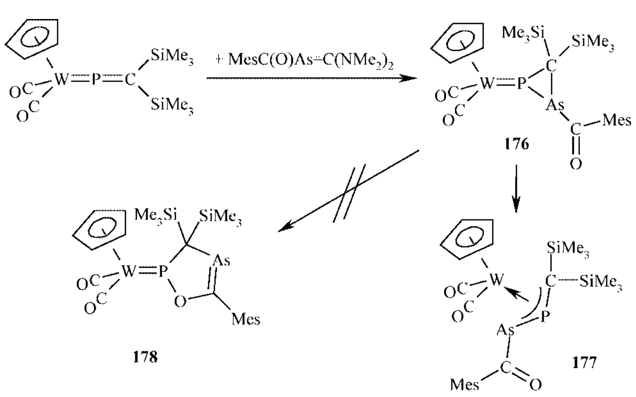
The attack of the carbonyl oxygen atom at the P atom is responsible for the ring enlargement to give final products **172**–**174**[79,80] (Scheme 73).

The increase of the steric demand of the substituent on going from the benzoyl and 4-ethylbenzoyl derivatives to MesC(O)As=C(NMe$_2$)$_2$ provided a situation where hetero-



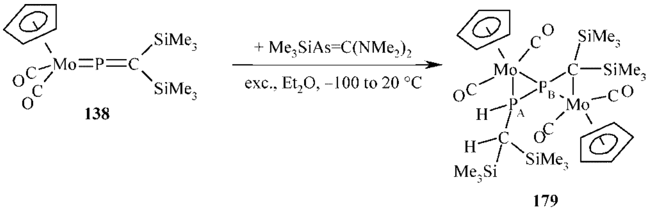
Scheme 73. Proposed mechanism for the formation of **172**–**174**.

cyclic ligands (e.g. in **178**) are no longer formed by CO incorporation. Instead, treatment of **139** with 1 equiv. of this arsaalkene generated the labile phosphenium complex **176**, which rearranged in solution within a few hours to the orange crystalline 2-phospha-1-arsaallyl complex **177** in 54% yield[80] (Scheme 74).



Scheme 74. Formation of 2-phospha-1-arsaallyl complex **177**.

The reaction of arsaalkene $Me_3SiAs=C(NMe_2)_2$ with molybdenum complex **138** proceeded with yet a different result. Combination of the reactants in a 2:1 molar ratio in diethyl ether at –100 to 20 °C afforded the As-free complex **179** as dark-red crystals after chromatographic work-up (yield 64%) [80] (Scheme 75).



Scheme 75. Formation of **179** from **138** and $Me_3SiAs=C(NMe_2)_2$.

8. Conclusions and Perspectives

Inversely polarized phosphaalkenes $RP=C(NMe_2)_2$ serve as convenient sources of the phosphinidene unit PR, which can be transferred onto a broad variety of electrophilic ligands in transition-metal complexes. Their combination with Fischer carbene complexes affords η^1-phosphaalkene complexes. This synthetic principle was extended to vinylidene complexes $[L_nM=CR'H]$ and phosphenium complexes $[L_nM=PRR']$, which are cleanly converted into η^1-phosphaallene and diphosphanido complexes, respectively. Phosphaalkenes, in which the phosphorus atom carries benzoyl-type substituents, reacted with phosphenium complexes with the incorporation of the CO group into five-membered metalloheterocycles. Phosphavinylidene complexes $[L_nM=P=C(SiMe_3)_2]$ are transformed into coordination compounds featuring the novel η^3-1,2-diphosphaallylic ligand. Inversely polarized arsaalkenes $RAs=C(NMe_2)_2$ also display a rich chemistry when allowed to react with organometallic electrophiles such as vinylidene and phosphavinylidene complexes. Here, the synthesis of phosphaallene, phosphaarsaallyl, diarsaphosphaallyl, and triarsaallyl complexes was achieved. Carbonyl-functionalized arsaalkenes led to phosphenium and spiro complexes featuring five-membered heterocycles.

Thus phospha- and arsaalkenes are valuable and versatile reagents in the arsenal of elementorganic and coordination chemists.

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