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Novel Approaches to Phosphorus-containing Heterocycles and Cumulenes

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Abstract

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Fast development in all areas of life and science over the last 50 years demands versatile, energy efficient and cheap materials with specific but easily tuneable properties which can be used for example in organic light emitting diodes (OLEDs), thin-film transistors, photovoltaic cells, etc. This thesis is devoted to the development of novel synthetic approaches to molecules with potential applications in the field of molecular electronics. The acquisition of a detailed mechanistic understanding of the newly developed reactions is central to the work presented in this thesis.

The first chapter is dedicated to the development of a new procedure for the preparation of phospha-Wittig-Horner (pWH) reagents, i.e. a reagents that has been known to convert carbonyl compounds into compounds with P=C double bonds. Each step of the synthetic sequence, i.e. preparation of the starting *P,P*-dichlorophosphines, their phosphorylation using the Michaelis-Arbuzov protocol, coordination to the metal centre and final hydrolysis, are presented in detail. A possible route to uncoordinated pWH reagents is also discussed.

The second chapter focuses on the reactivity of the pWH reagents with acetone under different reaction conditions. The results show how changes in the ratio of starting material *vs.* base as well as reaction time or structure of the pWH reagent can influence the reaction outcome and the stability of the obtained products. The possibility to prepare unusual phosphaalkenes with unsaturated *P*-substituents is presented.

The third chapter of the thesis is dedicated to the reactivity of pWH reagents towards symmetric and asymmetric ketones which contain one or two acetylene units. The proposed mechanisms of the reactions are studied by means of in situ FTIR spectroscopy as well as theoretical calculations. Physical-chemical properties of oxaphospholes, cumulenes and bisphospholes are presented.

The last chapter is dedicated to reactivity studies of pWH reagents towards ketenes, and the exploration of a reliable route to 1-phosphaallenes. Detailed mechanistic studies of the pWH reaction that are based on the isolation and crystallographic characterization of unique reaction intermediates are presented. The reactivity of phosphaallenes towards nucleophiles such as water and methanol are examined.

In summary, this thesis presents synthetic routes to novel phosphorus-containing molecules, together with detailed studies of the reaction mechanisms of the observed transformations.

Keywords: phosphorus, phosphole, oxaphosphole, cumulene, phospha-Wittig-Horner reagent, molecular electronics

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To Anuta

”To fly as fast as thought, to anywhere that is, you must begin by knowing that you have already arrived...”

Jonathan Livingstone Seagull
Richard Bach

List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I Arkhypchuk A. I., Santoni M.-P., Ott S. (2012) Revising the Phospha-Wittig-Horner-Reaction. *Organometallics,* 31(3): 1118-1126.

II Arkhypchuk A. I., Santoni M.-P., Ott S. (2012) Cascade Reactions Forming Highly Substituted, Conjugated Phospholes and 1,2-Oxaphospholes. *Angew. Chem. Int. Ed.,* 51(31): 7776-7780.

III Arkhypchuk A. I., Mihali V. A., Orthaber A., Ehlers A., Lammertsma K., Ott S. Phosphorus heterocycles from phosphinophosphonates and α,β-Unsaturated Ketones. *Manuscript*

IV Arkhypchuk A. I., Svyaschenko Y. V., Orthaber A., Ott S. (2013) Mechanism of the Phospha-Wittig-Horner Reaction. *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.201301469

Related papers not included in this thesis:

V Arkhypchuk A. I., Ott S. (2011) Reductive Diphosphene Formation from $W(CO)_5$-coordinated Dichlorophosphanes. *Phosphorus, Sulfur, and Silicon and the Related Elements*, 186: 664-665.

Contribution Report

Paper I. Performed all of the synthetic work and characterization, except for the X-ray crystallography. Major contribution to the interpretation of the results and to the writing of the manuscript.

Paper II. Performed all of the synthetic work and characterization, except for the X-ray crystallography. Major contribution to the interpretation of the results and to the writing of the manuscript.

Paper III. Performed major part of the synthetic work and characterization, except for the X-ray crystallography. Major contribution to the interpretation of the results and to the writing of the manuscript.

Paper IV. Performed major part of the synthetic work and characterization, except for the X-ray crystallography. Major contribution to the interpretation of the results and to the writing of the manuscript.

Contents

Abbreviations

CV	Cyclic Voltammetry
DABCO	1,4-Diazobicyclo[2.2.2]octane
DBU	1,5-Diazabicyclo[4.3.0]non-5-ene
DFT	Density Functional Theory
FTIR	Fourier Transform Infrared Spectroscopy
HOMO	Highest Occupied Molecular Orbital
HWE	Horner Wadsworth Emmons
LDA	Lithium diisopropylamide
LUMO	Lowest Unoccupied Molecular Orbital
m-CPBA	3-Chloroperbenzoic Acid
NMR	Nuclear Magnetic Resonance
OLED	Organic Light Emitting Diode
ORTEP	Oak Ridge Thermal Ellipsoid Plot
pWH	Phospha-Wittig-Horner
TES	triethylsilyl
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TMS	trimethylsilyl

1. Introduction

Life has dramatically changed over the last decades. Fast development in all areas of life and science over the last 50 years has caused a need for more and more powerful computers. Since the discovery of the integrated circuit by Jack Kilby in 1959, the number of transistors per unit area on integrated circuits, or functionality per chip, has doubled every 1.5 year. This is known as Moore's law which is expected to hold until 2020.[1] While in 2007 the 45 nm process technology was used for manufacturing, there are already published experimental results on a transistor with 10 nm gate length.[1,2] This "top-down" approach in nanotechnology is limited by processing restrictions. The cost of building fabrication facilities to manufacture chips has been increased exponentially by a factor of two for every chip generation. This is known as Moore's second law. One of the ways to overcome this economical problem is to use a "bottom-up" approach instead; i.e. an approach which would provide components made of single molecules, held together by covalent forces that are far stronger than those in macro-scale components. Over last two decades, a huge amount of literature has been devoted to molecular electronics. Scientists from all over the world turned their attention to the preparation of versatile, energy efficient and cheap materials with specific but easily tuneable properties.[2,3] While single molecule electronics is still challenging, the field of organic electronics has already matured considerably. Molecules and polymers ordered in special ways (e. g. in the form of structured mono- or multilayers) have found application as parts of displays in mobile phones and cameras where they play the role of electroluminescent materials.[4] This success story is rooted in the first organic electronic device which was made already in 1974 from melamine polymers.[5] In contrast, the field of single molecule electronics remains challenging as for industry as well as for academia, a high knowledge barrier needs to be overcame before first stable devices based on single molecules will become available on the market.

The term "molecular electronics" can be divided into two sub-categories – single molecule electronics and multi-molecule, or molecular material electronics. This distinction to some extent also underlines the two disciplines that need to be advanced to tap the full potential of molecular electronics – the development of techniques on the engineering side on one hand and the preparation of suitable molecules and molecular materials on the other. This thesis is devoted to the second task, i.e. the development of chemical ap-

proaches to intriguing molecules with potential applications in the field of molecular electronics. Special attention will be paid to π-conjugated systems. The first generation of π-conjugated materials was based on highly unsaturated all-carbon backbone polymers. Since the first organic electronic device was made in 1974,[5] these kind of polymers found applications in organic light emitting diodes (OLEDs), thin-film transistors, photovoltaic cells, etc.[2] Recently, it was shown that the incorporation of heavier elements into the carbon framework of π-conjugated systems has several important advantages compared to the traditional all-carbon based analogues. The heteroatom-containing systems exhibit reduced HOMO-LUMO gaps, some of them improved stability, etc. Phosphorus plays an outstanding role in this context since substances that contain multiple P-C bonds display similarities to their all-carbon analogues,[6] while the presence of the lone pair gives a possibility for unique modifications like oxidation, metal coordination or addition of electrophiles.[7,8] In general, all phosphorus-doped and phosphorus-containing π-conjugated materials can be divided into two larger groups: linear structures that contain phosphorus-carbon or phosphorus-heteroatom double bonds and phosphorus containing heterocyclic motives where the phosphorus atom is part of the ring system. This thesis describes the utilization of the phospha-Wittig-Horner reagents[9] for the preparation of representatives of both classes. Phosphaalkenes that feature a P=C double bond are a member of class I, while phospholes are one of the most important members of class II. Special attention is paid to the development of new reactions that lead to their preparations and to the acquisition of a mechanistic understanding. At the heart of this thesis is the reaction between phospha-Wittig-Horner reagents and unsaturated ketones. Theoretical, crystallographic and spectroscopic techniques were used to characterize the products, as well as to understand the reaction mechanism and to identify key reaction intermediates.

2. Background

This chapter gives an introduction to three classes of phosphorus containing compounds – phosphaalkenes, phospholes, and oxaphospholes – with the aim to make the reader familiar with their properties and possible applications. General synthetic approaches to these compounds are presented with particular focus on the phospha-Wittig-Horner approach towards phosphaalkenes.

2.1 Phosphaalkenes

2.1.1 Introduction

Phosphaalkenes are compounds which contain a three-valent two coordinated phosphorus atom which is doubly bonded to one adjacent carbon centre.[7] Even though those compounds contradict the double bond rule,[10-12] they have been known for more than 35 years.[13] Since the first phosphaalkene was prepared in 1976 by G. Becker through a condensation of bis(trimethylsilyl)phosphines with acid chloride, followed by a 1,3-silyl shift,[13] many different compounds of this class have appeared in the literature.[6,7,14-16] The popularity of phosphaalkenes originates in parts from the phosphorus-carbon analogy, i.e. the fact that low-valent phosphorus is rather similar to carbon in many respects. At the same time, the phosphorus heteroatom introduces unique properties into the system which are not present in the carbon analogues. Phosphorus, which is sometimes referred to as "the carbon copy"[6] has a similar electronegativity compared to carbon (C 2.5 vs. P 2.2). This property describes its ability to accept or release electrons, and is responsible for the reactivity of compounds which contain phosphorus. Since chemical reactivity is associated with the energies and localization of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), it is interesting to compare the parent phosphaalkene – phosphaethylene - with its carbon analogue – ethene (Figure 1).

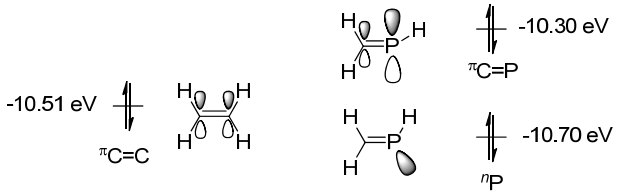


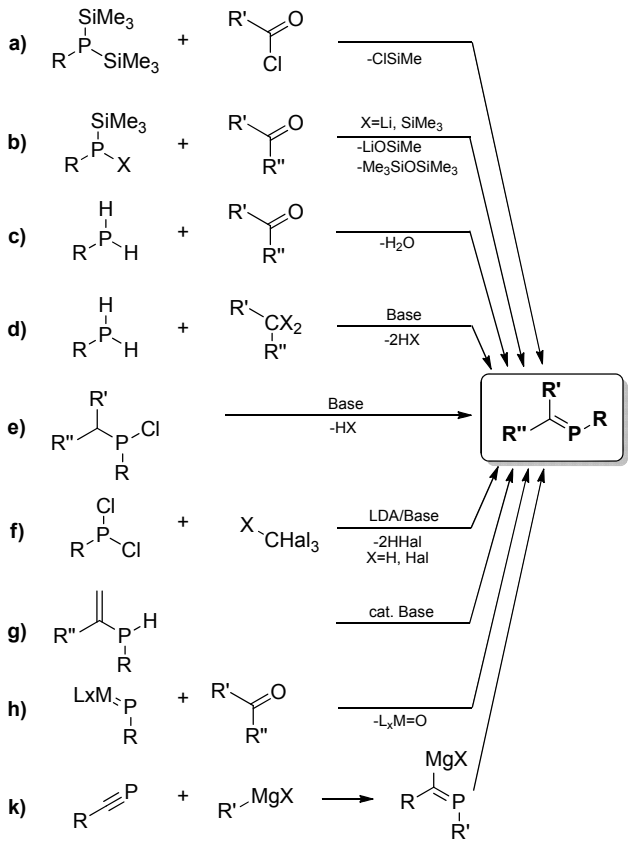
Figure 1. *HOMO of phosphaalkene and ethylene*

As can be seen from Figure 1, the HOMO of phosphaaethylene is the π-bond which is 0.21 eV higher in energy than the HOMO of ethylene. The former can thus be expected to exhibit a higher reactivity than the latter.[17] The lone pair in phosphaaethylene is only 0.40 eV more stable than the π-system and can thus be expected to have a tendency to participate in the reactions. A high reactivity of phosphaalkenes is also confirmed by thermodynamic data which show that the dissociation energy of the P=C double bond is smaller than that of the C=C bond as the result of much smaller contributions of the π-bond in case of the P=C system.[18] At the same time, the P=C double bond is almost nonpolar.[19] Its regioselectivity in reactions with polar reagents can be controlled by proper choice of substituents at both atoms.[20] Further similarities between P=C and C=C bonds are found in their chemical properties and reactivities. Like their carbon congeners, phosphaalkenes can participate in polymerisation reactions, addition and pericyclic reactions [6,8].

Beside the resemblance between alkenes and phosphaalkenes, the introduction of phosphorus offers unique possibilities compared to the all-carbon case. For example, the electronic properties of phosphorus containing compounds can be changed by simple chemical modifications such as oxidation of the heteroatom, or by metal coordination to the phosphorus lone pair or to the phosphorus-carbon double bond.[6-8,15] These properties suggest the utilisation of phosphaalkenes as ligands in catalysis,[14] as monomeric building blocks for the preparation of phosphorus containing polymers as well as for the construction of oligomeric and polymeric π-conjugated materials.[16,21,22]

2.1.2 Preparation of phosphaalkenes

Since the discovery of phosphaalkenes, a variety of synthetic protocols have been developed. A summary of the most well-known procedures is presented in Scheme 1. Route a) is historically the first one that was used for the preparation of phosphaalkenes. It consists of a condensation between bis(trimethylsilyl)phosphines and acid chloride with associated TMSCl elimination, followed by a 1,3-silyl shift.[13] This procedure has remained one of the most commonly used methods to-date.[23,24] Recently, this approach was successfully used for the preparation of the first poly(-p-phenylenephosphaalkene) (PPP) in the group of D. Gates.[25]

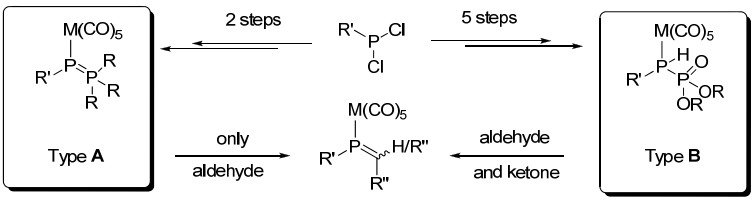


Scheme 1. *General approaches towards phosphaalkenes*

Another method to form P=C double bonds is the so-called phospha-Peterson approach (route b) which originates from the Peterson olefination.[26-29] In this procedure, carbonyl compounds are reacted with lithiated trimethylsilylphosphines or bis(trimethylsilyl)phosphines. Similarly to imines, phosphaalkenes can also be formed by elimination of water in a reaction between primary phosphines and carbonyl compounds (aldehydes or ketones, route c).[30] Elimination of other small molecules for example hydrogen chloride or bromide, can also be used to form P=C bonds (route d, e and f).[31-33] Special attention should be paid to route e) since this is one of the most common procedures that can be utilized for the preparation of phosphaalkenes with different substituents at both carbon and phosphorus.[34-39] An elegant approach towards *C,C*-dibromo-substituted phosphaalkenes was developed by Bickelhaupt (route f). In this case, the target compounds are obtained by treatment of *P,P*-dichlorophosphines with base in the presence of haloform or tetrahalomethane.[40,41] Even though the exact reaction mechanism is not clear, this approach allows the preparation of phosphalkenes in high yields. Synthetic protocols for the conversion of the bromide substituents to different alkyl or aryl groups were also developed.[42-44] 1,3-proton

shifts can also be used for the preparation of phosphaalkenes (route g),[45] while phosphinidine-metal complexes have been employed for the synthesis of the desired phosphorus compounds.[46-49] Addition of Grignard reagents to phosphaalkynes (compounds which contain phosphorus carbon triple bonds) results in the formation of metal-substituted phosphaalkenes where the metal can be exchanged by other electrophiles to yield phosphaalkenes with the desired substitution pattern.[50,51]

From our point of view, one of the most interesting approaches is the so-called phospha-Wittig reaction which has been known to convert simple aldehydes and ketones to phosphaalkenes with different substitution patterns at the carbon centre. The reaction also tolerates several types of substituents at the phosphorus side. The only restriction is a need for stabilization of the P^{III} centre either by relatively bulky *P*-substituents or by the coordination of metal-fragments. In analogy to the all-carbon case, two different types of reagents which differ in the nature of the P^{V} centre have been reported (Scheme 2).[52-56]

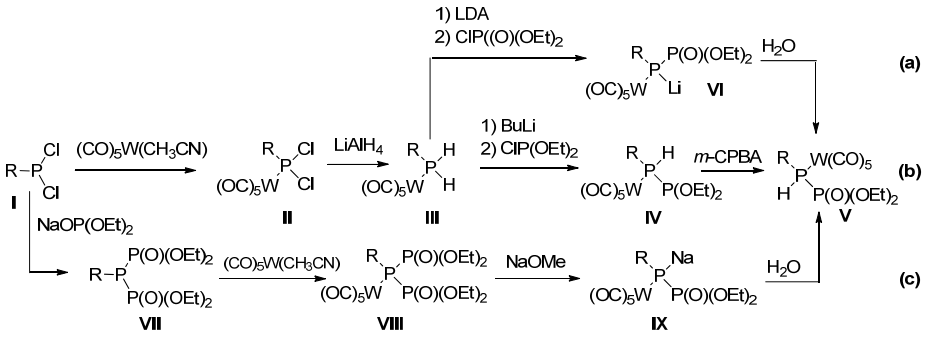


Scheme 2. *Phospha-Wittig (A) and phospha-Wittig-Horner (B) approach towards phosphaalkenes*

The compounds of type A (Scheme 2, left) which bear -PR_3 groups (R = alkyl, aryl, etc.) are usually referred to as phospha-Wittig reagents. They can be prepared from dichlorophosphines in only two steps, react however only with aldehydes to form phosphaalkenes where thus at least one *C*-substituent is a proton.[53,54,57,58] A metal-free version of these reagents is also known.[57] Compounds of type B (Scheme 2, right) which contain a $(RO)_2P{=}O$ unit are usually referred to as phospha-Wittig-Horner (pWH) reagents.[9,52] These compounds are more reactive and can also convert ketones into phosphaalkenes. Their preparation is described in a few publications and requires multistep synthesis.[9,52,59-61]

2.1.3 Preparation of pWH reagents

pWH reagents were first prepared in the group of Mathey in the early 90's, and alternative protocols were developed by the same group quickly thereafter.[9,52,59-61] A summary of the synthetic procedures that were available prior to the work described in this thesis is presented in Scheme 3.



Scheme 3 *Summary of literature procedures towards phospha-Wittig-Horner reagents. a) R=Ph, t-Bu,*[9] *b) R=Mes, Ment ,*[60] *c) R=Me, Ph, t-Bu, PhCH=CH, BuOCH=CH, 2-thieny .*[59]

All strategies presented in Scheme 3 start from *P,P*-dichlorophosphines. In case of routes a) and b), compounds **I** are first coordinated to a tungsten pentacarbonyl core and subsequently reduced to the primary phosphines with lithium aluminum hydride. Complexes **III** are stable towards water and oxygen and can be prepared on large scale and stored over a long period of time. Lithiation of **III** can be achieved by BuLi or LDA and the resulting salt can react with diethyl chlorophosphate and diethyl chlorophosphite in route a) and route b), respectively. In the first case, the reaction product is already the lithium salt of the target pWH reagent and quenching of the reaction mixture with water gives the desired pWH reagent **V** in 45-60% yield based on **III**. In route b), phosphinophosphite **IV** which is stable in solution and can be characterized by ^{31}P NMR is oxidized by *m*-chloroperbenzoic acid (*m*-CPBA) to afford product **V** in 84 % isolated yield based on **III**. Route c) represents a different approach towards pWH reagent **V** and, at the same time, offers a wider substrate scope. In this route, the starting *P,P*-dichlorophosphine **I** is treated with 2 eq. of sodium diethylphosphite to give bis(phosphonato)phosphines **VII** which is subsequently coordinated to the tungsten core to yield **VIII**. Selective cleavage of one P-P bond is achieved using sodium methoxide. The final pWH reagents **V** are isolated in 30-70% yield depending on the nature of the phosphorus substituent after quenching with water and purification by column chromatography.

The availability of several synthetic protocols for their preparation, as well as their relatively large substrate scope make pWH reagents versatile and highly interesting substrates for the preparation of phosphaalkenes with complex substitution patterns.[60,62]

2.2 Phospholes

2.2.1 Introduction to the field of phospholes

Phospholes are five-membered unsaturated heterocycles which contain a three-valent, three or two coordinated phosphorus atom. There are three possible isomers of phospholes – 1*H*-phospholes, 2*H*-phospholes and 3*H*-phospholes (Figure 2).

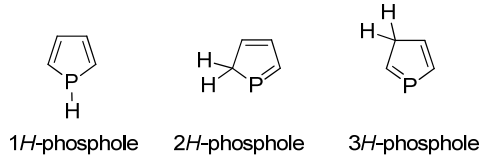
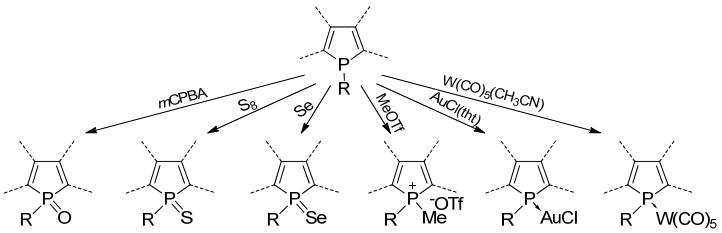


Figure 2. *Possible isomers of phospholes*

Even though it has been shown that 2*H*-phosphole is more stable than its 1*H*-isomer,[63] only few representatives of such 2*H*- or even 3*H*-phospholes have been described in the literature. Indeed, such structures can be stabilized only with special precautions, for example as highly substituted rings or as metal complexes.[8,63-65] To facilitate the reading of this thesis, the much more common 1*H*-phospholes which are also subject of this thesis will simply be referred to as phospholes hereafter.

One of the most interesting questions in the field of phosphole chemistry which caused an extensive debate in the scientific community is the extent and nature of aromaticity in these phosphorus heterocycles. Consensus has been found in the 1970s after efficient synthetic approaches to phospholes had been developed.[7,66-68] The phosphole ring is hardly aromatic, as for example visible from the first X-ray structure of a phosphole-containing compound.[69] The phosphorus centre within the phosphole ring is pyramidal and thus not co-planar with the four carbon centres. Furthermore, analysis of the C-C bond lengths showed that the phosphole ring contains localised C-C single and C=C double bonds. These findings unambiguously confirmed very low levels of aromaticity in the phosphole ring.[70] The pyramidalization of the phosphorus centre with relatively high inversion barrier (calculated to be 17.19 kcal/mol for parent phosphole[71]) leads also to the preserved reactivity of the phosphorus. At the same time, it was shown that a certain degree of aromaticity in the phosphole originates from the hyperconjugation of the diene unit with the exocyclic P-R σ-bond.[6,8] All-in-all, the above mentioned properties make the phosphorus centres perfectly suitable for fine tuning of the optical properties of the adjacent π-conjugated system by performing chemical modifications on the heteroatom without direct modifications of the conjugation paths. Examples of such modifications which include metal coordination, oxidation by oxygen, sulfur or selenium, and reactions with various Lewis acids are presented in Scheme 4.[6,8,16,72-74]



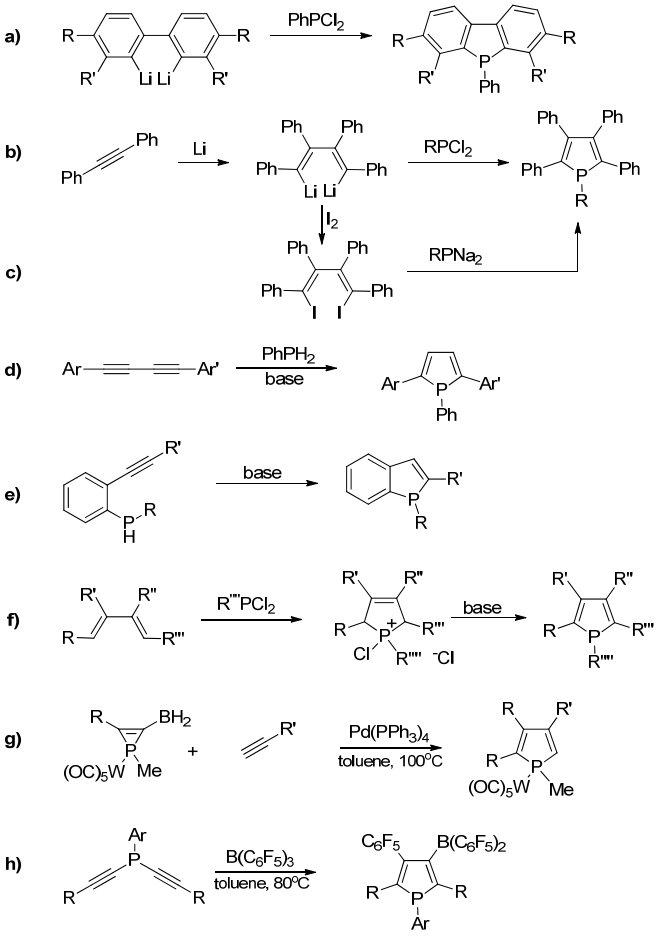
Scheme 4. *Examples of chemical modifications of the phosphorus centre in phospholes*

The influence that such modifications have on the optical properties of the π-conjugate have been intensively studied over the last decades. It is thus not surprising that phospholes are nowadays the most frequently employed building blocks for the preparation of π-conjugated, *P*-containing materials.[6,8,16]

2.2.2 Preparation of phospholes

Even though phospholes appeared in the literature for the first time already in 1953,[75] they remained relatively exotic compounds for the following 35 years. As the case for phosphaalkenes, several synthetic procedures also exist for the preparation of phospholes. The first phosphole was prepared by Wittig and Geissler by treatment of the 2,2'-dilithium salt of biphenyl with phenyl dichlorophosphine (Scheme 5, route a).[75] This approach remained one of the most frequently used for the preparation of dibenzophospholes, and was recently utilized by the groups of Baumgartner,[76,77] Matano[78] and Lammertsma.[79] Another way to form phosphole rings is to treat dilithium derivative prepared from acetylene and lithium with *P,P*-dichlorophosphine (Scheme 5, route b).[80,81] Alternatively, this dilithium derivative can be first quenched with iodine to give 1,4-diiodo-1,3-butadiene which can subsequently be treated with sodium phenylphosphide to give the desired phosphole (Scheme 5, route c).[82] Addition of primary and secondary phosphines to acetylenes was also utilized for the preparation of phospholes (Scheme 5, route d and e).[83,84] Phospholes can also be prepared from halophospholenium ions.[85-89] The latter can be formed in several ways, e.g. by treatment of cyclic phosphines with bromine or cyclic bromophosphines with alkylhalides.[85,86,88] However, the most common way is the so-called McCormack reaction (route f) where halophospholenium ions are formed in a reaction of 1,3-butadienes with *P,P*-dihalophosphines.[87] Treatment of the halophospholenium ions with DBU results in the smooth formation of the phosphole.[85,89] Mathey and coworkers reported a different approach towards phospholes in which terminal acetylenes can insert into phosphirane complexes in the presence of catalytic amounts of $Pd(PPh_3)_4$ (Scheme 5, route g).[90] The last example in Scheme 5 is the preparation of boryl-substituted phospholes from diacetylene substituted

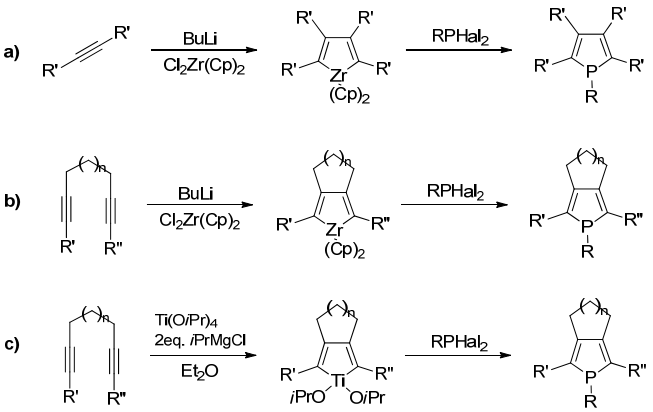
phosphines.[91] Boryl-substituted phospholes that are prepared in this fashion can be further used in Suzuki-Miuyara cross-coupling reactions.[91] All procedures described in Scheme 5 are rather specific and suffer from restrictions regarding substrate scope. They do thus not allow the preparation of compound libraries with large variations of the substituents in the final products.



Scheme 5. *Preparation of phospholes*

The development of the so-called Fagan-Nugen synthetic strategy in 1988 gave new life to phosphole chemistry.[92] This methodology is based on the treatment of acetylenes with an activated zirconocene complex, followed by quenching of the intermediately formed zirconium heterocycle by phosphorus dichloride or dibromide. This very versatile route allowed the preparation of large libraries of target structures (Scheme 6, route a).[93] The biggest drawback in the original reports is the low selectivity in case asymmetrically substituted acetylenes are used. This limitation could however be overcome by simple linking of the two reacting acetylenes by an inert bridge (Scheme

6, route b). This strategy resulted not only in increased selectivity but also improved yields.[94]



***Scheme 6**. Metallocycle-based synthetic approaches towards phospholes.*

The large scope and elegance of the Fagan-Nugen method permits the introduction of a large variety of substituents in the 2- and 5-positions of the phosphole ring, but also alterations of the substituent at the phosphorus.[95-100] Using a similar mechanism as the Fagan-Nugen route, an alternative transition metal complex– titanium tetra(isopropylate) – can also be used for the preparation of phospholes (Scheme 6, route c).[101-103] The latter synthetic strategy was successfully used for the preparation of for example 2,5-diacetylene-substituted phospholes.[99,100]

2.3 Oxaphospholes

Another important class of phosphorus containing molecules are heterophospholes. They are unsaturated heterocycles which contain at least one additional heteroatom besides the three valent phosphorus centre. Some of the possible structures are presented in Figure 3.

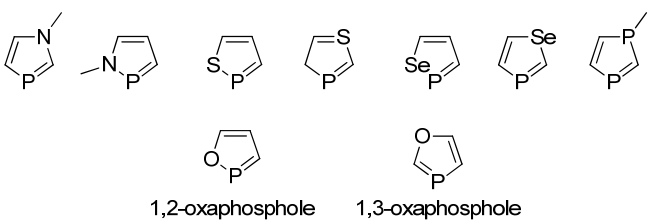


***Figure 3**. Structures of the mono-heterophospholes*

Heterophospholes can generally be of good stability and the development of a number of synthetic approaches to their preparations has led to a continu-

ous growth of this class of compounds.[6,7,65] Even though heterophospholes represent one of the biggest class of phosphorus containing molecules,[65] some of their members have still remained hardly accessible. This counts in particular for oxaphospholes, i.e. five-membered rings with one oxygen and one phospohorus heteroatom. 1,2-oxaphospholes have appeared in sporadic publications, but remain an almost unexplored type of phosphorus containing heterocycles due to the absence of broadly applicable synthetic approaches.[104,105] In contrast, 1,3-oxaphospholes have been known for some time,[106] and recently attracted high attention due to their intriguing luminescent properties.[107,108] In general, it should be stressed that the Fagan-Nugen method is not applicable to the preparation of heterophospholes.

3. Alternative approach to pWH reagents (Paper I)

This chapter is dedicated to the development of a new procedure for the preparation of pWH reagents. Each step of the synthetic sequence, i.e. preparation of the starting *P,P*-dichlorophosphines, their phosphorylation using the Michaelis-Arbuzov protocol, coordination to the metal centre and final hydrolysis, are presented in detail. A possible route to uncoordinated pWH reagents is also discussed.

3.1 Literature methods

As summarized and discussed in Scheme 3 (Chapter 2.1.3), numerous literature procedures for the preparation of pWH reagents are known.[9,52,59,60] In attempts to reproduce these literature reports, and to employ the published procedures for more complex substrates, for example those that carry unsaturated *P*-substituents, several problems and drawbacks were encountered.

For route (a) (Scheme 3), twofold lithiation of the primary phosphine tungsten complex **III** appears to be a challenging step. Following the reaction of **III** with *n*-BuLi and *t*-BuLi by ^{31}P NMR spectroscopy reveals that **III** undergoes only partial lithiation at temperatures higher than -20°C. At the same time, warming up to higher temperatures leads to decomposition. Complete *mono*-lithiation of **III** can be achieved using 1.25 equivalents of LDA (route b), but the reaction ultimately suffers from the addition of $[(^{i}Pr)_2N]^-$ to the phosphorous precursor and the formation of *N*,*N*-diisopropylamino,-*O*,*O*-diethylphosphonate. The latter is difficult to separate from the desired product by chromatography. Sequence (c) (Scheme 3) appears to be the most promising approach to pWH reagents. The difficulty in the approach lies in the preparation of $NaOP(OEt)_2$ that is used for the transformation of **I** to **VII**. $NaOP(OEt)_2$ needs to be employed at very high purity since excess sodium will reduce starting dichlorophosphine **I**, while residual methanol will react with **I** to form various solvolysis products. These limitations were found so severe that the reaction was not practicable to us. In our hands, all three routes a) – c) unfortunately produce substantial amounts of side products

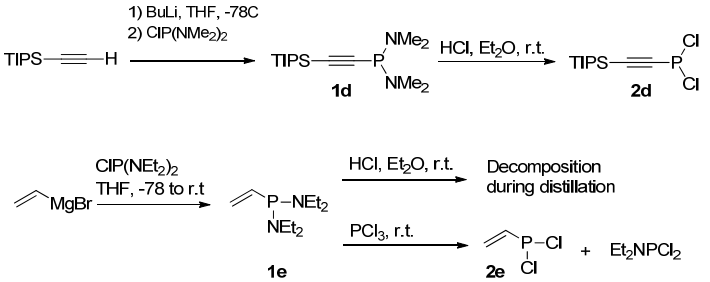
which are difficult, if not impossible, to remove by re-crystallization and/or by column chromatography.
Considering our interest in phosphaalkenes that are in π-conjugation with other unsaturated organic groups, protocols which would allow the preparation of pWH reagents with different substituents at the phosphorus side were of high need. At the same time, the development of a new protocol would hopefully circumvent some of the problems that were encountered in the published procedures.

3.2 Development of an alternative procedure

Phospha-Wittig-Horner reagents which bear vinyl and TIPS-acetylene, Ph, *t*-Bu, and Mes groups as substituents at the phosphorus centre were chosen as target structures.

3.2.1 Preparation of *P,P*-dichlorophosphines

A careful literature survey revealed that the Michaelis-Arbuzov reaction can be utilized for the conversion of *P,P*-dichlorophosphines to their corresponding phosphinodiphosphonates **VIII**.[109] We therefore decided to test this reaction on a small library of *P,P*-dichlorophosphines.
While $PhPCl_2$ (**2a**) and *t*$BuPCl_2$ (**2b**) are commercially available, three other dichlorophosphines needed to be prepared. In case of $MesPCl_2$ (**2c**), a well established literature procedure was available.[110] TIPS-$CCPCl_2$ (**2d**) can be prepared in analogy to the synthesis of $PhCCPCl_2$.[111]



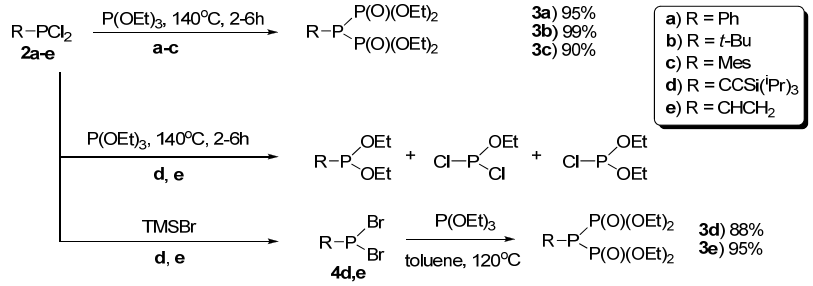
Scheme 7. *Preparation of $RPCl_2$* ***2d,e****.*

Since the literature procedure for the preparation of **2e** was based on highly toxic divinyl mercury,[112] we developed a new synthetic protocol (Scheme 7). Thus, treatment of vinyl magnesium bromide with bis-(diethylamino)chlorophosphine affords bis(diethylamino)vinyl-phosphine **1e** in good yield. Subsequent reaction of **1e** with an ethereal solution of anhydrous hydrochloric acid affords **2e**, albeit only in very low yields. Moreover,

2e is difficult to isolate from the reaction mixture due its considerable thermal, oxygen and moisture sensitivity. Alternatively, **2e** can be obtained in 75% yield by treatment of bis(diethylamino)vinylphosphine **1e** with two equivalents of phosphorus trichloride under solvent-free conditions at room temperature. After five minutes, the scrambling reaction is complete and the reaction mixture contains exclusively the desired *P*,*P*-dichlorovinylphosphine **2e** and dichloro(diethylamino)-phosphine. **2e** is isolated as a colorless liquid in high yield by vacuum distillation at -20°C.

3.2.2 Michaelis-Arbuzov phosphorylation of *P,P*-dichlorophosphines

With **2a-e** in hand, their reactivity in the Michaelis-Arbuzov reaction to prepare phosphinodiphosphonates **3a-e** was investigated (Scheme 8).

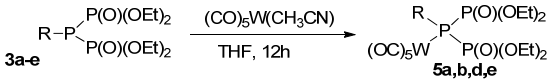


***Scheme 8**. Michaelis Arbuzov reaction of $RPCl_2$ **2a-e** to phosphinodiphosphonates **3a-e**.*

The formation of phosphinodiphosphonates **3a-c** proceeds smoothly and in good yields from compounds **2a-c**, while the transformation of **2d,e** under identical conditions results only in minor amounts of products. Investigation of the reaction mixtures by ^{31}P NMR showed that disproportionation between **2d,e** and triethylphosphite takes place which results in the formation of ethylchlorophosphites with varying numbers of chloro- and ethoxy groups (Scheme 8). In order to avoid undesired scrambling reactions, **2d,e** were converted into the corresponding *P*,*P*-dibromophosphines **4d,e**, since it is well known that bromides undergo phosphorylation with triethylphosphite under milder conditions.[113] The transformation was achieved by treatment of **2d,e** with trimethylsilylbromide under solvent-free conditions, giving bromides **4d,e** in good yields (88-92%).[114] Compounds **4d,e** react with $P(OEt)_3$ in a clean and selective manner to afford **3d,e** as colorless, oxygen and water sensitive liquids in good yields.

3.2.3 Coordination to $W(CO)_5$ core

To raise the stability of the pWH reagents as well as the products from subsequent reactions (i.e. phosphaalkenes), metal fragments were introduced at the phosphorus centre. One of the most commonly used metal fragment for this purpose is $W(CO)_5$.

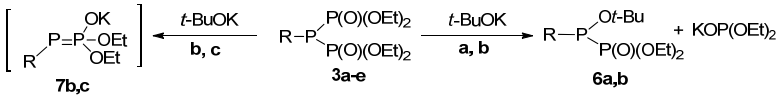


Scheme 9**. Coordination of $W(CO)_5$ to **3a-e

Treatment of compounds **3a-e** with freshly prepared $W(CO)_5CH_3CN$[9] in THF results in the formation of complexes **5a,b,d,e** in good yields (65-84%) (Scheme 9). In case of **3c**, no coordination could be achieved even after elongated reaction times and elevated temperatures, most probably due to steric crowding. Complexes **5** are moderately moisture sensitive oils which can be stored for several weeks at -20 °C under an atmosphere of argon without visible decomposition.

3.2.4 Metal-free pWH reagents

The possibility to prepare also metal-free pWH reagents by hydrolysis of the non-metal-coordinated compounds **3a-c** was investigated. Treatment of **3a** with a solution of potassium tert-butoxide in THF results in the substitution of one phosphonate group by a *tert*-butoxide and the formation of **6a** and $KOP(OEt)_2$ (Scheme 10).

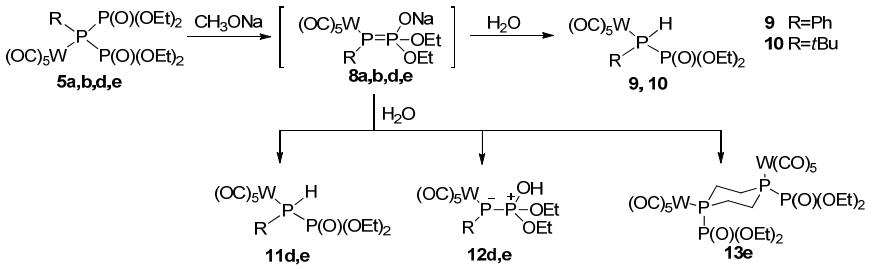


***Scheme 10**. Treatment of **3a-e** with potassium t-butoxide.*

Application of the same procedure to **3b** leads to a mixture of the desired product **7b** while **6b** is still observed as side product. Increasing the size of the substituent on the phosphorus centre further allows the preparation of **7c** as the only product of hydrolysis of **3c**. On the basis of the characteristic high-field ^{31}P NMR chemical shift of the P^{III} centre ($\delta(P^{III})$ = -165.6 ppm, $\delta(P^{V})$ = 79.8 ppm) and the unusually large $^{1}J_{P=P}$ = 569 Hz coupling constant,[7] compound **7c** was identified as the enolate form of the phospha-Wittig-Horner reagent. **7b,c** can only be generated *in situ*, and attempts to quench the salts and to isolate the meal-free pWH reagent result in decomposition.

3.2.5 Hydrolysis of phosphinodiphosphonate metal complexes

Treatment of complexes **5a,b,d,e** with NaOMe or KO^{t}Bu results in the formation of **8a,b,d,e**, i.e. the salts of the pWH reagents. These salts have characteristic ^{31}P NMR spectra with two doublets typically around 65 ppm (P^V) and between -113.4 (**8e**) and -75.4 (**8b**) ppm (P^{III}). The large $^1J_{P\text{-}P}$ coupling constants between 340 (**8e**) and 429.7 (**8b**) Hz are indicative of a higher bond order between the two phosphorus centres, and **8a,b,d,e** are thus best described as the enolate form with a formal P=P double bond (Scheme 11).



***Scheme 11**. Hydrolysis of phosphinodiphosphonates metal complexes.*

Quenching of the enolates **8a,b** with saturated ammonium chloride solution proceeds in the expected manner and compounds **9** and **10** can be isolated by column chromatography in good yield. In fact, **9** could be obtained from **2a** on a 15 g scale with a total yield of 62 % over 3 steps. Compound **9** is thermally unstable and needs to be stored at low temperatures under inert atmosphere to avoid decomposition which is clearly visible after several hours at room temperature. In our hands, the reliability and scalability of the discussed procedure that employs a Michaelis-Arbuzov reaction as the key step is a vast improvement compared to existing literature methods.

Crystals of **9** suitable for X-ray analysis were obtained be recrystallization from pentane at -30°C (Figure 4). The crystallographic cell of complex **9** consists of two molecules which interact with each other via a hydrogen bond (D-H…A = 2.676 Å and angle D-H…A = 168.7°) between the phosphine proton of the first and a phosphonate oxygen of the second molecule. The P-W distance is 2.497(2) Å, and thus in the expected range for compounds of the general formula $(CO)_5W\text{-}PR_3$[115].

Even though no complications were observed during aqueous work up of **8a,b**, a more complicated picture emerges during quenching of **8d,e** (Scheme 11). When a solution of **8d** which bears a TIPS-acetylene substituent at the *P*-atom was treated with aqueous NH_4Cl, the formation of a new compound **12d** was observed. Based on the analytical data, especially ^{31}P NMR which shows two doublets with chemical shifts of 37.2 ppm for P^V and -138.7 ppm for P^{III} and rather small coupling constant $^1J_{P\text{-}P}$ = 89 Hz, **12d** is probably best described as an ylide (Scheme 11).

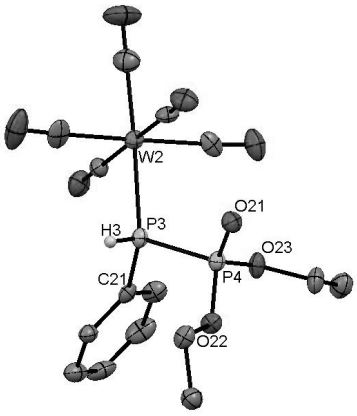


Figure 4. *Crystal structure of phospha-Wittig-Horner complex **9**. ORTEP drawing (50 % probability) All hydrogens except for H1 are omitted for clarity. Selected bond lengths: W2-P3 2.4966(16), P3-H3 1.000, P3-P4 2.187(2), P4=O21 1.471(5), P4-O22 1.575(5), P4-O23 1.565(5).*

The stability of the ylide form **12d** compared to the elusive "classical" pWH reagent can be explained in terms of π-conjugation of the lone pair at the low valent phosphorus centre with the adjacent acetylene substituent. This π-conjugation is also expressed in the UV/Vis spectrum of **12d** (in CH_3OH) which features a longest wavelength absorption maximum as a shoulder around 360 nm that trails well into the visible.

During quenching of THF solutions of **8e**, a new compound **13e** could be isolated as the main product. The structure of **13e** was assigned to a dimerization product of starting salt **8e** based on a comparison with existing ^{31}P and ^{13}C NMR data.[116] Its formation is the result of a nucleophilic attack of the ^{III}P on the vinyl group of a second molecule, followed by an intramolecular ring-closure following the same mechanism. Similar reactivity was observed by Mathey *et. al* on a divinylphosphine(pentacarbonyl)tungsten complex which forms 1,4-diphosphorinane upon treatment with BuLi.[117] Formation of **13e** can be avoided if **8e** is quenched under strongly acidic conditions *i.e.* in the presence of *p*-toluene sulfonic acid. Under these conditions, **11e** is formed, which however isomerizes to the more stable **12e** over hours. Phosphinylidenephosphites **12d,e** are stable compounds and can be purified by column chromatography.

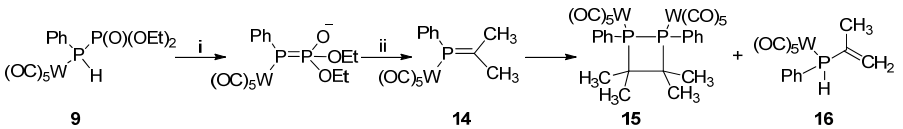
4. Reactivity of pWH reagents towards non-acetylenic ketones (Paper I)

This chapter focuses on the reactivity of the pWH reagents with acetone under different reaction conditions. The results show how changes in the ratio of starting material *vs.* base as well as reaction time or structure of the pWH reagent can determine the reaction outcome and the stability of the obtained products. The possibility to prepare unusual phosphaalkenes with unsaturated *P*-substituents is presented.

4.1 Test reaction of pWH reagents **9** with acetone

With the aim to study the reactivity of different isomeric forms of the pWH reagents and the effect different substituents have on the formation of phosphaalkenes, a series of reactions using **9** and acetone as starting materials was performed.

Following the literature procedure,[9] **9** was first treated with organic base (DABCO), followed by the addition of acetone (Scheme 12). The course of the reaction was monitored by ^{31}P NMR spectroscopy (Figure 5).



9 **14** **15** **16**

Scheme 12*. Phospha-Wittig-Horner reaction of **9** with acetone to form phosphaalkene **14**, and subsequent head-to-head dimerisation or 1,3-proton shift. i) LDA, THF, -78°C, 30min or DABCO, r.t. ii) dry acetone, r.t., 6-12h.*

As visible from Figure 5, formation of phosphaalkene **14** is complete already after five minutes. Phosphaalkene **14** can be unambiguously identified by its ^{31}P chemical shift at δ_{THF} = 170 ppm (δ_{CDCl3} = 176 ppm).[52] Prolongation of the reaction times (10h) results in complete consumption of **14** and the formation of a new species **15** with a ^{31}P chemical shift of δ = 105 ppm. The structural assignment of complex **15** was done based on HRMS data as well as ^{1}H, ^{31}P and ^{13}C NMR spectroscopic investigations. HRMS studies showed a molecular weight for **15** that is twice that of the starting phosphaalkene (m/z = 1092.89844 (**15**+2H_2O+Ag)). Compound **15** also features a character-

istic ABX coupling pattern in the ^{1}H NMR spectrum, indicating the presence of the two diasteriotopic methyl groups that couple to two phosphorus atoms. Together, these data suggest a 1,2-diphosphetane as the molecular structure of **15**. Formation of head-to-head dimers of phosphaalkenes that carry bulky substituents on the phosphorus atom was previously observed.[29] Their preferred formation over alternative head-to-tail dimers can be explained by steric factors, as the P-P bond in **15** is considerably longer than the C-P bonds in the elusive head-to-tail dimer. The longer P-P bond in **15** presumably accommodates the bulky $W(CO)_5$) groups in a better way, thus reducing steric repulsion.

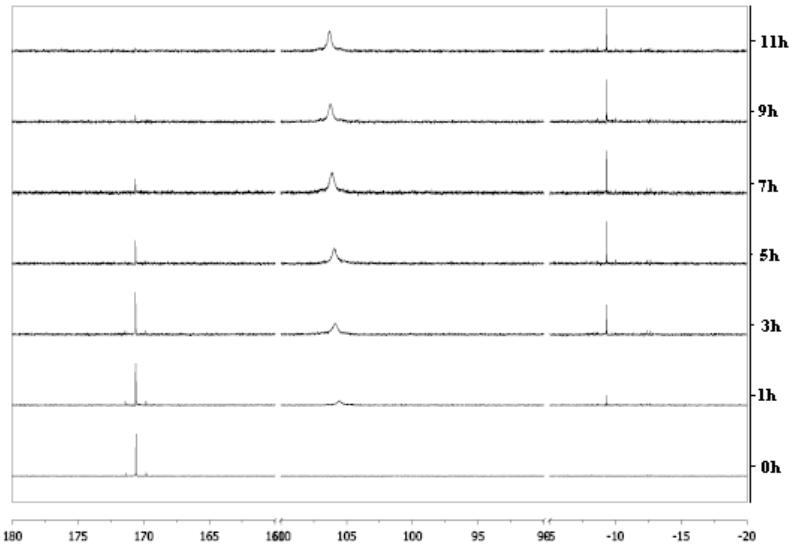


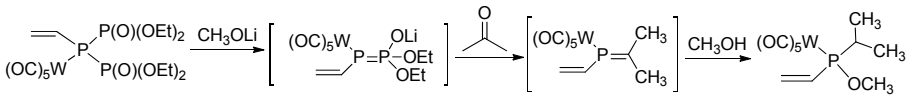
Figure 5. *^{31}P NMR spectroscopic study of the transformation of **14** to **15** in THF solution, using C_6D_6 as internal standard. ^{31}P NMR after 5min, 1h, 3h, 5h, 7h, 9h and 11h. Reaction was run at 22°C, using 20mg (0.035mmol) **9** in 0.5 ml THF and 4mg (0.035mmol) DABCO.*

Our observations of the subsequent chemistry of complex **14** and the formation of **15** differs from that reported in literature.[9] Marinetti et al. described a 1,3-proton shift which led to the formation of the secondary vinylphosphane **16**, which in our case was observed only as a side product in few percent yield according to NMR. Accurate reproduction of the literature procedure showed that the difference between our results and the literature report lies in the amount of DABCO that was used in the reaction. Increasing the amount of DABCO to two equivalents promotes the 1,3-proton shift and shifts the product distribution of **15** vs **16** to 1:1. Under such reaction conditions, the ^{31}P NMR signal of diphosphetane **15** is very broad and relatively easy to overlook.

Reaction between **9** and acetone can also be performed using one equivalent of LDA. In this case, the lithium salt of **9** is formed quantitatively after 30 minutes at -30°C as judged by ^{31}P NMR ($\delta(P^V)$ = 62.7 ppm and $\delta(P^{III})$ = -107.5 ppm ,$^1J_{P=P}$ = 383.3Hz). Addition of acetone and stirring of the reaction mixture at room temperature gives the expected compounds **14** and **15** in varying ratios depending on the reaction times.

4.2 One-pot pWH reagent preparation and condensation with acetone

Since the presence of unsaturated substituents at the P^{III} does not allow the isolation of the corresponding pWH reagents, an alternative one-pot procedure that is compatible with a subsequent reaction with acetone was developed. In analogy to what is presented in Scheme 11, the Li-salt **8e-Li** can be generated *in situ* starting from bis(phosphonato)phosphine **5e** upon treatment with lithium methoxide. **8e-Li** has a characteristic ^{31}P NMR chemical shift of 63.4 (P^V) and -113.2 (P^{III}) with $^1J_{P=P}$ = 350 Hz and was found to be suitable for the direct preparation of phosphaalkenes (Scheme 13).



5e **8e-Li** **17** **18**

Scheme 13. *In situ generation of **8e-Li** and its reaction with acetone*

Thus, treatment of the *in situ* prepared **8e-Li** with acetone results in the formation of the corresponding phosphaalkene **17** which is directly trapped by methanol that stems from used lithium methoxide. The reaction is complete after 8 hours at room temperature and compound **18** can be isolated in 28% yield after chromatographic purification. **8e-Li** can also be formed from **5e** by treatment with *t*BuOLi. The latter methanol-free conditions seem advantageous for the subsequent reaction with acetone as no trapped species of type **18** is observed. The formed phosphaalkene **17** however appears to be thermally unstable and decomposes in the absence of trapping reagents, presumably to polymeric material.

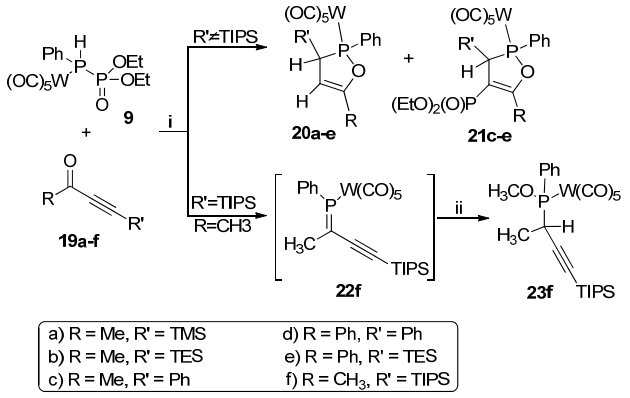
5. Reactions of pWH reagents with ketones bearing one or two acetylenic substituents (Paper II & III)

This chapter of the thesis is dedicated to the reactivity of pWH reagents towards symmetric and asymmetric ketones which contain one or two acetylenic units. The proposed mechanisms of the reactions are studied by means of *in situ* FTIR technique as well as theoretical calculations. Physical-chemical properties of oxaphospholes, cumulenes and bisphospholes are presented.

5.1 Reactivity of pWH reagents towards monoacetylenic ketones

Inspired by the results of the reactions between pWH reagents and saturated ketones, we decided to investigate the reactivity of the former towards unsaturated ketones that contain acetylene units. Already in the first experiments, it became very obvious that the reaction of pWH reagent **9** with ethynyl-methyl-ketones **19a-c** or ethynyl-phenyl-ketones **19d,e** exhibits a completely different reactivity as compared to the reaction of **9** with for example acetone. The results of the reactions are summarized in Scheme 14 and Table 1.

As for classical pWH reactions, all reactions presented in Scheme 14 are initiated by the addition of LDA. The desired phosphaalkene was however only observed in case of ketone **19f** which bears a very bulky *i*Pr_3Si (TIPS) group at the acetylene terminus. Phosphaalkene **22f** appears to be unstable and could be isolated only in form of its methanol addition product. The presence of two stereocentres (at the phosphorus and at the former carbonyl carbon atom) results in the formation of diasteromers in a ratio of ca 3:2 ($\delta(^{31}P)$ = 134.8 and 134.3). In case of less bulkier substituents such as Et_3Si (TES) groups in ketones **19b,e** or phenyl groups in ketones **19c,d**, the reaction outcome is very different. Formation of 1,2-oxaphospholes **20b,c,d,e** and **21c,d,e** are observed. Compounds **20b,c,d,e** and **21c,d,e** are the only products of the reaction. No compound of type **23f** can be observed even if



Scheme 14. *Reaction of pWH reagent* ***9*** *with monoacetylenic ketones. i) 1.1eq. LDA, -30°C, 30min after this 1eq. of* ***19*** *added, 1h at -50°C; ii) 10eq. of MeOH, -50°C, 30min.*

Table 1. *Product yields in the reaction of* ***9*** *with monoacetylenic ketones*

Entry	R	R'	Combined yield[a] Products **20** and **21**	Yield Product **23**
a	CH_3	TMS	38	0
b	CH_3	TES	35	0
c	CH_3	Ph	33	0
d	Ph	Ph	45	0
e	Ph	TES	43	0
f	CH_3	TIPS	0	65

a) Reaction outcome can be diverted by appropriate choice of the work-up procedure, as clearly demonstrated for the reaction with asymmetric diacetylenic ketones (Scheme 18, Table 3).

the reaction mixture is quenched by methanol at low temperatures to prevent decomposition of potential phosphaalkenes. Complexes **20** and **21** differ only in the phosphonate group at the C4 carbon of the ring which can be selectively removed during basic work up (*vide infra*). Heterocycles **20** have characteristic ^{31}P NMR chemical shifts, depending on the nature of the C3-substituent. Compounds that bear silyl-substituents (**20a,b,e**) exhibit a resonance at 132 ppm, while those having phenyl substitutions (**20c,d**) feature at 149 ppm. Heterocycles **21** show the expected AB spin-system in the ^{31}P NMR spectra with $^{3}J_{PP}$ coupling constants of 35 Hz (**21e**) and 28 Hz (**21c,d**). The phosphonate groups resonate around 15 ppm, while the oxaphosphole-*P* resonates between 162 (**21e**) and 152 ppm (**21c,d**). Compound **20e** was also characterised by X-ray diffraction analysis of single crystals obtained by slow evaporation of pentane solutions (Figure 6).

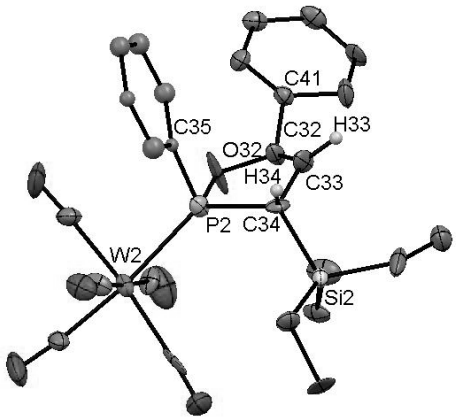
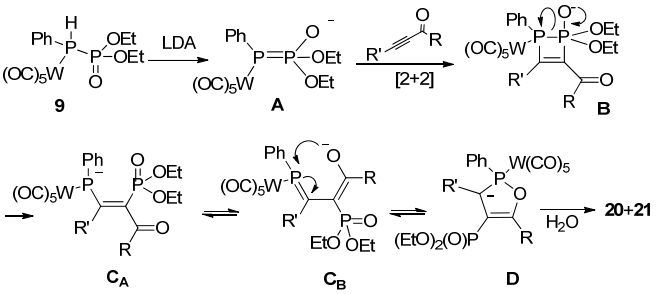


Figure 6. *Crystal structure of compound* ***20e*** *(ellipsoids set to 50% probability). All protons are omitted for clarity, except for those at the oxaphosphole.*

As visible from Figure 6, the phenyl group at the *P*-centre and the TES-substituent at the C3 carbon are *trans* to each other to avoid steric clashes. The system's desire to minimize steric repulsion between bulky substituents at C3 and the phenyl ring at the phosphorus centre results in the formation of only one out of two possible diastereomers in case of compounds **20b-e** and **21c-e**. In support of this hypothesis, it was found that when the steric demand of the C3 substituent is decreased, as in the case of a TMS group, the *trans* and *cis* diastereomers can both be isolated in a 5:1 ratio ($\delta(^{31}P)$ = 132.0 (*trans*) and 140.8 ppm (*cis*)).

5.1.1 Mechanism of oxaphosphole formation

Scheme 15 depicts the proposed mechanism for the formation of products **20a-e** and **21c-e**.



Scheme 15. *Mechanism for the formation of complexes* ***20*** *and* ***21****.*

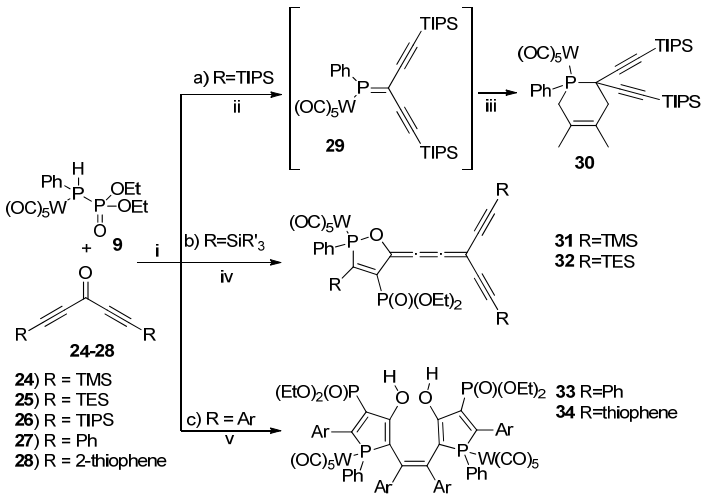
The reaction is initiated by LDA, which abstracts the proton from the pWH reagent and forms intermediate **A**. This intermediate can undergo [2+2] cycloaddition with the triple bond of the acetylenic ketone to form intermediate **B**. The cycloaddition is impossible in the presence of bulky TIPS groups at the acetylene termini and thus not observed in ketone **19f**. Ring opening of intermediate **B** gives intermediate **C** which can be presented by several tautomeric forms, the two most important of which are depicted in Scheme 18. One of them, $\mathbf{C_B}$, can undergo cyclisation to form **D** by nucleophilic attack of the formal alkoxide on the phosphorus centre. Aqueous work up of the reaction mixture results in the hydrolysis of **D** and the formation of the final products **20a-e** and **21c-e**. The reaction between ketones **19a-e** and pWH reagent **9** results exclusively in the formation of **20** and **21**. No products which would arise from the usual pWH reactivity was observed, even if the reaction was quenched with 1,3-butadiene or MeOH at low temperatures.

5.2 Reactivity of pWH reagents towards diacetylenic ketones.

The unusual reactivity of the pWH reagents with monoacetylenic ketones prompted us to investigate its reactivity also towards ketones that bear two acetylene substituents.

5.2.1 Symmetric ketones

The reaction of pWH reagent 9 with symmetric diacetylenic ketones **24-28** was studied and the results are summarized in Scheme 16 and Table 2.
As depicted in Scheme 16, the chemistry of the diacetylenic ketones has proven to be very rich. The reaction outcome is very much dependent on the nature of the substituent on the acetylene termini at the starting ketone. In analogy to the observed reactivity of the monoacetylenic ketones, only substrates with very bulky TIPS groups at the acetylene termini give phosphaalkenes (**29**). Their formation was indirectly proven by ^{31}P NMR and subsequent trapping experiments with 2,3-dimethyl 1,3-butadiene to give **30** as the product of a [4+2] hetero-Diels-Alder reaction.



Scheme 16. *Reaction of pWHr with symmetric diacetylenic ketones*

i) 1.1eq. BuLi, -30°C, 30min; ii) 1.05eq. of ***26****, -78°C, 30min.; iii) 10eq. of 2,3-dimethylbuta-1,3-diene, -78°C to r.t, 1h; iv) 2eq. of* ***24*** *or* ***25****, -78°C to -30°C, 1.5h; v) 1.05eq. of* ***27*** *or* ***28****, -50°C, 1.5-2h.*

Table 2. *Product yields of the reaction between pWH reagent* ***9*** *and symmetric di-acetylenic ketones*

Ketone	R	Product	Yield, %	$\delta(^{31}P)$, P^{III}	$\delta(^{31}P)$, P^{V}	J^{3}_{PP},Hz
24	TMS	31	7	168.2	6.4	59
25	TES	32	57	167.5	6.8	63
26	TIPS	30	35	9.7	-	-
27	Ph	33	38	38.4	13.6	38
28	Thiophene	34	10	37.2	13.4	32

Ketones that carry smaller silyl substituents at the acetylene termini such as **24** and **25** give rise to a completely different product class (Scheme 16). The reaction products, compounds **31** and **32**, are persubstituted 1,2-oxaphospholes in which one carbon centre is part of an exocyclic butatriene system. The butatriene is terminated by two acetylene units that bear the silyl groups that were present in the starting ketones **24** and **25**. Cumulenes **31** and **32** are the only isolated products of this reaction. Compounds **31, 32** were completely characterized by ^{13}C NMR spectroscopy which features 11 quaternary carbon atoms, ^{1}H NMR which shows the presence of three different silyl groups and ^{31}P NMR which indicates two distinct phosphorus centres ($\delta(P^{III})$ = 167.4 ppm, $\delta(P^{V})$ = 6.8 ppm) with a coupling of $J_{P\text{-}P}$ = 63 Hz.

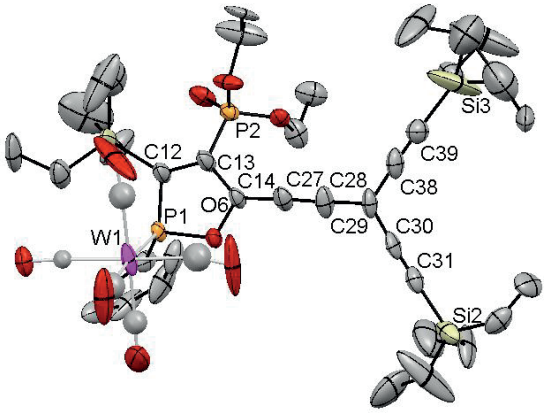


Figure 7. *Crystal structure of compound **32** (ORTEP drawing on 50% probability level). All protons are omitted to increase clarity of representation.*

Unambiguous structural confirmation of **32** was obtained by X-ray diffraction analysis of single crystals obtained by slow evaporation of pentane solution at -30°C (Figure 7). The oxaphosphole ring, the butatriene system and the two acetylene substituents describe one plane with a deviation of only 3.5° from ideal co-planarity (dihedral angle C12-C13-C14-C27 in Figure 7).

The reactivity of the system changes dramatically when aromatic substituents are introduced at the acetylene termini of the ketone, as in compounds **27** and **28**. The only isolated products of their reaction with pWH reagent **9** are complexes **33** and **34**, which were isolated as bright orange (**33**) and red solid (**34**) solids in 38% and 50% yield, respectively. Complete characterization using NMR, HRMS and X-ray analysis allowed the determination of the structures of compounds **33** and **34** as persubstituted bisphospholes. ^{31}P NMR spectra of **33** and **34** feature simple AB coupling pattern with two doublets at 37.2 and 13.4 ppm, ($^{3}J_{PP} = 32$ Hz) suggesting a symmetric structure of the compounds. Final structural proof was achieved by X-ray analysis of single crystals of **33** that were obtained by slow evaporation of a chloroform solution (Figure 8).

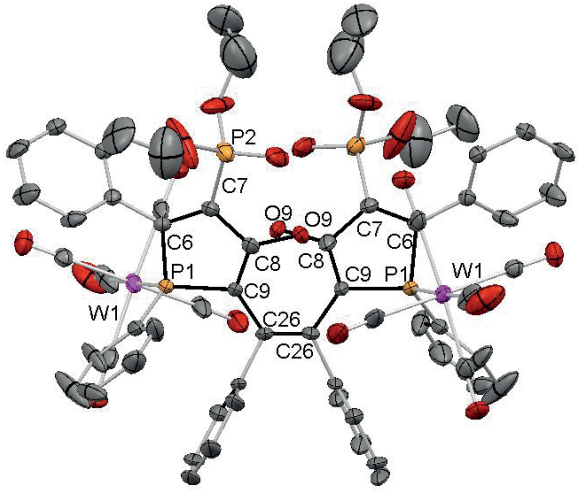
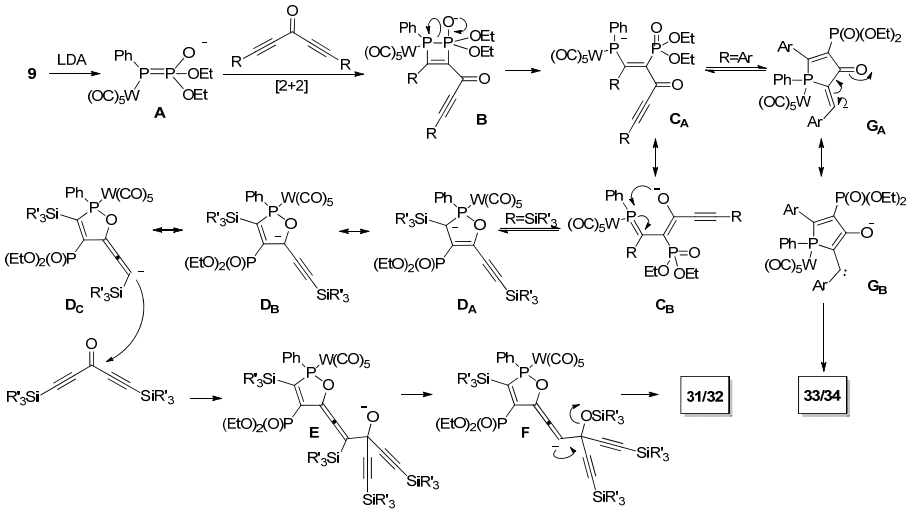


Figure 8. *Crystal structure of compound **33** (ORTEP drawing on 50% probability level). All protons are omitted to increase clarity of representation.*

As visible from Figure 8, compound **33** contains two fully substituted phosphole rings which are connected via an ethylene bridge in a *cis* fashion. Two hydroxy groups are in close proximity and cause helical twisting between the two phosphole parts of the molecule (dihedral angle C8-C9-C26-C26 = 37.5° in Figure 8). The OH protons of one phosphole subunit are in hydrogen-bonding distance to the oxygens of the phosphonate groups at the other phosphole (distance OH···O is 1.891 Å) which explains the unusually high ^{1}H NMR chemical shift of the OH proton (δ = 11.17 ppm). Complex **33** has a twofold rotational axis in the solid state and exhibits a C_2 point group symmetry.

5.2.2 Mechanism of the reaction between pWH reagents and diacetylenic ketones

Considering the small differences in the starting materials, the diversity of obtained products is truly stunning. It was thus a great challenge to find a coherent and detailed mechanistic model that would support all experimental findings. The proposed reaction mechanism is presented in Scheme 17.



***Scheme 17**. Mechanistic proposal for the formation of 1,2-oxaphosphole-terminated butatriene **31, 32** and ethene-bridged bisphosphole **33, 34**.*

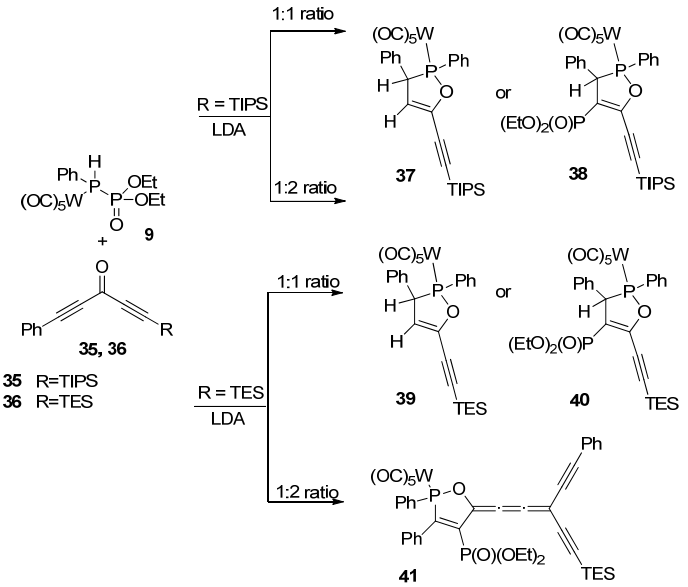
In case of ketones that bear small silyl substituents (TMS or TES), the first steps of the reaction sequence are identical to those suggested for monoacetylenic ketones in Schemes 15 and 17. However, one additional resonance form of **D** is possible due to the second acetylenic unit of the substrate. Intermediate $\mathbf{D_C}$ bears a negative charge on the allenic fragment which is perfectly set to undergo a nucleophilic attack on a second molecule of ketone to form intermediate **E**. The latter undergoes a 1,3-silyl shift with the formation of **F** in which the newly formed $OSiR_3$ can function as a leaving group to establish the final butatriene framework in **31** and **32**. Quenching the reaction at low temperatures allows the isolation of protonated **F** which already features the allene system but still contains the $OSiR'_3$ leaving group.

For the phenyl substituted ketones, the initial steps of the sequence are the same as in the previous case. At the stage of intermediate **C**, the sequences however divert. Tautomer $\mathbf{C_A}$ carries a formal negative charge on the phosphorus centre and can perform a 5-exo-dig attack on the carbon atom of the second acetylene unit. The resulting intermediate **G** can be represented again in two tautomeric forms. While $\mathbf{G_A}$ contains a localized negative charge on the exocyclic carbon centre, $\mathbf{G_B}$ exhibits a partial carbene character at the same centre. It is this carbene-type intermediate that is proposed to undergo dimerization that leads to the final products **33** and **34**.

5.2.3 Reactions with asymmetric ketones

Even though the reaction mechanism presented in Scheme 17 can explain the formation of all observed products, there are still a number of open questions. These include the determination of the rate limiting step, as well

as the identification of the factors that ultimately determine the structure of the final products. In order to elucidate some of these aspects, further experiments using asymmetric ketones like **35** and **36** were performed. Each of the ketones bears one phenyl group and one silyl group at the acetylene termini (TIPS for **35** and TES for **36**). The results of their reactions with pWH reagent **9** are presented in Scheme 18 and Table 3.



Scheme 18. *Reaction of pWH reagent **9** with asymmetric diacetylenic ketones*

Table 3*. Product yields for the reaction of pWH reagent **9** with asymmetric diacetylenic ketones*

Ketone	Ratio	Product	Yield, %	$\delta(^{31}P)$, P^{III}	$\delta(^{31}P)$, P^{V}	J^{3}_{PP},Hz
35	1:1	37[a]	37	150.0		
35	1:1	38[b]	30	155.9	12.4	27
35	1:2	37[a]	31	150.0		
36	1:1	39[a]	10	150.1		
36	1:1	40[b]	27	156.0	11.7	28
36	1:2	41[c]		150.7	6.0	43
				150.5	6.2	43

a) reaction was quenched by addition of water at -50°C; b) reaction was quenched by direct application on to the silica gel column; c) reaction was quenched by direct application on silica after 1.5h of reaction, only red colored fraction was collected and concentrated to obtain crude ^{31}P NMR data. Two isomers for complex **41** were found.

As expected, the TIPS group in **35** prevents the initial [2+2] cycloaddition of the lithiated pWH reagent **9-Li** at the silyl substituted terminus of the ketone. Thus, the initial attack takes place on the acetylene that contains the phenyl

substituent. The reaction leads to the formation of two oxaphospholes **37** ($\delta(^{31}P)$ = 150.0 ppm) and **38** ($\delta(^{31}P)$ = 155.9 ppm (d, $^{3}J_{PP}$ = 27 Hz, P^{III}) and 12.4 (d, P^{V}) ppm) that only differ in the presence of the phosphonate. A thorough investigation revealed that the ratio between oxaphospholes **37** and **38** strongly depends on the pH during quenching and subsequent work up. In case when the reaction mixture is directly poured onto silica gel (slightly acidic media), oxaphosphole **38** is formed exclusively, while quenching the reaction with water at -50° leads to the cleavage of the phosphonate group and exclusive formation of **37**. Careful control of the pH during work-up thus allows the selective preparation of heterocycles **37** and **38** with isolated yields of 37 and 30 %, respectively. Additional confirmation of the molecular structure of complex **38** was obtained by X-ray analysis of single crystal prepared by evaporation of DCM at -30° (Figure 9).

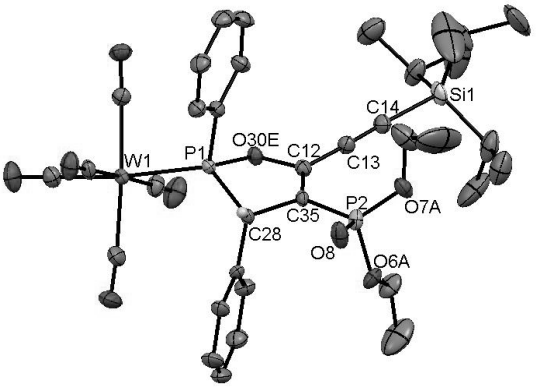


***Figure 9**. Crystal structure of compound **38** (ellipsoids set to 50% probability). All protons except for those at the oxaphosphole ring are omitted for clarity.*

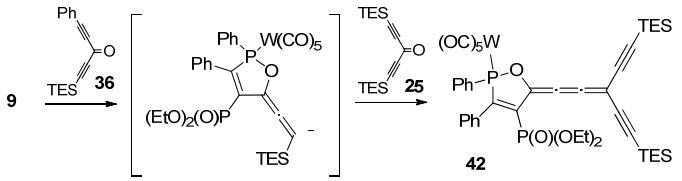
When the ratio between pWH reagent **9** and ketone **35** was increased to 1:2, no formation of cumulene type products was observed. This lack of reactivity can again be explained in terms of steric bulk of the TIPS group which does not allow nucleophilic attack on the second molecule of ketone (as depicted for $\mathbf{D_C}$ Scheme 17).

When ketone **36** is used in the reaction with pWH reagent **9**, oxaphospholes **39** ($\delta(^{31}P)$ = 150.0 ppm) and **40** ($\delta(^{31}P)$ = 156.0 ppm (d, $^{3}J_{PP}$ = 28Hz, P^{III}) and 11.7 (d, P^{V}) ppm) are formed in ratios that again depend on work-up procedures. As long as the ratio between the two starting materials **36** and **9** is kept 1:1, compounds **39** and **40** are the only observed products of the reaction. Based on this observation, two important conclusions can be drawn. First, the phenyl-acetylene in **36** is more reactive in the [2+2] cycloaddition reaction than the TES-acetylene. Second and most interestingly, the first part of the reaction sequence up to oxaphosphole formation is faster than the nucleophilic attack of $\mathbf{D_C}$ on the second molecule of ketone. This assignment

is in line with the observation that an increase of the ratio between **36** and **9** to 2:1 results in the formation of cumulene **41** as the only detectable reaction product. Cumulene **41** is however thermally unstable at room temperature and tends to polymerize during work up. However, compound **41** could be unambiguously identified in the bright red reaction mixture by ^{31}P NMR spectroscopy which indicated the presence of two isomers with chemical shifts of 150.7 ppm (d, $^{3}J_{PP}$=43Hz, P^{III}) and 6.0 ppm (d, P^{V}) for the first, and 150.5 ppm (d, $^{3}J_{PP}$=43Hz, P^{III}) and 6.2 ppm(d, P^{V}) for the second one. The formation of two isomers is expected due to the presence of *cis*/*trans* isomers across the butatriene system.

5.2.4 Reaction of pWH reagents with two different ketones

The reaction of ketone **36** with **9** suggests that intermediate **D** forms faster than any subsequent chemistry, and that it can thus be formed selectively. This observation encourages an experiment in which two different diacetylenic ketones are employed successively. Such a reaction would in principle allow free control over the substituents at C3 of the oxaphosphole, as well as the acetylene termini at the cumulene.

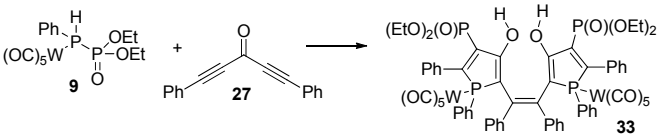


***Scheme 19**. Stepwise reaction of pWH reagent **9** with two different ketones*

Thus, pWH reagent **9** was treated with one equivalent of BuLi and then reacted with one equivalent of ketone **36** at -78°C. After stirring the resulting dark red solution for 30 minutes at this temperature, one equivalent of ketone **25** was added (Scheme 19). After quenching of the reaction mixture by direct application onto silica gel, compound **42** could be isolated as the single product in 18% yield. Neither oxaphospholes of type **39** and **40**, nor any other cumulene that would result from scrambling of the ketones could be observed. The exclusive formation of **42** illustrates the possibility to control the substitution pattern of the acetylenes at the cumulene and at the C3 carbon of the oxaphosphole ring by employing suitable ketones at different stages of the one-pot reaction.

5.3 Bisphosphole formation investigated by *in situ* IR spectroscopy

Further mechanistic details of the cascade reaction that ultimately leads to the formation of bisphosphole **16** was sought from *in-situ* FTIR spectroscopy. This method allows the acquisition of spectroscopic data in real time under authentic reaction conditions and is particularly appealing to investigate this transformation due to multiple characteristic IR absorptions in exclusive regions of the IR spectrum. The IR stretching frequencies of the CO ligands should be rather sensitive to changes at the *W*-coordinated phosphorus centre. At the same time, also C≡C triple and C=C double bonds have characteristic absorptions, and are thus promising probes to follow the reaction between **9** and **27** (Scheme 20).



Scheme 20. *Reaction followed by in situ IR. Reaction was performed using 0.43 mmol (247 mg) of* ***9*** *and 0.43 mmol (100 mg) of* ***27*** *in 10 ml of THF at -50°C over 3h, after which it was quenched by the addition of water at the same temperature.*

As visible from Figure 10, each step of the reaction sequence can be followed by a change of the vibrational frequencies of the carbonyl groups in the $W(CO)_5$ moiety. Treatment of the pWH reagent **9** (ν_{CO} = 1950 cm^{-1}) with one equivalent of BuLi results in the appearance of two new bands at ν_{CO} = 1920 and 1875 cm^{-1} and complete disappearance of signals attributed to **9**. The reaction seems completed already after 5 minutes, indicating a clean and fast lithiation of **9** even at low temperatures. Upon addition of ketone **27**, several new broad bands appear, the most prominent of which feature at ν_{CO} = 1940, 1880, 1840 cm^{-1}. It emerges that the lithium salt of **9** is thus fully consumed within several minutes after addition of ketone **27**. The presence of multiple vibrational frequencies indicates high complexity of the reaction mixture and the presence of multiple reaction intermediates and potential side products. Addition of water finally leads to the formation of complex **33** as the major product as evidenced by comparison with the IR spectrum of an authentic sample of **33** (Figure 10, inset).

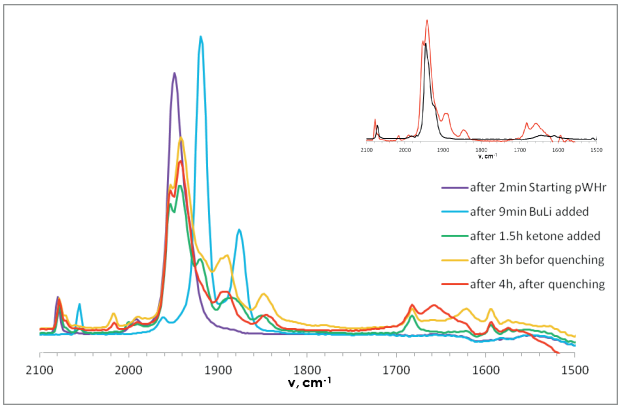
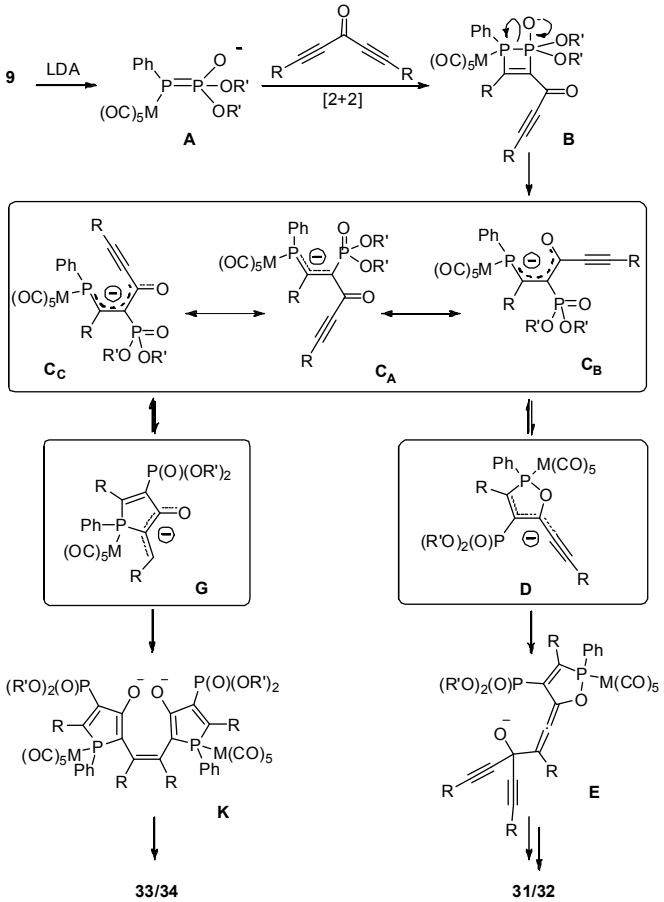


Figure 10. *Summary of the IR spectra from the in situ IR experiment (reaction between* ***9*** *with* ***27****, (the insertion shows overlaid IR spectra from pure complex* ***33*** *(black line) and last spectra of the reaction mixture in the in situ IR experiment (red line)).*

5.4 DFT calculations of the reaction mechanism between pWH reagent and acetylenic ketones

The reaction mechanism proposed to explain the observed products was scrutinized by DFT calculations. In particular, insights were sought into the reasons why aryl groups at the acetylene termini give rise to bisphospholes, while silyl groups promote oxaphosphole formation, To reduce computational time, the following modifications were made: ethyl groups in the phosphonate moiety were substituted by methyl groups, the transition metal was changed to chromium, and the groups at the acetylene termini which do not participate in the immediate reaction were changed to hydrogens. Scheme 21 summarizes all (model) intermediates with R being either Ph or TMS; in the text this is identified as, e.g., $\mathbf{D}_{\mathbf{R=Ph}}$ and $\mathbf{D}_{\mathbf{R=TMS}}$, respectively. For simplicity, we considered the following steps in this Scheme 21 irreversible: the P-P bond cleavage (**B→C**), the carbene dimerization (**G→K**), and the nucleophilic attack on a second ketone leading to the cumulene (**D→E**). This focuses the calculations on the distinguishing factors of **C** and conversion of **C** to **D** and **G**.



Scheme 21. *General mechanism of the reaction of pWH reagents with diacetylenic ketones*

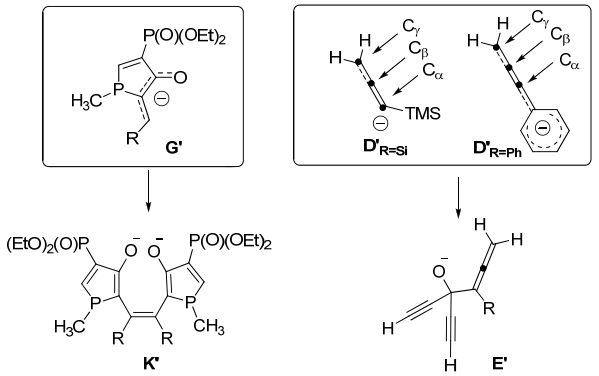
First, it was investigated if there is a conformational preference for intermediate **C** that depends on the substituent R, and whether such a preference could explain the product selectivity. Namely, conformer $\mathbf{C_C}$ is structurally closer to **G**, while $\mathbf{C_B}$ is more related to **D**. DFT calculations on the three conformers $\mathbf{C_A}$, $\mathbf{C_B}$, and $\mathbf{C_C}$ reveal similar stabilities with a slight preference for $\mathbf{C_C}$ and $\mathbf{C_A}$ irrespective of the substituent on the original ketone (Table 4).

Table 4. *Energies of the intermediates C for R=Ph and R=TMS.* [a]

Entry	C_A	C_B	C_C	C_A	C_B	C_C
R	TMS	TMS	TMS	Ph	Ph	Ph
ΔE, kcal/mol	n.a.	2.2[b]	0.2[c]	n.a.	1.5[b]	0.2[c]

a) Calculations were performed on the DFT level using B3LYP method with 6-31G-d bases set; b) $\Delta E = E_{CA}\text{-}E_{CB}$; c) $\Delta E = E_{CB}\text{-}E_{CC}$;

Phosphole formation ($\mathbf{C_C \rightarrow G}$) is slightly endothermic for both the phenyl- and silyl-derivatives by 4.5 and 8.7 kcal/mol, respectively, while oxaphosphole formation ($\mathbf{C_B \rightarrow D}$) is energetically favoured by 6.2 and 17.1 kcal/mol, respectively (Table 5). Combined, this is reflected in the **G→D** transformation, which is 23.8 kcal/mol exothermic for the TMS derivative and only 9.7 kcal/mol for the Ph derivative given that the intermediates **C**, **D** and **G** are in equilibrium. Put differently, the formation of $\mathbf{D_{R=TMS}}$ is energetically highly favoured, while formation of $\mathbf{G_{R=Ph}}$ is endothermic but still possible under the experimental conditions.



Scheme 22. *Structures of the intermediates that were used for the calculation of the irreversible steps*

Next, the irreversible reaction steps (**D→E** and (**G→K**)) were considered using the simplified structures that are depicted as **X'** in Scheme 22. The **D'→E'** transformation is thermodynamically downhill for R = phenyl and silyl by 17 and 27 kcal/mol, respectively. Similarly, also the **G'→K'** is exothermic by 23 and 17 kcal/mol) for the phenyl and silyl derivatives (Table 5). The calculations thus show that all transformations depicted in Scheme 22 are thermodynamically feasible. On the other hand, and in agreement with the experimental observations, bisphosphole formation is more favourable for the phenyl case, while the **D'→E'** transformation is preferable for the TMS substituent (Table 5).

Table 5. *Calculated energies for the transformation of selected intermediates*[a]

	ΔE				
R	$\mathbf{C_C \rightarrow G}$	$\mathbf{C_B \rightarrow D}$	**G'→K'**	**D'→E'**	TS(**D'→E'**)
TMS	8.7	-17.1	-17	-27	-12
Ph	4.5	-6.2	-23	-17	+10

a) All ΔE in kcal/mol.

The experimentally observed reaction outcome can be explained also by the electronic properties of **D'**. Namely, the negative charge in $\mathbf{D'_{R=Si}}$ is mainly localized at the carbon adjacent to the TMS group (Mulliken charges Cα -0.43 and Cβ +0.31) which gives rise to an angle of 149.9° between the allene and the Si. In contrast, $\mathbf{D'_{R=Ph}}$ is a much poorer nucleophile as its negative charge is fully delocalized with large contributions of the phenyl ring and an almost neutral allenic fragment that can equally well be described as a butatriene (average C_{Ph} -0.13, Cα 0.06, and Cβ 0.00). Large negative charges on Cγ probably result from truncation of the allenic fragment. The delocalization of the negative charge is also expressed in a linear geometry of $\mathbf{D'_{R=Ph}}$ that needs to be overcome if it is to react with a second ketone. Transition states (TS) for the conversion of **D'** into **E'** were located for substituents R = Ph and TMS at +9.9 and -12.1 kcal/mol relative to educts, respectively. The required energy for a charge localization on Cα in $\mathbf{D'_{R=Ph}}$ and concomitant bending of the carbon skeleton is estimated to be approximately 5.8 kcal/mol (compared to only 1.7 kcal/mol for $TS_{R=TMS}$). In summary, the calculations suggest that the high reaction barrier for the conversion of $\mathbf{D'_{R=Ph}}$ to $\mathbf{E'_{R=Ph}}$ makes this process kinetically unfavorable, and is responsible for the experimentally observed reaction outcome.

5.5 Physical-chemical properties of the oxaphospholes, bisphospholes and cumulenes

Since many compounds that are presented in this thesis belong to quite rare classes of phosphorus heterocycles, detailed studies of their physical-chemical properties was an important part of our investigations. Particular focus was given to the oxaphospholes, especially those that carry cumulene substituents, and the bisphospholes.

5.5.1 NMR studies

^{31}P NMR studies

The ^{31}P chemical shifts of all compounds presented in this chapter are summarized in Tables 2, 3 and 6. The ^{31}P NMR chemical shift of oxaphospholes **20**, **37** and **39** is close to 150 ppm, except for the C3-phenyl-substituted compound **20e** which resonates at higher field (132 ppm). The presence of a P^V phosphonate substituent at C4 as in **21**, **38** and **40** shifts the P^{III} resonance downfield, while its own chemical shift is rather conserved between 12 and 16 ppm. The presence of the cumulene substituent in **31**, **32** and **42** shifts the ^{31}P resonance of P^V upfield to ca. 6 ppm, an effect which allows unambiguous identification of this kind of compounds in the crude reaction mixtures.

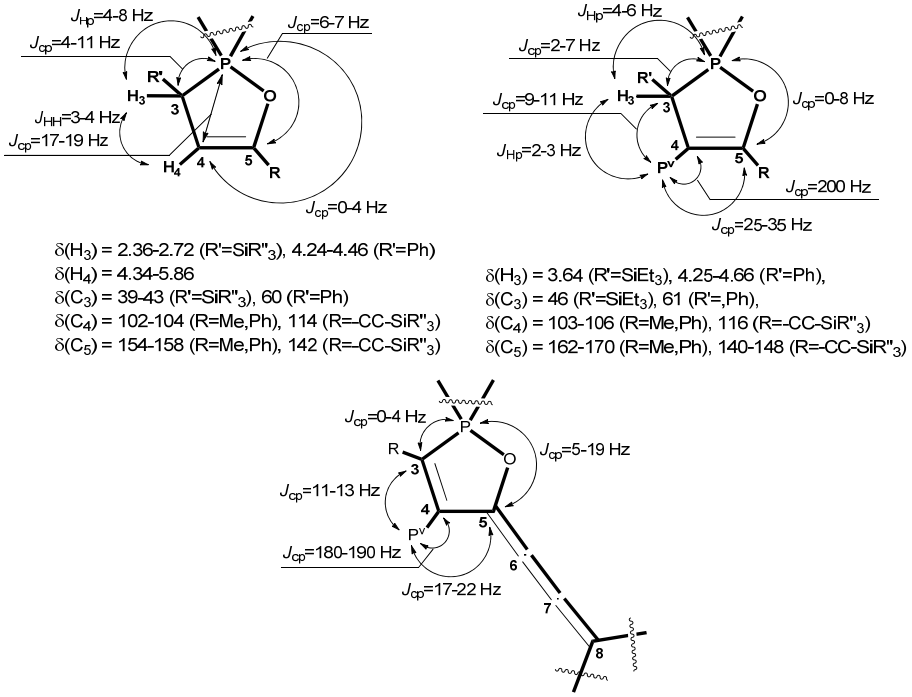
Table 6. *^{31}P chemical shifts and coupling constants for oxaphospholes.*

Comp.	$\delta(^{31}P)$	Comp.	$\delta(^{31}P^{III})$	$\delta(^{31}P^{V})$	$^{1}J_{PP}$, Hz
20a	132.0				
20b	132.0				
20c	149.6	**21c**	153.0	15.8	28
20d	149.6	**21d**	151.2	14.8	28
20e	132.8	**21e**	161.5	16.0	36
37	150.0	**38**	156.0	12.4	27
39	150.1	**40**	156.0	11.7	27

^{1}H and ^{13}C NMR

As oxaphospholes are rather rare heterocylces, we systematically studied their NMR spectroscopic signatures (Figure 11 and Tables 7-9). Ring proton H3 of the oxaphospholes has an exclusive position in the ^{1}H NMR spectrum (Figure 11) and is usually observed as a multiplet due to the presence of $^{2}J_{HP}$ (ca. 4-8 Hz), and $^{3}J_{HH}$ (3-4 Hz) or $^{3}J_{HP}$ couplings (ca. 3 Hz). Long range coupling of the H3 to the protons of the substituents on C5 can also be observed.

The ^{13}C chemical shift of the C3 carbon atom of the oxaphospholes is generally higher for compounds that bear phenyl group on C3 compared to their silyl-substituted congeners. The ^{1}J coupling constant to the P^{III} atom is in the range of $^{1}J_{(C3P^{III})}$ = 7-11 Hz for the compounds with R'=Ph and $^{1}J_{(C3P^{III})}$ = 2-6 Hz for compounds with R'=TES. In case of silyl-substituted cumulenes **31** and **32**, this coupling constant was not detected, while it was found to be $^{1}J_{(C3P^{III})}$ = 4 Hz for the phenyl-substituted analogue. The coupling constant between C3 and P^{V} atom is generally 9-13 Hz and not dependent on the substitution pattern of the ring. The C4 carbon resonates around 102-107 ppm for the oxaphospholes that do not contain any acetylene substituents in the C5 position of the ring and at circa 115 ppm for the complexes having an acetylene group. In case of complexes **21**, **38**, **40** and the cumulenic systems **31, 32 and 42**, a relatively large coupling constant ($^{1}J_{(C4P^{V}}$ = ca. 200 Hz) to the P^{V} atom is detected. The C5 carbon of the oxaphospholes has a chemical shift in the range of 155 to 170 ppm. In case of complexes **37-40**, the anisotropic influence of the acetylene unit causes a downfield shift of circa 15 ppm and C5 can be observed in the ^{13}C NMR spectrum between 141-148 ppm.



$\delta(H_3)$ = 2.36-2.72 (R'=SiR"$_3$), 4.24-4.46 (R'=Ph)
$\delta(H_4)$ = 4.34-5.86
$\delta(C_3)$ = 39-43 (R'=SiR"$_3$), 60 (R'=Ph)
$\delta(C_4)$ = 102-104 (R=Me,Ph), 114 (R=-CC-SiR"$_3$)
$\delta(C_5)$ = 154-158 (R=Me,Ph), 142 (R=-CC-SiR"$_3$)

$\delta(H_3)$ = 3.64 (R'=SiEt$_3$), 4.25-4.66 (R'=Ph),
$\delta(C_3)$ = 46 (R'=SiEt$_3$), 61 (R'=,Ph),
$\delta(C_4)$ = 103-106 (R=Me,Ph), 116 (R=-CC-SiR"$_3$)
$\delta(C_5)$ = 162-170 (R=Me,Ph), 140-148 (R=-CC-SiR"$_3$)

Figure 11. *Summary of the chemical shifts and carbon – phosphorus, proton-carbon coupling constants for ring carbons /protons*

Table 7. *Shemical shifts and coupling constants for ring carbons and protons of heterocycles* ***20a-e****,* ***37*** *and* ***39****.*

Comp.	$\delta(C_3)$	$^1J(C_3P)$	$\delta(C_4)$	$^2J(C_4P)$	$\delta(C_5)$	$^2J(C_5P)$	$\delta(H_3)$	$^2J(H_3P)$	$\delta(H_4)$	$^3J(H_4P)$
20a	42.5	4	101.9	3	154.8	7	2.36	8	4.81	18
20b	39.2	5	102.0	3	154.4	6	2.35	7	4.34	19
20c	59.8	11	103.7		158.3	7	4.24	5[a]	5.09	18
20d	60.1	11	102.5		158.4	7	4.46	5	5.86	18
20e	40.4	6	101.9	4	155.1	6	2.72	8	5.58	19
37	59.9	10	114.4		142.4	6	4.26	4	5.72	17
39	59.8	10	114.7		142.5	6	4.28	4	5.73	17

[a] Coupling constants were resolved by applying enhanced resolution work up method to the original spectra.

***Table 8**. Shemical shifts and coupling constants for ring carbons and protons of heterocycles **21c-e**, **38** and **40**.*

Comp.	δ (C_3)	^1J (C_3P^V)	^1J (C_3P^{III})	δ (C_4)	^1J (C_4P^V)	δ (C_5)	^1J (C_5P^V)	^1J (C_5P^{III})	δ (H_3	^3J (H_3P^V)	^2J (H_3P^{III})
21c	60.8	10	7	105.7	200	170.2	32	8	4.25	4	4
21d	62.4	11	7	106.9	200	166.7	28	8	4.72	3	6
21e	46.0	10	2	103.5	205	162.2	27		3.64	2	5
38	61.7	9	7	116.1	196	148.9	25	7	4.44	3	6
40	61.8	9	7	116.9	195	140.9	30	2	4.66	3	6

***Table 9**. Shemical shifts and coupling constants for ring carbons and protons of cumulenes **31**, **32**, **41** and **42**.*

Comp.	δ (C_3)	^1J (C_3P^V)	^1J (C_3P^{III})	δ (C_4)	^1J (C_4P^V)	^2J (C_4P^{III})	δ (C_5)	^1J (C_5P^V)	^1J (C_5P^{III})	δ (P^{III})	δ (P^V)	^1J (PP)
31	129.2	11		143.5	189		169.1	19	19	168.2	6.4	59
32	129.0	11		143.0	188		168.9	22	18	167.5	6.8	63
42	131.5	13	4	130.0	178	6	161.9	17	5	150.5	5.8	43
41										150.7	6.0	43

5.5.2 UV/Vis investigations

Due to the fact that complexes **32-34** and **42** are brightly colored compounds, we studied their optical absorption properties. The results of these measurements are summarized in Table 10.

***Table 10.** Electronic absorption spectra of compounds **15-17** and **25**.[a]*

Compound	λ_{max} , nm (ε [$M^{-1}cm^{-1}\times10^{-3}$])
32	470 (86), 342 (47.2), 322 (47), 303 (47.3)
33	445 (7.3), 316 (16.6)
34	484 (11.8), 329 (21.7)
42	460 (14.4), 334 (13.6), 300 (19)

[a] Measured in CH_2Cl_2

The compounds that contain a butatriene moiety (**42** and **32**) show relatively low energy longest wavelength absorption maxima (λ_{max}) which are however in the same range as those reported for comparable cumulenes.[118] Surprisingly, the introduction of a phenyl substituent instead of a TES group on the C3 carbon of the ring in complex **42** leads to a hypsochromic shift of 10 nm compared to the λ_{max} observed for **32**, as well as to a substantial decrease of the absorption coefficient (from ε = 86000 (**32**) to ε = 14400 $M^{-1}cm^{-1}$ (**42**)). At the same time, the presence of the thiophene substituents in bisphosphole

34 leads to a bathochromic shift of 39 nm as well as to an increase in molar absorptivity compared to that of the all-phenyl analogue **33**.

5.5.3 CV measurements

Complexes **32-34** and **42** that contain extended π-conjugated systems were studied by cyclic voltammetry (CV) and the obtained oxidation and reduction potentials correlated to the substitution patterns and extend of conjugation. Results of these measurements are presented in Table 11.

Table 11. *Electrochemical properties of compounds **32-34, 37, 38** and **42**[a]*

Compound	Reduction E_{cp} [V]		Oxidation E_{pa} [V]	
32[c]	-1.81	-1.40[b]	0.94	1.36
42	-1.67	-1.35[b]	0.96	
33	-2.38	-2.00	0.43	1.03
34	-2.34	-1.87	0.35	1.14
37			1.27	
38			1.12	

[a] Measured for 1 mM solutions of the analyte in CH_2Cl_2 (0.1 M NBu_4PF_6), glassy C-Electrode, ν = 100mV/s. All potentials are given versus Fc+/0. [b] Peak is reversible, reported value corresponds to $E_{1/2}$ = (Epa + Epc)/2. [c] Measured for 0.6 mM solution due to low solubility of the complex.

As visible from the data in Table 11, both cumulenes **32** and **42** feature redox processes at rather similar potentials, with the main differences being in the reductive scan. The phenyl substituted compound **42** is reduced at milder potential as compared to the TES substituted system **32**. The CVs of **32** and **42** are very different compared to those of simple oxaphospholes such as **37** and **38** which do not contain the cumulene system. It is thus possible to conclude that the reductions as well as the first oxidation that are observed in the CVs of compounds **32** and **42** are largely localized at the cumulene portion, since they are not observed for heterocycles **37** and **38**.

The CVs of bisphospholes **33** and **34** feature two electrochemically irreversible reductions and two irreversible oxidation processes. The presence of the thiophene substituents in **34** pushes the oxidation potentials to more positive values by 80 mV compared to that of phenyl substituted **33**. At the same time, also the first reduction of **34** occurs at milder potential by 130 mV. The sizeable impact that different substituents have on the electrochemically observed redox processes thus suggests that the phenyl and thiophene substituents are in significant conjugation with the bisphosphole π-system.

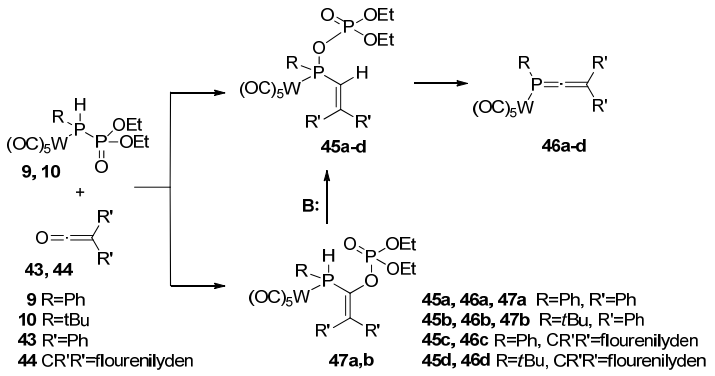
6. Reactions with ketenes (paper IV)

This chapter is dedicated to reactivity studies of pWH reagents towards ketenes, and the exploration of a reliable route to 1-phosphaallenes. Detailed mechanistic studies of the pWH reaction that are based on the isolation and crystallographic characterization of unique reaction intermediates are presented. The reactivity of phosphaallenes towards nucleophiles such as water and methanol is examined.

6.1 Preparation of phosphaallenes

Inspired by the work on the reaction of pWH reagents with acetylenic ketones presented in Chapter 5, we decided to investigate the reactivity of pWH reagents towards ketenes. To explore the possibility of preparing 1-phosphaallenes,[119,120] the reaction between two pWH reagents which differ by substituents on the P^{III}-side (**9** and **10**) and two ketenes, diphenylketene (**43**) and fluorenyl ketene (**44**) have been investigated.

As described in Chapter 4, we have demonstrated that organic bases such as DABCO or DBU promote phosphaalkene formation from pWH reagents and acetone in less than five minutes at ambient temperature. Hence, the same reaction protocol was also applied for the investigation presented in this chapter. Thus, the reaction between **9, 10** and **43, 44** was initiated by addition of one equivalent of base (DBU). No further changes in the reaction media were observed after 30 minutes and the reaction was thus quenched by an aqueous work up. Much to our surprise, the products that were obtained were not the expected phosphaallenes, but previously unknown phosphinophosphates **45a-d** (Scheme 23).



***Scheme 23**. Reaction between **9, 10** and **43, 44** using DBU as base*

Phosphinophosphates **45a-d** were isolated as pale yellow solids by column chromatography in good to excellent yields and characterized by ^{1}H, ^{13}C, ^{31}P NMR as well as HRMS which are all in agreement with the proposed structures. **45a-d** can be easily identified in the reaction mixture by characteristic ^{31}P NMR chemical shifts of -9.8 ppm for the P^{V} and 127 ppm (R = Ph, **45a,c**) or 148 ppm (R = *t*Bu, **45b,d**) for the P^{III} centre. Unambiguous proof for the structure of **45** was obtained by single crystal X-ray diffraction of compound **45c** (Figure 12).

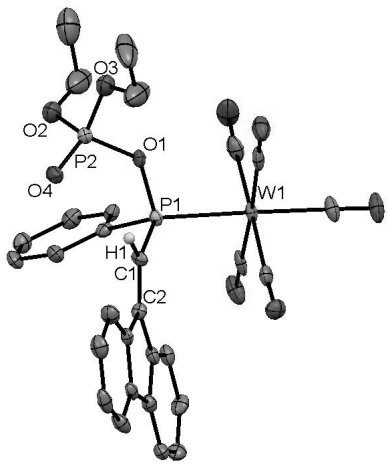
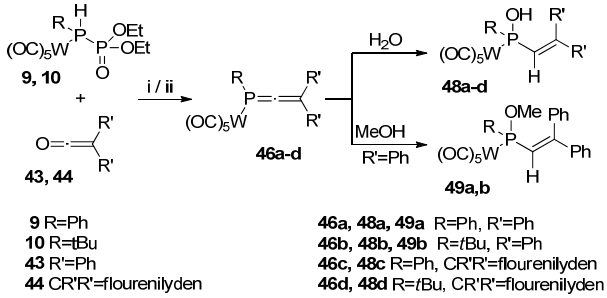


***Figure 12**. Crystal structure of compound **45c** (ellipsoids set to 50% probability). All protons are omitted for clarity, except for that at the vinyl moiety.*

When the reaction times were extended from 30 minutes to several days, complete conversion of the starting materials to the desired phosphaallenes **46a-d** was observed. Changing from DBU to LDA as a base accelerates the reaction and allows preparation of the phosphaallenes **46a-d** within one hour (Scheme 27). The target compounds are characterized by typical ^{31}P NMR chemical shifts of 57 ppm (**46a**), 98 ppm (**46b**), 60 ppm (**46c**) and 94 ppm

(**46d**), and are highly moisture sensitive which hampers their isolation and purification. Products that arise from the addition of water (**48**) or methanol (**49**) to **46** could however be isolated and characterized, in case of **48b** and **48c** even by single crystal X-ray studies (Scheme 24, Figure 13).



Scheme 24. *Isolated solvolysis products of phosphaallenes **46a-d**. i) In case of ketene **43**, the reaction was performed using 1eq. of BuLi, THF, -78°C, 30min; ii) in case when the ketene was generated in situ (**43 , 44**), the synthesis was performed by application of 2eq. of tBuOLi to 1eq. **9, 10** with subsequent addition of 1eq. of corresponding acid chloride at -78°C, THF, 1h.*

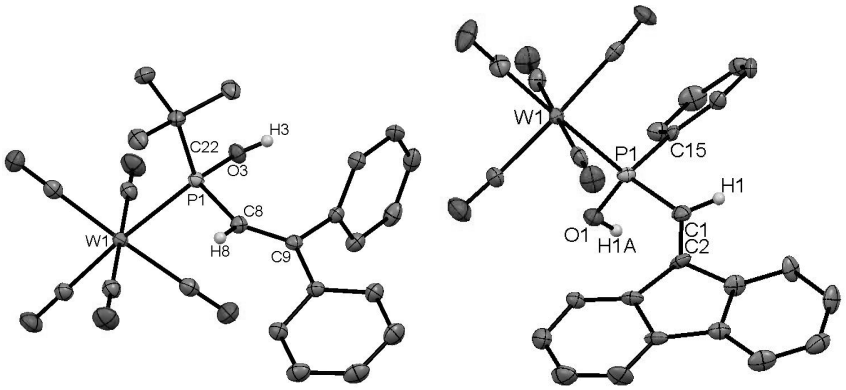


Figure 13. *Crystal structure of compounds **48b** (left) and **48c** (right) (ellipsoids set to 50% probability). All protons are omitted for clarity, except for that at the P^{III} atom.*

In order to investigate their role in the mechanism for phosphaallene formation, isolated compounds **45** were re-exposed to the basic reaction conditions. Formation of the corresponding phosphaallenes was observed at similar timescales as those observed in the original one-pot procedure (Scheme 23).

Further studies of the reaction between pWH reagents **9** and **10** and ketenes **43** and **44** allowed the isolation of another class of unexpected compounds **47a,b** (Scheme 23). Compounds **47** arise from the formal addition of the pWH reagent across the C=O portion of the ketenes. Their preparation is prompted by the addition of catalytic amounts of DBU to solutions contain-

ing equimolar amounts of pWH reagent and ketene. Under such conditions, the reaction neither goes to completion with the formation of phosphaallene **46** nor lead to the formation of phosphate **45**. Compounds **47a,b** are the only detectable products of the reaction, are stable, and can thus be isolated and completely characterized. Most gratifyingly, we were able to perform not only HRMS and NMR studies on complexes **47** but also X-ray crystallographic analysis on single crystals of **47a** (Figure 14).

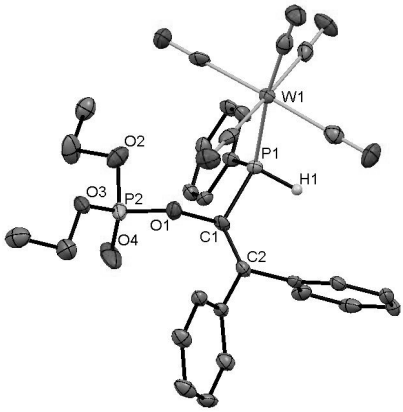
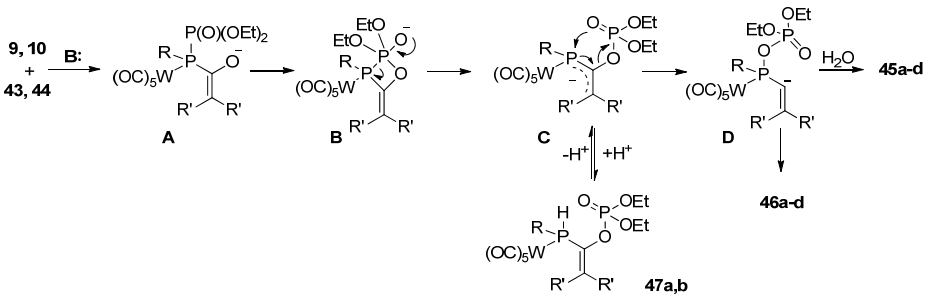


***Figure 14**. Crystal structure of compound **47a** (ellipsoids set to 50% probability). All protons are omitted for clarity, except for that at the P^{III} atom.*

Exposure of **47a,b** to equimolar amounts of base leads to the formation of **45a,b** within several minutes, followed by the final transformation to afford **46** on timescales similar as those observed in the one-pot procedure. Summarizing the observations described above, it appears that the step that leads to phosphaallene formation is the rate-limiting step of the reaction sequence. Considering that pWH reactions with simple ketones are relatively fast (chapter 4), it is tempting to suggest that the presence of the C=C double bond in the ketene substrate decelerates the final step and allows the detection and isolation of reaction intermediates that have never been observed before.

6.2 Mechanism of the pWH reaction

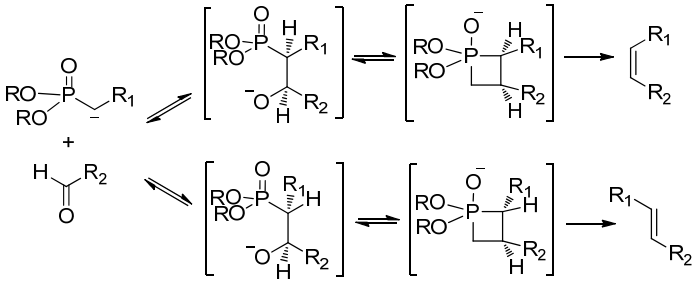
The discovery of compounds **45** and **47** allows us to suggest a detailed mechanistic proposal for the pWH reaction for the first time. The mechanism that is presented in Scheme 25 is in parts rather different to what is commonly believed for the analogous carbon-based reaction, i.e. the Horner-Wadsworth- Emmons (HWE) reactions (Scheme 26).[121-123]



Scheme 25. *Proposed mechanism of the pWH reaction*

The reaction starts with the formation of the salts of pWH reagents **9, 10** which have partial P=P double bond character, but also bear significant negative charge on the P^{III} centre. Nucleophilic attack of these salts on the carbonyl carbon of the ketene leads to the formation of intermediate **A** with negative charge on the oxygen. Nucleophilic attack of this oxygen on the P^{V} centre of the phosphonate group results in the formation of a four-membered ring. This oxadiphosphetane resembles the phosphaoxetane intermediate that is usually postulated in the HWE reaction. However, **B** does not undergo a single step phosphate elimination as is the case in the HWE reaction. In case of **B**, exclusive cleavage of the P-P single bond occurs, and intermediate **C** which carries a phosphate group at the former carbonyl carbon and a negative charge on the P^{III} centre is formed. Subsequent [2,3]-sigmatropic rearrangement leads to intermediate **D** in which the phosphate group can act as a leaving group to form phosphaallenes **46a-d**. When the reaction is performed with catalytic amounts of base, exclusive formation of product **47a,b** is observed. In this case, intermediate **C** acts as a base and deprotonates residual **9** or **10**. The reaction is thus self-propagating and compounds **47a,b** are the only observed products. In a separate experiment, it could be shown that **C** is indeed a stronger base than the anion of the pWH reagent. Thus, when both **9** and **47a** were exposed to anhydrous MeOH-d_4, only the *P*-bound proton in the former exchanged for a deuterium of the solvent. For compound **47a** no such exchange appears even at elevated temperatures. These results are consistent with the assignment that **C** must be the stronger conjugate base, as **9** is a stronger acid. Final step of the sequence is an E2 elimination of the phosphate to establish the phosphaallene system.

It is important to underline that neither an intermediate of type **45**, nor of type **47** has ever been observed in the HWE reaction. At a few instances, similar structures were suggested in order to explain different stereochemical outcomes in HWE reactions as compared to the classical Wittig reactions.[124,125] In general it is widely accepted that the HWE reaction goes through an oxaphosphetane intermediate which affords final product by *simultaneous* C-P and C-O bond cleavage (Scheme 26).



***Scheme 26**. Mechanism of the HWE reaction.*

Intermediates which arise from exclusive C-P bond cleavage have never been observed and are calculated to be high in energy and very short-lived, if ever produced.[125] Since phosphorus and carbon are believed to be closely related,[6] a comparison of the HWE reaction with the phosphorus analogous pWH reaction is interesting from theoretical as well as from practical point of view. The main difference between the two reactions arises from differences in the bonding situations in intermediate **B** (Scheme 25) and the corresponding oxaphosphetane in Scheme 26. It should be noted that the P-P bond in **B** is weaker than the corresponding C-P bond in the oxaphosphetane and can thus be cleaved more easily. At the same time, the C-O bond in **B** can be expected to be stronger since the carbonyl carbon contributes a sp^2-hybrid orbital to the C-O bond as compared to a sp^3-hybrid that participates in the oxaphosphetane. Accounting for these differences in bonding, it is no longer surprising that selective cleavage of the P-P bond is observed. Another interesting aspect is the [2,3]-sigmatropic rearrangement to form **D**. Related [3,3] rearrangements have however precedence in the isomerization of allylic phosphates.[126-128] Driving force for this rearrangement is the formation of a new O-P bond. The final elimination of the phosphate group is suggested to proceed via an E2 mechanism which requires s-*trans* arrangement of the vinyl-lone pair and the phosphate leaving group. As visible from the Newman projection in Figure 15, such a conformation is sterically very demanding since the phosphate needs to come into close proximity to the R' group. It is this unfavorable conformation that gives kinetic stabilization to intermediate **D** and that can be made responsible for the relatively long reaction times.

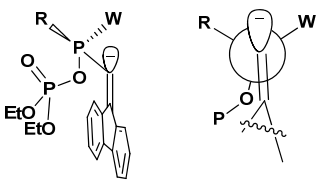


Figure 15.** Newman projections of intermediate **D

In summary, we have studied the reactivity of pWH reagents **9** and **10** towards ketenes and were able to establish a reliable route to 1-phosphaallenes. Characterization of unique reaction intermediates **47a,b** as well as **45a-d** provided a detailed picture of the reaction mechanism. It emerged that the pWH reaction is much more than a simple phosphorus analogue of the HWE reaction, with multiple intermediates being observed in the former that have never been observed in the latter.

7. Concluding remarks, summary and outlook

This thesis is devoted to the development new synthetic approaches to pWH reagents and the utilization of these compounds in reactions with acetylenic ketones and ketenes. The products that are obtained in these reactions are highly complex phosphorus-containing compounds based on phosphaalkene, oxaphosphole and phosphole skeletons.

More specifically, we were able to develop reliable synthetic protocols which allowed the preparation of pWH reagents with non-classical, unsaturated, π-conjugated substituents in only three steps with good overall yields on a multigram scale. pWH reagents can be prepared starting from *P,P*-dichlorophosphines which can be phosphorylated under Michaelis-Arbuzov conditions to give bis(phosphonato)phosphines. The latter, after coordination to a metal core, can undergo hydrolysis in the presence of metal alcoxides. Prepared in such a way, salts of the pWH reagents can be directly used in a one-pot reaction or quenched by addition of water. Obtained pWH reagents were proven to exist in two different forms depending on the nature of the substituent on the phosphorus side. While the more classical description that contains a secondary phosphine centre and a phosphonate group is observed for *tert*-butyl and phenyl substituted complexes, vinyl or acetylene *P*-substituents stabilize the ylide form.

The synthesized pWH reagents were used in reactions with various types of ketones. We were able to show that phenyl substituted pWH reagent **9** reacts quantitatively with acetone to give the corresponding phosphaalkene in less than 5 minutes. Prolongation of the reaction times results in subsequent transformation to 1,2-diphosphetane.

In case when the reactions were conducted with ketones that contain at least one acetylene unit, very different reactivity is observed. The outcome of the reactions was proven to be highly dependent on the nature of the substituent at the acetylene termini as well as the overall structure of the ketones. Several general conclusions can be drawn:

- ✓ Bulky substitutents (TIPS) at the acetylene termini prevent reactivity at the acetylene portion of the substrates and classical phosphaalkene formation is observed.
- ✓ Monoacetylenic ketones lead to the formation of highly functionalized 1,2-oxaphospholes. If required, the phosphonate group at the C4 carbon of the oxaphosphole ring can selectively be removed by raising the pH during the work up procedure.

- ✓ Diacetylenic ketone which bear TMS or TES groups at the acetylene termini give rise to cumulene substituted oxaphospholes.
- ✓ The reaction sequence that ultimately leads to cumulene-substituted oxaphospholes is highly modular, and allows the successive reaction with two different ketones, and thus offers good control over the substituents at the final compounds.
- ✓ Symmetric ketones with aromatic acetylene termini react entirely different and give rise to per-substituted bisphospholes.

Mechanisms that rationalize all presented transformations could be proposed and are corroborated by structural characterization of the final products using NMR, HRMS and X-ray analysis. Selected mechanistic models are further supported by theoretical methods and *in situ* FTIR spectroscopy.

Investigation of the reactivity of pWH reagents towards ketenes resulted in the establishment of a reliable route to 1-phosphaallenes. Even though these compounds appear to be sensitive towards nucleophiles, they could be isolated and completely characterized as water and methanol adducts. Characterization of unique reaction intermediates provided a detailed picture of the reaction mechanism. It emerged that the pWH reaction goes through multiple intermediates that can spectroscopically be observed, and structurally characterized. The pWH reaction is thus greatly different to its carbon-analogous HWE reaction, in which alkene formation from an oxaphosphetane intermediate occurs in one concerted step.

In summary, this thesis presents investigations on synthetic routes to novel phosphorus-containing molecules, together with detailed studies of the reaction mechanisms of the observed transformations. Even though this work is of fundamental character, some of the prepared compounds have a potential to be applied within the field of molecular electronics. Especially, the obtained bisphospholes are promising candidates for organic light emitting diodes. Even though the compounds are non-emissive in the current state, several post-synthetic modifications such as removal of the tungsten core and oxidation of the phosphole unit may result in improved optical properties and potential applications of the compounds as functional materials in organic electronic devices.

Svensk sammanfattning

Livet har förändrats dramatiskt de senaste årtiondena. Den snabba utvecklingen de sista 50 åren har lett till ett behov av både snabbare och kraftfullare datorer. Jack Kirby uppfann den integrerade kretsen 1959 och sedan dess har antalet transistorer per areaenhet, eller per chip, dubblerats var 18:e månad. Den här utvecklingen kallas Moores lag och förväntas gälla till 2020. Storleken på transistorerna spelar en avgörande roll då den gör att den totala storleken på komponenterna kan minskas och i och med detta kan elektronisk utrustning på mikroskala produceras. År 2007 tillverkades transistorer med 45 nm teknologi men redan nu finns publicerade resultat där man använder 10 nm teknologi. [1,2] Tillverkningen av transistorer och många andra komponenter inom nanoteknologin använder sig idag av en ”top-down”-process, dvs. man utgår från ett bulk-material från vilket man tillverkar mindre komponenter. Denna process börjar nå sina begränsningar. Kostnaderna för att bygga anläggningar för tillverkning av integrerade kretsar har ökat exponentiellt med en faktor två för varje ny generation av kretsar och kallas för Moores andra lag. Ett sätt att lösa det här ekonomiska problemet skulle kunna vara att använda en ”bottom-up”-process, där man tillverkar elektroniska komponenter från enskilda molekyler. Molekylerna hålls samman av kovalenta krafter som är mycket större än krafterna i de komponenter som finns på den makroskopiska skalan.

De senaste två årtiondena har det publicerats en stor mängd litteratur inom molekylär elektronik. Forskare över hela världen har riktat sin uppmärksamhet mot framställningen av flexibla, energi-effektiva och billiga material med specifika och lättmodifierade egenskaper.[2,3] De första stegen mot detta mål är redan tagna. Molekyler och polymerer som ordnats i speciella arrangemang (t.ex. mono- eller multilager) har redan använts i skärmar hos mobiltelefoner och kameror där de fungerar som ljus-emitterande material i organiska ljus-emitterande dioder (OLEDs).[4] Men trots att den första organiska elektronikkomponenten gjordes 1974 från melamin-polymerer[5], förblir molekylär elektronik ett forskningsfält som är utmanande både för industrin och för akademin. Vi måste ta klivet över en hög kunskapströskel innan den första komponenten baserad på en enda molekyl kommer att vara på marknaden.

Molekylär elektronik omfattar både elektronik baserad på en enda molekyl och elektronik med flera molekyler. Uttrycket molekylär elektronik innefattar två delar som är viktiga för forskningsfältets framsteg d.v.s. utveckling

och förbättring av nya och existerande tekniker på ingenjörssidan samt framställning av lämpliga molekyler. Den här avhandlingen behandlar den andra delen, utveckling av kemiska metoder och riktad syntes av molekyler för potentiella tillämpningar inom molekylär elektronik. Särskild uppmärksamhet bör riktas mot π-konjugerade system. Den första generationen av π-konjugerade material baserades på omättade kol-baserade polymerer. Sedan den första organiska elektronikkomponenten tillverkades 1974[5] har dessa polymerer tillämpats i OLEDs, tunnfilms-transistorer, fotovoltaiska celler etc.[2]

Man har nyligen kunnat visa att integrering av tyngre grundämnen i kol-baserade π-konjugerade system medför ett flertal fördelar såsom minskat HOMO-LUMO avstånd, förbättrad stabilitet etc. Fosfor spelar en framträdande roll i det här avseendet, dels eftersom man visat att ämnen som innehåller multipelbindningar mellan fosfor och kol har likheter med motsvarande kol-analoger[6], men också för att det fria elektronparet hos fosfor erbjuder en möjlighet till unika modifieringar såsom oxidation, koordination av metaller eller addition av elektrofiler.[7,8] Fosfor-dopade π-konjugerade material kan generellt delas in i två stora grupper. Den första gruppen omfattar linjära strukturer innehållande dubbelbindningar mellan fosfor och kol eller fosfor och en heteroatom. Den andra består av fosfor-innehållande heterocykliska motiv där fosforatomen är en del av ringsystemet. Den här avhandlingen behandlar utvecklingen av nya syntesvägar till fosfa-Wittig-Horner reagens och användningen av dessa föreningar i reaktioner med omättade ketoner för att ge olika klasser av fosforföreningar – fosfaalkener, oxafosfoler och fosfoler.

Vi har utvecklat pålitliga syntesvägar som medför att vi kan framställa pWH reagens med icke-klassiska, omättade, π-konjugerade substituenter i enbart tre steg med bra totalutbyte på en mulitgramskala. pWH reagens kan framställas från P,P-diklorofosfiner, vilka kan fosforyleras under Michaelis-Arbuzov-förhållanden för att ge bis(fosfonato)fosfiner. Bis(fosfonato)fosfinerna kan i sin tur, efter att ha koordinerats till en metall, hydrolyseras i närvaro av metallalkoholater. Salter av pWH reagens som erhållits genom denna syntesväg kan användas direkt eller neutraliseras genom tillsats av vatten. De erhållna pWH reagens existerar i två olika former beroende på fosforatomens substituenter. Tertbutyl eller fenyl-substituerade komplex ger den vanliga P-H formen medan vinyl- eller acetylengrupper resulterade i ylid-formen.

De syntetiserade pWH reagens kan sedan användas i reaktioner med olika typer av ketoner. Fenyl-substituerade pWH reagerar kvantitativt med aceton och resulterar i en fosfaalken på mindre än 5 minuter. Förlängs reaktionstiden omvandlas fosfaalkenen till en 1,2-difosfitan. I de fall då reaktionerna utfördes med ketoner innehållande minst en acetylen-grupp var resultatet av reaktionen starkt beroende av substituenten knuten till acetylengruppen samt av den övergripande strukturen hos ketonen. Ett flertal slutsatser kan dras:

Om monoacetylena ketoner används i reaktionen blir produkten en fosfaalken eller en oxafosfol. Fosfaalkenen fås från ketoner med skrymmande substituenter (TIPS) på acetylenen och oxafosfolen från ketoner med TES, TMS eller fenyl-grupper som substituenter.

Om reaktionen utförs med diacetylena ketoner med TIPS-substituerade acetylener erhålls en ostabil fosfaalken som den enda observerade produkten. Fosfaalkenen kan isoleras som en hetero-Diels-Alder addukt.
I de fall då en diacetylen keton med TMS- eller TES-substituenter används erhålls kumulen-substituerade oxafosfoler.

För symmetriska ketoner med aromatiska substituenter på acetylenerna är den enda isolerade produkten en persubstituerad bis-fosfol.

Om osymmetriska diacetylena ketoner med en fenyl- och en TIPS-grupp används är slutprodukterna två olika oxafosfoler. De skiljer sig från varandra genom närvaro/frånvaro av en fosfonatgrupp på kolatom C4. Förhållandet mellan dem beror på pH-värdet under upparbetningen.
För TES/fenyl-substituerade asymmetriska diacetylena ketoner beror produktens struktur på förhållandet mellan startmaterialen. Reaktionerna resulterar antingen i oxafosfoler eller kumulen-substituerade oxafosfoler.

Genom att kombinera karakterisering av slutprodukterna med NMR, HRMS och röntgenkristallografi tillsammans med teoretiska metoder och in situ FT IR–tekniker har en detaljerad reaktionsmekanism mellan pWH reagens och ketonerna kunnat presenteras.

Undersökningar av reaktiviteten för pWH reagens mot ketener resulterade i en ny syntesväg till 1-fosfaallener. Trots att dessa föreningar verkar vara känsliga mot nukleofiler har deras vatten- och metanoladdukter kunnat isoleras och karakteriserats fullständigt. Karakterisering av unika reaktionsintermediärer har gett en detaljerad bild av reaktionsmekanismen. Det framkom att pWH-reaktionen är mycket mer än bara en enkel fosfor-analog av HWE-reaktionen och ett flertal intermediärer har kunnat observeras.

Sammanfattningsvis presenterar denna avhandling en undersökning av syntesvägar till nya fosfor-innehållande molekyler samt en detaljerad studie av reaktionsmekanismerna för de olika omvandlingarna som leder till dessa föreningar. Även om denna studie är av mer fundamental karaktär, har vissa av de framställda föreningarna potential för att användas inom tillämpningar för molekylär elektronik. Detta gäller speciellt bisfosfolerna. För närvarande har inte dessa föreningar någon emission, men tillämpningar av ett flertal post-syntetiska modifieringar t.ex. borttagning av metallen koordinerad till fosforatomen och oxidation av fosfolen, kan resultera i förbättrade optiska egenskaper. Detta kan i sin tur leda till potentiella tillämpningar som funktionella organiska material i elektroniska komponenter.

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