ADANCING THE CHEMISTRY OF PHOSPHOLE

NANYANG TECHNOLOGICAL UNIVERSITY

ADVANCING THE CHEMISTRY OF PHOSPHOLE

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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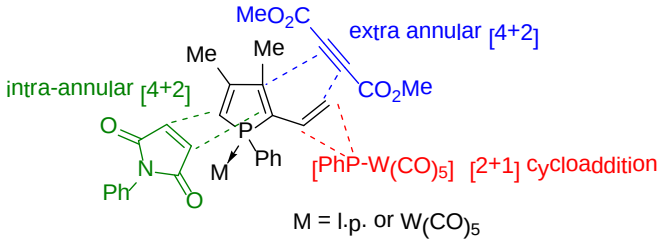
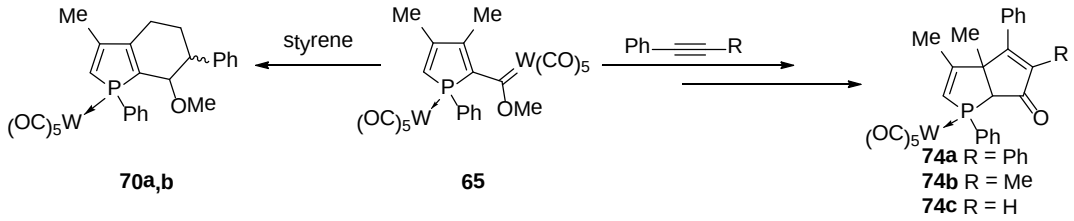
ABSTRACT

We have studied the influence of two types of unsaturated substituents on the α-position of the weakly aromatic phospholes. They include the vinyl group and the Fischer carbenes.

The presence of this vinylic group has induced linear π-conjugation with the diene unit of phosphole. This has in turn activated the dienic system resulting in a unique chemistry that is rarely (or never) observed in the other 5-membered heteroarene derivatives. Synthesis of the desired 2-vinylphosphole is via 2-formylphosphole which is prepared from 2-lithiophosphole. Then, it is complexed to $W(CO)_5$ and characterised by X-ray analysis. Both the trivalent 2-vinylphosphole and the complexed form are subjected to various cycloaddition reactions. Three reactive sites are created and the cycloaddition pathway selected is exclusive to the specific reagent.



Similarly, we started the synthesis of pentacarbonyl tungsten 2-phospholylcarbene derivatives from 2-lithiophosphole. Using the most general entry to Fischer carbenes, trivalent phospholylcarbene and tetravalent phospholylcarbene are obtained. Several trial experiments with the trivalent phosphole-substituted carbene have shown the lone pair on P will disturb the exclusive reaction at the carbenic carbon. Thus, the tetravalent phospholylcarbene became the main focus for the study. This complex behaves in the same way as a standard Fischer carbenes when subjected to oxidation and hydrolysis. However, a completely different picture emerged from the reaction with neat styrene and alkynes.



LIST OF PUBLICATIONS

1. "The Original Reactivity of a Phosphole-Substituted Fischer Carbene Complex."
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ABBREVIATIONS AND SYMBOLS

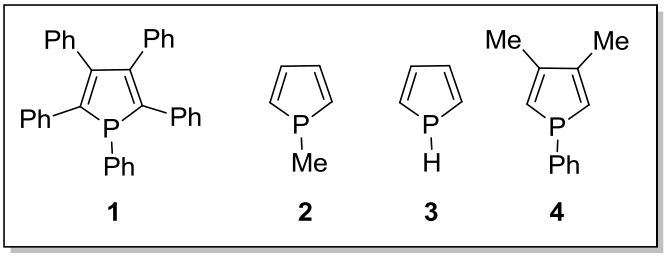
δ	NMR chemical shift in Hz
°	Degree
^{13}C	$^{13}C\{^{1}H\}$
^{31}P	$^{31}P\{^{1}H\}$
Å	Angstroms
ASE	Aromatic Stabilization Energy
BI	Bird Index
d	Doublet
dd	doublet of doublets
DCM	Dichloromethane
DFT	Density function theory
DMAD	Dimethyl acetylenedicarboxylate
DMSO	Dimethyl sulfoxide
et al.	*et aliae* = and others
etc.	et cetera = and others
HOMO	Highest occupied molecular orbital
HRMS	High resolution mass spectroscopy
kcal	kilocalorie
LUMO	Lowest unoccupied molecular orbital
MeOTf	Methyl trifluoromethansulfonate

m	*meta*
m-CPBA	*meta*-chloroperoxybenzoic acid
m	multiplet
mol	mole
NPM	N-phenylmaleimide
NICS	Nucleus-independent chemical shift
NMR	Nuclear magnetic resonance
ppm	Parts per million
THF	Tetrahydrofuran

CHAPTER 1

Introduction to Phosphole Chemistry

Phospholes, the five-membered unsaturated heterocycles containing phosphorus, only joined the family of pyrroles, furans and thiophenes in 1959, with the discovery of monocyclic phosphole, bearing structure **1**, by two different groups.[1,2] After several years, the C-unsubstituted phosphole **2** was synthesized[3], which was followed by the characterization of the parent phosphole **3** under low temperature in 1983 by Mathey.[4]

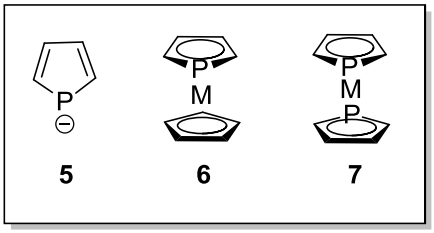


Since then, the fairly underexplored phosphole chemistry has started to gain greater attention. Further sophisticated research on the synthesis, chemical and physical properties of them has commenced.

Currently, it has been widely accepted that phospholes are the least (or weakly) aromatic in the class of five-membered unsaturated heterocycles of S, O and N. This unique property has proved to be a challenging yet valuable one. Hence, it is receiving a great amount of interests and have set the field of phosphole chemistry as the topic for numerous reviews, from as early as the 1970s to the mid 1999s[5-17] with the latest ones summarized by Mathey[18], Quin[19], Réau and Dyer[20], as well as Sinyashin's group in 2013.[21]

The practical applications of phospholes in homogeneous catalysis have long being explored.[15,16] Comparable or even superior results obtained in some reactions, together with the ease of handling, have made phospholes more favourable over phosphines as ligands. Thus, the recent trend is to develop more functionalized phospholes. One new venture worth mentioning is the use of optically active phospholes in metal catalysed asymmetric allylic alkylation.[22] The quest in phosphole chemistry, including coordination chemistry, has not stopped when it was realised that phospholide ions **5** (lithiated phospholes) have the ability to

act as *eta*-5 ligands due to their aromaticity.[23] Subsequently, a range of phosphametallocenes **6** and **7** were synthesized,[24,25] and pioneering research on the applications of such complexes in catalysis has started.[26] In brief, many recent metal catalysed reactions that phospholes participated in (such as hydroformylation, copolymerization and polymerization with ethylene, etc.) have been summarized.[19,21]



5 **6** **7**

One of the new and intriguing applications of phospholes is their ability to be used as the building block for electro-optic substances. The intrinsically low aromaticity of phospholes implies a polarizable endocyclic diene. This was demonstrated by including acetylenic substituents on the α-carbons of the phosphole, leading to the absorption and emission at relatively long wavelengths.[27] Moreover, the reactive P-centers allow chemical modifications which can alter the optical and electro-chemical properties of phosphole-based π-conjugated materials. These appealing properties place phosphole markedly above other commonly used aromatic organic synthons such as pyrrole, thiophene, fluorene, or benzene as the building blocks for electro-optical materials.

It is clear that phospholes deserve our attention for more novel advances. Thus, the contents of this thesis concentrate on functionalizing monophospholes with vinylic groups on the α-carbon. We envisaged that the α-vinylic substituent on phospholes would create a significant alteration in phospholes chemistry. In the near future, such vinylic-substituted phopholes may also serve as the building blocks for highly π-conjugated phospholes polymers.

1.1 Synthesis of Phosphole

The methods employed to construct the O, S and N ring systems are almost inadequate to synthesize the phosphole ring. Nearly all of the known carbonyl condensation approaches are not useful for phosphole synthesis due to the difference in chemistry between phosphines and amines. This is evidenced by the failure to obtain phospholes when Hughes[28] and

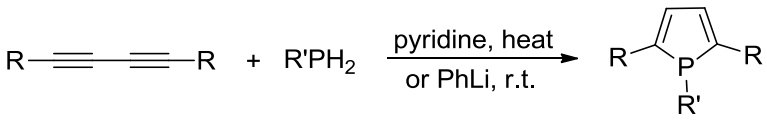
Vysotskii[29] used Paal-Knorr condensation of 1,4-dicarbonyl compounds with $PhPH_2$ and with PH_3 respectively for the synthesis. However, there is a single synthetic route which is common for both phosphole and pyrrole ring with some generality; the condensation of 1.3-diynes with primary phosphines or amines.

The limited scope in direct phosphole ring synthesis has prompted the search for other sophisticated and general synthesis methods. By far, the transformation of 3-phospholene ring to phospholes is one of the best methods. This leads to many techniques being developed to transform the monounsaturated ring to a fully unsaturated one.

Thus, a closer look at the synthetic methods available to construct phosphole rings is required. It has to be noted that the collections of phospholes presented in this section will mainly cover non-functionalized phospholes, while the techniques to prepare complex phospholes will be discussed in section 1.4 under functionalization.

1.1.1 Cycloaddition of alkynic compounds with primary phosphines

The only example of direct ring closure which is common for both phospholes and pyrrole ring was discovered in 1967 by Märkl.[30] This method uses 1,4-substituted diynes to react with primary phosphines to give 1,2,5-trisubstituted phospholes in 60% yield (R = Ph, R' = Ph) (Scheme 1.1). This is also one of the earliest process known that allows a range of substituents other than phenyl to be placed on the ring.



Scheme 1.1 Synthesis of 1,2,5-trisubstituted phosphole by 1,3-diynes with primary phosphines

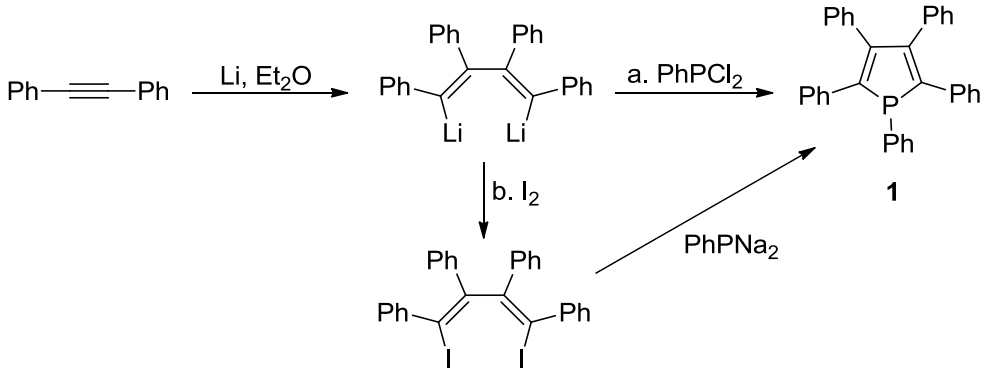
In order to counter the issue of handling reactive primary phosphines, an easier to handle phosphine with a dimethylol derivative, ($RP(CH_2OH)_2$) can be used. However, by doing so, the yield dropped significantly to 20.5%.

Märkl's work only dealt with symmetrical diynes, but unsymmetrical diynes have proven to work fairly well too. A comprehensive summary of phospholes synthesized by this method

can be found in the review by Mathey.[5] Also, more advanced investigations on how to improve the reactions have since been performed, such as the addition of bases and by free radicals.[31] However, the downside of this method is that only 1,2,5-tribsubstituted phospholes can be synthesized.

1.1.2 Condensation of RPX_2 with 1,4-dilithiobutadiene or 1,4-dihalobutadiene with $RPLi_2$

The first approach that place phospholes into the family of pyrroles, furans and thiophenes. Two independent laboratories successfully synthesized a monocyclic phospholes **1** where one of them used the 1,4-dilithiobutadiene to react with $PhPCl_2$ (Scheme 1.2).[2,32]



Scheme 1.2 Synthesis of 1,2,3,4,5-pentaphenylphosphole by 2 different pathways

The dilithiated-diene can be easily prepared from diphenylethyne and lithium, together with the excellent yield of the phosphole. It remains the best way to prepare this derivative. In addition, the P-benzyl substituted phosphole was also reported.[33]

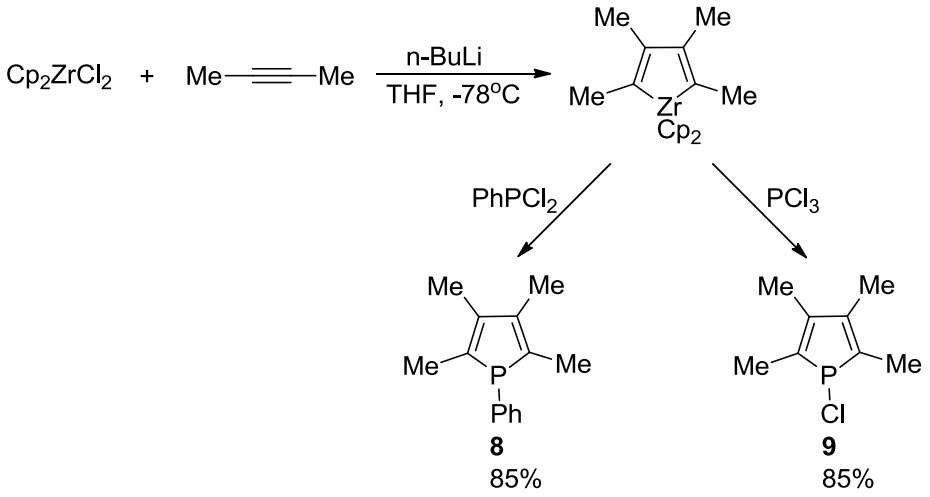
Conversely, a 1,4-dihalobutadiene can be used to react with the disodium salt of phosphine to give phosphole **1** with 88% yield[33] (Scheme 1.2). A related extension from this process is the usage of 1,4-dichlorobutadiene to react with $PhPLi_2$.[34]

1.1.3 Reaction of zirconacyclopentadiene with $PhPCl_2/PCl_3$

Transition metals are also being applied into making the 1,2,3,4,5-pentasubstituted phospholes. It involves a one-step approach by reaction of the easily prepared

zirconacyclopentadiene with phosphonous dichloride or PCl_3 to give compounds **8**[35,36] and **9**[37] respectively (Scheme 1.3).

An earlier example of using transition metals in a similar fashion was shown by Braye and Hübel in 1959. Their method made use of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with tolan to form an iron carbonyl complex, which then reacts with $PhPCl_2$ to give phosphole **1**.[1]

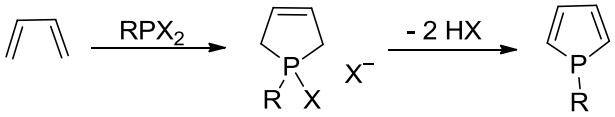


Scheme 1.3 Preparation of 1,2,3,4,5-pentasubstituted phospholes from zirconacyclopentadiene

1.1.4 Dehydrohalogenation of McCormack cycloadducts and its derivatives

The ring transformation of 3-phospholene derivatives from the McCormack cycloaddition to phospholes is a far more superior method than those direct ring closing methods. This earliest method allows the synthesis of asymmetrical phosphole with reasonable yield.

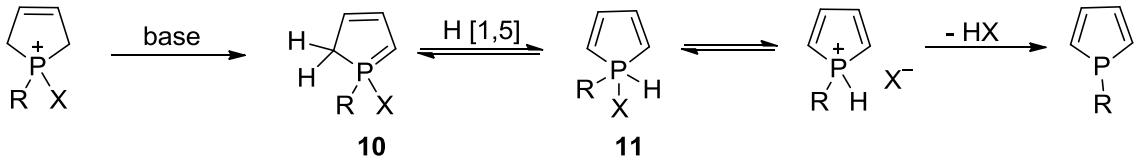
Halophospholenium halides which are the initial product formed from the McCormack cycloaddition of dienes and phosphorus (III) haldies, are able to form phosholes after dehydrohalogenation. Different reactant combinations sometimes produce unwanted halo-2-phospholenium salts. However, when the double bond is at the 3-position (Scheme 1.4), these adducts can undergo dehydrohalogenation to give phospholes.[28,38-42]



Scheme 1.4 Dehydrohalogenation of halo-3-phospholenium salts

Dehydrohalogenation of 3-phospholenium halides to phospholes has becomes the most versatile and clear cut method since Mathey proposed an efficient route in 1969.[43] Tertiary amine (DBU) is used for the dehalohydrogenation in boiling benzene. Its first improvement in 1970[44] which replaces benzene with a mixture of solvents (benzene, hexane, and DCM) allows the reaction to be performed at milder condition. Final optimization by changing the strong base, DBU, to *α*-picoline in 1981.[45] This optimized one-pot system has even allowed 1-phenyl-3,4-dimethylphosphole **4**, to be produced up to a 30kg scale.[46]

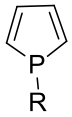
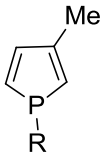
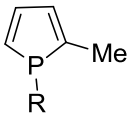
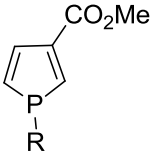
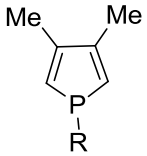
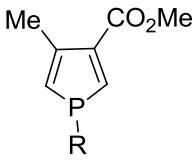
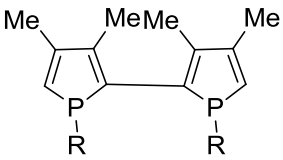
The mechanism of this dehydrohalogenation by base is difficult to prove. A reasonable description involves a reversible hydrogen [1,5]-sigmatropic shift (Scheme 1.5). This key step accounts for an equilibrium between the cyclic ylide **10** and the covalent form of phospholium salt **11** when phosphole is reacted with anhydrous HCl.[47]



Scheme 1.5 Proposed mechanism of dehydrohalogenation of halo-3-phospholene salt by base

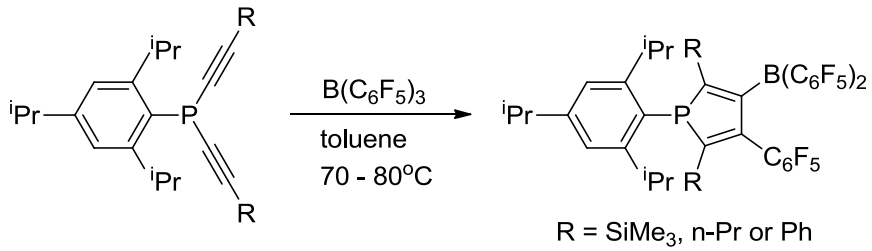
The scope of Mathey dehydrohalogenation is fairly general. The first C-functionalized phosphole, and the simple 1-methylphosphole are both synthesized using Mathey's method from 3-phospholene oxides. Table 1.1 summarises some of the phospholes synthesized by Mathey dehydrohalogenation of McCormack cycloadducts and its derivatives.

Table 1.1 Synthesis of phospholes by dehydrohalogenation of McCormack adducts

Phospholes	R,[ref] yield
	Ph,[45] 50%; n-Bu,[48] 14%
	Ph,[45] 75%; $PhCH_2$,[49] 7.4%; Me,[49] 12%; n-Bu,[48] 8%
	Ph,[50] 15%; Me,[49] 14%
	Me,[49] 23%
	Ph,[45] 86%; $PhCH_2$,[45] 75%; Me,[45] 30%; n-Bu,[48] 18%; n-$C_{12}H_{25}$,[51] 33%
	Me,[49] 23%
	Ph,[52] 50%

1.1.5 Wrackmeyer 1,1-carboboration reaction of bis(alkynyl)phosphines

A latest entry to generate phosphole rings has been proposed by Erker and co-workers.[53] This synthetic method is a straight forward one pot reaction which involves suitable bis(alkynyl)phosphines and strong Lewis acid, tris(pentafluorophenyl)borane. Upon heating in toluene, 3-boryl substituted phospholes will be produced (Scheme 1.6).



Scheme 1.6 Phosphole synthesis via 1,1-carboboration of bis(alkynyl)phosphines

These 3-borylphospholes are shown to be able to take part in the typical Suzuki-Miyaura cross coupling reaction with iodobenzene. Thus, replacing the boryl moiety by a phenyl substituent.

1.2 Computational and Theoretical Studies on Phospholes

Theoretical studies of phospholes were not compelling in the earlier days. The electronic structure of the phospholes rings was not well understood as compared to their related heterocyclopentadienes since there is no pure theoretical treatment to provide such insight. Nor has thermochemical measurement of the resonance energy been made with the correct compounds. Thus, the degree of cyclic electron delocalization in the ring system that governs the chemical and physical properties remains unclear.

The ambiguity of the electronic structure is solved when more sophisticated computational approach is taken beginning of the 90s. Many aspects of the ring system including those which have not been considered before are studied. Thus, this section provides the theoretical endeavours on the phospholes ring systems.

1.2.1 Aromaticity of phosphole

Aromaticity of phospholes has been a highly debated topic. This uncertainty only came to light gradually with the synthesis of simple phospholes[3,30,43] which allowed experimental examination to study the delocalization without the interference of the substituents on the ring. Before this, theoretical study proposed by Brown[54] was based on unsubstituted phosphole ring with a planar system assumed. It was concluded that the phosphole ring had considerable conjugation energy of 1.49β while pyrrole is 1.27β. However, when this simplified treatment was

compared to the available pentaphenylphospholes, a conclusive theory could not be drawn regarding the nature of the ring.

A clearer picture emerged when the synthesis and the X-ray diffraction analysis of a simple phosphole, 1-benzylphosphole, was published.[55,56] Immediately, Brown's assumption of the planarity of the ring was negated. The tricoordinate (σ^3) phosphorus in the 5-membered ring has retained its pyramidal conformation which contributes to phosphole's low aromaticity nature.[57,58] The inversion barriers of phosphole (16kcal/mol) are compared with a saturated counterpart phospholane, (36kcal/mol) using dynamic NMR spectroscopy. Clearly, the stabilizing effect of aromatic delocalization is unable to compensate the intrinsically high 35kcal/mol of planarization barrier.

Still, subsequent findings have not led to unanimity, with some believe the absolute absence of conjugations[59-61] while others insisting on the presence of it.[62-65] Mislow pointed out an extensive delocalization in the planar structure but felt unsettled about the aromaticity in the ground state (pyramidal structure).[64] Results from Findlay[61], on the other hand, doubts the presence of any delocalization.

Then, more prominent studies follow, such as the Bird Index (BI), the Nucleus Independent Chemical Shift (NICS), and Aromatic stabilization Energy (ASE). Bird's calculation indicates that phospholes have lower aromaticity than furan.[66] The BI of 1-benzylphosphole is also shown to be slightly higher than cyclopentadiene. This slight difference results from the σ^*/π hyperconjugation between P-R bond and the dienic system, which also explain phosphole's weak ASE.[63,67,68] Evidently, the NICS(0)π value of phosphole (-13.2)[69] is just marginally larger than cyclopentadiene (-12.1).[70] Till this point, it has very much accepted that the studied phospholes are weakly aromatic.

The next crucial question is how the aromaticity can be improved. Promising yet difficulty in developing the chemistry around phosphole due to its poor electron delocalization has pushed more computational studies to be performed. Earlier study conducted by Mislow suggested the presence of extensive delocalization in the planarized phospholes.[62] This has become the focal point which is heavily studied by various methods, including structural parameters,[70,71] calculation of NMR properties,[72] BI,[70] BDSHRT,[70] stabilization energy[70,73] and

NICS values.[70] It was demonstrated that Mislow's claim is true. Additionally, the optimized planar structure of phosphole in these studies possesses an even higher aromaticity than pyrrole or thiophene.

Theorectically, it is recognized that reducing the pyramidality of P can increase the electron delocalization in the ring. Thus, it is reasonable to consider substituents that might planarize the phosphole ring. Quin proposed placing bulky substituent on the P atom to reduce the pyramidality of phosphorus in the ring.[74,75] Surely, when 1-(2,4,6-tri-*tert*-butylphenyl)-3-methylphosphole[76] was characterised, the pyramidality of phosphorus is significantly reduced, with an out-of-plane (OOP) angle of 45.9° (Figure 1) while the usual is about 65°. Comparable to benzene, this phosphole with space demanding substituents easily undergoes Frieldel-Craft acylation in the presence of $AlCl_3$.

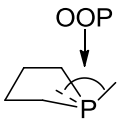


Figure 1.1 Definition of out-of-plane (OOP) angle in phospholes

Another possible alternative shown theorectically to induce planarity of the tricoordinate phosphorus is through the introduction of π-acceptor groups such as BH_2 at P atom (inversion barrier decreased to 1.5kcal/mol). Likewise, placing these π-acceptors groups on both the α-carbons render a similar effect. Though, the planarizing effect is larger when it is at the phosphorus.[77,78] Similarly, introducing a strong σ-donor group on the phosphorus has shown to minimize the degree of pyramidality. One good example is the boratabenzene group.[79]

It has to be mentioned that another option to flatten phosphole is by replacing the intracyclic CR units by one or more P atoms forming polyphospholes. However, since our focus is on monophosphole, detailed discussion can be found in several reviews.[21,80]

Till today, complete planarization of the parent phosphole **3** has not been accomplished.

The relationship between degree of aromaticity and planarity of phosphole is not in parallel. Reducing the planarity of phosphorus in phospholes does not always promise better aromaticity. As mentioned, placing a BH_2 group on the phosphorus does decrease the

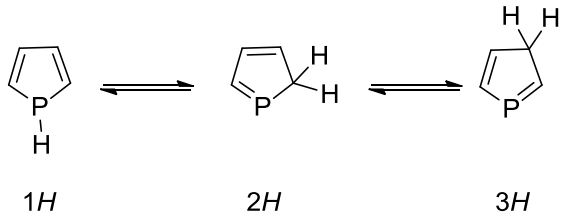
pyramidality of phospholes, but it also compromises the aromaticity.[71,77] The reason being, there is competition between the empty orbital of boron and the dienic system for the lone pair on phosphorus.[81]

Equally, Mattmann *et al.*[82] demonstrated that pyramidality is not a universal theory especially for a range of 1-substituted phospholes. The P-substituted phospholes studied are considered pyramidal (sum of bond angles between 293° and 309°) according to a previous theoretical study.[70] Yet, the 1-cyano and 1-alkoxyphospholes are able to undergo the [4+2] cycloadditions with dienophiles that is not observed with the 1-phenyl derivative. The reason behind this shift in delocalization of these phospholes examined is the hyperconjugation effect between the P-R σ bonds and the dienic system.

Summing up, the nonaromatic behaviour of monophospholes is a consequence of pyramidality of the tricoordinate phosphorus which causes the poor overlap between the lone pair of P and the dienic system. Thus, fairly planarized monophospholes can be achieved by placing bulky substituents on the phosphorus or, the addition of σ-donating and π-accepting groups. However, there is no direct connection between pyramidality and aromaticity when dealing with 1-substituted phospholes (electron withdrawing groups). To date, with the modern and refined computation studies, coupled with the less stringent criterion for aromaticity, phosphole is now considered as weakly aromatic.

1.2.2 Stability of the 1*H*, 2*H* and 3*H*- isomeric forms of phospholes and their Diels-Alder reactivity

In the midst of investigating the delocalization of phospholes in the early days, the isomeric forms of phosphole **3** have been explored to aid the understanding (Scheme 1).

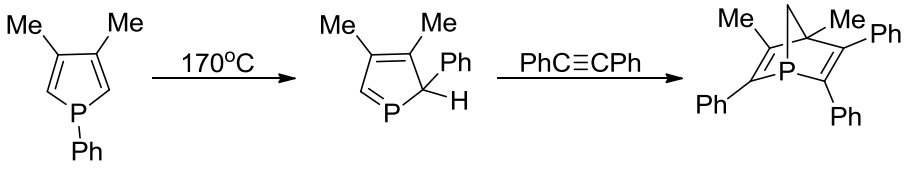


1*H* 2*H* 3*H*

Scheme 1.7 Isomers of parent phosphole **3**

It was realized then that the 2*H*-isomer of phosphole has the lowest energy among the 3 isomers and is more stable than the 1*H*-phosphole structure **3** by 6.53kcal/mol.[5,14,15,83,84]

This phenomenon has already been observed experimentally in 1981 by Mathey when he reacted 1-phenyl-3,4-dimethylphosphole **4** with tolan.[85] Contrary to the [4+2] cycloadduct (7-phosphanorbornene) obtained from the reaction of phosphole **4** with *N*-phenylmaleimide,[86] the reaction with tolan gives a totally different [4+2] cycloaddition product, i.e.1-phosphanorbornadiene **12** (Scheme 1.8).



4 **12**

Scheme 1.8 Formation of 1-phosphanorbornadiene **10**

He hypothesized that the substituent on P shifts to the adjacent carbon when subjected to high temperature, changing from the 1Ph-phosphole **4,** to the 2Ph-phosphole before undergoing the Diels-Alder reaction (Scheme 1.8).

Comprehensive studies on the mechanism of both the interconversions among the three isomers and the Diels-Alder cycloaddition have taken place recently with more reliable computational methods.

The newly computed relative stabilities of phospholes and their sigmatropic rearrangement[87] are in good agreement with reference to Bachrach et al. study in 1993.[88] Both stated that the 2*H*-phosphole is the most stable among the three isomers. It also reinforces Mathey's claim that the rearrangement happened before the [4+2] cycloaddition takes place. On top of that, it is theoretically demonstrated that the rearrangement of 1*H* to 2*H*-phospholes is irreversible which has been previously noticed by several experimental trials.[4,85,89-91]

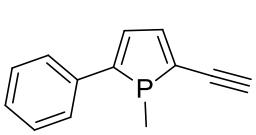
Thorough computational studies on the substituent effects on the Diels-Alder reaction, as well as the well-known Diels-Alder dimerization of phosphole oxide have been performed.[92-94] All these studies point towards exactly the product as in the experimental outcome.

To conclude, all the theoretical studies agree unanimously that the 2*H*-phosphole structure is of the lowest energy. Being the most active diene among its isomers, the Diels-Alder reaction of phosphole with dienophiles at high termperature yielded only the [4+2] adduct of the 2*H* phosphole.

1.2.3 Unsaturated α-C-substituents effect on conjugation

The poor cyclic π-conjugation of monophospholes indicates a set of polarisable diene and has very important consequences. Besides the deviation from the usual chemistry of pyrrole and thiophene mentioned,[5,15,16] it has the potential to be engineered into π-conjugated materials.

The electron excess cis-diene of phospholes has been theoretically proven that by grafting unsaturated moiety on either one of the α-carbon atoms or both of the rings, will exhibit a large extent of conjugation. Delaere's theoretical study on monophospholes clearly shows that, both the JI (closer to one) and NICS values increased (less negative) when two highly pronounced π-substituents, phenyl and ethynyl, are located respectively at the 2 and 5 positions, at the ends of butadiene unit, **13**. Thus, it can be deduce that there is a delocalization of π- electron in the carbon backbone since there is a decrease in aromaticity within the phosphole ring.[71]



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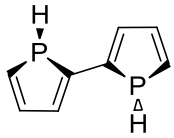

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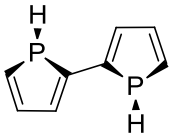
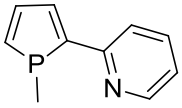


15

Nguyen and co-worker's extended the study on the influence of unsaturated substituents on phospholes to mono- (on one α-C) or di-substituted (both α-C) with pyridine or thiophene shown below.[95]



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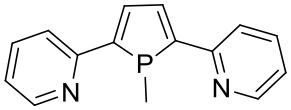

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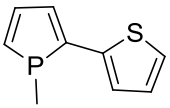

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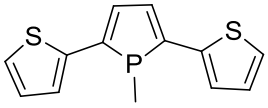

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The study illustrated that both the pyridine and thiophene lengthen the P-C bond length, and it is especially pronounced in the disubstituted phospholes, **17** and **19**. Moreover, both the JI and the NICS values increase. All this data indicates that the cyclic π-conjugation (responsible for the aromaticity of the phosphole ring) is decreased due to the competition from the heteroaryl substituents (linear π-conjugation). Electronic behaviours of the above four compounds are also examined. The energy level of HOMO is raised while the LUMO is lowered as a consequence of the extension of the π-conjugated system by the heteroaryl substituents. Red shift is observed (longer λ_{max}) as a result of the smaller HOMO-LUMO gap. Equally, oxidation by sulphur alters the geometric and electronic structures that reduce the cyclic π-conjugation within phospholes.

The existence of the first phosphole oligomer (Table 1.1) dates back to 1986 by Mathey's group[52] and it inspired Nguyen's group to conduct a computational study to provide insight of the parent phosphole oligomers.[96] Similarly, the geometries, influence on the aromaticity, and energy gaps of orbitals are studied. Calculations are confined to fully optimized structures and two isomers of the phosphole oligomers are considered. **14**, is the one with alternating hydrogens and the other with hydrogens pointing in same direction, **15**. It is realised that oligomers **14** are nearly coplanar but the other form are weakly distorted. This minor distortion does not significantly influence the delocalization of the π-electron along the conjugated bonds. However, large rotational disorder of about 90° would. Secondly, they found that by flattening the phosphole units raised the HOMO and LUMO orbital energy. Also, it lengthens the interring bond distance, $d_{C\alpha}$ between the inner rings of phosphole. This means linear π-conjugation becomes less significant. However, as the chain length increased, the HOMO energy rises and the LUMO energy lowers, regardless whether the phospholes used are aromatic or not, which is in line with other theoretical studies.[97-99]

To elucidate the structure-property relationships when substituting unsaturated moiety on the α-C of phospholes, three different systems have been investigated. On monophospholes, the grafting of unsaturated moiety on the 2,5-positions of phosphole extended the linear π-conjugations. This observation also applies when heteroaryl moieties are used. Furthermore, the electronic property is dramatically altered when the reactive P centre is oxidised by sulphur. While in the case of phosphole oligomers, it agrees with the other two studies that planarizing

the phosphole units will enhance the interaction of the phosphorus lone-pair and the endocyclic diene units. Also, significant linear π-conjugation is observed when the substituents are coplanar to dienic system on phosphole. In a nut shell, the extent of external conjugation weakens when endocyclic delocalization within phosphole increases.

1.3 Applications of Phospholes

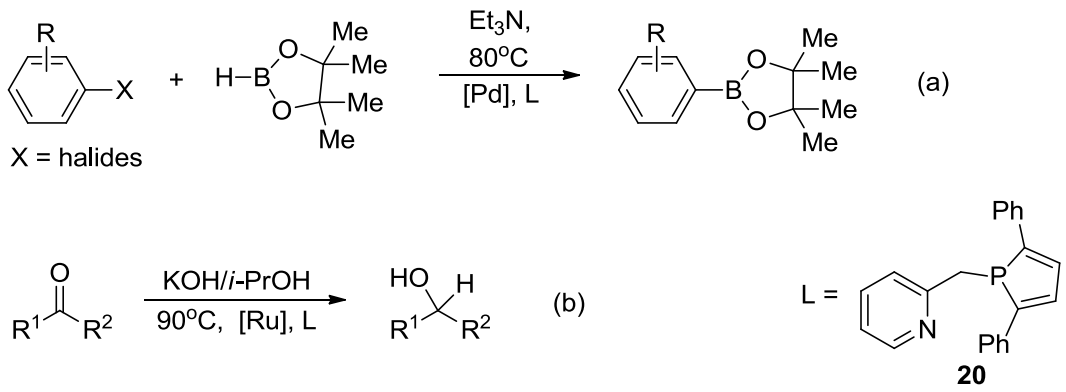
The drive to discover practical applications of monophospholes has not ceased, in fact it heightened recently due to the countless positive results obtained. Besides the ability to act as ligand in various metal catalysed organic reactions, new applications in the electrooptical and biological fields are also discovered.

1.3.1 Phospholes as ligands in homogeneous catalysis

The earliest and thoroughly explored application of trivalent monophospholes is the ability to act as ligand in coordination chemistry. Phospholes possess various bonding types; bonds formation through the lone pair on P, the diene system or the derived aromatic phospholide ions.[5,14,17,84] To date, phospholes which are well known to behave as classical two-electron donor tertiary phosphines, have complexed with numerous metals ranging from transition to group III and IV metals. A comprehensive list of these complexes has been summarised in Quin's paper.[19]

Generally, monophosphole ligands are π-acceptors and labile. One such common phosphole ligand is 3,4-dimethyl-1-phenylphosphole. However, recent demand for more complex phospholes with some functional groups has increased. This can be achieved by varying substituents at the P- and C-atoms of the phospholes rings.

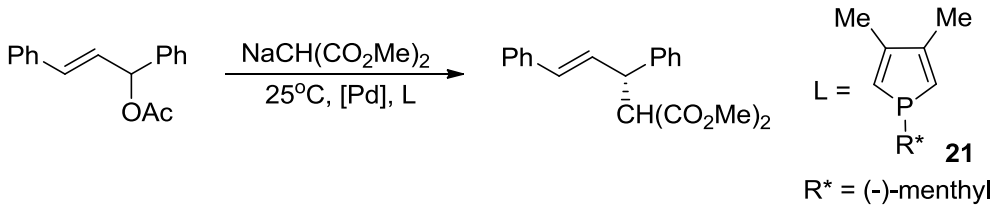
A variety of functionalized phospholes were synthesized and used to create catalysts which are successful in various organic reactions. A representative P-N-chelate **20**, exhibit excellent activity in the Suzuki-Miyaura cross-coupling when complexed with Pd (Scheme 1.9a).[100] With only 0.001 mol% of catalyst loading, the reaction of aryl halides with pinacolborane completed within 48h at 80°C with 100% yield.



Scheme 1.9 (a) Suzuki-Miyaura cross coupling and (b) Transfer hydrogen of ketones with ligand **20**

The ruthenium complex of this P,N-chelating ligand was also able to catalyze the transfer hydrogenation of various ketones (Scheme 1.9b). The activity was so high that the number of catalytic cycles can go up to 1×10^6 depending on the ketones used.[101]

Also, popularity of phosphole complexes is growing in the area of asymmetric catalysis. Reason being the striking good activity and selectivity obtained. Such as the asymmetry allylic alkylation using simple chiral monophospholes **21** as ligand afforded *ee* as high as 89% (Scheme 1.10).[22]



Scheme 1.10 Asymmetric allylic alkylation using chiral ligand **21**

The three examples shown above are just the few catalysis reactions which phospholes have taken part in. There are still a myriad of positive results achieved in various other catalysis reactions such as Heck reaction, hydroformylation, hydrogenation, etc. All of the recent catalysis reactions involving phospholes have been summarized comprehensively in reviews.[19,21]

1.3.2 Phospholes based electro-optical materials

The first phospholes which exhibit extended π-conjugation were prepared in the early 1960s, whereas the first α,α'-oligo(phosphole)s is discovered in the late 80s. Yet, the presence of the extended linear π-conjugation in these phospholes and its derivatives were not considered at that time. This may be due to the poor understanding of the behaviour of phospholes. Today, however, the chemistry of phospholes has reached a matured state, together with the advance in technology, and it becomes possible to incoporate phospholes into useful π-conjugated materials.

Characteristics of electro-optical substances consist of extended double bond conjugation; electronic absorption and emission are at relatively long wavelength due to the low HOMO-LUMO energy gap. From the theoretical standpoint, phospholes fit the bill as the geometric and electronic features allow extended linear π-conjugation. Secondly, the reactive phosphorus centres allow the fine tuning of the optical and electrochemical properties by chemical modifications.[71,95,98,102]

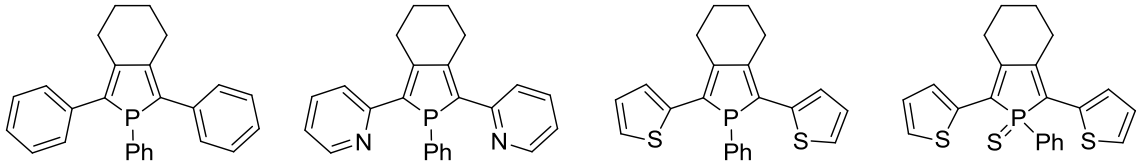
Practically, there are already many examples of monophosphole derivatives being developed as electro-optical substances, in particular, photovoltaic cells, thin-film transistors and light-emitting diodes (LED).[103-106]

Comprehensive and systematic investigation of phosphole-based π-conjugated systems which are suitable for OLED applications and conductive polymers was first proposed by Réau's group. Their studies focus on 2,5-di(heteroaryl)phospholes. Other than looking into the effect of substituents on the structure-property relationships, the thermal stability and the ease of handling were also studied.

Within the series of 2,5-di(heteroaryl)phospholes synthesized, substituents effects on the absorption and emission maximum were investigated. Also, the electrochemical properties were examined when chemical modifications (sulphurization, quaternization, and complexation to metals) are performed on the reactive P-centre.[107,108] Collectively, the metric data show the presence of an extended delocalization of the π-system along the heterocycles. Furthermore, absorption maximum was observed in the visible region and a red shift in λ_{max} was recorded

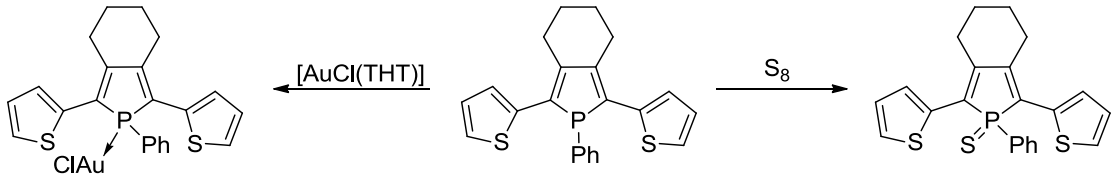
when the 2,5-substituents were varied or when the trivalent P-atom becomes tervalent. All these results are in good agreement with the theoretical calculations.[95,105]

Amazingly, supramolecular structures can be build when the σ^3-P are coordinated to transition metals.[109]



22a (354nm) **22b** (390nm) **22c** (412nm) **22d** (432nm)

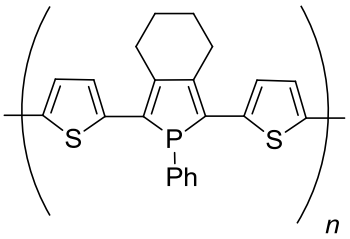
The chemical modifications on the nucleophilic P-centre also enhanced the thermal stability of the phospholes such that it can be used to develop into OLED materials. The heat sensitive trivalent phosphole **15c** (decomposes under high temperature) cannot be deposed by sublimation (preparation of single-layer OLED). In contrast, the thioxo-derivative, **22d** and phosphole gold(I) complex **22e**, were thermally stable to give homogeneous thin films upon sublimation. The gold(I) derivative **22e** gives encouraging results for developing white-emitting OLED as it exhibit an electroluminescence (EL) emission ranging from the 480-800nm domain.[110,111]



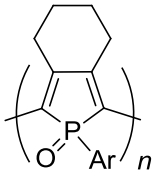
22e **22c** **22d**

Another valuable property of the extended conjugation phosphole-based system is that they can be electrochemically oxidized, creating conjugated cation radicals that polymerize on the electrode to give π-conjugated polymers. The absorption maximum of such polymers appears to be in the range of 550-600nm and show potential as conductive polymers.[103,105,106,112-114] In 2010, Matano has successfully synthesized α,α'-linked polyphophole **24** by using Stille-type coupling.[115] This phosphole polymer has a UV-absorption at λ_{max} = 655nm (109nm longer than λ_{max} of polythiophene **25**)[116,117], an especially long wavelength which implies

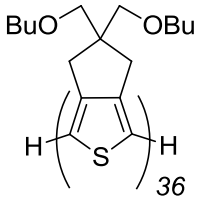
a strikingly narrow band gap. Evidently, this polyphosphole also showed high electron-accepting ability.



23 (550nm)



24 (655nm)



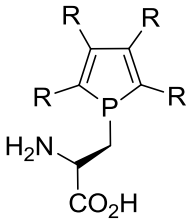
25 (546nm)

In addition, phospholes and its derivatives have shown to be suitable materials for non-linear optics (NLO). There were a few examples which demonstrate excellent NLO properties.[118,119]

Collectively, the easily polarized diene in phosphole allows the creation of extended π-conjugated system. Simultaneously, the reactive P atom allows chemical modifications which cause a profound impact on the optical and electrochemical properties of phospholes and its derivatives. These two unique properties are lacking in the aromatic thiophene and pyrrole. Thus, phosphole chemistry opens a gateway to novel P-based molecular materials[120] which might prove to be of better performance than polythiophene and polypyrrole.

1.3.3 Biological applications of phospholes

Phospholes and their derivatives have entered the field of biology and medicine recently. Again, the weak aromaticity and the nucleophilic properties of the P atom in monophospholes are the main attraction. There is considerable interest in utilising monophospholes and its metal complexes as inhibitor for disulphide reductases[121,122] or as antitumor drugs.[123,124] Also, polypeptides that incorporate phospholes are also gaining attention in scientific applications. Thus, phosphole-substituted alanines **26**, tyrosines and phenylalanines **27**, have been prepared.[125,126]



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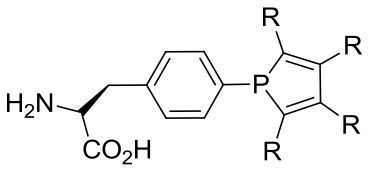

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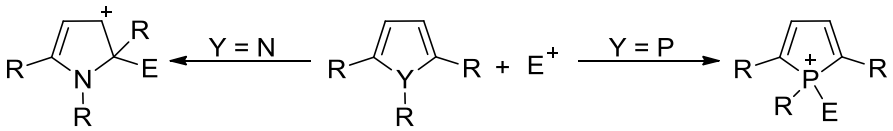
Preliminary results demonstrate the possibility of developing effective phosphole-based metallodrugs. Thus, efforts are geared towards this direction. While doing so, monophospholes also have been incorporated in proteins synthesis.

1.4 Functionalization of Monophospholes

Till this point, we have learnt that phospholes are usually made from synthetic routes that are different from making other aromatic 5-membered heterocycles. Secondly, the weak aromaticity of phospholes that is attributed to the hyperconjugation of the exocyclic P-R σ-bond with the π-system of the diene causes a huge deviation from the chemistry of thiophene and pyrroles. A good example is when electrophile is added to phospholes. One would expect the electrophile to be added to the carbon adjacent to the heteroatom as seen in pyrrole chemistry. Experimentally, the electrophile was added to the P-atom instead (Scheme 1.11). Furthermore, there has been a significant increase in demand of complex phospholes for various practical applications. Therefore, the following sections discuss the functionalization methods of the α-carbon(s) of phospholes that are not extrapolated from the N-and S-analogues.



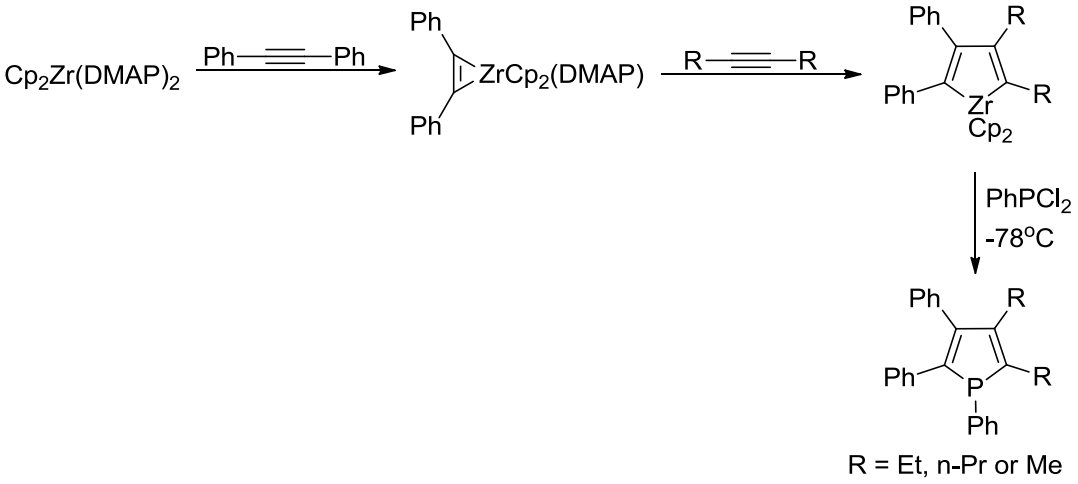
Scheme 1.11 Reactivity of pyrrole and phosphole towards electrophile

1.4.1 Fagan-Nugent method

This method was first introduced in 1988[35] and has proven to be relatively versatile method in phosphole synthesis that is still in use today. It allows novel substituents (silyl, 2-pyridyl, 2-thienyl) to be installed during the building of the ring. As mentioned (Section 1.1.3),

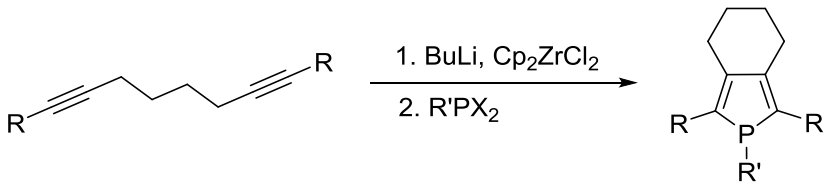
this method involves the formation of zirconacyclopentadiene from bimolecular coupling of an alkyne (bearing the desired C-substituents) with a zirconium-cyclopentadiene complex. Then reacting with PX_3 or RPX_2 (X = halides, R = aryl or alkyl) affords the desired phosphole.

Other than the usual symmetrical phospholes synthesized, asymmetrical phospholes have also been described[127] using similar concept but with an alternative route.[128] This method forms a zirconacyclopropene by reacting $Cp_2Zr(DMAP)_2$ complex with one equivalent of alkyne. Subsequently, it is coupled with a different alkyne to give the asymmetrical zirconacyclopentadiene (Scheme 1.12).



Scheme 1.12 Formation of zirconacyclopentadiene from zirconacyclopropene

Numerous phosphole-based electro-optical materials were synthesized using Fagan-Nugent method, including the formation of phosphole oligomers containing five[129] and seven[106] conjugated rings. All these materials were synthesized by the reaction of a diyne bearing the desired substituents (heteroaryl substituents) with zirconium-cyclopentadiene complex (Scheme 1.13).[103,105,130]



Scheme 1.13 Formation of 2,5-(heteroaryl)phospholes

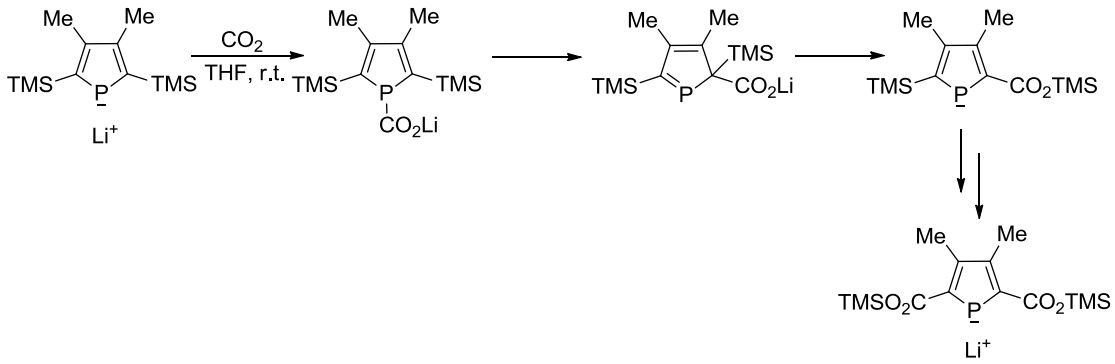
Matano and co-workers managed to replace the usual zirconium reagent by a low-valent titanium reagent called the Sato-Urabe reagent. This reagent can be generated *in situ* from Ti(O*i*-Pr)$_4$ and *i*-PrMgCl. Similar to the chemistry of zirconacyclopentadienes, a titanacyclopentadienes will be formed. Subsequent reaction with $PhPCl_2$ at low temperature will generate the desired phospholes. The discovery of this methodology is remarkable as it allowed functional groups such as ester to be grafted other than aryl substituents.[104]

The versatility of this old method has advanced the phosphole chemistry with excellent results which makes it viable for functionalizing phospholes till today.

1.4.2 [1,5]-Sigmatropic rearrangement

[1,5]-sigmatropic shift was reported in 1981[85] and it can be applied to the synthesis of α-functionalized phospholes. It has been shown that various substituents (even ferrocenyl substituents) on P can be induced to rearrange to one of the α-positions of the ring in the presence of a base under mild conditions.[131-136]

Phosphole-2,5-dicarboxylic acid has been synthesized presumably by a twofold [1,5]-sigmatropic rearrangement.[137] However, the double rearrangement is made possible due to the presence of the trimethylsilyl groups at the 2,5-positions on the phospholide. Generation of a new phospholide after one of the silyl group migrates to the carboxylate ions formed, makes a second rearrangement feasible (Scheme 1.14).



Scheme 1.14 Twofold of [1,5]-sigmatropic shift

As we can see, this technique allows a variety of substituents to be put onto the α-carbon in phospholes.

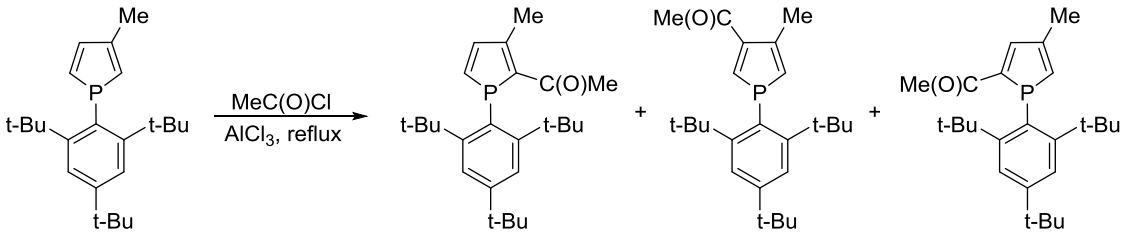
1.4.3 Classical Frieldel-Crafts reaction

The failure to replace hydrogen on the phosphole ring by electrophilic species is a result of the weak aromaticity and the presence of the nucleophilic lone pair on the P atom of phosphole. In order to perform classical Frieldel-Crafts reaction on phospholes either one of the following requirements has to be met. It is either by protecting the nucleophilic P-atom with Mo or grafting bulky substituents on trivalent P.

Complexation of phosphole with a low valent metals such as $M(CO)_5$ will eliminate the occurrence of electrophilic attack on the nucleophilic P. Thus, C-acetylation by Friedel-Crafts on this phosphole-$M(CO)_5$ complex can be performed.[138]

Aforementioned (Section 1.2.1), placing a bulky moiety on the P-atom such as 2,4,6-tri-*t*-butylphenyl can reduce the pyramidality of the P-atom. Thus, aromaticity will be improved and electrophilic substitution can be performed.

The few studies have shown the feasibility of such reaction conditions. 2-acetylphosphole derivatives are obtained as the main product which is consistent with the orientation on acetylation of 3-methylpyrrole. Two other side products, 4-acetyl and the 5-acetyl derivatives are also obtained (Scheme 1.15).[76]



Scheme 1.15 Friedel-Crafts acetylation on phosphole with bulky P-substituent

Acylation (propionyl and butyryl chlorides) with similar phosphole yielded the desired 2-acyl derivatives along with one other side product. However, reaction of benzoyl chloride with the phosphole did not take place.[139]

Overall, electrophilic substitution can be performed to functionalize phospholes as long as the lone pair on P is protected by $Mo(CO)_5$ or increasing the aromaticity character by having

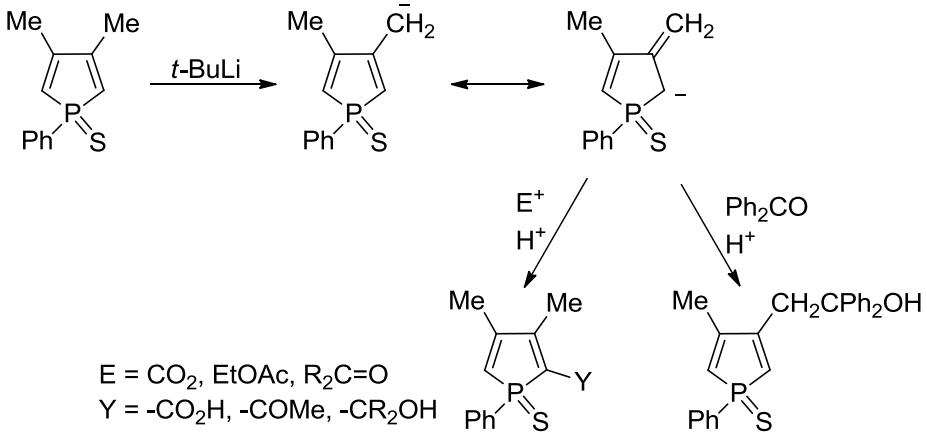
bulky P-substituent. However, it lacks generality as only certain substrates can be used and the yield of desired product is low.

1.4.4 Deprotonation from the ring methyl group of phosphole sulfide or phosphole-borane

Both phosphole sulfide and phosphole-borane are easily accessible. The former is prepared by adding elemental sulphur to phosphole, while the latter is generated by reaction of phosphole with borane dimethylsulfide. Similarity between these two compounds is the formation of a delocalised allylic anion by abstraction of a methyl proton with strong base. This then allows a few 2-functionalized phospholes to be synthesized.

In the case of phosphole sulphide, deprotonation by a strong base, *t*-butyllithium, from the methyl group is possible. Consequently, the allylic anion formed is resonance-delocalized. Addition of an electrophile will then be picked up either by the exocyclic carbon (undesired) or at the endocylic α-carbon (Scheme 1.16).[140,141]

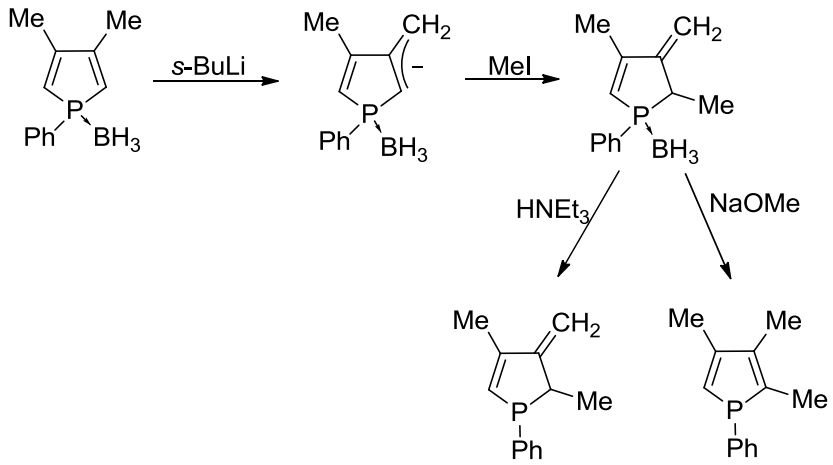
It has been shown that Ph_2PCl also reacted on the 2-position of the ring which is the important site.[142] Reduction of the P=S bond then gives the functionalized phospholes.



Scheme 1.16 Functionalization of phosphole sulphide

Likewise, resonance delocalized allylic anion is formed when phosphole-borane is reacted with a strong base, *sec*-butyllithium. Ideally, the electrophilic attack is more regioselective than phosphole sulfide; most of the electrophiles are added onto the carbon

adjacent to phosphorus except carbonyl substrates. However, 2-functionalized phospholes are only obtained when a stronger base like NaOMe is used for the decomplexation (Scheme 1.17).



Scheme 1.17 Functionalization of phosphole-borane

Although phosphole sulfide and phosphole-borane can be easily prepared, the low to moderate yield and limited functional groups which can be attached, render this method far from being general.

1.4.5 Lithiation of 2-bromophospholes

This is considered the most general and versatile route to 2-functionalized phospholes. 2-bromophospholes can be obtained through a sequence of chemical reactions from 1-phenyl-3,4-dimethylphosphole **4**. Then, lithiation with *n*-butyllithium via halogen exchange, giving the 2-lithiophospholes cleanly.[143] On top of that, the usual initial attack of alkyllithium at the phosphorus is avoided in this situation.[48,144,145]

The reactive 2-lithiophosphole generated *in situ* has to be kept at -100°C. Followed by the reaction with electrophiles, a series of 2-functionalized phospholes can be synthesized[143,146] including a 2,2'-bisphposphole with 75% yield (Scheme 1.18).

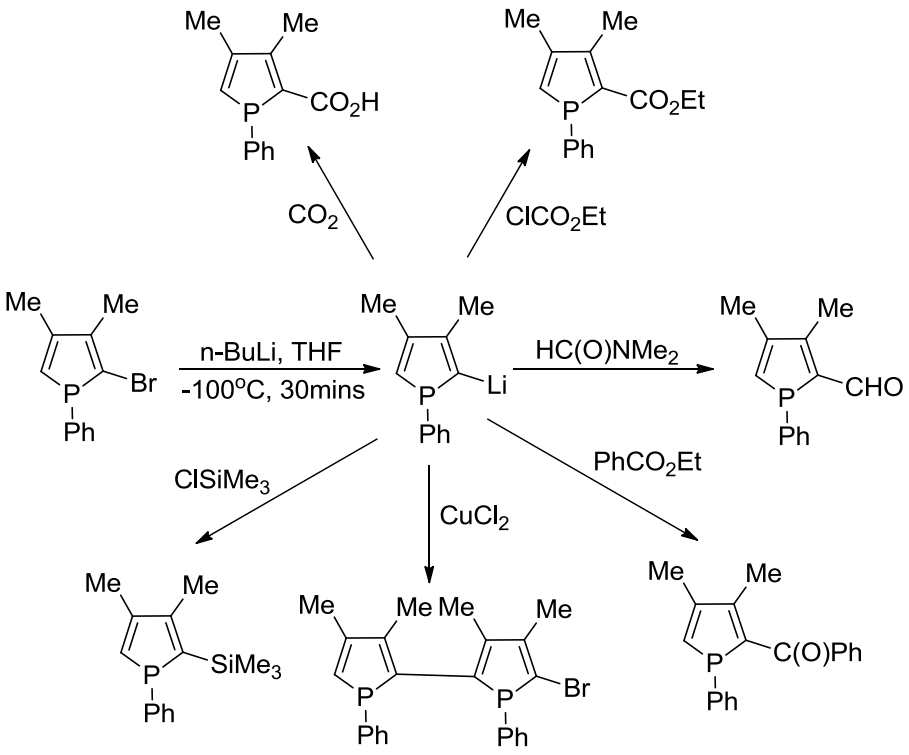
The success of this chemistry leads to the synthesis of 2,5-dibromophospholes.[147] When subject to mild condition (-90°C), even with an excess of buthyllithium, only one exchange of bromine atom is observed. Subsequently, this 5-bromo-2-lithiophosphole reacted just like the

2-lithiophosphole derivatives, producing a range of 5-bromophospholes functionalized in the 2-position. Successfully, an α-linked quaterphosphole was synthesized.

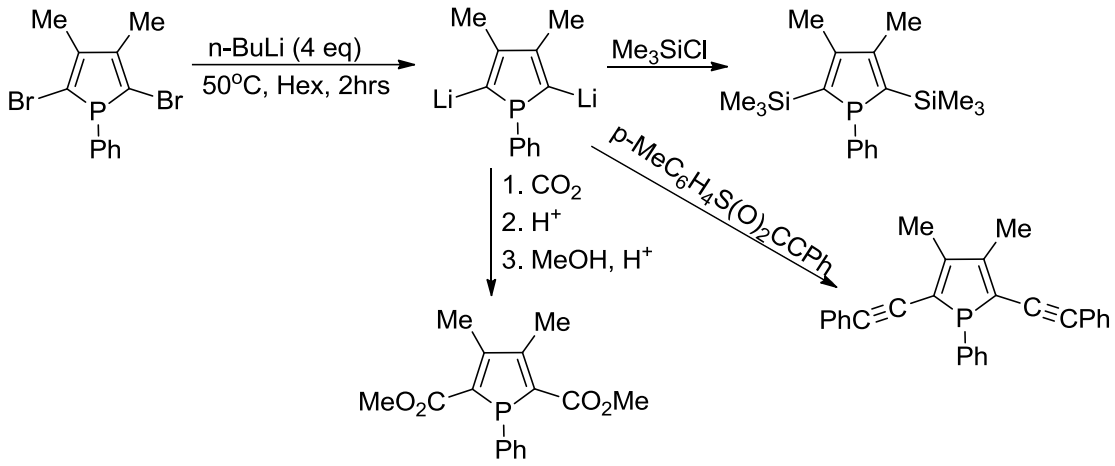
After a few years, Deschamp managed to achieve a double lithiation on 2,5-dibromophospholes, successfully obtaining the 2,5-dilithiophospholes. From there, 2,5-acetylenic, silyl and dicarboxylate functionalized phospholes are obtained with excellent yield (Scheme 1.19).

Coe *et al*. has also been studying the optimization of the chemistry of 2,5-dibromophospholes succeeded in preparing a vinylene-bridged phosphole dimer by McMurry coupling. Similarly, they also managed to obtain a 2-vinylphosphole derivative in the same work.[148]

2,5-dihalophospholes has also applied into Sonogashira coupling with terminal alkynes for the synthesis of 2-alkynylphospholes. However, this method is less efficient as compared to the nucleophilic substitution (S_N2) type of reaction between 2-lithiophospholes with alkynyl sulfinates because of the low yield.[149]



Scheme 1.18 Series of 2-functionalized phospholes synthesized from 2-lithiophosphole



Scheme 1.19 2,5-di(functionalized) phospholes from 2,5-dibromophosphole

In conclusion, 2-bromophosphole suffers slightly due to the low accessibility. However, this slight disadvantage is outweighed by the wide variety of functionalized phospholes produced with excellent yield. Furthermore, this valuable chemistry is extended to 2,5-dibromophospholes which expanded the collection of α-functionalized phospholes. Thus, it proved to be a versatile starting point for functionalizing phospholes.

1.5 Conclusion

Having summarised the literature thus far, we can draw the following conclusions. Monophosphole is generally nonplanar since it contains a rigid pyramidal tricoordinated phosphorus atom. This prevents strong endocyclic π-conjugation between the lone pair on P atom and the cis-1,3-butadiene unit which explains its poor aromaticity. The delocalization within the phosphole ring arises from the hyperconjugation of the exocyclic P-R σ-bond and the π-system of the dienic system. Consequently, phosphole contains a highly polarizable diene and a reactive lone pair on P-atom.

Structure-property relationships have been studied more intensively to better understand the behaviours of phospholes. These studies aided scientists in solving the unusual chemistry observed with phospholes. Also, it benefits the design of more functional phospholes for practical usage.

Recently, the maturity and deeper understanding of phosphole chemistry prompted the development of novel and effective phosphole-based catalysts, electro-optical materials and

metallodrugs. Hence, from both theoretical and practical standpoints, monophospholes offer much richer chemistry that cannot be extrapolated from its S, N, O counterparts.

1.6 Motivation

As we have seen, though there are a great variety of π-conjugated phospholes being synthesized, all of them focus on their electro-optical property. Till now, none has look into how this extended π-conjugation will affect the chemistry of phosphole. This is apparently because of the lack of a convenient technique for introducing a simple vinyl substituents at the α-position of the phosphole ring.

On the other hand, the chemistry of furans, thiophenes and pyrroles has been extensively examined. Modifications on these rings are easily realized with their good aromaticity. Their aromaticity has also been tempered by grafting different substituents on it.

One of the prized substituents that has been attached to the 5-membered heteroarenes is vinyl. The vinyl group has shown the ability to induce an extended conjugation with the aromatic ring, thus, creating two different reaction sites for Diels-Alder cycloaddition. This point will be discussed in Chapter 2.

Another recent development on these heteroarenes that involves vinylic π-orbitals is Fischer carbenes.[150-160] These aromatic 5-membered rings decorated with Fischer carbenes have attracted attention with their unique electronic properties. Before this, investigations on their chemical behaviour have brought about useful synthesis of many natural products. This will be reviewed later in Chapter 3.

Obviously, phospholes being a member in the family of 5-membered heteroarenes has been neglected. Hence, this has spurred the focus of this thesis. After evaluating the available pathways to functionalize α-C, we endeavour to establish an access to monophospholes with a vinylic π-orbital on the α-position via the direct and versatile 2-lithiophosphole. Then, the effect of the vinylic substituents on the polarisable diene of phosphole will be examined by various chemical reactions.

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CHAPTER 2

Synthesis and Chemistry of 2-Vinylphospholes

2.1 Introduction

The surpisingly robust monophosphole rings have two unique properties, intact reactivity of pyramidal phosphorus atom and the highly polarisable *cis*-1,3-butadiene unit. In contrast to pyrroles, thiophenes and furans, the nucleophilic P atom in phospholes easily undergoes oxidation, sulfurization, quaternization reactions and forms complexes with transition metals. Whereas the dienic system also reacts in many cyclopentadiene-like cycloadditions and it is known to produce a series of organophosphorus compounds.

Versatility of phospholes has thus opened new prospects for their applications. Recently, one area that is receiving major attention is the development of monophosphole derivatives as electro-optical materials. As we have seen (Section 1.3.2), it is the two unique properties that have set phospholes valuable in this area.

Thus, a series of π-conjugated phospholes, including 2-alkenylphospholes and the more recent 2-phosphaalkene-substituted phosphole[1] were synthesized. Yet, none has examined the modification on phosphole rings in the presence of such substituents other than their application as chromophores. The apparent reason being the lack of a general technique for introducing a simple vinyl moiety on the α-position of the ring.

In contrast, the chemistry of thiophenes, pyrroles and furans are more extensively studied. In spite of their aromaticity, which would be expected to reduce the diene reactivity, they have actually shown to undergo Diels-Alder reactions. The incorporation of vinyl moiety at the α-positions of these 5-membered heteroarenes has long been considered as well. Such as the synthesis of indoles can be acheived via the treatment of 2-vinylpyrroles derivatives with dienophiles. While a few pericyclic compounds are results of vinylfurans effectively function as diene component in intramolecular Diels-Alder reactions.[2-7]

Clearly, being part of the heteroarenes family, phospholes have been missed out in this particular area of study. On this basis, we set out to synthesize 2-vinylphosphole **50**. And,

judging from the theoretical and practical standpoints of the available π-conjugated phospholes, we would expect a significant conjugation between the vinyl group and the diene. Furthermore, the presence of the vinyl substituent might offer an alternative pathway for cyclo-addition reactions. Hence, the chemistry of the phosphole ring might be perturbed.

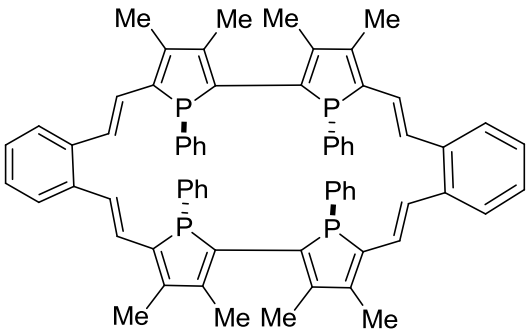
2.2 Reviews of Reactions of the Dienic System of σ^3- and σ^4-monophospholes

Before we move on to examine the chemistry of 2-vinylphosphole **50**, it is essential to review the existing α-vinylic phosphole derivatives and the typical reactions surrounding phosphole's dienic system. This review seeks to examine whether the presence of the vinyl substituent on phospholes would cause a deviation from the usual reaction on the diene unit.

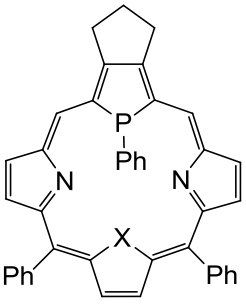
2.2.1 α-Functionalized monophopholes with vinylic π-orbitals

The library of 2,5-diarylphospholes has expanded when their application in the field of electro-optical materials was realized. As we have seen, most of these newly synthesized π-conjugated phospholes are classifiable to Fagan-Nugent method (Section 1.3.2 and 1.4.1).

In comparison, the number of alkenyl-substituted phospholes is countable. These few examples are prepared by introducing the vinyl-substituents on the preformed phosphole ring by a sequence of chemical reactions. Frequently, the starting point is the lithiation of 2-bromo- or 2,5-dibromo-phospholes (Section 1.4.5).



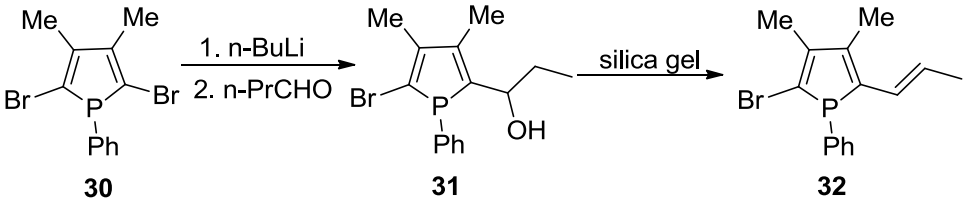
28



29a X = S
29b X = NH

The first example of vinylphopholes was prepared by Mathey *et al.* in 1995, a macrocylic vinylene-bridged tetraphosphole **28**.[8] Following this, phosphorus analogue of porphyrins **29a,b** were successfully synthesized.[9,10]

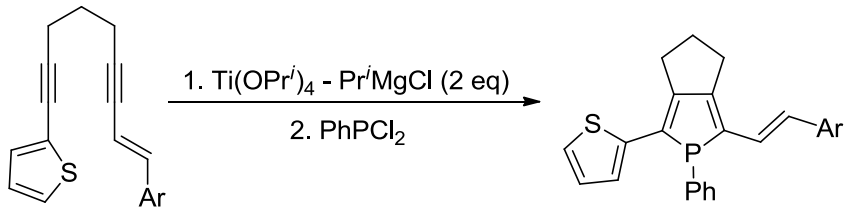
A simple monophosphole with an α-vinyl substituent **32** was obtained by Coe's group from the unexpected dehydration of **31** (Scheme 2.1) in silica. In the same work, a vinylene-bridged phosphole dimer was prepared as well.[11]



30 **31** **32**

Scheme 2.1 Synthesis of 2-(1-propenyl)phosphole **32**

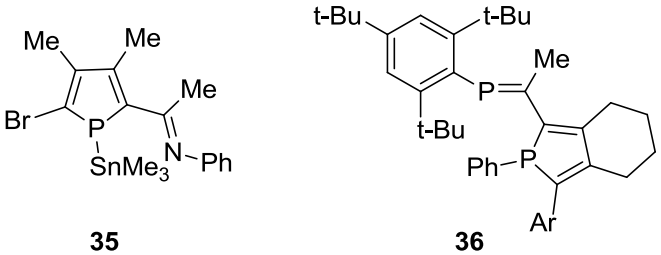
Lately, an easier and convenient method for the production 2-alkenylphospholes has been established by Matano. This technique which was described (Section 1.1.3), made use of the Sato-Urabe reagent with diynes **33** bearing a styryl moiety at the terminal carbons (Scheme 2.2).[12] Subsequently, treatment with $PhPCl_2$ afforded the phosphole **34**.



33 **34**

Scheme 2.2 Synthesis of 2-aryl-5-styrylphospholes

Although the context in this section emphasize on the vinyl substituents, it is also worth pointing out the existence of hetero-vinylic substituents on phospholes. Namely, an imine functionalized phosphole complex **35**[13] and a phosphaalkene-substituted phosphole **36**.[1]

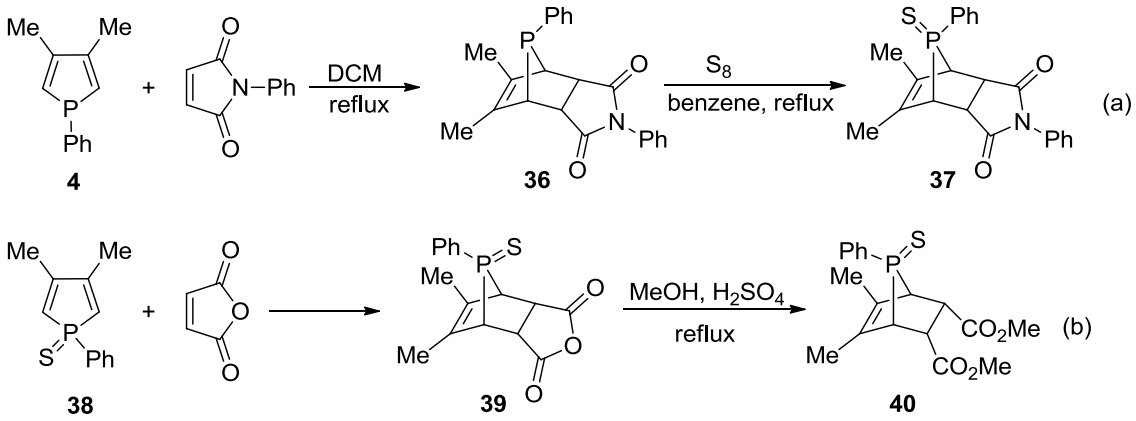


35 **36**

Clearly, the number of examples of 2-vinylphospholes is limited. Within all these available phospholes, most studies attend to the synthesis technique, physical data or the applications. None of them has examined the effect of the vinyl substituents on the chemistry of the diene in the phosphole ring.

2.2.2 Cycloaddition reactions at the diene of σ^3- and σ^4-phospholes

Monophospholes possess a dienic system that is generally weakly reactive despite the relative poor cyclic delocalization. This weak cyclic conjugation decreases the availability of the π-electrons.[14,15] This explains why cycloadditions of σ^3-phospholes are kind of rare. Mathey was the first to demonstrate such phenomenon when 3,4-dimethyl-1-phenylphosphole **4** was reacted with N-phenylmaleimide (NPM).[16] It yielded the [4+2]-cycloaddition product, 7-phosphanorbornene **36** (Scheme 2.3a).

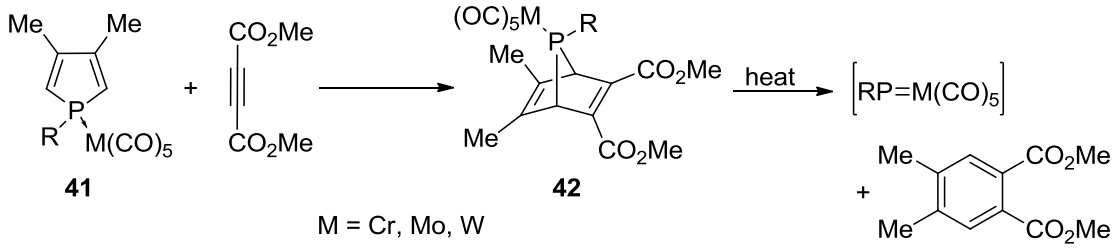


Scheme 2.3 [4+2]-cycloaddition of σ^3- and σ^4-phospholes

On the other hand, σ^4-phospholes (oxides, sulfides or W, Mo metal complexes) readily undergo [4+2]-cycloadditions such as Diels-Alder reactions with dienophiles. Most phosphole oxides are so reactive such that they dimerise spontaneously. This is due to the increased reactivity of the diene as the endocyclic conjugation weakens.

A surprising observation was made from the reaction above. When σ^3-phospholes were used in the cycloaddition, followed by sulfurization, the stereochemistry at P of the product was *anti* (Scheme 2.3a). However, if the phosphole was sulfurized before the cycloaddition, the cycloadduct bears the *syn* stereochemistry (Scheme 2.3b). This pattern has also been observed with another phosphole derivative.[17,18]

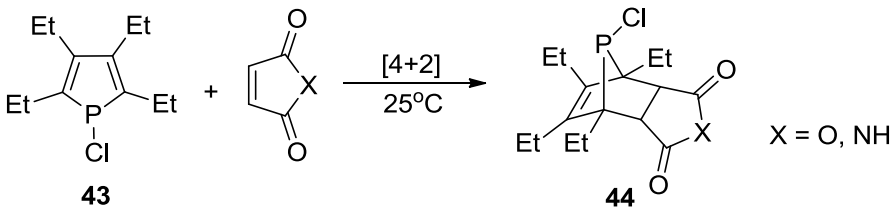
Besides the Diels-Alder reaction between phospholes and maleic anhydride, N-phenyl-, N-methylmaleimide and alkenes, this chemistry has also extended to alkynes. The cycloadduct **42** (7-phosphanorbornadiene) formed from the reaction between phosphole metal complexes (metal such as Mo, Cr and W) with alkyne (dimethyl acetylenedicarboxylate), generates a phthalate and a transient terminal phosphinidene complex [RP=M(CO)$_5$] upong high heating. This chemistry has been studied thoroughly with many different substituents on P (alkyl, cyano, chloro, *etc*). Reason being, these adducts serve as efficient precursor for transient terminal phosphinidene complexes which have further expanded the organophosphorus chemistry and are described in depth in many reviews.[14,19-23]



Scheme 2.4 Diels-Alder reaction of phosphole complexes with DMAD

As we have seen, it is difficult for σ^3-phospholes (with P-alkyl or P-aryl substituents) to take part in [4+2]-cycloaddition. Thus, from the understanding of theorectical study,[24] placement of appropriate groups on the phosphorus in phospholes greatly improve their reactivity to dienophiles. The suitable substituents are electron-withdrawing groups such as cyano-, alkoxy- or halo- because they reduced the aromaticity in the phosphole rings.[25] Thus, the failure for Diels-Alder to take place between σ^3-phosphole **4** with acrylonitrile at high temperature has been circumvented under mild condition. One very good example is the [4+2] reaction of 1-chlorophospholes **43** with maleic acid derivatives at room temperature in good yields (Scheme 2.5).[26]

Similarly, the presence of electron-withdrawing substituents at the P atom significantly speeds up the intramolecular cycloaddition at mild temperature. Previously, in the absence of these substituents, a harsher reaction condition was required.[27,28]



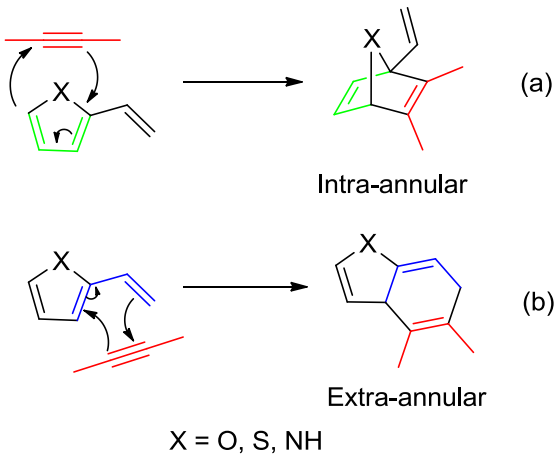
Scheme 2.5 [4+2]-cycloaddition of 1-chlorophospholes with maleic acid derivatives

Rarely, phospholes will act as dienophiles in Diels-Alder reaction. In fact, past examples of phospholes taking the role as dienophiles only involved σ^4-phospholes (oxidised or sulfurized phospholes).[14] Whereas, a [2+2]-cycloaddition of **4** with an alkene under UV irradiation has been discovered recently.[29] Other less known cycloadditions involving phospholes, such as [2+3]- and [4+3]-cycloadditions, have been described as well.[14,30]

Definitely, there are other types of reactions that have taken place on the diene of phospholes other than cycloaddition reactions. Some of them have been reviewed in section 1.4. Others include the reductive dimerization of phospholes induced by $NiCl_2$, ring opening and ring expansion reactions which all have been comprehensively summarised in many references.[20,21]

2.3 [4+2] Cycloadditions of 2-Vinyl Substituted 5-Membered Heterarenes

The presence of the vinyl group on furan, pyrroles or thiophenes, provides another site for the Diels-Alder to take place. Whilst cycloaddition across the endocyclic 4π-system of the heteroarenes (intra-annular) is still possible (Scheme 2.6a), the exocyclic vinyl group and the endo π-system of the heteroaryl rings can also act as a 4π diene in the Diels-Alder reaction, giving rise to the extra-annular cycloaddition (Scheme 2.6b). As a results, it expanded the access to natural products and several novel heterocycles.[31,32]

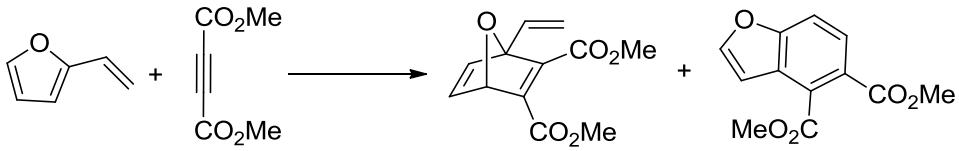


Scheme 2.6 Intra- and extra-annular cycloaddition of 5-membered α-vinylheteroarenes

A closer look at how these 2-vinylheteroarenes will react with DMAD and maleic acid derivatives is required as it allows us to understand which pathway would be preferred.

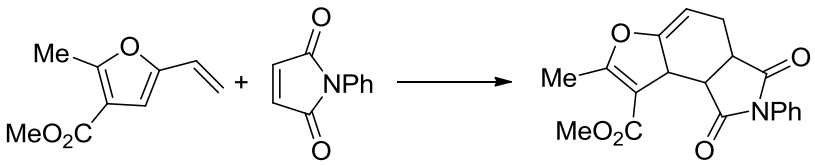
2.3.1 Diels-Alder reactions of 2-vinylfuran derivatives

In 1968, Davidson reported the cycloaddition of 2-vinylfuran with dimethyl acetylenedicarboxylate (DMAD).[33] It was observed that the cycloadducts from both pathways, intra- and extra-annular, were obtained (Scheme 2.7).[34] Recently, Ghobsi has shown the cycloaddition between DMAD and a 2-vinylfuran derivative took place exclusively at the exo-endo diene (extra-annular).[35]



Scheme 2.7 Diels-Alder reaction of 2-vinylfuran with DMAD

Interestingly, the reaction outcome between 2-vinylfuran derivatives and maleic aicd derivatives seems to favour the extra-annular route. In the case of 2-vinylfuran with maleic anhydride, Paul observed the cycloadduct was afforded via the extra-annular Diels-Alder reaction.[36] The experiments conducted by Drew also revealed such trend with N-phenylmaleimide and vinylfuran derivative **45** (Scheme 2.8).[37]



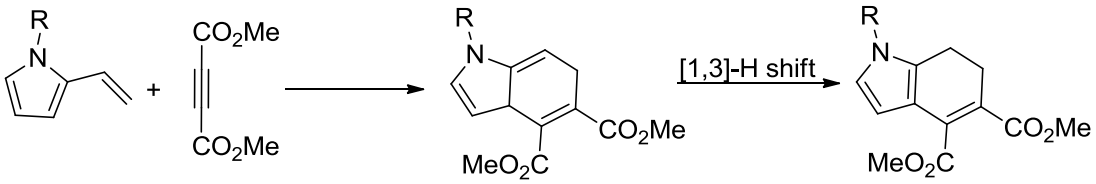
45 **46**

Scheme 2.8 Extra-annular Diels-Alder reaction

2.3.2 Diels-Alder reactions of 2-vinylpyrrole derivatives

The chemistry of vinylpyrroles only started to flourish around 1980s[38] when Hoseman *et al*. discovered a stable 2-(nitrovinyl)pyrrole. Though, the synthesis of 2-vinylpyrroles can be easily achieved through Wittig reaction from formylpyrroles in good yield.[39]

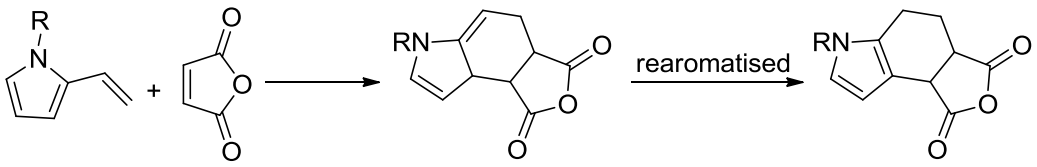
Following that, Jones examined the reaction outcome of N-methyl- and N-phenyl-2-vinylpyrroles with DMAD respectively. At high temperature (80°C), both derivatives yielded the dihydroindoles product which were transformed from the Diels-Alder adduct via [1,3]-H shift (Scheme 2.9).[40,41] Unlike 2-vinylfuran, cycloaddition of the endocyclic diene of pyrrole with DMAD was not detected.



R = Me, Ph

Scheme 2.9 Cycloaddition of 2-vinylpyrroles with DMAD

Jones also reacted both of the 2-vinylpyrrole derivatives with maleic anhydride. It was found that the reactions were completed within minutes at low temperature. However, they failed to isolate the Diels-Alder cycloadducts. Instead, the major product obtained was the rearomatised form (Scheme 2.10).



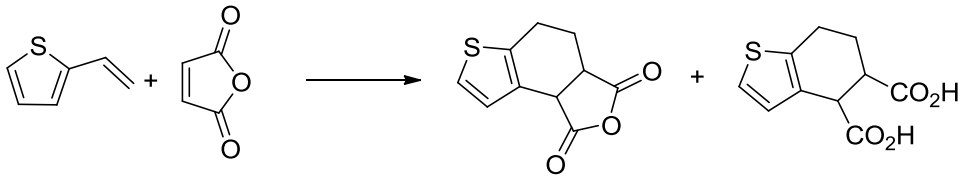
R = Me, Ph

Scheme 2.10 Diels-Alder reaction of 2vinylpyrrole derivatives with maleic anhydride

Many subsequent studies of 2-vinylpyrrole derivatives with maleic anhydride and N-phenyl maleimide also produced similar outcomes.[42]

2.3.3 Diels-Alder reactions of 2-vinylthiophene derivatives

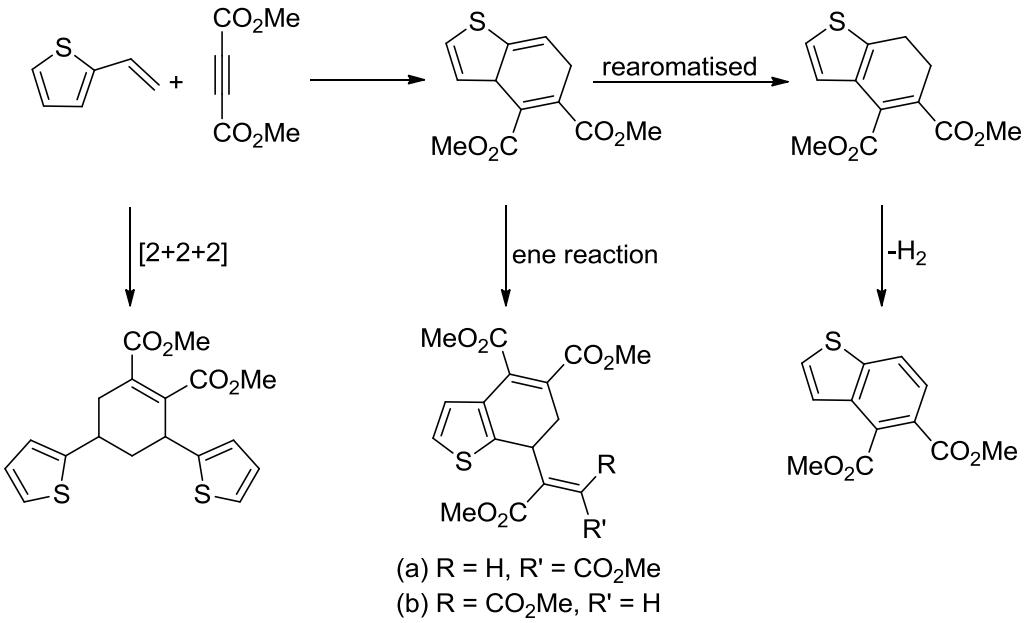
Before the discovery of the first cycloaddition of 2-vinylthiophene in 50s,[43] reports on vinylthiophenes are scattered. The result obtained between 2-vinylthiophene and maleic anhydride[44] seems doubtful till it was revisited by Abarca in 1985.[45] It was confirmed then that the initial cycloadduct was unobtainable. Instead, the rearomatised adduct and the corresponding dicarboxylic acid were isolated (Scheme 2.11).



Scheme 2.11 Cycloaddition of 2-vinylthiophene with maleic anhydride

However, two studies have succeeded in isolating the pre-aromatised cycloadduct by using a highly reactive dienophile, 4-phenyl-1,2,4-triazoline-3,5-dione at low temperature.[46,47]

The reaction of 2-vinylthiophene with DMAD was also studied by Abarca.[45] The reaction afforded four products which none consist of the Diels-Alder cycloadduct or the rearomatised form. This is because these two cycloadducts have undergone further reactions *in situ* to give three of the four products. The other one was a result of a [2+2+2] cycloaddition of two equivalents of 2-vinylthiophene with DMAD (Scheme 2.12).



Scheme 2.12 Cycloaddition of 2-vinylthiophene with DMAD

2.4 Summary

Summing up, examples of vinylphospholes derivatives are limited because of the lack of a general synthetic route. Among the references on vinylphospholes, not one of them has reported on their chemical behaviour. This leads us to examine the available references on how the other 2-vinyl substituted heteroarenes (furans, pyrroles and thiophenes) would have reacted when subjected to the similar cycloaddition reactions of phopsholes.

Thus, after understanding the chemistry of the analgoues of vinylphospholes, we shall report our findings herein.

2.5 Results and Discussion

In section 1.2.3, we have summarised the theoretical studies performed on a series π-conjugated phosphole derivatives. However, there is no report on simple 2-vinylphosphole derivatives. Hence, we first started out by carrying out DFT study on 1-methylphosphole **47** and 1-methyl-2-vinylphosphole **48** at the RB3LYP/6-311+G(d,p) level.[48] The comparison between these two molecules will provide a preliminary insight on the characteristics of 2-vinylphosphole.

Extracting from the computed structure of **48** (Figure 1), the vinyl moiety is coplanar with the diene of phosphole. Secondly, the bond length between the α-C of phosphole to the

vinyl carbon (C1-C13) is somewhat short at 1.451Å and quite similar to the endocyclic C-C bond (C2-C3) at 1.450Å. Furthermore, the significant difference between structure **47** and **48** is the alternation between the C-C and the C=C bonds. From the published work on **47** studied on a similar computational level,[24] the mean alternation is 0.103Å while molecule **48** is 0.089Å. Adding on, the sum of C-P-C angles for **48** and **47** are 297.9° and 301.0° respectively. This means that the pyramidality of the P atom of **48** is higher than that of **47**. As we recalled (Section 1.2.1 and 1.2.3), when there is a decrease in interaction between the diene and the phosphorus atom in phosphole, the P atom will become more pyramidal.[49] Thus, piecing together all this information, it points to the likelihood of a significant conjugation between the vinyl substituent and the diene of phosphole.

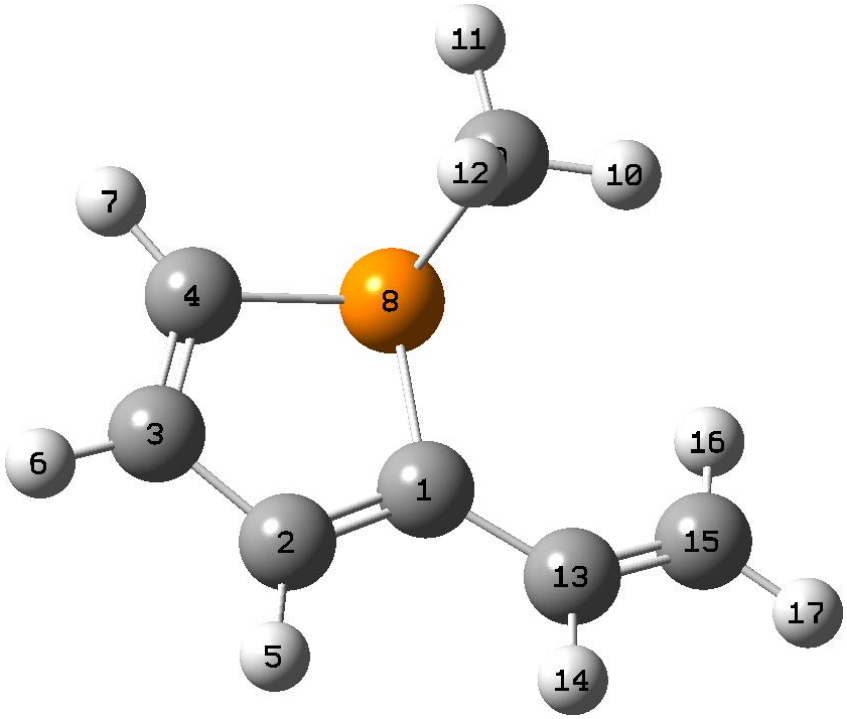


Figure 2.1 Computed structure of 1-methyl-2-vinylphosphole **48** Main distances (Å) and angles (deg.): C1-P8 1.835, C4-P8 1.811, C9-P8 1.867, C1-C2 1.365, C2-C3 1.450, C3-C4 1.356, C1-C13 1.451, C13-C15 1.341; C1-P8-C4 90.36, C1-P8-C9 103.44, P8-C1-C13 125.93

The study of the structural property of 2-vinylphosphole was further aided by examining the frontier orbitals (Kohn-Sham) of **48**. As illustrated (Figure 2.2), the HOMO of **48** lies 0.46eV higher than the HOMO of **47**. This is a result of the antibonding combination of the vinyl π bond with the diene HOMO. Also, the insignificant change in the energy of the lone pair orbitals

between the two structures (0.08eV lower between **48** and **47**) confirms the delocalization of the lone pair of P into the ring is weak. This equates to an increase of linear π-conjugation between the dienic system and the vinyl group.

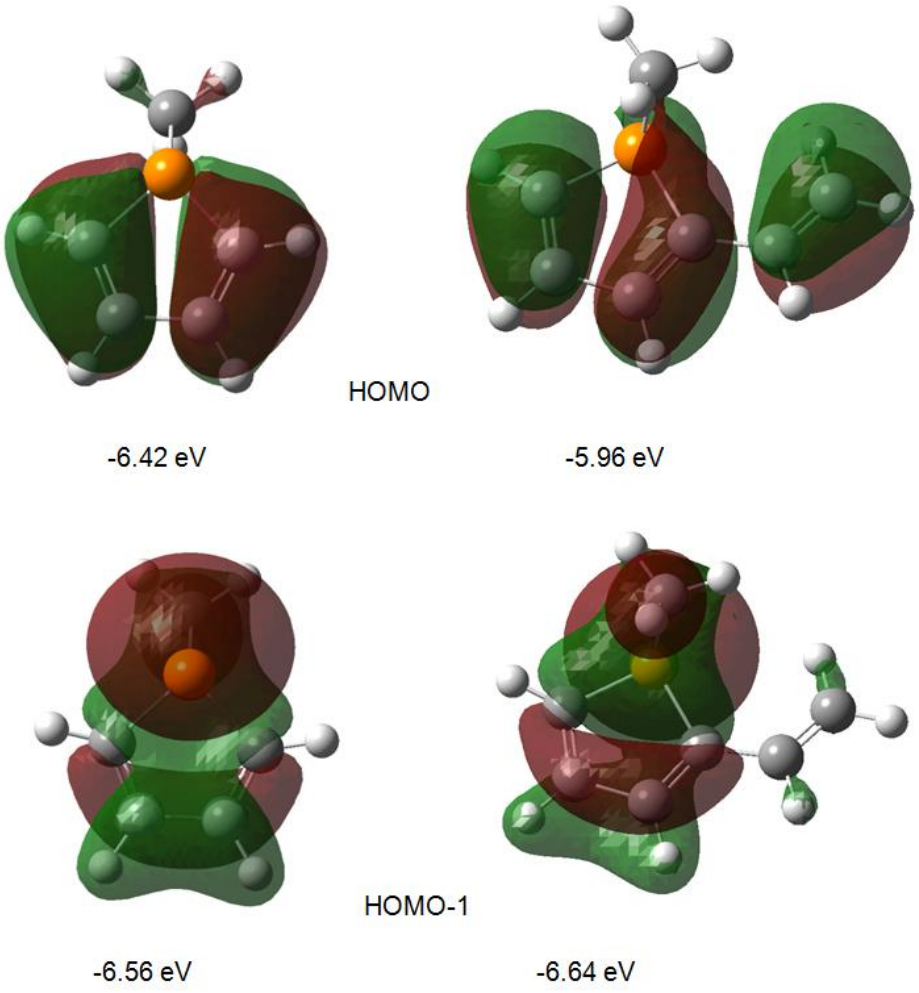
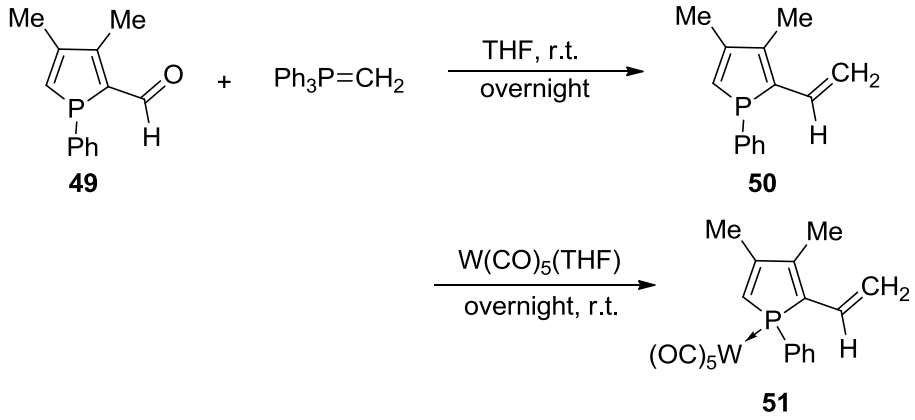


Figure 2.2 Highest occupied Kohn-Sham orbitals of 1-methylphosphole **47** and 1-methyl-2-vinylphosphole **48**

The outlook from the theoretical study suggests there will be an additional set of reactive diene (besides the diene of phosphole), which is made up of the exocyclic vinyl group and the adjacent endocyclic C=C of phosphole. This is indeed observed in the examples of 5-membered 2-vinyl substituted heteroarenes (Section 2.3). Thus, the experiments conducted on our 2-vinylphosphole focused on the cycloaddition reactions.

Synthesis of the 2-vinylphosphole **50** was easily attained with 67% yield through Wittig reaction of methylenetriphenylphosphorane with formylphosphole **49**[50] at room temperature (Scheme 2.13). This is a common technique employed in organic synthesis for introducing alkene substituents from an aldehyde.[51] Due to the unstability of compound **49**, one has to ensure it is freshly made on the day for the Wittig reaction in order to obtain a good yield of compound **50**.



Scheme 2.13 Synthesis of 2-vinylphosphole **50** and 2-vinylphosphole tungsten complex **51**

After stirring overnight and upon purification by flash chromatography with degassed hexane, 2-vinylphosphole **50** was then reacted with $W(CO)_5(THF)$ to give complex **51**. Full characterisations of complex **51** were performed and structurally confirmed by X-ray crystallography (Figure 2.3).

Comparing between the computed structure **48** and the X-ray study of **51**, it shows that the vinyl group in both cases points to the same side of the phosphorus atom. Also, the vinyl group in **51** is coplanar to the phosphole, which is in agreement with the computed structure **48**. So far the structural information matches both practically and theoretically. The next step would be to investigate the reactivity of these vinyphosphole derivatives towards cycloaddition.

Before venturing into that, it is essential to recall that the presence of the vinyl moiety might create several sites for cycloaddition to occur, which are seen in the cases of vinyl-substituted furans, pyrroles and thiophenes (Section 2.3).

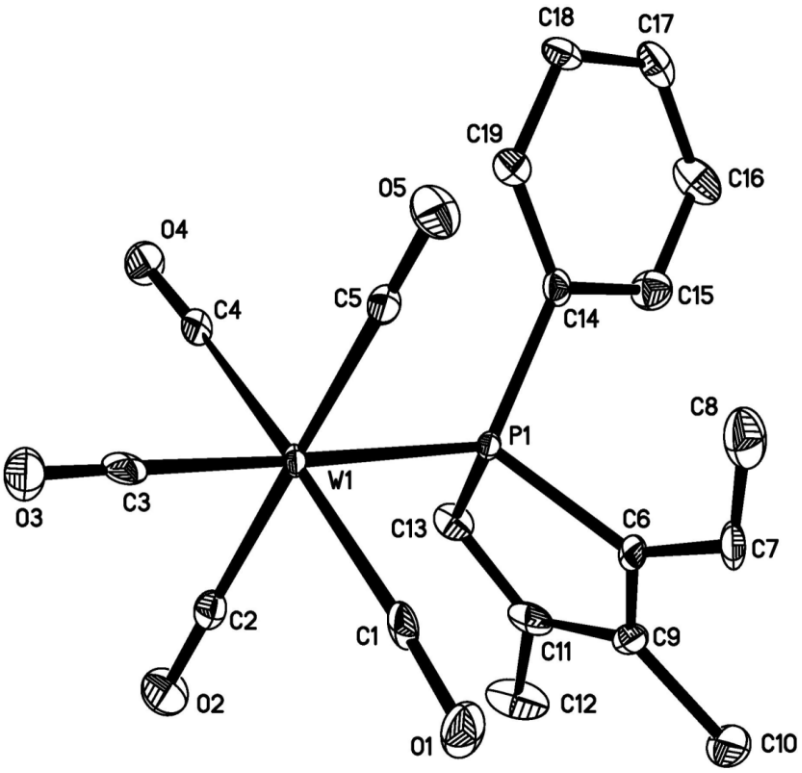


Figure 2.3 X-ray crystal structure of **51**. Main distances (Å) and angles (deg.): C6-P1 1.806(7), C13-P1 1.794(8), C14-P1 1.834(8), C6-C9 1.359(11), C9-C11 1.449(12), C11-C13 1.340(11), C6-C7 1.459(11), C7-C8 1.317(13); C6-P1-C13 91.3(4), C6-P1-C14 105.1, P1-C6-C7 123.6(6)

Thus, we tested the two common reagents for Diels-Alder reactions for phospholes and the other 5-membered heteroaryl rings. They are N-phenylmaleimide (NPM) and dimethyl acetylenedicarboxylate (DMAD).

Since, it has been shown that a σ^3-phosphole **4** is able to undergo Diels-Alder reaction with NMP.[16] This inspired us to examine the reactivity of the σ^3-vinylphosphole **50** under similar reaction condition. A trial reaction was performed in an NMR tube containing NMP and **50** dissolved in toluene. When the reaction mixture was heated at 40°C, there was no new peak observed from the ^{31}P NMR other than the starting material (δ = -3.3ppm) after 4 hours. Thus, temperature was slowly increased by 10°C every 2 hours. New observable peak appeared (δ = 74.4ppm) when it was heated at 80°C. Finally, the reaction was driven to completion at 100°C overnight. Upon purification through chromatography in silica, an *endo*-cycloadduct **52** was obtained. The [4+2] cycloaddition happened at the endocyclic diene of phosphole and led to the *endo* product **52**. The cycloadduct through the extra-annular pathway was not detected.

Surpringly, the X-ray crystallography of **52** (Figure 2.4) revealed that the P was oxidized, and it bears the *syn*-stereochemistry.

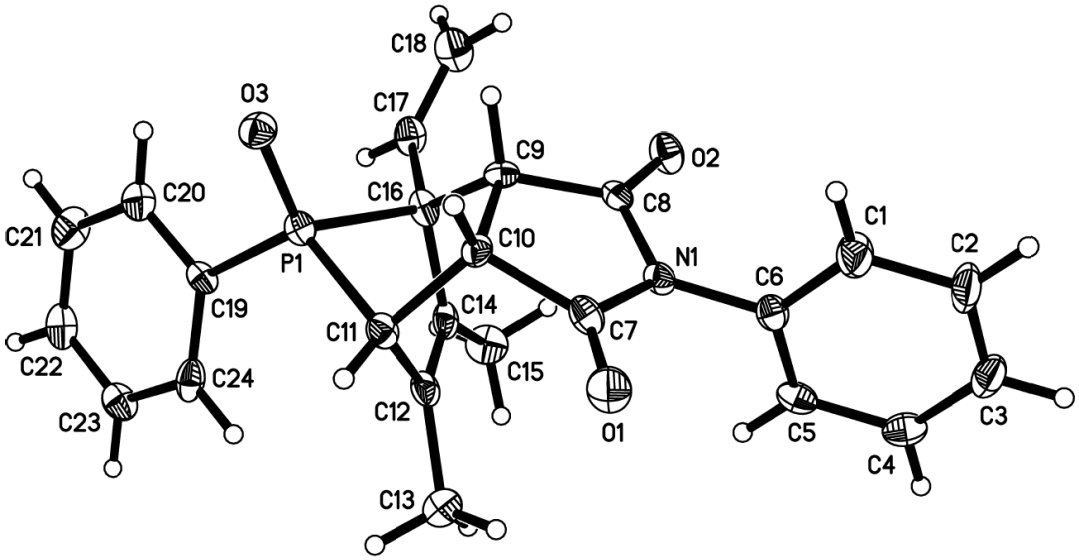


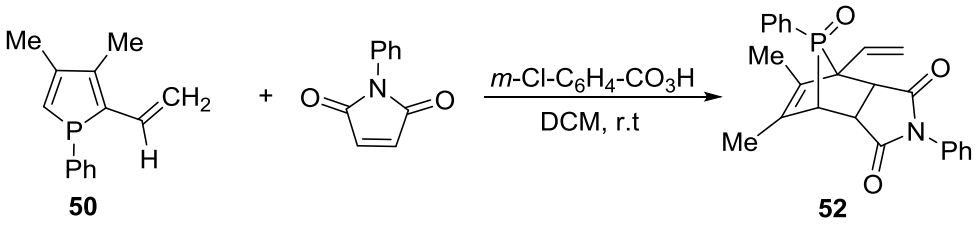
Figure 2.4 X-ray crystal structure of **52**. Main distances (Å) and angles (deg.): P1-C11 1.831(6), P1-C16 1.872(5), C9-C10 1.544(7), C9-C16 1.564(7), C10-C11 1.567(7), C16-C17 1.495(8), C17-C18 1.302(8); C11-P1-C16 83.5(3)

Attention must be brought back to the discussion in section 2.2.2 (Scheme 2.3). When σ^3-phosphole reacts with dienophile (maleic acid derivatives), followed by sulfurization, it leads to the formation of a cycloadduct bearing the *anti*-stereochemistry. However, when the phosphole is sulfurized and subsequently subject to cycloaddition reaction, the cycloadduct formed will bear the *syn*-stereochemistry. Thus, if our cycloadduct was oxidized during the chromatography, the P=O bond would be on the opposite side of the cycloaddition.

Undoubtedly, the oxidation of the cycloadduct in our reaction must not have occurred during the purification. We postulate that the poorly reactive vinylphosphole **50** was first oxidized by the oxygen from the atmosphere which diffused through the NMR cap. Then, the reactive σ^4-phosphole oxide formed underwent the cycloaddition with NMP, producing the cycloadduct with the *syn*-stereochemistry.

Our postulation was confirmed by repeating the experiment with oxidized 2-vinylphosphole. However, most phosphole oxides dimerize spontaneously at room temperature.

Thus, 2-vinylphosphole oxide was generated *in-situ* with *m*-chloroperoxybenzoic acid (*m*-CPBA) in the presence of NMP. In order to ensure that the [4+2] cycloadditions between the phosphole oxide and NMP take place before the self-dimerization of phosphole oxides, the *m*-CPBA solution was added dropwise (4 hours) into the reaction mixture of compound **50** and NMP at room temperature (Scheme 2.14). Indeed, cycloadduct **52** was obtained with 52% yield while traces of dimeric oxide of **50** were observed.

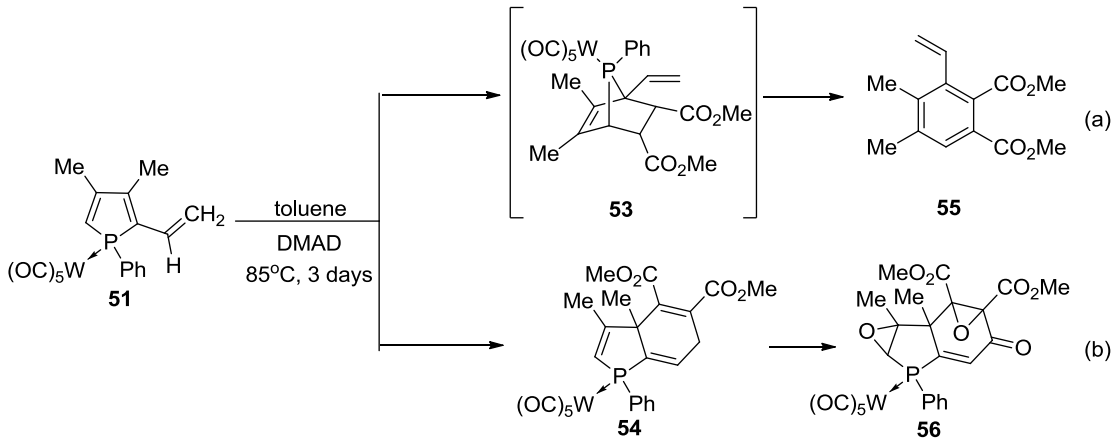


Scheme 2.14 Diels-Alder reaction of compound **50** with N-phenylmaleimide

Thus, the cycloaddition of 2-vinylphosphole **50** with NMP does not proceed unless the phosphole **50** is oxidised. Furthermore, it takes place exclusively via the intra-annular pathway unlike the examples of 2-vinylheteroarenes discussed.

Next, a more reactive dienophile, dimethyl acetylenedicarboxylate (DMAD) was tested. Since DMAD can react with the phosphole lone pair,[52] we used the P-$W(CO)_5$ complex **51**. Both reactants **51** and DMAD were dissolved in toluene in a sealed tube and heated at 85°C. This reaction is also a very common technique used by Mathey's group to generate the 7-phosphanorbornadiene complex, which is a [4+2] cycloaddition of the diene of phosphole-$M(CO)_5$ complexes with DMAD (intra-annular).[53] In the vinylphosphole system, the presence of the vinyl group might create a second pathway for the cycloaddition (extra-annular).

Indeed, the reaction proceeded with the two aforementioned routes. The usual route (intra-annular) produced the cycloadduct **53** which collapsed *in situ* generating a transient phosphinidene precursor and the vinylphthalate **55** (Scheme 2.15a). However, in the midst of the reaction, 7-phosphanorbonadiene complex **53** was not observed in the ^{31}P NMR (around 200ppm region).



Scheme 2.15 Diels-Alder cycloaddition of complex **51** with DMAD

The extra-annular pathway (Scheme 2.15b) afforded product **54** which was established definitively by X-ray crystallography (Figure 2.5). No rearomatization took place due to the presence of a quaternary carbon. In addition, the cyclohexadiene ring formed assumed a boat conformation, which is bent around C15-C20 with an angle of 35.7°.

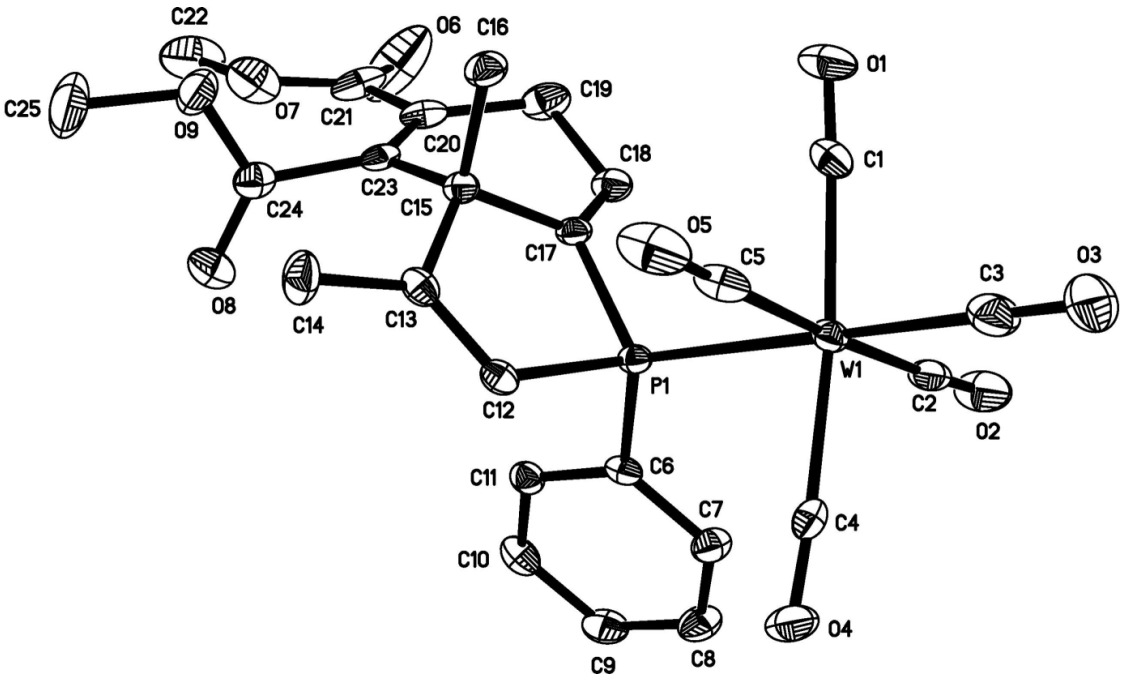


Figure 2.5 X-ray crystal structure of **54**. Main distances (Å) and angles (deg.): P1-C12 1.798(3), P1-C17 1.809(3), C12-C13 1.330(5), C13-C15 1.537(4), C15-C17, 1.527(4), C17-C18 1.323(4), C18-C19 1.497(5), C19-C20 1.511(5), C20-C23 1.345(5), C23-C15 1.530(4); C12-P1-C17 89.97(15)

However, upon careful separation by preparatory thin layer chromatography (PTLC), a minute amount of complex **56** was obtained and unambiguously identify by X-ray crystal structure analysis (Figure 2.6). We were perplexed by this product as two out of the three C=C bonds in **54** were expoxidized, and the vinylic carbon was oxidized to a ketone. After doing some thorough literature search, we realised that tungsten oxo species is known to have the ability to catalyse the epoxidation of olefins.[54,55] Since our reaction vessel was sealed, the only source of oxidative material would be the excess DMAD where the transfer of oxygen might be catalysed by the presence of a tungsten oxo species. If this hypothesis is acknowledged, then the epoxidation of only two C=C bonds out of the three can be easily explain by steric factor. As the two epoxide rings are situated at the P-phenyl side of the phosphole ring (less hindered), it explains why the C=C bond which is hindered by the bulky $W(CO)_5$ is not favourable for epoxidation.

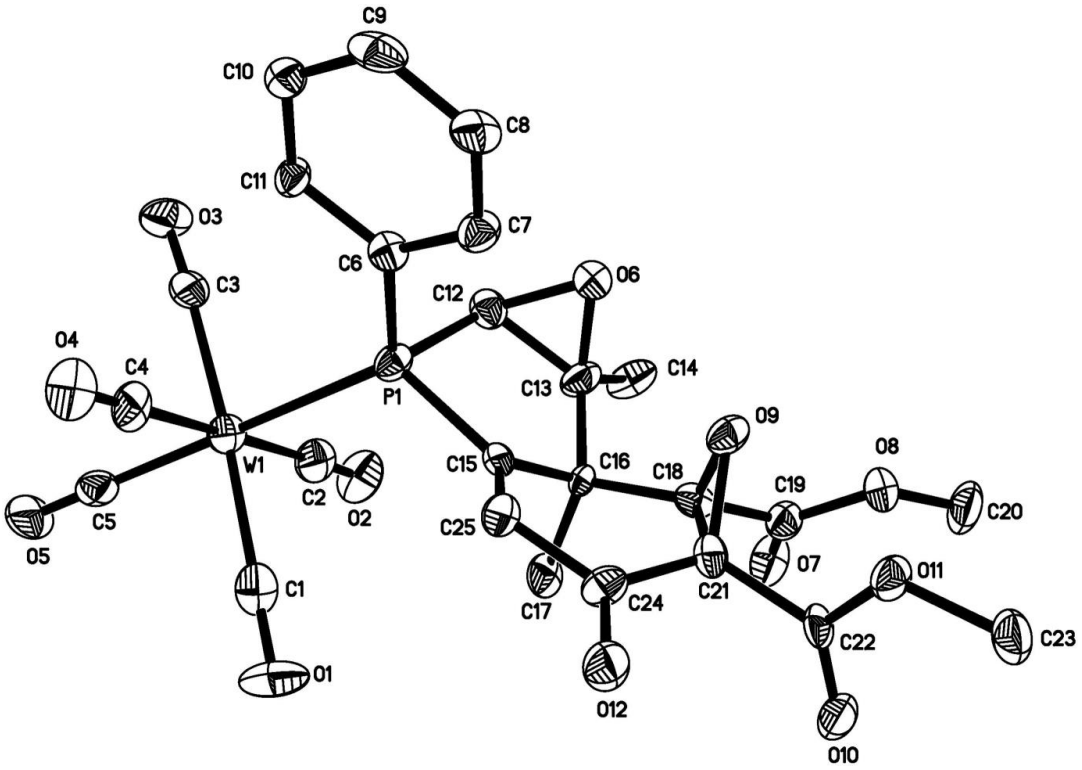
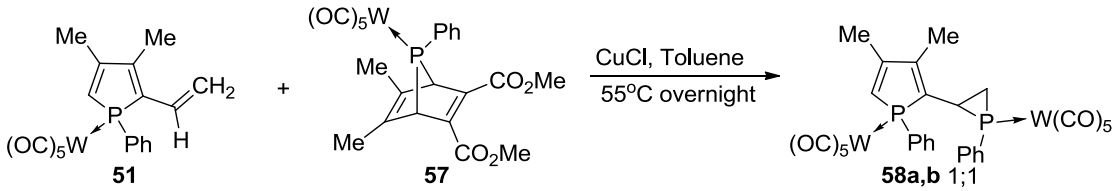


Figure 2.6 X-ray crystal structure of **56**. Main distances (Å) and angles (deg.): P1-C12 1.810(10), P1-C15 1.820(10), C12-C13 1.494(14), C13-C16 1.543(13), C16-C15 1.527(13), C15-C25 1.330(14), C25-C24, 1.483(14), C24-O12 1.212(12), C24-C21 1.494(14), C21-C18 1.463(14), C16-C18 1.510(13), C12-O6 1.449(12), C13-O6 1.455(13), C18-O9 1.420(12), C21-O9 1.434(12); C12-O6-C13 61.9(6), C18-O9-C21 61.7(6), C12-P1-C15 89.5(5)

Therefore, the reaction of complex **51** with DMAD happened through the two possible pathways. And the initial Diels-Alder cycloadduct did not rearomatise. These two outcomes were also observed from 2-vinylfuran but not from 2-vinylpyrroles and 2-vinylthiophenes. This may be due to the poor aromaticity of phospholes and furans as compared to thiophenes and pyrroles. On the other hand, the cycloaddition of **50** with NMP took place exclusively by the intra-annular route. Yet, direct comparison with other heteroarenes cannot be made since the phosphole was oxidised before the cycloaddition.

Last but not least, we also explored the reactivity of our 2-vinylphosphole complex **51** towards [1+2] cycloaddition. To do this, the classical [1+2] cycloaddition of terminal phosphinidene complex [PhP-W(CO)$_5$] with alkenes was selected,[56] In our case complex **51** served as the source of alkene.

The reaction of **51** with 7-phosphanorbornadiene complex **57** was completed overnight at 55°C cleanly (Scheme 2.16), showing two sets of AB signals in ^{31}P NMR. After separation through chromatography, isomer **58a** showed up at -155.5ppm and 22.1ppm while **58b** appeared at -156.9ppm and 20.29ppm. The upfield signals belong to the phosphiranes whereas the peaks at the positive region are due to the phospholes. The condensation took place solely at the vinyl substituent due to steric factor. This was evident by the equal amount of isomers **58** (40% and 41% yield) obtained because the exocyclic vinyl group is not sterically hindered.



Scheme 2.16 [1+2] cycloaddition of terminal phosphinidene with vinylphosphole complex **51**

Complex **58a** was identified by X-ray crystal structure (Figure 2.7). From the data of the crystallography examination, the phosphirane plane makes an angle of 45° with the plane of phosphole. Also, the formation of the phosphirane ring at the α-position of phosphole induces both the lengthening of the phosphole-substituent bond (C16-C17) and the increase of alternation within the diene by 0.138Å.

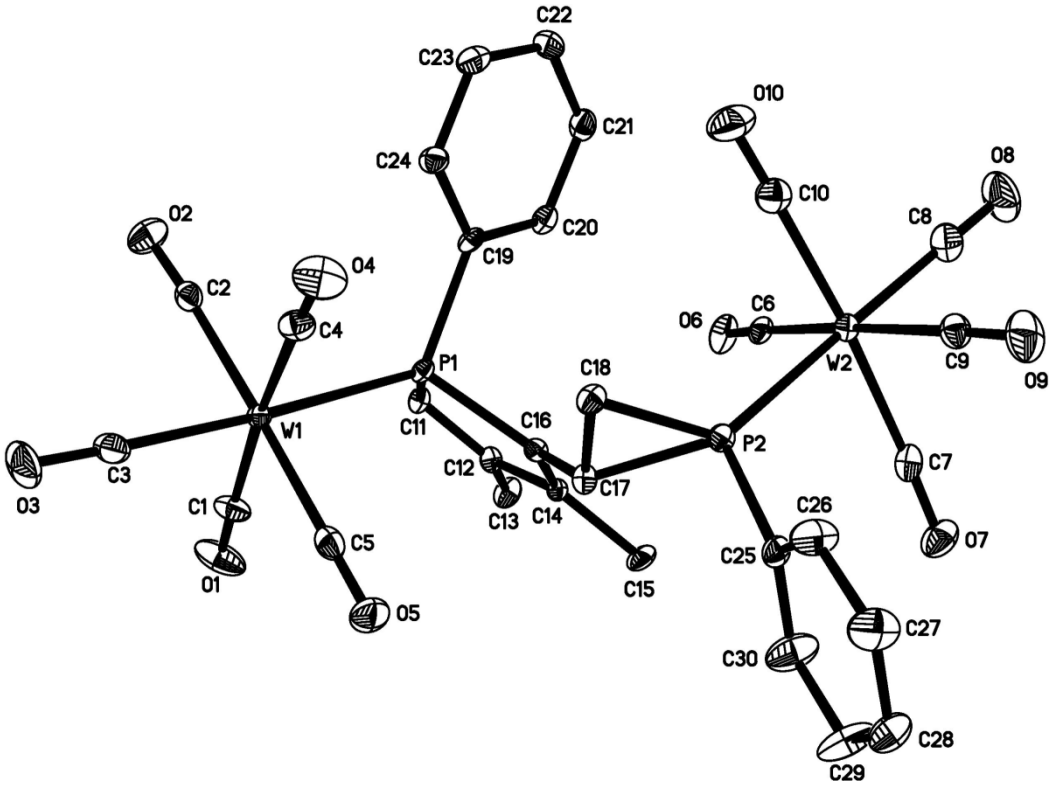


Figure 2.7 X-ray crystal structure of **58a**. Main distances (Å) and angles (deg.): P1-C11 1.794(4), P1-C16 1.824(4), C11-C12 1.343(5), C12-C14 1.482(5), C14-C16 1.345(5), C16-C17 1.479(5), C17-C18 1.516(5), C17-P2 1.837(4), C18-P2 1.818(4); C11-P1-C16 91.21(17), C17-P2-C18 49.02(17)

Then, complex **58** was heated to investigate the possibility of classical rearrangement of 2-vinylphosphiranes into phospholenes.[56,57] However, only decomposition products were observed upon heating at 100°C.

2.6 Conclusion

DFT calculations have shown the 1-methyl-2-vinylphosphole **48** to have significant conjugation between the vinyl substituent and the diene of phosphole by a few physical traits. These physical traits are namely, the vinyl moiety is coplanar to the phosphole, shortening of the phosphole-substituent bond length, alternation between the diene is decreased, and the pyramidality of the phosphorus atom. Furthermore, the frontier orbital (Kohn-Sham) revealed the weak delocalization of the lone pair on P into the ring. All these add up to suggest the

likelihood of increase linear π-conjugation along the diene of phosphole to the exocyclic vinyl group.

With this prospective outlook, 2-vinylphosphole derivatives **50** and **51** were prepared by a sequence of chemical reactions. In parallel to the computational study, the vinyl group in complex **51** is coplanar to the phosphole ring and is pointed to the phosphorus atom.

Thus, after reviewing the cycloaddition of 5-membered heteroarenes with α-vinyl substituents, compound **50** and **51** was subjected to the same series of reactions.

The trial reaction of 2-vinylphosphole **50** with NPM was completed at 100°C overnight. However, the X-ray crystal structure of the product **52** revealed that the P was oxidised and bears the *syn*-stereochemistry. This stereochemistry of P can only be obtained if oxidised or sulfurized phospholes (σ^4) are used for the cycloaddition. Thus, we revisited this reaction by generating the oxide of **50** *in situ* with slow addition of *m*-CPBA in the presence of NPM. Indeed, the 7-phosphanorbonene oxide **52** was obtained. By doing so, we confirm that the poorly reactive **50** was oxidised before the cycloaddition with NPM in the trial experiment. Unlike its analogues such as furans, pyrroles and thiophene, the [4+2] cycloaddition with NPM takes place via the intra-annular pathway.

Next, [4+2] cycloaddition between complex **51** and a stronger dienophile, DMAD, was carried out. And, it produced three products. The initial intra-annular cycloadduct **53** collapsed *in situ* to afford the by-product vinylphthalate **55**. At the same time, complex **54** was obtained through the extra-annular route, and rearomatization was not observed. This similar outcome was reported with 2-vinylfuran but not for the pyrroles and thiophenes analogues. A possible reason might be due to the low aromaticity of furans and phospholes.

However, the minute product **56** was the one that caught our attention. It was a by-product of complex **54**. We postulated that the two epoxidized C=C bonds result from the presence of a tungsten oxo species which mediated the transfer of oxygen from the excess DMAD.

Lastly, a [1+2] cycloaddition reaction was performed by reacting complex **51** with a source of terminal phosphinidene. Surprisingly, the reaction proceeded exclusively at the vinyl

substituent which mainly due to steric factor producing diastereomers **58a** and **58b** in equal amount.

Hence, in this work, we have demonstrated that the vinylphosphole derivative **50** and **51** possess three sites for cycloaddition reaactions. They are the intra- and extra-annular [4+2] cycloaddition and also the vinyl group for [1+2] cycloaddition. And the pathway selected is exclusive to the specific reagent. From this, it can be comprehend that 2-vinylphospholes display the potential for the synthesis of novel organophosphorus compounds.

2.7 Experimental

Oven-dried glasswares (105°C) were used and cooled under nitrogen atmosphere. All reactions were carried out with distilled dry solvents and under N_2 atmosphere. Silica gel (230-400mesh) was used for the chromatographic separations. Commercially available N-phenylmaleimide and DMAD were used without purification. The phosphinidene precursor **57** was synthesized as described in the literature.[11] NMR spectra were recorded on either a JEOL ECA 400, JEOL ECA 400 SL or Bruker BBFO2 400MHz spectrometer. All spectra were recorded at 298K. Proton decoupling was applied for ^{13}C and ^{31}P spectra. HRMS were obtained on a Water Q-Tof Premier MS. X-ray crystallographic analyses were performed on a Bruker X8 APEX CCD diffractometer or a Bruker Kappa CCD diffractometer.

*1-Phenyl-2-vinyl-3,4-dimethylphosphole **50***

n-BuLi (1.4 mL, 1.6 M in hexane, 2.2 mmol) was added dropwise into an oven-dried two-neck flask under N_2 containing methyltriphenylphosphonium iodide (0.8893, 2.2 mmol) suspended in THF (10 mL) at 0°C. The reaction mixture was left to stir at room temperature for 15 min. Subsequently, 3,4-dimethyl-1-phenylphosphole-2-carboxaldehyde **49** (0.4335 g, 2.0 mmol) dissolved in THF (3 mL) was added. The reaction was stirred overnight. The solvent was removed and the crude was purified using flash chromatography in degassed hexane. The phosphole was obtained in 67% yield (0.3715g).

^{31}P NMR ($CDCl_3$): δ -3.31ppm

^{1}H NMR ($CDCl_3$): δ 2.08-2.09 (m, 3H, Me), 2.10-2.11 (m, 3H, Me), 4.97 (d, $J_{(H-P)}$ = 10.6Hz, 1H, =CH_2), 5.31 (d, $J_{(H-P)}$ = 17.2Hz, 1H, =CH_2), 6.35 (d, $J_{(H-P)}$ = 39.7Hz, 1H, =CH-P), 6.70-6.81 (m, 1H, =CH), 7.25-7.28 (m, 3H, Ph), 7.30-7.34 (m, 2H, Ph).

^{13}C NMR ($CDCl_3$): δ 13.78 (d, $J_{(C-P)}$ = 2.1Hz, Me), 18.35 (d, $J_{(C-P)}$ = 3.4Hz, Me), 115.15 (d, $J_{(C-P)}$ = 12.3Hz, =CH_2), 127.92 (d, $J_{(C-P)}$ = 1.1Hz, P-CH), 128.68 (d, $J_{(C-P)}$ = 8.0Hz, Ph), 129.29 (s, Ph), 131.22 (d, $J_{(C-P)}$ = 17.5Hz, =CH), 133.29 (d, $J_{(C-P)}$ = 11.8Hz, P-C(Ph)), 133.61 (d, $J_{(C-P)}$ = 19.4Hz, Ph), 144.34 (s, P-C), 144.82 (d, $J_{(C-P)}$ = 10.2Hz, C-Me), 150.38 (d, $J_{(C-P)}$ = 6.2Hz, C-Me).

Exact mass: calcd $C_{14}H_{16}P$, 215.0990; found 215.0972.

*1-Phenyl-2-vinyl-3,4-dimethylphosphole pentacarbonyltungsten complex **51***

1-Phenyl-2-vinyl-3,4-dimethylphosphole **50** (0.135 g, 0.63 mmol) dissolved in THF (3 mL) was added to $W(CO)_5$(THF) (0.7mmol) and stirred overnight at room temperature. The solvent was removed under vacuum and the purification carried out by flash chromatography using hexane (0.3380 g, 99%).

^{31}P NMR ($CDCl_3$): δ 14.63 ppm ($J_{(P-W)}$ = 221.0 Hz)

^{1}H NMR ($CDCl_3$): δ 2.18 (m, 6 H, Me), 5.16-5.23 (m, 2 H, =CH_2), 6.43 (d, $^{2}J_{(H-P)}$ = 36.8 Hz, 1H, =CH-P), 6.71-6.83 (m, 1H, C-CH=), 7.36-7.51 (m, 5 H, Ph).

^{13}C NMR ($CDCl_3$): δ 13.77 (d, $^{3}J_{(C-P)}$ = 8.4 Hz, Me), 17.71 (d, $^{3}J_{(C-P)}$ = 10.5 Hz, Me), 118.97 (d, $^{3}J_{(C-P)}$ = 7.2 Hz, =CH_2), 128.65 (d, $^{2}J_{(C-P)}$ = 14.4 Hz, C-*C*H=), 129.21 (d, $J_{(C-P)}$ = 10.5 Hz, Ph), 129.61 (d, $J_{(C-P)}$ = 38.6 Hz, P-C(Ph)), 130.95 (d, $J_{(C-P)}$ = 44.1 Hz, P-CH=), 131.04 (d, $J_{(C-P)}$ = 2.3 Hz, Ph), 132.48 (d, $J_{(C-P)}$ = 13.0Hz, Ph), 142.40 (d, $J_{(C-P)}$ = 42.5 Hz, P-C), 145.90 (d, $J_{(C-P)}$ = 14.7 Hz, C-Me), 150.00 (d, $J_{(C-P)}$ = 7.5 Hz, C-Me), 196.61 (d, $J_{(C-P)}$ = 6.4 Hz, $W(CO)_5$ *cis* C=O), 198.83 (d, $J_{(C-P)}$ = 19.3 Hz, $W(CO)_5$ *trans* C=O).

Exact mass: calcd $C_{19}H_{15}O_5PW$, 538.0166; found 538.0166.

*7-Phosphanorbornene oxide **7***

m-Chloroperoxybenzoic acid (0.0814 g, 70% in H_2O, 0.33 mmol) was dissolved in 5 mL of dichloromethane and dried over $MgSO_4$. It was filtered into an addition funnel attached to a 2-neck flask containing 2-vinylphosphole **50** (0.0443 g, 0.33 mmol) and *N*-phenylmaleimide

(0.0629g, 0.36 mmol) dissolved in 2 mL of dichloromethane. Then, *m*-CPBA solution was added dropwise into the reaction mixture at room temperature for 4 h. The crude was purified by chromatography with a 2:3 ratio of hexane and ethyl acetate as the eluent. Oxide **52** was obtained (0.0692 g, 52%).

^{31}P (**7**) (CH_2Cl_2): δ 74.4 ppm.

^{1}H NMR (CD_2Cl_2): δ 1.65 (s, 3H, Me), 1.78 (s, 3H, Me), 3.54-3.57 (m, 1H, CH), 4.07-4.14 (m, 2H, CH), 5.52-5.55 (m, 1H, =CH_2), 5.68-5.73 (m, 1H, =CH_2), 6.14-6.24 (m, 1H, =CH), 7.06-7.08 (m, 2H, Ph), 7.38-7.58 (m, 8H, Ph).

^{13}C NMR (CD_2Cl_2): δ 13.27 (d, J_{P-C} = 3.0Hz, CH_3), 16.04 (d, J_{P-C} = 4.4Hz, CH_3),45.42 (d, J_{P-C} = 12.4Hz, CH), 48.46 (d, J_{P-C} = 87.3Hz, P-CH), 48.7 (d, J_{P-C} = 8.3Hz, CH), 60.48 (d, J_{P-C} = 66.0Hz, P-C),121.23 (d, J_{P-C} = 10.1Hz, =CH_2),127.31 (s, Ph), 129.25 (d, J_{P-C} = 8.9Hz, P-C(Ph)), 129.28 (s, Ph), 129.42 (d, J_{P-C} = 6.7Hz, Ph), 129.62 (d, J_{P-C} = 6.1Hz, =CH), 129.81 (s, Ph), 130.44 (d, J_{P-C} = 8.8Hz, =C), 132.59 (s, Ph), 132.79 (d, J_{P-C} = 8.0Hz, Ph), 133.15 (d, J_{P-C} = 2.7Hz, Ph), 133.84 (d, J_{P-C} = 10.8Hz, =C), 174.97 (d, J_{P-C} = 13.4Hz, C=O), 175.63 (d, J_{P-C} = 14.1Hz, C=O).

Exact mass: calcd $C_{24}H_{23}O_3PN$, 404.1416; found 404.1434.

*Reaction of **51** with dimethyl acetylenedicarboxylate*

Complex **51** (0.116 g, 0.22 mmol) was dissolved in 2 mL of toluene and dimethyl acetylenedicarboxylate (0.08 mL, 0.66 mmol) was added. The reaction tube was sealed and heated at 90°C for 3 d. Two new peaks were observed in the crude reaction mixture at 2.87 ppm (J_{P-W} = 233.5 Hz) and 21.0 ppm (J_{P-W} = 218.9 Hz) with the presence of starting material at 14 ppm. Purification was performed by gradient chromatography, with a mixture of dichloromethane and hexane as the eluent from 1:4 ratio to 100% dichloromethane. A mixture of products **54** and **56** was first eluted, followed by compound **55** (0.0175 g of colorless oil, 43.8 %). Compounds **54** and **56** were separated by PTLC, with a 4:1 mixture of dichloromethane and hexane as the eluent. 0.013 g of pale yellow solid **54** was obtained (12%) while compound **56** was recovered as a yellow oil (0.0029 g, 2%).

Compound **54**

^{31}P NMR (CD_2Cl_2): δ 2.73 ($J_{(P\text{-}W)}$ = 234.1 Hz)

^{1}H NMR (CD_2Cl_2): δ 1.53 (s, 3H, Me), 2.04 (s, 3H, Me), 3.07 (m,1H, CH_2), 3.33-3.41 (m, 1H, CH_2), 3.70 (s, 3H, OMe), 3.82 (s, 3H, OMe), 6.04 (d, $^{2}J_{(H\text{-}P)}$ = 33.6 Hz, 1H, P-CH=), 6.28-6.32 (m, 1H, =CH), 7.38-7.58 (m, 5H, Ph).

^{13}C NMR (CD_2Cl_2): δ 17.27 (d, $J_{(C\text{-}P)}$ = 10.0 Hz, Me), 27.11 (s, Me), 28.97 (d, $J_{(C\text{-}P)}$ = 10.1Hz, CH_2), 52.84 (s, OMe), 52.95 (s, OMe), 55.75 (d, $J_{(C\text{-}P)}$ = 13.5Hz, C-Me), 125.24 (d, $J_{(C\text{-}P)}$ = 46.8 Hz, P-CH=), 128.54 (s, C), 129.30 (d, $J_{(C\text{-}P)}$ = 10.1Hz, Ph), 131.11 (d, $J_{(C\text{-}P)}$ = 2.2 Hz, Ph), 132.39 (d, $J_{(C\text{-}P)}$ = 13.7 Hz, Ph), 133.84 (d, $J_{(C\text{-}P)}$ = 12.9 Hz, =CH), 137.72 (d, $J_{(C\text{-}P)}$ = 34.1 Hz, P-C(Ph)), 147.42 (d, $J_{(C\text{-}P)}$ = 41.7 Hz, P-C=), 148.97 (s, C), 156.63 (s, C), 165.80 (s, CO_2Me), 169.21 (s, CO_2Me), 197.44 (d, $J_{(C\text{-}P)}$ = 7.0 Hz, $W(CO)_5$ *cis* C=O), 200.03 (d, $J_{(C\text{-}P)}$ = 20.1 Hz, $W(CO)_5$ *trans* C=O).

Exact mass: calcd $C_{25}H_{21}O_9PW$, 680.0433; found 680.0413.

Compound **56**

^{31}P NMR (CD_2Cl_2): δ 21.39

Exact mass: calcd $C_{25}H_{19}O_{12}PW$, 726.0124; found 726.0128.

Compound **55**

^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3H, Me), 2.32 (s, 3H, Me), 3.85 (s, 3H, OMe), 3.87 (s, 3H, OMe), 5.33 (dd, $J_{(H\text{-}H)}$ = 18.0 Hz, $J_{(H\text{-}H)}$ = 1.6 Hz, 1H, CH_2), 5.49 (dd, $J_{(H\text{-}H)}$ = 12.8 Hz, $J_{(H\text{-}H)}$ = 1.6 Hz, 1H, CH_2), 6.70-6.78 (m, 1H, =CH), 7.73 (s, 1H, Ph).

^{13}C NMR (CD_2Cl_2): δ 16.96 (Me), 20.65 (Me), 52.48 (OMe), 52.51 (OMe), 121.00 (CH_2), 124.79 (Ph), 130.28 (C-H(Ph)), 133.08 (Ph), 134.26 (CH), 136.78 (Ph), 138.03 (Ph), 140.45 (Ph), 166.42 (CO_2Me), 170.09 (CO_2Me).

Exact mass: calcd $C_{14}H_{17}O_4$, 249.1127; found 249.1141.

*Phosphirane complexes **58a,b***

Complex **51** (0.199 g, 0.37 mmol), CuCl (0.019 g, 0.19 mmol) and 7-phenyl-7-phosphanorbornadiene tungsten complex[11] (0.726 g, 1.1 mmol) were dissolved in toluene. The mixture was heated at 55°C for 1 day in a sealed tube. Solvent was removed, followed by purification by chromatography with a 1:4 mixture of dichloromethane and hexane as the eluent. Isomer **58a** (0.074 g, 41%) was eluted before isomer **58b** (0.072 g, 40%).

Isomer **58a**

^{31}P NMR ($CDCl_3$): δ -155.46 (d, $J_{(P-P)}$ = 18 Hz, $J_{(P-W)}$ = 268.7 Hz), 22.11 (d, $J_{(P-P)}$ = 18 Hz, $J_{(P-W)}$ = 216.7Hz).

^{1}H NMR (CD_2Cl_2): δ 1.21-1.27 (m, 1H, CH_2), 2.24-2.30 (m, 1H, CH_2), 2.28 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.74 (m, 1H, CH), 6.65 (d, J_{P-H} = 36.0 Hz, 1H, =CH), 7.42-7.46 (m, 6H, Ph), 7.51-7.56 (m, 2H, Ph), 7.62-7.67 (m, 2H, Ph).

^{13}C NMR (CD_2Cl_2): δ 15.37 (d, J_{P-C} = 8.8 Hz, CH_3), 15.97 (dd, $^{1}J_{P-C}$ = 11.0 Hz, $^{3}J_{P-C}$ = 4.8 Hz, CH_2), 18.22 (d, J_{P-C} = 10.5 Hz, CH_3), 26.49 (pseudo t, J_{P-C} = 34.5 Hz, CH), 128.76 (d, J_{P-C} = 37.0 Hz, P-C(Ph)), 129.55 (d, J_{P-C} = 9.9 Hz, Ph), 129.76 (d, J_{P-C} = 10.5 Hz, Ph), 130.76 (d, J_{P-C} = 49.1 Hz, =CH), 131.58 (d, J_{P-C} = 1.9 Hz, Ph), 131.79 (d, J_{P-C} = 12.0 Hz, Ph), 132.43 (d, J_{P-C} = 2.4 Hz, Ph), 134.01 (d, J_{P-C} = 13.7 Hz, Ph), 136.13 (d, J_{P-C} = 29.3 Hz, P-C(Ph)), 140.78 (d, J_{P-C} = 39.5 Hz, P-C=), 150.09 (dd, J_{P-C} = 5.7 Hz, J_{P-C} = 17.3 Hz, C-Me), 152.71 (dd, J_{P-C} = 2.5 Hz, J_{P-C} = 7.9 Hz C-Me), 195.97 (d, $J_{(C-P)}$ = 8.1 Hz, $W(CO)_5$ *cis* C=O), 197.17 (d, $J_{(C-P)}$ = 6.3 Hz, $W(CO)_5$ *cis* C=O), 197.78 (d, $J_{(C-P)}$ = 31.9 Hz, $W(CO)_5$ *trans* C=O), 198.86 (d, $J_{(C-P)}$ = 19.0 Hz, $W(CO)_5$ *trans* C=O).

Exact mass: calcd $C_{30}H_{20}O_{10}P_2W_2Na$, 992.9448; found 992.9495.

Isomer **58b**

^{31}P NMR (CD_2Cl_2): δ -156.94 (d, $J_{(P-P)}$ = 5.7 Hz, $J_{(P-W)}$ = 261.1 Hz), 20.29 (d, $J_{(P-P)}$ = 5.7 Hz, $J_{(P-W)}$ = 216.7 Hz).

^{1}H NMR (CD_2Cl_2): δ 1.86-1.93 (m, 2H, CH_2), 2.17 (d, J_{P-H} = 0.9 Hz, 3H, CH_3), 2.29 (d, J_{P-H} = 1.0 Hz, 3H, CH_3), 2.66 (pseudo t, J_{P-H} = 19.6 Hz, 1H, CH), 6.38 (d, J_{P-H} = 36.0 Hz, 1H, =CH), 6.80-6.85 (m, 2H, Ph), 7.01-7.15 (m, 6H, Ph), 7.24-7.34 (m, 2H, Ph).

^{13}C NMR (CD_2Cl_2): δ 14.93-15.07 (m, CH_2), 15.44 (d, J_{P-C} = 8.9 Hz, CH_3), 18.04 (d, J_{P-C} = 10.5 Hz, CH_3), 27.71-28.07 (m, CH), 127.46 (d, J_{P-C} = 37.2 Hz, P-C(Ph)), 129.52 (d, J_{P-C} = 10.2 Hz, Ph), 129.74 (d, J_{P-C} = 10.4 Hz, Ph), 130.52 (d, J_{P-C} = 47.1 Hz, =CH), 130.83 (d, J_{P-C} = 1.9 Hz, Ph), 131.20 (d, J_{P-C} = 30.5 Hz, P-C(Ph)), 131.42 (d, J_{P-C} = 2.3 Hz, Ph), 132.27 (d, J_{P-C} = 12.3 Hz, Ph), 133.23 (d, J_{P-C} = 13.6 Hz, Ph), 139.99 (dd, J_{P-C} = 6.8 Hz, J_{P-C} = 38.8 Hz, P-C=), 148.79 (dd, J_{P-C} = 4.7 Hz, J_{P-C} = 17.1 Hz, C-Me), 151.76 (d, J_{P-C} = 8.0 Hz, C-Me), 196.17 (d, $J_{(C-P)}$ = 8.0 Hz, $W(CO)_5$ *cis* C=O), 197.06 (d, $J_{(C-P)}$ = 6.6 Hz, $W(CO)_5$ *cis* C=O), 198.53 (d, $J_{(C-P)}$ = 31.0 Hz, $W(CO)_5$ *trans* C=O), 198.73 (d, $J_{(C-P)}$ = 19.0 Hz, $W(CO)_5$ *trans* C=O).

Exact mass: calcd $C_{30}H_{20}O_{10}P_2W_2Na$, 992.9448; found 992.9495.

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CHAPTER 3

Synthesis of Phosphole-substituted Fischer Carbene and Examining its Reactivity

3.1 Introduction

In the previous chapter, we have shown the synthesis of 2-vinylphospholes derivatives. And, indeed, the introduction of the vinyl moiety at the 2-position of phosphole does enhance the linear conjugation between the diene of phosphole and the exocyclic vinyl group. This is evident by [4+2] cycloadditions taking place via both the intra- and extra-annular pathway.

Thus, we pondered about the effect of a more polarising substituent with vinylic π-orbitals if it is placed on the α-position of phosphole. At this point, the chemical property of the metal-carbon bond of Fischer carbenes caught our attention.

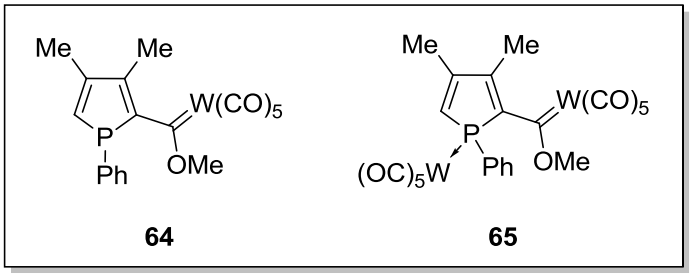
The first introduction of a stable carbene by Fischer in 1964[1] has opened a new class of organometallic complexes in chemistry. Since then, extensive studies on Fischer carbenes have been performed. Till today, their chemical versatility is still warmly embraced as a valuable tool in many organic and natural products syntheses.[2-6] Recently, their unique physical properties have grabbed the attention of material scientists dealing with organic non-linear optics materials.[7]

The synthesis and research on the first monocarbene complexes with 5-membered heteroaromatic substituents date back to 1971.[8] Also, it has been figured that conjugated Fischer carbene complexes, especially complexes with aromatic moiety (benzenes, furans, thiophenes and pyrroles) showed higher extension of π-electron delocalization.[9]

To our knowledge, nothing is known on the corresponding phosphole derivatives. Noticeably, the exploration of the chemistry and structural features of Fischer carbene complexes containing phosphole have been neglected compared to the other 5-membered heteroaryl analogues.

Therefore, the objective of this chapter is to prepare the phosphole-substituted Fischer carbene complexes **64** and **65**. Since, the aromaticity of phospholes is much poorer than that of other 5-membered heteroarenes,[10] better π-electron delocalization would be expected.

Furthermore, the presence of the metal moiety should induce a higher polarization of the π-electron density of the dienic unit of phosphole with the carbene.



In consequence, these Fischer carbene complexes substituted with phosphole might or might not react differently from the usual Fischer carbene complexes. In order to clear this uncertainty, phosphole Fischer carbene complexes **64** and **65** will be subjected to a series of chemical reactions which are usually used on Fischer carbene complexes. These reactions are namely; oxidation by DMSO, hydrolysis, reaction with alkenes and alkynes.

3.2 An Overview of Carbene Complexes

Carbenes are compounds with a neutral divalent carbon atom with six electrons on its valence shell. Their existence was first suggested in 1855 by Geuther and Hermann.[11] Continuous interrogations have yielded the discovery of two types of metal carbene complexes, Fischer cabenes and Schrock carbenes.

Generally, these two types of organometallic complexes differ by a few characteristic features which are summarised in the table below (Table 3.1). There are cases where the following criteria for the classifying become arbitrary. An example is the osmium carbene complex $[Os(CH_2)(PPh_3)_2(NO)Cl]$.[12]

Table 3.1 Characteristics of metal carbene complexes

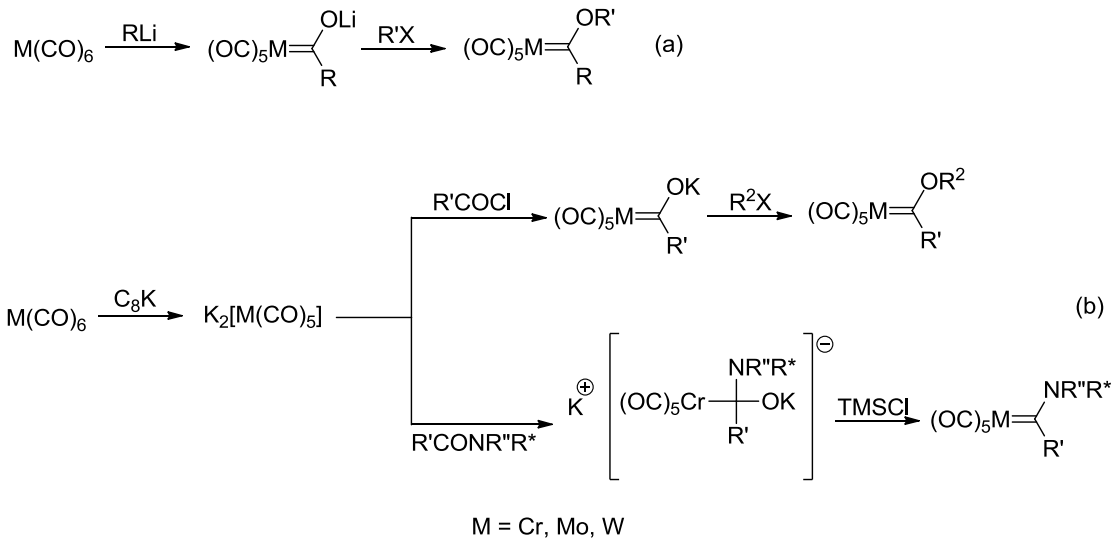
Fischer carbene	Schrock carbene
Low oxidation state metals	High oxidation state metals
Heteroatom at the carbenic centre	Alkyl group or H atom linked to carbene
π-acceptor ligands on metal	Variety of ligands on metal
Electrophilic carbenic centre	Nucleophilic carbene carbon

The scope of reactions of Fischer carbenes is very wide. Thus, these multifaceted complexes have earned a place as a valuable reagent in organic synthesis. While the fortes of Schrock carbenes lie in olefin metathesis[13] and as substitutes for phosphorus ylides in Wittig reactions.[14]

In this section, we will limit the discussion to the chemistry of Fischer carbene complexes especially those substituted with 5-membered heteroarenes. This will provide a better contrast between the phosphole-substituted carbene complexes formed with the O, N and S analogues. Thus, more in-depth information on Fischer carbenes and Schrock carbenes may be obtained in many references.[3,4,15-23]

3.2.1 Synthesis, structure and general reactivity of group VI Fischer carbene complexes

There are two methods available to generate Group VI metal Fischer cabene complexes. The Fischer method is the most general entry, it involves the coupling of organolithium reagents with $M(CO)_6$ (where M = Cr, Mo, W). Followed by the *in-situ O*-alkylation with hard alkylating reagents, such as trialkyloxonium tetrafluoroborates or alkyl fluorosulfonates (Scheme 3.1a). The second synthetic entry is via the Semmelhack-Hegedus route (Scheme 3.1b).[24-26] This method is recommended if the organolithium componds are not available.



Scheme 3.1 Fischer method (a) and Semmelhack-Hegedus (b) route to Group VI metal carbene complexes

Both techniques are still applicable today for the synthesis of a series of novel carbene complexes such as biscarbenes[27-30] and π σ polymetallic carbene complexes.[31]

Structurally, the metal-to-carbon bond in Fischer complexes is often represented as $L_nM=CR_2$. In fact, a better representation would be $R_2C\rightarrow ML_n$. This is because the metal-to-carbon bond arises from the ligand→metal σ donation and metal→ligand π back donation (Figure 3.1).[32]

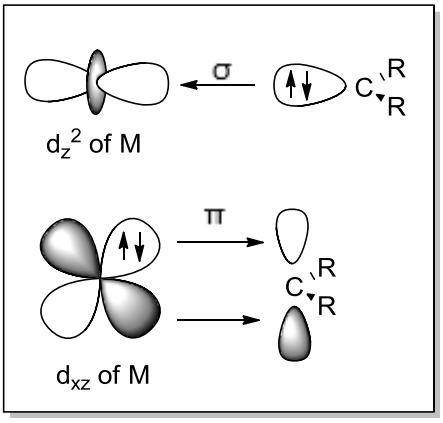


Figure 3.1 Dominant orbital interactions of Fischer carbene complexes

Consequently, this metal-to-carbon interaction is rendering the carbenic carbon its electrophilic nature. Predictably, Fischer carbene complexes act like carbonyl reagents (Figure 3.2). Wider range of reactions can be achieved by replacing the alkyl group by an unsaturated substituent. By doing so, the conjugated carbene complexes will possess the behaviour of an activated ester.[19] Within the varieties of chemical tranformations, Dötz discovered the useful benzannulation. It is a [3+2+1] cycloaddition of the Fischer complexes to alkynes with CO insertion, prevalently known as the Dötz reaction.[3,16]

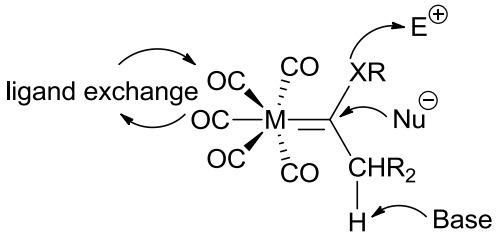
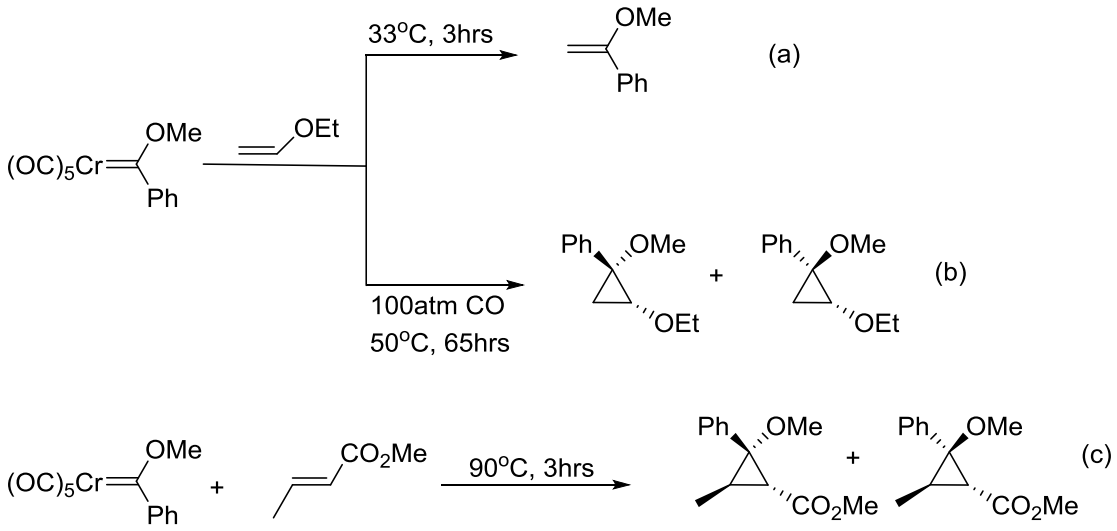


Figure 3.2 Possible reactions on group VI Fischer carbene complexes

Reviewing the references, Fischer carbene of group VI metal complexes with unsaturated substituents opened up an array of organic products to be formed. Since, the aim in this chapter is to compare the role of aromaticity of phospholes on the carbene moiety or vice versa. Thus, in the following discussions we will focus on complexes with aromatic substituents (concentrating mainly on 5-membered heteroarenes).

3.2.2 Reaction of (alkoxy)(aryl)carbene group VI metal complexes with alkenes

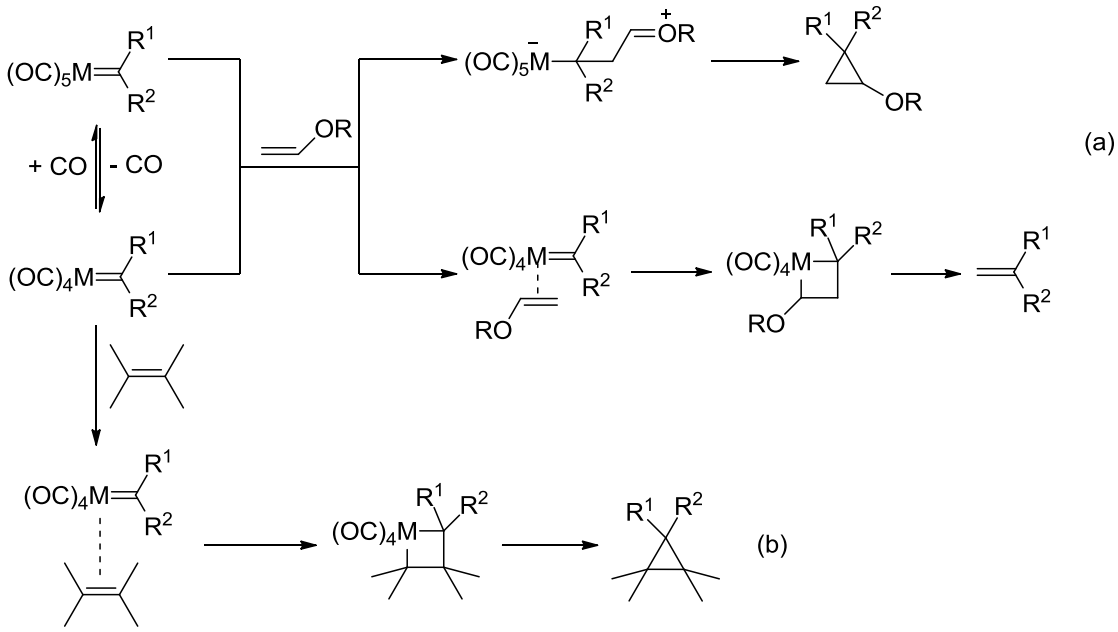
In general, the reaction between Fischer carbene complexes and alkenes proceed with two major routes, namely, olefin metathesis and cyclopropanation. The pathway which the reaction will undergo and the outcomes of the reactions depend on several factors.



Scheme 3.2 Reaction between (Ph)(OMe)C-Cr(CO)$_5$ with alkenes

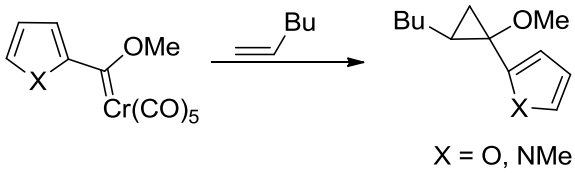
The examination of the reaction pathway between chromium complex of (alkoxy)(aryl)carbene with alkenes was reported by Fischer and Dötz. It has been illustrated that the alkenes is one of the factors. In the work, it was reported that if electron-rich alkenes were used, only the methatheses products were obtained (Scheme 3.2a). The cyclopropanated products can be obtained (in the absence of olefin metathesis product) when the experiment was conducted under high pressure of carbon monoxide (100atm) (Scheme 3.2b).[33] On the contrary, electron-deficient alkenes afforded only cyclopropanation products (Scheme 3.2c).[34,35] These early results suggest that different tranformative mechansims are involved when different alkenes are used (Scheme 3.3).[36,37]

Metal on the carbene complexes also plays a crucial role on the isomeric ratio of the cyclopropanation products. In the similar work (Scheme 3.2c), the molydenum derivative gave a higher isomeric ratio of the cyclopropanated products than the chromium or tungsten analogues. In order to show that metal does play a part in the product formation, Cooke and Fischer performed the [2+1] cycloaddition of diethyl fumarate with a chiral chromium carbene complex.[38] If free carbene was formed before the cycloaddition, then, non-chiral cyclopropanated product would be obtained. However, optically active products were isolated. Thus, indicating that the metal takes part in the product formation.



Scheme 3.3 Mechanisms of metal-carbenes complexes with electron-rich alkenes (a) and electron-poor alkenes (b)

The study of heteroaryl carbene complexes with alkenes emerged recently. Barluenga's group has explored the reaction between 2-furan- and 2-(N-methylpyrrole)-substituted Fischer carbene complexes with 1-hexyne (Scheme 3.4).[39] These complexes also go through cyclopropanation with moderate to good yield.



Scheme 3.4 Cyclopropanation of 1-hexyne with heteroaryl Fischer carbene complexes

The usefulness of Fischer carbenes in the formation of substituted cyclopropanes has led to an extensive study of different alkenes to be used, such as unactivated alkenes and 1,3-dienes.[16,17,40-42] In addition, the presence of the heteroaromatic rings on the Fischer carbenes did not disturb the cyclopropanation pathway. Thus, Fischer carbenes act as an excellent synthon for highly substituted cyclopropanes.

3.2.3 Annulations of group VI (alkoxy)(aryl/heteroaryl)carbene complexes with alkynes

After accessing the reaction with alkenes, one would expect the reaction of group VI carbene complexes and alkynes to give the 3-membered products, cyclopropenes. However, the unsaturated 3-membered ring was never obtained despite the continuous probing by chemists. Presumably, the only example of cyclopropenation was between the cationic iron-carbene complex with 2-butyne.[43]

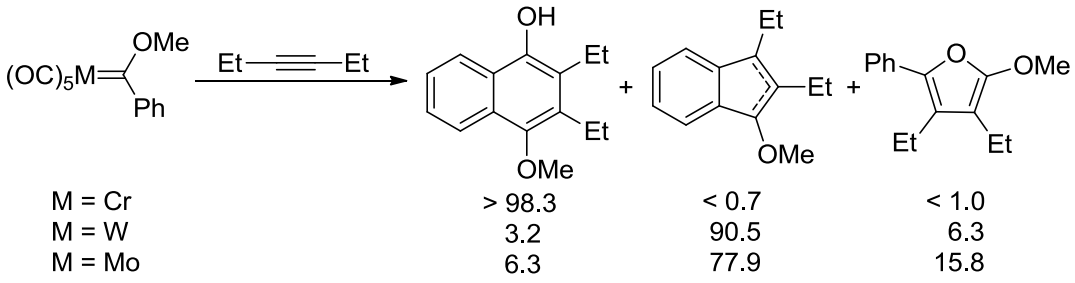
Although the inability to form cyclopropenes via this reaction, a major discovery, and probably the essence of Fischer carbenes in organic synthesis, was made in the reaction with alkynes. It is the discovery of benzannulation in 1975 by Dötz,[44] hence, the name, Dötz reaction. Today, this [3+2+1] cycloaddition reaction of α,β-unsaturated carbene ligands (C_3), alkynes (C_2) and CO (C_1), has been highly cited.[3,16,40,41,45-47]

However, the reaction between group VI metal carbonyl Fischer carbene complexes with α,β-unsaturated substituents and alkynes does not always occur in the [3+2+1] manner. Certain conditions will affect the occurence of this pathway. Thus, this leads to the diverse range of products formed which include cyclopentannulated products, furans, cyclobutenones, vinyl ketenes, etc.[19]

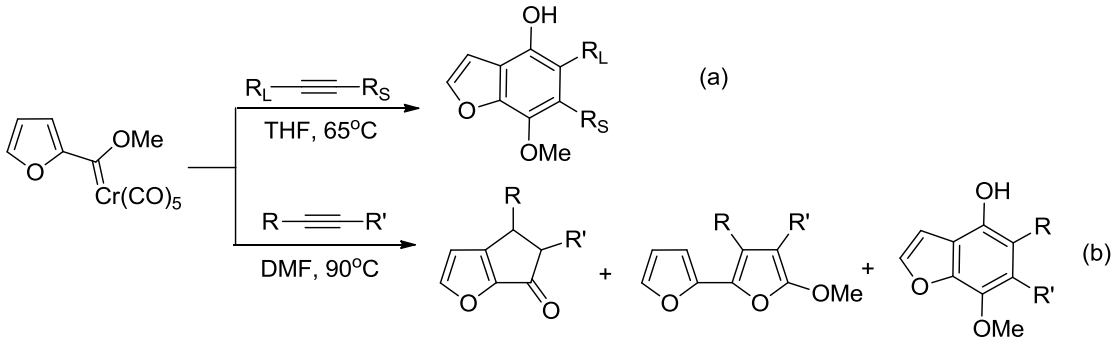
Within this short chapter, it is impossible to cover all aspects regarding the reaction of carbene complexes with alkynes. Thus, in order to serve as a reference for this project, only

examples of group VI metal (alkoxy)(aryl or heteroaryl)carbenes complexes will be analyzed. Detailed evaluations which are not found here can be obtained in the many reviews mentioned.[2-6,15,18,41,45,47]

In the reaction between carbene complexes and alkynes, many competing pathways might take place giving a range of products. Therefore, one of the aspects of annulation of carbene with alkynes is the metals employed. The three group VI metals carbene complexes give different percentages of products. This is proven by the example shown below (Scheme 3.5). In the case the chromium complex, hydroquinone was obtained almost exclusively. This product is formed from the benzannulation pathway. On the other hand, the tungsten and molydenum analogues favour the [3+2] cycloaddition, giving indene as the major product.[48] Comparing the ratio of the product distribution, complexes with Cr metal tend to undergo CO insertion. The reason for this trend observed is probably due to the weaker Cr-CO bond strength among the three metals.[49,50]



Scheme 3.5 Effect of metal on the cyclization reactions

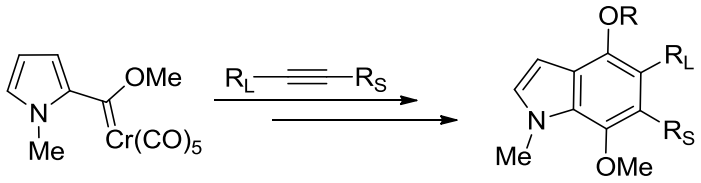


Scheme 3.6 Reaction between methoxy-2-furylcarbene complexes and alkynes under different condition

The other factors that may disturb the occurrence of benzannulation include solvent used, ligand on the carbene ligand, concentration and temperature applied. All these have been documented thoroughly.[51]

Furan- and thiophene-substituted Fischer carbene chromium complexes have been explored back in the late 1970s. Dötz *et al.* reacted (2-furyl or 2-thiophene)methoxycarbene chromium complexes with either tolan or 1-pentyne.[52] As expected, benzannulation took place giving benzofuran and benzothiophene derivatives. Also, the reaction with the terminal alkyne yielded the products bearing the larger substituent next to the phenol (Scheme 3.6a). This regioselectivity which is an important criterion of benzannulation, is generally observed in many other Dötz reactions. Then, Yamashita extended the chemistry of furan- and thiophene-substituted Fischer carbene with alkynes by changing the solvent used and the ligand on the carbene. Indeed, his work demonstrated that polar solvent (DMF) and the amino ligand (instead of OMe) on the carbene affect the occurrence of benzannulation (Scheme 3.6b).[53,54]

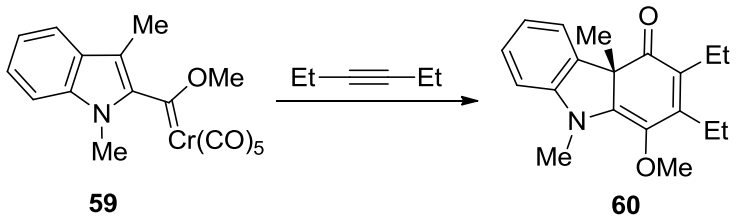
Yamashita's group also studied the reaction between alkoxy(pyrrole)carbene complexes and alkynes. In 1985, they studied the chromium carbene complex bearing N-methylpyrrole substituent with various alkynes.[55,56] Hydroindoloquinones were successfully obtained through benzannualtion. Again, when asymmetrical alkynes were used, the major regioisomer bears the larger alkyne substituent next to the phenol (Scheme 3.7).



Scheme 3.7 General product obtained between $[Cr(CO)_5C(OMe)(C_5H_6N)]$ with alkynes

A few years later, Wulff and co-workers addressed the reactivity of complex **59** with alkynes. This complex contained a methyl moiety on the ortho-position on the pyrrole ring with respect to the carbene functionality. It has been shown that 2-6-dibsubstituted-aryl carbene complex and alkynes does not undergo the usual benzannulation but instead pentannulation. Thus, curiosity grew about the reactivity of complex **59**. Unexpectedly, the methyl moiety did not

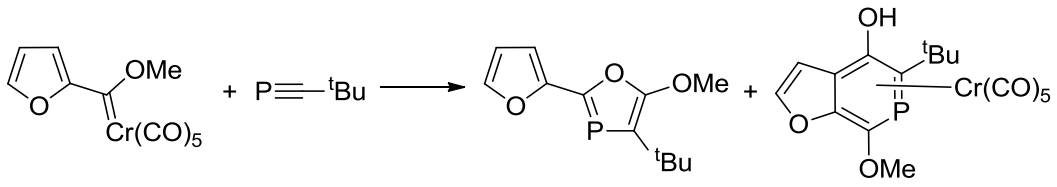
block the CO-insertion and product **60** was obtained in high yield (Scheme 3.8).[57] The poor aromaticity of the benzopyrrole moiety may be an explanation.



59 **60**

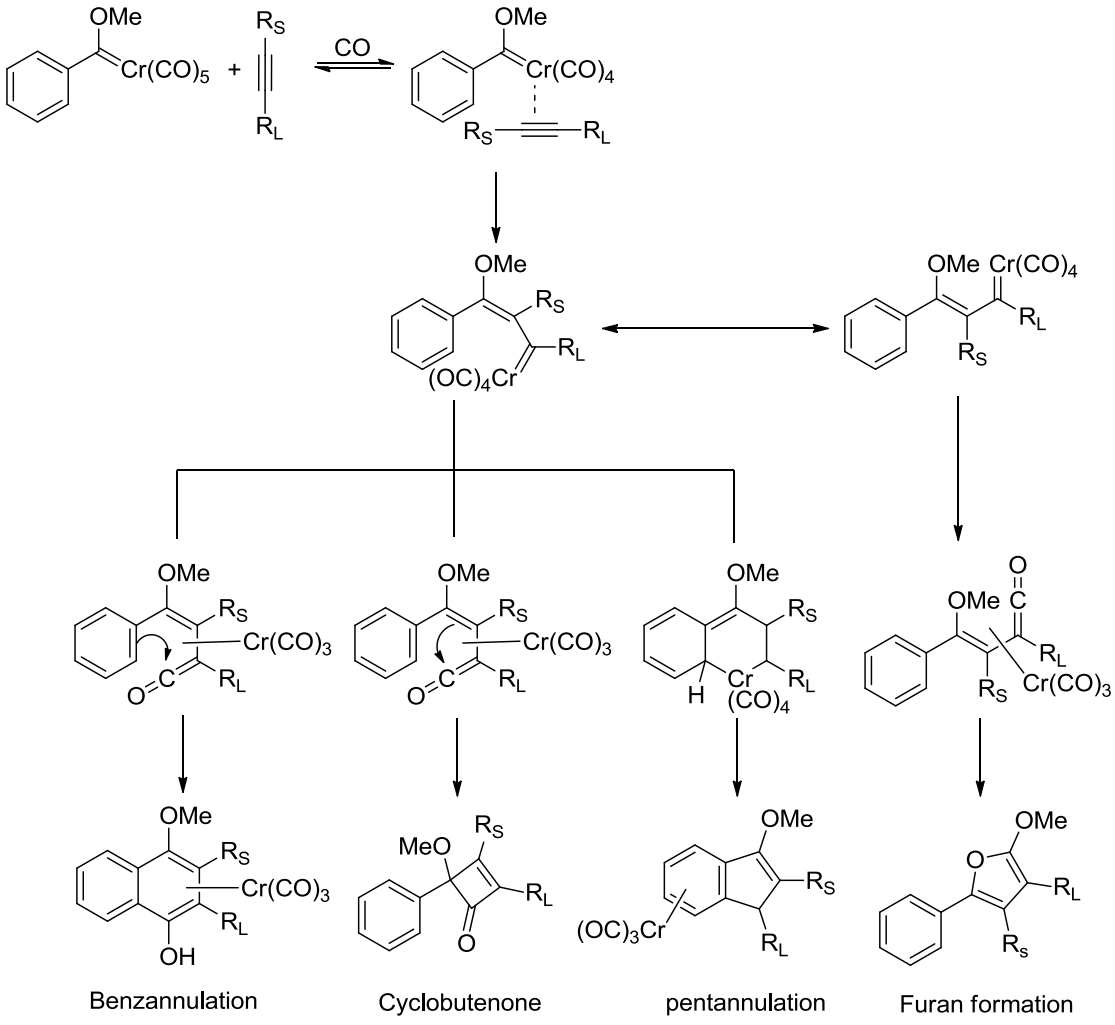
Scheme 3.8 Unexpected benzannulation of complex **56** with diethylacetylene

The scope of functionality on alkynes that can be used are found to be very wide and it has been extended to heteroalkynes. An alkyne mimic, *tert*-butylphosphaethyne was reacted with a series of α,β-unsaturated carbene chromium complexes generating phosphinine derivatives (Scheme 3.9).[58]



Scheme 3.9 Annulation with heteroalkyne

It is understood that more often than not chromium carbene complexes favour the Dötz pathway. However, from the examples shown, there are instances where other pathways will take place in the reaction between the metal-carbenes and alkynes. There are four possibilities through which the reaction can proceed. Out of the four, two are major routes, namely, [3+2] and [3+2+1] cycloadditions that produce cyclopentadiene (or indene) and benzannulation (or cyclohexadienone) respectively. The other two routes are [2+1+1] and [2+2+1] cycloadditions which give cyclobutenone and furan correspondingly. And the scheme below summarises the mechanisms between the four competitive pathways (Scheme 3.10).



Scheme 3.10 Four competitive pathways in annulation with alkynes

3.3 Summary

In a nutshell, Fischer carbenes complexes are stabilized carbenes which coordinate to low valent transition metals. They can be easily obtained by either reacting organolithium with metal carbonyl followed by alkylation or via the Semmelhack-Hegedus method. Since the carbenic carbon is electron deficient, it frequently bears a π-donating substituent which allows electronic stabilization. The other carbene substituent may be a saturated or unsaturated moiety.

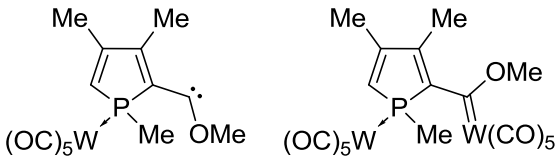
With the ease in obtaining Fischer carbene derivatives via the two synthetic routes mentioned, heteroaryl carbene complexes have long been introduced. As illustrated, all these

complexes possess similar chemical behaviour as the other Fischer carbenes bearing saturated and unsaturated substituents.

Thus, the next section will explore the behaviour of the phosphole-substituted Fischer carbene complexes **64** and **65**.

3.4 Results and Discussion

The complete lack of information about phospholylcarbene complex advises the need for some vision on the fundamental structure. Thus, compound **61** which is the free carbene and complex **61-W** which is the stabilized form, are computed by DFT at the B3PW91/6-31G(d)-Lanl2dz(W) level[59] (Figure 3.3 and 3.4 respectively).



61 **61-W**

These two compounds differ by two characteristics. Firstly, the bond length between C4-C22 in compound **61-W** is 1.466 Å, 0.024 Å longer than that of compound **61** (1.442 Å). This difference is attributed to the existence of backbonding between W metal and the p-orbital of carbenic carbon atom. As a consequence, the π conjugation between the diene unit of phosphole and the carbene may weaken, thus lengthening of the C4-C22 bond distance. Secondly, the dihedral angle of C=C-C-O in **61** has been calculated to be -68.5°. However, the two bulky $W(CO)_5$ groups in **61-W** may have caused spatial crowding. Therefore, the result is a drastic change in the dihedral angle of C=C-C-O in **61-W** (68.8°).

Besides the physical properties, these two characteristics also reveal the possible chemical reactivity of the phospholylcarbene complexes to be synthesized. The weakened linear π conjugation due to the backbonding in **61-W** hinted the possibility of a weak carbene-tungsten bond. Without a doubt, the energy required to break the C-W bond in **61-W** to get **61** and singlet $W(CO)_5$ is calculated to be 61.6 kcal/mol. Significantly lower by 20.4 kcal/mol when compared to $(CO)_5W{=}C(H)(OH)$ (D_e = 81.8 kcal/mol).[32] However, this direct comparison only provides an estimation of trends since different theorectical methods were used. The non-zero dihedral

angle of C=C-C-O of **61** illustrates that the carbene is not co-planar with the diene of phosphole so maximal overlap of the p-orbital and the π-orbital of diene may not be achieved. Nevertheless, the relatively short C4-C22 bond length (1.442 Å) suggests the presence of substantial delocalization of the π-electrons between the two units. The combination of p-orbital of carbene with the LUMO of diene seen from the Kohn-Sham orbitals (Figure 3.5) also verifies the existence of sizable conjugation. Altogether, this denotes that conjugation will be restored when the stabilized carbene **61-W** dissociates to the free carbene form **61**.

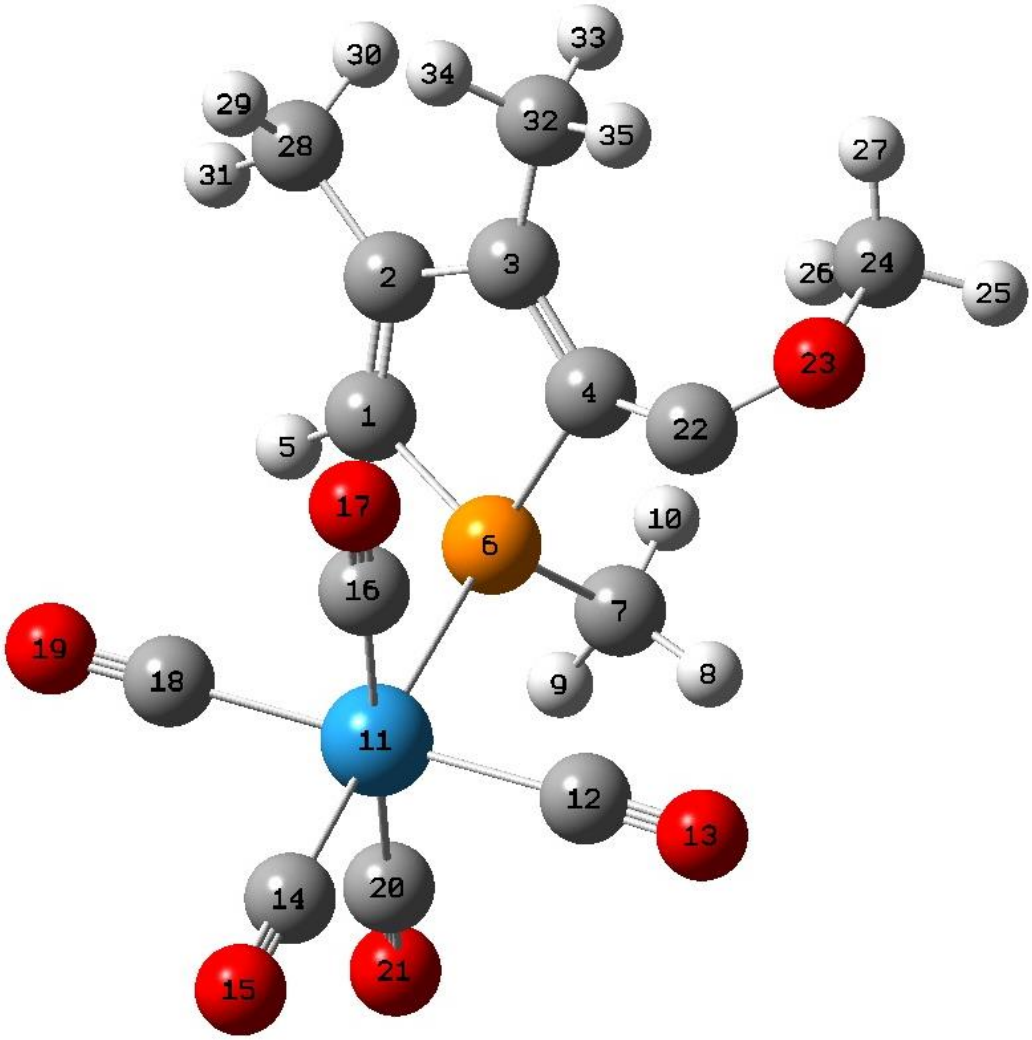


Figure 3.3 Computed structure of phospholylcarbene **61**. Main distances (Å) and angles (deg.): P-W 2.520, P-Me 1.849, P-C1 1.802, P-C4 1.840, C4-C22 1.442, C22-O23 1.301, C1-C2 1.354, C2-C3 1.475, C3-C4 1.377; C1-P-C4 91.0, C4-C22-O23 120.1, O23-C22-C4-C3 -68.5

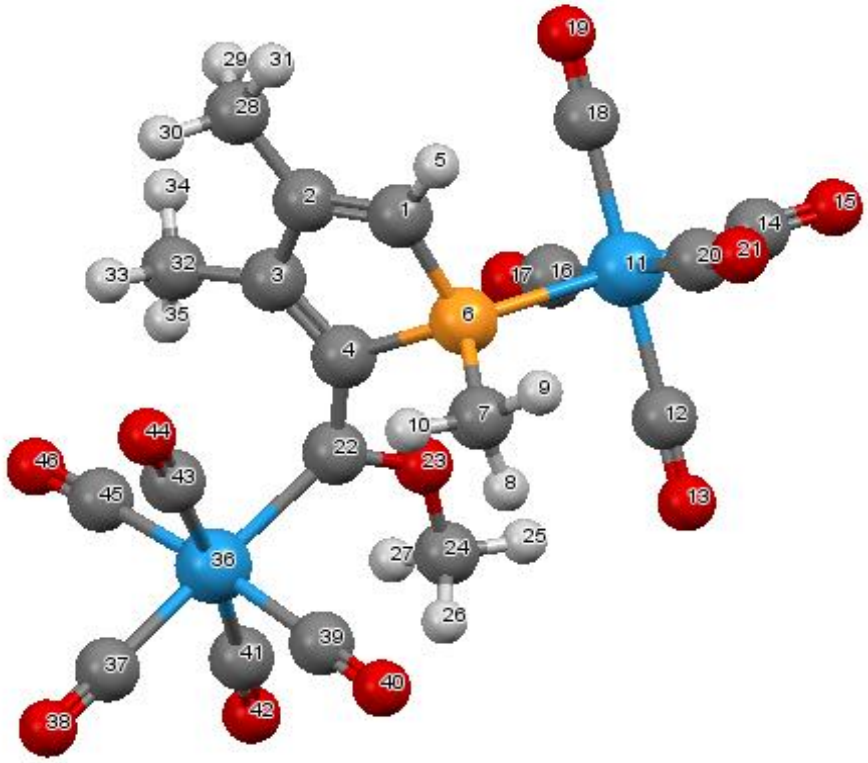


Figure 3.4 Computed structure of phospholylcarbene tungsten complex **61-W**. Main distances (Å) and angles (deg.): P-W11 2.543, P-Me 1.845, P-C1 1.797, P-C4 1.845, C4-C22 1.466, C22-O23 1.327, C22-W36 2.207, C1-C2 1.353, C2-C3 1.477, C3-C4 1.371; C1-P-C4 90.8, C4-C22-O23 106.1, O23-C22-C4-C3 68.8

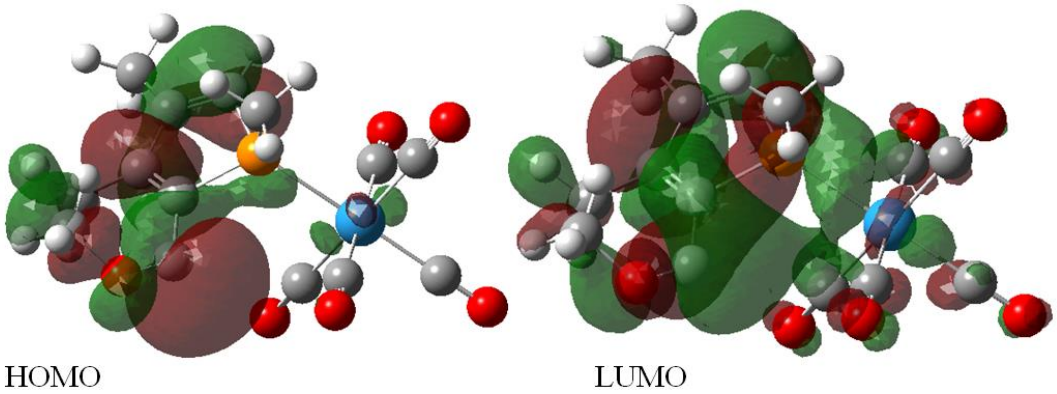


Figure 3.5 Computed HOMO and LUMO of compound **61** (Kohn-Sham)

Merging these bits of data from the computed structures, we can expect a reactive carbene-tungsten bond since the delocalization of π-electrons will be reinstalled in the free carbene. In addition, the poor aromaticy of phospholes will cause a more pronounced linear π-

conjugation. Thus, this appealing approach in combining Fischer carbene with phosphole will bring about a unique chemistry that has not been observed from the O,S and N analogues of Fischer carbene complexes (Section 3.2.2 and 3.2.3).

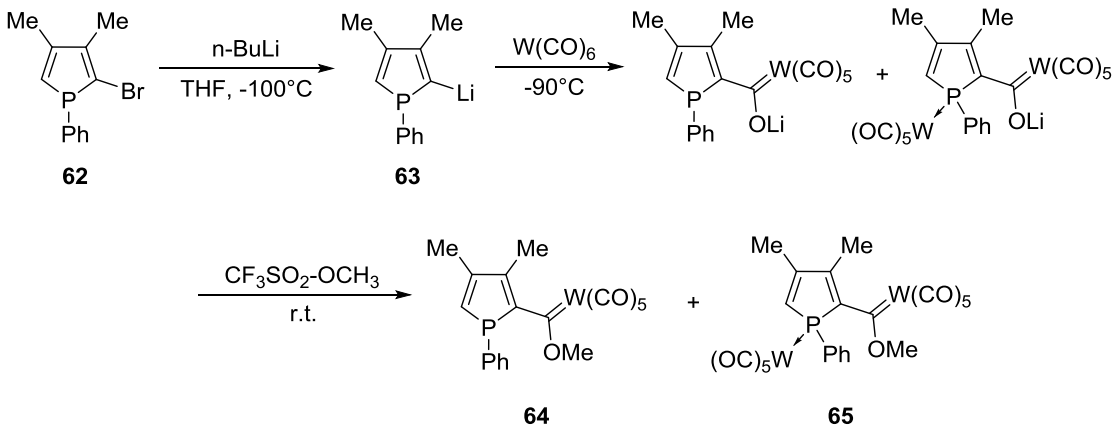
As we have seen in Section 1.4.5, the generation of lithiophosphole can be easily obtained via the lithiation of bromophospholes by n-BuLi at low temperature. Thus, phospholylcarbene tungsten complex **64** and **65** were synthesized via the most general entry by Fischer as discussed earlier (Section 3.2.1).

2-lithiophosphole **63** was reacted with $W(CO)_6$ at -90°C for 30mins. As the presence of excess n-BuLi added to lithiate 2-bromophosphole **62** will compete with **63** for $W(CO)_6$ to form butylcarbene tungsten complex, two equivalent of $W(CO)_6$ was added. This is followed by *in-situ* O-alkylation with MeOTf after the reaction mixture was warmed up to room temperature (Scheme 3.11). The crude mixture was monitored by ^{31}P NMR before purification and several peaks were present. Besides the desired complex **65** at 23ppm and at 14ppm for compound **64** (minor), there are several other peaks which fall between 33 and 46ppm.

During the purification on silica at -20°C with hexane, the bright yellow undesired (n-Bu)(OMe)C=$W(CO)_5$ was eluted first. As the polarity of eluent was gradually increased by the addition of DCM, bright red fraction of **64** was eluted. Following behind was the darker red band containing **65**. However, as the polarity of both compounds are quite similar, only enriched solution of **64** was obtained. The rest of the peaks which fall between 33 to 46ppm were attained only after flushing the column with ethyl acetate. Since further purifiaction of the last fraction was not successful after several attempts, it was not characterized.

Both complex **64** and **65** were fully characterised and structurally established by X-ray crystallography (Figure 3.6 and 3.7 respectively). From their ^{13}C NMR spectrum, the corresponding carbenoid carbon in each compound shows up at the significantly downfield shift at 316.94ppm and 316.87ppm as expected. The difference is so small that it can be assumed that they are practically identical. They are also fairly close in structure after comparing their structural parameters. There are some minute differences such as the slightly longer C=W bond in **64** than in **65** (2.202(2) vs. 2.137(4) Å) and a somewhat shorter ring-carbene length (1.462(3) vs. 1.475(6) Å). These differences may due to the stabilization of diene by delocalization of the

phosphorus lone pair and hyperconjugation is playing against the delocalization with the carbene. At this point, no conclusive comment on their chemical reactivity can be drawn, especially since compound **64** bears two reactive sites (lone pair on P and the electrophilic carbene).



62 **63** **64** **65**

Scheme 3.11 Formation of carbenes **64** and **65** by Fischer method

Correlating of the X-ray structure of **65** to the computed structure **61-W** shows some minor differences. Firstly, the bond length between the carbene carbon and diene (C6-C8) is 1.475(6)Å (similar to thiophene-carbene derivatives[9,27,29,30]) which is slightly longer than **61-W**. Secondly, the angle made between the plane of the diene with the plane of carbene (O6-C6-C8) is found to be 48.2°. Thus, the structure of **65** is highly similar to the computed one.

Later on, the experiment was revisited by changing $W(CO)_6$ to one equivalent. With the two equivalent of $W(CO)_6$ added, it was proposed that the first equivalent reacted with the carbanion whereas the lone pair on phosphole coordinated to the second equivalent with elimination of CO. Hence, giving complex **65** as the major product and the σ^3-phosphole-substituted Fischer carbene **64** as the minor one. In order to prove that this is true, the experiment was repeated with one equivalent of $W(CO)_6$ instead. This time round, the product distribution was reversed and uncomplexed-phosphole carbene **64** became the dominant product (isolated yield was 18% for **64** vs. 10% yield for **65**).

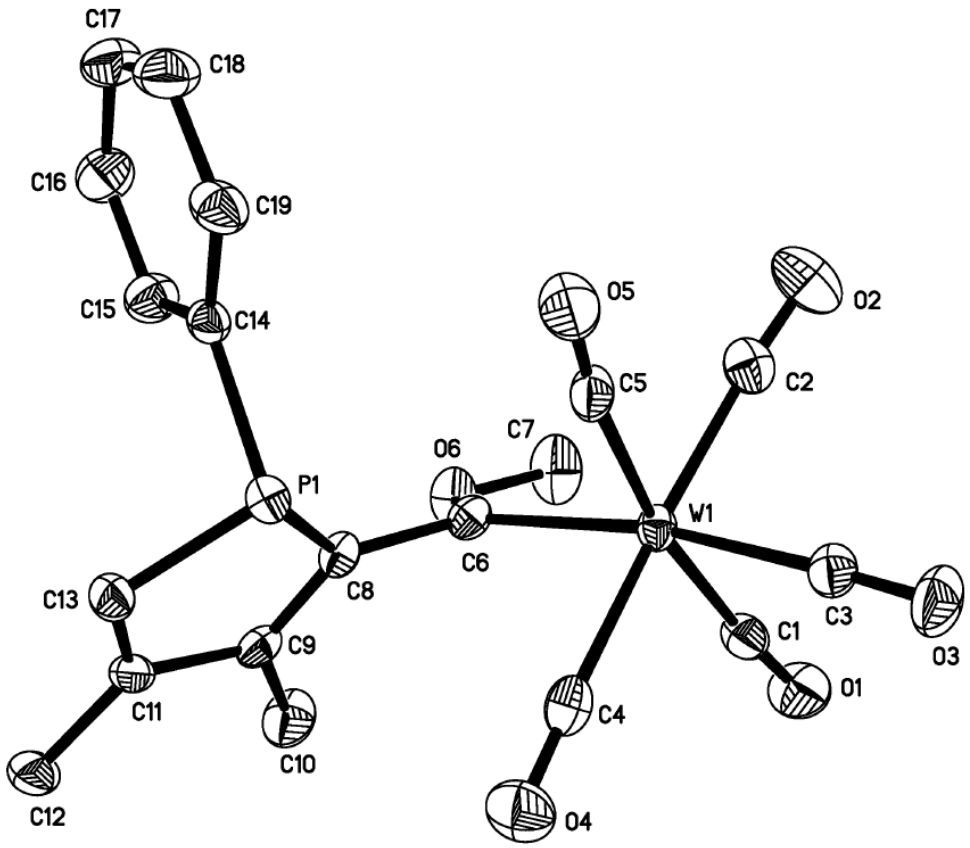


Figure 3.6 X-ray crystal structure of the σ^3-phosphole substituted Fischer carbene complex **64** Main distances (Å) and angles (deg.): P-C14 1.836(3), P-C8 1.820(2), P-C13 1.785(3), C8-C9 1.373(3), C9-C11 1.470(4), C11-C13 1.347(4), C8-C6 1.462(3), C6-O6 1.327(3), C6-W1 2.202(2); C8-P-C13 90.04(11), O6-C6-C8 106.7(2), O6-C6-W1 130.62(17), C8-C6-W1 122.19(17).

An interesting incident was noted between compound **64** and **65**. An NMR sample of **64** in DCM was left to stand at room temperature and monitored daily by ^{31}P NMR. Peak at 23ppm which belongs to complex **65** gradually appeared. Within a week, peak at 14ppm (compound **64**) was absent leaving behind a messy spectrum showing a major peak at 23ppm. This may be due to the lone pair on P in **64** coordinated to the tungsten on another molecule of **64** which results in the formation of complex **65**.

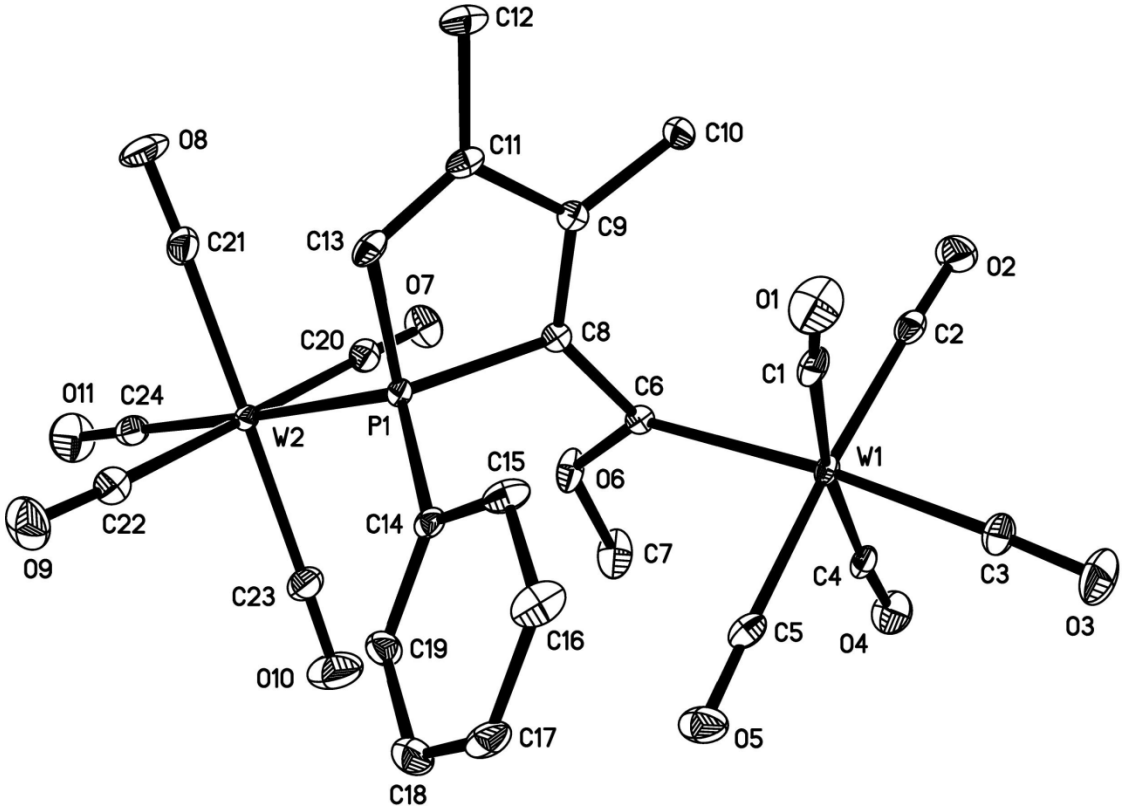
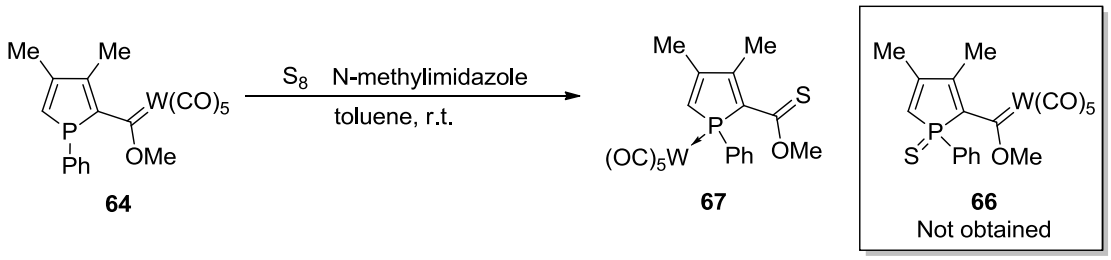


Figure 3.7 X-ray crystal structure of the phosphole substituted Fischer carbene complex **65** Main distances (Å) and angles (deg.): P-W 2.5263(12), P-C14 1.821(5), P-C8 1.836(4), P-C13 1.789(5), C8-C9 1.359(7), C9-C11 1.486(7), C11-C13 1.340(7), C8-C6 1.475(6), C6-O6 1.332(5), C6-W1 2.173(4); C8-P-C13 90.7(2), O6-C6-C8 104.7(4), O6-C6-W1 129.5(3), C8-C6-W1 124.1(3).

Up till now, the targeted phosphole carbene tungsten complex **65**, together with the σ^3-phosphole carbene complex **64** were successfully synthesized and characterized. In terms of structure, complex **65** resembles closely to the computed **61-W** and the thiophene carbene analogues. Thus, the next step would be to investigate the reactivity of these two phospholylcarbene complexes by a series of chemical reactions.

Compound **64** intrigued us because the P atom of the phosphole moiety is trivalent. Thus, it could serve as a basis of comparison to the other 5-membered heterarylcarbenes especially pyrrolylcarbenes. However, one has to recall that unlike the O, S and N analogues, phosphole which is weakly aromatic (Section 1.2.1) contains a nucleophilic lone pair. Thus, more than one reactive sites can be anticipated.

In order to test the reactivity of compound **64**, it was subjected to sulfurization by elemental sulfur. It has been shown many times that σ^3-phosphole can be sulfurized easily to σ^4-P.[60-62] Unexpectedly, after overnight reaction with elemental sulfur at room temperature, 2-thioester-phosphole tungsten complex **67** was obtained quasi-quantitatively (Scheme 3.12). Instead of sulfurization of the σ^3-P to give compound **66**, the carbene carbon was sulfurized and the $W(CO)_5$ group moved onto the P. Complex **67** was unambiguously characterized and X-ray analysis was performed (Figure 3.8). The thiocarbonyl carbon shows up at 204.6ppm in ^{13}C NMR and the P-W coupling is 225Hz.



Scheme 3.12 Sulfurization of compound **64**

A related work which involved elemental sulphur, CO and a Fischer-carbene-$Cr(CO)_5$ leading to the formation of thioester and $Cr(CO)_6$ was found after thoroughly reviewing the literature.[63] This published work reported the efficient sulfurization promoted by CO introduced at atmospheric pressure. In our case, the intramolecular σ^3-P of phosphole might have played the role of the CO as a ligand, thus promoting the sulfurization. The ability of tricoordinated P to act as a ligand can be supported by the observation mentioned earlier on the self-conversion of compound **64** to complex **65**. Hence, from the total absence of the sulfurized **66**, we can conclude that the carbene carbon is more reactive than the trivalent phosphole unit.

After identifying the more reactive site, compound **64** was then subjected to a few chemical reactions with unsaturated reagents (such as styrene and tolan) under different reaction conditions. However, all the trial experiments produced many undistinguishable peaks in the ^{31}P NMR. This may be a result of the presence of two reactive components in **64**. Thus, the multiple reactive sites in compound **64** caused the selective reaction at the carbene centre to be compromised.

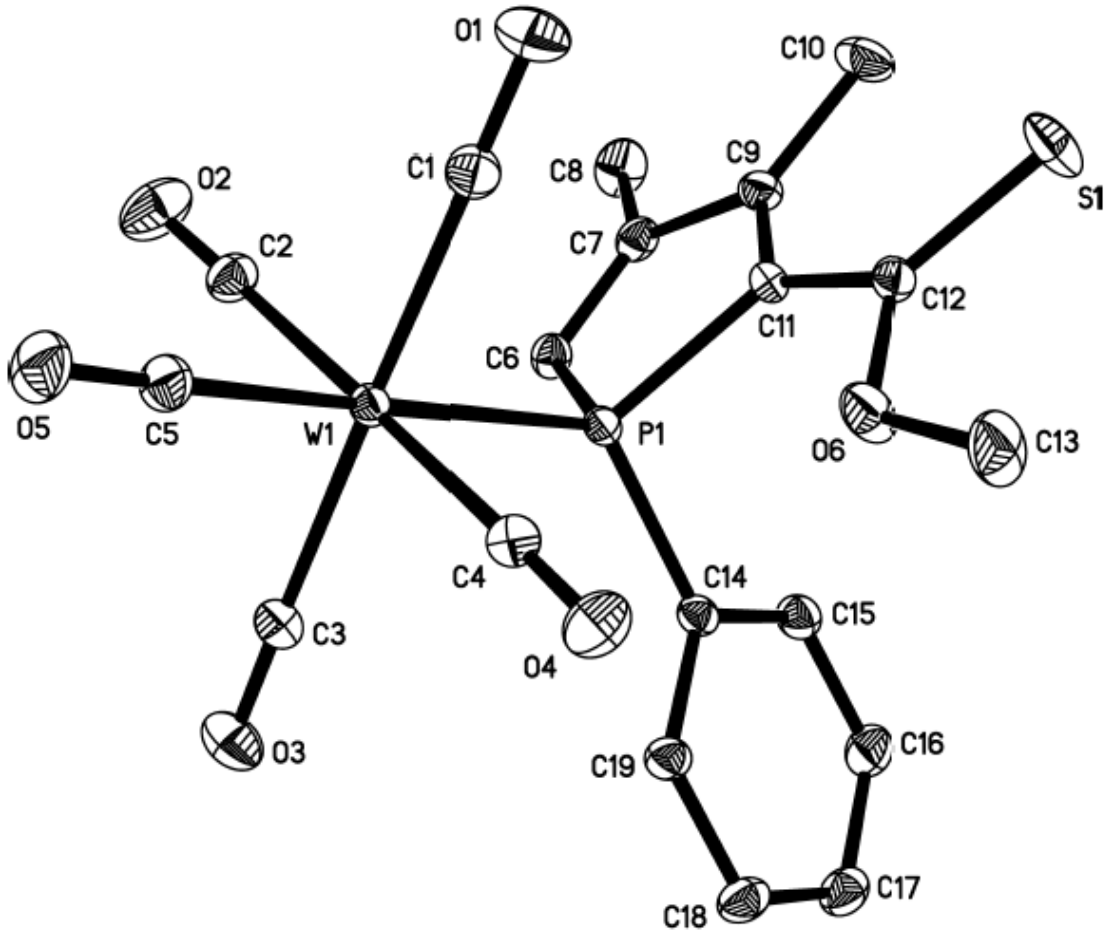
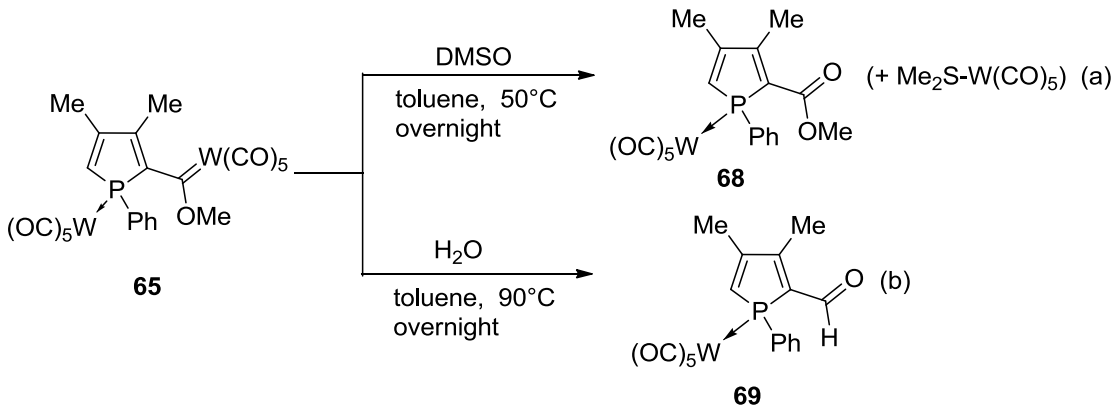


Figure 3.8 X-ray crystal structure of the 2-thioester-phosphole complex **67** Main distances (Å) and angles (deg.): P-W 2.5062(6), P-C11 1.820(2), P-C6 1.789(2), P-C14 1.825(3), C6-C7 1.343(4), C7-C9 1.480(4), C9-C11 1.373(3), C11-C12 1.451(3), C12-S 1.635(3), C12-O6 1.352(3); C6-P-C11 90.70(11), O6-C12-C11 109.3(2), O6-C12-S 122.34(19), C12-C11-P 121.16(17).

Now, the best candidate left to study the chemistry of phospholylcarbene is complex **65** since the reactive lone pair on P is now protected by $W(CO)_5$ group. Thus, no side reaction will take place other than those of the carbenic carbon.

It is known that the M=C functionality in Fischer carbene can be readily altered to other functional groups such as ester and aldehyde.[2,64] Therefore, these two most fundamental chemical modifications were selected to examine the chemistry of complex **65**.

Dimethyl sulfoxide (DMSO), a common reagent for oxidising Fischer carbene complexes, was added to complex **65** in toluene (Scheme 3.13a). Visible reaction (monitored by ^{31}P NMR) occured when the reaction mixture was heated to 50°C. After heating overnight, the reaction was completed. Upon purification, phospholylester complex **68** was obtained with 70% yield and characterized by X-ray crystallography (Figure 3.9). The C=O of the ester group appears 163.24ppm in ^{13}C NMR. Structurally, it resembles the thioester **67** where the ester group is almost coplanar to the diene of phosphole at an angle of 7.7°.



Scheme 3.13 Oxidation by DMSO (a) and reaction with water (b)

The reaction of **65** with water produced the aldehyde **69** with high yield (Scheme 3.13b). The characteristic proton of the aldehyde appears at 10.13ppm in ^{1}H NMR, and the carbonyl carbon shows up at 185.17ppm (^{13}C NMR). Formylphosphole complex **69** is also structurally established by X-ray analysis (Figure 3.10).

Till this point, phosphole carbene **65** followed the normal course of a standard Fischer carbene in these two reactions. This means the σ^4-phosphole moiety does not disturb the carbene functionality. Thus, the next objective is to test its reactivity towards alkenes and alkynes.

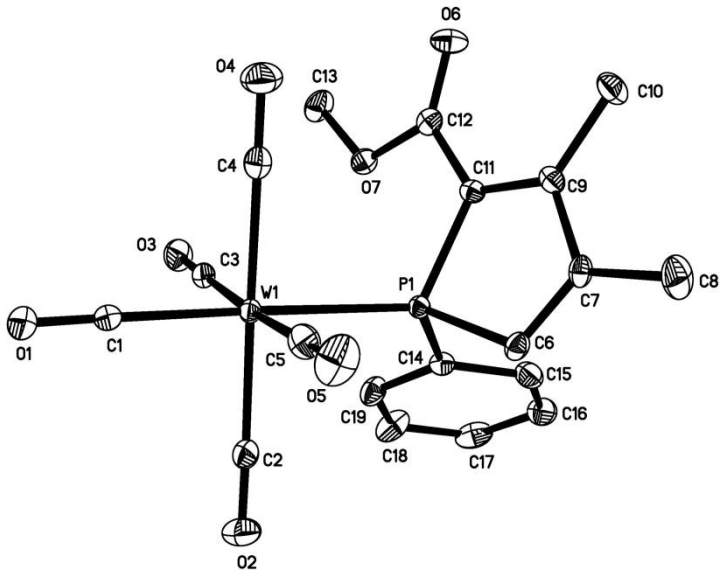


Figure 3.9 X-ray crystal structure of ester **68**. Main distances (Å) and angles (deg.): P-W 2.5196(7), P-C14 1.832(3), P-C6 1.794(3), P-C11 1.813(3), C6-C7 1.346(4), C7-C9 1.489(4), C9-C11 1.351(4), C11-C12 1.475(4), C12-O6 1.211(3), C12-O7 1.353(3); C6-P-C11 90.48(13), C11-C12-O6 127.3(3), C12-C11-P 121.9(2), O6-C12-O7 123.2(3).

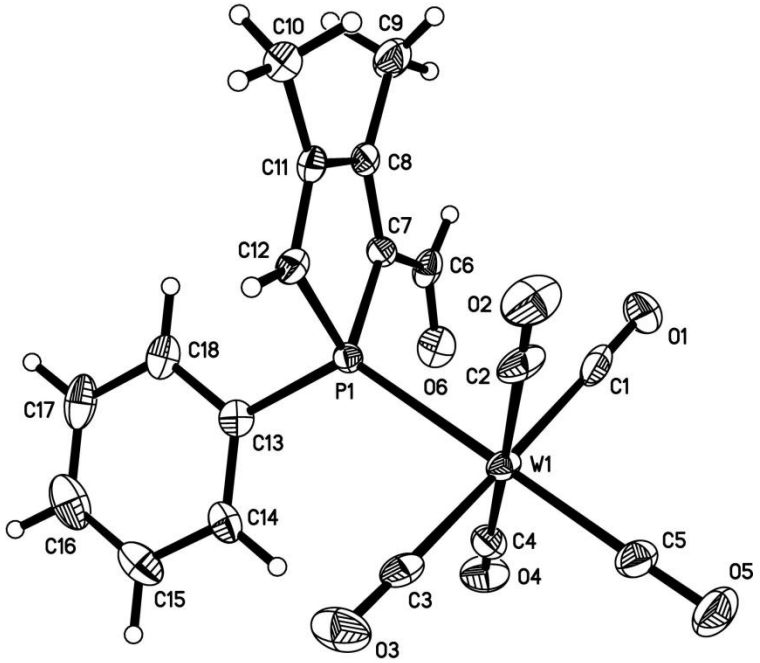
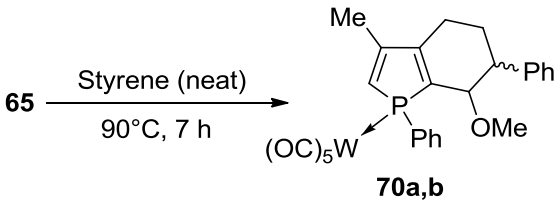


Figure 3.10 X-ray crystal structure of aldehyde **69**. Main distances (Å) and angles (deg.): P-W 2.4966(16), P-C13 1.837(6), P-C7 1.807(6), P-C12 1.802(6), C7-C8 1.352(9), C8-C11 1.488(9), C11-C12 1.335(9), C6-C7 1.456(9), C6-O6 1.221(8); C7-P-C12 89.9(3), C7-C6-O6 123.6(6), C6-C7-P 121.8(5).

One has to recall that there are two pathways that can happen when Fischer carbenes react with alkenes. The two pathways are olefin metathesis and cyclopropanation (Section 3.2.1). Also, the reaction between chromium complex of 2-furanyl- and 2-pyrrolylcarbenes with 1-pentyne gave the cyclopropanated products (Scheme 3.4).

With this knowledge in hand, a trial experiment between **65** and five equivalents of styrene was conducted in toluene. No visibile reaction was observed until the reaction was heated to 90°C. However, the product obtained was 2-formylphosphole complex **69**. This might be due to the presence of water in both the solvent and styrene. After several optimizations, the best condition is when the alkene is used as the solvent. Thus, the reaction was repeated in neat styrene heating at 90°C for 7 hours for complete consumption of **65** (Scheme 3.14). Two new peaks appeared at 13.12 and 16.08ppm in ^{31}P NMR in 1:1 ratio.



Scheme 3.14 Reaction of **65** with styrene

Surprisingly, both of the two products **70a**,**b** obtained after chromatography does not tally to cyclopropanated product nor the metathesis one. This confusion was cleared when structure of **70a** was established by X-ray analysis (Figure 3.11). Further analysis of the ^{13}C NMR spectra of **70a** and **70b** revealed that the *C*H$_2$ of the styrene is not coupled to the P while *C*HPh displays $^3J_{P\text{-}C}$ coupling (4.0 and 6.3 Hz respectively). Hence, this cycloaddition giving the two isomers have similar regiochemistry.

Although the mystery of the structures has been solved, the mechanism still remained unclear to us. It has to be mentioned that the computed D_e for changing **61-W** to **61** is 61.6kcal/mol. In view of the reaction temperature at 90°C, the dissociation of **65** to its free carbene form is improbable. Thus, a suitable mechanism via the cyclopropanation is proposed (Scheme 3.15).

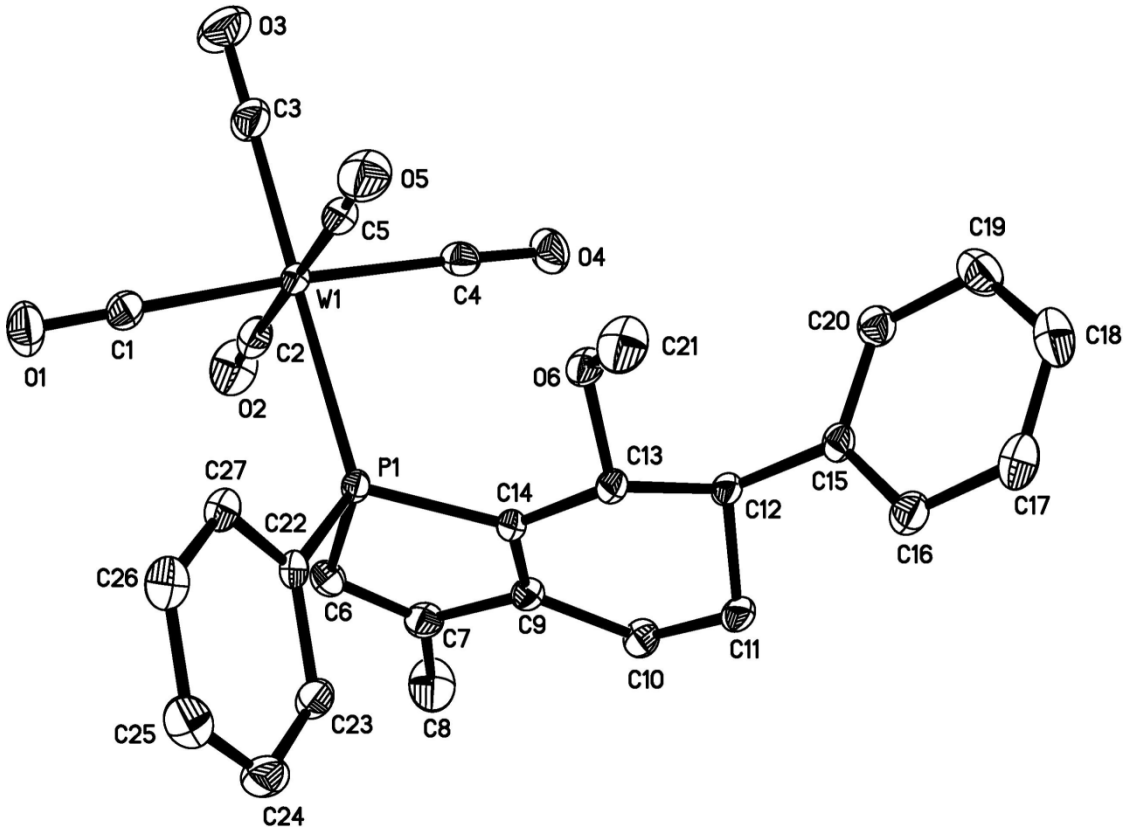
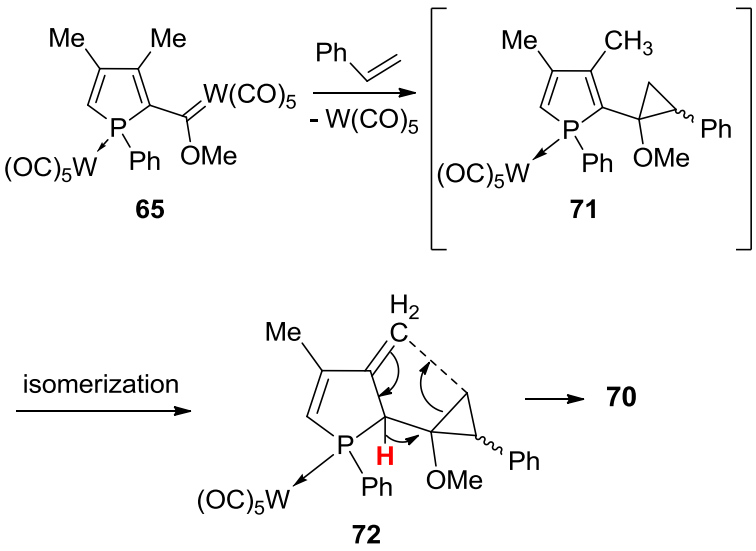


Figure 3.11 X-ray crystal structure of bicyclic product **70**. Main distances (Å) and angles (deg.): P-W 2.5131(5), P-C22 1.8272(19), P-C6 1.7972(19), P-C14 1.8134(19), C6-C7 1.341(3), C7-C9 1.478(3), C9-C14 1.349(2), C9-C10 1.499(3), C10-C11 1.521(3), C11-C12 1.535(3), C12-C13 1.545(2), C13-C14 1.502(3), C13-O6 1.421(2); C6-P-C14 90.99(9), C14-C13-O6 109.17(15), C13-C14-P 126.79(13).

We believe that cyclopropanation did take place producing the transient cyclopropane **71**. Since phosphole is weakly aromatic, isomerization of the tetracoordinated phosphole moiety in **71** is possble[65] which leads to the formation of **72**. After which, rearrangement occurred when the H from C_2 undergoes a 1,2-migration to the vicinal cyclopropyl carbon generating complex **70**. This outcome is startling as it has never been observed in other Fischer complexes, even those with aryl or heteroaryl substituents.

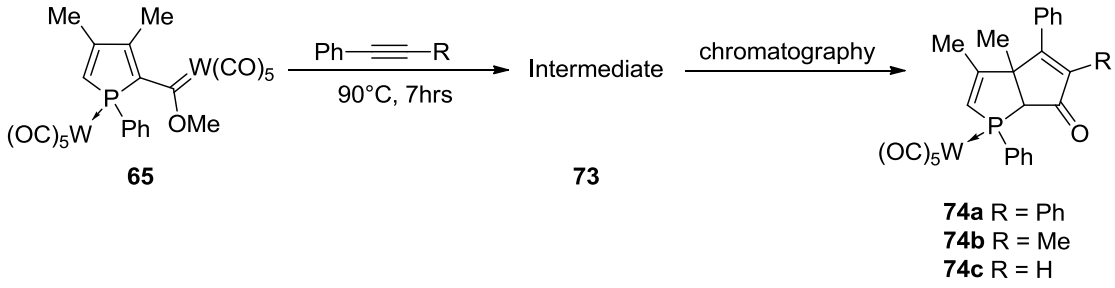


Scheme 3.15 Proposed mechanism for the formation of **70**

As carbenes are also known to dimerize upon thermolysis, carbene **65** was heated between 50 to 90°C in toluene. The system collapsed upon heating at 90°C and produced a convoluted ^{31}P NMR spectrum with a main peak of **69** observed. Thus, no conclusion can be drawn on whether **65** has underwent dimerization.

The interesting outcome from the reaction of styrene and carbene **65** prompted the investigation with alkynes. As we have seen (Section 3.2.2), many competing pathways could occur when Fischer carbene complexes are reacted with alkynes depending on the reaction conditions. For example, chromium metal favours benzannulation while tungsten favours cyclopentannulation.

To make the trial investigation simpler, we first tested the reaction with a symmetrical alkyne, diphenylacetylene. Using the optimized condition of styrene, indeed, the reaction goes to completion upon heating **65** in neat tolan at 90°C with almost no other side product formed. ^{31}P NMR analysis of the crude mixture showed an initial unknown intermediate at -2.25ppm ($J_{P\text{-}W}$ = 234Hz). After column chromatography with silica gel, complex **74a** was obtained which shows up at 14.27ppm in ^{31}P NMR. Again, characterization by X-ray analysis disclosed an unexpected structure (Figure 3.12). This final major product yielded is a cyclopentenone (Scheme 3.16).



Scheme 3.16 Annulation of complex **65** with alkynes

Expectedly, since the metal centre in **65** is tungsten, benzannulation did not happen. Also, we are aware that cyclopropanation does not take place between alkynes and group VI Fischer carbenes. Therefore, result as in the case of styrene cannot be obtained. However, cyclopentannulation generally leads to the formation of cyclopentadiene or indene. In our case, a cyclopentenone was obtained instead.

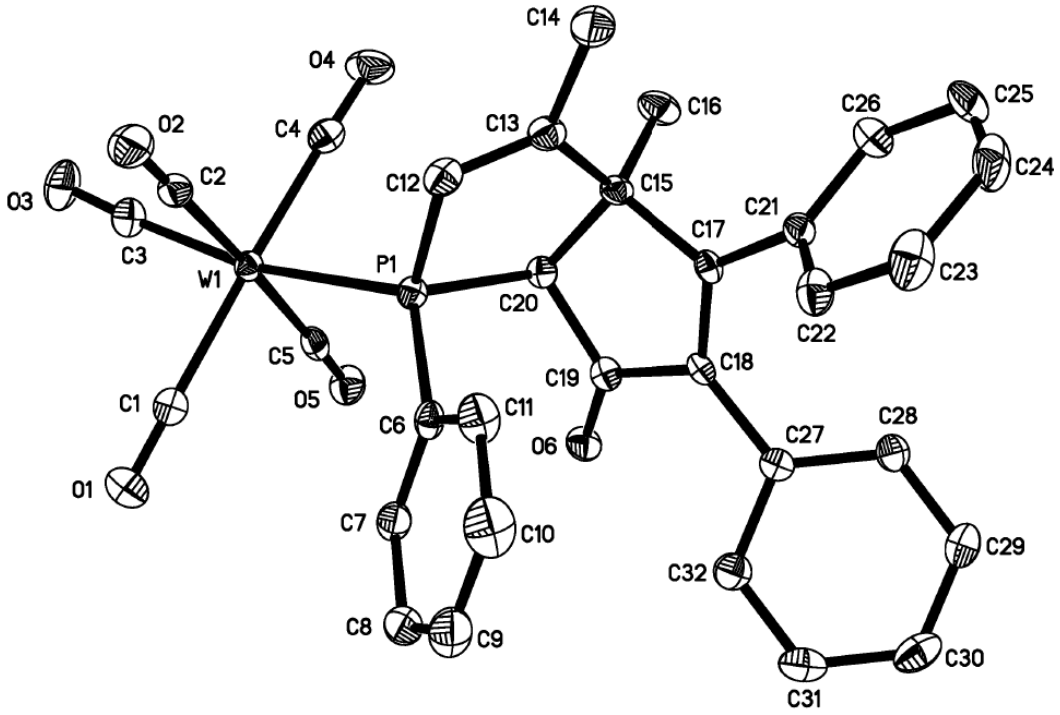
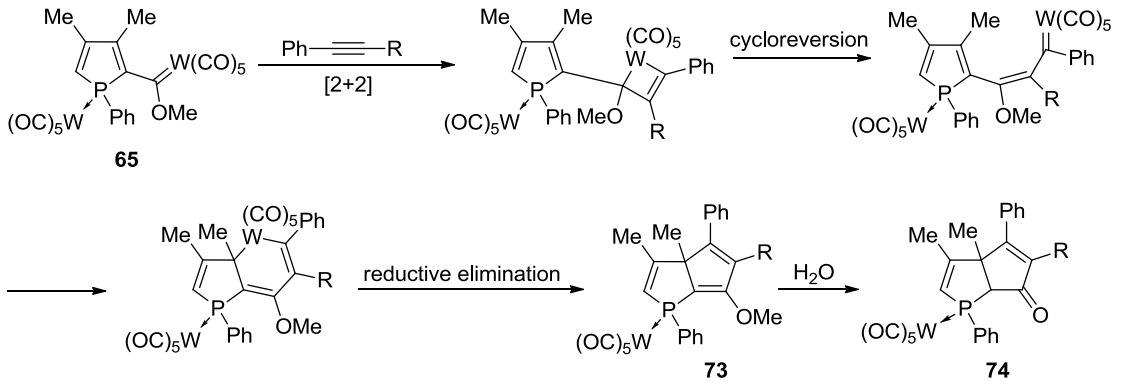


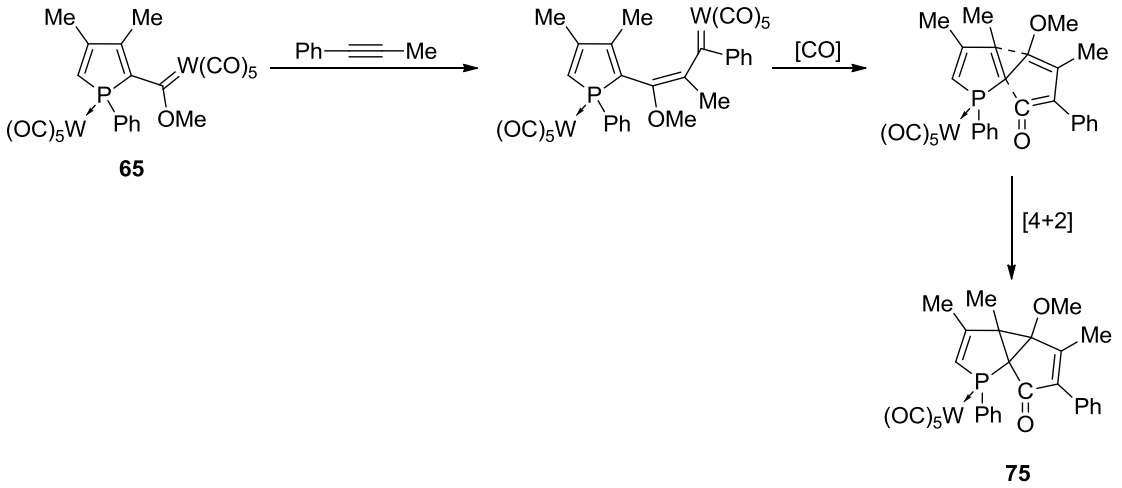
Figure 3.12 X-ray crystal structure of cyclopentenone **74a**. Main distances (Å) and angles (deg.): P-W 2.4985(6), P-C6 1.8232(2), P-C12 1.794(2), P-C20 1.860(2), C12-C13 1.325(4), C13-C15 1.525(3), C15-C17 1.537(3), C17-C18 1.349(3), C18-C19 1.480(3), C19-C20 1.509(3), C19-O6 1.215(3); C12-P-C20 91.36(11), C18-C19-C20 107.54(18), C19-C20-P 112.17(16).

We managed to find a similar published work which reports the formation of cyclopentenone between alkenyl Fischer carbenes and alkynes. However, the formation of cyclopentenone was catalyzed by the presence of a nickel (0) catalyst. Thus, a mechanism was proposed with reference to this published work (Scheme 3.17).[66]



Scheme 3.17 Proposed mechanism for the formation of **74**

Likewise, when the reaction was repeated with a terminal alkyne and a asymmetrical alkyne, unknown intermediates were observed (**73c**: -4.66ppm, $J_{P\text{-}W}$ = 234Hz and **73b**: -3.33ppm, $J_{P\text{-}W}$ = 238Hz). Upon subsequent purification, the final products obtained after chromatography were cyclopentenones **74c** and **74b** respectively. Both have been identified by X-ray analysis (Appendix). Hence, it is believed that these intermediates **73** are hydrolyzed during the purification by column chromatography.



Scheme 3.18 Proposed mechanism for the formation of **75**

Besides **74b**, an additional minor product **75** was isolated from the reaction between the asymmetical alkyne, 1-phenyl-1-propyne, and complex **65**. With the help of the X-ray study of **75** (Figure 3.13), a probable mechanism was proposed (Scheme 3.18). This mechanism was proposed on the basis of a report by Moser.[67]

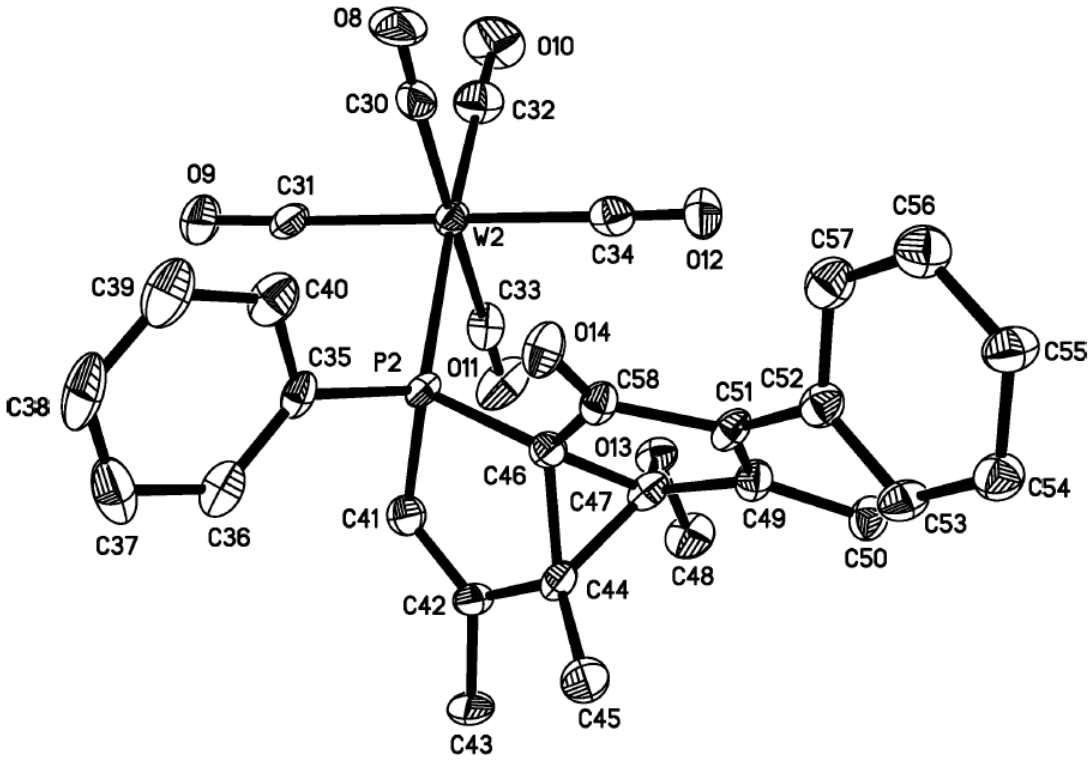


Figure 3.13 X-ray crystal structure of tricyclic compound **75**. Main distances (Å) and angles (deg.): P-W 2.5045(18), P-C6 1.837(7), P-C12 1.811(7), P-C17 1.822(7), C12-C13 1.329(10), C13-C15 1.469(9), C15-C17 1.562(10), C15-C18 1.546(9), C18-O6 1.429(9), C18-C20 1.505(10), C20-C22 1.341(11), C22-C29 1.493(10), C29-O7 1.209(9), C29-C17 1.504(10); C12-P-C17 90.7(3), C15-C17-C18 60.4(4), C18-C17-C29 105.4(6), C17-C29-C22 107.5(6).

On the whole, this annulation works with phosphole because the ring is poorly aromatic as compared to the other 5-membered heteroaryl rings. This is evident by the example shown in Section 3.2.2. The benzopyrrole carbene **59** which bears a methyl moiety on the ortho-position undergoes benzannulation. However, in the case of 2,6-disubstutited aryl carbene, benzannulation did not proceed. This goes to show that aromaticity plays a vital role.

3.5 Conclusion

The marriage of phosphole and Fischer carbene has created a few unique chemistry that was not observed in the other heteroaryl carbene complexes.

First of all, the DFT calculations have shown the free carbene **61** does not have maximal overlap with the diene unit. Nevertheless, significant delocalization can be expected since the bond length between the ring and carbene is relatively small. Also, the LUMO shows that there is an overlap between p-orbital of carbene with the LUMO of the diene. All these add up to suggest the chances of π-conjugation along the diene and the carbene.

Secondly, the structure of complex carbene **61-W** was also computed. Unlike compound **61**, the bond between the carbene and the ring is longer. This is suspected to be due to the presence of the backbonding between carbene and metal. Thus, weakening the conjugation between the diene and the carbene. To restore the conjugation, the dissociation energy was calculated to be 61.5kcal/mol which is smaller than the D_e of $(OC)_5W{=}CH(OH)$. This shows that the metal-carbene bond is weaker.

With this approving outlook from the theoretical studies. We went ahead to synthesize the phospholylcarbene complexes **64** and **65** via Fischer's method. Though there are some differences between the structurse of **65** and the computed **61-W**, the differences are very minute. Thus, it can be concluded that they both resemble each other.

Complex **64** which possesses two reactive sites prompted the study on its reactivity. When subjected to elemental sulfur, the σ^3-phosphole was not sulfurized. Instead, the carbene was sulfurized and the $W(CO)_5$ shifted and complexed onto the P. It is postulated that the lone pair on P might have acted as a ligand which results in the sulfurization of carbene. From the observed self-conversion **64** to **65**, the possibility of the P acting as a ligand is viable. Hence, this also suggests that the carbene is more reactive than the tricoordinated phosphorus. Even so, the presence of the nucleophilic lone pair on P caused many unwanted side reactions. Therefore, complex **64** was deemed unsuitable to be used to study the chemistry of phospholecarbene.

This brings us to focus on the complex **65** whose lone pair is protected. Indeed, this complex undergoes oxidation and hydrolysis as the standard Fischer carbene complexes.

Next, the classical cycloaddition with alkenes was performed. An unexpected product **70** was isolated. It was proposed to be formed via the transient cyclopropane **71**.

This interesting result advocated the need of deeper investigation. Thus, cycloaddition reactions between complex **65** and alkynes were examined. Again, the range of products obtained, cyclopentenone **74** and tricyclic compound **75**, were rarely (or never) observed in the examples of other heteroarylcarbene complexes. This phenomenon can happen in our phospholylcarbene system because of the weak aromaticity of phosphole. Hence, with the help of references, respective mechanism for the formation of **74** and **75** was proposed.

To conclude, the poor aromaticity of phosphole has bring about a unique reactivity that has never been noticed with other aryl- or heteroarylcarbene complexes.

3.6 Experimental

Oven-dried glasswares (105°C) were used and cooled under nitrogen atmosphere. All reactions were carried out with distilled dry solvents and under N_2 atmosphere. Silica gel (230-400mesh) was used for the chromatographic separations. Commercially available DMAD, styrene, diphenylacetylene, 1-phenyl-1-propyne and phenylacetylene were used without purification. NMR spectra were recorded on either a JEOL ECA 400, JEOL ECA 400 SL or Bruker BBFO2 400MHz spectrometer. All spectra were recorded at 298K. Proton decoupling was applied for ^{13}C and ^{31}P spectra. HRMS were obtained on a Water Q-Tof Premier MS. X-ray crystallographic analyses were performed on a Bruker X8 APEX CCD diffractometer or a Bruker Kappa CCD diffractometer.

*Phosphole-substituted Fischer carbene complexes **64** and **65***

1-Phenyl-2-bromo-3,4-dimethylphospole **62** (1.00g, 3.74mmol) was dissolved in THF (15mL) in a schlenk tube and cooled to -100°C. Then, n-BuLi (2.6mL, 1.6M in Hex, 4.11mmol) added dropwise into the solution. The reaction was left to stir for 0.5 hours at -100°C. To the mixture, $W(CO)_6$ (1.3161g, 3.74mmol) was added and stirred at -90°C for 0.5 hours followed by -80°C

for 0.5 hours. The reaction mixture was allowed to slowly warm up to room temperature. Subsequently, methyl trifluoromethansulfonate (0.42mL, 3.74mmol) added. The crude was purified using chromatography at -20°C with a 4:1 of hexane and DCM eluent mixture. Red oil of compound **64** (0.3730g, 18%) was obtained before its dark red P-$(WCO)_5$ complex, **65** (0.3284, 10%). Hexane was added and pure red crystalline **64** was obtained at -25°C, while complex **65** was crystallized with pentane at -25°C.

Complex **64**

^{31}P NMR (CD_2Cl_2): δ 13.66 ppm

^{1}H NMR (CD_2Cl_2): δ 2.09 (d, $^{4}J_{(H-P)}$ = 3.2Hz, 3H, Me), 2.12 (dd, $^{4}J_{(H-P)}$ = 4.4Hz, 3H, Me), 4.41 (s, 3H, OMe), 6.73 (d, $^{2}J_{(H-P)}$ = 38.8Hz, 1H, =CH-P), 7.24-7.32 (m, 5H, Ph).

^{13}C NMR (CD_2Cl_2): δ 16.97 (s, Me), 18.28 (d, $^{3}J_{(C-P)}$ = 1.9Hz, Me), 68.99 (s, OMe), 129.23 (d, $J_{(C-P)}$ = 7.7Hz, Ph), 130.37 (s, Ph), 130.55 (d, $J_{(P-C)}$ = 14.0Hz, P-C(Ph)), 134.21 (d, $J_{(P-C)}$ = 11.2Hz, P-CH=), 134.37 (d, $J_{(C-P)}$ = 19.7Hz, Ph), 143.61 (d, $J_{(C-P)}$ = 16.6Hz, P-C=), 150.23 (d, $J_{(C-P)}$ = 7.7Hz, C-Me), 167.56 (d, $J_{(C-P)}$ = 2.8Hz, C-Me), 198.39 (s, C-$W(CO)_5$ *cis* C=O), 205.22 (s, C-$W(CO)_5$ *trans* C=O), 316.94 (d, $J_{(C-P)}$ = 30.1Hz, C=W).

Exact mass: calcd $C_{19}H_{15}O_6PW$, 554.0116; found 554.0115.

Complex **65**

^{31}P NMR (DCM): δ 23.43 ($J_{(P-W)}$ = 221.1Hz)

^{1}H NMR (500MHz) ($CDCl_3$): δ 2.31 (d, $^{4}J_{(H-P)}$ = 1.4Hz, 3H, Me), 2.36 (s, 3H, Me), 4.53 (s, 3H, OMe), 6.72 (d, $^{2}J_{(H-P)}$ = 36.6Hz, 1H, =CH-P), 7.39-7.53 (m, 5H, Ph).

^{13}C NMR ($CDCl_3$): δ 17.79 (d, $^{3}J_{(C-P)}$ = 9.7Hz, Me), 17.99 (d, $^{3}J_{(C-P)}$ = 8.0Hz, Me), 69.63 (s, OMe), 128.04 (d, $J_{(P-C)}$ = 38.4Hz, P-C(Ph)), 129.43 (d, $J_{(C-P)}$ = 10.3Hz, Ph), 132.03 (s, Ph), 133.06 (d, $J_{(C-P)}$ = 13.1Hz, Ph), 133.15 (d, $J_{(P-C)}$ = 41.1Hz, P-CH=), 148.47 (d, $J_{(C-P)}$ = 15.3Hz, C-Me), 151.08 (d, $J_{(C-P)}$ = 8.5Hz, C-Me), 162.99 (d, $J_{(C-P)}$ = 23.1Hz, P-C=), 196.73 (d, $J_{(C-P)}$ = 6.3Hz, P-$W(CO)_5$ *cis* C=O), 197.00 (s, C-$W(CO)_5$ *cis* C=O), 198.42 (d, $J_{(C-P)}$ = 21.6Hz, P-$W(CO)_5$ *trans* C=O), 203.32 (s, C-$W(CO)_5$ *trans* C=O), 316.87 (s, C=W).

Exact mass: calcd $C_{24}H_{15}O_{11}PW_2Na$, 900.9268; found 900.9276.

*Sulfurization of **64***

Red solid **64** (20.0mg, 0.036mmol) dissolved in toluene (5mL) and sulphur powder (1.2mg, 0.036mmol) was added. A small drop of N-methylimidazole was added, and the reaction was left to stir overnight at room temperature. The mixture was purified by flash column with a 4:1 hexane and DCM mixture. Thiocarboxylate **67** (69.6mg, 95%) was obtained as an orange oil. Crystallization with pentane was achieved at -25°C.

^{31}P NMR (DCM): δ 20.96 ppm ($J_{(P-W)}$ = 225.4Hz)

^{1}H NMR ($CDCl_3$): δ 2.28 (d, $^{4}J_{(H-P)}$ = 0.9Hz, 3H, Me), 2.64 (s, 3H, Me), 4.02 (s, 3H, OMe), 6.68 (d, $^{2}J_{(H-P)}$ = 35.7Hz, 1H, =CH-P), 7.38-7.49 (m, 5H, Ph).

^{13}C NMR ($CDCl_3$): δ 17.64 (d, $^{3}J_{(C-P)}$ = 6.7Hz, Me), 17.98 (d, $^{3}J_{(C-P)}$ = 9.5Hz, Me), 57.97 (s, OMe), 128.44 (s, Ph), 128.92 (d, $J_{(C-P)}$ = 68.0Hz, P-C(Ph)), 129.07 (d, $J_{(C-P)}$ = 11.5Hz, Ph), 131.09 (s, Ph), 132.25 (d, $J_{(C-P)}$ = 13.4Hz, Ph), 137.04 (d, $J_{(C-P)}$ = 40.3Hz, P-CH=), 144.15 (d, $J_{(C-P)}$ = 45.0Hz, P-*C*-C(S)OMe), 150.02 (d, $J_{(C-P)}$ = 5.8Hz, C-Me), 158.69 (d, $J_{(C-P)}$ = 14.4Hz, C-Me), 196.51 (d, $J_{(C-P)}$ = 5.7Hz, $W(CO)_5$ *cis* C=O), 198.67 (d, $J_{(C-P)}$ = 21.1Hz, $W(CO)_5$ *trans* C=O), 204.60 (d, $J_{(C-P)}$ = 16.3Hz, C=S).

Exact mass: calcd $C_{17}H_{11}O_6PSW$, 557.9524; found 557.9539.

*Oxidation of complex **65***

Dimethyl sulfoxide (2.76μL, 0.04mmol) was added into compound **65** (34.0mg, 0.04mmol) dissolved in 3mL of toluene and heated at 50°C overnight. Reaction mixture turned yellow. Toluene was removed and purification by chromatography with 4:1 mixture of hexane and DCM. Yellow solid of **67** (16.0mg, 70%) was isolated, and crystallization with pentane at -25°C was achieved.

^{31}P NMR (DCM): δ 17.7 ppm ($J_{(P-W)}$ = 221.1Hz)

^{1}H NMR (CD_2Cl_2): δ 2.24 (d, $^{4}J_{(H-P)}$ = 1.4Hz, 3H, Me), 2.55 (s, 3H, Me), 3.68 (s, 3H, OMe), 6.71 (d, $^{2}J_{(H-P)}$ = 34.4Hz, 1H, =CH-P), 7.36-7.53 (m, 5H, Ph).

^{13}C NMR (CD_2Cl_2): δ 15.14 (d, $^3J_{(C\text{-}P)}$ = 6.4Hz, Me), 16.70 (d, $^3J_{(C\text{-}P)}$ = 9.7Hz, Me), 50.98 (s, OMe), 127.98 (s, Ph), 128.17 (d, $J_{(C\text{-}P)}$ = 36.9Hz, P-C(Ph)), 128.40 (d, $J_{(C\text{-}P)}$ = 10.5Hz, Ph), 130.53 (d, $J_{(C\text{-}P)}$ = 2.3Hz, Ph), 131.63 (d, $J_{(C\text{-}P)}$ = 12.9Hz, Ph), 133.73 (d, $J_{(C\text{-}P)}$ = 43.7Hz, P-*C*-CO_2Me), 135.13 (d, $J_{(C\text{-}P)}$ = 41.5Hz, P-CH=), 149.80 (d, $J_{(C\text{-}P)}$ = 6.2Hz, C-Me), 161.63 (d, $J_{(C\text{-}P)}$ = 12.7Hz, C-Me), 163.24 (d, $J_{(C\text{-}P)}$ = 16.9Hz, C=O), 195.89 (d, $J_{(C\text{-}P)}$ = 6.6Hz, $W(CO)_5$ *cis* C=O), 198.29 (d, $J_{(C\text{-}P)}$ = 20.1Hz, $W(CO)_5$ *trans* C=O).

Exact mass: calcd $C_{19}H_{15}O_7PW$, 570.0065; found 570.0068.

*Hydrolyzation of **65***

Compound **65** (34.0mg, 0.04mmol) was dissolved in 2mL of toluene in a sealed tube and a drop of water was added. The mixture was heated at 90°C overnight. Toluene was removed and purification by chromatography with 4:1 mixture of hexane and DCM. Formylphosphole **69** (15.1mg, 70%) was attained as yellow oil. and Crystallization with pentane at -25°C was accomplished.

^{31}P NMR (DCM): δ 14.87ppm ($J_{(P\text{-}W)}$ = 218.9Hz)

^{1}H NMR (CD_2Cl_2): δ 2.29 (d, $^4J_{(H\text{-}P)}$ = 1.4Hz, 3H, Me), 2.51 (s, 3H, Me), 6.94 (d, $^2J_{(H\text{-}P)}$ = 34.8Hz, 1H, =CH-P), 7.39-7.57 (m, 5H, Ph) 10.13 (d, $^3J_{(H\text{-}P)}$ = 16.5Hz, 1H, CHO).

^{13}C NMR ($CDCl_3$): δ 14.29 (d, $^3J_{(C\text{-}P)}$ = 6.8Hz, Me), 17.08 (d, $^3J_{(C\text{-}P)}$ = 9.4Hz, Me), 129.17 (d, $J_{(C\text{-}P)}$ = 41.8Hz, P-C(Ph) ipso), 129.14 (d, $J_{(C\text{-}P)}$ = 10.7Hz, Ph), 131.08 (s, Ph), 131.80 (d, $J_{(C\text{-}P)}$ = 12.6Hz, Ph), 137.85 (d, $J_{(C\text{-}P)}$ = 6.4Hz, P-CH=), 142.92 (d, $J_{(C\text{-}P)}$ = 35.9Hz, P-*C*-CHO), 150.23 (d, $J_{(C\text{-}P)}$ = 5.6Hz, C-Me), 162.37 (d, $J_{(C\text{-}P)}$ = 12.3Hz, C-Me), 185.17 (d, $J_{(C\text{-}P)}$ = 12.1Hz, CHO), 196.04 (d, $J_{(C\text{-}P)}$ = 6.6Hz, $W(CO)_5$ *cis* C=O), 198.61 (d, $J_{(C\text{-}P)}$ = 20.2Hz, $W(CO)_5$ *trans* C=O).

Exact mass: calcd $C_{18}H_{13}O_6PW$, 539.9959; found 539.9962.

*Reaction of **65** with styrene*

Compound **65** (80.0mg, 0.09mmol) was dissolved in styrene in a sealed tube. The mixture was heated at 90°C for 7 hours. Upon completion, styrene was removed, and purification by chromatography with 4:1 of hexane and DCM of eluent mixture. Complex **70a** (17.8mg, 40%)

was eluated first and yellow oil of **70b** (11.8mg, 20%) was obtained later. Crystallization of **70a** with DCM/hexane mixture at -25°C was achieved.

Isomer **70a**

^{31}P NMR ($CDCl_3$): δ 13.12 ppm ($J_{(P-W)}$ = 217.8Hz)

^{1}H NMR (CD_2Cl_2): δ 2.01-2.07 (m, 2H), 2.17 (d, $^{4}J_{(H-P)}$ = 1.4Hz, 3H, Me), 2.28-2.36 (m, 1H), 2.49-2.59 (m, 1H), 2.85 (s, 3H, OMe), 3.07-3.14 (m, 1H, C*H*-Ph), 3.90 (d, $J_{(H-H)}$ = 6.3Hz, C*H*-OMe), 6.54 (d, $^{2}J_{(H-P)}$ = 37.6Hz, 1H, =CH-P), 6.97-6.99 (m, 2H, Ph), 7.13-7.19 (m, 3H, Ph), 7.41-7.43 (m, 3H, Ph), 7.51-7.57 (m, 2H, Ph).

^{13}C NMR ($CDCl_3$): δ 16.92 (d, $^{3}J_{(C-P)}$ = 10.3Hz, Me), 24.23 (d, $^{3}J_{(C-P)}$ = 7.7Hz, CH_2), 27.88 (s, CH_2) 44.70 (d, $J_{(C-P)}$ = 4.0Hz, *C*H-Ph), 59.10 (s, OMe), 80.33 (d, $J_{(C-P)}$ = 8.3Hz, *C*H-OMe), 126.67 (s, CH, PhC) 126.68, 127.76 (s, CH, PhC), 128.47 (s, CH, PhC), 129.12 (d, CH, $J_{(C-P)}$ = 10.1Hz, PhP), 129.93 (d, C, $J_{(C-P)}$ = 38.5Hz, PhP), 130.88 (d, CH, $J_{(C-P)}$ = 2.2Hz, PhP), 130.90 (d, $J_{(C-P)}$ = 43.5Hz, P-CH=), 132.07 (d, CH, $J_{(C-P)}$ = 12.5Hz, PhP), 142.90 (s, PhC), 145.53 (d, $J_{(C-P)}$ = 41.3Hz, P-C=), 147.20 (d, $J_{(C-P)}$ = 13.7Hz, *C*-CH_2), 149.29 (d, $J_{(C-P)}$ = 8.1Hz, C-Me), 196.93 (d, $J_{(C-P)}$ = 6.9Hz, $W(CO)_5$ *cis* C=O), 199.49 (d, $J_{(C-P)}$ = 19.6Hz, $W(CO)_5$ *trans* C=O).

Exact mass: calcd $C_{27}H_{23}O_6PW$, 658.0742; found 658.0746.

Isomer **70b**

^{31}P NMR ($CDCl_3$): δ 16.08 ppm ($J_{(P-W)}$ = 216.7Hz)

^{1}H NMR (CD_2Cl_2): δ 1.93-1.99 (m, 2H), 2.19 (d, $^{4}J_{(H-P)}$ = 1.2Hz, 3H, Me), 2.55 (br, 2H), 2.60 (s, 3H, OMe), 2.90-2.96 (m, 1H, C*H*-Ph), 4.75 (d, $J_{(H-H)}$ = 6.6Hz, C*H*-OMe), 6.57 (d, $^{2}J_{(H-P)}$ = 36.2Hz, 1H, =CH-P), 7.19-7.31 (m, 5H, Ph), 7.33-7.40 (m, 3H, Ph), 7.55-7.60 (m, 2H, Ph).

^{13}C NMR (CD_2Cl_2): δ 17.04 (d, $^{3}J_{(C-P)}$ = 10.3Hz, Me), 25.79 (d, $^{3}J_{(C-P)}$ = 8.5Hz, CH_2), 30.76 (s, CH_2), 47.08 (d, $J_{(C-P)}$ = 6.3Hz, CH-Ph), 57.06 (s, OMe), 81.90 (d, $J_{(C-P)}$ = 9.5Hz, *C*H-OMe), 127.04 (s, CH, PhC), 127.92 (s, CH, PhC), 128.71 (d, CH, $J_{(C-P)}$ = 10.7Hz, PhP), 128.97 (s, CH, PhC), 130.50 (d, C, $J_{(C-P)}$ = 41.2Hz, PhP), 130.59 (d, $J_{(C-P)}$ = 46.7Hz, P-CH=), 130.87 (d, CH, $J_{(C-P)}$ = 2.2Hz, PhP), 133.08 (d, CH, $J_{(C-P)}$ = 13.1Hz, PhP), 144.30 (s, PhC), 144.84 (d, $J_{(C-P)}$ = 37.3Hz,

P-C=), 148.92 (d, $J_{(C-P)}$ = 12.7Hz, *C*-CH_2), 149.69 (d, $J_{(C-P)}$ = 8.5Hz, C-Me), 197.05 (d, $J_{(C-P)}$ = 6.7Hz, $W(CO)_5$ *cis* C=O), 199.08 (d, $J_{(C-P)}$ = 18.4Hz, $W(CO)_5$ *trans* C=O).

*Cyclopentenone **74a***

Compound **65** (42.6mg, 0.049mmol) was placed in an oven-dried NMR tube under a stream of N_2. Diphenylacetylene (neat) was added, and the tube was sealed and heated at 90°C for 7 hours. Upon completion, DCM was added to the crude mixture, ^{31}P NMR showed a major signal at -2.25 ppm. Purification by column chromatography with a 4:1 mixture of hexane and DCM gave product **74a** as yellow oil (19.4mg, 55%). It was crystallized with hexane at -25°C.

^{31}P NMR (CD_2Cl_2): δ 14.27 ppm ($J_{(P-W)}$ = 243.3Hz)

^{1}H NMR (CD_2Cl_2): δ 1.56 (s, 3H, Me), 1.80 (s, 3H, Me), 3.83 (s, 1H, C*H*), 6.04 (d, $^{2}J_{(H-P)}$ = 36.0Hz, 1H, =CH-P), 6.09-6.11 (m, 2H, Ph), 6.90-6.94 (m, 2H, Ph), 7.00-7.08 (m, 3H, Ph), 7.35-7.38 (m, 3H, Ph), 7.48-7.53 (m, 3H, Ph), 7.59-7.61 (m,2H, Ph).

^{13}C NMR (CD_2Cl_2): δ 18.50 (d, $^{3}J_{(C-P)}$ = 11.6Hz, Me), 25.24 (d, $^{3}J_{(C-P)}$ = 5.4Hz, Me), 64.98 (s, *C*-Me), 66.65 (d, $^{2}J_{(C-P)}$ = 19.4Hz, *C*-H), 122.49 (d, $J_{(C-P)}$ = 42.6Hz, P-CH=), 133.10 (d, $J_{(C-P)}$ = 29.9Hz, P-C(Ph)), 136.7 (s, =*C*-Ph), 140.51 (s, =*C*-Ph), 160.13 (d, $J_{(C-P)}$ = 3.8Hz, =*C*-Me), 197.36 (d, $J_{(C-P)}$ = 7.4Hz, $W(CO)_5$ *cis* C=O), 199.84 (d, $J_{(C-P)}$ = 3.9Hz, C=O), 200.20 (d, $J_{(C-P)}$ = 23.0Hz, $W(CO)_5$ *trans* C=O).

Exact mass: calcd $C_{32}H_{23}O_6PW$, 718.0742; found 718.0783.

*Cyclopentenone **74b** and tricyclic product **75***

The same reaction procedure as for **74a** was used with 1-phenyl-1-propyne. The crude mixture contains mainly two products at -3.33 (**74b**) and 5.0 ppm. Elution with a mixture of hexane and DCM (4:1) gave the product at 5.0ppm, which evolved overnight to give the tricyclic product **75** (2.8mg, 9%), while **73b** gave **74b** (11.8mg, 40%) which was eluated with a 3:2 hexane/DCM mixture.

Cyclopentenone **74b**

^{31}P NMR ($CDCl_3$): δ 13.12 ppm ($J_{(P-W)}$ = 241.8Hz)

^{1}H NMR ($CDCl_3$): δ 0.92 (s, 3H, Me), 1.60 (s, 3H, Me), 1.64 (s, 3H, Me), 3.68 (s, 1H, C-*H*), 5.97 (d, $^{2}J_{(H-P)}$ = 35.7Hz, 1H, =CH-P), 7.04-7.07 (m, 2H, Ph), 7.38-7.54 (m, 8H, Ph).

^{13}C NMR (CD_2Cl_2): δ 8.14 (s, Me), 18.18 (d, $^{3}J_{(C-P)}$ = 11.6Hz, Me), 24.58 (d, $^{3}J_{(C-P)}$ = 5.3Hz, Me), 64.39 (s, *C*-Me), 65.90 (d, $^{2}J_{(C-P)}$ = 19.8Hz, *C*-H), 121.56 (d, $J_{(C-P)}$ = 42.2Hz, P-CH=), 132.33 (d, $J_{(C-P)}$ = 28.5Hz, P-C(Ph)), 135.3 (s, PhC=*C*-Me), 137.77 (s, =*C*-Ph), 159.26 (d, $J_{(C-P)}$ = 3.8Hz, =*C*-Me), 196.59 (d, $J_{(C-P)}$ = 7.2Hz, $W(CO)_5$ *cis* C=O), 199.38 (d, $J_{(C-P)}$ = 23.1Hz, $W(CO)_5$ *trans* C=O), 200.94 (d, $J_{(C-P)}$ = 3.6Hz, C=O).

Exact mass: calcd $C_{27}H_{21}O_6PW$, 656.0585; found 656.0586.

Tricyclic product **75**

^{31}P NMR (CD_2Cl_2): δ 13.21 ppm ($J_{(P-W)}$ = 238.1Hz)

^{1}H NMR (CD_2Cl_2): δ 1.68 (s, 3H, Me), 2.31 (s, 3H, Me), 2.33 (s, 3H, Me), 3.69 (s, 3H, OMe), 6.07 (d, $^{2}J_{(H-P)}$ = 37.6Hz, 1H, =CH-P), 7.24-7.30 (m, 2H, Ph), 7.35-7.46 (m, 3H, Ph), 7.49-7.51 (m, 3H, Ph), 7.68-7.74 (m, 2H, Ph).

^{13}C NMR ($CDCl_3$): δ 12.49 (s, Me), 15.30 (s, Me), 18.87 (d, $^{3}J_{(C-P)}$ = 11.3Hz, Me), 48.75 (d, $^{2}J_{(C-P)}$ = 31.7Hz, P-*C*), 59.59 (s, OMe), 70.14 (s, *C*-Me), 84.27 (s, *C*-OMe), 128.63 (d, $J_{(C-P)}$ = 45.3Hz, P-CH=), 132.69 (d, $J_{(C-P)}$ = 34.6Hz, P-C(Ph)), 138.86 (d, $J_{(C-P)}$ = 6.4Hz, =*C*-Me), 150.75 (s, Ph-*C*=CMe), 161.08 (s, PhC=*C*-Me), 194.56 (d, $J_{(C-P)}$ = 3.3Hz, C=O), 196.86 (d, $J_{(C-P)}$ = 7.5Hz, $W(CO)_5$ *cis* C=O d), 199.51 (d, $J_{(C-P)}$ = 22.7Hz, $W(CO)_5$ *trans* C=O).

Exact mass: calcd $C_{29}H_{23}O_7PW$, 698.0691; found 698.0698.

Cyclopentenone ***74c***

Follows similar reaction condition as for **74a** with phenylacetylene. The crude mixture contained **73c** (-4.66ppm) and **74c**. Chromatography as usual gave pure **74c** (14.0mg, 42%).

^{31}P NMR ($CDCl_3$): δ 13.49 ppm ($J_{(P-W)}$ = 244.1Hz)

^{1}H NMR ($CDCl_3$): δ 1.72 (s, 3H, Me), 1.77 (s, 3H, Me), 3.69 (s, 1H, C-*H*), 5.34 (s, 1H, =C-*H*), 5.98 (d, $^{2}J_{(H-P)}$ = 35.2Hz, 1H, =CH-P), 7.17-7.20 (m, 2H, Ph), 7.42-7.44 (m, 6H, Ph), 7.48-7.52 (m, 2H, Ph).

^{13}C NMR ($CDCl_3$): δ 18.46 (d, $^3J_{(C-P)}$ = 11.6Hz, Me), 25.33 (d, $^3J_{(C-P)}$ = 5.2Hz, Me), 66.17 (s, *C*-Me), 67.16 (d, $^2J_{(C-P)}$ = 19.2Hz, *C*-H), 122.89 (d, $J_{(C-P)}$ = 42.3Hz, P-CH=), 131.47 (s, =*C*-H), 132.31 (d, $J_{(C-P)}$ = 30.2Hz, P-C(Ph)) 135.89 (s, =*C*-Ph), 158.25 (d, $J_{(C-P)}$ = 3.8Hz, =*C*-Me), 196.85 (d, $J_{(C-P)}$ = 7.1Hz, $W(CO)_5$ *cis* C=O), 199.52 (d, $J_{(C-P)}$ = 23.1Hz, $W(CO)_5$ *trans* C=O), 200.08 (d, $J_{(C-P)}$ = 3.9Hz, C=O).

Exact mass: calcd $C_{26}H_{19}O_6PW$, 642.0429; found 642.0443.

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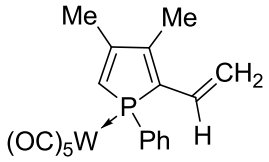
APPENDIX

Crystal data and structure refinement for compound **51**

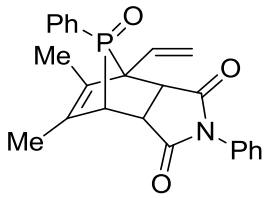


51

Identification code	mat172	
Chemical formula	$C_{19}H_{15}O_5PW$	
Formula weight	538.13	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.200 x 0.340 x 0.380 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 9.3460(7) Å	α = 90°
	b = 9.0127(5) Å	β = 93.896(4)°
	c = 22.2490(14) Å	γ = 90°
Volume	1869.8(2) $Å^3$	
Z	4	
Density (calculated)	1.912 g/cm^3	
Absorption coefficient	6.290 mm^{-1}	
F(000)	1032	
Theta range for data collection	1.84 to 31.23°	
Index ranges	-13<=h<=12, -13<=k<=13, -30<=l<=32	
Reflections collected	24376	
Independent reflections	6038 [R(int) = 0.0719]	
Coverage of independent reflections	99.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.3660 and 0.1980	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo2 - Fc2)2	

Data / restraints / parameters	6038 / 12 / 237	
Goodness-of-fit on F2	1.227	
Δ/σmax	0.001	
Final R indices	4710 data; I>2σ(I)	R1 = 0.0526, wR2 = 0.1199
	all data	R1 = 0.0733, wR2 = 0.1359
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0301P)^2+21.7769P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	2.954 and -2.094 eÅ^{-3}	
R.M.S. deviation from mean	0.277 eÅ^{-3}	

Crystal data and structure refinement for compound **52**

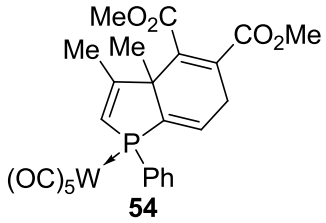


52

Identification code	mat175	
Chemical formula	$C_{24}H_{22}NO_3P$	
Formula weight	403.39	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.120 x 0.200 mm	
Crystal habit	colorless block	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.8173(17) Å	α = 90°
	b = 12.915(3) Å	β = 90°
	c = 19.645(4) Å	γ = 90°
Volume	1983.4(8) Å^3	
Z	4	
Density (calculated)	1.351 g/cm^3	
Absorption coefficient	0.165 mm^{-1}	
F(000)	848	
Theta range for data collection	2.80 to 28.30°	
Index ranges	-10<=h<=10, -16<=k<=17, -24<=l<=26	

Reflections collected	13563	
Independent reflections	4905 [R(int) = 0.1308]	
Coverage of independent reflections	99.6%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9840 and 0.9680	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	4905 / 0 / 264	
Goodness-of-fit on F2	0.963	
Final R indices	2429 data; I>2σ(I)	R1 = 0.0729, wR2 = 0.1004
	all data	R1 = 0.1816, wR2 = 0.1314
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0333P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.5(2)	
Largest diff. peak and hole	0.355 and -0.359 eÅ^{-3}	
R.M.S. deviation from mean	0.087 eÅ^{-3}	

Crystal data and structure refinement for compound **54**

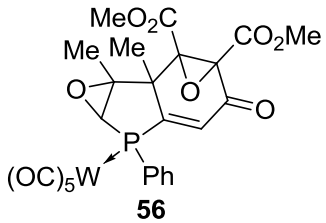


54

Identification code	mat182	
Chemical formula	$C_{25}H_{21}O_9PW$	
Formula weight	680.24	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.160 x 0.200 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.8997(2) Å	α = 66.3596(16)°

	b = 13.3814(4) Å	β = 89.6223(16)°
	c = 13.9890(4) Å	γ = 74.1012(16)°
Volume	1293.87(7) $Å^3$	
Z	2	
Density (calculated)	1.746 g/cm^3	
Absorption coefficient	4.576 mm^{-1}	
F(000)	664	
Theta range for data collection	1.74 to 29.75°	
Index ranges	-11<=h<=10, -18<=k<=18, -19<=l<=19	
Reflections collected	34777	
Independent reflections	7318 [R(int) = 0.0504]	
Coverage of independent reflections	99.3%	
Absorption correction	multi-scan	
Max. and min. transmission	0.6580 and 0.4610	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	7318 / 0 / 329	
Goodness-of-fit on F2	1.056	
Δ/σmax	0.002	
Final R indices	6318 data; I>2σ(I)	R1 = 0.0295, wR2 = 0.0596
	all data	R1 = 0.0409, wR2 = 0.0636
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0278P)^2+1.1972P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	2.511 and -1.857 $eÅ^{-3}$	
R.M.S. deviation from mean	0.146 $eÅ^{-3}$	

Crystal data and structure refinement for compound **56**

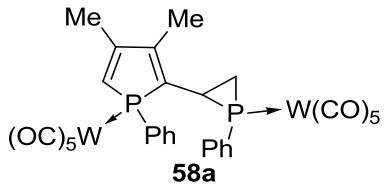


56

Identification code	mat179

Chemical formula	$C_{25}H_{19}O_{12}PW$	
Formula weight	726.22	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.040 x 0.100 x 0.180 mm	
Crystal habit	yellow plate	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.3976(9) Å	α = 108.019(5)°
	b = 10.0987(11) Å	β = 101.382(5)°
	c = 14.5996(13) Å	γ = 91.405(5)°
Volume	1286.2(2) $Å^3$	
Z	2	
Density (calculated)	1.875 g/cm^3	
Absorption coefficient	4.618 mm^{-1}	
F(000)	708	
Theta range for data collection	1.50 to 27.05°	
Index ranges	-11<=h<=11, -12<=k<=12, -18<=l<=18	
Reflections collected	21489	
Independent reflections	5600 [R(int) = 0.1174]	
Coverage of independent reflections	99.5%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8370 and 0.4900	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	5600 / 0 / 356	
Goodness-of-fit on F2	1.041	
Final R indices	3882 data; I>2σ(I)	R1 = 0.0543, wR2 = 0.1153
	all data	R1 = 0.0985, wR2 = 0.1632
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0738P)^2+2.2699P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.342 and -1.791 $eÅ^{-3}$	
R.M.S. deviation from mean	0.294 $eÅ^{-3}$	

Crystal data and structure refinement for compound **58a**

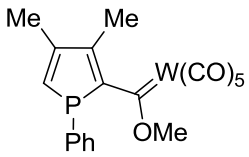


58a

Identification code	mat171	
Chemical formula	$C_{30}H_{20}O_{10}P_2W_2$	
Formula weight	970.10	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.028 x 0.200 x 0.300 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.5975(4) Å	α = 73.5805(15)°
	b = 11.3475(4) Å	β = 80.4996(15)°
	c = 14.5752(5) Å	γ = 68.8731(15)°
Volume	1564.34(10) $Å^3$	
Z	2	
Density (calculated)	2.060 g/cm^3	
Absorption coefficient	7.505 mm^{-1}	
F(000)	916	
Theta range for data collection	1.46 to 31.28°	
Index ranges	-15<=h<=15, -16<=k<=16, -21<=l<=21	
Reflections collected	55789	
Independent reflections	10163 [R(int) = 0.0560]	
Coverage of independent reflections	99.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8170 and 0.2120	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	10163 / 0 / 399	
Goodness-of-fit on F2	1.080	

Δ/σmax	0.002	
Final R indices	8520 data; I>2σ(I)	R1 = 0.0262, wR2 = 0.0521
	all data	R1 = 0.0372, wR2 = 0.0632
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0004P)^2+8.0779P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.534 and -1.640 eÅ^{-3}	
R.M.S. deviation from mean	0.201 eÅ^{-3}	

Crystal data and structure refinement for compound **64**

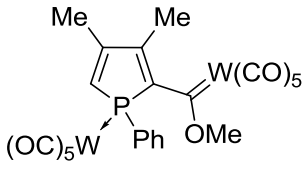


64

Identification code	mat158s	
Chemical formula	$C_{19}H_{15}O_6PW$	
Formula weight	554.13	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal size	0.320 x 0.360 x 0.380 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 12.0588(11) Å	α = 90°
	b = 10.7193(9) Å	β = 104.875(2)°
	c = 15.8075(14) Å	γ = 90°
Volume	1974.8(3) Å^3	
Z	4	
Density (calculated)	1.864 g/cm^3	
Absorption coefficient	5.962 mm^{-1}	
F(000)	1064	
Theta range for data collection	3.10 to 31.05°	
Index ranges	-17<=h<=17, -15<=k<=15, -22<=l<=22	
Reflections collected	29635	
Independent reflections	6319 [R(int) = 0.0384]	
Absorption correction	multi-scan	

Max. and min. transmission	0.2514 and 0.2103	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	6319 / 0 / 247	
Goodness-of-fit on F2	1.092	
Δ/σmax	0.003	
Final R indices	5325 data; I>2σ(I)	R1 = 0.0234, wR2 = 0.0513
	all data	R1 = 0.0332, wR2 = 0.0544
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0250P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.830 and -1.294 eÅ^{-3}	
R.M.S. deviation from mean	0.150 eÅ^{-3}	

Crystal data and structure refinement for compound **65**

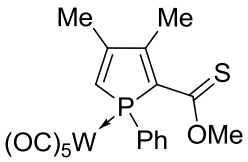


65

Identification code	mat139	
Empirical formula	C24 H15 O11 P W2	
Formula weight	878.03	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.8963(4) Å	a= 85.551(2)°.
	b = 11.8911(6) Å	b= 89.254(2)°.
	c = 12.3316(6) Å	g = 67.831(2)°.
Volume	1339.62(11) Å^3	
Z	2	
Density (calculated)	2.177 Mg/m^3	
Absorption coefficient	8.697 mm^{-1}	

F(000)	820
Crystal size	0.40 x 0.40 x 0.30 mm^3
Theta range for data collection	1.66 to 31.11°.
Index ranges	-14<=h<=14, -17<=k<=17, -17<=l<=17
Reflections collected	26318
Independent reflections	8354 [R(int) = 0.0491]
Completeness to theta = 31.11°	97.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.1801 and 0.1285
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8354 / 0 / 340
Goodness-of-fit on F^2	1.204
Final R indices [I>2sigma(I)]	R1 = 0.0361, wR2 = 0.0800
R indices (all data)	R1 = 0.0409, wR2 = 0.0826
Largest diff. peak and hole	1.631 and -2.969 e.$Å^{-3}$

Crystal data and structure refinement for compound **67**

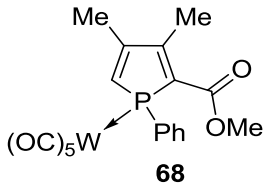


67

Identification code	mat161s	
Chemical formula	$C_{19}H_{15}O_6PSW$	
Formula weight	586.19	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.180 x 0.300 x 0.420 mm	
Crystal habit	brown block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.2561(2) Å	α = 64.5800(10)°
	b = 10.9951(2) Å	β = 69.8690(10)°
	c = 11.4642(3) Å	γ = 62.6370(10)°
Volume	1019.45(4) $Å^3$	
Z	2	

Density (calculated)	1.910 g/cm^3	
Absorption coefficient	5.879 mm^{-1}	
F(000)	564	
Theta range for data collection	2.00 to 45.50°	
Index ranges	-20<=h<=20, -22<=k<=21, -22<=l<=22	
Reflections collected	50219	
Independent reflections	17139 [R(int) = 0.0575]	
Coverage of independent reflections	99.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.4176 and 0.1915	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	17139 / 0 / 256	
Goodness-of-fit on F2	0.979	
Δ/σmax	0.003	
Final R indices	13356 data; I>2σ(I)	R1 = 0.0376, wR2 = 0.0793
	all data	R1 = 0.0588, wR2 = 0.1033
Weighting scheme	w=1/[$\sigma^2(F_o^2)$+(0.0509P)^2+0.0000P] where P=(F_o^2+2F_c^2)/3	
Largest diff. peak and hole	1.459 and -3.495 eÅ^{-3}	
R.M.S. deviation from mean	0.426 eÅ^{-3}	

Crystal data and structure refinement for compound **68**

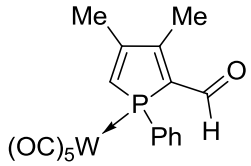


68

Identification code	mat142
Empirical formula	C19 H15 O7 P W
Formula weight	570.13

Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.8473(10) Å	a= 90°.
	b = 10.3999(9) Å	b= 105.103(2)°.
	c = 15.6057(13) Å	g = 90°.
Volume	2013.1(3) $Å^3$	
Z	4	
Density (calculated)	1.881 Mg/m^3	
Absorption coefficient	5.855 mm^{-1}	
F(000)	1096	
Crystal size	0.38 x 0.36 x 0.32 mm^3	
Theta range for data collection	1.64 to 31.15°.	
Index ranges	-18<=h<=18, -15<=k<=11, -22<=l<=22	
Reflections collected	27358	
Independent reflections	6450 [R(int) = 0.0488]	
Completeness to theta = 31.15°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2559 and 0.2144	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6450 / 0 / 256	
Goodness-of-fit on F^2	1.080	
Final R indices [I>2sigma(I)]	R1 = 0.0257, wR2 = 0.0601	
R indices (all data)	R1 = 0.0313, wR2 = 0.0619	
Largest diff. peak and hole	1.634 and -2.050 $e.Å^{-3}$	

Crystal data and structure refinement for compound **69**

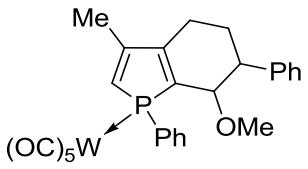


69

Identification code	mat146
Empirical formula	C18 H13 O6 P W
Formula weight	540.10
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	P2(1)/n	
Unit cell dimensions	a = 23.0500(13) Å	a= 90°.
	b = 10.6336(5) Å	b= 106.282(2)°.
	c = 31.9768(19) Å	g = 90°.
Volume	7523.3(7) $Å^3$	
Z	16	
Density (calculated)	1.907 Mg/m^3	
Absorption coefficient	6.257 mm^{-1}	
F(000)	4128	
Crystal size	0.40 x 0.24 x 0.14 mm^3	
Theta range for data collection	1.28 to 30.62°.	
Index ranges	-32<=h<=32, -11<=k<=15, -45<=l<=45	
Reflections collected	116951	
Independent reflections	23087 [R(int) = 0.0864]	
Completeness to theta = 30.62°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4746 and 0.1886	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	23087 / 346 / 1020	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0534, wR2 = 0.1024	
R indices (all data)	R1 = 0.1034, wR2 = 0.1290	
Largest diff. peak and hole	2.309 and -2.409 e.$Å^{-3}$	

Crystal data and structure refinement for compound **70**

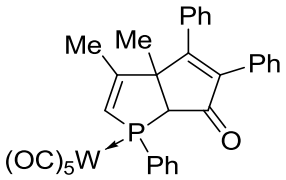


70

Identification code	mat151s	
Empirical formula	C27 H23 O6 P W	
Formula weight	658.27	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.4421(3) Å	a= 90°.
	b = 15.0036(4) Å	b= 99.8350(10)°.
	c = 14.0515(4) Å	g = 90°.
Volume	2584.53(12) $Å^3$	

Z	4
Density (calculated)	1.692 Mg/m^3
Absorption coefficient	4.570 mm^{-1}
F(000)	1288
Crystal size	0.38 x 0.34 x 0.30 mm^3
Theta range for data collection	3.09 to 31.10°.
Index ranges	-18<=h<=18, -14<=k<=21, -20<=l<=20
Reflections collected	33531
Independent reflections	8264 [R(int) = 0.0296]
Completeness to theta = 31.10°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3410 and 0.2756
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8264 / 0 / 318
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0206, wR2 = 0.0418
R indices (all data)	R1 = 0.0274, wR2 = 0.0437
Largest diff. peak and hole	0.706 and -0.751 $e.Å^{-3}$

Crystal data and structure refinement for compound **74a**

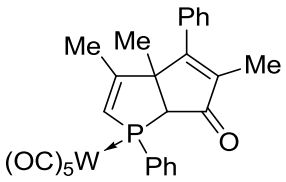


74a

Identification code	mat155s	
Empirical formula	C32 H23 O6 P W	
Formula weight	718.32	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.8561(3) Å	a= 90°.
	b = 18.8634(4) Å	b=105.5100(10)°.
	c = 10.3930(2) Å	g = 90°.
Volume	2806.44(10) $Å^3$	
Z	4	
Density (calculated)	1.700 Mg/m^3	
Absorption coefficient	4.217 mm^{-1}	
F(000)	1408	

Crystal size	0.22 x 0.12 x 0.10 mm^3
Theta range for data collection	2.98 to 31.07°.
Index ranges	-21<=h<=21, -27<=k<=27, -14<=l<=15
Reflections collected	38729
Independent reflections	8955 [R(int) = 0.0437]
Completeness to theta = 31.07°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6778 and 0.4572
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8955 / 0 / 363
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0257, wR2 = 0.0524
R indices (all data)	R1 = 0.0382, wR2 = 0.0563
Largest diff. peak and hole	1.370 and -0.873 e.$Å^{-3}$

Crystal data and structure refinement for compound **74b**

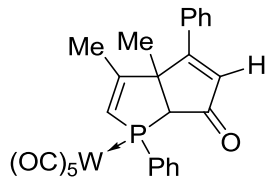


74b

Identification code	mat163s	
Chemical formula	$C_{27}H_{21}O_6PW$	
Formula weight	656.26	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.060 x 0.100 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 12.7092(11) Å	α = 90°
	b = 15.1650(11) Å	β = 98.073(3)°
	c = 12.9120(12) Å	γ = 90°
Volume	2463.9(4) $Å^3$	
Z	4	
Density (calculated)	1.769 g/cm^3	

Absorption coefficient	4.794 mm^{-1}	
F(000)	1280	
Theta range for data collection	2.08 to 31.06°	
Index ranges	-18<=h<=18, -20<=k<=21, -18<=l<=18	
Reflections collected	30069	
Independent reflections	7870 [R(int) = 0.0737]	
Coverage of independent reflections	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7619 and 0.6457	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	7870 / 0 / 319	
Goodness-of-fit on F2	1.067	
Δ/σmax	0.001	
Final R indices	5843 data; I>2σ(I)	R1 = 0.0394, wR2 = 0.0982
	all data	R1 = 0.0654, wR2 = 0.1383
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0713P)^2+0.1288P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.275 and -1.689 $eÅ^{-3}$	
R.M.S. deviation from mean	0.350 $eÅ^{-3}$	

Crystal data and structure refinement for compound **74c**

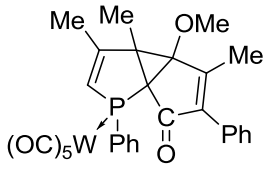


74c

Identification code	mat165s
Chemical formula	$C_{26}H_{19}O_6PW$
Formula weight	642.23
Temperature	103(2) K

Wavelength	0.71073 Å	
Crystal size	0.120 x 0.200 x 0.240 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 12.1714(3) Å	α = 90°
	b = 15.2546(4) Å	β = 100.9559(8)°
	c = 12.7074(3) Å	γ = 90°
Volume	2316.38(10) $Å^3$	
Z	4	
Density (calculated)	1.842 g/cm^3	
Absorption coefficient	5.097 mm^{-1}	
F(000)	1248	
Theta range for data collection	2.11 to 31.04°	
Index ranges	-17<=h<=17, -22<=k<=22, -18<=l<=18	
Reflections collected	49781	
Independent reflections	7396 [R(int) = 0.0498]	
Coverage of independent reflections	99.8%	
Absorption correction	multi-scan	
Max. and min. transmission	0.5800 and 0.3740	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	7396 / 0 / 309	
Goodness-of-fit on F2	1.033	
Δ/σmax	0.001	
Final R indices	6481 data; I>2σ(I)	R1 = 0.0208, wR2 = 0.0455
	all data	R1 = 0.0270, wR2 = 0.0481
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0186P)^2+1.3265P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.249 and -0.871 $eÅ^{-3}$	
R.M.S. deviation from mean	0.117 $eÅ^{-3}$	

Crystal data and structure refinement for compound **75**



75

Identification code	mat159s	
Chemical formula	$C_{29}H_{23}O_7PW$	
Formula weight	698.29	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.140 x 0.160 x 0.200 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 20.414(2) Å	α = 90°
	b = 12.6386(12) Å	β = 106.811(3)°
	c = 22.2892(18) Å	γ = 90°
Volume	5504.9(9) $Å^3$	
Z	8	
Density (calculated)	1.685 g/cm^3	
Absorption coefficient	4.299 mm^{-1}	
F(000)	2736	
Theta range for data collection	1.60 to 25.00°	
Index ranges	-24<=h<=24, -15<=k<=15, -26<=l<=26	
Reflections collected	62684	
Independent reflections	9697 [R(int) = 0.0745]	
Absorption correction	multi-scan	
Max. and min. transmission	0.5844 and 0.4801	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	9697 / 369 / 791	

Goodness-of-fit on F2	1.159	
Δ/σmax	0.001	
Final R indices	8016 data; I>2σ(I)	R1 = 0.0360, wR2 = 0.1011
	all data	R1 = 0.0522, wR2 = 0.1375
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0813P)^2+3.4694P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	2.885 and -2.644 eÅ^{-3}	
R.M.S. deviation from mean	0.360 eÅ^{-3}	