Six-membered Rings With One Phosphorus Atom

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1 Introduction

The chemistry of six-membered ring containing one phosphorus atom has seen remarkable development in the period of interest (2008–18). Noticeably, the use of λ^3-phosphinines in transition metal catalysis, coordination chemistry, and material science has been widely investigated.[1–7] This is due to their unique structural and electronic properties compared to other heterocycles.

During the last decade, methods enabling straightforward access of λ^5-phosphinines have also been developed and applications of those molecules in the development of highly fluorescent materials and in biological imaging are currently of high interest.

Fig. 1 shows the nomenclature of common six-membered ring containing one phosphorus atom, where λ refers to valency of the phosphorus atom. This nomenclature will be used throughout this article.

2 Theoretical methods

Similarly to benzene and pyridine, phosphinines are planar, aromatic and follow Hückel's rule. Theoretical calculations using bond separation and homodesmic reaction energies suggest their aromaticity to be as high as 88% of that of benzene.[8,9] As demonstrated by photoelectron and electron transmission spectroscopy and also by theoretical calculations, electronic properties of phosphinines differ significantly from pyridines.[10–13] In fact, as shown in **Fig. 2**, The $HOMO^{-2}$ orbital has a large coefficient at the phosphorus atom and represents essentially the lone-pair at the heteroatom. Additionally, the orbital on the phosphorus is more diffuse and less directional as reflected by the strong 3 s-orbital character (63.8%) versus 29.1% found for the nitrogen atom in pyridines. Consequently, phosphinines show very low basicity in aqueous solutions with a pK_a ($C_5H_6P^+$) = 16.1 ± 1.0, and are relatively inert towards electrophilic attack.[14]

Importantly, while the $HOMO^{-1}$ and HOMO orbitals contribute to π-donation, the LUMO orbital enables the heterocycle to act as a π-acceptor ligand, once coordinated to the metal center via the phosphorus atom. Consequently, phosphinines are now known as much better π-acceptor ligands, but less good σ donors compared to pyridines.[15–17]

The effect of the substituents on frontier orbitals has mainly been investigated computationally by the group of Müller.[18] For instance, the relative frontier energies of a series of pyridyl-functionalized phosphinines **2a–e** were studied and compared to the parent phosphinine (**Fig. 3**). Both the sequence and the shape of the π- and n-orbitals resemble those of phosphinine. It was found that electron-withdrawing substituents such as fluorine and trifluoromethyl reduce the energy of the LUMO leading to stronger π-acceptance properties. Inversely, introducing a Me- or MeS- substituent results in increasing the HOMO of **2d**,**e** compared to **2a**. For instance, the strong + M effect of the MeS- group increases the π-donor properties of **2e** by conjugative interactions through the HOMO. Importantly, the same group investigated the orbital energy of 2-(trimethylsilyl)-λ^3-phosphinine **3** and compared it to that of the parent phosphinine.[19] In this regard, while the LUMO energies of both heterocycles are almost similar, a change of the orbital sequence of the $HOMO^{-1}$ and $HOMO^{-2}$ was noticed when the —$Si(CH_3)_3$ group is introduced. While the phosphorus lone pair is represented by the $HOMO^{-2}$ in phosphinine, it becomes the $HOMO^{-1}$ in 2-(trimethylsilyl)-λ^3-phosphinine **3**. Consequently, the latter is a much better σ-donor than the parent phosphinine.

The NICS parameter is defined as a negative value of the absolute shielding measured in the center of a given ring. These calculations confirmed the aromaticity of phosphinine, resulting in a value of − 10.2 (− 11.5 and − 10.6 for benzene and pyridine, respectively).

The use of NICS to gauge the aromaticity of other six membered phosphorus heterocycles has also been investigated. In this context, Hansmann has recently studied the aromaticity of azaphosphinines and compared them to the corresponding phosphinin-2-olate and its methylated derivative. For this purpose, NICS(1), which are obtained by placing a dummy atom 1 Å above the geometrical center of the heterocycle, were used. As shown in **Fig. 4**, the aromaticity of both 1,3-azaphosphinin-6-olate **4b** (− 5.0) and 1,4-azaphosphinin-6-olate **4c** (− 5.2) are low, although slightly higher than the phosphinin-2-olate **4a** (− 4.8). Importantly, a noticeable increase of the aromaticity by about 4.5 ppm is achieved with methoxylated azaphosphinines. Although high, these values remain low compared to that of pyridine.[20]

In contrast to phosphinines **1** (NICS(1) = − 10.1 ppm), azaphosphinines ((NICS(1) = − 9.5 ppm), and phosphinin-2-olate (NICS(1) = − 4.8 ppm), the NICS values of a large variety of fused six-membered phosphorus heterocycles **5** were found positive, suggesting an anti-aromatic character (**Fig. 4**). This antiaromaticity is preserved independently of the structure of the fused heterocycles or the oxidation state at the phosphorus atom (**Fig. 5**).[21]

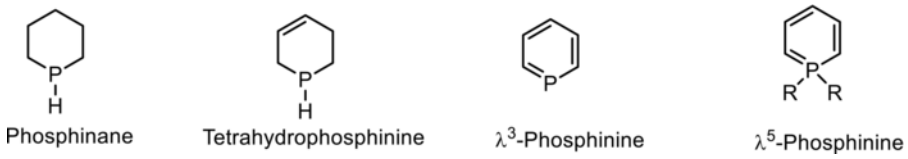


Fig. 1

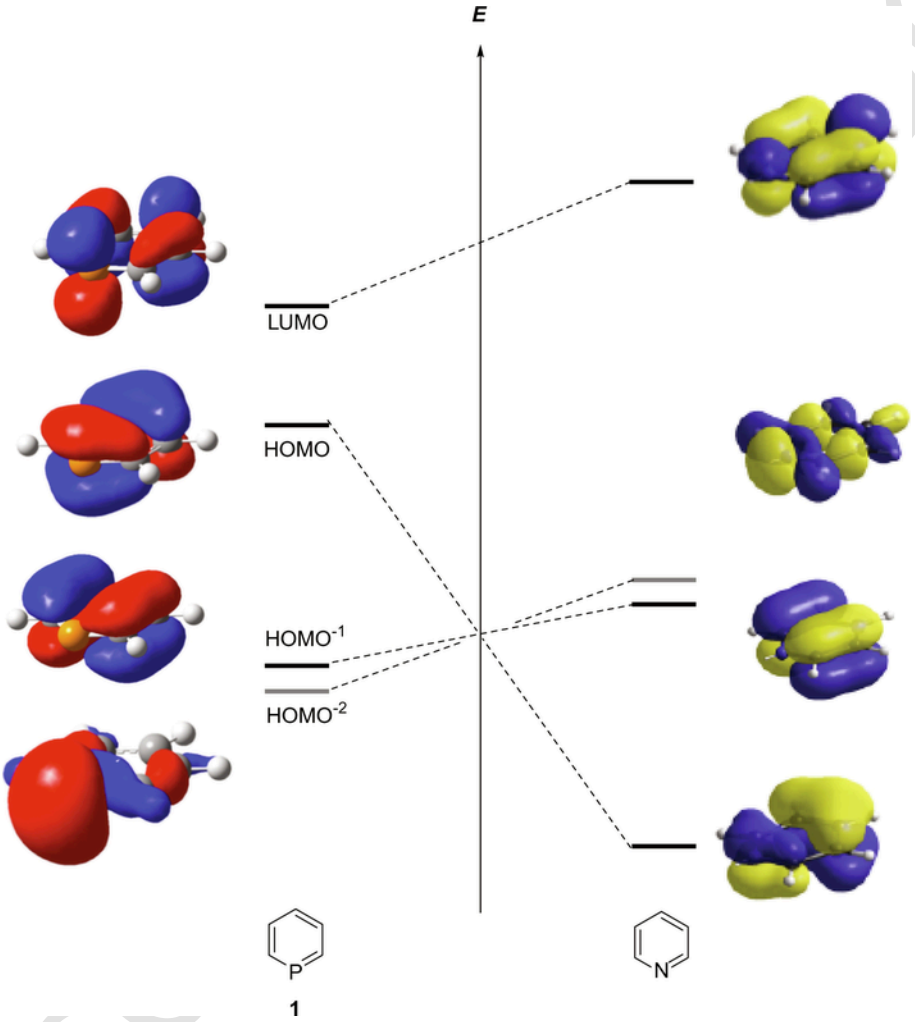


Fig. 2 Qualitative MO-diagram of the frontier orbitals of phosphinine **1** (left) and pyridine (right).

The aromaticity of two λ^5-phosphinines **6a,b** has recently been calculated. Despite the presence of electron withdrawing groups (CN) in **6a**, **6b** has the same NICS(0) value than the parent phosphinine **6a** (Fig. 6).[22]

3 Experimental structural methods

3.1 X-ray structures and NMR of 6 MR phosphines

3.1.1 Aryl-phosphines

A synthetic route to a phospha-naphthalene **8** was developed, and the reactivity of this aromatic phosphine was investigated in cycloaddition reaction with dimethyl-butadiene (Scheme 1). The phosphines **8** and **9** (as a molybdenum $Mo(CO)_5$ complex) were

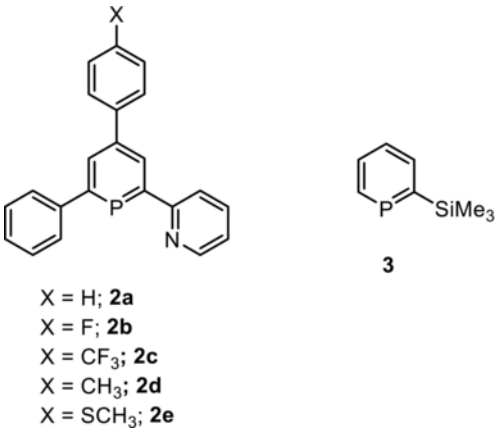


Fig. 3

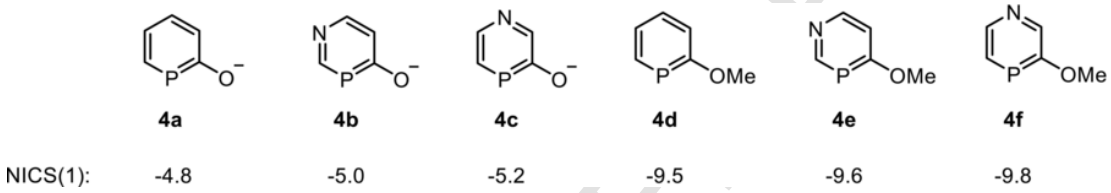


Fig. 4

characterized in the solid state by X-ray diffraction analysis.[23] The phospha-naphthalene scaffold is fully planar with the two P—C bonds of nearly equal lengths (1.710(7) Å for bond a and 1.734(8) Å for bond f) (**Scheme 1**).

The decoordination of tungsten from 6-MR phosphines was investigated and conveniently analyzed by NMR spectroscopy. Photolysis of **10** in a THF solution containing 1,2-bis(diphenylphosphino)ethane (dppe) afforded the free phosphine **11** in 81% featuring an interesting tricyclic core (**Scheme 2**).[24]

Formation of cyclic phosphonium cations from Au(III) complexes by carbon-phosphorus reductive elimination was described and compound **12** was structurally characterized. Noncatalyzed reaction to obtain analogous six-membered phosphorus-based architectures were developed and a number of polyaromatic triarylphosphine oxides **12–13** were characterized in the solid state (**Fig. 7**).[25]

A representative X-ray structure of the type of **13** bearing an annulated thiophene heteroaromatic ring (**Fig. 8**) showed that these structures are essentially planar and that the six-membered phosphorus heterocycle had C—C bonds of similar lengths, in the range of 1.43 and 1.46 Å.

3.1.2 Alkyl-phosphines

Aminophobanes and alkylphobanes were used as ligands in Pt and Co complexes and numerous complexes were characterized in the solid-state by X-ray diffraction analysis. Structures of the cobalt complexes with phobanes ligands evidenced the close contact between a CO ligand and two hydrogen atoms from one of the 6-membered rings of the phobane ligand (**Fig. 9**).[26]

Several seleno-phobanes were characterized in the solid state (**Fig. 10**A). The structure of *i*-butylphobane liganded Grubbs II catalyst showed a distorted square pyramid coordination geometry around the Ru center with the phobane and NHC ligands in trans relation (**Fig. 10**B).[27]

Several Pt complexes containing a cyclic diphosphine ligand were characterized in the solid state as part of a structural investigation of the size of the cycles on the geometry of the Pt complexes. The Tolman cone angles and bidentate angles of **12** and related diphosphines were determined (**Table 1**).

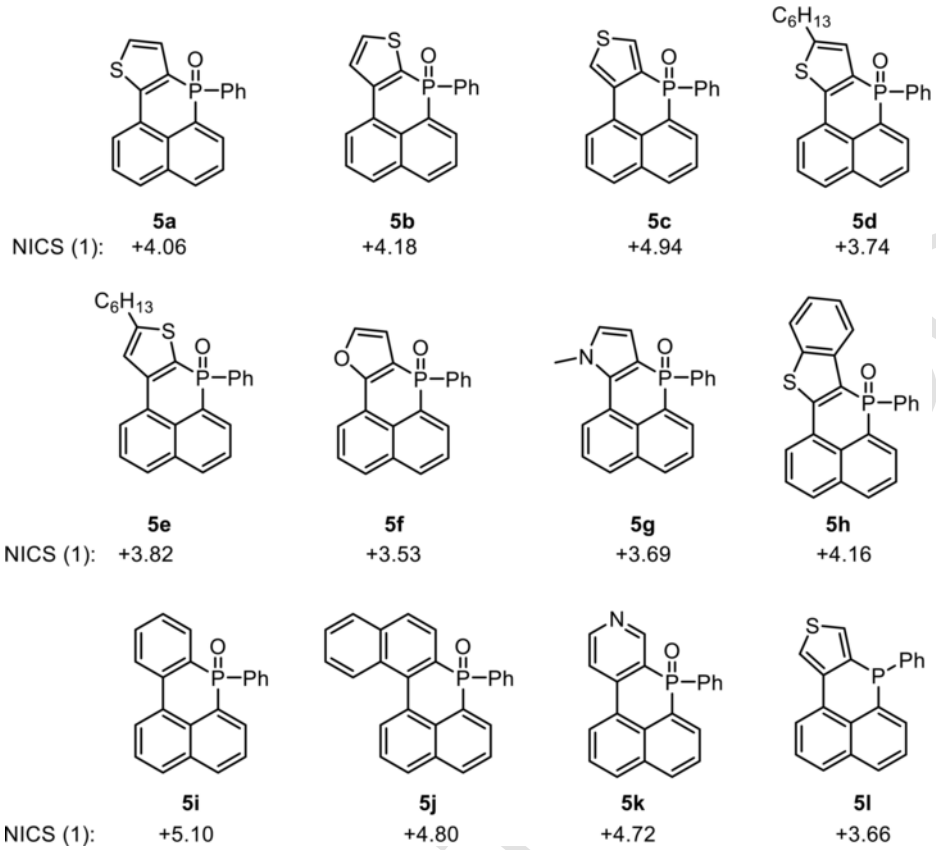


Fig. 5

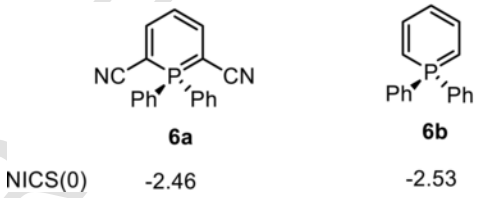


Fig. 6

4 Reactivity of nonconjugated rings

4.1 Reactions at the phosphorus atom

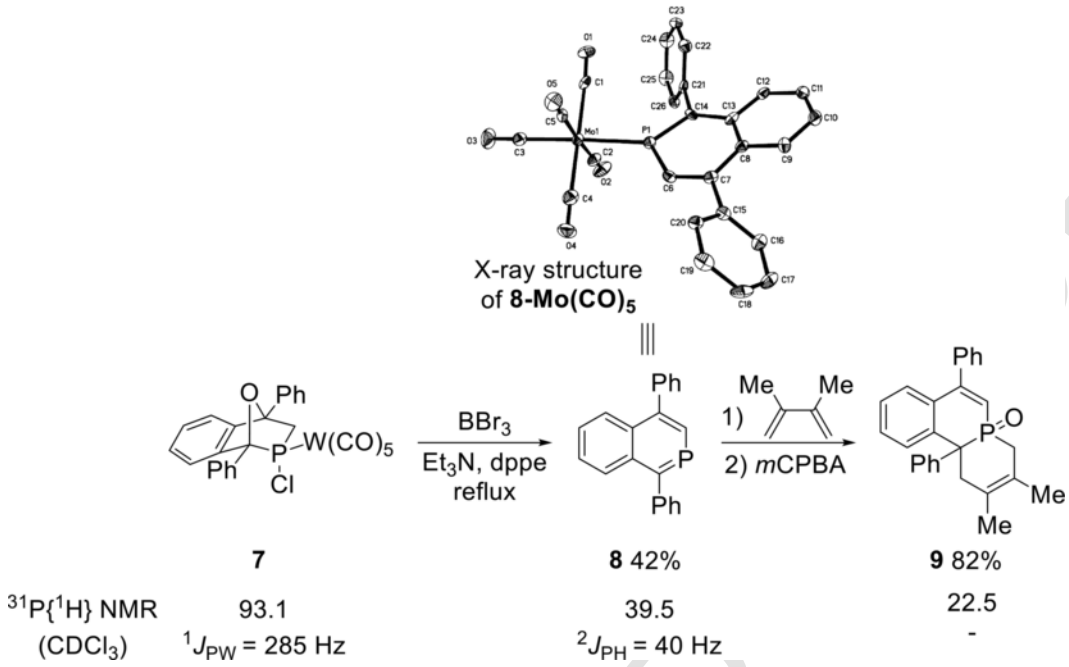
4.1.1 P-alkylation

Radical alkylation at the phosphorus atom of the bicyclic secondary phosphinane **16** was performed using the 2,2′-Azobis(2-methylbutyronitrile) (vazo) as a radical initiator at 100 °C (**Scheme 3**).[28]

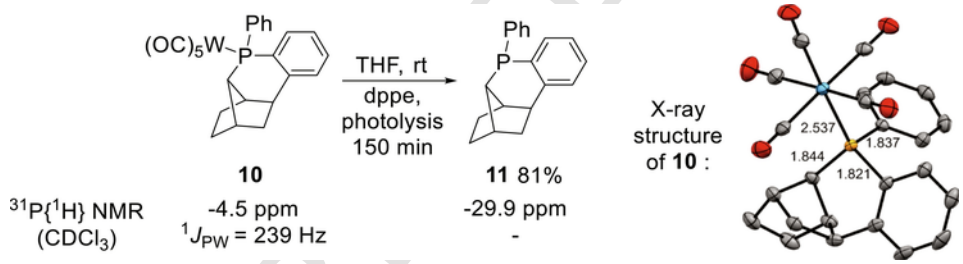
Another method consists of the transalkylation with methanol to synthesize new *P*-methylated phosphinane. However, this method has been described using cyclic phosphine oxide derivatives **18** and the desired product has not been isolated but engaged in a subsequent ring oxidation with chromium oxide (**Scheme 4**).[29]

4.1.2 Formation of P—BH_3 complex

The boration of cyclic phosphinanes has been considered by several research groups through different procedures. Borane•dimethylsulfide complex could perform the boration of several phosphinane rings, **20** or **22** (**Scheme 5**A and B).[30,31].



Scheme 1



Scheme 2

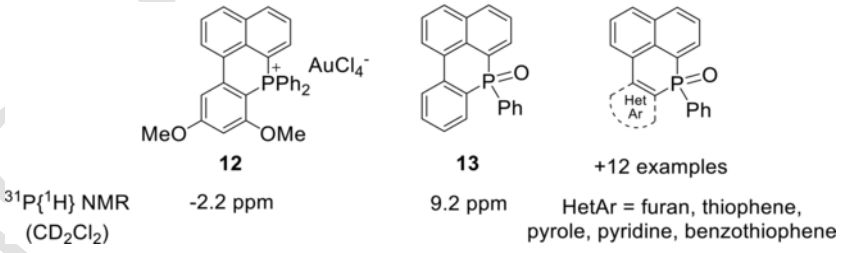


Fig. 7

A milder boration reaction of the phosphinane **24** was achieved with the borane•tetrahydrofuran complex at room temperature (**Scheme 6**).[32]

The boration of the phosphine oxide esters **26** was carried out through a sulfuration-reduction sequence. More precisely, phosphine oxide esters **26** were first converted into the corresponding thiophostones **27** using an excess of Lawesson's reagent and then subjected to reduction using Raney-Ni reagent. The trivalent phostone was then combined with borane dimethyl sulfide complex to yield the desired phosphonite-borane adducts **28** (**Scheme 7**).[33]

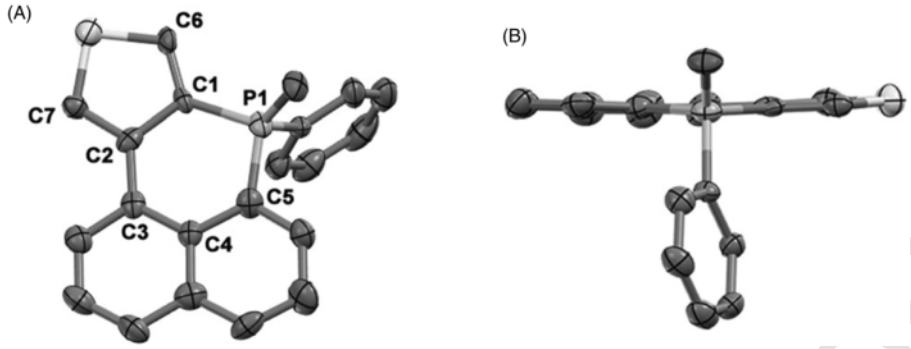


Fig. 8 Solid-state structure of a thiophene analogue of **13** with thermal ellipsoids at the 50% probability level; hydrogen atoms omitted for clarity. Selected bond lengths: C1—C2 1.441(8), C2—C3 1.465(9), C3—C4 1.439(9), C4—C5 1.434(8), C1—C6 1.364 (8), C2—C7 1.385(8).

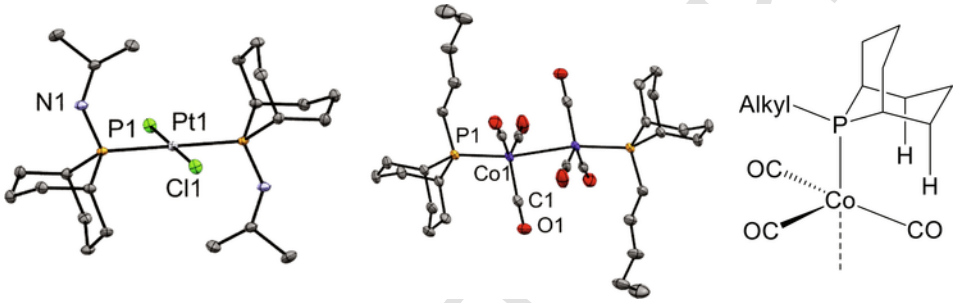


Fig. 9 (A) Crystal structure of trans-[$PtCl_2$(PhobPNHiPr)$_2$]. Selected bond lengths (Å) and angles (°): Pt(1)—P(1) 2.3241(10), Pt(1)—Cl(1) 2.3102(8), P(1)—N(1) 1.6594(16), Pt(1)—P(1)—N(1) 109.40(6); (B) Crystal structure of a Co complex Pt(1)—P(1) 2.3241(10), Pt(1)—Cl(1) 2.3102(8), P(1)—N(1) 1.6594(16), Pt(1)—P(1)—N(1) 109.40(6); (C) Scheme representing the axial protons repulsion with a CO ligands.

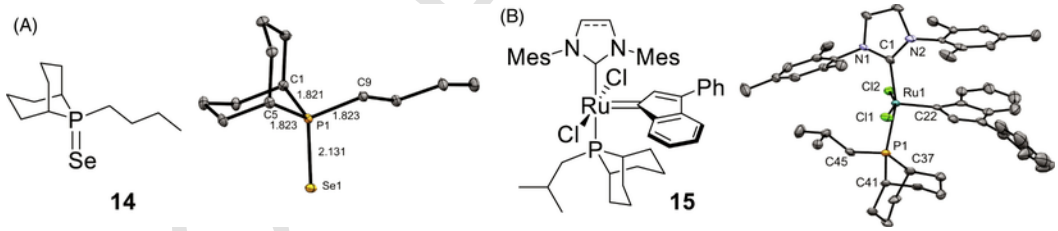


Fig. 10 (A) Structure and solid-state X-ray crystallographic structure of s-PhobP(*Se*)*n*Bu **14**; (B) Structure and ORTEP representation of complex **15** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for the sake of clarity. Selected bond lengths (Å) and angles (deg): Ru1—Cl1 2.3911(16), Ru1—Cl2 2.3999(15), Ru1—C1 2.090(6), Ru1—P1 2.4161(15), Ru1—C22 1.874(6), C1—Ru1—C22 102.4(2), C1—Ru1—Cl1 87.91(16), C1—Ru1—Cl2 91.57(16), C1—Ru1—P1 161.61(17), C22—Ru1—P1 96.01(16), Cl1—Ru—Cl2 162.68(5).

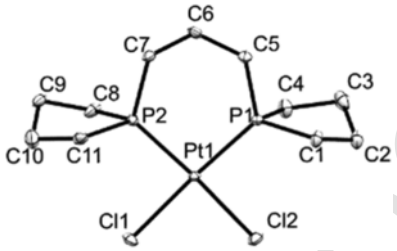
4.1.3 P-deboration

Amines are efficient reagents for the deboration of phosphonite borane derivatives. In particular, triethylamine in THF was used in the presence of 4-methoxybenzenethiol to provide decomplexation of the oxaphosphonite borane **29**. The yield greatly depends on the stereochemistry of the α-carbon of the phosphorus atom (**Scheme 8**).[34]

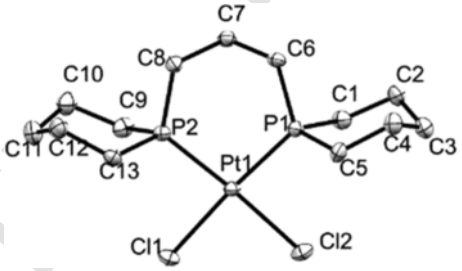
In another approach, the deboration of oxazaphosphinane **31** has been carried out using diethylamine in large excess for 3 h at 60 °C. This method allows the formation of phosphoramidite **32** with variable yields depending on the configuration of the phosphorus atom (**Scheme 9**).[31]

Table 1

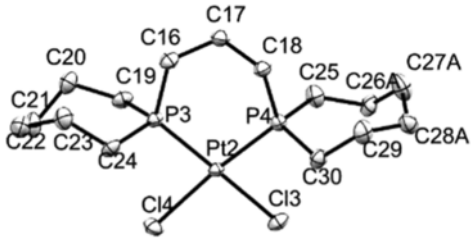
Bond distances/A°			
For compound A			
Pt1—P1	2.2143(11)	Pt1—P2	2.2089(11)



Pt1—Cl1	2.3604(10)	Pt1—Cl2	2.3533(10)
P1—C1	1.835(4)	P1—C4	1.828(4)
P1—C5	1.807(4)	P2—C7	1.819(4)
P2—C8	1.822(5)	P2—C11	1.838(4)
Intracyclic C—P—C: 96.0°			
P—Pt—P: 96.0°			
Tolman cone angle: 228°			
For compound B			
Pt1—P1	2.2228(12)	Pt1—P2	2.2289(13)



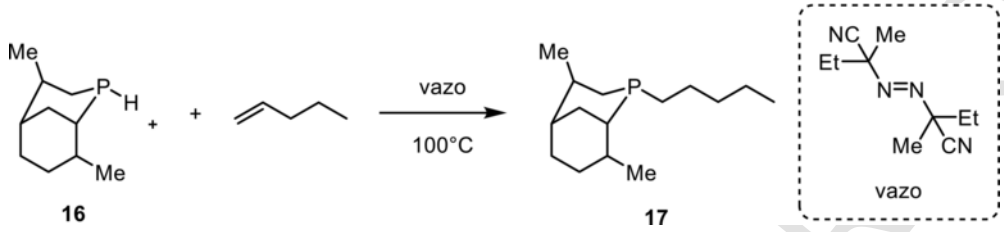
Pt1—Cl1	2.3716(13)	Pt1—Cl2	2.3774(13)
P1—C1	1.825(5)	P1—C5	1.822(5)
P1—C6	1.823(4)	P2—C8	1.817(5)
P2—C9	1.827(5)	P2—C13	1.827(5)
Intracyclic C—P—C: 104.3			
P—Pt—P: 96.5°			
Tolman cone angle: 229°			
For compound C			
Pt1—P1	2.2275(17)	Pt2—P3	2.2258(16)



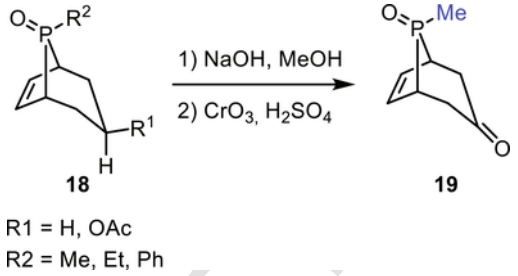
Pt1—P2	2.2330(15)	Pt2—P4	2.2293(15)
Pt1—Cl1	2.3719(16)	Pt2—Cl3	2.3740(16)
Pt1—Cl2	2.3884(16)	Pt2—Cl4	2.3898(15)
Pt1—P1	2.2275(17)	Pt2—P3	2.2258(16)
P1—C1	1.837(6)	P3—C16	1.835(6)
P1—C4	1.821(6)	P3—C19	1.829(6)
P1—C9	1.825(6)	P3—C24	1.821(6)
P2—C3	1.818(6)	P4—C18	1.810(6)

P2—C10	1.827(6)	P4—C25	1.823(6)
P2—C15	1.831(6)	P4—C30	1.825(6)

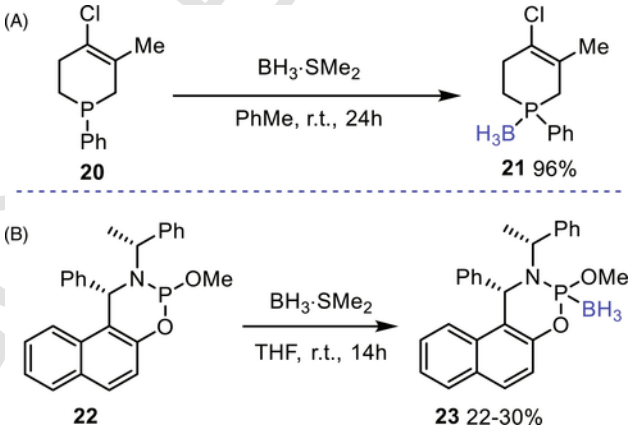
Intracyclic C—P—C: 109.8
P—Pt—P: 97.0
Tolman cone angle: 225°



Scheme 3

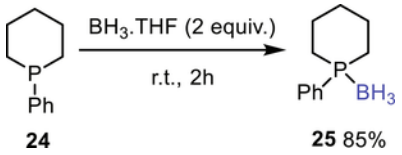


Scheme 4

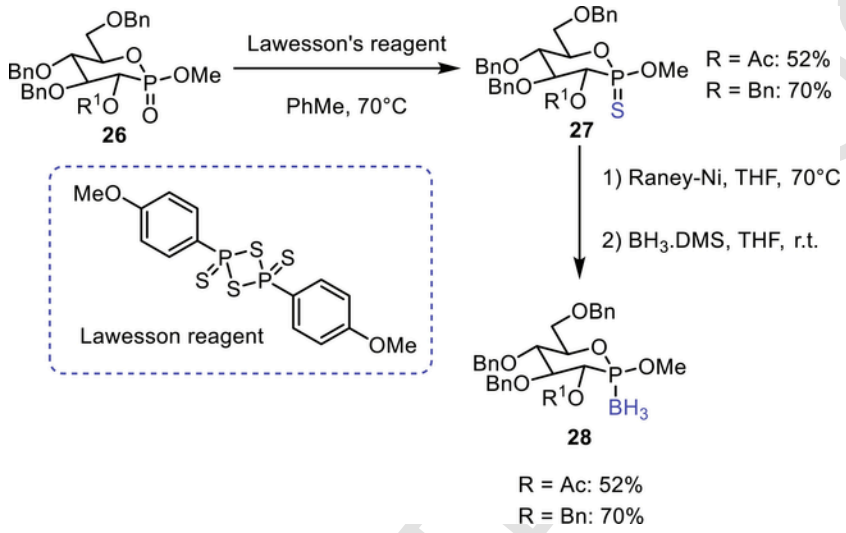


Scheme 5

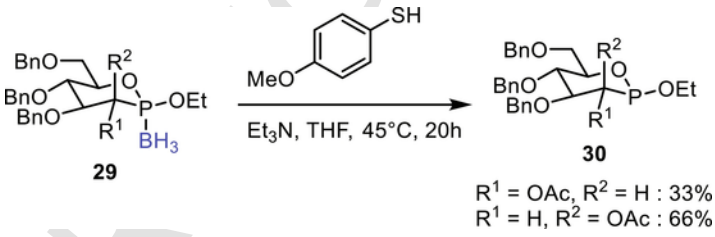
Finally, deboronation can occur at elevated temperatures in the presence of an olefin. For instance, the phosphine borane complex **33** could be converted to the phosphonium salt, which was not isolated but dealkylated in the presence of $LiAlH_4$ to form the phosphine **34** in 51% yield. (**Scheme 10**).[35]



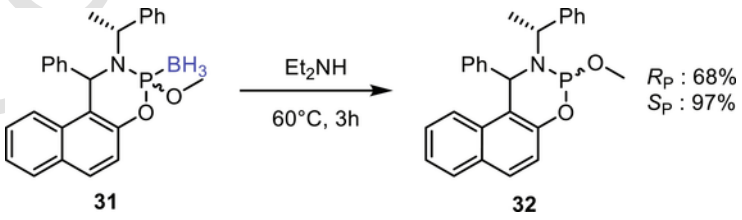
Scheme 6



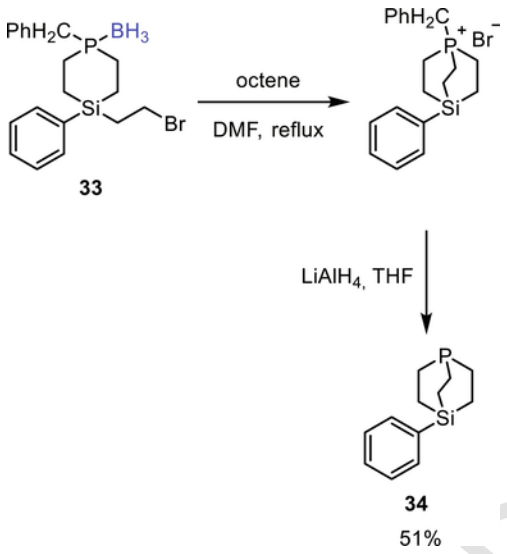
Scheme 7



Scheme 8



Scheme 9



Scheme 10

4.1.4 P-oxygenation

The formation of the P—O bond can be performed on 6MR chloro-phosphines. **35** was reacted with potassium phenylboronate in the presence of iodine and tetra-*n*-butylammonium bromide to give the corresponding benzoxazaphosphinyl phenylboronate **36** (**Scheme 11**).[36]

4.1.5 P-oxidation

The *meta*-chloroperoxybenzoic acid was shown to be an appropriate reagent for the oxidation of phosphine boranes **37** and the phosphine sulfide **39** to the corresponding phosphine oxides at room temperature (**Scheme 12**A and B).[1,37]

4.1.6 P-deoxygenation

Different silanes have been used for the deoxygenation of various six-membered phosphine rings, although moderate yields were obtained.

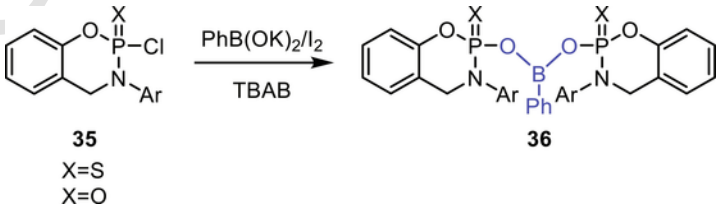
For example, diphenylsilane could reduce the 1-phenylphosphinane 1-oxide **41** when heated in dioxane at 100 °C, albeit with low conversion (**Scheme 13**A).[38] Similarly, the reduction of the phosphinane 1-oxide **43** by phenylsilane at 80 °C provided the corresponding phosphine **44** in 21% yield (**Scheme 13**B).[39]

In another approach, the use of trichlorosilane with pyridine improved the performance of the reduction in the case of unsaturated phosphine oxide rings **45** and **47** as quantitative yields were obtained (**Scheme 14**A and B).[29]

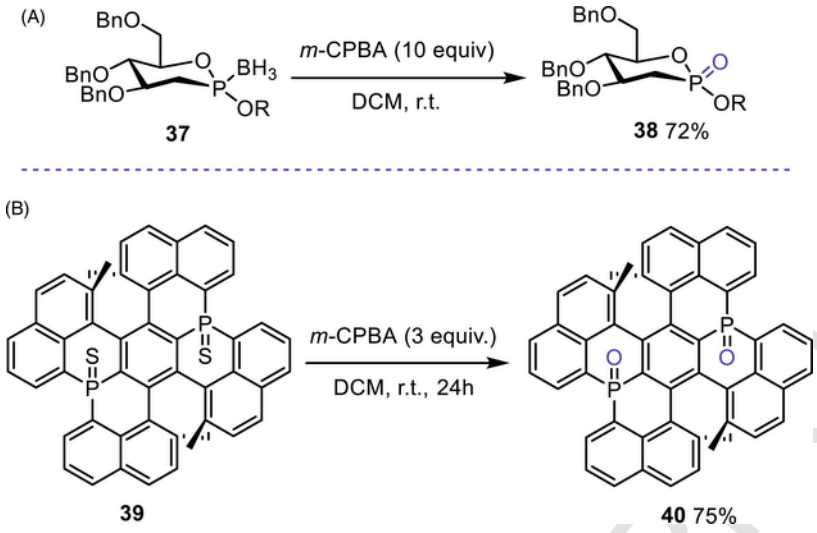
Finally, the combination of hexylsilane with a catalytic amount of trifluoromethanesulfonic acid (5 mol%) enabled the reduction of the phosphinane 1-oxide **41** in 85% yield (**Scheme 15**).[32]

4.1.7 P-chlorination

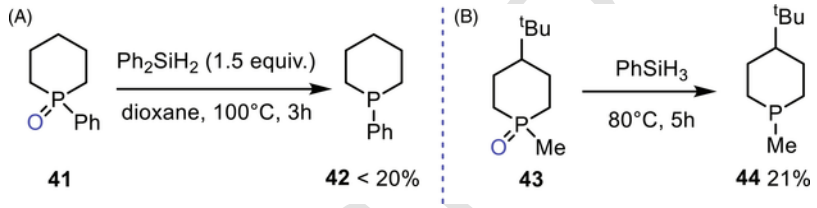
The chlorination of the phosphinic acid **45** was conducted with oxalyl chloride in the presence of a catalytic amount of dimethylformamide (**Scheme 16**).[39]



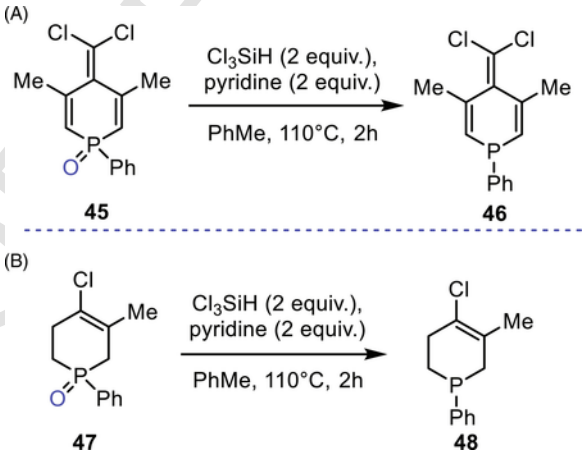
Scheme 11



Scheme 12

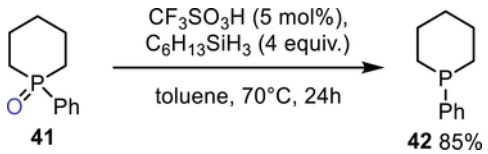


Scheme 13

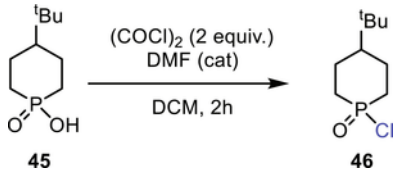


Scheme 14

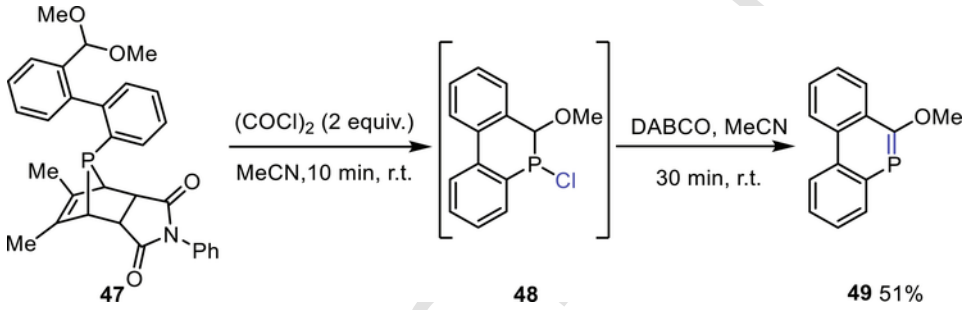
Moreover, oxalyl chloride was effective for the chlorination of bicyclic aryl phosphine **47**. The authors reported a decomposition of the bicyclic structure during the reaction accompanied by the creation of a new 6-membered ring. A dehydrochlorination of the resulting phosphine **48** with the 1,4-diazabicyclo[2.2.2]octane (DABCO) in CH_3CN leads to the formation of the corresponding polyaromatic compound **49** (Scheme 17).[40]



Scheme 15



Scheme 16



Scheme 17

4.1.8 P-sulfuration and P-selenation

The cyclic phosphine sulfide **51** could be synthesized by reacting **50** with an excess of elemental sulfur in toluene over 4 days at 60 °C (**Scheme 18**).

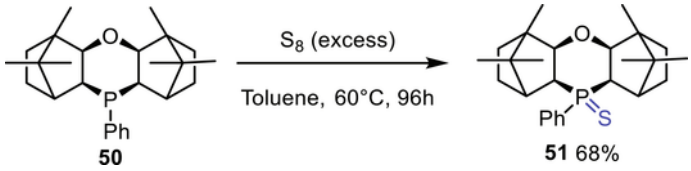
On the other hand, selenation of phosphine **50** by elemental selenium requires higher temperatures and results in the formation of the desired product **52** with a yield of 71% (**Scheme 19**).[41]

4.1.9 P-desulfuration

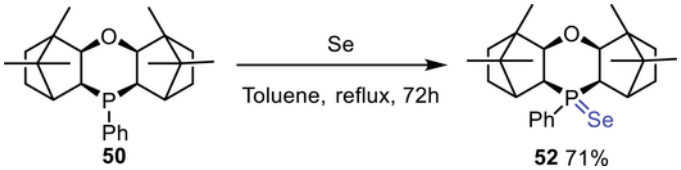
The reduction of phosphine sulfides can be performed utilizing the hexachlorodisilane in refluxed benzene (**Scheme 20**).[35]

Moreover, desulfuration of the P-fused double helicene **55** was achieved in the presence of 20 equivalents of triethylphosphine at 60 °C (**Scheme 21**).[37]

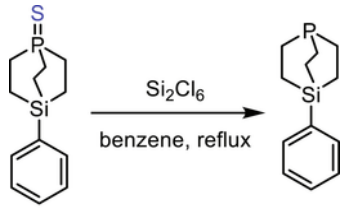
The Raney-Ni reagent was also effective in reducing phosphine sulfide **57** within 3 h at room temperature (**Scheme 22**).[42]



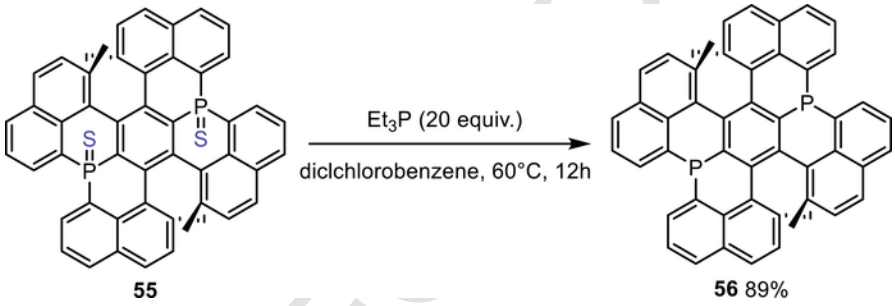
Scheme 18



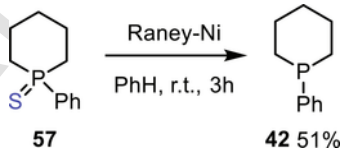
Scheme 19



Scheme 20



Scheme 21



Scheme 22

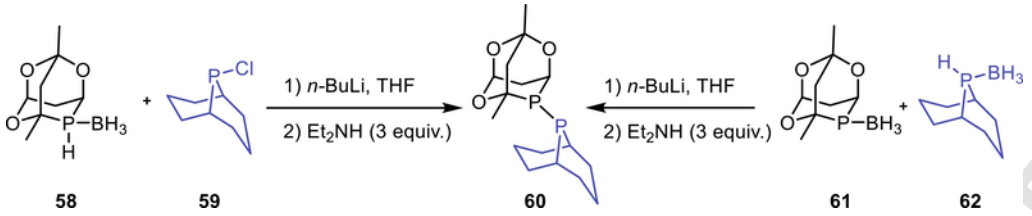
4.1.10 P-phosphorylation

The coupling of the borane•phosphinane complex **58** and 1-chlorophosphinane **59** occurs in the presence of *n*-BuLi to form the corresponding bicyclophosphonane **60** in 53% yield. Interestingly, the latter can also be obtained by combining **61** with **62** (**Scheme 23**).[43]

4.2 Ring reactions

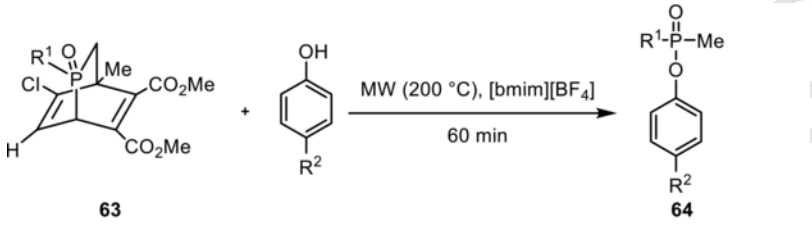
4.2.1 Ring rearrangements

The reaction of bicyclic phosphine oxides **63** with various phenols in ionic liquid [bmim][BF_4] under microwave activation at 200 °C leads to the formation of phosphinates **64** (**Scheme 24**).[44]



58 59 60 61 62

Scheme 23



63 64

Scheme 24

4.2.2 Baeyer-Villiger reaction

The extension of six-membered phosphinane oxide **65** into seven-membered phosphinate **66a,b** was achieved via Baeyer-Villiger using perbenzoic acids (**Scheme 25**).[29] A mixture of two isomers was obtained.

4.2.3 Diels-Alder reaction

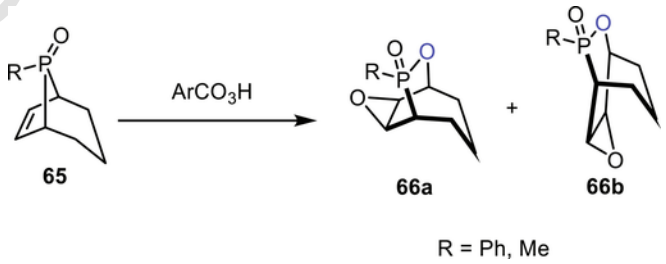
The cycloadducts **68** were obtained through the Diels Alder reaction of dihydrophosphinine oxides **67** (dienes) with *N*-phenylmaleimide (dienophile) in the ionic liquid [bmim][BF_4] and under microwave-activation (**Scheme 26**).

It should be mentioned that the intermolecular Diels-Alder reaction of two molecules of dihydrophosphinine oxide **67** is possible in the absence of solvents under microwave irradiation to give the dimer **69** in 70% yield (**Scheme 27**).[44]

4.2.4 Hydrogenation

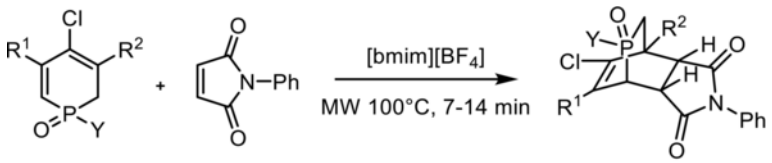
The hydrogenation of 4-chloro-dihydrophosphinine oxide **70** could be achieved using a palladium catalyst and in the presence of a large excess of ammonium formate in refluxing toluene for 4 h. The resulting mixture of hydrogenated products contains the chlorotetrahydrophosphinine oxide **71**, its dechlorinated congener **72**, and the fully saturated hexahydrophosphinine oxide **73** (**Scheme 28**).[45]

Later on, the same group conducted the selective mono-hydrogenation of *P*-phenyl-dihydrophosphinine oxide with the borane dimethyl sulfide complex (**Scheme 29**).[46]



65 66a 66b

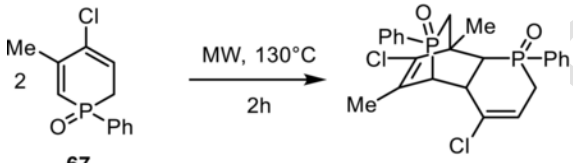
Scheme 25



67
R^1 = H, Me
R^2 = Me, H
Y = Ph, EtO

68 80-99%

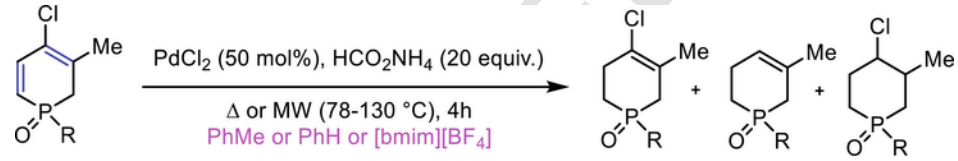
Scheme 26



67

69 70%

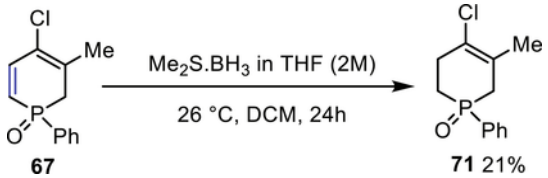
Scheme 27



70 **71** **72** **73**

R = Ph, PhMe, 110°C	22%	31%	47%
Ph, PhMe, MW 110°C	11%	79%	5%
Ph, [bmim][BF_4], 110°C	10%	41%	49%
Ph, [bmim][BF_4], (MW) 110°C	2%	59%	39%
Ph, PhH, 78°C	9%	44%	47%
Ph, [bmim][BF_4], 130°C	3%	45%	52%
EtO, PhMe, 110°C	10%	36%	54%

Scheme 28



67

71 21%

Scheme 29

4.3 Reactions at the ring carbons

4.3.1 Mannich reaction

The Mannich reaction of the unsaturated six-membered ring phosphorinanone **72** was carried out with methylamine and formaldehyde in ethanol to yield the air-stable bicyclic 1-aza-7-phosphabicyclo[3.3.1]nonan-9-ones **73** (**Scheme 30**).[47,48]

4.4 Reactivity of substituents attached to phosphorus atoms

4.4.1 O-esterification

Phosphinic acids cannot easily undergo direct esterification under conventional reaction conditions. In this context, microwave irradiation (200 °C) and high pressure were essential to perform the esterification reaction of phosphinic acid **74** to the corresponding phosphinate **75** in the presence of an excess of alcohol (**Scheme 31**).[49,50]

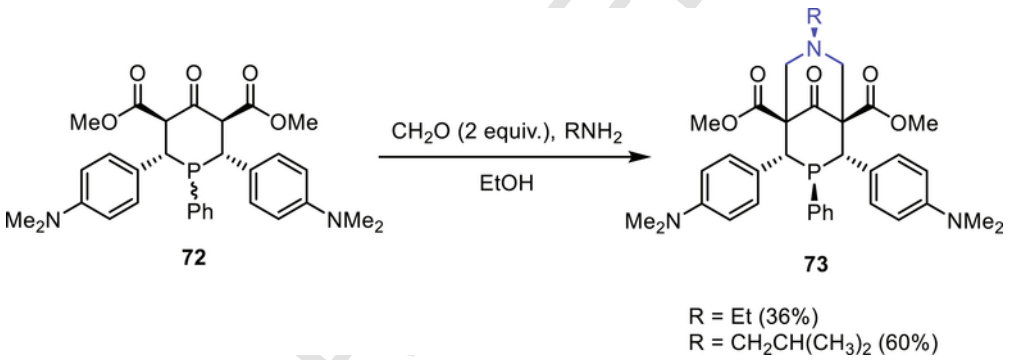
However, in order to avoid thermal degradation of some phosphinic acids, alkylation was performed instead of esterification, allowing to use milder conditions. For instance, esterification of 1-hydroxy-1,2,3,4,5,6-hexahydrophosphinine oxide **74** was carried out using TEBAC as catalyst (5%) under thermal (Δ) or MW activation (120 °C) for 1 h (**Scheme 32**).[49]

In an alternative approach, using K_2CO_3 in acetone under reflux enabled effective alkylation of several phosphinic acids **76a-c** (**Scheme 33**).[51]

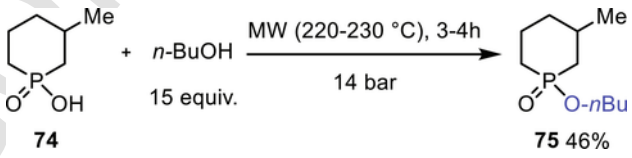
4.5 Monodentate 6-membered ring phosphine as ligands for TM catalysts

4.5.1 Catalysts for alkenes and alkynes metathesis

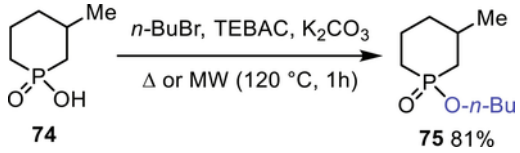
Isobutyl and cyclohexyl-bicyclononane phosphines (Phoban) are prevalent ligands in the ruthenium-carbene complexes [$Cl_2(PR_3)_2Ru(=CHR)$], known as Grubbs olefin catalysts (**Scheme 34**). Grubbs first and second generations of ruthenium complexes **77**–**79** bearing alkyl-



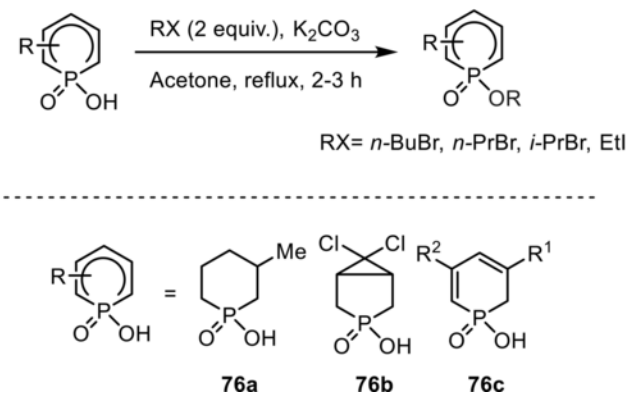
Scheme 30



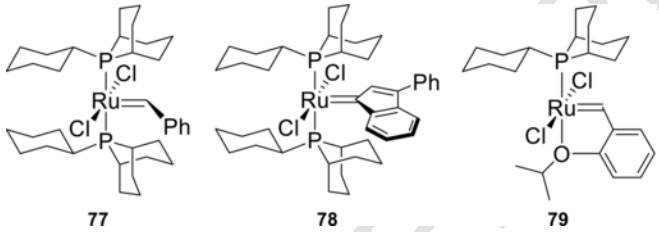
Scheme 31



Scheme 32



Scheme 33



Scheme 34 First generation ruthenium-alkylidene complexes bearing cyclohexylphobane ligands.

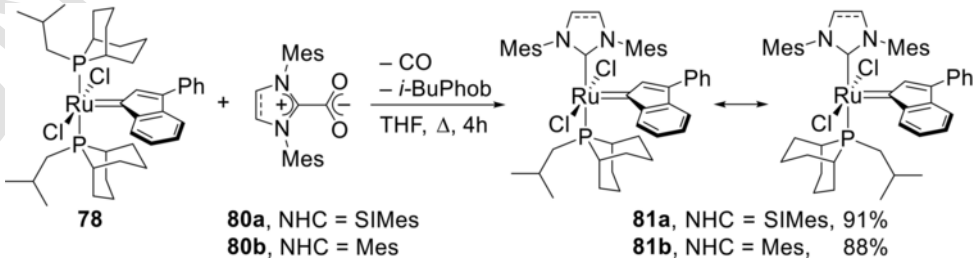
phobanes,[52] are widely used for ROMP, RCM and CM of alkenes,[18] for ethenolysis of long chain oleates, and in isomerizing olefin metathesis.[53]

Numerous structural modifications have been made on these alkyl-phosphine ligands to tailor the activity and stability of the ruthenium complex. Computational and kinetic investigations showed that further substitution of the bicyclic fused 6-membered rings of phobanes with Me, *i*Pr or *t*Bu groups had a limited effect on the yields and activity on the self-metathesis reaction of 1-octene.[54]

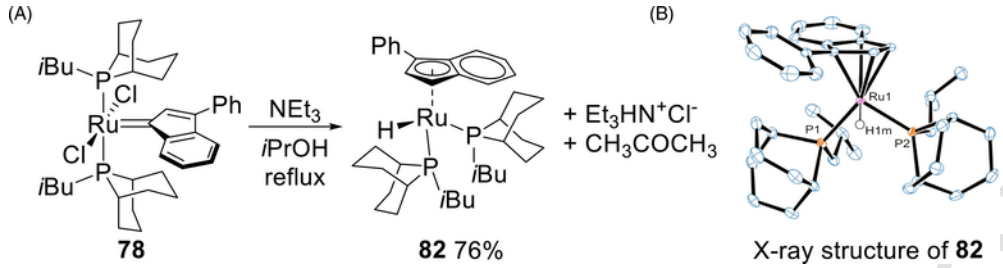
Modified Ru-complexes with a Phoban and an NHC ligand were prepared in high yields by a decarboxylative reaction from the NHC-CO_2 adducts **80a,b** (**Scheme 35**).[27] Variable temperature ^{31}P NMR spectroscopy showed that the isobutyl chain of the phobane ligands in the complexes **81a,b** point preferentially in the opposite direction of the ruthenium-indenyl moiety at low temperature (− 40 °C), which is also the case in the solid state. At this temperature in $CDCl_3$ as solvent, the signal of the phoban ligand in the transoid conformer **81a** was observed at 9.7 ppm whereas that of the cisoid congener **81b** was at − 0.3 ppm.

Using isobutyl phobanes as electron-rich bulky phosphines, Nolan reported a new rearrangement process of the metathesis pre-catalysts **78** under treatment with NEt_3, to form a ruthenium hydrido complex **82** which was characterized by X-ray diffraction analysis (**Scheme 36**B).[55]

Nolan and coworkers reported that the cyclohexylphobane Ru alkylidene complexes have superior performances over the isobutylphobane in the metathesis of 1-octene, and tested the scope of cross-metathesis reactions with a series of phoban containing pre-catalysts.[56]



Scheme 35



Scheme 36

4.5.2 Miscellaneous reactions

Iso-butylphobanes were used as ligands in dinuclear ruthenium ethylene complexes designed for atom transfer radical addition reaction of CCl_4 to styrene (**Scheme 37**). The dinuclear ruthenium ethylene complex **85b** obtained by coordination of ethylene to the corresponding Ru-precatalyst was characterized by XRD and had a typical piano-stool geometry.[57]

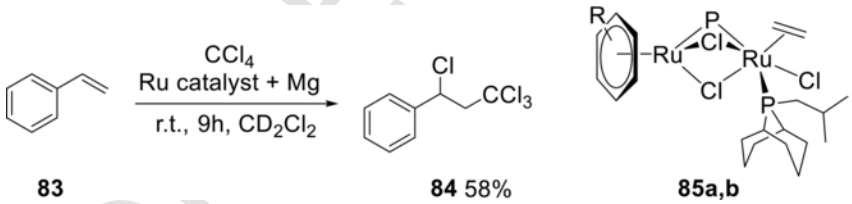
Substituted aminophobanes **87a,b** were employed for Cr-catalyzed ethene oligomerization and their coordination chemistry with rhodium, palladium, platinum was explored (**Scheme 38**).[58]

4.6 Bidentate 6-membered ring diphosphine ligands for TM catalysts

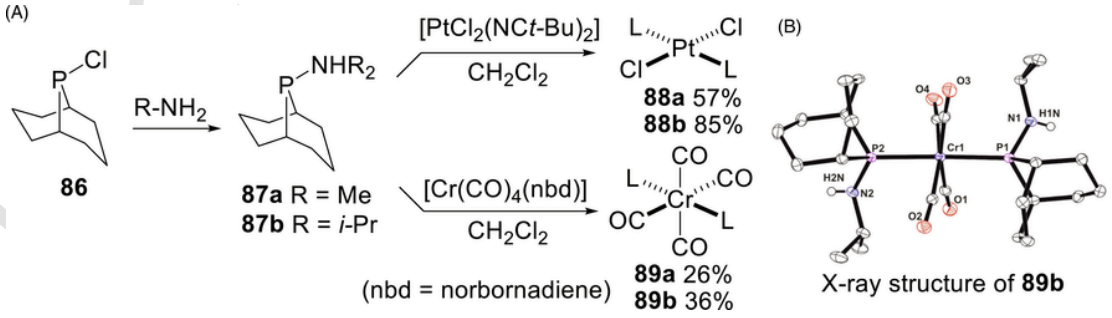
4.6.1 Bidentate phobane diphosphines derived ligands

The 1,2-bis(cyclooctylphosphanyl)ethane phosphines represent the most frequent occurrence of six-membered ring cyclic phosphines. Their coordination complexes with transition metals and the catalytic applications in which they have been applied are detailed in this section. The 1,2-bis(cyclooctylphosphanyl)ethane phosphines (bcope, **90**) were employed as electron-rich bidentate ligands for Pt[19] and Pd catalyzed alkynes hydrogenation and oligomerization (**Scheme 39**), in carbonylation reactions of alkynes, and in the palladium oxo process.[59] An arene palladium complex intermediate **91** with bcope ligands was characterized by multinuclear NMR with 2D $^{1}H—^{31}P$ HMQC correlations.[59]

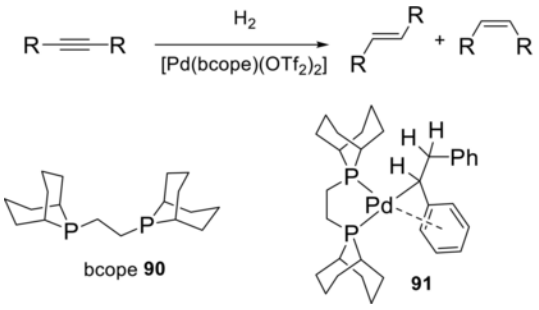
Finally, phobanes and other bidentate ligands could be used as ligands for the Rh-catalyzed homogeneous reductive amidation of aldehydes.[60]



Scheme 37 (**85a** arene = p-cymene **85b** arene = 1,3,5-*i*$Pr_3C_6H_3$)



Scheme 38



Scheme 39

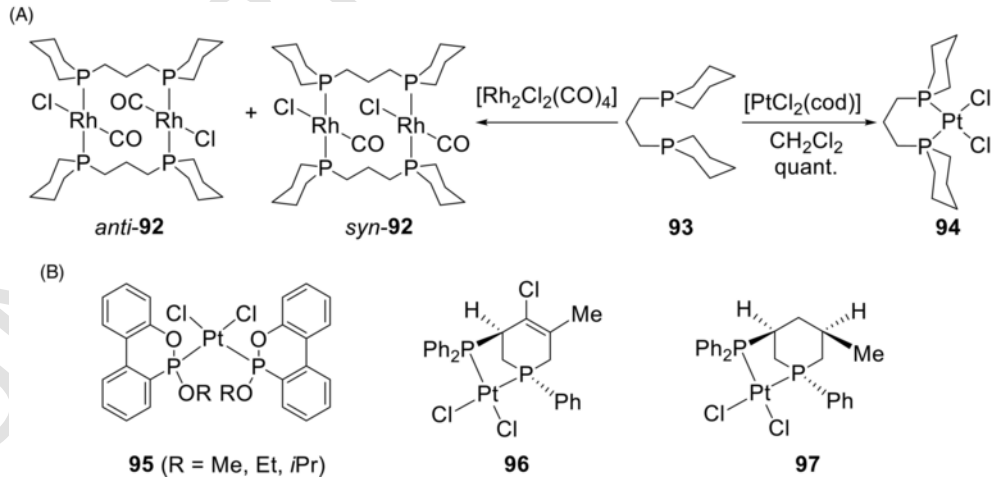
4.6.2 Alkyl-phosphinane derived ligands

Alkyl-phosphinane derivatives have been employed for the design of bidentate ligands for new Rh catalysts development. Bidentate propyl bis-phosphinane **93** was added to one equivalent of $[Rh_2Cl_2(CO)_4]$ or of $[PtCl_2(cod)]$ to form the binuclear trans-rhodium complexes *syn*-**92** and *anti*-**92**, and the air-stable cis-platinum(II) complex **94**, respectively (**Scheme 40**A). These Pt and Rh complexes were used for the hydroformylation of 1-octene in nonanals. The hydroformylation of styrene was also investigated with platinum(II) complex catalysts with cyclic phosphorus ligands **95** and with diphenylphosphino-tetrahydrophosphinine and hexahydrophosphinine derivatives **96–97** as bidentate ligands (**Scheme 40**B).[61]

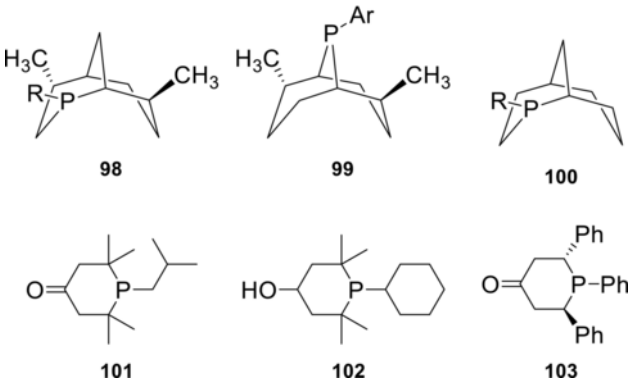
Several phobane and limonene-derived phosphine ligands **98–99** were investigated in hydrogenolysis reactions of cobalt acyl complexes. The unsymmetrical nature of these ligands, with specific regions of steric congestion, resulted in accelerated hydrogenolysis and efficient formation of acetaldehyde.[26] Chiral phosphorus ligands derived from **99** were used for enantioselective construction of all-carbon quaternary spirocenters by Pd-catalyzed asymmetric intramolecular *ipso* Friedel-Crafts allylic alkylation of phenols.[62]

The alkene to alcohol transformation via hydroformylation/reduction reaction catalyzed by cobalt-complexes in the presence of 6-membered ligands such as **98–100** was reported. Evaluation of the effects of ligands in the modified cobalt hydroformylation of 1-octene showed that the favorable catalytic properties of the Phoban and Lim ligands are due to their asymmetrical nature which gives them the ability to adopt beneficial geometries at several stages in the catalytic cycle (**Scheme 41**).

The bidentate role of the structurally similar P,O-type phosphorinane ligand **101** was demonstrated in Nickel-catalyzed Kumada coupling reactions, and a P—Ni—O bonded tricyclic intermediate complex was postulated leading to reductive elimination and biaryl formation. The tetramethylphosphorinan-4-ol **102** and other structural analogs with nitrogen substituents were used as bidentate ligands for the formation of new Pt, Pd and Rh coordination complexes, which were used as catalysts in Suzuki-Miyaura and Buchwald-Hartwig amination reactions. Chiral tertiary P-heterocycles **103** were synthesized with up to 95% ee and 98% yield by asymmetric intermolecular addition of $PhPH_2$ to bis(enones) using chiral palladacycles as catalysts.[63]



Scheme 40



Scheme 41

4.6.3 Cage-shaped tricyclic phosphines containing a six membered ring

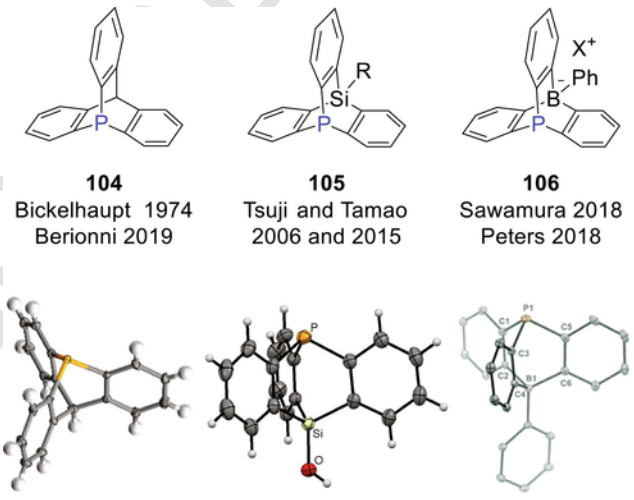
A series of tricyclic-type triarylphosphines derived from the phosphatriptycene **104** was recently used as ligands in a number of TM metal complexes. The 9-phospha-10-silatriptycene **105**, or 9-phospha-10-boratriptycene scaffold **106** (**Scheme 42**), were used as ligands in the Pd-catalyzed Suzuki-Miyaura cross-coupling reactions of chloroarenes as well as for the hydrosilylation and hydrogenation of ketones respectively.[64]

These phosphines, and the 9-phospha-10-silatriptycene analogs were also grafted to silica support and used for CH borylations of functionalized arenes, phenol derivatives, pyridines, and for the (Csp^3) —H borylation of amides.

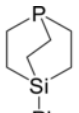
Investigations of their coordination with Pt, W, Co, Fe were also described and the X-ray structures of these triptycene-phosphines were determined before and after coordination with these transition-metals.[65]

Compact cage-shaped phosphines with a 1-phospha-4-silabicyclo[2.2.2]octane **107** was synthesized, characterized in the solid state, and employed as ligand for the iridium catalyzed hydrosilylation of ketones (**Scheme 43**).[66]

A phosphatrioxa-adamantane cage shaped phosphine **108** was shown to behave as a bulky ligand equivalent to a formal R_2P electro-withdrawing group. It is suitable for the Rh-catalyzed hydroformylation of 1-heptene and the Zn-catalyzed hydrocyanation of 3-pentenenitrile (**Scheme 44**A).[67] No applications of fluorophosphines in catalysis were described before this report, certainly because of the instability of R_2PF with respect to the disproportionation reaction shown in **Scheme 44**B.

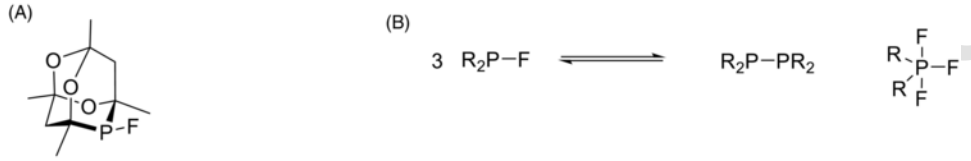


Scheme 42



Ph-SMAP **107**

Scheme 43



108

Scheme 44

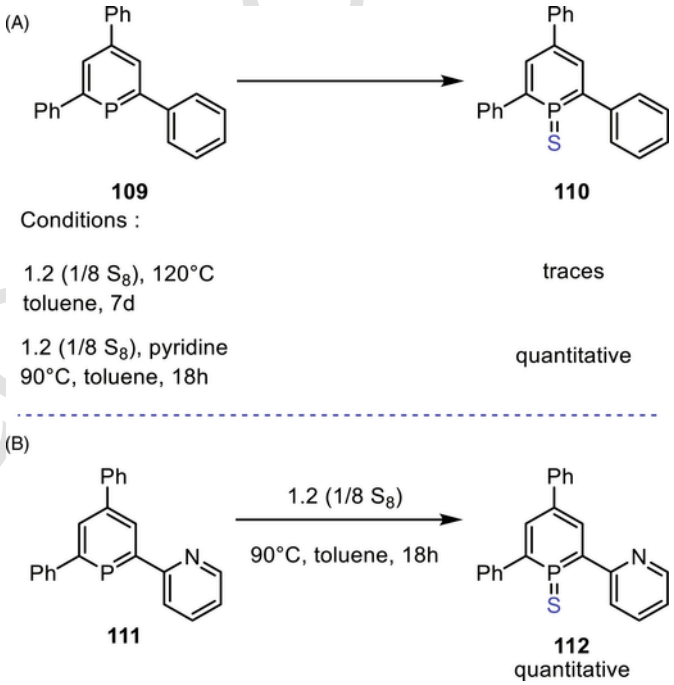
5 Reactivity of fully conjugated rings

5.1 Reactions at the phosphorus atom

5.1.1 P-sulfuration

Oxidation of phosphorus atom on phosphinine derivatives by elemental sulfur was investigated in different approaches.

First, the sulfuration of phenyl-substituted phosphinine **109** using elemental sulfur only lead to traces of the desired phosphinine sulfide **110** even after heating at 120 °C for seven successive days (**Scheme 45**A). Interestingly, the phosphinine **111** bearing a pyridyl



Scheme 45

function is more reactive and undergo a quantitative sulfuration reaction after 18 h at 90 °C (**Scheme 45**B). Other studies revealed that quantitative yields could be obtained using pyridine as an additive in the case on non-functionalized phosphinines.[68]

5.1.2 P-oxidation-oxygenation

The oxygenation of the phosphorus atom of phosphinines leads to the disruption of their ring aromaticity. Methanol could be used as a suitable agent for the addition on the phosphorus-carbon double bond of phosphinines **113** (**Scheme 46**).[68]

On the other hand, the oxidation can also be achieved by an exchange process from an aminophosphinine under acidic conditions. In particular, concentrated hydrochloric acid was used in the case of the λ^5-phosphinine **115** to synthesize the corresponding ester **116**. Using the same conditions, the phosphinine diamine **117** is converted to the corresponding phosphinic acid **118**. Interestingly, the use of trifluoromethanesulfonic acid and methanol allowed the obtention of the ester **116** (**Scheme 47**).[69]

5.1.3 P-reduction

Various reducing agents have been used to convert λ^5-to the corresponding λ^3-phosphinines. For example, $LiAlH_4$ was suitable for the reduction of *N,N*-dimethoxy phosphinine **119**. However, a low yield was obtained. Thus, and in order to improve the efficiency of the reaction, chlorotrimethylsilane was added, forming alane in situ and successfully carrying out the reduction reaction (**Scheme 48**).

While tetramethyldiamino phosphinine **117** was found to be inert towards $LiAlH_4$, it can be reduced with diisobutylaluminum hydride (DIBAL-H) under solvent-free conditions at room temperature (**Scheme 49**).[69]

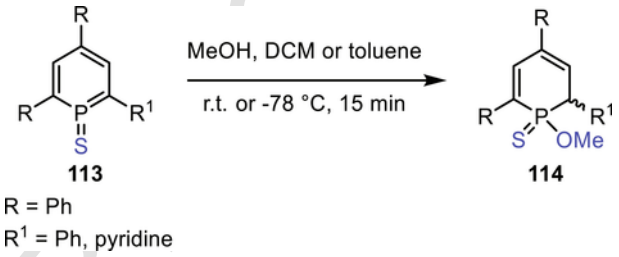
In addition, thermolysis at 260 °C could also be a good approach for the reduction of alkylated λ^5-phosphinine **118** (**Scheme 50**).[70] However, due to its high reactivity, 119 was not isolated by trapped with 2,3-dimethylbutadiene through a Diels-Alder reaction.

5.1.4 P-protonation

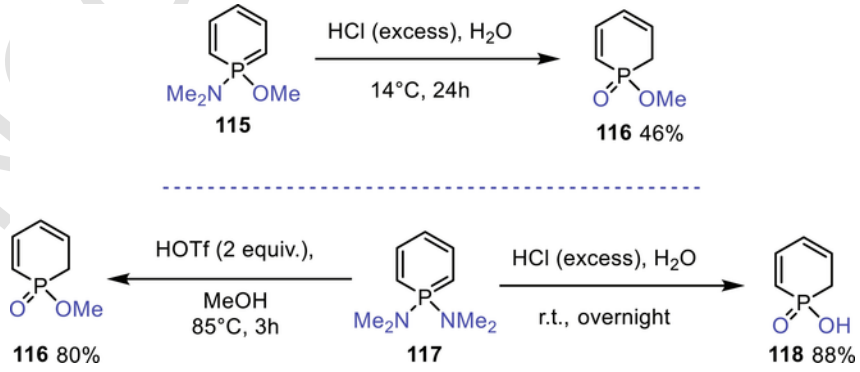
As discussed above, phosphinines are weak Brønsted bases. Thus, their protonation requires the use of a strong acid. For instance, protonation of the phosphinine **120** was achieved using a carborane acid generated in situ upon mixing $Et_3Si(CHB_{11}Me_5Cl_6)$ with triflic acid. The reaction resulted in the formation of the phosphinine salt with $CHB_{11}Me_5Cl_6$ as a weekly coordinating anion (**Scheme 51**).[71,72]

5.1.5 P-arylation

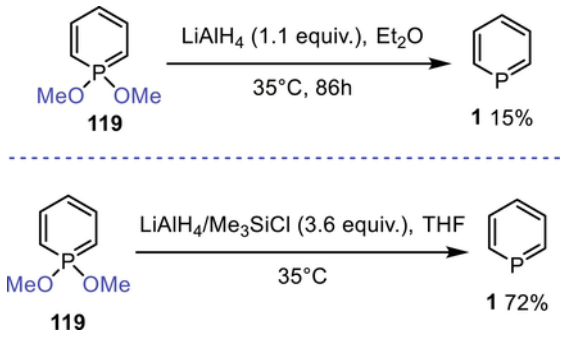
Quantitative arylation of phosphinine **111** and **122** can be achieved with phenyllithium (**Scheme 52**). Subsequent treatment of the resulting anions **123** with water leads to the formation of the corresponding dihydrophosphinine **124**. It should be mentioned that the hydrolysis



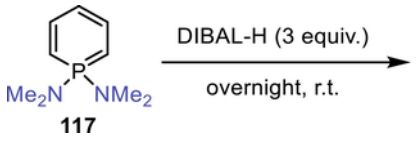
Scheme 46



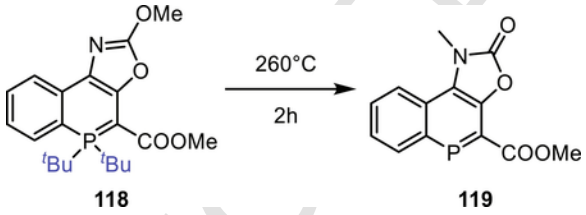
Scheme 47



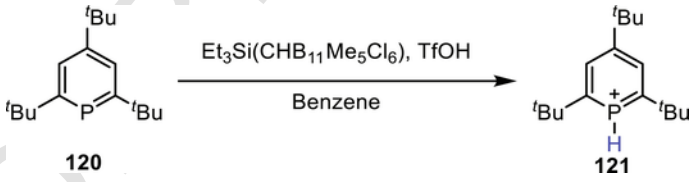
Scheme 48



Scheme 49



Scheme 50



Scheme 51

gives rise to a mixture of diastereoisomers, as two stereogenic centers have been formed at the phosphorus and the carbon atom of the heterocycle (**Scheme 52**).[73]

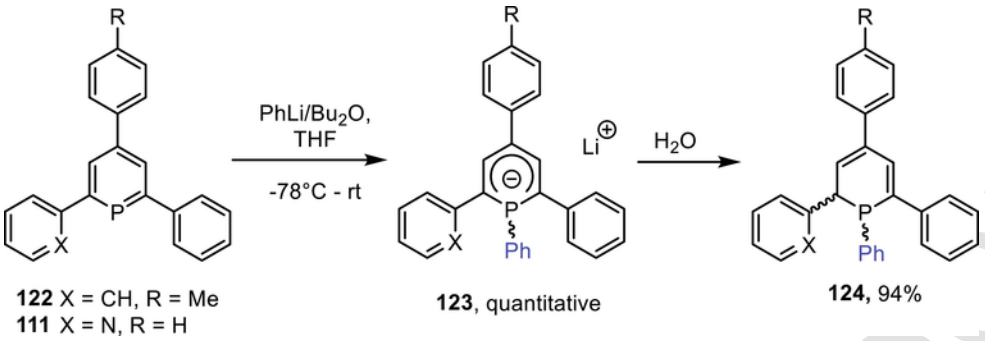
5.2 Reactions at the ring carbons

5.2.1 Halogenation reactions

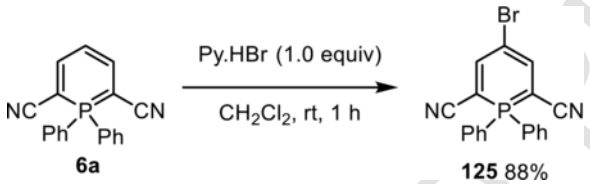
The bromination of the λ^5-phosphinine **6a** could be achieved using pyridinium bromide, furnishing the desired bromophosphinine in high yield (**Scheme 53**).[22]

5.2.2 Formylation reactions

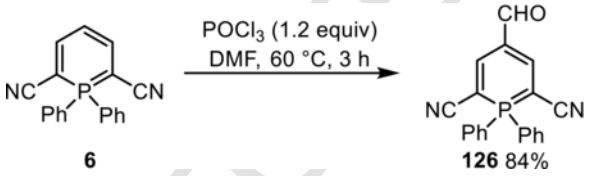
The phosphinine **6a** could be formylated using Vilsmeier-Haack reaction conditions to yield the 4-formyl derivative **126** in 84% yield (**Scheme 54**).[22]



Scheme 52



Scheme 53



Scheme 54

5.2.3 *Palladium catalyzed cross coupling reactions*

Functionalizations of bromophosphinines **127** and **129** were achieved via Pd-catalyzed Stille cross-coupling (**Scheme 61**A) as well as C—P cross coupling (**Scheme 55**B).[74]

A palladium catalyzed Suzuki cross coupling could be achieved on the λ^5-phosphinine **125** with phenylboronic acid providing **131** in 76% yield (**Scheme 56**).[22]

Finally, the λ^5-phosphinine **125** could be subjected to a palladium catalyzed Sonogashira cross coupling with phenylacetylene, furnishing the functionalized product **132** with 69% yield (**Scheme 57**).[22]

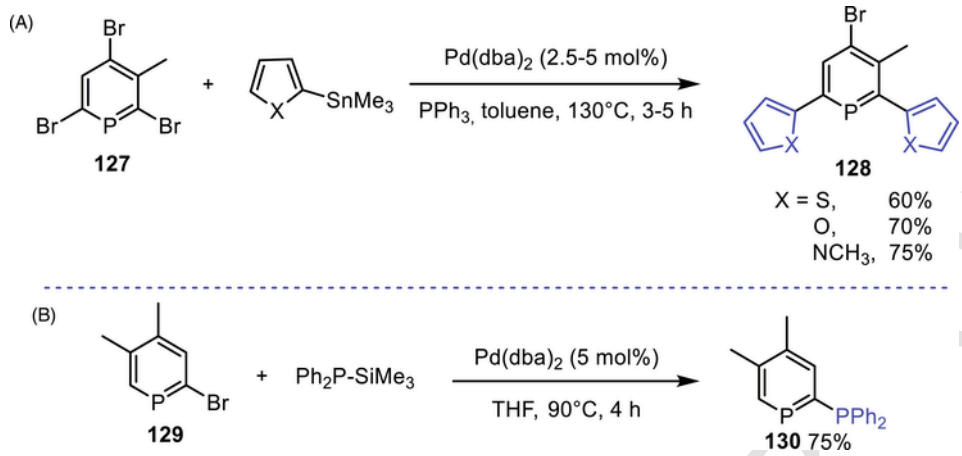
5.2.4 *Desilylation*

Efficient protodesilylation of different 2,6-di-(trimethylsilyl)-substituted phosphinines **133** was successfully achieved using ethereal hydrogen chloride (**Scheme 58**).[75]

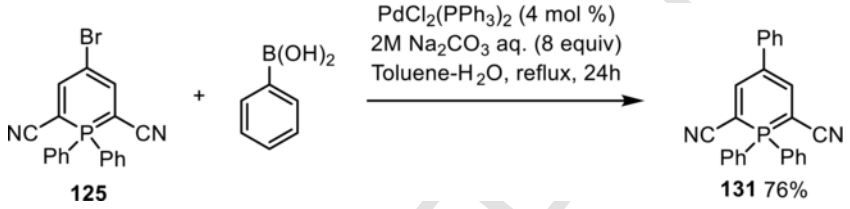
In another approach, the preparation of unsubstituted phosphinine **1** was achieved through the protodesilylation of silylphosphine **3** with HCl upon with heating at 50 °C for 3 days (**Scheme 59**).[19]

5.2.5 *Wittig reaction*

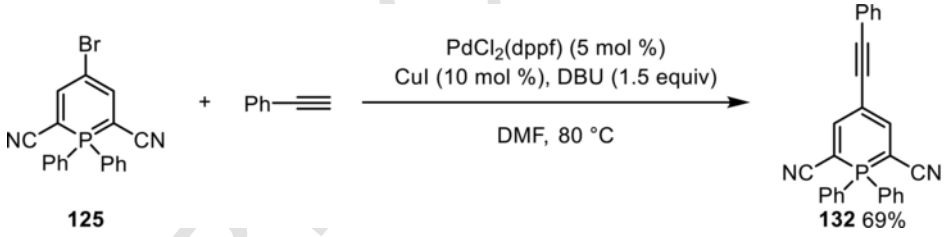
The 4-formylphosphinine **126** could be engaged in a Wittig reaction with the benzyltriphenylphosphonium ylide and furnished the corresponding olefin functionalized product **135** with 56% yield (**Scheme 60**).[22]



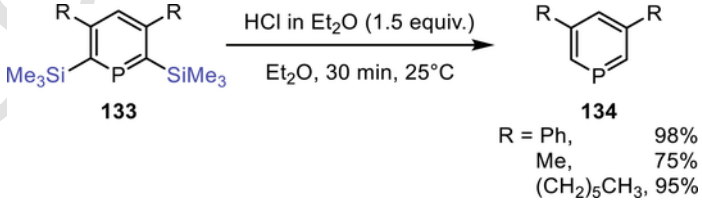
Scheme 55



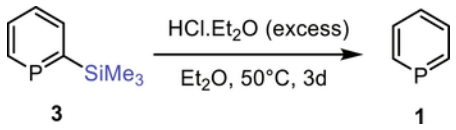
Scheme 56



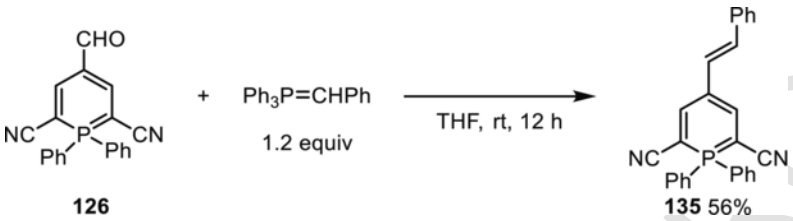
Scheme 57



Scheme 58



Scheme 59



Scheme 60

5.3 Ring reactions

5.3.1 Diels-Alder reaction

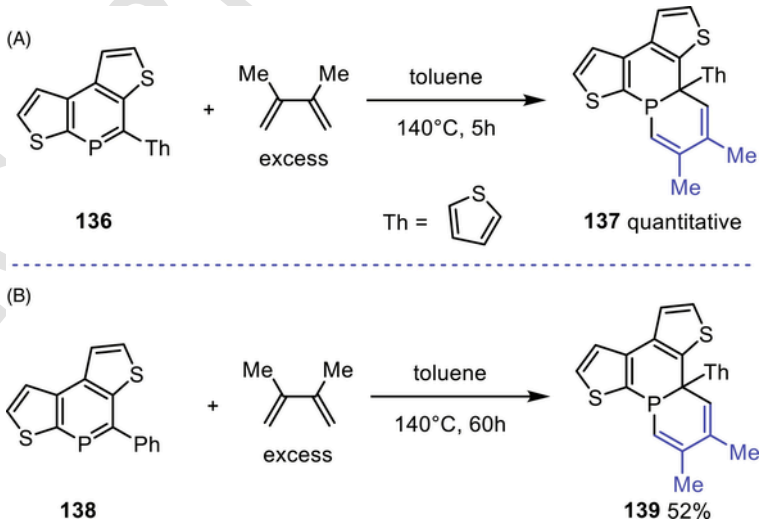
Phosphinines can be employed in Diels-Alder cycloaddition either as dienes or dienophiles depending on the reaction partners. These reactions usually require high temperatures.

For instance, when phosphinine **136** and **138** were used as a dienophiles, the reaction took place at 140 °C. However, the efficiency of the reaction depends on the substitution at the cycle. More precisely, the reaction of 2-thiophen-dithienophosphinine **136** was fast and quantitative (**Scheme 65**A), whereas the 2-phenylphosphinine derivative **138** reacted very slowly with the diene and provided the product in only 52% yield after extensive heating (**Scheme 61**B).[76,77]

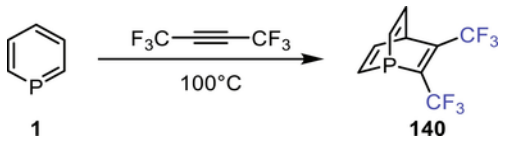
Phosphinine **1** can undergo a thermal Diels-Alder reaction with an activated dienophile such as hexafluorobutyne at 100 °C (**Scheme 62**).[77]

5.4 Cycloreversion reaction

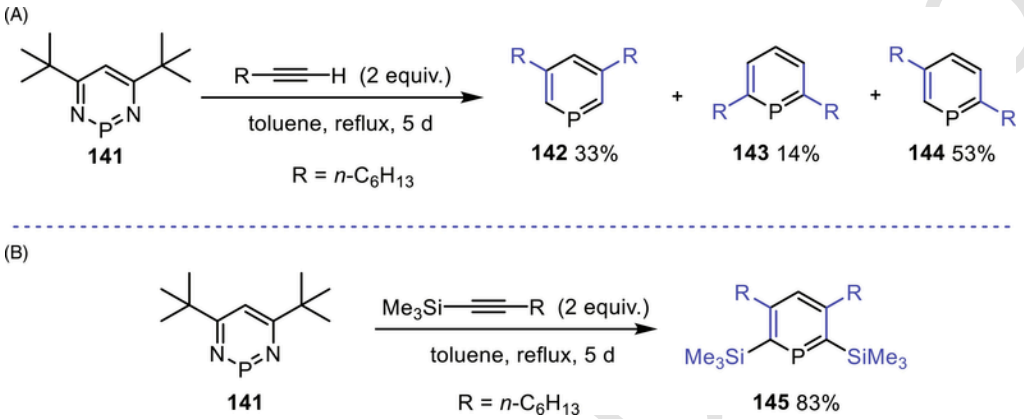
The reaction of diazaphosphinine **141** with 1-octyne resulted in the exchange of the *tert*-butyl cyanide group by the alkyne moiety. This reaction gives a mixture of the three disubstituted derivatives (**Scheme 63**A). Interestingly, when 1-trimethylsilyl-oct-1-yne was used



Scheme 61



Scheme 62



Scheme 63

instead of the non-activated octene, the reaction was found to be regioselective with only the 2,6-substituted isomer **145** obtained (**Scheme 63**B).[75]

6 Coordination chemistry

The coordination chemistry of phosphinines is broad and includes a range of different metals. In most cases, the formation of such complexes occurs by ligand exchange and is particularly favored in the case of triphenylphosphinine derivatives because of the high reactivity of the phosphorus atom towards transition metals.

For example, the coordination of triphenylphosphinine **109** with carbonyl tungsten led to the formation of the corresponding complex **146** in quantitative yield. This reaction consists in a ligand exchange between the tetrahydrofuran initially coordinated with the tungsten complex and the phosphinine **109**. More importantly, when acetonitrile was used instead of THF, the authors observed the double coordination reaction with phosphinine forming the dimer **147** (**Scheme 64**).[78]

In the same context, iron-carbonyl complexes have been used in the presence of 2,4,6-triphenylphosphinine **109** which can displace the carbonyl ligands of $Fe_2(CO)_9$ to form (2,4,6-triphenylphosphinine)$Fe(CO)_4$ **148** and the bis-liganded (2,4,6-triphenylphosphinine)$_2Fe(CO)_3$ **149** (**Scheme 65**).[79]

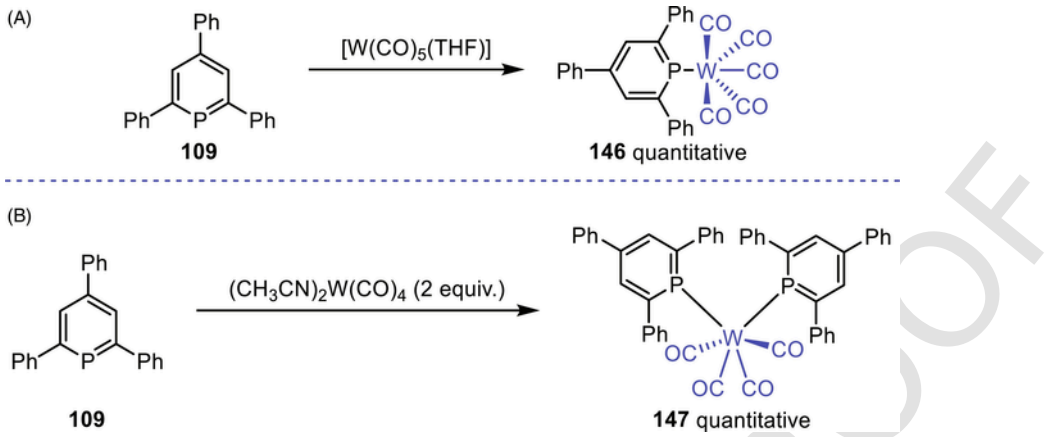
The reaction of the naphthalene iron salt [K([18]-crown-6){CpFe(η^4-$C_{10}H_8$)}] **150** with triphenylphosphinine also occurs by ligand exchange of naphthalene with phosphinine. The desired salt [K([18]crown-6)$(THF)_2$]-[Cp*Fe(η^4–2,4,6-triphenylphosphinine)}] **151** was obtained with a yield of 58%. The formed complex is highly sensitive to water, resulting in the simultaneous transfer of the oxygen to the phosphorus atom and the hydrogenation of the phosphinine to form the non-aromatic ionic complex [K([18]-crown-6)]{Cp*Fe(η^4–2,4,6-triphenyl-2,3-dihydrophosphinine 1-oxide)}] **152** (**Scheme 66**).

Furthermore, the oxidation of the aforementioned ionic iron phosphinine complex with $[Cp_2Fe]PF_6$ **151** led to the formation of the P-P-bound dimer [Cp*Fe(η^5–2,4,6-triphenylphosphinine)] **153**. In the presence of one equivalent of iodine, the iron phosphinine cation **154** was produced (**Scheme 67**A). Interestingly, the resulting cationic species can easily react with different nucleophiles such as $LiNMe_2$, LiCp, $LiBHEt_3$, and Ga(nacnacDipp) to yield new stable complexes **155**–**158** containing anionic phosphinine ligands (**Scheme 67**B).[80]

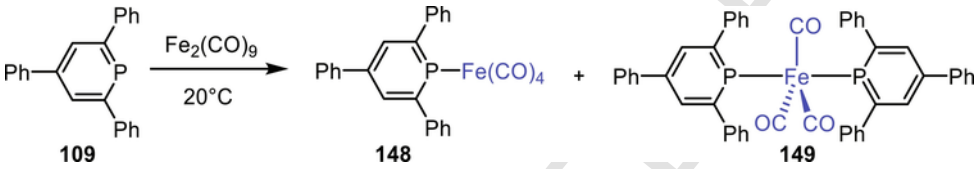
As in the case of ferrocene, the bimetallic iridium complex $[Cp^*IrCl_2]_2$ was effective for a ligand exchange in presence of phosphinines **159**, furnishing **160**. More importantly, this latter complex was subjected to a base-assisted C—H activation, affording the cyclometalated complex **161** (**Scheme 68**).[81] The latter were isolated in yields going from low (20%) to high (69%).

Likewise, iridium (**Scheme 69**A) and rhodium (**Scheme 69**B) complexes were used in the complexation reaction of 2-pyridyl diphenyl phosphinine **111** in CD_2Cl_2, which gave good yields for the corresponding cationic complexes **162** and **163**.

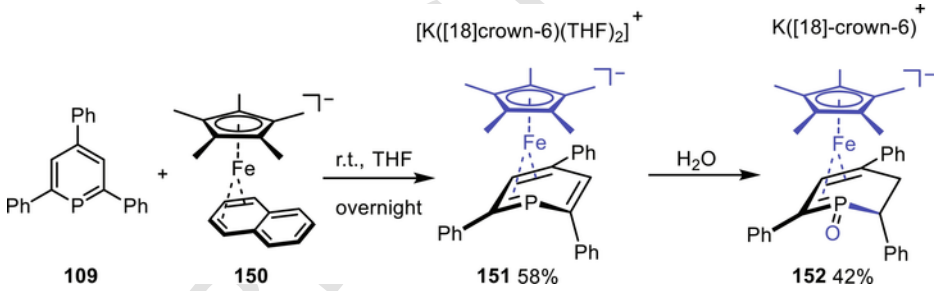
Finally, these complexes proved to be moisture sensitive and a mixture of diastereoisomers of the corresponding hydrogenated phosphinines **164** and **165** (**Scheme 70**A and B respectively) were obtained after adding a few drops of water in CD_2Cl_2.[82]



Scheme 64



Scheme 65



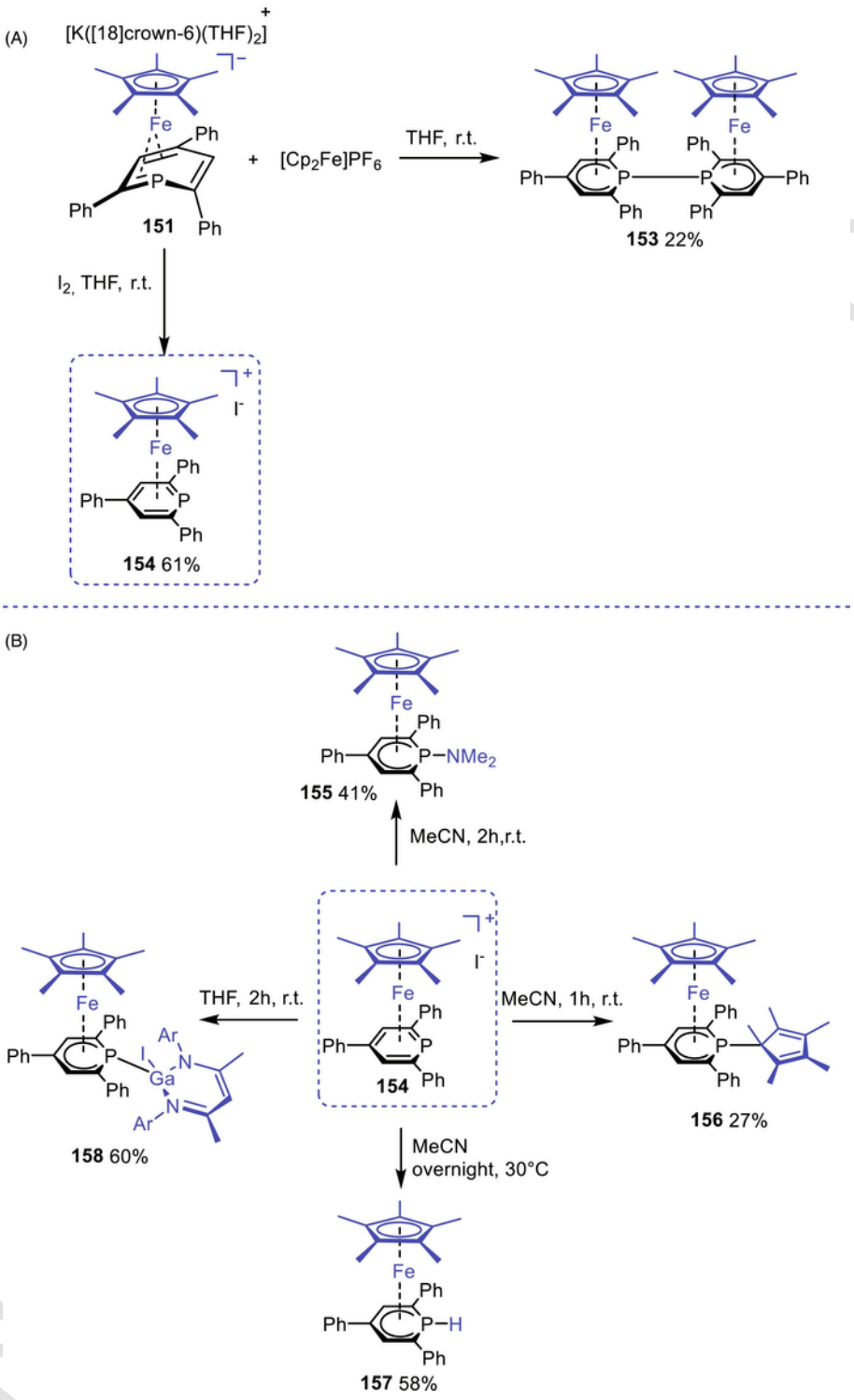
Scheme 66

7 Ring synthesis

Synthesis of phosphiranes **168** and **171** (**Scheme 71**A and B respectively) was achieved through a nickel-catalyzed hydrophosphinylation of alkenes with $(EtO)_2P(O)H$ followed by a nucleophilic ring formation.[83]

Elegant access to 2-hydroxyphosphinines **174** was reported by Mathey and coworkers by reacting furans with the methylenechlorophosphane-pentacarbonyltungsten complex **172** followed by a treatment with BBr_3 and triethylamine. It should be mentioned that the [4 + 2] cycloaddition (**Scheme 72**, first step) results in the formation of a mixture of *exo*- and -*endo* isomers **173**.[84,85] Structural investigations revealed that the major isomer has tungsten in the *exo*-position.

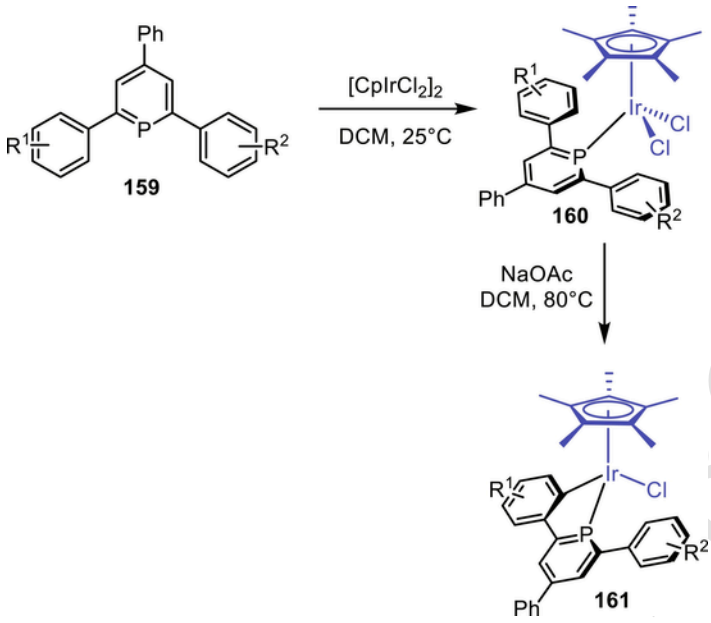
The same group has employed a similar methodology for the synthesis of 2-phosphanaphtalene via the reaction of methylenechlorophosphane-pentacarbonyltungsten **172** with isobenzofuran (**Scheme 73**). A mixture of *exo* and *endo* isomers **175a,b** was obtained in 2:1 ratio and both isomers were isolated. Interestingly, treatment of the mixture of isomers with BBr_3 and then with triethylamine formed the 2-phosphanaphthalenepentacarbonyltungsten complex that yielded the desired 2-phosphanaphtalene **176** after addition of 1,2-bis(diphenylphosphino)ethane (DPPE) in refluxing toluene.[23]



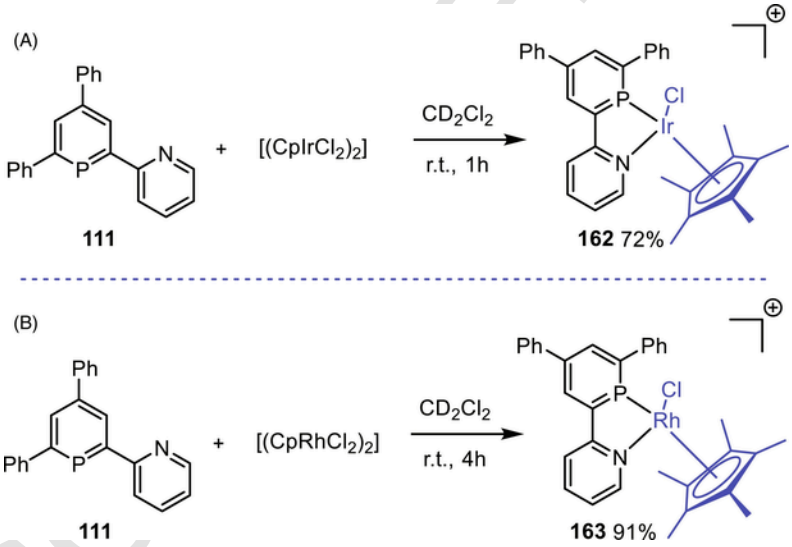
Scheme 67

The electron-accepting organophosphorus molecule **178** was synthesized by converting the 1,3-dioxolane-protected ketone **177** to the corresponding dilithiated species followed by reaction with dichlorophenylphosphine (Scheme 74).[86]

In 2011, Nakamura and coworkers reported the synthesis of curved π-conjugated molecules **180** with a phosphorus ring junction, namely phosphapyrelenes, through a tandem phospha-Friedel-Crafts reaction of dichloro(*m*-tetraryl)phosphine **179** (Scheme 75).[87]



Scheme 68



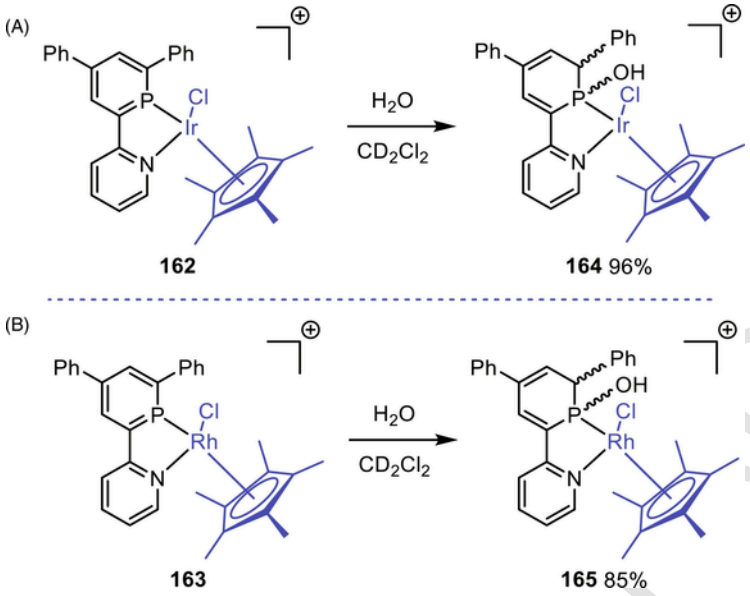
Scheme 69

A large variety of P-chiral 1,2-dihydro-2,1-benzazaphosphinine-1-oxides **184** was synthesized through the reaction of diarylphosphinic amides **182** with various alkynes **181** in the presence of a chiral rhodium catalyst **183** (Scheme 76).[88]

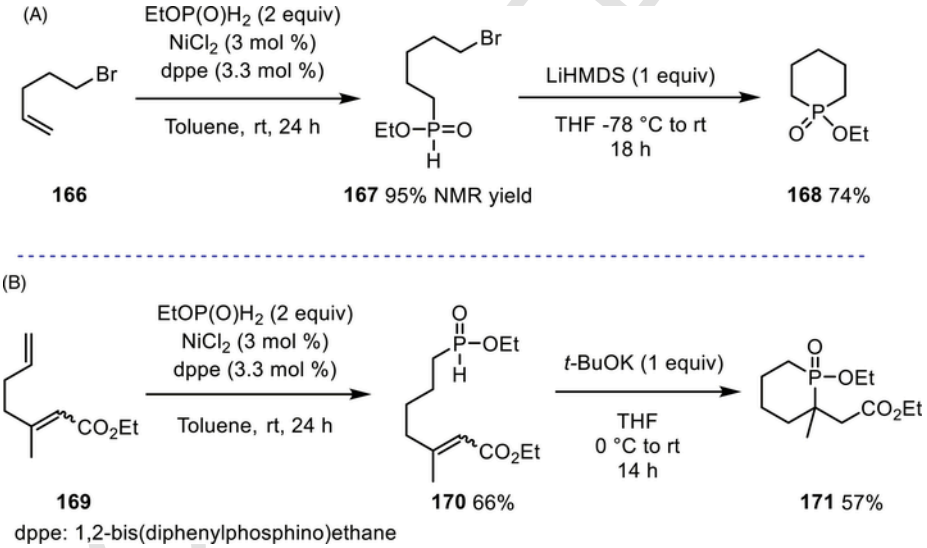
Access to phenophosphazine **186** was reported by Chatani and coworkers through palladium-catalyzed intramolecular cyclization of 2-bromo-*N*-2-(diphenylphosphino)phenylaniline **185** via carbon-phosphorus bond cleavage (Scheme 77).[89]

Synthesis of 1,2-phosphaborine **189** was synthesized through formal 1,1-insertion of a phosphinidene fragment into the pentaphenylboroles **187** with $[PPh]_5$ **188** under UV light irradiation (Scheme 78).[90]

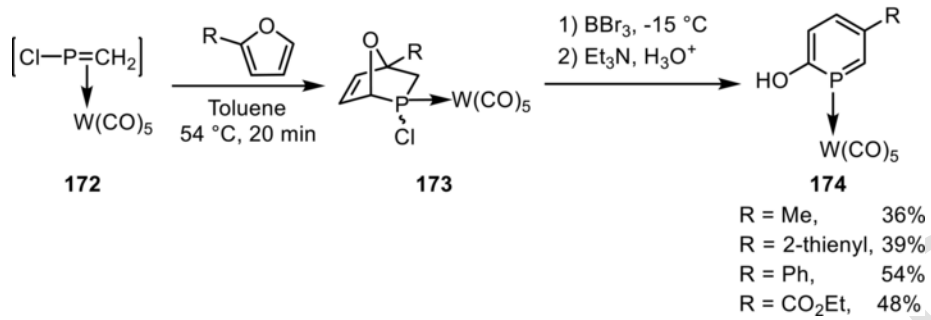
The reaction of phosphonium salt **190** with 1,3-dialdimine **191** in the presence of DBU gave the 2,6-dicyano-1,1-diphenyl-λ^5-phosphinine **192** as a sole product with a good 90% yield (Scheme 79).[22]



Scheme 70



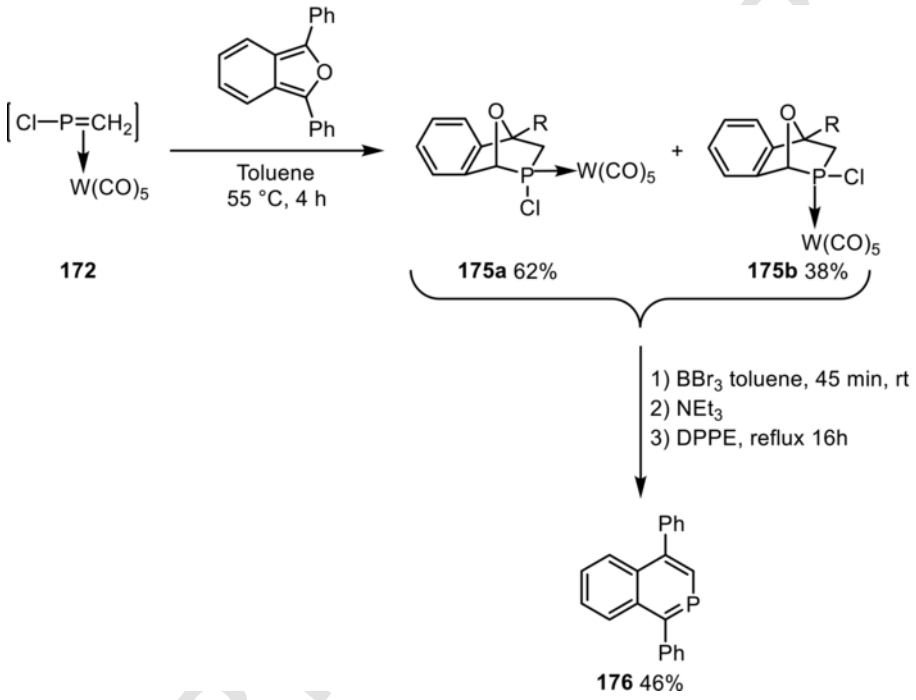
Scheme 71



172 **173** **174**

R = Me, 36%
R = 2-thienyl, 39%
R = Ph, 54%
R = CO_2Et, 48%

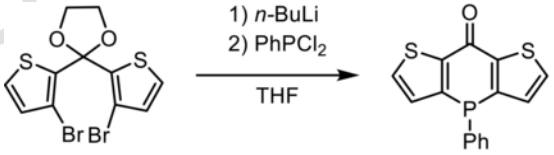
Scheme 72



172 **175a** 62% **175b** 38%

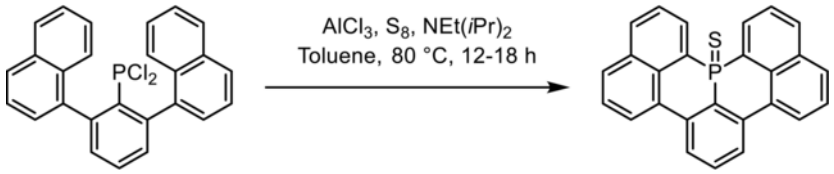
176 46%

Scheme 73



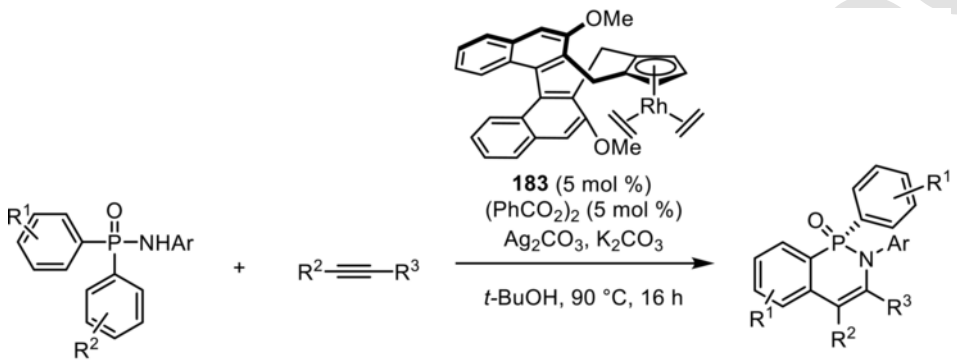
177 **178** 55%

Scheme 74



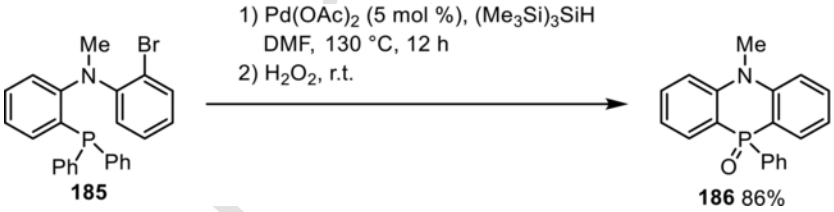
179 **180** 13%

Scheme 75



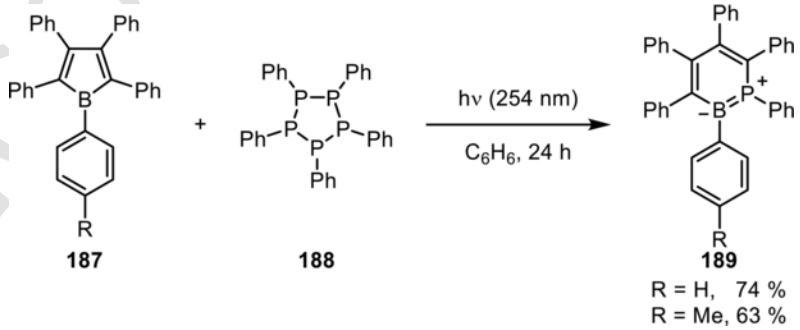
182 **181** **184** 25-85% (er 95:5-93:7)

Scheme 76



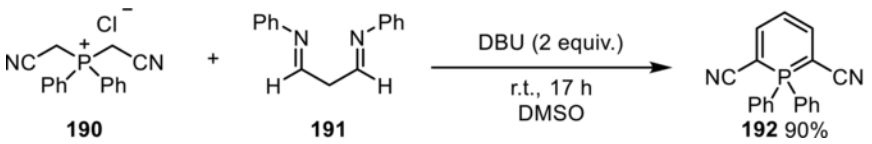
185 **186** 86%

Scheme 77



187 **188** **189**
R = H, 74 %
R = Me, 63 %

Scheme 78



Scheme 79

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