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Coordination Chemistry Reviews 251 (2007) 936–973

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Review

Stable compounds containing heavier group 15 elements in the +1 oxidation state

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Received 21 April 2006; accepted 20 July 2006
Available online 20 September 2006

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Abbreviations: 12-crown-4, 1,4,7,10-tetraoxacyclododecane; 15-crown-5, 1,4,7,10,13-pentaoxacyclopentadecane; 18-crown-6, 1,4,7,10,13,16-hexaoxacyclooctadecane; Ad, 1-adamantyl; $ArCF_3$, 2,4,6-tris(trifluoromethyl)phenyl; BAR^F, tris(pentafluorophenyl)borane; BIAN, 1,2-bis(imino)acenaphthene; Cy, cyclohexyl; dcypb, 1,4-bis(dicyclohexylphosphino)butane; dcype, 1,2-bis(dicyclohexylphosphino)ethane; dcypm, bis(dicyclohexylphosphino)methane; depe, 1,2-bis(diethylphosphino)ethane; depp, 1,3-bis(diethylphosphino)propane; Dipp, 2,6-diisopropylphenyl; dis, bis(trimethylsilyl)methyl; DKA, diketoamido; dme, 1,2-dimethoxyethane; dmp, 2,6-bis(mesityl)phenyl; dmpe, 1,2-bis(dimethylphosphino)ethane; dmpm, bis(dimethylphosphino)methane; dppb, 1,4-bis-(diphenylphosphino)butane; dppben, 1,2-bis(diphenylphosphino)benzene; dppe, 1,2-bis(diphenylphosphino)ethane; dppE, *cis*-1,2-bis(diphenylphosphino)ethylene; dppmE, 1,1-bis(diphenylphosphinomethyl)ethylene; dppmm, tetrakis(diphenylphosphinomethyl)methane; dppNap, 1,8-bis(diphenylphosphino)naphthalene; dppox, α,α′-bis(diphenylphosphino)-*o*-xylene; dppp, 1,3-bis(diphenylphosphino)propane; Dtp, 2,6-bis(2,4,6-triisopropylphenyl)phenyl; Fl^*, 2,7-di-*tert*-butylfluorenylidene; Mes, 2,4,6-trimethylphenyl; Mes^*, 2,4,6-tri-*tert*-butylphenyl; Np, neopentyl; opbp, *o*-phenylenebis(phenylphosphide); OTf, triflate; Pmdeta, pentamethyldiethylenetriamine; Py, pyridine; thf, tetrahydrofuran; tmeda, tetramethylethylenediamine; Tripp, 2,4,6-triisopropylphenyl

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doi:10.1016/j.ccr.2006.07.007

Abstract

This review provides an oxidation state model that emphasizes the similarities in the structural features, bonding and reactivities of molecules containing main group elements in a particular oxidation state. Using this model, the syntheses, structural features and selected aspects of the chemistry of stable compounds containing group 15 elements (pnictogens) in the +1 oxidation state are examined. Molecular types that are considered include: triphosphenium salts, phosphamethine cyanine dyes, phosphide anions, certain pnictaalkenes, certain phosphinidenes and their heavier analogues, among others. Theoretical models are presented to rationalize the factors that render such molecules stable.

Keywords: Low oxidation state; Main group; Group 15; Pnictogen; Phosphorus; Arsenic; Antimony; Bismuth; Molecular structure; Bonding

1. Introduction

The concept of an atom existing in a particular oxidation state is one of the fundamental ideas that may be used to rationalize the structural features, bonding and reactivity of a molecule. The utility of the oxidation state model derives from the understanding that the oxidation state of a particular atom in a molecule provides insight into the number of electrons directly associated with, and hence the chemistry of, the atom in question. In this review, the synthesis, structural features and reactivity of organo-element compounds containing group 15 centers in certain relatively low oxidation states is outlined. Because the assignment of oxidation states is sometimes ambiguous or contentious, the criteria used in this work and some reasons for their choice are presented prior to the discussion of the experimental and theoretical observations regarding the chemistry of the compounds that we consider to meet the criteria.

Although several methods may be used to assign an oxidation state, perhaps the most common method employed for organic and p-block compounds is the use of counting rules based on the relative electronegativities of the atoms in a compound and a few assumptions (e.g. H is always in the +1 oxidation state, O is always in the −2 oxidation state). Using such rules, the group 15 elements (pnictogens, Pn) are assigned formal oxidation states ranging from −3 to +5 under normal conditions [1–3]. The idea of elements having formal oxidation states or oxidation numbers is certainly useful in the context of balancing reduction–oxidation (RedOx) reactions however the rules used to assign such formal oxidation states sometimes yield results that are not chemically intuitive. For example, whereas the formal oxidation state of the phosphorus center in PH_3 is −3, the formal oxidation state of the phosphorus center in PMe_3 may be either +3 or −3 (depending on the electronegativity scale that is used) and the formal oxidation state of the phosphorus center in $P(NMe_2)_3$ is +3 in spite of the similar chemical behaviors and electronic structures of the three Lewis bases. Likewise, the formal oxidation state of the nitrogen in NPh_3 is −3, while that of the Pn center in each of the heavier $PnPh_3$ analogues (Pn = As, Sb, Bi) is +3 despite the obvious chemical, electronic and structural relationships observed for the series. In a similar vein, whereas the metathesis reaction of PCl_3 with LiMe to form PMe_3 and LiCl could be considered a RedOx reaction ($P^{III} \rightarrow P^{-I}$ and $C^{-IV} \rightarrow C^{-II}$), the analogous reaction of PCl_3 with $LiNMe_2$ to form $P(NMe_2)_3$ and LiCl is never considered to involve oxidation or reduction. Somewhat more oddly, the counting rules used to assign formal oxidation numbers suggest that the oxidation states of the nitrogen atoms in Li_3N, NMe_3 and $NMe_4{}^+$ are the same despite the drastic differences in the structures and reactivities exhibited by the nitride, the amine and the ammonium cation. Also from the perspective of chemical reactivity, such counting rules suggest that while the coordination of the "lone pair" of electrons on a molecule such as PH_3 to H^+ does not change the oxidation state of the phosphorus center, the identical Lewis acid–base reaction between PH_3 and $CH_3{}^+$ might change the oxidation state of P, and the related reaction of PH_3 with an O atom will certainly change the oxidation state of the phosphorus center. Such conclusions are seemingly absurd in the context that each of the three reactions produces a tetrahedral-shaped molecule with no remaining "lone pair" of electrons on the phosphorus atom and each of the reactions involves the formation of a new bond between phosphorus and an isolobal fragment. Given the foregoing, it is necessary to remember that the formal oxidation states obtained from the use of such counting methods are simply models that are useful in many instances but they should not be overly interpreted.

An alternative model one can use to define the oxidation state of an atom in a molecule is based on the number of non-bonding electrons associated with that particular atom. Such an approach corresponds perhaps more closely with the less-commonly used concept of a "valence state" [4] and is also more compatible with the use of the isolobal analogy [5] to understanding chemical structure and reactivity. This model, illustrated in Fig. 1, is advantageous in that it more obviously emphasizes the similarities in the electronic structures, geometrical features and perhaps chemical behaviors of compounds containing elements in a given "oxidation state". The implicit assumption in the model presented in Fig. 1 is that the Pn atom is less electronegative than all of the elements to which it may be bonded. While this assumption may be unrealistic when Pn = N, the model eliminates many of the ambiguities and oddities in the chemistry of compounds containing an element in a given oxidation state. For example, whereas the counting rules might suggest that the phosphorus atom in PMe_2H is +1, the phosphine has more structural and chemical similarities to $AsMe_2H$, containing As^{III}, than to a phosphinidene that contains P^I. Using the method outlined in Fig. 1, both $PnMe_2H$ compounds are considered to contain Pn^{III} and both are expected to have different structural properties and chemistry than the compound containing Pn^I.

There are a few notable generalizations that are apparent using the proposed oxidation state model. Firstly, organopnictogen compounds that contain pnictogen atoms in even oxidation states are anticipated to be paramagnetic and are rela-

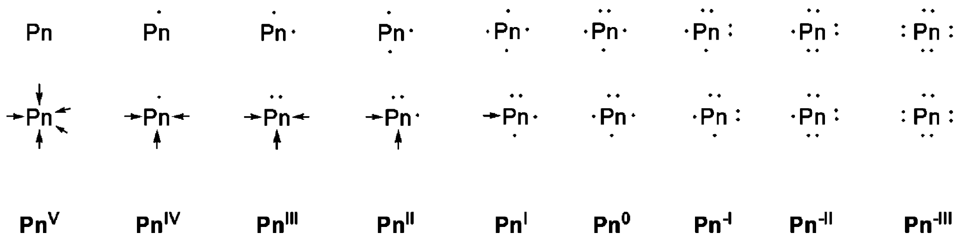


Fig. 1. Oxidation states of pnictogens; the arrows suggest a typical number of covalent bonds that may be made to an element in each oxidation state.

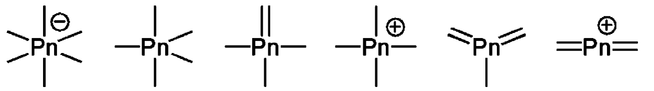


Fig. 2. Selected bonding environments observed for compounds containing Pn^V centers.

tively rare. Secondly, the negative oxidation states are unlikely to be found in organo-element compounds and are thus expected to be found primarily in salt-like ionic, inorganic, or Zintl-ion environments. Thirdly, in stable compounds under typical laboratory conditions (inert atmosphere at normal pressure and readily accessible temperatures), pnictogen centers generally occur in either the +3 or +5 oxidation state in spite of the incredible diversity in structural features and reactivity observed for the organo-element compounds.

When pnictogens are in the +5 oxidation state, Pn^V, there are no valence electrons that are not associated with a bond, i.e. there are no "lone pair" electrons, as illustrated in Fig. 2. The +3 oxidation state, Pn^{III}, corresponds to an environment in which there is a single "lone pair" of electrons as depicted in Fig. 3. Given the foregoing, this review examines the chemistry of isolable organo-element compounds that contain heavier group 15 elements in oxidation states lower than +3. In terms of the oxidation state model outlined in Fig. 1, the types of compounds that may be understood in this context are limited to those that contain either Pn^{II}, Pn^I, Pn^0, or Pn^{-I} centers. However, as outlined by Driess [6], compounds that contain Pn^{-I}, such as the dilithiated phosphides (phosphanides) of the form "$RPLi_2$", are best considered as hybrids of organo-element and ionic compounds that invariably form clusters in the solid state; such compounds will not be re-examined in this review. Furthermore, the absence of organo-element compounds containing true Pn^0 environments would limit the subject matter of this review to compounds containing Pn^{II} and Pn^I, of which the latter are considerably more prevalent. Given that the chemistry of main group radicals has been reviewed recently and extensively [7], and that the chemistry of the Pn^{II}-containing phosphinyl and arsinyl radicals has been reviewed in particular [8,9], this review will focus only on the chemistry of organo-element compounds containing heavier pnictogen atoms in the +1 oxidation state.

Finally, a comment about the chemical drawings used in this review is warranted. Because a given molecule can be depicted in various manners, the oxidation state of the Pn atom contained therein might seem ambiguous, as illustrated in Fig. 4. Such chemical drawings are often made using rules (e.g. minimize the number of formal charges) that suggest that one drawing is superior to another drawing on the basis of formalisms that have no relationship to the actual electronic structure of the molecule depicted. Again, one must remember that such Lewis-type structures are simple models that should not be accorded too much significance. More accurate models of the actual electronic structures of such molecules are obtained from computational investigations or inferred from structural and reactivity studies. For the purposes of this review, the authors will generally depict chemical structures in a manner that conforms to the drawings that have appeared in the literature (for example, many structures are often drawn in the manner of either of the Pn^{III} forms shown in Fig. 4) however it must be emphasized that the inclusion of a compound in this review indicates that there is evidence that compound behaves as if it contains a lower oxidation state pnictogen center. As a final note, for general structural types "R" represents a formally anionic ligand, such as an alkyl group, and "Do" represents a formally neutral ligand, such as a phosphine.

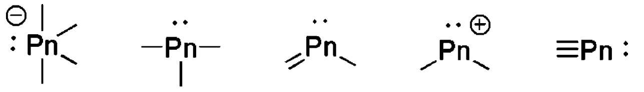


Fig. 3. Selected bonding environments for compounds containing Pn^{III} centers.

The subject matter in the following sections is divided in general by element and each section is subdivided into classes of related compounds. Within these subdivisions, families of related compounds that were prepared using a single synthetic approach are generally treated together. A final section explores the nature of the bonding in representative molecules that contain Pn^I centers. While many of the compounds and reactions outlined below have been reviewed in other contexts [10–17], it is the authors' wish to demonstrate the similarities in the structural features and reactivities of classes of compounds that are related on the basis of the oxidation state model outlined above. As a final note, all of the crystal structure pictures in this review

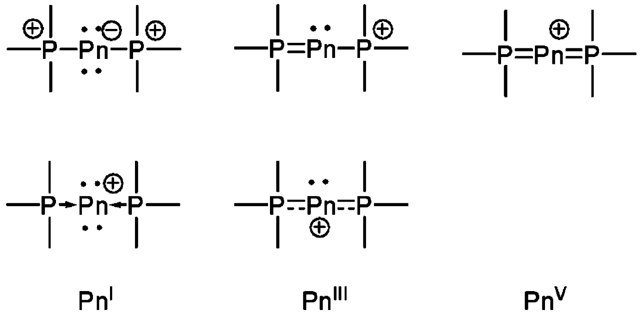


Fig. 4. Ambiguity in Lewis-type chemical structure drawings of a single cation having the formula $[Pn(PR_3)_2]$.

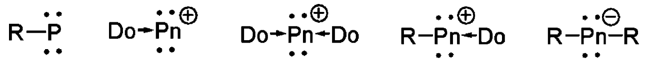


Fig. 5. General structural drawings for compounds containing P^I centers.

were generated using data obtained from the Cambridge Structural Database (CSD; the six-letter CSD codes are provided in parentheses for these cases) [18], from supporting information included with publications or from the authors' own crystallographic data.

2. Phosphorus

The most common of the lower oxidation state for phosphorus in organo-phosphorus compounds is +1, in which the phosphorus atom bears four non-bonding electrons. There are several different structural types that may be envisioned for P^I depicted in Fig. 5. The potential compounds include neutral, cationic and anionic species that contain either mono- or di-coordinate phosphorus centers however, in practice, only compounds containing the di-coordinate environments are found to be adequately stable to allow for their isolation under typical laboratory conditions.

In spite of their instability under standard laboratory conditions, one of the most widely studied families of Pn^I compounds are the neutral phosphinidenes having the general form R–P, which are a heavier analogue nitrenes [19]. Free phosphinidenes exist only as coordinatively unsaturated and highly reactive intermediates with either a triplet or, more rarely, a singlet ground state. In the absence of other reagents, phosphinidenes are prone to oligomerization to give either double-bonded diphosphenes or the more familiar cyclic polyphosphines of the form $(R–P)_n$, as pictured in Fig. 6, depending on the size of the R substituent. Although all of the compounds in Fig. 6 are formally considered to contain P^I centers, their structural features and reactivity is more typical of that expected by P^{III} centers as illustrated by the structure of $(Ph–P)_6$ **1** [20] in Fig. 7; the utility of such oligomers for the generation of Pn^I species is examined later in this section.

Work involving transient phosphinidenes has been extensively reviewed [21–23] and will not be discussed in detail in this review. In many instances, monomers of the transient species can be stabilized through coordination with either Lewis bases or metal centers. Such stabilized phosphinidenes, which have proven to be useful phospha-Wittig reagents for the formation of new carbon–phosphorus bonds that may otherwise be very difficult to produce [24], are examined in the section below covering the stable, di-coordinate neutral P^I species.

There is one class of molecule that has been described as being equivalent to a stabilized singlet phosphinidene, namely the so-called “10-P-3” (meaning a total of 10 electrons around a phosphorus center which is connected to three other atoms) hypervalent molecules initially described by Culley and Arduengo [25]. As shown in Fig. 8, such molecules consist of a phosphorus atom ligated by a substituted diketoamido (R–DKA) ligand. When the molecule has a planar bicyclic arrangement, the phosphorus atom is described as 10-P-3; this description implies a pseudo-trigonal bipyramidal (ψ-tbp) arrangement with two lone pairs of electrons in equatorial sites and thus merits classification as a P^I compound by the convention outlined in Fig. 1. Alternatively, such compounds can possibly adopt a folded bicyclic arrangement in which the phosphorus atom is described as 8-P-3; this would thus be classified as a P^{III} center. The crystal structures of several examples of (R–DKA)P compounds have been determined (R = ^{t}Bu, Ad, CMe$_2$Ph **2**) and each of them exhibits the planar bicyclic core consistent with the 10-P-3 (P^I) description, as illustrated for the cumyl substituted example in Fig. 9.

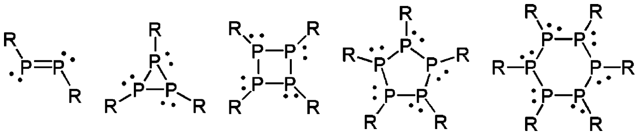


Fig. 6. Phosphinidene oligomerization products.

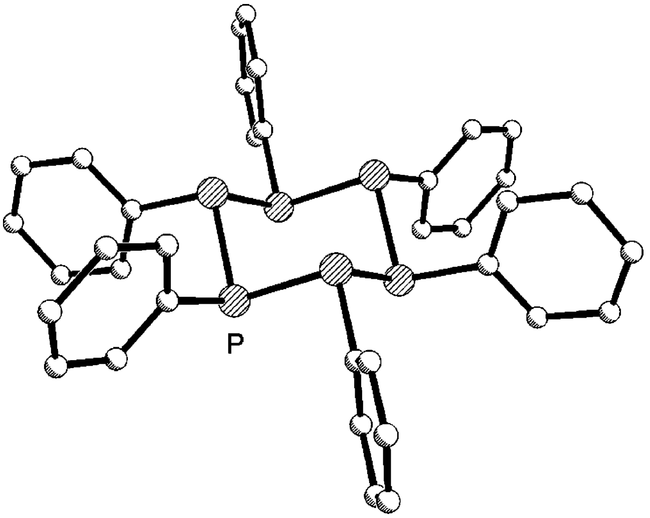


Fig. 7. Molecular structure of $(Ph–P)_6$ **1** (POBENZ) showing the pyramidal environment more typical of a P^{III} center.

While interest in such compounds has been renewed recently [26], almost all of the known chemistry of these interesting molecules has been reviewed comprehensively by Arduengo and Stewart [27] and will not be re-examined in detail in this review. There are, however, some salient features concerning

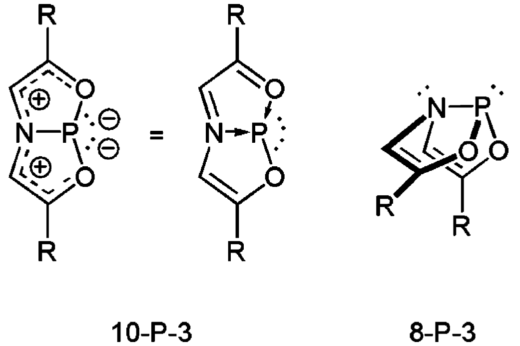


Fig. 8. Drawings of (R–DKA)P molecules illustrating difference between the planar 10-P-3, P^I arrangement and the folded 8-P-3, P^{III} arrangement.

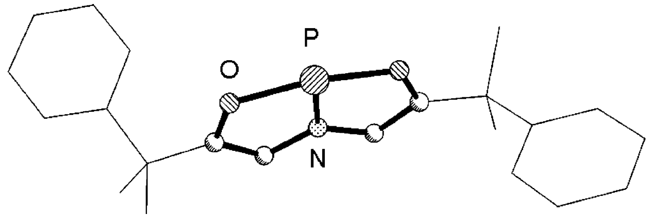


Fig. 9. Molecular structure of (PhMe$_2$C-DKA)P **2** (WEGJAT) illustrating the planar bicyclic core.

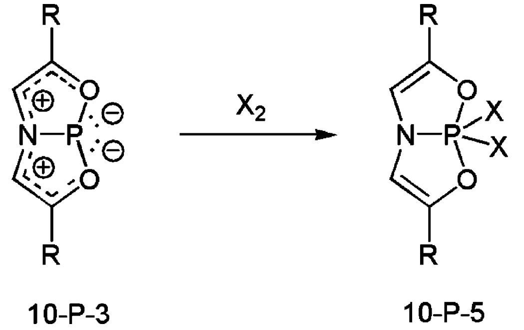


Fig. 10. Oxidation of (R–DKA)P compounds produces a 10-P-5, P^V compound consistent with oxidation of one lone pair by X_2 (X = Cl, Br) in addition to the transfer of two electrons the ligand.

the reactivity of such molecules that are worthy of mention. In particular, while the free compounds all exhibit the planar 10-P-3 arrangement, when compounds such as (^{t}Bu-DKA)P **3** are ligated to transition metal complexes, they often adopt the folded 8-P-3 geometry. In contrast, oxidation of the phosphorus center in such species with chlorine or bromine is reported to yield 10-P-5 molecules that retain the planar bicyclic core and have a distorted trigonal bipyramidal geometry around the phosphorus atom on the basis of ^{31}P NMR spectroscopy and the structures of alkyl derivatives (FEDPOT and FEDPUZ) [28] (Fig. 10). The apparent disappearance of the second "lone pair" of electrons in these cases is a consequence of electron transfer from the P atom to the R–DKA ligand. Alternatively, the fluorinated product (^{t}Bu-DKA)PF$_2$ **4**, pictured in Fig. 11, has a structure that may be describes as containing a pseudo-octahedral 12-P-5, which suggests that a "lone pair" is retained on the phosphorus center [29].

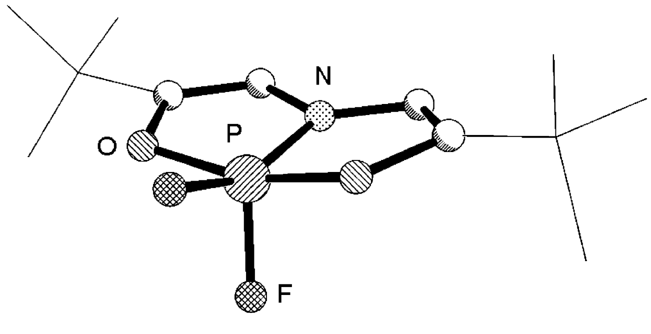


Fig. 11. Molecular structure of (tBu-DKA)PF$_2$ **4** (WEGHUL) illustrating the pseudo-octahedral 12-P-5, P^{III} arrangement of the compound.

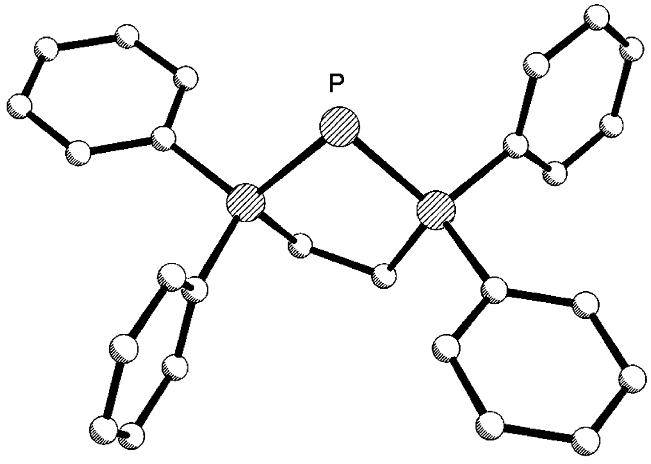


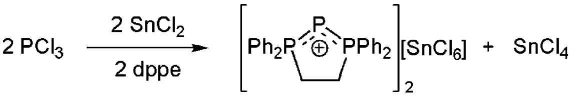
Fig. 12. Molecular structure of the cation [(dppe)P] **5**.

2.1. Phosphine-stabilized P^I cations

In the early 1980s, Schmidpeter began initial work on the synthesis of cations that contain phosphorus in the +1 oxidation state [30]. For the next 15 years there was very little work in the area, with examples being reported sporadically. More recently there has been an increasing interest in the investigation of not only the synthesis of such species but also of the unique reactivity and utility of compounds containing phosphorus and its heavier congeners in the +1 oxidation state.

2.1.1. Syntheses employing SnX$_2$ oxidation

In 1982, Schmidpeter published the first example of what he would later call a triphosphenium cation [31,32]. The reduction of phosphorus(III) chloride with tin(II) chloride in the presence of a chelating phosphine, namely bis(diphenylphosphino)ethane (dppe), generated the hexchlorostannate salt of the P^I cation [(dppe)P]$^+$ **5** (Eq. (1)):



5$_2$[SnCl$_6$] (1)

Schmidpeter characterized the salt of **5** using both ^{31}P NMR and X-ray crystallography, in addition to microanalysis. In solution, the composition of the cation was readily confirmed by its ^{31}P NMR spectrum, which consists of a doublet at 64 ppm (two P atoms) and a triplet at −232 ppm (one P atom). As shown in Table 1, symmetrical triphosphenium cations of the general form $[(R_3P)_2P]^+$ display the easily identifiable spectrum of an AX_2 spin system with very large $^1J_{P–P}$ coupling constants that typically exceed 400 Hz. The ligating phosphorus centers exhibit ^{31}P NMR signals that are usually deshielded relative to phosphoric acid, and that resonate between $\delta = +30$ and $+90$ depending on the nature of the R substituents. In contrast, the dicoordinate P^I center is significantly shielded and exhibits signals in the ^{31}P NMR spectrum that resonate in the range of $\delta = -175$ to -235.

The solid state structure, as depicted in Fig. 12, reveals short P–P bonds, 2.122(1) and 2.128(2) Å, which are interme-

Table 1
^{31}P NMR chemical shifts of symmetric triphosphenium salts $[L_2P][A]$

L	A	δP(L)	δP^I	$^1J_{PP}$	Ref.
L_2 = dppe **5**	$SnCl_6^{2-}$	64	−232	449	[31]
L_2 = dppe **5**	Cl^-, Br^-, I^-, $SnBr_6^{2-}$	64	−232	452	[36]
L_2 = dppe **5**	I^-	64	−231	451	[43]
L_2 = dppe **5**	BPh_4^-	64	−236	456	[43]
L_2 = depe **6**	Cl, $SnCl_6^{2-}$	81	−267	440	[37]
L_2 = dmpe **7**	Cl, $SnCl_6^{2-}$	60	−212	435	[37]
L_2 = dcype **8**	Cl^-	88	−290	458	[38]
L_2 = dppe **10**	Cl^-, Br^-, I^-, $SnCl_6^{2-}$, $SnBr_6^{2-}$	71	−248	473	[36]
L_2 = dppben **11**	Cl^-, Br^-, I^-, $SnCl_6^{2-}$, $SnBr_6^{2-}$	58	−213	453	[37]
L_2 = dmpm **12**	Cl^-	21	−154	449	[38]
L_2 = dcypm **13**	Cl^-, $SnCl_6^{2-}$	45	−214	333	[38]
L_2 = dppp **14**	Cl^-, Br^-, I^-, $SnCl_6^{2-}$	23	−209	422	[36]
L_2 = dppp **14**	I^-	22	−209	423	[44]
L_2 = dppp **14**	BPh_4^-, OTf^-, PF_6^-, $GaCl_4^-$	23	−210	424	[44]
L_2 = depp **15**	Cl^-, $SnCl_6^{2-}$	31	−253	417	[54]
L_2 = dppmE **16**	$SnCl_6^{2-}$	23	−213	431	[35]
L_2 = dppb **17**	Cl^-, $SnCl_6^{2-}$	34	−211	454	[36]
L_2 = dcypb **18**	Cl^-, $SnCl_6^{2-}$	48	−262	472	[54]
L_2 = dppox **19**	Cl^-, Br^-, 1^-, $SnCl_6^{2-}$, $SnBr_6^{2-}$	25	−216	437	[37]
L = PPh_3 **21**	$AlCl_4^-$	30	−174	502	[40]
L = $P(NMe_2)_3$ **22**	BPh_4^-	85	−194	513	[41]
L = dppNap **23**	I^-	26	−216	392	[45]
L_2 = dppmm **24**	$AlCl_4^-$	18	−250	440	[46]
L = PPh_2Me	$AlCl_4^-$	23	−176	464	[40]
L = $PPhMe_2$	$AlCl_4^-$	12	−159	451	[40]
L = PPh_2Net_2	$AlCl_4^-$	79	−164	508	[40]
L = $PPh(NEt_2)_2$	$AlCl_4^-$	64	−163	510	[40]
L = PPh_2NHPh	$AlCl_4^-$	47	−182	498	[40]
L = $P(N(CH_2)_5)_3$	$AlCl_4^-$	79	−193	560	[40]
L = $P(N(CH_2)_4O)_3$	$AlCl_4^-$	78	−207	566	[40]
L = $P(OEt)_3$	$AlCl_4^-$	82	−218	508	[40]
L = PBu_3	$AlCl_4^-$	33	−229	473	[40]

diate between what is considered typical for single (2.217(1) in $Ph_2P–PPh_2$ (BAPBOJ) [33]) and double (2.034(2) in Mes*P = PMes* (BALXOB) [34]) bonds. The very small P–P–P angle of 88.9(1) is largely a consequence of the constraints imposed of the chelating diphosphine however the strongly bent geometry is typical of all structurally characterized triphosphenium cations.

Related cyclic compounds have been synthesized by other groups using variations of Schmidpeter's approach using either different chelating diphosphines or using tin(II) bromide as the reducing agent. Whereas the salts **11**[$SnCl_6$] and **14**[A] (A = $SnCl_6^{2-}$, $AlCl_4^-$) were also structurally characterized (selected metrical parameters are included in Table 4), the presence of the other cations was inferred primarily on the basis of characteristic ^{31}P NMR data which is summarized in Table 1 [35–38]:

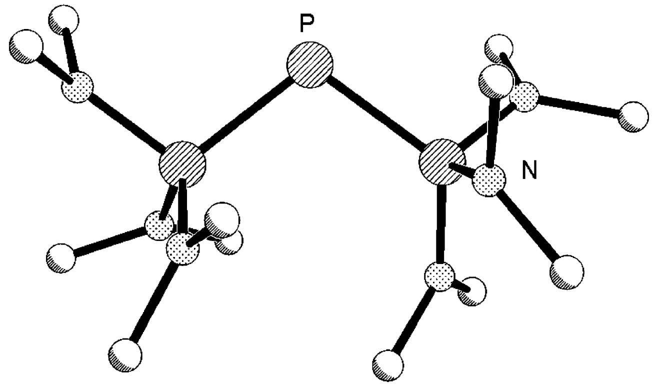
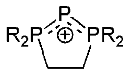
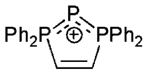


Fig. 13. Molecular structure of an acyclic triphosphenium cation **22** showing the distinctive bent geometry of the Pn^I center [42].



5 R = Ph
6 R = Et
7 R = Me
8 R = Cy
9 R = Ph,Et



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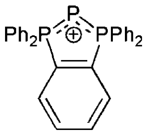

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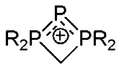
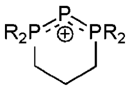
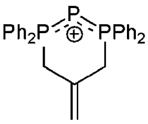


12 R = Me
13 R = Cy



14 R = Ph
15 R = Et



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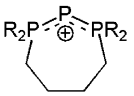
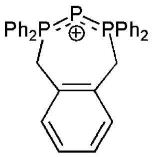
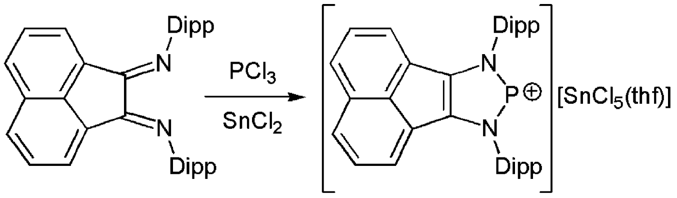


17 R = Ph
18 R = Cy



19

It is worthy of note that certain diimines (bis-nitrogen donors) have also been used recently to trap P^I centers generated using the $PCl_3/SnCl_2$ protocol. In the case of the readily-reduced BIAN system, the P^I center is oxidized to P^{III} and the diimine is reduced in the course of the reaction (Eq. (2)) as evidenced by both the metrical parameters in the solid-state structure (LECZOJ) and the high frequency ^{31}P NMR chemical shift of 232 ppm, which is in the range characteristic of dicoordinate $\mathrm{P^{III}}$ phosphenium cations [39]:

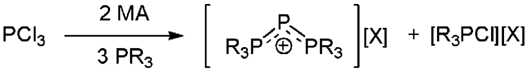


20[SnCl$_5$(thf)]

(2)

2.1.2. Syntheses employing ligand oxidation or PX$_3$ disproportionation

Examples of salts containing acyclic cations were reported by Schmidpeter shortly after his initial report of the cyclic compounds. The synthetic approach to the acyclic species involved reduction of phosphorus (III) chloride by an additional equivalent of the ligating phosphine ($\mathrm{PPh_3}$ or $\mathrm{P(NMe_2)_3}$), which is oxidized from $\mathrm{P^{III}}$ to $\mathrm{P^{V}}$ in the process (Eq. (3)) [32,40,41]. The tetrachloroaluminate salt of the $\mathrm{PPh_3}$ stabilized cation **21** was characterized using X-ray crystallography and ^{31}P NMR spectroscopy, in addition to microanalysis. The solid-state structure, shown in Fig. 13, again exhibits P–P bond lengths that are intermediate between single and double bonds. Importantly, the cation contains a strongly bent P–P–P arrangement even in the absence of the constraints imposed by the chelating ligands in the cyclic systems outlined above. The ^{31}P NMR chemical shift of the $\mathrm{P^{I}}$ center is less shielded than those found in the cyclic analogues:



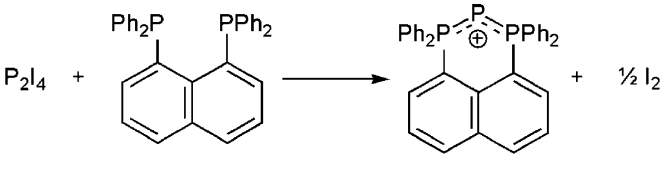
21[AlCl$_4$]: R = Ph, MA = AlCl$_3$, X = AlCl$_4^-$
22[BPh$_4$]: R = NMe$_2$, MA = [Na][BPh$_4$], X = BPh$_4^-$
loss of 2 [Na][Cl] (3)

In a similar manner, many of the cyclic cations that have been isolated with $\mathrm{SnX_6^{2-}}$ counter ions have also been prepared with halide anions ($\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$) using the ligand oxidation protocol [36,37]. A significant complication to using this approach on a preparative scale, for salts containing either acyclic or cyclic cations, is the similar solubilities of the halo-phosphonium salt by-products and the desired $\mathrm{P^{I}}$ salts. As a result, many of the cations prepared using this method have been characterized only by ^{31}P NMR (see Table 1). A variation of this approach involves the disproportionation of phosphorus (III) iodide (or phosphorus (II) iodide) in the presence of a chelating phosphine in a non-donor solvent, such as methylene chloride, to produce iodide salts of the $\mathrm{P^{I}}$ cations with the easily removed $\mathrm{I_2}$ by-product (Eqs. (4) and (5)). The compounds **5**[I], **14**[I] and **23**[I] have both been prepared using this approach and both have been comprehensively characterized by X-ray crystallography (Table 4), ^{31}P NMR and microanalysis [43–45].

$$\mathrm{PI_3} + \text{diphos} \rightarrow [(\text{diphos})\mathrm{P}][\mathrm{I}] + \mathrm{I_2} \quad (4)$$

diphos = dppe, [(diphos)P] = **5**,

diphos = dppp, [(diphos)P] = **14**



23

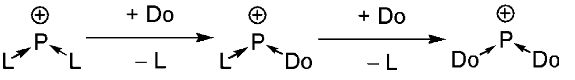
(5)

2.1.3. Ligand exchange and salt metathesis reactions

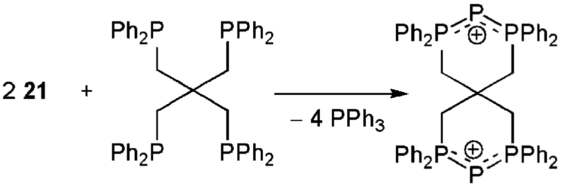
Other triphosphenium $\mathrm{P^{I}}$ salts are accessible through various exchange reactions employing the salts obtained using the syntheses outlined above. For example, access to different counter anions is readily available starting from the iodide salts of **5** and **14** through salt metathesis reactions involving the elimination of alkali metal iodides (Eq. (6)) [44]. The acyclic cation **21**[AlCl$_4$] can undergo sequential substitution by more basic phosphines to generate both symmetric and unsymmetric acyclic cations or cyclic $\mathrm{P^{I}}$ cations (Eq. (7)) [40]. Such reactivity is in keeping with the idea of cations such as **21** as being a “$\mathrm{P^{+}}$” cation coordinated by two neutral phosphine ligands. Similarly, unsymmetrical cyclic cations may also be obtained through the use of an asymmetric chelating diphosphine [37]. Even spirocyclic dications, such as **24**, are accessible through the use of an appropriate substituting ligand (Eq. (8)) [46]. While this type of ligand exchange reactivity has been verified extensively by ^{31}P NMR, side reactions often preclude the bulk isolation of pure products using this method [40,46]. ^{31}P NMR chemical shifts for asymmetric cations are summarized in Table 2:

$$\mathbf{5}[\mathrm{I}]\text{ or }\mathbf{14}[\mathrm{I}] \xrightarrow[-[\mathrm{M}][\mathrm{I}]]{+[\mathrm{M}][\mathrm{A}]} \mathbf{5}[\mathrm{A}]\text{ or }\mathbf{14}[\mathrm{A}] \quad (6)$$

[M][A] = [Na][BPh$_4$], [Ag][OTf], [K][PF$_6$], [Li][GaCl$_4$]



(7)



24 (8)

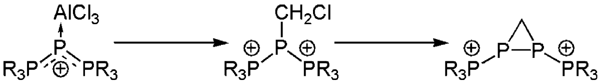
2.1.4. Reactivity

In spite of their positive charge, cations containing $\mathrm{P^{I}}$ centers can behave as electron donors. For example, acyclic $\mathrm{P^{I}}$ cations, $\mathrm{(R_3P)_2P^+}$ (R = Ph, NMe$_2$), are able to coordinate to aluminum trichloride in typical Lewis base/Lewis acid fashion. In the presence of hydrochloric acid, protonation (which is equivalent to oxidation in terms of the model described in Fig. 1) rapidly

Table 2
^{31}P NMR chemical shifts of asymmetric triphosphenium salts [L^1PL^2] [A]

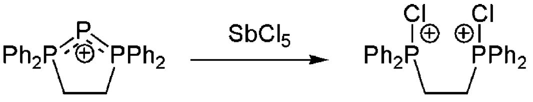
L^1	L^2	A	$\delta P(L^1)$	$\delta P(L^2)$	δP^I	$^1J_{PP(L^1)}$	$^1J_{PP(L^2)}$	$^2J_{PP}$	Ref.
PPh_3	PPh_2Me	$AlCl_4^-$	30	24	−180	482	480	25	[40]
PPh_3	$PPhMe_2$	$AlCl_4^-$	31	16	−173	481	463	26	[40]
PPh_3	PBu_3	$AlCl_4^-$	32	32	−199	503	458	41	[40]
PPh_3	PPh_2NEt_2	$AlCl_4^-$	30	64	−167	510	501	30	[40]
PPh_3	$PPh(NEt_2)_2$	$AlCl_4^-$	30	77	−170	524	479	27	[40]
PPh_3	PPh_2NHPh	$AlCl_4^-$	29	49	−178	479	524	27	[40]
PPh_3	$P(NMe_2)_3$	$AlCl_4^-$	29	84	−180	523	493	30	[40]
PPh_3	$P(N(CH_2)_5)_3$	$AlCl_4^-$	29	77	−173	542	497	32	[40]
PPh_3	$P(N(CH_2)_4O)_3$	$AlCl_4^-$	28	76	−181	526	528	32	[40]
PPh_3	$P(OEt)_3$	$AlCl_4^-$	32	80	−196	437	562	15	[40]
$Et_2P(CH_2)_2PPh_2$ **9**		Cl^-, Br^-, I^-, $SnCl_6^{-2}$	68	79	−251	462	433	10	[37]

occurs at P^I to give dications of the form $[(R_3P)_2PH][AlCl_4]_2$ [41,47]. Upon prolonged exposure to dichloromethane, both the $AlCl_3$ adduct and the dication are reported to be susceptible to oxidation at P^I by CH_2Cl^+ followed by loss of the phosphonium R_3PCl^+ to give diphosphiranes (Eq. (9)), as characterized by ^{31}P NMR data and in light of the crystal structure for the dication shown in Fig. 14 [41,48].



(9)

Whereas oxidation by a variety of other alkyl chlorides also readily occurs for acyclic cations [47], cyclic P^I cations are more resistant and typically require stronger oxidizing agents such as methyl triflate [38,49]. Cyclic cations can also be protonated/oxidized by H^+ from HCl, HOTf or ^{t}BuCl/$AlCl_3$ [47,49]. A summary of ^{31}P NMR data for oxidized P^I cations is given in Table 3. Attempted chlorination of P^I cations using $SbCl_5$ resulted in a breakdown of the P–P–P framework and oxidation of the P^{III} ligand to P^V (Eq. (10)) [50].



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(10)

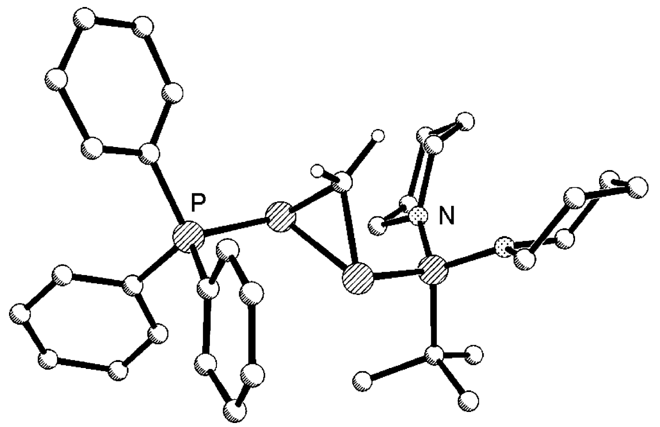


Fig. 14. Structurally characterized analogue (DOCNEO) of the oxidation product from the reaction outlined in Eq. (9).

The only structurally characterized oxidation product that retains the original P–P–P framework is $[(Ph_3P)_2PH][AlCl_4]_2$ **25**$[AlCl_4]_2$ [47] (Fig. 15). In comparison to $[(Ph_3P)_2P][AlCl_4]$ **21**$[AlCl_4]$, the solid-state structure shows a lengthening of the P–P bonds by 0.077 and 0.087 Å and a slight PPP angle increase from 102.2° to 106.4°. Of particular import is the strongly pyramidal arrangement of the substituents around the central phosphorus atom (the sum of the angles around P is 288.25°); this is consistent with the presence of a single "lone pair" of electrons on the phosphorus atom and thus it may be classified as a P^{III} center using the convention outlined above.

A rare well-characterized reduction of a P^I center occurs when the acyclic cation **22**$[BPh_4]$ is treated with Schwartz's reagent, $Cp_2Zr(H)Cl$. In conjunction with the destruction of the P–P–P framework and oxidation of the $P(NMe_2)_3$ ligands to $[ClP(NMe_2)_3][BPh_4]$, the P^I center is reduced to P^{-III} and trapped in an eight-membered ring composed of hydride-bridged zirconocene fragments [51–53] (Eq. (11)). The four coordinate "phosphonium cation" is bound to the zirconium centers in an unusual square-planar arrangement, as illustrated in Fig. 16; such an unprecedented product demonstrates some of the unique

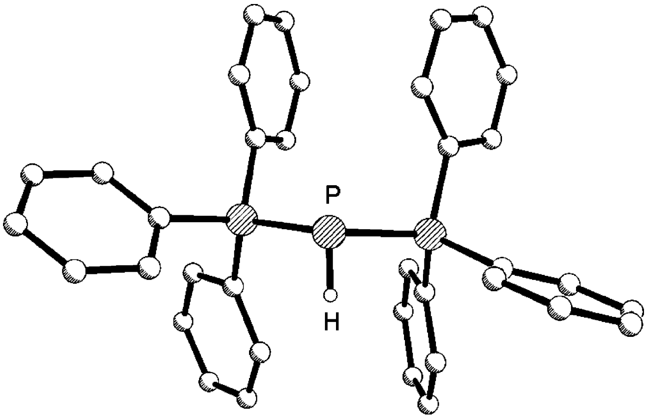


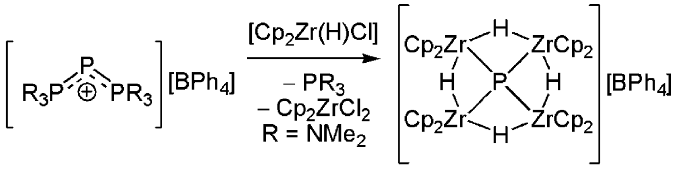
Fig. 15. Molecular structure of the protonated triphosphenium dication $[(Ph_3P)_2PH]$ **25** (DAWFAI) showing the pyramidal geometry of the central phosphorus atom.

Table 3
^{31}P NMR data for the cationic P^I oxidation products of the form $[L_2PE]$ [A], and for the reduction product **26**$[BPh_4]$

L	[Ox]	E	A	δP(L)	δP^I	$^1J_{PP}$	$^1J_{PH}$	Ref.
L = PPh_3 **21**	HCl	H	$AlCl_4^-$	23	−120	286	236	[47]
L = PPh_3 **21**	MeCl	Me	$AlCl_4^-$	23	−48	330		[47]
L = PPh_3 **21**	CH_2Cl_2	CH_2Cl	$AlCl_4^-$	25	−41	330		[47]
L = PPh_3 **21**	EtCl	Et	$AlCl_4^-$	22	−37	334		[47]
L = PPh_3 **21**	^{i}PrCl	^{i}Pr	$AlCl_4^-$	21	−23	354		[47]
L = PPh_3 **21**	PhCl	Ph	$AlCl_4^-$	24	−28	358		[47]
L = PPh_2Me	HCl	H	$AlCl_4^-$	18	−121	261	230	[47]
L = PPh_2Me	CH_2Cl_2	CH_2Cl	$AlCl_4^-$	20	−38	305		[47]
L = $PPhMe_2$	HCl	H	$AlCl_4^-$	18	−116	255	227	[47]
L = $PPhMe_2$	CH_2Cl_2	CH_2Cl	$AlCl_4^-$	21	−31	300		[47]
L = PBu_3	HCl	H	$AlCl_4^-$	38	−146	277	233	[47]
L = PBu_3	CH_2Cl_2	CH_2Cl	$AlCl_4^-$	39	−39	319		[47]
L_2 = dppmm **24**	CH_2Cl_2	CH_2Cl	$AlCl_4^-$	9	80	282		[46]
L_2 = dppe **5**	HCl	H	$AlCl_4^-$	53	−157	239	218	[47]
L_2 = dppe **5**	$AlCl_3$/^{t}BuCl	H	$AlCl_4^-$	54	−154	240	NR	[54]
L_2 = depe **6**	$AlCl_3$/^{t}BuCl	H	$AlCl_4^-$	68	−184	255	NR	[54]
L_2 = dppE **10**	$AlCl_3$/^{t}BuCl	H	$AlCl_4^-$	58	−157	258	231	[54]
L_2 = dppben **11**	$AlCl_3$/^{t}BuCl	H	$AlCl_4^-$	43	−133	241	218	[54]
L_2 = dppp **14**	$AlCl_3$/^{t}BuCl	H	$AlCl_4^-$	14	−156	226	223	[54]
L_2 = dppb **17**	$AlCl_3$/^{t}BuCl	H	$AlCl_4^-$	29	−134	255	236	[54]
L_2 = dppmm **24**	$AlCl_3$/^{t}BuCl	H	$AlCl_4^-$	12	177	232	NR	[46]
L_2 = dppe **5**	HOTf	H	OTf^-	53	−153	241	NR	[54]
L_2 = depe **6**	HOTf	H	OTf^-	72	−181	243	230	[54]
L_2 = dmpe **7**	HOTf	H	OTf^-	56	−149	240	218	[54]
L_2 = dcype **8**	HOTf	H	OTf^-	78	−203	259	228	[54]
L_2 = dppE **10**	HOTf	H	OTf^-	58	−159	272	NR	[54]
L_2 = depp **15**	HOTf	H	OTf^-	29	−182	232	223	[54]
L_2 = dcypb **18**	HOTf	H	OTf^-	49	−166	276	267	[54]
L_2 = dppe 5	MeOTf	Me	OTf^-	55	−91	284		[49]
L_2 = dppE **10**	MeOTf	Me	OTf^-	58	−96	311		[49]
L_2 = dppben **11**	MeOTf	Me	OTf^-	45	−69	291		[49]
L_2 = dppp **14**	MeOTf	Me	OTf^-	12	−89	262		[49]
L_2 = dppb **17**	MeOTf	Me	OTf^-	31	−76	308		[49]
L_2 = dppox **19**	MeOTf	Me	OTf^-	16	−73	296		[49]
26	$Cp_2Zr(H)Cl$	N/A	BPh_4^-		254		30	[51]

NR: not recorded.

chemistry of triphosphenium reagents.



22$[BPh_4]$ **26**$[BPh_4]$

(11)

2.2. Carbon-based-donor-stabilized P^I cations

Phosphamethine cyanines, which are the phosphorus analogues of methine cyanine dyes [56], are among the oldest class of compounds that may be considered to contain P^I centers in many cases. Although such compounds are traditionally regarded as special cases of 2-phosphaallylic cations, which contain P^{III} centers, many examples exhibit structural features and reactivities that are more consistent

Table 4
Structurally characterized triphosphenium salts $[L_2P][A]$

$[L_2P]$	A	P–L bonds (Å)	L–P–L angles (°)	CSD refcode	Ref.
5	$SnCl_6^{2-}$	2.122(1), 2.128(2)	88.9(1)	BEHMEG	[31]
5	I^-	2.131(2) [2.126(2)], 2.133(2) [2.129(2)]	89.35(6) [88.45(6)]	KACXIW	[43]
5	BPh_4^-	2.135(2), 2.122(2)	86.44(7)	KACXOC	[43]
11	$SnCl_6^{2-}$	2.124(1), 2.122(1)	90.67(4)	WUFYIF	[37]
14	$SnCl_6^{2-}$	2.132(1), 2.132(1)	96.44(6)	XEZLAP	[36]
14	$AlCl_4^-$	2.1259(5), 2.1310(5)	95.579(18)	FETJIY	[55]
21	$AlCl_4^-$	2.137(6), 2.128(6)	102.2(2)	DASTEW	[40]
23	I^-	2.1172(7), 2.1178(7)	91.48(3)		[45]
25	$2AlCl_4^-$	2.205(1), 2.224(1)	106.39(4)	DAWFAI	[47]

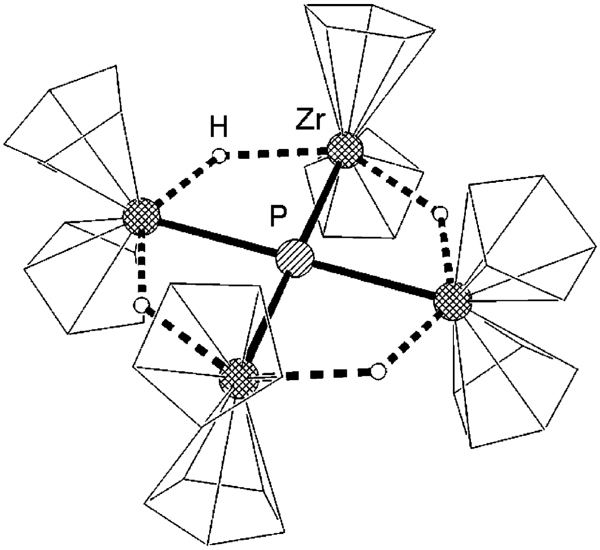


Fig. 16. Molecular structure of the planar phosphonium cation $[P(Cp_2ZrH)_4]$ **26** (CUPGUP) derived from the reaction of **22**$[BPh_4]$ with excess Cp_2ZrHCl.

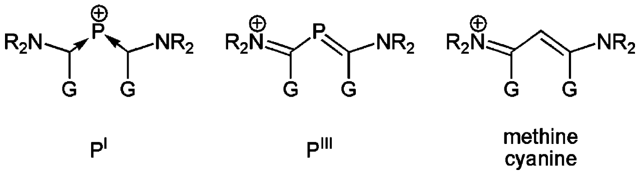


Fig. 17. Phosphamethine cyanines.

with their being understood as carbene-stabilized P^I cations (Fig. 17).

In a similar manner to the situation illustrated for triphosphenium-like cations in Fig. 4, different canonical forms may be used to depict the electronic structure of phosphamethine cyanine cations, as shown in Fig. 18. Although they are well-known for nitrogen analogues, linear structures which can be considered to contain P^V, have not been observed for phosphorus. Conversely, structural types containing P^{III} and P^I both predict bent geometries at the phosphorus center and both are thus more apt depictions of observed structures. Whereas the P^{III} structure could explain the presence of relatively short P–C bonds, the required planar structure is not observed in almost any of the examples that have been studied crystallographically. In this light, the pronounced twisting of the carbene fragments away from C–P–C plane, which diminishes the potential for π-overlap, suggests that the P^I drawing is generally the most realistic depiction of such species [57]; compounds containing such geometrical features are included herein. Computational evidence for this interpretation and potential reasons for the preference of the P^I structure over the P^{III} alternative are elucidated in the Electronic Structure and Bonding section (Section 5) of this review.

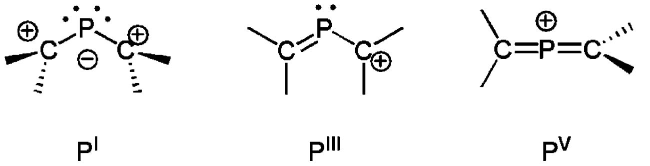
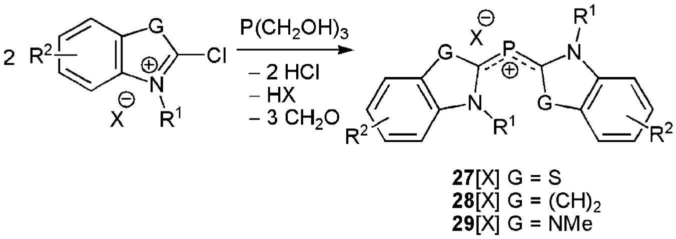


Fig. 18. Canonical structures of 2-phosphaallylic cations.

2.2.1. Syntheses

These P^I compounds were originally prepared by the elimination of acid from the product of cyclic imidoyl-type precursors and $P(CH_2OH)_3$ to provide salts containing cations of the type shown in Eq. (12) [58–60]. Similarly, the reaction of $P(SiMe_3)_3$ with similar precursors produced salts of cations containing either cyclic or acyclic carbenic ligands (Eq. (13)) [61,62]:



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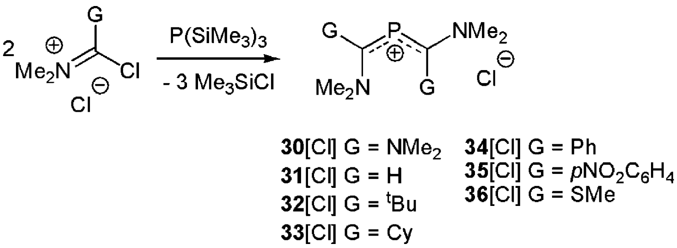
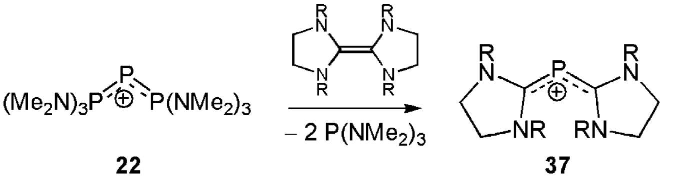


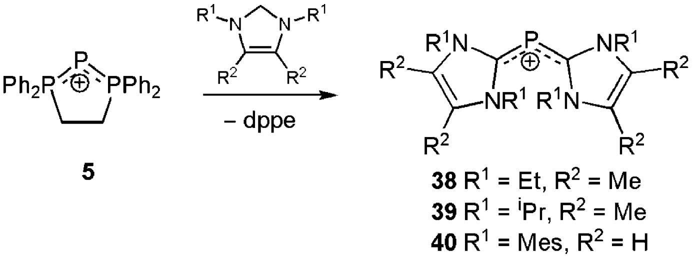
(13)

An alternative synthetic route to phosphamethinecyanine cations discovered by Schmidpeter et al. involved the insertion of a P^I center from the triphosphenium cation **22** into certain electron-rich olefins (Eq. (14)) [63,64]. More recently, it has been demonstrated that the substitution of the phosphine ligands in salts of **5** by stable *N*-heterocyclic carbenes [65] produces phosphamethine cyanine salts (Eq. (15)) [57]. Furthermore, the direct addition of stable *N*-heterocyclic carbenes to phosphorus trihalides also produces P^I halide salts **38–40**; the additional equivalent of carbene used in the reaction produces a halo-imidoyl halide by-product as part of the RedOx reaction [57]. Treatment of appropriate metallophosphaalkenes with tin (II) chloride can result in the release of **30** [66]. Cyclic four-membered cationic rings can be synthesized by treatment of phosphaalkynes with methylating reagents, which undergo cyclization to give cations such as **41** (Eq. (16)) [67].

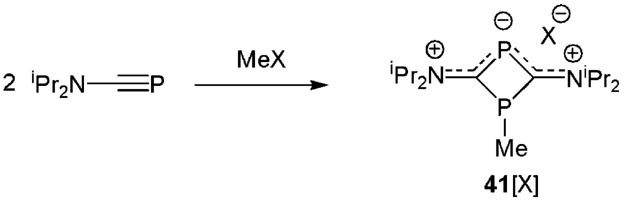
A completely different synthetic approach to 2-phosphaallylic cations proceeds through the silylation of carbonyl groups conjugated to phophaalkenes by trimethylsilyl triflate (TMS-OTf) (Eq. (17)) [68] however it must be noted that such cations are best-described as containing P^{III} centers on the basis of their structural features (*vide infra*):



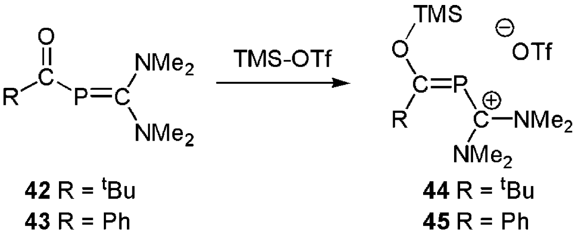
(14)



(15)



(16)



(17)

A summary of ^{31}P NMR data for carbon-based-donor-stabilized P$^{\mathrm{I}}$ cations is presented in Table 5. Although the chemical shifts of such cations are often found to be more shielded than that of phosphoric acid, the actual shift change markedly according to the nature of the G fragment. It should be noted that many phosphamethine cyanine cations, particularly those containing extended π-systems in the carbenic fragment, exhibit absorptions in the visible region, resulting in intensely colored compounds. These compounds have been investigated for their dye-like properties and relevant UV–vis absorption data is summarized in Table 6.

In spite of the large number of phosphamethine cyanine salts that have been synthesized, only a handful of examples have been structurally characterized. Depictions of the molecular structures of cations **27**–**39** are shown in Figs. 19–21 and a summary of metrical parameters from structurally characterized cations is presented in Table 7.

Table 5
^{31}P NMR data for carbon-based-donor-stabilized P$^{\mathrm{I}}$ salts [L$_2$P] [A]

[L$_2$P]	A	δP$^{\mathrm{I}}$	$^2J_{\mathrm{PH}}$	Ref.
27	BF_4^-	−26		[58]
28	ClO_4^-	−49		[59]
29	BF_4^-	104		[60]
30	Cl^-	−22		[62]
31	Cl^-	42	10	[62]
32	Cl^-	34		[62]
33	Cl^-	16		[62]
34	Cl^-	113		[62]
35	Cl^-	117		[62]
36	Cl^-	45		[62]
37	Cl^-	−93		[63]
38	Cl^-	−129		[57]
38	BPh_4^-	−127		[57]
39	Cl^-	−126		[57]
39	BPh_4^-	−124		[57]
40	Cl^-	−124		[57]
41	I^-	155		[67]
41	OTf^-	156		[67]
44	OTf^-	109		[68]
45	OTf^-	101		[68]

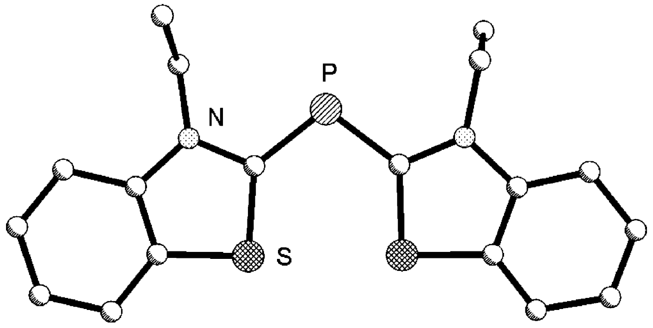


Fig. 19. Molecular structure of the planar cation **27** (EBSPMC).

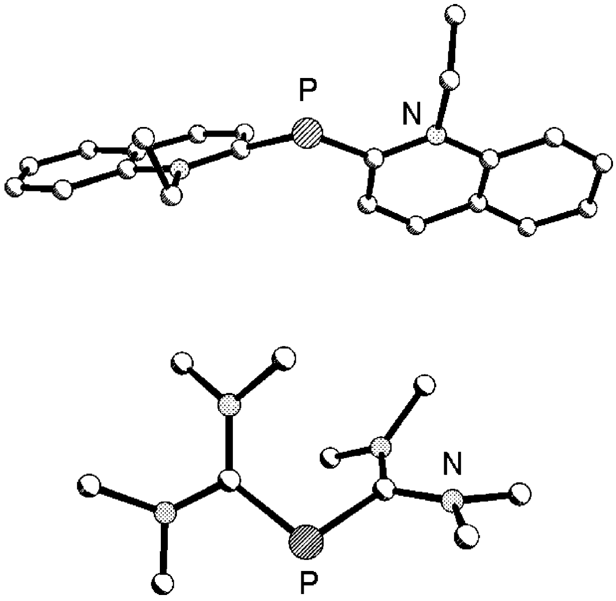
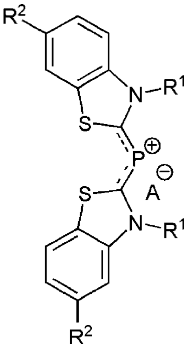
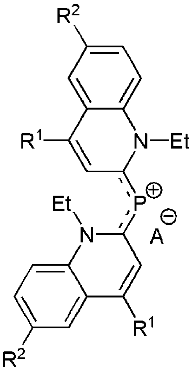
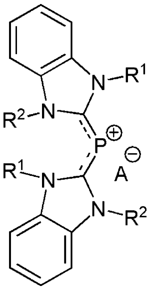
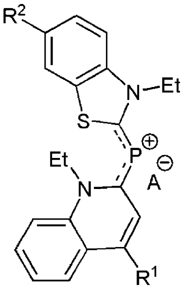


Fig. 20. Molecular structures of the cations **28** (QNLPHQ10—top) and **30** (DIBVOZ—bottom) illustrating the non-planar geometries.

Table 6
Spectrophotometric data for carbon-based-donor-stabilized P^I salts $[L_2P][A]$

	R^1	R^2	A	λ_{max} (nm)	ε (10^{-4})	Ref.
	Me	H	BF_4^-	472	4.37	[58]
	Me	H	ClO_4^-	476	5.04	[61]
	Et	H	BF_4^-	472	4.37	[58]
	Et	H	BF_4^-	478	5.35	[61]
	Et	H	ClO_4^-	478	5.14	[59]
	Et	Br	ClO_4^-	489	4.83	[59]
	Me	OMe	BF_4^-	485	4.34	[58]
	Et	OMe	BF_4^-	485	4.34	[58]
	Et	OMe	ClO_4^-	494	3.88	[59]
	H	H	BF_4^-	592	4.27	[58]
	H	H	ClO_4^-	605	5.15	[59]
	Me	H	BF_4^-	587	4.11	[58]
	Me	H	ClO_4^-	595	3.64	[59]
	H	Br	ClO_4^-	618	4.86	[60]
	Me	Me	BF_4^-	421	3.26	[60]
	Me	Et	BF_4^-	424	3.24	[60]
	Me	^{i}Pr	BF_4^-	424	3.02	[60]
	Et	Et	BF_4^-	437	3.00	[60]
	Et	^{i}Pr	BF_4^-	440	2.80	[60]
	H	H	ClO_4^-	562	3.45	[59]
	Me	H	ClO_4^-	557	3.51	[59]
	H	OMe	ClO_4^-	565	3.60	[59]

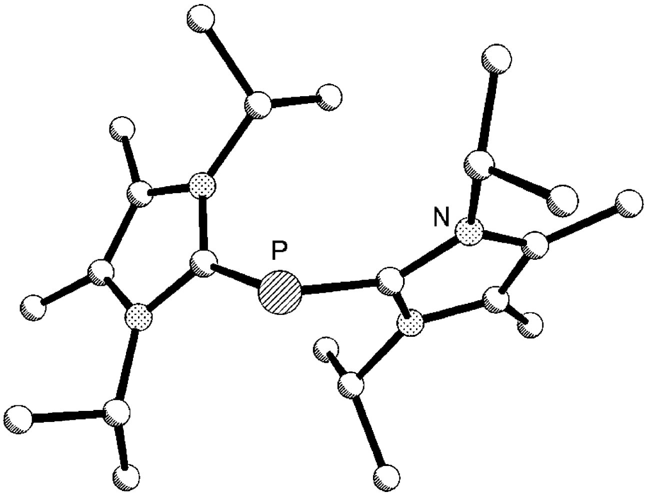


Fig. 21. Molecular structure of the cation **39** (RANGIX).

2.2.2. Reactivity

The chemistry of phosphamethine cyanines has not been examined in great detail, however the oxidation chemistry of such species supports their inclusion in this review. For example, the oxidation of the 2-phosphaallyl cations **30** with MeI (Eq. (18)) does not lead to a planar structure, but rather to a pyramidal product (Fig. 22) consistent with oxidation of the P^I center to a P^{III} center [69]. Oxidation of the same cation with either ozone, hydrogen peroxide or dimethyl sulfoxide (Eq. (19)) results in a complete oxidation of P^I to P^V, as shown by the structure in Fig. 22 [70]. The oxidation of other phosphamethine cyanines with hydrogen peroxide results in the oxidation of the carbon donors to generate the corresponding ketones and also in the complete oxidation of the P^I center to PO_4^{3-} (Eq. (20)) [59]. Treatment of the cations with H_2O or protic acids also decomposes the cation to form H_3PO_4 and imidazolium-type cations (Eq. (21)) [59,60]. A summary of metrical parameters for the oxidation products derived from phosphamethine cyanine cations

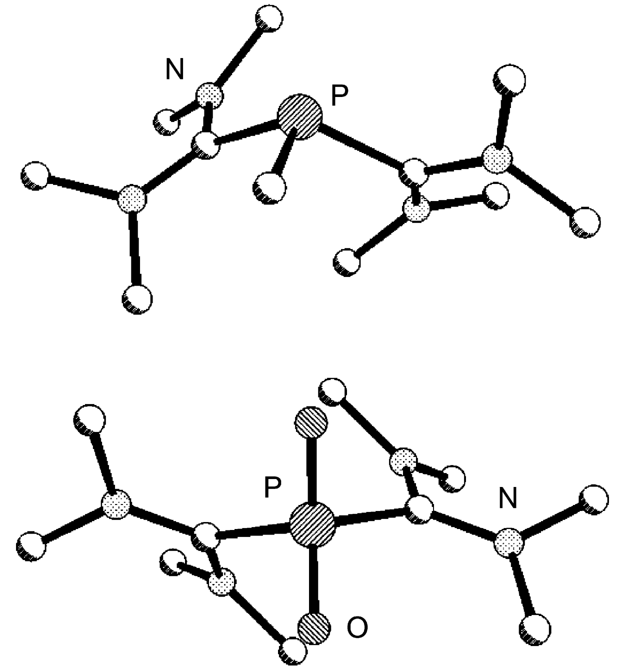
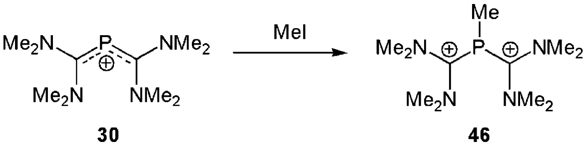
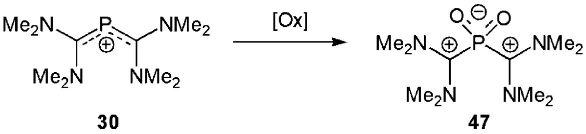


Fig. 22. Molecular structures of the methylated phosphamethine cyanine dication **46** (DIBVUF—top) and the oxidized phosphamethine cyanine cation **47** (FAGBUK—bottom).

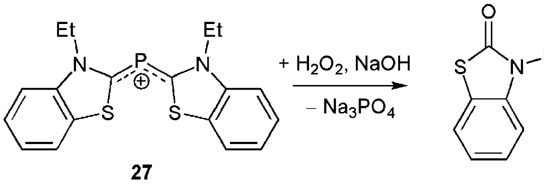
that have been structurally characterized cations are included in Table 7.



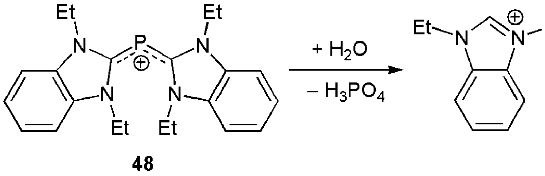
(18)



(19)



(20)



(21)

2.3. Anionic P^I compounds

2.3.1. Syntheses

Anionic P^I compounds are P^I ions stabilized by two anionic donor molecules (Table 8). The most well-known examples of anionic P^I compounds are phosphide (phosphanide) anions, PR_2^-, which are typically formed by the deprotonation (which is equivalent to reduction using the model outlined in Fig. 1) of the corresponding secondary phosphines (Eq. (22)) [2]. Stable phosphides are known for a variety of carbon-based donor groups (R = Ph, CF_3, Ar) and are useful reagents for the synthesis of phosphorus-containing compounds:

$$R_2PH \xrightarrow[-H_2 \text{ or } HR]{M,MH \text{ or } [M][R]} [M][PR_2] \tag{22}$$

$[M]49\ R = Ph, [M]50\ R = CF_3,\ [M]51\ R = Py,$

$[M]52\ R = SiH_3,\ [M]53\ R = 2,4,6\text{-}(CF_3)_3C_6H_2,$

$[M]54\ R = Mes$

There are numerous examples of diorganophosphides that have been characterized by X-ray crystallography in which there are close contacts between the phosphorus atom and the counter cation. To preclude any ambiguities in the description of the structures, only examples of salts containing phosphide anions in which the P^I center is not coordinated to the counter cation that have been structurally characterized are considered in this review; selected metrical parameters for such salts are summarized below in Table 9. All known organophosphides exhibit a strongly-bent C–P–C fragment and P–C distances that are "typical" of single bonds; two representative examples are illustrated in Fig. 23. Organic phosphides are used extensively for the generation of element–phosphorus bonds through salt metathesis reactions, however, given the considerable breadth of this approach, a detailed examination of the products of such reactions is beyond the scope of this review.

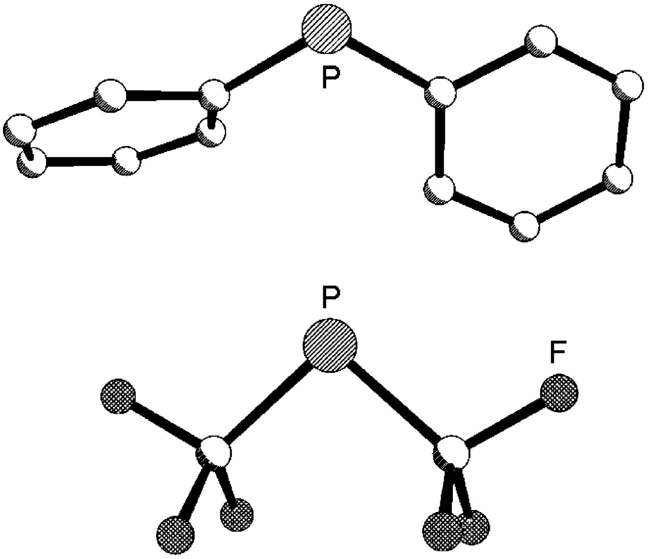
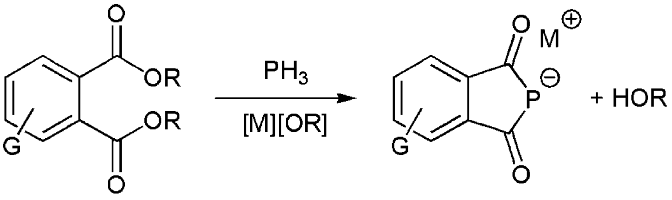


Fig. 23. Molecular structures of the diaryl anion **49** (CEVNAS) and the bis(trifluoromethyl) anion **50** (UJABIQ).

The reaction of PH_3 with dialkylphthalates and group 1 alkoxides results in the generation of alcohol and the trapping of P^I between two carbon centers (Eq. (23)). A variety of substituents on the aromatic ring and cations are possible using this approach [74]:



[M]**55** G = 5-H
[M]**56** G = 4-pyridyl N
[M]**57** G = 5-Me

(23)

A series of anionic P^I compounds stabilized by carbon donors that has been examined more extensively are the salts containing dicyanophosphide anions $P(CN)_2^-$ **58**. These anions are formed by either the addition of alkali metal cyanides to white phosphorus (Eq. (24)) or by the reduction of phosphorus (III) cyanide (Eq. (25)), however, the resultant salts are only stable in solution when the group 1 cations are ligated by crown ethers [75–77]. The potassium salt of $P(CN)_2^-$ can also be obtained through the reaction of $P(CN)_3$ with KF in the presence of a crown ether [76] or by double substitution of triphosphenium cations by cyanide anions (Eq. (26)) [46]. The structure of the anion, depicted in Fig. 24, exhibits the bent C–P–C geometry:

$$P_4 + 8[M][CN] \rightarrow \underset{[M]\mathbf{58}}{[M][P(CN)_2]} \tag{24}$$

Table 7
Structurally characterized phosphamethine cyanine salts $[L_2P][A]$ and products from their oxidation

$[L_2P]$	A	P–L bonds (Å)	L–P–L angles (°)	CSD refcode	Ref.
27	ClO_4^-	1.75(4), 1.75(7)	104.6	EBSPMC	[71,72]
28	ClO_4^-	1.77, 1.81	100.4	QNLPHQ	[73]
30	ClO_4^-	1.796(4) [average P–C]	103.6(2)	DIBVOZ	[69]
30	$FeCl_4^{2-}$	1.790(7), 1.795(7)	104.7(3)	TUKBAC	[66]
39	Cl^-	1.824(2), 1.823(2)	97.35(9)	RANGIX	[57]
41	OTf^-	1.776(3), 1.782(3), 1.862(10)	81.2(1)	YIBYAJ	[67]
46	$2I^-$	[average P–C], 1.816(10) [P–Me], 1.887(4)	107.1(4)	DIBVUF	[69]
47	ClO_4^-	[average P–C], 1.478(3) [average P–O]	103.8(3) [C–P–C], 122.5(3) [O–P–O], 103.8(3) [average O–P–C]	FAGBUK	[70]

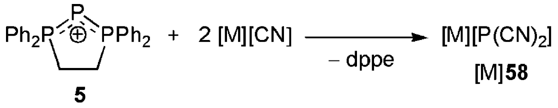
Table 8
^{31}P NMR data for selected anionic P^I compounds $[M][L_2P]$

L^1	L^2	M	δP (L or M)	δP^I	$^1J_{PP}$ or $^1J_{PH}$	Ref.
49		$(12\text{-crown-4})Li^+$		−7		[89]
50		(18-crown-6)K+		−2		[90]
51		$(thf)_2Li^+$		13		[91]
52		$(tmeda)_2Li^+$		−416		[92]
53		$MePPh_3$	−22	21		[93]
54		$(12\text{-crown-4})Cs^+$		−34		[94]
H^-	$2,4\text{-}(CF_3)C_6H_3^-$	$(18\text{-crown-6})K^+$		−73	163	[95]
H^-	$2,4\text{-}(CF_3)C_6H_3^-$	$(15\text{-crown-5})_2K^+$		−67	163	[95]
55		Cs^+		43		[74]
56		Cs^+		44		[74]
57		$(18\text{-crown-6})K^+$		59		[74]
58		$(18\text{-crown-6})Na^+$		−193		[75]
58		$(18\text{-crown-6})K^+$		−194		[77]
62		$(18\text{-crown-6})K^+$		−111		[80]
62		$^nBu_4N^+$		−109		[80]
62		$(Ph_3P)_2N^+$	21	−108		[80]
63		$(18\text{-crown-6})K^+$	0	−168	302	[78]
64		$(18\text{-crown-6})K^+$	56	−161	362	[78]
65		$(18\text{-crown-6})K^+$	68	−203	392	[78]
66		$(18\text{-crown-6})K^+$	74	−205	348	[78]
67		$(18\text{-crown-6})K^+$	54	−142	398	[78]
68		$(18\text{-crown-6})K^+$	23	−180	380	[78]
69		Li^+	79	−166	402	[82]
69		Na^+	77	−154	395	[82]
70		Li^+	59	−128	402	[82]
70		Na^+	56	−116	398	[82]
71		$(18\text{-crown-6})K^+$	75	−199	404	[78]
72		$(18\text{-crown-6})K^+$	68	−183	405	[78]
72		NH_4^+	67	−188	413	[83]
72		$Et_2NH_2^+$	68	−187	422	[83]
72		$(CH_2)_4NH_2^+$	68	−188	413	[83]
72		$(CH_2)_5NH_2^+$	67	−188	411	[83]
73		$(CH_2)_4NH_2^+$	69	−179	412	[96]
$P(NPh)Ph_2^-$	$P(NPh)Ph_2^-$	Li^+	32	−120	405	[97]
$P(NPPh_2)Ph_2^-$	$P(NPPh_2)Ph_2^-$	Li^+	46 (P–P) 50 (terminal)	−122	410 $^2J = 48$	[97]
74		$(18\text{-crown-6})K^+$	12	−102	323	[78]
75		$(thf)_2Li^+$	33	−180	313	[88]
$P^tBu_2^-$	$P^iPr_2^-$	$(thf)_2Li^+$	63,34	−158	314, 307	[88]
76		$(thf)_2Li^+$	62	−140	330	[88]
76		$(tmeda)Li^+$	62	−136	341	[88]
$P^tBu_2^-$	$P(NEt_2)_2$	$(thf)_2Li^+$	51, 158	−127	284, 308	[88]
$L_2 = opbp$		Li^+	31	−174	368	[98]

Table 9
Structurally characterized anionic P^I compounds $[M][L_2P]$

L or $[L_2P]$	M	P–L bonds (Å)	L–P–L angles (°)	CSD refcode	Ref.
49	(12-crown-4)Li^+	1.811(4), 1.804(4)	105.2(2)	CEVNAS	[89]
50	(18-crown-6)K^+	1.84(1)	96.9(5)	UJABIQ	[101]
51	$(thf)_2Li^+$	1.794(4), 1.798(4)	110.4(2)	SUDXOE	[91]
52	$(tmeda)_2Li^+$	2.175(1), 2.168(1)	92.3(1)	PIKWAH	[92]
53	$MePPh_3{}^+$	1.803(2), 1.841(2)	109.1(1)	SUTKAT	[93]
54	(12-crown-4)Cs^+	1.840(9), 1.858(10)	106.2(4)	BILBUU	[94]
$L^1 = H$, $L^2 = 2,6\text{-}(CF_3)_2C_6H_3$	(18-crown-6)K^+	1.794(9) [P–Ar]		AFISAJ	[95]
$L^1 = H$, $L^2 = 2,6\text{-}(CF_3)_2C_6H_3$	(15-crown-5)$_2$K	1.793(6) [P–Ar]		AFISEN	[95]
$L^1 = H$, $L^2 = Mes^*$	K^+	1.20(2) [P–H]	103(2)	RUNSAU	[102]
58	(18-crown-6)Na^+	1.72(2) 1.76(2)	95.0(10)	XOCCPN	[103]
58	(18-crown-6)K^+	1.691(10) 1.665(11)	95.2(6)	DIJXOJ	[76]
60	(18-crown-6)Na^+	1.775(9) [P–C], 2.486(1) [P–Br]	101.4(6) [C–P–C]	NACNPA	[79]
61	(18-crown-6)Na^+	1.823(6) [P–C], 1.810(8) [P–C], 3.058(1) [P–Br]	91.0(4), 92.9(2), [C–P–C]	NACNPB	[79]
62	$(Ph_3P)_2N^+$	1.79(2) [P–Ph], 1.76(2) [P–CN]	102(1)	CIWROP	[80]
69	Li^+	2.123(5), 2.159(5)	95.3(1)	CUFKAP	[82]
73	$(CH_2)_4NH_2{}^+$	2.124(2), 2.120(2)	95.1(1)	BOWXEQ	[96]
75	$(thf)_2Li^+$	2.1627(8)	94.21(4)	TIZLIX	[88]
76	$(thf)_2Li^+$	2.174(1), 2.174(1)	96.50(4)	TIZLAP	[88]
76	(tmeda)Li^+	2.1841(12), 2.1741(13)	95.55(4)	TIZLET	[88]
$L_2 = opbp$	$(thf)_3Li^+$	2.168(2), 2.153(2)	96.9(1)	DENGUY	[98]

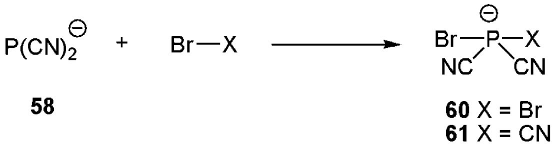
$$P(CN)_3 + [M][PO(OR)_2] \xrightarrow[-PO(CN)(OR)_2]{} \underset{[M]\mathbf{58}}{[M][P(CN)_2]} \qquad (25)$$



(26)

M = (18-crown-6)Na, (18-crown-6)K

The oxidation chemistry of dicyanophosphide anions has provided some interesting results. The oxidation of **58** anions with MeI occurs exclusively at the P^I center, which is more nucleophilic than the nitrogen atoms in the cyanide substituents, to yield $MeP(CN)_2$ **59** [75]; this chemical behavior is exactly analogous to that which was described above for the methylation cationic P^I compounds. Likewise, the P^I anions can also be oxidized by elemental chalcogens (O_2, S_8, Se) to either P^{III} or P^V through sequential oxidations [78]. Perhaps the most interesting oxidation chemistry is observed in the reaction of dicyanophosphide salts with halogens or pseudohalogens. For example, the reaction of **58** with Br_2 (Eq. (27)) results in the two-electron oxidation of the anion to produce a salt containing the $P(CN)_2Br_2{}^-$ **60** anion, which exhibits the disphenoidal shape expected for an anionic P^{III} center; the structure of the anion is illustrated in Fig. 25 [79]. The relevant NMR data is summarized below in Table 10 for the oxidized products:



(27)

Asymmetric anionic P^I compounds of the type $RPCN^-$ are available synthetically through the degradation of the cyclic $(PhP)_5$ species by cyanide salts (Eq. (28)), or through treatment of $P(CN)_2{}^-$ with alkyl or aryl lithium salts (Eq. (29)) [80]. Substitution of $P(CN)_2{}^-$ with a variety of phosphinite-type donors (PR_2E^-) leads to either asymmetric or symmetric P^I anions based on reaction stoichiometry (Eq. (30)). In a similar vein, the reaction of white phosphorus with a chelating diphosphide dianion also results in the trapping of a P^I center between to the two anionic donors [81]:

$$(PhP)_5 + 5[M][CN] \rightarrow \underset{[M]\mathbf{62}}{[M][PhPCN]} \qquad (28)$$

$$\underset{[M]\mathbf{58}}{[M][P(CN)_2]} + [Li][R] \xrightarrow[-[Li][CN]]{} \underset{[M]\mathbf{62}}{[M][RPCN]} \qquad (29)$$

$$\underset{[M]\mathbf{58}}{[M][P(CN)_2]} + [M][PR_2E] \rightarrow [M][(ER_2P)P(CN)] \qquad (30)$$

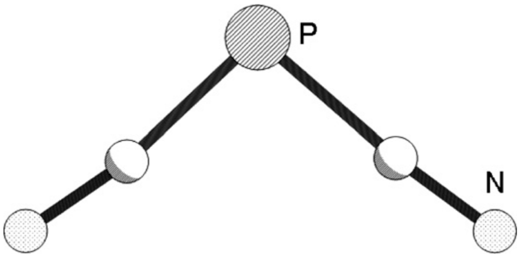


Fig. 24. Molecular structure of the anion $[P(CN)_2]$ **58** (DUXOJ).

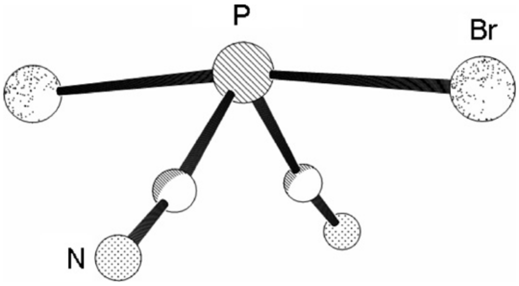


Fig. 25. Molecular structure of the anion $[P(CN)_2Br_2]$ **60** (NACNPA).

Table 10
^{31}P NMR data for oxidized products derived from P^I anions [M][L_2PE]

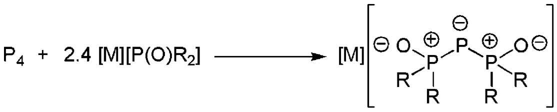
[L_2P]	[Ox]	E	M	δP(L)	δP^I	δSe	$^1J_{PP}$	$^1J_{PSe}$	Ref.
58	MeI	Me	(18-crown-6)Na^+		−82				[75]
58	S_8	S	(18-crown-6)K^+		8				[78]
58	S_8	2S	(18-crown-6)K^+		−8				[78]
58	Se	Se	(18-crown-6)K^+		−42	−240		530	[78]
58	Se	2Se	(18-crown-6)K^+		−85	172		774	[78]
58	S_8, Se	S + Se	(18-crown-6)K^+		−43	159		781	[78]
58	O_2, Se	O + Se	(18-crown-6)K^+		−40	72		814	[78]
58	Br_2	2Br	(18-crown-6)Na^+		−165				[99]
58	I_2	2I	(18-crown-6)Na^+		−172				[99]
58	BrCN	Br + CN	(18-crown-6)Na^+		−177				[100]
58	ICN	I + CN	(18-crown-6)Na^+		−168				[100]
70	Mel	Me	Na^+	42	−64		236		[81]
70	S_8	2S	Na^+	22	58		33		[81]

$$[M]63\,R = Ph, E = \text{lone pair}, [M]64\,R = Ph, E = O,$$

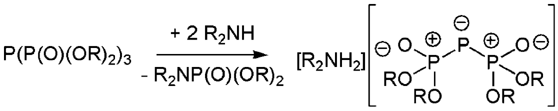
$$[M]65\,R = OEt, E = O, [M]66\,R = NMe_2,\ E = O,$$

$$[M]67\,R = Ph,\ E = S, [M]68\,R = Ph, E = NPh^-$$

Symmetric anionic P^I compounds stabilized by phosphorus donors may also be generated directly from the reaction of white phosphorus with phosphinite anions (Eq. (31)) [81,82]. Reaction stoichiometry is very important in such preparations, because either "P^+" or "$P_2{}^+$" fragments are ligated by the two phosphinite anions when 2.4 or 4 equiv. are used, respectively. An alternative route to such anions is provided by the reaction of tris(dialkylphosphoryl)phosphines, $P(P(O)(OR)_2)_3$, with two equivalents of a secondary amines (NH_3, Et_2NH, $(CH_2)_5NH$, $(CH_2)_5NH$), wherein one equivalent of the amine extracts a $P(O)(OR)_2$ moiety in exchange for a proton and the second equivalent deprotonates the resultant molecule to produce the anionic species (Eq. (32)) [83,84]. The crystal structures of the anion P–P–P species are, predictably, very similar to those of the triphosphenium cations described above; the structure of one example is shown in Fig. 26. Several related anions of the form $P(PR_2)_2{}^-$ have also been synthesized by the deprotonation of the corresponding diphosphinophosphine. Such anions have been used as chelating ligands for a variety of main group and transition metal fragments and the structure of one example is shown in Fig. 27:



[M]**69** R = Et
[M]**70** R = Ph
[M]**71** R = NMe_2 (31)



[R_2NH_2]**72** R = Et
[R_2NH_2]**73** R = ^{i}Pr (32)

Like the cyanide-stabilized species, these anions can also be oxidized at P^I by methyl cations or elemental sulfur, although they are resistant to both oxygen and moisture [81]. And as with many other phosphides, these anions may be used as ligand for transition metal complexes [85–87].

An alternative approach to such triphosphorus anions involves the elimination of Me_3SiBu following the treatment of the appropriate phosphorus–silyl compound with BuLi (Eq. (33)) [88]. These anionic P^I compounds can be used in the generation of related neutral low oxidation state phosphorus

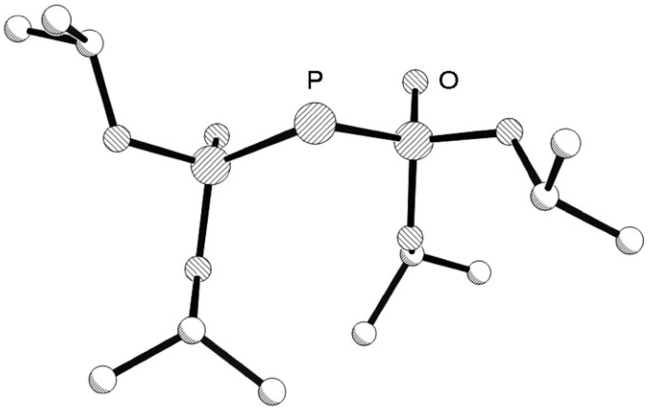


Fig. 26. Molecular structure of the anion [$P(PO(O^iPr)_2)_2$] **73** (BOWXEQ).

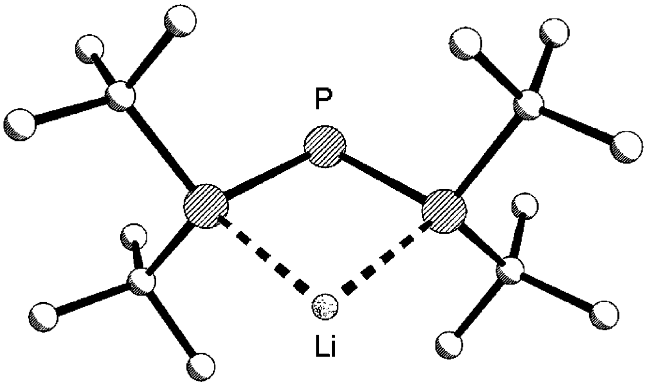
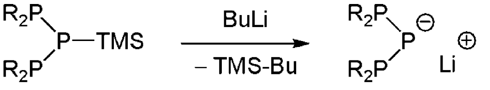


Fig. 27. Molecular structure of the anion [$P(P^tBu_2)_2$] **76** showing the closest contacts to the [Li] counter cation (TIZLAP).

compounds, which are discussed below:



[Li]**74** R = Ph
[Li]**75** R = ^{i}Pr
[Li]**76** R = ^{t}Bu

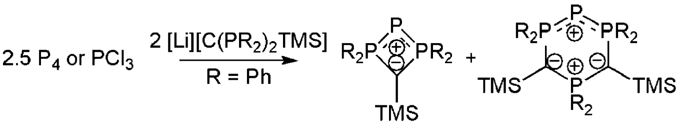
(33)

2.4. Neutral P^I compounds

Neutral P^I compounds (Tables 11–13) may be divided into two general categories: cyclic species with an anionic chelating ligand and acyclic species stabilized by one neutral donor and one anionic donor (Fig. 28).

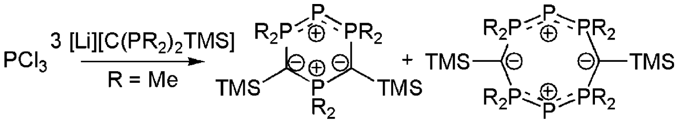
2.4.1. Syntheses

Lithium salts of the diphosphinomethanide carbanions [Li][C(PR_2)$_2$TMS] react with phosphorus trichloride to give P^I rings of various sizes depending on the carbanion substituents and reaction conditions (Eqs. (34)–(36)). In such reactions, the presence of bulkier substituent groups (such as when R = Ph) on the phosphine fragments appears to favor the formation of primarily four-membered rings exhibiting very acute P–P–P angles, as depicted in Fig. 29; such rings can be generated through the reaction of these salts with either PCl_3 or P_4 [104]. The presence of smaller substituents (R = Me) on the phosphine fragments tends to result in the formation of larger non-planar rings; either six-or eight-membered rings, such as the one pictured in Fig. 30, are obtained from the reaction of PCl_3 with three equivalents of the lithium diphosphinomethanide [105–107]. Somewhat in contrast to the case of the carbanion, the addition of two equivalents of the diphosphinoamide salt [Li][N(PPh_2)$_2$] to P_4 does not produce a four-membered ring but yields instead a symmetric, non-planar eight-membered ring, shown in Fig. 30, in which two P^I centers are bridged by the diphosphinoamide anions [108,109]. The product is obtained via an acyclic anionic P^I intermediate that was identified by ^{31}P NMR spectroscopy (Eq. (37)) [97]. Treatment of PCl_3 with three equivalents of the same amide generates an identical eight-membered ring, with the extra amide being oxidized in the process [110]. This neutral P^I compound **82** is able to coordinate to Pd(II) complexes through donation from both P^I centers [111]. The reaction of P_4 with the heavier diphosphinophosphide analogue [Li][Ph_2PPPPh_2], generates only the diphosphine $Ph_2P–PPh_2$ [111]. Reduction of a cyclic bis(amino)chlorophosphine with lithium metal eventually leads to the formation of a four-membered P_4 ring with alternating di- and tetra-coordinate phosphorus atoms **83** (Eq. (38)) [112]:



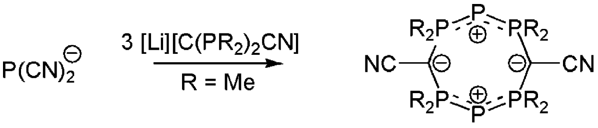
77 **78**

(34)



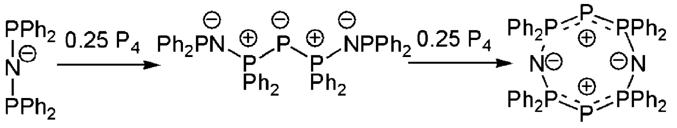
79 **80**

(35)



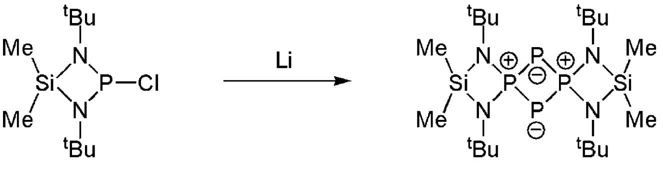
81

(36)



82

(37)



83

(38)

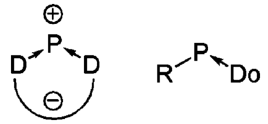


Fig. 28. General structural arrangements of neutral P^I compounds.

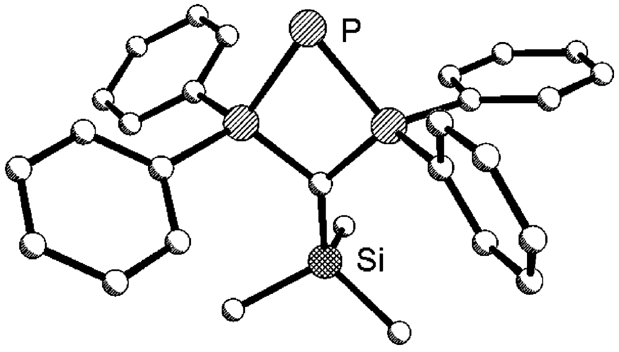


Fig. 29. Molecular structure of the neutral four-membered ring P^I compound **77** (TUJFAF01).

The lithium phosphide [Li]**51** or its parent secondary phosphine (2-Py)$_2$PH can be converted to a variety of zwitterions containing P^I centers, through reaction with group 13 Lewis acids. The product results from the loss of either a halide of alkyl substituent from aluminum or gallium during reaction with either the lithium phosphide or phosphines (Eqs. (39) and (40))

Table 11
^{31}P NMR data of neutral P$^{\mathrm{I}}$ compounds

P$^{\mathrm{I}}$ compound	δP$^{\mathrm{I}}$	δP$^{\mathrm{III}}$	δP$^{\mathrm{V}}$	$^{1}J_{\mathrm{PP}}$ or $^{1}J_{\mathrm{PSe}}$	$^{2}J_{\mathrm{PP}}$	$^{3}J_{\mathrm{PP}}$	Ref.
77	−86	20		261			[104]
78	−123	29	−3	282	64	28	[107]
79	−140	5	14	348	24	14	[105]
80	−110	8		251			[107]
81	−141	36		425			[97]
82	−142	35		429			[97]
83	63	102		372			[112]
84	26						[91]
85	24						[115]
88	94		22		4		[116]
89	97		87		18		[117]
90	92		54	688	22		[117]
91	−81	13		436			[118]
92	−54						[119]
93	−23						[120]
94	−12						[120]
95	−24						[120]
96	−64						[125]
97	−115	−3		582			[127]
98	−134	5		581			[127]
99	−151	24		589			[127]
100	−154	20		612			[127]
106	−46						[139]
107	68						[68]
108	73						[68]
109	63						[68]
110	73						[68]
111	78						[68]
112	65						[68]
113	145						[130]
114	−133						[131]
115	−38						[131]
116	−233	16		374			[35]
117	−89, 15	171		251, 681		37	[133]
118	−124, 16	158		252, 697		40	[134]
119	−43, 16	173		254, 651		38	[134]
120	−205, 32	57		275, 597		64	[135]
121	−169, 32	65		292, 617		53	[136]
122	−213, −81	57		238, 604		52	[135]
123	−99, −87	168		224, 706		33	[135]
124	−180, −73	61		254, 631		47	[136]
125	−132, 215	59		384, 510		59	[136]
126	−119, 242	59		390, 510		57	[136]

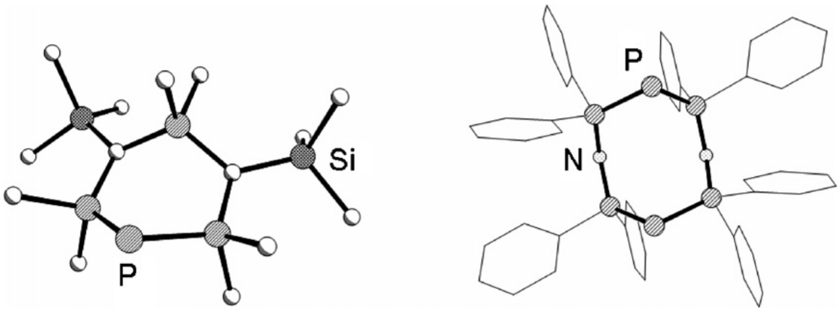


Fig. 30. Molecular structures of the neutral six- and eight-membered ring P$^{\mathrm{I}}$ compounds **79** (YOCNOT) and **82** (JEHXUP).

Table 12
^{31}P NMR data for oxidized or coordinated neutral P^{I} compounds [L_2PE][A]

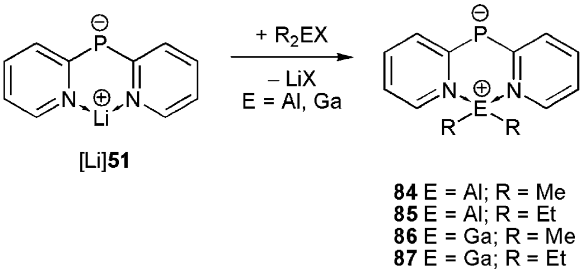
P^{I} compound	[Ox]	E	A	δP(L)	δP^{I}	$^{1}J_{PP}$	$^{1}J_{PH}$	Ref.
93	BH_3·THF	2BH_3	N/A		4			[128]
96	BH_3·THF	2BH_3	N/A		3			[125]
96	O_2	2O	N/A		91			[125]
97	TMS-OTf	TMS	OTf	16	−30	343		[126]
97	HOTf	H	OTf	17	−93	282	233	[126]
97	MeOTf	Me	OTf	17	−40	336		[126]
97	TMSl	TMS	I	17	−28	343		[126]
97	MeI	Me	I	18	−37	336		[126]
97	BH_3·THF	BH_3	N/A	5	−59	435		[126]

Table 13
Structurally characterized neutral P^{I} compounds and some oxidized or complexed products derived therefrom

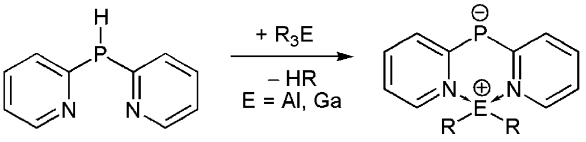
P^{I} compound	P–L bonds (Å)	L–P–L angles (°)	CSD refcode	Ref.
77	2.1489(5) [2.1526(5)], 2.1530(6) [2.1488(5)]	72.65(2) [72.21(2)]	TUJFAF	[104,107]
78	2.134(1)	98.1(3)	YOCNOT	[105,107]
82	2.133(1), 2.137(1)	95.86(2)	JEHXUP	[111]
84	1.786(2), 1.782(2)	106.6(1)	SUDXUK	[91]
85	1.777(3), 1.778(3), 1.815(9)	107.40(13)	MAZQIN	[115]
88	1.832(8), 1.798(9), 1.792(7), 1.839(2)	81.3(4) 82.9(4)	ZITPOH	[116]
89	1.839(2), 1.783(2), 1.777(2), 1.829(6)	79.62(7) 82.82(7)	CUTMOT	[117]
90	1.841(5), 1.782(6), 1.769(5), 1.794(3) [P–NHC]	79.2(3) 82.4(3)	CUTQAJ	[117]
92	1.816^{a} [P–Ph]	100.50^{a}	RULLIT	[119]
93	1.763(6) [P–NHC], 1.9773(3) [P–Ph]	99.9(3)	RUNWAY	[120]
94	1.746(4) [P–NHC], 1.843^{a} [P–Ph]	100.5(2)	RUNWUS	[120]
95	1.784(2) [P–NHC] 1.843(4) [P–CF_3]	101.66(8)	RUNWIG	[120]
97	1.843(4) [P–Ar], 2.084(2) [P–PMe_3]	106.79(13)	VETBF	[126]
102	1.856(2) [P–NHC], 1.828(2) [P–Ph]	104.78(7)	RUFSEQ	[128]
103	1.818(5) [P–NHC], 1.899(5) [P–R]	86.8(2)	ACEQUU	[125]
104	1.824(3) [P–NHC], 1.861(4) [P–R]	86.5(2)	ACEQOO	[125]
110	1.838(2) [P–L^1], 1.735(2) [P–L^2]	102.3(1)	CODNAK	[68]
111	1.844(2) [P–L^1], 1.728(2) [P–L^2]	104.1(1)	CODNEO	[68]
113	1.8264(16) [P–NHC], 1.7483(16) [P–C(S)R]	101.89(7)	GITQOP	[130]
114	1.771(5) [P–NHC], 1.680(13) [P–CN]	101.8(5)	CNPBZM	[131]
117	2.202(2) [2.205(2)], [P–PR_2], 2.077(2) [2.081(2)], [P–PR_3]	105.77(7) [105.98(7)]	LIKYAF	[140]
120	2.1791(4) [P–PR_2], 2.1263(4) [P–PR_3]	100.951(13)	YEVSB	[135]
122	2.1826(5) [P–PR_2], 2.1358(5) [P–PR_3]	100.29(2)	YEVSOH	[135]

[a] Value taken from the CSD.

[91,113–115]; the molecular structure of **84** is shown in Fig. 31:



(39)



(40)

Whereas the addition of alkyl halides to amino-substituted phosphaalkynes was shown above to generate P^{I} cations, treat-

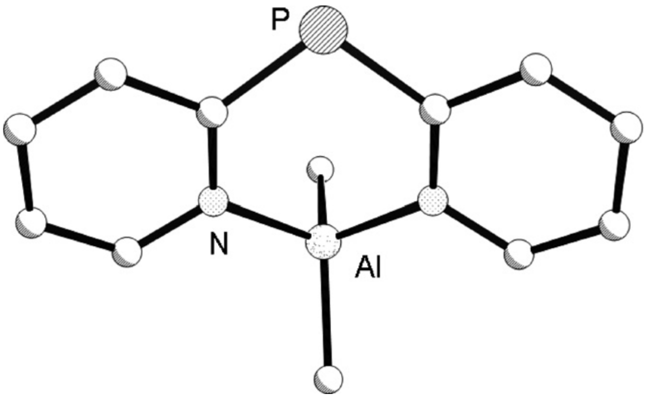


Fig. 31. Molecular structure of **84** (SUDXUK) illustrating the non-planarity of the central six-membered ring.

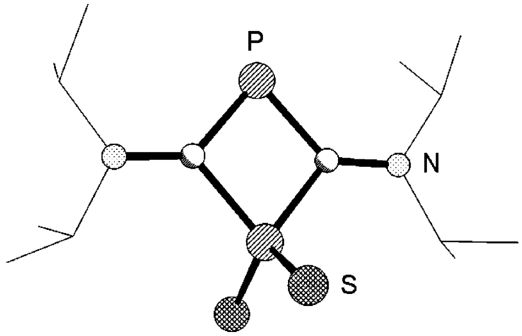
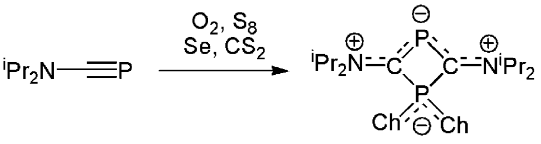


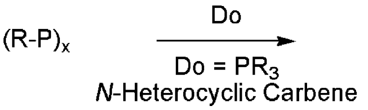
Fig. 32. Molecular structure of **89** (CUTMOT), illustrating the planar core of the molecule.

ment with elemental chalcogens (O_2, S_8, Se) or CS_2 yields the analogous neutral species where one of the P atoms has undergone complete oxidation to P^V (Eq. (41)) [116,117]. The molecular structure of one example of this family of chalcogenides is illustrated in Fig. 32:

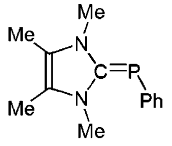


88 Ch = O
89 Ch = S
90 Ch = Se (41)

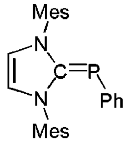
As outlined at the start of Section 2, cyclic phosphinidenes contain P^I centers on the basis of formal counting rules but have structural and electronic features that are more consistent with P^{III} centers. Such rings can, however, be broken apart by suitable strong donors (phosphines, *N*-heterocyclic carbenes) to produce neutral compounds that may be more accurately described as containing P^I; in appropriate cases, such compounds can be considered reasonably as being base-stabilized phosphinidenes (Eq. (42)) [118–120]. The first report of this approach was the reaction of four equivalents of PMe_3 with $(PCF_3)_4$, to yield the P^I compound Me_3PPCF_3 **91** [121]:



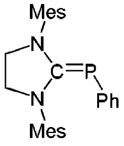
(42)



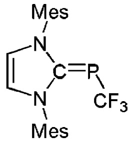
92



93



94



95

Whereas carbene-stabilized phosphindenes are often considered to be a type of phosphaalkene, which contain P^{III} centers [122,123], the structural features of the NHC-stabilized phosphinidenes are more consistent with their containing a P^I center [124]. In particular, the structural features exhibited by NHC-stabilized phosphinidenes are, predictably, virtually identical to those found in the corresponding NHC-stabilized cations and dialkylphosphides described above. Of particular note is the observation that neither of the groups attached to the phosphorus atom are co-planar with the C–P–C framework in structures such as that shown in Fig. 33.

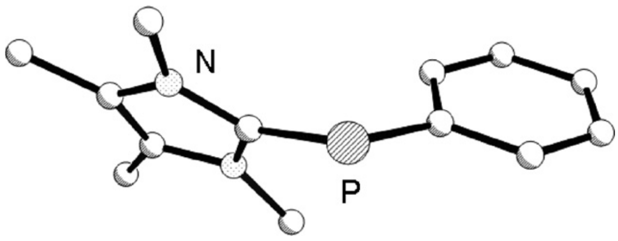
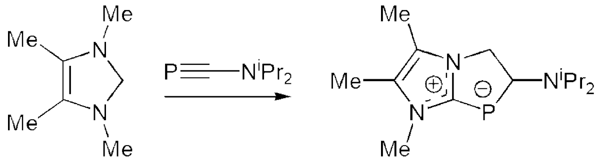


Fig. 33. Molecular structure of the neutral NHC-stabilized phosphinidene **92** (RULLIT).

Compounds that can be considered as intramolecularly carbene-stabilized phosphinidenes can also be isolated from the treatment of amino-substituted phosphaalkynes with *N*-heterocyclic carbenes (Eq. (43)) [125]:



96 (43)

Analogous phosphine-stabilized phosphinidenes can also be isolated when an aryldichlorophosphine, $ArPCl_2$, is reduced in the presence of PMe_3 (Eq. (44)) [126]. This method has only produced monomeric products when sterically demanding groups are affixed to the P^I center (Ar = 2,4,6-$^tBu_3C_6H_2$, Mes*; Ar = 2,6-$Mes_2C_6H_3$, Dmp, Mes = 2,4,6-$Me_3C_6H_2$) and the structure of one example is depicted in Fig. 34. When this synthetic approach is attempted with less bulky substituents on the phosphorus atom the only products that are isolated result from phosphinidene oligiomerization to give the corresponding cyclic polyphosphine. In contrast, the synthetic approach employing the Lewis-base phosphinidene extraction from cyclic polyphosphines allows for much smaller groups on the P^I center

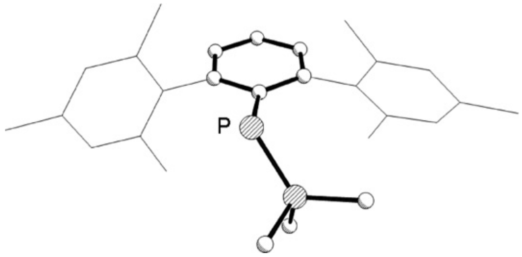


Fig. 34. Molecular structure of the phosphine-stabilized phosphinidene **97** (VETBIF).

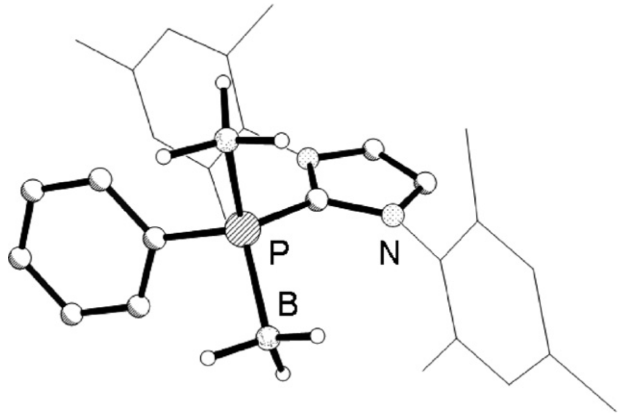
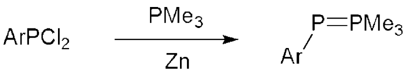


Fig. 35. Molecular structure of the bis-BH_3 adduct of the NHC-stabilized phosphinidene **102** (RUFSEQ).

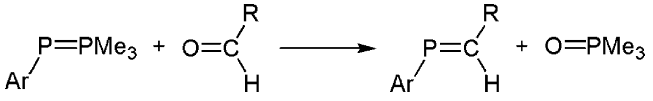
such as $-CF_3$ [120]:



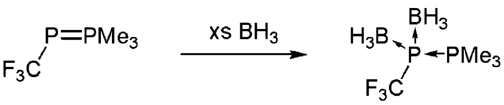
97 Ar = Dmp
98 Ar = Mes* (44)

2.4.2. Reactivity

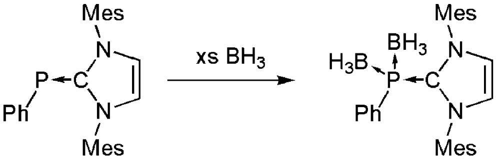
Phosphine-stabilized phosphinidenes **97** and **98** can undergo exchange of PMe_3 with other non-hindered trialkylphosphines, such as PBu_3 to give compounds **99** and **100** [127], and have proven useful as phospha-Wittig reagents; these can be employed for the formation of new P–C bonds (Eq. (45)) [127] and were the subject of a recent review [24]. Phosphine- and NHC-stabilized phosphinidenes have been shown to coordinate to two equivalents of BH_3 (Eqs. (46)–(48)); the structure of one such example is shown in Fig. 35 [128]. Bulkier substituents on the phosphinidene fragment seem to prevent the coordination of two borane molecules (Eq. (49)) [126]. Similar bis-adducts are also observed with the intramolecularly carbene-stabilized molecule **96**:



97, 98 (45)



91 **101** (46)



93 **102** (47)

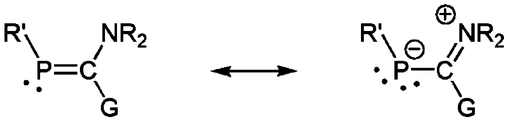


Fig. 36. “Inverse electron density” phosphaalkenes.

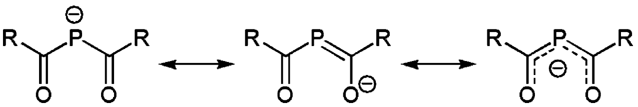
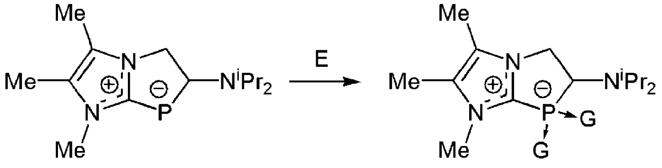
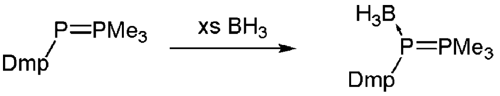


Fig. 37. Canonical structures of 2-phospha-dionato anions.



96

103 G = BH_3; E = BH_3
104 G = O; E = O_2 (48)



97 **105** (49)

As outlined by Weber [129], “inverse electron density” phosphaalkenes can be considered to contain P^I centers in that the canonical structure containing the phosphide-like fragment is an important resonance contributor to the actual electronic structure (Fig. 36). When G is an NR_2 fragment, such compounds are clearly analogous to the NHC-stabilized phosphinidenes described above. It must be noted, however, that the descrip-

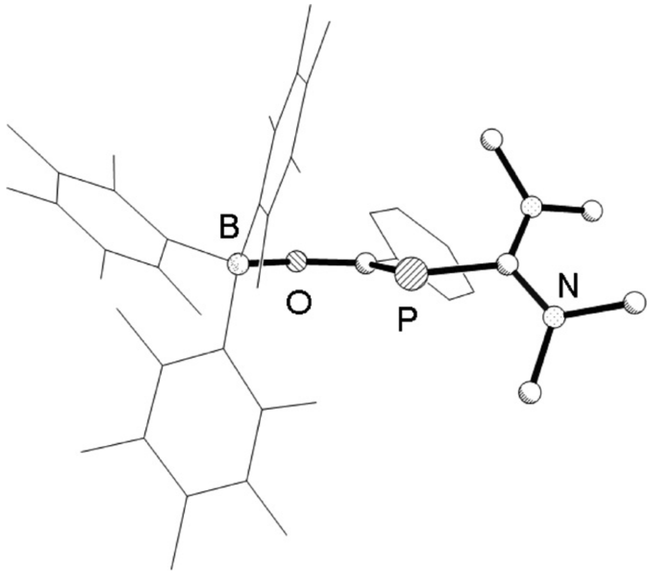
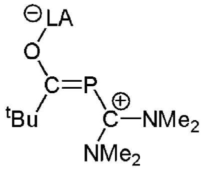
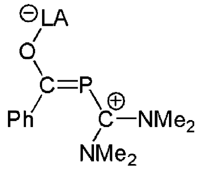


Fig. 38. Molecular structure of the P-acyl phosphaalkene–$B(C_6F_5)_3$ adduct **110** (CODNAK) showing the planar arrangement of the RC(O) fragment and the C–P–C moiety.

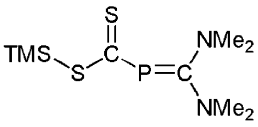
tion of such compounds as containing P^I centers is only justified when the R′ group is not able to form a P=C or (P=E) multiple bond. For example, whereas $(TMS)P{=}C(NMe_2)2$ **106** can reasonably be considered to contain a P^I center, the corresponding P-acyl phosphaalkenes (obtained through the reaction of **106** with organic acid chlorides [130]) are more aptly described as containing P^{III} centers; this description is a consequence of the enolate form of the RC(O)P fragment as depicted in Fig. 37. While the structures of free P-acyl phosphaalkenes of the type $RC(O)P{=}C(NMe_2)_2$ are not known, the structure of the $B(C_6F_5)_3$ adduct **110** is depicted in Fig. 38 and clearly shows that the acyl group is co-planar with the C–P–C moiety and is thus consistent with the presence of a P^{III} environment. In spite of this observation, the coordination chemistry of the P atom in such molecules is very similar to that which is observed for the other P^I compounds described above [68] and thus "inverse electron density" phosphaalkenes are worthy of inclusion in this review:



107 LA = $B(C_6F_5)_3$
108 LA = $AlCl_2{}^tBu$
109 LA = $AlMe_3$

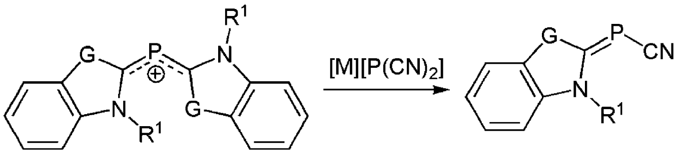


110 LA = $B(C_6F_5)_3$
111 LA = $AlCl_2{}^tBu$
112 LA = $AlMe_3$



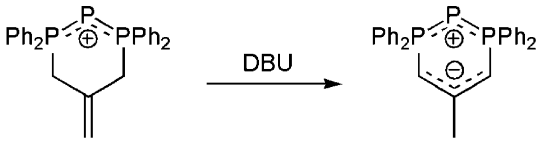
113

Finally, it should be noted that neutral P^I compounds can also be generated from existing P^I cations and anions. For example, displacement of cyanide from $P(CN)_2{}^-$ by $(Ph_2P)_2CCN^-$ generates an 8-membered ring identical to **82** in which each N atom has been replaced by a CCN fragment. Similarly, equimolar mixtures of carbene-stabilized P^I cations and cyanide-stabilized P^I anions leads to ligand scambling results in overall neutral P^I compounds with both carbene and cyanide donors (Eq. (50)) [131]. Lastly, some cyclic P^I cations can be deprotonated by DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) [132] to yield zwitterionic compounds as shown in Eq. (51) [35]:



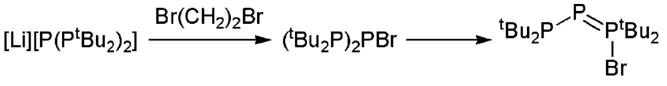
114 G = NMe
115 G = $(CH)_2$

(50)



16 **116** (51)

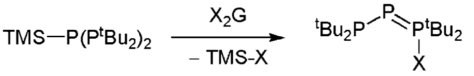
The reaction of the anionic bis-phosphide stabilized P^I salt $[Li][P(P^tBu_2)_2]$ [Li]**76** with 1,2-dibromoethane generates an oxidized phosphorus compound of the type $(R_2P)_2PBr$, which then undergoes a tautomerization involving the transfer of Br from the central phosphorus atom (providing a P^I-like center) to one of the phosphide fragments (producing a P^V-like center) leads to the product $^tBu_2P–P{=}P(Br)^tBu_2$ (Eq. (52)) [133], as shown in Fig. 39:



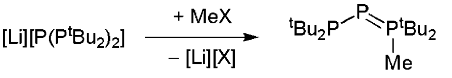
[Li]**76** **117**

(52)

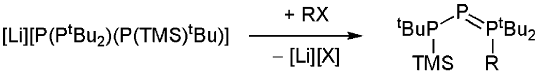
In a similar vein, the treatment of $(^tBu_2P)_2P$-TMS with various halogenating agents (X_2G) also results in the formation of compounds **118** and **119** (Eq. (53)) [134]. The methylated analogue **120** is accessible through the reaction of $[Li][P(P^tBu_2)_2]$ with either Me_2SO_4 or MeCl (Eq. (54)) [135]. Other analogous neutral P^I compounds, such as $^tBu(TMS)P–P{=}P(Me)^tBu_2$ **122**, are accessible using the same synthetic approach by altering the initial lithium diphosphinophosphide reagent (Eq. (55)) [135]. Such species can likewise be converted to the related halogenated species through treatment with halogenating reagents and concomitant loss of TMS-X (Eq. (56)) [136]:



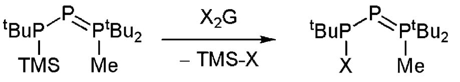
118 X = Cl
119 X = I (53)



[Li]**76** **120** (54)



122 R = Me
123 R = Br (55)



122 **125** X = Cl
126 X = Br (56)

The reaction of $^tBu_2P–P{=}P(Br)^tBu_2$ **117** with lithium phosphides produce diphosphines and result in the oxidation of the P^I center to yield $P(PR_2)(P^tBu_2)_2$ (Eq. (57)) [137]. Treatment of **117** with alkyl lithium reagents results in both the exchange of Br for R and the oxidation of the P^I center to give a phosphine of the form $PR(P^tBu_2)_2$ as the major project and some of the P^I species **118–120** (Eq. (58)) [137]. In contrast, alkyl lithium reagents abstract a proton from the methyl group in $R^tBuP–P{=}P(Me)^tBu_2$ (R = ^{t}Bu, TMS) to produce the lithium salt of the corresponding anion; such salts can be treated with TMS-Cl to re-generate a neutral P^I compound **121** or **123** [136]. The reaction of $R^tBuP–P{=}P(Me)^tBu_2$ with $Ni(CO)_4$ results in

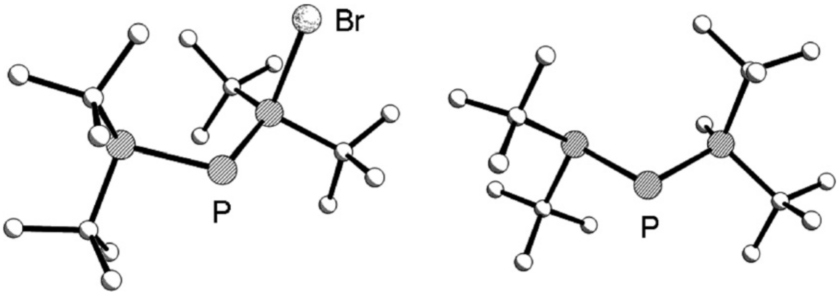


Fig. 39. Molecular structures of the related brominated and methylated neutral P^I species **117** (LIKYAF) and **120** (YEVSIB).

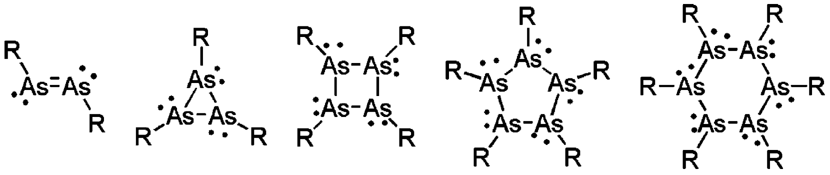
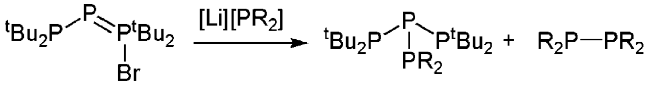


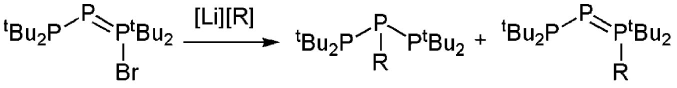
Fig. 40. Oligomeric organo-arsinidene structures.

the cyclization of the P–P^{t}Bu$_2$ phosphinidene-like units into a three-membered ring and coordination to nickel via the pendant P^{t}Bu$_2$ fragments [138]:



117

(57)



117

118 R = Cl
119 R = I
120 R = Me

(58)

3. Arsenic

As is the case for phosphorus, the traditional classes of compounds that are formally considered to contain As^I centers are exemplified by the molecules composed of oligomers of unstable arsinidene fragments pictured in Fig. 40.

Perhaps the most well-known example of such a compound is the drug "Salvarsan" **127** [141], which has been shown to consist of primarily three- and five-membered rings. Despite their classification as As^I compounds on the basis of counting rules, all of the cyclo-polyarsines [142] contain exclusively pyramidal environments around arsenic that are consistent with the As^{III} centers, as outlined above for the phosphorus analogues. In this light, the types of compounds that contain As^I centers as outlined in Fig. 1 are similar to the dicoordinate examples described above for phosphorus.

The R–DKA ligands used to obtain the "stabilized phosphinidenes" described above have also been used to prepare the arsenic congeners [28,143]. The structure of the 10-As-3 compound (^{t}Bu-DKA)As **128** is depicted in Fig. 41 and features the requisite planar bicyclic core. While the chemistry of these arsenic derivatives is much less developed than that of the phosphorus analogues, the molecule is reported to be more resistant to hydrolysis than the phosphorus congeners and the planar bicyclic core appears to be maintained upon ligation to transition metals.

3.1. Syntheses

While there are fewer examples of As^I compounds, they tend to be synthesized by synthetic routes that have been used to obtain the analogous P^I compounds. For example, cationic phosphines-stabilized As^I compounds may be synthesized by the reduction of $AsCl_3$ by $SnCl_2$ in the presence of a chelating phosphines (Eq. (59)) (Table 15) [35,37,144,145]. Several compounds that have been obtained using this synthetic approach have also been characterized crystallographically and examples of cations containing saturated and unsaturated backbones are depicted in Fig. 42. In every case the compounds exhibit As–P bonds that are intermediate in length between those of As–P single bonds (CSD average 2.34 Å) and As=P double bonds (2.124(4) Å in Mes*P = AsDis [146]). The P–As–P fragments in all of the cyclic cations are strongly bent with the angles being, expectedly, smaller than those of the corresponding phosphorus analogues. Selected metrical parameters for the crystallograph-

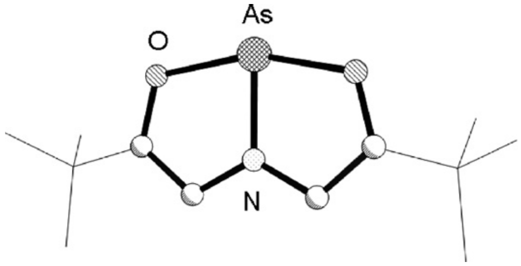


Fig. 41. Molecular structure of the stabilized arsinidene **128** (CUXCIH).

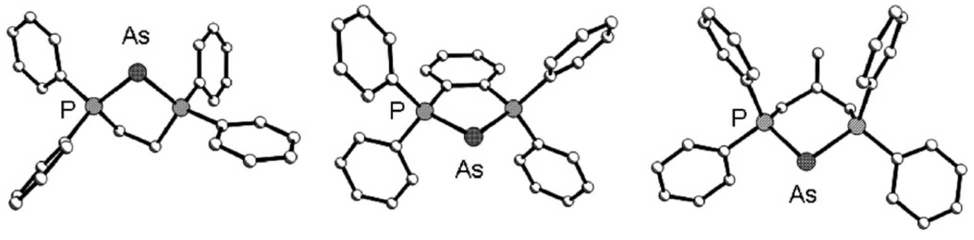
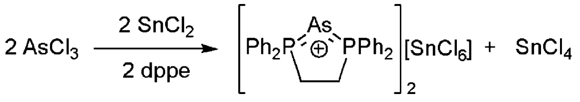


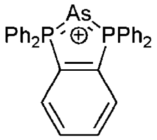
Fig. 42. Molecular structures of the diphosphine-stabilized As$^{\mathrm{I}}$ cations **129** (EBENAB), **133** (WUFYOL) and **135** (WAJGOD).

ically characterized molecules are compiled in Table 16:



129$_2$[SnCl$_6$] (59)

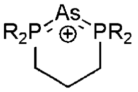
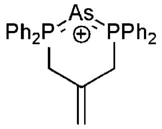
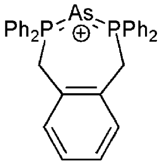




129 R = Ph
130 R = Et
131 R = Ph, Et

132

133

134

135

136

As demonstrated for the phosphorus analogues, diimines have recently been used to trap As$^{\mathrm{I}}$ centers generated using the AsCl$_3$/SnCl$_2$ protocol. The metrical parameters of the cation in the [(BIAN)As][SnCl$_5$(thf)] **137**[SnCl$_5$(thf)] (LECZID) thus obtained clearly demonstrate that the As$^{\mathrm{I}}$ center is oxidized to As$^{\mathrm{III}}$ (Eq. (60)) and the diimine is reduced to the corresponding diamide in the process [39]. More recently, Reeske and Cowley have shown if a diimine that is not easily reduced is used in analogous trapping reactions, the product obtained does indeed contain an As$^{\mathrm{I}}$ center (Eq. (61)) [147]. The structure of the cation is depicted in Fig. 43 and the structure is perhaps best described as containing a 10-As-3 center [27] with a ψ-tbp geometry; in this light, the compound can be considered to be equivalent to a base-stabilized arsidene in the same manner as the R–DKA molecules of Arduengo described above. In this context, the As–N distances are reported to be consistent with dative As–N bonds and the metrical parameters of the diimine fragment are almost identical to those of the free diimine ligand and thus are not indicative of ligand reduction:

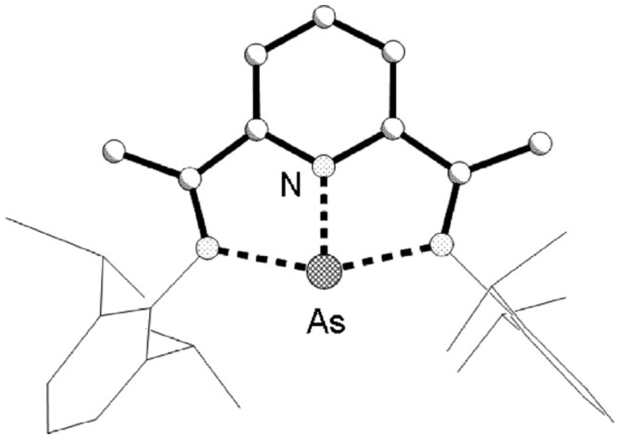
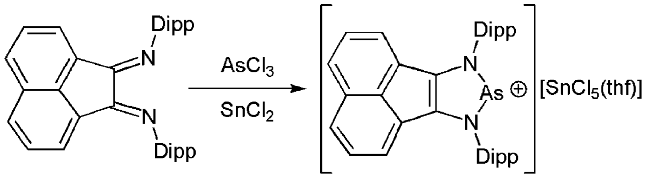
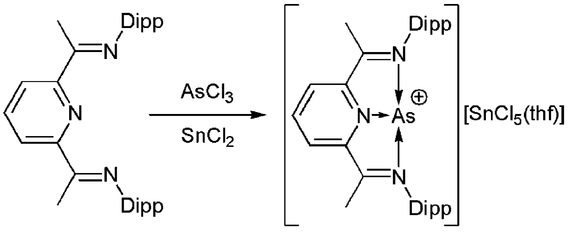


Fig. 43. Molecular structure of the diimine-stabilized As$^{\mathrm{I}}$ cation **138** (GEHCIG, GEHCOM).



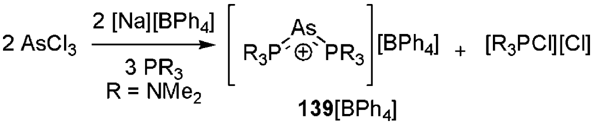
137[SnCl$_5$(thf)]

(60)

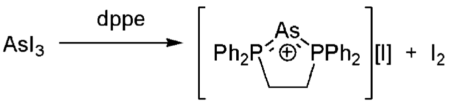


138[SnCl$_5$(thf)] (61)

In a similar manner to that which was described above for the phosphorus derivatives, an additional equivalent of ligating phosphine can also be used to reduce As$^{\mathrm{III}}$ to As$^{\mathrm{I}}$ to generate acyclic and cyclic cations (Eq. (62)) [37,52,53]. The molecular structure of the acyclic As$^{\mathrm{I}}$ cation **139** is depicted in Fig. 44 and displays the expected bent P–As–P fragment containing short P–As bonds. Arsenic (III) iodide also undergoes disproportionation, promoted by chelating phosphines that trap the low oxidation state As$^{\mathrm{I}}$ ion with either iodide (Eq. (63)) or the dinuclear As$^{\mathrm{III}}$ complex (dppe)As$_2$I$_7^-$ as the counter ion depending on reaction conditions [43,145]:



139[BPh$_4$] (62)



129[I] (63)

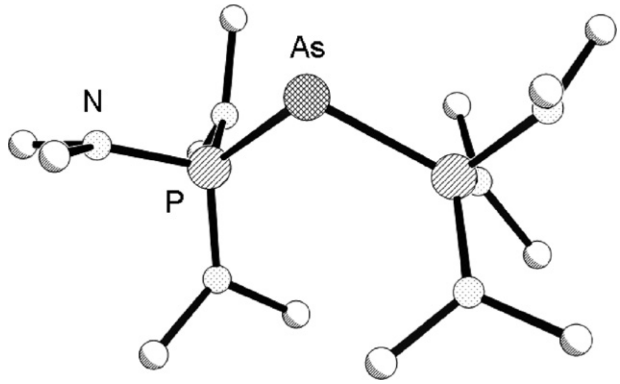


Fig. 44. Molecular structure of the acyclic cation $[As(PNMe_3)_2]$ **139** (IDUQON).

3.2. Reactivity

When the acyclic As^I compound **139** is treated with a large excess of the Schwartz reagent ($Cp_2Zr(H)Cl$) the triaminophosphine ligands are cleaved and oxidized to produce $ClP(NMe_2)_3^+$ cations and the arsenic center is reduced to As^{-III} and trapped in a Zr_4H_4 ring **140** (Eq. (64)) in a manner analogous that described above for the phosphorus congener [52,53]. A complication in the synthesis is the unexpected production of the P analogue during the reaction; thus the product crystallizes as the tetraphenylborate salt containing a mixture of P and As atoms at the center of the Zr_4H_4 ring.

In a related manner, the oxidative cleavage of the stabilizing phosphine ligands from cyclic As^I compounds can be effected through the reaction of salts containing such cations with either atmospheric oxygen or oxidizing agents such as Me_3NO (Eq. (65)). In the case of the iodide salt of **129**, the oxidative cleavage process appears to liberate arsinidine-like "As–I" fragments that cyclize into six-membered rings (presumably consistent with Baudler's observations of transient P_6X_6 species [148,149]) that are capped by two additional iodide anions to produce heterocubane dianions of the form $As_6I_8^{2-}$ **141** as depicted in Fig. 45 [145]:

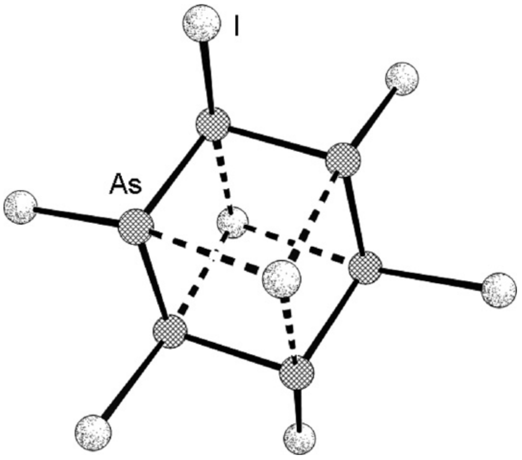
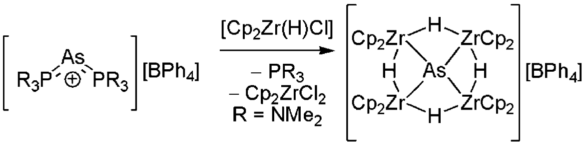
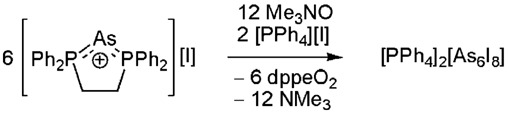


Fig. 45. Molecular structure of the dianion $[As_6I_8]$ **141** (IBUGUI).

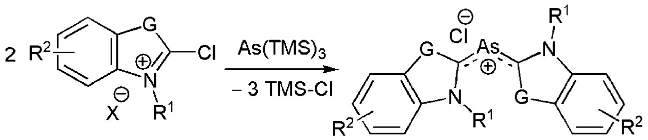


139$[BPh_4]$ **140**$[BPh_4]$ (64)



129[I] $[PPh_4]_2$**141** (65)

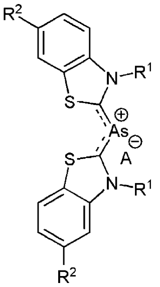
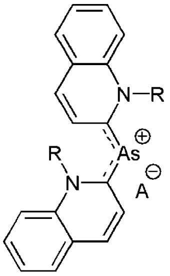
The arsenic analogues of phosphamethine cyanines, which are known as arsamethine cyanines, may also be considered as carbene-stabilized As^I centers, can be isolated from the reaction of 2-chlorobenzothiazolium and tris(trimethylsily)arsine, driven by the loss of TMS-Cl (Eq. (66)) [61]. While the arsenic analogues also exhibit transitions in the visible region and the pertinent data is summarized below in Table 14, no examples have been characterized by X-ray crystallography to date and the chemistry of such compounds has not been investigated in detail.



142[Cl] G = S
143[Cl] G = $(CH)_2$

(66)

Table 14
Spectrophotometric data for carbon-based-donor-stabilized As^I cations $[L_2As][A]$

	R^1	R^2	A	λ_{max}	ε (10^{-4})	Ref.
 **142**	Me	H	BF_4^-	489	3.63	[61]
	Et	H	BF_4^-	491	3.80	[61]
	Et	OMe	BF_4^-	500	2.83	[61]
 **143**	Me		BF_4^-	639	3.50	[61]
	Et		BF_4^-	642	3.80	[61]

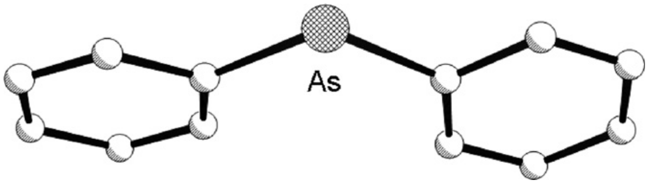


Fig. 46. Molecular structure of [$AsPh_2$] **144** (CEVMUL).

As with phosphorus, some of the most well-known As^I-containing species are the diorgano arsenide salts that contain anions of the type R_2As^- (**144** R = Ph; **145** R = H). Such species are useful reagents for the generation of other organoarsenic compounds through nucleophilic substitution or metathesis reactions [150–152]. In comparison with the phosphorus congeners there are considerably fewer examples of stable arsenides that do not feature coordination of the arsenic atom to the counter cations. One family of such salts are those that contain the diphenylarsenide anion, Ph_2As^- **144**. These anionic As^I compounds may be generated through the reaction of diphenylarsine with ^{n}BuLi. Coordination of the lithium cation with oxygen donors (crown ethers, dioxanes) allows for the collection of crystals suitable for examination by X-ray crystallography [89,153]. The molecular structure of the anion from one such salt is depicted in Fig. 46 and selected metrical parameters are listed in Table 16. The As–C bond distances are all greater than 1.93 Å and are thus consistent with typical single As–Ar distances found in the CSD and are certainly much larger than the distances reported for As=C double bonds (ca. 1.80 Å or smaller).

Cyclic, anionic As^I compounds of the type [$(RP)_nAs^-$] (**146** R = ^{t}Bu, $n = 3$; **147** R = Ad, $n = 3$) are accessible through the reaction of $As(NMe_2)_3$ with lithium salts of primary phosphines (Eq. (67)) [154,155]:

$$As(NMe_2)_3 \xrightarrow[\text{tmeda}]{[Li][RPH]} [(tmeda)Li][(RP)_nAs] \tag{67}$$

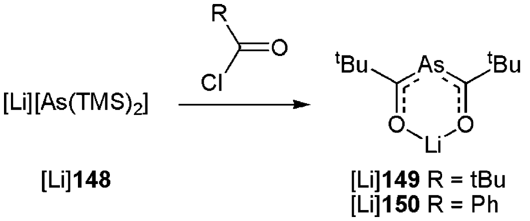
$$[(tmeda)Li]\mathbf{146}\,R={}^tBu, n = 3,\ [(tmeda)Li]\mathbf{147}\,R = Ad, n = 3$$

Table 15

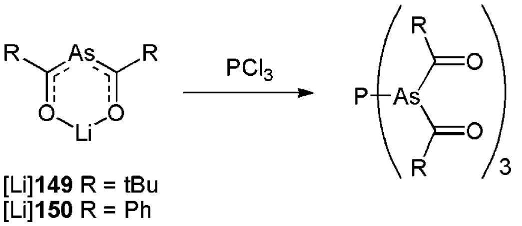
^{31}P NMR data of phosphine-stabilized As^I compounds

As^I compound	A	δP^{III}	Ref.
129	Cl^-	63	[37]
129	I^-	61	[43]
129	$SnCl_6^{2-}$	62	[144]
129	$(dppe)As_2I_7^-$	60 [cation], −14 [anion]	[145]
130	$SnCl_6^{2-}$	76	[37]
131	Cl^-	75, 63	[37]
131	$SnCl_6^{2-}$	74, 64	[37]
132	$SnCl_6^{2-}$	68	[37]
133	$SnCl_6^{2-}$	55	[37]
134	Cl^-	29	[37]
135	$SnCl_6^{2-}$	18	[35]
136	$SnCl_6^{2-}$	24	[37]
139	BPh_4^-	89	[52,53]
146	$(tmeda)(thf)Li^+$	8(t), −74 (d)	[154]
147	$(tmeda)(thf)Li^+$	−12 (t), −90 (d)	[155]
153	N/A	−0.5	[104]
154	N/A	42	[107]
155	I^-	44, 34 [P^{III}], 71 [P^V]	[163]
156	N/A	33	[163]
160	N/A	17	[165]

Another class of anionic compounds that may be considered to contain As^I centers are the 2-arsadionates, which are isovalent with β-diketonate anions. These arsenic compounds are readily available from the reaction [Li][$AsTMS_2$] [Li]**148** and two equivalents of acid chloride, which results in the elimination of TMS-Cl and the desired salt (Eq. (68)) [156]. Compounds of this type have the ability to coordinate to transition metal complexes through either the arsenic center or the oxygen atoms [157–159]. Coordination is not limited to the d-block, complexes with both the s- and p-blocks have also been reported [160]. For example, reaction of three equivalents of [Li]**149** or [Li]**150** with phosphorus (III) chloride results in loss of lithium chloride and formation of tris(diacylarsinido)phosphines (Eq. (69)) [161]. 2-Arsadionate anions invariably exhibit planar O–C–As–C–O fragments, as illustrated in Fig. 47, which suggest that such molecules contain an As^{III} center. While the planar structure is likely a consequence of π-delocalization, it should be noted that As–C bond distances in such complexes are relatively long and the structures are often constrained to be planar by the chelation of the anion to a single metal center. Regardless, such compounds have been included in this survey because the structures of the main group and transition complexes obtained through the formation of As–E bonds have pyramidal environments about the As atom and are thus more consistent with those obtained from arsenide anions than those obtained from normal arsaalkene ligands:



(68)



(69)

In contrast to the phosphorus congener, the As^I cation **135** cannot be deprotonated to produce the corresponding neutral species. However, in an analogous manner to the phosphorus derivatives, bis(pyridyl)arsenides **151** react with group 13 compounds to give zwitterions, such as when complexed with $AlMe_2$ cations **152** [113]. Most of the neutral As^I compounds that have been reported are generated through the reaction of arsenic trihalides with lithium diphosphinomethanide salts in a man-

Table 16
Structurally characterized As^I compounds [L_2As][A]

L	A	As–L bonds (Å)	L–As–L angles (°)	CSD refcode	Ref.
129	$SnCl_6^{-2}$	2.2508(12), 2.2518(12)	85.63(4)	EBENAB	[144,145]
129	$(dppe)As_2I_7^-$	2.2559(17), 2.2542(18)	85.44(6)	BUHET	[145]
132	$(HCPPh_2OSnCl_5)_2^-$	2.254(2), 2.252(1)	84.57(5)	WUFYUR	[37]
133	$SnCl_6^{2-}$	2.2517(8), 2.2468(9)	87.37(2)	WUFYOL	[37]
135	$SnCl_6^{2-}$	2.250(1), 2.244(1)	93.0(1)	WAJGOD	[35]
138	$SnCl_5(thf)^-$ [$As_2I_8^{2-}$]	1.862(5) [1.879(5)], 2.095(4) [2.076(4)]	154.2(2)	GEHCOM [GEHCIG]	[147]
139	BPh_4^-	2.266(2), 2.236(2)	103.26(6)	IDUQON	[53]
144	$(12\text{-crown-}4)_2Li^+$	1.972(5)	108.6(2)	CEVMUL	[89]
144	EtO_2Li^+	1.935(5), 1.955(6)	102.4(2)	DUWZAW	[153]
144	$(1,4\text{-dioxane})_3Li^+$	1.959(6), 1.962(6)	102.2(2)	DUWYUP	[153]
145	$(dme)_2Li^+$			CEJQEN	[166]
146	$(tmeda)(thf)Li^+$	2.333(4), 2.324(3)	85.1(1)	HOBDIL	[154]
147	$(tmeda)(thf)Li^+$	2.356(1), 2.350(1)	83.67(4)	LIRZER	[155]
149	$(dme)_{0.5}Li^+$	1.886(7) [1.887(7)], 1.945(6) [1.926(5)]	98.4(3) [98.9(3)]	TOGQOV	[156]
149	$(Et_2O)Li^+$	1.947(5), 1.901(5), 1.934(8)	100.2(2)	TOGQUB	[156]
150	$(dme)Li^+$	1.946(10), 1.869(10), 1.955(11)	98.1(4), 102.4(4)	HUXBIL	[160]
152	N/A	1.919(7), 1.893(8), 2.2710(7)	N/A	ZAFNUP	[113]
153	N/A	[2.2729(7)] 2.2692(7), [2.2681(7)]	69.90(2) [69.45(2)]	TUJFEJ	[104,107]
154	N/A	2.301(1), 2.256(1)	N/A	YETCAB	[107,162]
155	I^-	2.253(2), 2.260(2)	97.06(7)	NATQII	[163]
157	N/A	1.899(3) [As–NHC], 1.845(2) [As–Ph]	97.3(1)	RUNWEC	[120]
158	N/A	1.902(7) [As–NHC], 1.976(7) [As–CsFs]	99.8(3)	RUNWOM	[120]
160	N/A	2.2190(17) [As–PMe_3], 1.969(6) [As–Arl	101.53(17)	RAJRAW	[165]

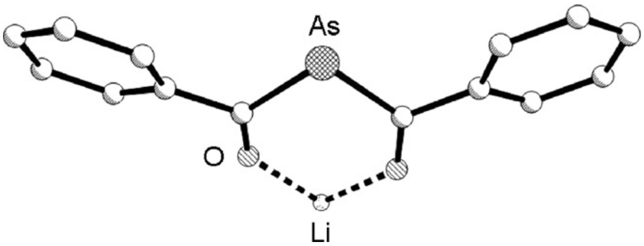
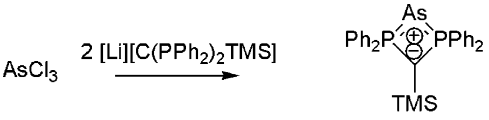


Fig. 47. Molecular structure of the a portion of the salt [Li]**150** (HUXBIL) showing the nearly planar O–C–As–C–O fragment in such anions and the *O*,*O*′-chelation of Li.

ner similar to that observed for phosphorus. For example, the reaction of arsenic(III) chloride with [Li][$C(PR_2)_2TMS$], where R = Ph results in the formation of the four-membered ring compound **153** and involves the oxidation of the additional equivalent of the carbanion (Eq. (70)) [104] (Fig. 48). In contrast, when R = Me, the eight-membered ring is not observed. Instead four arsenic centers with an average oxidation state of 0.5 are trapped between two carbanions (Fig. 49) and oxidation of the extra carbanion (Eq. (71)) [107,162]. The treatment of arsenic(III) iodide with either 2 or 3 equiv. of the lithium amide [Li][$N(PPh_2)_2$] results in the formation of either a seven-membered As^I cation with an iodide anion (Eq. (72)) (Fig. 50) or an eight-membered ring with two As^I centers (Eq. (73)) [163]. The application of heat drives the reduction to elemental arsenic and further oxidation of the remaining amides.



153 (70)

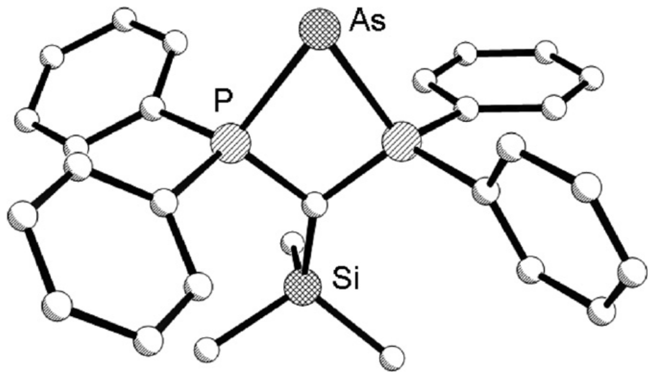


Fig. 48. Molecular structure of the neutral four-membered ring As^I compound **153** (TUJFEJ).

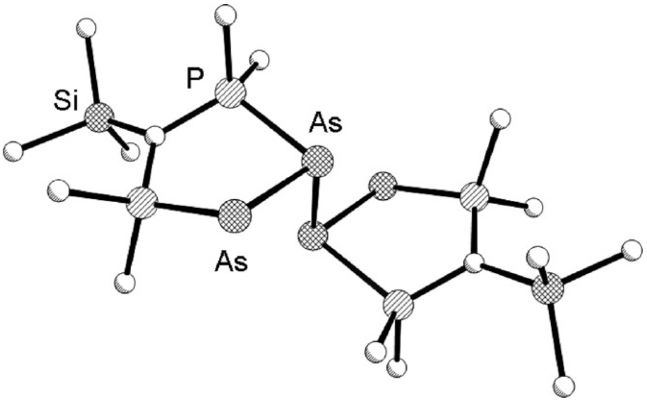


Fig. 49. Molecular structure of the As^I product **154** (YETCAB).

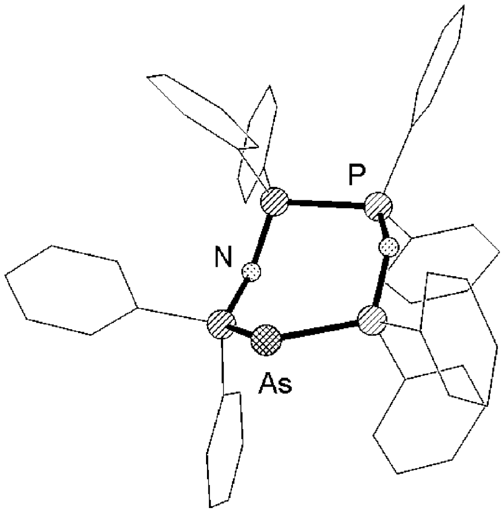


Fig. 50. Molecular structure of the cation **155** from the iodide salt (NATQII).

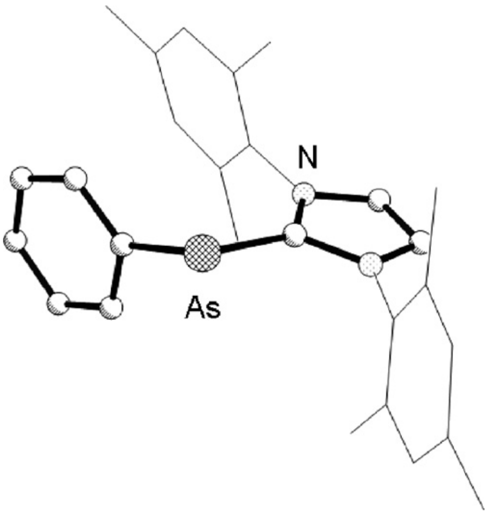
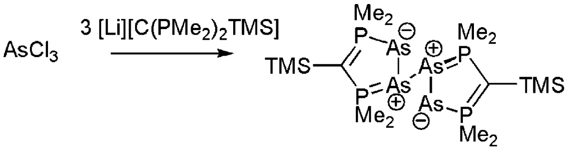
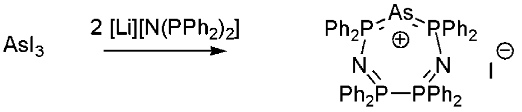


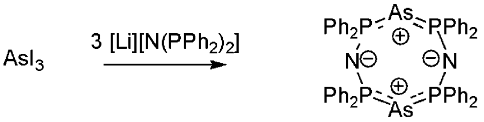
Fig. 51. Molecular structure of the neutral As^{I} compound **157** (RUNWEC).



154 (71)



155[I] (72)



156 (73)

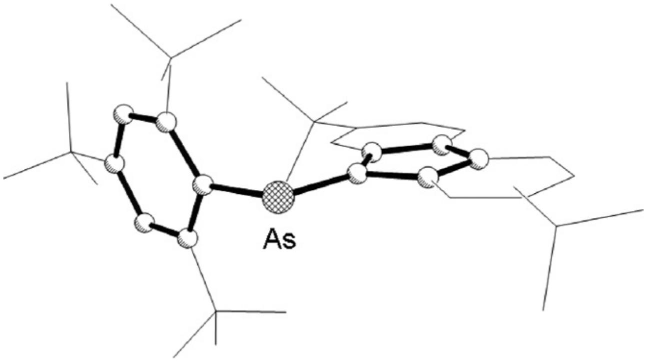


Fig. 52. Molecular structure of Fl*=As–Mes* **159** (RUQGUF), which features an As^{III} center involved in an arsenic–carbon double bond.

In a manner similar to that which is observed for cyclopolyphosphines, strong nucleophiles such as *N*-heterocyclic carbenes are able to break apart cyclic-polyarsines of the type (R–As)$_x$, to give neutral stabilized As^{I} centers (**157** R = Ph; **158** R = C_6F_5) [120]. The structures of the molecules produced using this method exhibit As–C distances of roughly 1.90 Å that fall in the range of single As–C bonds. Furthermore, as exemplified by Fig. 51, the twisting of substituents from the C–As–C plane reduces the possibility of As–C multiple bonding. For comparative purposes, the structure of the arsaalkene Fl*=As–Mes* **159** [164] is presented in Fig. 52; this molecule exhibits a carbenic fragment that is coplanar with the C–As–C unit and features an As–C distance of 1.794(11) Å, which is consistent with a double bond between the elements and the presence of an As^{III} center. A rationale for the differences observed between these seemingly similar compounds is presented in Section 5 of this review.

Reduction of sterically-demanding arylarsine dichlorides (aryl = 2,6-bis(2,4,6-triisopropylphenyl)phenyl) by zinc in the presence of PMe_3 stabilizes the arsinidene generated [165]. The structure of **160** is shown in Fig. 53 and is reminiscent of the phosphorus analogue described above. These As–P bonds are anticipated to undergo arsa-Wittig reactions in a manner similar to the phosphorus analogues, although has only so far been shown by indirect evidence. The loss of the PMe_3 ligand from the molecule results in the formation of the corresponding diarsene R–As=As–R, as one would expect for an arsinidene bearing such a large R substituent.

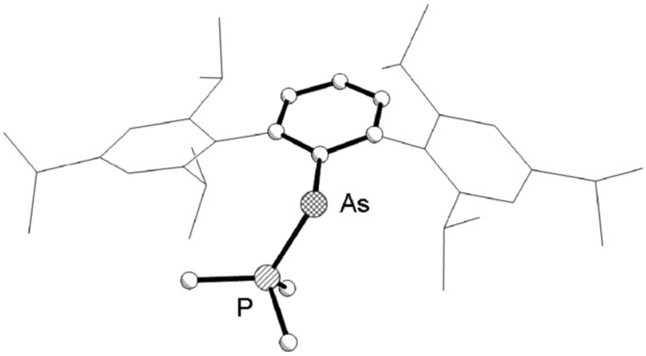


Fig. 53. Molecular structure of the arsinidene–phosphine adduct **160** (RAJRAW).

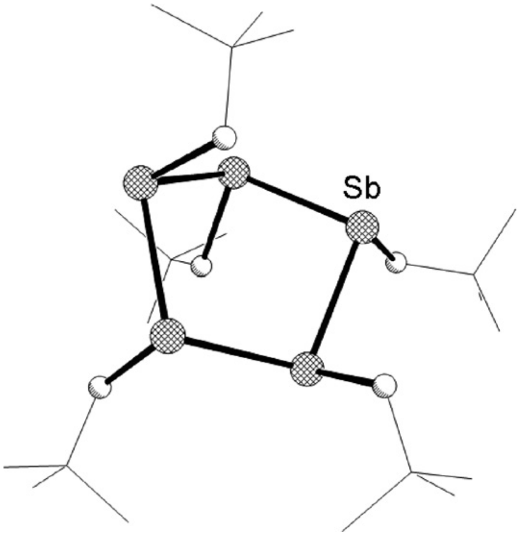


Fig. 54. Molecular structure of the cyclic-polystibine $(SbNp)_5$ (EMOHET).

4. Antimony and bismuth

There are significantly fewer examples of organo-element compounds that contain antimony or bismuth in Pn^I environments and, because the structural and chemical properties of these compounds is similar in many cases, the compounds containing Sb and Bi are treated together in this section.

As with the lighter congeners, whereas the free stibinidenes (R–Sb) or bismuthinidenes (R–Bi) are unstable, the cyclic-polypnictines formally derived from such fragments are well-known for both elements [167,168]. Examples of a five-membered ring composed of R–Sb fragments and a four-membered ring derivative containing bismuth are pictured in Figs. 54 and 55, respectively. In every such case, the geometry about each pnictogen atom is pyramidal and thus the molecules are best described as containing Pn^{III} centers.

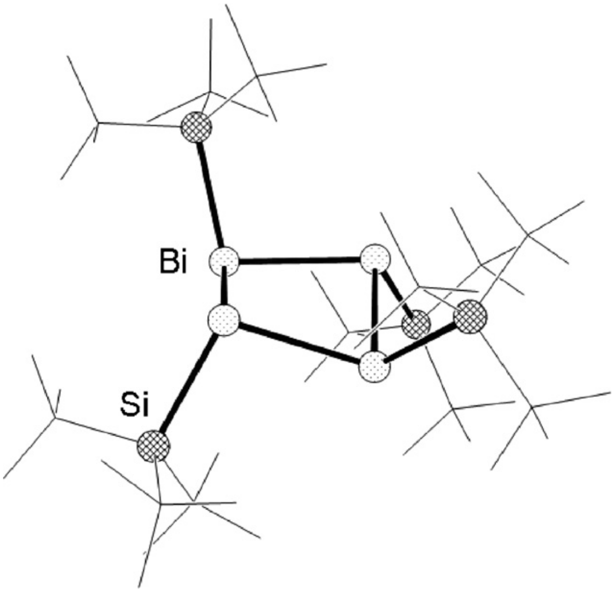


Fig. 55. Molecular structure of the cyclic-polybismuthine $(Bi(Si(^tBu_3))_4$ (OGOCOC).

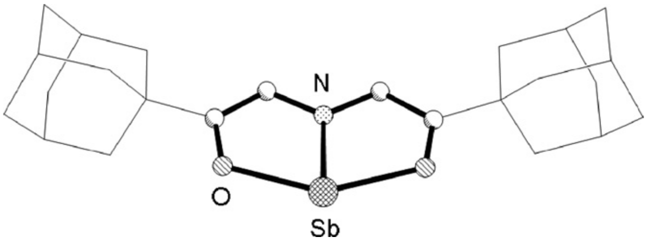


Fig. 56. Molecular structure of (Ad-DKA)Sb **161** (FEDMIK).

As observed for the lighter group 15 elements, the only stable monomeric “stibinidenes” that have been observed both contain 10-Sb-3 [25] centers supported by either adamantyl- or *tertiary*-butyl substituted DKA ligands. The molecular structure of the molecule containing the Ad-DKA ligand **161** is depicted in Fig. 56 and exhibits the necessary planar, ψ-tbp geometry indicative of the Sb^I center.

In contrast to the chemistry of some of the lighter DKA-substituted analogues, oxidation of the Sb^I center with halogens results in the formation of an umbrella-shaped environment about the antimony. The structural features are thus consistent with the presence of a single “lone-pair” of electrons on antimony and justify its description as a Sb^{III} center, as illustrated in Fig. 57 by the product **162** derived from the oxidation of $(^tBu\text{-}DKA)Sb$ **163** with I_2 [28,169].

In contrast to the observations of the phosphorus DKA analogues, **163** retains the planar bicyclo-core in every structurally characterized example in which it is used as a ligand (either terminal or bridging) for transition metal complexes [169–171].

Unlike all of the lighter pnictogen analogues, there are no examples of cationic or neutral antimony (I) or bismuth (I) compounds. The dearth of such species is often a consequence of the tendency of antimony and bismuth compounds to be completely reduced to Sb^0 and Bi^0 under most of the reduction conditions that have been used to synthesize the lighter congeners. For example, the syntheses employing lithium amides used to generate the neutral As^I zwitterions described above result in the deposition of either elemental Sb or Bi [163]. Conversely, the synthetic approaches involving the reaction of SbX_3 or BiX_3

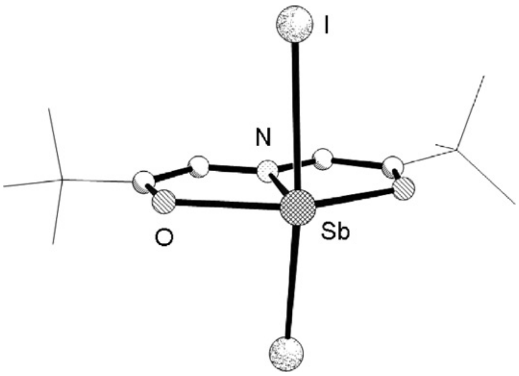


Fig. 57. Molecular structure of the I_2 oxidation product of $(^tBu\text{-}DKA)Sb$ **162** (JIMHAO).

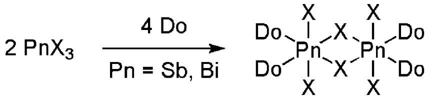
Table 17
Structurally characterized Sb^I compounds $[M][L_2Sb]$

$[L_2Sb]$	M	Sb–L bonds (Å)	L–Sb–L angles (°)	CSD refcode	Ref.
164	$(12\text{-crown-4})2Li^+$	2.154(9), 2.168(13), 2.157(10), 2.173(12), 2.129(12), 2.157(13)	96.8(4), 97.6(4), 102.4(4)	DUWZEA	[153]
165	$(12\text{-crown-4})2Li^+$	2.166(11), 2.190(12)	92.7(4)	DUWZIE	[153]
166	$(pmdeta)Na^+$	2.720(8), 2.776(2), 2.741(8), 2.762(2)	91.4(2), 89.80(7)	BALMAD	[179]
166	$(pmdeta)_2K^+$	2.7643(9), 2.7669(7)	86.23(3)	WOMFAF	[180]
166	$(tmeda)_2Li^+$	2.7706(5), 2.7678(5)	89.369(11)	LALSAT	[181]
167	$(dme)L^+$	2.532(1)	94.2(1)	BOJDEJ	[182]
171	$(tmeda)(Me_2NH)Na^+$	2.489(3), 2.541(3)	99.7(1)	HOBDEH	[154]

Table 18
Structurally characterized Bi^I compounds $[M][L_2Bi]$

$[L_2Bi]$	M	Bi–L bonds (Å)	L–Bi–L angles (°)	CSD refcode	Ref.
168	$(dme)Li^+$	2.633(14)	91.8(4)	CEBFOE	[183]
169	$(THF)_3Na^+$	2.726(10), 2.707(8)	122.3(2)	OGOCUI	[184]
170	$(THF)_4Li^+$	2.668(5), 2.672(4)	112.2(1)	OGOCI	[184]

with donors such as phosphines or *N*-heterocyclic carbenes do not result in the formation Pn^I species but instead generate donor–acceptor complexes that retain the Pn^{III} centers (Eq. (71) illustrates a typical result) [172–178]:



(74)

Anionic Sb^I and Bi^I compounds are known, although there are relatively few examples in comparison to those of phosphorus and arsenic. The compounds containing dicoordinate Sb or Bi atoms that are not ligated to metals and that have been structurally characterized are listed in Tables 17 and 18, respectively. Diphenylstibinide, Ph_2Sb^- **164**, depicted in Fig. 58, can be generated by the treatment of diphenylstibine with ^{n}BuLi, in a manner similar to that which is observed for the lighter group 15 elements [153].

The reduction of $SbPh_3$ with lithium yields the lithium salt of an anion that consists of a Sb^I center ligated by two Ph_2Sb moieties (Eq. (72)) [153], the structure of which is presented in Fig. 59. The ^{t}Bu analogue $(Sb^tBu_2)_2Sb^-$ **166** is obtained from the reduction of $(^tBuSb)_4$ with excess potassium [179,180] and the Li and Na analogues are prepared analogously (Eq. (73)) [179,181]. The reaction of $Sb(TMS)_3$ with MeLi yields a salt containing the anion $(TMS)_2Sb^-$ **167** in which the lithium cation is coordinated by dme molecules (Eq. (74)) [182]. The bismuth analogue $(TMS)_2Bi^-$ **168**, is accessible through the related procedure [183], and exhibits contacts with the counter cation, as illustrated in Fig. 60, as does the compound containing the $(^tBu_3Si)Bi^-$ anion **169** [184]. The only structurally characterized example of such an anion for Bi in which there are no obvious cation–anion contacts is found in the lithium salt of the extremely bulky anion $((TMS)_3Si)_2Bi^-$ **170**, which is drawn in Fig. 61 [184]:

$$\mathrm{SbPh_3}\xrightarrow[\text{tmeda}]{\text{Li}}\underset{[(\text{tmeda})\text{Li}]\mathbf{165}}{[(\text{tmeda})\text{Li}][(\text{Ph}_2\text{Sb})_2\text{Sb}]} \tag{75}$$

$$(^t\mathrm{BuSb})_4\xrightarrow[\text{L}]{\text{M}}\underset{[(\text{L})\text{M}]\mathbf{166}}{[(\text{L})\text{M}][(^t\text{Bu}_2\text{Sb})_2\text{Sb}]} \tag{76}$$

$$\mathrm{Sb(TMS)_3}\xrightarrow[\text{dme}]{\text{MeLi}}\underset{[(\text{dme})\text{Li}]\mathbf{167}}{[(\text{dme})\text{Li}][(\text{TMS})_2\text{Sb}]} \tag{77}$$

Finally, it is also worth noting that the only cyclic compound that contains either an Sb^I or Bi^I center is the anion $Sb(PCy)_4^-$ **171**, which crystallizes as a bis-Na-bridged dimer, as shown in Fig. 62. As with its arsenic analogue mentioned above, it is also prepared through the addition of primary phosphido alkali metal complexes to $Sb(NMe_2)_3$ [154,155].

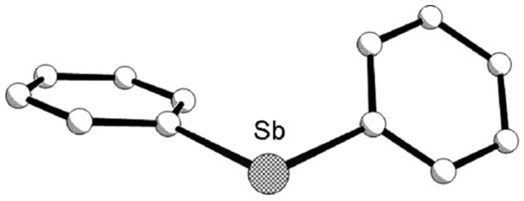


Fig. 58. Molecular structure of the anion $[SbPh_2]$ **164** (DUWZEA).

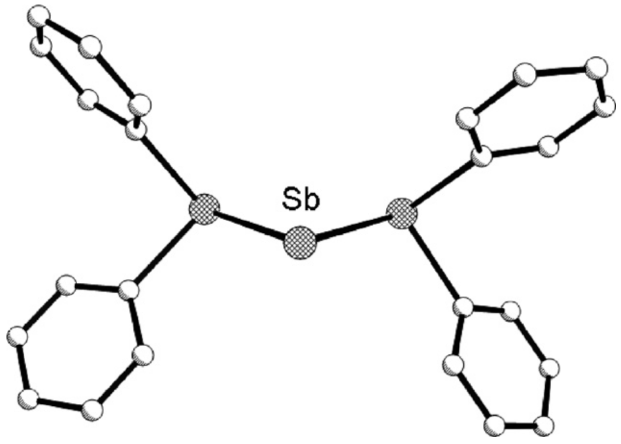


Fig. 59. Molecular structure of the anion $[(SbPh_2)_2Sb]$ **165** (DUWZIE).

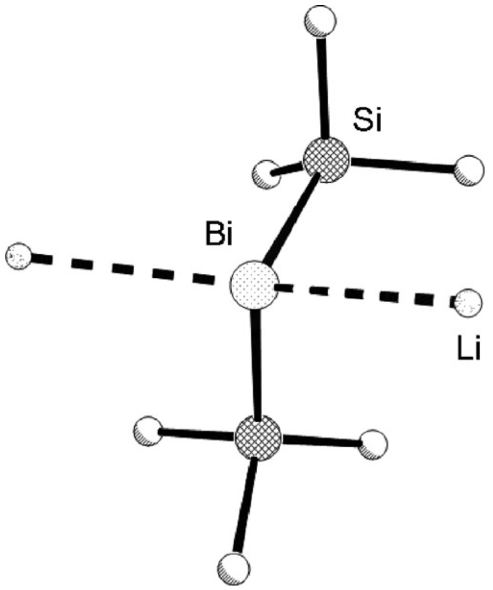


Fig. 60. Molecular structure of the anion $[(TMS)_2Bi]$ **168** (CEBFOE), illustrating the contacts between Bi and the nearest Li atoms.

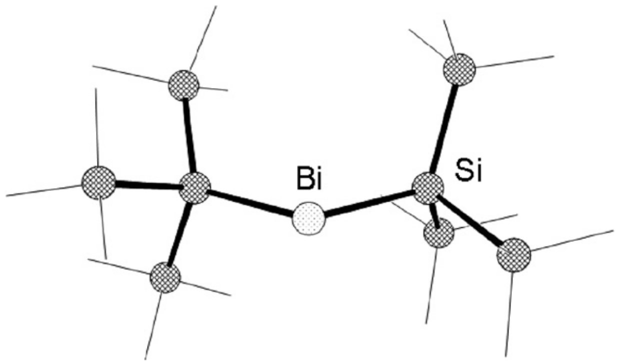


Fig. 61. Molecular structure of the anion $[(Si(TMS)_3)_2Bi]$ **170** (OGOCIW).

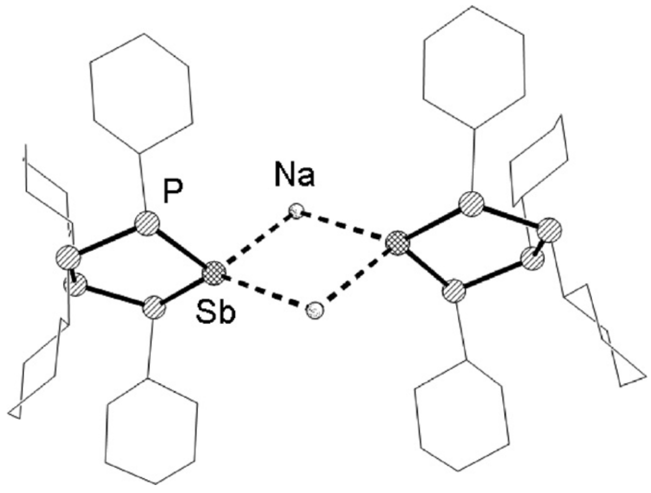


Fig. 62. Molecular structure of the salt [Na] **171** (HOBDEH), illustrating the Na-bridged dimeric nature of the salt.

5. Electronic structure and bonding considerations

While there have not been many computational investigations of stable molecules containing pnictogen atoms in unusually low oxidation states, the studies that have been reported provide insight into the nature of the bonding in such molecules and into the factors that render some of the molecules described above relatively stable.

5.1. Hypervalent pnictinidene species

In regard to stabilized pnictinidene molecules of the form (R–DKA)Pn, Arduengo and Stewart have used MP2/DZP calculations to determine that the planar hypervalent 10-P-3 arrangement is 58 kJ mol^{-1} more favorable than the pyramidal 8-P-3 for the H-DKA ligand [27]. The calculated metrical parameters of the model system were in good agreement with the values obtained experimentally only when the computational method accounted for electron-correlation. It should be noted that saturated analogues of the DKA ligand always produce pyramidal 8-P-3 molecules and it appears that the geometrical and electronic constraints of a delocalized π-system are necessary to stabilize the 10-P-3 arrangement. It is also noteworthy that the transition metal complexes of arsenic and antimony (R–DKA)Pn molecules exhibit metrical parameters that are consistent with the presence of two “lone pairs” of electrons on the pnictogen center. Other aspects concerning the nature of the bonding in this unique ligand system have been described in detail in the review by Arduengo and Stewart and will not be repeated herein.

5.2. Phosphine-stabilized Pn^I cations

As indicated in the Introduction, different Lewis-type drawings, such as those drawn in Fig. 63, have been used to depict cations having the composition $(R_3P)_2Pn^+$. The Pn^V drawing would predict a cation structure exhibiting a linear P–Pn–P arrangement and short P–Pn bonds. While such an arrangement is typical for the cations in the so-called “PNP” (bisphosphoranyliminim) salts, which contain $(R_3P)_2N^+$ cations, linear arrangements have never been observed for any of the heavier analogues. In contrast, both the Pn^{III} and Pn^I drawings suggest a cation structure that contains a bent P–Pn–P fragment. Both of these bent structures would also be predicted to exhibit shorter than single bonds because of delocalized π-bonding in the Pn^{III} case and because of coulombic attraction in the bis-ylidic Pn^I structure. Ultimately, the primary difference between the Pn^{III} and Pn^I drawings stems from the “location” of one pair of electrons and, given the deficiencies of such drawings, the true nature

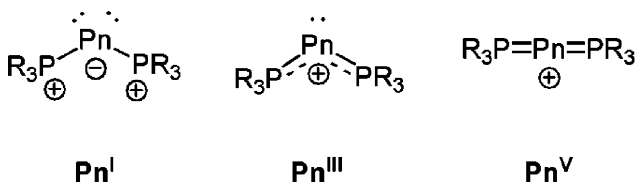


Fig. 63. Possible Lewis-type structures for cations of the form $(R_3P)_2Pn^+$.

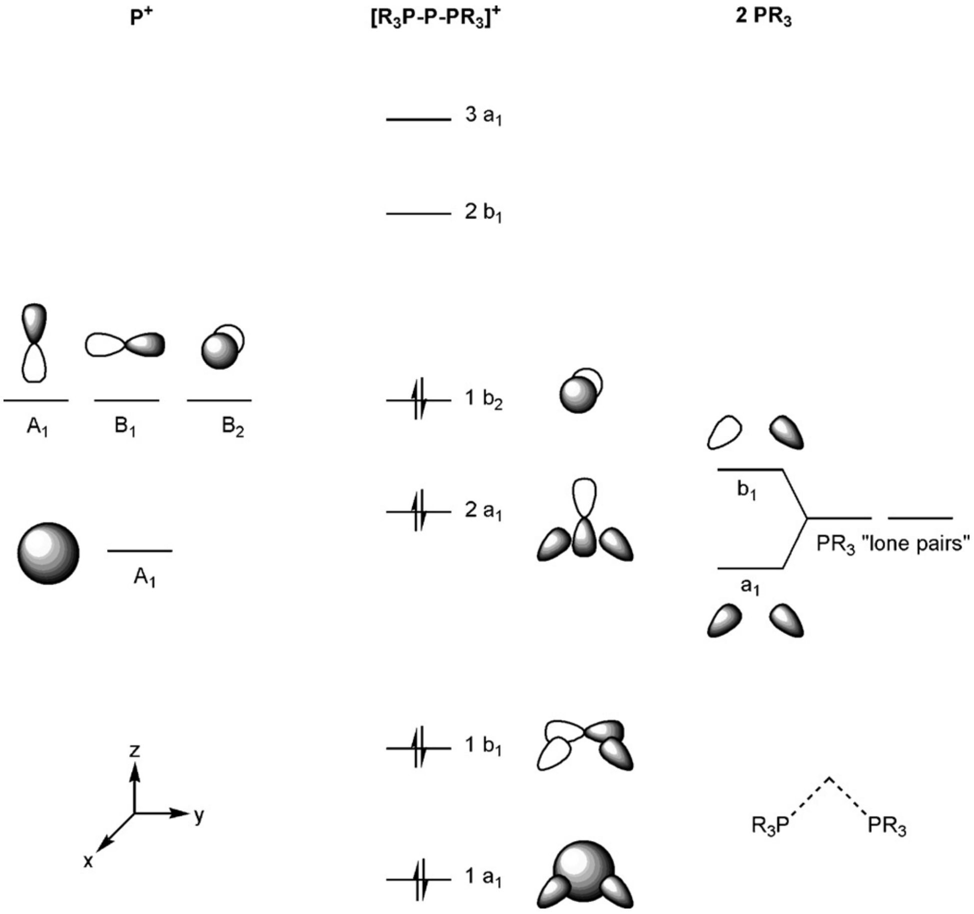


Fig. 64. Simplified qualitative molecular orbital diagram for an idealized triphosphenium cation having C_{2v} symmetry using only the symmetry-adapted linear combinations of “lone pair” orbitals on the PR_3 ligands.

of the electronic structure of such molecules is best provided by more sophisticated models. In this light, a simplified molecular orbital (MO) diagram for a triphosphenium cation is presented in Fig. 64.

The bonding molecular orbitals derived from the combination of the C_{2v} symmetry-adapted linear combinations (SALC) of “lone pair” orbitals on the phosphine ligands and the atomic orbitals on the P^+ center are shown schematically in Fig. 64. The MOs derived from such a scheme are virtually identical in appearance and construction to those that one would obtain in an MO diagram for water. Thus, in the absence of any other perturbations, one would suggest that the Pn^{I}-type description of the electronic structure with two “lone pairs” of electrons on the central atom should be the more suitable. The frontier orbitals associated with a phosphine ligand are, however, not limited to the “lone pair” (the highest occupied molecular orbital, HOMO) and other perturbations must be taken into account. In particular, one SALC derived from the lowest unoccupied molecular orbital (LUMO) of each phosphine ligand is of appropriate symmetry to interact with the b_2 orbital (i.e. the $3p_x$ orbital on P) to allow for a P-phosphine back-bonding interaction (such interactions are also described by the term “hypercongugation”), as illustrated in Fig. 65. If this back-bonding interaction is sufficient to turn the “lone pair” into a delocalized π-bond, then the Pn^{III} description would appear to be more appropriate.

Density functional theory (DFT) calculations on some simple model compounds have been reported and provide more quantitative insight into the true electronic structure of triphosphenium cations [43,44]. While calculations have been also been performed on more realistic models, the results obtained for the model compounds $(H_3P)_2P^+$ and $(H_3N)_2P^+$ are adequate for the purposes of this review. The energies and appearance of selected frontier orbitals obtained from DFT calculations at the B3PW91/6-311+G(d) level of theory for $(H_3P)_2P^+$ and $(H_3N)_2P^+$ are presented in Figs. 66 and 67, respectively [43].

The symmetries and appearances of the occupied orbitals for both models are consistent with those predicted using the qualitative MO diagram in Fig. 64, with the HOMO-1 orbital being a “lone pair” in the molecular plane and the HOMO being a “lone pair” largely composed of the $3p_x$ orbital on the dicoordinate

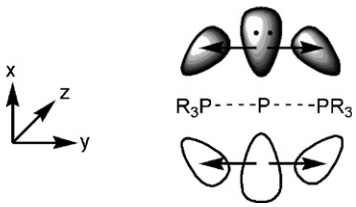


Fig. 65. Back-bonding interaction between the filled $3p_x$ orbital on P and the b_2 SALC obtained from the anti-bonding orbitals on the phosphine ligands.

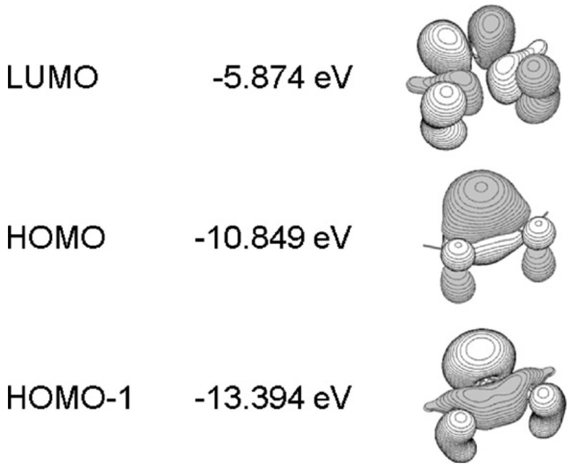


Fig. 66. Frontier orbitals for $(H_3P)_2P^+$ [43].

phosphorus atom. There are, however, some instructive differences between the two models. While the energies of the LUMOs in each case are similar, the energies of the HOMO in $(H_3P)_2P^+$ is significantly lower than that of $(H_3N)_2P^+$ and whereas the HOMO on $(H_3N)_2P^+$ contains an essentially undistorted $3p_x$ orbital on the phosphorus atom, the corresponding lobe in the phosphine-substituted model is obviously distorted toward the phosphine ligands. Both of these features are consistent with the presence of significant back-bonding in the case of $(H_3P)_2P^+$ that is largely absent in $(H_3N)_2P^+$, as one would expect on the basis of the well-known transition metal chemistry of amine and phosphine ligands. It should be noted that the presence of back-bonding in $(H_3P)_2P^+$ is also reflected by the smaller electron population of the $3p_x$ ($1.71e^-$) in comparison to the population of the corresponding $3p_x$ orbital ($1.93e^-$) in $(H_3N)_2P^+$, which is close to the value of $2e^-$ that one would expect for a "lone pair". Other calculations reveal that if the back-bonding orbital interactions are blocked, the optimized P–P bond distances are more consistent with those of single bonds [33]. Overall, the appearance of the orbitals and the largely localized b_2 "lone-pair" of electrons on the dicoordinate phosphorus atoms suggest that the P^I description of triphosphenium cations is probably the most appropriate; this interpretation is consistent with the observed oxidation and coordination chemistry of some of the examples described in Section 2. However, the significant stabilization of the HOMO attributable to the presence of phosphorus-ligand back-bonding indicates that the P^{III}-type model provides insight into the unusual stability of such cations. In this vein, it is noteworthy that no stable cations of the type $(R_3N)_2P^+$ have ever been reported.

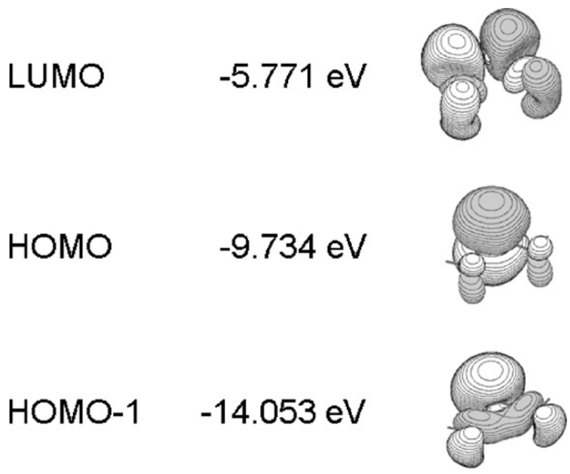


Fig. 67. Frontier orbitals for $(H_3N)_2P^+$ [43].

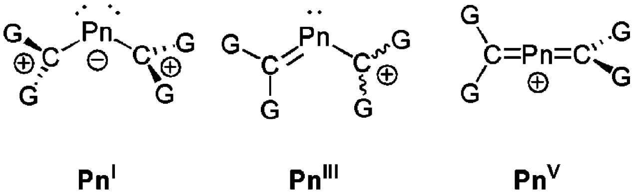


Fig. 68. Possible Lewis-type structures for cations of the form $[(G_2C)_2Pn^+]$, where G may represent one of many different types of substituent.

5.3. Carbene-stabilized Pn^I cations

The potential ambiguities in the geometrical features and electronic structures predicted for cations of the general forms $(G_2C)_2Pn^+$ (G = e.g. R, ChR, PnR_2, X, etc.) in Fig. 68 are similar to those of the triphosphenium cations outlined in the preceding section. Structurally characterized molecules containing the linear, allene-like arrangement suggested by the Pn^V drawing are rare for Pn = N and have never been observed for any of the heavier pnictogen atoms. All of the reported carbene-stabilized cations exhibit a significantly bent C–Pn–C arrangement consistent with either the Pn^I or Pn^{III} models. In the case of such ligands, however, there exist readily observable differences in the necessary alignment of the carbenic fragments in the different models. In particular, the Pn^{III} model requires at least one of the carbenic fragments to be coplanar with the C–Pn–C unit to allow for the formation of the multiple bond. If both carbene ligands are coplanar with the C–Pn–C fragment, the multiple bonding can be delocalized over both C–Pn bonds. In contrast, the Pn^I model requires no particular alignment of the carbene ligands with respect to the C–Pn–C plane and, while shortening of the C–Pn bond through coulombic interactions may occur, the model is consistent with the presence of C–Pn single bonds in such molecules.

The MO diagram in Fig. 64 is applicable (using the "lone pairs" on the carbenic carbon of the ligands in lieu of those on the phosphine ligands) to the understanding of the different geometries predicted by the Pn^{III} and Pn^I models. Again, in the absence of any interactions of the orbitals on the pnictogen atom with SALCs other than those derived from the ligand lone pair, one would anticipate the presence of two water-like "lone pairs" on the dicoordinate center. However, as in the case of the phosphine ligands described above, the chemically important frontier orbitals of carbene ligands are not limited to the "lone pair" orbitals and thus other interactions must be taken into account [65]. In particular, as illustrated schematically in Fig. 69, singlet carbene fragments have a lone pair in the molecular plane and a formally empty $2p_x$ orbital perpendicular to the

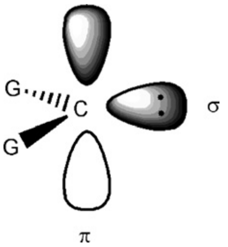


Fig. 69. Schematic frontier orbitals for an idealized singlet carbene ligand.

molecular plane. While the nature of the G substituent adjacent to the carbenic center can perturb the electron populations of these orbitals (e.g. if G is a π-donor group such as NR_2, the $2p_x$ orbital will be partially populated), the overall shape of the vacant orbital on C remains constant and it may be used to gain insight into the nature of the interactions between such ligands and the atoms to which they are bonded.

In the particular context of assessing the validity of Pn^{III} and Pn^{I} models for compounds of the type $(G_2C)_2Pn^+$, the presence of only a single, clearly oriented vacant orbital on the carbene ligand requires the carbene co-planar with the C–Pn–C fragment to maximize the overlap of the π-orbitals, as illustrated for Pn = P in Fig. 70. In the extreme situation where the G groups are not π-donors and carbene fragment is co-planar with C–Pn–C moiety, the back-bonding enabled by such overlap can be considered to result in the formation of a double bond between the carbon and pnictogen atoms; such a situation would result in a compound best described as containing a Pn^{III} center. Conversely, if the carbene ligand is twisted significantly from co-planarity with the C–Pn–C fragment, then the magnitude of the back-bonding interactions will be significantly smaller and the molecule is best described as containing a Pn^{I} center. The latter situation is more likely when the G groups on the carbene are π-donors, which partially populate the π orbital on the carbenic center and reduce its ability to act as a back-bond acceptor.

The simple model outlined above may be used to understand, for example, the difference in the C–P bond distances in molecules such as **110** and **111** that are described in Section 2.4. Each molecule has a short C–P bond to the C(Ph)O(LA) fragment (1.735(2) Å in **110**; 1.728(2) Å in **111**), which is coplanar with the C–P–C moiety, and a long C–P bond (1.838(2) Å in **110**; 1.844(2) Å in **111**) to the $C(NMe_2)_2$ fragment. Because this review is focused on molecules containing Pn^{I} centers, most of the molecules listed above contain carbene fragments in which both of the G groups are π-donors and thus limit the amount of Pn–carbene back-bonding.

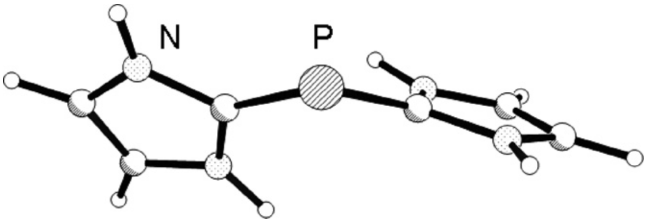


Fig. 71. Optimized structure in C_2 symmetry for the model compound **172**.

The only calculations on such molecules that have been reported to date were B3PW91 DFT calculations conducted on bis-NHC substituted phosphorus cations [57]. These calculations indicate that the perfectly coplanar (C_{2v}) arrangement of carbene ligands and the C–P–C framework are not minima on the potential energy surface even for the unsubstituted model compound $(NHC)_2P^+$ **172**. The optimized geometry of the most stable structure drawn in Fig. 71 shows that the carbene ligands are twisted by 36° from the C–P–C plane; the predicted C–P distance of 1.799 Å is only marginally shorter than those calculated for phosphorus bonded to an aromatic substituent. As such, the metrical parameters suggest that the P^{I} model is the most-representative of such molecules. However, despite the non-planarity of the molecule, several calculated features indicate that back-bonding is a significant feature in such species. In particular, the population of the $3p_x$ orbital on phosphorus ($1.49e^-$) is considerably less than 2 and the HOMO-2 orbital, pictured in Fig. 72, is consistent with a delocalized π-system in spite of the twisted arrangement of the NHC ligands.

In terms of experimental observations, it must be noted that the coordination and oxidation chemistry of the NHC-stabilized compounds described in Section 2.2 is consistent with the presence of two "lone pairs" on the di-coordinate phosphorus atom. This is consistent with the description of such compounds as containing Pn^{I} centers. However, it is necessary to recognize the important and real consequences of back-bonding in such molecules. In particular, the delocalized π-system in these molecules provides the color associated with these dye-like species, as illustrated by the UV–vis data in Table 6. Thus, as in the case with the phosphine stabilized species, while the Pn^{I} model provides the most accurate description of the molecules,

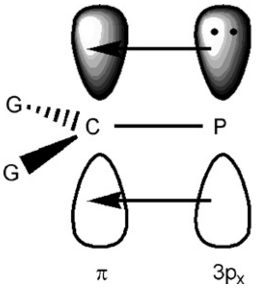


Fig. 70. Schematic representation of the possible back-bonding interaction between the vacant orbital (π) on a singlet carbene fragment and the filled $3p_x$ orbital on P.

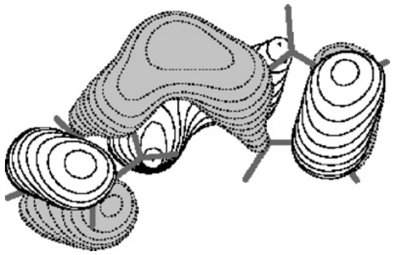
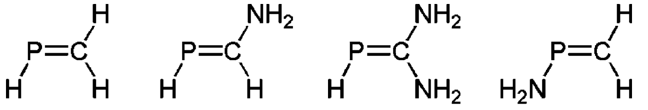


Fig. 72. Representation of the HOMO-2 orbital in **172**, showing the lobes derived from the interaction of the $3p_x$ orbital on P with the π-systems on the two NHC ligands.



173 **174** **175** **176**

Fig. 73. Model phosphaalkenes used for charge analysis calculations.

the importance of the contribution from the Pn^{III} model should not be neglected.

5.4. Neutral Pn^{I} compounds

Some models of the carbene-stabilized pnictinidenes of the type described in Section 2.4 have been investigated using computational methods. In particular, investigations of the charge distributions in “inverse electron density” phosphaalkenes have been performed on the model compounds drawn in Fig. 73 [68]. Whereas the Mulliken charges in the π-system on the P and C atoms in model **173** are almost equal ($qP = +0.039$, $qC = -0.039$), the presence of amino substituents on the carbon atom in models **174** and **175** result in increasingly negative charges on the P atom (**174**: $qP = -0.285$, $qC = +0.013$; **175**: $qP = -0.504$, $qC = +0.059$). In contrast the presence of an amino substituent on the phosphorus atom in model **176** results in a “normal electron density” phosphaalkene with a positive π-charge on the P atom (+0.094) and a negative π-charge on the carbon atom (−0.246). Because the changes in the overall charges observed are dominated in the changes in charges associated with the π-system described above, the results are in complete agreement with the back-bonding model described above for bis-carbene stabilized P^{I} cations.

A qualitative bonding model used to understand such molecules, while also related to the back-bonding model described in the previous section, is likewise worthy of mention [124]. Because of the isolobal relationship between carbenes and pnictinidenes, both types of molecule can exist in either singlet or triplet states. In theory, the combination of a singlet carbene with a singlet pnictinidene produces a donor–acceptor complex with a single bond between the carbon and pnictogen atoms, as illustrated in Fig. 74. Such complexes are analogous to Fisher-type transition metal carbene complexes. These complexes contain pnictogen atoms with two “lone pairs” of electrons and may thus be described as containing Pn^{I} centers; compound **92**, as depicted in Fig. 33, is an example of such a complex.

Alternatively, the theoretical combination of a triplet pnictinidene with a triplet carbene produces a pnictaaalkene with a double bond between pnictogen and carbon atoms, as depicted in Fig. 75. Such an arrangement is analogous to a Schrock-type transition metal carbene complex and predicts a Pn^{III} environment with the presence of only one “lone pair” of electrons on the pnictogen center. The fluorenylidene arsaalkene **159** pictured in Fig. 52 illustrates this type of molecule.

Pnictinidenes typically have triplet ground states so the difference between the type of carbene–pnictinidene complex observed is determined primarily by the preferred ground state of the carbene fragment. Since the presence of π-donor substituents on carbenes favors the adoption of a singlet ground state, carbenes such as NHCs yield Pn^{I}-type complexes, while carbenes substituted by other types of groups often produce Pn^{III}-type pnictaalkenes. Ultimately, the singlet–triplet model produces identical predictions as the back-bonding/hyperconjugation model outlined in the last section because the presence of the π-donor substituents that favor the singlet ground state for the carbene also limit the carbene’s ability to act as a back-bonding acceptor.

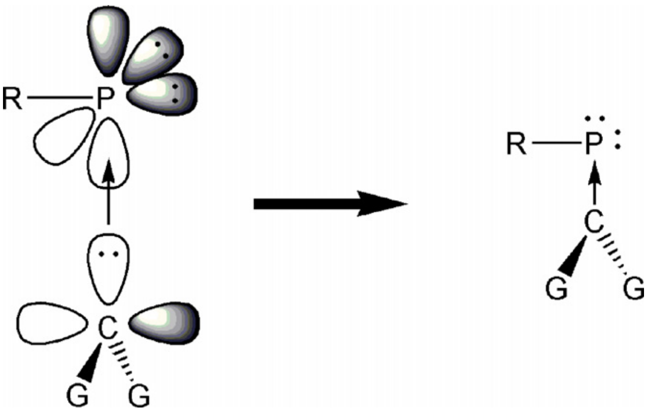


Fig. 74. Orbital interactions between singlet fragments to produce a Fischer-type carbene pnictinidene complex containing a Pn^{I} center.

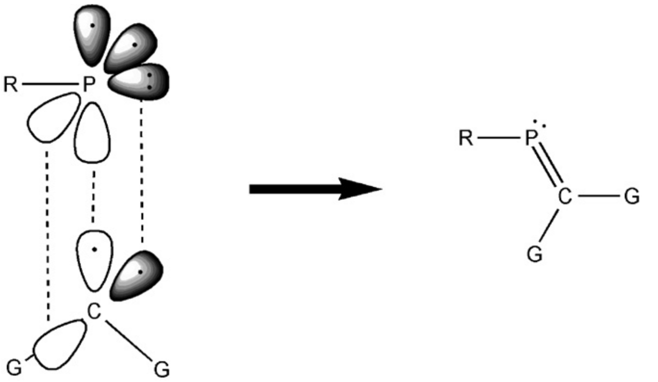


Fig. 75. Orbital interactions between triplet fragments to produce a Schrock-type carbene pnictinidene complex (a pnictaalkene) containing a Pn^{III} center.

6. Conclusions and outlook

The assignment of oxidation state on the basis of the number of “lone pairs” of electrons highlights the similarities in structural features and chemical reactivities associated with several different classes of compounds that contain group 15 elements. In this context, compounds containing pnictogen atoms bearing two “lone pairs” of electrons are described as containing Pn^{I} centers. While the chemistry of some Pn^{I} species, in particular the phosphides and their heavier analogues, has proven to be useful for the formation of new element–pnictogen bonds, the chemistry of many of the other types of compounds described above has not yet been exploited. For example, the unprecedented products such as the planar phosphonium and arsonium species obtained from the RedOx reactions involving such compounds represent only the tip of the iceberg in regard to the unique chemistry that may be possible for these electron-rich compounds. Likewise, the exploration of the application of pnicta-Wittig chemistry for the generation of new molecules and oligomers has only been initiated recently and the ligand chemistry of many of the electron-rich Pn^I species has yet to be investigated in detail.

The demonstrated applicability of synthetic methods derived from coordination chemistry to generate new Pn^I compounds greatly increases the scope and type of the Pn^I species that may be obtained. For example, the application of carbene–phosphine exchange chemistry for the synthesis of new types of phosphamethine cyanine dyes may be very lucrative given the tremendous recent progress in the synthesis of relatively stable carbenes. Furthermore, the understanding provided by experimental and theoretical investigations of electronic features that influence the stability of such compounds may now be used to “tune” the chemistry and properties of molecules containing Pn^I centers.

Given their unusually electron-rich nature and the “flexibility” in their modes of bonding, there appears to be a great deal of chemistry remaining to be discovered for compounds containing Pn^I centers.

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