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Journal of Organometallic Chemistry 646 (2002) 94–106

Journal of Organometallic Chemistry

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Account

Lithium phosphonium azayldiides $R_3P{=}NLi$. Applications in organic synthesis and coordination chemistry

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Received 12 September 2001; accepted 25 October 2001

Abstract

Lithium phosphonium azayldiide $Ph_3P{=}NLi$ easily prepared in large scale, is a very interesting tool in organic synthesis. It allows the synthesis of primary, secondary, cyclic or functional amines, of α,β-unsaturated, aromatic or heteroaromatic nitriles and of polyheteroatomic linkages (P=N–P, P=N–As, P=N–S). In coordination chemistry, [Ph_3PN^-] is a ligand involved in numerous transition metal complexes (Ni, Mo, La, W, Re, Ac: five kinds of structures). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Azayldiide; Phosphonium; Reactivity; Coordination; Phosphinimine; Nitrile

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1. Introduction

Lithium phosphonium azayldiides R_3PNLi (**1**) [1], which can be also be considered as *N*-lithiated phosphinimines, are isoelectronic structures with the lithium phosphonium methyldiides R_3PCHLi (**2**) [2,3]. These metalated phosphonium *yldiides* are named by simple extension of the original definition given as early as 1944 by Wittig [4] for the term 'ylide' (from the German 'ylid'). According to this definition, the 'onium ylide' denotes a species **3** with a carbon group indicated by the suffix 'yl' (from the radical 'alkyl'), bearing a negative charge (corresponding to a heteropolar bond), indicated by the suffix 'ide' (by analogy with acetylide), located on carbon directly linked to a heteroatom bearing a positive charge (onium). By extension of this definition [5], the term lithium phosphonium 'methyldiide' for R_3PCHLi (**2**) indicates the presence of one methyl group bearing formally two negative charges. Further extension leads to the term 'azayldiide' for R_3PNLi (**1**), thus taking into account the presence of a nitrogen atom (Scheme 1) [1–8].

This review deals with the recent developments in the uses of R_3PNLi, and more specifically of Ph_3PNLi, in organic synthesis and in coordination chemistry.

2. Syntheses of $R_3P{=}NLi$

Lithium phosphoniun azayldiides R_3PNLi (**1**) were initially prepared by Schmidbaur [1,9,10] by direct metalation with a base such as MeLi of the corresponding *N*-unsubsituted azaylides R_3PNH (**6**) [11], which can be obtained either from the aminophosphonium salts **5** [12], or from the *N*-silylated phosphinimines (**7**) [13]. Another method allows the direct *one-pot* preparation of R_3PNLi, by a double deprotonation, using two equivalents of *n*-butyllithium, of the corresponding aminophosphonium salts **5**, itself obtained from gazeous ammonia and dibromophosphorane [14–17] (Scheme 2).

3. Structure of $Ph_3P{=}NLi$

3.1. NMR spectroscopy

In DMSO-d_6 the ^{31}P-NMR signal of $Ph_3P{=}NLi$ (**10**) appears at −11.9 ppm. This value is the result of a strong shielding effect, induced by the mono-and di-

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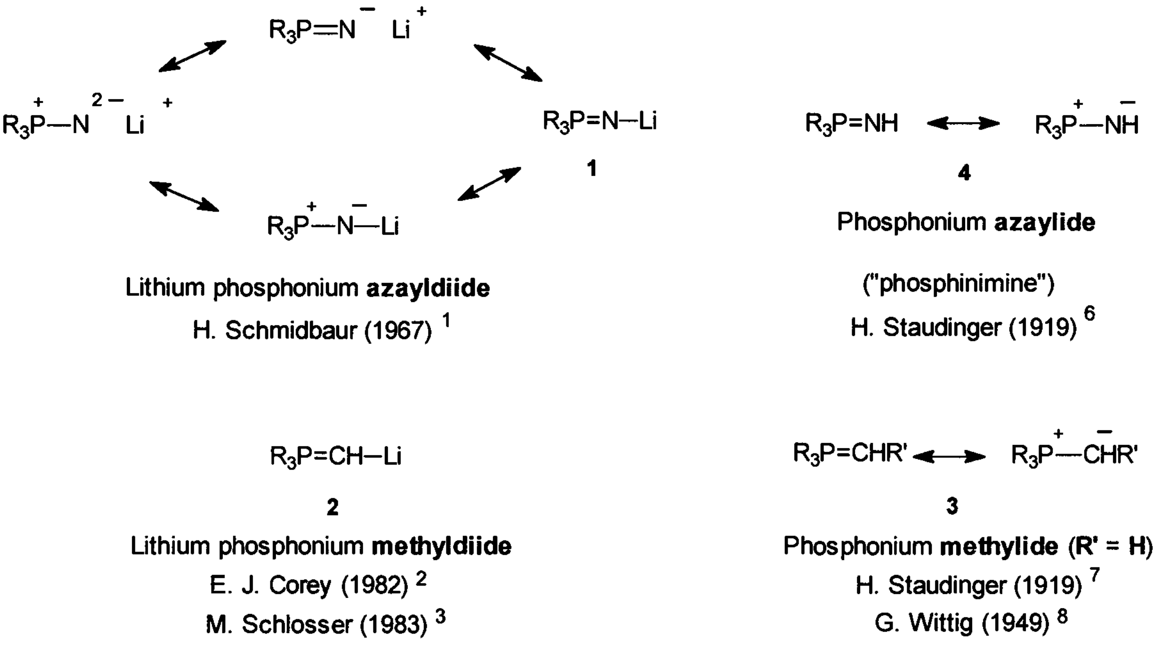
PII: S0022-328X(01)01430-9

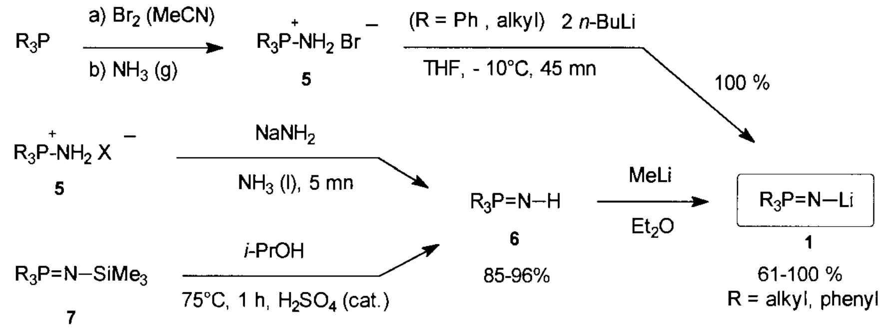
deprotonation of the starting aminophosphonium salt **8** (Table 1, Scheme 3),

In ^{13}C-NMR spectra the only perceptible difference concerns the aromatic *ipso* carbon atoms of $Ph_3P{=}NLi$ and $Ph_3P{=}NH$ which are deshielded (about 10 ppm) in comparison with the *ipso* carbon of $Ph_3PNH_2^+\ Br^-$. This was already observed for compounds of type $Ph_3P{=}X$ ($X = CH_2$, NH, O, S, Se) for which the chemical shifts of the aromatic carbon atoms, other than *ipso*, are less affected by the nature of the X groups [19].

The equilibrium between $Ph_3P{=}NH$ and $Ph_3P{=}NLi$ has been investigated in ^{31}P-NMR (DMSO-d_6) in the presence of *N*-lithiated aniline in order to determine the basicity of the lithium triphenylphosphonium azayldiide (**10**). A $pK_{a(H_2O)}$ value of 28.1, for the acidity of $Ph_3P{=}NH$, has thus been found, which corroborates the highest basicity of **10** in regard to the corresponding phosphinimine (**9**) ($pK_{a(H_2O)}$ of 20.6 for the pair $Ph_3PNH_2^+Br^-/Ph_3P{=}NH$: **8**/**9**) [18,20].



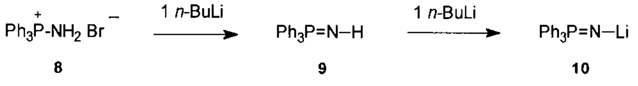
Scheme 1.



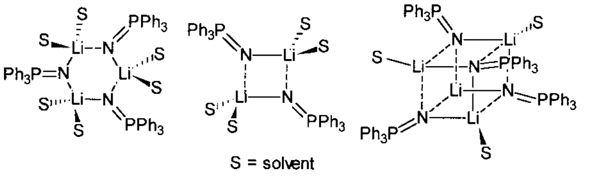
Scheme 2.

Table 1
^{31}P- and ^{13}C-NMR of $Ph_3PNH_2^+Br^-$ (**8**), $Ph_3P{=}NH$ (**9**) and $Ph_3P{=}NLi$ (**10**) [18]

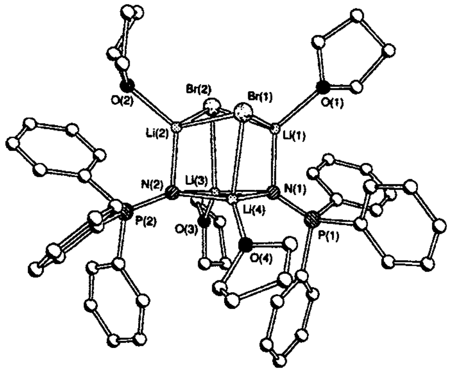
	δ ^{31}P (ppm)		δ ^{13}C (ppm)/J (Hz) (DMSO-d_6)							
	THF	DMSO-d_6	δ Ci	J_{CiP}	δ Cm	J_{CmP}	δ Co	J_{CoP}	δ Cp	J_{CpP}
$Ph_3PNH_2^+Br^-$ (**8**)	35.5	35.2	123.4	102.8	129.9	13.1	132.9	11.4	134.8	2.7
$Ph_3P{=}NH$ (**9**)	22	20.4	134.5	93.8	128.6	11.1	131.7	9.4	131.8	2.8
$Ph_3P{=}NLi$ (**10**)	−4.9 (75%) −7.5 (25%)	−11.9	134.6	93.5	128.6	11.4	131.7	9.4	131.3	2.7



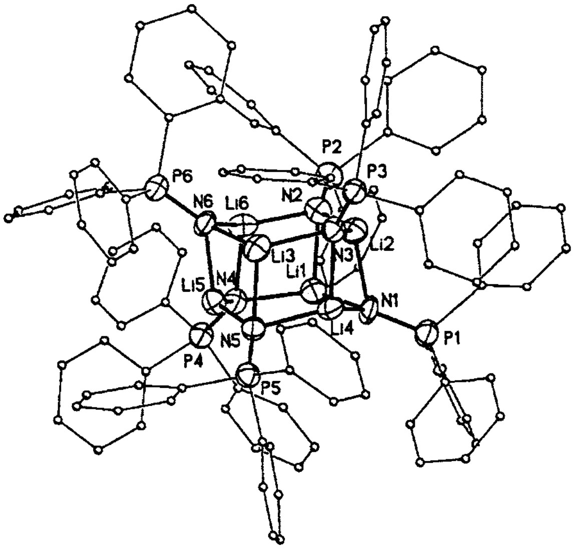
Scheme 3.



Scheme 4.



Scheme 5. X-ray structure of [$(Ph_3PNLi{\cdot}LiBr)_2{\cdot}4THF)$]·1.5 arene [24].



Scheme 6. X-ray structure of [$(Ph_3PNLi)_6{\cdot}5THF)$] [25].

The ^{31}P-NMR spectrum of $Ph_3P{=}NLi$ presents lone signal in DMSO ($\delta = -11.9$ ppm) or in DME ($\delta = -4.3$ ppm), which are strongly dissociative solvents, respectively, by donor and chelating effects [21]. On the contrary, the spectrum recorded using THF (less donor solvent) discloses two signals for **10** (Table 1). Taking into account the ability of lithium atoms to associate with anionic species or with donor sites of solvents [22], the presence of two signals can be attributed to the existence of aggregates with formation of piled cycles including four or six atoms, similar to those described for lithiated imines [14,23] (Scheme 4).

3.2. X-ray crystal structures

The X-ray crystal structure of the triphenylphosphonium azayldiide (**10**) has been published by two groups [24,25]. The first one studied the complex [$(Ph_3PNLi{\cdot}LiBr)_2{\cdot}4THF)$]·1.5 arene (arene = benzene or toluene), prepared by the reaction of two equivalents of n-BuLi with the aminophosphonium bromide (**8**) in arene-THF (Scheme 5) [24]. The structure consists of a pseudocubane $Li_4N_2Br_2$ core in which each lithium atom is four-coordinated by three μ_3-bridging anionic centres and one molecule of THF. The average distances Li–N (197.1 and 200.5 pm) and Li–Br (273.8 and 260.3 pm) within the core show that the interactions of the lithium atoms with the nitrogen of Ph_3PN^- are favoured in comparison with those with the bromide anions. This preference, and the strong ability of Ph_3PNLi to solvate LiBr, thus avoiding its association into an infinite (LiX) lattice, confirm the high Lewis basicity of the phosphonium azayldiides. The structural parameters show a high ratio of electrostatic interactions between Ph_3PN^- and Li^+. Thus, the P–N distance (154.1 pm) is here shorter than in other complexes also involving Ph_3PN^- as μ_3-bridged ligand ($\{Ph_3P{=}N[Au(PPh_3)]_3\}^{2+}$ $2BF_4^-$, P–N = 162 pm) [26]. Moreover, this distance is also shorter than in the parent $Ph_3P{=}NH$ **9**, in good agreement with an increased electrostatic interaction between the positive phosphorus atom and a more negative nitrogen atom after the deprotonation with n-BuLi.

A second research group [25] has published the structure of [$(Ph_3PNLi)_6{\cdot}5THF$] (Scheme 6), obtained avoiding the presence of LiBr. The crystal structure discloses hexameric molecules with a Li_6N_6 polyhedron peripherally shielded by the phenyl groups. As in the former case, the authors found a surprisingly short distance for the P–N bond (153.8 pm) regarding the range corresponding to the PN double bonds (155–164 pm) [27].

4. Applications of $Ph_3P{=}NLi$ in organic synthesis

As hereafter illustrated, the reagent $Ph_3P{=}NLi$ (**10**) is the most used phosphonium azayliide in organic synthesis as well as in coordination chemistry.

As a matter of fact, this reagent can be easily prepared in large scale, up to the mole, from commercially available starting materials [17] (Scheme 7).

Moreover, THF solutions of the reagent **10** can be kept for several weeks, under nitrogen, at 0 °C, without appreciable change. It is only slowly protonated into $Ph_3P{=}NH$ (**9**), by a long refluxing of the solvent (after 24 h refluxing: 23% protonation in THF and 36% in DME) [41].

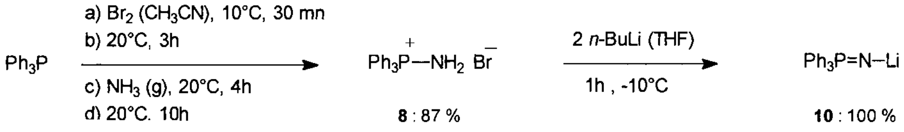
4.1. Reactivity towards carbon electrophiles

4.1.1. Reaction with alkylating agents

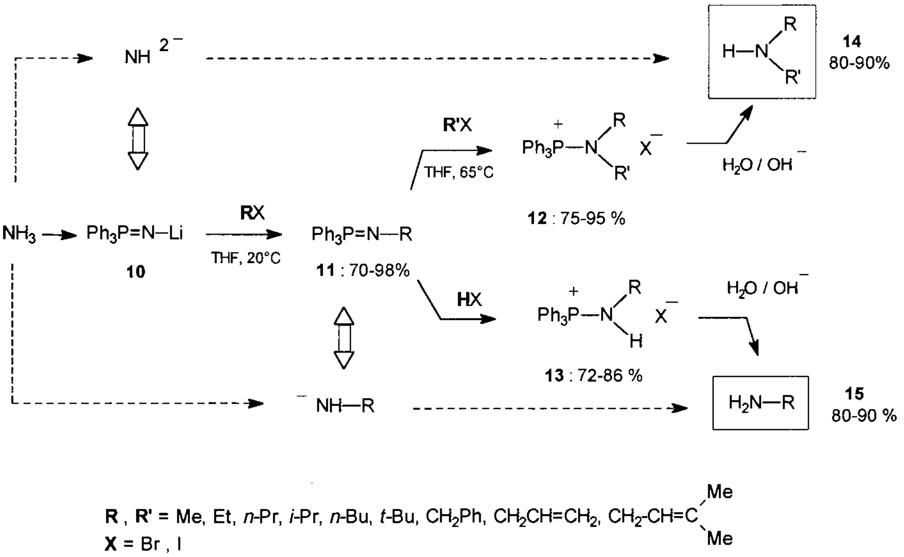
4.1.1.1. Reaction with alkyl halides: synthesis of aminophosphonium salts and corresponding amines. Lithium azayldiide (**10**) exhibits a high nucleophilicity towards alkylating agents RX. Thus, the stepwise mono- or dialkylation of $Ph_3P{=}NLi$ can be controlled and give very good yields of, respectively, *N*-alkyl phosphinimines (**11**) and unsymmetrically disubstituted aminophosphonium salts (**12**) [15,28–30]. The aminophosphonium salt (**13**) can also be obtained by treatment of **11** by HCl. $Ph_3P{=}NLi$ can be considered as a synthetic equivalent of dimetalated ammonia (NH^{2-}). Indeed it affords a new synthetic approach to primary and secondary amines **14** and **15**, obtained in high yields by hydrolysis of the corresponding aminophosphonium salts [31,32] (Scheme 8).

4.1.1.2. Reaction with ω-dihaloalkanes: synthesis of cyclic aminophosphonium salts [18]. With diiodomethane or 1,2-diiodoethane, the azayldiide (**10**) acts only as a base leading to the quantitative formation of the phosphinimine (**9**). The reaction of 1,3-diiodopropane with the azayldiide affords two different *N*-allylaminophosphonium salts, **16** and **18**. They result from a *N*-mono- or *N*-dialkylation, followed or preceded by a dehydrohalogenation step by **10**. In the presence of other ω-diiodoalkanes ($n = 4$–6), the reaction with **10** allows the synthesis of the corresponding cyclic aminophosphonium salts (**19**–**21**) in good isolated yields in the case of diiodobutane or pentane (for diiodopentane the corresponding cyclic amine (**22**) was also isolated after basic hydrolysis). This means that inside the transient *N*-(4-iodo-butyl or 5-iodo-pentyl) triphenylphosphinimine (**17**) ($n = 4$, 5), the cyclisation is promoted by an entropic effect. Notice that with an excess of diiodobutane (five equivalents), small amounts of **23** were obtained together with the main product **19** (89%), after the final work-up. In the case of 1,6-diiodohexane, the azepane derivative (**21**) is obtained in medium yield together with a mixture of unidentified phosphonium salts (Scheme 9).

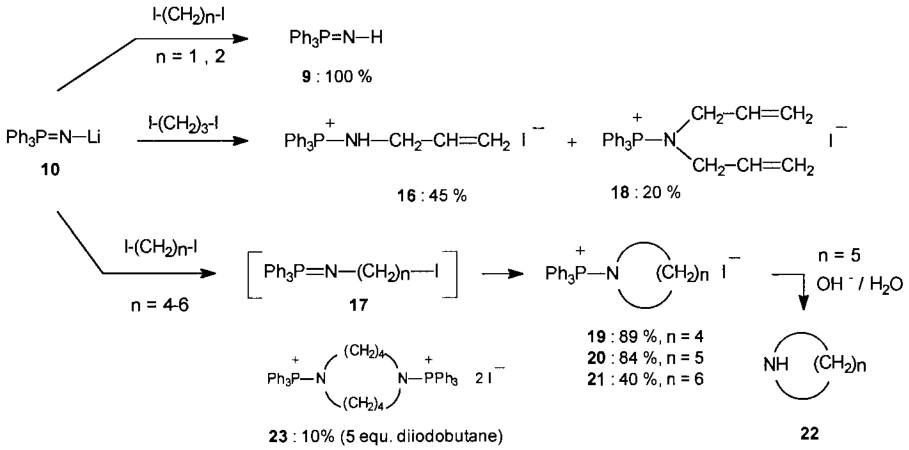
Furthermore, some particular dihalogenated compounds such as $Y(CH_2X)_2$ (**24**) were also considered. The α,α′-dibromo *o*-xylene (**24b**) ($Y = o\text{-}C_6H_4$, $X = Br$) reacts with one equivalent of **10** to give the corresponding triphenyl 2-*iso*indolylphosphonium bromide (**25**) in high yield (93%). On the other hand, the azayldiide (**10**) in the presence of one equivalent of *Z*-1,4-dichloro-2-



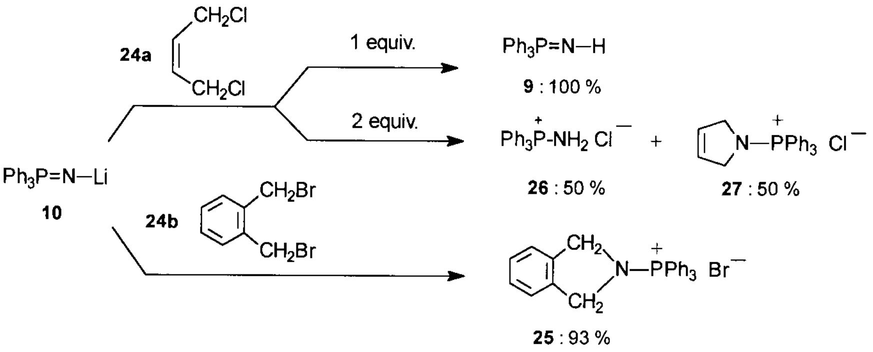
Scheme 7.



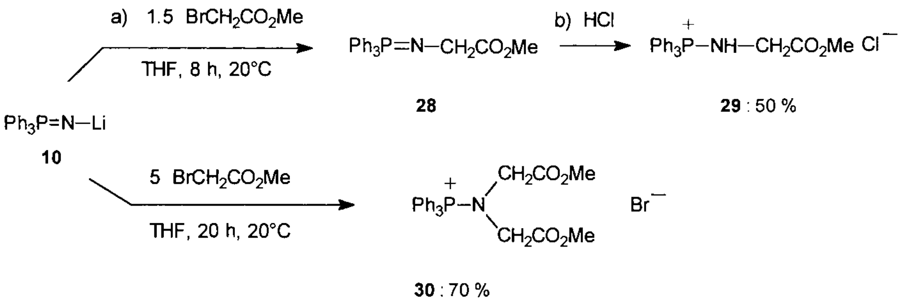
Scheme 8.



Scheme 9.



Scheme 10.



Scheme 11.

butene (**24a**) (Y = CH=CH, X = Cl) is quantitatively protonated into **9** which is the only phosphorus compound recovered. It is noteworthy that, when **10** reacts with two equivalents of **24a**, a 1/1 mixture of the starting salt **26** and of one cyclic aminophosphonium salt **27** (isolated) is obtained, probably as a result of a consecutive transyluration reaction between the in situ formed azaylide (**9**) and the *N*-substituted aminophosphonium resulting from the alkylation of **9** by a second dichlorobutene molecule **24a** [18] (Scheme 10).

4.1.2. Reaction with α-halogenated esters

The reaction of **10** with α-bromoesters allows the synthesis of functional amino phosphonium salts, which are amino acid precursors [33a,33b]. One and half equivalents of ester are required to obtain about 50% yield in monosubstituted phosphinimine intermediate **28** and in the corresponding salt **29** after acidolysis (whatever the type of ester used: methyl, ethyl, *t*-butyl, or benzyl esters). In the presence of an excess of α-bromoester the *N*-disubstituted aminophosphonium salt (**30**) is obtained in good yield. Compounds **29** and **30** are potentially convertible into the corresponding amino acids under basic conditions [34] (Scheme 11).

4.1.3. Reaction with acylating agents

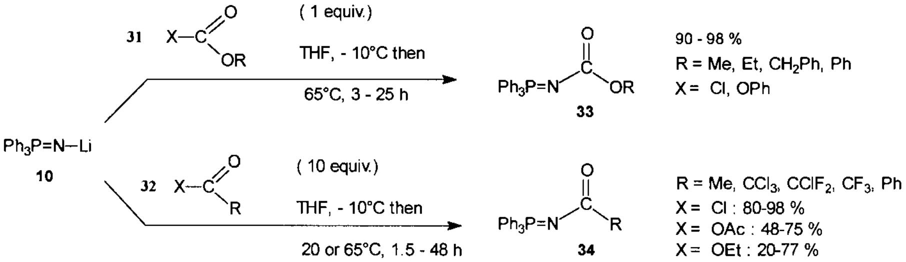
The authors describe the one-pot activity of $Ph_3P{=}NLi$ towards acylating agents [17]. By this procedure, a high yielding synthesis of varied *N*-alkoxycarbonyl- and *N*-acyltriphenylphosphinimines **33** and **34**, are achieved. Depending on the reactivity of the carbonyl derivatives, the acylations are carried out in THF at 65 °C or at room temperature within a few hours. The reactivity of **10** is nearly the same towards anhydrides and acyl chlorides, and its affinity towards various carbonyl compounds is very important. Notice, that the azayldiide (**10**) is acylated only by non-enolisable esters, because of its basicity which induces the enolisation and therefore lowers down strongly the electrophilicity of the carbonyl functions (Scheme 12).

The azayldiide is a simple and efficient reagent for the general synthesis of *N*-acylphosphinimines in comparison with other synthetic routes already reported [35], which require the use of: (i) hazardous conditions owing to the explosive nature of organic azides used [36]; (ii) *N*-silylated phosphinimines, difficult to prepare and considerably less reactive than **10** [37]; (iii) Ph_3PNH (**9**), also less reactive than **10** and moreover used in twofold excess [38]; (iv) the Kirsanov reaction followed by a Grignard reaction [39].

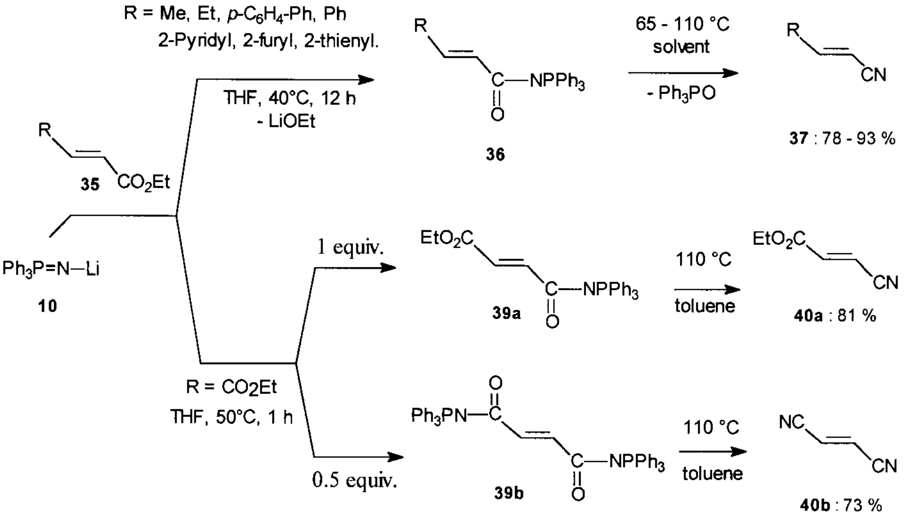
4.1.4. Reaction with α,β-unsaturated esters and with aromatic or heteroaromatic esters: synthesis of the corresponding nitriles

The azaylide (**10**) reacts with numerous esters (**35**) to give via a nucleophilic substitution at the carbonyl group, the corresponding new *N*-acylated phosphinimines (**36**) (by comparison the azaylide $Ph_3P{=}NH$ (**9**) does not react with esters in the same experimental conditions: THF at 40 °C) [40]. The hardness of the nucleophile (**10**) is here well demonstrated by its reactivity with the α,β-unsaturated esters (**35**), occurring at the carboxylate group rather than at the β-vinylic carbon. In a second step the phosphinimines (**36**), isolated or in situ, undergo an intramolecular aza-Wittig reaction to afford the corresponding α,β-unsaturated nitriles (**37**) in good yields. When Ph_3PNLi reacts with the diester ($R = CO_2Et$:diethyl maleate) the ratio of monoacylation–diacylation can be controlled (one or two equivalents of **10**) to give the corresponding phosphinimines **39a** or **39b** which can be transformed in the way into the mono- or dinitrile **40a** or **40b** (Scheme 13).

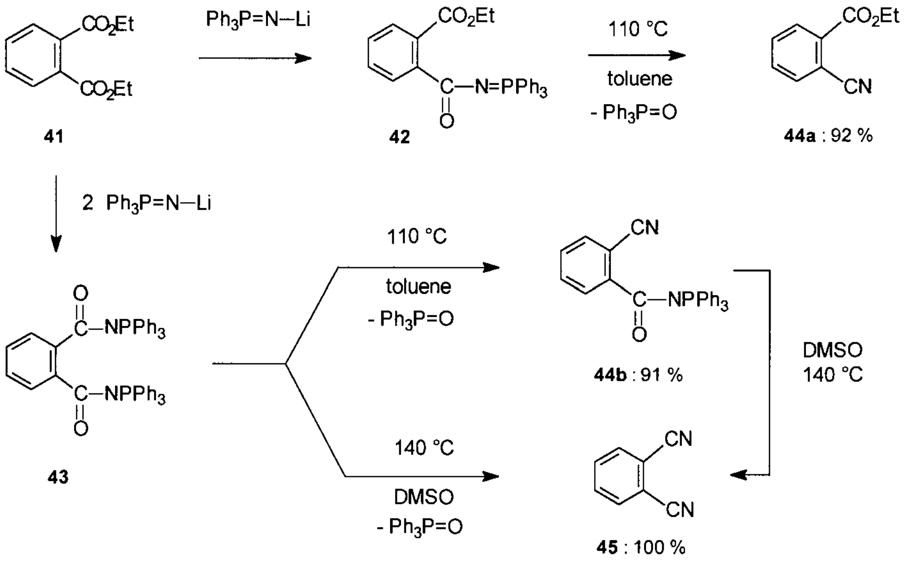
Depending on the conditions, the diethyl phthalate (**41**) is also converted mainly either into the monoester



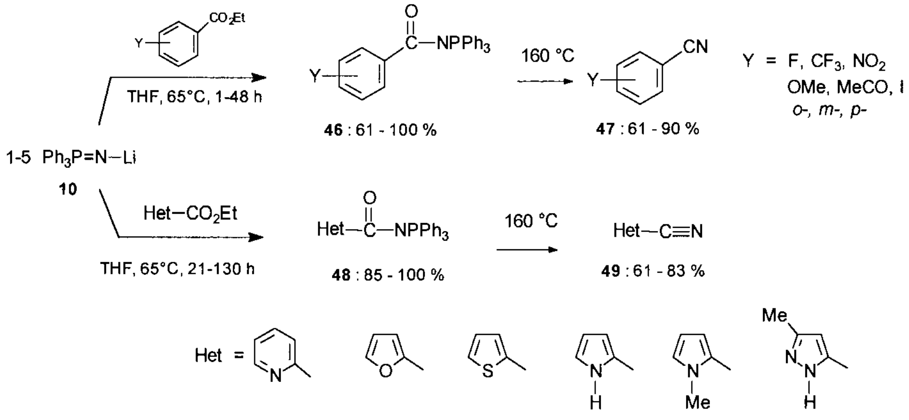
Scheme 12.



Scheme 13.



Scheme 14.



Scheme 15.

(**42**) or into the diphosphinimine (**43**). The corresponding mono- or dinitrile, **44a**, **44b** or **45** are here also obtained by intramolecular aza-Wittig reactions [40] (Scheme 14).

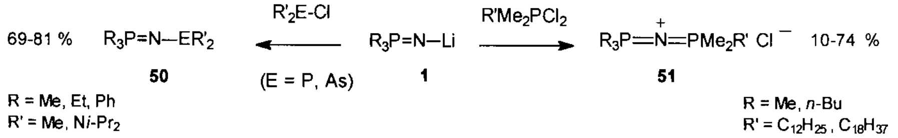
The method has been successfully extended to the *one-pot* synthesis of a large family of functionalised aromatic and heteroaromatic nitriles **47** and **49** [41] (Scheme 15).

In the case of substituted ethyl benzoates the corresponding nitriles can be obtained chemoselectively in good overall yields (61–90%) with various functional groups (F, I, CF_3, OMe, MeCO, NO_2), wherever their position on the aromatic ring may be. Only the compounds with the nitro group in the *meta* or *ortho* position give a lower yield (20–28%). It is noteworthy that the kinetic of the two steps of the nitrile synthesis are differently depending on the nature of the substituents. The first step, the *N*-acylphosphinimine (**46**) formation, is accelerated by electron withdrawing substituents and, on the contrary, slowed down by electron donating groups. The reverse and stronger effects are verified for the second step the intramolecular aza-Wittig reaction. Accordingly, the synthesis of nitriles from the corresponding esters is all in all favoured by electron donating substituents and disfavoured by electron withdrawing substituents of the aromatic ring.

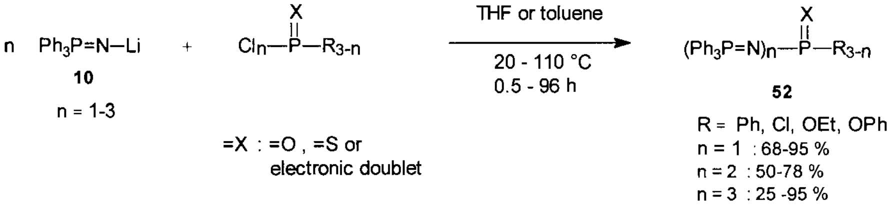
4.2. Reactivity towards heteroatomic electrophiles

4.2.1. Reaction with phosphorus and arsenic halides: synthesis of PNAs or PNP bonds

Phosphorus and arsenic chlorides undergo nucleophilic substitution, under mild conditions, with R_3PNLi (**1**), thus leading to the formation of the corresponding *N*-substituted phosphinimines with P=N–P and P=N–As bonds (**50**) [9,42]. In the presence of one equivalent of dichlorophosphorane the same reaction, also under mild conditions, affords the corresponding unsymmetrical bis(phosphoranylidene)ammonium chlorides (**51**) [16] (Scheme 16).



Scheme 16.



Scheme 17.

A systematic study of the reactivity of Ph_3PNLi towards P^{III} and P^{IV} phosphorus electrophiles has been recently performed [41]. The results show the possibility to obtain (*one-pot*) in very good yields a large range of *N*-substituted phosphinimines which are valuable precursors for the (poly-)phosphazene chemistry. Thus mono-, -di- and also triphosphinimines (**52**) have been synthesised. The triphosphinimine (P^{III}, $n = 3$) is very basic and similar to a Schwesinger's base [43] (Scheme 17).

4.2.2. Reaction with halogens: synthesis of PNP bonds

The reaction of Ph_3PNLi with bromine probably proceeds via the intermediate formation of a highly reactive halogenated phosphinimine (**53**), which leads in the presence of triarylphosphine to the formation of unsymmetrical bis(phosphoranylidene)ammoniun bromides (**54**), with charged P=N–P linkages [33] (Scheme 18).

These bulky cations are mainly used to stabilise air-sensitive anions in metal carbonyl chemistry, allowing the formation of suitable crystals which are extensively used in order to determine the X-ray structure of a lot of anionic metal carbonyls type $[M_m(CO)_n]^{p-}$ (M = Mo, W, Cr, Ni, Fe, Co) [44,45].

4.2.3. Reactivity towards sulphur electrophiles

The reaction of Ph_3PNLi towards sulphur electrophilic substrates (tosyl or sulphuryl chloride), affords an easy *one-pot* preparation for a range of *N*-substituted phosphinimines (**55**–**57**), which are valuable precursors for the sulphonamide chemistry [29,46]. Moreover, the intermediate **58** can be isolated or alkylated [47] using other nucleophiles such as ammonia, more hindered amines and alcohols, aromatic amines and hydrazines (Scheme 19).

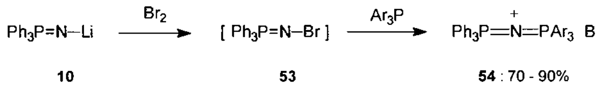
4.2.4. Reaction with metallic halides

Azayldiides $R_3P{=}NLi$ (R = Me, Et, *t*-Bu, Ph) by reaction with silyl, germanium and tin-halides lead to the formation of the corresponding metallated phosphinimines [1,10,16,48,49]. Phosphinimines with different substituents on the phosphorus atom are also described by similar synthetic ways [16] (Scheme 20).

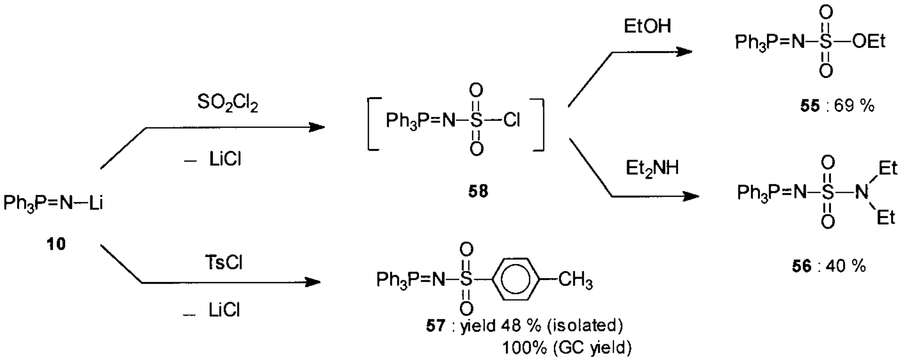
5. Applications of $Ph_3P{=}NLi$ in coordination chemistry

5.1. Introduction

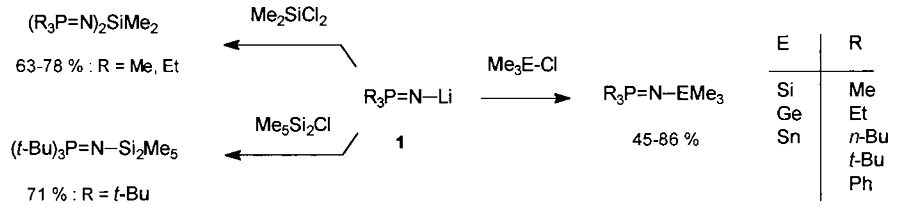
The anions $[R_3PN^-]$ of the phosphonium azayldiides (**1**), are potentially able to give two to six electrons to one (structures A or B), two (structures C or D) or three (structure E) metallic atoms [M] (Scheme 21) [50,51]. Thus, the anions $[R_3PN^-]$ which behave like versatile phosphoraneiminato ligands, are involved in numerous transition metal complexes. We will only focus here on those of these phosphoraneiminato complexes obtained directly from R_3PNLi. Five types of structures are described in the literature: (i) in the structures A and B, $[R_3PN^-]$ is a terminal function of the metal and the axis P–N–M is, respectively, closed to the linearity or bent; (ii) in the structures C and D $[R_3PN^-]$ is symmetrically or unsymmetrically μ_2-bridged; (iii) in the structure E $[R_3PN^-]$ is μ_3-bridged. The observed structures being connected to the oxidation state of the metal in the complexes (structure A for high oxidation states and E, on the opposite, for low oxidation states), we will choose this criterion already recently adopted [51], to present the results from the literature (Scheme 21).



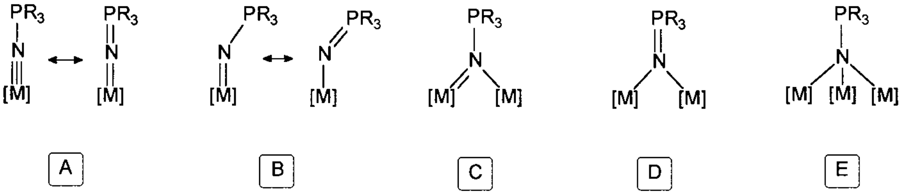
Scheme 18.



Scheme 19.



Scheme 20.



Scheme 21.

5.2. Formation of complexes with a metal at the oxidation state (+VII)

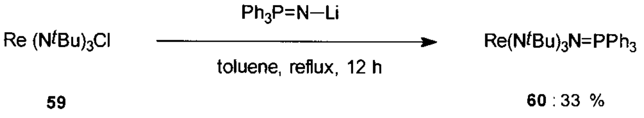
The interaction between a slight excess of Ph_3PNLi and $Re(N^tBu)_3Cl$ in refluxing toluene allows the formation of the phosphoraneiminato complex $Re(N^tBu)_3$ $(N{=}PPh_3)$ (+VII) (**60**) [52] (Scheme 22).

The structure of complex **60** has been proposed on the basis of IR spectra. Indeed, the phosphoraneiminato complexes are characterised by a strong absorption in the range of about 1100 cm^{-1}, corresponding to the antisymmetric stretching vibration of the MNP group. For ν_{as} at the lower limit of the ν(MNP) region (1052–1200 cm^{-1}), structures of type B are usually observed (1050 cm^{-1} for $[Mo(NO)(NPMePh_2)(dttd)]$ with a P–N–Mo bond angle of 130°) [53]. On the contrary, a ν_{as} at a higher limit would rather correspond to the structure A (1128 cm^{-1} for $[MoCl_4(NPPh_3)]_2$ with a P–N–Mo bond angle of 166°) [53]. For the authors, the structure B seems then to be the main contributor for $Re(N^tBu)_3(N{=}PPh_3)$, because of the presence of the characteristic band at 1094 cm^{-1}.

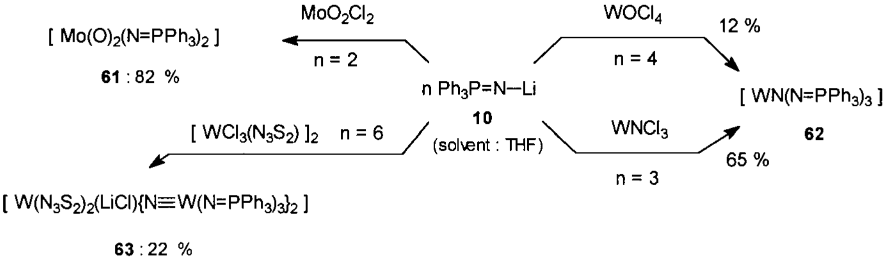
5.3. Formation of complexes with a metal at the oxidation state (+VI)

Various dioxo- or nitrido-phosphoraneiminato complexes of molybdenum(VI) (**61**) and tungsten(VI) (**62**) have been synthesised by reaction of Ph_3PNLi (two to four equivalents) with the corresponding oxo- or nitrido-halides. The complex **61** is a monomeric molecule, which forms a colourless crystal with a tetrahedrally coordinated molybdenum atom. The structure is similar to A: the interatomic distances MoN (185.9 pm) and NP (157.6 pm) correspond to double bonds and the Mo–N–P angle (161.7°) is near 180° corresponding to the linearity [54] (Scheme 23).

A cyclothiazeno complex of tungsten(VI) (type $M[N_3S_2]$) (**63**) ($n = 6$) has also been obtained from Ph_3PNLi [55].



Scheme 22.



Scheme 23.

5.4. Formation of complexes with a metal at the oxidation state (+IV)

Ph$_3$PNLi forms with actinides (thorium, uranium) monomeric complexes Cp$_3$AcNPPh$_3$ (+IV) (**66**), starting from the corresponding cyclopentadienyl halides [51,56] (Scheme 24).

A linear structure type A has been attributed for these compounds on the basis of the X-ray crystallographic data. Indeed, the length observed for the U–N bond is 47 pm longer than the appropriate Pauling metallic radius corresponding to the tetravalent uranium. This difference between the metal–nitrogen distance and the metallic radius, larger by 41 pm than expected for a bond order of 3, but less by 48 pm than expected for a bond order of 2.5, suggests a near triple bond for U–N (a value of about 60 pm is consistent with a metal–nitrogen bond order of about 2) [57]. Moreover, the P–N bond length, 161 pm, is not significantly different from 161.5 observed for [Ph$_3$P–NH$_2$]-Cl·CH$_2$Cl$_2$ which shows a simple P–N bond [12a]. Accordingly this result is in good agreement with a structure A.

The observed value of the U–N–P angle (172°), confirms a linear geometry type A. For the authors, it corresponds to p_π–p_π, d_π–p_π and/or f_π–p_π orbital overlaps, optimised in the case of U–N–P angle to 180° (the slight bending observed is caused by steric interactions).

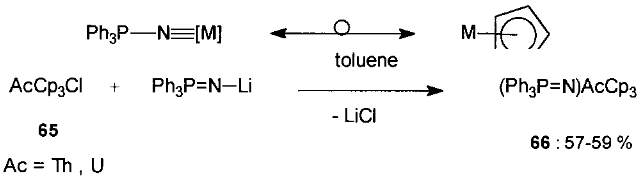
These conclusions are reinforced by extended Hückel molecular orbital calculations performed with H$_3$PNUCp$_3$ as model which show a highly polarised P–N bond with high negative charge located on nitrogen atom. This indicates that among the two limit resonance forms **67** and **68**, the second one is more appropriate to describe the bond within R$_3$PN$^-$ in complexes Cp$_3$AcNPPh$_3$. The prevalence of **68** which indicates that the R$_3$PN$^-$ ligand is potentially a three-electron pair donor agrees then well with the geometry A [56] (Scheme 25).

Notice that Ph$_3$PO, isoelectronic with Ph$_3$PN$^-$, is less multiple electron pair donor. As a result Ph$_3$PN$^-$ exhibits for example a U–N bond (207 pm) for Cp$_3$UNPPh$_3$ shorter than the U–O bond (238 pm) in (MeC$_6$H$_4$)$_3$UOPPh$_3$ [56].

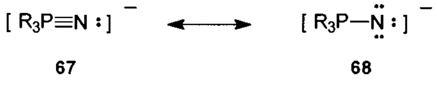
5.5. Formation of complexes with a metal at the oxidation state (+III)

Transition metal complexes with such an oxidation state and involving Ph$_3$PN$^-$ as ligand are very often bound to two or three metallic centres [51]. However, an exception has been observed in the reaction of Ph$_3$PNLi with the chloro-bridged bis(cyclopentadienyl)chlorides [LaCp$_2$Cl] and [YCp$_2$Cl] [58,59] (Schemes 26–28).

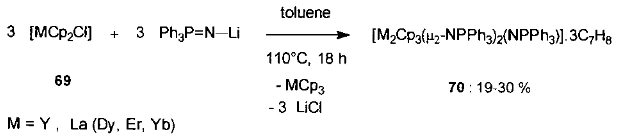
Indeed, whereas two of the three Ph$_3$PN$^-$ ligands link the metallic atoms via μ_2-N nitrogen thus forming almost planar M$_2$N$_2$ four-membered rings, the third Ph$_3$PN$^-$ is terminally coordinated to one metallic atom with a geometry type A (the P–N$_{\text{exocyclic}}$ distance corresponds to a double bond and the P–N$_{\text{exo}}$–M angle between 168 and 171.1° indicate an almost linear geometry). The bonding mode of the two other bridged Ph$_3$PN$^-$ corresponds to a symmetrical geometry D (same M–N distances in the M$_2$N$_2$ cycles and bond order of 2 for PN$_{\text{cyclic}}$). It is interesting to note that these results are also indicative of the isolobal relationship between Ph$_3$PN$^-$ coordinated in a terminal mode (A) and the cyclopentadienyl anion [60].



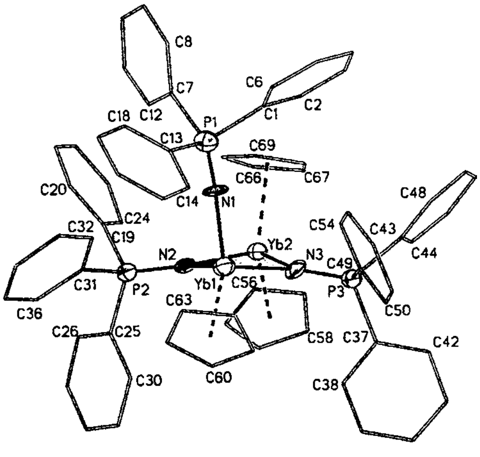
Scheme 24.



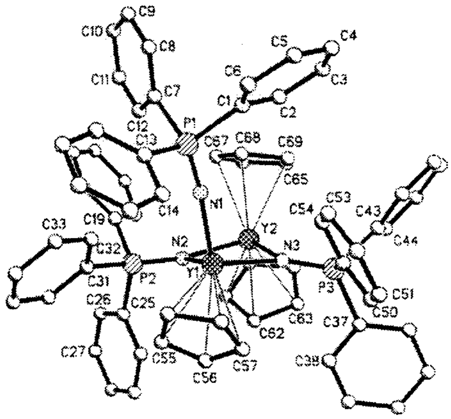
Scheme 25.



Scheme 26.



Scheme 27. X-ray structure of $[Yb_2Cp_3(NPPh_3)_3]$.



Scheme 28. X-ray structure of $[Y_2Cp_3(NPPh_3)_3]$.

Indeed, these two ligands in complexes $[M_2Cp_3(NPPh_3)_3]$ both involve comparable orbitals (σ, 2π), and are sterically and electronically equivalents (ex: N_{exo}–Yb–Cp and Cp–Yb–Cp have very close angles, respectively, 118.3 and 125.5°).

Ph_3PNLi reacts also with cyclooctatetraenide complexes of cerium and samarium to give the corresponding phosphoraneiminato complexes of lanthanide **71** [25]. The X-ray analyses disclose for these compounds a central heterocubane structure with the participation of two Ph_3PN^- via their nitrogen atom. Each nitrogen is trebly-bridged (μ_3) with, respectively, two lithium and one lanthanide atom (Scheme 29).

5.6. Formation of complexes with a metal at oxidation state (+II)

The phosphoraneiaminato complexes (II) are widely described but only one example seems to be obtained from the azayldiides R_3PNLi (R = Me) [50,51] (Scheme 30).

A μ_3-$NPMe_3$ unit and a cubane-type molecular structure with Ni and N atoms in alternating corners are proposed on the basis of the mass spectrum. This structure would be then of type E.

6. Conclusions

As shown in this review, among the lithium phosphonium azayldiides (**1**), compound **10**, $Ph_3P{=}NLi$, is particularly interesting.

It is now easily prepared in large scale, from commercially available starting materials, and can be kept for several days in THF solution, under nitrogen at 0 °C, without appreciable evolution.

In organic synthesis, it can be used as nucleophilic aminating agent, as synthetic equivalent of NH_2^- or NH^{2-} synthons, affording with appropriate alkylating agents, primary, secondary or cyclic amines and also functional amines. Another important synthetic application consists in the functional transformation of α,β-unsaturated, aromatic or heteroaromatic esters into nitriles. In heteroatom chemistry, $Ph_3P{=}NLi$ is also a good starting reagent to access easily to polyheteroatomic linkages (P=N–P, P=N–As, P=N–S...) which can be interesting structural elements in molecules or materials.

For further applications in organic synthesis, may be the recent preparation of potassium (**73**) [61] or magnesium (**74**) [62], analogs of the reagent **10**, can bring some possibilities (Scheme 31).

$$[La(C_8H_8)Cl(THF)_2]_2 + 4\ Ph_3P{=}N{-}Li + 2\ LiCl \xrightarrow[20°C]{THF} 2\ [La(C_8H_8)Li_3Cl_2(NPPh_3)_2(THF)_3]$$

La = Ce , Sm

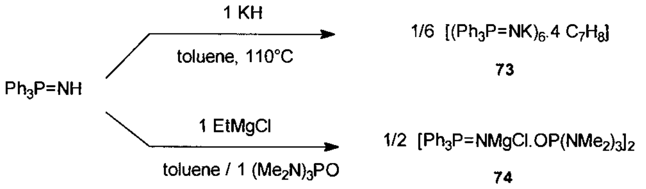
71 : 20-30 %

Scheme 29.

$$4\ ClNi(PMe_3)_2N_3 + 4\ Me_3P{=}N{-}Li \xrightarrow{toluene} [NiCl(NPPh_3)]_4 + LiCl + 4\ LiN_3 + 8\ PMe_3$$

72 : 20 %

Scheme 30.



Scheme 31.

Scheme 32.

But more likely, the most promising developments would result in the future from the prospective preparation and synthetic uses of adequate palladium, nickel or copper derivatives.

It is also noteworthy that another interesting direction of developments in the azayldiide chemistry started recently with the first results obtained on the analogous aminosulphonium azaylidiide (**75**), for S_NAr reactions with activated halogenoaromatic compounds [63] (Scheme 32).

In coordination chemistry, the anion $[Ph_3PN^-]$ is a versatile phosphoraneiminato ligand involved in numerous transition metal complexes: the oxidation states of the metal [Ni, Mo, La (Ce, Sm, Dy, Er, Yb), W, Re, Ac (Th, U)...] are ranging from II to VII, and five different kinds of structures are known for the complexes, involving either a monocoordination of $[Ph_3PN^-]$ or a μ_2, even μ_3, bridging behaviour of the ligand.

Therefore, the various applications in organic synthesis or in coordination chemistry illustrate the general interest of the phosphonium azayldiide (**1**) and particularly of the reagent $Ph_3P{=}NLi$ (**10**).

Acknowledgements

We thank le Conseil Régional de la *Région Languedoc Roussillon* for financial support, and also Wiley-VCH and The Royal Society of Chemistry for permission of X-ray structures reproductions.

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