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Review

Stabilised phosphazides

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ABSTRACT

The Staudinger reaction between phosphines and azides provides a straightforward route to azaylides. Until the 1980s, it was thought that the putative intermediates of this reaction, namely phosphazides, were merely transient species that could be detected only by spectroscopic methods. This review summarises the achievements reported over the last 25 years on the preparation, structure and properties of phosphazides stabilised by substitution effects and/or coordination to transition metals or main group elements. Relevant computational studies on the Staudinger reaction are included.

1. Introduction

The reaction between azides [1] and phosphines leading to aza-ylides was discovered by Hermann Staudinger in 1919 [2] (Scheme 1). Applications in organic synthesis are numerous, such as for the preparation of C=N bonds (*via* the aza-Wittig reaction) [3] and also for chemical ligation of biologically relevant moieties [4]. Until the 1980s, it was thought that the putative intermediates

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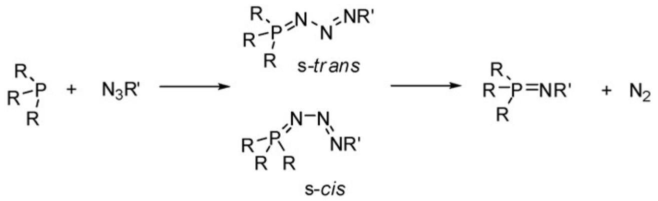


Scheme 1. The Staudinger reaction.

of this reaction, namely *phosphazides*, (Scheme 1) were merely transient species, unstable to elimination of dinitrogen at or below room temperature, that could be detected only by spectroscopic methods. However, it has since been shown that substitution effects and/or coordination of the N lone pairs to Lewis acid centres stabilise them sufficiently to permit their full structural characterisation (*vide infra*). There has been a resultant rapid growth in research in this area, which forms the focus of this review.

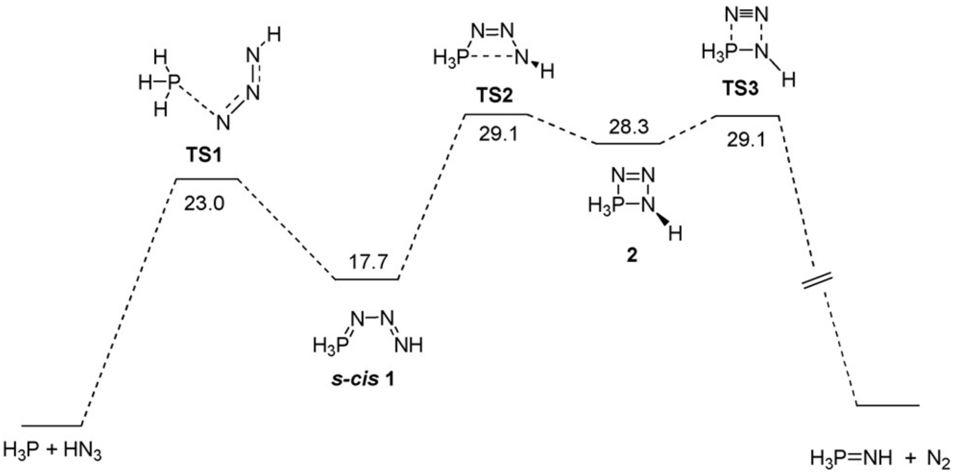
We therefore intend to discuss the preparation and properties of both free phosphazides that are stabilised by their inherent structural characteristics and those stabilised by coordination to transition metals or main group elements. Relevant computational studies will be included, along with our own recent photochemical isomerisation of N_α- to N_β-coordinated phosphazides. We will conclude with an analysis of current trends and some suggestions for future avenues of research in this field.

2. Computational studies

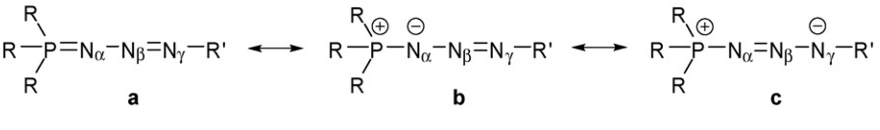
Although stable phosphazides have been known for more than 20 years, only recently have modern quantum methods provided firm theoretical insight into this area of research. The first computational mechanistic studies were carried out simultaneously and independently by Rzepa [5] and Grützmacher [6]. Their work predicts that the Staudinger reaction proceeds according to the mechanism shown in Scheme 2. Thus, nucleophilic attack of the phosphorus lone pair on the terminal nitrogen atom of the azide (N_α) leads to the formation of phosphazide ***s-cis* 1** in preference to ***s-trans* 1** [7]. Not only is ***s-cis* 1** calculated to be more stable (by about 6–9 kcal/mol), but also the reaction pathway leading to it is lower in energy. The greater stability of the s-*cis* isomer is somewhat paradoxical given that the vast majority of isolated phosphazides adopt the s-*trans* conformation in the solid state (*vide infra*).

The stability of ***s-cis* 1** is thought to arise from a favourable electrostatic interaction between the positively charged P atom and the negatively charged N_γ atom (Scheme 3), as substantiated by the rather short $P\cdots N_\gamma$ distance (2.40 Å), and the NBO atomic charges (P: 0.95, N_γ: −0.55) [6]. The second step of the Staudinger reaction is the cyclisation of the phosphazide ***s-cis* 1** to afford the four-membered cyclic intermediate **2** that subsequently extrudes dinitrogen with almost no energy barrier [8]. This pathway is lower in energy than the isomerisation of the s-*cis* to the s-*trans* phosphazide (by 5–10 kcal/mol for the parent compounds). Variations of the substituents such that the P atom was more electron-rich or the N-atom more electron-poor were both found to stabilise the s-*trans* phosphazide relative to its s-*cis* isomer. For R = OMe, R′ = H, the s-*trans* form was even found to be slightly favoured thermodynamically, although the s-*cis* isomer remained favoured kinetically [5].

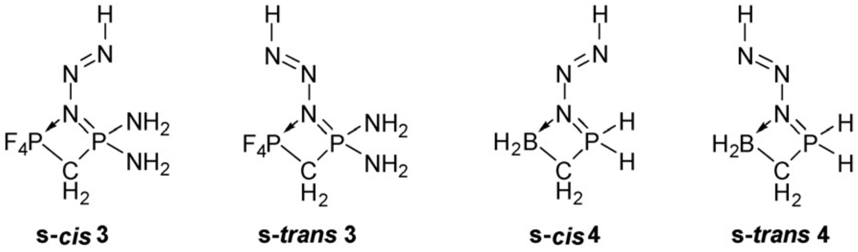
Furthermore, the group of Grützmacher hypothesised that the necessary change in hybridisation at the N atoms required for extrusion of dinitrogen could be hampered kinetically if the N-lone pair was involved in a donor–acceptor interaction, in this case with a suitably positioned electron-deficient P atom [6]. This was demonstrated experimentally and this aspect of the work will be detailed in Section 4.2 of this review. Additional calculations on the simplified model **3** suggested the s-*cis* form is once again more stable, but by only 3 kcal/mol, meaning that the s-*trans* form is *more* stabilised by the $N_\alpha \rightarrow P(V)$ interaction. Due to the expense of calculations on **3**, the still simpler P/B compound **4** was examined (Scheme 4). Once again, the s-*cis* form was found to be the more stable (by 5 kcal/mol). Decomposition of ***s-cis* 4** by loss of dinitrogen was still found to be very thermodynamically favourable (−46 kcal/mol), although there is a significant energy barrier to this process (20 kcal/mol vs. 8 kcal/mol for the parent system, at the same level of theory). These results are consistent with a kinetic stabilisation of s-*cis* phosphazides by the $N_\alpha \rightarrow B$ interaction.



Scheme 2. Potential energy surface for the Staudinger reaction computed by Rzepa (B3LYP/6-311G** level of theory, energies in kcal/mol, relative to the separated reactants).



Scheme 3. Limiting structures for phosphazides.



Scheme 4. Phosphazides stabilised by a donor–acceptor interaction.

Scheme 5. Alternative transition states for the first step of the Staudinger reaction.

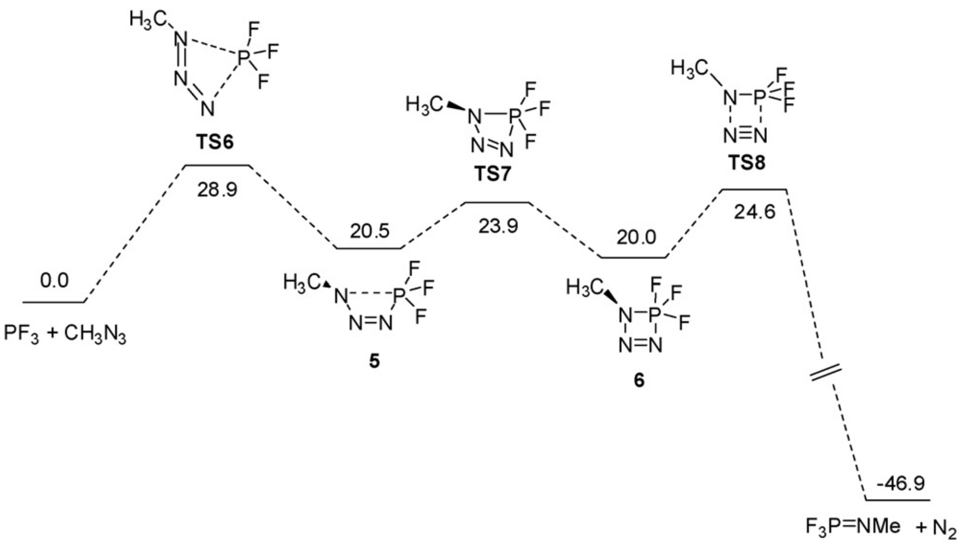
More recently, Tian and Wang reported a detailed mechanistic study of the Staudinger reaction [9]. Their results are in agreement with previous work, and reveal some new insights. In addition to a more detailed investigation of substitution effects, a possible mechanism involving initial nucleophilic attack of the phosphine on N_γ (the substituted nitrogen) leading to **TS4** was investigated, as was the likelihood of concerted attack of P at N_α and N_γ *via* **TS5** (Scheme 5).

NBO partial charge analysis confirmed a stabilising electrostatic interaction between the P and N_γ atoms in the transition state for the formation of the s-*cis* phosphazide **s-*cis* 1**, as proposed by Rzepa et al. [5] and Grützmacher et al. [6]. Interestingly, the reaction *via* initial nucleophilic attack on N_γ (**TS4**) was predicted to proceed along a lower energy pathway than that *via* formation of the s-*trans* intermediate. This is a one-step mechanism, with simultaneous attack of the phosphine and loss of dinitrogen. It is still a higher energy pathway than the formation of the s-*cis* phosphazide, which is therefore confirmed to be the most favoured pathway in the Staudinger reaction. The energies of transition states comparable to **TS2**, intermediate **2** and transition state **TS3** (Scheme 2) are found to be so close in energy that the elimination of nitrogen was predicted to occur in an essentially concerted step from the s-*cis* phosphazide **s-*cis* 1**, without the intermediacy of the four-membered heterocycle **2**.

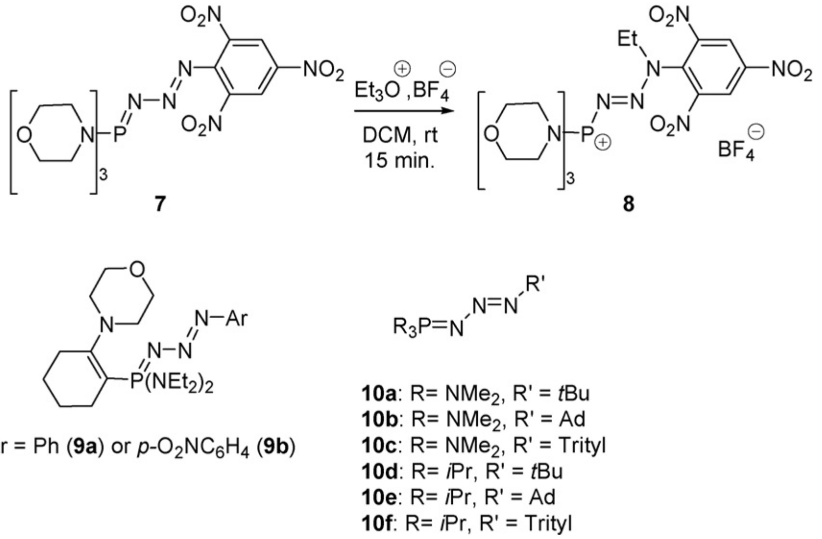
Substituent effects were found to be as expected given the donor/acceptor properties as compared to H. Thus, a drop in the initial transition state energy of ~10 kcal/mol was observed for most alkyl and aryl substituted systems. This is explained by a greater electrostatic interaction between the P and N_γ atoms as a result of the greater partial charges induced by the substituents.

A new reaction pathway was found for the reaction between PF_3 and N_3CH_3. A concerted attack of the phosphine on both N_α and N_γ atoms *via* transition state **TS6** which then leads to a closed intermediate **5** similar to that found on the 'conventional' pathway *via* the s-*cis* phosphazide (Scheme 6). Transition state **TS7**, intermediate **6** and transition state **TS8** essentially show a 1,3 P shift along the $N_\alpha N_\beta N_\gamma$ unit.

In addition, solvent effects were evaluated *via* the Onsager dipole interaction model. Accordingly, dimethyl sulfoxide (DMSO), as a polar solvent, was found to stabilise the intermediates and transition states more than the reactants, in line with the acceleration typically observed in polar solvents [10]. This solvent effect was more pronounced when electron-withdrawing substituents such as fluorine atoms were introduced at the P or N centre. These conclusions were recently further supported by *ab initio* molecular dynamic simulations using the Atom-centered Density Matrix Propagation (ADMP) approach [11]. For the initial attack of PH_3 to HN_3, the phosphorus atom first approaches simultaneously N_α and N_γ up to about 3.0 Å, and then moves toward N_α as the result of electrostatic and covalent interactions. Moreover, the variation of energy along the potential surface was found to correlate intimately and positively with the change of the average polarisability.



Scheme 6. Potential energy surface for the Staudinger reaction of PF_3 and CH_3N_3 (energies in kcal/mol, relative to the separated reactants).



Scheme 7. Some electronically and sterically stabilised phosphazides.

3. Free phosphazides

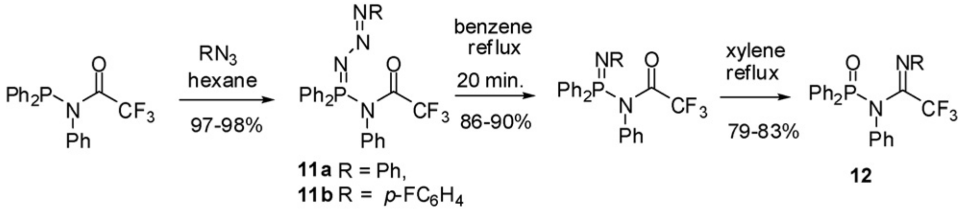
Having examined the structural and mechanistic insights provided by the recent computational studies, it is now appropriate to discuss some of the reported experimental data on isolated phosphazides within this theoretical framework, beginning with those which are *not* involved in coordination to transition metals or main group elements.

3.1. Open chain phosphazides

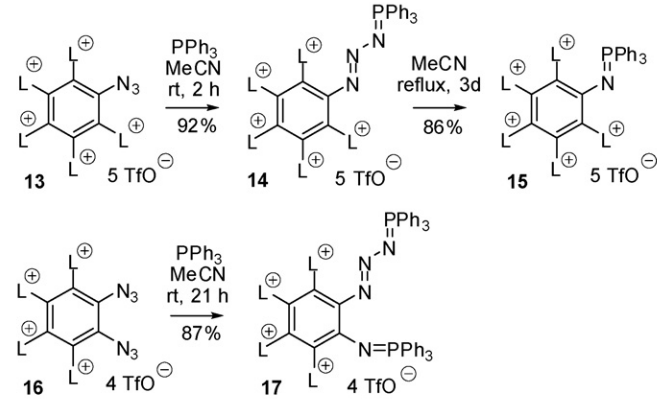
3.1.1. Phosphazides derived from classical phosphines

A number of phosphazides have been prepared from classical phosphines in cases where certain structural features impart unusual stability. In the early-1980s, Russian workers carefully examined the effects of the substituents at phosphorus and nitrogen [12]. Phosphazides Ph_3PN_3Ar were found to be stable at room temperature only when the two *ortho*-positions of the aryl group are substituted by electron-withdrawing groups (typically NO_2). In addition, the presence of morpholino substituents at phosphorus was found to significantly accelerate the formation of phosphazides $(EtO)_{3-n}(\text{morpholino})_nPN_3Ph$, and to simultaneously slow down their decomposition. This study culminated with the first structural characterisation of a free phosphazide from the reaction of the tris(morpholino)phosphine with 2,4,6-trinitrophenylazide [13]. Phosphazide **7** was isolated as red crystals stable up to 155–158 °C, but the expected iminophosphorane could not be authenticated among the decomposition products. In the solid state, the PN_3 skeleton adopts an s-*trans* conformation and manifests a significant contribution from the zwitterionic resonance form **c** (Scheme 3), as favoured by the strongly electron-withdrawing 2,4,6-trinitrophenyl group at nitrogen. The PN_α bond is slightly longer than those formed with the morpholino substituents (1.638 Å vs. 1.623–1.631 Å) and the $N_\alpha N_\beta$ distance (1.298 Å, nominally a single-bond) is shorter than the $N_\beta N_\gamma$ distance (1.316 Å, nominally a double bond) (Scheme 7). The increased electron density at N_γ was further illustrated by the formation of the corresponding γ-alkylated salt **8** upon reaction of **7** with triethyloxonium tetrafluoroborate [13,14]. The sterically hindered phosphazides **9a** and **9b** were also isolated from the corresponding Staudinger reactions [15]. The stability of **9a**, derived from phenyl azide, demonstrates that the nitro groups are not essential for phosphazide stability if the phosphine is appropriately chosen. In both of these examples, the PNNN unit adopts an s-*trans* conformation. Compared with **7**, the presence of a phenyl instead of picryl substituent at nitrogen results in **9a** in a slightly shorter PN_α bond (1.623 Å) and in greater double bond character between $N_\beta N_\gamma$ than between $N_\alpha N_\beta$ (as judged by the respective bond distances of 1.273 and 1.324 Å). The presence of sterically demanding substituents on the PN_3 skeleton was suspected to disfavour the isomerisation of s-*trans* into s-*cis* phosphazides and to prevent the formation of the four-membered ring structure responsible for the dinitrogen extrusion [16].

Schmutzler was able to illustrate the general stability of phosphazides derived from tris(dialkylamino)phosphines and hindered azides by the preparation and isolation of derivatives **10a–c** [17]. Triisopropylphosphine was employed in the preparation of the analogous series **10d–f**, in which the bulk of the substituents is largely responsible for the phosphazide stability, making the steric requirements for extrusion of nitrogen prohibitive (Scheme 7). The solid-state structure of **10c** reveals the s-*trans* conformation of the PN_3 skeleton, and very much resembles that of **9a** (PN_α 1.620 Å, $N_\alpha N_\beta$ 1.376 Å $N_\beta N_\gamma$ 1.261 Å).



Scheme 8. Synthesis and reactivity of phosphazides **11** derived from *N*-(diphenylphosphino)-trifluoroacetamides.



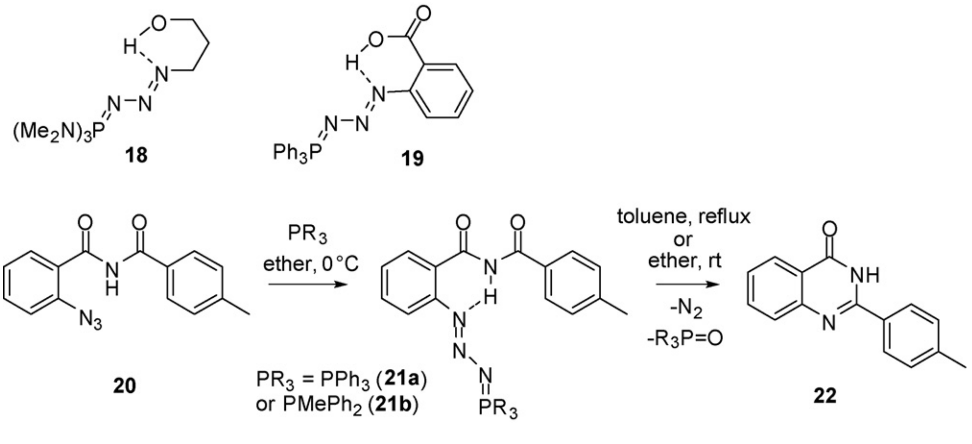
Scheme 9. Stable phosphazides **14** and **17** derived from polycationically substituted phenyl azides.

Recently, introduction of a *N*-trifluoroacetamido group at phosphorus was reported to also impart significant stability, and phosphazides **11a** and **11b** derived from simple aryl azides were found to be stable for several days in the absence of solvents. Upon heating to 40–50 °C, they readily eliminate dinitrogen to afford the corresponding phosphazenes that further rearrange into *N*-phosphorylated trifluoroacetamidines **12** *via* intramolecular aza-Wittig reaction when heated to reflux for a few hours in xylene (Scheme 8) [18].

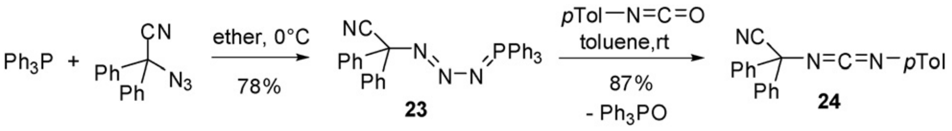
Weiss et al. recently investigated the stability of phosphazides featuring polycationically substituted phenyl rings at nitrogen. The *in situ* generated azide **13** readily reacts with triphenylphosphine within 2 h at room temperature to afford the corresponding phosphazide **14** in 92% yield (Scheme 9). The structure of **14** was unambiguously established by NMR spectroscopy, FAB mass spectrometry and elemental analysis. Phosphazide **14** slowly extrudes dinitrogen in refluxing acetonitrile to give the corresponding phosphazene **15** in 86% yield after 3 days (decomposition starts at 34 °C in the solid state) [19]. Upon reaction with two equivalents of triphenylphosphine under the same conditions, the related *ortho*-diazide **16** does not lead to the *ortho*-bisphosphazide but to a mixed adduct **17** featuring one phosphazide group and one phosphazene unit. Compared with the monophosphazide **14**, the spontaneous extrusion of one dinitrogen molecule most likely results from the reduction of both steric hindrance (one stiff DMAP ligand is substituted by a more flexible phosphazide unit) and electrostatic stabilisation (the number of cationic ligands per phosphazide unit decreases from five to two).

The presence of an intramolecular hydrogen bond can also confer special stability upon phosphazides, as first illustrated crystallographically by Freeman and co-workers [20]. Reaction of 3-azidopropan-1-ol and tris(dimethylamino)phosphine led to compound **18** (Scheme 10). Despite its instability above −10 °C, crystals of phosphazide **18** suitable for an X-ray diffraction study could be obtained. In the solid state, the PN_3 skeleton adopts an s-*trans* conformation and there is an O–H···N_γ hydrogen bond (O···N distance: 2.845 Å, OHN_γ angle: 173°). A similar situation was found in the phosphazide **19** derived from triphenylphosphine and 2-azidobenzoic acid [21]. The X-ray diffraction study [21b] revealed, as expected, even stronger hydrogen bonding (O···N distance: 2.525 Å, OHN_γ angle: 162°). In line with the mechanistic issues detailed above, the presence of the H-bond probably impedes the isomerisation of the s-*trans* phosphazide into the s-*cis* conformer necessary for extrusion of dinitrogen. Furthermore, Molina and co-workers isolated the phosphazide **21a** following reaction of triphenylphosphine with azido imide **20** (Scheme 10) [22]. Subsequent conversion of **21a** to the 4(3*H*)-quinazolinone **22** by extrusion of dinitrogen and intramolecular aza-Wittig reaction was achieved only by prolonged heating in toluene. As the result of reduced steric protection, a similar process spontaneously occurs at room temperature for phosphazide **21b**. Although no X-ray diffraction study could be performed on either **21a** or **21b**, the retention of N_2 was established by mass spectrometry and the presence of the H-bond was subtantiated by the broad, strongly absorbing N–H stretch in the IR spectra at 3500–2900 cm^{-1}. Both H-bonding and steric effects thus contribute to the stability of this series of phosphazides.

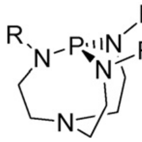
An unusual (and so far the only) example of a free acyclic s-*cis* phosphazide **23** was isolated from the reaction of triphenylphosphine and α-azido diphenylacetonitrile (Scheme 11) [23]. The PN_α,



Scheme 10. Phosphazides stabilised by hydrogen bonding.



Scheme 11. Synthesis and reactivity of the only free acyclic s-*cis* phosphazide **23**.



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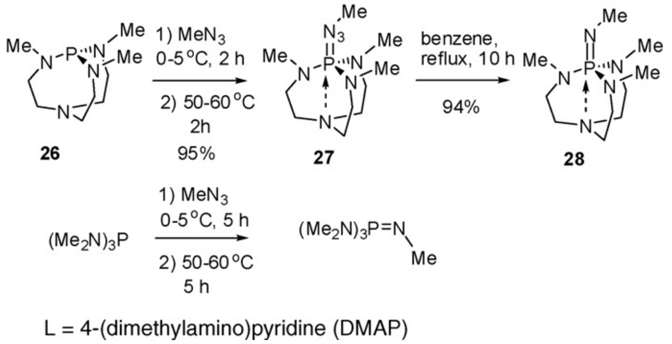
Scheme 12. The proazaphosphatrane core as developed by Verkade.

$N_{\alpha}N_{\beta}$ and $N_{\beta}N_{\gamma}$ bond lengths (1.641, 1.339 and 1.262 Å, respectively) suggest extensive electronic delocalisation along the PN_3 fragment. The PN_{γ} distance (2.800 Å) significantly exceeds the sum of covalent radii (1.78 Å), but remains noticeably shorter than the sum of the van der Waals radii (3.55 Å). In addition, the tetrahedral environment around the phosphorus atom is strongly distorted towards a trigonal bipyramid with a phenyl group and N_{γ} in apical positions. Phosphazide **23** decomposes in refluxing benzene to give a complex mixture from which the expected phosphazene could not be detected. However, it readily reacts at room temperature with *p*-tolylisocyanate to afford the corresponding carbodiimide **24**. This demonstrates that phosphazides themselves can undergo aza-Wittig reaction, probably *via* six-membered cycloadducts.

3.1.2. Phosphazides derived from proazaphosphatranes

Many of the stable phosphazides covered so far are derived from tris-(dialkylamino)phosphines. Donation of electron density from the N lone pairs to phosphorus is a contributing factor in the increased stability of these phosphazides as compared to those derived from trialkyl or triaryl phosphines. A highly significant structural variation of these aminophosphines is achieved by their incorporation into cage systems, as pioneered by Verkade with *proazaphosphatranes* **25** (Scheme 12) [24].

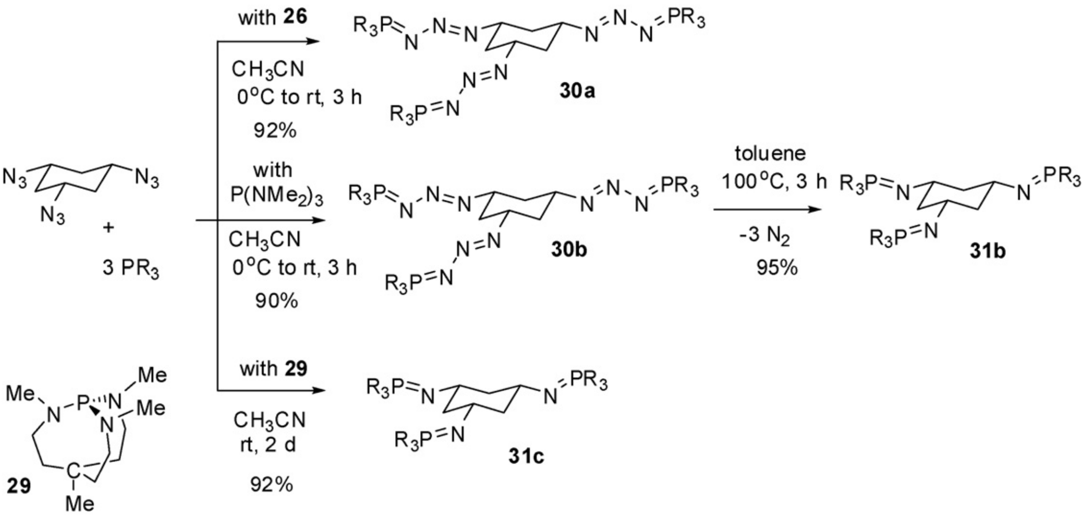
The fact that the three amino substituents are “tied back” has profound consequences for the reactivity of this class of compounds compared to their acyclic analogues. For example, they are more basic than the acyclic systems partly because of electron donation from *all three* N lone pairs to phosphorus. This is not the case in conformationally less restricted examples, where only two of the nitrogen atoms donate electron density to the phosphorus atom, while the third amino substituent acts merely as an electron-withdrawing group [25]. In addition, the lone pair on the axial nitrogen atom may engage in transannular bonding upon quaternarisation of the phosphorus atom.



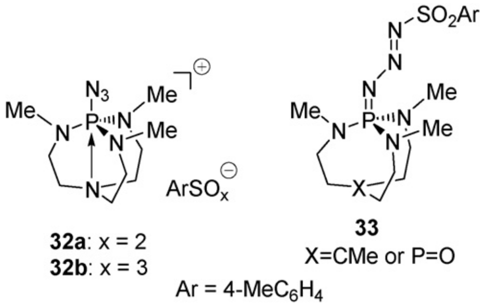
Scheme 13. Comparison of a proazaphosphatrane and related acyclic tris(amino)phosphine in the Staudinger reaction.

Similar effects also confer great stability on phosphazides derived from these systems by reducing the partial positive charge on the phosphorus atom. Hence, phosphazide **27** could be isolated in nearly quantitative yield from the reaction of the permethylated proazaphosphatrane **26** with methyl azide (Scheme 13) [24]. Crystallographic data could not be obtained, but its structure was established by multi-nuclear NMR spectroscopy and mass spectrometry. Furthermore, heating **27** for 10 h in refluxing benzene induces the elimination of dinitrogen and cleanly affords the corresponding phosphazene **28**. The critical role of the cage structure and transannular nitrogen atom is clearly substantiated by the direct formation of the phosphazene $(Me_2N)_3P{=}N{-}Me$ when tris(dimethylamino)phosphine is reacted with MeN_3 under the same conditions.

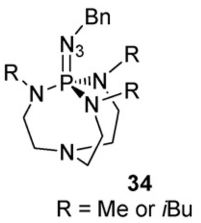
More insight into the influence of the cage structure was subsequently obtained by comparing the behaviour of the three related phosphines **26**, $(Me_2N)_3P$ and **29** toward tris-1,3,5-azidocyclohexane (Scheme 14) [26]. Both trisphosphazides **30a** and **30b** could be readily isolated from room temperature reactions, but only **30b** could be decomposed thermally into the corresponding trisphosphazene **31b**. The trisphosphazide **30a** is thermally stable when refluxed in toluene for 24 h and when heated in neat at 100 °C under vacuum (0.5 Torr, 10 h). Crystals suitable for X-ray diffraction analysis were grown from hot acetonitrile. In the solid state, all three PNNN units adopt the s-*trans* conformation. In addition, all of the equatorial nitrogen atoms are in essentially planar envi-



Scheme 14. Trisphosphazides from 1,3,5-trisazidocyclohexane.



Scheme 15. The effect of a transannular lone pair on the reaction of cage trisaminophosphines with tosyl azide.

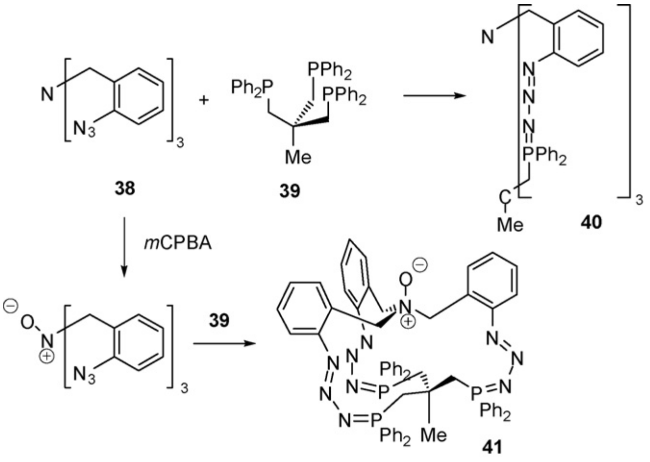


Scheme 16. Structurally characterised monophosphazides derived from proazaphosphatranes and benzyl azide.

ronments, indicating N → P electron donation, but the rather long PN_{ax} distances (3.06–3.16 Å) suggest weak, if any, transannular interaction. Strikingly, the related cage trisaminophosphine **29** free of axial nitrogen directly afforded the trisphosphazene **31c** under the same conditions, further demonstrating that subtle variations in the electronic and steric properties may dramatically influence the stability of phosphazides.

The proazaphosphatrane **26** forms an azidophosphonium salt **32a** upon reaction with tosyl azide, whereas the related bicyclic phosphines, which lack a transannular N-lone pair, afford stable *covalent* phosphazides **33** (Scheme 15) [27]. The ionic character of **32a** was attributed to the presence of a transannular N → P interaction, as evidenced structurally on the related sulfonate salt **32b** obtained by atmospheric oxidation (PN_{ax} 1.940–1.945 Å).

Finally, additional structural data were recently reported for the two phosphazides **34** derived from benzyl azide (Scheme 16) [28]. Both compounds adopt an s-*trans* conformation and the key PN_{α}, $N_{\alpha}N_{\beta}$ and $N_{\beta}N_{\gamma}$ bond lengths (1.619–1.620 Å, 1.354–1.360 Å and 1.260–1.267 Å, respectively) are very similar to those observed in the trisphosphazide **30a**. An interesting difference between the two phosphazides is that for R = Me, there is a *cis* arrangement around the $N_{\beta}N_{\gamma}$ bond, whereas for R = *i*Bu, there is a *trans* arrangement. At the moment, it is not clear if this isomerism is dictated by the alkyl group at the equatorial nitrogen atoms, or by crystal-packing forces.



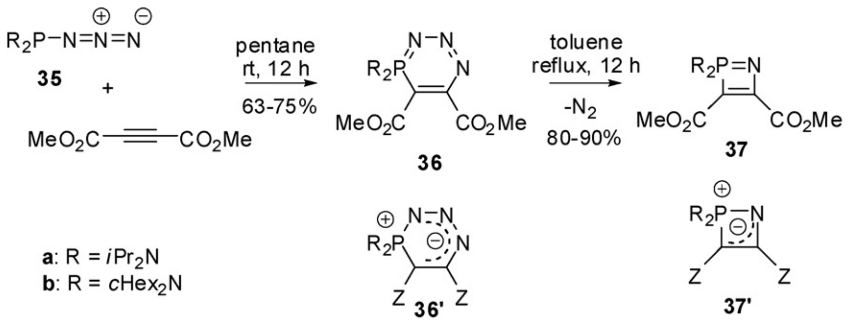
Scheme 18. Macrocyclic polyphosphazides derived from *ortho*-substituted tris(azides).

3.2. Cyclic phosphazides

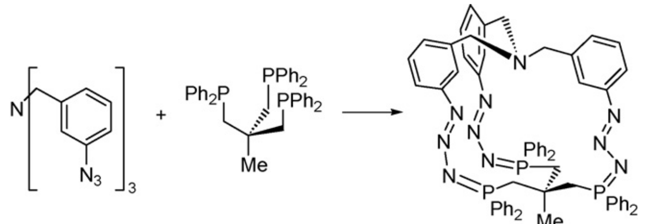
In early studies, Bertrand et al. demonstrated that phosphazides may be stabilised by incorporation of the PN_3 unit into cyclic 6π electron systems. Taking advantage of the peculiar stability of the bisaminophosphino azides **35**, the cyclic phosphazides **36a** and **36b** were readily obtained by 1,4-dipolar cycloadditions with dimethyl acetylenedicarboxylate (Scheme 17) [29,30]. The X-ray diffraction study carried out on **36a** revealed a very flat boat conformation of the six-membered ring. The s-*cis* conformation is obviously imposed by the cyclic structure. The endocyclic bond lengths revealed extensive electron delocalisation, suggesting that these phosphazides are best described by the non-aromatic charge-separated resonance form **36**′. Both the geometric constraints and π-delocalisation disfavour the loss of dinitrogen, so that the phosphazides decompose only in refluxing toluene. The resulting phosphazenes **37**, namely 1,2λ^5-azaphosphetes, were isolated in high yields and fully characterised. Due to the interrupted π delocalisation (form **37**′), they escape from antiaromaticity and are rare examples of stable four-π-electron rings [31].

3.3. Macrocylic trisphosphazides

Alajarín et al. have pioneered the synthesis of polyphosphazides derived from tris(azides) and trisphosphines (Scheme 18) [32]. The reaction is quite general and results in a spectacular build-up of complexity. The macrocyclic products show considerable variation



Scheme 17. *s-cis* phosphazides incorporated into delocalised 6π electron cyclic systems.



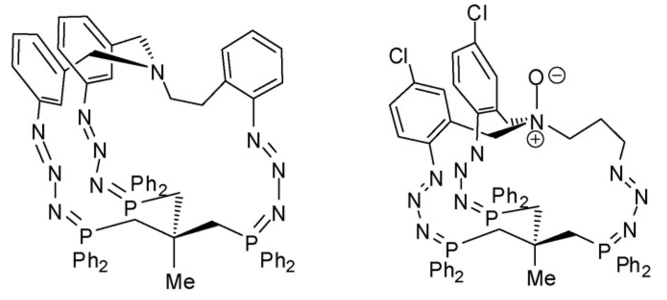
42 **39** **43**

Scheme 19. Macrocyclic polyphosphazides derived from a *meta*-substituted tris(azide).

in structure according to the substitution pattern of the reactants. The first macrobicyclic tris(phosphazide) **40** was prepared by reaction of the tris(*o*-azidobenzyl)amine **38** and trisphosphine **39**, a well-known ligand for transition metals [33]. However, this compound was found to be rather unstable and crystals suitable for X-ray diffraction analysis could not be obtained. In order to prevent inversion of configuration at the apical nitrogen atom, the *N*-oxide of **38** was prepared by treatment with *m*-chloroperbenzoic acid (*m*CPBA). The product **41** of its reaction with **39** was found to be sufficiently stable for a crystal structure to be obtained. In this instance, the three PN_3 units all adopt an s-*cis* conformation and the molecule is C_3-symmetric in the solid state, resulting in a three-blade propeller shape. Such symmetry is also likely in solution in this case, as substantiated by the single sharp peak observed in the ^{31}P NMR spectrum ($\delta = -1.4$ ppm at 298 K). No significant variations in any of the NMR spectra were observed from 203 to 330 K, suggesting that the compound is conformationally stable in this temperature range.

An interesting structural change is induced by the use of the *meta*-substituted tris(azide) **42** in place of the *ortho*-compound **38** used above [34]. In this case, formation of the *N*-oxide was not required for the preparation of a stable derivative. Thus, tris(*meta*-azidobenzyl)amine **42** was reacted with trisphosphine **39** to give the tris(phosphazide) **43** (Scheme 19). In solution the compound **43** had spectroscopic data consistent with a chiral C_3-symmetric structure related to that found for **41**. However, a broad singlet at $\delta = +4$ ppm in the ^{31}P spectrum suggested a more fluxional system than in **41**. An X-ray diffraction study led to the discovery of two major differences between **41** and **43** in the solid state. First, the configuration at the apical nitrogen in **43** is inverted compared to **41**, with the lone pair pointing towards the interior of the macrocyclic cage, and second, one of the PNNN units adopts an s-*trans* conformation. This was therefore the first polyphosphazide found to contain phosphazides of different geometries. The molecule is nevertheless *pseudo*-C_3-symmetric and, like **41**, has a propeller-like appearance. The magnetic inequivalence of the phosphorus atoms was further demonstrated in solution by low temperature ^{31}P NMR spectroscopy. The two distinct signals observed at $\delta = +2$ and +23 ppm on cooling to 243 K were tentatively assigned to the s-*cis* and s-*trans* PNNN units, respectively.

More detailed investigations by this group concerning substitution effects were subsequently carried out [35]. Few new major insights were provided by the substituted systems, as an increase in steric bulk either in the *ortho*-position of the azide or on the benzylic carbon atoms led to a decrease in the stability of the tris(phosphazide) adducts [35a]. Attempts to form diastereomerically pure products expected from reactions of racemic chiral tris(azides) and triphos **39**, were disappointingly not successful, further demonstrating the sensitivity of these systems to subtle steric variation at the benzylic carbon. The *ortho*/*meta* substitution of the tris(azidobenzyl)amine skeleton was found to also affect the thermal behaviour of the resultant tris(phosphazide).



44 **45**

Scheme 20. Macrocyclic polyphosphazides derived from more flexible non-*C*3-symmetric tris(azides).

Indeed, *ortho*-substituted compounds decompose in solution to give complex mixtures as a result of reversible dissociation of the phosphazide arms into phosphine and azide, [35a] whereas the *meta*-substituted derivatives generally undergo triple extrusion of dinitrogen upon heating for several hours at 60 °C to afford the corresponding cage tris(phosphazenes) with retention of the three-blade propeller structure [35b,d]. In addition, variation of the tris(azide) component to non-C_3-symmetric precursors has allowed to extend the variety of cage tris(phosphazides) to compounds featuring more flexible skeletons, as illustrated by **44** and **45** (Scheme 20) [35c].

Recently, macrocyclic tris(phosphazides) were shown to readily undergo reversible exchange of their tripodal components via a dynamic disassembly–reassembly process. Taking advantage of the propensity of the phosphazide moiety to dissociate into its phosphine and azide precursors, the tris(phosphazide) **40** was quantitatively converted into the less sterically congested and more thermodynamically stable derivative **43** by displacement of the *ortho*-substituted tris(azide) **38** with its *meta*-substituted analog **42** [34c].

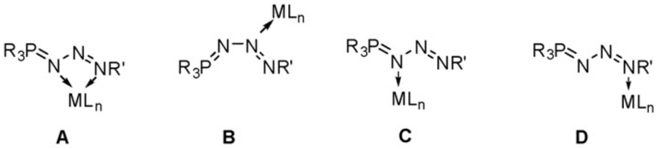
4. Coordinated phosphazides

4.1. Transition metal complexes

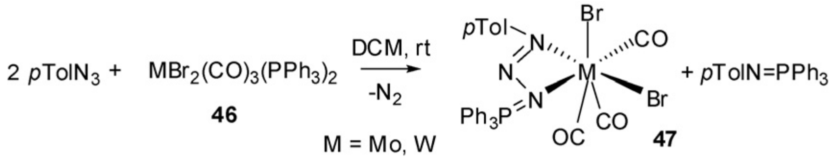
Although phosphazides have been known to act as ligands for transition metals for some time, their use for this purpose is relatively underexplored, probably due to their reputation for instability. The four different coordination modes evidenced so far are given in Scheme 21. The two possible preparative routes, namely (i) formation of the phosphazide in the coordination sphere of a transition metal and (ii) coordination of a preformed phosphazide to a transition metal, have each been exploited and will be successively presented hereafter.

4.1.1. Phosphazides generated in the coordination sphere of transition metals

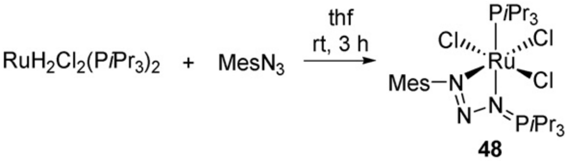
More than 25 years ago, Haymore and co-workers prepared the tungsten and molybdenum complexes **47** by reaction of the bisphosphine complexes **46** with an aromatic azide (Scheme 22)



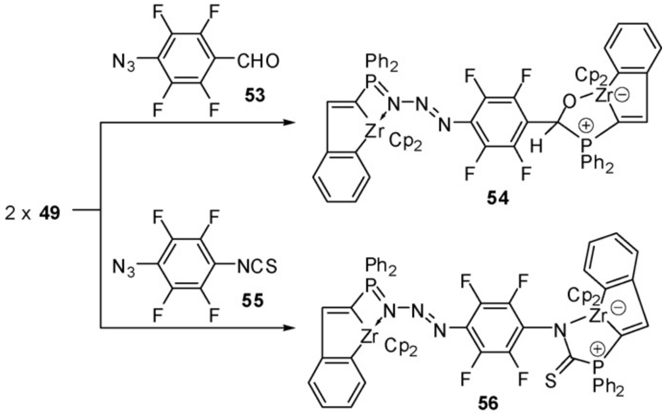
Scheme 21. The four coordination modes evidenced so far for phosphazides.



Scheme 22. Formation of molybdenum and tungsten phosphazide complexes.



Scheme 23. Formation of the Ru(III) phosphazide complex **48**.



Scheme 25. Bimetallic zwitterionic phosphazide complexes.

[36]. Two molecules of azide are consumed for every phosphazide complex produced. Careful control of the reaction conditions was required to obtain an acceptable yield of complexes **47**, since the phosphazide was readily displaced from the metal by the phosphazene by-product at extended reaction times. A crystal structure was obtained for the tungsten complex. The phosphazide ligand adopts the s-*trans* conformation and chelates the metal through N_α and N_γ, forming a quasi-planar four-membered metallacycle (coordination mode **A**). The metal is seven coordinate and adopts a capped octahedron geometry distorted by the NN chelate. The WN_α and WN_γ distances (2.163 and 2.220 Å) are indicative of normal MN single bonds, while the PN_α, $N_\alpha N_\beta$ and $N_\beta N_\gamma$ bond lengths (1.672, 1.364 and 1.279 Å) suggest significant delocalisation within the PN_3 unit, rather than strict conformity to one of the possible limiting structures. Chelation explains the thermal stability of these complexes, as the appropriate geometry for extrusion of dinitrogen is unattainable as long as the ligand remains bound to the metal.

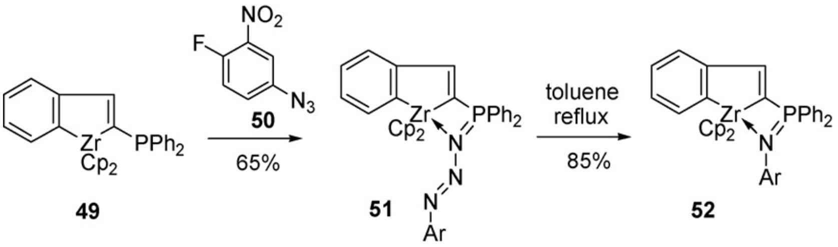
Following the same strategy, Hursthouse and co-workers isolated the paramagnetic Ru(III) phosphazide complex **48** upon reaction of the Ru(IV) complex $[RuH_2Cl_2(PiPr_3)_2]$ with mesityl azide (Scheme 23) [37]. Although no other product was detected, complex **48** was isolated in 45% yield, suggesting that a disproportionation reaction accounts for the reduction of ruthenium. In this case also, the phosphazide adopts an s-*trans* conformation and coordinates through N_α and N_γ, resulting in a distorted octahedral arrangement around the metal with *mer* chloride ligands. In contrast to the tungsten complex **47**, the phosphazide is unsymmetrically coordinated in **48** (RuN_α and RuN_γ: 2.151 and 1.671 Å, respectively), but the PN_α, $N_\alpha N_\beta$ and $N_\beta N_\gamma$ bond lengths (1.672, 1.361 and 1.286 Å) are very similar to those of **47**, suggesting little influence on the electronic delocalisation within the phosphazide.

Majoral et al. have developed the preparation of zirconated phosphines **49** and employed them as novel donor–acceptor compounds in reactions with organic substrates [38]. To extend their utility further, their formal [3 + 1] cycloaddition with azides was investigated, leading to the discovery of yet another coordination mode. Reaction of azide **50** with **49** led to the isolation of phosphazide complex **51** (Scheme 24), in which only the N_α atom is coordinated to the metal centre (ZrN_α: 2.401 Å, coordination mode **B**). The phosphazide also adopts here the s-*trans* conformation, and the PN_α, $N_\alpha N_\beta$ and $N_\beta N_\gamma$ bond lengths (1.653, 1.338 and 1.294 Å) only marginally differ from those found previously in complexes **47** and **48**. Dinitrogen is produced only by heating a solution of **51** to reflux in toluene, giving rise to the expected phosphazene complex **52**. Interestingly, the choice of azide has a profound effect on the course of these complexation reactions, with diphenyl phosphorylazide and trimethylsilyl azide directly giving rise to coordinated phosphazenes similar to **52**.

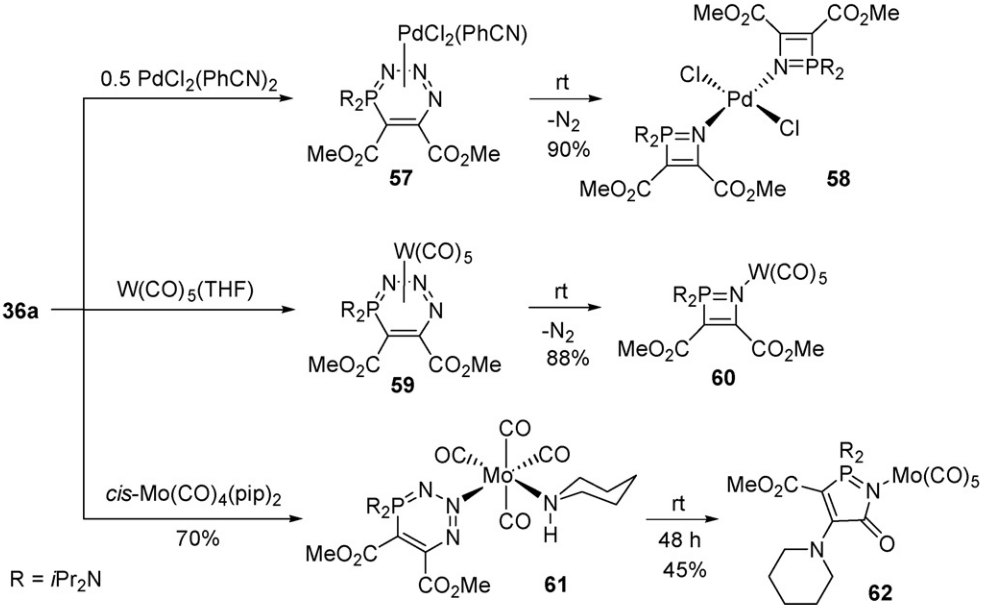
As an extension of this chemistry, bimetallic complexes derived from azido aldehyde **53** and azidoisothiocyanate **55** were also prepared from **49** (Scheme 25). Both phosphazide complexes **54** and **56** were isolated and found to possess similar thermal stability to that found for **51**, although the corresponding phosphazenes were not recovered from these decomposition reactions.

4.1.2. Coordination of preformed phosphazides

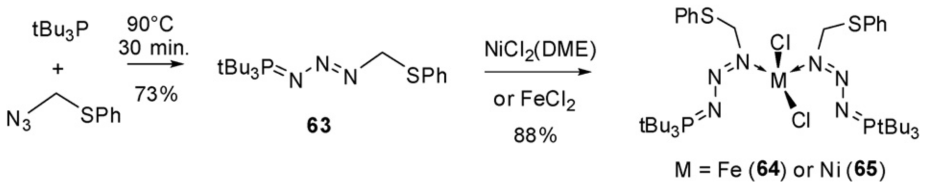
Taking advantage of the peculiar stability of the cyclic s-*cis* phosphazide **36a**, Bertrand and co-workers studied its coordination to metal fragments (Scheme 26) [39]. In the presence of metal



Scheme 24. Preparation of a phosphazide complex involving $N_\alpha \rightarrow Zr$ interaction.



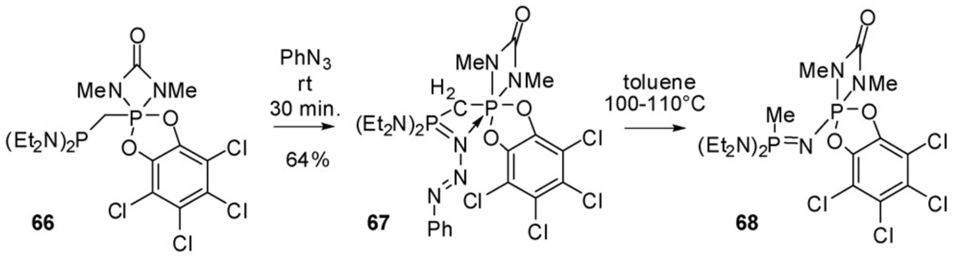
Scheme 26. Some complexes derived from the cyclic s-*cis* phosphazide **36a**.



Scheme 27. Synthesis and coordination of the (phenylthio)phosphazide **63**.

salts, **36a** tended to eliminate dinitrogen, so that palladium- and tungsten-bound phosphazides **57** and **59** could only be characterised by ^{31}P NMR spectroscopy, on the way to the corresponding azaphosphete complexes **58** and **60**. However, the molybdenum complex **61** could be isolated and crystallised. The previously unseen coordination mode **C** involving the less sterically hindered N_β atom was observed in the solid state (MoN_β: 2.258 Å). In addition, a hydrogen bond was found between the N_γ atom of the phosphazide and the NH of the piperidine ligand. Complexation does not have a significant effect on the endocyclic bonds of the phosphazide ligand (the PN_α, $N_\alpha N_\beta$ and $N_\beta N_\gamma$ bond lengths vary by less than 0.02 Å). Although stable in the solid state, complex **61** slowly decomposed in solution to afford the five-membered ring complex **62**. In contrast to what is usually encountered, complexation has a destabilising effect on phosphazide **36a**, and since even a catalytic amount of $PdCl_2$ induces the loss of nitrogen at room temperature, this is an efficient and mild route to the azaphosphete **37a** (Scheme 17).

In 2001, Stephan reported another example of coordination of a stable phosphazide [40]. In the course of this work, it was discovered that free (phenylthio)phosphazide **63** is stable to loss of nitrogen at >100 °C, presumably for steric reasons (the reaction of P_iPr_3 with N_3CH_2SPh proceeds directly to the phosphazene). Structural data were not obtained and it is included here for continuity with its coordination chemistry. Thus, reaction of **63** with $FeCl_2$ or $NiCl_2$(DME) gave rise to the paramagnetic bis(phosphazide) complexes **64** and **65** (Scheme 27). In contrast to the complexes **47** and **48** prepared by Haymore and Hursthouse, coordination of the phosphazides occurs essentially *via* the N_γ atom (coordination mode **D**), with only very weak interactions between the metal and N_α atoms (FeN_γ: 2.101 Å, FeN_α: 2.998 Å; NiN_γ: 2.024 Å, NiN_α: 2.712 Å). This difference may be related to the smaller size of Ni and Fe compared to W and Ru, resulting in greater sensitivity to the steric bulk of the phosphazide ligand in the former systems. These are the only examples so far in which a preformed open-chain phosphazide has been used to form metal complexes.



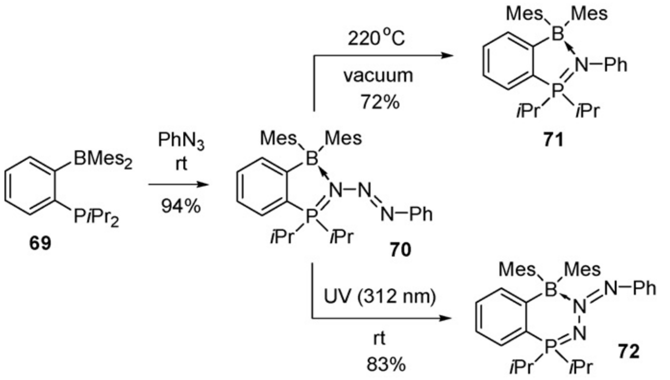
Scheme 28. A *s-cis* phosphazide stabilised by an adjacent P(V) functionality.

4.2. Main group complexes

As mentioned in Section 2, the group of Grützmacher evidenced computationally the effect of a nearby electron-acceptor on phosphazide stability [6]. This was also illustrated experimentally by the reaction of **66**, featuring both P(III) and P(V) centres, and phenyl azide, leading to the stable phosphazide **67** (Scheme 28). This compound was isolated and successfully studied by X-ray crystallographic analysis. N_α forms a dissymmetric bridge between the two P atoms [N_αP(V): 1.812 Å, N_αP(III): 1.626 Å], resulting in an almost planar four-membered heterocycle. The PN_3 adopts an s-*cis* conformation, with a PN_γ distance of 2.977 Å. Heating of the compound to about 100 °C led not to simple loss of dinitrogen but to aza-ylide **68**, a reaction for which the mechanism is not yet understood.

Bourissou and co-workers have investigated the chemistry of so-called ambiphilic ligands containing both donor and acceptor groups. A series of phosphine-boranes have been prepared and found to have both interesting coordination properties with respect to transition metals [41] and the ability to trap reactive intermediates [42]. Reaction of phenyl azide with phosphine–borane **69** led to the formation of a stable Staudinger adduct **70** (Scheme 29).

The X-ray diffraction study showed the phosphazide in the s-*cis* conformation and the $N_\alpha \rightarrow B$ coordination mode, despite the encumbered environment around the boron (BN_α: 1.649 Å). This effect was quantified by a notable pyramidalisation of the geometry at boron ($\Sigma_\alpha = 340°$, ^{11}B NMR: $\delta = 2.1$ ppm). Loss of dinitrogen occurred only at the melting point of the solid under vacuum to give the phosphazene **71** in 72% isolated yield. While investigating photochemical conditions for loss of dinitrogen under milder conditions, it was found that irradiation of **70** at 312 nm led to the formation of a new product with a markedly different ^{31}P NMR chemical shift from the starting material ($\delta = +34$ ppm vs. $\delta = +61$ ppm). The products were found to be in a photostationary equilibrium (about 15:85), and at low temperature it was possible to crystallise the major isomer. An X-ray diffraction study allowed the identification of this compound as the isomerised material **72**, which features $N_\beta \rightarrow B$ coordination and has the phosphazide in the s-*trans* conformation. The geometry of the N=N double bond has also changed its configuration from *E* to *Z*. This is the first example of the direct interconversion of phosphazide isomers [42a]. Although the N_β isomer could not be cleanly converted back to the N_α form, neither thermally nor photochemically, the generality and eventual reversibility of the unusual photoisomerisation process of such heterodienes was demonstrated for the related phosphazine adducts **73** and **74** derived from ethyl diazoacetate (Scheme 30).



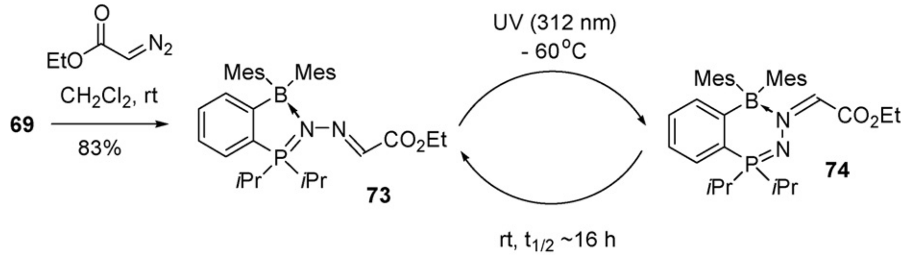
Scheme 29. A phosphazide stabilised by an adjacent borane group, and its photoisomerisation.

5. Synthetic applications

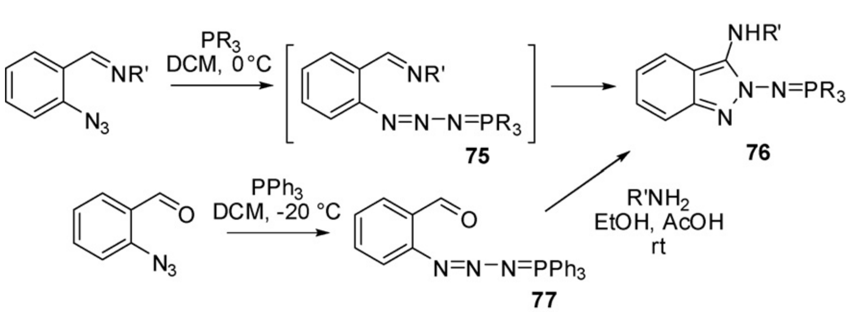
In this last section, the few studies dealing with the synthetic applications of phosphazides, rather than as transient precursors of the corresponding aza-ylides, will be discussed.

5.1. Synthesis of 2H-indazole derivatives

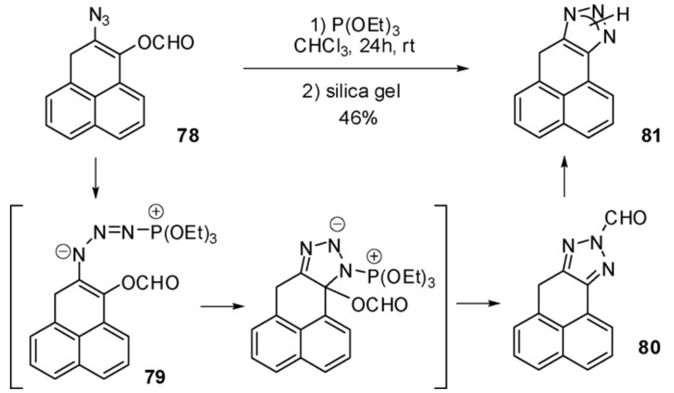
Molina et al. observed an unusual reaction between *o*-azidobenzaldimines and phosphines (Scheme 31) [43]. Before extruding dinitrogen, the transient phosphazides **75** are trapped intramolecularly *via* a formal heterocyclisation of the 1,2,6-triazahexatriene skeleton. After aromatisation, phosphazenes **76**



Scheme 30. Synthesis and isomerisation of a phosphazine.



Scheme 31. Formation of 2*H*-indazole derivatives from the heterocyclisation of 1,2,6-triazahexatrienes.



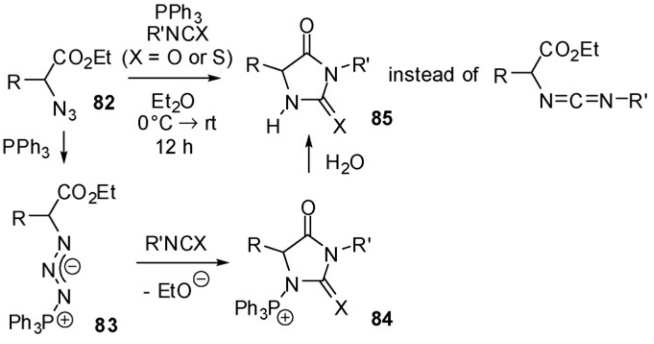
Scheme 32. Triazole formation via 1,5-electrocyclisation of the vinyl phosphazide intermediate **79**.

derived from 2,3-diamino-2*H*-indazoles are readily obtained, and can be further transformed by simple hydrolysis or aza-Wittig reaction. Interestingly, the reaction of *o*-azidobenzaldehyde with triphenylphosphine at −20 °C allowed the isolation of the intermediate phosphazide **77** [41c] that could then be reacted with primary aromatic amines at room temperature to obtain the 2*H*-indazole derivatives.

Somewhat related is the formation of the 1,2,3-triazole **81** upon reaction of the corresponding β-(formyloxy)vinyl azide **78** with triethylphosphite (Scheme 32) [44]. The putative vinyl phosphazide **79** is believed to undergo a fast 1,5-electrocyclisation reaction, leading to **80** after *o*-to-*N*-formyl transfer and elimination of triethylphosphate. The *N*-formyl group is hydrolysed during chromatography, and **81** is finally obtained in 46% yield.

5.2. Reaction with iso(thio)cyanates and carbon disulfide

As mentioned in Section 3.1.1, the reluctance of the *s*-*cis* phosphazide **23** (Scheme 11) to eliminate dinitrogen led to the first unambiguous evidence for an aza-Wittig reaction proceeding with a phosphazide, using *p*-tolylisocyanate as a partner [23,45].

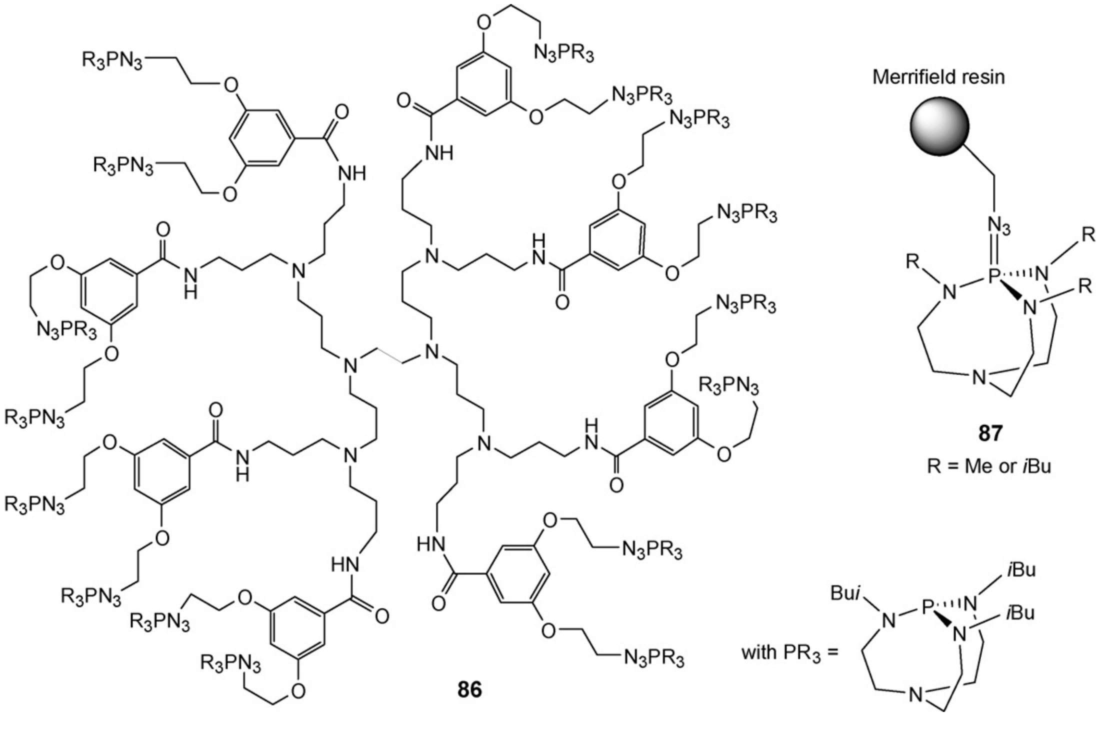


Scheme 33. Formation of (thio)hydantoins from α-azido esters.

Similar behaviour was postulated recently by Fresneda and Molina to account for the unexpected formation of (thio)hydantoins from the reaction of α-azido ethyl esters **82** with triphenylphosphine and iso(thio)cyanates (Scheme 33) [46]. The transient formation of the phosphazide adduct **83** was substantiated by *in situ* ^{31}P NMR monitoring. The (thio)hydantoins **85** are very likely formed by hydrolysis of the corresponding phosphonium salts **84**, that result from the cyclisation onto the ester functionality. So far, the precise stage at which nitrogen elimination occurs during the conversion of the phosphazide **83** into the cyclised phosphonium salt **84** is not known.

5.3. Dendritic and polymer-supported phosphazides derived from proazaphosphatranes

Taking advantage of the propensity of proazaphosphatranes to form stable phosphazides, the group of Verkade recently reported the preparation of the dendritic polyphosphazide **86** (Scheme 34),



87

R = Me or *i*Bu

Scheme 34. Dendritic polyphosphazide **86** and polymer-supported monophosphazides **87**.

and its application in the catalysis of various C–C coupling reactions [47]. Starting from the appropriate dendritic polyazide, 16 phosphazide units were introduced at the surface. The structure of **86** was established by multi-nuclear NMR spectroscopy and elemental analysis. The use of *iso*-butyl groups at the nitrogen atoms was necessary to avoid the penetration of the proazaphosphatrane within the dendrimer and deprotonation of the amide groups. The dendritic polyphosphazide **86** proved to be very efficient at promoting a variety of C–C bond forming reactions, including Michael, Henry, tandem Michael/aldol reactions and the cyclotrimerisation of isocyanates. In addition, polymer-supported phosphazides **87** were readily obtained from the reaction of an azido-functionalised Merrifield resin with proazaphosphatranes. These immobilised catalysts were very active even at room temperature towards a broad range of 1,4-addition and transesterification reactions, and their reusability for up to 10–20 batches was demonstrated [28,48].

6. Conclusion and Outlook

The chemistry of phosphazides has progressed remarkably from the initial postulation of their existence as transient intermediates of the Staudinger reaction, to a point where they occupy their own niche in research. Although many important advances have been made, much work is still required for this area to achieve its full potential.

There has been an increasing trend in recent years towards catalysis using organic molecules [49]. The compatibility of the Staudinger reaction with many functional groups means that there is potential for the rapid construction of architectures that contain multiple catalytically active moieties, such as acids and bases of various strengths. Precedent for this is provided by the work of Alajarín, [32,34,35] in which complex polycyclic systems are available in only a few steps.

Computational studies have provided significant mechanistic and structural insight, leading to a better understanding of the course of the Staudinger reaction and the factors affecting phosphazide stability. Despite the increasing number of reports on stable phosphazides, relatively few of them have been tested as ligands, and preparation of phosphazide–metal complexes is normally carried out by reaction of azides with phosphine complexes. More efficient preparations of these complexes would be effected if the formation of a stable phosphazide and subsequent complexation to a metal fragment would be carried out in a single-pot procedure, representing a modular approach to these systems. In order for this to happen, a better understanding of phosphazide stability is needed, underpinned by the theoretical work described above. Formation of the phosphazide within the coordination sphere of the metal is also likely to remain an important method for complex preparation, particularly for complexes of ordinarily unstable phosphazides.

Given the thermal stability of certain transition metal–phosphazide complexes, it is conceivable that they would be of value as catalysts for typical carbon–carbon bond-forming processes. The possible variation inherent in phosphazide structure may lead to their development as tunable ligands for a range of synthetic transformations. The foundations have now been laid for a significant expansion to occur in this research area.

Note added in proof

Through reaction of phosphine complexes with mesityl azide, Liu and Cui recently obtained the first lanthanide phosphazides complexes (coordination mode A): Dalton Trans. in press.

Acknowledgments

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[7] Key structural parameters vary significantly between the examples of stable phosphazides covered in this review. Differences in the NN bond distances have led to a dichotomy in the nomenclature used to describe these compounds. When referring to the geometrical arrangement of the PN_3 unit, it is common to see both *s-cis*/*s-trans* conformational descriptors (for systems where the central $N_\alpha N_\beta$ interaction has single bond character) and *E*/*Z* configurational descriptors (for systems where the zwitterionic form predominates and the central $N_\alpha N_\beta$ interaction has double bond character). To avoid confusion, *s-cis* and *s-trans* will be preferred hereafter as most of the stable phosphazides are structurally better suited to this. This allows easier comparison of geometrical parameters in different systems.

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