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Exploring organic reactions using simple cyclodiphosphazanes ☆

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ABSTRACT

Phosphine-activated reactions of alkynes/alkenes/allenes as well as the Mitsunobu reaction involve a rich phosphorus chemistry. With the aid of simple cyclodiphosphazanes, characterization of many compounds analogous to the proposed intermediates in such reactions has been accomplished. Use of a cyclodiphosphazane in Pd-catalyzed *N*-arylation reactions is highlighted. Results on molecular non-stoichiometry in phosphorus compounds and on the use of chiral phosphorus systems are discussed. Synthesis of allenylphosphoramides involving a cyclodiphosphazane is also described. X-ray structures of the new compounds [(*t*-BuNH)($PhCH_2CH(CN)CH_2$–)P(μ-N-*t*-Bu)$_2$P(NH-*t*-Bu)]$^+$[HCO_3]$^-$ (**13**), [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P(=N-*t*-Bu)-C(=CH_2)CH(C_6H_4-4-Me)-P(O)($OCH_2CMe_2CH_2O$)] (**18**), [(*i*-PrNH)P(μ-N-*t*-Bu)$_2$P(=N-*i*-Pr)-N(CO_2-*i*-Pr)-NH(CO_2-*i*-Pr)] (**24**), [(*S*)-(2-OH-1-$C_{10}H_6$-1′-$C_{10}H_6$-2′-O-P(O)(NH-*t*-Bu)$_2$] (**36**) and [(*t*-BuNH)(O)P(μ-N-*t*-Bu)$_2$P(O)(CH=C=CMe_2)] (**40**) are also reported.

1. Introduction

Cyclodiphosph(III)azanes, $[ClPNR]_n$ constitute well-known examples of inorganic ring systems [1]. Much of the chemistry investigated earlier is on the substitution reactions involving the P–Cl bond and on the relative geometry of the substituents on phosphorus [1,2]. In later years, the potential of these compounds as highly versatile ligands as well as macrocyclic precursors has been exploited by several groups of workers [3,4]. It is to be noted that in these compounds, both phosphorus and nitrogen are trivalent and hence have unshared electron pairs, but in the majority of cases it is the one on phosphorus that takes part in the reactions. While the ligand chemistry is fairly well-exploited, use of cyclophosphazane as a nucleophile is not explored in detail. That such a feature can be utilized effectively in exploring the mechanistic details of traditional organic reactions is one of the objectives of our work and is discussed in this paper. In addition, the *in situ* generated metal-complexes may actually be put to use in organic transformations is another aspect that we wish to describe herein. In the course of our studies on cyclophosphazanes we have also made some new observations related to molecular non-stoichiometry that involves lone pair/phosphoryl bonds in cyclodiphosphazanes. In addition to giving a brief review of our work in this paper, we present the X-ray structures of the new compounds [(*t*-BuNH)($PhCH_2CH(CN)CH_2$–)P(μ-N-*t*-Bu)$_2$P(NH-*t*-Bu)]$^+$[HCO_3]$^-$ (**13**), [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P(=N-*t*-Bu)-C(=CH_2)CH(C_6H_4-4-Me)-P(O)($OCH_2CMe_2CH_2O$)] (**18**), [(*i*-PrNH)P(μ-N-*t*-Bu)$_2$P(=N-*i*-Pr)-N(CO_2-*i*-Pr)-NH(CO_2-*i*-Pr)] (**24**), [(*S*)-(2-OH-1-$C_{10}H_6$-1′-$C_{10}H_6$-2′-O-P(O)(NH-*t*-Bu)$_2$] (**36**) and [(*t*-BuNH)(O)P(μ-N-*t*-Bu)$_2$P(O)(CH=C=CMe_2)] (**40**) along with relevant details on their synthesis.

2. Results and discussion

2.1. P(III) promoted organic transformations of activated alkenes/alkynes/allenes

As mentioned above, several organic transformations are activated in the presence of a phosphine. The primary intermediates in these reactions are the phosphonium salts (betaines) depicted as [(MeO_2C)C^-=C(CO_2Me)-PR_3^+] (**1**), [R′(O)C-C(H)$^-$C(=CH_2)-PR_3^+] (**2**), [R′(O)C-C(H)=C(CH_2)$^-$-PR_3^+] (**3**) and [(EWG)CH^--CH_2-PR_3^+] (**4**) EWG=CN, CO_2R) in Scheme 1 [5]. It must be noted that if the phosphorus(III) compound bears functionalities like –NCO, –NCS or –N_3, the reaction with activated alkynes would involve these groups also [6]. One of the most important reactions among those shown in Scheme 1 is the Morita–Baylis–Hillman reaction [7] that leads to a diverse number of functionalized and synthetically useful allylic systems. Another useful reaction wherein the phosphine induces an 'umpolung addition' to an alkyne system involves the formation of a compound such as [(*E*)-$PhCH_2OCH_2CH$=CH(CO_2Me)] (**5**) in which an intermediate of type **1** is involved [5a]. Our interest in this connection was to identify/isolate compounds analogous to those proposed in these reactions and in this context, we have utilized the cyclodiphosph(III)azane [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**6**), which is an excellent nucleophile. When this P(III) compound

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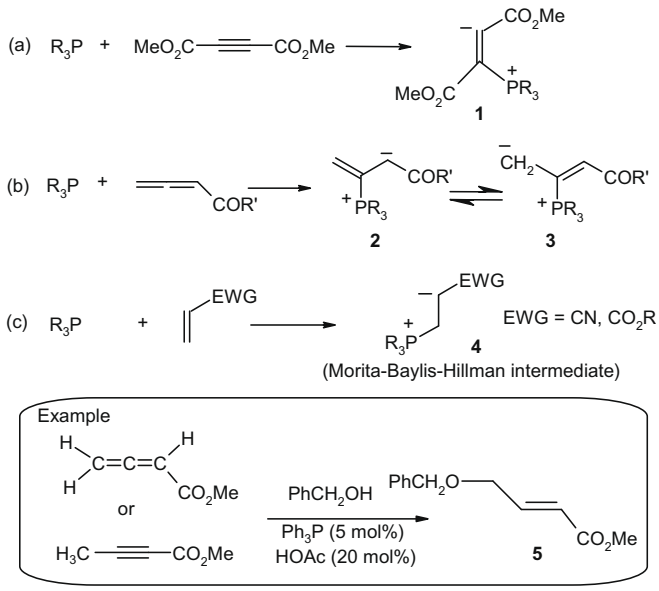
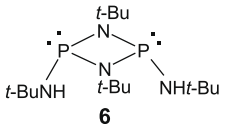


Scheme 1.

was treated with dimethylacetylene dicarboxylate (DMAD), instead of the expected phosphonium salt or any of its tautomeric form, we obtained the novel five-membered ring heterocycle (*t*-Bu-NH)P(μ-N-*t*-Bu)$_2$P{=C(CO$_2$Me)-CH(OMe)-C(O)-N-*t*-Bu} (**7**), however, use of methyl propiolate afforded the tautomeric form (*t*-Bu-NH)P(μ-N-*t*-Bu)$_2$P(=N-*t*-Bu)[CH=CH(CO$_2$Me)] (**8**) of the expected phosphonium salt [8]. Despite the fact that **7** or **8** is not a phosphonium salt, the formation of P–C bond vindicates the involvement of the postulated intermediates shown in Scheme 1.



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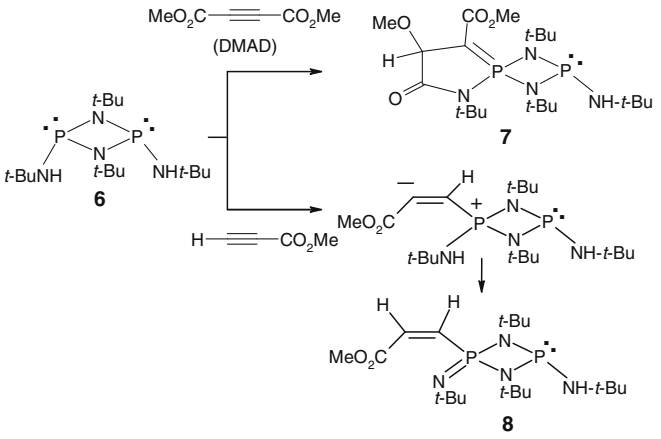
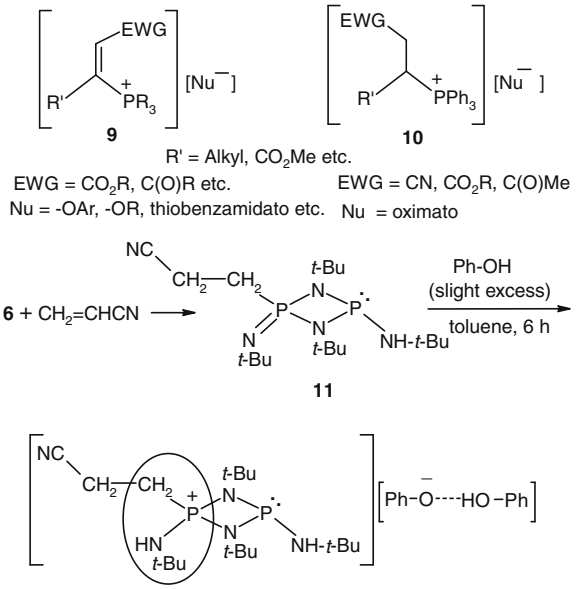
In the reactions shown in Scheme 1, the first stage intermediates so formed undergo reactions with nucleophiles ArOH/ROH to lead to the phosphonium salts of types [(EWG)CH=C(R′)(PR$_3$)]$^+$[Nu]$^-$ (**9**) and [(EWG)CH$_2$CH(R′)(PPh$_3$)]$^+$[Nu]$^-$ (**10**) [EWG=electron withdrawing group] prior to the formation of the required products [9]. We have observed that it is indeed possible to isolate such products {e.g. [(*t*-BuNH)((CN)CH$_2$CH$_2$-)P(μ-N-*t*-Bu)$_2$P(NH-*t*-Bu)]$^+$-[PhOH···OPh]$^-$ (**12**)} (Scheme 3) as shown by the isolation of (*t*-Bu-NH)P(μ-N-*t*-Bu)$_2$P(=N-*t*-Bu)(CH$_2$CH$_2$CN) (**11**) (see Scheme 2).

In contrast to the above, the reaction of [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**6**) with PhCH$_2$C(CN)=CH$_2$ is slightly different. Although at room temperature there was no reaction, when the mixture was refluxed in toluene for 2 d, the signal for **6** disappeared in the ^{31}P NMR spectrum and the reaction mixture showed mainly four peaks [−17.6 and −7.1 (tetracoordinate) 72.1 and 74.1 (tricoordinate)] (Fig. 1). These peaks are most likely due to two isomeric species that differ about the P=N bond (or two tautomeric forms). Upon attempted purification through silica gel column, only the new ionic compound [(*t*-BuNH)(PhCH$_2$CH(CN)CH$_2$-)P(μ-N-*t*-Bu)$_2$P(NH-*t*-Bu)]$^+$[HCO$_3$]$^-$ (**13**) was isolated (Scheme 4). The anion, analyzed as [HCO$_3$]$^-$ by X-ray crystallography (Fig. 2), could have come from the absorption of adventitious carbon dioxide-moisture. In a similar way, compound (*t*-Bu-NH)P(μ-N-*t*-Bu)$_2$P(=N-*t*-Bu)(CH$_2$CH$_2$CN) (**11**) [δ(P) −12.9, 71.6], prepared as described above, on passing through silica gel column gave the ionic product [(*t*-BuNH)((CN)CH$_2$CH$_2$-)P(μ-N-*t*-



Scheme 2.



Scheme 3.

Bu)$_2$P(NH-*t*-Bu)]$^+$[HCO$_3$]$^-$ (**14**) [δ(P) 21.1, 83.4]. The P(1)–N(3) distance of 1.607(3)Å in **13** is longer than that reported for **11** [1.526(2) Å] [8] as expected for the P–N single bond in **13** and double bond in **11**.

We have also explored the reaction of allenylphosphonates with the cyclodiphosphazane [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**6**). Interestingly, we could isolate both the enantiomers of the product [(*t*-Bu-NH)P(μ-N-*t*-Bu)$_2$P(=N-*t*-Bu)C(=CH$_2$)-CH(Ph)-P(O)(OCH$_2$CMe$_2$CH$_2$O)] (**16**) from the reaction of **6** with the allene (OCH$_2$CMe$_2$CH$_2$O)P(O)C(Ph)=C=CH$_2$ (**15**) [10]. The identity of the two enantiomers (separated by spontaneous resolution) has been confirmed by X-ray crystallography as well as CD spectra of the crystals. In the present work, the reaction of the *p*-tolyl substituted allene (OCH$_2$CMe$_2$CH$_2$O)P(O)C(C$_6$H$_4$-4-Me)=C=CH$_2$ (**17**) was performed. We did obtain the expected new product [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P(=N-*t*-Bu)-C(=CH$_2$)CH(C$_6$H$_4$-4-Me)-P(O)(OCH$_2$CMe$_2$CH$_2$O)] (**18**), but it crystallized as a racemic mixture (Fig. 3). Nevertheless, the results clearly show that the initial attack of the P(III) species (in this case compound **6**) occurs at the central carbon of the allene part giving a reasonable proof for the proposed intermediate of the

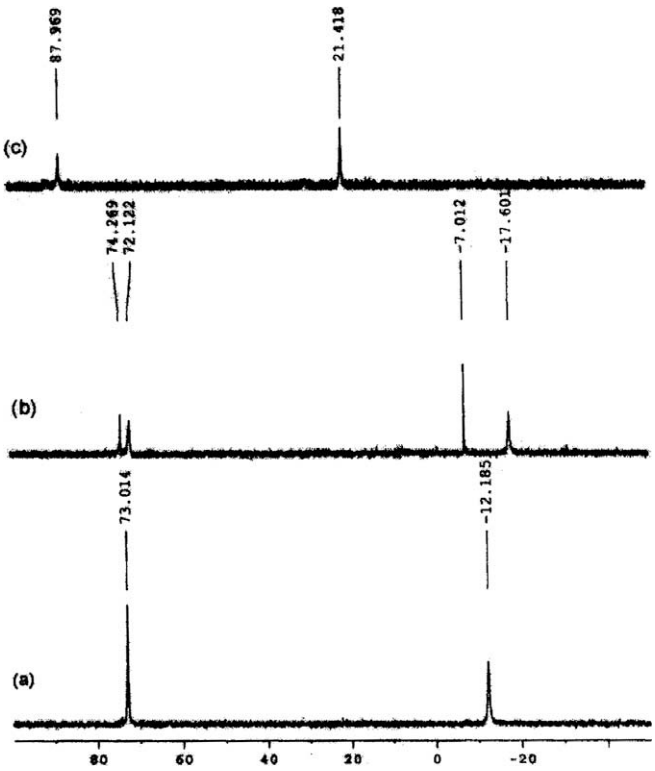


Fig. 1. The ^{31}P NMR spectra of (a) pure compound **11**, (b) reaction mixture of compound **6** + $(PhCH_2)(CN)C{=}CH_2$ containing (**A**) and (c) pure compound **13**.

type $[(R'(O)C)\text{-}C(H)^{-}C(=CH_2)\text{-}PR_3^{+}]$ (**2**) or $[R'(O)C\text{-}C(H){=}C(CH_2^{-})\text{-}PR_3^{+}]$ (**3**) shown in Scheme 1 (see Scheme 5).

2.2. Reaction of compound $[(t\text{-BuNH})P(\mu\text{-}N\text{-}t\text{-Bu})]_2$ (**6**) and related cyclodiphosphazanes with dialkyl azodicarboxylates-implications for the mechanism of Mitsunobu reaction

The redox combination of a phosphine and a dialkyl azodicarboxylate is the key to the success of the well-known Mitsunobu reaction in which esterification of an acid (and related reactions) with inversion of configuration for asymmetric alcohols can be accomplished under very mild conditions [5b]. Several phosphorus based intermediates like $[Ph_3P^{+}\text{-}N(CO_2R)\text{-}N^{-}\text{-}CO_2R]$ (**19**), $[Ph_3P\text{-}N(CO_2R)\text{-}NH\text{-}CO_2R]^{+}[R'CO_2]^{-}$ (**20**) and $[Ph_3P(OR'')]^{+}[R'CO_2]^{-}$ (**21**) have been proposed in this synthetically useful reaction. However,

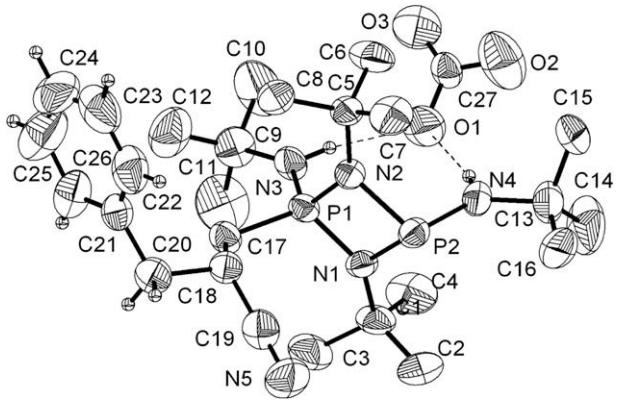


Fig. 2. Molecular structure of **13**. Selected bond distances (Å): P(1)–N(1) 1.633(3), P(1)–N(2) 1.639(3), P(1)–N(3) 1.607(3), P(1)–C(17) 1.792(4), P(2)–N(1) 1.756(3), P(2)–N(2) 1.763(3), P(2)–N(4) 1.641(4). Bicarbonate proton was not located. Hydrogen bond parameters: N(3)–H(4N)···O(1) 0.88(4), 2.00(4), 2.870(5) Å, 171(4)°; N(4)–H(3N)···O(1) 0.87(4), 2.19(5), 3.042(5) Å, 166(4)°.

detailed characterization of these or analogous species had eluded detection prior to our work [11]. By making use of the cyclodi-

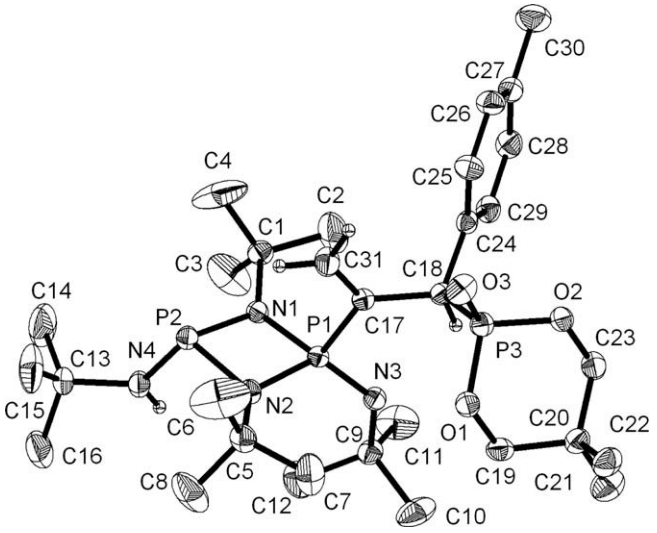
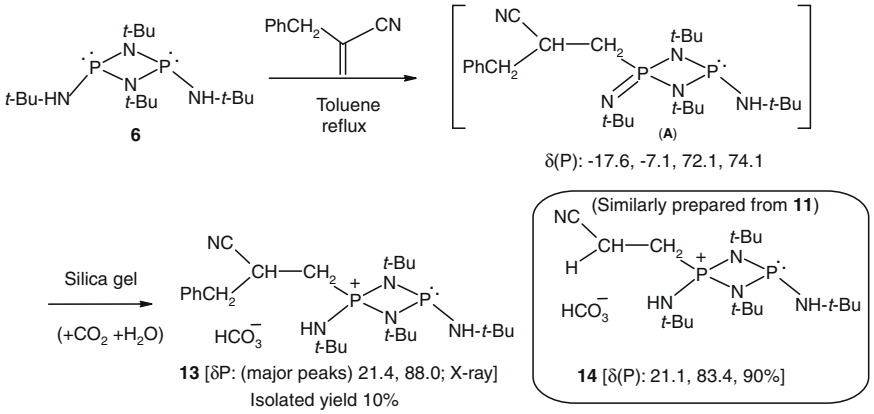
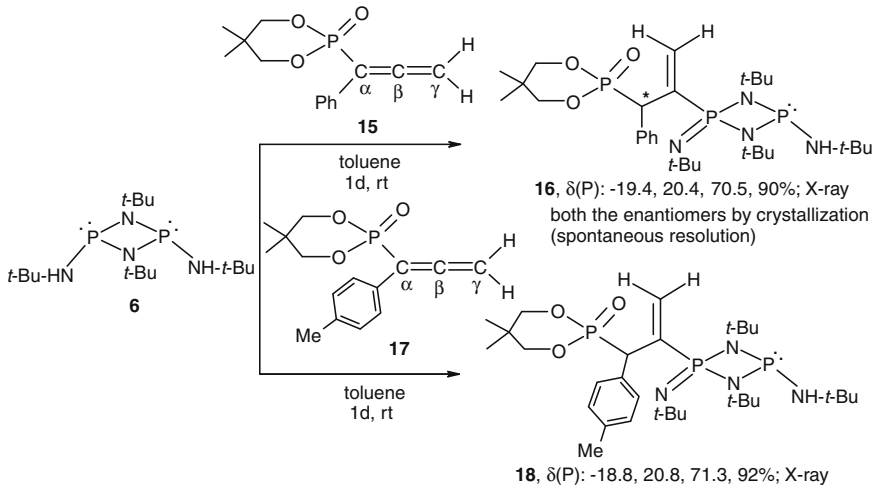


Fig. 3. Molecular structure of **18**. Selected bond distances (Å): P(1)–N(1) 1.683(2), P(1)–N(2) 1.680(2), P(1)–N(3) 1.540(2), P(1)–C(17) 1.828(3), P(2)–N(1) 1.735(2), P(2)–N(2) 1.743(2), P(2)–N(4) 1.660(3).

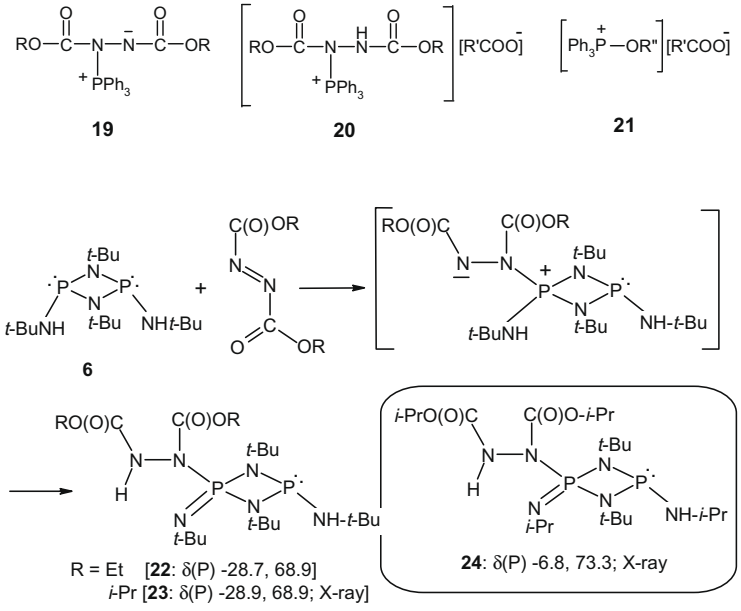


Scheme 4.



Scheme 5.

phosphazane [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**6**), we have been able to characterize several compounds, which include [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P(=N-*t*-Bu)-N(CO$_2$R)-NH(CO$_2$R] [R = Et (**22**), *i*-Pr (**23**)] (Scheme 6). It may be noted that **22**–**23** are the tautomeric forms of the expected betaine analogous to [Ph$_3$P$^+$-N(CO$_2$R)-N$^-$-CO$_2$R] (**19**); thus a reasonable (though not exact) evidence for the proposed first stage intermediate in the Mitsunobu reaction is provided from our work. The question as to whether the *t*-BuNH group on the cyclophosphazane is really required or not is answered by isolating the *i*-PrNH analogue [(*i*-PrNH)P(μ-N-*t*-Bu)$_2$P(=N-*i*-Pr)-N(CO$_2$-*i*-Pr)-NH(CO$_2$-*i*-Pr)] (**24**) which is a new compound (Fig. 4). This result indicates that the availability of a proton on N is necessary for the success of this reaction. However, it is important to note that in aminophosphites with an –NH-*i*-Pr group, a pentacoordinate derivative was obtained [12]. We have also attempted to use other secondary amino groups like morpholino or dimethylamino, but in these cases the reaction led only to the corresponding oxidized species of type [(R$_2$N(O)P-N-*t*-Bu]$_2$ as isolatable products. Another important point in these systems is the ^{31}P NMR chemical shift of the phosphinimine part. While in **23** this value is -28.9 ppm, in the morpholino compound [(*cycl*-OC$_4$H$_8$N)P(μ-N-*t*-Bu)$_2$P(=N-*t*-Bu)-N(CO$_2$-*i*-Pr)-NH(CO$_2$-*i*-Pr)] (**25**) prepared similarly [11c] it is −51.5, which is well inside the pentacoordinate region Fig. 5; cf. (*cycl*-OC$_4$H$_8$N)P(μ-N-*t*-Bu)$_2$P(NH-*t*-Bu)(N(CO$_2$-*i*-Pr)-N=C(O-*i*-Pr)O-) (**25**″) and hence it is likely that in solution, there is a significant contribution from this form [12]. This observation also suggests that the nature of the species in the reaction of P(III) compounds with DIAD/DEAD depends on the substituents present on the phosphorus that include the betaine, imine (where proton shift is possible) and pentacoordinate phosphorane [cf. **25**, (*cycl*-OC$_4$H$_8$N)P(μ-N-*t*-Bu)$_2$P$^+$(NH-*t*-Bu)-N(CO$_2$-*i*-Pr)-N$^-$(CO$_2$-*i*-Pr) (**25**′) and **25**″]. This point is also of some relevance since it is known that similar pentacoordinate derivatives take part in the Mitsunobu esterification [13].



Scheme 6.

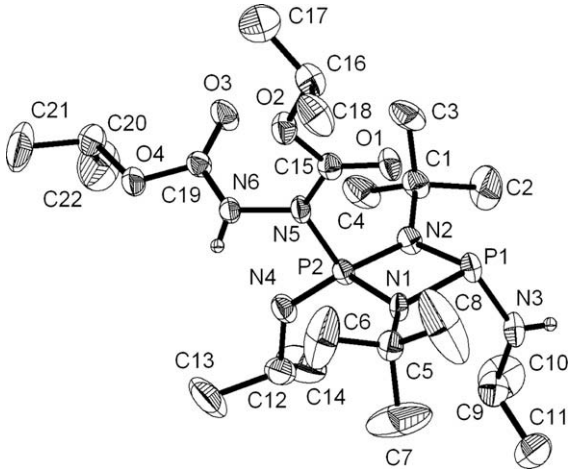
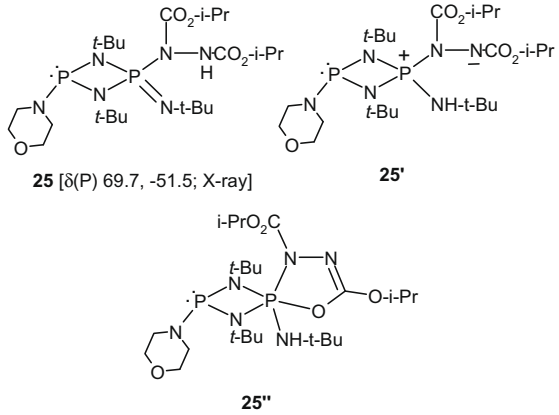


Fig. 4. Molecular structure of **24**. Selected bond distances (Å): P(1)–N(1) 1.744(3), P(1)–N(2) 1.768(2), P(1)–N(3) 1.655(2), P(2)–N(1) 1.647(3), P(2)–N(2) 1.649(4), P(2)–N(4) 1.531(4), P(2)–N(5) 1.727(4). Hydrogen bond parameters (intermolecular): N(3)–H(3N)···O(3) 0.72(5), 2.35(5), 3.067(5) Å, 170(5)°. Symmetry code: $-x+1/2, y-1/2, -z+1/2$.



As shown in Scheme 1, at the second stage of the Mitsunobu reaction, species of type $[Ph_3P\text{-}N(CO_2R)\text{-}NH\text{-}CO_2R]^+[R'CO_2]^-$ (**20**) are the proposed intermediates. Here we had better success and could isolate compounds $[(t\text{-BuNH})P(\mu\text{-}N\text{-}t\text{-Bu})_2P(NH\text{-}t\text{-Bu})\text{-}N(CO_2\text{-}i\text{-Pr})\text{-}NH(CO_2\text{-}i\text{-Pr}]^+[RCO_2]^-$ [R = Ph (**26**), 4-Cl-$C_6H_4CH_2$ (**27**), 4-Br-C_6H_4 (**28**), and 4-O_2N-C_6H_4 (**29**) by the addition of carboxylic acids to $(t\text{-BuNH})P(\mu\text{-}N\text{-}t\text{-Bu})_2P(=N\text{-}t\text{-Bu})\text{-}N(CO_2\text{-}i\text{-Pr})\text{-}NH(CO_2\text{-}i\text{-Pr})$ (**23**) [11c]. Interestingly, these compounds undergo the Mitsunobu esterification and thus lend credence to the postulated intermediates like **20** [11c] (see Scheme 7).

2.3. Molecularly non-stoichiometric crystals of cyclodiphosphazane derivatives

Between the two most prevalent oxidation states for phosphorus, three and five, a significant number of compounds in the latter oxidation state can be simply prepared by treating P(III) compounds with suitable oxidizing agents, to lead to compounds with a phosphoryl bond. This part of our work was originally intended for the synthesis of chiral phosphoramidates based on a cyclodiphosphazane system for use in asymmetric synthesis such as reduction [14]. However, while synthesizing the required binaphthoxy-substituted cyclophosphazanes, we found that the P(III) precursor and its oxidized products had similar cell parameters, as shown by X-ray structure determination. A Cambridge database

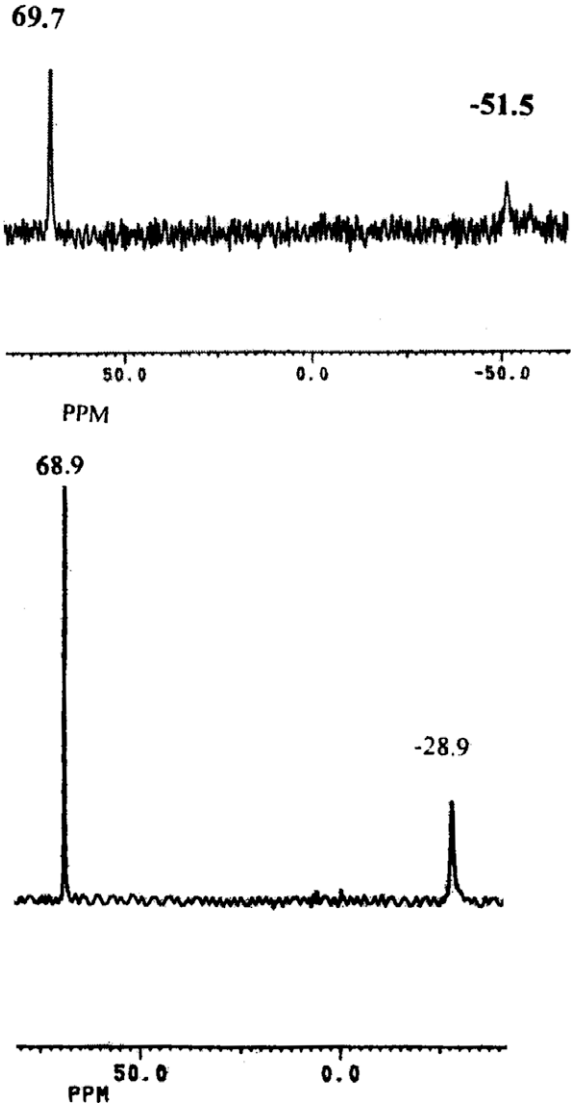
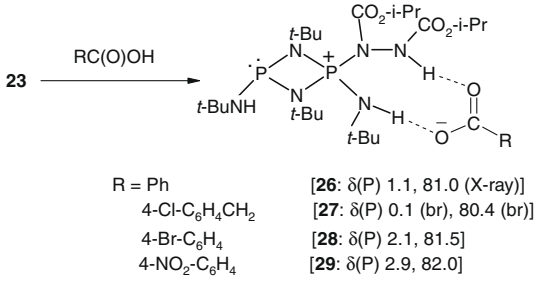
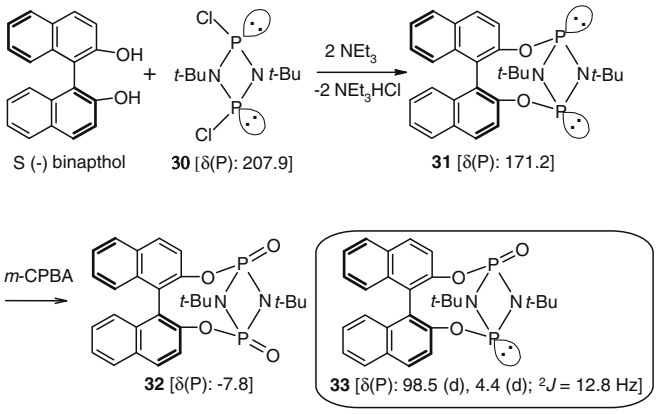


Fig. 5. The ^{31}P NMR spectra of **23** (bottom) and **25**, illustrating the significant difference in the chemical shift at the phosphinimine region.

survey of X-ray structures for several other P(III) and their corresponding P(V) compounds revealed that the difference in cell volume due to the extra oxygen per molecule in the crystals is only about 6 Å^3. Thus in the crystallization process of sufficiently large molecules, it can be expected that a compound with the phosphoryl group (P═O) may co-crystallize with the corresponding P(III) derivative to form solid solutions. The individual compounds will be intact, but can interchangeably pack in the crystal lattice,

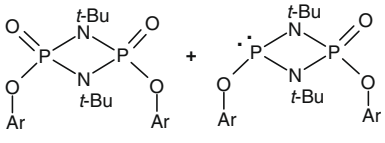


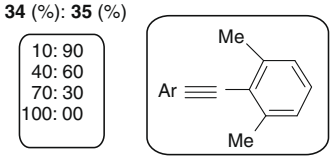
Scheme 7.



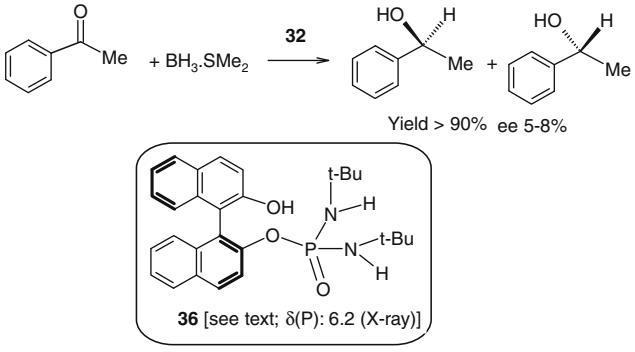
Scheme 8.

thus leading to crystals which can be termed as molecularly non-stoichiometric. Although the concept looks simple, this aspect had not been investigated prior to our work. The importance of this observation can be appreciated when we realize that obtaining single crystals does not guarantee the purity of the compound. The first system in cyclodiphosphazanes that we encountered is shown in Scheme 8. Compounds (*S*)-(O-$C_{10}H_6$-$C_{10}H_6$-O-)[P(μ-N-*t*-Bu)$_2$P] (**31**) and (*S*)-(O-$C_{10}H_6$-$C_{10}H_6$-O-)[(O)P(μ-N-*t*-Bu)$_2$P(O)] (**32**) crystallize in the same space group $P2_12_12_1$ with very similar unit cell dimensions; upon mixing, they form the co-crystal readily in the ratio 1:2.3 as evidenced by X-ray crystallography and ^{31}P NMR spectra for the crystals after dissolution in $CDCl_3$ [15]. This observation was useful in explaining the difficulty in obtaining pure mono-oxidized compound (*S*)-(1,1′-O-$C_{10}H_6$-$C_{10}H_6$-O-)[(O)P(μ-N-*t*-Bu)$_2$P] (**33**); the crystals of this compound also belonged to the same space group with (again) similar unit cell dimensions and contained ca 5% of the fully oxidized product **32**. More dramatic is the system represented by compounds [(2,6-$Me_2C_6H_3O$)(O)P(μ-N-*t*-Bu)]$_2$ (**34**) and (2,6-$Me_2C_6H_3O$)(O)P(μ-N-*t*-Bu)$_2$P(O-2,6-$Me_2C_6H_3$) (**35**) [15b]. Here, three different types of crystals with varying stoichiometry of **34** and **35** are obtained (cf. the structural drawings). The results are proven by the combined use of ^{31}P NMR spectroscopy and X-ray crystallography. Thus it is imperative that in synthesis involving oxidation of P(III) systems, we should be careful not to assume that the crystals are necessarily pure compounds.





As regards our original objective of using (*S*)-(O-$C_{10}H_6$-$C_{10}H_6$-O-)[(O)P(μ-N-*t*-Bu)$_2$P(O)] (**32**) for chiral catalysis, we have tried the reduction of acetophenone (Scheme 9). The chiral induction was low, but in addition, we noted that the phosphoramidate **32** was not particularly stable under these conditions. We were able to isolate the new ring-cleaved product [(*S*)-(2-OH-1-$C_{10}H_6$-1′-$C_{10}H_6$-2′-O-P(O)(NH-*t*-Bu)$_2$] (**36**) (Fig. 6). It is thus possible that even in the reactions reported in the literature [14] the true catalyst may not be the original N–P═O compound.



Scheme 9.

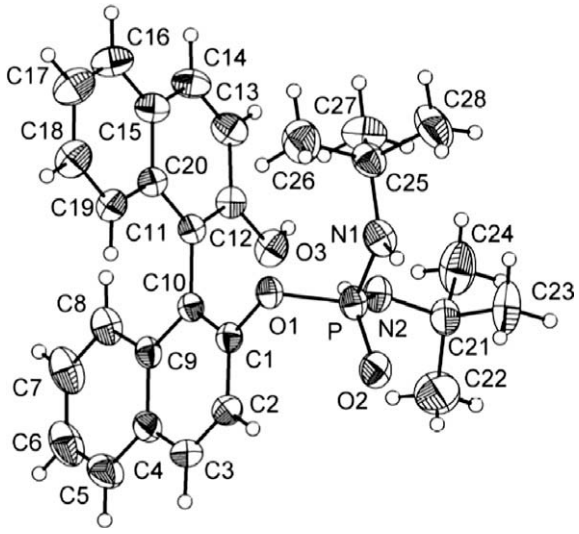


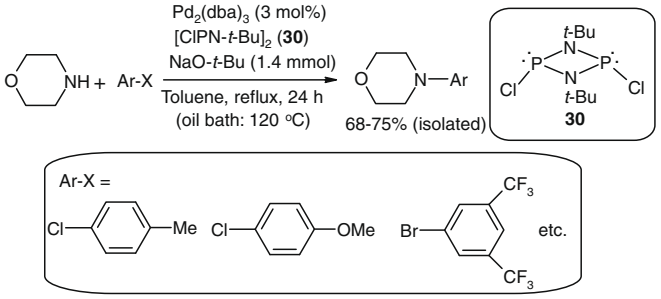
Fig. 6. An ORTEP drawing of compound **36**. Selected bond distances (Å): P–O(1) 1.601 (2), P–O(2) 1.472 (2), P–N(1) 1.615(3), P–N(2) 1.620(3). H-bond parameters O(3)–H(1)···O(2) 0.77(5) Å, 1.88(5) Å, 2.614(3) Å, 160(5)°. Symmetry code: $1 - x$, $0.5 + y$, $0.5 - z$.

*2.4. The cyclodiphosphazane [ClP(μ-N-t-Bu)]$_2$ (**30**) as a co-ligand for the palladium catalyzed amination of aryl bromides and chlorides*

C–N Bond formation by palladium catalyzed cross coupling reaction is one of the powerful techniques in synthetic organic chemistry. To the best of our knowledge, only two reports have appeared describing the utility of chloro(amino)phosphines as ligands in this type of coupling [16]. In this context, we felt that cyclodiphosphazane derivative [ClP(μ-N-*t*-Bu)]$_2$ (**30**) bearing a bulky *t*-butylamino substituent as a ligand should be quite useful. Thus we have been fairly successful in using **30** and three examples from our recent work are presented in Scheme 10 [17]. Using this route, we have been able to effect *N*-arylation of aniline using the bulky aryl bromide, 1-bromo-2,4,6-trimethylbenzene, albeit in somewhat lower yields (38%). Currently, we are trying to extend the use of cyclodiphosphazanes to other reactions that include the Suzuki coupling.

2.5. Allenes derived from cyclodiphosphazanes

Allenes have two cumulative orthogonal double bonds and are versatile intermediates in organic chemistry. The P–Cl bond in [ClP(μ-N-*t*-Bu)]$_2$ (**30**) can be readily converted to allenylphosphoramidates by treating it with suitable propargylic alcohols. This has been shown by us recently and the compounds



Scheme 10.

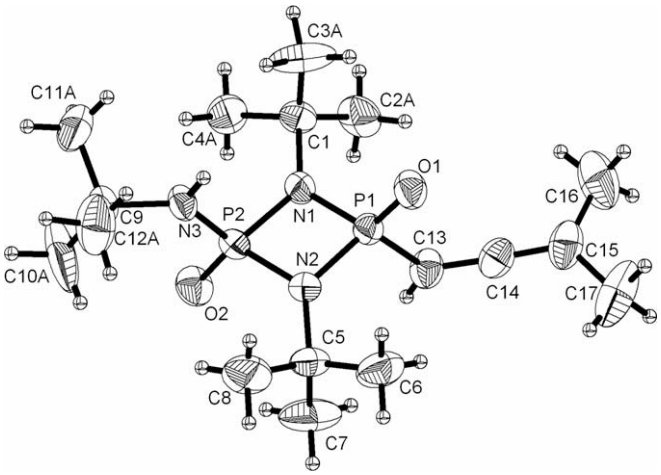
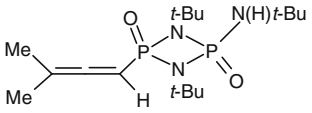


Fig. 7. Molecular structure of **40**. The other set of positions for *t*-butyl atoms connected to C1 are omitted for clarity. Selected bond distances (Å): P(1)–N(1) 1.667(2), P(1)–N(2) 1.662(2), P(1)–O(1) 1.463(2), P(1)–C(13) 1.782(2), P(2)–N(1) 1.676(2), P(2)–N(2) 1.703(2), P(2)–N(3) 1.616(2), P(2)–O(2) 1.462(2). Hydrogen bond parameters (intermolecular): N(3)–H(3D)···O(1) 0.75(2), 2.28(2), 3.014(3) Å, 164(3)°. Symmetry code: 1 − x, 2 − y, −z.

[(RR′C═C═CH)(O)P(μ-N-*t*-Bu)$_2$P(O)(CH═C═CRR′)] [R = R′ = H (**37**), R = R′ = Me (**38**), R = Me, R′ = Et (**39**)] have been prepared and structurally characterized [18]. It can be readily noted that both *cis*- and *trans*- isomers are possible and both of these have been isolated in two cases. In addition to these, the new partially oxidized allenyl product [(*t*-BuNH)(O)P(μ-N-*t*-Bu)$_2$P(O)(CH═C═CMe$_2$)] (**40**) (Fig. 7) was obtained in traces. Although we are yet to ascertain the details of its formation, its isolation could open up further opportunities for exploration. Finally, we believe that compounds **37**–**39** have the potential to be used as polymer precursors, but this work still needs to be done (see Scheme 11).



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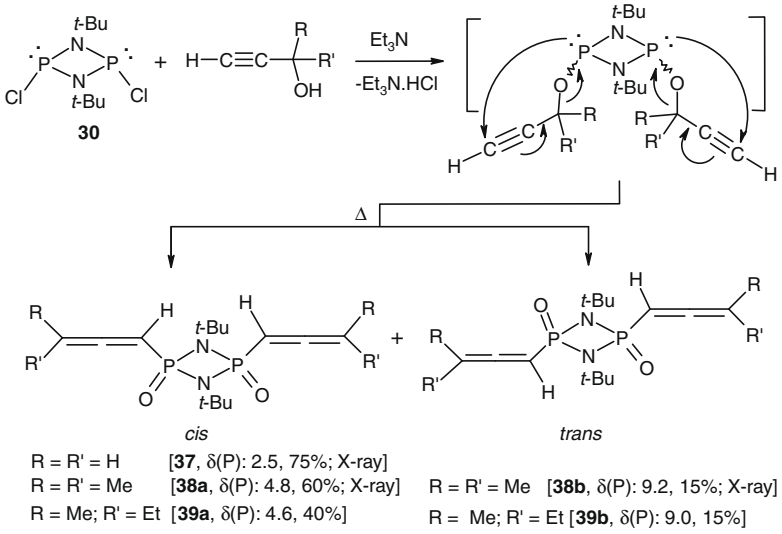
3. Conclusion

By means of five different systems, we have shown the synthetic potential of simple cyclodiphosphazanes. These involve the use of (i) [(*t*-BuNH)PN-*t*-Bu]$_2$ as a mechanistic probe for the Mitsunobu and phosphine catalyzed reactions of alkenes/alkynes/allenes (ii) generation of molecularly non-stoichiometric crystals via derivatives of [ClP-μ-N-*t*-Bu]$_2$, (iii) Pd(0) catalyzed *N*-arylation reactions mediated by [ClP-μ-N-*t*-Bu]$_2$ and (iv) syntheses of new allenylphosphoramides. We believe that further exploration, in particular in homogeneous catalysis, will bear more fruits in the coming years.

4. Experimental

General experimental conditions are available in a recent paper [19]. Compounds [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**6**) [8,11c], (*t*-BuNH)P(μ-N-*t*-Bu)$_2$P{═C(CO$_2$Me)-CH(OMe)-C(O)-N-*t*-Bu} (**7**) [8,11c], (*t*-Bu-HN)P(μ-N-*t*-Bu)$_2$P(═N-*t*-Bu)[CH═CH(CO$_2$Me)] (**8**) [8,11c], (*t*-Bu-NH)P(μ-N-*t*-Bu)$_2$P(═N-*t*-Bu)(CH$_2$CH$_2$CN) (**11**) [8], [(*t*-BuNH)((CN)CH$_2$CH$_2$-)P(μ-N-*t*-Bu)$_2$P(NH-*t*-Bu)]$^+$[PhOH···OPh]$^-$ (**12**) [8], (OCH$_2$CMe$_2$CH$_2$O)P(O)C(Ph)═C═CH$_2$ (**15**) [10], [(*t*-Bu-HN)P(μ-N-*t*-Bu)$_2$P(═N-*t*-Bu)C(═CH$_2$)-CH(Ph)-P(O)(OCH$_2$CMe$_2$CH$_2$O)] (**16**) [10], (OCH$_2$CMe$_2$CH$_2$O)P(O)C(C$_6$H$_4$-4-Me)═C═CH$_2$ (**17**) [20], [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P(═N-*t*-Bu)-N(CO$_2$R)-NH(CO$_2$R] [R = Et (**22**), *i*-Pr (**23**)] [11c], [(*cycl*-OC$_4$H$_8$N)P(μ-N-*t*-Bu)$_2$P(═N-*t*-Bu)-N(CO$_2$-*i*-Pr)-NH(CO$_2$-*i*-Pr)] (**25**) [11b], [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P(NH-*t*-Bu)-N(CO$_2$-*i*-Pr)-NH(CO$_2$-*i*-Pr]$^+$[RCO$_2$]$^-$ [R = Ph (**26**), 4-Cl-C$_6$H$_4$CH$_2$



Scheme 11.

(**27**), 4-Br-C_6H_4 (**28**), and 4-O_2N-C_6H_4 (**29**) [11b,c], $[ClP(\mu\text{-N-}t\text{-Bu})]_2$ (**30**) [18], (*S*)-(1,1′-O-$C_{10}H_6$-$C_{10}H_6$-O-)[$P(\mu\text{-N-}t\text{-Bu})_2P$] (**31**) [15a], (*S*)-(1,1′-O-$C_{10}H_6$-$C_{10}H_6$-O-)[$(O)P(\mu\text{-N-}t\text{-Bu})_2P(O)$] (**32**) [15a], (*S*)-(1,1′-O-$C_{10}H_6$-$C_{10}H_6$-O-)[$(O)P(\mu\text{-N-}t\text{-Bu})_2P$] (**33**) [15a], [(2,6-$Me_2$-$C_6H_3O$)$(O)P(\mu\text{-N-}t\text{-Bu})]_2$ (**34**) [15b], (2,6-$Me_2C_6H_3O$)$(O)P(\mu\text{-N-}t\text{-Bu})_2P$(O-2,6-$Me_2C_6H_3$) (**35**) [15b], and [$(RR'C{=}C{=}H)(O)P(\mu\text{-N-}t\text{-Bu})_2P(O)(CH{=}C{=}CRR')$] [R = R′ = H (**37**), R = R′ = Me (**38**), R = Me, R′ = Et (**39**)] **37–39** [18] have been reported before**.** Compound [(*t*-BuNH)$(O)P(\mu\text{-N-}t\text{-Bu})_2P(O)(CH{=}C{=}CMe_2)$] (**40**) (CCDC 749655) was obtained in very small quantities along with **38a**,**b**, probably as an impurity from the starting material **30**; this aspect is still under study. The procedure for the *N*-arylation of 1-bromo-2,4,6-trimethylbenzene was similar to that reported by us recently [17]. Details on the other new compounds are presented below.

4.1. Synthesis of compounds [(t-BuNH)($PhCH_2CH(CN)CH_2$-)$P(\mu\text{-N-}t\text{-Bu})_2P(NH\text{-}t\text{-Bu})]^+[HCO_3]^-$ (13) and [(t-BuNH)($(CN)CH_2CH_2$-)$P(\mu\text{-N-}t\text{-Bu})_2P(NH\text{-}t\text{-Bu})]^+[HCO_3]^-$ (14)

To a solution of $[(t\text{-BuNH})P(\mu\text{-N-}t\text{-Bu})]_2$ (**6**) (0.706 g, 2.02 mmol) in toluene (10 mL), 2-benzyl-acrylonitrile (0.433 g, 3.03 mmol) was added *via* syringe at room temperature and mixture heated under reflux for 2 d. At this stage, the ^{31}P NMR spectrum showed mainly four peaks [−17.6 and −7.1 (tetracoordinate) 72.1 and 74.1 (tricoordinate)] corresponding to two species. This solution was concentrated *in vacuo* and chromatographed (silica gel, 85% ethyl acetate – 15% hexane) to get $[(t\text{-BuNH})(PhCH_2CH(CN)CH_2\text{-})P(\mu\text{-N-}t\text{-Bu})_2P(NH\text{-}t\text{-Bu})]^+[HCO_3]^-$ (**13**). The product eluted from column was different from that present before. The silica gel was tested for the presence of nitrate after washing with water several times, but no detectable amount of nitrate was found. Crystals were obtained at room temperature from dichloromethane-hexane mixture. Yield (isolated): 0.11 g (10%). M.p. 206 °C (dec.). IR (KBr): 3208, 3102, 2971, 2241, 1493, 1454, 1367, 1196 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.35, 1.38, 1.52, 1.68 (4 s, 36H, $C(CH_3)_3$), 2.82 (br m, 2H, PCH_2), 3.02 (br m, 3H, PCC*H* + $PCCCH_2$), 3.38 (br, 1H, N*H*), 7.25–7.37 (m, 5H, Ar–*H*), 8.10 (br, 1H, N*H*) (C–O*H* proton peak was too broad). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.6 (s, PCCH), 30.9 (d, ^1J(P–C) ∼ 121.0 Hz, P*C*, one of the peaks merged with peaks due to *t*-Bu carbons), 31.1, 31.4 (2 s, $C(CH_3)_3$), 32.5 (d, ^3J(P–C) ∼ 10.0 Hz, $C(CH_3)_3$), 40.4 (d, ^3J(P–C) = 15.0 Hz, CH_2Ph), 52.9–56.1 (many lines, $C(CH_3)_3$), 120.0 (s, *C*N), 128.1, 129.2, 129.6, 134.9 (the peak due to bicarbonate was too weak to be observed). ^{31}P NMR (160 MHz, $CDCl_3$): δ 21.4, 88.0. Anal. Calc. for $C_{27}H_{49}N_5O_3P_2$: C, 58.57; H, 8.92; N, 12.64. Found: C, 58.72; H, 8.81; N, 12.66%. CCDC number 749651.

Compound $[(t\text{-BuNH})((CN)CH_2CH_2\text{-})P(\mu\text{-N-}t\text{-Bu})_2P(NH\text{-}t\text{-Bu})]^+[HCO_3]^-$ (**14**) was obtained by passing compound (*t*-Bu-NH)$P(\mu\text{-N-}t\text{-Bu})_2P(=N\text{-}t\text{-Bu})(CH_2CH_2CN)$ (**11**) through a silica gel column using ethyl acetate–hexane (9:1) mixture as eluent. Yield: 0.59 g (90%). M.p.: 182–183 °C (dec.). IR (KBr): 3451, 3216, 2974, 2249, 1370, 1198 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.34, 1.46, 1.52 (3s, 36H, $C(CH_3)_3$), 2.38 (br, 2H, PCH_2CH_2), 3.05 (br, 2H, PCH_2), 3.35 (br, ∼1H, N*H*), the other N*H* and C–O*H* proton peaks were too broad. ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.9 (s, $PCCH_2$), 23.4 (d, ^1J(P–C) = 97.0 Hz, P*C*), 31.8, 32.3, 32.5 (3 s, $C(CH_3)_3$), 53.0 (d, ^2J(P–C) = 15.0 Hz, $C(CH_3)_3$), 54.7 and 56.1 (2 s, $C(CH_3)_3$), 117.5 (s, *C*N) (The peak due to bicarbonate was perhaps too weak to be observed). ^{31}P NMR (160 MHz, $CDCl_3$): δ 21.1, 83.4. Anal. Calc. for $C_{20}H_{43}N_5O_3P_2$: C, 51.79; H, 9.34; N, 15.17. Found: C, 51.86; H, 9.32; N, 15.08%.

4.2. Synthesis of compound [(t-BuNH)$P(\mu\text{-N-}t\text{-Bu})_2P(=N\text{-}t\text{-Bu})$-$C(=CH_2)CH(C_6H_4\text{-}4\text{-Me})\text{-}P(O)(OCH_2CMe_2CH_2O)]$ (18)

Cyclodiphosphazane $[(t\text{-BuNH})P(\mu\text{-N-}t\text{-Bu})]_2$ (**6**) (0.484 g, 1.38 mmol) and allenylphosphonate ($OCH_2CMe_2CH_2O$)-$P(O)C(C_6H_4\text{-}4\text{-Me}){=}C{=}CH_2$ (**17**) [20] (0.386 g, 1.38 mmol) were dissolved in dry toluene (8 mL), and the mixture was stirred at room temperature for 1 d. The solution was concentrated *in vacuo* (to ca 3 mL) and cooled for 1 d at −4 °C to obtain crystals of [(*t*-BuNH)$P(\mu\text{-N-}t\text{-Bu})_2P(=N\text{-}t\text{-Bu})$-$C(=CH_2)CH(C_6H_4$-4-Me)-$P(O)(OCH_2C$-$Me_2CH_2O)]$ (**18**). Yield: 0.804 g (92%). M.p.: 178–180 °C. IR (KBr): 3335, 2970, 2901, 2629, 2550, 2262, 1819, 1606, 1512, 1473, 1361, 1280, 1215, 1062 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.89, 1.17, 1.27, 1.39 and 1.40 (5s, 42H, $C(CH_3)_2 + C(CH_3)_3$), 2.28 (1s, 3H, Ar–CH_3), 2.67 (d, ^2J(P–H) = 8.0 Hz, 1H, N*H*), 3.80–4.35 (m, 4H, OCH_2), 5.75 (dd, ^3J(P–H) ∼ 26.8 Hz, ^4J(P–H) = 3.6 Hz, 1H,=CH_AH_B, *cis* to P), 6.01 (dd, ^3J(P–H) ∼ 11.6 Hz, ^2J(P–H) ∼ 14.8 Hz, 1H, P(O)C*H*), 6.79 (d, ^3J(P–H) ∼ 51.6 Hz, 1H, = CH_AH_B, *trans* to P), 7.04 (d, ^3J(H–H) = 8.0 Hz, 2H, Ar–*H*), 7.42 (d, ^3J(H–H) = 7.6 Hz, 2H, Ar–*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.91 and 21.07 (2s, $C(CH_3)_2$), 21.96 (Ar–CH_3), 31.07 (d, ^3J(P–C) = 24.3 Hz, $C(CH_3)_3$), 32.38 (d, ^3J(P–C) = 6.3 Hz, $C(CH_3)_3$), 32.87 (d, ^3J(P–C) ∼ 9.6 Hz, $C(CH_3)_3$), 34.54 (d, ^3J(P–C) = 12.0 Hz, $C(CH_3)_3$), 41.09 (dd, ^1J(P–C) ∼ 125.0 Hz, ^2J(P–C) = 4.6 Hz, P(O)*C*(Ar)), 51.37 (d, ^2J(P–C) = 14.6 Hz, $C(CH_3)_3$), 52.22 (dd → t, ^2J(P–C) ∼ 9.5 Hz, $C(CH_3)_3$), 52.55 (d, ^2J(P–C) = 8.1 Hz, $C(CH_3)_3$), 76.46 and 76.52 (2s, OCH_2), 128.21, 128.86, 129.01, 129.97, 133.04 (d, ^2J(P–C) ∼ 7.4 Hz) and 136.53 (Ar–*C* + PC=CH_2), 143.47 (d, ^1J(P–C) = 163.0 Hz, PC=CH_2). ^{31}P NMR (160 MHz, $CDCl_3$): δ −18.71 (dd, ^2J(P–P) ∼ 6.4 Hz, ^3J(P–P) ∼ 35.2 Hz), 20.86 (d, ^3J(P–P) ∼ 35.2 Hz), 71.30 (d, ^2J(P–P) ∼ 6.4 Hz). LC–MS: *m/z* 627 $[M+1]^+$. CCDC number 749652.

4.3. Synthesis of compound [(i-PrNH)$P(\mu\text{-N-}t\text{-Bu})_2P(=N\text{-}i\text{-Pr})$-$N(CO_2\text{-}i\text{-Pr})\text{-}NH(CO_2\text{-}i\text{-Pr})]$ (24)

Cyclodiphosphazane $[i\text{-PrNHPN-}t\text{-Bu}]_2$ [δ(P) 90.69; 0.609 g, 1.9 mmol] was dissolved in dry toluene (6 mL). To this, diisopropyl azodicarboxylate (0.384 g, 1.9 mmol) was added drop-wise at 25 °C. The mixture was stirred for 1 d, concentrated *in vacuo* (to ca 2 mL) and cooled for 1 d at −4 °C to obtain crystals of [(*i*-PrNH)$P(\mu\text{-N-}t\text{-Bu})_2P(=N\text{-}i\text{-Pr})$-$N(CO_2\text{-}i\text{-Pr})\text{-}NH(CO_2\text{-}i\text{-Pr})]$ (**24**). Yield: 0.885 g (89%). M. p.: 105–108 °C. IR (KBr): 3339, 2980, 2733, 2602, 1747, 1716, 1498, 1369, 1304, 1205, 1107, 920, 869 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.14–1.44 (br, 42H, $(C(CH_3)_2 + C(CH_3)_3)$, 2.23 (d, ^2J(P–H) = 4.4 Hz, 1H, N*H*-*i*-Pr), 3.54–3.67 (m, 2H, $NCH(CH_3)_2$), 4.90–4.98 (m, 2H, $OCH(CH_3)_2$), 6.83 (1s, 1H, N*H*–C(O)). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.87, 21.99, 22.12, 22.29, 26.08, 26.64, 27.55, 27.75, 30.88 (s, $C(CH_3)_2 + C(CH_3)_3$), 43.46, 50.84, 52.44, 52.74, 53.11, 67.28, 68.47, 69.33, 69.98, 153.82 (d, ^2J(P–C) = 15.4 Hz, P–N–C(O)), 159.23 (P–N–N–C(O)). ^{31}P NMR (160 MHz, $CDCl_3$): δ −6.89, 73.38. LC–MS: *m/z* 523 $[M+1]^+$. Anal. Calc. for $C_{22}H_{48}N_6O_4P_2$: C, 50.56; H, 9.26; N, 16.08. Found: C, 50.48; H, 9.22; N, 16.17%. CCDC number 749653.

4.4. Synthesis of compound [(S)-(2-OH-1-$C_{10}H_6$-1′-$C_{10}H_6$-2′-O-$P(O)(NH\text{-}t\text{-Bu})_2$] (36)

To a solution of (*S*)-(1,1′-O-$C_{10}H_6$-$C_{10}H_6$-O-)[$(O)P(\mu\text{-N-}t\text{-Bu})_2P(O)$] (**32**) (0.258 g, 0.50 mmol) in toluene, $BH_3.SMe_2$ (0.200 g, 2.7 mmol) was added *via* syringe. This mixture was stirred for 30 min and then the acetophenone (0.300 g, 2.5 mmol) was added. The contents were stirred for 8 h more. The reaction mixture was quenched with water and extracted with dichloromethane. The alcohol $PhCH(OH)(CH_3)$ [0.270 g (90%)] was isolated using column chromatography (EtOAc-hexane); from later fractions, compound [(*S*)-(2-OH-1-$C_{10}H_6$-1′-$C_{10}H_6$-2′-O-$P(O)(NH\text{-}t\text{-Bu})_2$] (**36**) was isolated. Crystals of (*S*)-**36** were obtained from 1:1 CH_2Cl_2–hexane. Yield: 0.156 g (60%). M.p.: 238–240 °C. IR (KBr): 3382, 3310, 2967, 1622, 1595, 1507, 1462, 1387, 1209, 1161, 1067 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.99 and 1.05 (2 s, 18H, *t*-Bu-*H*), 2.24 and 2.30 (2 d, ^2J(PH) = 8.0 Hz each, 2H, 2 N*H*-t-Bu), 6.80 (s, br, 1H, –O*H*), 7.07 (d, ^3J(HH) = 8.0 Hz, 2H, Ar–

Table 1
Crystallographic data for the compounds **13**, **18**, **24**, **36** and **40**.[a]

Compound	**13**	**18**	**24**	**36**	**40**
Empirical formula	$C_{27}H_{49}N_5O_3P_2$	$C_{31}H_{47}N_4O_3P_3$	$C_{22}H_{48}N_6O_4P_2$	$C_{28}H_{33}N_2O_3P$	$C_{17}H_{35}N_3O_2P_2$
Formula weight	553.67	626.72	522.60	561.46	375.42
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
a (Å)	10.4784(15)	10.3463(7)	10.786(3)	9.8138(6)	9.4506(8)
b (Å)	17.994(3)	10.7424(7)	16.708(4)	14.8809(9)	13.7169(12)
c (Å)	16.762(5)	16.4625(11)	17.788(4)	20.8118(13)	16.9175(14)
α (°)	90	87.232(2)	90	90	90
β (°)	94.75(4)	89.947(3)	104.188(4)	90	96.5510(10)
γ (°)	90	82.1340(10)	90	90	90
V /Å^3	3149.5(12)	1810.3(2)	3107.9(13)	3039.3(3)	2178.7(3)
Z	4	2	4	4	4
D_{calc} (g cm^{-3})	1.166	1.150	1.117	1.227	1.145
μ (mm^{-1})	0.172	0.199	0.174	0.297	0.213
F(0 0 0)	1196	680	1136	1184	816
Data/restraints/parameters	5534/0/342	7113/0/389	5425/0/329	7153/0/352	3838/12/296
GOF (S)	1.079	1.079	1.055	1.021	1.048
R_1 [$I > 2\sigma(I)$]	0.0558	0.0684	0.0907	0.0577	0.0456
wR_2 [all data]	0.1259	0.1672	0.2244	0.1546	0.1323
Max./min. residual elec. dens. [e Å^{-3}]	0.272/−0.256	0.694/−0.366	0.671/−0.328	0.383/−0.342	0.269/−0.242

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$.

H), 7.22–7.99 (m, 10H, Ar–*H*). ^{13}C NMR (400 MHz, $CDCl_3$): δ 31.0 and 31.2 (2 d, ^3J(PC) ~ 4.7 Hz, C(*C*H$_3$)$_3$), 50.9 (d, ^2J(PC) ~ 21.9 Hz *C*(CH$_3$)$_3$), 116.5, 119.6, 121.6, 121.7, 123.5, 124.7, 125.4, 125.6, 126.8, 127.0, 128.0, 128.1, 129.3, 130.0, 130.3, 131.2, 133.7, 148.7, 148.8, 152.4. ^{31}P NMR (160 MHz, $CDCl_3$): δ 6.2. $[\alpha]^{27}_D$ = (−) 51.75 (c = 0.40, $CHCl_3$). CCDC number: 749654.

4.5. X-ray crystallography

X-ray data were collected on a Bruker AXS SMART diffractometer using Mo Kα (λ = 0.71073 Å) radiation. The structures were solved and refined by standard methods [21]. The N–H and O–H protons were located from difference maps and refined isotropically. The anion in [(*t*-BuNH)(PhCH$_2$CH(CN)CH$_2$-)P(μ-N-*t*-Bu)$_2$P(NH-*t*-Bu)]$^+$[HCO$_3$]$^-$ (**13**) fits in as nitrate also, but we did not have any evidence for the presence of this in the system and hence this was analyzed as the bicarbonate anion; reactions of (*t*-Bu-NH)P(μ-N-*t*-Bu)$_2$P(=N-*t*-Bu)(CH$_2$CH$_2$CN) (**11**) with acids has phenols has been investigated before [8] and is consistent with the assignment as reported here. Some of the *t*-butyl carbon atoms in these compounds have high thermal parameters, but these do not affect the overall structure and hence we have not tried to model these rigorously. Crystallographic data are summarized in Table 1.

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Appendix A. Supplementary material

CCDC 749651, 749652, 749653, 749654 and 749655 contain the supplementary crystallographic data for compounds **13**, **18**, **24**, **36** and **40**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.11.001.

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