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Synthesis of the 2,4,5-Tri-*tert*-butyl-1,3-diphospholide Anion by Phosphinidene Elimination from 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene on Treatment with the Amide Li[NPh(SiMe$_3$)]

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Abstract: Treatment of the lithium amide Li[NPh(SiMe$_3$)] with 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene, $P_3C_3t\mathrm{Bu}_3$, in a 1:2 ratio afforded equimolar amounts of the lithium salt of the five-membered 2,4,5-tri-*tert*-butyl-1,3-diphospholide anion, $\mathrm{LiP_2C_3}t\mathrm{Bu_3}$ (isolated as its *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA) adduct), and the tricyclic compound 6-[phenyl(trimethylsilyl)amino]-3,5,7-tri-*tert*-butyl-1,2,4,6-tetraphosphatricyclo[3.2.0.0^{2,7}]hept-3-ene. Both compounds have been structurally characterised by single-crystal X-ray diffraction studies. The mechanism of this remarkable reaction has been elucidated by theoretical methods at the B3LYP/6-311+G** level of theory. The reaction involves a hitherto unobserved aminophosphinidene, which was formed by abstraction of a phosphorus atom from triphosphabenzene. The intermediate aminophosphinidene, which is further stabilised by the solvent THF, shows, in agreement with previous theoretical predictions, enhanced stability and reacts then with a second molecule of triphosphabenzene.

Keywords: amides • density functional calculations • phosphinidenes • phosphorus heterocycles • reaction mechanisms • reactivity

Introduction

The chemistry of unsaturated compounds containing low-coordinate phosphorus has developed rapidly over recent years.[1–3] These compounds exhibit many similar properties to their better-known unsaturated hydrocarbons. Interest in these compounds, typified by phospha-alkenes, -alkynes and -benzenes (phosphinines), as well as polyphosphacyclopentadienyls and -metallocenes, has mainly concerned synthetic, structural and spectroscopic aspects. Recently a variety of useful catalytic processes utilising these compounds has also been reported. Breit et al.[4] have shown that substituted phosphinines coordinated in a η^1 fashion to rhodium can act as highly activated and selective catalysts for the hydroformylation of olefins. Likewise, complexes containing η^6-phosphinines catalyse the synthesis of pyridines from alkynes and nitriles[5] and the cyclodimerisation of 1,3-butadiene.[6]

In previous studies[7–10] we showed that the 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene, $P_3C_3t\mathrm{Bu}_3$ (**1a**), readily undergoes [1+4] cycloaddition reactions with isoelectronic silylenes and (transition-metal-complexed) phosphinidenes (and in unpublished work[11]) with isolobal In$^\mathrm{I}$ and Ga$^\mathrm{I}$ compounds. On the other hand, the analogous reaction of **1a** with the Arduengo-type carbene, tetramethylimidazol-2-ylidene, unexpectedly led to a ring contraction reaction involving the extrusion of a C*t*Bu fragment from the 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene ring leading to the quantitative formation of the aromatic five-membered 1,2,4-triphosphole, $P_3C_2t\mathrm{Bu}_2$ (carbene), ring system.[12] (Scheme 1). In these reactions the reactant is a nucleophile that attacks the low-lying[13] LUMO of the triphosphabenzene.

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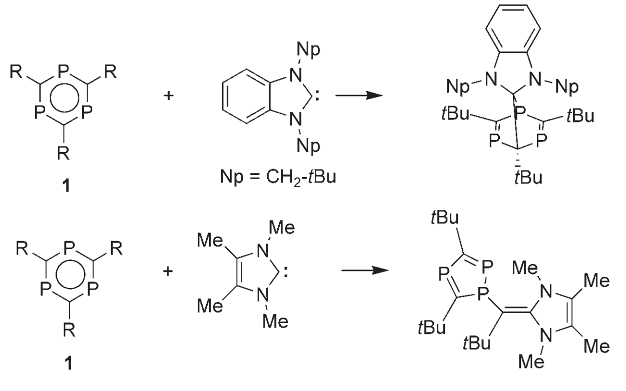
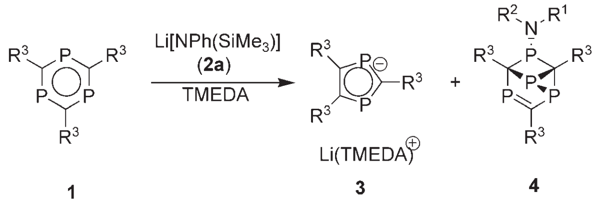


Scheme 1.

Results and Discussion

In view of this differing behaviour, we explore the reaction of 1,3,5-triphosphabenzene with other nucleophiles. Herein, we describe its remarkable reaction with lithium and sodium amides. Thus, treatment of Li[NPh(SiMe$_3$)] (**2a**) with P_3C_3tBu$_3$ (**1a**) in a 1:2 ratio in THF at 50 °C for three days readily afforded the lithium salt of the 1,3-diphospholide anion, Li[P_2C_3tBu$_3$] (**3a**) in quantitative yield together with the unusual tricyclic compound 6-[phenyl(trimethylsilyl)amino]-3,5,7-tri-*tert*-butyl-1,2,4,6-tetraphosphatricyclo[3.2.0.0^{2,7}]hept-3-ene (**4a**) (Scheme 2).



Scheme 2. **a**: R^1 = Ph, R^2 = SiMe$_3$, R^3 = tBu. **b**: R^1 = R^2 = R^3 = H.

An interesting feature of this two-step reaction is that **4a** results from the trapping of the initially formed novel reactive aminophosphinidine fragment, PN(Ph)SiMe$_3$, by the second molecule of P_3C_3tBu$_3$. Hence we have investigated the detailed mechanisms of both these reactions using theoretical calculations at the B3LYP/6-311+G** level of theory for the model system $NH_2^- + 2P_3C_3H_3$ and also for the system with real substituents at the B3LYP/6-31+G* level of theory. The formation of an uncomplexed aminophosphinidene intermediate is of particular interest. Substitution of the phosphinidene by an amino group results in considerable stabilisation of the singlet state.[14] Me$_2$NP was reported to have a singlet ground state, the triplet being 1.7 kcal mol^{-1} less stable (QCISD(T)/6-311G(d,p)//MP2/6-31G**).[14a] For H$_2$NP, however, the triplet was more stable than the singlet by 1.2 kcal mol^{-1} (QCISD(T)/6-311++G-(3df,2p)//MP2/6-31G**).[14a] In spite of the computationally predicted stabilisation achieved by the amino group, no report seems to have appeared about this type of compound,[3,15,16] however, complexed aminophosphinidenes are known.[17]

Addition of TMEDA to **3a** afforded [Li(TMEDA)]-[P_2C_3tBu$_3$] (**3A**) as a pale orange powder that was purified by vacuum sublimation and subsequently crystallised. Compounds **3A** and **4a** were both characterised by their ^{31}P, ^{13}C, ^{7}Li and ^{1}H NMR spectra, their mass spectra and by single-crystal X-ray diffraction studies. The ^{31}P{^{1}H} NMR spectrum of **3A** exhibited a singlet at $\delta = 186.8$ ppm which is in excellent agreement with literature values reported for both Na-[P_2C_3tBu$_3$][17] and our previously reported, fully structurally characterised K[(THF)P_2C_3tBu$_3$],[18] which were made by completely different synthetic routes.

The ^{7}Li NMR spectrum of **3A** revealed a sharp singlet at $\delta = 3.28$ ppm and in the ^{13}C{^{1}H} NMR spectrum the ring carbon atoms appeared as a triplet ($\delta = 188.9$ ppm, $^1J_{C,P} = 49.9$ Hz) and a multiplet ($\delta = 163.4$ ppm) as a result of second-order coupling. Strong peaks at m/z 270 arising from the protonated ring ion, P_2C_3tBu$_3$H$^+$, and fragmentation products were observed in the EI (positive-ion mode) mass spectrum.

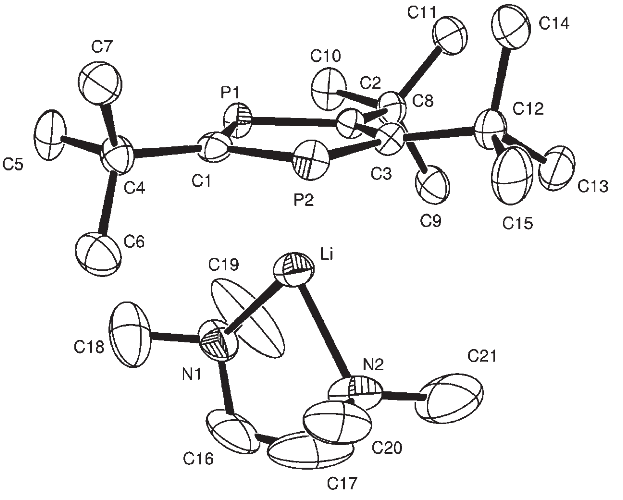


Figure 1. Molecular structure of [Li(TMEDA)][P_2C_3tBu$_3$] **3A**. Selected bond lengths [Å] and bond angles [°]: Li–ring$_{\text{centroid}}$ 2.128(6), P1–C1 1.732(2), P1–C2 1.789(3), P2–C1 1.745(3), P2–C3 1.782(3), C2–C3 1.420(4); C1-P1-C2 97.62(14), C1-P2-C3 97.58(12), P1-C1-P2 114.73(15), C3-C2-P1 114.9(2), C2-C3-P2 115.0(2).

A single-crystal X-ray diffraction study of **3A** revealed the monomeric structure shown in Figure 1 and establishes a planar P_2C_3tBu$_3$ ring η^5-coordinated to the lithium centre with a lithium–ring$_{\text{centroid}}$ distance of 2.128(6) Å. As expected the C–C and C–P ring bond lengths lie between those of single and double bonds, indicating significant ring π-electron delocalisation (d(P–C) = 1.732(2)–1.789(3), d(P–C)$_{\text{average}}$ = 1.762; d(C–C) = 1.420(4) Å). Interestingly, although the literature bond lengths for the μ-η^5:η^5-bridging P_2C_3tBu$_3$ ring in (Me$_3$Si)$_3$SiLi(μ-η^5:η^5-P_2C_3tBu$_3$)Li(toluene) are 1.768 Å[18] for the average C–P ring bond length and

1.399(6) Å for the C–C ring bond length, in close agreement with those of **3A**, the Li–ring$_{centroid}$ distances of 2.024 and 1.988 Å are significantly shorter. Similar ring bond lengths (d(P–C)$_{average}$ = 1.753(5) and d(C–C) = 1.416(6) Å) have been reported for the polymeric [K(THF)P_2C_3*t*Bu_3],[19] which exists as an infinite chain of alternating [K^+(THF)] ions η^5-ligated to the P_2C_3*t*Bu_3 rings.

The ^{31}P, ^{29}Si, ^{13}C and ^{1}H NMR and mass spectral data for compound **4a** are in accord with its formulation as the tricyclic organophosphorus compound 6-[phenyl(trimethylsilyl)amino]-3,5,7-tri-*tert*-butyl-1,2,4,6-tetraphosphatricyclo[3.2.0.0^{2,7}]hept-3-ene containing five-, four- and three-membered rings. Of the four ^{31}P NMR resonances, only the multiplet at $\delta_{P(A)}$ = 348.8–348.5 ppm is indicative of an unsaturated phosphorus environment. A doublet of doublets of doublets at $\delta_{P(C)} = -14.4$ ppm and $\delta_{P(D)} = -59.1$ ppm have been ascribed to the two phosphorus atoms in the three-membered diphosphirane ring on the basis of their large one-bond coupling constant, $^{1}J_{P,P}$ = 186.0 Hz. The broad doublet at −15.6 ppm has been attributed to the saturated P^B centre bearing the amino substituent and this phosphorus splits the signal arising from the $SiMe_3$ atom at δ = 11.1 ppm in the ^{29}Si NMR spectrum ($^{2}J_{Si,P}$ = 36.4 Hz). A low-field doublet of doublets at δ = 204.4 ppm in the ^{13}C{^{1}H} NMR spectrum can be assigned to the unsaturated phosphaalkene carbon atom which is also split by the adjacent diphosphirane P^D atom ($^{1}J_{C,P}$ = 69.3 and 47.6 Hz). The broadness of the *ortho*-phenyl proton signal in the ^{1}H NMR spectrum at room temperature implies that the rotation of the phenyl group is sterically constrained as a sharp signal at δ = 6.9 ppm is obtained when **4a** is heated to 70 °C. Further support for the structural formula came from the satisfactory elemental analysis and the observation in the EI(positive-ion mode) mass spectrum of a strong molecular ion at *m*/*z* 495 with the expected fragmentation pattern.

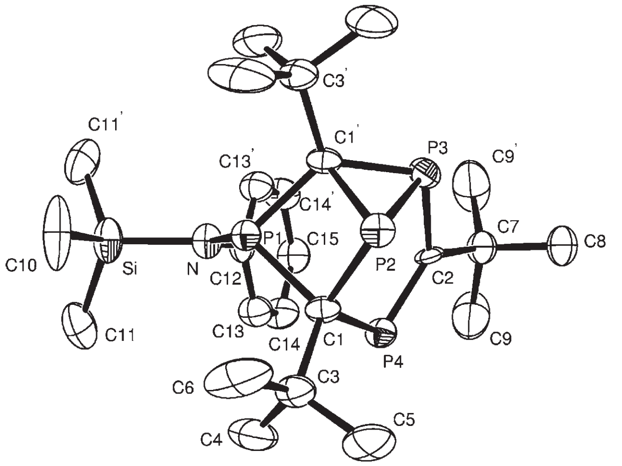


Figure 2. Molecular structure of 6-[phenyl(trimethylsilyl)amino]-3,5,7-tri-*tert*-butyl-1,2,4,6-tetraphosphatricyclo[3.2.0.0^{2,7}]hept-3-ene, P_4C_3*t*Bu_3N(Ph)$SiMe_3$ (**4a**). Selected bond lengths [Å] and bond angles [°] (the second set of data refer to the B3LYP/6-31+G* computed data (see also text)): P1–N 1.693(7)/1.743, Si–N 1.785(7)/1.806, N–C12 1.450(10)/1.442, P1–C1 1.856(6)/1.860, P2–C1 1.913(6)/1.930, P2–P3 2.165(4)/2.199, P3–C1 1.824(6)/1.919, P3–C2 1.83(2)/1.842, P4–C2 1.65(2)/1.687, P4–C1 1.924(6)/1.884; P1-N-Si 117.9(4)/116.9, C12-N-P1 129.8(5)/129.8, C12-N-Si 112.3(5)/113.3.

The atom connectivities in **4a** were fully established by a single-crystal X-ray diffraction study (Figure 2), the rather high *R* factor (9.4 %) resulting from the close, but not exact, mirror symmetry of the molecule, excluding the C2, P3 and P4 atoms, resulting in the molecule being disordered across a crystallographic mirror plane with half-occupancy atom sites for C2, P3 and P4. Furthermore, the unit cell contains one CH_2Cl_2 solvate molecule lying on an inversion centre with disordered carbon and hydrogen atoms that could not be resolved. Although any discussion of bond lengths and angles must therefore be treated with caution, the proposed P=C distance, P4–C2, of 1.65(2) Å is clearly much shorter than other C–P single bond lengths, which all lie in the range of 1.924(6) to 1.824(6) Å. The PNPh($SiMe_3$) fragment is essentially planar, the sum of the angles around the nitrogen atom being 359.1°.

In the hope that metal complexation at any one of the phosphorus atoms would break the pseudosymmetry, we attempted to make a Pt^{II} complex of **4a**. Although the complex has been successfully characterised by multinuclear NMR spectroscopy, we were not able to grow crystals suitable for an X-ray study.

Theoretical calculations: To better understand the mechanism for the formation of the 1,3-diphospholide anion from **1** we considered the intermediates shown in Figure 3,

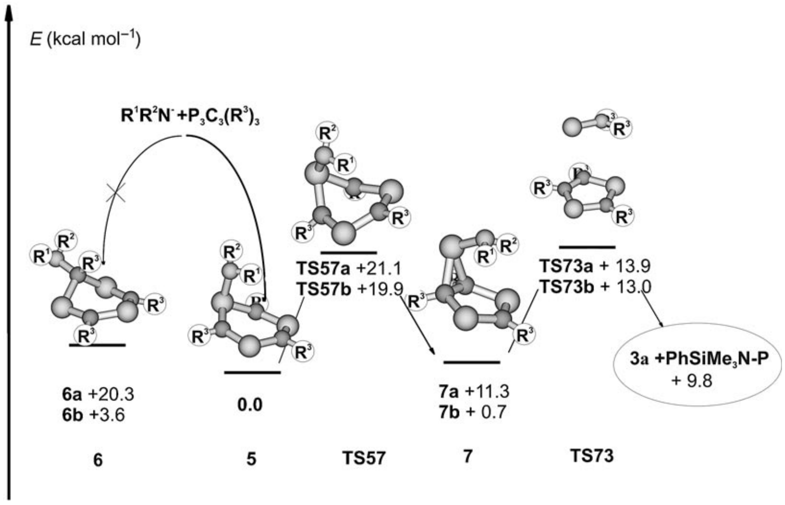


Figure 3. Computed reaction path after the attack of the amido group on triphosphabenzene. **a**: R^1 = Ph, R^2 = $SiMe_3$, R^3 = *t*Bu. **b**: R^1 = R^2 = R^3 = H.

formed by initial nucleophilic attack at the carbon or phosphorus atom of **1**. Previously we established[12] analogous intermediates for the reaction of the Arduengo-type carbene $C(NMe)_2C_2Me_2$ and the triphosphabenzene $P_3C_3tBu_3$ (**1a**).

The model reaction system $NH_2^- + P_3C_3H_3$ (**1b**) was studied theoretically at the B3LYP/6-311+G** level of theory (Figure 3), but, as discussed in detail elsewhere,[20] in the real system it is important to take account of the significant steric repulsion of the bulky *t*Bu substituents in unsaturated phosphorus rings which plays a significant role in affecting the relative energies of both intermediate and transition-state structures. Our theoretical analysis will therefore address this point later. For the real system, unless otherwise stated, we have used the more economical B3LYP/6-31+G* level of theory for geometry optimisation throughout (see also Computational methods in the Experimental Section).

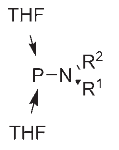
In the first step of the model $NH_2^- + $**1b** reaction, the amide ion can attack the triphosphabenzene ring either at the phosphorus or the carbon atom and, according to the calculations, both result in intermediates **5b** and **6b**, respectively, with attack at phosphorus (**5b**) being favoured over that at carbon (**6b**) by 3.6 kcal mol^{-1} (Figure 3).

As found previously[12] for the reaction of the nucleophilic Arduengo carbene with **1b** a second intermediate **7b** can be formed upon ring closure via transition-state structure **TS57b**. The energy of the latter is 19.9 kcal mol^{-1} greater than that of **5b**, with **7b** being slightly less stable (by 0.7 kcal mol^{-1}) than **5b**. A further possible structure in which the NH_2^- unit bridges the 1 and 4 positions of the 1,3,5-triphosphabenzene ring could not be located as a minimum. The diphosphacyclopentadienide anion and the transient aminophosphinidene PNH_2 can be obtained from **7b** via the transition state **TS73b**, which is 13.0 kcal mol^{-1} higher in energy than **5b**. Thus, the entire reaction has a reasonably low energy barrier, in accord with the observed production of aminophosphinidene at room temperature.

Computation of the real system (at the B3LYP/6-31+G* level of theory) alters somewhat the relative energies, but the main conclusion remains the same. Thus, **5a** is significantly more stable (by 20.3 kcal mol^{-1}) than **6a** as the attacking amino and the *t*Bu groups repel each other in **6a**. Also **7a** is destabilised (it is ca. 11.3 kcal mol^{-1} higher in energy than **5a**) as a result of the repulsion between the two *t*Bu groups located on two neighbouring carbon atoms in **7a**. Nevertheless, the energy of **TS57a** is still only 21.1 kcal mol^{-1} greater than **5a** and thus the overall reaction barrier is not significantly influenced by the substituents.

The energy change of reaction (1) has been calculated; the triphosphabenzene and the attacking amide is more stable by 9.5 kcal mol^{-1}. Note, however, that this model calculation refers to gas-phase ions and neither solvation effects nor counterions were taken into account. Furthermore, the energy of the open-shell singlet $Ph(Me_3Si)NP$ phosphinidene has been considered; the triplet is the ground state, being more stable by 1.5 kcal mol^{-1} (see below). The solvent THF can play an important role as its lone pair stabilises the closed-shell phosphinidene, interacting with the empty orbital of phosphorus. Phosphinidenes are known to be stabilised by different nucleophiles.[16,21] Likewise, germylenes are known to be stabilised by diethyl ether.[22] Indeed, the complex formed between $Ph(Me_3Si)NP$ and THF was computed to have a closed-shell singlet ground state (B3LYP/6-31+G*). The stability of this complex is between 6.1 (B3LYP/6-31+G*) and 13.0 kcal mol^{-1} (MP2/6-31G*)[23] depending on the level of the theory applied. Since for $GeCl_2$ a complex with two THF molecules has been reported, we have also computed the structure of **8** in which two THF molecules form a complex with $Ph(Me_3Si)NP$. The stability of this complex, depending on the level of the theory, is 7.3 (B3LYP/6-31+G*) and 19.3 kcal mol^{-1} (MP2/6-31G*). As highly correlated calculations using larger basis sets are not feasible for these systems the extent of the stabilisation of $Ph(Me_3Si)NP$ by THF remains unclear, but it is apparent that the solvent (which is in large excess, therefore shifting the equilibrium towards complex formation) stabilises the phosphinidene intermediate as a singlet.

$$\mathbf{1a} + Ph(Me_3Si)N^- \rightarrow \mathbf{3a} + Ph(Me_3Si)NP \qquad (1)$$



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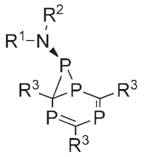

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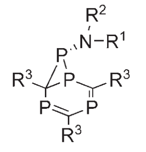

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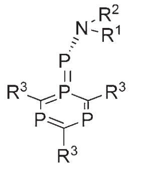

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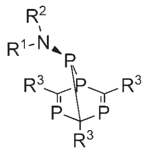

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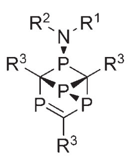

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a: R^1= Ph, R^2= $SiMe_3$, R^3= *t*Bu
b: R^1= R^2= R^3= H

The second triphosphabenzene ring can then be attacked by the newly generated phosphinidene PNH_2 at either the carbon or the phosphorus atoms, by analogy with our previous studies[7–10] on the structurally characterised [1+4] silylene and (metal-complexed) phosphinidene adducts of $P_3C_3tBu_3$. The phosphorus atom of the aminophosphinidene can adopt either a 1,4- or a 1,2-bridging position over the triphosphabenzene ring. Both of these possibilities (as reaction intermediates) were modelled for the parent system ($P_3C_3H_3 + PNH_2$) at the B3LYP/6-311+G** level of theory in a search for minima on the potential energy surface.

When the PNH_2 species approaches either the phosphorus or the carbon atom from above the plane of the parent triphosphabenzene ring, $P_3C_3H_3$, no structures analogous to **5** or **6** were obtained as minima. Instead, both of these optimisations resulted in the 1,2-bridged structure. In the most stable structure **9b**, the amino group is situated above the plane of the ring; structure **10b**, in which the amino moiety points away from the ring, is less stable than **9b** by 2.2 kcal mol^{-1} at the B3LYP/6-311+G** level of theory. We were unable to locate transition-state structures for the formation of **9b** and **10b** apart from weakly bound van der Waals complexes at a reactant separation of 3.4 Å. Attack at the ring phosphorus atom can also result in the formation of planar **11b**, which is less stable than **9b** by 8.5 kcal mol^{-1}. Structure **12b**, in which the phosphorus is in a 1,4-bridging position, has also been located; it is more stable than **9b** by 5.8 kcal mol^{-1}. Structure **4b** (the model compound for the observed product **4a**) is 7.2 kcal mol^{-1} more stable than **9b**, being the thermodynamic sink, in agreement with the observed reactivity. Structure **13b**, in which the amino moiety is in an *exo* position, is less stable than its isomer **4b** by 7.6 kcal mol^{-1}. The transition-state structures connecting the most stable intermediates and the product (**9b**, **12b** and **4b**) were also located. The highest energy transition-state structure lies only 19.3 kcal mol^{-1} above **9b**, indicating a rather facile reaction.

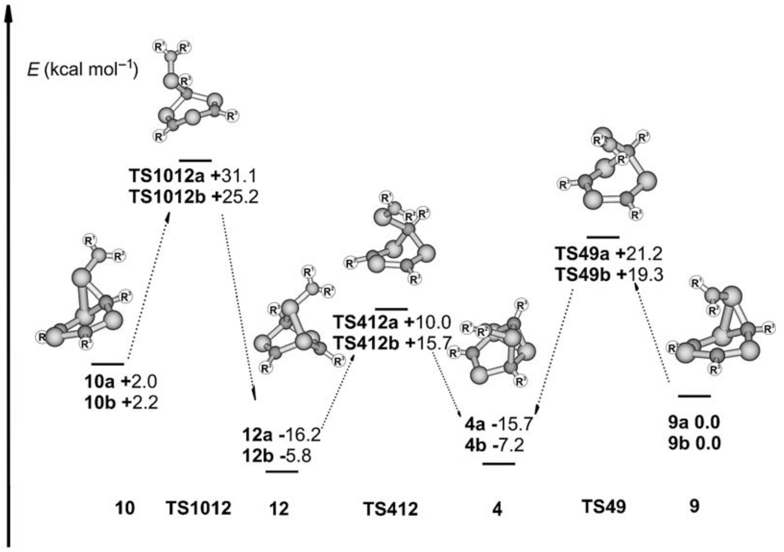


Figure 4. Computed reaction path after the attack of an aminophosphinidene on triphosphabenzene. **a**: R^1 = Ph, R^2 = $SiMe_3$, R^3 = *t*Bu. **b**: R^1 = R^2 = R^3 = H.

It can be surmised that **11** might also be a reaction intermediate, complexation with the lone pair of the triphoshabenzene ring stabilising the aminophosphinidene. Recent examples have shown that phosphinidenes are stabilised by phosphines as ylides.[21f,24] However, because **11** is less stable than **9** (or **10**), and as the latter structures are formed without a barrier from aminophosphinidene and triphosphabenzene, it seems unlikely that **11** would play a role in the reaction. Thus, we assume that the first reaction step is the barrierless formation of **9** (or **10**).

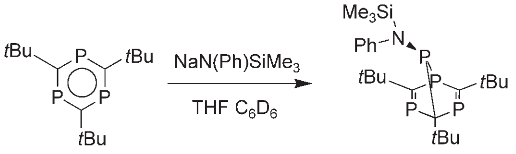
Further studies were carried out on analogous structures bearing the real substituents (**4a** and **9a**–**12a**) at the B3LYP/6-31+G* level of theory. The transition-state structures connecting the minima were located. Structure **13a** has not been considered further as it is less stable than **4a** by 22.5 kcal mol^{-1} (the observed reaction product). The results showing the relative energies of the minima and the connecting transition-state structures are summarised in Figure 4. Interestingly, at the B3LYP/6-31+G* level of theory, the bridged structure **12a** was found to be slightly (by 0.5 kcal mol^{-1}) more stable than **4a** (the observed product), whereas at the B3LYP/3-21G(*) level of theory **4a** was more stable than **12a** by 0.4 kcal mol^{-1}. The two isomeric structures are evidently similar in energy and it is likely that solvent effects or crystal forces can influence their relative stability[25] (see also below).

The computed structural features of **4a** are close to those obtained by the X-ray study (see Figure 2). The amino moiety is planar and the P–C bonds in the three- and four-membered rings are rather long. For the P3–C1 bond, however, the computed distance is longer than the value obtained from the X-ray analysis by nearly 0.1 Å. This difference is likely to be caused by the observed disorder in P3.

Likewise, as in the case of the parent compounds, both **9a** and **10a** can be obtained barrierless from triphosphabenzene and the aminophosphinidene and have similar energies. The observed product **4a** can be obtained via a 21.2 kcal mol^{-1} barrier **TS94a** (37.4 kcal mol^{-1} above **12a**) directly from **9a**. The transition-state structure connecting **10a** and **12a** (**TS1012a**), is, however, 47.3 kcal mol^{-1} higher in energy than **12a**, which in turn is a 29.1 kcal mol^{-1} barrier on the reaction path from **10a**. The transition-state structure connecting **9a** and **10a** (**TS910a**), as well as the one between **12a** and **4a** (**TS412a**), does not exclude the possible interconversion of these molecules. The reaction pathway suggested from these computations is shown in Figure 4.

In the above reaction sequence, the reactivity of the aminophosphinidene is of particular interest. According to the calculations described herein, it reacts with **1a** as a singlet without a barrier to form **9a**. The interaction of the singlet $PN(Ph)SiMe_3$ with THF results in complex **8**, which has a closed-shell singlet ground state, as discussed above. The free aminophosphinidene $PN(Ph)SiMe_3$, however, is a ground-state triplet, the triplet–(closed-shell) singlet splitting being 5.4 kcal mol^{-1} (B3LYP/6-31+G*). The triplet-state reaction product from $PN(Ph)SiMe_3$ and triphosphabenzene (the phosphinidene unit is attached to a ring carbon atom, the adduct at phosphorus being less stable) was calculated to be 23.1 kcal mol^{-1} less stable than the singlet. Thus, the reaction of the triplet state is rather demanding in energy, whereas the singlet reacts without any barrier with the excess triphosphabenzene. Note that the stabilised phosphinidene[14] tBu$_2$PP reacts similarly with multiply bonded compounds, resulting in the formation of three-membered rings.[24] On the other hand, Jones and co-workers[26] very recently proposed a MeP elimination step in the formation of the known tetraphosphaferrocene, Fe(P$_2$C$_3t$Bu$_3$)$_2$,[27] from the reaction of FeCl$_2$ and LiMeP$_3$C$_3t$Bu$_3$ and they successfully characterised the resulting (MeP)$_n$ polyphosphane rings. MeP, the phosphinidene eliminated in this reaction, has a large triplet–singlet splitting (the triplet is favoured by as much as 26 kcal mol^{-1}) so that the (otherwise forbidden, therefore rather slow) triplet–singlet conversion is more likely than with a small triplet–singlet splitting. The known reaction product from the non-stabilised triplet phosphinidenes are polyphosphanes, as has been observed experimentally.

To provide further support for the mechanism proposed above, we carried out the additional reaction of **1a** with sodium phenyl(trimethylsilyl)amide, Na[NPh(SiMe$_3$)], which proceeded smoothly at ambient temperature in a solution of THF and C$_6$D$_6$. Owing to the greater reactivity of the sodium amide compared with the corresponding lithium reagent, the progress of the reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy which revealed the presence of a long-lived intermediate attributed to the [1+4] cycloaddition product **12a** shown in Scheme 3.



1 **12**

Scheme 3.

The ^{31}P NMR spectrum of compound **12a** displays four coupled phosphorus atoms ($\delta = 335.8$ ppm, dd, $J_{P,P} = 25.1$, 15.6 Hz; $\delta = 310.1$ ppm, ddd, $J_{P,P} = 64.0$, 20.5, 15.6 Hz; $\delta = 178.6$ ppm, dd, $J_{P,P} = 245.0$, 64.0 Hz and $\delta = 10.3$ ppm, ddd, $J_{P,P} = 245.0$, 25.1, 20.5 Hz) and shows strong similarities to the ^{31}P{^{1}H} NMR spectrum of other fully structurally characterised [1+4] cycloadducts of the phosphinidene complex [MePW(CO)$_5$] and P$_3$C$_3t$Bu$_3$.[10,11] The reaction was complete after 3 days at room temperature, yielding, as expected, NaP$_2$C$_3t$Bu$_3$ (singlet, $\delta_P = 187.4$ ppm in THF) and the tricyclic compound **4a**. Note that this rearrangement clearly shows that the stability in THF differs from the relative stabilities of **12a** and **4a** computed at the B3LYP/6-31+G* level of theory, however, it is in agreement with the relative energies computed by some other functionals.[25] Considering the small (0.5 kcal mol^{-1}) computed energy differences between the two isomeric structures, the contradiction between the B3LYP results and the experimental results can either be explained by the effect of the THF solvent or by the approximate nature of the density functional theory applied.

This ready formation of alkali metal salts of the 1,3-diphospholide anion M[P$_2$C$_3t$Bu$_3$] (M = Li, Na) by treatment of the 1,3,5-triphosphabenzene with a metal amide offers synthetic advantages over our previously reported synthesis involving the reaction of **1a** with a potassium mirror, in which metal phosphides were also formed. Interestingly, Regitz and co-workers[28] recently described the ready formation of Li[RP$_3$C$_3t$Bu$_3$] from **1a** and LiR, which subsequently led to LiP$_2$C$_3t$Bu$_3$ on refluxing in THF for 3 h. However, the fate of the presumed eliminated phosphinidene, PR, was not established.[29]

Conclusion

The two-step reaction between lithium amide Li[NPh(SiMe$_3$)] and 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene, P$_3$C$_3t$Bu$_3$ (in a 1:2 ratio), afforded equimolar amounts of the lithium salt of the five-membered 2,4,5-tri-*tert*-butyl-1,3-diphospholide ring anion LiP$_2$C$_3t$Bu$_3$ (isolated as its TMEDA adduct) and the tricyclic compound 6-[phenyl(trimethylsilyl)amino]-3,5,7-tri-*tert*-butyl-1,2,4,6-tetraphosphatricyclo[3.2.0.0^{2,7}]hept-3-ene. The first step in the reaction is the extrusion of a stabilised aminophosphinidene from the aromatic six-membered ring, resulting in the stable, aromatic five-membered diphospholide anion. Computational studies indicate that the aminophosphinidene reacts as the singlet state stabilised (apart from the amino substituent) by the solvent THF, attacking the second molecule of triphosphabenzene to give, after a series of transformation steps, a cage compound.

This series of reactions is remarkable from several aspects. First, the transformation of the highly aromatic six-membered ring[30] to the highly aromatic polyphospholide anion[30] deserves attention. Apart from its aromaticity, the symmetrical arrangement of the bulky *tert*-butyl substituents further stabilises the 1,3,5-triphosphabenzene.[20] The angle strain induced by the small bonding angles at the doubly bonded σ^2-phosphorus (nearly 95° in H$_2$C=PH)[31] is destabilising in the six-membered ring. Although the five-membered diphospholide ion suffers from less ring strain than triphosphabenzene, the repulsion of the two neighbouring *tert*-butyl groups is disadvantageous. As a result of these counterbalancing effects, the stability of the eliminated phosphinidene is crucial in shifting the equilibrium of the reaction. Thus, triphosphabenzene can be used as a mild phosphinidene source.

The aminophosphinidene formed during the reaction described herein is significantly stabilised and reacts with a second triphosphabenzene molecule as a singlet, which is stabilised by interaction with the solvent ether molecule. This reactivity differs remarkably from that of the triplet PMe, which oligomerises.

Experimental Section

All manipulations were carried out under rigorously anhydrous and oxygen-free conditions using standard high vacuum-line techniques or in inert atmosphere Schlenk tubes using glassware that had been flame-dried in vacuo or by repeated alternate evacuation and purging with either dry argon or nitrogen. Some manipulations were performed under catalytically dried and deoxygenated nitrogen in either a Mbraun or a Miller Howe glove box. $P_3C_3t\mathrm{Bu}_3$ and $\mathrm{Li[N(Ph)SiMe_3]}$ were prepared in accord with literature procedures.[32,33] The NMR spectra were recorded by using DPX300 or AMX 500 Bruker instruments and calibrated internally to residual solvent resonances for ^{1}H and ^{13}C; external H_3PO_4 (85% aqueous solution) and LiCl were used as references for ^{31}P and ^{7}Li spectra, respectively. MS data were obtained by using a VG Autospec Fisons instrument; EI 70 eV.

Synthesis of 3a, 3A and 4a: $P_3C_3t\mathrm{Bu}_3$ (**1a**) (312.0 mg, 1.04 mmol) and $\mathrm{Li[N(Ph)SiMe_3]}$ (102.2 mg, 0.60 mmol) were combined and dissolved in THF (15 mL) with stirring to afford an orange solution of **3a**. The reaction mixture was heated at 50 °C for three days. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA, 118 μL, 90.6 mg, 0.78 mmol) was added at room temperature and the orange solution stirred for 18 h. Removal of the solvent in vacuo afforded an orange oil which dissolved in hexane (5 mL). Cooling to −50 °C with stirring led to the precipitation of [Li(TMEDA)][$P_2C_3t\mathrm{Bu}_3$] (**3A**) as a pale orange powder, which was isolated by filtration and washed with hexane (2×3 mL) at −50 °C (121.0 mg, 59 %). Crystals suitable for X-ray diffraction study were grown from a saturated diethyl ether solution at −4 °C. The combined filtrate and hexane washings were transferred to a sublimation tube. The solvent was removed in vacuo to afford a yellow oil which was sublimed over several days (1.0×10^{-6} mbar, 85 °C) to afford another yellow oil which gradually crystallised. The sublimate was recovered through dissolution in hexane. Removal of the solvent afforded **4a** as a yellow powder (148.6 mg, 58 %). Crystals suitable for X-ray diffraction study were grown from a dichloromethane solution slowly cooled to −85 °C.

3A: ^{1}H NMR (300.13 MHz, [D$_5$]pyridine): $\delta=2.37$ (s, 4H; NCH_2CH_2N), 2.15 [s, 12H; N(CH_3)$_2$], 2.06 (s, 18H; *t*Bu), 2.02 ppm (s, 9H; *t*Bu); ^{7}Li NMR (116.6 MHz, [D$_5$]pyridine): $\delta=3.28$ ppm (s). ^{13}C{^{1}H} NMR (75.5 MHz, [D$_5$]pyridine): $\delta=188.9$ (t, $^1J_{\mathrm{C,P}}=49.9$ Hz; ring C), 163.9–162.9 (m; ring C), 58.0 (s; N*C*H$_2$*C*H$_2$N), 45.8 (s; N*C*H$_3$), 38.7–38.0 [m; *C*(CH$_3$)$_3$], 38.1 [t, $^2J_{\mathrm{C,P}}=20.6$ Hz; *C*(CH$_3$)$_3$], 37.9 [pseudo-t, $J_{\mathrm{C,P}}=8.4$ Hz; C(*C*H$_3$)$_3$], 37.7 ppm [t, $^3J_{\mathrm{C,P}}=10.0$ Hz; C(*C*H$_3$)$_3$]; ^{31}P{^{1}H} NMR (121.5 MHz, [D$_5$]pyridine): $\delta=186.8$ ppm (s). MS (EI+): *m*/*z* (%): 270 (55) [$P_2C_3t\mathrm{Bu}_3\mathrm{H}$]$^+$, 231 (25), 214 (40) [$P_2C_3t\mathrm{Bu}_3\mathrm{H}-t\mathrm{Bu}$]$^+$, 57 (100); elemental analysis calcd (%) for $C_{21}H_{43}LiN_2P_2$: C 64.3, H 11.04, N 7.14; found: C 64.3, H 10.80, N 7.22.

Crystal data for 3A: $C_{21}H_{43}LiN_2P_2$, $M_r=392.45$, orthorhombic, space group *Pna*2$_1$ (no. 33), $a=11.5527(4)$, $b=18.6719(7)$, $c=11.4096(5)$ Å, $U=2461.2(2)$ Å^3, $Z=4$, $\rho_{\mathrm{calcd}}=1.06$ Mg m^{-3}, crystal dimensions 0.2×0.2×0.2 mm, $F(000)=864$, $T=173(2)$ K, Mo$_{K\alpha}$, radiation $\lambda=0.71073$ Å. Data collection: Kappa CCD. Of the total 5420 independent reflections measured, 3938 with $I>2\sigma(I)$. The final indices [$I>2\sigma(I)$] were $R_1=0.053$, $wR_2=0.101$ and $R_1=0.087$, $wR_2=0.114$ (for all data). Full-matrix least-squares refinement on F^2 was carried out using SHELXL-97.[34] There is some minor conformational disorder of the TMEDA ligand which was only resolved for the C(16)/C(16a) atoms in the ratio 0.70:0.30.

CCDC-646619 (**3A**) and CCDC-646620 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4a: ^{1}H NMR (500.13 MHz, C$_6$D$_6$): $\delta=7.1$–6.7 (br s, 2H; *ortho*-Ph), 6.96–6.91 (m, 2H; *meta*-Ph), 6.85–6.82 (m, 1H; *para*-Ph), 1.50 (s, 9H; *t*Bu), 1.46 (s, 9H; *t*Bu), 1.13 (s, 9H; *t*Bu), 0.19 ppm [s, 9H; Si(CH_3)$_3$]; ^{13}C{^{1}H} NMR (125.76 MHz, C$_6$D$_6$): $\delta=204.4$ (dd, $^1J_{\mathrm{C,P}}=69.3$, 47.6 Hz; unsaturated ring C), 147.5 (d, $^2J_{\mathrm{CP}}=7.8$ Hz; *ipso*-Ph), 129.0 (br s; *meta*-Ph), 125.5 (s; *para*-Ph), 91.8–90.5 (m; saturated ring C), 78.4–77.3 (m; saturated ring C), 40.8 [dd, $^2J_{\mathrm{C,P}}=22.3$, 15.6 Hz; *C*(CH$_3$)$_3$], 37.5 [pseudo-t, $^2J_{\mathrm{C,P}}=15.3$ Hz; *C*(CH$_3$)$_3$], 37.2–36.8 [m; *C*(CH$_3$)$_3$], 33.6 [pseudo-t, $^3J_{\mathrm{C,P}}=10.1$ Hz; C(*C*H$_3$)$_3$], 33.0 [dd, $^3J_{\mathrm{C,P}}=13.2$, 10.1 Hz; C(*C*H$_3$)$_3$], 30.8 [pseudo-quartet, $^3J_{\mathrm{C,P}}=9.0$ Hz; C(*C*H$_3$)$_3$], 2.1 ppm [d, $^3J_{\mathrm{C,P}}=11.2$ Hz; Si(*C*H$_3$)$_3$]; ^{29}Si{^{1}H} NMR (99.3 MHz, C$_6$D$_6$): $\delta=11.1$ ppm (d, $^2J_{\mathrm{Si,P}}=36.4$ Hz). ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): $\delta=348.8$–348.5 (m, C=*P*), −14.4 (ddd, $^1J_{\mathrm{P,P}}=186.0$ Hz, $^2J_{\mathrm{P,P}}=65.0$, 19.0 Hz; diphosphirane ring *P*), −15.6 (br d, $^2J_{\mathrm{P,P}}=65$ Hz; saturated N*P*C$_2$), −59.1 ppm (ddd, $^1J_{\mathrm{P,P}}=186.0$ Hz, $^2J_{\mathrm{P,P}}=26.0$, 8.0 Hz; diphosphirane ring *P*). MS (EI+): *m*/*z* (%): 495 (40) [*M*]$^+$, 395 (100) [*M*−*t*BuCP]$^+$, 231 (90), 195 (20): elemental analysis calcd (%) for $C_{24}H_{41}NP_4Si$: C 58.17, H 8.34, N 2.83; found: C 58.12, H 8.49, N 2.71.

Crystal data for 4a: $C_{25}H_{43}Cl_2NP_4Si$, $M_r=580.47$, orthorhombic, space group *Pnma* (No. 62), $a=19.1533(14)$, $b=16.8732(13)$, $c=9.9062(4)$ Å, $U=3201.5(4)$ Å^3, $Z=4$, $\rho_{\mathrm{calcd}}=1.20$ Mg m^{-3}, crystal dimensions 0.4×0.2×0.2 mm, $F(000)=1232$, $T=173(2)$ K, Mo$_{K\alpha}$, radiation $\lambda=0.71073$ Å. Data collection: Kappa CCD. Of the total 2289 independent reflections measured, 1968 with $I>2\sigma(I)$. The final indices [$I>2\sigma(I)$] were $R_1=0.094$, $wR_2=0.238$ and $R_1=0.107$, $wR_2=0.246$ (for all data). Program package WinGX. Full-matrix least-squares refinement on F^2 was carried out using SHELXL-97.[34] Absorption correction was not applied. Structures were drawn using ORTEP-3 for Windows. The molecule is disordered across a crystallographic mirror plane with half-occupancy atom sites for C2, P3 and P4 and other atoms are unresolved. The high *R* factor and large ADPs for some of the atoms are a consequence of the close, but not exact, mirror symmetry of the molecule, excluding atoms C2, P3 and P4. Residual density was interpreted as the chlorine atoms of a molecule of solvate CH_2Cl_2 lying on an inversion centre with the disordered carbon and hydrogen atoms not located.

Computational methods: Computations were carried out using the Gaussian 03 suite of programs.[35] The structures were first optimised at the B3LYP level of the density functional theory[36] using the 3-21G(*) basis set, followed by calculation of the second derivatives to establish whether minima or transition-state structures (first-order saddle points) were obtained. These minima, which are connected by transition-state structures along the reaction path were located by IRC calculations. Subsequent optimisations were then carried out at the B3LYP/6-311+G** level of theory for the parent systems (hydrogen at the carbon and nitrogen atoms), whereas for systems with real substituents, B3LYP/6-31+G* optimisations were carried out using the B3LYP/3-21G(*) second derivatives. For the parent systems, further second-derivative calculations were also performed resulting in second derivatives similar to those derived using the B3LYP/3-21G(*) level of theory. For larger systems with real substituents, no further second-derivative calculations were performed. The stability of the wavefunction was tested at the stationary points and unless otherwise stated the closed-shell wavefunctions were found to be stable. The structures were visualised using the MOLDEN program.[37]

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