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Abstract: Two [3+1] fragmentations of the Lewis acid stabilized bicyclo[1.1.0]tetraphosphabutane \( \text{Li}[\text{Mes*P}_4] \) (\( \text{Mes}^* = 2,4,6-i\text{Bu}_3\text{C}_6\text{H}_2 \)) are reported. The reactions proceed by extrusion of a \( \text{P}_4 \) fragment, induced by either an imidazolium salt or phenylisocyanate, with release of the transient triphosphirene \( \text{Mes*P}_3 \), which was isolated as a dimer and trapped by 1,3-cyclohexadiene as a Diels–Alder adduct. DFT quantum chemical computations were used to delineate the reaction mechanisms. These unprecedented pathways grant access to both \( \text{P}_2^- \) and \( \text{P}_4^- \)-containing organophosphorus compounds in two simple steps from white phosphorus.

The conversion of white phosphorus (\( \text{P}_4 \)) directly into organophosphorus compounds avoids the use of environmentally taxing phosphorus halides,[1] but is hampered by the unpredictably reactivity of the \( \text{P}_4 \) tetrahedron.[2] Increased control is possible with a stepwise strategy, in which \( \text{P}_4 \) is converted into an “activated” product to enable subsequent selective functionalization. Exemplary are the \( \text{P}_4^- \)-derived \( \text{R}_2\text{P}_2^- \) cages reported by Weigand and co-workers (Scheme 1a).[3] The carbene-stabilized diphenyl \( \text{B} \) reported by Bertrand and co-workers,[4] the transition-metal-activated \( \mu_3\text{P}^- \)-coordinated diruthenium dication \( \text{C} \) of Stopponi and co-workers,[5] the terminal niobium phosphide \( \text{D} \) reported by Figueroa and Cummins,[6] and the bimetallic, butterfly-type bicyclo[1.1.0]tetraphosphabutanes \( \text{E} \) reported by the research groups of Scheer (\( \text{M} = \text{Fe} \)),[7] Scherer (\( \text{M} = \text{Fe} \)),[8] and Wolf (\( \text{M} = \text{Ni} \)).[9–11]

We discovered that the nucleophilic addition of sterically encumbered aryl lithium reagents to \( \text{P}_4^- \) in the presence of triarylboration Lewis acids (LAs) grants access to stable Li

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[D_J]THF at room temperature, thus giving full conversion into two isomers of the H-substituted bicyclo-[1.1.0]tetraphosphabutane 1 (Figure 1). Simulation of the 31P[1H] NMR resonance revealed AMX2 spin systems (inset; inverted) consisting of neutral exo,endo-2 and exo,exo-2 in a 1:0.7 ratio (J_{P,PM} = 19.1 and 303.9 Hz, respectively). The 1H NMR spectrum confirmed the protonation of anion 1a (δ(P) = -1.34 (J_{P,PM} = 147.5 Hz, 1H; exo,endo-Mes*P/H) and 0.65 (J_{P,PM} = 133.2 Hz, 1H; exo,exo-Mes*P/H) ppm), which occurred with concurrent P-BPh3 bond cleavage, as confirmed by the presence of only free BPh3 and Li[BPh4] in the 31P[1H] NMR spectrum (see the Supporting Information). Thus, the protonation of 1a provides a unique and facile route to a highly unsheilded LA-free R,P2 derivative to enable the study of its controlled fragmentation.

As expected, 2 decomposed slowly at room temperature; after 2 h only Mes*PH2 could be detected by 31P NMR spectroscopy. We envisioned a more controlled fragmentation by the formation of 2 in the presence of strong donors, for example, by the use of Brønsted acidic imidazolium chlorides, which produce an NHC in situ. Indeed, the addition of [IDippH][Cl] (1.1 equiv; IDipp = 1,3-bis(2,6-disopropylphenyl)imidazol-2-ylidene) to a solution of 1a in THF (Scheme 2) resulted in its instant and complete consumption.

The 31P NMR spectrum of the reaction mixture showed the formation of the phosphinidene adduct 3 (IDipp=PH, 13% by 31P NMR; δ(P) = -137.3 ppm, J_{P,PM} = 163.6 Hz), thus suggesting that the fragmentation of 2 had occurred by transfer of the wing-tip PH to the carbene. Recently, the research groups of Driess, Grützmacher, and Tamm synthesized 3 by using instead a phosphasilene, Na[OPr], or P(SiMe3), respectively. Mes*PH2 was the other observable P-containing product (8% by 31P NMR; δ(P) = -132.1 ppm), whereas the 31B NMR spectrum revealed a weak resonance signal at 2.6 and a larger signal at -7.4 ppm originating from [IDippH][BPh4] and IDipp-BPPh3, respectively (see the Supporting Information). The formation of the latter adduct frustrates the conversion into 3 and results in the decomposition of remaining labile 2 (see above).

DFT calculations carried out at the oB97X-D/6-311+G(2d,p)/6-31G(d) level by using the phenyl analogue of both exo,endo-2 (2; Ph instead of Mes*) and the NHC (Ph instead of Dipp) provided insight into the remarkable
formation of 3 (Scheme 3; comparable energies were obtained for exo,exo-2', see the Supporting Information). Nucleophilic attack of the NHC at the most accessible wing-tip P atom was computed to first give van der Waals complex 4' (ΔE = -10.3 kcal mol⁻¹), which undergoes cleavage of an edge P–P bond with a modest barrier (8.4 kcal mol⁻¹) to afford zwitterionic 5' (ΔE = -6.6 kcal mol⁻¹). Extrusion of the NHC–phosphinidene adduct 3' with the concomitant formation of triphosphirene 6 is endothermic (ΔE = 8.2 kcal mol⁻¹). It is likely that 6' dimerizes (ΔΔE = -46.1 kcal mol⁻¹) to afford the intriguing hexaphosphane 8', which was recently synthesized by Schulz and co-workers (Ph = Mes⁺) from P₁ building blocks.[22] We did not observe 8 in the 31P NMR spectrum, probably owing to its complex high-order splitting pattern.

Next, we wondered whether [3+1] fragmentation of the anionic precursor 1a would also be feasible and whether P₁ compounds would be isolable. Neutral heteroallenes, such as isocyanates, emerged from substrate screening as suitable reagents. In fact, the treatment of 1a in THF with excess phenylisocyanate (PhNCO; 20 equiv) afforded directly spirophosphorane Li[PhP₂]₂ (70%) by 3¹P NMR: δ(3¹P)'[H] = -62.6 ppm) as well as the tricyclic hexaphosphate Mes⁺P₁₈ (8; 19% by ³¹P NMR; δ(³¹P)'[H] = -96.1 (m, P2/P3), -107.2 ppm (m, P1); Scheme 4).[22] The two compounds were isolated as analytically pure white powders in 80 (Li[7]) and 18% yield (8); they were fully characterized by multinuclear NMR spectroscopy, HRMS, and X-ray crystal-structure determination (see the Supporting Information for 8).

The molecular structure of Li[7] revealed a distorted trigonal-bipyramidal geometry around the central phosphorus atom (A-isomer; Figure 2), with the most apicophilic nitrogen atoms in the axial positions and the carbonyl groups and the P lone pair in the equatorial plane. Ion pairing through complexation of the Li⁺ cation to the oxygen atoms of the anion (Li···O₁ = 1.866(10) Å) creates along the crystallographic a-axis a stable (m.p.: 149°C) one-dimensional coordination polymer, which was found to be insoluble in THF. The formation of Li[7] from 1a is fully reminiscent of the reaction of Na[OCP] with RNCO (R = Ph, Cy, nBu),[29] in which the 2-phosphaethynolate anion acts as a formal “P⁺” source, with CO as the leaving group, akin to Mes⁺P in our case. Note that Na[OCP] provides the living isocyanate trimerization catalyst [7⁺] as the unstable Na⁺ salt, whereas Li[7] showed only slight decomposition in [D₆]DMSO over a 24 h period.

We resorted again to DFT calculations to provide detailed insight into the fragmentation of Li[PhP₂-BPh₃] (1a); Scheme 5: Li⁺ counterions are included, but not shown). Our proposed mechanism starts with the coordination of PhNCO to 1a to give complex 9' (ΔE = -21.2 kcal mol⁻¹),[25] which affords 10' after P–C bond formation (ΔE = 0.0 kcal mol⁻¹; ΔE₁ = -15.9 kcal mol⁻¹) at the BPh₃-coordinated wing-tip phosphorus atom. The anionic carboxamide of 10' then attacks the electrophilic C atom of a second phenylisocyanate molecule to give 12' (ΔE_{relativ} = -36.4 kcal mol⁻¹) via coordination complex 11'.[25,26] In 12', the nucleophilic N2 atom and the wing-tip P4 atom are in close proximity (2.08 Å), which enables P–N bond formation with concurrent P–P bond cleavage (TS₁₂₋₁₃; ΔE₁ = -12.0 kcal mol⁻¹). Fragmentation of the resulting compound 13' generates the BPh₃ adduct of heterocycle 14' and triphosphirene 6'. Whereas this step is energetically uphill (ΔE = 21.2 kcal mol⁻¹), it is significantly moderated by the dimerization of 6' (ΔE = -46.1 kcal mol⁻¹) as well as by the nucleophilic addition of 14' to two additional PhNCO molecules to afford the spiro compound Li[7] with the liberation of BPh₃ (ΔE = -29.1 kcal mol⁻¹; ΔE_{relativ} = -90.4 kcal mol⁻¹).

**Scheme 3.** Relative coB97X-D/6-311 + G(2d, p)/6-31G(d) energies (in kcal mol⁻¹) for the computed fragmentation pathway leading from exo,endo-2' to 3' and 8'.

**Scheme 4.** Fragmentation of 1a with PhNCO.
organotriphosphirane with a shorter P1–C1 bond (1.8766–14 Å) than the P2–C22 and P3–C19 bonds (1.9149(16) and 1.9149(16) Å, respectively) owing to the different hybridization of their carbon substituents (sp² versus sp³). The product was formed as a single (endo) stereoisomer with the C=C double bond (C23–C24 1.332(2) Å; C20–C21 1.538(2) Å) positioned opposite to the P1 lone pair. Also, DFT calculations, again at the B97X-D/6-311+G(2d,p)//6-31G(d) level, revealed endo-15 (Mes* = Ph) to be thermodynamically and kinetically favored over exo-15 (ΔE = −3.4 kcal mol⁻¹; ΔEₕ = 3.5 versus 6.3 kcal mol⁻¹, respectively), which may be attributed to secondary orbital interactions in the transition state leading to the endo adduct (see the Supporting Information).[29] Diels–Alder adduct 15 is a unique example of a nonsymmetrically substituted tris-(organyl) P₃ species derived directly from P₃⁺ as well as the obtained P₃ products, the formation of adduct 15 illustrates the versatility of 1a as a platform for the stepwise preparation of organophosphorus compounds from white phosphorus.

In conclusion, we have shown that the P₃⁺-derived Lewis acid stabilized bicyclo[1.1.0]tetraphosphabutanide compound 1a can be utilized as a source of P₃⁺ and P₃⁻-containing organophosphorus compounds through unprecedented [3+1] fragmentation reactions. Their formation proceeds by the extrusion of a P₃⁻ fragment, as induced by either an imidazolium salt or isocyanate, with concurrent release of the transient triphosphirene Mes*P₃, which can be isolated as a dimer or trapped with 1,3-cyclohexadiene. The latter approach afforded the unique tris(organyl) triphosphirane 15. We anticipate the presented chemistry of 1a to be a versatile entry point for the design of selective strategies for the fragmentation and functionalization of P₃⁺.

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Note that the reaction of 1a with the metal carbonyl complex [(McCN)(W(CO))₂] affords anionic Li[Mes*P⁺(W(CO)₅)]₂ (see Ref. [136]).

Spectral parameters were determined by iterative full shape-analysis by using the gNMR simulation program: P.H. Budzelaa, gNMR, version 5.06.0, 2006.


DIipp-BPh₄ can be considered as a quenched frustrated Lewis pair (FLP) in equilibrium with its constituents.


CCDC 1491988, 1491989, and 1491990 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.


Complexes 9 and 11 feature a PhNCO-Li⁺ interaction, the energy of which is overestimated and is moderated in solution by the coordination of THF solvent molecule to the Li⁺ cation.

The addition reactions are templated by the Li⁺ cation.

A similar diphasphene intermediate was proposed by Weigand for the NHCl-induced [3+2] fragmentation of an [RP₂Li⁺] e cage.
cation (see Ref. [3c]) and by Bertrand for the reaction of $P_4$ with cyclic (alkyl)(amino)carbenes (CAACs; see Ref. [4]).


[29] This selectivity was also observed by Cossairt and Cummins:

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