P_4 Fragmentation

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Selective [3+1] Fragmentations of P_4 by "P" Transfer from a Lewis Acid Stabilized $[RP_4]^-$ Butterfly Anion

*Jaap E. Borger, Andreas W. Ehlers, Martin Lutz, J. Chris Slootweg, and Koop Lammertsma**

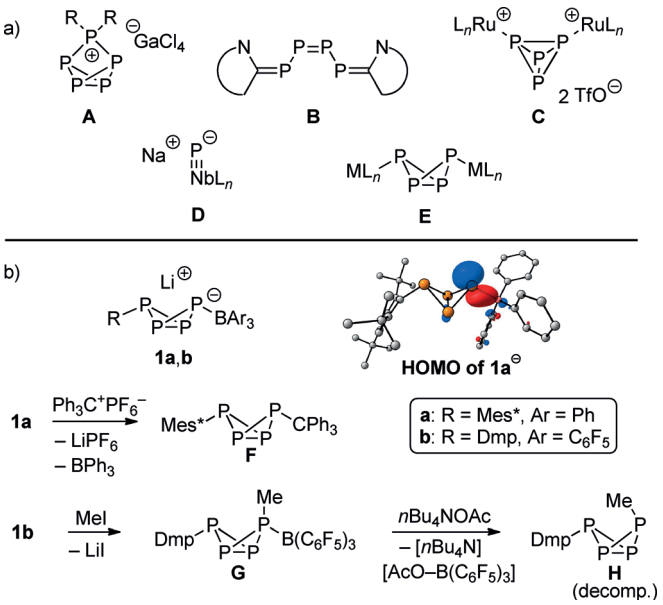
Abstract: *Two [3+1] fragmentations of the Lewis acid stabilized bicyclo[1.1.0]tetraphosphabutanide Li[Mes*P_4·BPh_3] (Mes* = 2,4,6-$tBu_3C_6H_2$) are reported. The reactions proceed by extrusion of a P_1 fragment, induced by either an imidazolium salt or phenylisocyanate, with release of the transient triphosphirene 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 P_1- and P_3-containing organophosphorus compounds in two simple steps from white phosphorus.*

The conversion of white phosphorus (P_4) directly into organophosphorus compounds avoids the use of environmentally taxing phosphorus halides,[1] but is hampered by the unpredictable reactivity of the P_4 tetrahedron.[2] Increased control is possible with a stepwise strategy, in which P_4 is converted into an "activated" product to enable subsequent selective functionalization. Exemplary are the P_4-derived $R_2P_5^+$ cages **A** reported by Weigand and co-workers (Scheme 1 a),[3] the carbene-stabilized diphosphene **B** reported by Bertrand and co-workers,[4] the transition-metal-activated $\mu,\eta^{1:1}$-P_4-coordinated diruthenium dication **C** of Stoppioni and co-workers,[5] the terminal niobium phosphide **D** reported by Figueroa and Cummins,[6] and the bimetallic, butterfly-type bicyclo[1.1.0]tetraphosphabutanes **E** reported by the research groups of Scheer (M = Fe),[7] Scherer (M = Fe),[8] and Wolf (M = Ni).[9–11]

We discovered that the nucleophilic addition of sterically encumbered aryl lithium reagents to P_4 in the presence of triarylborane Lewis acids (LAs) grants access to stable Li^+ salts **1** of the elusive $[RP_4]^-$ butterfly anion (Scheme 1 b).[12] The lone pair at the B-coordinated wing-tip P atom (see HOMO in Scheme 1 b) can be alkylated to give the neutral disubstituted bicyclotetraphosphanes **F** and **H** in high yield.[13] The Lewis acid strength plays an important role in these reactions. That is, the weak Lewis acid BPh_3 in **1a** spontaneously dissociates from the RP_4 core upon endocyclic substitution (subsequent isomerization gives **F**),[13b] whereas removal of the strong Lewis acid $B(C_6F_5)_3$ in **1b** requires an additional step (**G**→**H**; Scheme 1 b).[13a] The stability of the nonsymmetrical R_2P_4 derivatives is governed by steric effects: **F** with a bulky trityl substituent is indefinitely stable, whereas methyl-substituted **H** decomposes in solution. This notion inspired us to target the controlled and selective fragmentation of even smaller tetraphosphabutanes R_2P_4.

As a starting point, we focused on protonating BPh_3-stabilized **1a**[13b] and found that the Mes*P_4H formed in situ could be trapped by an N-heterocyclic carbene (NHC) to affect an unprecedented [3+1] fragmentation. After screening various organic carbonyl compounds, we further found that the anionic precursor **1a** itself also undergoes [3+1] fragmentation with phenylisocyanate.[14]

The protonation of **1a** proceeded readily upon addition of the mild proton donor $[Me_3NH][BPh_4]$ (1.0 equiv) in



Scheme 1. a) Examples of P_4-activation products used for subsequent controlled functionalization. b) Lewis acid stabilized $[RP_4]^-$ anions and subsequent alkylation reactions. Mes* = 2,4,6-$tBu_3C_6H_2$, Dmp = 2,6-dimesitylphenyl; HOMO of the DFT-optimized geometry of $\mathbf{1a}^-$.

[*] J. E. Borger, Dr. A. W. Ehlers, Dr. J. C. Slootweg, Prof. Dr. K. Lammertsma
Department of Chemistry and Pharmaceutical Sciences
Vrije Universiteit Amsterdam
De Boelelaan 1083, 1081 HV Amsterdam (The Netherlands)
E-mail: K.Lammertsma@vu.nl
Dr. M. Lutz
Crystal and Structural Chemistry
Bijvoet Center for Biomolecular Research, Utrecht University
Padualaan 8, 3584 CH Utrecht (The Netherlands)
Dr. A. W. Ehlers, Prof. Dr. K. Lammertsma
Department of Chemistry, University of Johannesburg
Auckland Park, Johannesburg, 2006 (South Africa)
Dr. A. W. Ehlers, Dr. J. C. Slootweg
Current address: Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam (The Netherlands)

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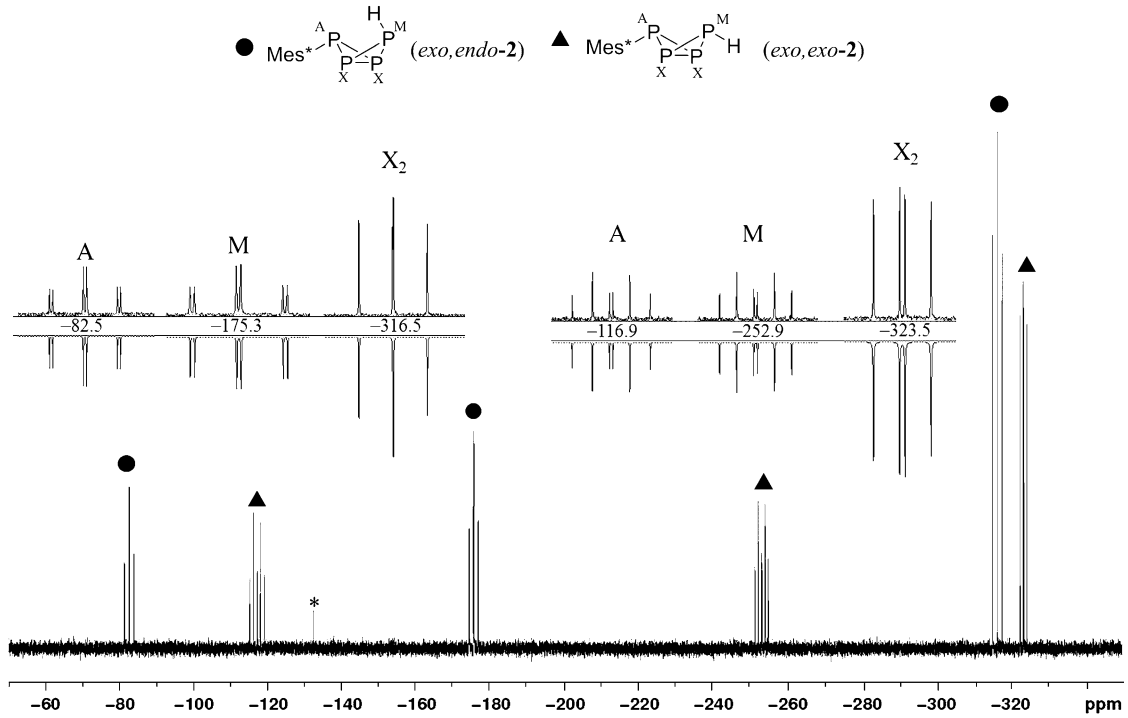
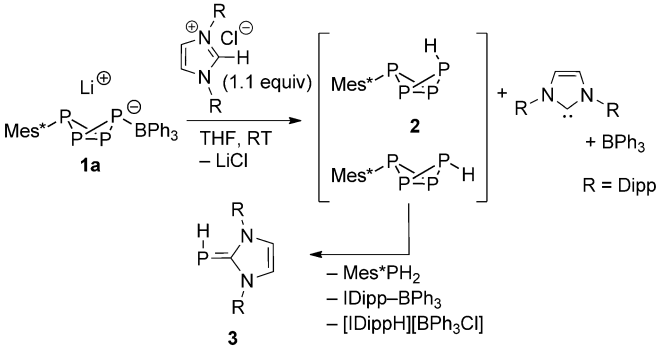


Figure 1. $^{31}P\{^1H\}$ NMR spectrum (162.0 MHz, [D_8]THF, 291 K) recorded directly after mixing **1a** and [Me_3NH][BPh_4]. Inset shows expanded experimental and simulated (inverted) regions. *exo,endo*-**2**: ($\delta_{PA} = -82.5$, $\delta_{PM} = -175.3$, $\delta_{PX} = -316.5$ ppm; $^1J_{PA,PX} = -202.7$, $^1J_{PM,PX} = -198.5$, $^2J_{PA,PM} = 19.1$, $^1J_{P,H} = 147.8$, $^2J_{P,H}$ not resolved, $^3J_{P,H} = 17.2$ Hz); *exo,exo*-**2** ($\delta_{PA} = -116.9$, $\delta_{PM} = -252.9$, $\delta_{PX} = -323.5$ ppm; $^1J_{PA,PX} = -165.5$, $^1J_{PM,PX} = -137.0$, $^2J_{PA,PM} = 303.9$, $^1J_{P,H} = 133.9$, $^2J_{P,H} = 11.7$, $^3J_{P,H} = 111.1$ Hz). The signal marked with an asterisk (*) was assigned to Mes^*PH_2.

[D_8]THF at room temperature, thus giving full conversion into two isomers of the novel H-substituted bicyclo-[1.1.0]tetraphosphabutane **2** (Figure 1). Simulation of the $^{31}P\{^1H\}$ NMR resonances[15] revealed AMX_2 spin systems (inset; inverted) consistent with neutral *exo,endo*-**2** and *exo,exo*-**2** in a 1:0.7 ratio ($^2J_{PA,PM} = 19.1$ and 303.9 Hz, respectively). Also, the ^1H NMR spectrum confirmed the protonation of anion **1a** ($\delta(^1H) = -1.34$ ($^1J_{H,P} = 147.5$ Hz, 1H; *exo,endo*-Mes*P_4H) and 0.65 ($^1J_{H,P} = 133.2$ Hz, 1H; *exo,exo*-Mes*P_4H) ppm), which occurred with concurrent P–BPh_3 bond cleavage, as confirmed by the presence of only free BPh_3 and Li[BPh_4] in the $^{11}B\{^1H\}$ NMR spectrum (see the Supporting Information). Thus, the protonation of **1a** provides a unique and facile route to a highly unshielded LA-free R_2P_4 derivative to enable the study of its controlled fragmentation.

As expected, **2** decomposed slowly at room temperature; after 2 h only Mes^*PH_2 could be detected by ^{31}P 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.[3c,16] Indeed, the addition of [IDippH][Cl] (1.1 equiv; IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) to a solution of **1a** in THF (Scheme 2) resulted in its instant and complete consumption.

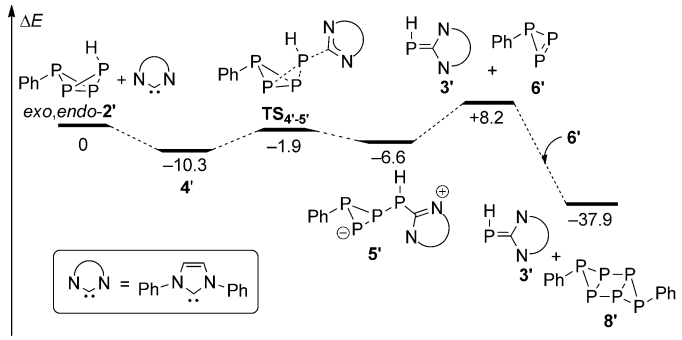
The ^{31}P NMR spectrum of the reaction mixture showed the formation of the phosphinidene adduct **3** (IDipp=PH, 13% by ^{31}P NMR; $\delta(^{31}P) = -137.4$ ppm, $^1J_{P,H} = 163.6$ Hz), thus suggesting that the fragmentation of **2** had occurred by transfer of the wing-tip PH to the carbene. Recently, the



Scheme 2. Fragmentation of **1a** with [IDippH][Cl].

research groups of Driess,[17] Grützmacher,[18] and Tamm[19] synthesized **3** by using instead a phosphasilene, Na[OCP], or $P(SiMe_3)_3$, respectively. Mes^*PH_2 was the other observable P-containing product (8% by ^{31}P NMR; $\delta(^{31}P) = -132.1$ ppm), whereas the ^{11}B NMR spectrum revealed a weak resonance signal at 2.6 and a larger signal at −7.4 ppm originating from [IDippH][BPh_3Cl] and IDipp-BPh_3, 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).[20,21]

DFT calculations carried out at the ωB97X-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



Scheme 3. Relative ωB97X-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′**.

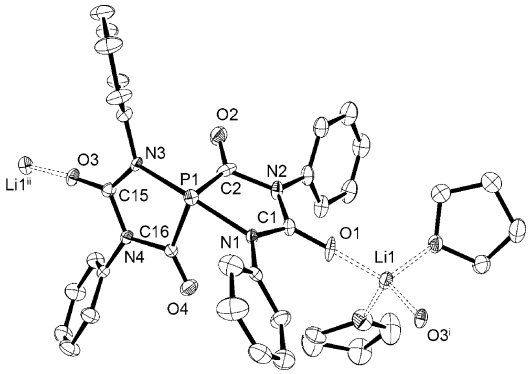
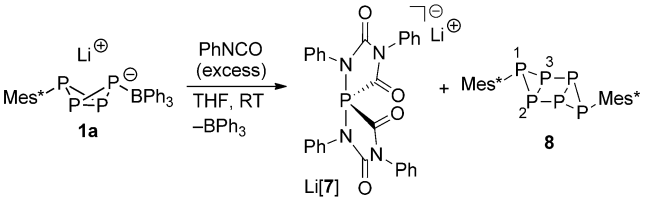


Figure 2. Polymeric coordination chain of Li[**7**] in the crystal (ellipsoids at 30% probability; hydrogen atoms are omitted for clarity; only the major disorder component is shown).[23] Selected bond lengths [Å] and angles [°]: P1–C2/C16 1.768(8)/1.855(6), P1–N1/N3 1.979(5)/1.911(5), Li1–O1 1.866(10), Li1–O3^{i} 1.870(9); C2-P1-N1 85.3(3), N3-P1-C16 85.5(3), C16-P1-C2 96.8(3), N1-P1-N3 168.3(3). Symmetry codes i: $x+0.5, 0.5-y, 1-z$; ii: $x-0.5, 0.5-y, 1-z$.

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′** ($\Delta E = -10.3$ 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′** ($\Delta E = -6.6$ kcal mol^{-1}). Extrusion of the NHC–phosphinidene adduct **3′** with the concomitant formation of triphosphirene **6′** is endothermic ($\Delta E = 8.2$ kcal mol^{-1}). It is likely that **6′** dimerizes ($\Delta\Delta E = -46.1$ kcal mol^{-1}) to afford the intriguing hexaphosphane **8′**, which was recently synthesized by Schulz and co-workers (Ph = Mes*) from P_1 building blocks.[22] We did not observe **8** in the ^{31}P 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 P_3 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 spirophosphoranide Li[**7**] (100% by ^{31}P NMR; $\delta(^{31}P\{^1H\}) = -62.6$ ppm) as well as the tricyclic hexaphosphane Mes*$_2$P$_6$ (**8**; 19% by ^{31}P NMR; $\delta(^{31}P\{^1H\}) = -96.1$ (m, P2/P3), -107.2 ppm (m, P1); Scheme 4).[22] The two compounds

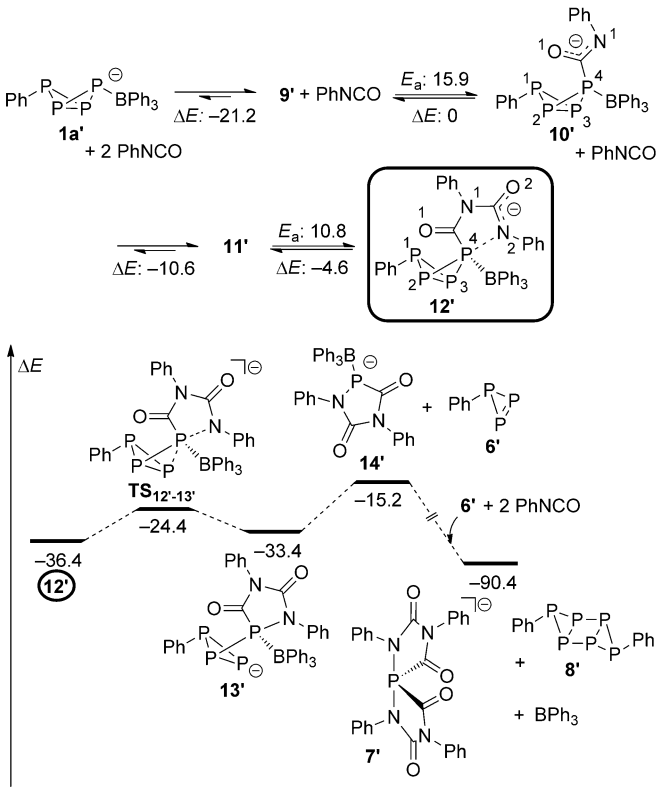


Scheme 4. Fragmentation of **1a** with PhNCO.

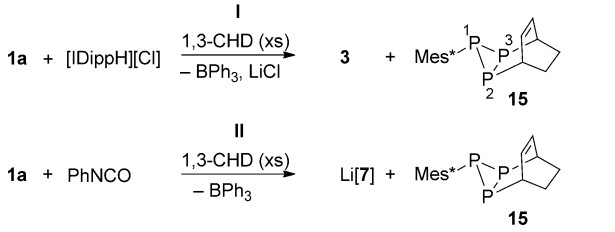
were isolated as analytically pure white powders in 80 (Li[**7**]) and 18% yield (**8**); they were fully characterized by multinuclear NMR spectroscopy, HRMS, and X-ray crystal-structure determination (see the Supporting Information for **8**).

The molecular structure of Li[**7**] revealed a distorted trigonal-bipyramidal geometry around the central phosphorus atom (Λ-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 (Li1···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, *n*Bu),[24] in which the 2-phosphaethynolate anion acts as a formal "P^{-}" source, with CO as the leaving group, akin to Mes*P_3 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 [D$_6$]DMSO over a 24 h period.

We resorted again to DFT calculations to provide detailed insight into the fragmentation of Li[PhP_4·BPh_3] (**1a′**; Scheme 5; Li^+ countercations are included, but not shown). Our proposed mechanism starts with the coordination of PhNCO to **1a′** to give complex **9′** ($\Delta E = -21.2$ kcal mol^{-1}),[25] which affords **10′** after P–C bond formation ($\Delta E = 0.0$ kcal mol^{-1}; $\Delta E_a = 15.9$ kcal mol^{-1}) at the BPh_3-coordinated wing-tip phosphorus atom. The anionic carboxamide group of **10′** then attacks the electrophilic C atom of a second phenylisocyanate molecule to give **12′** ($\Delta E_{total} = -36.4$ 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 (**TS$_{12'\text{-}13'}$**; $\Delta E_a = 12.0$ kcal mol^{-1}). Fragmentation of the resulting compound **13′** generates the BPh_3 adduct of heterocycle **14′** and triphosphirene **6′**. Whereas this step is energetically uphill ($\Delta E = 21.2$ kcal mol^{-1}), it is significantly moderated by the dimerization of **6′** ($\Delta E = -46.1$ 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 BPh_3 ($\Delta E = -29.1$ kcal mol^{-1}; $\Delta E_{overall} = -90.4$ kcal mol^{-1}).



Scheme 5. Relative ωB97X-D/6-311 + G(2d,p)//6-31G(d) energies (in kcal mol^{-1}) for the computed fragmentation pathway leading from **1a′** to **7′**, **8′**, and BPh_3. A Li^+ countercation was included in all anionic species, but is not shown.



Scheme 6. Fragmentation reactions in the presence of 1,3-CHD. Dipp = 2,6-*i*$Pr_2C_6H_3$, Mes* = 2,4,6-*t*$Bu_3C_6H_2$. I) [IDippH][Cl] (1.1 equiv), THF, room temperature; II) PhNCO (4 equiv), THF, room temperature.

To confirm the intermediacy of triphosphirene Mes*P_3 in the reactions,[27,28] we sought to trap this important P_3 building block by a Diels–Alder reaction with 1,3-cyclohexadiene (1,3-CHD). Satisfyingly, the addition of an excess amount of 1,3-CHD (50 equiv) to the reaction mixture of **1a** and either [IDippH][Cl] or PhNCO (Scheme 6) afforded the desired cycloaddition product **15** in 27 (^{31}P NMR) and 69% yield (isolated), respectively, in addition to the "P"-transfer products **3** (30% by ^{31}P NMR) and Li[**7**] (> 99% isolated).

The two $^{31}P\{^1H\}$ NMR resonances of **15** at −160.9 (P1) and −195.2 ppm (P2/P3) show a second-order AB_2 spin system with $^1J_{PA,PB}$ coupling constants of 192.0 Hz.[15] The molecular structure (Figure 3) reveals a 1-aryl-2,3-dialkyl-substituted organotriphosphirane with a shorter P1–C1 bond (1.8766(14) Å) than the P2–C22 and P3–C19 bonds (1.9210(16) and 1.9149(16) Å, respectively) owing to the different hybridization of their carbon substituents (sp^2 versus sp^3). 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 ωB97X-D/6-311 + G(2d,p)//6-31G(d) level, revealed *endo*-**15′** (Mes* = Ph) to be thermodynamically and kinetically favored over *exo*-**15′** ($\Delta E = -34.2$ versus −30.4 kcal mol^{-1}; $\Delta E_a = 3.5$ 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) P_3 species derived directly from P_4; as well as the obtained P_1 products, the formation of adduct **15** illustrates the versatility of **1a** as a platform for the stepwise preparation of organophosphorus compounds from white phosphorus.

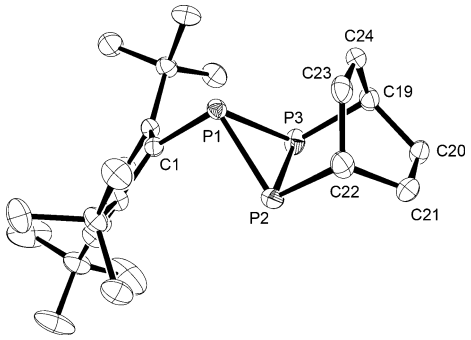


Figure 3. Molecular structure of **15** in the crystal (ellipsoids at 50% probability; hydrogen atoms are omitted for clarity).[23] Only the major form of the disordered *tert*-butyl group is shown. Selected bond lengths [Å] and torsion angles [°]: P1–P2/P3 2.2096(5)/2.2139(5), P2–P3 2.1755(6), P1–C1 1.8766(14), P2–C22 1.9210(16), P3–C19 1.9149(16), C23–C24 1.332(2), C21–C20 1.538(2); P1-P2-P3-C19 101.35(6).

In conclusion, we have shown that the P_4-derived Lewis acid stabilized bicyclo[1.1.0]tetraphosphabutanide compound **1a** can be utilized as a source of P_1- and P_3-containing organophosphorus compounds through unprecedented [3+1] fragmentation reactions. Their formation proceeds by the extrusion of a P_1 fragment, as induced by either an imidazolium salt or isocyanate, with concurrent release of the transient triphosphirene Mes*P_3, 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 P_4.

Acknowledgements

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Keywords: anions · fragmentation · Lewis acids · organophosphorus compounds · phosphorus

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[26] The addition reactions are templated by the Li^+ cation.

[27] A similar diphosphene intermediate was proposed by Weigand for the NHC-induced [3+2] fragmentation of an $[RP_5Cl]^+$ cage

cation (see Ref. [3c]) and by Bertrand for the reaction of P_4 with cyclic (alkyl)(amino)carbenes (CAACs; see Ref. [4]).
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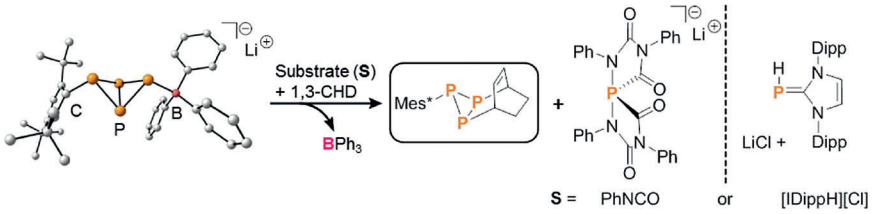
Communications

P_4 Fragmentation

J. E. Borger, A. W. Ehlers, M. Lutz,
J. C. Slootweg,
K. Lammertsma* _____ ■■■■–■■■■

Selective [3+1] Fragmentations of P_4 by "P" Transfer from a Lewis Acid Stabilized $[RP_4]^-$ Butterfly Anion



Cracking P_4: Two [3+1] fragmentations of the Lewis acid stabilized bicyclo[1.1.0]-tetraphosphabutanide Li[Mes*P_4·BPh_3] (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) were induced by an imidazolium salt or phenylisocyanate (see scheme). These unprecedented pathways provided access to P_1- and P_3-containing organophosphorus compounds in two straightforward steps from white phosphorus.