UvA-DARE (Digital Academic Repository)

Selective [3+1] Fragmentations of P₄ by “P” Transfer from a Lewis Acid Stabilized [RP₄]⁻ Butterfly Anion

Borger, J.E.; Ehlers, A.W.; Lutz, M.; Slootweg, J.C.; Lammertsma, K.

DOI

[10.1002/ange.201607234](https://doi.org/10.1002/ange.201607234)

[10.1002/anie.201607234](https://doi.org/10.1002/anie.201607234)

Publication date

2017

Document Version

Author accepted manuscript

Published in

Angewandte Chemie

[Link to publication](#)

Citation for published version (APA):

Borger, J. E., Ehlers, A. W., Lutz, M., Slootweg, J. C., & Lammertsma, K. (2017). Selective [3+1] Fragmentations of P₄ by “P” Transfer from a Lewis Acid Stabilized [RP₄]⁻ Butterfly Anion. *Angewandte Chemie*, 129(1), 291-296. <https://doi.org/10.1002/ange.201607234>, <https://doi.org/10.1002/anie.201607234>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)

Author Manuscript

Title: Selective [3+1]-Fragmentations of P4 by "P" Transfer from a Lewis Acid Stabilized [RP4]-Butterfly Anion

Authors: Jaap E. Borger; Andreas W. Ehlers; Martin Lutz; J. Chris Slootweg; Koop Lammertsma

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record.

To be cited as: 10.1002/ange.201607234

Link to VoR: <https://doi.org/10.1002/ange.201607234>

Selective [3+1]-Fragmentations of P₄ by “P” Transfer from a Lewis Acid Stabilized [RP₄][−] 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*P₄BPh₃] (Mes* = 2,4,6-*t*Bu₃C₆H₂) are reported. The reactions proceed by extrusion of a P₁ fragment induced by either an imidazolium salt or phenylisocyanate with release of the transient triphosphirene Mes*P₃, 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 P₁ and P₃ containing organophosphorus compounds in two simple steps from white phosphorus.

Converting white phosphorus (P₄) directly into organophosphorus compounds avoids using environmentally taxing phosphorus halides,^[1] but is hampered by the unpredictable reactivity of the P₄-tetrahedron.^[2] Increased control is achievable with a stepwise strategy, converting P₄ to an “activated” product to allow subsequent selective functionalization. Exemplary are the P₄-derived R₂P₅⁺ cages reported by Weigand (A; Scheme 1a),^[3] the carbene stabilized diphosphene B by Bertrand,^[4] the transition metal activated μ,η^{1:1}-P₄ coordinated diruthenium dication C of Stoppioni,^[5] the terminal niobium phosphide D by Cummins,^[6] and the bimetallic, butterfly type bicyclo[1.1.0]tetraphosphabutanes E of Scheer (M = Fe),^[7] Scherer (M = Fe)^[8] and Wolf (M = Ni).^[9,10,11]

We discovered that nucleophilic addition of sterically encumbered aryllithium reagents to P₄ in the presence of triarylborane Lewis acids (LA) grants access to stable Li⁺ salts of the elusive [RP₄][−] butterfly anion (1; Scheme 1b).^[12] The lone pair at the B-coordinated wing-tip P-atom (see HOMO in Scheme 1b) 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 BPh₃ in 1a spontaneously dissociates from the RP₄ core upon endocyclic substitution (subsequent isomerization gives F),^[13b] whereas removal of the strong B(C₆F₅)₃ in 1b requires an additional step (G → H; Scheme 1b).^[13a] The stability of the non-symmetrical R₂P₄ derivatives is governed by sterics, as the bulky trityl-substituted F is indefinitely stable, while the methyl-substituted H decomposes in solution. This notion inspired us to target the controlled and selective fragmentation of even smaller tetraphosphabutanes R₂P₄.

As starting point, we focused on protonating the BPh₃ stabilized 1a^[13b] and found that the *in situ* formed Mes*P₄H can 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 also anionic precursor 1a itself undergoes [3+1]-fragmentation with phenylisocyanate.^[14]

Scheme 1. a) Examples of P₄ activation products used for subsequent controlled functionalization. b) Lewis acid stabilized [RP₄][−] anions and subsequent alkylation reactions; Mes* = 2,4,6-*t*Bu₃C₆H₂, Dmp = 2,6-dimesitylphenyl; HOMO of the DFT optimized geometry of 1a[−].

Protonation of 1a proceeds readily upon addition of the mild proton donor [Me₃NH][BPh₄] (1.0 equiv.) in [d₈]THF at room temperature, giving full conversion to two isomers of the novel *H*-substituted bicyclo[1.1.0]tetraphosphabutane 2 (Figure 1). Simulation of the ³¹P{¹H} NMR resonances^[15] revealed AMX₂ 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 Hz and 303.9 Hz, respectively). Also the ¹H NMR spectrum confirmed protonation of anion 1a (δ¹H: −1.34 (¹J_{H,P} = 147.5 Hz, 1H; *exo,endo*-Mes*P₄H) and 0.65 (¹J_{H,P} = 133.2 Hz, 1H; *exo,exo*-Mes*P₄H) ppm) that occurred with concurrent P–BPh₃ bond cleavage, as confirmed by the presence of only free BPh₃ and Li[BPh₄] in the ¹H{³¹P} NMR spectrum (see the Supporting Information). Thus, the protonation of 1a provides a unique facile route toward a highly unshielded LA free R₂P₄ derivative, allowing study of its controlled fragmentation.

As expected, 2 decomposed slowly at room temperature; after two hours only Mes*PH₂ could be detected by ³¹P NMR spectroscopy. We envisioned a more controlled fragmentation by forming 2 in the presence of strong donors, such as using Brønsted acidic imidazolium chlorides that produce *in situ* an NHC.^[3c, 16] Indeed, 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.

[*] 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
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

Supporting information for this article is given via a link at the end of the
document.

Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162.0 MHz, $[\text{d}_8]\text{THF}$, 291 K) recorded directly after mixing **1a** and $[\text{Me}_3\text{NH}][\text{BPh}_4]$. Inset shows expanded experimental and simulated (inverted) regions. *Exo,endo-2*: ($\delta_{\text{P}_A} -82.5$, $\delta_{\text{P}_M} -175.3$, $\delta_{\text{P}_X} -316.5$ ppm; $^1J_{\text{P}_A-\text{P}_X} = -202.7$, $^1J_{\text{P}_M-\text{P}_X} = -198.5$, $^2J_{\text{P}_A-\text{P}_M} = 19.1$, $^1J_{\text{P},\text{H}} = 147.8$, $^2J_{\text{P},\text{H}}$ not resolved, $^3J_{\text{P},\text{H}} = 17.2$ Hz); *exo,exo-2* ($\delta_{\text{P}_A} -116.9$, $\delta_{\text{P}_M} -252.9$, $\delta_{\text{P}_X} -323.5$ ppm; $^1J_{\text{P}_A-\text{P}_X} = -165.5$, $^1J_{\text{P}_M-\text{P}_X} = -137.0$, $^2J_{\text{P}_A-\text{P}_M} = 303.9$, $^1J_{\text{P},\text{H}} = 133.9$, $^2J_{\text{P},\text{H}} = 11.7$, $^3J_{\text{P},\text{H}} = 111.1$ Hz). Signal marked with an asterisk (*) was assigned to Mes^*PH_2 .

The ^{31}P NMR spectrum of the reaction mixture showed the formation of phosphinidene adduct $\text{IDipp}=\text{PH}$ **3** (13% by ^{31}P NMR; $\delta^{31}\text{P}$: -137.4 ppm, $^1J_{\text{P},\text{H}} = 163.6$ Hz), suggesting that fragmentation of **2** had occurred by transfer of the wing-tip PH to the carbene. Recently, Driess,^[17] Grützmacher^[18] and Tamm^[19] synthesized **3**, using instead a phosphasilene, $\text{Na}[\text{OCP}]$ or $\text{P}(\text{SiMe}_3)_3$, respectively. Mes^*PH_2 is the other observable P-containing product (8% by ^{31}P NMR; $\delta^{31}\text{P}$: -132.1 ppm), while the ^{11}B NMR spectrum revealed a weak resonance signal at 2.6 and a larger one at -7.4 ppm, originating from $[\text{IDippH}][\text{BPh}_3\text{Cl}]$ and $\text{IDipp}-\text{BPh}_3$, respectively (see the Supporting Information). Formation of the latter adduct frustrates the conversion to **3** and results in decomposition of remaining labile **2** (*vide supra*).^[20,21]

Scheme 2. Fragmentation of **1a** using $[\text{IDippH}][\text{Cl}]$.

DFT calculations at $\omega\text{B97X-D}/6\text{-311+G(2d,p)}/6\text{-31G(d)}$, 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'** ($\Delta E = -10.3$ 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 $^{-1}$). Extruding NHC-phosphinidene adduct **3'** with concomitant formation of triphosphirene **6'** is endothermic ($\Delta E = 8.2$ kcal mol $^{-1}$). Likely **6'** dimerizes ($\Delta\Delta E = -46.1$ kcal mol $^{-1}$) to afford the intriguing hexaphosphane **8'**, which was recently synthesized by Schulz et al. (Ph = Mes^*) from P_1 building blocks.^[22] We did not observe **8** in the ^{31}P NMR spectrum likely due to its complex high-order splitting pattern.

Scheme 3. Relative $\omega\text{B97X-D}/6\text{-311+G(2d,p)}/6\text{-31G(d)}$ energies (in kcal mol $^{-1}$) for the computed fragmentation pathway leading from *exo,endo-2'* to **3'** and **8'**. NHC = N-heterocyclic carbene.

Next, we wondered if [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, treatment of **1a** in THF with excess phenylisocyanate (PhNCO; 20 equiv.) afforded directly spirophosphorane $\text{Li}[\text{7}]$ (100% by ^{31}P NMR; $\delta^{31}\text{P}\{^1\text{H}\}$: -62.6 ppm) as well as the tricyclic hexaphosphane Mes^*_2P_6 **8** (19% by ^{31}P NMR; $\delta^{31}\text{P}\{^1\text{H}\}$: -96.1 (m, P2/P3), -107.2 (m, P1) ppm; Scheme 4).^[22] Both compounds could be isolated as analytically pure white powders in 80% (**Li[7]**) and 18% (**8**) yield; they were fully characterized by multinuclear NMR spectroscopy, HR-MS and X-ray crystal structure determination (see the Supporting Information for **8**).

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

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

The molecular structure of $\text{Li}[\text{7}]$ revealed a distorted trigonal bipyramidal geometry around the central phosphorus (Λ -isomer; Figure 2), bearing 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 ($\text{Li1}\cdots\text{O1} = 1.866(10)$ $\text{\AA}$) creates a stable (m.p. 149 $^\circ\text{C}$) one-dimensional coordination polymer along the crystallographic a -axis, which was found to be insoluble in THF. The formation of

Li[7] from **1a** is fully reminiscent to the reaction of Na[OCP] with RNCO (R = Ph, Cy, *n*Bu),^[24] where the 2-phosphaethynolate anion acts as a formal “P” source with CO as leaving group, akin to Mes*P₃ in our case. Note that Na[OCP] provides the living isocyanate trimerization catalyst [7][−] as 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[PhP₄·BPh₃] (**1a'**) (Scheme 5; Li⁺ counter cations are included, but not shown). Our proposed mechanism starts by coordination of PhNCO to **1a'** giving 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 BPh₃-coordinated wing-tip phosphorus atom. The anionic carboxamide group of **10'** then attacks the electrophilic C-atom of a second phenylisocyanate to give **12'** ($\Delta E_{\text{total}} = -36.4$ 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'-13'}; $\Delta E_a = 12.0$ kcal mol^{−1}). Fragmentation of the resulting **13'** generates the BPh₃-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 affording spiro compound Li[7'] under liberation of BPh₃ ($\Delta E = -29.1$ kcal mol^{−1}; $\Delta E_{\text{overall}} = -90.4$ kcal mol^{−1}).

Scheme 5. Relative ω B97X-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 BPh₃. A Li⁺ counter cation was included in all anionic species, but is not shown.

To confirm the intermediacy of triphosphirene Mes*P₃ in the reactions,^[27,28] we sought to trap this important P₃ building block by a Diels-Alder reaction with 1,3-cyclohexadiene (1,3-CHD). Satisfyingly, addition of an excess of 1,3-CHD (50 equiv.) to the reactions of **1a** with either [IDippH][Cl] or PhNCO (Scheme 6) afforded the desired cycloaddition product **15** in 27% (³¹P NMR) and 69% (isolated) yield, respectively, in addition to the “P” transfer products **3** (30% by ³¹P NMR) and Li[7] (>99% isolated).

Scheme 6. Fragmentation reactions in the presence of 1,3-CHD. Dipp = 2,6-*i*Pr₂C₆H₃, Mes* = 2,4,6-*i*Bu₃C₆H₂. **I**) 1.1 equiv. [IDippH][Cl], THF, RT; **II**) 4 equiv. PhNCO, THF, RT.

The two ³¹P{¹H} NMR resonances of **15** at −160.9 ppm (P1) and −195.2 ppm (P2/P3) show a second order AB₂ spin-system with ¹J_{P_AP_B} 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) Å and 1.9149(16) Å, respectively) due to the different hybridization of their carbon substituents (sp² vs. sp³). The product is 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 ω B97X-D/6-311+G(2d,p)//6-31G(d), 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 second 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 non-symmetrically substituted tris(organyl)-P₃ species derived directly from P₄, which in addition to the obtained P₁ products illustrates the versatility of **1a** as 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 *n*-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 P₄-derivatized Lewis acid stabilized bicyclo[1.1.0]tetraphosphabutane **1a** can be utilized as a source for P₁ and P₃ containing organophosphorus compounds through unprecedented [3+1]-fragmentation reactions. Their formation proceeds by extrusion of a P₁ fragment induced by either an imidazolium salt or isocyanate with concurrent release of the transient triphosphirene Mes*P₃ that can be isolated as a dimer or trapped with 1,3-cyclohexadiene. The latter affords the unique tris(organyl) substituted triphosphirane **15**. We anticipate the presented chemistry of **1a** to be a versatile entry point for the design of selective fragmentation and functionalization strategies of P₄.

Acknowledgements

This work was supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (NWO/CW).

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

- [1] D. E. C. Corbridge, *Phosphorus 2000*, Elsevier, Amsterdam, **2000**.
- [2] For reviews, see: a) M. Peruzzini, L. Gonsalvi, A. Romerosa, *Chem. Soc. Rev.* **2005**, 34, 1038–1047; b) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, 110, 4164–4177; c) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* **2010**, 110, 4178–4235; d) M. Scheer, G. Balázs, A. Seitz, *Chem. Rev.* **2010**, 110, 4236–4256; e) N. A. Giffin, J. D. Masuda, *Coord. Chem. Rev.* **2011**, 255, 1342–1359.
- [3] a) M. H. Holthausen, J. J. Weigand, *J. Am. Chem. Soc.* **2009**, 131, 14210–14211; b) J. J. Weigand, M. Holthausen, R. Fröhlich, *Angew. Chem. Int. Ed.* **2009**, 48, 295–298; *Angew. Chem.* **2009**, 121, 301–304; c) M. H. Holthausen, S. K. Surmiak, P. Jerabek, G. Frenking, J. J. Weigand, *Angew. Chem. Int. Ed.* **2013**, 52, 11078–11082; *Angew. Chem.* **2013**, 125, 11284–11288; d) M. H. Holthausen, J. J. Weigand, *Chem. Soc. Rev.* **2014**, 43, 6639–6657.
- [4] J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2007**, 46, 7052–7055; *Angew. Chem.* **2007**, 119, 7182–7185. For more carbene activations by the group of Bertrand, see: a) O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2009**, 48, 5530–5533; *Angew. Chem.* **2009**, 121, 5638–5641; b) C. D. Martin, C. M. Weinstein, C. E. Moore, A. L. Rheingold, G. Bertrand, *Chem. Commun.* **2013**, 49, 4486–4488.
- [5] P. Barbaro, C. Bazzicalupi, M. Peruzzini, S. Seniori Costantini, P. Stoppioni, *Angew. Chem. Int. Ed.* **2012**, 51, 8628–8631; *Angew. Chem.* **2012**, 124, 8756–8759.
- [6] a) J. S. Figueroa, C. C. Cummins, *J. Am. Chem. Soc.* **2003**, 125, 4020–4021; b) J. S. Figueroa, C. C. Cummins, *Angew. Chem. Int. Ed.* **2004**, 43, 984–988; *Angew. Chem.* **2004**, 116, 1002–1006; c) J. S. Figueroa, C. C. Cummins, *J. Am. Chem. Soc.* **2004**, 126, 13916–13917; d) N. A. Piro, J. S. Figueroa, J. T. McKellar, C. C. Cummins, *Science* **2006**, 313, 1276–1279.
- [7] a) M. Scheer, S. Deng, O. J. Scherer, M. Sierka, *Angew. Chem. Int. Ed.* **2005**, 44, 3755–3758; *Angew. Chem.* **2005**, 117, 3821–3825; b) S. Deng, C. Schwarzmaier, C. Eichhorn, O. Scherer, G. Wolmershäuser, M. Zabel, M. Scheer, *Chem. Commun.* **2008**, 4064–4066; c) C. Schwarzmaier, S. Heinl, G. Balázs, M. Scheer, *Angew. Chem. Int. Ed.* **2015**, 54, 13116–13121; *Angew. Chem.* **2015**, 127, 13309–13314.
- [8] a) O. J. Scherer, T. Hilt, G. Wolmershäuser, *Organometallics* **1998**, 17, 4110–4112; b) O. J. Scherer, T. Hilt, G. Wolmershäuser, *Angew. Chem. Int. Ed.* **2000**, 39, 1425–1427; *Angew. Chem.* **2000**, 112, 1483–1485.
- [9] a) S. Pelties, D. Herrmann, B. de Bruin, F. Hartl, R. Wolf, *Chem. Commun.* **2014**, 50, 7014–7016; b) S. Pelties, A. W. Ehlers, R. Wolf, *Chem. Commun.* **2016**, 52, 6601–6604.
- [10] For other examples of P₄-derived bicyclo[1.1.0]tetraphosphabutane derivatives, see: a) R. Riedel, H.-D. Hausen, E. Fluck, *Angew. Chem. Int. Ed. Engl.* **1985**, 24, 1056–1057; *Angew. Chem.* **1985**, 97, 1050; b) M. B. Power, A. R. Barron, *Angew. Chem. Int. Ed. Engl.* **1991**, 30, 1353–1354; *Angew. Chem.* **1991**, 103, 1403–1404; c) J.-P. Bezombes, P. B. Hitchcock, M. F. Lappert, J. E. Nycz, *Dalton Trans.* **2004**, 499–501; d) A. R. Fox, R. J. Wright, E. Rivard, P. P. Power, *Angew. Chem. Int. Ed.* **2005**, 44, 7729–7733; *Angew. Chem.* **2005**, 117, 7907–7911; e) B. M. Cossairt, C. C. Cummins, *New J. Chem.* **2010**, 34, 1533–1536; f) D. Holschumacher, T. Bannenberg, K. Ibrom, C. G. Daniliuc, P. G. Jones, M. Tamm, *Dalton Trans.* **2010**, 39, 10590–10592; g) S. Khan, R. Michel, J. M. Dieterich, R. A. Mata, H. W. Roesky, J.-P. Demers, A. Lange, D. Stalke, *J. Am. Chem. Soc.* **2011**, 133, 17889–17894; h) N. A. Giffin, A. D. Hendsbee, T. L. Roemmele, M. D. Lumsden, C. C. Pye, J. D. Masuda, *Inorg. Chem.* **2012**, 51, 11837–11850; i) S. Heinl, S. Reisinger, C. Schwarzmaier, M. Bodensteiner, M. Scheer, *Angew. Chem. Int. Ed.* **2014**, 53, 7639–7642; *Angew. Chem.* **2014**, 126, 7769–7773; j) C. Schwarzmaier, A. Y. Timoshkin, G. Balázs, M. Scheer, *Angew. Chem. Int. Ed.* **2014**, 53, 9077–9081; *Angew. Chem.* **2014**, 126, 9223–9227; k) S. Heinl, M. Scheer, *Chem. Sci.* **2014**, 5, 3221–3225.
- [11] For two cationic examples prepared from P₁ building blocks, see: a) M. Donath, E. Conrad, P. Jerabek, G. Frenking, R. Fröhlich, N. Burford, J. J. Weigand, *Angew. Chem. Int. Ed.* **2012**, 51, 2964–2967; *Angew. Chem.* **2012**, 124, 3018–3021; b) J. Bresien, K. Faust, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2015**, 54, 6926–6930; *Angew. Chem.* **2015**, 127, 7030–7034.
- [12] The anion has never been isolated, but was detected by ³¹P NMR spectroscopy by Baudler et al., who after reduction of P₄ with Na/K naphthalenide observed [HP₄][−] at low temperature; [HP₄][−] was recently also detected by Mézailles using borohydrides: a) M. Baudler, C. Adamek, S. Opiela, H. Budzikiewicz, D. Ouzounis, *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 1059–1061; *Angew. Chem.* **1988**, 100, 1110–1111; b) K. X. Bhattacharyya, S. Dreyfuss, N. Saffon-Merceron, N. Mézailles, *Chem. Commun.* **2016**, 52, 5179–5182.
- [13] a) J. E. Borger, A. W. Ehlers, M. Lutz, J. C. Sloatweg, K. Lammertsma, *Angew. Chem. Int. Ed.* **2014**, 53, 12836–12839; *Angew. Chem.* **2014**, 126, 13050–13053; b) J. E. Borger, A. W. Ehlers, M. Lutz, J. C. Sloatweg, K. Lammertsma, *Angew. Chem. Int. Ed.* **2016**, 55, 613–617; *Angew. Chem.* **2016**, 128, 623–627.
- [14] Note that the reaction of **1a** with metal carbonyl (MeCN)W(CO)₅ affords anionic Li[Mes*P₄·(W(CO)₅)₂], see Ref. [13b].
- [15] Spectral parameters were determined by iterative full line shape analysis using the gNMR simulation program: P. H. M. Budzelaar, gNMR, Version 5.0.6.0, **2006**.
- [16] J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2007**, 129, 14180–14181.
- [17] K. Hansen, T. Szilvási, B. Blom, S. Inoue, J. Epping, M. Driess, *J. Am. Chem. Soc.* **2013**, 135, 11795–11798.
- [18] A. M. Tondreau, Z. Benkő, J. R. Harmer, H. Grützmacher, *Chem. Sci.* **2014**, 5, 1545–1554. Recently, also P₄ could be directly converted to **3**: M. Cicač-Hudi, J. Bender, S. H. Schlindwein, M. Bispinchoff, M. Nieger, H. Grützmacher, D. Gudat, *Eur. J. Inorg. Chem.* **2016**, 649–658.
- [19] A. Doddi, D. Bockfeld, T. Bannenberg, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2014**, 53, 13568–13572; *Angew. Chem.* **2014**, 126, 13786–13790.
- [20] IDipp-BPh₃ can be considered as a quenched frustrated Lewis pair (FLP) in equilibrium with its constituents.
- [21] For a related FLP system using the B(C₆F₅)₃ Lewis acid to activate dihydrogen, see: D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2008**, 47, 7428–7432; *Angew. Chem.* **2008**, 120, 7538–7542.
- [22] J. Bresien, A. Schulz, A. Villinger, *Chem. Eur. J.* **2015**, 21, 18543–18546.
- [23] CCDC 1491988–1491990 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [24] D. Heift, Z. Benkő, H. Grützmacher, A. R. Jupp, J. M. Goicoechea, *Chem. Sci.* **2015**, 6, 4017–4024.
- [25] Complexes **9'** and **11'** feature a PhNCO[−]Li⁺ interaction of which the energy is overestimated and is moderated in solution by coordination of THF solvent molecules to the Li⁺ cation.
- [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 [RP₅Cl]⁺ cage cation, see Ref. [3c], and by Bertrand for the reaction of P₄ with CAACs (cyclic (alkyl)(amino)carbenes), see Ref. [4].
- [28] Cummins et al. isolated the triphenyltin analogue through liberation of the corresponding phosphene from a niobium precursor, see: B. M. Cossairt, C. C. Cummins, *Angew. Chem. Int. Ed.* **2010**, 49, 1595–1598; *Angew. Chem.* **2010**, 122, 1639–1642.
- [29] This selectivity was also observed by Cummins et al., see: a) B. M. Cossairt, C. C. Cummins, *Angew. Chem. Int. Ed.* **2008**, 47, 8863–8866; *Angew. Chem.* **2008**, 120, 8995–8998; b) Ref [28].

COMMUNICATION

Cracking P₄: Two [3+1]-fragmentations of the Lewis acid stabilized bicyclo[1.1.0]tetraphosphabutanide Li[Mes*P₄·BPh₃] (Mes* = 2,4,6-*t*Bu₃C₆H₂) induced by an imidazolium salt or phenylisocyanate are reported. These unprecedented pathways grant access to P₁ and P₃ containing organophosphorus compounds in two simple steps from white phosphorus.

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

Page No. – Page No.

Selective [3+1]-Fragmentations of P₄ by
“P” Transfer from a Lewis Acid
Stabilized [RP₄][−] Butterfly Anion

Supporting Information

1.	Experimental Details	S2
2.	Computational Details	S10
3.	X-ray Structure Determinations	S55
4.	NMR Spectra	S57
5.	References	S62

Author Manuscript

1. Experimental Details

All manipulations regarding the preparation of air-sensitive compounds were carried out under an atmosphere of dry nitrogen, using standard Schlenk and drybox techniques. Solvents were purified, dried and degassed according to standard procedures.

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance 400 and internally referenced to the residual solvent resonances (THF- d_8 : ^1H δ 3.58, 1.72 ppm, $^{13}\text{C}\{^1\text{H}\}$ δ 67.2, 25.3 ppm; C_6D_6 : ^1H δ 7.16 ppm, $^{13}\text{C}\{^1\text{H}\}$ δ 128.1 ppm; CD_2Cl_2 : ^1H δ 5.32, $^{13}\text{C}\{^1\text{H}\}$ δ 53.8; DMSO- d_6 : ^1H δ 2.50, $^{13}\text{C}\{^1\text{H}\}$ δ 39.5). $^{31}\text{P}\{^1\text{H}\}$, ^{31}P , $^{11}\text{B}\{^1\text{H}\}$, ^{11}B and ^7Li NMR spectra were recorded on a Bruker Avance 400 and externally referenced (85% H_3PO_4 , $\text{BF}_3\cdot\text{OEt}_2$ and LiCl , respectively). Chemical shifts are reported in ppm. Melting points were measured on samples in sealed capillaries and are uncorrected. ESI Mass spectra were recorded on a Bruker Daltonics micrOTOF spectrometer in negative or positive (capillary potential of 4500 V) ion mode and the IR spectrum was recorded on a Shimadzu FTIR-8400S spectrophotometer.

Phenyl isocyanate (PhNCO) and 1,3-cyclohexadiene (1,3-CHD) were purchased from commercial resources and distilled prior to use and stored over molecular sieves (4 Å). $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$,^[S1] $[\text{IDippH}][\text{Cl}]$ ^[S2] and $[\text{Me}_3\text{NH}][\text{BPh}_4]$ ^[S1,S3] were prepared according to previously published procedures.

Protonation of $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$ using $[\text{Me}_3\text{NH}][\text{BPh}_4]$

$[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$ (0.015 g, 0.019 mmol, 1.0 equiv.) and $[\text{Me}_3\text{NH}][\text{BPh}_4]$ (0.007 g, 0.019 mmol, 1.0 equiv.) were loaded in an NMR tube and THF- d_8 (0.6 mL) was added to give a crème colored mixture which was directly analyzed using $^{31}\text{P}\{^1\text{H}\}$, ^{31}P and $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum revealed full conversion of the starting material and the formation of two new bicyclic tetraphosphabutane species (Figure S1). The $^{31}\text{P}\{^1\text{H}\}$ resonances of the two products were simulated^[S4] as AMX_2 spin systems (inset; inverted), consistent with those expected for the neutral *exo,endo* and *exo,exo* isomers of $\text{Mes}^*\text{P}_4\text{H}$ (1:0.7 ratio respectively). The former being easily distinguished from the latter by the smaller $^2J_{\text{P,P}}$ coupling constant (19.1 Hz vs. 303.9 Hz). The ^{31}P NMR spectrum (Figure S2) showed additional splitting of nearly all signals into doublets (*exo,endo*- $\text{Mes}^*\text{P}_4\text{H}$: $^1J_{\text{P,H}} = 147.8$ Hz, $^2J_{\text{P,H}}$ = not resolved, $^3J_{\text{P,H}} = 17.2$ Hz; *exo,exo*- $\text{Mes}^*\text{P}_4\text{H}$: $^1J_{\text{P,H}} = 133.9$ Hz, $^2J_{\text{P,H}} = 11.7$ Hz, $^3J_{\text{P,H}} = 111.1$ Hz). The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum showed two signals at 34.4 ppm and -6.5 ppm corresponding to BPh_3 (the signal is observed at 56.3 ppm in $\text{Tol}-d_8$ ^[S1]) and $[\text{Li}][\text{BPh}_4]$ respectively,^[S5] confirming both neutral P_4 derivatives to be devoid of Lewis acid.

In addition to the two tetraphosphanes, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum revealed the presence of Mes^*PH_2 by a sharp singlet signal at -132.2 ppm. Within 2 h, this primary phosphane was the only observable product suggesting complete decomposition of $\text{Mes}^*\text{P}_4\text{H}$ toward Mes^*PH_2 and other undetected P-containing species.

Exo,endo-Mes*P₄H:

³¹P{¹H} NMR (162.0 MHz, THF-*d*₈, 291 K): AMX₂ spin system, $\delta_{\text{PA}} -82.5$, $\delta_{\text{PM}} -175.3$, $\delta_{\text{PX}} -316.5$ ppm, $^1J_{\text{PA,PX}} = -202.7$, $^1J_{\text{PM,PX}} = -198.5$, $^2J_{\text{PA,PM}} = 19.1$ Hz.

¹H NMR (400.1 MHz, THF-*d*₈, 291 K): δ 7.22 (d, $^4J_{\text{H,P}} = 1.2$ Hz, 1H; *m*-C₆H₂), 1.71 (s, 18H; *o*-C(CH₃)₃), 1.27 (s, 9H; *p*-C(CH₃)₃), -1.34 (dd, $^1J_{\text{H,P}} = 147.5$ Hz, $^3J_{\text{H,P}} = 17.3$ Hz, 1H; Mes*P₄H).

Exo,exo-Mes*P₄H:

³¹P{¹H} NMR (162.0 MHz, THF-*d*₈, 291 K): AMX₂ spin system, $\delta_{\text{PA}} -116.9$, $\delta_{\text{PM}} -252.9$, $\delta_{\text{PX}} -323.5$ ppm, $^1J_{\text{PA,PX}} = -165.5$, $^1J_{\text{PM,PX}} = -137.0$, $^2J_{\text{PA,PM}} = 303.9$ Hz.

¹H NMR (400.1 MHz, THF-*d*₈, 291 K): δ 7.23 (d, $^4J_{\text{H,P}} = 1.2$ Hz, 1H; *m*-C₆H₂), 1.68 (s, 18H; *o*-C(CH₃)₃), 1.27 (s, 9H; *p*-C(CH₃)₃), 0.65 (ddt, $^1J_{\text{H,P}} = 133.2$ Hz, $^2J_{\text{H,P}} = 11.3$ Hz, $^3J_{\text{H,P}} = 109.0$ Hz, 1H; Mes*P₄H).

Figure S1. ³¹P{¹H} NMR spectrum (162.0 MHz, THF-*d*₈, 291 K) recorded directly after mixing [Li(THF)_{2.2}][Mes*P₄·BPh₃] and [Me₃NH][BPh₄]: expansion (inset) shows the experimental (top) and simulated^[S4] (inverted) spectrum. The resonance signal corresponding to Mes*PH₂ is marked with an asterisk (*).

Figure S2. ^{31}P NMR spectrum (162.0 MHz, $\text{THF-}d_8$, 291 K) recorded directly after mixing $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$ and $[\text{Me}_3\text{NH}][\text{BPh}_4]$.

Fragmentation of $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\text{BPh}_3]$ using $[\text{IDippH}][\text{Cl}]$

$[\text{IDippH}][\text{Cl}]$ (0.012 g, 0.028 mmol, 1.1 equiv.) was added to a solution of $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\text{BPh}_3]$ (0.020 g, 0.026 mmol, 1.0 equiv.) in $\text{THF-}d_8$ (0.6 mL), in an NMR tube containing $(\text{MeO})_3\text{PO}$ in a sealed capillary as an internal standard, at room temperature. The orange suspension was left for 2.5 h at room temperature and analyzed using ^{31}P NMR spectroscopy, showing ca. 13% conversion toward $\text{IDipp}=\text{PH}$ and ca. 8% to Mes^*PH_2 (see Figure S3). The recorded $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum showed signals at 2.6 and -7.4 ppm, corresponding to the adducts $[\text{IDippH}][\text{BPh}_3\text{Cl}]$ and IDipp-BPh_3 , respectively. These species were independently confirmed by analysis of the reaction solutions obtained after stirring a stoichiometric mixture of either $[\text{IDippH}][\text{Cl}]$ or IDipp with BPh_3 in $\text{THF-}d_8$, revealing one signal at 3.2 ppm in case of the former and -7.2 ppm in case of the latter, in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum.

Figure S3. ^{31}P NMR spectra (ppm scale) of $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\text{BPh}_3]$ in $\text{THF-}d_8$ prior to the addition of $[\text{IDippH}][\text{Cl}]$ (left) and 2.5 h thereafter (right).

Fragmentation in the presence of 1,3-CHD:

$[\text{IDippH}][\text{Cl}]$ (0.012 g, 0.028 mmol, 1.1 equiv.) was added to a solution of $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\text{BPh}_3]$ (0.020 g, 0.026 mmol, 1.0 equiv.) and 1,3-CHD (0.12 mL, 1.3 mmol, 50 equiv.) in $\text{THF-}d_8$ (0.6 mL), in an NMR tube containing $(\text{MeO})_3\text{PO}$ in a sealed capillary as an internal standard, at room temperature. The orange suspension was left for 2.5 h at room temperature and analyzed using ^{31}P NMR spectroscopy, showing ca. 30% conversion toward $\text{IDipp}=\text{PH}$, ca. 27% conversion to $\text{Mes}^*\text{P}_3(\text{C}_6\text{H}_8)$ and ca. 8% to Mes^*PH_2 (see Figure S4). The recorded $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum showed signals at 2.6 and -7.4 ppm, corresponding to the adducts $[\text{IDippH}][\text{BPh}_3\text{Cl}]$ and IDipp-BPh_3 , respectively.

Figure S4. ^{31}P NMR spectra (ppm scale) of $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$ in $\text{THF}-d_8$ prior to the addition of $[\text{IDippH}][\text{Cl}]$ (left) and 2.5 h thereafter (right).

Fragmentation of $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$ using PhNCO

An excess of PhNCO (0.041 mL, 0.38 mmol, 20 equiv.) was added to a solution of $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$ (0.015 g, 0.019 mmol, 1.0 equiv.) in $\text{THF}-d_8$ (0.6 mL), in an NMR tube containing $(\text{MeO})_3\text{PO}$ in a sealed capillary as an internal standard, at room temperature. The clear brown solution was quickly analyzed using $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, showing ca. 100% conversion toward $[\text{Li}(\text{THF})_{1.5}][\mathbf{7}]$ and ca. 19% conversion to Mes^*_2P_6 (see Figure S5). The ^{11}B NMR spectrum revealed a signal at 57.9 ppm corresponding to BPh_3 .

Figure S5. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (ppm scale) of $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$ in $\text{THF}-d_8$ prior to the addition of excess PhNCO (left) and directly thereafter (right).

Isolation of Mes^*_2P_6 and $[\text{Li}(\text{THF})_{1.5}][\mathbf{7}]$:

An excess of PhNCO (0.62 mL, 5.66 mmol, 20 equiv.) was added to a solution of $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$ (0.220 g, 0.283 mmol, 1.0 equiv.) in THF (10 mL) at room temperature. Within one minute the clear solution colored red and then brown with the precipitation of a white solid. After standing for 16 h the solid was collected by filtration and subsequently washed with THF (2 x 10 mL). Drying *in vacuo* yielded spiro-phosphoramide $[\text{Li}(\text{THF})_{1.5}][\mathbf{7}]$ as analytically pure white powder in 80% yield (0.140 g, 0.225 mmol). The filtrate and the THF washings were combined and evaporated to dryness to give an oily red residue which was washed with acetone (2 x 10 mL), cold DCM (1 mL, 0 °C) and *n*-pentane (5 mL) to give Mes^*_2P_6 as a white powder in 18% yield (0.017 g, 0.025 mmol).

Characterization of spiro-phosphoranide [Li(THF)_{1.5}][7]:

Crystals suitable for X-ray diffraction were obtained directly from the reaction solution upon standing overnight without stirring.

Mp. (nitrogen, sealed capillary): 149 °C.

¹H NMR (400.1 MHz, DMSO-*d*₆, 294 K): δ 7.46 (d, ³*J*_{H,H} = 7.9 Hz, 4H; *o*-C₆H₅), 7.42 (d, ³*J*_{H,H} = 7.9 Hz, 4H; *o*-C₆H₅), 7.34 (t, ³*J*_{H,H} = 7.3 Hz, 2H; *p*-C₆H₅), 7.22 (br. t, ³*J*_{H,H} = 7.3 Hz, 8H; *m*-C₆H₅), 6.96 (t, ³*J*_{H,H} = 7.3 Hz, 2H; *p*-C₆H₅).

⁷Li (155.5 MHz, DMSO-*d*₆, 294 K): δ -1.1 (s).

¹³C{¹H} NMR (100.6 MHz, DMSO-*d*₆, 294 K): δ 175.8 (d, ¹*J*_{C,P} = 23.8 Hz; P-C(O)), 153.1 (d, ²*J*_{C,P} = 7.1 Hz; PN-C(O)), 142.6 (d, ²*J*_{C,P} = 4.3 Hz; *ipso*-PN-C₆H₅), 136.2 (s; *ipso*-PC(O)N-C₆H₅), 128.6 (s; *m*-PC(O)N-C₆H₅), 128.3 (*o*-PC(O)N-C₆H₅), 127.8 (*m*-PN-C₆H₅), 127.2 (*p*-PC(O)N-C₆H₅), 124.0 (d, ³*J*_{C,P} = 4.5 Hz; *o*-PN-C₆H₅), 122.2 (s; *p*-PN-C₆H₅).

³¹P{¹H} NMR (162.0 MHz, DMSO-*d*₆, 293 K): δ -67.1 (s).

HR-MS (ESI): 269.0499 [M - 2 PhNCO]⁻. Calcd.: for C₁₄H₁₀N₂O₂P 269.0485.

IR (cm⁻¹): 2976 (w), 2876 (w), 1706 (m), 1678 (m), 1642 (s), 1595 (m), 1488 (s), 1378 (s), 1322 (m), 1166 (m), 1048 (m), 891 (m), 833 (m), 761 (s), 690 (s), 647 (m), 569 (m).

Comment on the solubility and stability of [Li(THF)_{1.5}][7]:

The product was found to be insoluble in THF but soluble and moderately stable in DMSO-*d*₆, showing only trace impurities in the recorded ¹H NMR spectrum after standing for 24 h in.

Characterization of Mes*₂P₆:^[S6]

The obtained multinuclear NMR data were found to be in full agreement with the previously reported data for Mes*₂P₆ by Schulz et al.^[S6]

¹H NMR (400.1 MHz, CD₂Cl₂, 294 K): δ 7.00 (s, 4H; *m*-C₆H₂), 1.63 (s, 36H; *o*-C(CH₃)₃), 1.14 (s, 18H; *p*-C(CH₃)₃).

¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂, 294 K): δ 158.0 (s; *o*-C₆H₂), 149.3 (s; *p*-C₆H₂), 123.2 (s; *m*-C₆H₂), 40.2 (s; *o*-C(CH₃)₃), 34.8 (s; *o*-C(CH₃)₃), 34.6 (s; *p*-C(CH₃)₃), 31.1 (s; *p*-C(CH₃)₃), not observed (*ipso*-C₆H₂).

³¹P{¹H} NMR (162.0 MHz, CD₂Cl₂, 293 K): δ -96.1 (m, 4P; Mes*P₂(P₄)), -107.2 (m, 2P; Mes*P₂(P₄)).

Crystals suitable for X-ray diffraction were grown by layering a THF solution of Mes*₂P₆ with *n*-pentane.

Figure S6. Molecular structure of Mes*₂P₆ in the crystal (ellipsoids are set at 50% probability; H-atoms omitted).

Isolation of Mes*P₃(C₆H₈):

PhNCO (0.112 mL, 1.03 mmol, 4.0 equiv.) was added to a solution of [Li(THF)_{2.2}][Mes*P₄BPh₃] (0.200 g, 0.257 mmol, 1.0 equiv.) and 1,3-CHD (1.22 mL, 12.9 mmol, 50 equiv.) in THF (10 mL) at room temperature. Within one minute the clear solution colored red and then brown with the precipitation of a white solid.* The mixture was stirred for 15 min. after which the volatiles were removed *in vacuo*. The product was extracted into *n*-pentane (20 mL), evaporated to dryness and washed with acetonitrile (2 x 5 mL) at 0 °C to give Mes*P₃(C₆H₈) as a pale yellow powder in 69% yield (0.074 g, 0.177 mmol). Crystals suitable for X-ray diffraction were grown from a saturated *n*-hexane solution at +6 °C.

*Though not required to obtain pure Mes*P₃(C₆H₈), the white solid can be collected by filtration giving pure [Li(THF)_{1.5}][7] after washing with THF in quantitative yield.

Mp. (nitrogen, sealed capillary): 129–144 °C (trajectory).

¹H NMR (400.1 MHz, C₆D₆, 291 K): δ 7.30 (d, ⁴J_{H,P} = 2.0 Hz, 2H; C₆H₂), 5.53–5.50 (m, 2H; C(H)=C(H)), 2.81–2.75 (m, 2H; C(H)-C(H)=C(H)), 1.82 (s, 18H; *o*-C(CH₃)₃), 1.21 (s, 9H; *p*-C(CH₃)₃), 0.89–0.80 (m, 4H; C(H)₂-C(H)).

¹³C{¹H} NMR (100.6 MHz, C₆D₆, 291 K): δ 158.3 (s; *o*-C₆H₂), 148.2 (s; *p*-C₆H₂), 123.2 (s; *m*-C₆H₂), 121.5 (d, ³J_{C,P} = 11.3 Hz; C(H)=C(H)), 40.0 (s; *o*-C(CH₃)₃), 34.9 (d, ⁴J_{C,P} = 9.0 Hz; *o*-C(CH₃)₃), 34.4 (s; *p*-C(CH₃)₃), 31.3 (s; *p*-C(CH₃)₃), 26.7 (td, ¹J_{C,P} = 20.4 Hz, ²J_{C,P} = 13.8 Hz; C(H)-C(H)=C(H)), 23.0 (m; C(H)₂-C(H)), not observed (*ipso*-C₆H₂).

³¹P{¹H} NMR (162.0 MHz, C₆D₆, 291 K): δ –160.9 (1P; Mes*P), –195.2 (2P; P₂(C₆H₈)); AB₂ second order spin-system: ¹J_{P_A,P_B} = 192.0 Hz (Figure S7).^[S4]

HR-MS (ESI): 441.2012 [M + Na]⁺. Calcd.: for C₂₄H₃₇NaP₃ 441.2000.

Figure S7. Experimental (top) and simulated (inverted) ³¹P{¹H} NMR spectra (ppm scale) of Mes*P₃C₆H₈.

2. Computational Details

Density functional calculations were performed at the ω B97X-D^[S7] level of theory using Gaussian09, revision D.01.^[S8] Geometry optimizations were performed using the 6-31G(d) basis set^[S9,S10] and uncorrected energies were obtained from single point calculations using the 6-311+G(2d,p) basis set.^[S10,S11,S12] The nature of each stationary point was confirmed by frequency calculations.

Calculated minimum energy reaction pathway for the fragmentation of *exo,endo-2'* using IPh (NHC^{Ph})

Scheme S1. Relative ω B97X-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'. NHC = *N*-heterocyclic carbene.

Calculated minimum energy reaction pathway for the fragmentation of *exo,exo-2'* using IPh (NHC^{Ph})

Scheme S2. Relative ω B97X-D/6-311+G(2d,p)//6-31G(d) energies (in kcal mol⁻¹) for the computed fragmentation pathway leading from *exo,exo-2'* to 3' and 8'. NHC = *N*-heterocyclic carbene.

Optimized geometries (Cartesian coordinates) and uncorrected energies (in a.u.)**IPh:**

E = -688.218086101

C	0.000036000	0.340490000	-0.091191000
C	0.673457000	-1.770164000	0.534193000
C	-0.673520000	-1.770109000	0.534367000
H	1.373936000	-2.540778000	0.813925000
H	-1.374192000	-2.540811000	0.813332000
N	1.060505000	-0.487865000	0.152216000
N	-1.060475000	-0.487922000	0.151684000
C	2.410998000	-0.063807000	0.014792000
C	3.405335000	-0.976440000	-0.330025000
C	2.731357000	1.276140000	0.228135000
C	4.724995000	-0.548733000	-0.444343000
H	3.152627000	-2.012200000	-0.533938000
C	4.049413000	1.694839000	0.098902000
H	1.936226000	1.968175000	0.479779000
C	5.052656000	0.785766000	-0.230510000
H	5.495327000	-1.264286000	-0.715312000
H	4.293687000	2.739771000	0.264535000
H	6.081944000	1.117491000	-0.325771000
C	-2.410924000	-0.063790000	0.014373000
C	-2.731385000	1.276039000	0.228473000
C	-3.405236000	-0.976262000	-0.330853000
C	-4.049491000	1.694655000	0.099638000
H	-1.936156000	1.967894000	0.480344000
C	-4.724969000	-0.548619000	-0.444786000
H	-3.152615000	-2.011908000	-0.535502000
C	-5.052730000	0.785725000	-0.230113000
H	-4.293678000	2.739515000	0.265931000
H	-5.495205000	-1.264177000	-0.716008000
H	-6.082059000	1.117443000	-0.324921000

exo,endo-2':

E = -1597.68320194

Author Manuscript

P	-1.561812000	-1.095181000	-0.599801000
P	-1.563545000	1.101210000	-0.588227000
P	-3.378814000	-0.001756000	0.055957000
P	-0.503992000	-0.004656000	1.031830000
C	1.232837000	-0.001239000	0.407097000
C	1.918830000	-1.206054000	0.215459000
C	1.915538000	1.205154000	0.213823000
C	3.253931000	-1.203473000	-0.176222000
C	3.250682000	1.205567000	-0.177830000
C	3.921380000	0.001822000	-0.374671000
H	3.771719000	-2.145770000	-0.327794000
H	3.766015000	2.149012000	-0.330614000
H	-3.149637000	-0.009153000	1.463023000
H	1.403141000	2.151809000	0.365426000
H	1.408825000	-2.153821000	0.368276000
H	4.963200000	0.003015000	-0.680647000

exo,exo-2':

E = -1597.68286819

P	-1.529007000	-1.027237000	-0.708765000
P	-1.557386000	1.142380000	-0.493549000
P	-3.304562000	-0.047177000	0.221134000
P	-0.514485000	-0.091574000	1.044613000
C	1.218757000	-0.025226000	0.412762000
C	1.934410000	-1.214358000	0.230703000
C	1.870864000	1.195409000	0.207137000
C	3.266730000	-1.182972000	-0.168242000
C	3.204044000	1.224465000	-0.191252000
C	3.903491000	0.036395000	-0.381416000
H	3.805913000	-2.114100000	-0.314278000
H	3.695523000	2.178855000	-0.354305000
H	-4.037324000	0.067912000	-0.994583000
H	1.337244000	2.130895000	0.353195000
H	1.447302000	-2.172362000	0.393976000
H	4.943179000	0.060642000	-0.693631000

4':

E = -2285.91762683

P	-1.042116000	-0.891341000	-0.938179000
P	-1.568266000	-2.842545000	-0.028272000
P	0.458434000	-1.958829000	0.265269000
P	-2.309155000	-0.949363000	0.877486000
C	-4.010218000	-0.721579000	0.200790000
C	-4.855810000	0.083918000	0.972188000
C	-4.498221000	-1.258961000	-0.995563000
C	-6.157729000	0.350626000	0.559403000
C	-5.800342000	-0.994814000	-1.407071000
C	-6.631881000	-0.189356000	-0.632188000
H	-6.801630000	0.977128000	1.169703000
H	-6.168168000	-1.420998000	-2.335787000
H	0.261966000	-1.310458000	1.513511000
H	-3.862826000	-1.889115000	-1.613244000
H	-4.489147000	0.506986000	1.904817000
H	-7.648338000	0.013660000	-0.956216000
C	2.343268000	0.752734000	0.264893000
N	1.674027000	1.823911000	-0.259038000
N	3.559059000	0.858149000	-0.349937000
C	2.438579000	2.556628000	-1.161919000
C	3.637821000	1.944285000	-1.217201000
H	2.072567000	3.443790000	-1.654269000
H	4.516796000	2.164082000	-1.802315000
C	4.638474000	-0.037622000	-0.105252000
C	5.940487000	0.453094000	-0.031031000
C	4.386612000	-1.397199000	0.060189000
C	6.995435000	-0.424326000	0.199609000
H	6.126174000	1.518443000	-0.128522000
C	5.446180000	-2.263082000	0.303940000
H	3.367806000	-1.761825000	-0.008419000
C	6.752304000	-1.783425000	0.370276000
H	8.008172000	-0.037470000	0.260412000
H	5.247989000	-3.322459000	0.434790000
H	7.575442000	-2.466390000	0.556348000
C	0.341963000	2.159467000	0.109113000

Author Manuscript

C	-0.559185000	2.603803000	-0.856910000
C	-0.053469000	2.033615000	1.438231000
C	-1.862745000	2.920317000	-0.488246000
H	-0.253381000	2.664380000	-1.896979000
C	-1.359096000	2.349002000	1.795975000
H	0.663566000	1.673566000	2.167287000
C	-2.266853000	2.793957000	0.837859000
H	-2.568443000	3.249380000	-1.244357000
H	-1.668474000	2.237764000	2.830552000
H	-3.288580000	3.029786000	1.118442000

4th:

E = -2285.91535138

P	-0.913529000	-0.923332000	-0.558464000
P	-1.571563000	-2.778681000	0.420281000
P	0.241882000	-1.681161000	1.163653000
P	-2.503525000	-0.832380000	0.981637000
C	-4.028086000	-0.733337000	-0.050334000
C	-4.995067000	0.166786000	0.411041000
C	-4.279287000	-1.446707000	-1.227858000
C	-6.184268000	0.354941000	-0.286868000
C	-5.468825000	-1.260408000	-1.923856000
C	-6.422935000	-0.359156000	-1.456648000
H	-6.924210000	1.057979000	0.084232000
H	-5.651131000	-1.820976000	-2.836009000
H	1.159737000	-2.434401000	0.377800000
H	-3.546067000	-2.153956000	-1.607774000
H	-4.814220000	0.724842000	1.326730000
H	-7.351402000	-0.217505000	-2.001832000
C	2.386905000	0.786566000	0.276609000
N	1.628641000	1.789465000	-0.258080000
N	3.492759000	0.810518000	-0.527367000
C	2.234097000	2.403534000	-1.350390000
C	3.417541000	1.783163000	-1.521204000
H	1.788458000	3.228922000	-1.882543000
H	4.182713000	1.929249000	-2.266507000
C	4.602980000	-0.059653000	-0.338986000

C	5.884030000	0.342863000	-0.711709000
C	4.403177000	-1.316477000	0.229040000
C	6.959511000	-0.521993000	-0.531925000
H	6.051097000	1.335345000	-1.117874000
C	5.484912000	-2.166997000	0.416567000
H	3.401706000	-1.603204000	0.525091000
C	6.766162000	-1.778517000	0.031681000
H	7.955114000	-0.201422000	-0.823555000
H	5.322672000	-3.143491000	0.862578000
H	7.607369000	-2.449495000	0.174807000
C	0.358581000	2.163183000	0.263651000
C	-0.656954000	2.576433000	-0.596680000
C	0.135822000	2.095243000	1.637171000
C	-1.897801000	2.932451000	-0.076368000
H	-0.492887000	2.583925000	-1.669819000
C	-1.108111000	2.446958000	2.145811000
H	0.935436000	1.749903000	2.282235000
C	-2.126074000	2.871526000	1.294754000
H	-2.691052000	3.240272000	-0.750433000
H	-1.283568000	2.381231000	3.214801000
H	-3.096396000	3.143798000	1.698576000

TS₄₋₅:

E = -2285.9043779

P	-0.530693000	-1.183481000	-0.490460000
P	-0.955240000	-2.550210000	1.179805000
P	1.097257000	-0.770079000	0.938087000
P	-2.089761000	-0.676239000	1.017743000
C	-3.653567000	-1.049830000	0.090249000
C	-4.610011000	-0.028704000	0.048719000
C	-3.936748000	-2.258066000	-0.553914000
C	-5.817224000	-0.204977000	-0.621829000
C	-5.140357000	-2.434547000	-1.229274000
C	-6.083670000	-1.410157000	-1.265578000
H	-6.552123000	0.595509000	-0.638357000
H	-5.345202000	-3.379475000	-1.725078000
H	0.402423000	0.070528000	1.835692000

H	-3.207968000	-3.064439000	-0.511399000
H	-4.406258000	0.912705000	0.554616000
H	-7.025680000	-1.553362000	-1.787616000
C	1.933612000	0.873297000	0.121168000
N	1.317570000	1.981528000	-0.354069000
N	3.135403000	0.854037000	-0.504407000
C	2.116124000	2.638678000	-1.272783000
C	3.263056000	1.929536000	-1.367138000
H	1.799435000	3.553442000	-1.747624000
H	4.164498000	2.100565000	-1.933245000
C	-0.001072000	2.415914000	0.007374000
C	-0.998708000	2.413542000	-0.960551000
C	-0.251432000	2.833381000	1.308498000
C	-2.274798000	2.842885000	-0.614248000
H	-0.784142000	2.044635000	-1.958382000
C	-1.531508000	3.257642000	1.645313000
H	0.546532000	2.817755000	2.043740000
C	-2.539137000	3.266346000	0.685388000
H	-3.066554000	2.822485000	-1.355515000
H	-1.741584000	3.574198000	2.661465000
H	-3.539131000	3.592441000	0.954238000
C	4.145206000	-0.143736000	-0.322873000
C	4.579003000	-0.460668000	0.959603000
C	4.683011000	-0.769887000	-1.442087000
C	5.563044000	-1.428864000	1.119952000
H	4.143800000	0.041293000	1.816894000
C	5.677284000	-1.727225000	-1.270993000
H	4.307157000	-0.529227000	-2.431838000
C	6.116096000	-2.058226000	0.007785000
H	5.898545000	-1.689066000	2.118434000
H	6.097700000	-2.223943000	-2.139314000
H	6.885079000	-2.812874000	0.138314000

TS_{4^u-5^v}:

E = -2285.90586027

P	-0.727500000	-0.928663000	-0.580885000
P	-0.953772000	-2.590878000	0.853435000

Author Manuscript

P	0.825958000	-0.688658000	0.938670000
P	-2.187575000	-0.786358000	1.090637000
C	-3.748223000	-1.062955000	0.126564000
C	-4.663167000	-0.003028000	0.124020000
C	-4.076972000	-2.231360000	-0.567425000
C	-5.870007000	-0.100908000	-0.561647000
C	-5.283343000	-2.330057000	-1.255031000
C	-6.182946000	-1.267207000	-1.254763000
H	-6.569386000	0.730928000	-0.552028000
H	-5.523643000	-3.245504000	-1.788811000
H	1.768620000	-1.599205000	0.407373000
H	-3.379314000	-3.065186000	-0.563041000
H	-4.423787000	0.909351000	0.666461000
H	-7.126789000	-1.350231000	-1.786366000
C	1.989697000	0.813483000	0.055525000
N	1.474067000	2.018678000	-0.271257000
N	3.259584000	0.846717000	-0.412975000
C	2.398228000	2.791080000	-0.955478000
C	3.527153000	2.054650000	-1.043670000
H	2.167549000	3.789966000	-1.289568000
H	4.494837000	2.278046000	-1.463622000
C	0.137827000	2.444250000	0.039023000
C	-0.786784000	2.586307000	-0.989280000
C	-0.204056000	2.691068000	1.363152000
C	-2.083896000	2.981115000	-0.680152000
H	-0.501324000	2.353081000	-2.010027000
C	-1.503041000	3.084826000	1.661417000
H	0.535221000	2.554078000	2.145129000
C	-2.439889000	3.231280000	0.642523000
H	-2.821046000	3.071353000	-1.470954000
H	-1.784892000	3.262590000	2.693641000
H	-3.456332000	3.529057000	0.880600000
C	4.206542000	-0.214713000	-0.277379000
C	4.406006000	-0.801271000	0.968325000
C	4.921245000	-0.636870000	-1.393969000
C	5.327703000	-1.835001000	1.090672000
H	3.843247000	-0.450258000	1.827531000

C	5.853578000	-1.659774000	-1.256552000
H	4.732761000	-0.184000000	-2.362499000
C	6.055104000	-2.261330000	-0.017380000
H	5.479193000	-2.303448000	2.057526000
H	6.410961000	-1.996553000	-2.124627000
H	6.777355000	-3.064978000	0.084067000

5':

E = -2285.91175449

P	0.193055000	-1.459443000	-0.113988000
P	0.776280000	-3.210003000	-1.108142000
P	-1.259600000	0.012586000	-1.489148000
P	1.998147000	-1.402174000	-1.382206000
C	3.359851000	-1.394139000	-0.112188000
C	4.418308000	-0.509936000	-0.352723000
C	3.397004000	-2.179859000	1.042914000
C	5.475967000	-0.395015000	0.547227000
C	4.450261000	-2.065396000	1.945095000
C	5.490367000	-1.170051000	1.703630000
H	6.290348000	0.295071000	0.342046000
H	4.462416000	-2.681800000	2.840101000
H	-0.234590000	0.902990000	-1.881799000
H	2.595924000	-2.892253000	1.226946000
H	4.413144000	0.092566000	-1.259624000
H	6.311609000	-1.084340000	2.409672000
C	-1.716567000	1.044159000	-0.078598000
N	-1.067344000	2.097207000	0.480362000
N	-2.823622000	0.855390000	0.683910000
C	-1.783969000	2.580406000	1.562988000
C	-2.879275000	1.801913000	1.692603000
H	-1.427548000	3.417567000	2.140581000
H	-3.682436000	1.809448000	2.411211000
C	-3.815687000	-0.157676000	0.474235000
C	-5.100923000	0.227606000	0.107421000
C	-3.481924000	-1.495076000	0.659496000
C	-6.071821000	-0.750413000	-0.077167000
H	-5.326760000	1.278323000	-0.046226000

Author Manuscript

C	-4.457886000	-2.465095000	0.457999000
H	-2.472904000	-1.767853000	0.955325000
C	-5.749945000	-2.094478000	0.094921000
H	-7.077454000	-0.462177000	-0.365949000
H	-4.204852000	-3.511711000	0.589552000
H	-6.508294000	-2.855800000	-0.057958000
C	0.191150000	2.643870000	0.056272000
C	0.198128000	3.846942000	-0.641484000
C	1.370733000	1.981459000	0.380359000
C	1.416355000	4.397699000	-1.024810000
H	-0.740646000	4.334052000	-0.886670000
C	2.582528000	2.539312000	-0.012848000
H	1.339234000	1.036288000	0.913214000
C	2.605424000	3.743717000	-0.711256000
H	1.434623000	5.334226000	-1.572849000
H	3.504039000	2.019201000	0.226678000
H	3.554188000	4.173845000	-1.016414000

5”:

E = -2285.91346587

P	0.245242000	-1.370226000	-0.130355000
P	0.933515000	-3.010511000	-1.253872000
P	-1.223243000	-0.002659000	-1.508855000
P	2.068532000	-1.128580000	-1.353587000
C	3.413665000	-1.180718000	-0.068270000
C	4.484580000	-0.303807000	-0.274143000
C	3.432569000	-1.998112000	1.065373000
C	5.536356000	-0.226137000	0.636036000
C	4.476688000	-1.917391000	1.981741000
C	5.530198000	-1.029114000	1.773199000
H	6.360699000	0.459271000	0.455856000
H	4.473122000	-2.557541000	2.860126000
H	-2.343461000	-0.864230000	-1.452014000
H	2.626487000	-2.711911000	1.219752000
H	4.489004000	0.330870000	-1.158387000
H	6.345998000	-0.972287000	2.488566000
C	-1.809518000	1.009558000	-0.128838000

Author Manuscript

N	-1.081298000	2.014385000	0.416435000
N	-2.945804000	0.940518000	0.611136000
C	-1.761178000	2.577610000	1.481729000
C	-2.929346000	1.912002000	1.601490000
H	-1.341498000	3.396448000	2.042851000
H	-3.745850000	2.015821000	2.297288000
C	-3.988419000	-0.032187000	0.469146000
C	-5.239126000	0.374366000	0.019603000
C	-3.730890000	-1.357432000	0.807847000
C	-6.255066000	-0.569869000	-0.094282000
H	-5.406384000	1.413501000	-0.246303000
C	-4.749725000	-2.293988000	0.677984000
H	-2.741329000	-1.644372000	1.152113000
C	-6.009518000	-1.900974000	0.230655000
H	-7.234920000	-0.264983000	-0.447332000
H	-4.556687000	-3.332404000	0.925690000
H	-6.801107000	-2.636971000	0.132172000
C	0.253303000	2.373029000	0.022798000
C	0.462637000	3.045100000	-1.174881000
C	1.307463000	2.017767000	0.857420000
C	1.765366000	3.363602000	-1.543522000
H	-0.379244000	3.294616000	-1.812149000
C	2.603434000	2.352572000	0.485001000
H	1.114001000	1.454626000	1.764436000
C	2.830311000	3.021290000	-0.714977000
H	1.946140000	3.873007000	-2.484192000
H	3.435364000	2.055747000	1.113929000
H	3.845999000	3.263102000	-1.012000000

3':

E = -1030.19541279

C	0.001716000	-0.204665000	-0.037281000
C	-0.678701000	1.972465000	-0.133462000
C	0.663111000	1.977971000	-0.132607000
H	-1.397288000	2.775232000	-0.161879000
H	1.373702000	2.786628000	-0.185612000
N	-1.089329000	0.640908000	-0.069191000

N	1.085128000	0.651605000	-0.080011000
H	-1.302965000	-2.120083000	0.032337000
P	0.106646000	-1.957402000	0.039875000
C	-2.460620000	0.262709000	-0.007979000
C	-3.291672000	0.547127000	-1.087202000
C	-2.968084000	-0.337338000	1.142346000
C	-4.646096000	0.234926000	-1.011253000
H	-2.871622000	1.002011000	-1.979012000
C	-4.318600000	-0.658139000	1.205401000
H	-2.298182000	-0.557380000	1.967008000
C	-5.159544000	-0.368762000	0.132321000
H	-5.297298000	0.457671000	-1.850790000
H	-4.717236000	-1.129370000	2.098288000
H	-6.215272000	-0.615499000	0.188825000
C	2.456615000	0.272487000	-0.037299000
C	3.275555000	0.814033000	0.950867000
C	2.977939000	-0.595704000	-0.993745000
C	4.628347000	0.490473000	0.976371000
H	2.848142000	1.475230000	1.698769000
C	4.327166000	-0.926428000	-0.949714000
H	2.325166000	-1.010732000	-1.753447000
C	5.155059000	-0.383123000	0.029722000
H	5.267349000	0.912375000	1.745968000
H	4.732973000	-1.608969000	-1.689805000
H	6.209090000	-0.641860000	0.056733000

6':

E = -1255.69276001

P	-2.309804000	-0.362757000	1.010464000
P	-2.312926000	-0.389118000	-0.996738000
P	-1.009917000	1.111192000	-0.014624000
C	0.668888000	0.335626000	-0.005571000
C	1.730876000	1.248734000	-0.003188000
C	0.960034000	-1.032058000	-0.002376000
C	3.049904000	0.807405000	0.002751000
C	2.279878000	-1.473721000	0.003028000
C	3.327000000	-0.556660000	0.005922000

Author Manuscript

H	3.860555000	1.529860000	0.004746000
H	2.489093000	-2.539397000	0.005168000
H	0.161125000	-1.768260000	-0.004140000
H	1.523782000	2.316590000	-0.006099000
H	4.355692000	-0.904514000	0.010398000

8':

E = -2511.45902234

P	-0.509851000	1.003685000	-1.125093000
P	0.509851000	-1.003685000	-1.125093000
P	0.509837000	-1.003692000	1.125022000
P	-0.509837000	1.003692000	1.125022000
P	1.104311000	2.025105000	-0.000052000
P	-1.104311000	-2.025105000	-0.000052000
C	-0.411425000	-3.737500000	-0.000009000
C	-0.206717000	-4.417199000	1.205968000
C	-0.206531000	-4.417230000	-1.205933000
C	0.206531000	-5.745641000	1.204385000
H	-0.362083000	-3.905608000	2.151961000
C	0.206717000	-5.745675000	-1.204248000
H	-0.361747000	-3.905666000	-2.151965000
C	0.414677000	-6.411875000	0.000093000
H	0.368532000	-6.258783000	2.147543000
H	0.368864000	-6.258841000	-2.147367000
H	0.739704000	-7.448003000	0.000132000
C	0.411425000	3.737500000	-0.000009000
C	0.206717000	4.417199000	1.205968000
C	0.206531000	4.417230000	-1.205933000
C	-0.206531000	5.745641000	1.204385000
H	0.362083000	3.905608000	2.151961000
C	-0.206717000	5.745675000	-1.204248000
H	0.361747000	3.905666000	-2.151965000
C	-0.414677000	6.411875000	0.000093000
H	-0.368532000	6.258783000	2.147543000
H	-0.368864000	6.258841000	-2.147367000
H	-0.739704000	7.448003000	0.000132000

Calculated minimum energy reaction pathway for the fragmentation of 1a' using PhNCO

Scheme S3. Relative ω B97X-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 BPh₃. A Li⁺ counter cation was included in all anionic species but is not shown.

Optimized geometries (Cartesian coordinates) and uncorrected energies (in a.u.)

PhNCO:

E = -399.703737546

C	0.853686000	-1.290537000	-0.000030000
C	-0.090604000	-0.264583000	-0.000096000
C	0.322618000	1.070387000	-0.000118000
C	1.679795000	1.369027000	0.000005000
C	2.627107000	0.348355000	0.000090000
C	2.208647000	-0.979603000	0.000061000
H	0.513109000	-2.320454000	-0.000035000
H	-0.418096000	1.864569000	-0.000225000
H	1.996643000	2.407554000	0.000025000
H	3.686043000	0.586526000	0.000218000
H	2.940790000	-1.781129000	0.000104000
N	-1.444932000	-0.614230000	-0.000133000
C	-2.526681000	-0.080795000	0.000068000

O -3.631421000 0.313630000 0.000121000

BPh₃:

E = -719.761820912

B	-0.003002000	-0.001125000	0.000212000
C	0.973861000	-1.228024000	-0.000521000
C	0.641630000	-2.431150000	0.647674000
C	2.220134000	-1.168356000	-0.649162000
C	1.513219000	-3.514940000	0.660755000
H	-0.313990000	-2.512419000	1.159073000
C	3.085956000	-2.256317000	-0.663293000
H	2.509046000	-0.253674000	-1.160256000
C	2.735704000	-3.430440000	-0.001232000
H	1.238258000	-4.427761000	1.181572000
H	4.036995000	-2.187520000	-1.183622000
H	3.414877000	-4.278539000	-0.001228000
C	-1.554029000	-0.231377000	0.000640000
C	-2.427077000	0.663751000	0.644035000
C	-2.128823000	-1.341686000	-0.643146000
C	-3.802131000	0.456240000	0.656951000
H	-2.016453000	1.532709000	1.151720000
C	-3.504815000	-1.542398000	-0.657378000
H	-1.482931000	-2.053953000	-1.149941000
C	-4.343835000	-0.645461000	-0.000762000
H	-4.453004000	1.156127000	1.173115000
H	-3.923796000	-2.400642000	-1.174857000
H	-5.418590000	-0.804838000	-0.001462000
C	0.573906000	1.457314000	0.001191000
C	-0.096594000	2.510592000	-0.645689000
C	1.784396000	1.764279000	0.647952000
C	0.419829000	3.801772000	-0.659543000
H	-1.035112000	2.308927000	-1.155419000
C	2.294239000	3.057969000	0.661290000
H	2.329118000	0.973698000	1.157289000
C	1.614594000	4.078334000	0.000530000
H	-0.111027000	4.594533000	-1.178904000
H	3.224658000	3.270404000	1.180040000

H	2.015977000	5.087950000	0.000071000
---	-------------	-------------	-------------

6':

E = -1255.69276001

P	-2.309804000	-0.362757000	1.010464000
P	-2.312926000	-0.389118000	-0.996738000
P	-1.009917000	1.111192000	-0.014624000
C	0.668888000	0.335626000	-0.005571000
C	1.730876000	1.248734000	-0.003188000
C	0.960034000	-1.032058000	-0.002376000
C	3.049904000	0.807405000	0.002751000
C	2.279878000	-1.473721000	0.003028000
C	3.327000000	-0.556660000	0.005922000
H	3.860555000	1.529860000	0.004746000
H	2.489093000	-2.539397000	0.005168000
H	0.161125000	-1.768260000	-0.004140000
H	1.523782000	2.316590000	-0.006099000
H	4.355692000	-0.904514000	0.010398000

Li[**1a'**]:

E = -2324.44060227

P	1.573662000	0.186425000	0.778547000
P	1.581949000	-0.586950000	-1.265334000
P	-0.071268000	0.709746000	-0.611086000
P	2.794961000	1.227925000	-0.776305000
C	-2.356233000	1.334642000	0.650802000
C	-3.179801000	2.160370000	-0.141530000
C	-1.781467000	1.945007000	1.788541000
C	-3.367517000	3.518756000	0.137862000
C	-1.961884000	3.299456000	2.082276000
C	-2.742744000	4.103494000	1.243842000
C	-2.735662000	-0.654523000	-1.142057000
C	-3.932267000	-1.328310000	-0.846367000
C	-2.457010000	-0.442689000	-2.498776000
C	-4.804120000	-1.756347000	-1.841774000
C	-3.320484000	-0.868576000	-3.507690000
C	-4.501502000	-1.526153000	-3.182205000

Author Manuscript

C	-1.599622000	-1.253751000	1.223245000
C	-0.843923000	-2.402343000	0.934944000
C	-2.195784000	-1.200369000	2.490890000
C	-0.663202000	-3.420265000	1.864617000
C	-2.029063000	-2.217072000	3.430366000
C	-1.253162000	-3.328958000	3.123429000
B	-1.834730000	-0.124976000	0.096097000
C	4.449949000	0.451908000	-0.485681000
C	5.085421000	0.558651000	0.756541000
C	5.129556000	-0.171885000	-1.538379000
C	6.362771000	0.039623000	0.945272000
C	6.405630000	-0.692726000	-1.348309000
C	7.024639000	-0.588483000	-0.105776000
H	6.839947000	0.123907000	1.917184000
H	6.915410000	-1.182470000	-2.172780000
H	-1.137361000	1.349620000	2.430452000
H	-1.536713000	0.063289000	-2.788475000
H	-3.065928000	-0.689821000	-4.549301000
H	-1.484648000	3.731582000	2.957314000
H	-5.177578000	-1.862157000	-3.963587000
H	-2.878789000	5.158549000	1.460470000
H	-3.995621000	4.122738000	-0.511066000
H	-5.720105000	-2.276265000	-1.572944000
H	-4.178838000	-1.528952000	0.194215000
H	-3.647208000	1.732495000	-1.024092000
H	-0.398189000	-2.510743000	-0.052417000
H	-2.823429000	-0.351179000	2.753680000
H	-2.510609000	-2.139488000	4.401884000
H	-1.115680000	-4.121643000	3.853677000
H	-0.065784000	-4.290103000	1.604644000
H	4.577652000	1.042536000	1.587089000
H	4.655122000	-0.260581000	-2.512446000
H	8.019314000	-0.997864000	0.043308000
Li	-0.893993000	3.032497000	-0.209706000

Li[9']:

E = -2724.17809876

Author Manuscript

P	0.655727000	-0.427202000	0.460495000
P	0.222350000	-1.770173000	-1.212158000
P	-0.984714000	0.059978000	-0.952011000
P	1.892713000	-0.302790000	-1.390090000
C	-2.846861000	1.459736000	0.431773000
C	-3.611763000	2.308289000	-0.394244000
C	-2.011519000	2.104631000	1.370946000
C	-3.525975000	3.703084000	-0.316631000
C	-1.925080000	3.494590000	1.466580000
C	-2.673875000	4.305703000	0.610791000
C	-3.920627000	-0.654359000	-0.863079000
C	-5.198905000	-0.841720000	-0.309843000
C	-3.796348000	-0.887281000	-2.238180000
C	-6.288915000	-1.228901000	-1.081198000
C	-4.880074000	-1.279804000	-3.024403000
C	-6.133446000	-1.450122000	-2.448494000
C	-2.594240000	-1.112860000	1.416675000
C	-2.265017000	-2.467772000	1.240290000
C	-2.868623000	-0.707627000	2.730443000
C	-2.175107000	-3.354964000	2.306204000
C	-2.788988000	-1.587908000	3.809362000
C	-2.431773000	-2.915200000	3.603258000
B	-2.736239000	-0.150992000	0.125537000
C	3.371656000	-1.340293000	-0.991500000
C	3.562557000	-2.072173000	0.185003000
C	4.390463000	-1.340521000	-1.951572000
C	4.742265000	-2.779385000	0.395327000
C	5.568251000	-2.051596000	-1.745182000
C	5.748089000	-2.770519000	-0.566978000
H	4.874599000	-3.339227000	1.316694000
H	6.344521000	-2.044389000	-2.504854000
H	-1.389450000	1.495701000	2.021830000
H	-2.827350000	-0.768745000	-2.721380000
H	-4.739509000	-1.456292000	-4.087807000
H	-1.258351000	3.945906000	2.196150000
H	-6.980474000	-1.758111000	-3.055586000
H	-2.596132000	5.386850000	0.669064000

H	-4.125596000	4.318378000	-0.981856000
H	-7.261342000	-1.365948000	-0.614962000
H	-5.336863000	-0.687325000	0.758620000
H	-4.271660000	1.859752000	-1.131750000
H	-2.097254000	-2.843622000	0.232409000
H	-3.174046000	0.318033000	2.924308000
H	-3.013286000	-1.233679000	4.812587000
H	-2.366952000	-3.605107000	4.440290000
H	-1.914911000	-4.394436000	2.124461000
H	2.789708000	-2.093661000	0.948534000
H	4.261622000	-0.774176000	-2.871393000
H	6.667619000	-3.324246000	-0.400666000
Li	-1.211612000	2.673674000	-0.923933000
O	0.529373000	3.593728000	-0.958850000
C	1.518077000	3.195928000	-0.421261000
N	2.486456000	2.902076000	0.184783000
C	3.617762000	2.135500000	0.473153000
C	3.696496000	1.485676000	1.702988000
C	4.637701000	2.025129000	-0.469808000
C	4.807558000	0.698184000	1.978692000
H	2.886798000	1.585499000	2.417493000
C	5.743229000	1.235448000	-0.176542000
H	4.547446000	2.534936000	-1.422919000
C	5.829993000	0.570674000	1.042540000
H	4.867600000	0.174385000	2.927028000
H	6.530438000	1.125224000	-0.914764000
H	6.685778000	-0.060742000	1.255702000

Li[TS₉₋₁₀]:

E = -2724.15276292

P	-1.694964000	-1.634815000	-0.979287000
P	-1.688701000	-0.401641000	0.853795000
P	-0.013493000	-0.279112000	-0.554914000
P	-2.852491000	0.269409000	-0.927895000
B	1.595688000	-1.315947000	0.186352000
C	0.756023000	2.019633000	-1.238860000
O	1.731590000	1.730485000	-1.899663000

Author Manuscript

N	-0.041551000	2.747327000	-0.675123000
C	-4.553655000	-0.330422000	-0.513201000
C	-5.600203000	0.469514000	-0.985851000
C	-4.868252000	-1.484553000	0.214762000
C	-6.927217000	0.130185000	-0.737764000
H	-5.374446000	1.369288000	-1.553805000
C	-6.194100000	-1.824561000	0.461148000
H	-4.079634000	-2.128592000	0.596203000
C	-7.226608000	-1.018855000	-0.013104000
H	-7.725740000	0.764494000	-1.111377000
H	-6.421054000	-2.723996000	1.026047000
H	-8.260927000	-1.286385000	0.181878000
C	0.114929000	4.082009000	-0.254641000
C	1.372632000	4.678949000	-0.130052000
C	-1.035637000	4.793681000	0.083766000
C	1.468731000	5.988646000	0.326915000
H	2.267045000	4.116069000	-0.380712000
C	-0.928189000	6.105330000	0.530849000
H	-1.999262000	4.304489000	-0.011092000
C	0.321827000	6.706792000	0.656142000
H	2.446967000	6.449903000	0.425242000
H	-1.826872000	6.657559000	0.788721000
H	0.402875000	7.729171000	1.012056000
C	2.553697000	-0.115699000	0.802854000
C	3.949919000	-0.092663000	0.610428000
C	2.019624000	0.984767000	1.501621000
C	4.751525000	0.969362000	1.041729000
H	4.432393000	-0.934565000	0.114397000
C	2.806166000	2.043568000	1.943783000
H	0.951383000	1.022430000	1.698616000
C	4.178902000	2.049415000	1.702623000
H	5.823973000	0.939060000	0.868024000
H	2.340811000	2.876870000	2.462500000
H	4.793089000	2.880840000	2.035331000
C	1.101112000	-2.386075000	1.290909000
C	0.540008000	-3.610672000	0.891135000
C	1.163536000	-2.142956000	2.669896000

C	0.058363000	-4.536088000	1.811171000
H	0.482809000	-3.847129000	-0.169772000
C	0.687322000	-3.063684000	3.600934000
H	1.598544000	-1.214303000	3.031450000
C	0.130389000	-4.265148000	3.175095000
H	-0.373041000	-5.470578000	1.462157000
H	0.756544000	-2.842362000	4.662841000
H	-0.241337000	-4.985338000	3.898723000
C	2.341473000	-2.021640000	-1.093063000
C	3.320250000	-3.005367000	-0.851348000
C	2.165331000	-1.649854000	-2.439217000
C	4.087090000	-3.555028000	-1.871364000
H	3.471072000	-3.348149000	0.169519000
C	2.939092000	-2.187336000	-3.474582000
H	1.380546000	-0.939696000	-2.707715000
C	3.909100000	-3.139381000	-3.191796000
H	4.829765000	-4.313231000	-1.638424000
H	2.760095000	-1.874019000	-4.499566000
H	4.509162000	-3.567540000	-3.989133000
Li	2.946874000	0.337158000	-1.460558000

Li[10⁺]:

E = -2724.17806291

P	2.357382000	0.418495000	-1.026760000
P	2.158125000	0.048504000	1.176020000
P	0.404141000	0.110313000	-0.108034000
P	2.797043000	-1.602758000	-0.186586000
C	-2.233049000	0.920017000	-0.938034000
C	-3.376373000	0.326955000	-0.377055000
C	-2.129953000	0.867535000	-2.341848000
C	-4.371224000	-0.266623000	-1.161054000
C	-3.120401000	0.297099000	-3.142512000
C	-4.254553000	-0.274491000	-2.553740000
C	-1.486038000	1.741027000	1.556953000
C	-1.927414000	2.988440000	2.023776000
C	-1.511806000	0.678373000	2.475246000
C	-2.376878000	3.169091000	3.329367000

Author Manuscript

C	-1.951680000	0.851722000	3.785535000
C	-2.388715000	2.099716000	4.219484000
C	-0.413508000	2.955905000	-0.599058000
C	0.777182000	3.469171000	-0.056861000
C	-1.034624000	3.734824000	-1.584564000
C	1.342309000	4.658891000	-0.502337000
C	-0.485887000	4.935544000	-2.032267000
C	0.713024000	5.397240000	-1.501792000
B	-1.073352000	1.602974000	-0.004815000
C	4.629077000	-1.443261000	0.004541000
C	5.444434000	-1.182614000	-1.102940000
C	5.229500000	-1.687413000	1.245213000
C	6.828552000	-1.145576000	-0.966484000
C	6.613709000	-1.648580000	1.379296000
C	7.415388000	-1.374980000	0.274579000
H	7.448557000	-0.933942000	-1.832475000
H	7.066065000	-1.830344000	2.349475000
H	-1.244062000	1.274048000	-2.821485000
H	-1.193500000	-0.314309000	2.160997000
H	-1.948160000	0.007303000	4.470447000
H	-3.003833000	0.287502000	-4.222393000
H	-2.731263000	2.238492000	5.241296000
H	-5.032507000	-0.715855000	-3.170022000
H	-5.233330000	-0.722950000	-0.683960000
H	-2.712366000	4.150929000	3.653310000
H	-1.916822000	3.841431000	1.350051000
H	-3.487615000	0.320153000	0.702831000
H	1.264866000	2.938722000	0.759518000
H	-1.981016000	3.410505000	-2.008905000
H	-1.000980000	5.511455000	-2.796686000
H	1.148251000	6.328407000	-1.853351000
H	2.268832000	5.015812000	-0.061118000
H	4.998461000	-1.003656000	-2.077888000
H	4.614513000	-1.905280000	2.114847000
H	8.495437000	-1.342054000	0.381055000
C	-0.396620000	-1.532123000	-0.505993000
O	-0.549588000	-1.768792000	-1.741432000

N	-0.962906000	-2.035024000	0.551773000
C	-2.006885000	-2.959777000	0.386397000
C	-3.093458000	-2.837040000	1.269773000
C	-2.071791000	-3.949025000	-0.614604000
C	-4.216230000	-3.641379000	1.138374000
H	-3.035182000	-2.080791000	2.046794000
C	-3.207260000	-4.753744000	-0.737729000
H	-1.225724000	-4.093110000	-1.277066000
C	-4.286074000	-4.599702000	0.126235000
H	-5.044318000	-3.521226000	1.831214000
H	-3.234173000	-5.516171000	-1.511460000
H	-5.165498000	-5.227890000	0.024049000
Li	-2.425908000	-1.708730000	-1.823647000

Li[11*]:

E = -3123.89878575

P	2.266460000	-0.949133000	1.139080000
P	1.866720000	-0.403833000	-0.997926000
P	0.284434000	-0.273690000	0.502351000
P	3.065059000	0.955217000	0.304028000
C	4.771652000	0.388400000	-0.136800000
C	5.142747000	-0.894203000	-0.559973000
C	5.762484000	1.371214000	-0.024671000
C	6.470481000	-1.181532000	-0.858542000
C	7.090747000	1.082571000	-0.322332000
C	7.446931000	-0.196128000	-0.739442000
H	6.741889000	-2.181343000	-1.184200000
H	7.846433000	1.856664000	-0.228204000
H	4.400892000	-1.682460000	-0.661716000
H	5.491876000	2.373482000	0.299689000
H	8.483002000	-0.424770000	-0.970759000
C	-0.072414000	1.491361000	1.027513000
O	-0.645051000	1.595092000	2.159892000
N	0.224378000	2.401646000	0.144916000
C	0.027063000	3.749324000	0.473504000
C	0.387316000	4.306147000	1.718423000
C	-0.535766000	4.601094000	-0.489894000

C	0.138091000	5.650832000	1.994387000
H	0.884600000	3.679834000	2.453067000
C	-0.781563000	5.938621000	-0.205806000
H	-0.783391000	4.189549000	-1.463644000
C	-0.459947000	6.471627000	1.041454000
H	0.434100000	6.060137000	2.956603000
H	-1.227593000	6.572181000	-0.966899000
H	-0.652822000	7.517127000	1.259048000
C	-3.008504000	2.537077000	-0.144851000
O	-3.177937000	3.072549000	0.914344000
N	-2.879811000	2.075084000	-1.214883000
C	-2.487904000	1.276038000	-2.285385000
C	-3.448916000	0.517648000	-2.948867000
C	-1.150175000	1.267699000	-2.681927000
C	-3.061909000	-0.251286000	-4.039979000
H	-4.471517000	0.516831000	-2.589401000
C	-0.782909000	0.496111000	-3.778815000
H	-0.419360000	1.830955000	-2.108392000
C	-1.735230000	-0.253880000	-4.464641000
H	-3.801839000	-0.853725000	-4.557007000
H	0.257602000	0.471704000	-4.086919000
H	-1.440279000	-0.854437000	-5.319604000
B	-1.068386000	-1.932195000	0.583949000
C	-0.364268000	-2.818991000	-0.574381000
C	-0.970495000	-2.509394000	2.092494000
C	-2.579381000	-1.425566000	0.298659000
C	0.585942000	-3.811156000	-0.289667000
C	-0.605684000	-2.549911000	-1.932542000
C	-1.332186000	-3.850180000	2.300213000
C	-0.672276000	-1.754433000	3.234602000
C	-3.160066000	-0.379098000	1.032334000
C	-3.434139000	-2.147227000	-0.546508000
C	1.251831000	-4.502295000	-1.299734000
H	0.814475000	-4.043802000	0.747151000
C	0.050737000	-3.234436000	-2.949370000
H	-1.317542000	-1.773530000	-2.198986000
C	-1.369742000	-4.415026000	3.570806000

H	-1.594697000	-4.467279000	1.443482000
C	-0.704467000	-2.310405000	4.511980000
H	-0.427479000	-0.697885000	3.137232000
C	-4.506831000	-0.049243000	0.907922000
H	-2.543793000	0.175860000	1.737020000
C	-4.785570000	-1.832322000	-0.673435000
H	-3.040653000	-2.987941000	-1.110717000
C	0.985713000	-4.217883000	-2.635427000
H	1.983018000	-5.263380000	-1.040496000
H	-0.163381000	-2.994461000	-3.987874000
C	-1.047810000	-3.646509000	4.686480000
H	-1.649650000	-5.458456000	3.690821000
H	-0.459869000	-1.693748000	5.373256000
C	-5.328553000	-0.773302000	0.046510000
H	-4.920467000	0.767185000	1.495393000
H	-5.416434000	-2.422959000	-1.333058000
H	1.504233000	-4.754627000	-3.425303000
H	-1.070503000	-4.084689000	5.680447000
H	-6.383168000	-0.527540000	-0.045450000
Li	-1.711365000	3.120568000	2.214280000

Li[TS_{11'-12'}]:

E = -3123.88159176

P	-0.888746000	-1.998396000	-1.476012000
P	-1.510338000	-1.021175000	0.430010000
P	0.467824000	-0.652556000	-0.428471000
P	-2.258494000	-0.230201000	-1.513835000
B	2.127249000	-1.543165000	0.475328000
C	0.757892000	0.998943000	-1.338145000
O	1.000012000	0.896667000	-2.531299000
N	0.852451000	2.044279000	-0.498512000
C	-0.501168000	2.140360000	1.058973000
O	0.213159000	1.923480000	2.015580000
N	-1.546943000	2.417687000	0.485177000
C	1.415653000	3.278049000	-0.904566000
C	1.471555000	4.296418000	0.064613000
C	2.014473000	3.521616000	-2.152264000

C	2.113043000	5.502983000	-0.191629000
H	0.987963000	4.157656000	1.028861000
C	2.653080000	4.732956000	-2.394903000
H	1.969615000	2.762510000	-2.919442000
C	2.715045000	5.728891000	-1.424452000
H	2.130495000	6.269655000	0.577355000
H	3.108885000	4.896831000	-3.367359000
H	3.214924000	6.670250000	-1.629621000
C	-2.855965000	2.340445000	0.990287000
C	-3.161612000	1.746481000	2.219791000
C	-3.882715000	2.830564000	0.180379000
C	-4.488420000	1.651058000	2.627843000
H	-2.365225000	1.357746000	2.847697000
C	-5.204223000	2.738725000	0.601711000
H	-3.624445000	3.271480000	-0.776430000
C	-5.512954000	2.147222000	1.824818000
H	-4.719440000	1.183874000	3.580408000
H	-5.996301000	3.119953000	-0.035372000
H	-6.546082000	2.069248000	2.149108000
C	-3.890134000	-1.094744000	-1.499359000
C	-4.252098000	-1.992030000	-2.509930000
C	-4.830007000	-0.757651000	-0.517512000
C	-5.523593000	-2.557169000	-2.525865000
H	-3.539200000	-2.256221000	-3.286836000
C	-6.101002000	-1.321839000	-0.539396000
H	-4.570378000	-0.054113000	0.268944000
C	-6.449539000	-2.223365000	-1.541292000
H	-5.790849000	-3.259961000	-3.309249000
H	-6.818486000	-1.053507000	0.230276000
H	-7.441016000	-2.665932000	-1.555981000
C	1.399193000	-2.438889000	1.613972000
C	0.723743000	-1.855876000	2.703036000
C	1.331170000	-3.836647000	1.517001000
C	0.058169000	-2.618403000	3.657880000
H	0.688677000	-0.771398000	2.797217000
C	0.662606000	-4.610185000	2.463153000
H	1.808070000	-4.333969000	0.677692000

C	0.029935000	-4.005342000	3.543813000
H	-0.448368000	-2.127514000	4.484570000
H	0.631700000	-5.690424000	2.349449000
H	-0.492252000	-4.606570000	4.282711000
C	3.040202000	-0.281120000	0.975381000
C	3.638794000	0.565473000	0.017611000
C	3.285600000	0.035381000	2.322279000
C	4.367763000	1.698622000	0.374209000
H	3.498946000	0.350890000	-1.038861000
C	4.027494000	1.161835000	2.696346000
H	2.881734000	-0.602847000	3.100832000
C	4.554408000	2.011861000	1.724201000
H	4.764771000	2.350322000	-0.397831000
H	4.183227000	1.377163000	3.749377000
H	5.108377000	2.900610000	2.009823000
C	2.946233000	-2.347166000	-0.667283000
C	3.965437000	-3.210726000	-0.229607000
C	2.813562000	-2.183771000	-2.052139000
C	4.785098000	-3.894723000	-1.119980000
H	4.118112000	-3.351984000	0.838530000
C	3.633333000	-2.861348000	-2.954314000
H	2.073735000	-1.495898000	-2.457364000
C	4.618039000	-3.726108000	-2.492817000
H	5.557107000	-4.560170000	-0.742678000
H	3.496784000	-2.707895000	-4.021253000
H	5.254226000	-4.260237000	-3.192887000
Li	2.010771000	1.883860000	1.231440000

Li[12*]:

E = -3123.90608572

P	2.002123000	0.593095000	-1.628913000
P	2.383356000	0.059134000	0.532565000
P	0.328542000	0.064207000	-0.193975000
P	2.740565000	-1.428448000	-1.089132000
C	4.572698000	-1.246016000	-1.257752000
C	5.282890000	-0.041770000	-1.190548000
C	5.280290000	-2.434254000	-1.468264000

Author Manuscript

C	6.666461000	-0.031080000	-1.327644000
C	6.665533000	-2.422841000	-1.608013000
C	7.360929000	-1.220415000	-1.536962000
H	7.203264000	0.911407000	-1.273568000
H	7.198540000	-3.354550000	-1.772994000
H	4.759269000	0.899252000	-1.037878000
H	4.743133000	-3.377999000	-1.526495000
H	8.441313000	-1.207525000	-1.647279000
C	-0.530115000	-1.336655000	-1.153160000
O	-0.363487000	-1.547467000	-2.325739000
N	-1.538661000	-1.949666000	-0.403599000
C	-2.627841000	-2.609978000	-1.059797000
C	-3.329223000	-1.925210000	-2.050782000
C	-2.976557000	-3.909749000	-0.709344000
C	-4.392458000	-2.551679000	-2.689961000
H	-3.032656000	-0.919282000	-2.335033000
C	-4.049543000	-4.523508000	-1.347260000
H	-2.419767000	-4.428022000	0.062482000
C	-4.757225000	-3.848494000	-2.337641000
H	-4.935225000	-2.021432000	-3.466173000
H	-4.326267000	-5.536658000	-1.072575000
H	-5.590747000	-4.333381000	-2.836645000
C	-1.473181000	-1.827708000	0.986121000
O	-2.329560000	-2.335717000	1.736501000
N	-0.480840000	-1.024786000	1.386336000
C	0.114455000	-1.232306000	2.649536000
C	0.160115000	-0.208591000	3.600676000
C	0.710552000	-2.465252000	2.951308000
C	0.779948000	-0.414025000	4.833340000
H	-0.278831000	0.755155000	3.366151000
C	1.318445000	-2.666212000	4.181258000
H	0.694432000	-3.253874000	2.205465000
C	1.356910000	-1.642073000	5.128763000
H	0.813017000	0.395028000	5.556678000
H	1.776908000	-3.625791000	4.399835000
H	1.841671000	-1.802598000	6.086380000
B	-0.876366000	1.798427000	-0.082566000

C	0.212604000	2.941456000	0.301304000
C	-1.610123000	2.070833000	-1.513462000
C	-2.060017000	1.527352000	1.024660000
C	0.473459000	4.005617000	-0.575247000
C	0.962628000	2.923012000	1.490514000
C	-2.626917000	3.045594000	-1.497690000
C	-1.336703000	1.487262000	-2.756144000
C	-3.181854000	0.747160000	0.673620000
C	-2.096585000	2.097979000	2.306944000
C	1.407306000	4.995636000	-0.279563000
H	-0.063130000	4.060890000	-1.517334000
C	1.896913000	3.906678000	1.800576000
H	0.837774000	2.103107000	2.194107000
C	-3.328861000	3.410024000	-2.639866000
H	-2.870638000	3.539634000	-0.559223000
C	-2.046043000	1.832727000	-3.908414000
H	-0.558236000	0.740073000	-2.854082000
C	-4.241659000	0.508862000	1.547944000
H	-3.232376000	0.314678000	-0.320580000
C	-3.145234000	1.865213000	3.204150000
H	-1.290699000	2.757841000	2.614413000
C	2.121732000	4.954283000	0.912935000
H	1.579850000	5.799707000	-0.989915000
H	2.455946000	3.846202000	2.730521000
C	-3.045903000	2.794988000	-3.857697000
H	-4.100549000	4.172975000	-2.579634000
H	-1.804099000	1.344318000	-4.848481000
C	-4.224413000	1.059722000	2.834602000
H	-5.071167000	-0.115314000	1.229919000
H	-3.125636000	2.328230000	4.186751000
H	2.852571000	5.723727000	1.145279000
H	-3.594972000	3.068228000	-4.754515000
H	-5.045419000	0.883872000	3.523233000
Li	-2.397940000	-0.597575000	2.684111000

Li[TS_{12'-13'}]:

E = -3123.88698772

Author Manuscript

P	2.419396000	0.416492000	-2.289133000
P	2.471323000	0.563149000	-0.100867000
P	0.323640000	0.135625000	-0.114701000
P	3.029422000	-1.333052000	-1.126555000
B	-1.253442000	1.522388000	-0.549088000
C	-0.226395000	-1.513581000	-0.827944000
O	-0.136883000	-1.949780000	-1.940742000
N	-1.000679000	-2.134052000	0.169954000
C	-0.957790000	-1.574344000	1.450000000
O	-1.709898000	-2.003201000	2.342627000
N	-0.122627000	-0.526540000	1.517102000
C	-1.901405000	-3.204130000	-0.128513000
C	-2.835992000	-3.042301000	-1.153125000
C	-1.872898000	-4.375508000	0.628169000
C	-3.754541000	-4.057450000	-1.407460000
H	-2.820542000	-2.144517000	-1.760751000
C	-2.802175000	-5.377529000	0.372474000
H	-1.133862000	-4.489732000	1.412560000
C	-3.745018000	-5.219828000	-0.641555000
H	-4.473167000	-3.937721000	-2.211825000
H	-2.781977000	-6.288559000	0.961847000
H	-4.464319000	-6.007563000	-0.841726000
C	0.290015000	0.051116000	2.754010000
C	0.551184000	1.418501000	2.825392000
C	0.491322000	-0.755767000	3.876178000
C	0.991266000	1.978426000	4.020215000
H	0.412061000	2.056868000	1.960547000
C	0.920578000	-0.183103000	5.066547000
H	0.311921000	-1.822529000	3.820023000
C	1.171464000	1.184596000	5.146744000
H	1.188580000	3.044924000	4.056346000
H	1.070806000	-0.817075000	5.935031000
H	1.513804000	1.624109000	6.078231000
C	4.864799000	-1.224076000	-0.858804000
C	5.688917000	-0.224398000	-1.382728000
C	5.444260000	-2.247921000	-0.100446000
C	7.059581000	-0.242583000	-1.141351000

H	5.246008000	0.566758000	-1.983727000
C	6.814464000	-2.267316000	0.139953000
H	4.814680000	-3.037273000	0.304700000
C	7.625499000	-1.261788000	-0.379753000
H	7.689249000	0.541284000	-1.553069000
H	7.249534000	-3.067888000	0.731755000
H	8.696096000	-1.275253000	-0.195649000
C	-1.564046000	1.659935000	-2.134925000
C	-2.448492000	2.701962000	-2.471244000
C	-1.142481000	0.832787000	-3.181733000
C	-2.899724000	2.899574000	-3.770494000
H	-2.789015000	3.381911000	-1.692791000
C	-1.585885000	1.027268000	-4.490886000
H	-0.427353000	0.039702000	-2.999377000
C	-2.469784000	2.055504000	-4.792328000
H	-3.580946000	3.718178000	-3.988191000
H	-1.224251000	0.368809000	-5.276118000
H	-2.812621000	2.207495000	-5.812211000
C	-2.565248000	0.882270000	0.228396000
C	-2.793452000	0.993776000	1.615238000
C	-3.599691000	0.271683000	-0.507191000
C	-3.990095000	0.596368000	2.217230000
H	-2.023098000	1.416006000	2.251930000
C	-4.798411000	-0.150972000	0.076949000
H	-3.476905000	0.162029000	-1.580775000
C	-5.013238000	0.031354000	1.447565000
H	-4.123289000	0.730394000	3.286554000
H	-5.573343000	-0.593966000	-0.542290000
H	-5.957599000	-0.252064000	1.903854000
C	-0.729856000	2.940391000	0.040799000
C	-1.457488000	3.744734000	0.929027000
C	0.489503000	3.465374000	-0.421958000
C	-0.972429000	4.970987000	1.382260000
H	-2.434923000	3.422748000	1.277099000
C	0.991101000	4.679043000	0.033702000
H	1.058474000	2.915404000	-1.167632000
C	0.264830000	5.435160000	0.950930000

H	-1.567912000	5.564256000	2.071279000
H	1.946216000	5.039289000	-0.337733000
H	0.652938000	6.383880000	1.310841000
Li	-3.376947000	-1.645446000	1.438353000

Li[13*]:

E = -3123.90126941

P	1.200850000	-1.369321000	-0.896280000
P	2.499309000	-1.636396000	0.852258000
P	1.244284000	-3.318974000	0.093146000
C	-1.858662000	-0.809737000	-1.071053000
C	-2.360607000	-1.174294000	1.228515000
P	-0.427575000	-0.038275000	-0.154996000
O	-1.970078000	-0.888160000	-2.267751000
O	-3.021886000	-1.559069000	2.158109000
N	-2.739100000	-1.308831000	-0.126982000
N	-1.131026000	-0.531642000	1.331873000
C	-3.928868000	-2.011793000	-0.496717000
C	-4.825806000	-1.421456000	-1.381542000
C	-4.164537000	-3.282690000	0.019546000
C	-5.971956000	-2.116359000	-1.752558000
H	-4.621177000	-0.435519000	-1.784076000
C	-5.320894000	-3.961453000	-0.345537000
H	-3.455505000	-3.725084000	0.709535000
C	-6.224178000	-3.382753000	-1.232952000
H	-6.671030000	-1.661994000	-2.447663000
H	-5.511953000	-4.948485000	0.063755000
H	-7.124211000	-3.918176000	-1.519549000
C	-0.594277000	-0.290196000	2.644446000
C	-0.815670000	0.930003000	3.275146000
C	0.126598000	-1.299001000	3.275895000
C	-0.261657000	1.156845000	4.531028000
H	-1.414628000	1.689020000	2.788730000
C	0.669277000	-1.067817000	4.534716000
H	0.251390000	-2.254983000	2.776671000
C	0.485406000	0.163726000	5.158096000
H	-0.422257000	2.114135000	5.016814000

H	1.237050000	-1.851559000	5.026356000
H	0.917561000	0.345304000	6.137693000
B	-0.054188000	2.015595000	-0.594317000
C	1.524505000	2.197574000	-0.273382000
C	-0.458914000	2.076898000	-2.162246000
C	-1.054838000	2.786074000	0.412275000
C	2.406054000	2.760855000	-1.207127000
C	2.069327000	1.862842000	0.978068000
C	-1.517765000	2.876814000	-2.615392000
C	0.253768000	1.368863000	-3.144826000
C	-2.427053000	2.486577000	0.470317000
C	-0.595688000	3.790743000	1.274105000
C	3.754254000	2.971626000	-0.916162000
H	2.027962000	3.050486000	-2.183422000
C	3.413878000	2.057435000	1.278351000
H	1.424645000	1.442743000	1.748445000
C	-1.852008000	2.961474000	-3.964898000
H	-2.088716000	3.462189000	-1.900962000
C	-0.075656000	1.437514000	-4.493493000
H	1.098514000	0.749652000	-2.850287000
C	-3.289009000	3.124730000	1.355637000
H	-2.839820000	1.730718000	-0.197187000
C	-1.449582000	4.446411000	2.159372000
H	0.457039000	4.057994000	1.262616000
C	4.266456000	2.614559000	0.327504000
H	4.403508000	3.419422000	-1.664415000
H	3.793729000	1.773631000	2.255961000
C	-1.135979000	2.236339000	-4.910863000
H	-2.674548000	3.599887000	-4.276635000
H	0.496099000	0.865405000	-5.219321000
C	-2.798523000	4.108459000	2.212212000
H	-4.340420000	2.852506000	1.381658000
H	-1.057022000	5.218136000	2.816250000
H	5.317086000	2.771636000	0.555747000
H	-1.397108000	2.296804000	-5.963802000
H	-3.464130000	4.608651000	2.909868000
C	4.104993000	-1.770756000	-0.096354000

C	4.918249000	-2.910786000	0.028136000
C	4.528803000	-0.734949000	-0.943248000
C	6.107245000	-3.024164000	-0.694994000
H	4.610406000	-3.717835000	0.691230000
C	5.721600000	-0.846704000	-1.654384000
H	3.920130000	0.159587000	-1.047851000
C	6.508488000	-1.991610000	-1.540640000
H	6.720509000	-3.914218000	-0.588405000
H	6.031742000	-0.034604000	-2.305037000
H	7.433717000	-2.076905000	-2.101996000
Li	3.075098000	-3.253316000	-1.559375000

Li[14*]:

E = -1868.17947674

C	1.393442000	0.888566000	-1.234428000
C	1.665296000	-1.376450000	-0.610084000
P	-0.298399000	0.229423000	-1.508052000
O	1.789054000	2.015566000	-1.402496000
O	2.265562000	-2.406742000	-0.213163000
N	2.262824000	-0.160575000	-0.786072000
N	0.358610000	-1.355058000	-0.950788000
C	3.622386000	0.088881000	-0.430044000
C	4.472831000	0.679140000	-1.359845000
C	4.075454000	-0.231531000	0.846917000
C	5.791196000	0.944602000	-1.006308000
H	4.097068000	0.940260000	-2.342287000
C	5.398944000	0.025085000	1.186443000
H	3.390559000	-0.673416000	1.561677000
C	6.258312000	0.613854000	0.262683000
H	6.454875000	1.411152000	-1.727544000
H	5.756084000	-0.226741000	2.180474000
H	7.289701000	0.819493000	0.532452000
C	-0.330143000	-2.589232000	-0.855891000
C	-0.265881000	-3.500382000	-1.915111000
C	-0.918950000	-2.963759000	0.356787000
C	-0.744666000	-4.799993000	-1.744761000
H	0.192457000	-3.188162000	-2.848118000

C	-1.397191000	-4.264439000	0.520469000
H	-0.966318000	-2.235576000	1.161405000
C	-1.296329000	-5.188737000	-0.522100000
H	-0.682422000	-5.509716000	-2.563626000
H	-1.849072000	-4.552032000	1.464503000
H	-1.663736000	-6.201367000	-0.389030000
B	-1.372727000	1.004080000	0.104025000
C	-0.720816000	0.471712000	1.500614000
C	-1.248846000	2.597513000	-0.181583000
C	-2.907769000	0.492145000	-0.085717000
C	0.609686000	0.736045000	1.875577000
C	-1.467536000	-0.297300000	2.409880000
C	-0.672021000	3.506147000	0.714906000
C	-1.771768000	3.134953000	-1.371013000
C	-3.922034000	1.199822000	0.582846000
C	-3.317009000	-0.639207000	-0.801406000
C	1.165226000	0.245772000	3.055057000
H	1.228612000	1.366570000	1.242345000
C	-0.923301000	-0.800176000	3.592277000
H	-2.510342000	-0.508657000	2.186522000
C	-0.606743000	4.870487000	0.440435000
H	-0.274918000	3.146146000	1.659918000
C	-1.702822000	4.492883000	-1.661378000
H	-2.264176000	2.471193000	-2.080193000
C	-5.252102000	0.795057000	0.554430000
H	-3.653314000	2.095981000	1.138055000
C	-4.647341000	-1.056187000	-0.846336000
H	-2.587478000	-1.218318000	-1.365902000
C	0.404086000	-0.539842000	3.917848000
H	2.193993000	0.492625000	3.306810000
H	-1.544709000	-1.387131000	4.264925000
C	-1.115154000	5.370099000	-0.753478000
H	-0.156695000	5.545486000	1.164256000
H	-2.115203000	4.869669000	-2.594014000
C	-5.623240000	-0.341577000	-0.162091000
H	-6.004412000	1.371593000	1.086908000
H	-4.919348000	-1.937654000	-1.422463000

H	0.833255000	-0.921093000	4.840661000
H	-1.059765000	6.433167000	-0.972260000
H	-6.662363000	-0.658184000	-0.193480000
Li	1.333054000	-3.950637000	0.079457000

Li[7']:

E = -1947.87146257

C	0.549833000	-1.583212000	-0.058907000
C	2.363265000	-0.060242000	-0.527482000
O	0.060355000	-2.571253000	0.435788000
O	3.298433000	0.582785000	0.004713000
N	1.867321000	-1.212150000	0.135193000
N	1.650999000	0.245281000	-1.602875000
C	2.707482000	-1.934071000	1.041939000
C	2.312415000	-2.130728000	2.361519000
C	3.922678000	-2.434428000	0.585142000
C	3.140362000	-2.839174000	3.225178000
H	1.358281000	-1.744356000	2.703311000
C	4.752247000	-3.129363000	1.457419000
H	4.213082000	-2.275325000	-0.448429000
C	4.361351000	-3.336450000	2.777303000
H	2.830048000	-3.000251000	4.252921000
H	5.701400000	-3.517292000	1.100812000
H	5.005550000	-3.888008000	3.455131000
C	1.945421000	1.390758000	-2.360200000
C	0.891756000	2.039614000	-3.029555000
C	3.241710000	1.928248000	-2.499617000
C	1.116706000	3.186041000	-3.777426000
H	-0.107450000	1.624175000	-2.964307000
C	3.453222000	3.084321000	-3.252420000
H	4.081054000	1.429369000	-2.031109000
C	2.397482000	3.726028000	-3.887898000
H	0.280010000	3.662953000	-4.279597000
H	4.463364000	3.472812000	-3.347563000
H	2.568496000	4.626372000	-4.469282000
P	-0.487026000	-0.369772000	-1.113068000
C	-0.422928000	1.022265000	0.185451000

N	-2.067338000	-0.803308000	-0.343276000
O	0.457471000	1.870910000	0.344569000
N	-1.521123000	0.972689000	0.978457000
C	-2.520321000	-0.015693000	0.666671000
C	-2.967533000	-1.680709000	-1.022918000
C	-1.726364000	1.903673000	2.047361000
O	-3.584116000	-0.038067000	1.240041000
C	-2.593483000	-3.001132000	-1.259602000
C	-4.186961000	-1.201867000	-1.505806000
C	-0.832676000	1.924291000	3.113249000
C	-2.808781000	2.775126000	2.004862000
C	-3.435939000	-3.836581000	-1.988800000
H	-1.657444000	-3.364821000	-0.850575000
C	-5.028273000	-2.046733000	-2.217716000
H	-4.474750000	-0.174022000	-1.313265000
C	-1.017458000	2.841782000	4.141598000
H	-0.002710000	1.225164000	3.132594000
C	-2.992459000	3.682737000	3.042165000
H	-3.505038000	2.729699000	1.175359000
C	-4.653343000	-3.365299000	-2.467763000
H	-3.139110000	-4.864911000	-2.172044000
H	-5.977105000	-1.669601000	-2.587676000
C	-2.096524000	3.721263000	4.107045000
H	-0.320435000	2.863022000	4.973493000
H	-3.838577000	4.362131000	3.016749000
H	-5.309298000	-4.020605000	-3.032857000
H	-2.241422000	4.434666000	4.912515000
Li	2.257990000	2.226678000	-0.102763000

8':

E = -2511.45902234

P	-0.509851000	1.003685000	-1.125093000
P	0.509851000	-1.003685000	-1.125093000
P	0.509837000	-1.003692000	1.125022000
P	-0.509837000	1.003692000	1.125022000
P	1.104311000	2.025105000	-0.000052000
P	-1.104311000	-2.025105000	-0.000052000

Author Manuscript

C	-0.411425000	-3.737500000	-0.000009000
C	-0.206717000	-4.417199000	1.205968000
C	-0.206531000	-4.417230000	-1.205933000
C	0.206531000	-5.745641000	1.204385000
H	-0.362083000	-3.905608000	2.151961000
C	0.206717000	-5.745675000	-1.204248000
H	-0.361747000	-3.905666000	-2.151965000
C	0.414677000	-6.411875000	0.000093000
H	0.368532000	-6.258783000	2.147543000
H	0.368864000	-6.258841000	-2.147367000
H	0.739704000	-7.448003000	0.000132000
C	0.411425000	3.737500000	-0.000009000
C	0.206717000	4.417199000	1.205968000
C	0.206531000	4.417230000	-1.205933000
C	-0.206531000	5.745641000	1.204385000
H	0.362083000	3.905608000	2.151961000
C	-0.206717000	5.745675000	-1.204248000
H	0.361747000	3.905666000	-2.151965000
C	-0.414677000	6.411875000	0.000093000
H	-0.368532000	6.258783000	2.147543000
H	-0.368864000	6.258841000	-2.147367000
H	-0.739704000	7.448003000	0.000132000

Calculated minimum energy reaction pathway for the Diels-Alder reaction of **6'** with 1,3-CHD

Scheme S4. Relative ω B97X-D/6-311+G(2d,p)//6-31G(d) energies (in kcal mol⁻¹) for the computed Diels-Alder reaction leading from **6'** to *endo*-**15'**.

Scheme S5. Relative ω B97X-D/6-311+G(2d,p)//6-31G(d) energies (in kcal mol⁻¹) for the computed Diels-Alder reaction leading from **6'** to *exo*-**15'**.

Optimized geometries (Cartesian coordinates) and uncorrected energies (in a.u.)

1,3-CHD:

E = -233.404661857

C	-0.303155000	0.704456000	-1.191086000
C	-0.049312000	1.420877000	0.112316000
C	0.049312000	0.732441000	1.255873000
C	-0.049312000	-0.732441000	1.255873000
C	0.049312000	-1.420877000	0.112316000
C	0.303155000	-0.704456000	-1.191086000

H	-1.392287000	0.637250000	-1.343689000
H	-0.008857000	2.507140000	0.112175000
H	0.184641000	1.245432000	2.204256000
H	-0.184641000	-1.245432000	2.204256000
H	0.008857000	-2.507140000	0.112175000
H	-0.090483000	-1.280055000	-2.035362000
H	0.090483000	1.280055000	-2.035362000
H	1.392287000	-0.637250000	-1.343689000

6':

E = -1255.69276001

P	-2.309804000	-0.362757000	1.010464000
P	-2.312926000	-0.389118000	-0.996738000
P	-1.009917000	1.111192000	-0.014624000
C	0.668888000	0.335626000	-0.005571000
C	1.730876000	1.248734000	-0.003188000
C	0.960034000	-1.032058000	-0.002376000
C	3.049904000	0.807405000	0.002751000
C	2.279878000	-1.473721000	0.003028000
C	3.327000000	-0.556660000	0.005922000
H	3.860555000	1.529860000	0.004746000
H	2.489093000	-2.539397000	0.005168000
H	0.161125000	-1.768260000	-0.004140000
H	1.523782000	2.316590000	-0.006099000
H	4.355692000	-0.904514000	0.010398000

16':

E = -1489.10702713

P	0.408644000	-0.854059000	-1.107530000
P	0.339987000	-1.291149000	0.855828000
P	-0.570580000	0.618833000	0.222626000
C	-2.380816000	0.262932000	0.067236000
C	-3.209532000	1.389128000	0.144758000
C	-2.972182000	-0.991805000	-0.108241000
C	-4.591822000	1.266426000	0.045140000
C	-4.354705000	-1.115837000	-0.204256000
C	-5.168064000	0.011726000	-0.129907000

H	-5.218405000	2.151606000	0.103979000
H	-4.798301000	-2.098010000	-0.339396000
C	3.507433000	-0.127688000	1.367997000
H	3.597419000	-0.555856000	2.362901000
C	3.358408000	1.065952000	-1.204714000
H	3.228299000	1.481765000	-2.200353000
C	2.903932000	1.059115000	1.188737000
C	2.725047000	1.608639000	-0.153341000
H	2.052826000	2.451397000	-0.283851000
H	2.498029000	1.606048000	2.034848000
C	4.036053000	-0.920207000	0.199757000
C	4.369317000	-0.036006000	-1.009339000
H	3.275784000	-1.662783000	-0.087363000
H	4.920060000	-1.494052000	0.497533000
H	4.451011000	-0.652300000	-1.910255000
H	5.355137000	0.433676000	-0.866442000
H	-2.767451000	2.373339000	0.284036000
H	-2.357154000	-1.884935000	-0.173396000
H	-6.246436000	-0.088509000	-0.209066000

TS_{16'-15'}:

E = -1489.1014183

P	0.594601000	-0.946636000	-1.017438000
P	0.601869000	-0.900794000	1.021621000
P	-0.453348000	0.719080000	-0.033356000
C	-2.242828000	0.248480000	-0.011253000
C	-3.133952000	1.328366000	-0.012439000
C	-2.764181000	-1.049333000	0.005500000
C	-4.509669000	1.119225000	0.003591000
C	-4.139296000	-1.258812000	0.021410000
C	-5.015946000	-0.176719000	0.020753000
H	-5.186034000	1.969123000	0.002829000
H	-4.528182000	-2.273015000	0.034579000
C	2.975402000	0.444739000	1.406194000
H	2.886606000	0.464860000	2.489099000
C	3.025081000	0.368889000	-1.404749000
H	2.973123000	0.330449000	-2.489569000

C	2.611616000	1.536093000	0.679901000
C	2.643826000	1.498889000	-0.751433000
H	2.217369000	2.328888000	-1.306010000
H	2.154192000	2.389122000	1.171146000
C	3.829184000	-0.654840000	0.819586000
C	3.815482000	-0.728101000	-0.730617000
H	3.546079000	-1.618355000	1.254435000
H	4.854337000	-0.467113000	1.165054000
H	3.454631000	-1.703986000	-1.070949000
H	4.844079000	-0.651170000	-1.105824000
H	-2.746377000	2.344745000	-0.026048000
H	-2.096015000	-1.905606000	0.006370000
H	-6.088962000	-0.343951000	0.033817000

endo-15':

E = -1489.15190831

P	-0.667041000	-1.096898000	-0.634131000
P	-0.668037000	1.102050000	-0.626135000
P	0.335321000	-0.002851000	1.016960000
C	2.061097000	-0.000575000	0.344766000
C	2.750348000	-1.204029000	0.161654000
C	2.748289000	1.203727000	0.159795000
C	4.092647000	-1.202864000	-0.204809000
C	4.090627000	1.204170000	-0.206670000
C	4.766325000	0.001088000	-0.389540000
H	4.610976000	-2.146274000	-0.349133000
H	4.607422000	2.148196000	-0.352459000
C	-2.436190000	1.351039000	0.080905000
H	-2.572786000	2.432590000	0.162571000
C	-2.435117000	-1.352437000	0.070673000
H	-2.570916000	-2.434672000	0.144307000
C	-2.639464000	0.664183000	1.389330000
C	-2.638969000	-0.675571000	1.384200000
H	-2.717609000	-1.260179000	2.295606000
H	-2.718624000	1.241769000	2.305151000
C	-3.411654000	0.777090000	-0.978220000
C	-3.410742000	-0.771376000	-0.984387000

H	-3.157438000	1.172495000	-1.968040000
H	-4.414970000	1.145919000	-0.741797000
H	-3.155415000	-1.158549000	-1.977183000
H	-4.413753000	-1.143304000	-0.751568000
H	2.233031000	-2.150074000	0.297659000
H	2.229435000	2.149126000	0.294299000
H	5.813837000	0.001753000	-0.676012000

16'':

E = -1489.10530744

P	0.253742000	-1.349892000	-1.046590000
P	0.317503000	-1.241150000	0.959498000
P	-0.501155000	0.512267000	-0.113820000
C	-2.337908000	0.298939000	-0.033444000
C	-3.074270000	1.489493000	-0.070448000
C	-3.027965000	-0.913122000	0.061450000
C	-4.464230000	1.469589000	-0.013326000
C	-4.418190000	-0.933724000	0.119787000
C	-5.139590000	0.256202000	0.082798000
H	-5.019134000	2.402699000	-0.043418000
H	-4.938456000	-1.884094000	0.194971000
C	3.374291000	0.507436000	1.461704000
C	3.689021000	0.160004000	-1.343530000
C	3.429218000	1.752524000	0.612445000
C	3.121886000	1.472959000	-0.866571000
C	3.654185000	-0.695211000	0.938614000
C	3.932804000	-0.844725000	-0.490528000
H	-2.554831000	2.442363000	-0.145400000
H	-2.484763000	-1.853512000	0.090329000
H	-6.224421000	0.237597000	0.129399000
H	3.858301000	0.030114000	-2.409369000
H	4.309616000	-1.797521000	-0.851943000
H	3.676840000	-1.580105000	1.569405000
H	3.183356000	0.615857000	2.526225000
H	2.736375000	2.508966000	0.994997000
H	4.438539000	2.182214000	0.710726000
H	3.498636000	2.295461000	-1.484053000

Author Manuscript

H	2.033090000	1.459398000	-1.021905000
---	-------------	-------------	--------------

TS_{16''-15'}:

E = -1489.09521651

P	0.616581000	-0.918428000	-1.027146000
P	0.616563000	-0.918158000	1.027344000
P	-0.450302000	0.727271000	-0.000127000
C	-2.241145000	0.273881000	-0.000064000
C	-3.137593000	1.349968000	-0.000140000
C	-2.754329000	-1.027032000	0.000055000
C	-4.511552000	1.132661000	-0.000095000
C	-4.128543000	-1.245082000	0.000099000
C	-5.010024000	-0.167271000	0.000026000
H	-5.193782000	1.977868000	-0.000151000
H	-4.512624000	-2.261181000	0.000193000
C	3.048218000	0.157340000	1.398775000
H	2.994096000	0.108528000	2.483055000
C	3.048280000	0.157037000	-1.398756000
H	2.994191000	0.107985000	-2.483027000
C	2.819147000	1.514311000	0.775698000
C	2.819183000	1.514142000	-0.775981000
H	3.629502000	2.159389000	-1.139451000
H	1.894654000	1.954673000	1.159685000
C	3.674705000	-0.847187000	0.709770000
C	3.674731000	-0.847343000	-0.709508000
H	-2.754370000	2.368154000	-0.000236000
H	-2.079656000	-1.878888000	0.000114000
H	-6.082279000	-0.340095000	0.000064000
H	4.018530000	-1.731805000	-1.238318000
H	4.018483000	-1.731532000	1.238787000
H	3.629449000	2.159637000	1.139066000
H	1.894710000	1.954425000	-1.160105000

exo-15':

E = -1489.14597723

P	-0.668109000	-1.041373000	-0.788122000
P	-0.680419000	1.149983000	-0.628014000

P	0.316263000	-0.059532000	0.952351000
C	2.062380000	-0.016440000	0.355425000
C	2.771922000	-1.211328000	0.193409000
C	2.732092000	1.197671000	0.173604000
C	4.120579000	-1.191768000	-0.147003000
C	4.081552000	1.215466000	-0.166164000
C	4.778808000	0.021716000	-0.326979000
H	4.655955000	-2.127905000	-0.275337000
H	4.586825000	2.165997000	-0.309719000
C	-2.464882000	1.341236000	0.045118000
H	-2.625823000	2.419511000	0.130797000
C	-2.451654000	-1.345347000	-0.153765000
H	-2.603024000	-2.425753000	-0.229410000
C	-2.735899000	0.663778000	1.408570000
C	-2.727197000	-0.878591000	1.294747000
H	-3.705871000	-1.277369000	1.582300000
H	-2.007997000	1.006898000	2.149635000
C	-3.373901000	0.733618000	-0.989312000
C	-3.366787000	-0.600217000	-1.087997000
H	2.265287000	-2.163866000	0.325094000
H	2.195435000	2.135545000	0.288262000
H	5.831443000	0.036784000	-0.593492000
H	-3.985388000	1.366731000	-1.624967000
H	-3.972358000	-1.139555000	-1.809989000
H	-3.719651000	1.005056000	1.748514000
H	-1.992941000	-1.317003000	1.977172000

3. X-ray Structure Determinations

X-ray crystal structure determination of Li[7]

$C_{36}H_{36}LiN_4O_6P$, Fw = 658.60, colourless block, $0.36 \times 0.33 \times 0.22 \text{ mm}^3$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 18.7146(8)$, $b = 18.2933(10)$, $c = 9.9827(6) \text{ \AA}$, $V = 3319.0(3) \text{ \AA}^3$, $Z = 4$, $D_x = 1.318 \text{ g/cm}^3$, $\mu = 0.14 \text{ mm}^{-1}$. 67455 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073 \text{ \AA}$) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{\max} = 0.65 \text{ \AA}^{-1}$. The Eval15 software^[S13] was used for the integration of the intensities. A model for large mosaicity [1.6°] appeared to be necessary for the prediction of the reflection profiles. Multiscan absorption correction and scaling was performed with SADABS^[S14] (correction range 0.62-0.75). 7612 Reflections were unique ($R_{\text{int}} = 0.046$), of which 6609 were observed [$I > 2\sigma(I)$]. The structure was solved with Patterson superposition methods using SHELXT.^[S15] Least-squares refinement was performed with SHELXL-2014^[S16] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The monophosphorus anion was refined with whole molecule disorder resulting in a ratio of 0.740(4):0.260(4) between the two disorder components. One of the THF molecules showed ring puckering disorder. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 601 Parameters were refined with 489 restraints (displacement parameters, distances, angles, and planarity of the phenyl rings and in the disordered moieties). $R1/wR2$ [$I > 2\sigma(I)$]: 0.0775 / 0.2017. $R1/wR2$ [all refl.]: 0.0877 / 0.2090. $S = 1.070$. Flack parameter^[S17] $x = 0.09(3)$. Residual electron density between -0.39 and $0.58 \text{ e/\AA}^3$. Geometry calculations and checking for higher symmetry were performed with the PLATON program.^[S18]

X-ray crystal structure determination of 15

$C_{24}H_{37}P_3$, Fw = 418.44, colourless plate, $0.27 \times 0.23 \times 0.07 \text{ mm}^3$, monoclinic, $P2/c$ (no. 13), $a = 20.4101(9)$, $b = 6.2198(3)$, $c = 19.0401(10) \text{ \AA}$, $\beta = 97.006(2)^\circ$, $V = 2399.01(19) \text{ \AA}^3$, $Z = 4$, $D_x = 1.159 \text{ g/cm}^3$, $\mu = 0.26 \text{ mm}^{-1}$. The crystal appeared to be cracked into two fragments related by a 3.9° rotation about an arbitrary vector. Consequently two orientation matrices were used for the integration with Eval15.^[S13] 120873 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073 \text{ \AA}$) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{\max} = 0.65 \text{ \AA}^{-1}$. Multiscan absorption correction and scaling was performed with TWINABS^[S14] (correction range 0.68-0.75). 6016 Reflections were unique ($R_{\text{int}} = 0.034$), of which 5363 were observed [$I > 2\sigma(I)$]. The structure was solved with Patterson superposition methods using SHELXT.^[S15] Least-squares refinement was performed with SHELXL-2014^[S16] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The t-butyl group was refined with a disorder model. Slight whole molecule disorder was present but has been ignored in the refinement. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 285 Parameters were refined with 187 restraints (distances, angles and displacement parameters in the disordered t-butyl moiety). $R1/wR2$ [$I > 2\sigma(I)$]: 0.0398 / 0.1043. $R1/wR2$ [all refl.]: 0.0450 / 0.1079. $S = 1.026$. Residual electron density between -0.21 and $1.18 \text{ e/\AA}^3$. Batch scale factor for the second crystal fragment BASF = 0.0537(10). Geometry calculations and checking

for higher symmetry were performed with the PLATON program.^[S18]

X-ray crystal structure determination of 8

$C_{36}H_{58}P_6$, Fw = 676.64, yellow block, $0.57 \times 0.24 \times 0.14 \text{ mm}^3$, triclinic, $P\bar{1}$ (no. 2), $a = 6.1532(3)$, $b = 9.7600(8)$, $c = 16.4721(11) \text{ \AA}$, $\alpha = 93.816(3)$, $\beta = 91.486(4)$, $\gamma = 103.156(3)^\circ$, $V = 960.29(11) \text{ \AA}^3$, $Z = 1$, $D_x = 1.170 \text{ g/cm}^3$, $\mu = 0.30 \text{ mm}^{-1}$. The crystal was twinned with a twofold rotation about $uvw = [1,0,0]$ as twin operation. Additional crystal fragments were present. In total four orientation matrices were therefore used for the integration with Eval15.^[S13] 50104 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073 \text{ \AA}$) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{\max} = 0.65 \text{ \AA}^{-1}$. Multiscan absorption correction and scaling was performed with TWINABS^[S14] (correction range 0.52-0.75). 4510 Reflections were unique ($R_{\text{int}} = 0.052$), of which 3749 were observed [$I > 2\sigma(I)$]. The structure was solved with Patterson superposition methods using SHELXT.^[S15] Least-squares refinement was performed with SHELXL-2014^[S16] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier maps and refined with a riding model. 202 Parameters were refined with no restraints. $R1/wR2 [I > 2\sigma(I)]$: 0.0740 / 0.2146. $R1/wR2 [\text{all refl.}]$: 0.0862 / 0.2226. $S = 1.141$. Residual electron density between -0.67 and $1.06 \text{ e/\AA}^3$. Batch scale factors for the other crystal fragments BASF = 0.326(5), 0.188(6), 0.076(5). Geometry calculations and checking for higher symmetry were performed with the PLATON program.^[S18]

CCDC 1491988-1491990 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Author Manuscript

5. NMR Spectra

[Li(THF)_{1.5}][7]:

Author Manuscript

Spiro-Phosphoramide 13C APT

```

NAME          JBI1367
EXPNO         12
PROCNO        1
Date_         20151212
Time          3.03
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zgpg30
TD            65536
SOLVENT       DMSO
NS            10240
DS            4
SWE           23980.814 Hz
FIDRES        0.365918 Hz
AQ            0.3664756 sec
RG            16384
DM            20.850 usec
DE            6.00 usec
TE            294.1 K
CNST12        145.0000000
CNST11        1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00001120 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            8.60 usec
P2            17.60 usec
PL1           -1.00 dB
SFO1          100.6282298 MHz

===== CHANNEL f2 =====
CPOPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           3.00 dB
PL12          18.00 dB
SFO2          400.1316005 MHz
SI            65536
SF            100.618180 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40

```

JB1367 / 31P{1H} DMSO-d6 / P(PhNCO)4Li

```

NAME          JBI1367
EXPNO         8
PROCNO        1
Date_         20151210
Time          16.35
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zgpg30
TD            65536
SOLVENT       DMSO
NS            65
DS            4
SWE           75387.869 Hz
FIDRES        1.147277 Hz
AQ            0.4358644 sec
RG            7296.2
DM            6.650 usec
DE            6.00 usec
TE            294.1 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0           1

===== CHANNEL f1 =====
NUC1          31P
P1            6.25 usec
P2            -1.00 dB
SFO1          161.9674942 MHz

===== CHANNEL f2 =====
CPOPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           3.00 dB
PL12          18.00 dB
PL13          18.00 dB
SFO2          400.1316005 MHz
SI            65536
SF            161.9755590 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40

```

Mes*₂P₆ (8):

4. References

- [S1] J. E. Borger, A. W. Ehlers, M. Lutz, J. C. Slootweg, K. Lammertsma, *Angew. Chem. Int. Ed.* **2016**, *55*, 613–617.
- [S2] Prepared in two steps starting from the corresponding aniline: a) L. Delaude, M. Szypa, A. Demonceau, A. F. Noels, *Adv. Synth. Catal.* **2002**, *344*, 749–756; b) P. Tang, W. Wang, T. Ritter, *J. Am. Chem. Soc.* **2011**, *133*, 11482–11484.
- [S3] K. E. Reynard, R. E. Sherman, H. D. Smith Jr., L. F. Hohnstedt, G. Gassenheimer, T. Wartik, Trimethylammonium Tetraphenylborate (*A ready source of Triphenylborane*) in *Inorganic Syntheses, Volume XIV* (Eds. A. Wold, J. K. Ruff), John Wiley & Sons, Inc., Hoboken, NJ, USA, **1973**, pp. 52-55.
- [S4] Spectral parameters were determined by iterative full line shape analysis using the gNMR simulation program: P. H. M. Budzelaar, gNMR, Version 5.0.6.0, **2006**.
- [S5] R. T. Baker, J. C. Gordon, C. W. Hamilton, N. J. Henson, P.-H. Lin, S. Maguire, M. Murugesu, B. L. Scott, N. C. Smythe, *J. Am. Chem. Soc.* **2012**, *134*, 5598–5609.
- [S6] J. Bresien, A. Schulz, A. Villinger, *Chem. Eur. J.* **2015**, *21*, 18543–18546.
- [S7] J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.
- [S8] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
- [S9] a) R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724–728; b) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257–2261; c) P. C. Hariharan, J. A. Pople, *Theoret. Chim. Acta* **1973**, *28*, 213–222; d) P. C. Hariharan, J. A. Pople, *Mol. Phys.* **1974**, *27*, 209–214; e) M. S. Gordon, *Chem. Phys. Lett.* **1980**, *76*, 163–168; f) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654–3665; g) C. Binning Jr., L. A. Curtiss, *J. Comput. Chem.* **1990**, *11*, 1206–1216; h) J.-P. Blaudeau, M. P. McGrath, L. A. Curtiss, L. Radom, *J. Chem. Phys.* **1997**, *107*, 5016–5021; i) V. A. Rassolov, J. A. Pople, M. A. Ratner, T. L. Windus, *J. Chem. Phys.* **1998**, *109*, 1223–1229; j) V. A. Rassolov, M. A. Ratner, J. A. Pople, P. C. Redfern, L. A. Curtiss, *J. Comput. Chem.* **2001**, *22*, 976–984.
- [S10] For the polarization functions, see: M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265–3269.
- [S11] a) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654; b) A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648.
- [S12] For the diffuse functions, see: T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294–301.
- [S13] A. M. M. Schreurs, X. Xian, L. M. J. Kroon-Batenburg, *J. Appl. Crystallogr.* **2010**, *43*, 70-82.
- [S14] G. M. Sheldrick, SADABS and TWINABS, Universität Göttingen, Göttingen (Germany), **2008**.
- [S15] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3-8.
- [S16] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3-8.
- [S17] S. Parsons, H. D. Flack, T. Wagner, *Acta Crystallogr.* **2013**, *B69*, 249-259.
- [S18] A. L. Spek, *Acta Crystallogr.* **2009**, *D65*, 148-155.