Stabilization and Transfer of the Transient [Mes*P$_4$]$^-$ Butterfly Anion Using BPh$_3$

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Abstract: *The transient bicyclo[1.1.0]tetraphosphabutane anion, generated from white phosphorus (P$_4$) and Mes*Li (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$), can be trapped by BPh$_3$ in THF. This Lewis acid stabilized anion can be used as an [RP$_4$]$^-$ transfer agent, reacting cleanly with neutral Lewis acids (B(C$_6$F$_5$)$_3$, BH$_3$, and W(CO)$_5$) to afford unique singly and doubly coordinated butterfly anions, and with the trityl cation to form a neutral, nonsymmetrical, all-carbon-substituted P$_4$ derivative. This reaction path enables a simple, stepwise functionalization of white phosphorus.*

Scheme 1. Previous approaches toward the stepwise functionalization of P$_4$.

Functionalizing white phosphorus directly is imperative if chlorinated intermediates are to be avoided in producing organophosphorus compounds.[1] However, the high and unpredictable reactivity of the P$_4$ tetrahedron makes it a challenge to develop such processes.[2] Lately, encouraging progress has been made by several groups aimed at the controlled, stepwise functionalization of P$_4$. For example, Scheer and co-workers[3] generated symmetrically disubstituted bicyclo[1.1.0]tetraphosphabutanes (**A**) with Cp^R organic radicals[4] (Scheme 1; Cp^R = C$_5$R$_5$), Wolf et al.[5,6] used an organometallic nickel(I) radical to obtain a similar P$_4$ butterfly, Bertrand et al. demonstrated diverse P$_4$ activations with various carbenes,[7] Weigand et al. reported stepwise R$_2$P$^+$ cation insertions into the P$_4$ cage (**B**)[8] with subsequent NHC-induced fragmentation into P$_3^+$ and P$_2$ species,[9] and Hill and co-workers used a nucleophilic approach to obtain the [nBu$_2$P$_4$]$^{2-}$ dianion (**C**)[10] with coordinating Mg^{2+} complexes to stabilize the otherwise unstable phosphides.[11] The group of Schulz addressed the role of Lewis acids (LA) in, for example, the interconversion of *exo–exo* and *endo–exo* disubstituted P$_4$ isomers,[12] which can also serve as chelating ligands for Cu$^+$, as reported recently by Scheer.[13] In an exploratory study, mimicking a frustrated Lewis pair (FLP) approach, we showed that P$_4$

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reacts in toluene with ArLi (Ar = Dmp (2,6-dimesitylphenyl) or Mes* (2,4,6-tBu$_3$C$_6$H$_2$)) and B(C$_6$F$_5$)$_3$ to give the stabilized [ArP$_4$]$^-$ anion (**D**) of which the nucleophilic LA-coordinated phosphorus atom can be *endo*-alkylated with MeI, thereby illustrating that P$_4$ can be substituted with two different C groups in two controlled steps.[14] However, there are also limitations. Not only does the strongly stabilizing B(C$_6$F$_5$)$_3$ reduce the reactivity of **D** to a degree that an analogy with neutral phosphanes (R$_3$P) may be more appropriate, also the apolar solvent hampers their synthesis. The further development of this novel chemistry demands that the role of the Lewis acid is addressed. In the present study, we begin by describing the use of the far milder BPh$_3$ as trapping agent, which provides a convenient source of the stabilized [RP$_4$]$^-$ ion in THF. We show that this weaker adduct enables the smooth transfer of the tetraphosphide anion to other Lewis acids and C electrophiles, which significantly facilitates the selective, stepwise functionalization of the P$_4$ scaffold.

Addition of Mes*Li to a THF solution of P$_4$ and BPh$_3$ at 0 °C gave only bicyclo[1.1.0]tetraphosphabutanide **1** (76% yield of the isolated product after washing with benzene/n-pentane; Scheme 2), according to the ^{31}P{^{1}H} NMR spectrum that shows only three signals in a 1:1:2 ratio (AMX$_2$ spin system) at δ = −112.5 (P4), −149.0 (P1), and −306.5 ppm (P2,3).[15] The synthesis is suited for multigram scale and is, because of the solubility of Mes*Li in THF, complete within 1 hour, as opposed to the 4 weeks needed for **D**. Notably, in contrast to B(C$_6$F$_5$)$_3$, BPh$_3$ does not form an adduct with ethers, which allows the use of THF as solvent for the synthesis of **1**.
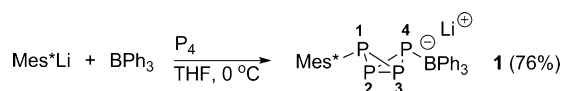
Crystals of **1**, suitable for X-ray diffraction, were grown by layering a THF solution with n-hexane. The molecular structure of **1** (Figure 1a) reveals the BPh$_3$ adduct of the Mes*P$_4$ anion with the Li$^+$ cation coordinated by four THF molecules (not shown) and shows an *exo,exo* configuration. The bridgehead P2−P3 bond (2.1562(12) Å), the slightly longer bonds connecting the flanking P1 and P4 atoms

Scheme 2. Synthesis of the BPh₃-stabilized [Mes*P₄]⁻ butterfly anion.

Scheme 3. The exchange of BPh₃ in **1** with B(C₆F₅)₃ to give **2**.
a) B(C₆F₅)₃ (1.1 equiv), toluene, RT.
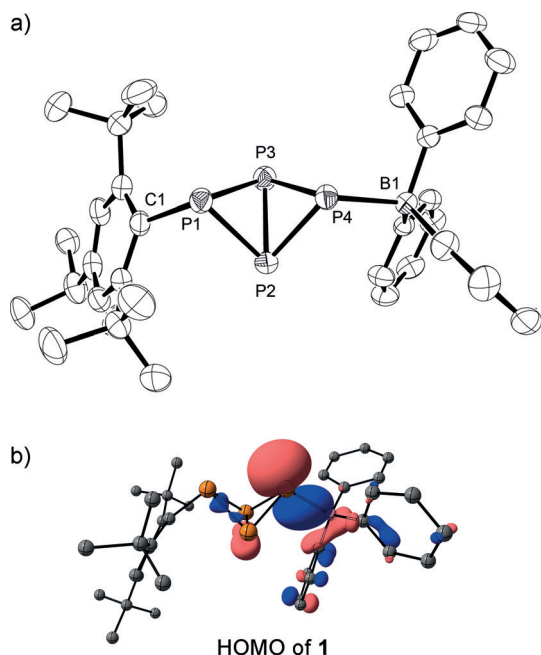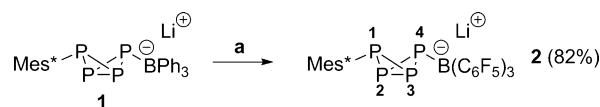
a)

b)

HOMO of **1**

Figure 1. a) Molecular structure of **1a** in the crystal[17] (thermal ellipsoids are set at 30% probability; H atoms, the [Li(THF)₄]⁺ counterion, and noncoordinated THF are omitted for clarity). Only one conformation of the disordered *tert*-butyl group is shown. Selected bond lengths [Å] and torsion angle [°]: P1–P2/P3 2.2234(12)/2.2245(12), P4–P2/P3 2.2117(12)/2.2048(12), P2–P3 2.1562(12), C1–P1 1.881(3), P4–B1 2.064(3); P1-P2-P3-P4 95.87(5). b) HOMO of the optimized geometry of anion **1**.

(P1–P2/P3 2.2234(12)/2.2245(12) Å, P4–P2/P3 2.2117(12)/ 2.2048(12) Å), and the P1-P2-P3-P4 torsion angle (95.87(5)°) are similar to those found for **D**[14] and related neutral P₄ compounds.[3,4–6,12] Importantly, the 37.7 kcal mol⁻¹ strong P–B bond of **1**⁻, computed at the ωB97X-D/6-311 + G(d,p)// 6-31 + G(d,p) level of theory,[16] is 24.4 kcal mol⁻¹ weaker than that computed for **D**⁻ ($\Delta E = 62.1$ kcal mol⁻¹), whereas the bond lengths are similar (P–BPh₃ 2.0785 Å, observed 2.064(3) Å; P–B(C₆F₅)₃ 2.0877 Å, observed[14] 2.064(2) Å). The highest occupied molecular orbital (HOMO) of **1** shows the expected strong nucleophilic character with a large coefficient on the readily accessible wingtip P4 atom (Figure 1 b).

Functionalizing the P₄ core of BPh₃-stabilized [RP₄]⁻ effectively calls for convenient replacement of its LA. To obtain the necessary insight, we first examined borane exchange and reacted 1.1 equiv of B(C₆F₅)₃ with a suspension of **1** in toluene at room temperature to selectively obtain the known *exo,exo*-**2** (**D**; Ar = Mes*)[14] which was isolated in 82% yield (Scheme 3; $\delta = -132.2$ (P1), −159.9 (P4), and −310.4 ppm (P2,P3)). Transferring [Mes*P₄]⁻ from *exo,exo*-

1 to obtain *exo,exo*-**2** and not the *exo,endo* isomer may suggest a dissociative process by first breaking the P–B bond ($\Delta E = 37.7$ kcal mol⁻¹), but an associative path is more likely in light of the mild and apolar reaction conditions (toluene, RT). This pathway would entail the intermediate formation of the mixed bisborane [Mes*P₄·(*endo*-B(C₆F₅)₃)(*exo*-BPh₃)]⁻ and subsequently formation of *exo,endo*-**2** by dissociation of BPh₃.[18] Compound *exo,endo*-**2** should then convert into the *exo,exo* isomer, for example, via a bis(B(C₆F₅)₃) adduct, as has been reported for the related phosphide [Li(12-crown-4)]- [H₂P·(B(C₆F₅)₃)₂].[19] DFT calculations at the ωB97X-D/6- 311 + G(d,p)/PCM(toluene)//6-31G(d) level of theory support this course of events (Scheme 4), revealing the 13.4 kcal
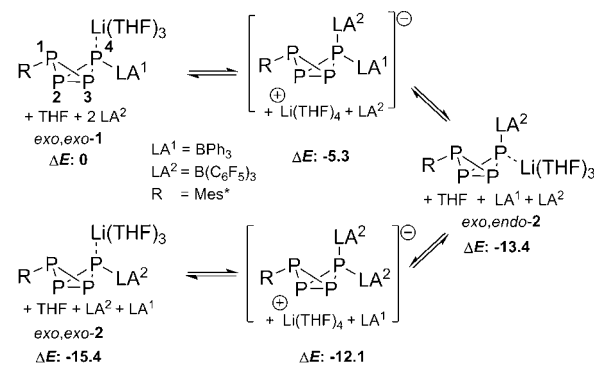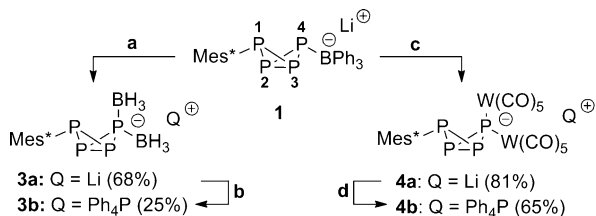

Scheme 4. Relative computed ωB97X-D/6-311 + G(d,p)/PCM-(toluene)//6-31G(d) energies (in kcal mol⁻¹) for the conversion of *exo,exo*-**1** into *exo,exo*-**2**.

mol⁻¹ favored formation of *exo,endo*-**2**. The formation of the *exo,exo* isomer from *exo,endo*-**2**, via the congested symmetrical bisborane adduct [Mes*P₄·(B(C₆F₅)₃)₂]⁻ ($\Delta E = 1.3$ kcal mol⁻¹), is favored by a further 2.0 kcal mol⁻¹.

The B(C₆F₅)₃-induced exchange between *exo,endo*-**2** and *exo,exo*-**2** is supported by analysis of the ³¹P and ¹¹B NMR spectra.[20] A stoichiometric mixture of B(C₆F₅)₃ and *exo,exo*-**2** in [D₈]toluene showed at room temperature broadened ³¹P{¹H} resonance signals and a single ¹¹B{¹H} signal at $\delta = -14.5$ ppm, but the bridgehead P2 and P3 atoms gave two nonequivalent, baseline-separated signals at −60°C ($\delta = -316.7$ and −323.8 ppm, ratio 1.5:1; coalescence at −10°C; estimated $\Delta G^{\ddagger}_{263K} = 11.2$ kcal mol⁻¹)[21] at which temperature also the resonance signals for the wingtip atoms ($\delta = -124.1$ (P1) and −152.9 ppm (P4)) and the borane broadened. A control experiment showed that rapid cooling of a [D₈]toluene solution of only *exo,exo*-**2** to −60°C (no B(C₆F₅)₃ present) did not show broadening or splitting of the ³¹P{¹H} and ¹¹B{¹H} NMR resonance signals. We interpret these results as supportive of an associative mechanism[22] for

the rapidly exchanging isomers of **2**.[23] In contrast, at ambient temperature *exo,exo-***1** does not undergo exchange with BPh$_3$ as it shows a sharp AMX$_2$ spin system in the ^{31}P{^{1}H} NMR spectrum and an additional ^{11}B signal for the free borane at $\delta = 49.4$ ppm. DFT calculations concur with the apparent lack of dynamics, as the bis(BPh$_3$) intermediate (compare with Scheme 4) is a significant 15.3 kcal mol^{-1} less stable than *exo,exo-***1**, which inhibits rapid exchange at room temperature.

We next set out to investigate whether or not a bisborane–[RP$_4$]$^-$ is experimentally accessible. We felt that two boranes should be able to effectively stabilize both lone pairs of the wingtip phosphorus, but that the size of their substituents (Ph, C$_6$F$_5$) might be sterically too demanding to allow isolation of the bisborane adduct. The smallest of the boranes, BH$_3$, was targeted successfully for stabilizing [Mes*P$_4$]$^-$. Adding an excess of Me$_2$S·BH$_3$ to a suspension of **1** in *n*-pentane enabled isolation of the desired bisborane **3a**, which was isolated in 68% yield (Scheme 5a). Its ^{11}B NMR spectrum showed two

Figure 2. Molecular structure of **3b** in the crystal[17] (thermal ellipsoids are set at 50% probability; H atoms, the [PPh$_4$]$^+$ counterion, and a cocrystallized THF molecule are omitted for clarity). Selected bond lengths [Å], angle, and torsion angle [°]: P1–P2/P3 2.2249(6)/2.2287(6), P4–P2/P3 2.1884(6)/2.1868(6), P2–P3 2.1985(6), C1–P1 1.8787(16), P4–B1 1.961(2), P4–B2 1.957(2); B1-P4-B2 122.84(10); P1-P2-P3-P4 105.41(3).

Scheme 5. Transfer reactions of the BPh$_3$-stabilized Mes*P$_4$ butterfly-type anion **1**. a) Me$_2$S·BH$_3$ (2.5 equiv), *n*-pentane, RT; b) **3a**, Ph$_4$PBr (1.1 equiv), THF, RT; c) [(MeCN)W(CO)$_5$] (2.1 equiv), THF, RT; d) **4a**, Ph$_4$PBr (1.1 equiv), THF, RT.

broad quartets at $\delta = -30.9$ and -37.9 ppm and the expected AMX$_2$ spin system in the ^{31}P{^{1}H} NMR spectrum with resonance signals at $\delta = -60$(P4), -109.0(P1), and -275.3 ppm (P2,P3). The resonance signal for the P4 nucleus is significantly deshielded compared to that of *exo,exo-***1** and compares well to that of the structurally related neutral DmpP$_4$Me·B(C$_6$F$_5$)$_3$ (-57.5 ppm)[14] and Ga$_2$P$_4$*t*Bu$_6$ (-50.7 ppm).[24] Salt metathesis enabled exchange of the Li$^+$ cation for Ph$_4$P$^+$ to give **3b** which was isolated in 25% yield (Scheme 5b). Crystals of **3b** suitable for X-ray diffraction were grown and the obtained molecular structure confirmed its identity as a bis(BH$_3$)-stabilized [Mes*P$_4$]$^-$ anion (Figure 2). The P1-P2-P3-P4 torsion angle of 105.41(3)° is nearly 10° larger than for **1**, which suggests repulsion between the *endo*-BH$_3$ group (B2) and the lone pair on P1. This widening of the butterfly is also observed in the related trisubstituted DmpP$_4$Me·B(C$_6$F$_5$)$_3$ (102.98(2)°)[14] and cationic [Mes*$_2$P$_4$Cl]$^+$ ($-101.68(3)°$) on which the group of Schulz reported recently,[25] but is less pronounced than in the tetrasubstituted [{CpRu(PPh$_3$)$_2$}$_2$($\mu^{1:3}$,$\eta^{1:1}$-P$_4$H$_2$)]$^{2+}$ cation (134.2°) isolated by Stoppioni et al.[26] The P4–P2 and P4–P3 bonds (2.1884(6), 2.1868(6) Å) are slightly contracted compared to the P1–P2 and P1–P3 bonds (2.2249(6), 2.2287(6) Å), likely as a result of the Lewis acidity of the BH$_3$ groups. The calculated P–B bond strengths of anionic **3**
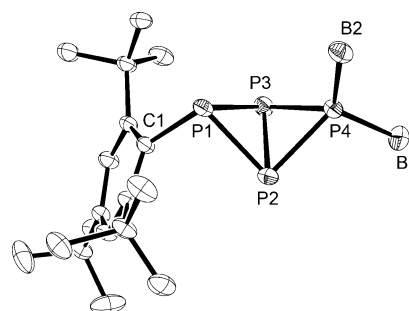
differ slightly from each other (P4–B1 39.8, P4–B2 36.4 kcal mol^{-1}) with the *exo*-BH$_3$ group having the strongest bond. We note **3** to be the first isolable P$_4$ butterfly with two small coordinating groups on a flanking phosphorus atom that maintains its anionic character, thereby favorably contrasting bicyclic tetraphosphanes with large, sterically encumbered groups that hamper controlled functionalization.[3–6,12,14,25]

Next, we targeted the transfer of [Mes*P$_4$]$^-$ to the metal-based Lewis acid W(CO)$_5$, which is isolobal with BH$_3$, expecting a similar trisubstituted anion as **3**. Stirring **1** and [(MeCN)W(CO)$_5$] in THF in a 1:2.1 ratio showed indeed the selective formation of the anticipated new ditungstate **4a**, which was isolated in 81% yield as a thick brown oil (Scheme 5c).[27] The ^{31}P NMR spectrum of compound **4a** shows characteristic resonance signals at $\delta = -56.4$(P1), -171.3(P4), and -259.0 ppm (P2,P3; AMX$_2$ spin system). Salt metathesis using Ph$_4$PBr afforded phosphonium salt **4b** (65% yield; Scheme 5d) of which crystals suitable for X-ray structure determination were obtained.

The molecular structure of **4b** (Figure 3) confirms the presence of two W(CO)$_5$ groups coordinating to P4 at similar distances (P4–W1 2.5811(4), P4–W2 2.5912(4) Å) with a W1-P4-W2 angle of 125.069(16)°. These structural parameters are akin to those reported for the related diphosphide [Ph$_4$P][((CO)$_5$W)$_2$PH$_2$].[28] In the IR spectrum, the CO stretching modes (**4b**: 2060, 2048, 1921 and 1861 cm^{-1}; [((CO)$_5$W)$_2$PH$_2$]$^-$: 2048, 1930, 1872 cm^{-1}) also suggest that the donor strength of the anionic [RP$_4$]$^-$ core is similar to that of PH$_2^-$. The P$_4$ fold angle of **4b** (101.83(2)°) is, like that for **3b** (105.41(3)°), larger than for bifunctionalized P$_4$ species.[3–6,14] However, the P1–P2/P3 (2.2170(6)/2.2296(6) Å) and P4–P2/P3 (2.2113(6)/2.2175(6) Å) bond lengths are similar to those of bifunctionalized P$_4$ species and no ring contraction like in **3b** is found.

The *exo* P–W(CO)$_5$ bond of **4** is slightly stronger (1.5 kcal mol^{-1}) than its *endo* bond, just like for the borane groups of **3**, but both are about 25 kcal mol^{-1} stronger (ΔE: P4–W1 63.7; ΔE: P4–W2 62.2 kcal mol^{-1}) than the P–B bonds, suggesting a more prominent charge transfer from the [RP$_4$]$^-$ core to the metal complexes. This effect is also
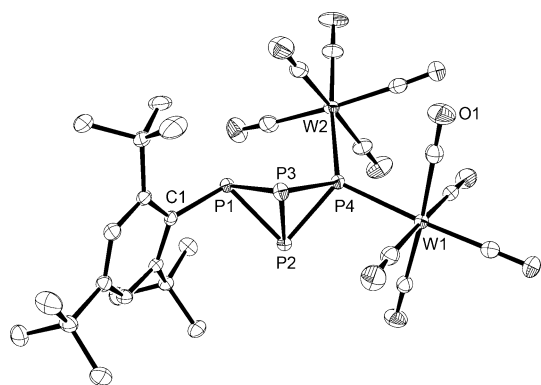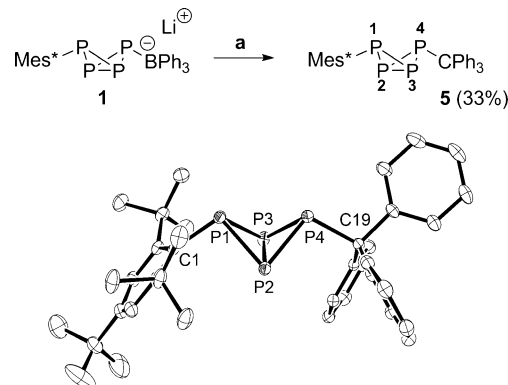
Figure 3. Molecular structure of **4b** in the crystal[17] (thermal ellipsoids are set at 50% probability; H atoms and the [PPh$_4$]$^+$ counterion are omitted for clarity). Selected bond lengths [Å], angle, and torsion angle [°]: P1–P2/P3 2.2170(6)/2.2296(6), P4–P2/P3 2.2113(6)/2.2175(6), P2–P3 2.1780(6), C1–P1 1.8707(16), P4–W1 2.5811(4), P4–W2 2.5912(4); W1-P4-W2 125.069(16); P1-P2-P3-P4 101.83(2).

Scheme 6. Top: Reaction of **1** with Ph$_3$C$^+$ PF$_6^-$; a) Ph$_3$C$^+$PF$_6^-$ (1.1 equiv), pyridine (5 equiv), DME, RT. Bottom: Molecular structure of **5** in the crystal[17] (thermal ellipsoids are set at 50% probability; H atoms are omitted for clarity). Selected bond lengths [Å], angle, and torsion angle [°]: P1–P2/P3 2.2257(6)/2.2294(6), P4–P2/P3 2.2001(6)/2.2243(6), P2–P3 2.1737(6), C1–P1 1.8700(16), P4–C19 1.9446(15); P1-P2-P3-P4 93.93(2).

reflected in the different energies of the MOs of the lone pair on P1, that is, −0.18 eV (HOMO) for **3**, −0.21 eV (HOMO-6) for **4**. Equally indicative is the ^{31}P NMR resonance signal for the P1 center of **4a** at $\delta = -56.4$ ppm, which is significantly deshielded ($\Delta\delta = 52.6$ ppm) from that of **3a** as a result of the difference in overlap of the HOMO of [Mes*P$_4$]$^-$ with the LUMO of the two Lewis acids; W(CO)$_5$ gives a better overlap than BH$_3$, resulting in a smaller energy gap of 0.01 versus 0.08 eV, respectively.

Extending the [RP$_4$]$^-$ transfer strategy, we aimed for P–C bond formation using the carbon-based Lewis acid Ph$_3$C$^+$PF$_6^-$. Stirring **1** with 1.1 equiv of the tritylium salt in dimethoxyethane (DME) resulted indeed directly in full conversion to the desired borane-free **5**, which on separation from BPh$_3$ by addition of pyridine to form the insoluble Py·BPh$_3$ adduct could be isolated in 33% yield (Scheme 6). In the ^{31}P NMR spectrum of **5**, resonance signals at $\delta = -105.5$ (P4), −127.5 (P1), and −308.8 ppm (P2,P3) confirm that the bicyclic P$_4$ framework remained intact. The molecular structure of **5** (Scheme 6; bottom), obtained by an X-ray crystal structure determination, shows an *exo,exo*-disubstituted P$_4$ butterfly with comparable peripheral P–P bonds and a fold angle of 93.93(2)°, similar to those of other bifunctionalized species.[3–6,12,14] Interestingly, in contrast to the previously reported *endo* methylation of [DmpP$_4$·B(C$_6$F$_5$)$_3$]$^-$ with MeI,[14] addition of the tritylium salt only yields the *exo,exo* product devoid of the Lewis acid. Presumably, BPh$_3$ departs on *endo* P–C bond formation between the [RP$_4$]$^-$ ion and the Ph$_3$C$^+$ ion with concurrent isomerization. The resulting *exo,exo*-bicyclo[1.1.0]tetraphosphane **5** is the first stable, nonsymmetrical all-hydrocarbon-substituted butterfly derivative generated directly from P$_4$ in two simple steps.

In summary, transient [Mes*P$_4$]$^-$ can be conveniently trapped with the mild Lewis acid BPh$_3$. The [Mes*P$_4$]$^-$ core of the stabilized anion can be transferred to both the bulky B(C$_6$F$_5$)$_3$ and small BH$_3$ Lewis acid as well as to W(CO)$_5$ to afford unique singly and doubly coordinated [RP$_4$]$^-$ tetraphosphides. Transfer to the tritylium cation leads to formation of a new P–C bond, thereby further functionalizing the

P$_4$ core. This novel transfer approach enables facile additional functionalization of bicyclo[1.1.0]tetraphosphabutane anions. We are now exploring the reactivity pattern of these intriguing new P$_4$-derived species and their utility in subsequent controlled transformations.

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[18] The mixed borane complex $[Mes*P_4\cdot(endo\text{-}B(C_6F_5)_3)(exo\text{-}BPh_3)]^-$ could not be detected by ^{31}P NMR spectroscopy.

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[20] While the *exo,exo* isomer is the most documented form of bicyclo[1.1.0]tetraphosphabutanes (see Refs. [3–6,14,25]), examples of the *exo,endo* product, or evidence thereof, have been reported: a) E. Niecke, R. Rüger, B. Krebs, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 544–545; *Angew. Chem.* **1982**, *94*, 553–554; b) 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; c) Ref. [9]; d) Ref. [12].

[21] See the Supporting Information for further details.

[22] The *endo* isomer could not be detected by $^{31}P\{^1H\}$ NMR spectroscopy when **1** was reacted with a "deficit" (0.8 equiv) of $B(C_6F_5)_3$ in $[D_8]$toluene.

[23] The chemical shift differences for the two products detected at −60 °C are in the same range as detected for the *rac* and *meso* isomers of the symmetrically substituted 1,4-$P_4[P(N-(SiMe_3)_2(NiPr_2)]_2$, reported by Lappert et al.[4a], which show three resonance signals for the bridgehead P atoms ($\delta = -325.8$ (*rac*), −332.9 (*meso*), and −338.0 ppm (*rac*)) and also only one for the wingtip P atoms (−139.5 ppm).

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