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On the Reactivity of Phosphaalumenes towards C–C Multiple Bonds

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Dedicated to Professor Robert West.

Abstract: Heterocycles containing group 13 and 15 elements such as borazines are an integral part of organic, biomedical and materials chemistry. Surprisingly, heterocycles containing P and Al are rare. We have now utilized phosphaalumenes in reactions with alkynes, alkenes and conjugated double bond systems. With sterically demanding alkynes 1,2-phosphaalumetes were afforded, whereas the reaction with HCCH or HCCSiMe$_3$ gave 1,4-phosphaaluminabarrelenes. Using styrene saturated 1,2-phosphaalumates were formed, which reacted further with additional styrene to give different regio-isomers of 1,4-aluminaphosphorinanes. Using ethylene, a 1,4-aluminaphosphorinane is obtained, while with 1,3-butadiene a bicyclic system containing an aluminacyclopentane and a phosphirane unit was synthesized. The experimental work is supported by theoretical studies to shed light on the mechanism governing the formation of these heterocycles.

Introduction

Main group element multiple bond systems have fascinated synthetic chemists for ages and to date multiple bonding between almost all combinations of main group elements has been realized. Forging multiple bonds between trielenes and pnictogens poses a significant challenge though. This is due to adjacent Lewis acidic group 13 and basic group 15 atoms, that result in a pronounced oligomerization tendency of these so-called pnictatrielenes.[1] Thirty years ago it was shown that in the mass spectra of the diboradiphosphetanes [RPBTmp]$_2$ (Scheme 1, **A**, R=CEt$_3$, Mes*=2,4,6-*t*Bu$_3$-C$_6$H$_2$; Tmp=2,2,6,6-tetramethylpiperidyl) bearing bulky substituents the molecular ion peaks of the monomeric [RP=BTmp]$^+$ ions were detected (Scheme 1, i).[2] The thermal cleavage of [Mes*PBTmp]$_2$ in solution was revisited by Michael Cowley and co-workers, showing that Mes*P=BTmp can be generated in situ in benzene solution at 80°C, which agreed with DFT calculations showing that the dimer is favored over the monomer by 46 kJmol^{-1}. That the monomer was indeed generated in solution was shown by intercepting it with the Lewis bases 4-dimethylaminopyridine (dmap) or IMe$_4$ (IMe$_4$=(MeCNMe)$_2$C) to afford the base-stabilized boraphosphenes [Mes*PB-(LB)Tmp] (LB=dmap, IMe$_4$). Heating a benzene solution of [Mes*PBTmp]$_2$ in the presence of HC≡CPh to 80°C afforded the four-membered 1,2-phosphaborete **B** in a [2+2] cycloaddition reaction in regio-selective manner (Scheme 1, ii).[3] Similarly, [Mes*PBTmp] was found to undergo a formal [2+2] cycloaddition with ^{Mes}TerP=Ch (Ch=S, Se), to give P$_2$BCh-heterocycles (**C**) (Scheme 1, ii).[4] Recently, novel base-stabilized cyclic,[5] and acyclic phosphaborenes, which have been shown to engage in metathesis reactions,[6] were reported, yet their reactivity towards alkynes has not been studied. In contrast, the base-stabilized iminoalane (**D**) reacted with HC≡CPh through addition across the Al–N bond with H being added to N and the acetylenide moiety being added at Al with the concomitant release of the LB (LB=I*i*Pr$_2$Me$_2$=(MeCN*i*Pr)$_2$C; Scheme 1, iii).[7] Interestingly, the heavier analogs, so-called phosphaalumenes and phosphagallenes, have been synthetically realized only recently. The groups of Goicoechea and Schulz independently reported on the reaction of phosphanyl-[8] or gallium-substituted phosphaketenes[9] with the Ga^I species ^{Dip}Nac-nacGa (^{Dip}Nacnac=HC{(CMe)(NDip)}$_2$; Dip=2,6-*i*Pr$_2$C$_6$H$_3$), which after extrusion of CO, gave the phosphagallenes **E** and **F**, respectively (Scheme 1). **E** mainly shows

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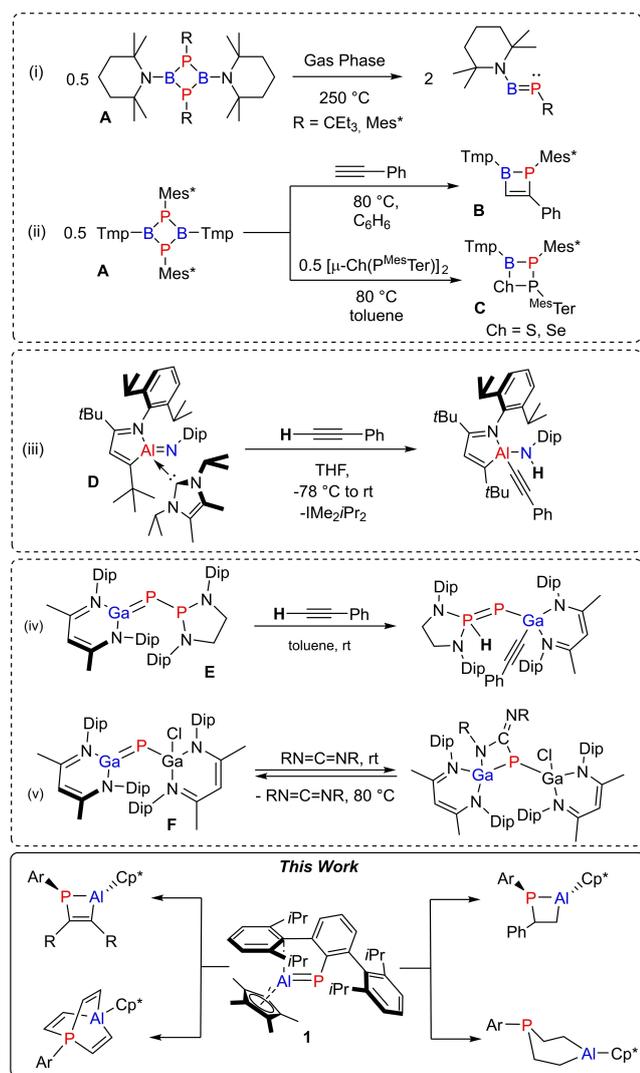
Scheme 1. Selected reactivities of boraphosphenes (ii), iminoalanes (iii) and gallaphosphenes (iv, v) towards multiple bond systems and summary of this study (bottom).

1,3-dipolar reactivity, which can also be understood as frustrated Lewis pair (FLP) reactivity, towards a range of protic substrates. For example HC≡CPh reacted cleanly with **E** at room temperature with [C≡CPh]⁻ being added to Ga, while the phosphanyl P atom is protonated, giving phosphanylidenephosphoranes (Scheme 1, iv).[10] **F** mainly reacts at the P–Ga double bond in 1,2-fashion,[11] and with carbodiimides [2+2] cycloaddition reactions to give four-membered GaPCN-heterocycles in reversible fashion were reported.[11a] Phosphaalumenes were predicted to be synthetically accessible by the installation of sterically demanding groups on both P and Al and theoretical studies showed ^{Tip}TerP=Al^{Tip}Ter to possess a strongly polarized P–Al multiple bond, with considerable zwitterionic character.[12] We have utilized phospha-Wittig reagents,[13] aryl-substituted phosphanylidenephosphoranes, as a formal source of phosphinidenes to deliver Ar–P fragments.[14] The combination of the phosphanylidenephosphorane ^{Dip}TerP(PMe$_3$)

(^{Dip}Ter=2,6-Dip-C$_6$H$_3$) with the Al^I compound (Cp*Al)$_4$ afforded the phosphaalumene ^{Dip}TerP=AlCp* (**1**) after a PMe$_3$ for Cp*Al substitution at 80 °C in benzene solution.[15]

Considering that the chemistry of B,N-[16] and B,P-heterocycles[5,17] has evolved into an integral part of synthetic inorganic and materials chemistry, the question arose whether the heavier Al,P-heterocycles can be accessed via cycloaddition reactions of alkenes and alkynes with ArPAlCp*. Erker and Uhl had previously shown that geminal-P/Al FLPs, accessed by the hydroalumination of P-substituted alkynes, reacted with HCCPh, to give a five-membered 1,3-phosphaalumina cyclopentene derivative.[18]

In this contribution we report on a second phosphaalumene and then outline first reactivity studies of phosphaalumenes **1** and **2** towards a variety of alkynes, alkenes und 1,3-butadiene, giving a plethora of unprecedented P,Al-heterocycles. Among these heterocycles four-membered 1,2-phosphaalumetes, and -alumates, as well as 1,4-aluminaphosphorinanes and bicyclic systems containing both an aluminacyclopentane and phosphorinane unit. With acetylene a 1,4-phosphaaluminabarrelene was afforded. The experimental work is supported by theoretical studies to determine the underlying reaction mechanisms.

Results and Discussion

We first wanted to extend the number of phosphaalumenes and therefore treated ^{Tip}TerP(PMe$_3$)[19] (^{Tip}Ter=(2,4,6-iPr$_3$C$_6$H$_2$)$_2$-C$_6$H$_3$) with (Cp*Al)$_4$ by analogy to the synthesis of **1** (Scheme 2).

After heating a 4:1 mixture of (Cp*Al)$_4$ and ^{Tip}TerP (PMe$_3$) to 80 °C for 16 h the formation of ^{Tip}TerPAlCp* (**2**) was confirmed by a new signal in the ^{31}P{^{1}H} NMR spectrum at −208.8 ppm (cf. **1** $\delta(^{31}$P{^{1}H}) = −203.9 ppm). When carrying out the reaction on a smaller scale or when treating **2** with 0.25 eq of (Cp*Al)$_4$ an additional broad resonance at −96.3 ppm, assigned to ^{Tip}TerP(AlCp*)$_2$ (**3**) ($\delta_{calc.}(^{31}$P) = −101.8 ppm),[20] was observed (ratio **2:3** = ca. 3:1). Purple crystals of **2** for single crystal X-Ray diffraction (SC-XRD) experiments were grown by placing a saturated *n*-heptane solution of **2** at −30 °C over a period of 24 h. This confirmed the formation of the expected phosphaalumene ^{Tip}Ter-PAlCp* (**2**) with a P–Al atomic distance of 2.2022(6) Å and an Al–P–C$_{Ter}$ angle of 112.00(5)° (Figure 1, left). By analogy to **1**, a contact between Al and the *ipso*-C (C7) of one of the flanking Tip-groups is detected at 3.1258(15) Å (cf. **1**: 2.9999(13) Å), longer than in **1** and might contribute to the fact that ^{Tip}TerP(AlCp*)$_2$ (**3**) is formed as a minor component through addition of Cp*Al to **2**. To investigate whether
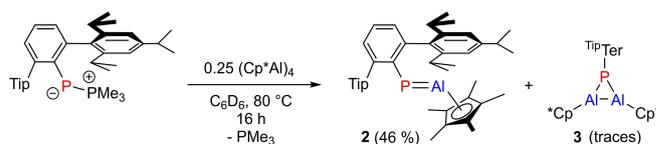
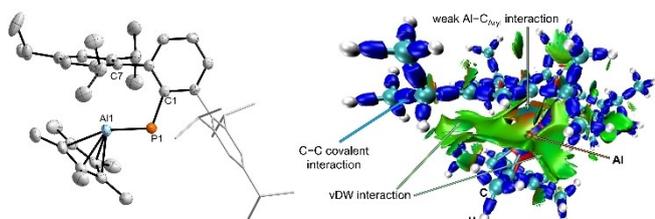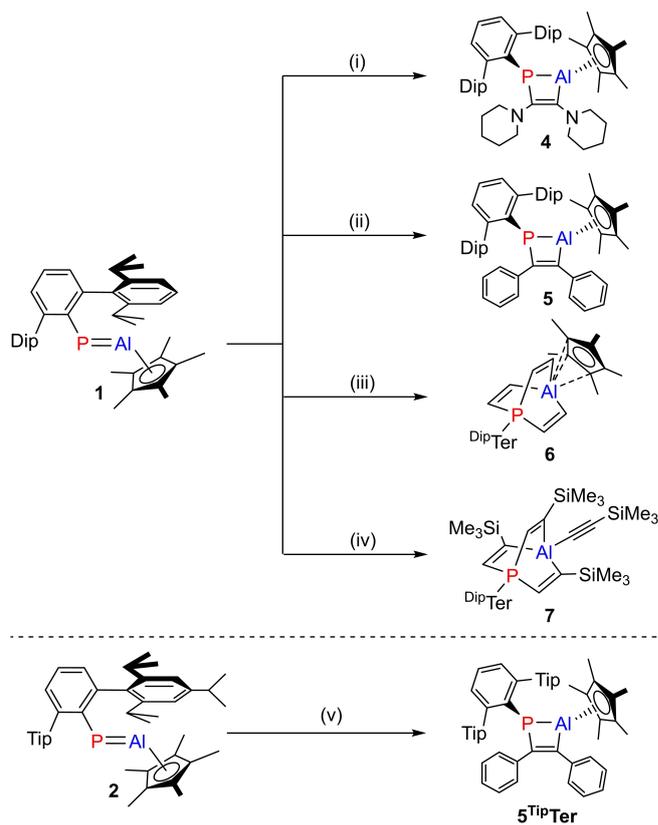**Scheme 2.** Synthesis of phosphaalumene **2**.

Figure 1. Molecular structure of **2** (left). Ellipsoids drawn at 50% with C-*H*-atoms omitted, Tip-groups rendered as wire-frame for clarity. Selected bond lengths [Å] and angles [°], **2**: Al1−P1 2.2022(6), P1−C1 1.8209(16), Al1−C7 3.1258(15), Al1−C38 2.2609(17), Al1−C37 2.2333(18), Al1−C39 2.2274(17), Al1−C40 2.1583(18), Al1−C41 2.1603(18); C1−P1−Al1 112.00(5), Al1−P1−C1−C2 −174.04(9), C1−C6−C7−C12 −98.23(18). Isosurface plot of IRI = 1.0 (right). vdW interactions are indicated by green areas, whereas dark blue areas indicate chemical bonding. Grid spacing for IRI is 0.12 Bohr.

Scheme 3. Reactivity studies on **1** towards alkynes: (i) PipC≡CPip, C_6D_6, rt., 1 h; (ii) PhC≡CPh, C_6D_6, 80°C, 6 d; (iii) HC≡CH, C_6D_6, rt., 15 min; (iv) HC≡CSiMe₃, C_6D_6, rt. vibratory plate, 16 h; (v) PhC≡CPh, C_6D_6, 80°C, 20 h.

the *p*-*i*Pr group of the ᵀⁱᵖTer-moiety resulted in repulsive interactions with the Cp* group on Al, an interaction region indicator (IRI) analysis was carried out, which allows to visually reveal both chemical bonds and weak interactions in molecules.[21]

This indicated a region of van der Waals (vdW) interactions between the Cp* Me-groups and all three *i*Pr-groups of the ᵀⁱᵖTer-moiety, as well as weak Al−C_{aryl} interactions (Figure 1, right).[20]

3 was elucidated by SC-XRD experiments of yellow crystals, which grew beside purple crystals of **2** from a saturated *n*-heptane solution, which was stored at −30°C for 72 h (Figure S1). **3** is an analogue of ᴹᵉˢTerP(AlCp*)₂,[15] with a planar PAl₂-heterocycle (d(P1−Al) 2.3531(6), 2.3575(6); d(Al−Al) 2.5113(7) Å; Σ(∡P1) = 359.36(4)°), rendering this a 2π-aromatic ring.[22] Nevertheless, it was not possible to obtain pure **3** by fractional crystallization and only four resonances could be unambiguously identified in the ¹H NMR spectrum (Figure S10).[20] The potential co-formation of **3** makes it more difficult to isolate **2** in good quantities (46%) and to test the reactivity of phosphaalumenes we therefore mainly turned to **1**, which can now be synthesized in high purity on a 0.735 g scale (see Supporting Information, p. S15).[20]

We started our investigations with the alkyne PipC≡CPip (Pip = piperidyl),[23] which was shown to have diaminodicarbene character in bimetallic complexes and is considered electron-rich.[24] Combination of **1** with PipC≡CPip in C_6D_6 at room temperature gave a new singlet signal in the ³¹P{¹H} NMR spectrum at 27.1 ppm after 1 h, indicative of the formation of a 1,2-phosphaalumete (cf. 1,2-phosphaborete **B**[3] δ(³¹P) = −47.3 ppm) (Scheme 3, i). This was confirmed by SC-XRD experiments on orange crystals grown from a saturated toluene solution at −30°C, which showed the formation of the 1,2-phosphaalumete [ᴰⁱᵖTerP(Pip₂C₂)AlCp*] (**4**) ($\delta_{calc.}$(³¹P) = 36.0 ppm, Table 1)[20] (Figure 2, left), with a P−Al atomic distance of 2.3493(6) Å and a C−C distance of 1.383(2) Å in the four-membered ring which is close to a double bond. The P atom is in a distorted trigonal pyramidal coordination environment with the ᴰⁱᵖTer and Cp* group being oriented *trans* with respect to the P−Al

Table 1: Characteristic ³¹P{¹H} NMR data of **2–11**. Calculated ³¹P NMR shifts (PBE0-D3/def2-TZVP//PBE0-D3/def2-SVP) and P−Al atomic distances [Å].

Compound	δ (³¹P{¹H})[a]	$\delta_{calc.}$ (³¹P)[b]	d (P−Al)
2	−208.9	−189.5	2.2022(6)
3	−96.3	−101.8	2.3531(6)
			2.3575(6)
4	27.1	36.0	2.3493(6)
5	35.3	43.8	2.3953(12)
5ᵀⁱᵖTer	33.8	43.5	2.3855(16)
6	−38.0	−39.8	3.0230(16)
7	−50.7	−53.5	3.0059(12)
8	76.0	98.4	2.3992(5)
8ᵀⁱᵖTer	75.0	86.3	2.4054(7)
9a	−19.3	−19.1	2.9546(7)
9b	−10.4	−11.5	3.0754(7)
10	−7.9	−1.4	3.3871(7)
11	−183.9	−197.1	3.2631(20)

[a] In C_6D_6 at room temperature; values given in ppm (δ).- [b] Referenced to the experimental absolute shift of 85% H_3PO_4 in the gas phase using PH₃ as a secondary standard.[20]

axis. The angles at Al (P−Al−C 78.55(5)°) and P (Al−P−C 69.85(5)°) are rather acute within the PAlC₂-heterocycle, which deviates from planarity (P−Al−C−C 20.42(11)°). In accordance with the molecular structure in the solid state
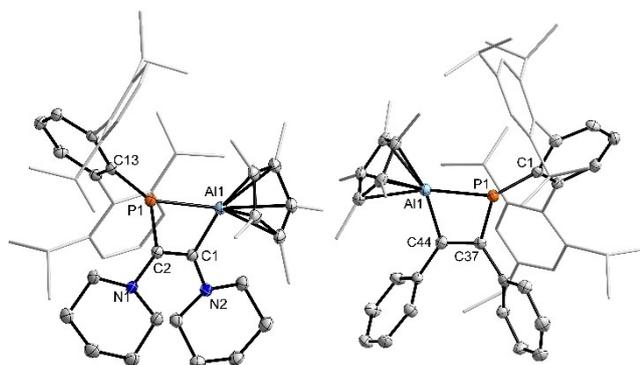
Figure 2. Molecular structure of **4** (left) and **5$^{\text{Tip}}$Ter** (right). Ellipsoids drawn at 50% with C-*H*-atoms omitted, Dip- (**4**), Tip- (**5$^{\text{Tip}}$Ter**) and Cp*-Me-groups rendered as wire-frame for clarity. Selected bond lengths [Å] and angles [°] (**4**): Al1–P1 2.3493(6), P1–C2 1.8589(15), Al1–C1 1.9532(16), C1–C2 1.383(2); C2–P1–Al1 69.85(5), P1–Al1–C1 78.55(5), P1–C2–C1 114.63(11), Al1–C1–C2 92.53(10); Al1–C1–C2–P1 20.42(11). (**5$^{\text{Tip}}$Ter**): Al1–P1 2.3855(16), P1–C37 1.849(4), Al1–C44 1.942(4), C32–C39 1.372(5); C1–P1–Al1 125.12(12), P1–Al1–C44 75.94 (12), P1–C37–C44 112.1(3), Al1–C39–C32 99.1(2); Al1–P1–C37–C44 0.9(2).

the Cp* group is η^5-coordinated, indicated by a sharp singlet signal at 1.73 ppm in the ^{1}H NMR spectrum in C$_6$D$_6$ at room temperature.

Crystals of **4** were found to be poorly soluble in C$_6$D$_6$, or toluene-d$_8$, however, sufficient NMR data was obtained when a toluene-d$_8$ solution of **4** was heated to 75°C, clearly showing four doublet signals for the *i*Pr-CH$_3$ protons of the Dip groups (Figure S13), indicating hindered rotation about the C$_{\text{Ter}}$–P bond in solution.

Encouraged by this outcome we turned to the less activated PhC≡CPh and no conversion with **1** or **2** was detected at room temperature after 24 h in C$_6$D$_6$. Heating **1** and PhC≡CPh to 80°C over a period of 6 d gave full conversion into a new species with a ^{31}P NMR shift of 35.3 ppm ($\delta_{\text{calc.}}(^{31}\text{P}) = 43.8$ ppm),[20] which was assigned to the 1,2-phosphaalumete [$^{\text{Dip}}$TerP(Ph$_2$C$_2$)AlCp*] (**5**) (Scheme 3, ii). Surprisingly, with **2** full conversion was reached after just 20 h at 80°C, giving [$^{\text{Tip}}$TerP(Ph$_2$C$_2$)AlCp*] (**5$^{\text{Tip}}$Ter**; $\delta = (^{31}\text{P}) = 33.8$ ppm; $\delta_{\text{calc.}}(^{31}\text{P}) = 43.5$ ppm)[20] as yellow crystalline solid after recrystallization from *n*-heptane (Scheme 3, v). This clearly shows that **2** is more reactive than **1**. In the ^{1}H NMR spectrum of **5** and **5$^{\text{Tip}}$Ter** one of the *i*Pr-methyl and the methine resonances of the $^{\text{Dip}}$Ter-moiety or of the *o-i*Pr groups in **5$^{\text{Tip}}$Ter**, respectively, appeared as broad featureless singlet signals and the Ph-groups gave two sets of signals in the expected ratio. Crystals grown by slowly evaporating a C$_6$D$_6$ solution of **5** or by placing a saturated *n*-heptane solution of **5$^{\text{Tip}}$Ter** at −30°C for 72 h, respectively, verified the formation of 1,2-phosphaalumetes, which showed **5** (Figure S2)[20] and **5$^{\text{Tip}}$Ter** (Figure 2, right) to have a nearly planar PAlC$_2$-ring (P–Al–C–C 1.11(17) (**5**), 0.9(2)° (**5$^{\text{Tip}}$Ter**)), with slightly different metrical parameters (d-(P–Al) 2.3953(12) (**5**), 2.3855(16) (**5$^{\text{Tip}}$Ter**); d(C–C) 1.372(4) (**5**), 1.372(5) Å (**5$^{\text{Tip}}$Ter**)) compared with **4**. Having shown that the bulky and rather unreactive PhC≡CPh reacted with

1 and **2**, albeit slowly in the case of **1**, we next tested whether acetylene gas would react in [2+2] fashion or whether further insertion into the P–Al bond of the 1,2-phosphaalumete was possible. It was shown for example that iso-valence electronic ditetrylenes reacted with two alkyne molecules giving 1,2- or 1,4-ditetrelbenzene derivatives.[25] The latter were furthermore shown to add a third alkyne giving 1,4-ditetrel-barrelene derivatives.[26] When purging a degassed C$_6$D$_6$ solution of **1** with freshly purified C$_2$H$_2$ (to remove traces of acetone, see Supporting Information for details)[20] we noticed that the characteristic purple color of **1** vanished within 15 min at room temperature (Scheme 3, iii)). In the ^{31}P{^{1}H} NMR spectrum a broad signal at −38.0 ppm indicated the formation of a molecule succinctly different from **4** and **5**. After workup and recrystallization of the crude product from a saturated *n*-pentane solution at −30°C X-ray quality crystals were obtained, which revealed the formation of the zwitterionic 1,4-phosphaaluminabarre-lene [$^{\text{Dip}}$TerP(C$_2$H$_2$)$_3$AlCp*] (**6**), in which three molecules acetylene have inserted into the P=Al bond to give a P,Al-congener of the parent bicyclo[2.2.2]octa-2,5,7-triene.[27] 1-phosphabarrelenes have been reported and can for example be obtained in [4+2]-cycloaddition reactions between phos-phinines and activated alkynes.[28] The calculated ^{31}P NMR shift of **6** ($\delta_{\text{calc.}}(^{31}\text{P}) = -39.8$ ppm)[20] is in reasonable agree-ment with the experimentally determined shift ($\delta_{\text{exp.}}(^{31}\text{P}) = -38.0$ ppm). The ^{1}H NMR spectrum is indicative of a C_s-symmetric structure in solution, with a septet and two doublets for the *i*Pr groups of the $^{\text{Dip}}$Ter-substituent. The bridging C*H*-protons show a $^3J_{\text{HH}}$ coupling constant of 15 Hz, in line with *cis*-alkenes, with the AlC*H* protons being significantly deshielded ($\delta(^1\text{H}) = 8.02$ ppm, $J_{\text{PH}} = 60.2$ Hz) compared to the PC*H* protons ($\delta(^1\text{H}) = 6.35$ ppm, $J_{\text{PH}} = 39.5$ Hz). X-ray quality crystals of **6** were grown from a saturated *n*-pentane solution at −30°C and SC-XRD experi-ments revealed that the Al and P atoms in **6** reside in distorted tetrahedral environments, with average bridging C–C distances of 1.334(6) Å, being indicative of a double bond (Figure 3, left). The P–Al separation of ca. 3.0510(17) Å is within the sum of the van der Waals radii of both atoms ($\Sigma r_{\text{vdw}}(\text{PAl}) = 3.64$ Å)[29] and due to the four-coordinate nature of both atoms, bonding between P and Al can be excluded. In the solid state the Cp*-group on Al is found to be η^3-coordinated, whereas in solution a singlet is detected in the ^{1}H NMR spectrum, indicating a fast sigmatropic rearrangement in solution.

The formation of **6** was further probed by theoretical studies with geometry optimizations carried out at the PBE0-D3[30]/def2SVP[31] level of theory. More accurate electronic energies were obtained at the DLPNO-CCSD-(T)[32] level of theory with the def2-TZVPP basis set,[31] which were corrected to include zero-point correction (ΔE_{ZPE}), thermal correction (ΔE_{therm}), entropy correction ($\Delta E_{\text{entropy}}$) and solvent correction (ΔE_{solv}) (notation: DLPNO-CCSD(T)/def2-TZVPP//PBE0-D3/def2-SVP). These investigations clearly showed **6** to be thermodynami-cally favored over a 1,2-phosphaalumete (IM1, via a [2+2]-cycloaddition) or a 1,4-phosphaalumine (IM2, via HCCH insertion into the P–Al bond of IM1, Figure 4). Starting
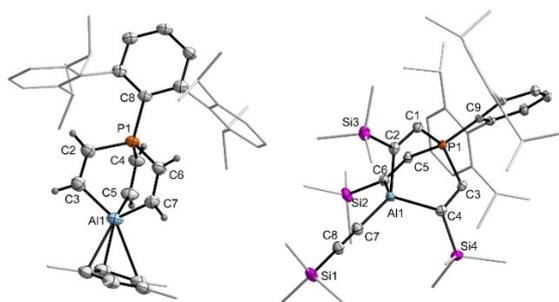
Figure 3. Molecular structures of **6** (left) and **7** (right). Ellipsoids drawn at 50% with C-*H*-atoms omitted (except those on C2-C7 in **6**), Dip- and Cp*-Me-groups rendered as wire-frame for clarity. Selected bond lengths [Å] and angles [°] **6**: Al1–P1 3.0510(17), Al1–C3 2.020(2), Al1–C5 2.016(2), Al1–C7 1.995(2), P1–C2 1.820(2), P1–C4 1.807(2), P1–C6 1.8152(19), P1–C8 1.8309(19), C3–C2 1.334(3), C4–C5 1.330(3, C6–C7 1.337(3); C2–P1–C4 105.66(10), C4–P1–C6 107.18(9), C6–P1–C2 103.98(9), C3–Al1–C5 95.92(9), C5–Al1–C7 99.09(9) [96.11 (17)], C7–Al1–C3 96.09(9). **7**: Al1–P1 Al1–C2 2.011(4), Al1–C4 2.007(4), Al1–C6 1.969(4), P1–C1 1.819(2), P1–C3 1.824(2), P1–C5 1.832(2), P1–C9 1.8269(19); C1–P1–C3 107.43(9), C1–P1–C5 103.71(9), C3–P1–C5 105.12(9), C2–Al1–C4 101.75(8), C2–Al1–C6 97.17(9), C4–Al1–C6 99.44(8).

from a reactant complex (RC), in which a weak H-bond between the P atom in **1** (which remains nearly unperturbed) and H–CCH is found (P⋯H–CCH 2.66 Å), acetylene first forms a π-complex with Al in TS1 ($\Delta G = 8.2$ kcal mol^{-1}) with a minimally elongated Al–P bond (Al–P 2.22 Å), to eventually form a 1,2-phosphaalumete (IM1) akin to **4** and **5** as the first intermediate. The second molecule HCCH again interacts with IM1 through a weak π-interaction with the Al atom (IM1′) and in a low-barrier step ($\Delta G = 4.3$ kcal mol^{-1}) via a more activated π-complex (Al–C 2.20; C–C 1.24 Å, TS2) a 1,4-phosphaalumine with a nearly planar AlC$_4$P-ring is formed as the second intermediate (IM2). In IM2 the Al⋯P separation is 3.50 Å, with an η^5-

coordinated Cp*-substituent on Al and the ^{Dip}Ter-substituent is oriented below the AlC$_4$ plane. Like in IM1′ the third HCCH molecule is first weakly bound to the Al atom resulting in minimal folding of the AlC$_4$P ring now adopting a boat conformation, with the Cp*-substituent shifting from η^5 to η^1 clearly reflected by two localized C=C bonds in the Cp*-ring (IM2′).

Through a low-lying transition state ($\Delta G = 5.1$ kcal mol^{-1}, TS3), the final 1,4-phosphaaluminabarrelene **6** is obtained. The overall reaction is strongly exergonic ($\Delta_R G = -134.5$ kcal mol^{-1}). In TS3 the boat conformation is more pronounced for the AlC$_4$P-ring, with an Al⋯P separation of 3.19 Å and the HCCH is associated to Al via a σ-bond (Al–C 2.21 Å) and the second C atom is oriented towards P (P–C 2.81 Å). The low activation barriers along the reaction pathway are in line with a facile reaction at room temperature and the high barriers for the reverse reactions also indicate that **6** is indeed a "thermodynamic sink" in this transformation. Calculations on the activation of HCCPh by a geminal Al/P-FLP revealed a similar pre-coordination at aluminum, pointing to the crucial role of the Lewis acidic center.[18] The reaction of **1** and **2** with tolane only proceeded at elevated temperature, which can be rationalized by a considerably higher barrier for the first reaction step ($\Delta G = 22.8$ kcal mol^{-1}).[20] A second transition state for the addition of a second tolane could not be determined, indicating that the sterically more demanding alkyne only reacted in [2+2] fashion, while the effect of the ^{Tip}Ter-moiety was not considered theoretically.

The SiMe$_3$-group has been termed as "fat proton",[33] and switching to HC≡CSiMe$_3$ a different outcome was observed. After reacting **1** with an excess of HC≡CSiMe$_3$ in C$_6$D$_6$ after 1 h, the ^{31}P{^{1}H} NMR spectrum was diagnostic of the formation of a 1,4-phosphaaluminabarrelene (Scheme 3, iv), giving a singlet at −50.7 ppm, with one set of signals in the alkyl-region for the ^{Dip}Ter-substituent, in line with the spectroscopic data of **6**. However, two singlets in a 1:3 ratio
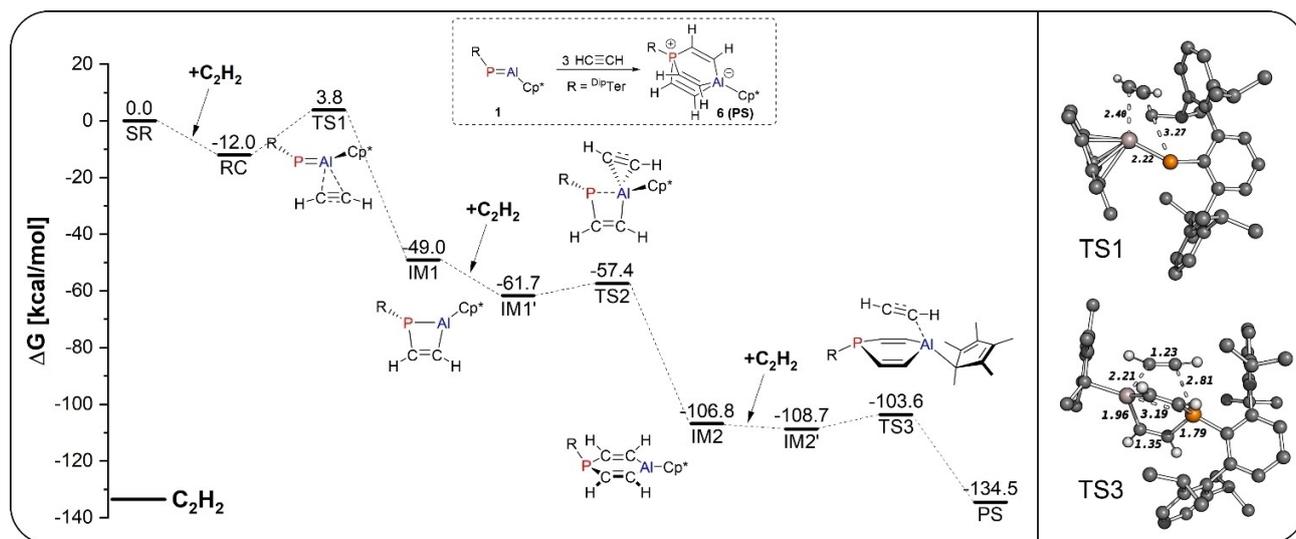

Figure 4. Free energy profile of the reaction of **1** with acetylene to give **6** (PS) calculated at the DLPNO-CCSD(T)/def2-TZVPP//PBE0-D3/def2-SVP level of theory.

were observed in the ^{1}H NMR spectrum for the Me$_3$Si-groups at 0.29 and 0.21 ppm, respectively and surprisingly no signal for the Cp*-moiety was detected. SC-XRD experiments on crystals grown from a saturated *n*-pentane solution at -30°C revealed (Figure 3, right), that in the presence of HC≡CSiMe$_3$ the Cp*-group was removed (in the form of Cp*H) and the tetravalent Al is now substituted by a terminal (Me$_3$Si)C≡C-group to give [^{Dip}TerP(HC=CSiMe$_3$)$_3$Al(C≡CSiMe$_3$)] (**7**) as a colorless crystalline solid ($\delta_{calc.}(^{31}$P$) = -53.5$ ppm). HCCSiMe$_3$ inserted into the Al=P-bond in regio-selective fashion with the CH-group at P, as also indicated by a doublet in the ^{1}H NMR spectrum at 6.51 ppm with a J_{PH} coupling constant of 50.4 Hz, similar to that in **6**. The metrical parameters of **7** match closely those of **6**, with average bridging C–C atom

distances of 1.338(3) Å and a P–Al separation of 3.0059(12) Å. The formation of **6** indicates that it is possible to remove the Cp*-substituent by protonation, which should in the future allow to further functionalize 1,4-phosphaaluminabarrelenes and other heterocycles presented in this study. It was for example recently shown that one of the Cp*-groups in (Cp*Al)$_4$ can be selectively removed by addition of Li[Al(OR^F)$_4$] (R^F = C(CF$_3$)$_3$) to give [Al(AlCp*)$_3$][Al(OR^F)$_4$].[34]

Having shown that bulky alkynes undergo a formal [2+2]-cycloaddition, we next set to investigate the reactivity towards alkenes. Addition of an excess of styrene H$_2$C=C(Ph)H to **1** and heating to 80°C for 10 min afforded a product with a singlet in the ^{31}P{^{1}H} NMR spectrum at 76.0 ppm, with one set of signals in the ^{1}H NMR spectrum indicating the formation of the saturated four-membered ring species [^{Dip}TerP(H(Ph)CCH$_2$)AlCp*] (**8**, $\delta_{calc.}(^{31}$P$) = 98.4$ ppm) in regio-selective fashion (Scheme 4, i). Whereas **1** did not react with styrene at room temperature, **2** reacted with an excess of styrene at room temperature within 0.5 h to give [^{Tip}TerP(H(Ph)CCH$_2$)AlCp*] (**8^{Tip}Ter**; δ (^{31}P$) = 75.0 ppm; $\delta_{calc.}(^{31}$P$) = 86.3$ ppm)[20] (Scheme 4, ii). Pale yellow crystals suitable for SC-XRD experiments were obtained after evaporation of the solvent and extraction with *n*-pentane for **8** or *n*-heptane for **8^{Tip}Ter** and concentration to incipient crystallization at -30°C, which confirmed the formation of **8** (Figure S3)[20] and **8^{Tip}Ter** (Figure 5, left) as the first examples of saturated 1,2-phosphaalumates, in which the Ph-group is located on the C atom attached to P. The P–Al separation (**8** 2.3992(5), **8^{Tip}Ter** 2.4054(7) Å) is longer compared to 1,2-phosphaalumete **4** (cf. 2.3493(6) Å) and similar to that found in **5** (cf. 2.3953(12) Å). The four-membered ring is non-planar (Al–C–C–P 30.82(8) (**8**), 28.62(11)° (**8^{Tip}Ter**)) with a C–C single bond (**8** 1.5636(19), **8^{Tip}Ter** 1.572(2) Å) in the ring and acute angles within the
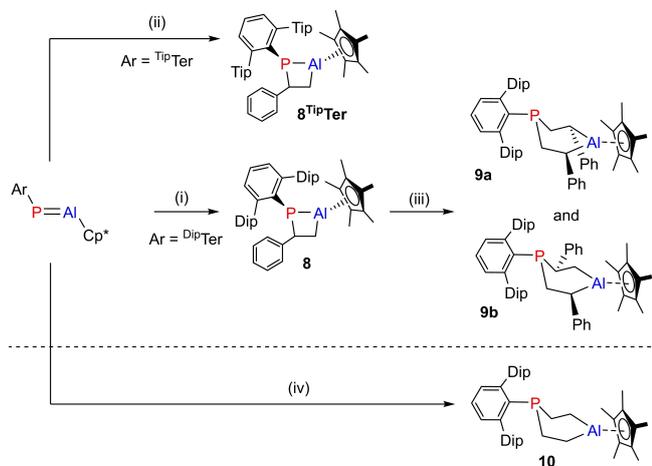
Scheme 4. Reactivity studies on **1** towards alkenes. (i) exc. styrene, C$_6$D$_6$, 80°C, 10 min; (ii) exc. styrene, C$_6$D$_6$, rt, 30 min; (iii) exc. styrene, C$_6$D$_6$, 80°C, 3 d; (iv) H$_2$C=C$_2$H, C$_6$D$_6$, rt, 15 min.
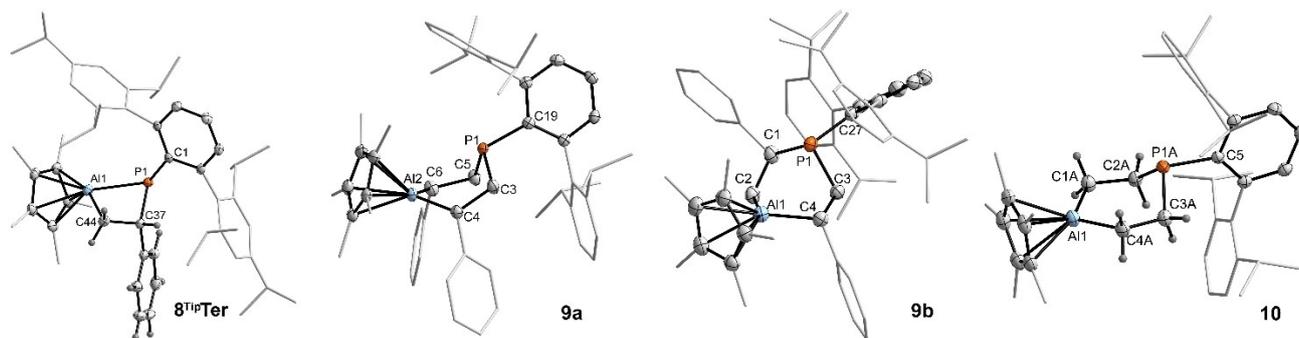

Figure 5. Molecular structures of **8^{Tip}Ter** (left), **9a** and **9b** (middle) and **10** (right). Ellipsoids drawn at 50% with C-H-atoms omitted (except some in **8^{Tip}Ter** and **10)**, Tip-, Dip- and Cp*-Me-groups rendered as wire-frame for clarity. Selected bond lengths [Å] and angles [°] **8^{Tip}Ter**: Al1–P1 2.4054(7), P1–C37 1.9153(18), Al1–C3 1.9636(19), C37–C44 1.572(2); C37–P1–Al1 72.01(6), P1–Al1–C44 79.18(6), P1–C37–C44 106.69(12), Al1–C44–C37 92.61(11); P1–C37–C44–Al1 28.62(11). **9a**: Al1–P1 2.9546(7), P1–C3 1.8445(14), P1–C5 1.8500(14), Al2–C4 2.0430(14), Al2–C6 1.9980(16), C3–C4 1.5565(19), C5–C6 1.543(2); C3–P1–C5 100.70(7), C3–P1–C19 108.38(6), C5–P1–C19 103.31(6), C6–Al2–C4 108.20(6); C5–P1–C3–C4 $-65.33(11)$, C5–C6–Al1–C4 $-28.86(12)$, C3–C4–Al1–C6 48.45(12). **9b**: Al1–P1 3.0754(7), P1–C1 1.8604(18), P1–C3 1.8563(18), Al1–C2 1.9896(19), Al1–C4 2.0217(19), C1–C2 1.571(3), C3–C4 1.546(2); C3–P1–C27 97.48(8), C3–P1–C1 100.84(8), C1–P1–C27 112.27(8), C2–Al1–C4 103.03(8) ; C1–P1–C3–C4 $-93.58(13)$, C2–Al1–C4–C3 21.16(14), C1–C2–Al1–C4 $-60.47(16)$. **10**: Al1–P1 A 3.3870(7), P1 A–C5 1.8659(17), P1–C2 A 1.840(2), P1–C3 A 1.842(2), Al1–C1 A 1.981(2) [1.93(5)], Al1–C4 A 1.992(3) [2.00(4)], C1 A–C2 A 1.552(3) [1.61(6)], C3 A–C4 A 1.544(3) [1.60(4)]; C2 A–P1 A–C3 A 100.46(9), C2 A–P1 A–C5 106.43(8), C3 A–P1–C5 103.34(8), C1 A–Al1–C4 A 109.07(11); C4 A–C3 A–P1–C5 173.58(15), C1 A–C2 A–P1 A–C3 A 77.49(16), C3–C4–Al1–C6 48.45(12).

ring at P (**8** 71.55(4), **8^{TipTer}** 72.01(6)°) and Al (**8** 78.98(4), **8^{TipTer}** 79.18(6)°). These distorted highly strained rings suggested that addition of a second molecule of styrene should be feasible and when heating the reaction mixture of **1** and an excess of styrene for 72 h the appearance of new signals in the $^{31}P\{^1H\}$ NMR spectrum at −10.4, −19.3 and −20.9 ppm indicated insertion of a second styrene unit into the P–Al bond with three different regio-isomers being formed (Scheme 4, iii). After removal of the solvent and recrystallization from *n*-pentane two of these regio-isomers were structurally authenticated by means of SC-XRD experiments, showing formation of the 6-membered 1,4-aluminaphosphorinane species **9a** and **9b** (Figure 5, middle). In **9a**, both of the Ph groups are situated at the C atom attached to Al and both are oriented below the almost planar AlC$_4$ unit, with an Al–P separation of 2.9546(7) Å. Based on calculations of the ^{31}P NMR shift in the gas phase **9a** was assigned to the species at −19.3 ppm ($\delta_{calc.}(^{31}P)$ = −19.1 ppm, Table 1). In **9b** the six-membered ring is considerably more distorted with one of the Ph groups attached to the C at Al and P, respectively. Both Ph-groups in **9b** are in-plane with the AlC$_4$P ring with an Al–P distance of 3.0754(7) Å and this species was assigned to the resonance at −10.4 ppm in the $^{31}P\{^1H\}$ NMR spectrum ($\delta_{calc.}(^{31}P)$ = −11.5 ppm, Table 1). Considering the different conformers of cyclohexane,[35] **9a** is best described as a half-chair-conformer, whereas **9b** adopts a twist-boat conformation. Consequently, the Al–P separation in **9a** and **9b** differs significantly. Attempts to separate **9a** and **9b** and the third regio-isomer from the reaction mixture in pure form have so far been unsuccessful. Nevertheless, it is shown that conformational differences provide a tool to modify the Al–P separation in 1,4-aluminaphosphorinanes as a potential dial to tailor their reactivity.

With acetylene the formation of the 1,4-phosphaaluminabarrelene **6** was observed and we therefore tested the reactivity towards ethylene. Exposure of **1** to an atmosphere of ethylene resulted in the loss of the characteristic purple color after 15 min at room temperature and the formation of the 1,4-aluminaphosphorinane [^{Dip}TerP(H$_2$CCH$_2$)$_2$AlCp*] (**10**) was observed (Scheme 4, iv), which was confirmed by ^{31}P NMR spectroscopy ($\delta_{exp.}(^{31}P)$ = −7.9 ppm, $\delta_{calc.}(^{31}P)$ = −1.4 ppm)[20] as well as by SC-XRD experiments (Figure 5, right). The molecular structure of **10** shows a half-chair conformation for the 1,4-AlPC$_4$ ring with an Al–P distance of 3.3871(7) Å and C–C distances of 1.551(3) and 1.558(4) Å in the AlC$_4$P ring. The Al atom is bent out of the C1–C2–C4–C5 plane by −14.4°, with the P atom being above that plane. The P atom is in a trigonal pyramidal environment ($\Sigma(\angle P3)$ = 310.03 °) and the Cp*-ring at Al is η^5-coordinated. When keeping the reaction mixture under an C$_2$H$_4$ atmosphere for an extended period of time, a new signal was detected in the ^{31}P NMR spectrum, indicating that further addition of C$_2$H$_4$ might be possible and could give rise to the formation of a saturated 1,4-phosphaaluminabar-relane, which will be the subject of future studies. The formation of **10** was again probed theoretically at the DLPNO-CCSD(T)/def2-TZVPP//PBE0-D3/def2-SVP level of theory (Figure 6). These investigations showed that **10** is formed in an exergonic reaction ($\Delta_R G$ = −71.7 kcal mol^{-1}).

Again starting from a reactant complex (RC), in which ethylene is oriented towards the P atom in **1** (which remains nearly unperturbed) through weak H-bonding, ethylene first forms a loose adduct with the Al=P unit (Al–C 2.77, P–C 2.72, P–Al 2.24 Å) in TS1 with the Al–P multiple bond slightly elongated, to eventually form a 1,2-phosphaalumate akin to **8** and **8^{TipTer}** as the first intermediate (IM1, Figure 6). The second molecule H$_2$C=C$_2$H again interacts with the P atom in IM1 through a weak H-bond (IM1′), and in a low-barrier step (ΔG = 9.9 kcal·mol^{-1}, TS2), in which the Al–P bond widens significantly (Al–P 2.46 Å) in a rather unsymmetric AlPC$_2$ ring (Al–C 2.36, P–C 2.86 Å), the 1,4-
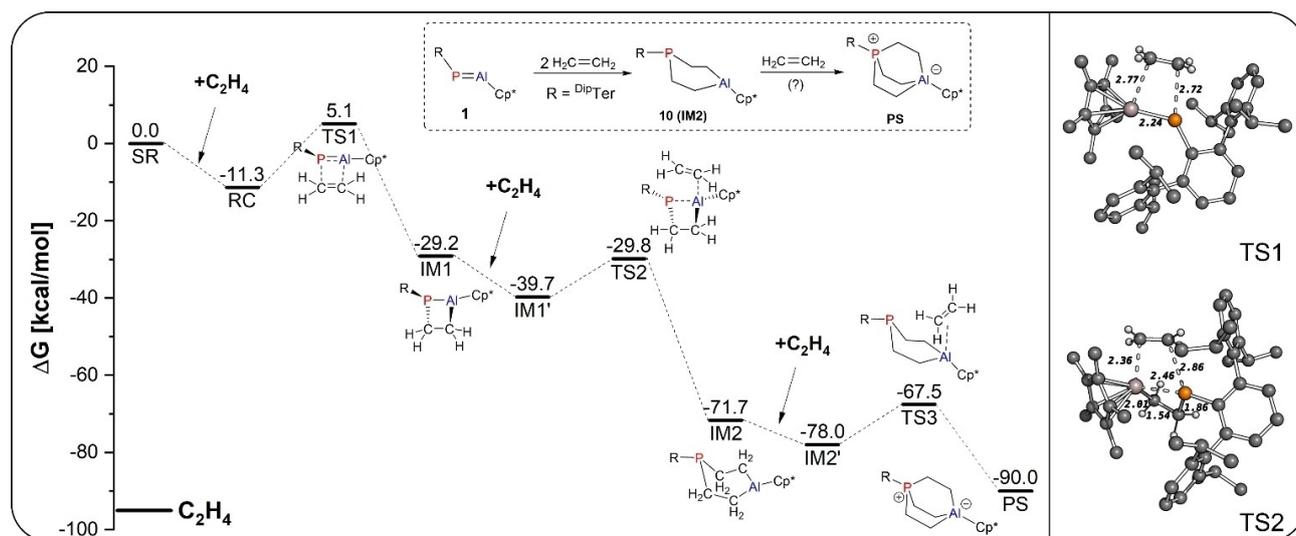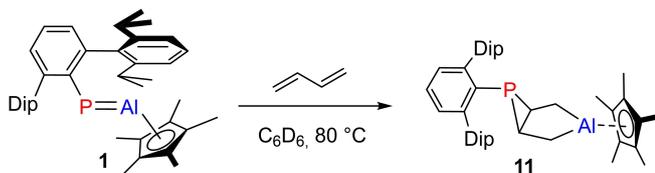

Figure 6. Free energy profile of the reaction of **1** with ethylene to give **10** (IM2) calculated at the DLPNO-CCSD(T)/def2-TZVPP//PBE0-D3/def2-SVP level of theory.

aluminaphosphorinane **10** with a saturated AlC₄P-ring is formed as the final product (IM2). The addition of a third ethylene was found to be exergonic by −18.3 kcal mol⁻¹ with respect to **10**. However, this third addition is associated with a barrier of 10.5 kcal mol⁻¹, which might explain why **10** is the major product of the reaction with ethylene at room temperature.

In a last series of experiments, we tested the reactivity of **1** towards 1,3-butadiene to elucidate the effect of a conjugated double-bond system (Scheme 5). Combination of **1** with an excess of a 15 wt% solution of 1,3-butadiene in hexane in C₆D₆ and heating to 80 °C over a period of 20 min gave a pale-yellow solution, which showed the formation of a new species in the ³¹P{¹H} NMR spectrum at −183.9 ppm, which indicated the formation of a species with a phosphirane unit (cf. (*t*BuC)₃PCH(Ph)CH₂ δ(³¹P) = −170.4 ppm).[36]

Evaporation of the solvent and recrystallization from a saturated *n*-pentane solution at −30 °C afforded crystals for SC-XRD experiments and the formation of bicyclic compound **11** (Figure 7), containing both a cycloaluminapentane and phosphirane unit was confirmed. The five-membered cycloaluminapentane unit is minimally folded along the C3–C6 axis (16.7(2) °) and the plane of the three-membered phosphirane-ring is bend away from the planar C3–C4–C5–C6 unit by 109.49(18) °. The Cp*-substituent on Al is η⁵-coordinated, with Al–C distances ranging from 2.199(12) to 2.294(10) Å. The P atom is in a trigonal

pyramidal coordination environment (Σ(∢P) = 255.54(8)°), with an acute C4–P2–C5 angle (48.47(9)°) in the phosphirane unit, indicating significant ring strain. The Al–P distance is 3.2631(20) Å, which is similar to the one observed in **10** and should in principle allow addition of other substrates along the Al–P axis following a FLP-type reactivity. FLPs based on P and Al have attracted considerable attention and pioneering work by Zargarian has paved the way for P/Al-FLPs to be applied in a variety of stoichiometric and catalytic activation reactions of small molecules.[37]

Mechanistically the formation of **11** might proceed via two pathways, however, initial formation of an aluminacyclopentene in a [4+1] cycloaddition involving only Cp*Al, akin to reports by Crimmin and co-workers,[38] which then reacts with the free phosphinidene in a [2+1] cycloaddition can be excluded based on experimental observations. Protasiewicz and co-workers had shown earlier that the phosphinidene ᵀⁱᵖTer–P, generated upon irradiation of ᵀⁱᵖTerP(PMe₃),[19] attacked the ᵀⁱᵖTer-moiety to give a phosphafluorene.[39] In the case of **11** there are no indications for the formation of a phosphafluorene and thus a different mechanism is suggested. Based on theoretical studies, the initial pre-organization of 1,3-butadiene and **1** through H-bonding with the P atom (RC, Figure 8), which then migrates to form a π-complex with aluminum through one of the conjugated double bonds (TS1), with a barrier of 12.9 kcal mol⁻¹. Through this transition state the first intermediate (IM1), a 1,2-phosphaalumate with a tangling double bond in vinylic position, is formed in a strongly exergonic

Scheme 5. Reactivity of **1** towards 1,3-butadiene giving bicyclic compound **11**.
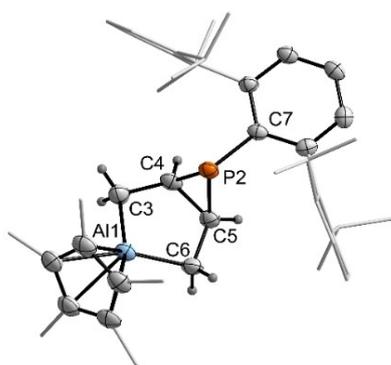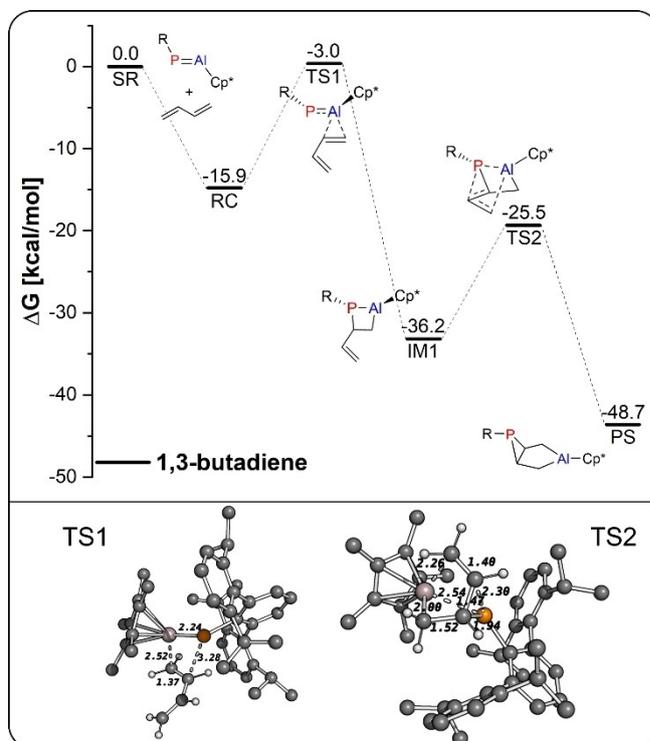

Figure 7. Molecular structure of **11**. Ellipsoids drawn at 50% with C-*H*-atoms omitted (except those on C3-C6), Dip- and Cp*-Me-groups rendered as wire-frame for clarity. Selected bond lengths [Å] and angles [°]: Al1–P1 3.2631(20), P2–C4 1.852(2), P2–C5 1.856(2), P2–C7 1.8395(18), Al1–C3 1.992(2), Al1–C6 1.977(2), C3–C4 1.518(3), C5–C6 1.517(2); C4–P2–C5 48.47(9), C4–P2–C7 104.34(8), C5–P2–C7 102.73(8), C6–Al2–C3 94.33(9); C5–P1–C3–C4 −65.33(11), Al1–C3–C4–P1 −57.85(16), Al1–C3–C4–C5 16.7(2).

Figure 8. Free energy profile of the formation of **11** (PS) starting from **1** and 1,3-butadiene (SR) calculated at the DLPNO-CCSD(T)//def2-TZVPP//PBE0-D3/def2-SVP level of theory.

reaction. The final product **11** is then formed by going through a second transition state (TS2) with allylic character and an energy barrier of ca. 10.7 kcal mol^{-1}, in line with the facile formation of **11** at 80 °C.

Conclusion

In this study we have systematically studied the reactivity of phosphalumene **1** towards alkynes and alkenes and have in part compared it to the reactivity of ^{Tip}TerPAlCp* (**2**), which is the second example of a phosphaalumene. With the sterically demanding alkynes Pip_2C_2 and Ph_2C_2 the first examples of 1,2-phosphaalumetes **4** and **5** were synthesized. Surprisingly, **2** reacted considerably faster with Ph_2C_2 to give **5^{Tip}Ter**, showing the influence of the terphenyl substituent in phosphaalumenes. A completely different outcome was observed with acetylene, which gave threefold insertion into the P=Al-bond and afforded the unique 1,4-phosphaalumi-nabarrelene **6**. Theoretical studies point to the Lewis acidic Al atom playing an important role in the activation of acetylene prior to insertion, to give the barrelene as the thermodynamically favored product. With Me$_3$SiCCH barrelene **7** was obtained, however, in this case the Al center now carries an ethynyl-substituent, through removal of the Cp*-substituent by protonation. This observation should prove crucial to access differently substituted 1,4-phosphaalumina-barrelenes through functionalization of the Cp*-group. With styrene the saturated four-membered rings **8** and **8^{Tip}Ter**, 1,2-phosphaalumates were afforded. Whereas **8** only formed at 80 °C, **8^{Tip}Ter** was readily obtained at room temperature. **8** was shown to be susceptible for the insertion of a second styrene unit at elevated temperatures, giving the two regio-isomers of 1,4-aluminaphosphorinanes **9a** and **9b**. With ethylene the formation of the 1,4-aluminaphosphorinane **10** was detected and theoretical studies show that the addition of a third equivalent of ethylene to give a saturated 1,4-phosphaluminabarrelane should be possible. Attempts to access the saturated congener of barrelene **6** are currently underway. Lastly, with 1,3-butadiene the bicyclic system **11** comprising an aluminacyclopentane and a phosphirane unit was afforded, which proceeded in a two-step reaction according to computational studies, excluding the intermediate formation of a free phosphinidene. Considering the presence of Lewis acidic and basic centers in these Al,P ring systems the reactivity towards small molecules is currently investigated.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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