

Main Group Chemistry

Cyclo-Dipnictadialanes

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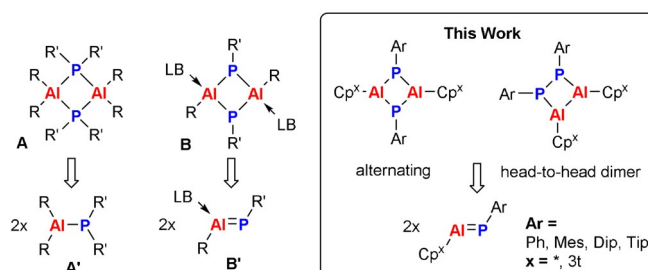
Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 80th birthday

Abstract: Using the Al^I precursor Cp^{3t}Al in conjunction with triphosphiranes (PAr)₃ (Ar = Mes, Dip, Tip) we have succeeded in preparing Lewis base-free cyclic diphosphadialanes with both the Al and P atoms bearing three substituents. Using the sterically more demanding Dip and Tip substituents the first 1,2-diphospha-3,4-dialuminacyclobutanes were obtained, whereas with Mes substituents [Cp^{3t}Al(μ-PMes)]₂ is formed. This divergent reactivity was corroborated by DFT studies, which indicated the thermodynamic preference for the 1,2-diphospha-3,4-dialuminacyclobutane form for sterically more demanding groups on phosphorus. Using Cp^{3t}Al we could extend this concept to the corresponding cyclic diarsadialanes [Cp^{3t}Al(μ-AsAr)]₂ (Ar = Dip, Tip) and additionally add the phosphorus variants [Cp^{3t}Al(μ-PAr)]₂ (P = Mes, Dip, Tip). The reactivity of one variant [Cp^{3t}Al(μ-PPh)]₂ towards NHCs was tested and resulted in double NHC-stabilised [Cp^{3t}(iPr)₂Al(μ-PPh)]₂.

Introduction

Heterocycles composed of phosphorus and the group 13 elements have been first reported by Davidson and Brown, who accidentally synthesised the trimer of Me₂Al–PMe₂ (Type A', Scheme 1), [Me₂AlPMe₂]₃.^[1] A growing interest in the use of single-source precursors for metalorganic chemical vapor deposition (MOVCD), for making group 13/15 semi-conducting materials, sparked the development of cyclic heteroatomic group 13/15 compounds. Among the early examples, Cowley and Jones reported the aluminium and gallium cycles [iBu₂AlP(H)SiPh₃]₂ (Type A, Scheme 1)^[2] and [Me₂GaP*t*Bu₂]₂,^[3] respectively. In these systems both phosphorus and the group 13 element are four-coordinate, and these are therefore the dimers of the respective phosphinoalanes and -gallanes. Pioneering work by Scheer et al. has

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Scheme 1. Known Al/P ring systems (A and B) and their respective monomers (A' and B') (left). Two potential dimers of phosphoaluminanes investigated in this study (right).

revealed that the parent phosphinoalane H₂Al–PH₂ can be intercepted by using Lewis bases (LB) and Lewis acids (LA) on aluminium and phosphorus, respectively.^[4] Dehydrogenative trimerisation in CH₂Cl₂ solution afforded the six-membered species [(CO₅W)P(H)–Al(H)NMe₃]₃, which transforms into a bicyclic species upon further loss of H₂.^[5] By judicious choice of a sterically demanding (kinetically stabilising) LB, e.g., IDip₂ = (HCNDip)₂C, Dip = 2,6-*i*Pr₂C₆H₃, the first only LB-stabilised parent compounds IDip₂-H₂EPhH₂ (E = Al, Ga; Pn = P,^[6] As^[7]) have recently been realised. In general, dimeric species of the type [R₂Al–PR'₂]₂ (A, Scheme 1) are obtained by condensation reactions. The driving force in these reactions is the formation of volatile by-products with thermodynamically stable bonds (e.g., H₂, alkanes, silanes, halosilanes).^[8] In particular, the extrusion of H₂ takes advantage of the protic and hydridic nature of the P–H^{δ+} and Al–H^{δ-} bonds, respectively.^[9]

In contrast, the formally doubly bonded pnictatrielenes RE=PnR' (E = Al, Ga; Pn = P, As, Sb) have eluded facile synthesis until recently. Phospha- and arsaaluminanes were

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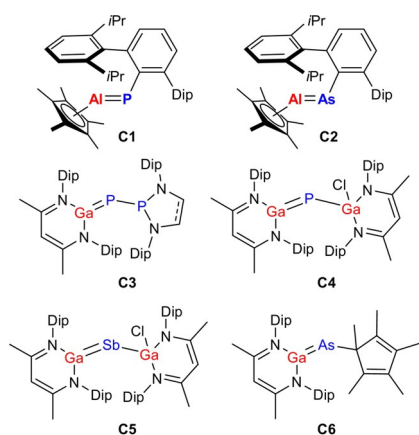
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prepared using a Cp^*Al for PMe_3 exchange starting from the pnicta-Wittig reagents $^{\text{Dip}}\text{TerPnPMe}_3$ ($^{\text{Dip}}\text{Ter} = 2,6\text{-Dip}_2\text{C}_6\text{H}_3$, $\text{Pn} = \text{P, As}$) and $(\text{Cp}^*\text{Al})_4$ to give $^{\text{Dip}}\text{TerPnAlCp}^*$ ($\text{Pn} = \text{P}$ (**C1**), As (**C2**), Scheme 2) as base-free monomeric compounds.^[10] The corresponding phosphagallenes were synthesised using phosphanyl- or gallaphosphaketenes in the reaction with $(^{\text{Dip}}\text{Nacnac})\text{Ga}$ ($^{\text{Dip}}\text{Nacnac} = \text{HC}[\text{C}(\text{Me})\text{NDip}]_2$) facilitating CO cleavage and formation of $[(\text{S})\text{P}]=\text{P}=\text{Ga}(^{\text{Dip}}\text{Nacnac})$ ($[(\text{S})\text{P}] = (\text{H}_n\text{CNDip})_2\text{P}$; $n = 1, 2$) (**C3**, Scheme 2),^[11] or $(^{\text{Dip}}\text{Nacnac})\text{Ga}=\text{P}=\text{Ga}(\text{Cl})(^{\text{Dip}}\text{Nacnac})$ (**C4**, Scheme 2),^[12] respectively. The arsagallene $(^{\text{Dip}}\text{Nacnac})\text{Ga}=\text{AsCp}^*$ (**C6**, Scheme 2) was obtained when Cp^*AsCl_2 was reacted with two equiv of $(^{\text{Dip}}\text{Nacnac})\text{Ga}$.^[13] Moreover, the stibagallene $(^{\text{Dip}}\text{Nacnac})\text{Ga}=\text{Sb}=\text{Ga}(\text{Cl})(^{\text{Dip}}\text{Nacnac})$ (**C5**, Scheme 2) has been reported.^[14] In all these doubly bonded species the E–Pn (E = Al, Ga; Pn = P, As, Sb) multiple bond is highly polarised towards the group 15 element.

Due to their Lewis-acidic group 13 centre and electron-rich pnictogen centre, E–Pn multiple bonds are prone to oligomerisation. LB-stabilised variants of cyclo-1,3-diphospha-2,4-dialanes (**B**, Scheme 1), formally the dimers of LB-coordinated $\text{RP}=\text{AlR}'$ (**B'**, Scheme 1), are known and were synthesised from silyl-substituted phosphanes $\text{R}_3\text{Si}-\text{PH}_2$ and H_3AlNMe_3 , giving after dehydrocoupling the four-membered heterocycle $[\text{RPAIH}(\text{NMe}_3)]_2$ ($\text{R} = \text{Si}^i\text{BuPh}_2$, $i\text{Pr}_3\text{Si}$, Me_2 ($i\text{PrMe}_2\text{C}$)Si). Attempts to generate the NHC-adduct of the corresponding phosphaalumene ($\text{RP}=\text{Al}(\text{NHC})\text{H}$) by addition of a free carbene to the four-membered ring resulted in base-exchange and formation of the respective bis-carbene adducts $[\text{RPAIH}(\text{NHC})]_2$ ($\text{NHC} = (\text{HCN}i\text{Pr})_2\text{C}$, $i\text{Pr}_2$).^[15] The reaction of Mes^*AlH_2 ($\text{Mes}^* = 2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2$) with H_2EPh (E = P, As) in a 1:1 ratio at 160 °C afforded under H_2 -elimination the trimers of $\text{Mes}^*\text{Al}=\text{EPh}$ (Mes^*AlPPh)₃ and $(\text{Mes}^*\text{AlAsPh})_3$,^[16] respectively, which are formal heavier analogues of borazine. Four-membered 1,3-diphospha-2,4-diboretanes, the boron congeners of **B** (Scheme 1), have been reported,^[17] mostly originating from unsuccessful attempts to access monomeric $\text{RP}=\text{BR}$ species.^[18] These phosphorus–boron heterocycles contain pyramidalised phosphorus atoms, making them potential ligands for transition metals.^[17e,19] The related ring systems $[\text{RE}(\mu\text{-PR}')_2]_2$ (E = B,^[20] $\text{R} = t\text{Bu}$, $\text{R}' = i\text{Pr}$; E = Al,^[21] $\text{R} = \text{Pr}t\text{Bu}_2$, $\text{R}' = t\text{Bu}$) with formally three



Scheme 2. Known base-free pnictatrielenes (**C1–C6**).

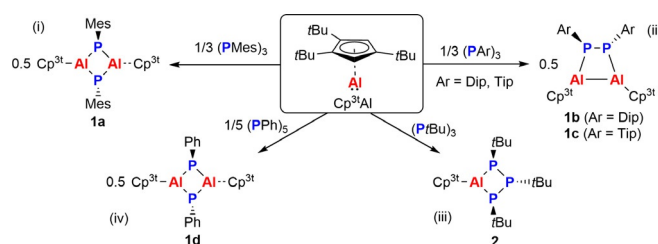
coordinate B and Al centres, respectively, have been shown to be biradicals. The cyclo-1,3-dipnicta-2,4-dialanes in which the group 13 centre is not stabilised by a Lewis-base have eluded facile synthesis to date. Herein, we close this gap and show that using cyclo-tripnictanes of the type Pn_3Ar_3 ($\text{Pn} = \text{P}$,^[22] As ;^[23] $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, Mes ; Dip ; $2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2$, Tip) in conjunction with the Al^{I} synthons $(\text{Cp}^*\text{Al})_4$ ^[24] and Cp^3Al ($\text{Cp}^3 = 1,2,4\text{-}t\text{Bu}_3\text{C}_5\text{H}_2$)^[25] four-membered heterocycles with group 13 and 15 centres bearing three substituents, respectively, become synthetically feasible. Interestingly, two distinct forms were obtained, for example, the expected cyclo-1,3-dipnicta-2,4-dialanes $[\text{Cp}^*\text{Al}(\mu\text{-PnAr})]_2$ ($x = *$, $3t$) and the head-to-head dimers 1,2-diphospha-3,4-dialuminacyclobutanes. The experimental findings were corroborated by DFT-studies shedding light on the divergent reactivity of differently substituted precursors.

Results and Discussion

Diphosphadialanes from Cp^3Al and $(\text{PR})_3/(\text{PAr})_3$

Triphosphiranes $(\text{PR})_3$ and cyclo-oligophosphanes are, in general, the formal oligomers of phosphinidenes.^[26] Especially $(\text{PhP})_3$ has been shown to react with NHCs to give NHC phosphinidene adducts of the type $\text{NHC}=\text{PPh}$,^[27] by formal phosphinidene transfer. We thus hypothesised that the combination of three equiv of Cp^3Al with $(\text{ArP})_3$ ($\text{Ar} = \text{Mes}$, Dip , Tip) would facilitate formation of $\text{Cp}^3\text{Al}=\text{PAR}$, which might exist either in its monomer form or as a dimeric cyclo-diphosphadialane (Scheme 3).

At first, we monitored the reaction of $(\text{MesP})_3$ with three equiv of Cp^3Al in C_6D_6 at room temperature.^[28] This resulted in an initial colour change to orange and after a few minutes a yellow solution was obtained, which showed one signal in the ^{31}P NMR spectrum at $\delta(^{31}\text{P}) = -174.3$ ppm and full consumption of $(\text{MesP})_3$ was noted. In the ^1H NMR spectrum four characteristic signals were detected in the alkyl region, indicative of a Mes to Cp^3Al ratio of 1:1. X-ray quality crystals of this compound were grown from a saturated toluene solution at -30 °C and confirmed the formation of $[\text{Cp}^3\text{Al}(\mu\text{-PMe}_3)]_2$ (**1a**). It needs to be pointed out that **1a** precipitates from C_6D_6 solutions after 30 minutes, therefore precluding collection of satisfactory ^{13}C NMR data. We therefore switched to more polar NMR solvents, but even using $\text{C}_6\text{D}_5\text{Br}$ the compound could not be redissolved. We next turned to $(\text{DipP})_3$ and $(\text{TipP})_3$, with bulkier aryl groups. When



Scheme 3. Reactivity of the alanedyl Cp^3Al towards triphosphiranes (reactions i, ii, and iv) and a cyclo-pentaphosphane (iii).

combining the respective triphosphirane with three equiv of $\text{Cp}^{\text{st}}\text{Al}$, a gradual colour change of the reaction mixture to orange was observed, accompanied by the precipitation of a microcrystalline red solid. In both cases broad, unresolved multiplet resonances at ca. -117 ppm were detected in the ^{31}P NMR spectrum. Recrystallisation of the red microcrystalline solid from C_6H_6 ($\text{Ar}=\text{Dip}$) or slow evaporation of a saturated toluene solution ($\text{Ar}=\text{Tip}$) afforded X-ray quality crystals, which showed that $[\text{Cp}^{\text{st}}\text{AlPAr}]_2$ ($\text{Ar}=\text{Dip}$ (**1b**), Tip (**1c**)) had formed, although in this case the first 1,2-diphospha-3,4-dialuminacyclobutanes were obtained. This is reminiscent of the reactivity of two equiv of $^{\text{Dip}}\text{TerGa}$ with $\text{TolN}=\text{NTol}$ ($\text{Tol}=4\text{-Me-C}_6\text{H}_4$), giving the corresponding 1,2-diaza-3,4-digallacyclobutanes $[\text{Dip}^{\text{TerGaNTol}}]_2$.^[29] This was rationalised by initial addition of ArGa to give a three-membered N_2Ga ring system followed by insertion of a second ArGa , which then affords $[\text{Dip}^{\text{TerGaNTol}}]_2$. Consequently, diphosphenes were considered to be potential intermediates in the formation of **1b** and **1c**. In a related study we have shown that $(\text{TipP})_2$ reacted with $\text{Cp}_2\text{Ti}(\text{btmsa})$ to give the corresponding formal diphosphene complexes $[\text{Cp}_2\text{Ti}(\text{P}_2\text{Tip}_2)]$ selectively.^[22] Moreover, we have recently shown that the diphosphene $\text{DipP}=\text{PDip}$ can be obtained in the PEt_3 -catalysed reductive coupling reaction of DipPBr_2 using Zn as a sacrificial reductant.^[30] We therefore treated $(\text{DipP})_2$ with two equiv of $\text{Cp}^{\text{st}}\text{Al}$ and noted an immediate colour change of the reaction mixture to deep orange, and the formation of **1b** was ascertained by detection of the broad ^{31}P NMR resonance at $\delta(^{31}\text{P}) = -117$ ppm, as well as by cell determination of X-ray quality crystals precipitating from the reaction mixture. Similarly to **1a**, comprehensive characterisation of **1b** and **1c** by multi-nuclear NMR spectroscopy is hampered by its poor solubility in common NMR solvents, such as C_6D_6 , C_7D_8 , thf-d_8 or even $\text{C}_6\text{D}_5\text{Br}$. LIFDI-MS studies showed the expected molecular ion peaks. **1a-c** crystallise in the triclinic space group $P\bar{1}$ with two molecules in the unit cell (Figure 1).^[28] **1a** is situated on a crystallographically imposed

centre of inversion, resulting in a central Al_2P_2 rectangle with alternating P and Al atoms and P–Al distances of 2.3176(7) and 2.3317(7) Å, respectively, which agrees well with the six-membered species $(\text{Mes}^*\text{AlPPh})_3$ [cf. $d_{\text{avg.}}(\text{Al-P}) = 2.328(3)$ Å].^[16] The angles at aluminium [$90.11(2)^\circ$] and phosphorus [$89.89(2)^\circ$] are nearly identical and the Mes groups on P are *trans*-oriented with respect to the Al_2P_2 plane. The $\text{Al-C}_{\text{Cp}^{\text{st}}}$ distances range from 2.2455(17) to 2.3584(18) Å, which renders the Cp^{st} group η^5 -coordinated. In contrast to **1a**, **1b** and **1c** show a puckered 1,2- P_2 -3,4- Al_2 four-membered ring which is folded along the $\text{Al1}\cdots\text{P2}$ axis by ca. 17° . The P–P [**1b** 2.1677(9) Å; **1c** 2.1676(4) Å] bonds are contracted and closer to a single bond [cf. $(\text{DipP})_2$ 2.0293(7); $(\text{TipPBr})_2$ 2.2402(8)]. In contrast the Al–Al distances [**1b** 2.6947(11) Å; **1c** 2.6933(5) Å] are rather long [cf. $[\text{Al}(\text{CH}(\text{SiMe}_3)_2)_2]$ 2.660(1) Å,^[31] $(\text{Cp}^{\text{st}}\text{AlBr})_2$ 2.586(3) Å, $(^{\text{Dip}}\text{TerAl})_2(\text{CSiMe}_3)_2$ 2.4946(9) Å] and almost equidistant P1–Al1 and P2–Al2 bonds [**1b** 2.4057(9), 2.4090(9) Å; **1c** 2.4090(5), 2.3977(5) Å] are detected within the ring. The Dip and Tip substituents are *trans*-oriented with respect to the P_2 -unit [$\angle(\text{C}_{\text{Ar}}\text{-P-P-C}_{\text{Ar}})$ **1b** 94.31° ; **1c** 93.73°], which agrees well with the structure of $[\text{Dip}^{\text{TerGaNTol}}]_2$ [$\angle(\text{C}_{\text{Tol}}\text{-N-N-C}_{\text{Tol}})$ 77.5°].^[29] The angles at P within the four-membered ring are larger than 90° [**1b** $94.96(3)$, $94.66(3)$; **1c** $93.617(13)$, $96.732(13)^\circ$], while the angles at Al are rather acute [**1b** $82.58(3)$, $82.47(3)$; **1c** $81.798(13)$, $83.846(13)^\circ$].

In order to investigate the bonding situation of these distinct three-coordinate phosphorus–aluminium heterocycles, we conducted DFT calculations for **1a** and **1b** at the PBE0-D3(BJ)/def2-SVP level of theory.^[34] For **1a**, the Mayer bond orders of the P–Al bonds are ca. 0.88,^[35] indicating that no double bond character is found for these bonds, in agreement with the X-ray data. Charge analyses reveal that the phosphorus atoms are partially negative, whereas the aluminium centres are positive. Accordingly, natural bond orbital (NBO)^[36] and intrinsic bond orbital (IBO)^[37] calculations indicate that the Al–P bonds are polarised to

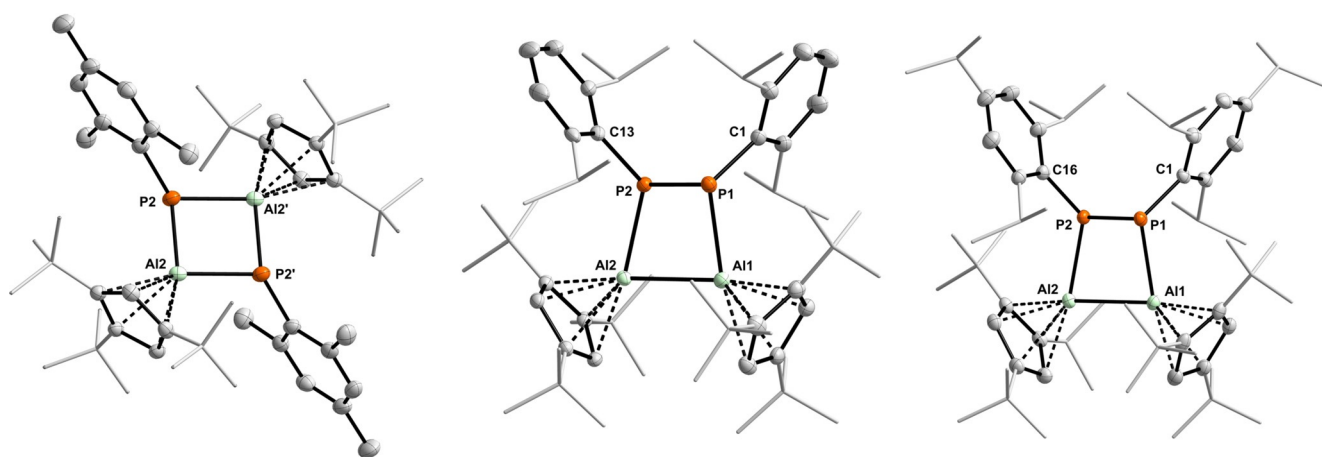


Figure 1. Molecular structures of **1a**, **1b**, and **1c**. ORTEPs drawn at 50% probability. For clarity, all H atoms have been omitted and the alkyl groups on the Cp^{st} , Dip, and Tip substituents have been rendered as wireframe. Selected bond lengths (Å) and angles ($^\circ$) of **1a**: P2–Al2 2.3176(7), P2–Al2' 2.3317(7); Al2–P2–Al2' $90.11(2)$, P2–Al2–P2' $89.89(2)$; **1b**: P1–P1 2.1677(9), Al1–P1 2.4057(9), Al2–P2 2.4090(9), Al1–Al2 2.6947(11); P2–P1–Al1 $94.66(3)$, P1–P2–Al2 $94.96(3)$, P1–Al1–Al2 $82.58(3)$, P2–Al2–Al1 $82.47(3)$; **1c**: P1–P1 2.1676(4), Al1–P1 2.4090(5), Al2–P2 2.3977(5), Al1–Al2 2.6933(5); P2–P1–Al1 $93.617(13)$, P1–P2–Al2 $96.732(13)$, P1–Al1–Al2 $83.846(13)$, P2–Al2–Al1 $81.798(13)$.

phosphorus (see Figure S41). The HOMO of **1a** is composed majorly by contributions at the phosphorus centres, while the LUMO is located mainly on the π system of the Mes substituents (Figure 2, left). At the PBE0-D3(BJ)/def2-SVP level of theory, the HOMO–LUMO gap of **1a** is 4.50 eV.

According to the Mayer bond order calculations, P–P (1.06) and Al–Al (0.86) single bonds are found in **1b**, supporting the attribution based on the crystal structures. The HOMO of **1b** is composed of a linear combination of the phosphorus lone pairs, while the LUMO is located at the π space of the Al–Al motif (Figure 2, right). The HOMO of **1b** is destabilised by ca. 0.7 eV in comparison to that of **1a**, while the LUMO is stabilised by ca. 0.5 eV. As a consequence, the HOMO–LUMO gap of **1b** (3.25 eV) is significantly smaller than that of **1a**. This indicates that the alternating Al_2P_2 heterocycle is more stable than its head-to-head counterpart if steric hindrance caused by the substituents is negligible, which is confirmed by further calculations (see below).

We then set out to test alkyl-substituted cyclo-oligophosphanes as phosphinidene source to determine the influence of the P substituent. When $(\text{PrBu})_3$ ^[38] was treated with three equiv of Cp^{Al} (Scheme 3, reaction iii), a new species with an AX_2 spin system was detected in the ^{31}P NMR spectrum ($\delta(^{31}\text{P}) = 76.1, -60.6$ ppm; $J_{\text{PP}} = 210.6$ Hz) and in the ^1H NMR spectrum unreacted Cp^{Al} was detected as well, indicating the formation of the four-membered ring $[\text{Cp}^{\text{Al}}(\text{PrBu})_3]$ (**2**). This is in analogy to the formation of $[\text{Cp}^{\text{Al}}(\text{PrBu})_3]$ ^[39] and $[(\text{SiMe}_3)_3\text{CGa}(\text{PrBu})_3]$ ^[40] which are formed in a ring-expansion reaction starting from $(\text{PrBu})_3$ and the respective E(I) source. Using cyclo-pentaphosphane (PPh_5), the reaction with five equiv of Cp^{Al} gave rise to the formation of a new species with a ^{31}P NMR signal at $\delta(^{31}\text{P}) = -130.6$ ppm and a Ph to Cp^{Al} ratio of 1:1 according to ^1H NMR spectroscopy (Scheme 3, reaction iv). The formulation as the 1,3-diphospha-2,4-dialane $[\text{Cp}^{\text{Al}}(\mu\text{-PPh})_2]$ (**1d**) was corroborated by X-ray analysis of crystals grown by slow

evaporation of a saturated C_6H_6 solution of **1d**. The metrical parameters of **1d** are nearly identical with **1a** and the Ph rings are *trans*-oriented with respect to the Al_2P_2 plane. The AlP_3 ring in **2** is minimally folded along the $\text{P1}\cdots\text{P3}$ axis by ca. 10.7° with an all-*trans* orientation of the *t*Bu groups at phosphorus and an η^5 -coordinated Cp^{Al} ring on aluminium. The P–Al distances [$\text{P1}-\text{Al1}$ 2.3764(11), $\text{P3}-\text{Al1}$ 2.3829(12)] are minimally longer than in $[\text{Cp}^{\text{Al}}(\text{PrBu})_3]$ [2.359(1), 2.360(1) Å]^[39] indicating the influence of the sterically more demanding Cp^{Al} group. Consequently, the fold angle in **1d** is smaller than in $\text{Cp}^{\text{Al}}(\text{PrBu})_3$ [18.7°].^[39]

Dipnictadialanes from Cp^{Al} and $(\text{PAr})_3$

We next investigated whether Cp^{Al} , generated from $(\text{Cp}^{\text{Al}})_4$ at 80°C ,^[24a,41] would show a reactivity like Cp^{Al} . Firstly, $(\text{PAr})_3$ was combined with 0.75 equiv of $(\text{Cp}^{\text{Al}})_4$ in C_6D_6 and the mixtures were heated to 80°C overnight resulting in colourless solutions (Scheme 4). Analysis by ^{31}P NMR spectroscopy revealed full conversion of the starting triphosphiranes and species with a singlet at $\delta(^{31}\text{P}) = -208.2$ (Ar = Mes), -230.6 (Ar = Dip) and -231.6 ppm (Ar = Tip) were detected. In the ^1H NMR spectrum one sharp signal for the Cp^{Al} group, indicating η^5 -coordination, and signals for the aryl groups were detected in a 1:1 ratio. It needs to be noted that for **3a–c** the aryl groups can rotate freely on the NMR time-scale, as evident from a minimal set of signals in the ^1H NMR spectrum (e.g., no splitting observed for the *o*-Me groups (**3a**) or the *o*-iPr groups (**3b–c**)). After evaporation of the solvent and extraction with *n*-hexane, X-ray quality crystals were obtained from concentrated filtrate solutions at -30°C . In all three cases the base-free 1,3-diphospha-2,4-dialanes $[\text{Cp}^{\text{Al}}(\mu\text{-PAr})_2]$ (Ar = Mes **3a**, Dip **3b**, Tip **3c**; Figure 3, left; Table 1) had formed. **3a–c** crystallise in the triclinic spacegroup $P\bar{1}$ with one molecule in the unit cell, with the Al_2P_2 ring being situated on a centre of inversion. In agreement with **1a** and **1d**, the central planar Al_2P_2 ring is a parallelogram with two distinct Al–P distances [**3a** 2.3218(16), 2.3226(15); **3b** 2.3068(11), 2.3448(12); **3c** 2.3099(6), 2.3395(6) Å] and the angles at P [**3a** 86.06(4); **3b** 89.00(3); **3c** 91.205(18)] and Al [**3a** 93.94(4); **3b** 91.00(3); **3c** 88.796(19)] deviate minimally from 90° . The phosphorus atoms are trigonal pyramidally coordinated, even though a considerable degree of planarisation is observed according to the sum of angles at P [**3a** 326.01; **3b** 334.60; **3c** 332.816°].

Four-membered Al_2As_2 heterocycles are rare and, for example, the butterfly-shaped cyclic species $[(\text{Et}_3\text{N})\text{ClAl}(\mu\text{-AsSi}(\text{CMe}_2\text{iPr})\text{Me}_2)]_2$ ^[42] and $[(\text{Me}_3\text{N})\text{HAl}(\mu\text{-AsR})_2]$ (R =

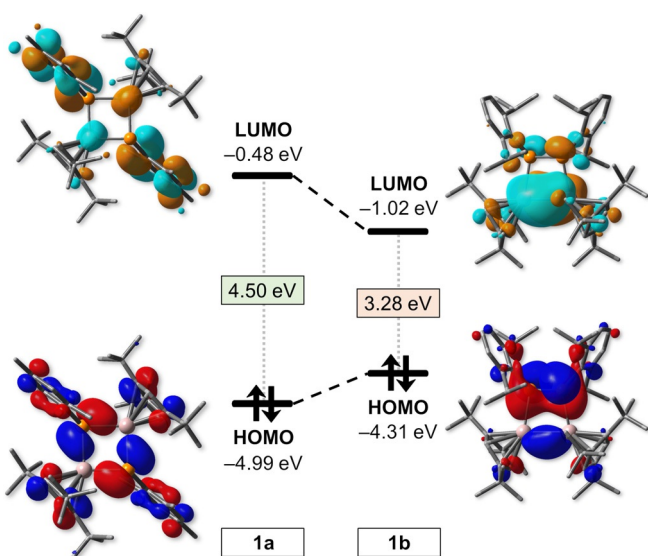
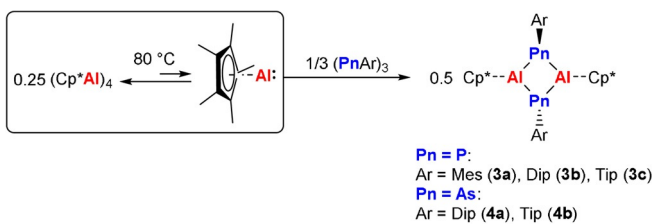


Figure 2. Canonical Kohn–Sham molecular orbitals of **1a** and **1b** at the PBE0-D3(BJ)/def2-SVP level of theory. Isovalues: 0.03 a.u.



Scheme 4. Reactivity of Cp^{Al} towards aryl-substituted cyclotripnic-tanes giving $[\text{Cp}^{\text{Al}}(\mu\text{-PnAr})_2]$ (Pn = P, **3a–c**; Pn = As, **4a–b**).

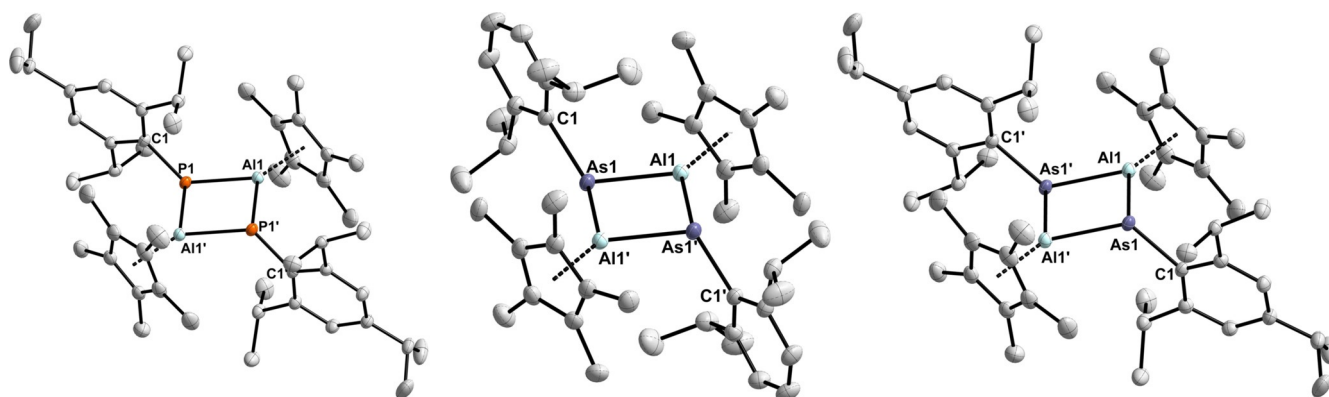


Figure 3. Molecular structures of **3c** (left), **4a** (middle), and **4b** (right). ORTEPs drawn at 50% probability. All H atoms have been omitted and the η^5 -coordination mode of Cp* is indicated by a dotted line from Al to the centroids of the Cp ring. Selected bond lengths (Å) and angles ($^\circ$) are summarised in Table 1.

Table 1: Selected bond lengths and angles of the Cp*-substituted ring systems **3a–c**, **4a**, and **4b**.

	3a	3b	3c	4a	4b
Pn1–Al1 [Å]	2.3218(16)	2.3068(11)	2.3099(6)	2.4106(8)	2.4160(5)
Pn1–Al1' [Å]	2.3226(15)	2.3448(12)	2.3395(6)	2.4462(16)	2.4445(5)
Al1–Pn1–Al1' [$^\circ$]	86.06(4)	89.00(3)	91.205(18)	87.27(5)	86.990(15)
Pn1–Al1–Pn1' [$^\circ$]	93.94(4)	91.00(3)	88.796(19)	92.73(5)	93.009(15)
$\Sigma(\angle, \text{Pn})$ [$^\circ$]	326.01	334.60	332.816	328.51	324.49

Stability of Diphosphadialanes from DFT Calculations

In this section, we analyse the steric and electronic factors dictating the preferential formation of Al_2P_2 (alternating or head-to-head) and AlP_3 heterocycles based on thermodynamic arguments. All calculations were performed at the SMD(solvent = benzene)^[45]/PBE0-D3(BJ)/def2-TZVP^[34] level of theory from gas-phase-optimised structures at the PBE0-D3(BJ)/def2-SVP level (see SI for more details).

Our experiments revealed that, while an alternating Al_2P_2 ring is formed from Cp^3tAl and $(\text{PAr})_3$ (Ar = Mes), a head-to-head Al_2P_2 structure is achieved if sterically more demanding Ar groups (Dip, Tip) are used. The relative free energies of **1a**, **1b**, and their unobserved isomers, $[\text{Cp}^3\text{tAlPMe}_3]_2$ and $[\text{Cp}^3\text{tAl}(\mu\text{-PDip})]_2$, respectively, are shown in Figure 4a. The head-to-head compound **1b** (Ar = Dip) is 27.7 kcal mol⁻¹ more stable than its alternating isomer $[\text{Cp}^3\text{tAl}(\mu\text{-PDip})]_2$.

This indicates that for sterically more demanding substituents, the thermodynamic reaction product is the head-to-head isomer, and its isomerization to the alternating structure is thermodynamically unfavoured. However, if sterically less demanding substituents at the phosphorus atoms are used, such as Mes, the alternating isomer becomes the thermodynamic product (for Ar = Mes, a free energy of 18.6 kcal mol⁻¹ favouring the alternating isomer is found). These results are in excellent agreement with the experimental findings, revealing that thermodynamic reasoning is already enough to predict the preference of head-to-head or alternating isomers during the course of the reaction. Another important experimental finding is that the reaction of Cp^3tAl with $(\text{PR})_3$ (R = *t*Bu) leads to an AlP_3 heterocycle, while an alternating Al_2P_2 system is formed if R = Mes. In order to explain this distinct reactivity profile, in Figure 4b we compare the free energy of reaction leading to compounds $[\text{Cp}^3\text{tAl}(\mu\text{-PMes})]_2$ (**1a**, Scheme 3, reaction i), $[\text{Cp}^3\text{tAl}(\mu\text{-PrBu})]_3$ (**2**, Scheme 3, reaction iii), and to the corresponding species $[\text{Cp}^3\text{tAl}(\text{PMes})_3]$ and $[\text{Cp}^3\text{tAl}(\mu\text{-PrBu})]_2$. Our results show that for both R groups,

SiPr_3 , $\text{SiMe}_2(\text{CMe}_2\text{iPr})$ ^[43] have been described in which the arsenic centre is three-coordinate and the aluminium centre is four-coordinate due to Lewis-base adduct formation. Other examples with four-coordinate Al and As centres have been synthesised by the Power group through the combination of the kinetically stabilised primary alane $\text{Me}^{\text{es}}\text{TerAlH}_2$ with liquid PhAsH_2 in the bulk phase, giving $[\text{Me}^{\text{es}}\text{Ter}(\text{H})\text{Al}(\text{As}(\text{H})\text{Ph})_2]$ ^[44] In analogy to the synthesis of **3a–c** we reasoned that aryl-substituted cyclo-triarsanes $(\text{AsAr})_3$ (Ar = Dip, Tip)^[23] would give base-free cyclo-diarsadialanes in the reaction with $(\text{Cp}^*\text{Al})_4$ and combination of both in a 4:3 ratio in C_6D_6 and heating to 80 $^\circ\text{C}$ overnight afforded colourless solutions that showed ^1H NMR spectra, which are similar to those of **3b** and **3c**. X-ray quality crystals grown from saturated *n*-hexane solutions at -30 $^\circ\text{C}$ showed that $[\text{Cp}^*\text{Al}(\mu\text{-AsAr})]_2$ (Ar = Dip **4a**, Tip **4b**) had indeed formed. **4a** and **4b** are colourless solids, which crystallise in the triclinic space group $P\bar{1}$, with one molecule on a crystallographically imposed centre of inversion in the unit cell (Figure 3, middle, right; Table 1). Again, the central $[\text{Al}(\mu\text{-As})]_2$ ring is best described as a parallelogram with different As–Al distances [**4a** 2.4106(8), 2.4462(16); **4b** 2.4160(5), 2.4445(5)] and intra-ring angles at arsenic smaller than 90 $^\circ$ [**4a** 87.27(5); **4b** 86.990(15) $^\circ$] and wider angles on aluminium [**4a** 92.73(5); **4b** 93.009(15) $^\circ$], with the arsenic atoms being considerably planarised [$\Sigma(\angle, \text{As})$ **4a** 328.51; **4b** 324.49 $^\circ$]. This agrees well with the six-membered species $(\text{Mes}^*\text{AlAsPh})_3$ reported by Power and co-workers [cf. $d_{\text{avg}}(\text{Al}(\text{As})) = 2.430(5)$ Å; $\Sigma(\angle, \text{As}) = 319.7(3.0)^\circ$].^[16]

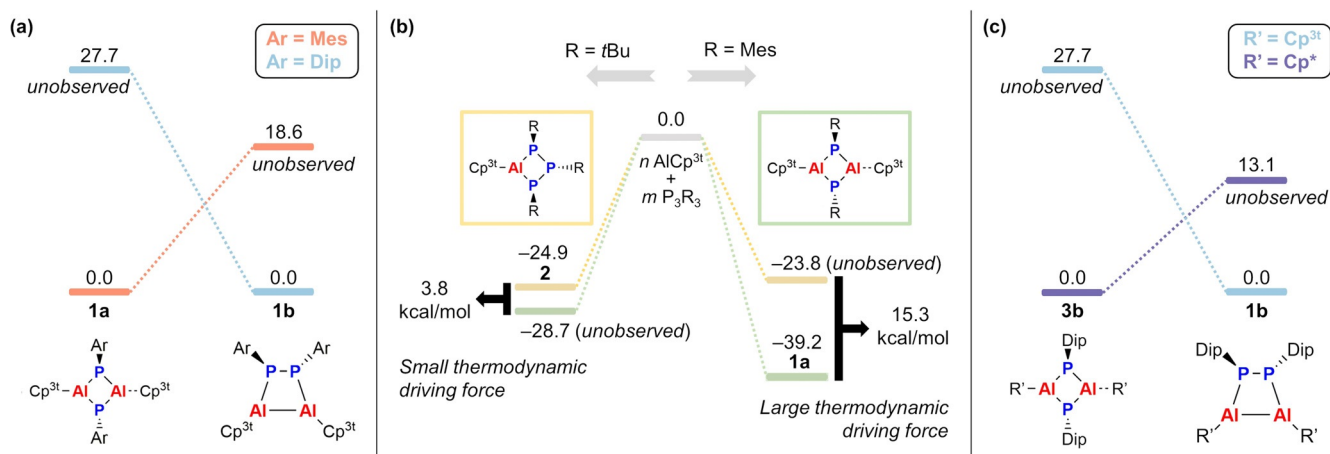


Figure 4. Thermodynamic profiles of the distinct phosphorus–aluminium heterocycles depicted in this work. a) Comparison of the alternating $[\text{Cp}^{\text{3t}}\text{Al}(\mu\text{-PAR})_2]$ and head-to-head $[\text{Cp}^{\text{3t}}\text{AlPAR}]_2$ structures for $\text{Ar} = \text{Mes}$, Dip . b) Comparison of the free energies of reaction forming the $[\text{Cp}^{\text{3t}}\text{Al}(\text{PR})_3]$ and $[\text{Cp}^{\text{3t}}\text{Al}(\mu\text{-PR})_2]$ ($\text{R} = t\text{Bu}$, Mes) heterocycles. c) Comparison of the alternating $[\text{R}'\text{Al}(\mu\text{-PDip})_2]$ and head-to-head $[\text{R}'\text{AlPDip}]_2$ structures for $\text{R}' = \text{Cp}^{\text{3t}}$, Cp^* . All energies are in kcal mol^{-1} .

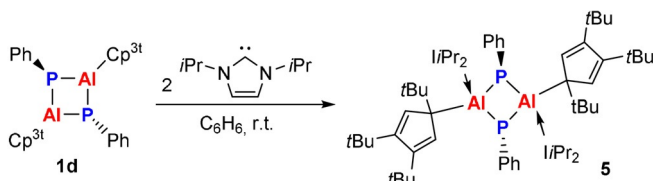
the alternating Al_2P_2 heterocycle is the thermodynamic product. However, in the case of $\text{R} = \text{Mes}$, a larger thermodynamic driving force for forming the alternating Al_2P_2 system is found, as the free energy difference between the two reactions is ca. 15 kcal mol^{-1} . Conversely, the free energy difference for $\text{R} = t\text{Bu}$ is merely 4 kcal mol^{-1} . These results indicate that steric factors are responsible for the distinct reactivity patterns observed for different R groups, with the sterically demanding $t\text{Bu}$ groups precluding the formation of alternating Al_2P_2 heterocycles by decreasing their stabilities in comparison to the AlP_3 system, presumably the first intermediate formed after interaction of $\text{Cp}^{\text{3t}}\text{Al}$ and $(\text{PR})_3$.

Finally, we also performed DFT calculations to investigate the reactivity trends observed in our experiments if the Cp^*Al species is considered. As shown in Scheme 4, if Cp^*Al is used, the alternating $[\text{Cp}^*\text{Al}(\mu\text{-PR})_2]$ isomer is found for $\text{R} = \text{Mes}$, Dip , Tip , whereas for Cp^{3t} the head-to-head $[\text{Cp}^{\text{3t}}\text{AlPDip}]_2$ isomer is found for $\text{R} = \text{Dip}$, Tip . The relative free energies of the diphosphadialane systems with $\text{R} = \text{Dip}$ and $\text{Cp}^{\text{3t}}\text{Al}$ and Cp^*Al fragments are shown in Figure 4c. Our results indicate that while **1b** is preferred over its alternating isomer if $\text{R} = \text{Dip}$, reduction of the steric demands in the Al substituents inverts the free energy trends, with the head-to-head $[(\text{Cp}^*\text{Al})_2(\text{PDip})_2]$ isomer lying $13.1 \text{ kcal mol}^{-1}$ above **3b**. Similarly to the previous cases, steric demands on the substituents drastically influence the free energy trends of the corresponding heterocycles, ultimately dictating the reactivity profile of the diphosphadialane systems studied herein. The preferred products from the reactions depicted in this work are effectively predicted by thermodynamic reasoning.

Reactivity of Diphosphadialanes with Lewis Bases

Lewis-base-stabilised dipnictadialanes have been described,^[15,43] and as an entry, **1d**, with a rather small Ph group on the phosphorus atoms, was combined with two equiv of the

NHC IiPr_2 ($\text{IiPr}_2 = (\text{HCN}i\text{Pr})_2\text{C}$). The ^{31}P NMR spectrum showed one new species at $\delta(^{31}\text{P}) = -123.3 \text{ ppm}$, which is minimally deshielded compared to **1d** and indicates formation of the bis-NHC adduct $[\text{Cp}^{\text{3t}}(\text{IiPr}_2)\text{Al}(\mu\text{-PPh})_2]$ (**5**, Scheme 5), which was corroborated by X-ray analysis of crystals grown from slow evaporation of a C_6H_6 solution (Figure 5). The molecular structure revealed that IiPr_2 is coordinated to Al and in *trans*-arrangement with respect to the Al_2P_2 ring resulting in a haptotropic shift from η^5 to η^1 of the Cp^{3t} group.^[46] This is reminiscent of the cluster compound $[(\text{Cp}^*\text{Al}(\text{IME}_4))(\mu, \eta^3: \eta^4\text{-P}_5)\text{FeCp}^*]$ with an η^1 Cp^* group on aluminium, which displays an $\text{Al}\text{-C}_{\text{NHC}}$ distance [$2.017(6) \text{ \AA}$] shorter than those of **5** [$2.100(2)$, $2.083(2)$].^[47] In the related compound $[(\text{IiPr}_2)\text{HAL}(\mu\text{-PSiPh}_2t\text{Bu})_2]$ the NHCs are in a *cis*-arrangement.^[15] Surprisingly, one of the ring phosphorus atoms is now in a nearly planar coordination environment ($\Sigma(\angle\text{P}2) = 347.87^\circ$), whereas the other is now closer to an ideal trigonal pyramidal coordination environment ($\Sigma(\angle\text{P}1) = 299.83^\circ$). This is accompanied by deformation of the formerly planar near-rectangular Al_2P_2 ring, which is now folded by ca. 16° along the $\text{P}1\cdots\text{P}2$ axis giving a butterfly structure, in accord with $[(\text{IiPr}_2)\text{HAL}(\mu\text{-PSiPh}_2t\text{Bu})_2]$. The $\text{Al}\text{-P}$ bonds show a pair of longer [$\text{Al}3\text{-P}4$ $2.4206(6)$, $\text{Al}1\text{-P}4$ $2.4009(5) \text{ \AA}$] and shorter [$\text{P}2\text{-Al}1$ $2.3371(7)$, $\text{P}2\text{-Al}3$ $2.3335(5) \text{ \AA}$] bonds, with the shorter distances to the more planar phosphorus atom. The molecular structure would imply two chemically and magnetically distinct phosphorus atoms and, consequently, a set of two doublets in the ^{31}P NMR spectrum.



Scheme 5. Reaction of **1d** with the NHC IiPr_2 , giving rise to the formation of the bis-NHC adduct **5**.

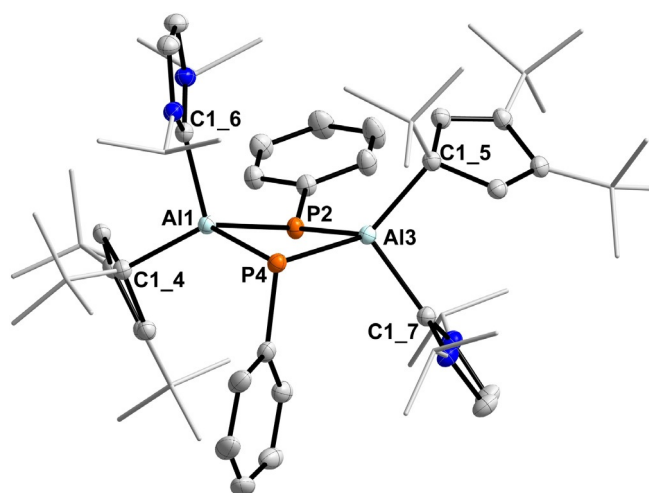


Figure 5. Molecular structure of **5**. ORTEPs drawn at 50% probability, all H atoms omitted and alkyl substituents on Cp^{3t} and iPr₂ rendered as wireframe. Selected bond lengths (Å) and angles (°) of **5**: P2–Al1 2.3371(7), P2–Al3 2.3335(5), Al3–P4 2.4206(6), Al1–P4 2.4009(5), P2–C1 1.825(2), P4–C1 1.846(2), Al1–C1_4 2.084(1), Al3–C1_5 2.092(1), Al1–C1_6 2.100(2), Al3–C1_7 2.083(2); Al1–P2–Al3 91.49(2), P2–Al3–P4 87.98(2), Al3–P4–Al1 87.87(2), P4–Al1–P2 88.37(2), Al1–P2–C1 128.61(6), Al1–P4–C1 104.08(5).

Thus, a solution of **5** in [D₈]toluene was cooled to –80 °C, which resulted in splitting of the singlet resonance at room temperature into two doublets at $\delta(^{31}\text{P}) = -122.6$ and -129.7 ppm ($J_{\text{pp}} = 67.1$ Hz). This indicates rapid exchange in solution between the phosphorus positions at room temperature, but even at lower temperatures, as a significant deshielding of the planarised P atom would be expected.

Conclusion

Pnictaalumenes are characterised by alternating Lewis acidic group 13 and electron-rich group 15 atoms, which results in a propensity to oligomerise. To date the corresponding cyclo-dipnictadialanes have only been synthesised as their Lewis base adducts. Herein, we show that using cyclo-tripnictanes (ArPn)₃ (Ar = Mes, Dip, Tip; Pn = P, As) in conjunction with Cp^xAl ($x = *, 3t$) afforded the first examples of base-free cyclo-dipnictadialanes. With small aryl substituents on the pnictogen, Cp^{3t}Al (**1a**, **1d**) and with Cp^{*}Al (**3a–c**, **4a–b**) in all cases the rings with alternating P and Al atoms [Cp^xAl(μ-PnAr)]₂ are thermodynamically favoured. Interestingly, the head-to-head-connected 1,2-diphospha-3,4-dialuminacyclobutanes, **1b** and **1c**, are preferred when both the substituents on phosphorus and aluminium are sterically demanding. This study clearly demonstrates (i) the potential of cyclo-tripnictanes as building blocks to implement PnAr units into unusual small molecules and (ii) that base-free cyclo-dipnictadialanes are synthetically feasible by judicious choice of the substituents on aluminium and the pnictogen. Studies on the reactivity of the ring systems presented in here with respect to their potential to act as a source of the monomeric pnictaalumenes are currently underway.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: aluminium · carbene ligands · main group elements · phosphorus · small ring systems

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