

Stabilised $(H_2)Al-E(H)R$ species, $E = P$ or As , $R^- = C(SiMe_3)_2(6-Me-2-pyridyl)^-$

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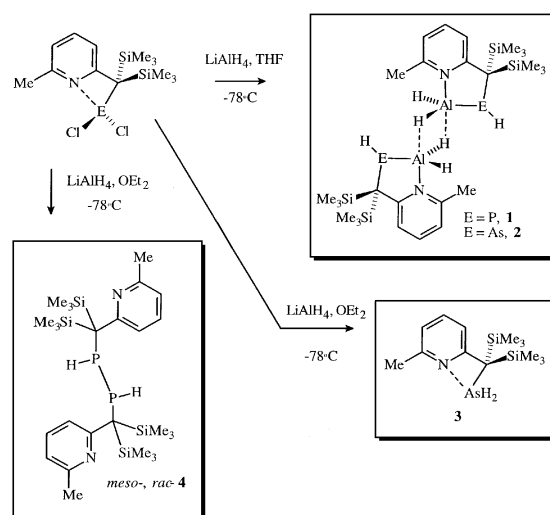
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Reaction of $RECl_2$ ($R^- = C(SiMe_3)_2(6-Me-2-pyridyl)^-$, $E = P$ or As) with $LiAlH_4$ in THF affords directly bonded aluminium hydride–pnictide hydride complexes as weakly associated hydride bridged dimers, $[RE(H)-Al(H)_2]_2$; a strong solvent dependency of these reactions, which had previously been observed with the formation of the dissecondary diphosphane in Et_2O ($E = P$), is further confirmed by the formation of $RAsH_2$ from $RAsCl_2$ and $LiAlH_4$ in Et_2O .

Compounds containing group 13–15 bonds are of interest as potential precursors to group 13–15 ceramic and semiconductor materials.^{1,2} Access to the class of compounds possessing aluminium(III) to phosphorus(III) or arsenic(III) bonds has mainly involved dehydrosilylation reactions of $E(SiMe_3)_3$ with lithium aluminium hydride, $LiAlH_4$,³ or the trimethylamine adduct of alane, H_3AlNMe_3 ,¹ affording $(Et_2O)_2Li\{\mu-E(SiMe_3)_2\}_2AlH_2$, $[H_2Al\{\mu-P(SiMe_3)_2\}_3]$ and $[H_2AlAs(SiMe_3)_2(NMe_3)]$. Analogous compounds with gallium to phosphorus or arsenic bonds have similarly been prepared.^{4,5} Another approach to making compounds with group 13–15 bonds where the metal has exclusively hydrido anionic ligands, other than the simple Lewis base adducts MH_3 ,^{6–9} is transmetalation involving $H_2(X)MPCy_3$ and $LiPCy_2(THF)_m$, $Cy =$ cyclohexyl, $M = Ga$, $X = Cl$,¹⁰ $M = In$, $X = H$.⁹ All the aforementioned phosphide and arsenide compounds are based on secondary phosphines or arsines, the pnictide bearing two substituents, either a trimethylsilyl group or a C-centred ligand. The prospect of forming dihydrido metal complexes based on primary phosphines and arsines is a synthetic challenge because of the likely propensity of spontaneous elimination of hydrogen and formation of polymeric material, although we have noted in earlier studies that secondary amine adducts of alane can be stabilised by the bulk of the amine ligand itself; 2,2,6,6-tetramethylpiperidine forms a stable Lewis base adduct with alane,⁶ as does $H\{N(SiMe_3)_2\}$ for which the adduct is a distillable liquid.⁷

Our approach in gaining access to dihydridoaluminium(III) compounds based on primary phosphide and arsenide species, $(H_2)Al-P/As(H)R$, is to incorporate a bulky alkyl group bearing an N-donor centre on the pnictide, notably $(6-Me-2-pyridyl)(SiMe_3)_2C^- (= R^-)$, which has been shown to stabilise unusual bonding configurations, as has the related ligand, $C(2-(SiMe_3)_2(2-pyridyl))^-$, allowing access to a range of new compounds.^{11–17} The combined steric hindrance of R^- coupled with the N-donor group has the tendency to reduce the degree of aggregation of the target species. In this context its noteworthy that $[H_2Al\{\mu-P(SiMe_3)_2\}_3]$ is trimeric whereas the NMe_3 adduct of the arsenic analogue is monomeric, $[H_2Al-As(SiMe_3)_2(NMe_3)]$.¹ Herein we report the synthesis of the first alane compounds based on primary phosphine and arsenine moieties, and also the synthesis of a primary arsine, $RAsH_2$, and its structure determination, a first for this class of compound.

The new phosphide and arsenide compounds, $(H_2)Al-P/As(H)R$, **1** (P) and **2** (As), were prepared by the reaction of $RECl_2$ with $LiAlH_4$ in THF, Scheme 1.† The choice of solvent in their synthesis is crucial. We have previously reported that



Scheme 1

the reaction of $RPdCl_2$ with $LiAlH_4$ in Et_2O affords reproducibly the dissecondary diphosphane, **4**, as a mixture of the *rac* and *meso* isomers, and not the expected dihydride species,¹² Scheme 1. In contrast we have now established that the analogous reaction of $RAsCl_2$ with $LiAlH_4$ in Et_2O does in fact result in the target dihydride species, $RAsH_2$, **3**.†

Single crystals of **1**, **2** (Fig. 1) and **3** suitable for single crystal X-ray diffraction were obtained from hexane solutions at $-30^\circ C$.‡ Compound **1** decomposes at temperatures above

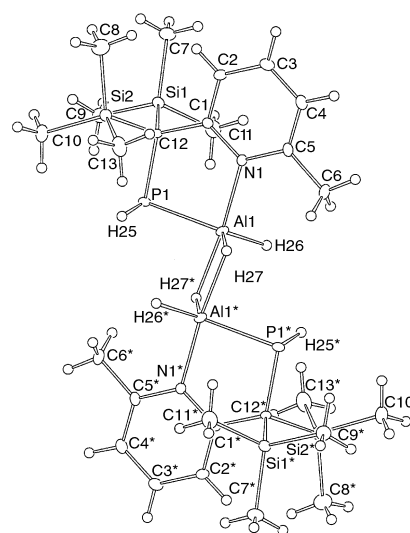


Fig. 1 Projection of $[H_2Al\{P(H)R\}]_2$, **1**. Important bond distances (Å) and angles ($^\circ$) (values for the arsenic analogue, **2**, in square brackets): Al–N 2.040(2) [2.043(1)], Al–E 2.330(1) [2.4184(5)], Al–H, 1.668, 1.633 [1.60, 1.52(20)], E–H 1.303 [1.54], E–C, 1.913(2) [2.041(2)]; N–Al–P 88.85(6) [89.96(4)], Al–E–C 96.29(8) [92.76(5)], Al–N–C 119.2(2), 120.9(2) [119.5(1), 120.5(1)], Al–E–H 94.6 [93.8].

116 °C to a dark red oil, whereas **2** melts at 206–208 °C. **3** decomposes above 50 °C, darkening in colour from yellow to orange at around 120 °C and at 160 °C it becomes dark red and gradually melts.

Complexes **1** and **2** are isostructural in the solid state (monoclinic, $P2_1/n$) and are dimeric, being weakly associated *via* metal–hydride bridging. The central feature of the two structures is the novel five membered heteroatomic rings containing Al–E bonds, with bond distances of 2.330(1) and 2.418(5) for Al–P and Al–As respectively. The P–Al bond distance is short in comparison to other alkylaluminium–phosphorus complexes, in particular 2.681(4) Å in $[(\text{Me}_3\text{C}-\text{CH}_2)_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3]$, 2.498(7) Å in $[(\text{Me}_3\text{SiCH}_2)_2(\text{Br})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3]$, 2.436(2) Å in $[(\text{Me}_3\text{SiCH}_2)_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_2]_2$,² 2.3916(16) Å and 2.4041(14) Å in $[\text{H}_2\text{AlP}(\text{SiMe}_3)_2]_3$ ¹ and 2.4001(13) Å in $[(\text{Et}_2\text{O})_2\text{Li}[\mu\text{-P}(\text{SiMe}_3)_2]_2\text{AlH}_2]$,³ a factor most likely attributable to the steric crowding around the metal centre. The Al–As bond distance is comparable to that found in $[\text{H}_2\text{AlAs}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$,¹ 2.438(2) Å, and in $[(\text{Et}_2\text{O})_2\text{Li}[\mu\text{-P}(\text{SiMe}_3)_2]_2\text{AlH}_2]$,³ 2.4934(7) Å, while it is shorter than in $[(\text{Me}_3\text{SiCH}_2)(\text{Br})\text{AlAs}(\text{SiMe}_3)_2]_2$, $[(\text{Me}_3\text{CCH}_2)_3\text{AlAs}(\text{SiMe}_3)_3]$ and $[(\text{Me}_3\text{SiCH}_2)_2\text{AlAs}(\text{SiMe}_3)_2]_2$ which have Al–As bond distances of 2.505(3) Å, 2.72(2) Å and 2.567(2) Å respectively. For **1** and **2**, the H atom on E and the bridging H on Al are coplanar; however, in geometrical terms they point away from each other, and at 3.185 Å, **1**, and 3.263 Å, **2**, there is no significant interaction. The non-bridging H on Al and the H on E point away from each other in **1** and **2**.

Despite many attempts we have been unable to obtain a satisfactory refinement for the crystals of RAsH_2 , **3**, as we have for **1** and **2**. This is due to an inherent twinning disorder and as such the *R*-factor converged at 18%. Although this prejudices discussion on bond distances and angles within the crystal lattice, it is evident that the As centre is involved in a planar four membered chelate with the pyridine ring, through a $\text{N}\cdots\text{As}$ interaction, similar to that observed in RECl_2 . Complex **3** is the only arsenic dihydride complex to exhibit N–As connectivity. Given the thermal instability of arsenic hydride it is not surprising that only four other AsH_2 complexes have been structurally characterised^{18–20} in the solid state, and these have been stabilised through attachment either to a transition metal, *e.g.* $[\text{Ir}(\text{CO})\text{Cl}(\text{Pet}_3)_2(\text{AsH}_2)]$,¹⁸ or to silicon in $[(2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2)(\text{tBu})\text{Si}(\text{AsH}_2)_2]$.²⁰

In order to assess the potential of complexes **1** and **2** as possible single source precursors for CVD the solids were slowly heated *in vacuo* to 200 °C which resulted in decomposition to an orange solid for **1** and a black solid for **2**. Microprobe analysis on the decomposed solids showed an approximate 1 : 1 ratio for Al : P for **1**, but not so for the As : Al ratio for **2**, which was 1 : 26. There was also evidence of a high percentage of Si present in the samples, indicating that decomposition *via* β -hydrogen transfer to form an intermediate $\text{HAL}=\text{ER}$, followed by β -hydrogen elimination of HR, is not evident. While it appears that compounds **1** and **2** are not a direct route to aluminium phosphide and arsenide, a new class of compounds has been established, and the ability of N-functionalised donor alkyl ligands to stabilise an unusual bonding configuration is noteworthy; extending the work to other donor alkyl ligand systems (group 15 and 16), and to the heavier group 13 elements is a synthetic challenge.

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Notes and references

† All ¹H and ¹³C NMR spectra were referenced internally to *d*₆-benzene. ³¹P NMR was referenced to a 5% solution of H_3PO_4 .

Synthesis of $[\text{H}_2\text{Al}\{\text{P}(\text{H})\text{R}\}]_2$, **1**: LiAlH_4 0.44 g, 11.57 mmol, thf 30 ml, $\text{R}'\text{PCl}_2$ 1.85 g, 5.26 mmol (yield 42%). Mp > 116 °C (decomp). ¹H NMR (400 MHz, C_6D_6 , 298 K): δ 0.15 (18H, s, SiMe_3), 1.63, 2.18 (1H, d, ¹*J*_{PH} 164 Hz), 2.49 (3H, s, Me), 4.96 (2H, br, AlH_2), 5.97 (1H, m, H_3), 6.64 (1H, m, H_5), 7.11 (1H, m, H_4). ¹³C NMR (75.0 MHz, C_6D_6 , 298 K): δ 1.27 (SiMe_3), 24.00 (C_7), 25.76 (C_1), 120.75 (C_5), 123.97 (C_3), 138.44 (C_4), 157.48 (C_6), 170.45 (C_2). ³¹P{¹H} (162 MHz, C_6D_6 , 298 K): δ –192.20. ³¹P

(162 MHz, C_6D_6 , 298 K): δ –194.91, –192.17 (¹*J*_{PH} 164 Hz). Microanalysis: Calc. (found) C 50.13 (49.85), H 8.74 (8.74), N 4.50 (4.37%). IR (Nujol mull): Al–H 1821.6 cm^{-1} .

Synthesis of $[\text{H}_2\text{Al}\{\text{As}(\text{H})\text{R}\}]_2$, **2**: LiAlH_4 0.28 g, 7.38 mmol, thf 30 ml, $\text{R}'\text{AsCl}_2$ 1.34 g, 3.39 mmol (yield 35%). Mp 206–208 °C. NMR: (¹H, 400 MHz, C_6D_6 , 298 K): δ 0.22 (18H, s, SiMe_3), 1.84 (1H, s, As–H), 2.26 (3H, s, Me), 4.91 (2H, br, AlH_2), 6.07 (1H, m, H_3), 6.74 (1H, m, H_5), 6.96 (1H, m, H_4); (¹³C, 75.0 MHz, C_6D_6 , 298 K): δ 1.17 (SiMe_3), 24.26 (C_7), 26.45 (C_1), 120.25 (C_5), 123.75 (C_3), 138.62 (C_4), 157.46 (C_6), 169.35 (C_2). Microanalysis: Calc. (found) C 43.98 (44.10), H 7.66 (7.92), N 3.94 (4.00%). IR (Nujol mull): Al–H 1819.8 cm^{-1} , As–H 2096 cm^{-1} .

Synthesis of **3** ($\text{R}'\text{AsH}_2$): LiAlH_4 0.17 g, 4.54 mmol, Et_2O 30 ml, $\text{R}'\text{AsCl}_2$ 0.90 g, 2.27 mmol (yield 0.45 g, 60.3%). Mp > 50 °C decomp. (orange)–120 °C (red) > 160 °C (melt). NMR: (¹H, 400 MHz, C_6D_6 , 298 K): δ 0.057 (18H, s, SiMe_3), 2.43 (3H, s, Me), 3.91 (2H, br, As–H₂), 6.78 (1H, m, H_3), 6.88 (1H, m, H_5), 7.51 (1H, s, H_4); (¹³C, 75.0 MHz, C_6D_6 , 298 K): δ 1.2 (SiMe_3), 21.2 (C_7), 50.9 (C_1), 119.1 (C_5), 120.3 (C_3), 137.9 (C_4), 155.7 (C_6), 163.6 (C_2). Microanalysis: Calc. (found) C 47.68 (47.69), H 8.00 (8.26), N 4.28 (4.21%).

‡ Crystal data: $[\text{H}_2\text{Al}\{\text{P}(\text{H})\text{R}\}]_2$, **1**: $\text{C}_{26}\text{H}_{54}\text{N}_2\text{Al}_2\text{P}_2\text{Si}_4$, monoclinic, $P2_1/n$ (no. 14), $a = 9.3949(2)$, $b = 13.7790(3)$, $c = 14.2939(3)$ Å, $\beta = 99.330(2)^\circ$, $V = 1825.90(6)$ Å³, $F(000) = 648$, $D_{\text{calc}} = 1.089$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 3.14$ cm^{-1} , $0.16 \times 0.13 \times 0.39$ mm³, $Z = 2$; Enraf-Nonius CCD diffractometer, Mo-K α radiation, $T = 123$ K, 4510 unique reflections (3554 observed, $I > 2.0\sigma(I)$), $2\theta = 70.8^\circ$, $R = 0.051$, $R' = 0.057$ (sigma weights, $n = 4 \times 10^{-4}$).

$[\text{H}_2\text{Al}\{\text{As}(\text{H})\text{R}\}]_2$, **2**: $\text{C}_{26}\text{H}_{54}\text{N}_2\text{Al}_2\text{As}_2\text{Si}_4$, monoclinic, $P2_1/n$ (no. 14), $a = 9.4334(2)$, $b = 13.7645(3)$, $c = 14.4634(2)$ Å, $\beta = 99.734(1)^\circ$, $V = 1850.97(6)$ Å³, $F(000) = 744$, $D_{\text{calc}} = 1.27$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 20.00$ cm^{-1} , $0.15 \times 0.15 \times 0.40$ mm³, $Z = 4$; Enraf-Nonius CCD diffractometer, Mo-K α radiation, $T = 123$ K, 5445 unique reflections (4150 observed, $I > 3.0\sigma(I)$), $2\theta = 60.1^\circ$, $R = 0.030$, $R' = 0.030$ (sigma weights, $n = 4 \times 10^{-4}$).

$[\text{RAsH}_2]$, **3**: $\text{C}_{13}\text{H}_{26}\text{NAsSi}_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.7896(7)$, $b = 9.1611(7)$, $c = 11.7955(6)$ Å, $\alpha = 100.069(5)^\circ$, $\beta = 96.977(5)^\circ$, $V = 854.6(1)$ Å³, $F(000) = 344$, $D_{\text{calc}} = 1.272$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 21.13$ cm^{-1} , $0.12 \times 0.13 \times 0.35$ mm³, $Z = 2$; Enraf-Nonius CCD diffractometer, Mo-K α radiation, $T = 123$ K, 4208 unique reflections (3087 observed, $I > 3.0\sigma(I)$), $2\theta = 60.1^\circ$, $R = 0.183$, $R' = 0.233$ (sigma weights, $n = 4 \times 10^{-4}$).

CCDC 182/1752. See <http://www.rsc.org/suppdata/cc/b0/b003990j/> for crystallographic files in .cif format.

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