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Sterically encumbered terphenyl substituted primary pnictanes $ArEH_2$ and their metallated derivatives ArE(H)Li ($Ar = –C_6H_3$-2,6-$Trip_2$; Trip = 2,4,6-triisopropylphenyl; E = N, P, As, Sb)

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Abstract

A series of sterically crowded primary pnictanes of formula $ArEH_2$ ($Ar = C_6H_3$-2,6-$Trip_2$; $Trip = C_6H_2$-2,4,6-*i*-Pr_3; E = N, **2**; P, **4**; As, **5**; Sb, **6**) and their lithiated pnictide salts ArE(H)Li (E = N, **7**; P, **8**; As, **9**; Sb, **10**) have been synthesized and characterized by X-ray crystallography (**2-6**), NMR, IR spectroscopy, and by combustion analysis. Details of the synthesis and structures of the azide derivative ArN_3 (**1**) and the arylphosphinic acid ArP(O)(OH)H (**3**) are also given. The amine compound **2** displays a planar geometry (within the limits of experimental error) at nitrogen which is attributable to interactions between the N–H moieties and the *ortho*-aryl rings. The antimony compound **6** is a rare instance of a stable primary stibane and its X-ray crystal structure represents the first structural determination of such a species. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Pnictanes; Sterically encumbered; Lithiated pnictanes; Terphenyls; Azide; Phosphinic acid

1. Introduction

The hydrogen derivatives of the Group 15 elements (i.e. the pnictanes EH_3; E = N, P, As, Sb or Bi) display increasingly positive values for ΔG_f^o as the group is descended [1], and their decreased stabilities with increasing atomic number are consistent with this trend. Nonetheless, the bond enthalpies for the E–H bonds remain surprisingly large for the heavier group members (e.g. Sb–H = ca. 60 kcal mol^{-1}) [1,2] which suggests that their stability might be kinetically enhanced with use of large substituents. Indeed, the substitution of one or two hydrogens by bulkier organic groups is already known to increase the stability of pnictanes. For example, phenylstibane, $PhSbH_2$, decomposes at room temperature [3], whereas *t*-$BuCH_2SbH_2$ [4] and $Me_3SiCH_2SbH_2$ [5] are colorless liquids which are stable for long periods under a H_2 atmosphere at ambient temperature. Recent work has shown that sterically encumbering *m*-terphenyl substituents are particularly effective at stabilizing unusual bonding and coordination numbers in compounds of the pnictogens and many other groups in the periodic table [6]. We were therefore interested in examining the effectiveness of these substituents in stabilizing primary pnictanes. Accordingly we have prepared the pnictane series $ArEH_2$ (E = N (**2**), P (**4**), As (**5**) or Sb (**6**); $Ar = C_6H_3$-2,6-$Trip_2$, $Trip = C_6H_2$-2,4,6-*i*-Pr_3) via reduction of the corresponding azide (ArN_3, **1**) or halides [7] with $LiAlH_4$ and characterized them spectroscopically and structurally. Attempts to synthesize the primary bismuthane $ArBiH_2$ via reduction of 2,6-$Trip_2H_3C_6BiCl_2$ with $LiAlH_4$ resulted in the isolation of the previously reported dibismuthene 2,6-$Trip_2H_3C_6BiBiC_6H_3$-2,6-$Trip_2$ [7]. In addition, we report the structures of the azide ArN_3 (**1**), the precursor of **2**, and the arylphosphinic acid ArP(O)(OH)H (**3**) which results from the hydrolysis of the halide $ArPCl_2$. The generation of the monolithio salts ArE(H)Li (E = N (**7**), P (**8**), As (**9**) or Sb (**10**) by reaction with *n*-BuLi as well as the spectroscopic (^1H, ^{13}C, NMR, IR) characterization of **1**–**10** and the structural characterization of **4**–**6** are also described.

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2. Experimental

2.1. General procedures

All manipulations were carried out using modified Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from Na–K alloy and degassed immediately before use. The compounds TsN_3 [8], 2,6-$Trip_2H_3C_6Li(OEt_2)$ [9], 2,6-$Trip_2H_3C_6PCl_2$ [7], 2,6-$Trip_2H_3C_6AsCl_2$ [7], and 2,6-$Trip_2H_3C_6SbCl_2$ [7] were prepared according to literature procedures. MeLi, nBuLi and $LiAlH_4$ were purchased commercially and used as received. ^{1}H-, ^{13}C-, ^{7}Li- and ^{31}P-NMR spectra were recorded on a Bruker 300 MHz instrument and referenced to the deuterated solvent. ^{7}Li- and ^{31}P-NMR spectra were referenced to LiCl and H_3PO_4, respectively. Infrared data were recorded as Nujol mulls on a Perkin–Elmer PE-1430 instrument.

2.2. 2,6-$Trip_2H_3C_6N_3$ (**1**)

TsN_3 (1.97 g, 10 mmol) was added dropwise via syringe to a solution of 2,6-$Trip_2H_3C_6Li(OEt_2)$ (5.63 g, 10 mmol) in Et_2O (50 ml) which had been cooled to ca. − 78°C. The solution was stirred ca. 1 h and then warmed to ca. − 10°C. Further stirring (5 h) at ca. − 10°C resulted in a pale yellow solution. An aqueous solution of NaOH (30 ml, 0.01 M) was then added to decompose excess lithium reagents. The mixture was stirred overnight at room temperature (r.t.) and the organic layer was separated and dried over $MgSO_4$. Filtration and evaporation of the solvent afforded pale yellow crystals of **1**, which were suitable for X-ray crystallographic analysis. Yield 4.24 g, 81%. M.p. 174–175°C N_2 evolution; IR $\nu_{(N\text{–}N)}$ 2085 cm^{-1} vs; ^{1}H (300 MHz, $CDCl_3$) δ 1.12 (d, 12H, p-CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 1.14 (d, 12H, o-CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 1.29 (d, 12H, o-CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 2.66 (sept, 4H, o-CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 2.94 (sept, 2H, p-CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 7.05 (s, 4H, m-Trip), 7.11 (d, 2H, m-C_6H_3) $^3J_{HH} = 6.6$ Hz, 7.19 (t, 1H, p-C_6H_3) $^3J_{HH} = 6.6$ Hz; ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$) δ 23.5 (CH(CH$_3$)$_2$), 24.0 (CH(CH$_3$)$_2$), 24.5 (CH(CH$_3$)$_2$), 30.7 (o-CH(CH$_3$)$_2$), 34.3 (p-CH(CH$_3$)$_2$), 120.6 (m-Trip), 123.98 (p-C_6H_3), 130.44 (m-C_6H_3), 132.61 (p-Trip), 133.8 (o-C_6H_3), 137.0 (i-C_6H_3), 147.0 (o-Trip), 148.99 (i-Trip).

2.3. 2,6-$Trip_2H_3C_6NH_2$ (**2**)

A solution of **1** (2.65 g, 5.0 mmol) in Et_2O (50 ml) was added dropwise to a suspension of $LiAlH_4$ (1.0 g, 26.3 mmol) in Et_2O (20 ml) at ca. − 78°C. The mixture was allowed to warm to ca. 25°C and stirred ca. 2 h. The mixture was then refluxed for 5 h, and cooled to ca. − 78°C. A solution of NaOH (15 ml, 0.01 M) was added very slowly and a vigorous reaction occurred. The mixture was warmed to room temperature whereupon the grey precipitate became white. The mixture was filtered and the organic filtrate was dried over $MgSO_4$. Filtration and evaporation of the ether layer resulted in colorless crystals of **2**. Yield 1.86 g, 75%. M.p. 169–172°C; IR $\nu_{(N\text{–}H)}$ 3378, 3472 cm^{-1} vs; ^{1}H (300 MHz, $CDCl_3$) δ 1.31 (d, 12H, p-CH(CH_3)$_2$) $^3J_{HH} = 6.6$ Hz, 1.33 (d, 12H, o-CH(CH_3)$_2$) $^3J_{HH} = 6.6$ Hz, 1.51 (d, 12H, o-CH(CH_3)$_2$) $^3J_{HH} = 6.6$ Hz, 2.97 (sept, 4H, o-CH(CH$_3$)$_2$) $^3J_{HH} = 6.6$ Hz, 3.15 (sept, 2H, p-CH(CH$_3$)$_2$) $^3J_{HH} = 6.6$ Hz, 3.36 (br s, 2H, NH_2), 7.02 (t, 1H, p-C_6H_3) $^3J_{HH} = 7.2$ Hz, 7.18 (d, 2H, m-C_6H_3) $^3J_{HH} = 7.2$ Hz, 7.29 (s, 4H, m-Trip); ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$) δ 24.0 (CH(CH$_3$)$_2$), 24.1 (CH(CH$_3$)$_2$), 24.5 (CH(CH$_3$)$_2$), 30.5 (o-CH(CH$_3$)$_2$), 34.3 (p-CH(CH$_3$)$_2$), 116.93 (p-C_6H_3), 121.1 (m-Trip), 124.99 (m-C_6H_3), 129.2 (p-Trip), 133.1 (o-C_6H_3), 142.6 (i-C_6H_3), 147.5 (o-Trip), 148.2 (i-Trip).

2.4. 2,6-$Trip_2H_3C_6P(O)(OH)H$ (**3**)

A solution of 2,6-$Trip_2H_3C_6PCl_2$ (3.80 g, 6.51 mmol) in Et_2O (250 ml)was added to $LiAlH_4$ (2.50 g, 65.10 mmol) and stirred overnight. The mixture was heated to reflux (3 h), cooled to ca. 25°C and stirred for a further 8 h. Excess $LiAlH_4$ was destroyed by the careful addition of dil. HCl (80 ml) at ca. − 8°C. The mixture was warmed to r.t., and extracted with Et_2O (3 × 50 ml). The organic fractions were combined, dried over $MgSO_4$, and filtered (Celite). The solvent was removed under reduced pressure and the white residue was extracted with hexane (200 ml), filtered (Celite), and concentrated under reduced pressure to 150 ml. The precipitates were redissolved by warming, and upon cooling while standing overnight, colorless crystals of **3** were obtained. Yield 0.24 g, 7%. M.p. turns opaque at 140°C, melts at 233–237°C. IR $\nu_{(PH)}$ 2410s, $\nu_{(P=O)}$ 1460s,br cm^{-1}, ^{1}H (300 MHz, $CDCl_3$) δ 1.16 (d, 9H, CH(CH_3)$_2$) $^3J_{HH} = 6.3$ Hz, 1.28 (d, 9H, CH(CH_3)$_2$) $^3J_{HH} = 6.6$ Hz, 1.37 (d, 3H, CH(CH_3)$_2$) $^3J_{HH} = 7.2$ Hz, 1.38 (d, 9H, CH(CH_3)$_2$) $^3J_{HH} = 7.2$ Hz, 1.50 (d, 6H, CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 2.66 (sept. 3H, CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 2.76 (sept., 1H, CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 2.91 (sept., 1H, CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 3.14 (sept., 1H, CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 4.64 (d, 1H, PH) $J_{PH} = 588$ Hz, 7.12 (s, 4H, m-Trip), 7.22–7.64 (m, 3H, p,m-C_6H_3), 10.96 (s, br, 1H, OH); ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$) δ 22.3 (CH(CH$_3$)$_2$), 24.1 (CH(CH$_3$)$_2$), 25.4 (CH(CH$_3$)$_2$), 30.8 (o-CH(CH$_3$)$_2$), 33.7 (p-CH(CH$_3$)$_2$), 120.3 (m-Trip), 128.5 (p-C_6H_3), 130.3 (m-C_6H_3), 133.6 (i-Trip), 143.6 (i-C_6H_3 $J_{CP} = 12$ Hz), 145.9 (o-C_6H_3), 146.7 (o-Trip), 148.0 (p-Trip); ^{31}P-NMR (121 MHz, $CDCl_3$) δ 26.77 ($J_{PH} = 582$ Hz, $J_{PC} = 4144$ Hz).

*2.5. 2,6-Trip$_2$H$_3$C$_6$PH$_2$ (**4**)*

The supernatant liquid from the above synthesis of **3** was isolated and concentrated to ca. 30 ml under reduced pressure. The precipitates were redissolved upon warming and upon cooling slowly to ca. 25°C, colorless needles of **4** were obtained. Yield 2.03 g, 61%. M.p. 215–218°C; IR $\nu_{(P-H)}$ 2308, 2304 cm^{-1}; ^{1}H (300 MHz, CDCl$_3$) δ 1.09 (d, 12H, CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 1.18 (d, 12H, CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 1.31 (d, 12H, CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 2.57 (sept, 4H, *o*-CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 2.95 (sept, 2H, *p*-CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 3.05 (d, 2H, PH_2) $^3J_{PH}$ 212 Hz, 7.07 (s, 4H, *m*-Trip), 7.11 (d, 1H, *m*-C$_6$H$_3$) $^3J_{HH} =$ 7.5 Hz, 7.12 (d, 1H, *m*-C$_6$H$_3$) $^3J_{HH} = 7.8$ Hz, 7.32 (t, br, 1H, *p*-C$_6$H$_3$) $^3J_{HH} = 7.5$ Hz; ^{13}C{^{1}H}-NMR (75 MHz, CDCl$_3$) δ 23.4 (CH(CH$_3$)$_2$), 24.1 (CH(CH$_3$)$_2$), 25.1 (CH(CH$_3$)$_2$), 30.7 (*o*-CH(CH$_3$)$_2$), 34.3 (*p*-CH(CH$_3$)$_2$), 120.9 (*m*-Trip), 126.6 (*p*-C$_6$H$_3$), 128.5 (*m*-C$_6$H$_3$) 132.6 (d, *i*-C$_6$H$_3$, $J_{CP} = 7.95$ Hz), 136.9 (*i*-Trip), 144.4, 144.6 (*o*-C$_6$H$_3$), 145.9 (*o*-Trip), 148.4 (*p*-Trip); ^{31}P-NMR (121 MHz, CDCl$_3$) -139.8 (t, $J_{PH} = 208$ Hz).

*2.6. 2,6-Trip$_2$H$_3$C$_6$AsH$_2$ (**5**)*

This compound was synthesised in a similar manner to **4**. A solution of 2,6-Trip$_2$-H$_3$C$_6$AsCl$_2$ (3.84 g, 6.12 mmol) in Et$_2$O (100 ml) was added to a suspension of LiAlH$_4$ (1.39 g, 36 mmol) at 0°C. The mixture was stirred overnight then heated to reflux temperature (2 h), cooled to ca. -78°C, and dilute HCl (20%, 90 ml) added. The mixture was warmed to 25°C, stirred overnight, and extracted with Et$_2$O (3 × 50 ml). The organic fractions were combined, dried over MgSO$_4$, and filtered (Celite). The solvent was removed under reduced pressure and the white residue was extracted with hexane (50 ml), filtered (Celite), and concentrated under reduced pressure to ca. 20 ml. The precipitates were redissolved by warming, and on standing overnight in a ca. 5°C refrigerator, colorless crystals of **5** were obtained. Yield 1.81 g, 53%. M.p. 225–226°C; IR $\nu_{(As-H)}$ 2105 cm^{-1} br; ^{1}H-NMR (300 MHz, CDCl$_3$) δ 1.09 (d, 12H, *p*-CH(CH_3)$_2$) $^3J_{HH} = 6.6$ Hz, 1.18 (d, 12H, *o*-CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 1.31 (d, 12H, *o*-CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 2.59 (sept, 4H, *o*-CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 2.63, (s, 2H, AsH_2), 2.95 (sept, 2H, *p*-CH(CH$_3$)$_2$) $^3J_{HH} = 6.6$ Hz, 7.06 (s, 4H, *m*-Trip), 7.14 (d, 2H, *m*-C$_6$H$_3$) $^3J_{HH} = 7.5$ Hz, 7.33 (t, br, 1H, *p*-C$_6$H$_3$) $^3J_{HH} = 7.5$ Hz; ^{13}C{^{1}H}-NMR (75 MHz, CDCl$_3$) δ 23.3, 23.5 (CH(CH$_3$)$_2$), 24.1, 24.2 (CH(CH$_3$)$_2$), 25.1, 25.2 (CH(CH$_3$)$_2$), 30.6 (*o*-CH(CH$_3$)$_2$), 34.2 (*p*-CH(CH$_3$)$_2$), 120.8, 120.9 (*m*-Trip), 126.8 (*p*-C$_6$H$_3$), 128.2 (*m*-C$_6$H$_3$) 135.5 (*i*-C$_6$H$_3$), 138.0 (*i*-Trip), 145.5 (*o*-C$_6$H$_3$), 145.8 (*o*-Trip), 148.3 (*p*-Trip).

*2.7. 2,6-Trip$_2$H$_3$C$_6$SbH$_2$ (**6**)*

This compound was prepared in a similar manner to **5** by using 2,6-Trip$_2$-H$_3$C$_6$SbCl$_2$ (2.90 g, 4.81 mmol) in Et$_2$O (30 ml) and LiAlH$_4$ (1.83 g, 48.1 mmol). It crystallized as colorless needles from a concentrated hexane solution at ca. 5°C. Yield 1.20 g, 41%. M.p. turns yellow at 160°C and decomposes at 195°C; IR $\nu_{(Sb-H)}$ 1875 cm^{-1} br; ^{1}H-NMR (300 MHz, CDCl$_3$) δ 1.07 (d, 12H, CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 1.20 (d, 12H, CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 1.30 (d, 12H, *o*-CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 2.60 (sept, 4H, *o*-CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 2.66, (s, 2H, SbH_2), 2.94 (sept, 2H, *p*-CH(CH$_3$)$_2$) $^3J_{HH} = 7.2$ Hz, 7.04 (s, 4H, *m*-Trip), 7.17 (d, 2H, *m*-C$_6$H$_3$) $^3J_{HH} = 7.2$ Hz, 7.34 (t, br, 1H, *p*-C$_6$H$_3$) $^3J_{HH} =$ 7.2 Hz; ^{13}C{^{1}H}-NMR (75 MHz, CDCl$_3$) δ 23.3 (CH(CH$_3$)$_2$), 24.2 (CH(CH$_3$)$_2$), 25.4 (CH(CH$_3$)$_2$), 30.6 (*o*-CH(CH$_3$)$_2$), 34.3 (*p*-CH(CH$_3$)$_2$), 120.9 (*m*-Trip), 127.2 (*p*-C$_6$H$_3$), 127.7 (*m*-C$_6$H$_3$), 136.3 (*i*-C$_6$H$_3$), 140.2 (*i*-Trip), 145.7 (*o*-C$_6$H$_3$), 148.2 (*p*-Trip), 148.5 (*o*-Trip).

*2.8. 2,6-Trip$_2$H$_3$C$_6$N(H)Li (**7**)*

A solution of **2** (2.49 g, 5.0 mmol) in Et$_2$O (30 ml) was cooled to ca. 0°C and methyllithium (3.13 ml, 1.6 M solution in Et$_2$O) was added via syringe. The solution was allowed to warm to ca. 25°C and stirred for 2 h. The yellow solution was concentrated under reduced pressure to ca. 15 ml and placed in a -20°C freezer for 3 days. No crystals formed. The addition of hexane (20 ml) resulted in a white precipitate. The supernatant liquid was decanted and the product was isolated as a white solid. Yield 1.60 g, 64%. ^{1}H-NMR (300 MHz, C$_6$D$_6$), δ 1.00 (d, 12H, *o*-CH(CH_3)$_2$) $^3J_{HH} = 6.6$ Hz, 1.07 (12H, *o*-CH(CH_3)$_2$) $^3J_{HH} = 6.6$ Hz, 1.28 (12H, *p*-CH(CH_3)$_2$) $^3J_{HH} = 6.6$ Hz, 2.06 (s, 1H, N(H)Li), 2.90 (sept, 8H, CH(CH$_3$)$_2$) $^3J_{HH} = 6.6$ Hz, 6.55 (t, 1H, *p*-C$_6$H$_3$) $^3J_{HH} = 7.5$ Hz, 6.79 (d, 2H, *m*-C$_6$H$_3$) $^3J_{HH} = 7.5$ Hz, 7.11 (s, 4H, *m*-Trip); ^{13}C{^{1}H}-NMR (75 MHz, C$_6$D$_6$) δ 24.3 (CH(CH$_3$)$_2$), 24.7 (CH(CH$_3$)$_2$), 25.1 (CH(CH$_3$)$_2$), 30.5 (*o*-CH(CH$_3$)$_2$), 34.4 (*p*-CH(CH$_3$)$_2$), 112.9 (*p*-C$_6$H$_3$), 122.1 (*m*-Trip), 126.8 (*m*-C$_6$H$_3$), 130.3 (*p*-Trip), 138.2 (*o*-C$_6$H$_3$), 146.9 (*o*-Trip), 147.9 (*i*-Trip), 157.5 (*i*-C$_6$H$_3$); ^{7}Li-NMR (C$_6$D$_6$) δ -9.17 s, br.

*2.9. 2,6-Trip$_2$H$_3$C$_6$P(H)Li (**8**)*

Crystals of **4** (2.0 g, 3.89 mmol) were dissolved in Et$_2$O (50 ml) and cooled to ca. 0°C whereupon *n*-BuLi (4.86 ml, 1.6 M in hexanes) was added dropwise (10 min). The colorless solution became an opaque yellow color. The mixture was warmed to r.t. and stirred overnight. The mixture was then heated to reflux for 0.5 h, cooled and the solvent removed under reduced pressure. The orange residue was then suspended in pentane (50 ml) and the product, a fine pale yellow powder, was isolated by filtration. Yield 1.40 g, 69%. M.p. 215°C sticky, partial melt at 230°C, with a complete melt at 245–250°C while becoming an orange color. ^{1}H-NMR (400 MHz, THF-d^8), δ 1.16 (d, 12H, p-CH(CH_3)$_2$) $^3J_{HH} = 6.8$ Hz, 1.26 (12H, o-CH(CH_3)$_2$) $^3J_{HH} = 6.8$ Hz, 1.30 (12H, o-CH(CH_3)$_2$) $^3J_{HH} = 6.8$ Hz, 1.41 (d, 1H, PH) $J_{HP} = 178$ Hz, 2.85 (sept, 2H, p-CH(CH$_3$)$_2$) $^3J_{HH} = 6.8$ Hz, 3.00 (sept, 4H, o-CH(CH$_3$)$_2$) $^3J_{HH} = 6.8$ Hz, 6.43 (s, 2H), 6.95 (s, 4H), 7.11 (s, 1H); ^{13}C{^{1}H}-NMR (75 MHz, THF-d^8) d 24.7–25.6 (m, CH(CH_3)$_2$), 31.1 (o-CH(CH$_3$)$_2$), 35.3 (p-CH(CH$_3$)$_2$), 115.3 (p-C$_6$H$_3$), 120.7, 120.8 (m-Trip), 127.8 (m-C$_6$H$_3$), 139.1, 139.2 (i-Trip), 143.4 (o-C$_6$H$_3$), 145.9 (p-Trip), 147.9 (o-Trip), 161.1 (i-C$_6$H$_3$) $J_{CP} = 37.5$ Hz; ^{31}P-NMR (121 MHz, THF-d^8) δ −111.1 (d, $J = 183$ Hz); ^{7}Li-NMR (THF-d^8) δ 0.50.

2.10. 2,6-Trip$_2$H$_3$C$_6$As(H)Li (**9**)

This compound was prepared in the same manner as **8** by using **5** (1.00 g, 1.79 mmol) in Et$_2$O (60 ml) and n-BuLi (1.12 ml, 1.6 M in hexanes). Yield 0.80 g, 79%. M.p. 178–179°C, (dec). ^{1}H-NMR (300 MHz, THF-d^8), δ 0.62 (s, 1H AsH), 1.02 (d, 12H, p-CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 1.26 (12H, o-CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 1.32 (12H, o-CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 2.85 (sept, 2H, p-CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 2.99 (sept, 4H, o-CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 6.45 (d, 2H, m-C$_6$H$_3$) $^3J_{HH} = 6.9$ Hz, 6.55 (t, 1H, p-C$_6$H$_3$) $^3J_{HH} = 6.3$ Hz, 6.94 (s, 4H, m-Trip); ^{13}C{^{1}H}-NMR (75 MHz, THF-d^8) d 24.9, 25.1, 25.4, 25.66, 25.7 (CH(CH_3)$_2$), 31.2 (o-CH(CH$_3$)$_2$), 35.4 (p-CH(CH$_3$)$_2$), 116.8 (p-C$_6$H$_3$), 120.6 (m-Trip), 127.3 (m-C$_6$H$_3$), 141.8 (i-Trip), 143.9 (o-C$_6$H$_3$), 145.8 (p-Trip), 147.6 (o-Trip), 162.2 (i-C$_6$H$_3$); ^{7}Li-NMR (THF-d^8) δ 0.67.

2.11. 2,6-Trip$_2$H$_3$C$_6$Sb(H)Li (**10**)

This compound was prepared in the same manner as **8** by using **6** (1.20 g, 1.98 mmol) in Et$_2$O (50 ml) and n-BuLi (1.24 ml, 1.6 M in hexanes). Yield 0.62 g, 51%. M.p. 120°C darkens, 135–140°C dec. ^{1}H-NMR (300 MHz, THF-d^8), δ −0.89 (s, 1H, SbH), 0.99 (d, 12H, p-CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 1.26 (d, 12H, o-CH(CH_3)$_2$) $^3J_{HH} = 6.9$ Hz, 1.36 (d, 12H, o-CH(CH_3)$_2$) $^3J_{HH} = 6.6$ Hz, 2.85 (sept, 2H, p-CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 2.97 (sept, 4H, o-CH(CH$_3$)$_2$) $^3J_{HH} = 6.9$ Hz, 6.42 (d, 2H, m-C$_6$H$_3$) $^3J_{HH} = 7.2$ Hz, 6.63 (t, 1H, p-C$_6$H$_3$) $^3J_{HH} = 7.2$ Hz, 6.89 (s, 4H, m-Trip); ^{13}C{^{1}H}-NMR–not obtainable due to rapid decomposition in THF-d^8; ^{7}Li-NMR (THF-d^8) δ −0.65.

2.12. X-ray data collection, the solution and refinement

Crystals of **1**–**4** and **6** were coated with hydrocarbon oil, mounted on a glass fiber and placed in the N$_2$ cold stream on the diffractometer (**5** was coated with epoxy resin and mounted at ca. 25°C) [10]. Data for **1**, **2**, **4** were obtained on a Siemens P4 Rotating Anode at 130 K using Cu–K$_\alpha$ radiation ($\lambda = 1.54178$ Å), those for **3** on a Siemens R3m/v at 130 K using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å), and data for **5**,**6** were measured on a Bruker SMART AXS 1000 at 299 and 93 K using Mo–K$_\alpha$ radiation. The SHELXTL-Plus v. 5.03 and SHELXTL v. 5.10 program suite was used for the structure solution and refinements [11]. The structures were solved by direct methods and refined by full-matrix least-squares procedures. Absorption corrections were applied to **1**–**4** using the program XABS2 [12] and to **5**,**6** using the program SADABS. Hydrogen atoms bonded directely to the pnictogen atom were located on the Fourier difference map and refined with fixed distances. Other hydrogen atoms were included in the refinement at calculated positions using a riding model included in the SHELXTL program. The structures of **1** and **4** are subject to disorder, which could be modelled successfully by using partial occupancies for the disordered atoms as described in the Supporting Information. Crystals of **3** included disordered solvent, which could not be successfully modelled, see the Supporting Information. Details of the data collection and refinement are given in Table 1. Selected bond distances and angles for **1**–**6** are provided in Table 2.

3. Discussion

3.1. The azide ArN$_3$, **1** and the amine ArNH$_2$, **2**

The azide **1** and the primary amine **2** were synthesized in a manner analogous to Yoshifuji's scheme for the synthesis of 2,6-dimesityl-4-methyl aniline [13]. The compound **1** resulted from the reaction of LiC$_6$H$_3$-2,6-Trip$_2$ with TsN$_3$ (Ts = C$_6$H$_5$SO$_3$–) [8] in ether solution. Further reduction of **1** with LiAlH$_4$ afforded the target primary amine **2** in 75% yield. Although **1** and **2** are members of compound classes for which numerous examples have been structurally characterized, there are a number of noteworthy features in both structures. The molecule **1** (Fig. 1) has a plane of symmetry containing the C(4), C(1) and N(1) atoms which is perpendicular to the central aryl ring. The azide moiety may occupy two positions (only one of which is illustrated in Fig. 1) on either side of this plane with equal probability and there is an angle of 22° between the perpendiculars to the axial ring and the coordination plane at N(1). The C($ipso$)–N–N angle is 135.4(3)° which is considerably wider than those seen in other aryl azide structures (typical angles range 115–120°) [14,15]. The azide moiety is not quite linear and has an N(1)–N(2)–N(3) angle of 173.5(7)°. The C($ipso$)–N(1) distance 1.408(5) Å is normal (cf. C–N = 1.417(7) Å in

4-$O_2NH_4C_6N_3$ [14]). However, both N–N distances, N(1)–N(2) (1.047(4) Å) and N(2)–N(3) (1.144(7) Å), are unusually short (cf. 1.270(6) and 1.127(17) Å in 4-$O_2NH_4C_6N_3$ [14]). We have no obvious explanation for this shortening although we draw attention to the fact that the use of a closely related terphenyl ligand in diphosphenes resulted in the shortest known PP double bond [16]. In the IR spectrum the NN stretching band was observed at 2085 cm^{-1} which is close to the 2104 cm^{-1} observed for $PhSCH_2N_3$ [17].

The most notable feature of the structure of **2** (Fig. 2) is that the sum of bond angles at the nitrogen atom is 359°, which indicates an almost trigonal planar coordination geometry at the nitrogen. Fukuyo et al. [18] have shown that the geometry at the nitrogen in primary amines may be strongly affected by inter- or

Table 1
Crystallographic data for compounds **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{36}H_{49}N_3$	$C_{36}H_{51}N$	$C_{37.75}H_{51}O_2P$	$C_{36}H_{51}P$	$C_{36}H_{51}As$	$C_{36}H_{51}Sb$
Formula weight	523.78	497.78	567.76	514.74	558.69	605.52
Color	Pale yellow	Colorless	Colorless	Colorless	Colorless	Colorless
Crystal dimensions (mm)	0.44 × 0.22 × 0.05	0.28 × 0.22 × 0.04	0.28 × 0.28 × 0.14	0.40 × 0.16 × 0.10	0.20 × 0.20 × 0.20	0.38 × 0.16 × 0.05
Crystal habit	Block	Block	Cube	Needle	Needle	Needle
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbcm*	*Pnma*	$P2_1/n$	*Pnma*	*Pnma*	*Pnma*
Unit cell dimensions						
a (Å)	10.930(2)	8.586(2)	15.512(3)	8.0950(16)	8.167(2)	8.167(2)
b (Å)	12.120(2)	25.579(5)	14.376(3)	25.562(5)	25.828(7)	25.828(7)
c (Å)	25.210(5)	14.512(3)	16.999(3)	15.904(3)	16.083(5)	16.083(5)
α (°)						
β (°)			111.42(3)			
γ (°)						
V ($Å^3$)	3339.6(12)	3187.1(11)	3528.9(12)	3290.9(11)	3392.3(16)	3392.3(16)
Z	4	4	4	4	4	4
d (g cm^{-3})	1.042	1.037	1.069	1.039	1.094	1.186
Absorption coefficient (mm^{-1})	0.454	0.432	0.107	0.869	1.022	0.833
F(000)	1144	1096	1234	1128	1200	1272
Radiation, λ (Å)	Cu–K_α; 1.54178	Cu–K_α; 1.54178	Mo–K_α; 0.71073	Cu–K_α; 1.54178	Mo–K_α; 0.71073	Mo–K_α; 0.71073
Temperature (K)	130	130	130	130	299	93
2θ (°)	113	113	45	56.35	52.98	63.32
Total data	2576	2471	5037	2523	23291	11158
Unique data	2270	2155	4595	2222	3591	6066
Observed data $I>2\sigma I$	1883	1201	2616	1450	2274	4343
R_{int}	0.0167	0.0730	0.0497	0.0000	0.0482	0.0438
Parameters	191	182	388	183	202	181
R_1/R_w (all data)	0.0508/0.1358	0.0631/0.1999	0.0759/0.2041	0.0822/0.2279	0.0469/0.1317	0.0295/0.0774
Difference map (e $Å^{-3}$)	0.449/−0.252	0.189/−0.188	0.45/−0.334	0.435/−0.302	0.439/−0.403	0.605/−0.419

Table 2
Selected bond lengths (Å) and angles (°) for **1**–**6**

Compound	E–C [a]	E–H	C–E–H	H–E–H	C–C(*ipso*)–E	C–C(*ipso*)–C
ArN_3 [b] (**1**)	1.408(5)		135.4(3) [c]		119.24(14)	121.4(3)
$ArNH_2$ (**2**)	1.378(8)	1.00(5)	120(3)	119(2)	120.0(3)	120.0(5)
$\{ArP(O)(OH)H\}_2$ (**3**)	1.813(5)	1.342(19) (H(2))		118.6(4)	120.1(5)	
		1.552(4) (O(1))	107.6(2) (O(1))		121.1(4)	
		1.512(4) (O(2))	112.5(2) (O(2))			
$ArPH_2$ (**4**)	1.845(7)	1.39(2)	105(3)	102(2)	119.7(3)	120.3(6)
$ArAsH_2$ (**5**)	1.968(3)	1.484(18)	104.0(17)	107(1)	119.83(13)	120.3(3)
$ArSbH_2$ (**6**)	2.17 (av)	1.67 (av)	103.8 (av)	111 (av)	119.56(8) (av)	120.51(15)

[a] E = N, P, As or Sb.

[b] Ar = C_6H_3-2,6-$Trip_2$.

[c] C–N–N angle.

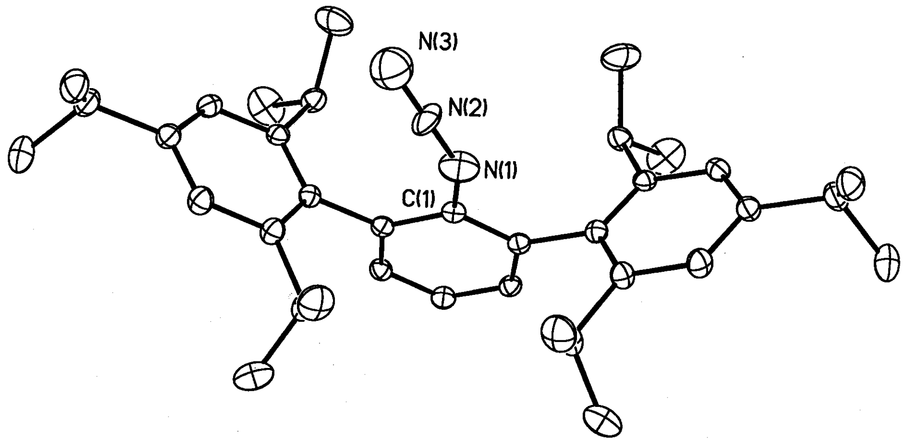


Fig. 1. Thermal ellipsoidal plot (30%) of ArN_3 (**1**). No hydrogen atoms and only one of the disordered azide moieties are shown. Important bond lengths and angles are in the text and Table 2.

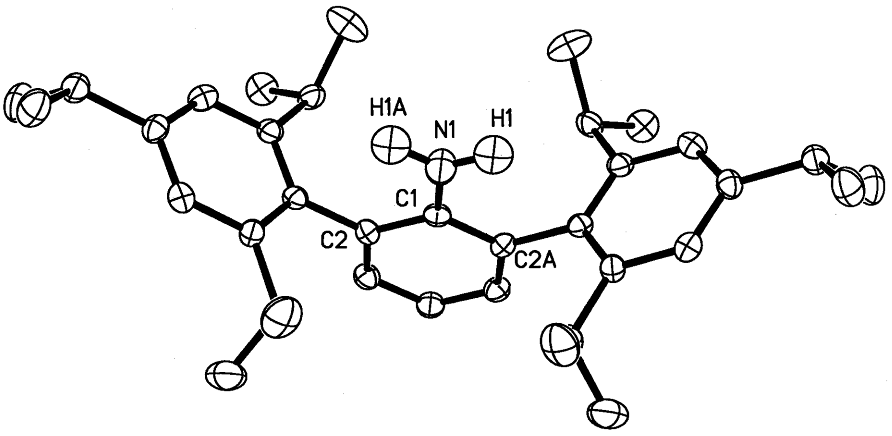


Fig. 2. Thermal ellipsoidal plot (30%) of $ArNH_2$ (**2**). Hydrogen atoms except those bound to nitrogen are not shown. Important bond lengths and angles are in Table 2.

intra-molecular interactions, e.g. hydrogen bonding between amine molecules. For example, *p*-nitro- or trinitro-anilines, which feature strong inter-molecular hydrogen bonding involving the N(H)–O unit, have trigonal planar nitrogen coordination, while unsubstituted aniline has a pyramidal nitrogen geometry [19,20]. Examination of the environment of the hydrogens bound to the nitrogen in **2** indicates that there is no possibility of inter-molecular hydrogen bonding in the solid state structure. However, the structure of **2** does suggest that there is an intra-molecular interaction between the amine hydrogen atoms and the ortho phenyl rings of the *m*-terphenyl ligand [21]. The N(H)-ring centroid distance, 3.013 Å; lies within the range of 2.9–3.1 Å which is predicted by from the sum of the van der Waals radii of H and sp^2 hybridized carbon [22]. This interaction may cause the trigonal planar geometry at the nitrogen atom in **2**.

*3.2. The phosphinic acid ArP(O)(OH)H (**3**)*

The phosphinic acid compound ArP(O)(OH)H (**3**) results from the reaction of the halide $ArPCl_2$ (the precursor for **4**) with trace amounts of water. Although it is produced only in small amounts by this process in the synthesis of $ArPCl_2$, its low solubility in comparison with $ArPCl_2$ ensure its ready crystallization and purification. Its IR spectrum displays a P–H stretching band at 2410 cm^{-1} and the ^{1}H-NMR spectrum displays peaks at centered 4.64 and 10.96 ppm which are attributable to the P–H hydrogen ($J_{PH} = 588$ Hz) and the O–H hydrogen. The $^{31}P\{^1H\}$-NMR spectrum reveals a peak at 26.77 ppm ($J_{PC} = 4144$ Hz). These spectroscopic parameters are very similar to those recently observed [16] for the closely related compound 2,6-$Mes_2H_3C_6P(O)(OH)H$. In the X-ray crystal structure dimerization occurs through hydrogen bonding involving the OH and PO moieties as shown in Fig. 3.

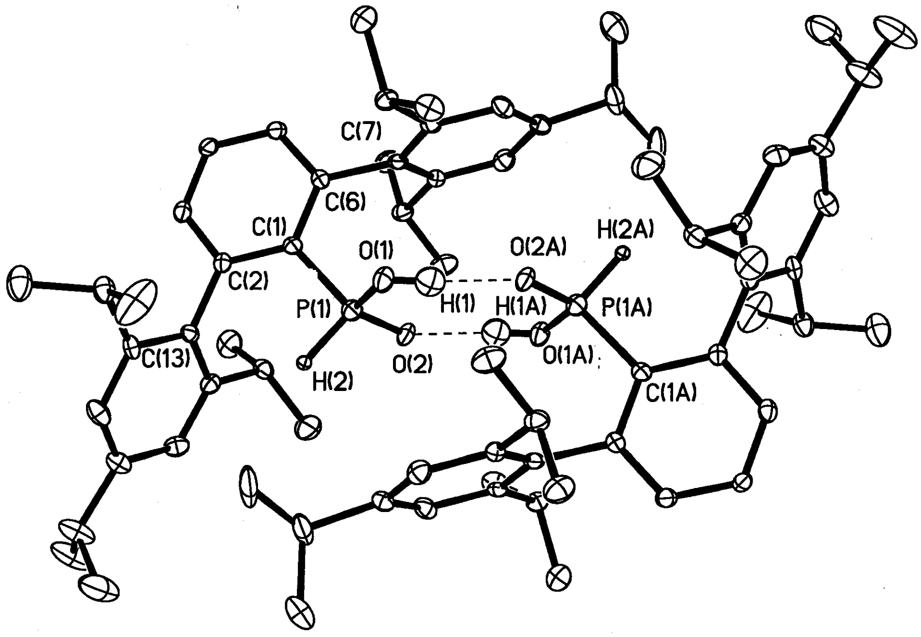


Fig. 3. Thermal ellipsoidal plot of $\{ArP(O)(OH)H\}_2$ (**3**). Hydrogen atoms except those bound to oxygen and phosphorus are not shown. Important bond lengths and angles are in the text and Table 2.

Surprisingly perhaps, the size of very large -C_6H_3-2,6-$Trip_2$ substituent is insufficient to prevent aggregation. The centrosymmetric dimers feature a P=O and P–OH distances of 1.512(4) and 1.552(4) Å and the O–H and O···HO distances (H atoms located and refined) are 0.84(3) and 1.71(4) Å. These structural parameters resemble those found for the dimers in the crystal structure of $\{2,6\text{-}Mes_2H_3C_6P(O)(OH)H\}_2$ [16].

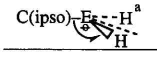
*3.3. The primary pnictanes $ArEH_2$ (E = P (**4**), As (**5**) and Sb (**6**)*

The compounds **4**–**6** were synthesized by the reduction of the $ArECl_2$ precursors [7] with $LiAlH_4$. The yield obtained decreased with increasing pnictogen atomic number from ca. 60% for the phosphane to ca. 40% for the stibane. Attempted reduction of $ArBiCl_2$ with $LiAlH_4$ gave ArBiBiAr [7] as the only crystalline product. Presumably, the $ArBiH_2$ species is too unstable to isolate near room temperature. The ^{1}H- and ^{13}C-NMR spectra of **4**–**6** displayed no unusual characteristics and the ^{31}P-NMR spectrum of **4** featured a resonance at − 139.8 ppm with $J_{P\text{–}H} = 208$ Hz. These values are typical for primary phosphanes [22]. The ^{31}P-NMR chemical shift of **4** is very similar to the − 137.8 ppm in 2,6-$Mes_2H_3C_6PH_2$ [16] but the $J_{P\text{–}H}$ for the latter (178 Hz) is somewhat lower than the coupling in **4**. The reason for the ca. 40 Hz difference in the coupling constant is not clear at present.

The major spectroscopic features and selected structural parameters of the pnictane series **2**, **4**, **5**, and **6** are presented in Table 3. With the exception of **2** (previously discussed) the coordination geometries show the expected increased pyramidal character. The IR stretching frequencies of the E–H bonds are of medium to strong intensity which undergo the expected shift to lower energy with increasing atomic number. The frequencies are within the expected range. For example, the frequency of the Sb–H band in **6**, 1875 cm^{-1}, is similar to the 1865 cm^{-1} observed in $Me_3SiCH_2SbH_2$ [5] or the 1870 cm^{-1} in *t*-$BuCH_2SbH_2$ [4]. The range of the chemical shifts of the E–H resonances in the ^{1}H-NMR spectra, 3.36–2.66 ppm, is relatively narrow. However, the 2.66 ppm shift of **6** is somewhat downfield of the 1.79 and 1.75 ppm values reported for $Me_3SiCH_2SbH_2$ and *t*-$BuCH_2SbH_2$. Perhaps, this is due to the partial shielding of the hydrogens by the *ortho*-aryl rings of the terphenyl ligands. The ^{13}C-NMR spectra of **2**, **4**, **5** and **6** also display a relatively narrow range of chemical shift values (142.6–132.6 ppm) for the key C(*ipso*) atom of the central aryl ring.

As can be seen from Table 1, the crystals of **4**, **5**, and **6** are isomorphous. The structures of the three compounds are very similar and are characterized by a

Table 3
Key spectroscopic and structural data for the pnictanes **2**, **4**, **5**, and **6**

Compound	**2**	**4**	**5**	**6**
Σ E (°)	359.8	311.8	314.9	299.6
IR $\nu_{(E\text{-}H)}$ (cm^{-1})	3378, 3472	2308, 2304	2105	1875
^{1}H NMR EH_2 (ppm)	3.36	3.05	2.63	2.66
^{13}C NMR $C_{(ipso)}$ (ppm)	142.6	132.6	135.5	136.3
 C(ipso)–E- - -H [a]	176	116	114	118 (av)

[a] out of plane angle

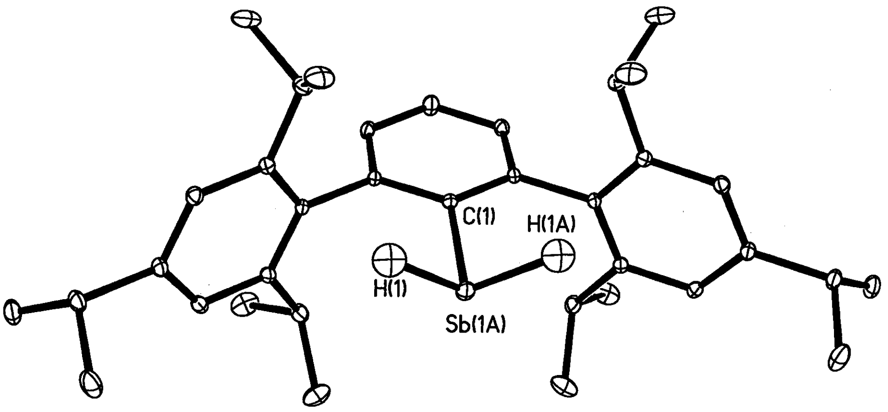


Fig. 4. Thermal ellipsoidal plot (30%) of $ArSbH_2$ (**6**). Hydrogen atoms except those bound to antimony are not shown. Important bond lengths and angles for **6** (and the analogues **4** and **5**) are given in Table 2.

plane of symmetry perpendicular to the central aryl ring plane which incorporates the *ipso* and *para* carbon and pnictogen atom as illustrated by the drawing of the stibane **6** in Fig. 4. The E–C bonds are of normal length and are close to those seen in the corresponding $ArECl_2$ species [7]. The increasing lengths of the P–C, As–C and Sb–C bonds almost exactly mirror the differences in covalent radii (P, 1.11 Å; As, 1.21 Å; Sb, 1.43 Å) between these atoms [23]. In contrast to the structure of **2**, the coordination of the pnictogens in **4**, **5** and **6** is pyramidal and the amount of pyramidal character increases for the P and As derivatives although in the Sb compound it seems to decrease slightly. This is of course consistent with the large inversion barriers in these compounds [24]. There does not appear to be much tendency toward flattening of the geometries as in the nitrogen case. Presumably, the less polar nature of the E–H bonds in the heavier pnictanes does not promote the existence of dipolar interactions between the E–H moieties and the ortho aryl rings which might favor a more planar geometry at E atom.

A few crystal structures of heavier primary pnictanes have been reported. These concern $MesPH_2$ [25], 9-phosphinotriptycene [26], $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4PH_2)$ [27] and a dibenzobarrellene phosphane [28]. The P–H distance of 1.39(2) Å in **4** is comparable to the 1.36(3) Å in the dibenzobarrellene [28] but is shorter than the 1.42 and 1.437 Å P–H values determined for PH_3 [29]. The As–H distance in **5**, 1.484(18) Å, is also consistent with the ca. 0.1 Å difference in covalent radii between P and As and the 1.519 Å As–H bond length in AsH_3 [30]. Similarly the average Sb–H bond length, 1.67 Å, is comparable to the 1.707 Å distance determined for SbH_3 [31].

The most remarkable feature of compounds **4**, **5**, and **6** is their thermal stability. Both **4** and **5** melt without decomposition at temperatures in excess of 200°C. The stibane **6** decomposes at 195°C and is indefinitely stable at room temperature under an N_2 atmosphere in the absence of light. Thus **6** probably has similar stability to the crystalline secondary stibane Mes_2SbH [32]. Presumably, the very large Ar ligands hinder the decomposition, which might involve an association pathway that would be made more difficult by the large substituent.

3.4. The lithium salts ArE(H)Li (E = N (7), P (**8**), As (**9**), Sb (**10**))

The pnictanes **2**, **4**–**6** may be readily deprotonated by organolithium reagents. Thus the addition of LiMe to an ether solution of **2** results in the in situ generation of ArN(H)Li in solution. The addition of hexane results in the precipitation of spectroscopically pure **7** as a white solid. The ^{1}H-NMR spectrum of C_6D_6 displays an N–H hydrogen signal at 2.06 ppm which is ca. 1 ppm upfield of the N–H hydrogens in **2**. The ^{13}C-NMR spectrum of C(*ipso*) resonance appears at 157.5 ppm or ca. 15 ppm downfield of the corresponding resonance in **2**.

The heavier pnictanes **4**, **5**, **6** are readily deprotonated by *n*-BuLi in a Et_2O–hexane solvent to afford **8**, **9**, **10** as yellow powders in 50–80% yield. The ^{1}H-NMR in C_6D_6 confirms that the compounds contain just one E–H proton, which is shifted upfield by 1.6–3.5 ppm. In the case of the phosphorus derivative **8** the $J_{P–H}$ is 178 Hz. In the ^{13}C-NMR spectra, the key resonance of the *ipso*-carbon of the central aryl ring appear at 161.1(**8**), 162.2(**9**), which are 18.5 and 16.7 ppm downfield of the precursors **4** and **5**. The ^{13}C-NMR of **10** in THF-d^8 was not observable due to rapid decomposition in solution.

4. Supplementary material

The X-ray data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-141058-63. Copies of the data can be obtained on application to CCDC, 12 Union Rd., Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.-ac.uk).

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