JOM 23757PC

# Preliminary Communication

## Monomeric arsinoboranes. The question of arsenic–boron π-bonding

Miguel A. Mardones, Alan H. Cowley,
Leopoldo Contreras and Richard A. Jones

*Department of Chemistry and Biochemistry,*
*The University of Texas at Austin, Austin, TX 78712 (USA)*

Carl J. Carrano

*Department of Chemistry, Southwest Texas State University,*
*San Marcos, TX 78666 (USA)*

### Abstract

The monomeric arsinoboranes $R_2AsB(Mes)_2$ (R = $^i$Pr (1); $^t$Bu (2); Mes = mesityl) have been prepared via the reaction of $LiAsR_2$ with $Mes_2BF$ in $Et_2O$ solution; compound 1 has been characterized by X-ray crystallography: monoclinic, space group $P2_1/c$ with $a = 8.883(2)$, $b = 29.190(6)$, $c = 9.146(2)$ Å, $\beta = 100.46(3)°$, and $Z = 4$.

Aminoboranes, $R_2NBR_2'$, constitute an important and extensively studied class of compound; [1]. Significantly less information, however, is available regarding the heavier analogues such as the arsinoboranes, $R_2$-$AsBR_2'$. Elegant early work by Stone and Burg [2] established the existence of a trimer, tetramer, and polymer based on the $Me_2AsBH_2$ unit. This development was followed by the synthesis of three arsinoboranes of empirical composition $Ph_2AsB(aryl)_2$ by Coates and Livingstone [3]. To our knowledge, no compounds of the above type have been characterized structurally. Indeed, structural data are available for only for compounds with arsenic–boron bonds [4–7]. Herein we report the preparation of the first monomeric hydrocarbyl-substituted arsinoboranes, $R_2$-$AsB(Mes)_2$ (R = $^i$Pr (1), $^t$Bu (2), Mes = mesityl). The X-ray crystal structure of 1 is also described.

In a typical reaction, a solution of $LiAs^iPr_2$ was prepared by addition of 2.2 ml of a 1.6 m hexane solution of $^nBuLi$ to a solution of $^iPr_2AsH$ (0.58 g, 3.6 mmol) in 20 ml of $Et_2O$. After it had warmed slowly to room temperature, the $LiAs^iPr_2$ solution was added via cannula to a cooled (−78°C) solution of $Mes_2BF$

(0.97 g, 3.6 mmol) in 30 ml of $Et_2O$. The mixture was allowed to warm to 25°C and was stirred for an addition 12 h at this temperature. After stripping the solvent and volatiles, the resulting yellow residue was extracted with 40 ml of toluene. Filtration, concentration, and cooling (−20°C) of this solution afforded yellow crystalline 1 (m.p. 84–85°C) in 65% yield. The chemical ionization ($CH_4$) mass spectrum revealed a peak at $m/e$ 411 which corresponds to the addition of $H^+$ to $^iPr_2AsBMes_2$, and the $^1H$ and $^{13}C\{^1H\}$ NMR data indicated the presence of equal abundances of $^iPr$ and Mes groups. * However, to confirm the monomeric nature of 1 it was necessary to carry out an X-ray analysis. ** The solid state of 1 comprises monomeric $^iPr_2AsBMes_2$ units with no short intermolecular contacts (Fig. 1). The boron and arsenic atoms adopt trigonal planar and tetrahedral geometries respectively and the overall "propeller-like" arrangement of mesityl and isopropyl moieties is one that minimizes steric repulsions. The most interesting facet of the structure relates to the question of π bonding. The As–B bond distances in boron arsenide (2.069 Å) [4] and an $AsB_2N$ ring system (2.063(4) and 2.069(4) Å) [5] are close to the sum of covalent radii for these elements (2.07 Å) and thus correspond to a bond order of unity. Two

---

\* MS (+CI, $CH_4$). 1: 411 (M⁺ + H), 367 (M⁺ − $^i$Pr), 291 (M⁺ − Mes), 249 ($Mes_2B^+$), 173 ($BAs^iPr_2$). 2: 439 (M⁺ + H), 381 (M⁺ − $^t$Bu), 319 (M⁺ − Mes), 249 ($Mes_2B^+$). $^1H$ NMR (300.15 MHz, 298 K $C_6D_6$). 1: $\delta = 1.17$ (12H, d, $J = 7.2$ Hz, $(CH_3)_2CH$), 2.12 (6H, s, para-$CH_3$), 2.47 (12H, s, ortho-$CH_3$), 2.50 (2H, septet, $J = 7.2$ Hz, $HC(CH_3)_2$), 6.74 (4H, s, meta-H). 2: $\delta = 1.33$ (18 H, s, $(CH_3)_3C$), 2.12 (6H, s, para-$CH_3$), 2.56 (12H, s, ortho-$CH_3$), 6.74 (4H, s, meta-$CH_3$). $^{13}C\{^1H\}$ NMR (75.47 MHz, 298 K, $C_6D_6$). 1: $\delta = 21.06$ (s, para-$CH_3$), 23.99 (s, $CH(CH_3)_2$), 24.16 (s, $(CH_3)_2C$), 26.97 (s, ortho-$CH_3$), 129.05 (s, meta-C), 138.10 (s, para-C), 138.12 (s, ortho-C), 143.10 (s, br, ipso-C). 2: 21.0 (s, para-$CH_3$), 25.2 (s, ortho-$CH_3$), 33.7 (s, $(CH_3)_3C$), 41.5 (s, $C(CH_3)_3$), 129.2 (s, meta-C), 137.7 (s, para-C), 138.6 (s, ortho-C).

\*\* Crystal data for 1 (24°C). $C_{24}H_{36}AsB$, $M = 410.3$, monoclinic, space group $P2_1/c$, $a = 8.883(2)$, $b = 29.190(6)$, $c = 9.146(2)$ Å, $\beta = 100.46(3)°C$, $V = 2332.1(9)$ Å³, $D_c = 1.168$ g cm⁻³, $Z = 4$, $\lambda(Mo-K\alpha) = 0.71073$ Å, $\mu(Mo-K\alpha) = 14.62$ cm⁻¹. A total of 3024 reflections was collected at 298 K on a Siemens P4 diffractometer with $2\theta$ between 3.0 and 45.0°. The data were corrected for Lorentz-polarization, and absorption effects. The structure was solved by direct methods and refined (full-matrix, least-squares) using 2149 reflections with $I > 2.0\sigma(I)$. The final R and $R_w$ values were 5.77 and 5.69%, respectively.
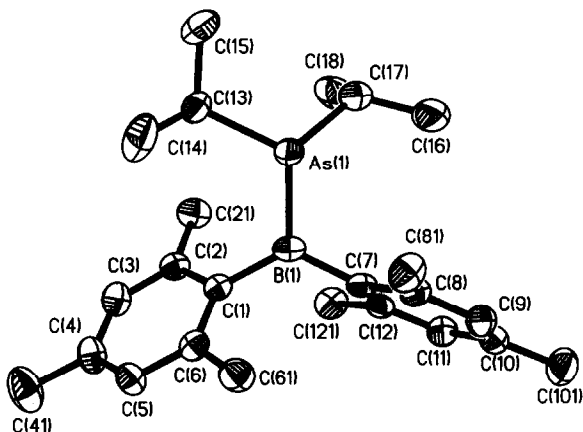
---

Correspondence to: Professor A.H. Cowley.

Fig. 1. Molecular structure of 1 including the atom numbering system. Pertinent bond distances (Å) and bond angles (deg): B(1)–As(1) 2.019 (7), B(1)–C(1) 1.589(9), B(1)–C(7) 1.564(9), As(1)–C(13) 1.968(6), As(1)–C(17) 1.975(8), C(1)–B(1)–C(7) 123.8(6), As(1)–B(1)–C(7) 116.2(5), C(1)–B(1)–As(1) 119.2(4), B(1)–As(1)–C(14) 110.8(3), B(1)–As(1)–C(17) 109.3(3), C(13)–As(1)–C(17) 105.4(3).

values are available for the arsenic–boron double bond distance, namely 1.868 Å in $[As-B-As]^{3-}$ and 1.926(6)–1.936(11) Å in $[PhAsBMes_2]^-$ [6,7]. Taking a value of 1.93 Å for the arsenic–boron double bond distance and a value of 2.07 Å for the corresponding single bond distance, one arrives at an estimated As–B bond order of 1.6 in 1. However, not too much emphasis should not be placed on this estimate because of the differences in coordination numbers. Nevertheless, the implication of some arsenic–boron multiple bonding in 1 is consistent with the relatively small twist angle of 12.1°. (The twist angle is defined as the angle between the normals to the C–As–C and C–B–C planes as viewed down the As–B axis.)

The analogous arsinoborane $^tBu_2AsB(Mes)_2$ (2) was prepared from $LiAs^tBu_2$ and $Me_2BF$ in $Et_2O$ at $-78°C$ in a manner similar to that described for 1. After extraction with $CH_2Cl_2$, the crude product was recrys-

tallized from pentane at $-40°C$ to afford a 30% yield of pure orange crystalline 2 (m.p. = 114–118°C). Unfortunately, crystals of 2 were not suitable for X-ray diffraction study. Nevertheless, the similarity in the spectral data * leaves little doubt that the structures of 1 and 2 are alike.

Attempts were made to synthesize arsinoboranes by the alkane elimination route. No reaction was evident when an equimolar mixture of $^tBu_2AsH$ and $^iPr_3B$ was refluxed in toluene solution. However, when the same mixture was heated in the absence of a solvent the arsenic cluster $^tBu_6As_8$ [8,9] was produced along with as yet unidentified products.

## Acknowledgments

## References

1 Gmelin Handbook of Inorganic and Organometallic Chemistry, 4th Supplement, Volume 3a, Boron and Nitrogen, 1991, and earlier volumes in this series.

2 F.G.A. Stone and A.B. Burg, J. Am. Chem. Soc., 76 (1954) 386.

3 G.E. Coates and J.G. Livingstone, J. Chem. Soc., (1961) 1000.

4 J.A. Perri, S. La Placa and B. Post, Acta Crystallogr., 11 (1958) 310.

5 K.H. Van Bonn, P. Schreyer, P. Paetzold and R. Boese, Chem. Ber., 121 (1988) 1045.

6 H.-G. von Schnering, M. Somer, M. Hartweg and K. Peters, Angew. Chem., Int. Ed. Engl., 29 (1990) 65.

7 M.A. Petrie, S.C. Shoner, H.V. Rasika Dias and P.P. Power, Angew. Chem., Int. Ed. Engl., 29 (1990) 1033.

8 M. Baudler and P. Bachmann, Z. Anorg. Allg. Chem., 485 (1982) 129.

9 For examples of As–As bond formation in the context of Ga–As chemistry, see R.L. Wells, Coord. Chem., Rev., 112 (1992) 273 and references therein.