

## Synthesis and Crystal Structure of Tris-[3,5-bis(trifluoromethyl)phenyl]arsine

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The title compound,  $\text{As}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_3$ , has been synthesised by Grignard reaction from arsenic trichloride and 3,5-bis(trifluoromethyl)phenylmagnesium bromide. It crystallises in the triclinic space group  $P\bar{1}$  with two formula units in the asymmetric unit. The most prominent feature of the crystal structure is the protrusion of a phenyl group of one molecule into the cavity at the base of the pyramid of a second molecule. The crystal structure is then built up by densely packing these units of interlocked molecules to form columns, which are arranged in parallel in a distorted hexagonal pattern.

**Key words:** Triphenyl Arsine, Grignard Reaction, Arsenic, Trifluoromethyl Groups

### Introduction

Phosphines and arsines are widely used as ligands in transition metal complexes. Their coordinating properties are determined by the substituents attached to the heteroatom [1]. In the case of triphenylphosphine and -arsine, the electronic properties of the ligand can be tuned through substitution at the aromatic ring, which in turn influences the stability and properties of the resulting metal complex. The pentafluorophenyl ligand, for instance, is strongly electron withdrawing and therefore stabilises complexes with electron rich metals. The common 2,4,6-tris(trifluoromethyl)phenyl (fmes) ligand is intermediate between the phenyl and the pentafluorophenyl ligand in its electron deficiency and offers the additional advantage that it sterically protects metal atoms favouring low coordination numbers [2]. The 3,5-bis(trifluoromethyl)phenyl ligand is less demanding sterically and consequently might be utilised more advantageously with metal centers that prefer higher coordination numbers. Electronically, it should display less of an  $-I$  effect than the fmes ligand.

In this report we describe the synthesis and crystal structure of tris[3,5-bis(trifluoromethyl)phenyl]arsine.

### Experimental Section

The synthesis of the title compound followed the general procedure for preparing triphenylstibine [3]. 7.7 g (0.317 mol) of magnesium granules (99%, Aldrich) and 200 ml of dry diethyl ether were placed into a round-bottomed, three-necked flask equipped with a magnetic stirrer, a reflux condenser cooled to  $-40^\circ\text{C}$ , and a 100 ml dropping funnel, into which 88.05 g (0.3005 mol) of 3,5-bis(trifluoromethyl)bromobenzene (98%, Avocado) and 75 ml of dry ether are filled. The latter solution was slowly added under stirring to the flask, the rate being adjusted to cause only gentle boiling. This took approximately 2 h, after which the solution was heated to  $45^\circ\text{C}$  for 30 min. Another 300 ml of dry ether were added, followed by 16.125 g (7.5 ml, 0.089 mol) of arsenic trichloride (Ventron) in 120 ml of dry ether over a period of 90 min. Afterwards, the mixture was heated to  $50^\circ\text{C}$  for 1 h. Upon cooling to  $-78^\circ\text{C}$  the product crystallised. It was filtered and recrystallised from petroleum ether. Crystals suitable for data collection were grown by cooling a saturated solution of the title compound in diethyl ether to  $-78^\circ\text{C}$ . Yield: 94% (59.75 g, 0.084 mol).

$^1\text{H}$  NMR (300.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.78 (s, 2 H, 2/6-H), 7.99 (s, 1 H, 4-H). –  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 123.0 (q,  $^1J$  = 273 Hz, C-7,8), 124.3 (sept,  $^3J$  = 3.7 Hz, C-4), 133.2 (q,  $^2J$  = 34 Hz, C-3/5), 133.5 (m, C-2/6), 140.1 (s, C-1).

**X-ray structure determination:** Formula  $\text{C}_{24}\text{H}_9\text{AsF}_{18}$ ,  $M$  = 714.23 g mol $^{-1}$ , colorless crystal  $0.24 \times 0.24 \times 0.06$  mm $^3$ ,  $a$  = 9.9763(12),  $b$  = 11.9917(14),  $c$  = 12.5499(15) Å,  $\alpha$  = 113.910(2) $^\circ$ ,  $\beta$  = 103.612(2) $^\circ$ ;  $\gamma$  = 100.977(3) $^\circ$ ,  $V$  = 1263.1(3) Å $^3$ ,  $\rho_{\text{calcd}}$  = 1.878 g cm $^{-3}$ ,  $\mu$  = 1.493 cm $^{-1}$ , empirical multi-scan absorption correction ( $0.6879 \leq T \leq 0.9105$ ),  $Z$  = 2, triclinic, space group  $P\bar{1}$ ,  $\lambda$  = 0.71073 Å,  $T$  = 100 K,  $\omega$  scans, 17807 reflections collected ( $-15 \leq h \leq 14$ ,  $-17 \leq k \leq 18$ ,  $-18 \leq l \leq 18$ ),  $[(\sin \theta)/\lambda]_{\text{max}}$  = 0.756 Å $^{-1}$ , 8932 independent ( $R_{\text{int}}$  = 0.0678) and 5004 observed reflections [ $I \geq 2\sigma(I)$ ], 388 refined parameters,  $R$  = 0.0597,  $wR_2$  = 0.1259, max. residual electron density 1.072 (–1.150) e Å $^{-3}$ . Intensity data was collected on a Bruker SMART Apex CCD diffractometer, employing graphite-monochromated Mo- $\text{K}\alpha$  radiation. The structure was solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on  $F^2$  (SHELXL-97) [5]. The atomic displacement parameters were treated anisotropically for all non-hydrogen atoms. The hydrogen atoms were calculated in ideal positions and allowed to

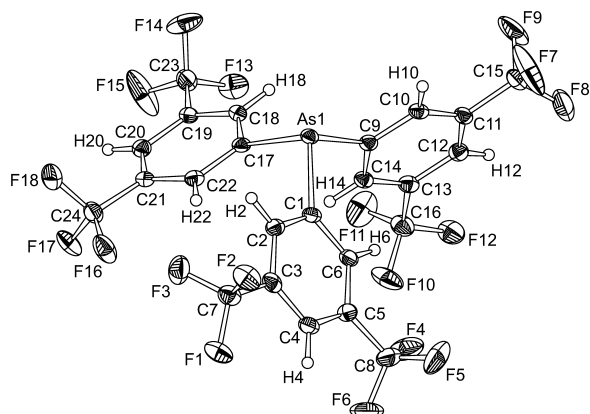


Fig. 1. Molecular structure of  $\text{As}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_3$  with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): As1–C1 1.979(3), As1–C9 1.961(3), As1–C17 1.987(3), C1–As1–C9 99.8(2), C1–As1–C17 98.3(2), C9–As1–C17 98.2(2).

ride on their parent atoms with fixed isotropic contributions. Graphics were prepared using DIAMOND [6]. Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre, CCDC-226276. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

## Results and Discussion

A convenient route to the title compound is the Grignard reaction of arsenic trichloride with 3,5-bis(trifluoromethyl)phenylmagnesium bromide. While there have been reports that phenyl Grignard reactants containing trifluoromethyl groups can explode spontaneously [4], in the present case the Grignard reagent was successfully prepared from 3,5-bis(trifluoromethyl)bromobenzene and magnesium. Following the subsequent reaction with arsenic trichloride, crystals of tris-[3,5-bis(trifluoromethyl)phenyl]arsine were obtained at  $-78^\circ\text{C}$  by recrystallisation from diethyl ether.

The molecular structure of the title compound is shown in Fig. 1. Due to the increased *s* character of the free electron pair at the arsenic atom the C–As–C angle of approximately  $99^\circ$  is significantly smaller than the tetrahedral angle. It is larger than in arsine and comparable to the value in triphenylarsine. This reflects the increased steric demand of the phenyl substituents in comparison to the hydrogen atom.

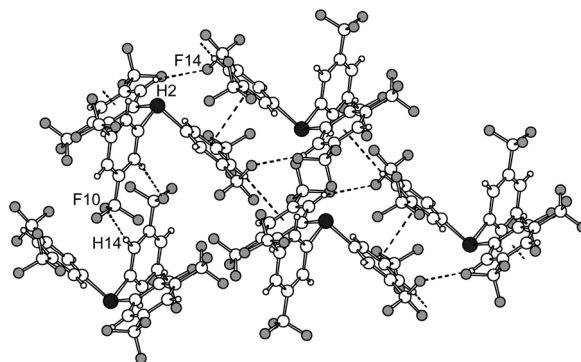


Fig. 2. Short intermolecular distances (dotted lines) indicating the C–H...F bonds between the interlocking molecules [leftmost pair of molecules,  $d(\text{C14} \cdots \text{H14} \cdots \text{F10}) = 3.561(4) \text{ Å}$ ,  $d(\text{H14} \cdots \text{F10}) = 2.63 \text{ Å}$ ,  $\angle(\text{C14} \cdots \text{H14} \cdots \text{F10}) = 166.7^\circ$ ] and between C2–H2...F14 [ $d(\text{C2} \cdots \text{H2} \cdots \text{F14}) = 3.460(4) \text{ Å}$ ,  $d(\text{H2} \cdots \text{F14}) = 2.58 \text{ Å}$ ,  $\angle(\text{C2} \cdots \text{H2} \cdots \text{F14}) = 153.7^\circ$ ]. Also shown are a possible C–H... $\pi$  interaction between H20 and the C1–C6 phenyl ring and a  $\pi \cdots \pi$  stacking between two C17–C22 phenyl rings.

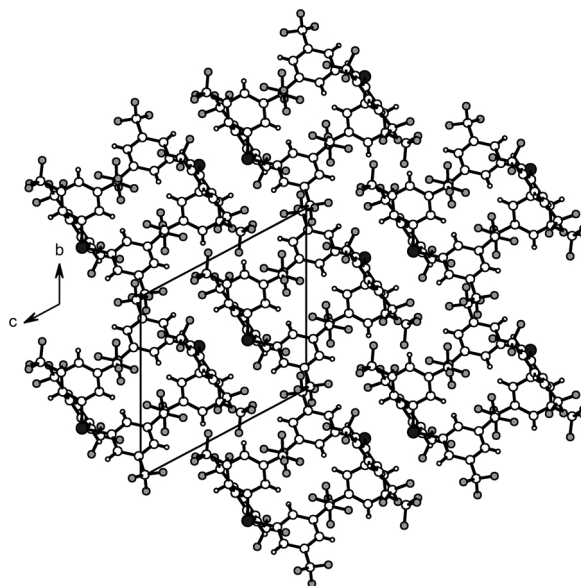


Fig. 3. Distorted hexagonal arrangement of the columns along [100].

The C–F bond distances in the trifluoromethyl groups, which range from 1.300(4) to 1.360(4) Å, show a much larger variation than the other bonds between non-hydrogen atoms in the molecular structure. In addition, some of the fluorine atoms have considerably elongated displacement ellipsoids. These findings illustrate the fact that the trifluoromethyl groups still possess a noticeable degree of freedom to move

even at the low temperature of 100 K, or have been locked in slightly disordered positions even though we have slowly cooled the crystal from room temperature to 100 K, at a rate of 10 K/h.

In the crystal structure, two molecules of the title compound are interlocked in such a way that one trifluoromethylphenyl group of each component protrudes into the cavity formed by the trigonal pyramidal shape of the second molecule (Fig. 2, leftmost pair of molecules). In this moiety two C–H...F contacts are found between H14 and F10. The aromatic rings are arranged ecliptically. Thus, this packing results in a compact unit that roughly resembles a parallelepiped with extrusions.

An analysis of the intermolecular distances reveals that there may be one weak C–H... $\pi$  interaction be-

tween H20 and the phenyl ring C1 to C6. The distance from H20 to the center of the ring is 3.19 Å and the angle between C20–H20 and the centroid is 169.40°. Also, two of the C17–C22 rings are found parallel and stacked well above each other with a centroid to centroid distance of 3.81 Å, which is rather long but still may be associated with a very weak  $\pi$ ... $\pi$  interaction. These interactions and additional short C–H...F distances (C2–H2...F14, Fig. 2) effectively link the molecules that are not part of the dimeric unit described above.

The crystal structure can therefore be described as consisting of columns which are formed by stacking the interlocked units along the *a* axis. The columns themselves are arranged in a distorted hexagonal pattern (Fig. 3).

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- [1] N.G. Andersen, B.A. Keay, *Chem. Rev.* **101**, 997 (2001).  
[2] M. Bardají, P.G. Jones, A. Laguna, A. Moracho, A. K. Fischer, *J. Organomet. Chem.* **648**, 1 (2001).  
[3] G.S. Hiers, in *Org. Synth., Coll. Vol. I*, 550 (1956).  
[4] E.C. Ashby, D.M. Al-Fekri, *J. Organomet. Chem.* **390**, 275 (1990).  
[5] G.M. Sheldrick, SHELX-97, Programs for crystal structure analysis, University of Göttingen, Germany (1997).  
[6] K. Brandenburg, DIAMOND. Release 2.1e. Crystal Impact, Bonn, Germany (2001).