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FULL PAPER

New group 15 compounds containing the 2,4,6-$(CF_3)_3C_6H_2$ (fluoromes = Ar), 2,6-$(CF_3)_2C_6H_3$ (fluoroxyl = Ar′) or 2,4-$(CF_3)_2C_6H_3$ (Ar″) ligands

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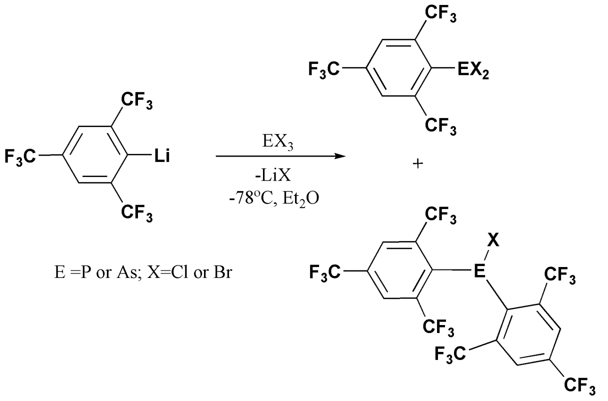
Several new P or As compounds containing the 2,4,6-$(CF_3)_3C_6H_2$ (Ar), 2,6-$(CF_3)_2C_6H_3$ (Ar′) and/or 2,4-$(CF_3)_2C_6H_3$ (Ar″) ligands have been synthesised, and characterised by multinuclear NMR spectroscopy and (for all isolated compounds) elemental analysis. The crystal and molecular structures of $ArPBr_2$ **1**, Ar_2PCl **2**, Ar''_2PCl **3**, Ar''_2PBr **4**, Ar′Ar″AsCl **5**, Ar′Ar″AsBr **6** and Ar′Ar″AsH **7** have been determined by single-crystal X-ray diffraction. A particularly interesting feature of these structures is close contacts between *ortho*-fluorines and the P or As atoms, as observed previously in Ar′Ar″PCl and Ar_2AsCl.

Introduction

The ability of the 2,4,6-$(CF_3)_3C_6H_2$ (fluoromes = Ar) group to stabilise both main group and transition metal species is well-documented.[1–25] Comparatively little has been published about the 2,6-$(CF_3)_2C_6H_3$ (fluoroxyl = Ar′) group as a substituent, however,[6,24,26–28] partly because there are complications in the chemistry of the precursor 1,3-bis(trifluoromethyl)benzene, Ar′H.[24,27,28] This can lithiate in two positions, giving rise to a mixture of 2,6-$(CF_3)_2C_6H_3$ (Ar′) and 2,4-$(CF_3)_2C_6H_3$ (Ar″) derivatives. The latter ligand is unlikely to stabilise low-coordinate species such as diphosphenes, because of only one bulky substituent in the *ortho*-position. In group 15, the hydrides and halides $ArPH_2$,[1,2] $ArPCl_2$,[1,2] ArPClF,[1] $ArPF_2$,[1] $Ar'PH_2$,[26] $Ar'PCl_2$,[26] Ar_2PH,[20] Ar_2PCl,[1] Ar′Ar″PCl,[24] Ar′Ar″PF,[27] Ar''_2PF,[27] $ArAsCl_2$,[16] Ar_2AsH,[2] Ar_2AsCl,[22] Ar_2AsF,[2] $ArSbCl_2$,[1] Ar_2SbCl,[1,21,22] Ar_2BiCl[5] and Ar_3Bi[5] have been reported. Of these, only Ar′Ar″PCl,[24] Ar_2AsCl,[22] Ar_2SbCl,[22] Ar_2BiCl[5] and Ar_3Bi[5] have been characterised crystallographically. In a very recent paper we described the synthesis, X-ray crystal structure and a detailed multinuclear NMR study in both solid state and solution of Ar′Ar″PCl.[24] In the present work, we report the synthesis and characterisation of several new group 15 derivatives containing Ar, Ar′ and/or Ar″ substituents. The X-ray crystal and molecular structures have been determined at low temperature for $ArPBr_2$ **1**, Ar_2PCl **2**, Ar''_2PCl **3**, Ar''_2PBr **4**, Ar′Ar″AsCl **5**, Ar′Ar″AsBr **6** and Ar′Ar″AsH **7**.

Results and discussion

The halogeno-derivatives were synthesised by reaction of the appropriate group 15 trihalide with the lithiated materials ArLi (from ArH) or a mixture of Ar′Li/Ar″Li (from Ar′H), as shown in Schemes 1 and 2, respectively. Even when an excess of the halide was used, some of the twice-substituted derivative Ar_2EX (except for Ar_2PBr), Ar′Ar″EX or Ar''_2EX (E = P or As; X = Cl or Br) was isolated, as described for Ar′Ar″AsCl **5** and Ar''_2PCl **3**. No evidence was found in the Ar′Li/Ar″Li reactions for the formation of the more sterically hindered second substitution product Ar'_2EX. The compounds could be identified by means of their ^{19}F and (where appropriate) ^{31}P NMR solution-state spectra (Experimental section). The hydrido-species Ar′Ar″PH **8** and Ar′Ar″AsH **7** were prepared by $LiAlH_4$ reduction of the corresponding chlorides; the synthesis of Ar′Ar″PCl, and its X-ray crystal structure, have been described in a previous paper.[24]



Scheme 1 Reaction of ArLi with EX_3 (E =P or As; X = Cl or Br).

A mixture of the chloro-derivatives ArAr′PCl **9** and ArAr″PCl **10** was also prepared by reaction of Ar′Li/Ar″Li with $ArPCl_2$ in an overall 1:1 molar ratio. Both compounds could be distinguished by their ^{19}F and ^{31}P NMR solution spectra, but they could not be separated by distillation.

A very notable feature of the room temperature ^{19}F NMR spectra for all compounds with one Ar″ substituent and one Ar or Ar′ substituent was the occurrence of a broad, unresolved resonance for the two *ortho*-CF_3 groups of the Ar or Ar′ moiety. Similar observations have been reported previously by us for Ar′Ar″PCl,[24] and in the literature for Ar′Ar″PF[27] and Cp*ArPCl,[29] with $^4J_{PF}$ not resolved, although interestingly a $^4J_{PF}$ value of 31.6 Hz was recorded for Cp*ArPH.[29] These results suggest strongly that there is a rotational barrier present in the more sterically hindered species. A detailed ^{19}F NMR temperature-dependence study is in progress, together with theoretical calculations, and these results will be reported elsewhere when complete.[30]

Eight of the compounds have been isolated as solids, and low-temperature X-ray crystal structures have been determined for seven of these. The only failure was Ar′Ar″PH **8**, for which

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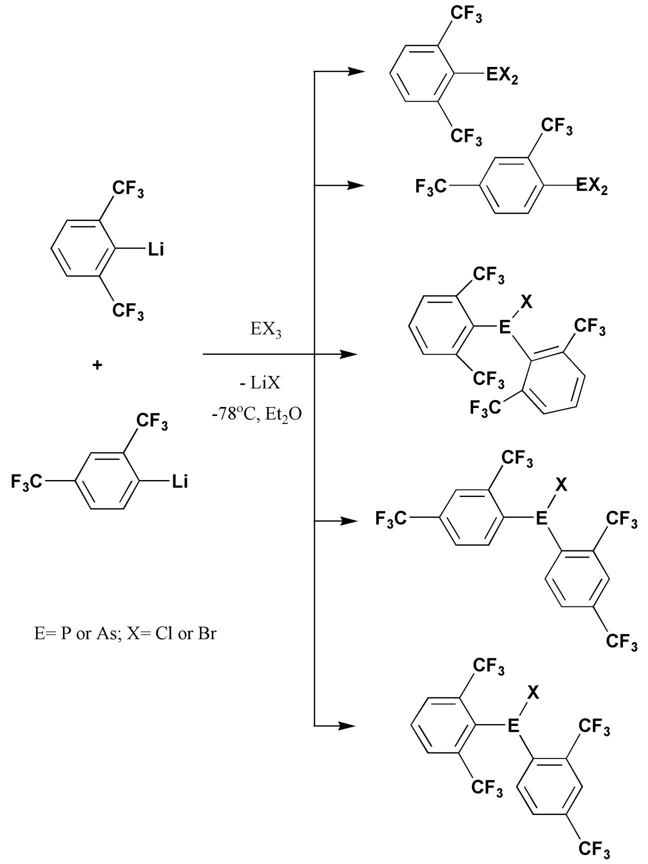

Scheme 2 Reaction of Ar′Li/Ar″Li with EX_3 (E = P or As; X = Cl or Br).

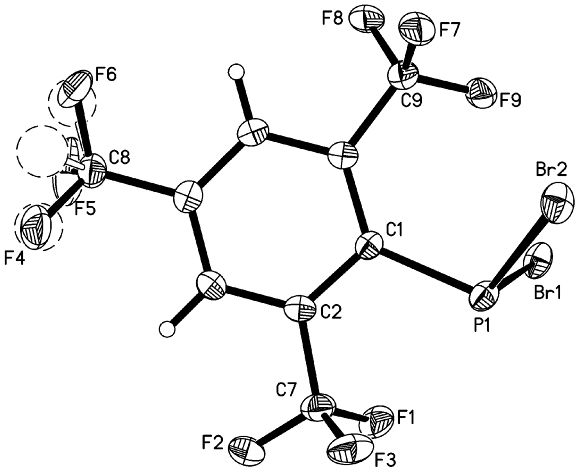

Fig. 1 Thermal ellipsoid drawing of $ArPBr_2$ **1**, showing 50% probability displacement ellipsoids for non-H atoms, and the disorder in the *p*-CF_3 group.

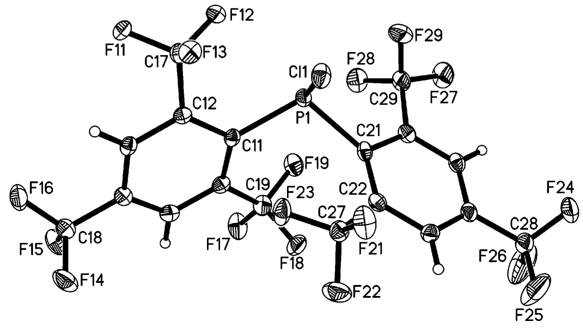

Fig. 2 Thermal ellipsoid drawing of Ar_2PCl **2**, showing 50% probability displacement ellipsoids for non-H atoms.

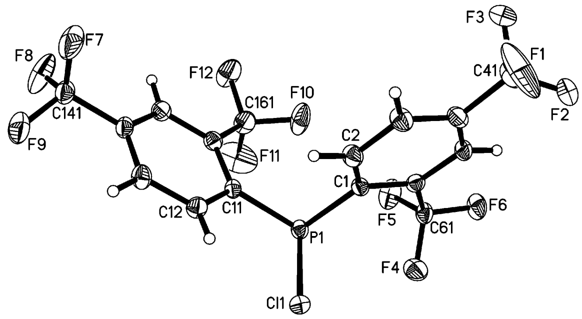

Fig. 3 Thermal ellipsoid drawing of Ar''_2PCl **3**, showing 50% probability displacement ellipsoids for non-H atoms.

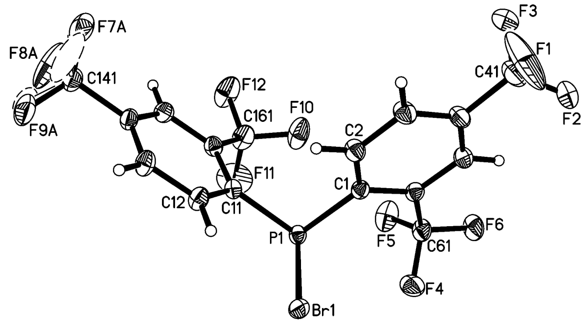

Fig. 4 Thermal ellipsoid drawing of Ar''_2PBr **4**, showing 50% probability displacement ellipsoids for non-H atoms, and the disorder in one of the *p*-CF_3 groups.

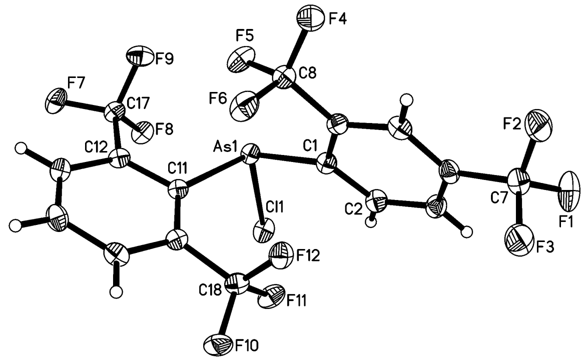

Fig. 5 Thermal ellipsoid drawing of $Ar'Ar''AsCl$ **5**, showing 50% probability displacement ellipsoids for non-H atoms.

data were collected but the structure could not be solved, because of poor crystal quality. The crystal and molecular structures have been established for $ArPBr_2$ **1**, Ar_2PCl **2**, Ar''_2PCl **3**, Ar''_2PBr **4**, $Ar'Ar''AsCl$ **5**, $Ar'Ar''AsBr$ **6** and $Ar'Ar''AsH$ **7**; these are illustrated in Figs. 1–7, respectively. Selected bond distances and angles are listed in Table 1 for phosphorus compounds and in Table 2 for arsenic derivatives. It is noteworthy that the crystals of **3** and **4** are isomorphous, while **5** is isomorphous with **6**.

Compound **1** crystallises with two independent molecules in the asymmetric unit, as shown in Fig. 1 and Table 1. The October 2001 release of the Cambridge Structural Database (Version 5.22)[31] contains only three structures of $RPBr_2$ compounds, *viz*. $Ph_3P{=}C(Me)PBr_2$,[32] $Ph_3P{=}C(SiMe_3)PBr_2$[32] and $C_5H(CHMe_2)_4PBr_2$.[33] The Br–P–Br angle in these compounds is smaller than in **1**, ranging from 93.5(1) to 96.06(7)°;[32] it is noteworthy, however, that the sum of the bond angles around phosphorus is also larger in **1** (*ca.* 310°) compared with the first two compounds above, where it varies from 295.8[32] to 305.7°,[31,33] reflecting the greater steric demands of the *ortho*-CF_3 groups. The P–Br bond lengths in **1** and **4** are slightly shorter than usually found in organophosphorus bromides (*e.g.* values between 2.268(2) and 2.489(3) Å),[32–38] although shorter

Table 1 Selected bond distances (Å) and angles (°) for phosphorus compounds **1–4**

$ArPBr_2$ **1**				Ar_2PCl **2**		Ar''_2PCl **3**		Ar''_2PBr **4**	
P(1)–Br(1)	2.2228(8)	P(2)–Br(3)	2.2166(8)	P(1)–Cl(1)	2.0628(10)	P(1)–Cl(1)	2.0619(9)	P(1)–Br(1)	2.2340(5)
P(1)–Br(2)	2.2153(8)	P(2)–Br(4)	2.2194(8)	P(1)–C(11)	1.882(3)	P(1)–C(1)	1.854(2)	P(1)–C(1)	1.8572(18)
P(1)–C(1)	1.879(3)	P(2)–C(11)	1.887(3)	P(1)–C(21)	1.885(3)	P(1)–C(11)	1.857(2)	P(1)–C(11)	1.8591(17)
C(1)–P(1)–Br(2)	102.10(8)	C(11)–P(2)–Br(4)	102.41(8)	C(11)–P(1)–C(21)	109.87(12)	C(1)–P(1)–C(11)	100.37(10)	C(1)–P(1)–C(11)	100.51(8)
C(1)–P(1)–Br(1)	102.52(9)	C(11)–P(2)–Br(3)	103.22(8)	C(11)–P(1)–Cl(1)	103.68(9)	C(1)–P(1)–Cl(1)	97.38(7)	C(1)–P(1)–Br(1)	96.99(6)
Br(2)–P(1)–Br(1)	105.35(3)	Br(3)–P(2)–Br(4)	104.90(3)	C(21)–P(1)–Cl(1)	92.95(9)	C(11)–P(1)–Cl(1)	100.95(7)	C(11)–P(1)–Br(1)	101.63(6)

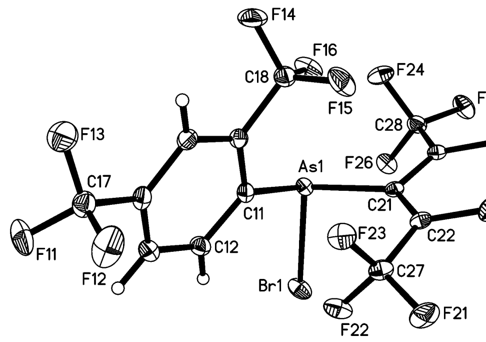

Fig. 6 Thermal ellipsoid drawing of Ar′Ar″AsBr **6**, showing 50% probability displacement ellipsoids for non-H atoms.

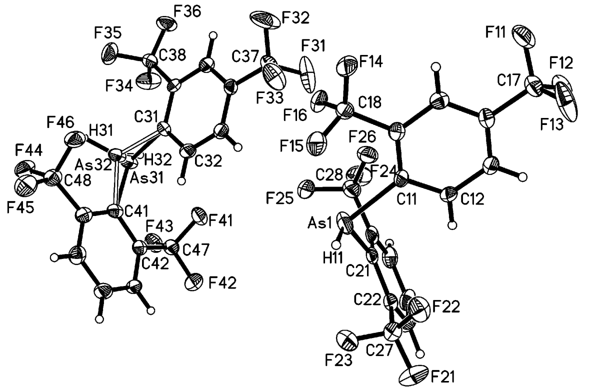

Fig. 7 Thermal ellipsoid drawing of Ar′Ar″AsH **7**, showing 50% probability displacement ellipsoids for non-H atoms; both independent molecules in the asymmetric unit are shown, because of the disorder in one As atom position.

P–Br distances of 2.203(3)–2.212(3) Å have been observed in PBr_3 complexes with $Cr(CO)_5$[39,40] and $W(CO)_5$.[40] This parallels the observation of a fairly short P–Cl bond in Ar′Ar″PCl of 2.061(1) Å, which was attributed to the electron-withdrawing properties of the CF_3 groups,[24] and of 2.063(1) Å in **2** and 2.062(1) Å in **3** (Table 1).

One striking feature of the crystal structure of **2** is the very marked asymmetry in the C–P–Cl bond angles, which differ by more than 10°. Similar observations have been reported in the literature for Ar_2AsCl (which exists in two different crystalline modifications, orthorhombic at 130 K and monoclinic at 296 K, with similar structures[22]), Ar_2SbCl[22] and Ar_2BiCl,[5] as shown in Table 3, although no comments thereon were included in these reports. This asymmetry probably arises as a consequence of secondary interactions between the group 15 element and fluorines of the *ortho*-CF_3 groups, as discussed in more detail below. Only minor differences in the C–E–X (E = P or As; X = Cl or Br) angles are apparent for the less sterically hindered compounds Ar′Ar″PCl,[24] Ar''_2PCl **3**, Ar''_2PBr **4**, Ar′Ar″AsCl **5** and Ar′Ar″AsBr **6**, with a maximum value of *ca.* 3.7° in **4**, as shown in Tables 1 and 2.

The As–Cl bond length in **5** of 2.2074(5) Å is similar to that in the orthorhombic modification of Ar_2AsCl (2.1920(12) Å),[22] and slightly shorter than in $AsCl_3$,[41] or other organo-derivatives with one As–Cl bond.[42–44] The As–Br distance of 2.3530(3) Å in **6** also appears normal, lying between the values of 2.31 Å for $AsBr_3$[45] and 2.40(1) Å for Ph_2AsBr,[46] and is similar to the corresponding bond length in Mes_2AsBr of 2.34(2) Å at low temperature and 2.3846(4) Å at higher temperature.[47] In structure **7**, there are two distinct molecules in each asymmetric unit, one of which has the arsenic atom disordered over two almost equally-populated sites (55 and 45% occupation, respectively). Data for the non-disordered As(1) atom are quoted in Table 2. The As–C distances are very similar in all instances, ranging from 1.980(4) to 2.007(6) Å, but even for As(1) it is not possible

Table 2 Selected bond distances (Å) and angles (°) for arsenic compounds **5**–**7**

Ar′Ar″AsCl **5**		Ar′Ar″AsBr **6**		Ar′Ar″AsH **7**[a]	
As(1)–Cl(1)	2.2074(5)	As(1)–Br(1)	2.3530(3)	As(1)–H(11)	See text
As(1)–C(1)	1.9880(18)	As(1)–C(11)	1.9827(19)	As(1)–C(11)	1.980(5)
As(1)–C(11)	2.0182(17)	As(1)–C(21)	2.0099(19)	As(1)–C(21)	1.995(5)
C(1)–As(1)–C(11)	102.98(7)	C(11)–As(1)–C(21)	103.15(8)	C(11)–As(1)–C(21)	98.11(18)
C(1)–As(1)–Cl(1)	100.08(6)	C(11)–As(1)–Br(1)	101.43(6)	C(11)–As(1)–H(11)	See text
C(11)–As(1)–Cl(1)	98.84(5)	C(21)–As(1)–Br(1)	98.91(5)	C(21)–As(1)–H(11)	See text

[a] Data for As(1): see text for further discussion.

Table 3 Comparison of key bond distances (Å) and angles (°) for Ar_2ECl (E = P, As, Sb or Bi)

Compound	Ar_2PCl	Ar_2AsCl[a]	Ar_2SbCl	Ar_2BiCl
E–Cl	2.0628(10)	2.1920(12)	2.358(11)	2.463(3)
E–C(1)	1.882(3)	2.023(4)	2.22(3)	2.356(8)
E–C(2)	1.885(3)	2.016(4)	2.25(3)	2.338(7)
C(1)–E–C(2)	109.87(12)	107.53(16)	107.0(12)	106.9(3)
C(1)–E–Cl	103.68(9)	100.57(12)	101.3(9)	99.5(2)
C(2)–E–Cl	92.95(9)	92.04(11)	88.4(9)	87.8(2)
Reference	This work	22	22	5

[a] Data for the orthorhombic modification at 130 K.

to be precise about distances or bond angles involving the H atom attached to As. The results indicate 1.37(6) Å for As(1)–H(11), and in the disordered molecule 1.42(10) Å for As(32)–H(32), and 1.63(12) Å for As(31)–H(31). These compare with 1.484(18) Å in a primary organoarsine,[48] a calculated value of 1.519 Å in AsH_3,[49] 1.520 Å in $[Cp^*Mn(CO)_2]AsH$,[50] and 1.5(2) Å in $Cp_2Nb(HAsEt_2)(H_3BAsEt_2)$.[51]

Disorder was found for the *para*-CF_3 groups in $ArPBr_2$ **1** and Ar″PBr **4**. This is often observed in compounds with these substituents, for example in Ar_2AsCl,[22] Ar_2SbCl,[22] Ar_2BiCl[5] and Ar_3Bi.[5] In all of the compounds studied there appear to be secondary interactions between the group 15 element and some of the fluorines of the *ortho*-CF_3 groups, as observed previously in Ar_2AsCl (both forms),[22] Ar_2SbCl[22] and Ar′Ar″PCl.[24] This is illustrated in Table 4, where the range of short E ··· F contacts (E = P, As or Sb), and number of such contacts, are listed, together with the number of fluorines in *ortho*-CF_3 groups. (There are often further E ··· F contacts at only slightly longer distances.) At least three such interactions are found for six fluorines in *o*-CF_3 groups, four for nine fluorines, and five for the only example studied here with twelve fluorines, *i.e.* Ar_2PCl **2**. The distances are shorter in all instances than the sum of the empirical van der Waals radii of P (1.91 Å) and F (1.40 Å),[52] as well as the theoretical ones (estimated as 2.05 and 1.42 Å respectively[53]). Since the van der Waals radii of As and Sb are expected to be larger than that of P, this deduction applies *a fortiori* to the heavier elements. These secondary interactions are expected to play a vital role in stabilising the structures, and almost certainly account for the large asymmetry in C–E–Cl bond angles in Ar_2ECl, described above. Similar interactions of fluorines from *ortho*-CF_3 groups in Ar ligands with the transition metals V,[18] Cr[19,25] and Mo[25] have also been reported.

Experimental

All manipulations, including NMR sample preparation, were carried out either under an inert atmosphere of dry nitrogen or *in vacuo*, using standard Schlenk procedures or a glovebox. Chemicals of the best available commercial grades were used, in general without further purification. The ^{31}P NMR spectra of phosphorus-containing starting materials were checked, to confirm the absence of any major impurities. ^{19}F NMR spectra were recorded on a Varian Mercury 200, Varian VXR 400, or Varian Inova 500 Fourier-transform spectrometer at 188.18, 376.35, and 470.26 MHz, respectively. ^{31}P NMR spectra were recorded on the same instruments at 80.96, 161.91 or 202.32 MHz. Chemical shifts were measured relative to external $CFCl_3$ (^{19}F) or 85% H_3PO_4 (^{31}P), with the higher frequency direction taken as positive. Microanalyses were performed by the microanalytical services of the Department of Chemistry, University of Durham.

Solutions containing ArLi or a mixture of Ar′Li/Ar″Li were prepared as described previously.[24,54]

Synthesis of $ArPBr_2$ 1

A solution of ArLi (100 ml, 48 mmol) was added to a PBr_3 (2.25 ml, 24 mmol) solution in diethyl ether (100 ml) at −78 °C. The solution was allowed to warm to room temperature and stirred for 2 h. A white precipitate of LiBr appeared. The solution was filtered and the solvents and excess PBr_3 were removed *in vacuo* leaving an orange oil. This oil was distilled under reduced pressure (0.03 Torr) giving colourless crystals. Yield (based on ArH): 4.80 g (20.3%).

Elemental analysis for $C_9H_2Br_2F_9P$ (M = 472). Calc: C 22.88, H 0.4%. Found: C 22.76, H 0.45%.

Table 4 Short E–F contacts (E = P, As or Sb)

Compound	Range (Å)		No. of contacts	No. of fluorines	Ref.
$ArPBr_2$ **1**	P(1)	2.865–3.208	3	6	This work
	P(2)	2.877–3.217	3	6	
Ar_2PCl **2**		2.843–3.111	5	12	This work
Ar′Ar″PCl		2.890–3.25	4	9	24
Ar''_2PCl **3**		2.874–3.124	3	6	This work
Ar''_2PBr **4**		2.887–3.122	3	6	This work
Ar_2AsCl	130(2) K	2.991–3.012	3	12	22
	296(1) K	2.935–3.110	3	12	22
Ar′Ar″AsCl **5**		2.701–3.292	4	9	This work
Ar′Ar″AsBr **6**		2.707–3.277	4	9	This work
Ar′Ar″AsH **7**	As(1)	2.934–3.186	4	9	This work
	As(31)	2.859–3.326	4	9	
	As(32)	2.880–3.247	4	9	
Ar_2SbCl		2.821–3.107	4	12	22

^{31}P NMR (CDCl$_3$): δ 130.1 (septet, $^4J_{\mathrm{P–F}}$ 62.3 Hz); ^{19}F NMR (CDCl$_3$): δ −53.1 (d, $^4J_{\mathrm{P–F}}$ 62.4 Hz, 6F, *o*-CF$_3$), −64.1 (s, 3F, *p*-CF$_3$).

Synthesis of Ar$_2$PCl 2

A solution of ArLi (100 ml, 48 mmol) was added dropwise to a solution of PCl$_3$ (2.09 ml, 24 mmol) in diethyl ether at −78 °C. The solution was allowed to warm to room temperature and stirred for 2 h. A white precipitate of LiCl appeared. The solution was filtered and the solvents and excess PCl$_3$ were removed under vacuum leaving a yellow oil, which was distilled under reduced pressure (0.01 Torr). Fractions were collected at 60 °C (ArPCl$_2$; ~65% of distillate) and 100 °C (Ar$_2$PCl; ~35% of distillate). Crystals were grown by recrystallisation from dichloromethane.

Elemental analysis for C$_{18}$H$_4$ClF$_{18}$P (M = 628.5). Calc.: C 34.36, H 0.6%. Found: C 34.1, H 0.6%.

^{31}P NMR (CDCl$_3$): δ 74.9 (m, $^4J_{\mathrm{P–F}}$ 41.9 Hz); ^{19}F NMR (CDCl$_3$): δ −54.4 (d, $^4J_{\mathrm{P–F}}$ 41.2 Hz, 12F, *o*-CF$_3$), −64.1 (s, 6F, *p*-CF$_3$).

Synthesis of Ar″$_2$PCl 3

A solution of Ar′Li/Ar″Li (100 ml, 94 mmol) in diethyl ether was added dropwise over 20 min to a solution of PCl$_3$ (25.2 g, 16 ml, 162 mmol) in diethyl ether (100 ml) at −78 °C. This solution was allowed to warm to room temperature and stirred for 4 h. A white precipitate of LiCl appeared. The solution was filtered through a fine sinter, and solvent and PCl$_3$ in excess were removed *in vacuo* giving a brown oil. The product was purified by distillation under vacuum (0.02 Torr) and two different fractions were collected at 86 °C (Ar′PCl$_2$/Ar″PCl$_2$; yield 9.2 g, 31% based on Ar′H) and 140 °C (Ar″$_2$PCl). Crystals of Ar″$_2$PCl were obtained by recrystallisation from hexanes. Yield (based on Ar′H) 11.68 g (25%).

Elemental analysis for C$_{16}$H$_6$ClF$_{12}$P (M = 492.5). Calc.: C 38.97, H 1.22%. Found: C 38.96, H 1.35%.

^{31}P NMR (CDCl$_3$) δ 68.3 (septet, $^4J_{\mathrm{P–F}}$ 65.5 Hz); ^{19}F NMR (CDCl$_3$) δ −57.3 (d, $^4J_{\mathrm{P–F}}$ 65.8 Hz, 6F, *o*-CF$_3$), −63.7 (s, 6F, *p*-CF$_3$); ^{13}C NMR (C$_7$D$_8$) δ 140.3 (d, $^1J_{\mathrm{P–C}}$ 56.8 Hz), 133.1 (q, $^2J_{\mathrm{F–C}}$ 33.9 Hz), 129.1 (s), 123.7 (br s), 123.6 (d, $^2J_{\mathrm{P–C}}$ 1.9 Hz), 123.6 (q, $^1J_{\mathrm{F–C}}$ 275.8 Hz), 123.4 (qd, $^1J_{\mathrm{P–C}}$ 273.1 Hz, $^3J_{\mathrm{P–C}}$ 1.74 Hz).

Synthesis of Ar″$_2$PBr 4

A solution of Ar′Li/Ar″Li (100 ml, 94 mmol) was added slowly to a PBr$_3$ (8 ml, 85 mmol) solution in diethyl ether (100 ml) at −78 °C. The solution was allowed to warm to room temperature and stirred for 5 h. A white precipitate of LiBr appeared. The solution was filtered and the solvents and excess PBr$_3$ were removed *in vacuo* leaving a brown oil. This oil was distilled under reduced pressure (0.01 Torr), fractions were collected at 60 °C (Ar′PBr$_2$/Ar″PBr$_2$; ~65% of distillate) and 120 °C (Ar″$_2$PBr; ~35% of distillate). Yield (based on Ar′H): 4.52 g (9%).

Elemental analysis for C$_{16}$H$_6$BrF$_{12}$P (M = 537). Calc.: C 35.78, H 1.13%. Found: C 35.69, H 1.15%.

^{31}P NMR (CDCl$_3$): δ 57.4 (septet, $^4J_{\mathrm{P–F}}$ 65.8 Hz); ^{19}F NMR (CDCl$_3$) δ −57.7 (d, $^4J_{\mathrm{P–F}}$ 65.8 Hz, 6F, *o*-CF$_3$), −63.7 (s, 6F, *p*-CF$_3$).

Synthesis of Ar′Ar″AsCl 5

A solution of Ar′Li/Ar″Li (100 ml, 94 mmol) in diethyl ether was added dropwise to a solution of AsCl$_3$ (13.5 ml, 160 mmol) in hexanes (100 ml) over a period of 20 min at −78 °C. The mixture was allowed to warm to room temperature and stirred for 4 h. A precipitate of LiCl formed. This was filtered off and the solvents and excess AsCl$_3$ removed *in vacuo*, leaving a brown oil. This oil was distilled under reduced pressure (0.01 Torr), and three different fractions were collected at 100 °C (Ar′AsCl$_2$; ~30% of distillate), 115 °C (Ar″AsCl$_2$; ~20% of distillate) and 145 °C (Ar′Ar″AsCl; ~50% of distillate). Ar′Ar″AsCl was purified by recrystallisation from hexanes. Yield (based on Ar′H): 4.5 g (9%)

Elemental analysis for C$_{16}$H$_6$AsClF$_{12}$ (M = 536.4). Calc.: C 35.79, H 1.12%. Found: C 35.33, H 1.10%.

^{19}F NMR (CDCl$_3$): δ −54.8 (br s, 6F, *o*-CF$_3$ in Ar′), −58.8 (s, 3F, *o*-CF$_3$ in Ar″), −63.5 (s, 3F, *p*-CF$_3$); ^{1}H NMR (CDCl$_3$): δ 8.1 (d, $^3J_{\mathrm{H–H}}$ 8 Hz), 7.7 (s), 7.28 (d, $^3J_{\mathrm{H–H}}$ 8 Hz), 7.26 (d, $^3J_{\mathrm{H–H}}$ 7.6 Hz), 6.6 (t, $^3J_{\mathrm{H–H}}$ 7.6 Hz).

Synthesis of Ar′Ar″AsBr 6

An Ar′Li/Ar″Li (20 ml, 19 mmol) solution in diethyl ether was added dropwise to a solution of AsBr$_3$ (3.2 g, 10.2 mmol) in hexanes at room temperature. The solution was stirred for 4 h, giving a brown solution. Solvents were removed under vacuum leaving a brown oil which was distilled under reduced pressure (0.01 Torr). Fractions were collected at 81 °C (Ar′AsBr$_2$/Ar″AsBr$_2$; ~60% of distillate) and 110 °C (Ar′Ar″AsBr/Ar″$_2$AsBr; ~40% of distillate).

The Ar′Ar″AsBr/Ar″$_2$AsBr mixture was dissolved in hexanes and left in the freezer. After one month colourless crystals of Ar′Ar″AsBr appeared. Yield 0.98 g (31%).

Elemental analysis for C$_{16}$H$_6$AsBrF$_{12}$ (M = 581.03). Calc.: C 33.08, H 1.04%; Found: C 33.46, H 1.04%.

^{19}F NMR (CDCl$_3$): δ −54.9 (br s, 6F, *o*-CF$_3$ in Ar′), −58.8 (s, 3F, *o*-CF$_3$ in Ar″), −63.5 (s, 3F, *p*-CF$_3$).

Synthesis of Ar′Ar″AsH 7

LiAlH$_4$ (0.2 ml, 1 M in diethyl ether, 0.2 mmol) was slowly added at 0 °C to an Ar′Ar″AsCl (0.2 g, 0.4 mmol) solution in hexanes. The solution was left to warm to room temperature and stirred for four days. Solvents were removed *in vacuo* and the resulting white solid washed three times with hexanes (3 × 2 mL). Crystals were grown by sublimation under vacuum. Yield 0.15 g (71%).

Elemental analysis for C$_{16}$H$_7$AsF$_{12}$ (M = 502.1). Calc.: C 38.27, H 1.41%. Found: C 37.98, H 2.03%

^{19}F NMR (C$_7$D$_8$): δ −58.2 (d, $^5J_{\mathrm{F–H}}$ 7.1 Hz, 6F, *o*-CF$_3$ in Ar′), −61.2 (s, 3F, *o*-CF$_3$ in Ar″), −63.8 (s, 3F, *p*-CF$_3$); ^{1}H NMR (C$_7$D$_8$): δ 8.06 (d, $^3J_{\mathrm{H–H}}$ 8 Hz), 7.9 (s), 7.7 (t, $^3J_{\mathrm{H–H}}$ 8 Hz), 7.4 (d, $^3J_{\mathrm{H–H}}$ 8 Hz), 6.9 (t, $^3J_{\mathrm{H–H}}$ 7.6 Hz), 5.99 (br s, As–H).

Synthesis of Ar′Ar″PH 8

LiAlH$_4$ (0.09 ml, 1.0 M in diethyl ether, 0.09 mmol) was added to an Ar′Ar″PCl (0.08 g, 0.18 mmol) solution in diethyl ether (5 ml). The solution was stirred for one day. A white precipitate of LiCl appeared; the solution was then filtered and solvents were removed under vacuum leaving a white solid, which was washed three times with diethyl ether (3 × 2 ml). Yield 0.05 g (60%).

Elemental analysis for C$_{16}$H$_7$PF$_{12}$ (M = 458.2). Calc.: C 41.90, H 1.54%. Found: C 39.95, H 2.12%.

^{19}F NMR (CDCl$_3$): δ −57.7 (br s, 6F, *o*-CF$_3$ in Ar′), −61.2 (d, $^4J_{\mathrm{P–F}}$ 43.7 Hz, 3F, *o*-CF$_3$ in Ar″), −63.4 (s, 3F, *p*-CF$_3$); ^{31}P{^{1}H} NMR (C$_7$D$_8$): δ −67.2 (m); ^{31}P(^{1}H coupled) NMR (C$_7$D$_8$): δ −67.6 (dm, $^1J_{\mathrm{P–H}}$ 240.7 Hz); ^{1}H NMR (C$_7$D$_8$): δ 7.5–6.2 (aromatic region), 5.7 (d, $^1J_{\mathrm{P–H}}$ 240.4 Hz, P–H).

Synthesis of ArAr′PCl 9/ArAr″PCl 10

A solution of Ar′Li/Ar″Li (20 ml, 6.6 mmol) was added dropwise to a solution of ArPCl$_2$ (2.52 g, 6.6 mmol) in diethyl ether. A precipitate of LiCl immediately formed. The solution was filtered and distilled under reduced pressure (0.01 Torr) giving a yellow oil, bp 110 °C.

^{19}F NMR (CDCl$_3$): ArAr′PCl **9**: δ −54.1 (d, $^4J_{\mathrm{P–F}}$ 42.1 Hz, 6F, *o*-CF$_3$), −54.3 (d, $^4J_{\mathrm{P–F}}$ 42.1 Hz, 6F, *o*-CF$_3$), −64 (s, 3F,

Table 5 Crystal data and structure refinement parameters

	$ArPBr_2$ **1**	Ar_2PCl **2**	Ar''_2PCl **3**	Ar''_2PBr **4**	$Ar'Ar''AsCl$ **5**	$Ar'Ar''AsBr$ **6**	$Ar'Ar''AsH$ **7**
Empirical Formula	$C_9H_2Br_2F_9P$	$C_{18}H_4ClF_9P$	$C_{16}H_6ClF_{12}P$	$C_{16}H_6BrF_{12}P$	$C_{16}H_6AsClF_{12}$	$C_{16}H_6AsBrF_{12}$	$C_{16}H_7AsF_{12}$
M_r	471.90	628.63	492.63	537.09	536.4	581.04	502.14
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$I2/a$	$I2/a$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Crystal size/mm	0.42 × 0.26 × 0.22	0.10 × 0.08 × 0.01	0.22 × 0.16 × 0.10	0.40 × 0.50 × 0.75	0.18 × 0.20 × 0.40	0.35 × 0.30 × 0.2	0.30 × 0.10 × 0.05
T/K	110(2)	120(2)	100(2)	103(2)	100(2)	120(2)	120(2)
a/Å	8.000(1)	8.0347(6)	18.734(6)	19.0725(13)	13.436(3)	13.7761(8)	8.1315(10)
b/Å	10.501(1)	8.5325(6)	8.170(3)	8.2148(6)	9.055(1)	8.9308(5)	14.9159(18)
c/Å	16.153(2)	29.833(2)	23.559(7)	23.6350(15)	14.644(3)	14.6416(8)	28.272(4)
α/°	101.39(1)	90.00	90.00	90.00	90.00	90.00	90.00
β/°	98.48(1)	94.572(2)	96.820(5)	97.447(4)	100.98(1)	99.6590(10)	96.389(2)0
γ/°	90.91(1)	90.00	90.00	90.00	90.00	90.00	90.00
V/Å^3	1314.3(3)	2038.7(3)	3580.2(19)	3671.8(4)	1749.0(6)	1775.84(17)	3407.7(7)
Z	4	4	8	8	4	4	8
D_c/g cm^{-3}	2.385	2.048	1.828	1.943	2.043	2.173	1.957
μ/mm^{-1}	6.385	0.436	0.423	2.444	2.219	4.285	2.119
R_{int}	0.0247	0.0486	0.0507	0.0354	0.0303	0.0324	0.0565
Observed data [$I > 2\sigma(I)$]	5691	3233	3420	4504	3749	3532	5199
R_1 [$I > 2\sigma(I)$]	0.0287	0.0430	0.0435	0.0294	0.0257	0.0220	0.0592
R_1 (all data)	0.0385	0.0761	0.0656	0.0325	0.0326	0.0294	0.0888
wR_2 [$I > 2\sigma(I)$]	0.0727	0.0952	0.1053	0.0713	0.0647	0.0472	0.1203
wR_2 (all data)	0.0755	0.1087	0.1158	0.0732	0.0687	0.0494	0.1329
Goodness of fit (S)	1.065	1.044	1.037	1.040	1.048	1.067	1.139
No. of variables	399	343	295	280	295	271	536

p-CF$_3$); ArAr″PCl **10**: δ −55.5 (br s, 6F, o-CF$_3$ in Ar), −58.6 (d,$^4J_{P\text{–}F}$ 58.3 Hz, 3F, o-CF$_3$ in Ar″), −63.6 (s, 3F, p-CF$_3$), −64.1 (s, 3F, p-CF$_3$); ^{31}P NMR (CDCl$_3$): ArAr′PCl **9**: δ 76.6 (m);ArAr″PCl **10**: δ 69.9 (m).

X-Ray crystallography

Single crystal X-ray diffraction experiments were carried out at low temperature, 100–120 K (see Table 5), using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART (CCD 1 K area detector) diffractometer equipped with a Cryostream N2 flow cooling device.[55] Series of narrow ω-scans (0.3°) were performed at several ϕ-settings in such a way as to cover a sphere of data to a maximum resolution between 0.70 and 0.77 Å. Cell parameters were determined and refined using the SMART software,[56] and raw frame data were integrated using the SAINT program.[57] The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL software.[58] Crystal data and structure refinement parameters are shown in Table 5.

The reflection intensities were corrected by numerical integration based on measurements and indexing of the crystal faces for **4** and **5** (using SHELXTL software).[58] For the remaining structures, the absorption corrections were carried out by the multi-scan method, based on multiple scans of identical and Laue equivalent reflections (using the SADABS software).[59]

Non-hydrogen atoms were refined anisotropically, except in some cases where there was disorder (see Results and discussion). For structures **1**, **3** and **5** the hydrogen atoms were found in difference Fourier maps and in the case of **1** constrained accordingly. For structures **2**, **4** and **6**, the hydrogen atoms were positioned geometrically and refined using a riding model. In the special case of Ar′Ar″AsH **7**, the hydrogen atoms were found in the Fourier difference map, one constrained and the other allowed to refine freely. The remaining hydrogen atoms were positioned geometrically and refined using a riding model.

CCDC reference numbers 189700–189706.

See http://www.rsc.org/suppdata/dt/b2/b207327g/ for crystallographic data in CIF or other electronic format.

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