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^{19}F NMR studies on positional variations of trifluoromethyl groups in CF_3-substituted aromatic group 15 trivalent chlorides

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ABSTRACT

Several Group 15 trivalent chlorides with CF_3-substituted aromatic groups R present, including at least one *ortho*-CF_3 substituent, R_nECl_{3-n} (n = 1 or 2; E = P, As, Sb or Bi) have been studied by ^{19}F solution-state NMR spectroscopy. In compounds with both *ortho*- and *para*-CF_3 groups, the chemical shifts of the *para*-CF_3 fluorines are very similar, irrespective of the central element E. Much more variation is found in the shifts of the *ortho*-CF_3 fluorines, which may be correlated with the nature of the aromatic group, the electronegativity of E and the occurrence of short E–F contacts, as demonstrated by previous crystallographic studies of some of these compounds.

1. Introduction

The bulky highly electronegative fluoromes ligand Ar (2,4,6-$(CF_3)_3C_6H_2$) has been used extensively to stabilise both main group and transition metal low-coordinate species [1–42]. This substituent is usually attached to the central element E by displacement of halide, using the lithio-derivative ArLi of the parent hydrocarbon 1,3,5-$(CF_3)_3C_6H_3$ (ArH). Much less use has been made of the fluoroxyl ligand 2,6-$(CF_3)_2C_6H_3$ (Ar′), because although the precursor hydrocarbon 1,3-$(CF_3)_2C_6H_4$ (Ar′H) is readily available, it 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 [37–39,43–50]. While both ligands are again highly electronegative, there is clearly more steric protection in the *ortho*-positions for the Ar′ species. A procedure has subsequently been described for preparing 2,4-$(CF_3)_2C_6H_3$ (Ar″) derivatives, including Ar″$_2$PCl (**7**), selectively in high yield [51]. More recently we have carried out some reactions with 1,4-$(CF_3)_2C_6H_4$ (Ar‴H). Monolithiation of Ar‴H leads to a single product Ar‴Li, but this leads to one *ortho*-CF_3 group only in the 2,5-$(CF_3)_2C_6H_3$ (Ar‴)-substituted compounds, hence giving less steric protection than in the Ar or Ar′ species, but comparable with that in Ar″ derivatives [52,53]. While ^{19}F solution-state NMR spectra for the reaction products have been recorded routinely in most instances, the results have not been considered in detail until very recently, and then only for several chloro-compounds of the Group 14 elements Si, Ge or Sn with Ar, Ar′ or Ar″ substituents [54]. The results showed that in compounds with *para*-CF_3 groups their ^{19}F chemical shifts were comparatively little affected by changing the central element, whereas the shifts of the *ortho*-CF_3 groups showed much larger variations, which could be correlated with both the electronegativity of the central element and the existence of intramolecular E–F contacts between the central element and fluorines in the *o*-CF_3 groups, (at least one interaction per CF_3 group), at distances appreciably shorter than the sum of the van der Waals radii. Analysis of the spectra enabled structures to be assigned, even in mixtures of products. We have now extended this study to a large number of chloro-derivatives of Group 15 elements E (E = P, As, Sb or Bi) with Ar, Ar′, Ar″ or Ar‴ substituents, using both data from the literature and some recorded for new compounds. The ^{31}P NMR solution-state spectra have also been obtained for the phosphorus(III) species.

2. Results and discussion

The phosphorus compounds studied are shown in Fig. 1, and their ^{19}F and ^{31}P NMR data are collected in Table 1. It is worth noting that the more sterically hindered disubstituted possible product Ar′$_2$PCl (**6**) from the reaction of the Ar′Li/Ar″Li mixture with PCl_3 was not detected in solution; the other two possible disubstituted products Ar′Ar″PCl (**11**) and Ar″$_2$PCl (**7**) have both been isolated from this mixture, and characterised by single-crystal X-ray diffraction [37,46]. Nevertheless there is a report of the crystal and molecular structures of Ar′$_2$PCl (**6**) in the Cambridge

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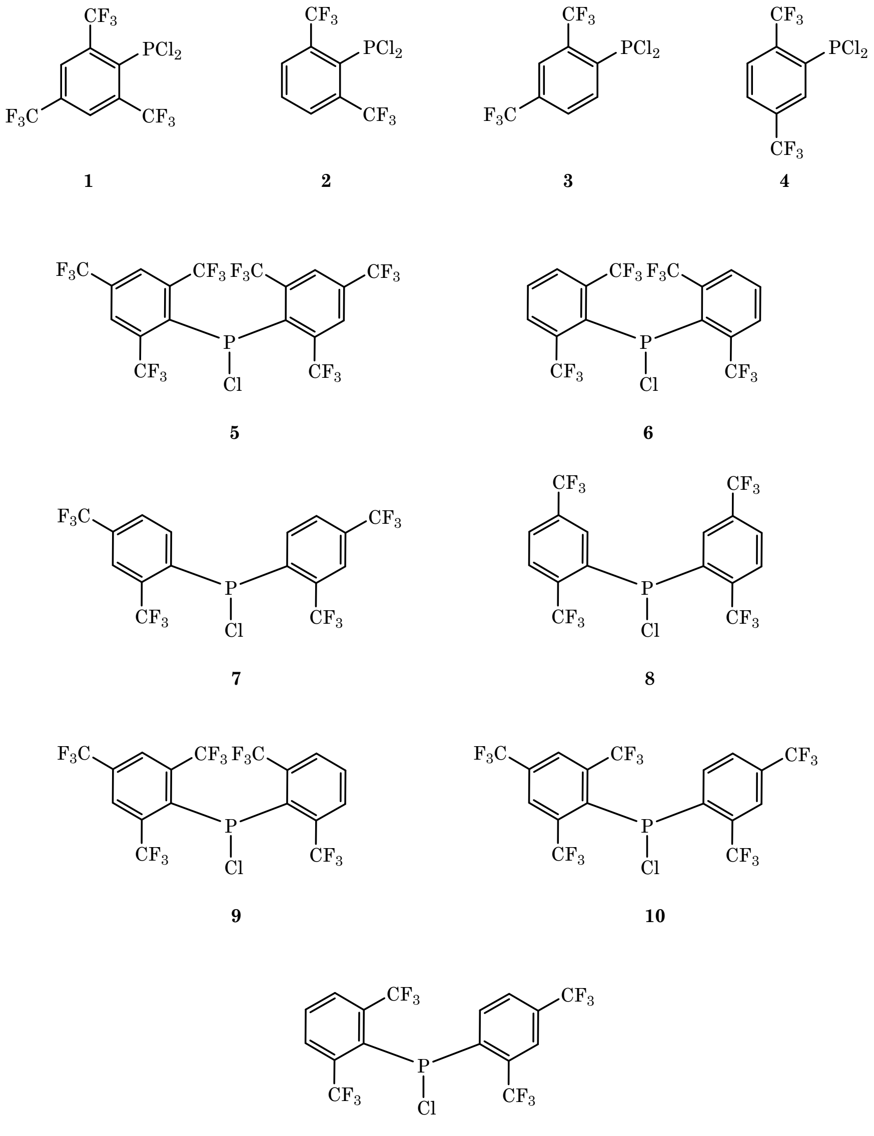


Fig. 1. Structures of phosphorus(III) compounds (**1**)–(**11**).

Table 1
^{19}F and ^{31}P NMR data for P(III) chlorides (**1**)–(**11**).

Compound	Number	δ ^{19}F (ppm)		$^{4}J_{PF}$ (Hz)	δ ^{31}P (ppm)	Ref.
$ArPCl_2$	(**1**)	−53.7	−64.6	61	144.7	[3]
$Ar'PCl_2$	(**2**)	−53.1[a]		61	146.6	[43]
$Ar''PCl_2$	(**3**)	−56.5	−63.6	84	151.6	this work
$Ar'''PCl_2$	(**4**)	−56.8	−64.3	84	151.2	[52]
Ar_2PCl	(**5**)	−54.4	−64.1	42	74.9	[37]
Ar'_2PCl	(**6**)					[57]
Ar''_2PCl	(**7**)	−57.3	−63.7	66	68.3	[37]
Ar'''_2PCl	(**8**)	−58.0	−64.5	66	67.6	[52]
ArAr′PCl	(**9**)	−54.1[b]	−64.0[b]	42	76.6	[52]
		−54.3[c]		42		
ArAr″PCl	(**10**)	−55.5[b*]	−63.6[b]		69.9	[37]
		−58.6	−64.1	58		
Ar′Ar″PCl	(**11**)	−55.0[c,*]			67.3	[46]
		−58.9	−63.6	58		

[a] Converted from CF_3COOH as reference;

[b] Resonances for Ar group;

[c] Resonance for Ar′ group;

[*] Broad.

structural database [55,56], from a private communication (reference code BADLAU) [57], although no preparative details or NMR data are available. Ar″PCl_2 (**3**) could not be separated from Ar′PCl_2 (**2**), but was identified as a minor component in the solution produced by a 1: 1 reaction between PCl_3 and the Ar′Li/Ar″Li mixture (Experimental section). All the ^{31}P shifts are entirely as expected for compounds of the type $RPCl_2$ (between 152 and 144 ppm), and R_2PCl (between 77 and 67 ppm), where R is an aromatic group (Table 1) [58].

^{19}F NMR data for some analogous derivatives of arsenic(III), antimony(III) and bismuth(III) are shown in Table 2, and their structures are illustrated in Fig. 2. The results for Bi are limited to

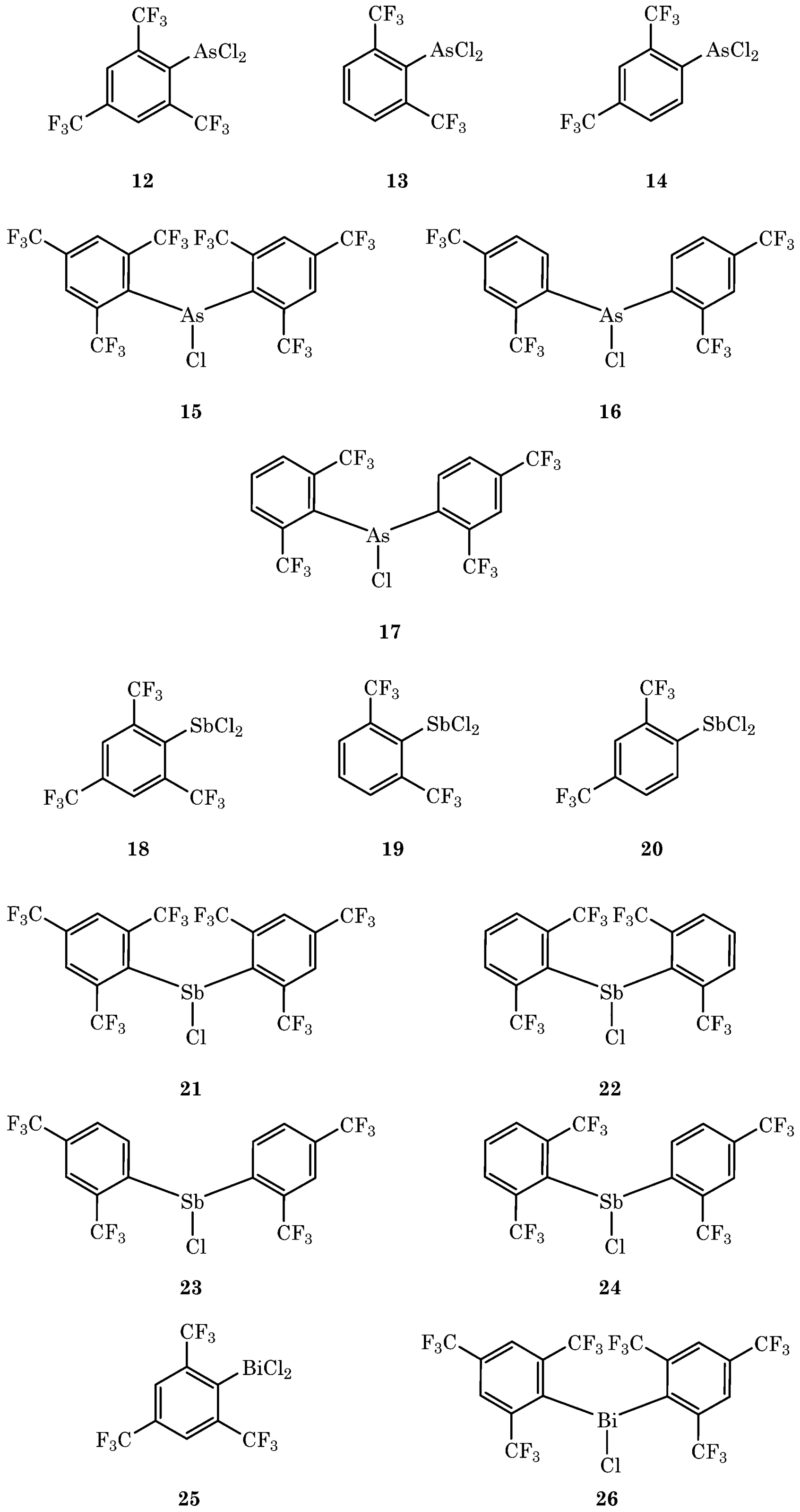


Fig. 2. Structures of heavier Group 15 compounds (**12**)–(**26**).

Table 2
^{19}F NMR data for group 15 compounds (**12**)–(**26**).

Compound	Number	δ ^{19}F (ppm)		Reference
$ArAsCl_2$	(**12**)	−53.5	−64.2	[25]
$Ar'AsCl_2$	(**13**)	−52.9		This work
$Ar''AsCl_2$	(**14**)	−57.7	−63.7	This work
Ar_2AsCl	(**15**)	−54.5	−63.9	[33]
Ar''_2AsCl	(**16**)	−58.4	−63.6	This work
$Ar'Ar''AsCl$	(**17**)	−54.8[a]		[37]
		−58.8[b]	−63.5	
$ArSbCl_2$	(**18**)	−55.6	−64.9	This work
$Ar'SbCl_2$	(**19**)	−53.2		[50]
$Ar''SbCl_2$	(**20**)	−54.9	−63.6	[50]
Ar_2SbCl	(**21**)	−55.1	−63.6	[14]
Ar'_2SbCl	(**22**)	−55.1		[50]
Ar''_2SbCl	(**23**)	−58.4	−63.7	[50]
$Ar'Ar''SbCl$	(**24**)	−55.5[a]		[50]
		−58.4[b]	−63.6[b]	
$ArBiCl_2$	(**25**)	−56.2	See text	[9]
Ar_2BiCl	(**26**)	−56.0	−63.3	[9]

[a] Resonance for Ar′ group.
[b] Resonances for Ar″ group.

literature data for Ar_2BiCl (**26**), which has been fully characterised by single-crystal X-ray diffraction, and a mention in the same paper of a very weak ^{19}F NMR signal at −56.2 ppm, ascribed to the fluorines from the *ortho*-CF_3 groups of $ArBiCl_2$ (**25**), which is a probable precursor [9]. The non-observation of the signal for the *para*-CF_3 group fluorines from (**25**), which would be half the intensity of that from the *ortho*-CF_3 group fluorines, is thus not surprising. Results are included for three new arsenic compounds (**13**), (**14**) and (**16**), and one new antimony compound (**18**) (Experimental section), as shown in Table 2. The ^{19}F NMR spectra for the Ar′Li/Ar″Li–$AsCl_3$ reaction mixture, together with those for Ar′Ar″AsCl, which has been characterised crystallographically [37], and for Ar''_2AsCl, are shown as a stackplot in Fig. 3.

As in the Group 14 elements, the ^{19}F NMR signals for *p*-CF_3 groups show little variation (Tables 1 and 2); the entire range of shifts for *p*-CF_3 substituents is only from −63.3 to −64.9 ppm, irrespective of the central element E. Significant differences are found for *ortho*-CF_3 ^{19}F resonances, however. There are variations depending on the nature of the organic group attached to E, on the element E itself, and on the probable number of short E–F contacts between fluorines from *ortho*-CF_3 groups and E, as shown in some instances by X-ray crystallography. These aspects are discussed in more detail below.

For all P and As compounds, the ^{19}F NMR shift sequences for the *o*-CF_3 fluorines follow the frequency pattern Ar′ > Ar > Ar″, with a larger difference between the values for Ar and Ar″ (Tables 1 and 2).

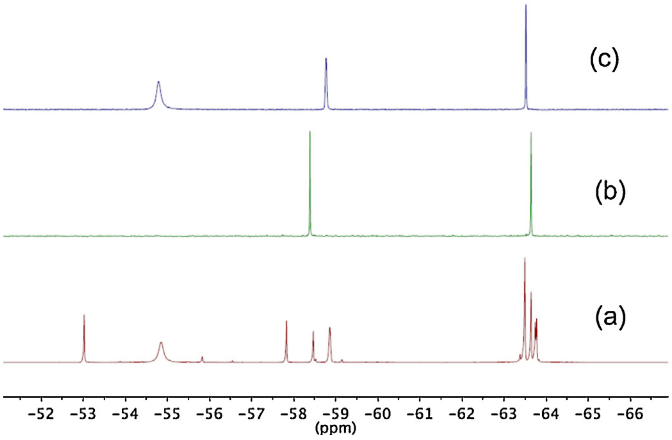


Fig. 3. Stackplot of ^{19}F NMR spectra for the products of the $AsCl_3$–Ar′Li/Ar″Li reaction where: (a) initial reaction mixture, showing $Ar'AsCl_2/Ar''AsCl_2/Ar'Ar''AsCl/Ar''_2AsCl$; (b) Ar''_2AsCl; (c) Ar′Ar″AsCl.

Table 3
Electronegativities and van der Waals Radii for elements E [59].

E	Electronegativity	van der Waals Radius (Å)	Sum of van der Waals Radii (Å)
P	2.20	1.95	3.42
As	2.28	2.05	3.52
Sb	1.97	2.25	3.72
Bi	1.93	2.35	3.82

Results for Ar‴ are only available for phosphorus, where replacement of Ar″ by Ar‴ leads to an even lower frequency shift for both $RPCl_2$ and R_2PCl. For Sb, while Ar′ gives rise to the highest frequency shift again, there is a discrepancy in the sequence for Ar and Ar″ substituents between $RSbCl_2$, where the reported shift for $Ar''SbCl_2$ is at higher frequency than that for $ArSbCl_2$, and R_2SbCl, where the compounds follow the same shift sequence as in the P and As compounds. This variation with substituent is particularly evident in mixed species R_1R_2ECl, where R_1 has two *o*-CF_3 groups and R_2 only has one. The results for ArAr″PCl (−55.5 and −58.6 ppm), Ar′Ar″PCl (−55.0 and −58.9 ppm), Ar′Ar″AsCl (−54.8 and −58.8 ppm) and Ar′Ar″SbCl (−55.5 and −58.4 ppm) fall into this category, with the higher frequency shift in each compound for the substituent with two *o*-CF_3 groups. This property can, of course, be used diagnostically in the analysis of mixtures of products in solution (see Fig. 3).

The electronegativities of the elements E are listed in Table 3, together with their van der Waals radii, and, on the assumption of a van der Waals radius for fluorine of 1.47 Å, the sum of these radii for E and fluorine [59]. For most types of compound studied, including $ArECl_2$, $Ar'ECl_2$ (no Bi data) and Ar_2ECl, the ^{19}F NMR shifts of the *ortho*-CF_3 groups follow the frequency sequence As > P > Sb > Bi, which parallels the order of electronegativities of E. There tends to be only a small difference between the values for As and P in corresponding compounds, but a larger change from P to Sb, again in accordance with electronegativity values (Table 3). This behaviour is parallel to that observed in Group 14 derivatives [54]. The exception appears to be for $Ar''ECl_2$, where the frequency order is Sb > P > As (there are again no data for Bi). There is no obvious explanation for this apparent discrepancy.

Some of the species in this work have been previously characterised by single-crystal X-ray diffraction; these comprise compounds (**5**), [37] (**6**), [57] (**7**), [37] (**8**), [52] (**11**), [46] (**15**), [33] (**17**), [37] (**21**) [33] and (**26**).[9] In all instances, careful examination of the molecular structures in the Cambridge Structural Database [55,56] confirms that there is at least one E–F contact at a distance less than 3.2 Å for the fluorines in every *ortho*-CF_3 group. (Some of these have been mentioned in the relevant papers, but in other compounds they were not discussed.) As shown in Table 3, these distances are appreciably shorter than the sum of the van der Waals radii for the elements concerned. The shortest E–F contact distance in each of these compounds is listed in Table 4. Although

Table 4
Shortest E–F distances in compounds of known structure.

Compound	Number	Shortest E–F distance (Å)	Temperature (K)	Reference
Ar_2PCl	(**5**)	2.843		[37]
Ar'_2PCl	(**6**)	2.800*	2.817[a,*]	[57]
Ar''_2PCl	(**7**)	2.874		[37]
Ar'''_2PCl	(**8**)	2.709		[52]
$Ar'Ar''PCl$	(**11**)	2.890		[46]
Ar_2AsCl	(**15**)	2.991	130(2)	[33]
		2.935	296(1)	
$Ar'Ar''AsCl$	(**17**)	2.701		[37]
Ar_2SbCl	(**21**)	2.821		[33]
Ar_2BiCl	(**26**)	2.885*		[9]

[a] Two molecules in the unit cell.
* Calculated from the Cambridge Structural Database.

the remaining species in Tables 1 and 2 have not been characterised crystallographically, it seems a reasonable assumption that similar short E–F interactions will be found in each case. Such interactions have been considered to contribute to the stabilities of both main group and transition metal derivatives in the solid state. As pointed out above, in mixed derivatives R_1R_2ECl with one aromatic group having two *ortho*-CF_3 groups and the other having only one, the shift is invariably at higher frequency for the fluorines in the R group which has two *ortho*-CF_3 substituents. Hence the number of E–F interactions is likely to be higher, and may make a significant contribution to the observed shifts.

3. Conclusions

Detailed investigation of the ^{19}F NMR solution-state shifts of a large number of Group 15 chloro-derivatives R_1ECl_2 or R_1R_2ECl (R_1 and R_2 are aromatic substituents with at least one *o*-CF_3 group; *E* = P, As, Sb or Bi) has shown that the shifts for *p*-CF_3 fluorines are very little affected by variation in E, R_1 or R_2. The shifts of the *o*-CF_3fluorines are much more sensitive, and may be correlated with the nature of the substituents R_1 and R_2, the electronegativity of the element E (apart from one apparent exception), and the occurrence of short E–F contacts. In compounds which have been previously characterised crystallographically, for every *o*-CF_3 group there is at least one such contact at a distance of 3.2 Å or less, appreciably shorter than the sum of the van der Waals radii. In mixed species ($R_1 \neq R_2$), the fluorines for R groups with two *o*-CF_3 substituents resonate at higher frequency than those with only one *o*-CF_3 group, irrespective of E. This may be correlated with the increased number of E–F interactions in the former case, and may be useful diagnostically in the analysis of mixtures of products, as in the reaction of the Ar′Li/Ar″Li mixture with ECl_3.

4. Experimental

4.1. General

All manipulations, including NMR sample preparation, were carried out either under dry N_2 or *in vacuo*, by means of standard Schlenk procedures or a glovebox. Chemicals of the best available commercial grades were used, in general without further purification. ^{19}F solution-state NMR spectra were usually recorded on a Varian Mercury 200 spectrometer at 188.18 MHz, and chemical shifts are expressed in ppm relative to external $CFCl_3$. Occasionally ^{19}F spectra were recorded on a Bruker AC 250 (235.36 MHz), Varian VXR 400 (376.35 MHz) or Varian Inova 500 (470.26 MHz) instrument. ^{31}P NMR spectra were similarly recorded at the apposite frequencies, and chemical shifts are given relative to external 85% H_3PO_4.

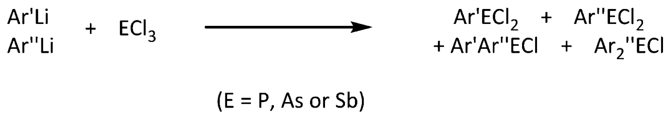
4.2. Lithiations

ArH and Ar‴H were treated separately with 2.5 M BuLi in Et_2O at −78° C (acetone/dry ice bath) to produce ArLi or Ar‴Li, respectively, according to the methods of Goodwin and Roden [12,46]. Ar′H reacted with BuLi under the same conditions to yield a mixture of Ar′Li and Ar″Li, in a *ca.* 1: 1 ratio as shown by NMR spectroscopy. **WARNING** It is important in these reactions to maintain a slight excess of the hydrocarbon with respect to BuLi at all times, to avoid any attack on a CF_3 group and the possible explosive formation of LiF. The reactions for formation of Group 15 chloro-derivatives from ArLi and Ar‴Li are shown in Scheme 1. The more complicated reactions of ECl_3 with a mixture of Ar′Li and Ar″Li are depicted in Scheme 2.

$$RLi + ECl_3 \longrightarrow RECl_2 + R_2ECl + LiCl$$

$$(R = Ar, E = P, As, Sb \text{ or } Bi; R = Ar''', E = P)$$

Scheme 1. Reactions for formation of Group 15 chloro-derivatives from ArLi and Ar‴Li.



$$\begin{matrix} Ar'Li \\ Ar''Li \end{matrix} + ECl_3 \longrightarrow \begin{matrix} Ar'ECl_2 + Ar''ECl_2 \\ + Ar'Ar''ECl + Ar_2''ECl \end{matrix}$$

$$(E = P, As \text{ or } Sb)$$

Scheme 2. Reactions of ECl_3 with a mixture of Ar′Li and Ar″Li.

4.3. Synthesis of Ar″PCl_2 (**3**)

Ar″PCl_2 (**3**) was prepared in a mixture with Ar′PCl_2 (**4**), which could not be separated by distillation *in vacuo*. A solution of Ar′Li/Ar″Li (96 mmol) was added dropwise over 20 min to a solution of PCl_3 (25.2 g, 16 ml, 183 mmol) in diethyl ether (100 ml) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 4 h. The white solid (LiCl) which appeared was removed by filtration, and solvent and any excess PCl_3 removed *in vacuo*, giving a brown oil. The product was purified by distillation under vacuum (Bp 86 °C, 0.01 Torr). The components were identified by ^{19}F and ^{31}P solution-state NMR spectroscopy (Table 1).

4.4. Synthesis of Ar′$AsCl_2$ (**13**)/Ar″$AsCl_2$ (**14**)/Ar′Ar″AsCl (**17**)/Ar''_2AsCl (**16**)

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 was distilled under reduced pressure (0.01 Torr), and fractions were collected at 115 °C (a mixture of all four products) and 145 °C (mainly Ar′Ar″AsCl (**17**)). Some solid appeared in the first fraction. This was separated, redissolved in CH_2Cl_2 and left in the freezer, producing a white microcrystalline product unsuitable for X-ray diffraction. ^{19}F solution-state NMR spectroscopy showed that this product was Ar''_2AsCl (**16**). The solid isolated from the higher-boiling fraction was successfully recrystallized from hexane, and has been fully characterised as Ar′Ar″AsCl (**17**) by single-crystal X-ray diffraction [37].

4.5. Synthesis of Ar$SbCl_2$ (**18**)

ArLi (100 ml, 45 mmol, 0.45 M solution in Et_2O) was added dropwise over 10 min to a stirred solution of $SbCl_3$ (10.8 g, 47.3 mmol) in Et_2O (50 ml) at −78 °C. An orange-brown solution was formed, with no visible precipitation of LiCl. The reaction mixture was stirred for 2 h at room temperature. Pentane (150 ml) was added, and the mixture was shaken vigorously. Two layers formed. The lower dense brown oil gave no ^{19}F NMR signal, so was thought to be excess $SbCl_3$ and LiCl. The pentane was removed *in vacuo* from the upper layer, yielding a yellow powdery solid which was recrystallized from CH_2Cl_2 (25 ml). The isolated solid was extremely unstable, even in a glovebox, and rapidly turned into a red oil. Nevertheless the ^{19}F solution-state NMR spectrum was successfully recorded (Table 2).

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