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PAPER

Stereochemically inactive lone pairs in phosphorus(III) compounds: the characterisation of some derivatives with the 2,5-$(CF_3)_2C_6H_3$ (Ar) substituent and their complexation behaviour towards Pt(II) species†

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Some new phosphorus(III) derivatives Ar_2PX (X = Br, Cl, F or H), $ArPX_2$ (X = Br or Cl), Ar_3P and Ar^tBuPCl, with the 2,5-bis(trifluoromethyl)phenyl (Ar) substituent on phosphorus, have been prepared, and characterised by ^{31}P and ^{19}F NMR solution-state spectroscopy. The complexing ability of Ar_2PX, Ar_3P and Ar^tBuPCl towards the dimeric platinum(II) complexes $[PtY(\mu\text{-}Y)(PEt_3)]_2$ (Y = Cl or Br, the latter for X = Br only) has also been investigated. Single-crystal X-ray diffraction studies at low temperature have been carried out for Ar_3P, Ar_2PCl and the hydrolysis or oxidation products $Ar_2P(H)OH$ and $Ar_2P(O)OH$. The structures of Ar_3P and Ar_2PCl are particularly interesting as in each compound the geometry around P is approximately octahedral. In Ar_3P there are three short contacts to fluorine as well as the three bonded C atoms for both of the independent molecules in the unit cell. For Ar_2PCl there are two short P–F contacts, and the octahedron is completed by a weak P–P interaction to a neighbouring molecule. In both instances the lone pair on the P(III) centre appears to be stereochemically inactive, and does not play a significant role in the structure.

Introduction

The bulky electron-withdrawing ligand 2,4,6-$(CF_3)_3C_6H_2$ (fluoromes) has been used extensively in recent years to stabilise both main group and transition metal species,[1] including phosphorus compounds, some of which have been structurally characterised.[2–15] The combination of steric bulk in the *ortho*-positions and the electron-withdrawing ability of the $-CF_3$ substituents enables many derivatives to be isolated which would be thermodynamically unstable, but are stabilised kinetically. This stability often seems to be enhanced by secondary short contacts between the central element and one or more fluorines of the *ortho*-CF_3 groups.[12,15] Less work has been carried out using the 2,6-$(CF_3)_2C_6H_3$ group, for good reasons.[14,16–20] While this ligand, too, is strongly electron-withdrawing and has bulky *ortho*-substituents, synthesis of its derivatives is usually accomplished *via* lithiation of the hydrocarbon precursor 1,3-bis(trifluoromethyl)benzene. The problem is that lithiation occurs in two positions, either between the two $-CF_3$ groups, giving the desired 2,6-$(CF_3)C_6H_3$ species, or *ortho* to one but *meta* to the second, leading to the isomeric 2,4-derivatives, and often a mixture of products. Only one of the two possible lithiated compounds has the steric protection afforded by two *ortho*-CF_3 groups, although both have the same electron-withdrawing substituents. Separation of products can then be difficult or impossible.

For comparison purposes, we decided to attempt the preparation of some 2,5-$(CF_3)_2C_6H_3$ compounds of phosphorus, *via* lithiation of 1,4-bis(trifluoromethyl)benzene, ArH. The advantage is that all four non-substituted positions on the aromatic ring are equivalent in ArH, so there is only one possible monolithiated derivative, ArLi. This ligand will provide only one *ortho*-CF_3 group, of course, like the 2,4-substituted compounds mentioned above, but will similarly possess two electron-withdrawing substituents. It thus provides much less steric protection than the 2,6- or 2,4,6-derivatives, but should have similar electronic properties. This ligand has so far been very little utilised. The only previous report of phosphorus compounds containing this substituent which have been structurally characterised is a very recent one, in which two zwitterionic species with Ar as one of the substituents on a phosphonium centre have been described.[21] There are also only two articles where the ligand has been attached to metals in structurally-characterised complexes, either as ArH in the π-complex $[Cr(ArH)_2]$,[22] or with the Ar group directly bound to platinum in $[ArPtCl(d^tBupm)]$, where d^tBupm = bis(di-t-butylphosphino)methane.[23]

We report the synthesis and characterisation in solution by ^{31}P and ^{19}F NMR spectroscopy of the compounds Ar_2PCl (**1**),

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Table 1 ^{31}P NMR data for Phosphorus(III) derivatives with the 2,5-$(CF_3)_2C_6H_3$ (Ar) substituent

Compound	Number	δ^{31}P, ppm	δ ^{19}F (*ortho* CF_3), ppm	δ ^{19}F (*para* CF_3), ppm	δ ^{19}F, ppm	$^4J_{P-F}$, Hz	$^1J_{P-F}$, Hz	$^1J_{P-H}$, Hz
Ar_2PCl	**1**	67.6	−58.0	−64.5	—	66	—	—
$ArPCl_2$	**2**	151.2	−56.8	−64.3	—	84	—	—
Ar_3P	**3**	−16.4	−58.9	−64.9	—	55	—	—
Ar_2PBr	**4**	56.9	−58.0	−64.0	—	66	—	—
$ArPBr_2$	**5**	140.8	−57.3	−64.6	—	86	—	—
Ar_2PF	**6**	145.1	−57.9	−64.4	−189.4	64	930	—
Ar_2PH	**7**	−47.5	−61.0	−65.0	—	39	—	228
Ar^tBuPCl	**8**	97.7	−55.2	−63.7	—	71	—	—
$Ar_2P(O)H$	**9**	8.8	−58.5	−64.0	—	8	—	550
$Ar_2P(O)(OH)$*	**10**	14.9	−58.0	−63.7	—	nr	—	—

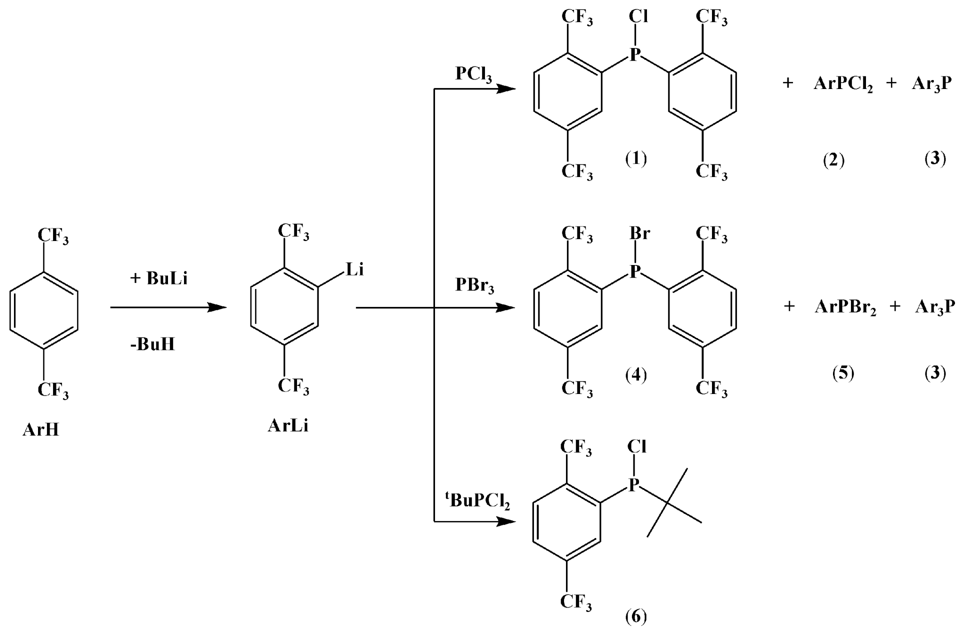
nr = not resolved. ^{31}P NMR spectrum showed a singlet and the ^{19}F NMR spectrum showed two 1 : 1 singlets.

$ArPCl_2$ (**2**), Ar_3P (**3**), Ar_2PBr (**4**), $ArPBr_2$ (**5**), Ar_2PF (**6**), Ar_2PH (**7**), Ar^tBuPCl (**8**), and the hydrolysis or oxidation products $Ar_2P(O)H$ (**9**) and $Ar_2P(O)OH$ (**10**). The monosubstituted phosphanes $ArPX_2$ are only present as minor components in solutions formed by the action of ArLi on PX_3, even from equimolar proportions of the reagents, although they may be readily recognised from their characteristic NMR coupling patterns (quartets in their ^{31}P spectra and doublets in their ^{19}F spectra, due to $^4J_{P-F}$ coupling.) It seems evident that ArLi reacts more readily with $ArPX_2$ than it does with PX_3, leading to the ready formation of Ar_2PX. The complexing behaviour of Ar_2PX, Ar^tBuPCl and Ar_3P towards the dimeric platinum(II) complexes $[PtY(\mu\text{-}Y)(PEt_3)]_2$ has also been investigated (Y = Cl in all instances except for X = Br, where Y is also Br to avoid any complications from halogen exchange). In general monomeric *trans*-$[PtY_2L(PEt_3)]$ complexes are formed initially as the kinetic products, though isolation after some time and partial characterisation by single-crystal X-ray diffraction of the product where L = Ar_2PCl, Y = Cl have shown that the *cis*-isomer may eventually be formed as the more thermodynamically stable product (although the crystals were not of sufficiently good quality to make the detailed results publishable the connectivities were clearly established). Ar_2PCl (**1**), Ar_3P (**3**), $Ar_2P(O)H$ (**9**) and $Ar_2P(O)OH$ (**10**) have been fully characterised by single-crystal X-ray diffraction at low temperature.

Results and discussion

(a) Synthesis of new phosphorus derivatives

1,4-Bis(trifluoromethyl)benzene ArH was treated with n-BuLi at −78° C to form the lithiated derivative ArLi. This was then reacted separately *in situ* with PX_3 (X = Cl or Br) or $^tBuPCl_2$, Scheme 1. In the reaction with the phosphorus trihalides, there was always more of the disubstituted species Ar_2PX formed than of $ArPX_2$ as shown by ^{31}P NMR spectroscopy, whether a 1 : 1 or 1 : 2 molar ratio of PX_3 to ArLi was used. Some Ar_3P (**3**) was also present. The yield of Ar_3P was increased by adding PX_3 dropwise to the cooled ArLi solution, rather than by adding a solution of ArLi to PX_3, thus keeping ArLi in excess relative to PX_3 during the early stages of reaction. The results suggested strongly that $ArPX_2$ is more reactive towards ArLi than is PX_3. ^{31}P and ^{19}F NMR data for the new phosphorus species prepared are shown in Table 1.



Scheme 1 Reactions of ArLi with PCl_3, PBr_3 and $^tBuPCl_2$.

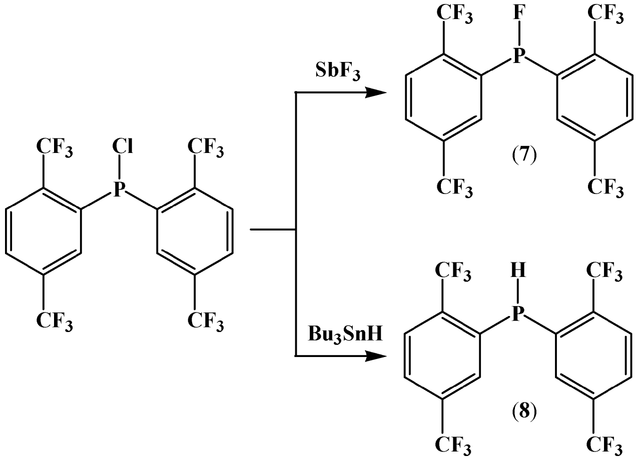
Table 2 ^{31}P NMR data for Pt(II) complexes synthesised containing phosphorus(III) derivatives with the 2,5-$(CF_3)_2C_6H_3$ (Ar) substituent

trans-[PtX_2 (L_A)(P_BEt_3)]			^{31}P						^{19}F			
Number	L_A =	X =	δ P_A, ppm	δ P_B, ppm	$^1J_{Pt-PA}$, Hz	$^1J_{Pt-PB}$, Hz	$^2J_{P-P}$, Hz	δ ^{19}F, ppm	δ *ortho* CF_3, ppm	δ *para* CF_3, ppm	$^1J_{P-F}$, Hz	$^4J_{P-F}$, Hz
11	Ar_2PCl	Cl	91.9	17.8	2694	2748	565	—	−55.9	−63.8	—	6
12	Ar_3P	Cl	43.6	15.7	~2400	2847	488	—			—	
13	Ar_2PBr	Br	72.1	11.5	2523	2678	563	—	−54.9	−63.6	—	5
14	Ar_2PF	Cl	146.5	17.4	3088	2570	567	−152.5	−58.7	−64.3	1009	nr
15	Ar_2PH	Cl	−6.2	16.3	2806	2985	420	—	−60.3	−65.0	—	8
16	Ar^tBuPCl	Cl	112.0	13.6	2466	2754	529	—	−52.3	−63.8	—	19

nr = not resolved.

In the reaction of ArLi with $^tBuPCl_2$, no evidence was found for formation of the tertiary phosphane $Ar_2{}^tBuP$, irrespective of the sequence of addition, probably because of too much steric hindrance around the central phosphorus atom.

Ar_2PF (**6**) and Ar_2PH (**7**) were synthesised from Ar_2PCl in solution by the action of SbF_3 and Bu_3SnH respectively, Scheme 2. The products could be readily recognised by the ^1J coupling between P and F or H, Table 1. When a solution from an ArLi – PCl_3 reaction was layered with hexane and left to stand for some time in a crystal tube, crystals eventually formed that were suitable for X-ray diffraction (Section c). These proved to be of the hydrolysis product $Ar_2P(O)H$ (**9**), rather than Ar_2PCl or Ar_3P. Crystals of Ar_2PCl (**1**) and Ar_3P (**3**) were obtained by alternative procedures (experimental section). A sample of Ar_2PF solution was exposed to air, and produced crystals of the oxidised and hydrolysed compound, $Ar_2P(O)OH$ (**10**). NMR data for these species are included in Table 1.

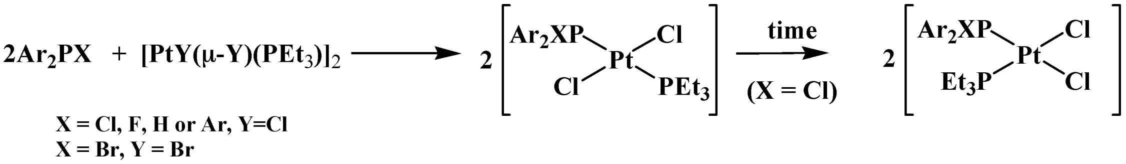


Scheme 2 Synthesis of Ar_2PF and Ar_2PH from Ar_2PCl.

(b) Complexation behaviour

These experiments were carried out on an NMR tube scale, by adding a solution of the chloro-dimer *trans*-[PtCl(μ-Cl)(PEt_3)]$_2$ in a 1 : 2 molar ratio to a solution of the appropriate phosphane Ar_2PX (X = Cl, F or H), Ar^tBuPCl or Ar_3P at room temperature (Scheme 3). *Trans*-complexes were formed in each case, confirmed by the ^{31}P NMR spectra which showed the expected large $^2J_{P-P}$ (488–567 Hz, Table 2) between the inequivalent phosphorus ligands. The $^1J_{Pt-P}$ values were also as expected, between 2300 and 3100 Hz (Table 2).

In a solution containing both Ar_2PCl and Ar_3P the chlorophosphane appeared to react preferentially with the platinum(II) starting material, with Ar_3P remaining largely unaffected. It proved possible to obtain reaction between Ar_3P and the chloro-dimer when no Ar_2PCl was present, even though some of the unreacted ligand still remained in solution. As a result of line broadening it was difficult to obtain a value of $^1J_{PtP}$ for the Ar_3P ligand, though this was estimated as *ca.* 2400 Hz. For Ar_2PBr the corresponding reaction was carried out with the bromo-dimer *trans*-[PtBr(μ-Br)(PEt_3)]$_2$ [24] (Scheme 3), to avoid any complications from halogen exchange. A *trans*-complex was again produced (Table 2). Reaction of Ar_3P with the bromo-dimer was also attempted, in the expectation that the Pt–Br bonds would be more labile, but surprisingly no reaction was apparent from the NMR spectra, with both starting materials remaining in solution. This behaviour is discussed further in section (c), where the molecular structure of Ar_3P at low temperature is considered. An interesting observation in *trans*-[$PtCl_2$(PEt_3)(Ar_2PH)] (**15**), is that the proton-coupled ^{31}P NMR spectrum showed an apparent triplet for the resonance of the Ar_2PH ligand, *J* 420 Hz, instead of the expected doublet of doublets. This result implies that $^1J_{PH}$ and $^2J_{PP}$ are virtually identical, leading to accidental equivalence. A value of 420 Hz for $^1J_{PH}$ in a Pt(II) complex of a secondary phosphane is entirely reasonable; for example, $PMes_2H$ gives $^1J_{PH}$ values between 361 and 430 Hz in a range of Pt(II) complexes.[25]



Scheme 3 Synthesis of Pt(II) complexes from *trans*-[PtY(μ-Y)(PEt_3)]$_2$.

Table 3 Selected bond lengths and angles for compounds (**1**), (**3**), (**9**) and (**10**)

Compound	Ar_2PCl(**1**)	Ar_3P(**3**)	$Ar_2P(O)(H)$ (**9**)	$Ar_2P(O)(OH)$ (**10**)
P-C1A	1.858(3)	1.847(3)	1.825(2)	1.818(2)
P-C1B	1.858(3)	1.855(3)	1.819(2)	1.816(2)
P-C1C	—	1.854(3)	—	—
P-Cl1	2.0681(12)	—	—	—
P-O1	—	—	1.4835(13)	1.5034(17)
P-O2	—	—	—	1.5401(17)
C1A-P-C1B	101.61(13)	101.51(12)	111.28(7)	112.96(10)
C1A-P-C1C	—	101.08(12)	—	—
C1B-P-C1C	—	100.91(13)	—	—
C1A-P-Cl1	101.12(10)	—	—	—
C1B-P-Cl1	97.26(10)	—	—	—
C1A-P-O1	—	—	113.44(7)	109.07(10)
C1A-P-O2	—	—	—	106.30(9)
C1B-P-O1	—	—	111.56(7)	108.45(10)
C1B-P-O2	—	—	—	106.65(10)
O1-P-O2	—	—	—	113.49(10)

The formation of *trans*-complexes by these phosphanes with electron-withdrawing aromatic substituents parallels behaviour previously observed for ligands L such as $PPh_x(C_6F_5)_{3-x}$ (x = 0, 1 or 2), where reaction with the chloro-dimer in refluxing acetone led to *trans*-$[PtCl_2L(PEt_3)]$.[26] Similarly, reaction of the dimer with L' = $PPh_x(C_6H_3F_2\text{-}2,6)_{3-x}$ (x = 0, 1 or 2) on gentle heating in acetone yielded the *trans*-isomers; the complexes $[PtCl_2L'_2]$ were also found to have *trans*-configurations.[27] All the complexes $[PtCl_2L_2]$, where L = $PPh_2(C_6H_4CF_3\text{-}2)$, $PPh_2(C_6H_4C_6F_{13}\text{-}2)$, $PPh_2(C_6H_4C_6F_{13}\text{-}3)$, $P(C_6H_4C_6F_{13}\text{-}4)_3$ or $P(C_6H_4C_6F_{13}\text{-}4)_2(2\text{-}C_6H_4C_6F_{13}\text{-}2)$, prepared in refluxing dichloromethane (DCM), had *trans*-configurations.[28] Both *cis*- and *trans*-complexes were found for $[PtCl_2\{P(C_6H_4C_6F_{13}\text{-}4)_3\}(PEt_3)]$ and $[PtCl_2\{P(C_6H_4C_6F_{13}\text{-}4)_3\}_2]$, after preparation by refluxing in DCM, and indeed the isomers of the latter complex co-crystallised.[28] For $[PtCl_2\{PPh_2(C_6H_4C_6F_{13}\text{-}4)\}_2]$ and $[PtCl_2\{PPh(C_6H_4C_6F_{13})_2\text{-}4\}_2]$ only *cis*-isomers were found under similar conditions.[28] Hence normally there is a marked preference for formation of the *trans*-complex with one or two strongly electron-withdrawing aromatic substituents on a phosphane ligand, which is the kinetic reaction product. Interestingly, in the present work when a few crystals were isolated from the Ar_2PCl reaction after some time, they were discovered to be of the *cis*-complex (Section c), even though only the *trans*-complex had been observed in solution, and had remained stable over a minimum of a two-week period. This result indicates that slow conversion to the thermodynamically more stable *cis*-isomer is feasible in some cases in solution (Scheme 3). Mild preparative conditions were generally used here, which would again favour formation of the kinetic product in the initial stages.

Table 4 Shortest P···F contacts in each Ar ligand for compounds (**1**), (**3**), (**9**) and (**10**)

Compound	P···F contact distance (Å)		
Ar_2PCl (**1**)	2.7092 (21)	3.0111 (22)	—
Ar_3P1 (**3**)	2.8419(18)	2.9232(18)	2.9677 (19)
Ar_3P2	2.9040 (18)	2.9369 (18)	2.9423 (17)
$Ar_2P(O)(H)$ (**9**)	2.896(1)	2.968(1)	—
$Ar_2P(O)(OH)$ (**10**)	2.9248 (15)	3.0094 (16)	—

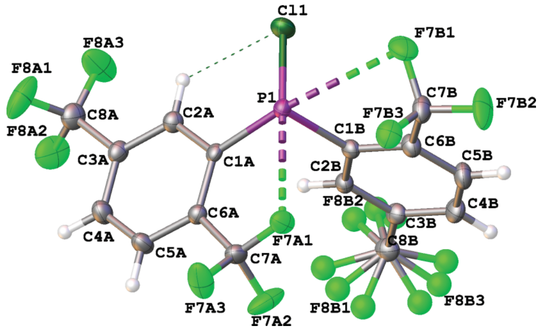


Fig. 1 The molecular structure of Ar_2PCl (**1**) showing the numbering scheme for the key atoms. Atomic Displacement Parameters (ADPs) are drawn at 50% probability.

(c) X-ray crystallography

The molecular structure of Ar_2PCl (**1**) is shown in Fig. 1; selected bond lengths and angles are listed in Table 3. The most striking feature of this structure is the short P–P distance, compared with the sum of the van der Waals radii,[28] of 3.19 Å between two adjacent molecules, completing approximately octahedral coordination about P (Fig. 2). This arises from one P–Cl and two P–C bonds, and two short P–F contacts to *ortho*-CF_3 groups (Fig. 1 and Table 4). The lone pair on phosphorus thus appears to be stereochemically inactive. The angles between *trans*-groups in the octahedron are Cl1-P1-F7A1 = 173.13, C1A-P1-F7B1 = 172.46 and P1′-P1-C1B = 165.78° respectively. Examples of stereochemically inactive lone pairs in Group 15 octahedral species are known for Sb(III) and Bi(III), in $[Sb_2Cl_{11}]^{5-}$,[30] $SbBr_6^{3-}$,[31] $BiCl_6^{3-}$,[32,33] and $[Bi_2Cl_{11}]^{5-}$,[34,35] but to the best of our knowledge this is the first such report for a P(III) compound.

The molecular structure of Ar_3P (**3**) also demonstrates slightly distorted octahedral coordination about P, as shown in Fig. 3. In this structure there is no P–P interaction, however, the octahedral geometry arising from three P–C bonds and three short P–F interactions to *ortho*-CF_3 groups. Selected bond distances and angles are given in Table 3, while the shortest P–F contact distances are listed in Table 4. There are two independent molecules in the asymmetric unit, with very similar structures. The angles

Table 5 Experimental data from crystallographic studies of compounds (**1**), (**3**), (**9**) and (**10**)

Identification code	(**1**)	(**3**)	(**9**)	(**10**)
Compound	Ar_2PCl	Ar_3P	$Ar_2P(O)(H)$	$Ar_2P(O)(OH)$
Empirical formula	$C_{16}H_6F_{12}PCl$	$C_{24}H_9F_{18}P$	$C_{16}H_7F_{12}OP$	$C_{32}H_{14}O_4F_{24}P_2$
Formula weight	492.63	670.28	474.19	980.37
Temperature	120(2) K	100(2) K	120(2) K	120(2) K
Crystal system	Triclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	*Pbca*	$P2_1/c$
a/Å	8.400(2),	9.9017(6),	16.1273(3),	12.8361(6),
b/Å	10.220(3),	14.8952(9),	8.2646(2),	16.8192(8),
c/Å	11.474(3)	18.3713(11)	25.3157(5)	8.1211(4)
α (°)	72.765(3),	100.382(1),	90,	90,
β (°)	72.896(3),	93.644(1),	90,	99.455(1),
γ (°)	78.100(3)	108.896(1)	90	90
Volume/Å^3	891.4(4)	2499.8(3)	3374.22(12)	1729.47(14)
Z	2	4	8	2
ρ_{calc}/mg mm^{-3}	1.835	1.781	1.867	1.883
μ/mm^{-1}	0.425	0.259	0.296	0.296
F(000)	484	1320	1872	968
Crystal size/mm	0.18 × 0.13 × 0.09	0.19 × 0.17 × 0.11	0.32 × 0.28 × 0.21	0.2 × 0.18 × 0.17
Theta range for data collection	1.92 to 30.22°	1.14 to 26.38°	1.61 to 29.50°	1.61 to 28.27°
Index ranges	$-11 \le h \le 11$, $-14 \le k \le 14$, $-15 \le l \le 16$	$-12 \le h \le 12$, $-18 \le k \le 18$, $-22 \le l \le 22$	$-22 \le h \le 22$, $-11 \le k \le 11$, $-35 \le l \le 35$	$-17 \le h \le 17$, $-21 \le k \le 22$, $-10 \le l \le 10$
Reflections collected	9022	21478	41514	16428
Independent reflections	4696 [R(int) = 0.0429]	10178 [R(int) = 0.0403]	4694 [R(int) = 0.0207]	4265 [R(int) = 0.0271]
Data/restraints/parameters	4696/54/272	10178/0/775	4964/1/299	4265/54/290
Goodness-of-fit on F^2	1.029	1.028	1.070	1.065
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0591$, $wR_2 = 0.1085$	$R_1 = 0.0507$, $wR_2 = 0.1052$	$R_1 = 0.0406$, $wR_2 = 0.1079$	$R_1 = 0.0461$, $wR_2 = 0.1120$
Final R indices [all data]	$R_1 = 0.1108$, $wR_2 = 0.1253$	$R_1 = 0.0820$, $wR_2 = 0.1162$	$R_1 = 0.0433$, $wR_2 = 0.1100$	$R_1 = 0.0559$, $wR_2 = 0.1180$
Largest diff. peak/hole (e Å^{-3})	0.663/– 0.582	0.640/– 0.480	0.607/– 0.388	0.702/– 0.801

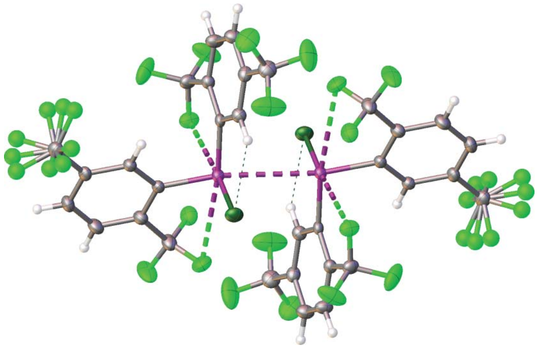


Fig. 2 Ar_2PCl dimer illustrating the octahedral coordination of the P atoms, completed by the P–P intermolecular bond. ADPs are drawn at 50% probability.

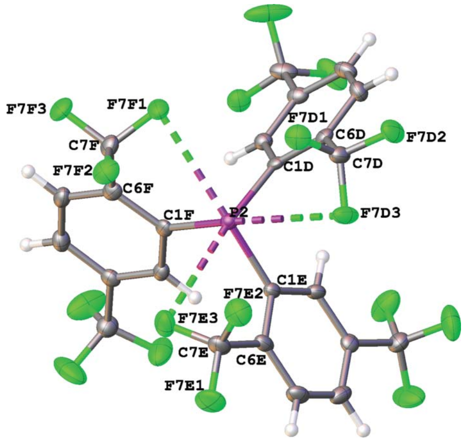


Fig. 3 The molecular structure of Ar_3P (**3**), showing the numbering scheme for the key atoms. ADPs are drawn at 50% probability.

between *trans*-groups about P1 range from 169.16 – 171.76°, and those about P2 from 169.37 – 173.15°, with the lone pair again stereochemically inactive. In section (b) it was noted that Ar_3P (**3**) reacts only to a limited extent with the platinum chloro-dimer *trans*-[PtCl(μ-Cl)(PEt$_3$)]$_2$, and not at all with its bromo-analogue, although the electronegative ligands on P would be expected to favour coordination. This behaviour may thus be attributed to the unavailability of a directed lone pair in (**3**). Ar_2PCl (**1**) did react more readily than Ar_3P with the chloro-dimer (section (b)), so a possible explanation could be the scission of the P–P interaction in solution, breaking up the ψ-octahedral structure and facilitating coordination to a transition metal. There will also be more steric hindrance to complex formation by Ar_3P than by Ar_2PCl, because of the three *ortho*-CF_3 groups in the former. This factor seems unlikely to predominate, however, since [2,4,6-$(CF_3)_3C_6H_2$]$_2$PCl, with four *ortho*-CF_3 groups, reacts readily with the platinum chloro-dimer.

Compound (**9**), $Ar_2P(O)H$, exists in the phosphorus(V) form in the solid state with a P–H bond, Fig. 4. The P═O bond length of 1.4835(13) Å may be compared with recent literature values of 1.476(3) Å,[36] 1.4819(19) Å[37] and 1.4894(15) Å[38] in

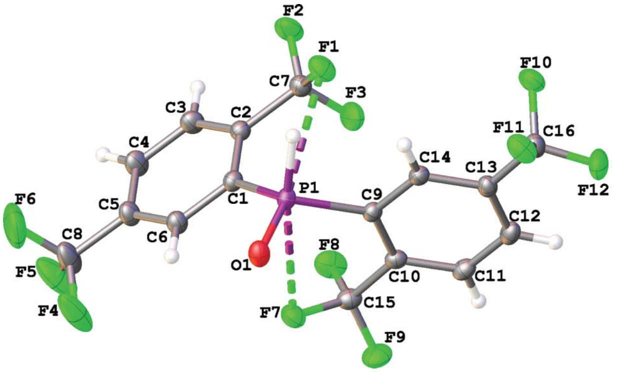


Fig. 4 The molecular structure of $Ar_2P(O)(H)$ (**9**), showing the numbering scheme for the key atoms. ADPs are drawn at 50% probability.

other compounds of this type. There is an H-bonding interaction between H1P on P1 and the oxygen atom O1A of an adjacent molecule, at a distance of 2.868(10) Å; the P–H–O bond angle is 149.8(11)°.

The oxidation product (**10**), $Ar_2P(O)OH$, (Fig. 5) shows only a small difference in the phosphorus-oxygen bond lengths (Table 3), with the nominal double bond at 1.5034(17) Å and the P-OH bond at 1.5401(17) Å. This again compares well with recent literature data for similar acids, *e.g.* 1.5053(14) and 1.5584(15) Å,[39] 1.4851(19) and 1.561(3) Å,[40] 1.502 and 1.524 Å,[41] and 1.503(1) and 1.532(1) Å respectively.[42] It forms strongly H-bonded symmetrical dimers between the P-OH group in one molecule and the P=O group in an adjacent molecule (and *vice versa*). The O–O distance of 2.479 Å compares well with that of 2.497(2) Å in the H-bonded dimer of the isomeric acid $[2,4\text{-}(CF_3)_2C_6H_3]_2P(O)OH$,[42] and with similar O–O distances between 2.441(3) and 2.554(3) Å in other recent structure determinations for compounds of this type.[40,41]

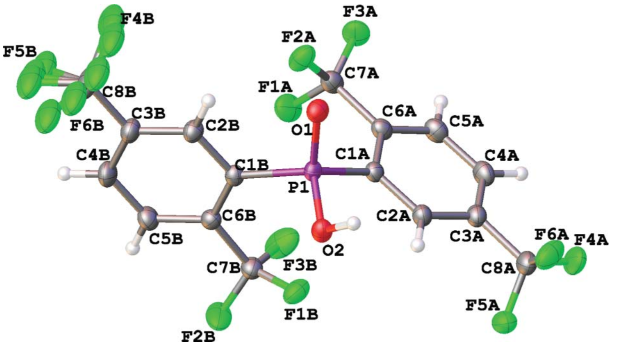


Fig. 5 The molecular structure of $Ar_2P(O)(OH)$ (**10**) showing the numbering scheme for key atoms. ADPs are drawn at 50% probability.

All of the new structures have P–F contacts at distances appreciably shorter than the sum of the van der Waals radii,[29] as shown in Table 4. These contacts clearly play a crucial role in determining the geometry in (**1**) and (**3**), and apparently the chemical reactivity in (**3**) in particular, as discussed above, while compounds (**9**) and (**10**) also have some comparatively short P–F interactions. The shortest P–F contacts reported to an *ortho*-CF_3 group are at 2.554(2) and 2.562(11) Å in a phosphenium salt,[18] while P–F distances of between 2.843 and 3.250 Å have been ascertained previously in several other arylphosphorus compounds with one or two *o*-CF_3 groups on the aromatic ring.[12,15,17] The distance of 2.7092(21) Å in Ar_2PCl thus lies towards the shorter end of the normal range.

As mentioned earlier a few crystals were isolated from the reaction of Ar_2PCl with *trans*-$[PtCl(\mu\text{-}Cl)(PEt_3)]_2$. The crystals showed signs of twinning and disorder, making the results unsuitable for publication, although the connectivities were confirmed. These showed that the *cis*-isomer of $[PtCl_2(Ar_2PCl)(PEt_3)]$ had formed, suggesting that this is the thermodynamic product, as expected.

Conclusions

Several phosphorus(III) derivatives containing the $2,5\text{-}(CF_3)_2C_6H_3$ (Ar) substituent have been successfully prepared, four of which have been fully characterised by single-crystal X-ray diffraction at low temperature. Two of these structures, for Ar_2PCl (**1**) and Ar_3P (**3**), are particularly interesting, since in each case the phosphorus has an approximately octahedral geometry, and the P lone pair appears to be stereochemically inactive. Ar_3P (**3**) proved reluctant to react with the platinum(II) species, possibly arising from this enclosed pseudo-octahedral environment. Ar_2PCl (**1**) reacted readily with *trans*-$[PtCl(\mu\text{-}Cl)(PEt_3)]_2$, suggesting that the P–P interaction found in the solid state may break up in solution, giving a geometry more receptive to coordination to a transition metal.

Other ArP(III) derivatives reacted with dimeric platinum(II) species to form the *trans*-complexes in solution as the kinetic products, although the few crystals isolated from the Ar_2PCl reaction proved to be of the more thermodynamically stable *cis*-isomer.

Experimental

All manipulations, including NMR sample preparation, were carried out either under an inert atmosphere of dry nitrogen or *in vacuo*, using standard Schlenk line or glovebox techniques. Chemicals of the best available commercial grade were used, in general without further purification. All solvents, unless otherwise stated were dried prior to use. The ^{31}P NMR spectra of all phosphorus-containing starting materials were recorded, to verify that no major impurities were present. ^{31}P NMR spectra were obtained on Varian Mercury 200, Varian Unity 300, Mercury 400 or Inova 500 Fourier-transform spectrometers at 80.96, 121.40, 161.91 or 202.3 MHz, respectively; chemical shifts are referenced to 85% H_3PO_4, with the high frequency direction taken as positive. ^{19}F spectra were recorded on Varian Mercury 200 or Mercury 400 at 188.18 and 376.34 MHz, respectively; chemical shifts are referenced to external $CFCl_3$, with the high frequency direction taken as positive. Microanalyses were performed by the microanalytical services of the Department of Chemistry, Durham University.

Synthesis of ArLi

BuLi (9.2 ml; 23 mmols) was added dropwise to a solution of 1,4-bis(trifluoromethyl) benzene (4 ml; 26 mmol) in Et_2O (30 ml) at −78 °C. The solution was allowed to warm to room temperature slowly.

Synthesis of Ar_2PCl (1)

ArLi solution (as prepared above) was added dropwise to a solution of PCl_3 (1 ml; 12 mmols) in Et_2O (30 ml) at −78 °C. The solution was allowed to warm to room temperature and left to stir for 18 h. Following filtration to remove LiCl, the solution was concentrated and then cooled to afford large colourless crystals. (Found: C 39.20% H 1.30% N 0.00% $C_{16}H_6ClF_{12}P$ requires C 39.01% H 1.23% N 0.00%). ^{31}**P** (121.40 MHz, $CDCl_3$): δ 67.6 ppm (sept, $^4J_{P\text{–}F}$ = 66 Hz). ^{19}**F** (376.34 MHz, $CDCl_3$): δ -58.0 ppm (d, $^4J_{P\text{–}F}$ = 66 Hz, *ortho*-CF_3), δ -64.5 ppm (s, *para*-CF_3). 78% yield from ^{31}P NMR spectra.

Synthesis of Ar_3P (3)

PCl_3 (1 ml; 12 mmols) was added dropwise to a solution of ArLi (as prepared above) at −78 °C. The solution was allowed to warm to room temperature and left to stir for 18 h. Following filtration to remove LiCl, the solution was concentrated and then cooled to afford large colourless crystals. (Found: C 42.85% H 1.38% N 0.00% $C_{24}H_9F_{18}P$ requires C 43.01% H 1.35% N 0.00%). ^{31}**P** (121.40 MHz, $CDCl_3$): δ −16.4 ppm (10 line multiplet). ^{19}**F** (376.34 MHz, $CDCl_3$): δ −58.9 ppm (d, $^4J_{P\text{–}F}$ = 55 Hz, *ortho*-CF_3), δ −64.9 ppm (s, *para*-CF_3); *m/z* (EI) 670 (100%, M^+) and 319 (89%, M^+ – Ar – 2CF_3); m.p. 111–113 °C; Isolated yield: 65%.

Synthesis of Ar_2PBr (4)

ArLi solution (38 ml, 24 mmols) was added dropwise to a solution of PBr_3 (1.1 ml; 11 mmols) in Et_2O (30 ml) at −78 °C. The solution was allowed to warm to room temperature and left to stir for 18 h. The solvent was removed in vacuo, and the product extracted using DCM. ^{31}**P** (161.9 MHz, $CDCl_3$): δ 56.9 ppm (sept, $^4J_{P\text{–}F}$ = 66 Hz). ^{19}**F** (376.34 MHz, $CDCl_3$): δ −58.0 ppm (d, $^4J_{P\text{–}F}$ = 66 Hz, *ortho*-CF_3), δ −64.0 ppm (s, *para*-CF_3). 58% yield from ^{31}P NMR spectra.

Synthesis of Ar_2PF (6)

SbF_3 was added to a solution of Ar_2PCl (1 : 1 ratio) in DCM. The solution was stirred and heated to reflux for 24 h. The solution was filtered to afford a dark orange solution.^{31}**P** (121.40 MHz, $CDCl_3$): δ 145.1 ppm (d of sept$^1J_{P\text{–}F}$ = 930 Hz, $^4J_{P\text{–}F}$ = 64 Hz). ^{19}**F** (376.34 MHz, $CDCl_3$): δ -57.9 ppm (d, $^4J_{P\text{–}F}$ = 64 Hz, *ortho*-CF_3), δ −64.41 ppm (s, *para*-CF_3), δ −189.4 ppm (d of sept, $^1J_{P\text{–}F}$ = 930 Hz, P-*F*). From the ^{31}P and ^{19}F NMR spectra, the conversion of Ar_2PCl to Ar_2PF appeared to be essentially quantitative.

Synthesis of Ar_2PH (7)

Bu_3SnH (0.37 ml, 12 mmols) was added dropwise to a solution of Ar_2PCl (0.5 ml, 12 mmols) at room temperature. The solution was stirred for 4 h to afford a yellow solution. ^{31}**P** {^{1}**H**} (121.40 MHz, $CDCl_3$): δ −47.5 ppm (sept, $^4J_{P\text{–}F}$ = 39 Hz). ^{31}**P** (121.40 MHz, $CDCl_3$): δ −47.5 ppm (d of sept, $^1J_{P\text{–}H}$ = 228 Hz, $^4J_{P\text{–}F}$ = 39 Hz). ^{19}**F** (376.34 MHz, $CDCl_3$): δ −61.0 ppm (d, $^4J_{P\text{–}F}$ = 39 Hz, *ortho*-CF_3), δ −65.0 ppm (s, *para*-CF_3). The conversion of Ar_2PCl to Ar_2PH also appeared to be quantitative from the ^{31}P and ^{19}F NMR spectra.

Synthesis of Ar^{t}BuPCl (8)

ArLi solution (19 ml, 2.6 mmols) was added dropwise to a solution of ^{t}BuPCl_2 (0.142 g; 2.6 mmols) in Et_2O (20 ml) at −78 °C. The solution was allowed to warm to room temperature and left to stir for 18 h. Following filtration to remove LiCl, the solution was concentrated. ^{31}**P** (161.9 MHz, $CDCl_3$): δ 97.7 ppm (q, $^4J_{P\text{–}F}$ = 71 Hz). ^{19}**F** (376.34 MHz, $CDCl_3$): δ −55.2 ppm (d, $^4J_{P\text{–}F}$ = 71 Hz, *ortho*-CF_3), δ −63.7 ppm (s, *para*-CF_3). Quantitative conversion of ArLi to Ar^{t}BuPCl was observed from ^{31}P NMR spectra.

Isolation of $Ar_2P(O)H$ (9)

A solution from one of the ArLi-PCl_3 reactions was layered with hexane and place in a crystal tube. White crystals suitable for X-ray analysis eventually formed, proved to be of the hydrolysis product $Ar_2P(O)H$, presumably formed by ready rearrangement of $Ar_2P(OH)$. This compound was also prepared from Ar_2PCl by adding reagent grade DCM and leaving the mixture to stand until conversion was complete. Found: C 40.29% H 1.50% N 0.00% $C_{16}H_7F_{12}OP$ requires C 40.53% H 1.49% N 0.00%. ^{31}**P** {^{1}**H**} (161.9 MHz, $CDCl_3$): δ 8.8 ppm (sept). ^{31}**P** (161.9 MHz, $CDCl_3$): δ 8.8 ppm (d of sept, $^1J_{P\text{–}H}$ = 550 Hz). ^{19}**F** (376.34 MHz, $CDCl_3$): δ −58.5 ppm (d, $^4J_{P\text{–}F}$ = 8 Hz, *ortho*-CF_3), δ −64.0 ppm (s, *para*-CF_3). *m/z* (EI) 474 (20%, M^+), 405 (100%, M^+ – CF_3) and 144 (70%, $C_6H_3CF_3$); m.p. 96–100 °C.

Isolation of $Ar_2P(O)(OH)$ (10)

A solution of Ar_2PF was exposed to air. Crystals were isolated after some time and X-ray analysis showed that these were $Ar_2P(O)(OH)$. Found: C 39.02% H 1.99% N 0.00% $C_{16}H_7F_{12}O_2P$ requires C 39.20% H 1.44% N 0.00%. ^{31}**P** (161.9 MHz, $CDCl_3$): δ 14.9 ppm (s). ^{19}**F** (376.34 MHz, $CDCl_3$): δ −58.0 ppm (d, $^4J_{P\text{–}F}$ = 64 Hz, *ortho*-CF_3), δ −63.7 ppm (s, *para*-CF_3).

Synthesis of *trans*-$[PtCl_2(Ar_2P_ACl)(P_BEt_3)]$ (11)

A solution of *trans*-$[PtCl(\mu\text{-}Cl)(PEt_3)]_2$ (0.0276g; 0.04 mmols) in $CDCl_3$ was added to Ar_2PCl (0.0419g; 0.08 mmols) in a Young's NMR tube. ^{31}**P** (161.9 MHz, $CDCl_3$): δ_{PA} 91.9 ppm (d + sats, $^1J_{Pt\text{–}P}$ = 2694 Hz, $^2J_{P\text{–}P}$ = 565 Hz) δ_{PB} 17.8 ppm (d + sats, $^1J_{Pt\text{–}P}$ = 2748 Hz, $^2J_{P\text{–}P}$ = 565 Hz). ^{19}**F** (376.34 MHz, $CDCl_3$): δ −55.9 ppm (d, $^4J_{P\text{–}F}$ = 6 Hz, *ortho*-CF_3), δ −63.8 ppm (s, *para*-CF_3).

Synthesis of *trans*-$[PtCl_2(Ar_3P_A)(P_BEt_3)]$ (12)

A solution of *trans*-$[PtCl(\mu\text{-}Cl)(PEt_3)]_2$ (0.0500g; 0.065 mmols) in $CDCl_3$ was added to Ar_3P (0.0871g; 0.13 mmols) in a Young's NMR tube. ^{31}**P** (161.9 MHz, $CDCl_3$): δ_{PA} 43.6 ppm (d + sats, $^1J_{Pt\text{–}P}$ = ~2400 Hz, $^2J_{P\text{–}P}$ = 488 Hz) δ_{PB} 15.7 ppm (d + sats, $^1J_{Pt\text{–}P}$ = 2847 Hz, $^2J_{P\text{–}P}$ = 488 Hz).

Synthesis of *trans*-$[PtCl_2(Ar_2P_ABr)(P_BEt_3)]$ (13)

A solution of *trans*-$[PtCl(\mu\text{-}Cl)(PEt_3)]_2$ (0.0601g; 0.065 mmols) in $CDCl_3$ was added to Ar_2PBr (0.0710g; 0.13 mmols) in a Young's NMR tube. ^{31}**P** (161.9 MHz, $CDCl_3$):): δ_{PA} 72.1 ppm (d + sats, $^1J_{Pt\text{–}P}$ = 2523 Hz, $^2J_{P\text{–}P}$ = 563 Hz) δ_{PB} 11.5 ppm (d + sats, $^1J_{Pt\text{–}P}$ = 2678 Hz, $^2J_{P\text{–}P}$ = 563 Hz). ^{19}**F** (376.34 MHz, $CDCl_3$): δ −54.9 ppm (d, $^4J_{P\text{–}F}$ = 5 Hz, *ortho*-CF_3), δ −63.6 ppm (s, *para*-CF_3).

Synthesis of *trans*-[PtCl$_2$(Ar$_2$P$_A$F)(P$_B$Et$_3$)] (14)

A solution of *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$ in CDCl$_3$ was added to Ar$_2$PF (1 : 2 ratio) in a Young's NMR tube. **^{31}P** (121.40 MHz, CDCl$_3$): δ_{PA} 146.5 ppm (d + sats, $^1J_{Pt-P}$ = 3088 Hz, $^2J_{P-P}$ = 567 Hz) δ_{PB} 17.4 ppm (d + sats, $^1J_{Pt-P}$ = 2570 Hz, $^2J_{P-P}$ = 567 Hz). **^{19}F** (376.34 MHz, CDCl$_3$): δ −52.3 ppm (d, $^4J_{P-F}$ = 19 Hz, *ortho*-CF$_3$), δ -63.8 ppm (s, *para*-CF$_3$).

Synthesis of *trans*-[PtCl$_2$(Ar$_2$P$_A$H)(P$_B$Et$_3$)] (15)

A solution of *trans*-[PtCl(μ-Cl)(PEt$_3$)]$_2$ (0.0570g; 0.075 mmols) in CDCl$_3$ was added to Ar$_2$PH (0.15 mmols) in a Young's NMR tube. **^{31}P** (161.9 MHz, CDCl$_3$): δ_{PA} −7.6 ppm (d + sats, $^1J_{Pt-P}$ = 2362 Hz, $^2J_{P-P}$ = 420 Hz) δ_{PB} 17.1 ppm (d + sats, $^1J_{Pt-P}$ = 2798 Hz, $^2J_{P-P}$ = 420 Hz). **^{19}F** (376.34 MHz, CDCl$_3$): δ −60.3 ppm (d, $^4J_{P-F}$ = 8 Hz, *ortho*-CF$_3$), δ −65.0 ppm (s, *para*-CF$_3$).

Synthesis of *trans*-[PtCl$_2$(Ar^{t}BuP$_A$Cl)(P$_B$Et$_3$)] (16)

A solution of *trans*-[PtCl(μ-Cl)(PEt$_3$)]$_2$ (0.0192 g; 0.025 mmols) in CDCl$_3$ was added to Ar^{t}BuPCl (0.05 mmols) in a Young's NMR tube. **^{31}P** (161.9 MHz, CDCl$_3$): δ_{PA} 112.0 ppm (d + sats, $^1J_{Pt-P}$ = 2466 Hz, $^2J_{P-P}$ = 529 Hz) δ_{PB} 13.6 ppm (d + sats, $^1J_{Pt-P}$ = 2754 Hz, $^2J_{P-P}$ = 529 Hz). **^{19}F** (376.34 MHz, CDCl$_3$): δ -52.3 ppm (d, $^4J_{P-F}$ = 19 Hz, *ortho*-CF$_3$), δ −63.8 ppm (s, *para*-CF$_3$).

X-ray Crystallography

Single crystal structure determinations were carried out from data collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART-CCD 1 K diffractometer. The temperature was controlled using an open flow N$_2$ Cryostream cooling device.[43] In each case, a series of narrow ω-scans (0.3°) were performed at several φ-settings to maximise data coverage. Cell parameters were determined and refined using the SMART software,[44] and raw frame data were integrated using the SAINT program.[45] The structures were solved using direct methods,[46] and refined by full-matrix least-squares on F^2 using SHELXTL,[46] and the graphical user interface Olex2.[47]

Due to rotational disorder of the CF$_3$ groups in the Ar ligand, different cooling strategies were employed. Crystals of (**1**), (**9**) and (**10**) were 'flash frozen' at 120 K and data were collected at that temperature. However Ar$_3$P (**3**) underwent significant stress when rapidly cooled, resulting in degradation of crystallinity. Slow cooling from room temperature resulted in no significant structural change, except thermal contraction of the unit cell dimensions and reduced thermal motion of the CF$_3$ groups. Hence only the lowest temperature data are reported. These data were collected at 100 K to minimise the disorder present, having been cooled slowly from room temperature at 60 K h^{-1}.

Additionally, the disorder in the CF$_3$ groups of (**1**) and (**10**) was modelled to give the most sensible structural refinement. In (**1**) the one disordered CF$_3$ group is modelled using multiple split occupancy isotropic atoms. The additional parameters for anisotropic refinement did not significantly improve the model statistics. In (**10**) a constrained anisotropic refinement of the disordered CF$_3$ group resulted in the more suitable model. It is noteworthy that all of the disorder present in the Ar ligands is constrained to those CF$_3$ groups not involved in P–F contacts, again highlighting the importance of these interactions.

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