Structural diversity in nonafluoromesityl chemistry†

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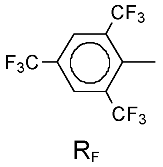
Received* (*in Strasbourg, France*) *10th May 1999, Accepted 3rd June 1999

Several new compounds containing the nonafluoromesityl substituent [2,4,6-tris(trifluoromethyl)phenyl, abbreviated as R_F] have been prepared and structurally characterized. Solid state structures are reported for $C_5Me_5P(Cl)R_F$ (**1**), $Sn(SeR_F)_4$ (**3**), $Te(R_F)_2$ (**4**) and $(AgR_F)_4$ (**5**). **1** and **4** crystallize in space group $P2_1/c$, **3** in space group $P\bar{1}$, and **5** in space group $I4_1/a$. While **1** and **3** are monomeric in the solid state, the telluride **4** is dimerized *via* Te···F secondary bonds and **5** adopts a tetrameric structure containing a central Ag_4 ring. Furthermore the preparation of $C_5Me_5P(H)R_F$ (**2**) is described.

During the past 10 years the 2,4,6-tris(trifluoromethyl)phenyl substituent "nonafluoromesityl", abbreviated as R_F, has been shown to be a highly versatile building block in main group chemistry.[1–3]



R_F

Due to its ideal combination of sterically and electronically stabilizing effects this ligand has been successfully employed in the stabilization of low coordination numbers around various main group elements such as phosphorus,[2,4-9] arsenic,[10] tin,[11-17] lead,[18] indium,[19] or thallium.[20] Of special interest are the readily accessible and unusually stable nonafluoromesityl derivatives of divalent tin and lead.[3,13] $(R_F)_2Pb$ was the first diarylplumbylene ever made.[17] We report here the preparation and crystallographic characterization of four new compounds containing the R_F substituent, namely $C_5Me_5P(Cl)R_F$ (**1**), $Sn(SeR_F)_4$ (**3**), $Te(R_F)_2$ (**4**) and $(AgR_F)_4$ (**5**). This investigation once more demonstrates the synthetic value of nonafluoromesityl in main group chemistry.

Syntheses and structures

Chloropentamethylcyclopentadienyl [2,4,6-tris(trifluoromethyl)-phenyl] phosphine, $C_5Me_5P(Cl)R_F$ (1)

Nonafluoromesityl derivatives of phosphorus form a fairly large and well-investigated class of compounds. Among the known examples are R_FPF_2, R_FPClF, R_FPCl_2, $(R_F)_2PCl$,[2,5,6] as well as the diphosphene derivative $R_FP{=}PR_F$ [2] and transition metal complexes thereof.[6,8,9] The hitherto unknown compound $C_5Me_5P(Cl)R_F$ (**1**) was prepared in 77% yield by treatment of lithium pentamethylcyclopentadienide with R_FPCl_2 in diethyl ether solution:

$$\mathrm{Li(C_5Me_5)} + \mathrm{R_FPCl_2} \rightarrow \underset{\mathbf{1}}{\mathrm{C_5Me_5P(Cl)R_F}} + \mathrm{LiCl} \qquad (1)$$

The product is easily isolated by vacuum distillation. Compound **1** forms bright yellow crystals, which melt without decomposition at 68 °C. A FI mass spectrum shows the molecular ion at *m*/*z* 482, and the spectroscopic data are in agreement with the formation of a mono(pentamethylcyclopentadienyl) product.

The chloro function in **1** can be replaced by hydrogen. Reduction of the chlorophosphine is readily achieved by treatment of **1** with $LiAlH_4$ in diethyl ether solution (65% yield):

$$\mathrm{C_5Me_5P(Cl)R_F} \xrightarrow[\text{2. H}_2\text{O}]{\text{1. LiAlH}_4} \underset{\mathbf{2}}{\mathrm{C_5Me_5P(H)R_F}} \qquad (2)$$

The secondary phosphine **2** is readily isolated by vacuum distillation as a yellow, highly air- and moisture-sensitive liquid. All spectroscopic data are in good agreement with the presence of $C_5Me_5P(H)R_F$. The FI mass spectrum shows the molecular ion with 10% relative intensity.

Single crystals of **1** suitable for X-ray diffraction were obtained by recrystallization from hexane. In the crystal structure (Fig. 1, Tables 1 and 5) the asymmetric unit contains two nearly identical but independent molecules. The phosphorus

Table 1 Selected bond lengths (Å) and angles (°) for $C_5Me_5P(Cl)R_F$ (**1**)

P(1)–Cl(1)	2.087(2)	C(22)–C(23)	1.348(6)
P(1)–C(1)	1.906(4)	C(23)–C(24)	1.461(6)
P(1)–C(21)	1.889(4)	C(24)–C(25)	1.354(6)
C(21)–C(22)	1.519(6)	C(21)–C(25)	1.504(6)
P(2)–Cl(2)	2.094(2)	C(42)–C(43)	1.347(6)
P(2)–C(11)	1.899(4)	C(43)–C(44)	1.467(6)
P(2)–C(41)	1.893(4)	C(44)–C(45)	1.353(6)
C(41)–C(42)	1.517(5)	C(41)–C(45)	1.515(5)
C(1)–P(1)–C(21)	110.6(2)	C(1)–P(1)–Cl(1)	101.6(1)
C(21)–P(1)–Cl(1)	107.3(1)	C(11)–P(2)–C(41)	108.4(2)
C(11)–P(2)–Cl(2)	100.6(1)	C(41)–P(2)–Cl(2)	109.2(1)

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† Dedicated to Professor Reinhard Schmutzler on the occasion of his 65th birthday.

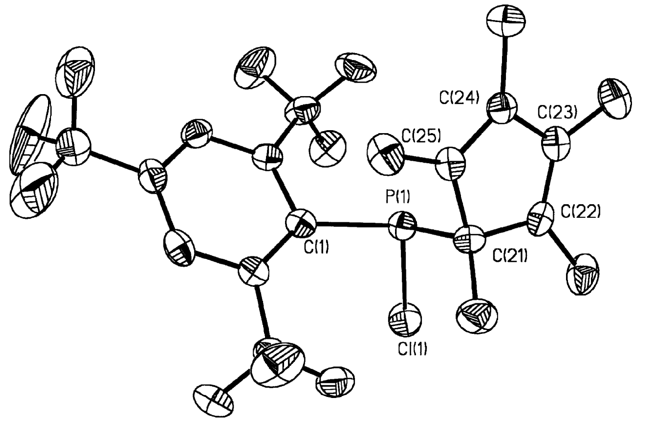

Fig. 1 Molecular structure of the phosphorus compound **1**.

atom is at the apex of a trigonal pyramid described by phosphorus, chlorine, and the *ipso*-carbon atoms of the R_F and C_5Me_5 substituents. With values of 2.087(2) [P(1)–Cl(1)] and 2.094(2) Å [P2–Cl(2)] the P–Cl distances are typical for phosphorus–chlorine single bonds.[21b] The P–C bond lengths are marginally longer than a standard phosphorus–carbon single bond.[21b] There is no π-bonding between the pentamethylcyclopentadienyl ring and the phosphorus atom. The double bonds are localized between C(22)–C(23) [C(42)–C(43)] and C(24)–C(25) [C(44)–C(45)] (see Table 1.)

Tetrakis[2,4,6-tris(trifluoromethyl)phenylseleno]tin(IV), $Sn(SeR_F)_4$ (3)

The recent discovery of the stable selenol 2,4,6-tris(trifluoromethyl)selenophenol, R_FSeH,[22,23] allowed the preparation of various main group and transition metal selenolate derivatives containing the R_FSe moiety. A straightforward synthetic method involves treatment of metal bis(trimethylsilyl)amides with appropriate amounts of the free selenophenol:[22,23]

$$M[N(SiMe_3)_2]_2 + 2R_FSeH \xrightarrow{\text{hexane}} M(SeR_F)_2 + 2HN(SiMe_3)_2 \quad (3)$$

with M = Mn, Zn, Cd, Hg, Ge, Sn, Pb. Alternatively, transition metal halides can be reacted with the corresponding alkali metal selenophenolates. The latter route has been employed, for example, in the preparation of indium(III), antimony(III) and bismuth(III) SeR_F derivatives:[22,23]

$$MCl_3 + 3NaSeR_F \rightarrow M(SeR_F)_3 + 3NaCl \quad (4)$$

The title compound $Sn(SeR_F)_4$ (**3**) was obtained in an unexpected manner when the tin(II) complex of bis[bis(trimethylsilyl)amide] was treated with two equivalents of R_FSeH.[22–24] In this case a disproportionation reaction took place with formation of **3** and elemental tin:

$$2Sn[N(SiMe_3)_2]_2 + 4R_FSeH \rightarrow \underset{\mathbf{3}}{Sn(SeR_F)_4} + Sn^0 + 4HN(SiMe_3)_2 \quad (5)$$

Single crystals of **3** suitable for X-ray diffraction were grown by slowly cooling a saturated solution in toluene from room temperature to −30 °C. In the molecular structure of **3** the central tin atom is tetrahedrally surrounded by four SeR_F substituents (Figs. 2 and 3, Tables 2 and 5). Both the Sn–Se (ave. 2.536 Å) and the Se–C (ave. 1.932 Å) distances are in good agreement with corresponding values taken from the literature.[25–27] The Sn–Se–C angles are in the range of 96.3° to 99.8°. A packing diagram (Fig. 3) reveals that in the crystal the molecules are dimerized *via* very weak Se···F secondary bonding. With a value of 3.394 Å the selenium–fluorine distances are almost identical with the sum of the van der Waals radii of selenium and fluorine (3.35 Å).[21a]

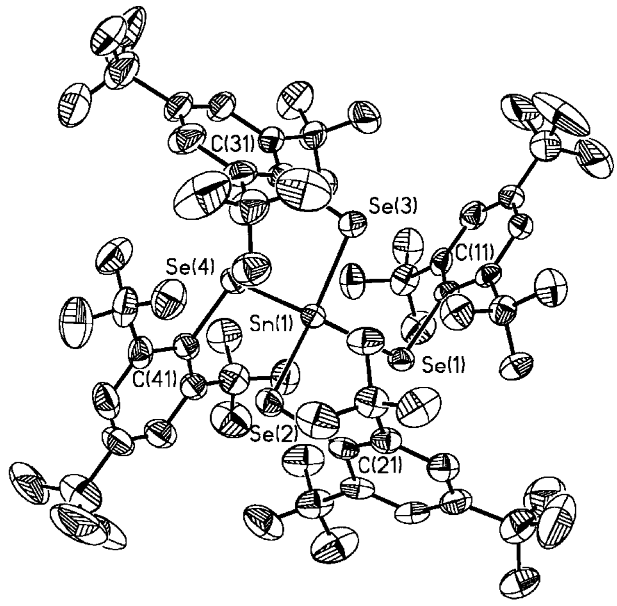

Fig. 2 Molecular structure of the tin complex **3**.

Bis[2,4,6-tris(trifluoromethyl)phenyl]telluride, $Te(R_F)_2$ (4)

The chemistry of tellurium compounds containing nonafluoromesityl substituents is currently not well-developed.[3] It was found that 2,4,6-tris(trifluoromethyl)phenyllithium, R_FLi, does not react directly with elemental tellurium to form the corresponding lithium tellurolate R_FTeLi. However, this inter-

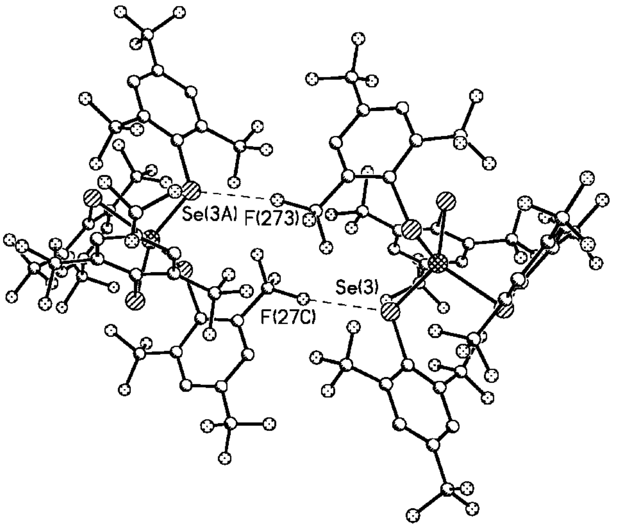

Fig. 3 Dimeric structure of **3** showing the Se···F secondary bonding.

Table 2 Selected bond lengths (Å) and angles (°) for $Sn(SeR_F)_4$ (**3**)

Sn(1)–Se(1)	2.532(1)	Sn(1)–Se(3)	2.535(1)
Sn(1)–Se(2)	2.538(1)	Sn(1)–Se(4)	2.541(1)
Se(1)–C(11)	1.936(5)	Se(2)–C(21)	1.936(5)
Se(3)–C(31)	1.924(5)	Se(4)–C(41)	1.932(5)
Se(1)–Sn(1)–Se(2)	103.20(2)	Se(1)–Sn(1)–Se(3)	104.13(2)
Se(1)–Sn(1)–Se(4)	119.26(3)	Se(2)–Sn(1)–Se(3)	119.66(3)
Se(2)–Sn(1)–Se(4)	106.25(3)	Se(3)–Sn(1)–Se(4)	105.26(3)
C(11)–Se(1)–Sn(1)	99.8(1)	C(21)–Se(2)–Sn(1)	96.3(1)
C(31)–Se(3)–Sn(1)	99.8(2)	C(41)–Se(4)–Sn(1)	98.8(2)

mediate is readily formed when $\mathrm{Bu}^n_3\mathrm{PTe}$ is used as a soluble tellurium source. $\mathrm{R_FTeLi}$ has not been isolated as a pure compound, as it is very readily oxidized to form bis[2,4,6-tris(trifluoromethyl)phenyl]ditelluride, $\mathrm{Te_2(R_F)_2}$. Surprisingly, the oily dark red ditelluride has also been found to be quite unstable. It decomposes under the influence of heat and/or light to form bis[2,4,6-tris(trifluoromethyl)phenyl]telluride, $\mathrm{Te(R_F)_2}$ (**4**), besides elemental tellurium. In fact, thermal decomposition of $\mathrm{Te_2(R_F)_2}$ was found to be the most convenient access to **4**. Scheme 1 depicts the reaction sequence leading to the monotelluride.[3,28]

Single crystals of **4** were obtained simply by heating a solution of $\mathrm{Te_2(R_F)_2}$ in ethanol under reflux until the red color of the ditelluride had disappeared. Filtration while hot and slow cooling of the filtrate to room temperature afforded bright yellow needles of **4** (Figs. 4 and 5, Tables 3 and 5).[24,28] The angle at tellurium is 107.4(2)° and thus differs only slightly (2.1°) from the ideal tetrahedral geometry. This unusually small deviation can be traced back to the high steric demand of the $\mathrm{R_F}$ substituents. With 84.7° the $\mathrm{R_F}$ rings are oriented almost perpendicular to each other. Once again this is a result of the large steric bulk of these ligands. The observed orientation minimizes steric interactions between opposite *ortho*-$\mathrm{CF_3}$ groups.

$$\mathrm{R_FLi + Bu^n{}_3PTe \longrightarrow R_FTeLi + Bu^n{}_3P}$$

$$\mathrm{2\,R_FTeLi + O_2 \xrightarrow[\Delta]{} Te_2(R_F)_2 + Li_2O}$$

$$\mathrm{Te_2(R_F)_2 \longrightarrow \underset{\mathbf{4}}{Te(R_F)_2} + Te}$$

Scheme 1

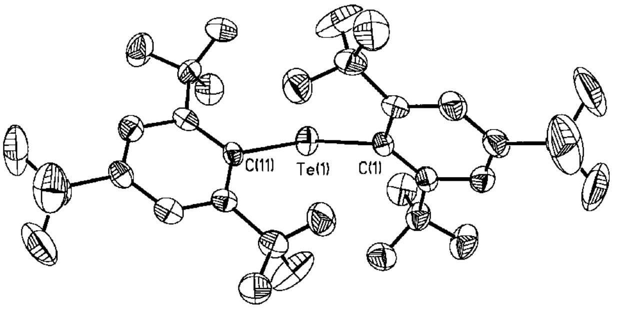

Fig. 4 Molecular structure of the tellurium compound **4**.

Table 3 Selected bond lengths (Å) and angles (°) for $\mathrm{Te(R_F)_2}$ (**4**)

Te(1)–C(1)	2.151(5)	Te(1)–C(11)	2.151(5)
C(1)–Te(1)–C(11)	107.4(2)		

In the crystal structure the molecules of **4** are dimerized *via* weak Te···F secondary interactions. The intermolecular Te···F distance is 3.546 Å and corresponds exactly to the sum of the van der Waals radii of tellurium and fluorine (3.55 Å).[21a]

Tetrakis[2,4,6-tris(trifluoromethyl)phenylsilver], $(\mathrm{AgR_F})_4$ (5)

The hitherto unknown arylsilver derivative 2,4,6-tris(trifluoromethyl)phenylsilver(I) (**5**) was formed in an unexpected reaction between bis[2,4,6-tris(trifluoromethyl)phenyl]lead(II), $\mathrm{Pb(R_F)_2}$,[17] and silver hexafluoroarsenate. Originally this reaction (carried out in liquid $\mathrm{SO_2}$) was expected to yield the cationic lead derivative $\mathrm{[Pb(R_F)_2]AsF_6}$ *via* an oxidation process. Instead, elimination of $\mathrm{Pb(AsF_6)_2}$ occurred and 2,4,6-tris(trifluoromethyl)phenylsilver (**5**) was formed in reasonably good yield (64%):[22]

$$\mathrm{Pb(R_F)_2 + 2AgAsF_6 \xrightarrow{SO_2} \tfrac{1}{2}(AgR_F)_4 + Pb(AsF_6)_2} \qquad (6)$$

Recrystallization of the crude reaction product from liquid $\mathrm{SO_2}$ afforded the colorless, air- and moisture-sensitive arylsilver complex **5**. As a solid as well as in solution **5** is also photosensitive and slowly turns black under the influence of light. The ^{1}H NMR spectrum of **5** shows a 13-line multiplet resulting from coupling of the aromatic protons with the three $\mathrm{CF_3}$ groups. The first indication that **5** is oligomeric in the solid state came from the mass spectrum, in which a peak at *m*/*z* 1275 corresponds to the fragment $[\mathrm{4M - R_F}]^+$. Fragments with one to four silver atoms were also identified. The assumption of a tetrameric structure was confirmed by an X-ray structure determination of **5** (Fig. 6, Tables 4 and 5). A four-membered, nearly planar $\mathrm{Ag_4}$ ring forms the central unit of the molecular structure of **5**. The torsion angle between the planes [Ag(2), Ag(1a), Ag(2a)] and [Ag(1a), Ag(2a), Ag(1)] is 8.4°, thus indicating a slight distortion towards a butterfly conformation (Fig. 6). In this respect the molecular structure

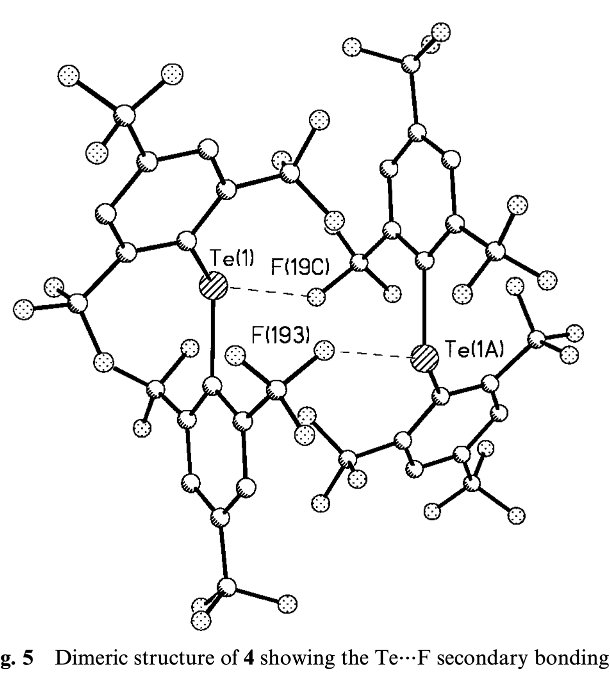

Fig. 5 Dimeric structure of **4** showing the Te···F secondary bonding.

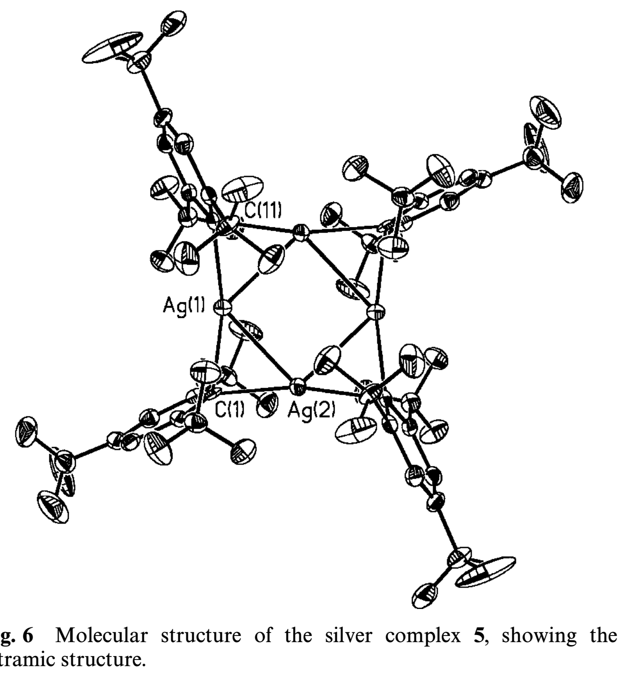

Fig. 6 Molecular structure of the silver complex **5**, showing the tetramic structure.

Table 4 Selected bond lengths (Å) and angles (°) for $(R_FAg)_4$ (**5**)

Ag(1)–Ag(2)	2.754(1)	Ag(1)–Ag(2a)	2.726(1)
Ag(1)–C(1)	2.262(4)	Ag(1)–C(11)	2.200(5)
Ag(2)–C(1)	2.191(5)	Ag(2a)–C(11)	2.275(4)
C(11)–Ag(1)–C(1)	166.2(2)	Cl(1)–Ag(2)–C(11a)	166.7(2)
Ag(2)–C(1)–Ag(1)	76.4(1)	Ag(1)–C(11)–Ag(2a)	75.0(1)

of **5** differs from that of the related tetrameric mesitylsilver(I),[29] in which the Ag_4 ring is exactly planar.

Two silver atoms in the Ag_4 unit are each bridged by a R_F substituent. Short distances of 2.726(1) and 2.754(1) Å between the silver atoms are in agreement with significant Ag–Ag interactions in **5**.

The present study underlines the ability of the 2,4,6-tris(trifluoromethyl)phenyl ligand to stabilize unusual coordination numbers and bonding situations in both main group and transition metal chemistry. Its unique stabilizing influence results from a combination of steric bulk and the possibility of forming weak E···F (E = main group or transition element) secondary interactions. While the chemistry of low-coordinated main group derivatives containing the R_F ligand is now well-explored, much less is known about related transition metal compounds. Future work in this area is expected to focus on this aspect of nonafluoromesityl chemistry.

Experimental

All reactions were carried out under dry, purified nitrogen. Solvents were dried with Na–benzophenone and freshly distilled under N_2 prior to use. Liquid SO_2 was predried and stored over P_4O_{10}. IR spectra were taken on Bio-Rad FTS 7 and Perkin Elmer 325 (Nujol : KBr) instruments while NMR spectra were obtained on Bruker WP 80 SY and Bruker 250 M. Elemental analyses were carried out at the analytical laboratories of the Department of Inorganic Chemistry at the University of Göttingen and the Department of Chemistry at Magdeburg. The starting materials nonafluoromesitylene,[2] LiR_F,[1] pentamethylcyclopentadiene,[30] $Pb(R_F)_2$,[17] and $AgAsF_6$ [31] were prepared according to literature procedures.

Syntheses

Chloropentamethylcyclopentadienyl[2,4,6-tris(trifluoromethyl)phenyl]phosphine, $C_5Me_5P(Cl)R_F$ (1). A 1.6 M solution of *n*-butyllithium (12.3 mL, 19.7 mmol) in hexane is added dropwise to 2.67 g (19.6 mmol) of C_5Me_5H in diethyl ether (120 mL) and the mixture is stirred for 30 min at room temperature. The resulting white suspension of $Li(C_5Me_5)$ is cooled to 0 °C and a solution of 7.50 g (19.6 mmol) R_FPCl_2 in diethyl ether (50 mL) is added with stirring. The reaction mixture is allowed to warm to room temperature and then heated to reflux for 1 h. The solution is filtered through a thin layer of Celite filter aid, the residue washed with diethyl ether (20 mL) and the solvent is removed *in vacuo*. The remaining yellow oil is purified by vacuum distillation. The main fraction is collected at 96 °C/0.4 mmHg and solidifies in the receiving flask. **1** (7.3 g, 77% yield) is isolated as a bright yellow, air- and moisture-sensitive solid. Mp 68 °C. Anal. calcd for $C_{19}H_{17}ClF_9P$ (482.76): C, 47.3; H, 3.6; Cl, 7.3. Found: C, 47.2; H, 3.6; Cl, 7.8%. IR: 1623 s, 1290 vs, 1193 s, 1149 vs, 1119 vs, 1076 vs, 1024 s, 914 s, 860 s, 800 s, 685 s cm^{-1}. FI-MS: *m*/*z* (%): 482 (M, 100). ^1H NMR (C_6D_6): δ 7.90 (s, 2 H, C_6H_2), 1.40 (s, 15 H, C_5Me_5). ^{19}F NMR (C_6D_6): δ − 52.9 (br, s, 6 F, *o*-CF_3), −63.7 (s, 3 F, *p*-CF_3). ^{31}P NMR (C_6D_6): δ 70.0–74.0 (m).

Pentamethylcyclopentadienyl[2,4,6-tris(trifluoromethyl)phenyl]phosphine, $C_5Me_5P(H)R_F$ (2). **1** (6.80 g, 14.1 mmol) in diethyl ether (820 mL) is added at 0 °C to a stirred suspension of 0.64 g (16.9 mmol) $LiAlH_4$ in diethyl ether (100 mL). The reaction mixture is allowed to warm to room temperature and then heated to reflux for 1 h. After cooling to room temperature, water (5 mL) is carefully added, the resulting precipitate is removed by filtration and washed with two portions of 20 mL Et_2O. The light yellow filtrate is dried over $MgSO_4$. Distillation affords 4.1 g (65%) of **2** as a pale yellow liquid. Bp 80 °C/1 Pa. Anal. calcd for $C_{19}H_{18}F_9P$ (448.31): C, 51.0; H, 4.1; P, 6.9. Found: C, 52.9; H, 4.7; P, 6.7%. IR: 1624 vs, 1574 s, 1292 vs, 1274 vs, 1201 vs, 1191 vs, 1141 vs, 1086 vs, 1040 s, 915 s, 860 s, 807 s, 701 s, 685 vs cm^{-1}. FI-MS: *m*/*z* (%): 448 (M, 10), 281 (M − R_F, 4), 135 (C_5Me_5, 100). ^1H NMR (C_6D_6): δ 7.80 (s, 2 H, C_6H_2), 5.00–3.90 (d sept, $^1J_{PH} = 240$ Hz, $^5J_{PF} = 6$ Hz, 1 H, P–H), 1.60 (m, 3 H, Me^1), 1.55 (d, $^5J_{PH} = 1.5$ Hz, 6 H, Me^3, Me^4), 1.20 (s, 6 H, Me^2, Me^5). ^{19}F NMR (C_6D_6): δ − 56.0 (d, $^4J_{PF} = 31.6$ Hz, 6 F, *o*-CF_3), −63.7 (d, $^6J_{PF} = 1.5$ Hz, 3 F, *p*-CF_3). ^{31}P NMR (C_6D_6): δ − 30.6 to −32.5 (m).

Tetrakis[2,4,6-tris(trifluoromethyl)phenylsilver], $(R_FAg)_4$ (5). In a pressure-bottle, dry SO_2 (20 mL) is condensed onto a mixture of 2.15 g (2.8 mmol) $Pb(R_F)_2$ and 1.66 g (5.6 mmol) $AgAsF_6$. The mixture is allowed to slowly warm to room temperature and stirred for 3 days under exclusion of light. An insoluble solid is removed by filtration and the filtrate is evaporated to dryness. The resulting colorless crystals are

Table 5 Summary of crystal data and structure solution for **1**, **3**, **4** and **5**

	1	3	4	5
Formula	$C_{19}H_{17}ClF_9P$	$C_{36}H_8F_{36}Se_4Sn \cdot 1.5C_7H_8$	$C_{18}H_4F_{18}Te$	$C_{36}H_8Ag_4F_{36}$
Formula weight	482.75	1697.16	689.81	1555.90
Crystal system	Monoclinic	Triclinic	Monoclinic	Tetragonal
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$I4_1/a$
a/Å	18.136(4)	13.136(4)	8.874(1)	16.504(1)
b/Å	11.396(2)	13.253(3)	17.781(2)	16.504(1)
c/Å	19.734(4)	17.247(4)	13.383(1)	30.677(2)
α/°	90	88.80(1)	90	90
β/°	94.21(3)	68.28(1)	97.22(1)	90
γ/°	90	75.47(1)	90	90
U/Å^3	4068(1)	2692(1)	2094.9(4)	8355.9(9)
Z	8	2	4	8
μ (calc.)/mm^{-1}	0.350	3.340	1.584	2.041
Reflections collected	10 388	9993	3247	4241
Unique reflections	5290	8494	2739	2281
R_{int}	0.0274	0.0932	0.0145	0.0068
R_1	0.0406	0.0411	0.0345	0.0249
wR_2	0.0978	0.1010	0.0833	0.0662
T/°C	− 120 ± 2	− 85 ± 2	− 90 ± 2	− 120 ± 2

dried under vacuum and recrystallized from liquid SO_2 to afford 1.39 g (64%) of **5** as a colorless crystalline solid. Mp 179 °C (decomp.). Anal. calcd for $C_{36}H_8Ag_4F_{36}$ (1555.88): C, 27.8; H, 0.5; Ag, 27.7. Found: C, 26.7; H, 0.8; Ag, 27.3%. IR: 1618 m, 1296 vs, 1279 vs, 1198 vs, 1170 s, 1132 vs, 1109 vs, 1082 s, 914 s, 687 s cm^{-1}. FI-MS: *m/z* (%): 1275 ($M - R_F$, 3), 885 [$(R_F)_2Ag_3$, 56], 497 [$(R_F)Ag_2$, 100], 369 ($R_FAg - F$, 11). ^1H NMR (C_6D_6): δ 7.96 (qqq, 8 H, $^4J_{HF}(p\text{-}CF_3) = 0.8$ Hz, $^4J_{HF}(o\text{-}CF_3) = 0.4$ Hz, $^6J_{HF}(o\text{-}CF_3) = 0.4$ Hz, C_6H_2). ^{19}F NMR (CD_3CN, ^1H-coupled): δ − 61.5 (t, 6 F, $^4J_{FH} = 0.4$ Hz, $^6J_{FH} = 0.4$ Hz, *o*-CF_3), −62.0 (t, 3 F, $^4J_{FH} = 0.8$ Hz, *p*-CF_3).

X-Ray structure determination of compounds 1, 3, 4, and 5

Crystal data are summarized in Table 5. The data were collected on a Stoe-Siemens-AED diffractometer with monochromated Mo-Kα radiation (λ = 0.71073 Å). For structures **3** and **4** a semiempirical and for **5** an empirical absorption correction was employed. The structures were solved by direct (**1**, **5**) or Patterson and Fourier methods (**3**, **4**).[32] All non-hydrogen atoms were refined anisotropically.[33] For the hydrogen atoms the riding model was used. The structures were refined against F^2 of all unique reflections. The *R* values are defined as

$$R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$$

and

$$wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{0.5}.$$

In all four structures the *para*-CF_3 groups were disordered over two positions. They were refined with distance restraints. The anisotropic displacement parameters of fluorine atoms lying opposite to each other were fixed to the same values. In structure **3** the toluene molecules are disordered. They were refined with distance restraints and restraints for the anisotropic displacement parameters.

CCDC reference number 440/128. See http://www.rsc.org/suppdata/nj/1999/905/ for crystallographic files in .cif format.

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