Donor Properties of Arylphosphines towards Selenium: *X*-Ray Crystal Structure of Tris(*m*-trifluoromethylphenyl)phosphine Selenide †

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Crystals of the title compound are orthorhombic, space group *Pbca*, with $a = 31.822(15)$, $b = 11.047(6)$, $c = 12.426(7)$ Å, and $Z = 8$. The structure was solved using multisolution direct methods and refined by least squares to R 0.054 (R' 0.059) for 1 964 observed diffractometer data. Phosphorus adopts a distorted tetrahedral geometry with mean Se–P–C and C–P–C angles of 113.1 and 105.6° respectively. The P–Se bond length [2.094(2) Å] is the shortest reported for a tertiary phosphine selenide and is attributed to the electron-withdrawing properties of the ($C_6H_4CF_3$-*m*) groups and the consequent increased *s* character of the phosphorus orbital involved in bonding with selenium.

In a recent paper [1] we described an investigation of the donor properties of a series of heteroaryl- and triaryl-phosphines towards selenium and platinum(II) acceptors, as indicated by ^{31}P n.m.r. studies of one-bond coupling constants $^{1}J(^{77}\text{Se}-^{31}\text{P})$ and $^{1}J(^{195}\text{Pt}-^{31}\text{P})$. We showed that the respective coupling constants increased as the groups attached to phosphorus became more electron-withdrawing, indicating an increased *s* character for the phosphorus lone-pair orbital involved in bonding to selenium or platinum, in accordance with Bent's rule.[2] Consequently, in such compounds, the bonds from phosphorus to the acceptor atom would therefore be expected to be shorter than in related molecules derived from phosphines bearing less electron-withdrawing groups. There are a number of indications in the literature that an increase in the magnitude of single-bond coupling constants, *e.g.* between phosphorus and platinum in phosphine or phosphite complexes of platinum(II) halides (as a result of the increased electron-withdrawing character of the phosphorus substituents), is in fact paralleled by a shortening of the phosphorus–platinum bond, although it has also been pointed out that such a shortening may not necessarily lead to a strengthening of the bond.[3–7] We have also shown recently that the increase in $^{1}J(^{77}\text{Se}-^{31}\text{P})$ in a series of dibenzophosphole selenides compared to that observed in a series of related, acyclic phosphine selenides can be correlated with a corresponding increase in the selenium–phosphorus i.r. stretching frequency, presumably indicating that the phosphorus–selenium bond is stronger in the dibenzophosphole selenides as a result of the increased *s* character of the phosphorus lone pair caused by the geometric constraints imposed by the ring system on the intervalence angles at phosphorus.[8]

In view of these results, it was of interest to see whether such increases in $^{1}J(^{77}\text{Se}-^{31}\text{P})$ in triarylphosphine selenides could be correlated with an observable shortening of the phosphorus–selenium bond. In this Note, we describe the structure of tris(*m*-trifluoromethylphenyl)phosphine selenide for which $^{1}J(^{77}\text{Se}-^{31}\text{P}) = 766$ Hz, compared to a value of 732 Hz for triphenylphosphine selenide.[1] Such a change in the coupling constant is much smaller than those that have been the subject of earlier correlations between coupling constants and bond lengths in phosphineplatinum(II) halide complexes,[3–7] and it was therefore expected that any shortening would be very small.

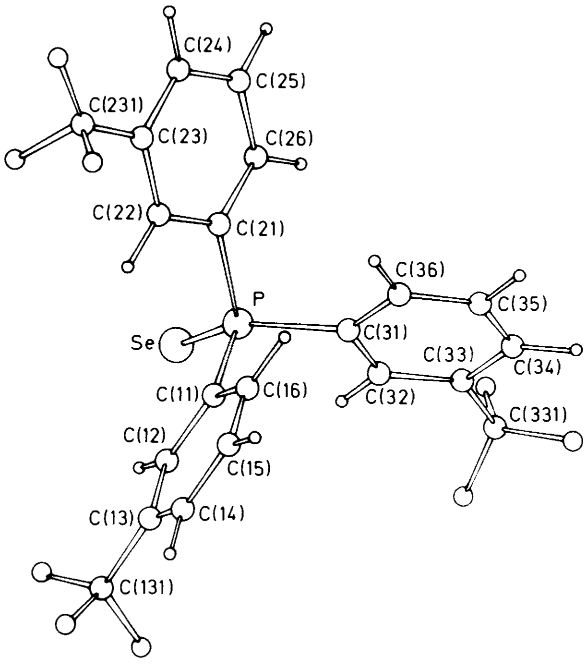

Figure. Molecular structure of $P(C_6H_4CF_3\text{-}m)_3Se$

Results and Discussion

The main features of the molecule are as expected with the selenium atom and the three aryl groups adopting a distorted tetrahedral arrangement about phosphorus (Figure). The aromatic rings are interleaved to give the characteristic propeller arrangement which facilitates an opening up of the Se–P–C(n1) (n = 1—3) angles from the regular tetrahedral value to a mean of 113.1°. This angular distortion is accompanied by a compression of the C(n1)–P–C(n1) angles such that the mean value of 105.6° is significantly smaller than the regular tetrahedral value. The feature of most interest is the

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† *Supplementary data available* (No. SUP 23802, 12 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Phosphorus–selenium bond distances in arylphosphine selenides, together with ^{77}Se–^{31}P coupling constants

R in PR_3Se	Bond distance (Å)	$^1J(^{77}Se-^{31}P)$/Hz
C_6H_4Me-*o*	2.116(5) [a]	708 [b]
C_6H_4Me-*m*	2.109(5) [c]	726 [b]
Ph	2.106(1) [d]	733 [e]
$C_6H_4CF_3$-*m*	2.094(2)	766 [e]

[a] T. S. Cameron and E. Dahlen, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1737. [b] R. P. Pinnell, C. A. Megerle, S. L. Manatt, and P. A. Kroon, *J. Am. Chem. Soc.*, 1973, **95**, 977. [c] T. S. Cameron, K. D. Howlett, and K. Miller, *Acta Crystallogr., Sect. B*, 1978, **34**, 1639. [d] P. W. Codding and K. A. Kerr, *Acta Crystallogr., Sect. B*, 1979, **35**, 1261. [e] Ref. 1.

Table 2. Final fractional co-ordinates for non-hydrogen atoms (Se, × 10^5; other atoms, × 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Se	9 698(2)	39 250(7)	42 693(5)
P	1 114(1)	3 306(2)	2 721(1)
C(11)	1 225(2)	4 521(6)	1 785(5)
C(12)	1 246(2)	5 694(6)	2 150(6)
C(13)	1 346(2)	6 626(7)	1 435(6)
C(14)	1 423(2)	6 383(6)	376(6)
C(15)	1 407(2)	5 209(7)	9(6)
C(16)	1 306(2)	4 278(7)	687(6)
C(21)	697(2)	2 431(6)	2 126(5)
C(22)	410(2)	2 956(7)	1 423(5)
C(23)	79(2)	2 276(9)	1 030(6)
C(24)	28(3)	1 084(8)	1 328(8)
C(25)	310(3)	546(8)	2 000(8)
C(26)	645(3)	1 219(7)	2 417(7)
C(31)	1 583(2)	2 339(6)	2 679(5)
C(32)	1 874(2)	2 416(7)	3 483(5)
C(33)	2 241(2)	1 740(7)	3 435(7)
C(34)	2 313(3)	998(7)	2 575(8)
C(35)	2 019(3)	899(7)	1 780(7)
C(36)	1 662(2)	1 574(6)	1 788(6)
C(131)	1 368(5)	7 883(8)	1 834(8)
C(231)	−221(3)	2 842(11)	296(11)
C(331)	2 541(3)	1 827(13)	4 365(11)
F(131)	1 728(4)	8 090(6)	2 315(10)
F(132)	1 334(3)	8 714(5)	1 115(6)
F(133)	1 102(5)	8 149(6)	2 562(8)
F(231)	−378(4)	3 817(9)	550(9)
F(232)	−88(3)	3 083(18)	−593(8)
F(233)	−546(3)	2 253(9)	105(12)
F(331)	2 643(2)	2 942(8)	4 594(7)
F(332)	2 902(2)	1 273(7)	4 166(6)
F(333)	2 388(2)	1 388(10)	5 251(7)

Table 3. Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

	$n = 1$	$n = 2$	$n = 3$
P–C(*n*1)	1.811(7)	1.801(7)	1.834(7)
C(*n*1)–C(*n*2)	1.374(10)	1.391(9)	1.364(9)
C(*n*2)–C(*n*3)	1.398(10)	1.382(10)	1.388(10)
C(*n*3)–C(*n*4)	1.365(11)	1.378(13)	1.367(12)
C(*n*4)–C(*n*5)	1.376(10)	1.363(13)	1.366(13)
C(*n*5)–C(*n*6)	1.368(10)	1.400(12)	1.357(11)
C(*n*6)–C(*n*1)	1.413(9)	1.396(10)	1.416(10)
C(*n*3)–C(*n*31)	1.476(12)	1.462(14)	1.503(15)
Average C–F	1.290	1.228	1.309
Se–P	2.094(2)		
Se–P–C(*n*1)	113.0(2)	113.0(2)	113.2(2)
P–C(*n*1)–C(*n*2)	119.7(5)	121.2(5)	119.7(5)
P–C(*n*1)–C(*n*6)	121.0(5)	119.7(5)	121.0(5)
C(*n*2)–C(*n*1)–C(*n*6)	119.2(6)	119.1(6)	119.2(6)
C(*n*1)–C(*n*2)–C(*n*3)	119.7(6)	119.7(7)	120.4(7)
C(*n*2)–C(*n*3)–C(*n*4)	120.6(7)	121.0(7)	119.9(7)
C(*n*3)–C(*n*4)–C(*n*5)	119.9(7)	120.1(8)	119.9(8)
C(*n*4)–C(*n*5)–C(*n*6)	120.8(7)	119.9(8)	121.6(8)
C(*n*5)–C(*n*6)–C(*n*1)	119.7(7)	120.2(7)	118.9(7)
C(*n*2)–C(*n*3)–C(*n*31)	119.4(7)	119.1(9)	117.9(8)
C(*n*4)–C(*n*3)–C(*n*31)	120.0(7)	119.9(8)	122.2(8)
Average C–C–F	113.9	116.8	112.6
Average F–C–F	104.6	101.3	106.1
C(11)–P–C(21)	106.1(3)		
C(11)–P–C(31)	104.8(3)		
C(21)–P–C(31)	106.0(3)		

length of the phosphorus–selenium bond which is found to be 2.094(2) Å and is compared with values reported for other arylphosphine selenides in Table 1. The P–Se bond length does appear to show a small dependence on the nature of the substituents at phosphorus. In particular a comparison of this distance in the title compound with that reported for triphenylphosphine selenide reveals a small, but nevertheless significant shortening of the bond, consistent with the increased *s* character of the phosphorus orbital involved in bonding with selenium as indicated by the one-bond coupling-constant data. The present P–Se bond length is the shortest reported so far for a tertiary phosphine selenide. It could, of course be argued that the slight shortening of this bond is attributable to an increase in the extent of $Se_{4p\pi} \rightarrow P_{3d\pi}$ back donation, as a result of the presence of the electron-withdrawing CF_3 substituents, leading to greater double-bond character. However, it has been concluded by several workers that the P–Se bond in phosphine selenides has little multiple-bond character.[9,10] Inspection of the data in Table 1 at first sight suggests that there is indeed an inverse correlation between the P–Se bond length and the magnitude of $^1J(^{77}Se-^{31}P)$. However, the differences in bond length between the *o*-tolyl-, *m*-tolyl-, and phenyl-phosphine selenides are not crystallographically significant.

Experimental

Crystals of the title compound were prepared as previously described.[1]

Crystal Data.—$C_{21}H_{12}F_9PSe$, $M = 545.2$, Orthorhombic, space group *Pbca*, $a = 31.822(15)$, $b = 11.047(6)$, $c = 12.426(7)$ Å, $U = 4\ 368.0$ Å^3, $D_m = 1.68$, $Z = 8$, $D_c = 1.66$ Mg m^{-3}, $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 1.97 mm^{-1}, $F(000) = 2\ 144$.

X-*Ray Intensity Measurements.*—A crystal of approximate dimensions 0.10 × 0.15 × 0.38 mm was mounted with the *c* axis coincident with the ω axis of a Stöe Stadi 2 two-circle diffractometer. Data were collected using the background–ω scan–background technique. Corrections for Lorentz and polarisation effects were applied but not for absorption. Of the 3 389 unique reflections collected, 1 964 had $I \geqslant 3.0\sigma(I)$ and were used in the subsequent structure analysis.

Structure Determination and Refinement.—All non-hydrogen atoms were located using multisolution direct methods. Although successive difference electron-density maps revealed the positions of the hydrogen atoms, the latter were not refined but included in positions calculated from the geometry of the molecule (C–H 1.08 Å). A common isotropic thermal parameter was applied to the located hydrogen atoms and refined to a final value of $U = 0.070(10)$ Å^2. Scattering factors were calculated [11] using an analytical approximation and the weighting scheme adopted was $w = 1.3571/[\sigma^2(F_o) + 0.0025(F_o)^2]$. Full-matrix refinement with anisotropic thermal parameters for all non-hydrogen atoms gave the final $R = 0.054$ and $R' = 0.059$.

The very high thermal parameters associated with the fluorine atoms indicate extensive vibrational motion of all three CF_3 groups. While the possibility of disorder cannot be excluded, the extent appears to be limited for not only were the nine fluorine atoms readily located in the early stages of the analysis, but attempts to represent the CF_3 groups by disordered sets of fluorine atoms were less successful than the present model. Final atomic parameters are given in Table 2, bond distances and angles in Table 3. All calculations were carried out on a IBM 4341 computer using the SHELX computing package.[12]

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