The structural characterisation of $Ph_3PSe(Ph)I$. The first charge transfer (CT) complex of a tertiary phosphine containing a pseudohalogen

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The reaction of 2 mol equivalents of triphenylphosphine with diphenyldiselenyldiiodine ($Ph_2Se_2I_2$) produces the charge transfer (CT) complex $Ph_3PSe(Ph)I$ in quantitative yield; this compound represents the first report of a CT complex of a tertiary phosphine that contains a pseudohalogen.

The ability of organic molecules that contain a group 15 or 16 donor atom to form charge transfer (CT) complexes with dihalogens or interhalogens has long been recognised,[1] however, it is only relatively recently that such complexes have been crystallographically characterised. The structural identification of these materials has now proved to be a topical area with several research groups currently involved in investigating a variety of these materials that have shown remarkable diversity in their solid-state structure. Thus, the dihalogen adducts of tertiary phosphines,[2–6] arsines,[7] stibines,[8] tertiary phosphine sulfides,[9–11] selenides,[12,13] diorgano sulfides[14] and selenides[15,16] and selenoamides[17,18] have all received considerable study. In addition, very recently the CT complexes of cyclic thioethers with I_2 and IBr have been extensively studied by Schröder and coworkers.[19–21] Generally speaking, adducts of diiodine or IX (X = Br, Cl) are CT compounds which contain an approximately linear E–I–X arrangement (E = P, As, S, Se) whereas adducts of the lighter dihalogens usually produce an X–E–X arrangement with the E atom in trigonal bipyramidal, disphenoidal see-saw or T-shaped geometry depending on the E atom and the organic substituents, although some exceptions to this rule have been identified. Despite the ongoing interest in these dihalogen adducts, very little is known regarding the pseudohalogen adducts of these donor molecules, despite the fact that the solid-state structures of such systems are likely to be quite different to the dihalogen analogues owing to electronic and especially steric factors. We have recently reported[22] that reaction of R_3P with XCN results in the formation of ionic compounds $[R_3PCN]X$ [R = 2,4,6-$(MeO)_3C_6H_2$, 2,6-$(MeO)_2C_6H_3$, $NCCH_2CH_2$, C_6H_{11} or $PhCH_2$; X = Br or I] which display no cation–anion interaction regardless of the nature of R or X. In order to establish the identity of a CT complex of a tertiary phosphine adduct containing both halide and pseudohalide moieties, we have turned our attention to the reaction of 2 mol equivalents of triphenylphosphine with diphenyldiselenyl diiodide. The very interesting structure of $Ph_2Se_2I_2$, itself a CT adduct, has been described by du Mont and coworkers[23] and consists of a dimeric centrosymmetric moiety containing short [2.775(1) Å] and long [3.588(1) Å] iodine–iodine distances. $Ph_2Se_2I_2$ was reacted with 2 mol equivalents of Ph_3P in dichloromethane according to eqn. (1).

$$2\,Ph_3P + Ph_2Se_2I_2 \xrightarrow[N_2(g),\ \text{room temp.}]{ca.\ 1\ d,\ CH_2Cl_2} Ph_3PSe(Ph)I \qquad (1)$$

Triphenylphosphine reacts very rapidly with $Ph_2Se_2I_2$, this being evident from the dramatic colour change in the reaction vessel (from the deep burgundy of $Ph_2Se_2I_2$ to bright yellow upon addition of Ph_3P). Nevertheless, the reaction mixture was allowed to stir for *ca.* 1 d to ensure reaction completion. The resultant compound, $Ph_3PSe(Ph)I$, was isolated in quantitative yield. Recrystallisation of this bright yellow powder from dichloromethane–diethyl ether solution (*ca.* 1 : 1) produced a large quantity of well formed crystals, one of which was selected for analysis by single crystal X-ray diffraction. The crystal structure of $Ph_3PSe(Ph)I\cdot CH_2Cl_2$ is illustrated in Fig. 1 (the dichloromethane solvate molecule is omitted for clarity). This compound is clearly shown to adopt a CT structure analogous to triphenylphosphine diiodine, Ph_3P–I–I. The *d*(Se–I) in $Ph_3PSe(Ph)I$, 3.2564(5) Å, lies well within the van der Waals' radius for the iodine and selenium atoms (4.1 Å) and is similar to *d*(I–I) in Ph_3PI_2, 3.142(2) Å,[2] and significantly shorter than *d*(I–I) in $PhMe_2PI_2$, 3.408(2) Å.[24] There are no non-bonded long-range contacts between $Ph_3PSe(Ph)I$ and the dichloromethane solvate molecule (which shows no sign of disorder) or between $Ph_3PSe(Ph)I$ and an adjacent molecule.

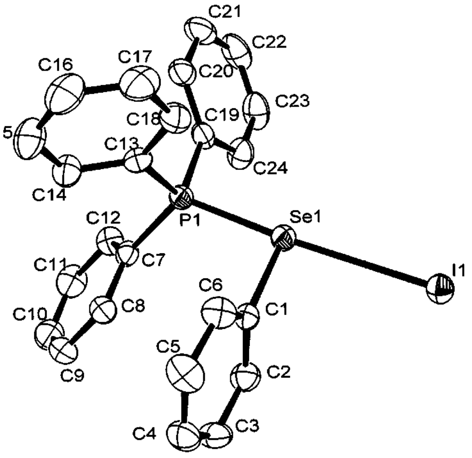

Fig. 1 Perspective view of the molecular structure of $Ph_3PSe(Ph)I$. Selected bond lengths (Å) and angles (°): Se(1)–I(1) 3.2564(5), Se(1)–P(1) 2.2585(9), Se(1)–C(1) 1.921(3), C(1)–Se(1)–P(1) 93.59(9), P(1)–Se(1)–I(1) 176.09(5), C(1)–Se(1)–I(1), 88.84(5).

There is great similarity between Ph_3PI_2 and $Ph_3PSe(Ph)I$ in the $^{31}P\{^1H\}$ NMR spectra of the two materials. We have previously reported that Ph_3PI–I ionises in $CDCl_3$ to produce the ionic $[Ph_3PI]I$ (δ 44). Remarkably, the $^{31}P\{^1H\}$ NMR spectrum of $Ph_3PSe(Ph)I$ in CD_2Cl_2 shows a single peak at δ 44 *i.e.* identical to that observed for $[Ph_3PI]I$. No phosphorus–selenium coupling constant was obtained from this spectrum; however, $^1J(^{13}C–^{31}P)$ = 111 Hz. This preliminary NMR data would seem to suggest, therefore, that either (a) $[Ph_3PI]^+$ and $Ph_3PSe(Ph)I$ are electronically very similar, or (b) in solution $Ph_3PSe(Ph)I$ exists as $[Ph_3PI][SePh]$. The absence of P–Se coupling seems to suggest that the latter option is correct; our investigations into the structure of $Ph_3PSe(Ph)I$ in solution are continuing and will be discussed in detail in a full report of this work. The solid-state CT nature of $Ph_3PSe(Ph)I$ is confirmed by the geometry at the selenium centre which is T-shaped [P(1)–Se(1)–C(1) 93.59(5)°, P(1)–Se(1)–I(1) 176.09(5)°, C(1)–Se(1)–I(1) 88.84(5)°] and not bent, as would be expected for an ionic compound. The *d*(P–Se) of 2.2585(9) Å lies within the range expected for a P–Se single bond and is very similar to the *d*(P–Se) we have previously observed for T-shaped dibromine adducts of tertiary phosphine selenides [*e.g.* *d*(P–Se) for $(Me_2N)_3PSeBr_2$ = 2.262(2) Å].[13] No compound of formula $R_3PSe(R)X$ has previously been reported. However, the related ionic compound $[Ph_3PSeMe][ClO_4]$ has been described by Jones and Thöne[25] and exhibits a P–Se–C bond angle of 97°, closer to that expected for bent geometry at the selenium centre. As previously stated, $Ph_3PSe(Ph)I$ represents the first reported CT complex of a tertiary phosphine which contains a pseudohalogen and we are currently investigating whether this compound is able to oxidise crude metal powders analogous to our previous studies concerning R_3PI_2. Our results will form the basis of a forthcoming paper.

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Notes and references

† *Crystal data* for $C_{25}H_{22}Cl_2IPSe$: M = 630.16, triclinic, space group $P\bar{1}$ (no. 2), a = 9.2713(11), b = 10.329(3), c = 13.245(2) Å, α = 91.77(2), β = 93.31(1), γ = 95.35(1)°, U = 1259.9(4) Å^3, T = 203 K, Z = 2, μ(Mo-Kα) = 30.01 cm^{-1}, 4714 reflections measured, 4411 unique (R_{int} = 0.0108) which were all used in calculations. The final $wR(F^2)$ was 0.0543 (all data). Single crystals of $Ph_3PSe(Ph)I$ were recrystallised from diethyl ether–dichloromethane solution (1 : 1) at *ca.* 50 °C. On cooling to RT a large crop of yellow crystals appeared after *ca.* 3 d. A chosen crystal was mounted in inert oil and transferred to the cold N_2 gas stream of the diffractometer. The structure was solved using direct methods and refined by full-matrix least squares on F^2.

CCDC 182/1400. See http://www.rsc.org/suppdata/cc/1999/2159/ for crystallographic files in .cif format.

1 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley Interscience, New York, 5th edn., 1990, ch. 14, p. 549.

2 N. Bricklebank, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and P. J. Kobryn, *J. Chem. Soc., Dalton Trans.*, 1993, 101.

3 W. W. du Mont, M. Bätcher, S. Pohl and W. Saak, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 912.

4 S. M. Godfrey, C. A. McAuliffe, I. Mushtaq, R. G. Pritchard and J. M. Sheffield, *J. Chem. Soc., Dalton Trans.*, 1998, 3815.

5 S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard, J. M. Sheffield and G. M. Thompson, *J. Chem. Soc., Dalton Trans.*, 1997, 4823.

6 F. Ruthe, W. W. du Mont and P. G. Jones, *Chem. Commun.*, 1997, 1947.

7 N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe, R. G. Pritchard and J. M. Moreno, *J. Chem. Soc., Dalton Trans.*, 1995, 3873.

8 N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1994, 1694.

9 D. C. Apperley, N. Bricklebank, S. L. Burns, D. E. Hibbs, M. B. Hursthouse and K. M. Abdul Malik, *J. Chem. Soc., Dalton Trans.*, 1998, 1289.

10 W. I. Cross, S. M. Godfrey, S. L. Jackson, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1999, 2225.

11 M. Arca, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis, G. Verani and F. Demartin, *Z. Anorg. Allg. Chem.*, 1998, **624**, 745.

12 S. M. Godfrey, S. L. Jackson, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1996, 4499.

13 S. M. Godfrey, S. L. Jackson, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1998, 4201.

14 B. Regelmann, K. W. Klinkhammer and A. Schmidt, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1633.

15 S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and S. Sarwar, *J. Chem. Soc., Dalton Trans.*, 1997, 1031.

16 S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and S. Sarwar, *J. Chem. Soc., Dalton Trans.*, 1997, 3504.

17 F. Bigoli, A. M. Pellinghelli, P. Deplano, F. A. Devillanova, V. Lippolis, M. L. Mecuri and E. F. Trogu, *Gazz. Chim. Ital.*, 1994, **124**, 445.

18 F. Cristiani, F. Demartin, F. A. Devillanova, F. Isaia, V. Lippolis and G. Verani, *Inorg. Chem.*, 1994, **33**, 6315.

19 A. J. Blake, F. Cristiani, F. A. Devillanova, A. Garau, L. M. Gilby, R. O. Gould, F. Isaia, V. Lippolis, S. Parsons, C. Radek and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1997, 1337.

20 A. J. Blake, F. Cristiani, F. A. Devillanova, A. Garau, L. M. Gilby, R. O. Gould, F. Isaia, V. Lippolis, S. Parsons, C. Radek and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1998, 2037.

21 A. J. Blake, F. Cristiani, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis, S. Parsons and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1999, 525.

22 S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and J. M. Sheffield, *J. Chem. Soc., Dalton Trans.*, 1998, 1919.

23 S. Kubiniok, W. W. du Mont, S. Pohl and W. Saak, *Angew. Chem., Int. Ed. Engl.*, 1987, **27**, 431.

24 N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe, R. G. Pritchard and J. M. Moreno, *J. Chem. Soc., Dalton Trans.*, 1995, 2421.

25 P. G. Jones and C. Thöne, *Z. Kristallogr.*, 1994, **209**, 78.

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