DALTON
COMMUNICATION

Structural isomerism in $R_3PSe(Ph)I$ compounds: the ionic structure of $[(Me_2N)_3PSePh]I$

Stephen M. Godfrey, Ruth T. A. Ollerenshaw, Robin G. Pritchard and Claire L. Richards

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester, UK M60 1QD. E-mail: Stephen.m.godfrey@umist.ac.uk

Received 24th January 2001, Accepted 24th January 2001
First published as an Advance Article on the web 9th February 2001

The reaction of two mole equivalents of $(Me_2N)_3P$ with $Ph_2Se_2I_2$ produces the ionic compound $[(Me_2N)_3PSePh]I$ which contains a long Se–I contact, 3.825(1) Å, and a bent P–Se–I angle, 114.5(2)°.

Structural characterisation of the dihalogen derivatives of organic molecules containing either a Group 15 or 16 atom is a topic of considerable current interest. The principle reason for this is the remarkable structural diversity they exhibit in the solid state, which is dependent on the identity of the dihalogen and, in some cases, the nature of the solvent in which they are prepared. Thus the dihalogen adducts of tertiary phosphine sulfides[1–3] and selenides,[4,5] diorgano sulfides and selenides,[6–8] thioamides[9] and selenoamides[10–14] have all received considerable attention by a variety of research groups world wide. The bonding exhibited by some of these adducts may be complicated and has proved controversial.[15] As previously stated, the identity of the halogen is of paramount importance in determining the structural nature of the organogroup 16 adduct. In general, adducts of diiodine or the interhalogens IX (X = Br, Cl) are charge-transfer (CT) adducts, containing an approximately linear E–I–X arrangement (E = S, Se; X = I, Br, Cl) whereas adducts of the lighter dihalogens usually produce an X–E–X arrangement with the E atom in a seesaw or T-shaped geometry, depending on the organic substituents and the E atom. Some exceptions to this rule have been identified however, *e.g.* the CT structure of Me_2SBr_2[6] and the ionic structure of $[\{(H_2N_2)CS\}_2I]I$.[16] Indeed, a recent study concerning the reaction of thioamides with diiodine suggests that the adducts formed are more complicated than first thought.[9] Recently, we have turned our attention to the synthesis of organogroup 15 adducts which contain a pseudohalide. Reaction of $Ph_2Se_2I_2$ with $2PPh_3$ or $Ph_4Te_4I_4$ with $4PPh_3$ produces the CT complexes $Ph_3PE(Ph)I$ (E = Se,[17] Te,[18] respectively). These species may be thought of as similar in nature to the CT complex Ph_3PI_2,[19] but containing the pseudohalide PhE (E = Se, Te). The group 16 atoms in these CT complexes have a T shaped geometry and the P–E–I bond sequences are essentially linear, consistent with the formation of a CT complex. In order to investigate the effect of the basicity of the parent tertiary phosphine on the resultant adduct, $R_3PSe(Ph)I$, we decided to react two mole equivalents of the very basic $(Me_2N)_3P$ with $Ph_2Se_2I_2$ in dichloromethane, eqn. (1).

$$2(Me_2N)_3P + Ph_2Se_2I_2 \xrightarrow[N_2(g)\ \text{room temp.}]{ca.\ 1\ \text{d.}\ CH_2Cl_2} (Me_2N)_3PSe(Ph)I \quad (1)$$

Reaction occurred almost instantaneously, producing a very pale yellow product† in quantitative yield. Recrystallisation of this material from diethyl ether–dichloromethane solution (*ca.* 1 : 1) produced a large crop of pale yellow crystals, one of which was selected for analysis by single crystal X-ray diffraction.‡ The crystal structure of $(Me_2N)_3PSe(Ph)I$ is illustrated in Fig. 1. Surprisingly, changing the nature of the parent tertiary phosphine has changed the structural nature of the $R_3PSe(Ph)I$ adduct. We have previously described the structure of $Ph_3PSe(Ph)I$, a CT adduct with a linear P–Se–I arrangement [176.09(5)°]. In contrast, $(Me_2N)_3PSe(Ph)I$ contains a bent P–Se–I linkage, [114.5(2)°] and, as a consequence, is probably better thought of as ionic, $[(Me_2N)_3PSePh]I$. Despite this fact, there remains a weak electrostatic contact between the selenium and iodine atoms [*d*(Se–I) = 3.825(1) Å], van der Waals radius for a selenium and iodine atom = 4.1 Å. This distance is significantly longer than that exhibited by $Ph_3PSe(Ph)I$, 3.2564(5) Å, and the change in geometry for the molecule indicates that a CT description for $(Me_2N)_3PSe(Ph)I$ is not appropriate, rather an ionic formulation is preferred. Only one compound containing a $[R_3PSeR]$ cation has previously been crystallographically characterised, $[Ph_3PSeMe]^+$ by Jones and Thöne[20] which contained the discrete anion $[ClO_4]^-$. The geometry of this cation is generally quite similar to $[(Me_2N)_3PSePh]^+$, described here. The *d*(P–Se) for $[(Me_2N)_3PSePh]I$, 2.250(1) is similar to that exhibited by $Ph_3PSe(Ph)I$, 2.2585(9) (slightly shorter, as expected) and similar to *d*(P–Se) for the T-shaped tertiary phosphine selenide dibromide complexes [*e.g.* *d*(P–Se) for $(Me_2N)_3PSeBr_2$ = 2.262(2) Å], all of which contain single phosphorus–selenium bonds.

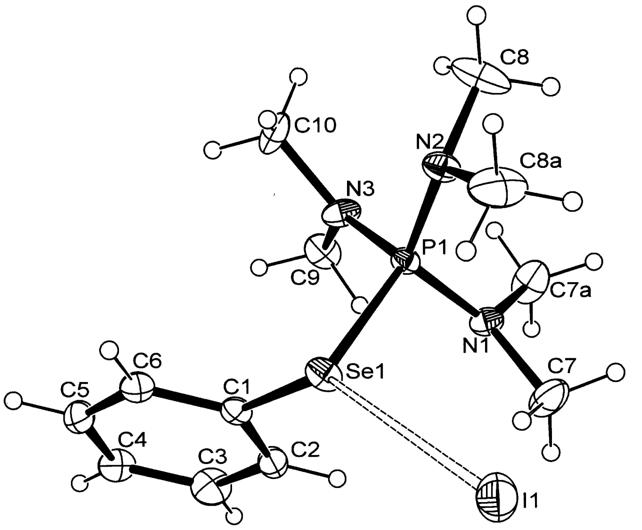

Fig. 1 Perspective view of the molecular structure of $(Me_2N)_3PSe(Ph)I$. Selected bond lengths (Å) and angles (°): Se(1)–I(1) (contact) 3.825(1), Se(1)–P(1) 2.250(1), Se(1)–C(1) 1.923(1), P(1)–N(1) 1.614(7), P(1)–N(2) 1.631(7), P(1)–N(3) 1.551(14); N(1)–P(1)–N(2) 118.9(4), N(2)–P(1)–N(3) 105.1(4), N(1)–P(1)–N(3) 107.0(5), N(2)–P(1)–Se(1) 105.05(14), N(3)–P(1)–Se(1) 114.9(4), N(1)–P(1)–Se(1) 106.36(14), C(1)–Se(1)–P(1) 94.1(3), P(1)–Se(1)–I(1) 114.5(2), C(1)–Se(1)–I(1) 143.1(3).

In conclusion, this study reveals the structural sensitivity of $R_3PSe(Ph)I$ compounds on R and that both CT and ionic derivatives are available for these previously unreported materials. It should be pointed out, however, that changing the

DOI: 10.1039/b100882j

R groups on the parent tertiary phosphine from Ph to Me_2N is quite a drastic change, Me_2N being a strong electron donating group. Recent work by Husebye *et. al.* reviewed analogous compounds and illustrated that the lone pair on an Me_2N group may be partially transferred towards the selenium atom.[21] An inspection of *d*(P–N) reveals two quite similar P–N distances [1.614(7) and 1.631(7) Å] and one rather short distance, 1.551(14) Å. A marked discrepancy is also noted in the N–P–N angles, two being similar, 105.1(4) and 107.0(5)° with the third being significantly greater, 118.9(4)°. Similarly significant variations are observed in the N–P–Se angles, again two being similar, 105.05(14) and 106.36(14)°, with the third greater, 114.9(4)°. Husebye and co-workers[21] proposed that if the lone pair on N is partially transferred towards the selenium atom, there is a resultant sp^2 hybridisation on N and partial double bond character of the N to P bond. Furthermore, these workers noted that in $(R_2N)_3PSe$ compounds only two dialkylamino groups are strong donors (N is sp^2), while the third is more or less neutral (N is sp^3), which was termed the *special* nitrogen atom. Analysing the bond angles for $[(Me_2N)_3PSePh]I$, broadly speaking, they support Husebye's theory,[21] *i.e.* N(3) would be considered the *special* nitrogen, with a large N–P–Se angle and the N–P–N angle involving the *non-special* nitrogen atom is relatively large as well. However, the *d*(P–N) for the *special* nitrogen is very short compared to the other two, which contrasts starkly with the theory. This appears curious and work is underway to examine a variety of $R_3PSe(Ph)I$ compounds (containing both alkyl and alkylamino R groups) to investigate the structure of these materials further. This will form the basis of a forthcoming paper.

We would like to thank the EPSRC for a research studentship to R. T. A. O.

Notes and references

† $(Me_2N)_3PSe(Ph)I$: Anal. Found (calc.): C, 33.6(34.0); H, 5.8(5.5); I, 30.8(30.3)%: $^{31}P\{H\}$ NMR (81.01 MHz, reference 85% H_3PO_4, solvent $CDCl_3$) singlet at δ 61.6, Se satellites at δ 64.7 and δ 58.6. ^1H NMR (200.2 MHz, reference $SiMe_4$, solvent $CDCl_3$) multiplet at δ 7.7–7.9 (due to phenyl protons): doublet at δ 2.4 (due to methyl protons) ratio *ca.* 1 : 4.

‡ Crystal data for $C_{12}H_{29}N_3IPSe$: $M = 452.21$, orthorhombic, space group *Cmca*, $a = 10.164(2)$, $b = 12.526(2)$, $c = 26.427(2)$ Å, $U = 3364.7(8)$ Å^3, $T = 203(2)$ K, $Z = 8$, μ(Mo-Kα) = 41.53 cm^{-1}, 1569 reflections ($R_{int} = 0.0647$) which were all used in calculations. The final $wR(F^2)$ was 0.1321 (all data). Single crystals of $(Me_2N)_3PSe(Ph)I$ were recrystallised from diethyl ether–dichloromethane solution (1 : 1) at *ca.* 50 °C. On cooling to room temperature a large crop of pale yellow crystals appeared after *ca.* 4 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 based on F^2. CCDC reference number 186/2331. See http://www.rsc.org/suppdata/dt/b1/b100882j/ for crystallographic files in .cif format.

1 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.

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

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

4 S. M. Godfrey, S. L. Jackson, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1997, 4201.

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

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

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

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

9 P. D. Boyle, J. Christie, T. Dyer, S. M. Godfrey, I. R. Howson, C. McArthur, B. Omar, R. G. Pritchard and G. Rh. Williams, *J. Chem. Soc., Dalton Trans.*, 2000, 3106.

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

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

12 P. D. Boyle, W. I. Cross, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and S. J. Teat, *J. Chem. Soc., Dalton Trans.*, 1999, 2219.

13 P. D. Boyle, W. I. Cross, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and S. J. Teat, *J. Chem. Soc., Dalton Trans.*, 1999, 2845.

14 P. D. Boyle, S. M. Godfrey and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1999, 4245.

15 P. D. Boyle and S. M. Godfrey, *J. Chem. Soc., Dalton Trans.*, 2000, 1960.

16 H. Hope and G. Hung-Yin Lin, *J. Chem. Soc., Chem. Commun.*, 1970, 169.

17 P. D. Boyle, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and J. M. Sheffield, *Chem. Commun.*, 1999, 2159.

18 P. D. Boyle, W. I. Cross, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard, S. Sarwar and J. M. Sheffield, *Angew. Chem., Int. Ed.*, 2000, **29**, 1796.

19 S. M. Godfrey, D. G. Kelly, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and S. M. Watson, *J. Chem. Soc., Chem. Commun.*, 1991, 1163.

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

21 M. D. Rudd, S. V. Lindeman and S. Husebye, *Acta Chem. Scand.*, 1996, **50**, 759.