Protonation of an Ylide Leads to a Unique C–H···O Hydrogen-bonded Dimer: The First Synthesis, Isolation and X-Ray Structural Characterisation of a Phosphonium Aryloxide

Matthew G. Davidson

University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW

The phosphonium ylide triphenylphosphonium methylide Ph_3PCH_2 reacts with 2,4,6-trimethylphenol to give the phosphonium aryloxide dimer $[(Ph_3PMe)^+(OC_6H_2Me_3\text{-}2,4,6)^-]_2$ **1**, in the solid state, in which aggregation is solely through C–H···O hydrogen bonding from both alkyl and aryl donors within the phosphonium cation, resulting in each phenoxide oxygen acceptor being five-coordinate (tetrafurcated).

Following our recent interest in the interactions of phosphonium ylides with main group metals,[1] and the long-standing interest of others in the inorganic chemistry of ylides,[2] we have prepared new phosphonium salts by protonation of ylide precursors, with the aim of subsequently metallating such species to give ylide-complexed metalloorganics. It is in this context that the present study was undertaken and 2,4,6-trimethylphenol was reacted with triphenylphosphonium methylide (Ph_3PCH_2) to give the phosphonium salt, $[(Ph_3PMe)^+(OC_6H_2Me\text{-}2,4,6)^-]_2$ **1**. Isolation and characterisation of **1** has revealed some surprising features in the solid state.

Stirring a 1 : 1 dry toluene solution of Ph_3PCH_2 and 2,4,6-trimethylphenol under nitrogen resulted in precipitation of an orange solid. Warming of this solid into solution and slow cooling to room temperature afforded orange crystals of **1**† shown by X-ray crystallography‡ to be $[(Ph_3PMe)^+(OC_6H_2Me_3\text{-}2,4,6)^-]_2$. The discrete dimeric structure of **1** is shown in Fig. 1. The acidic proton from the phenol has been transferred to the basic carbon of the ylide resulting in the formation of a phosphonium aryloxide salt. Such protonation of an ylide to give a phosphonium salt may be seen as an intermediate in the formation of five-coordinate alkoxy- or aryloxy-phosphoranes of the general formula $R_3(Me)POR'$ previously reported to result from the addition of R′OH to an ylide R_3PCH_2.[3] All bond lengths and angles within the cation and anion are normal. Most unusual, however, is the salt's observed mode of aggregation, which is through a series of C–H···O hydrogen bonds from the phosphonium cations to the aryloxide anions. In the subsequent description of C–H···O hydrogen bonds, D is defined as the C···O distance, d as the H···O distance and θ as the C–H···O angle. The central motif is a $(O\cdots H\text{–}C\text{–}H\cdots)_2$ eight-membered ring in which the methyl group of each cation bridges the two anions through two of its three hydrogen atoms: [C(19a)–H(19c)···O(1b) D = 3.242(7), d = 2.269(7) Å, θ = 171.8(9)°; C(19a)–H(19b)···O(1a) D = 3.196(6), d = 2.237(7) Å, θ = 165.6(9)°]. In addition, each oxygen atom is clamped between two *ortho* hydrogen atoms of phenyl groups belonging to different cations, thereby providing each oxygen atom with four hydrogen bonds [C(14a)–H(14a)···O(1a) D = 3.360(7), d = 2.428(7) Å, θ = 166.6(2)°; C(2a)–H(2a)···O(1b) D = 3.302(7), d = 2.375(7) Å, θ = 164.9(2)°]. All four of these C–H···O hydrogen bonds lie well within the accepted criteria of distance and angle used to define the existence of an electrostatic C–H···O interaction.[4,5] That these interactions are genuine is further emphasised by the orientation of the donor groups involved; despite being free to rotate, all are ideally oriented to participate in the observed hydrogen bonding.

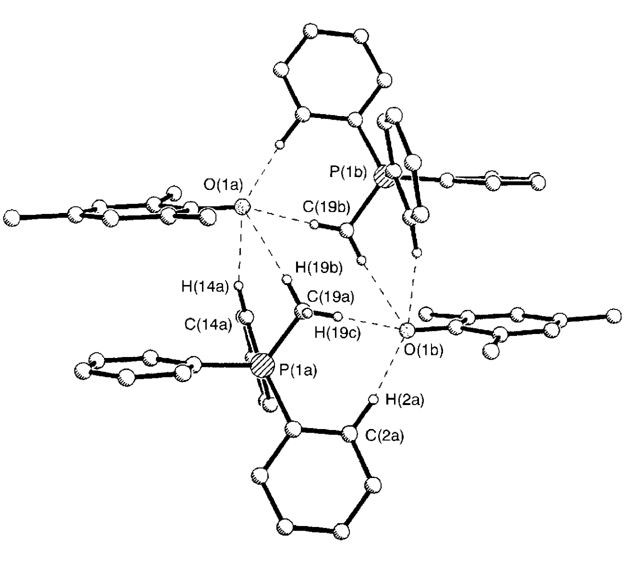

Fig. 1 Molecular structure of $[(Ph_3PMe)^+(OC_6H_2Me_3\text{-}2,4,6)^-]_2$ **1**

Searches of the Cambridge Structural Database (CSD) reveal **1** to be unique in several respects. No phosphonium aryloxides or alkoxides were found in the CSD although phosphonium thiolates and selenates are known.[6] Furthermore, no examples were found where such an alkyl phosphonium cation has been reported as a hydrogen-bond donor, although the CSD contains a number of examples where such hydrogen bonding is evident. Seven structures which exhibit short intermolecular C–H···O distances between an alkyl phosphonium cation and oxygen were found. Of these, four involve C–H interactions with neutral solvent molecules (methanol,[7] water,[8,9] and dimethylformamide[10]), two with perchlorate anions[11,12] and one involves close contacts to both acetate anions and neutral acetic acid in the same structure.[13] None, however, lead to a discrete dimeric structure such as is seen in **1**. The observation of one oxygen atom functioning as an acceptor for four C–H hydrogen bonds is unprecedented (by extension of established nomenclature such an acceptor should be termed tetrafurcated). The occurrence of such extensive and structurally significant C–H···O hydrogen bonding in the structure of **1** is favoured by a combination of factors: firstly, the alkyl phosphonium hydrogen atoms are inherently acidic (a property familiarly exploited in the base-promoted formation of ylides from phosphonium halides) and are, therefore potentially good hydrogen-bond donors; secondly, the highly anionic oxygen atom of the aryloxide provides an excellent hydrogen-bond acceptor; and thirdly, there is an absence of either a metal cation or a stronger hydrogen-bond donor (*e.g.* O–H, N–H *etc.*) with which the oxygen centre might interact preferentially.

The synthesis and characterisation of **1** provides considerable potential for development. Preliminary results suggest that the original aim of this study has been achieved: **1** can be metallated with Bu^nLi to provide an ylide complex of a lithium aryloxide and the crystalline product is awaiting X-ray characterisation. Such complexes are expected to provide potentially useful Wittig reagents, the anion present perhaps enhancing selectivity over conventional reagents. Synthetically, though a known method,[14] the use of ylides as precursors for phosphonium salts has not up to now been fully explored. This synthetic route, coupled with the observation that alkyl phosphonium salts can promote C–H···O hydrogen-bond formation, has implications for the study of solid-state structures both in terms of the synthesis of advanced materials[15,16] and in the study of crystal engineering.[17] These and other aspects of the chemistry of phosphonium ylides and their salts are currently being investigated

The author thanks Dr F. H. Allen (Cambridge Crystallographic Data Centre) and Professor J. A. K. Howard (University of Durham) for very useful discussions. This work was supported by St John's College, Cambridge (Research Fellowship for M. G. D.).

Received, 25th January 1995; Com. 5/00457H

Footnotes

† Triphenylphosphonium methylide, Ph_3PCH_2, was prepared according to literature procedures[18] and stored under an argon atmosphere in a dry box. To Ph_3PCH_2 (0.69 g, 2.5 mmol) and 2,4,6-trimethylphenol (0.42 g, 2.5 mmol) was added 20 cm^3 of dry toluene. Stirring for 15 min at room temperature gave an orange precipitate which dissolved into a red solution on heating and stirring to 80 °C in an oil bath. Slow cooling of this solution over 4 h to room temperature afforded a crop of orange crystals. Yield 80%; mp 148–150 °C; satisfactory C, H and P analyses; ^1H NMR (250 MHz, C_6D_6, 25 °C): δ 2.21 (s, 6H, *o*-ArMe), 2.51 (s, 3H, *p*-ArMe), 4.55 (br s, 3H, P–Me), 7.04 (m, 11H, Ar H), 7.75 (m, 6H, Ar H).

‡ *Crystal data* for **1**: $(Ph_3PMe)^+(OC_6H_2Me_3\text{-}2,4,6)^-$, $C_{28}H_{29}OP$, M = 412.48, monoclinic, space group $C2/c$, a = 20.038(4), b = 13.383(3), c = 18.623(4) Å, β = 112.66(3)°, U = 4609(2) $Å^3$, T = 153 K, Z = 8, D_c = 1.189 Mg m^{-3}, $F(000)$ = 1760, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.136 mm^{-1}. Data were collected on a Stoe four-circle diffractometer in the range $5 \leqslant 2\theta \leqslant 45°$ [3306 reflections collected, 3002 independent reflections (R_{int} = 0.0377)]. The structure was solved by direct methods[19] and refinement, based on F^2, was by full-matrix least-squares techniques[20] (non-hydrogen atoms were refined anisotropically, all hydrogen atoms were placed in idealised positions and allowed to ride on the relevant C-atom) to R_1 = 0.0552, wR_2 = 0.1464 for 1995 reflections with $F > 4\sigma(F)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at The Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 D. R. Armstrong, M. G. Davidson and D. Moncrieff, *Angew. Chem.*, 1995, **107**, 514; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 478.

2 For reviews of the inorganic chemistry of phosphonium ylides see: H. Schmidbaur, *Acc. Chem. Res.*, 1975, **8**, 62; *Angew. Chem.*, 1983, **95**, 980; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 907; A. W. Johnson, with special contributions by W. C. Kaska, K. A. O. Starzewski and D. A. Dixon, *Ylides and Imines of Phosphorus*, Wiley, New York, 1993.

3 H. Schmidbaur and H. Stühler, *Angew. Chem.*, 1972, **84**, 166; *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 145; *J. Am. Chem. Soc.*, 1974, **96**, 6208.

4 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063.

5 G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290.

6 J. M. Ball, P. M. Boormon, J. F. Fait, A. S. Hinman and P. J. Lundmark, *Can. J. Chem.*, 1989, **67**, 751.

7 H. Schmidbaur, C. Paschalidis, O. Steigelmann, D. L. Wilkinson and G. Muller, *Chem. Ber.*, 1989, **122**, 1857.

8 Mazar-Ul-Haque, W. Horne and S. E. Cremer, *J. Crystallogr. Spectrosc. Res.*, 1988, **18**, 533.

9 Mazar-Ul-Haque, W. Horne, S. E. Cremer and J. T. Most, *J. Crystallogr. Spectrosc. Res.*, 1989, **19**, 317.

10 H. J. Bestmann, D. Hadawi, H. Behl, M. Bremer and F. Hampel, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1205.

11 M. Cygler and J. Solimovski, *Can. J. Chem.*, 1983, **61**, 427.

12 M. R. Churchill, L. A. Buttrey, W. G. Feighery, J. B. Keister and J. W. Ziller, *J. Crystallogr. Spectrosc. Res.*, 1989, **20**, 1990.

13 E. Vedejs and S. T. Diver, *J. Am. Chem. Soc.*, 1993, **115**, 3358.

14 K. Jödden, *Methoden der Organischen Chemie (Houben-Weyl).* Thieme-Verlag, Stuttgart, 1982, vol. E1, pp. 491–579.

15 P. A. Chaloner, R. M. Harrison and P. B. Hitchcock, *Acta Crystallogr., Sect. C*, 1993, **49**, 1852.

16 *Materials for Nonlinear Optics: Chemical Perspectives*, ed. S. R. Marder, J. E. Sohn and G. D. Stucky, *ACS Symp. Ser.*, 1991, **455**.

17 C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, **22**, 39.

18 H. Schmidbaur, H. Stühler and W. Vornberger, *Chem. Ber.*, 1972, **105**, 1084.

19 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

20 G. M. Sheldrick, SHELXL-93, Program for crystal structure refinement, University of Göttingen, 1993.