Crystal and Molecular Structure of the Trimethyltin Chloride Complex of Triphenylphosphine–acetylmethylene

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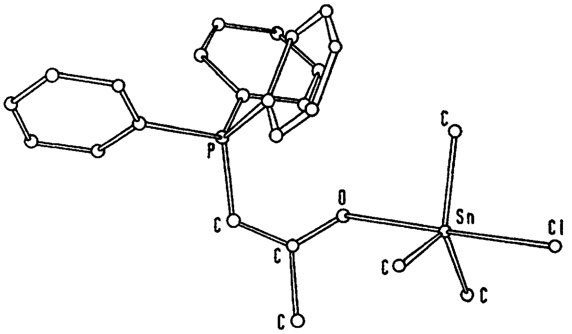
Summary Trimethyltin chloride–triphenylphosphine–acetylmethylene is *O* rather than *C*-bonded.

MERCURY(II) halides react with α-carbonyl phosphorus ylides to give stable *C*-mercurated phosphonium salts.[1] Triphenylphosphinemethylene gives analogous *C*-stannylated salts with organotin halides.[2] Structural assignment for the derivatives of trialkyltin halides with α-carbonyl ylides using normal spectroscopic techniques is not unequivocal.[3] We have, therefore, determined the structure of the trimethyltin chloride complex of triphenylphosphine-acetylmethylene[3] by single-crystal *X*-ray diffraction.

Colourless crystals of the complex are monoclinic, space group $P2_1/c$, $a = 9{\cdot}30$, $b = 10{\cdot}22$, $c = 26{\cdot}34$ Å, $\beta = 102{\cdot}43°$ $U = 2445{\cdot}7$ Å^3, $Z = 4$. The intensities of 2950 independent non-zero reflections were recorded on a Hilger-Watt four-circle diffractometer using Cu-K_α radiation. The tin atom was located from the three-dimensional Patterson function, and the positions of the lighter atoms determined by successive Fourier syntheses. Block-diagonal least squares refinement with anisotropic temperature factors for all atoms gave a final value for the conventional '*R*-index' of 0·049.



The structure of the complex is shown in the Figure. Contrary to expectation, the ylide residue is attached to tin *via* the carbonyl oxygen rather than the methylene carbon atom. The configuration at tin is trigonal bipyramidal with an essentially planar trimethyltin moiety. The tin–chlorine bond length is longer (2·57 Å) than that in the structurally similar pyridine complex (2·42 Å),[4] whilst the tin–oxygen co-ordinate bond distance is almost identical to that found previously for triphenyltin *N*-phenyl-*N*-benzoylhydroxylamine.[5]

The ylidic skeleton is planar with the angle P=C–C = 120·3° and the sum of the angles at the carbonyl carbon exactly 360°. The phosphorus–methylene multiple bond length (1·75 Å), the longest such yet reported,† approaches the single bond distance, mean r[P–C(aryl)] = 1·81 Å. This, together with the short (P=)C–C (1·36 Å) and the long C=O (1·27 Å) bond distances of the acetylmethylene group illustrates the substantial contribution of the enol form, $\overset{-}{O}.C(CH_3):CH\text{-}\overset{+}{P}Ph_3$, in the stabilisation of the ylide.

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† *cf.* Triphenylphosphinemethylene, where r (P=C) = 1·66 Å [6] and the bond order is estimated to be 1·3.[7]

[1] N. A. Nesmeyanov, V. M. Novikov, and O. A. Reutov, *J. Organometallic Chem.*, 1965, **4**, 202.
[2] D. Seyferth and S. O. Grim, *J. Amer. Chem. Soc.*, 1961, **83**, 1610.
[3] J. Buckle and P. G. Harrison, to be submitted for publication to *Inorg. Chem.*
[4] R. Hulme, *J. Chem. Soc.*, 1963, 1524.
[5] P. G. Harrison and T. J. King, *Chem. Comm.*, 1972, 815.
[6] J. C. J. Bart, *J. Chem. Soc.* (*B*), 1969, 350.
[7] W. Lüttke and K. Wilhelm, *Angew. Chem.*, 1965, **77**, 867.