Synthesis and Structure of the Tris(tetrathiafulvalenyl)phosphine, P(TTF)$_3$

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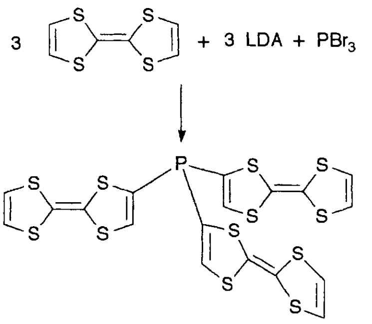
An efficient synthesis of P(TTF)$_3$ (TTF = tetrathiafulvalene), a unique electron-rich phosphine, is reported together with its complete characterisation by ^{31}P NMR, cyclic voltammetry and an analysis of its single-crystal X-ray structure.

Main group elements offer a unique opportunity to link together several redox units like tetrathiafulvalene (TTF). This would give rise to rich structural and electronic variations in TTF dimers, trimers and tetramers, depending upon the nature of the heteroatom. The recently described reaction of TTF–Li with TeCl$_4$[1] for the synthesis of dimeric Te(TTF)$_2$ and our own recent similar reactions with HgCl$_2$ and Me$_2$SiCl$_2$[2] demonstrate the feasibility of this method for the synthesis of TTF dimers.

We now report that this reaction has been successfully extended to Group 15 elements like phosphorus, thus providing a ready access to a new set of phosphines with multiple redox functionalities, like the prototypical P(TTF)$_3$. Compared with the usual aryl phosphines, P(TTF)$_3$ is expec-



Scheme 1 LDA = lithium diisopropylamide

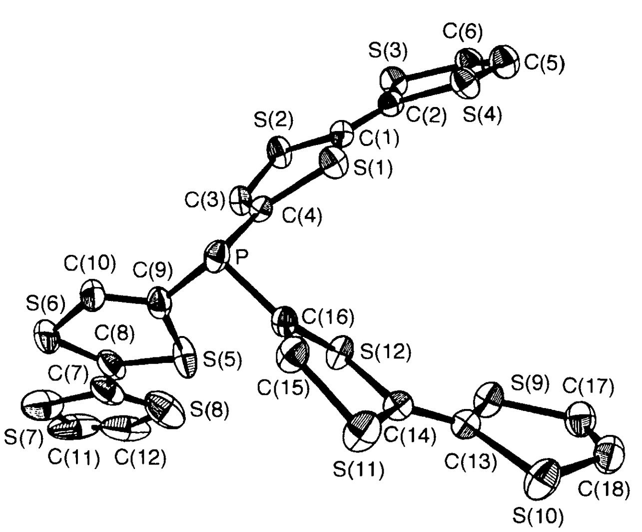


Fig. 1 ORTEP drawing and numbering scheme for $P(TTF)_3$. Thermal ellipsoids are drawn at the 30% probability level. Relevant bond lengths (Å) and angles(°): P–C(4) 1.839(4), P–C(9) 1.806(5), P–C(16) 1.807(4); C(4)–P–C(9) 101.4(2), C(4)–P–C(16) 100.8(2), C(9)–P–C(16) 103.5(2).

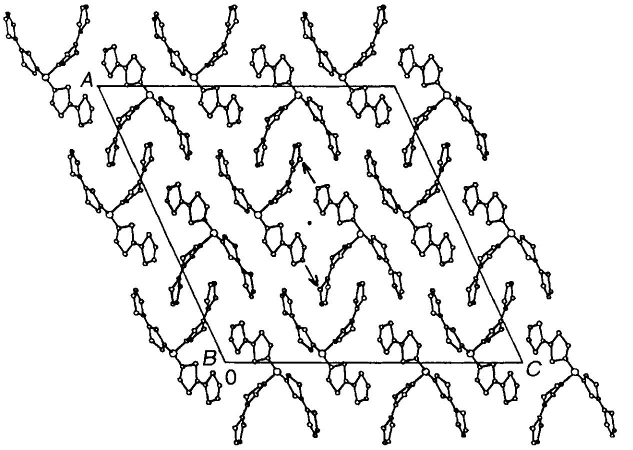


Fig. 2 PLUTO drawing of the unit cell, as viewed down the *b*-axis

ted to show a higher basicity as well as novel redox and structural properties, *per se* or when engaged in organometallic complexes and/or cation-radical salts.

The reaction of TTF–Li[3] and PBr_3 in dry diethyl ether at −78 °C yields $P(TTF)_3$ in 40% yield (Scheme 1). Elution of the reaction mixture on a SiO_2 column with cyclohexane eliminates unreacted TTF; further elution with toluene affords the pure material.† The ^{31}P chemical shift of $P(TTF)_3$ (−33.6 ppm *vs.* H_3PO_4) is remarkably shifted upfield when compared with PPh_3 ($\delta^{31}P$ = −6 ppm). It follows that the contribution[4] of a single TTF substituent on a phosphine amounts to −11.2 ppm, a value comparable to those of alkyl groups like propyl or butyl.

In cyclic voltammetry experiments,‡ two reversible oxidation waves of equal heights, are observed at +0.28 and + 0.52 V *vs.* saturated calomel electrode (SCE). By comparison, TTF exhibits two reversible waves at + 0.30 and + 0.56 *vs.* SCE under the same experimental conditions. This demonstrates that the three TTFs do not interact strongly with each other across the phosphorus atom. This is consistent with Extended Hückel calculations which show that the electron density at the branching carbon in the TTFs HOMO is small. Therefore, one expects very weak through-bond interaction between TTF units in such dimers, trimers or tetramers, regardless of the nature of the link.

This electron-rich phosphine has been further characterised by single crystal X-ray diffraction (Fig. 1).§ The molecule is located on a general position in the monoclinic unit-cell. The angles relative to the central phosphorus atom (101.4, 100.8 and 103.5°) are comparable, albeit a bit smaller, to that reported for PPh_3 (103°).[5] $P(TTF)_3$ may then be considered as slightly less bulky than triphenylphosphine itself. Thus, the observed ^{31}P chemical shift may be essentially ascribed to the electron-donating ability of the TTF substituents. Of particular note are the large deviations from planarity adopted by the three TTF units in the solid state. Each dithiole ring is bent along the S–S axis, up to an angle of 24° for the folding along S(11)–S(12). The latter is one of the largest values reported so far for TTF-like molecules.[6] We suggest that a possible explanation for these distortions is to be found in the peculiar mode of packing of the $P(TTF)_3$ molecules in the crystal (Fig. 2). In that respect, it is of interest to note that numerous (C)H · · · S short intermolecular contacts are revealed, ranging from 2.85 to 3.42 Å. In fact, every C–H group of $P(TTF)_3$ is engaged in such specific, directional weak intermolecular forces. The resulting pattern of association of the $P(TTF)_3$ molecules is quite striking. Consider for example the inversion-related molecules at the centre of Fig. 2. They are in fact connected by the shortest such (C)H · · · S contacts, as symbolised by the arrows. This leaves large, bimolecular units, which neatly fit into each other by the proper adjustment of their two molecular claws, hence the bending of the TTF substituents, the remarkable two-dimensional pattern and the striking hexagonal-like unit-cell.

Further work in these directions, as well as the potential of this and other phosphines in organometallic chemistry will be reported soon.

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† M.p. 177–180 °C (toluene). Satisfactory elemental analysis was obtained. δ_H (60 MHz, $CDCl_3$, TMS) 6.16 (6 H, s) and 6.6 (3 H, d, J_{PH} 10 Hz); *m/z* (chemical ionisation) 641 (M^+).

‡ Cyclic voltammograms were recorded using a PAR 273 potentiostat with Pt working and auxiliary electrodes, a SCE reference electrode, and $Bu_4N^+PF_6^-$ as supporting electrolyte in dry dimethylformamide (DMF). A ferrocene internal standard ($Fc^{+/0}$ couple) was measured after each experiment at 0.39 V *vs.* the SCE reference.

§ *Crystal data* for $P(TTF)_3$: $C_{18}H_9PS_{12}$, monoclinic space group *C*2/*c*, a = 29.774(2) b = 6.354(1), c = 28.930(2) Å, β = 114.656(7)°, V = 4974.8 Å^3, Z = 8, μ = 10.859 cm^{-1}, $F(000)$ = 2592, graphite-monochromated Mo-Kα radiation, λ = 0.71069 Å. The data were collected on an Enraf-Nonius CAD4-F diffractometer ($\omega/2\theta$ scan). No absorption corrections were applied. The structure was solved by direct methods using the Enraf-Nonius SDP programs[7] and refined by least-squares analysis (anisotropic for non-hydrogen atoms) to R = 0.038, R_w = 0.054 for 2479 observed ($F_0 > 3\sigma F_0$) reflections out of 4808 unique data. The goodness-of-fit value is 1.361. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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References

1 J. Y. Becker, J. Bernstein, S. Bittner and S. Shaik, *Proceedings of the International Conference on Science and Technology of Synthetic Metals, Tübingen (FRG)*, September 1990, *Synth. Metals*, 1991, **42**, 2523; *cf.* J. Y. Becker, Tetrahedron Lett., 1988, **29**, 6177.

2 Y. S. Huang, M. Fourmigué and P. Batail, unpublished work.

3 D. C. Green, *J. Org. Chem.*, 1979, **44**, 1476.

4 S. O. Grim, W. McFarlane and E. F. Davidoff, *J. Org. Chem.*, 1967, **32**, 781.

5 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.

6 J. J. Novoa, M. H. Whangbo and J. M. Williams, *Mol. Cryst. Liq. Cryst.*, 1990, **181**, 25; M. H. Whangbo, D. Jung, J. Ren, M. Evain, J. J. Novoa, F. Mota, S. Alvarez, J. M. Williams, M. A. Beno, A. M. Kini, H. H. Wang and J. R. Ferraro, *The Physics and Chemistry of Organic Superconductors*, ed. G. Saito and S. Kagoshima, Springer Verlag, Berlin, 1990, p. 262.

7 B. A. Frenz, *Computing in Crystallography*, Delft University Press, Delft, The Netherlands, 1978.