

Synthesis and Characterisation of 2,4,6-Tri-*t*-Butylphenylphosphines; X-Ray Structure of $[P(C_6H_2Bu^t_{3-2,4,6})S]_3^\dagger$

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Whereas treatment of phosphorus(III) chloride with an equimolar portion of LiAr (Ar = C₆H₂Bu^t_{3-2,4,6}) affords PArCl₂, with 2LiAr there is obtained ArP=PAR, which has low-lying MO's (photoelectron spectroscopy) and a LUMO (reversible electrochemical 1-electron reduction); other reactions of LiAr lead to PAr(Cl)X [X = CH(SiMe₃)₂ (and a 1-phosphabenzocyclopentene therefrom), Ph, C₆H₂Me_{3-2,4,6} (interesting variable temperature n.m.r. spectra), or OC₆H₂Bu^t_{3-2,4,6}], or the puckered six-membered (PS)₃ cyclic title compound (ring torsion angles all 80° with the S atoms 1.0 Å out of the P₃ plane) which with PPh₃ yields ArP=PAR.

We have demonstrated that persistent phosphinyl radicals $\cdot PR_2$ are accessible from their monochlorophosphine precursors PClR₂ [R = CH(SiMe₃)₂].¹ In seeking to extend these findings to sterically hindered diarylphosphinyl radicals $\cdot PAR_2$, we turned to the 2,4,6-tri-*t*-butylphenyl ligand (= Ar⁻, henceforth). However this led to quite different chemistry in that PAr₂Cl was not directly accessible. Results for trivalent phosphorus compounds are summarised in Scheme 1; some of these substances are precursors for novel phosphorus-centred radicals, as described in a previous communication.²

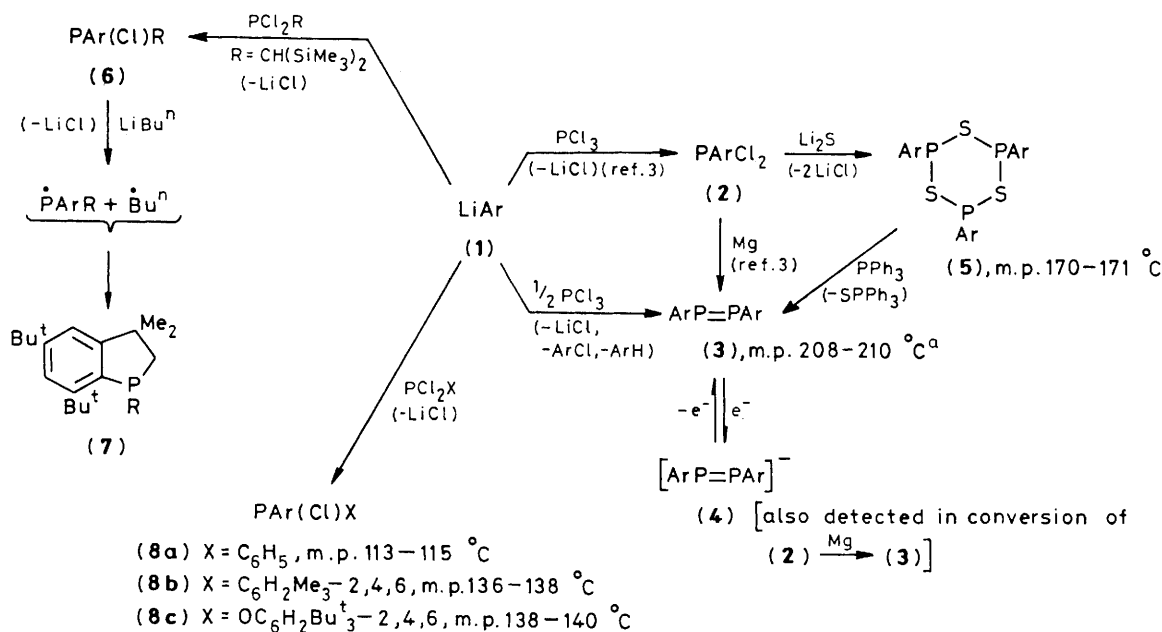
Yoshifuji, Inamoto, and their coworkers had already shown that the dichlorophosphine PArCl₂ (**2**) is obtained from phosphorus(III) chloride and an equimolar portion of LiAr (**1**) and moreover that (**2**) is reduced by magnesium metal to the very interesting orange-red azo-arene analogue *trans*-ArP=PAR (**3**).³ We now report an alternative, and in our hands a more convenient, synthesis of (**3**) (55%, but concentration dependent): from PCl₃ + 2LiAr (12 mmol) in tetrahydrofuran (thf) (25 cm³) at 78 °C and successive heating under reflux,

removal of volatile material (including ArCl and ArH) at up to 150 °C at 10⁻³ Torr, cooling, addition of *n*-C₆H₁₄, and low-temperature crystallisation (*n*-C₅H₁₂).

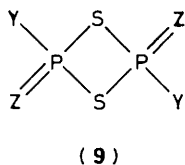
trans-Bis-(2,4,6-tri-*t*-butylphenyl)diphosphene (**3**) has low-lying HOMO's and a LUMO as shown by respectively (i) the He-I photoelectron spectrum (p.e.s.) [the three bands at lowest ionisation energy are at 7.24, 8.05, and 8.73 eV (*cf.*, 8.46 eV in ArH)], and (ii) cyclic voltammetry at a Pt electrode using [NBu₄][BF₄] in MeCN showing reversible 1-electron reduction: $E_1^{\text{red}} = -1.74$ V vs. s.c.e. (standard calomel electrode) {[Fe(η-C₅H₅)₂]⁺/[Fe(η-C₅H₅)₂], 0.54 V} *cf.*, -1.31 V for PhN=NPh (see also ref. 4); no oxidation was observed up to a potential of +1 V. The radical anion [ArP=PAR]⁻, (**4**), was alternatively obtained from (**3**) and Na[C₁₀H₈] in thf and was characterised by its e.s.r. spectrum;² it was also detected in the PArCl₂-Mg reaction.

In Scheme 1 are shown four further reactions of LiAr with a phosphorus(III) dichloride PCl₂X in equimolar proportions to yield PAr(Cl)X [X = R, (**6**); X = Ph, (**8a**); X = C₆H₂Me_{3-2,4,6}, (**8b**); or X = OC₆H₂Bu^t_{3-2,4,6}, (**8c**)]. These compounds are precursors for the radicals $\cdot PARX$, by treatment with an electron-rich olefin.² Such a radical appears (e.s.r.)

† No reprints available.



Scheme 1. The synthesis of some trivalent 2,4,6-tri-*t*-butylphenylphosphorus compounds (Ar = C₆H₂Bu^t₃-2,4,6). Satisfactory analytical and spectroscopic results were obtained for the new compounds (5)–(8).^a Our data on compound (3) differ considerably from those reported in ref. 3 with respect to m.p. (176–177 °C in ref. 3) and ³¹P n.m.r. chemical shift (relating to H₃PO₄) (we find -493.6 p.p.m. vs.³ -59.0 p.p.m.)



also to be formed as an intermediate in the cyclisation reaction of PAr(Cl)R with LiBuⁿ to yield the fused-ring phosphorus heterocycle (7). Additionally there is e.s.r. evidence for $\cdot\text{PAR}_2$ as an intermediate in the reaction $2\text{LiAr} + \text{PCl}_3 \rightarrow \text{ArP}=\text{PAR}$; it is possible that the reactive PClAr₂ is the first formed product.

The variable temperature ¹H n.m.r. spectra of the mesityl compound PAr(Cl)X (8b) in CCl₄ and the tri-*t*-butylphenoxy-compound (8c) in CDCl₃ show that there is restricted rotation on the n.m.r. time-scale about the P–C₆H₂Me₃, P–Ar (8b and 8c), and O–Ar (8c) bonds.

Although the bulky 2,4,6-tri-*t*-butylphenyl ligand permits the isolation of the diphosphene (3), rather than a cyclic oligomer (PR')_n ($n > 2$; e.g.,⁵ $n = 5$ or 6 for R' = Ph), it is interesting that 2,4,6-tri-*t*-butylphenylphosphonous sulphide (see Scheme 1) is the cyclic trimer (SPAr)₃ (5) in the solid state, rather than the sterically less hindered monomer or dimer. It appears to be the first monocyclic P^{III} sulphur compound containing a (PS)_n ring for which there are X-ray data, although the structures of pentavalent phosphorus compounds (9) [e.g. Z = S, Y = Me;⁶ or Z = NSiMe₃, Y = N(SiMe₃)₂⁷] have been described. The cyclic sulphide (5) is desulphurised by treatment with PPh₃ to generate the diphosphene (3).

The structure of (SPAr)₃ (5) (Figure 1) consists of molecules lying across the 3-fold crystallographic axis but with a random arrangement of molecules of opposite ring pucker in equivalent sites in the ratio of 3:2. The P and S atoms could be resolved but the carbon atoms could not.

The P₃S₃ ring is puckered, with the internal ring torsion angles all 80° and with the S atoms 1.0 Å out of the plane of

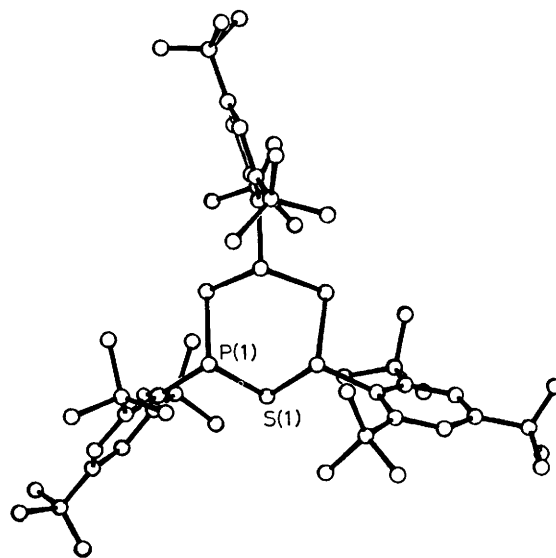


Figure 1

the three P atoms. For the ring orientation of higher occupancy the P–S bond lengths are 2.115(3) and 2.142(3) Å and the angle P–S–P is 91.9(2)° with S–P–S 105.9(2)°. The phenyl group is at an angle of 102° to the plane of the three P atoms and the P atom attached to C(1) of the phenyl ring is 0.6 Å out of the plane of the phenyl ring. This is presumably a steric effect due to the two *ortho-t*-butyl groups as seen elsewhere.⁸ It is interesting that while (SPAr)₃ has the chair conformation, the related compound (OPNPr₂)₃ has the boat conformation.⁹

Crystal data: C₅₄H₈₇P₃S₃·0.5C₅H₁₂, (5), rhombohedral, space group $R\bar{3}$, $a = 14.272(3)$ Å, $\alpha = 87.24(2)^\circ$, $Z = 2$. The structure was determined by heavy atom methods using 1582 reflections with $I > \sigma(I)$ measured on an Enraf-Nonius CAD4

diffractometer with Mo- K_{α} radiation. All atoms were refined anisotropically by least squares to give a final $R_F = 0.128$.[‡]

We thank Dr. C. J. Pickett and Mr R. G. Taylor for the electrochemical data and Dr. R. J. Suffolk for the p.e.s. results; N.A.T.O. for a grant to B. C., H. G., and M. F. L.; the S.E.R.C. and Dow Corning, Ltd., for a CASE studentship for A. J. T., and the S.E.R.C. also for assistance in the purchase of the diffractometer.

Received, 23rd March 1982; Com. 335

[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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