

PHOSPHORUS–PHOSPHORUS SINGLE OR DOUBLE BOND FORMATION FROM $\text{PCl}_{3-n}\text{R}_n$ ($n = 1$ or 2) AND A BIS-IMIDAZOLIDINE REDUCING AGENT

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Summary

1,3,1',3'-Tetraethyl-bis(2,2'-imidazolidene), L_2^{Et} (I), is a mild homogeneous reducing agent which reduces P–Cl bonds in phosphonous or phosphinous chlorides to give compounds with phosphorus–phosphorus bonds. High yields of diphosphines P_2R_4 are produced from the corresponding phosphinous chlorides (PClR_2). Phenyl- and t-butyl-phosphonous dichlorides are reduced to cyclopolyphosphines $(\text{PR})_n$, which appear to be the kinetically controlled products. 2,4,6-Tri(t-butyl)phenylphosphonous dichloride (PArCl_2) is reduced to either 1,2-dichloro-1,2-bis(2,4,6-tri-t-butylphenyl)diphosphine (PArCl_2) or *trans*-bis[(2,4,6-tri-t-butylphenyl)diphosphene (P_2Ar_2)] depending on the initial stoichiometry.

Introduction

Heterogeneous reduction of phosphinous halides (PR_2X) to diphosphines (P_2R_4) or of phosphonous dihalides (PRX_2) to cyclopolyphosphines $(\text{PR})_n$ by metals is a sluggish reaction which needs high temperatures and long reaction times [1]. In contrast, the homogeneous reduction of a hindered phosphinous halide by a bis-imidazolidine [$=\text{CN}(\text{R})\text{CH}_2\text{CH}_2\text{NR}$] ($\equiv \text{L}_2^{\text{R}}$) to the persistent phosphinyl radical (PR_2), which is generally in equilibrium with its dimer, the diphosphine (P_2R_4), is rapid at room temperature when initiated photolytically [2,3]. Consequently, we decided to explore the synthetic utility of a bis-imidazolidine, such as I, as a reducing agent for phosphonous dihalides as well as less hindered phosphinous halides.

Results and discussion

Reductions of diarylphosphinous chlorides to the tetra-aryldiphosphines proceeded much more rapidly and under much milder conditions with the bis-imidazolidene (I) than with the metal reducing agents used previously [1]. The stoichiometry of the reaction was that shown in eq. 1 ($R = \text{aryl}$).

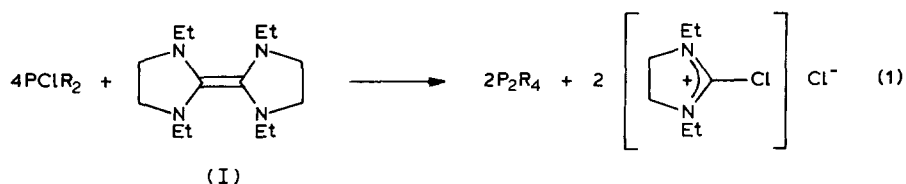


Photo-initiation was not required for the reactions reported here. The carbonium salt by-product precipitated out from the toluene solution during the reaction; hence, the mixture was easy to work up, and P_2R_4 was obtained in good yield (see Table 1). Since the reduction of hindered phosphinous chlorides by bis-imidazolidenes leads to phosphinyl radicals [2,3], it seems likely that the present reactions also proceed via phosphinyl radicals ($\text{PR}_2\cdot$), which dimerise to yield the diphosphines.

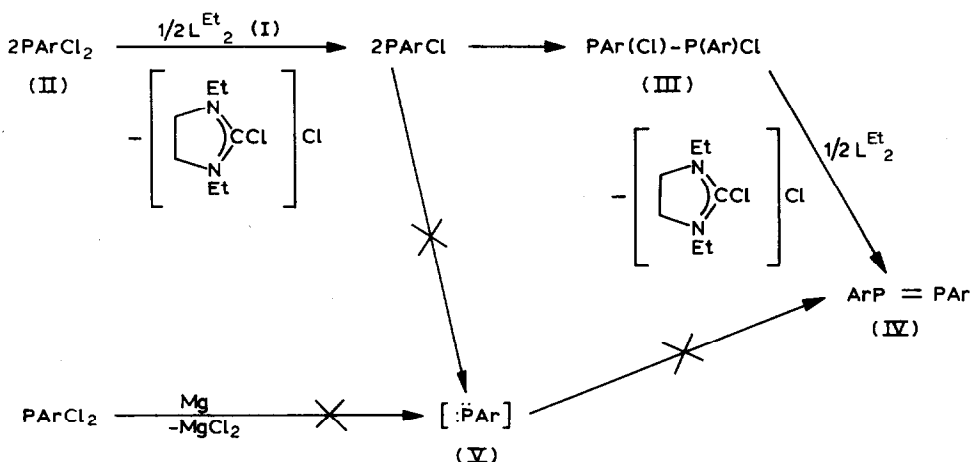
Reduction of *t*-butylphosphonous dichloride by the bis-imidazolidene (I) led cleanly to the cyclotetraphosphine (P^{Bu^t})₄ as the sole product; this was also obtained by reduction of the dichloride by a metal [4].

Reduction of phenylphosphonous dichloride by zinc, in a slow thermal reaction, yielded the cyclopentaphosphine (PPh)₅ as the major product, together with smaller amounts of cyclotetraphosphine and cyclohexaphosphine [5]. It seems probable that this was the thermodynamic product mixture under these conditions. In contrast, we now report that bis-imidazolidene reduction of PCl_2Ph gives a mixture of 55% of cyclotetraphosphine and 45% of cyclopentaphosphine, with no detectable cyclohexaphosphine. This mixture, obtained at ambient temperature under mild conditions, may be kinetically determined. It is possible that bis-imidazolidene reduction will prove to favour the formation of cyclopolyphosphines which are not as readily accessible by other reduction methods.

The preparation of phosphorus-phosphorus double-bonded compounds, diphosphenes, from P^{III} precursors is a topic of current interest [9-15]. The work described below on the bis-imidazolidene reduction of PARCl_2 helps to elucidate the mechanism of the reactions whereby a symmetrical diphosphene is prepared from a

TABLE 1
PREPARATION OF DIPHOSPHINES P_2R_4 BY REACTION 1

R in P_2R_4	Yield (%)	M.p. (lit.) (°C)
C_6H_5	88	120 (121-122 [6])
2,4,6-(CH_3) ₃ C_6H_2	73	210-215 (dec.) (200-215 [7])
(CH_3) ₃ C	57	47 (48 [4])
c- C_6H_{11}	50	171 (173 [8])



SCHEME 1. Reaction sequence in the reduction 2,4,6-tri(t-butyl)phenylphosphonous dichloride PArCl_2 (II) and the bis-imidazolidene L_2^{Et} (I), and inoperative alternatives (via V).

phosphonous dichloride. 2,4,6-Tri-(t-butyl)phenylphosphonous dichloride, PArCl_2 (II), was treated with L_2^{Et} (I). The initial product was the 1,2-dichlorodiphosphine (III) together with a small amount of the diphosphene (IV). Use of a slight excess of I under more vigorous conditions gave only IV.

Thus, in the preparation of diphosphenes by reduction from phosphonous dichlorides there is unlikely to be a phosphinidene intermediate (V), as has been proposed [9]. Formation of the dichlorodiphosphine (III) is now demonstrated to occur along the pathway from II to IV. Compound III has not previously been observed because an excess of a dechlorinating/reducing agent has always been employed.

These data are summarised in Scheme 1. From earlier ESR experiments [11], it was demonstrated that the initial transient product of reduction of PCl_2Ar by L_2^{Et} is the radical $\dot{\text{P}}\text{ArCl}$. It is now evident that $\dot{\text{P}}\text{ArCl}$ dimerises to the diphosphine III; this radical, as well the analogous $\dot{\text{P}}\text{ArX}$ ($\text{X} = \text{OBu}^t$, SPr , SBu^t , Cl , $\text{N}(\text{SiMe}_3)_2$, $\text{CH}(\text{SiMe}_3)_2$, Ph , $\text{C}_6\text{H}_2\text{Me}_3$ -2,4,6, Ar , or OAr), have previously been identified as products from L_2^{Et} (I) and PAr(Cl)X [11].

Experimental

General procedures

Except where otherwise noted starting materials were commercial products (Aldrich, Strem, or Alfa), and were distilled or crystallised before use; their purities were checked by NMR spectroscopy. Proton NMR spectra were recorded with a Varian EM-60 or an EM-90 spectrometer; ^{31}P NMR spectra were recorded at 36.4 MHz with a Bruker HFX-10 spectrometer; positive values of δ correspond to resonances at low field relative to external 85% H_3PO_4 at $\delta = 0$. Reactions were run under argon in a Schlenk line. Solvents were dried over sodium and distilled under nitrogen.

Starting materials

A mixture of *N,N*-dimethylformamide dimethylacetal (17.9 g, 20.0 cm³, 151 mmol) and *N,N'*-diethylethylenediamine (15.1 g, 18.3 cm³, 130 mmol) in dry benzene was heated in a distillation vessel during 3 h to 110°C and the methanol/benzene azeotrope that was produced was collected. The vessel was cooled and the remaining benzene was removed in vacuo. The residue was distilled under vacuum to yield 1,3,1',3'-tetraethyl-2,2'-bis(imidazolidene) (I) (11.5 g, 70%, b.p. 86–88°C at 3 Torr), which is sensitive to air and moisture; I is a low melting solid (m.p. 48°C) [16], and is conveniently used in toluene solution.

Bromomesitylene (19.9 g, 15.1 cm³, 100 mmol) in diethyl ether (30 cm³) was added slowly to *n*-butyllithium in hexane (52 cm³ of a 2.53 mol dm⁻³ solution; 130 mmol of LiBuⁿ) and the mixture was heated at reflux for 3 h. A copious deposit of crystalline mesityllithium was produced. The mixture was cooled to 0°C and phosphorus trichloride (6.8 g, 4.36 cm³, 50 mmol) in diethyl ether (20 cm³) was slowly added. The mixture was stirred at 25°C for 15 h and then filtered. Vacuum distillation gave mesitylphosphonous dichloride (1.5 g, b.p. 145–150°C at 2 Torr; ³¹P NMR: δ 161 ppm) and dimesitylphosphinous chloride (4.8 g, 31%, b.p. 180–185°C at 2 Torr; ¹H NMR (δ in ppm, CD₂Cl₂): 2.20 (s), 6-CH₃; 2.30 [d, *J*(PH) 2.4 Hz], 2,4-CH₃; 6.8 (d), 3,5-H, *J*(PH) 3.2 Hz; ³¹P NMR, δ 76 ppm).

Diphosphines: general procedure

A solution of the bis-imidazolidene (I) (0.60 mmol, 20% excess) in toluene (1 cm³) was added slowly at 0°C to a stirred solution of the phosphinous chloride (2.0 mmol) in toluene (5 cm³). The mixture was stirred at 0°C for 2 h, and then filtered. Toluene was evaporated from the filtrate in vacuo at room temperature to yield the diphosphine.

Tetra-*t*-butylcyclotetraphosphine

This was prepared by the above general procedure, starting from *t*-butylphosphonous dichloride (2.0 mmol) and the bis-imidazolidene (I) (1.0 mmol) in toluene (8 cm³). Examination of the product solution after filtration by ³¹P NMR spectroscopy showed only one peak, at 62.9 ppm, characteristic of the cyclotetraphosphine (cf. [4]: δ 58 ppm); this compound was isolated in 57% yield.

Phenylcyclopolyphosphines

Reaction between phenylphosphonous dichloride (2.0 mmol) and the bis-imidazolidene (I) (1.0 mmol) in toluene (8 cm³) was carried out by the above general procedure. Examination of the product solution after filtration by ³¹P NMR spectroscopy showed peaks only at 9.9 ppm (singlet; integrated area, 55% of total signal) attributed to the cyclotetraphosphine (cf. [5] δ 9.0 ppm), and at 5.1 ppm (complex multiplet, 45% of signal) attributed to the cyclopentaphosphine (cf. [17] δ 4.7 ppm) [7]. The isolated yield of the combined cyclopolyphosphines was 72%.

1,2-Dichloro-1,2-bis(2,4,6-tri-*t*-butylphenyl)diphosphine and trans-bis(2,4,6-tri-*t*-butylphenyl)diphosphene

A solution of the bis-imidazolidene (I) (0.23 g, 0.90 mmol) in toluene (10 cm³) was added dropwise to 2,4,6-tri-*t*-butylphenylphosphonous dichloride [9] (1.17 g, 3.37 mmol) in toluene (20 cm³). A white flocculent precipitate was immediately

formed and the solution became yellow. After 2 h stirring the precipitate was filtered off and the solvent removed from the filtrate in vacuo at room temperature. Examination of the residue by ^{31}P NMR spectroscopy showed it to be the almost pure diphosphine (δ 75.7 ppm) containing a little diphosphene (δ 494 ppm).

The diphosphene was formed quantitatively (^{31}P NMR) when an excess of the bis-imidazolidene (I) (ca. 10%) was used, and the mixture refluxed for 1 h.

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References

- 1 H. Heydt and M. Regitz in M. Regitz (Ed.), *Houben-Weyl, El, Phosphorverbindungen 1*, Georg Thieme Verlag, Stuttgart, 1982, pp. 191–192.
- 2 M.J.S. Gynane, A. Hudson, M.F. Lappert, P.P. Power, and H. Goldwhite, *J. Chem. Soc., Chem. Commun.*, (1976) 623.
- 3 M.J.S. Gynane, A. Hudson, M.F. Lappert, P.P. Power, and H. Goldwhite, *J. Chem. Soc., Dalton Trans.*, (1980) 2428.
- 4 K. Issleib and M. Hoffmann, *Chem. Ber.*, 99 (1966) 1320.
- 5 W.A. Henderson, M. Epstein, and F.S. Seichter, *J. Am. Chem. Soc.*, 85 (1963) 2462.
- 6 W. Kuchen and W. Grunewald, *Chem. Ber.*, 98 (1965) 480.
- 7 B.I. Stepanov, E.N. Karpova, and A.I. Bokanova, *Zh. Obshch. Khim.*, 39 (1969) 1544.
- 8 K. Issleib and W. Seidel, *Chem. Ber.*, 92 (1959) 2681.
- 9 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, 103 (1981) 4587.
- 10 B. Çetinkaya, P.B. Hitchcock, M.F. Lappert, A.J. Thorne, and H. Goldwhite, *J. Chem. Soc., Chem. Commun.*, (1982) 691.
- 11 B. Çetinkaya, A. Hudson, M.F. Lappert, and H. Goldwhite, *J. Chem. Soc., Chem. Commun.*, (1982) 609.
- 12 A.H. Cowley, J.E. Kilduff, T.H. Newman, and M. Pakulski, *J. Am. Chem. Soc.*, 104 (1982) 5820.
- 13 G. Bertrand, C. Couret, J. Escudié, S. Majid, and J.-P. Majoral, *Tetrahedron Lett.*, (1982) 3567.
- 14 C. Couret, J. Escudié, and J. Satgé, *Tetrahedron Lett.*, (1982) 4941.
- 15 A.H. Cowley, *Acc. Chem. Res.*, 17 (1984) 386; *Polyhedron*, 3 (1984) 389.
- 16 H.E. Winberg, U.S.P. 3,361,757; *Chem. Abs.* 69 (1968) 19155a.
- 17 L.R. Smith and J.L. Mills, *J. Chem. Soc., Chem. Commun.*, (1974) 808.