

Generation and E.S.R. Spectra of Some New Phosphorus-centred Radicals \dot{P}_2Ar_2X , $\dot{P}(Ar)X$, $\dot{P}(OAr)_2$, $\dot{P}Ar_2(:O)$, $\dot{P}Ar[N(SiMe_3)_2](:NSiMe_3)$, and $[P_2Ar_2]^{•-}$ derived from the Bulky Group $C_6H_2Bu^t_{3-2,4,6}$ ($= Ar$)†

Bekir Çetinkaya,^a Andrew Hudson,^a Michael F. Lappert,^a and Harold Goldwhite^b

^a School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, U.K.

^b Department of Chemistry, California State University, Los Angeles, California 90032, U.S.A.

The photochemical reaction of X_2 and the diphosphene *trans*- $ArP=PAR$ ($Ar = C_6H_2Bu^t_3$), (1), leads successively to \dot{P}_2Ar_2X , (2), $\dot{P}(Ar)X$, (3), and upon cooling $[P(Ar)X]_2$ [for $X = OBU^t$, $\Delta H_{diss} = 107 \pm 7$ kJ mol⁻¹] for $X = OBU^t$ or SPr^n , whereas for $X = SBU^t$ only (3) was detected; the radicals $\dot{P}(Ar)X$, $\dot{P}(OAr)_2$, and $\dot{P}Ar_2(:O)$ were formed by reduction of the appropriate diamagnetic P^{III} or P^V chloride, while $[P_2Ar_2]^{•-}$ was obtained from (1) and $Na[C_{10}H_8]$.

We describe the preparation and characterisation by e.s.r. spectroscopy of persistent radical intermediates formed by addition to the P=P double bond of the novel¹ $ArP=PAR$, (1), ($Ar = 2,4,6$ -tri-*t*-butylphenyl). A number of phosphorus-centred radicals stabilised by the bulky Ar ligand are also reported: \dot{P}_2Ar_2X (2), $\dot{P}(Ar)X$ (3), $\dot{P}(OAr)_2$, $\dot{P}Ar_2(:O)$, $\dot{P}Ar[N(SiMe_3)_2](:NSiMe_3)$, and $[P_2Ar_2]^{•-}$. E.s.r. data on these radicals are in Table 1. The preparation of the diamagnetic precursors will be described in a forthcoming communication² or in ref. 3 for $PAR_2(Cl)(:O)$.

Photolysis of di-*t*-butyl peroxide in a toluene solution of (1) at ambient temperature gave an e.s.r. spectrum consisting of a doublet of doublets [see (A) in Figure 1, and Table 1], and a less intense doublet [(B) in Figure 1]. The larger splitting in (A) is characteristic of phosphinyl radicals⁴ and the spectrum is assigned to the adduct (2; $X = OBU^t$), equation (1). [Photolysis of (1) under identical conditions (1 kW Hanovia Hg-Xe lamp) but without $Bu^t_2O_2$ did not afford a paramagnetic species.] The concentration of the doublet (B), assigned to the species (3), increased as that of (2) diminished. The intensity of this e.s.r. signal (B) was also found to depend reversibly on temperature; it was barely detectable at 0 °C but was strong at

50 °C. We attribute this to the phosphinyl radical (3; $X = OBU^t$) being in equilibrium with its dimer, equation (2). From the temperature dependence of the e.s.r. signal intensity we estimate $\Delta H_{diss} = 107 \pm 10$ kJ mol⁻¹ for the equilibrium (2).

Analogous radicals were detected when di-*n*-propyl disulphide but no marked temperature dependence was found for the concentration of (3; $X = SPr$). When di-*t*-butyl disulphide was employed as a radical source the spectrum of the adduct (2; $X = SBU^t$) was very weak and only (3; $X = SBU^t$) was readily detectable. These observations are consistent with increased steric requirements for SBU^t compared with OBU^t , leading to an enhanced formation of (3) from (2); the decreased tendency for (3) to dimerise may in part be due to stabilisation by the neighbouring sulphur.

A series of persistent phosphinyl radicals (3) was formed when a solution of $PAR(Cl)X$ [$X = Cl, Ph, C_6H_2Me_3-2,4,6, OC_6H_2Bu^t_3-2,4,6$, or $CH(SiMe_3)_2$] was photolysed in toluene in the presence of the electron-rich olefin (4) at ca. 25 °C, equation (3). {We had previously used this procedure for the synthesis of the persistent radicals \dot{MR}_2 [$M = P$ or As , $R = CH(SiMe_3)_2$ or $N(SiMe_3)_2$].⁴} Similarly, the radical $\dot{P}(OAr)_2$ was obtained at ca. 28 °C from $PCl(OAr)_2 + (4)$ in toluene by photolysis.

The radical $\dot{P}Ar_2$ was most readily prepared by treating $PARCl_2$ with an excess of $LiAr$. It was also slowly formed when

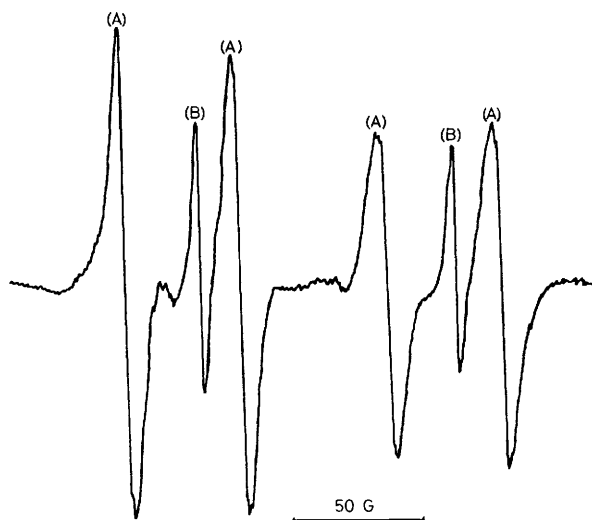
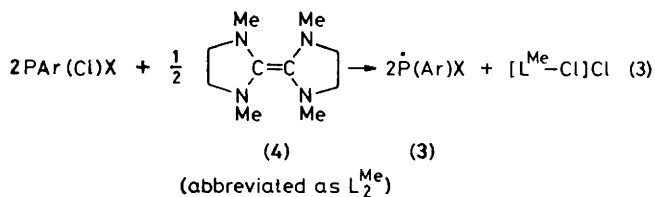
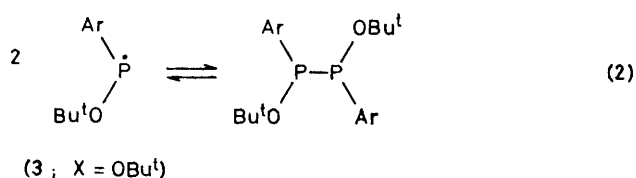
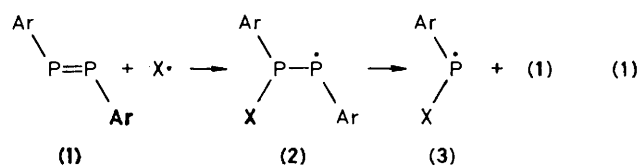
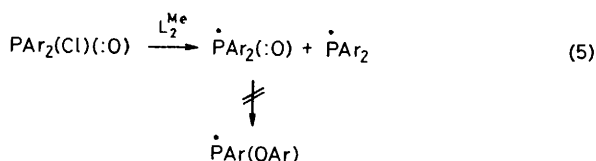
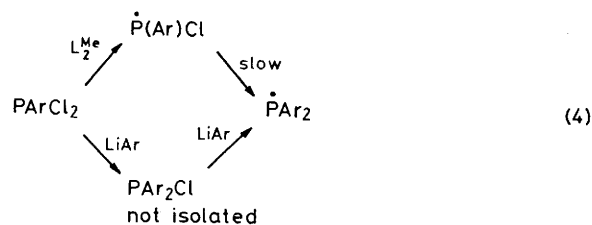


Figure 1. The e.s.r. spectrum of radicals produced by photolysis of $ArP=PAR + Bu^tOOBu^t$ in toluene at 30 °C; the signals marked (A) are attributed to $Ar(Bu^tO)PPAr$ (2; $X = OBU^t$), and (B) to $\dot{P}(Ar)OBU^t$ (3; $X = OBU^t$).



† No reprints available.



a solution of $\dot{\text{P}}(\text{Ar})\text{Cl}$ was kept for 1 week at room temperature, presumably by disproportionation. These findings are interpreted in terms of equations (4).

When $\text{PAr}_2(\text{Cl})(:\text{O})$ was reduced with the electron-rich olefin L_2^{Me} a 365 G doublet ($g_{\text{av.}} = 2.005$) was observed, which we assign to $\dot{\text{P}}\text{Ar}_2(:\text{O})$ [*cf.*, $\dot{\text{P}}\text{Me}_2(:\text{O})$ which has⁵ $a(^{31}\text{P}) = 375$ G, $g_{\text{av.}} = \text{ca. } 2.005$]. A second smaller doublet found in this system proved to be due to $\dot{\text{P}}\text{Ar}_2$. An alternative possibility, that instead of deoxygenative reduction a molecular rearrangement takes place to afford $\dot{\text{P}}(\text{Ar})\text{OAr}$, is discounted, since (3; X = OAr) has significantly smaller $a(^{31}\text{P})$ (see Table 1). Hence the reduction is interpreted in terms of equations (5).

When PArCl_2 was treated with $\text{LiN}(\text{SiMe}_3)_2$ a large doublet (336 G) signal with superimposed hyperfine structure was observed. This is assigned to a phosphorimidoyl radical, probably $\dot{\text{P}}\text{Ar}[\text{N}(\text{SiMe}_3)_2](:\text{NSiMe}_3)$ [*cf.*,⁶ $\dot{\text{P}}\text{Bu}^t[\text{N}(\text{SiMe}_3)_2](:\text{NSiMe}_3)$ which has $a(^{31}\text{P}) = 336.5$, $a(^{14}\text{N}) = 5.2$, $a(^{15}\text{N}') = 4.0$ G, $g_{\text{av.}} = 2.0032$]. A smaller doublet detected in this reaction is attributed to the phosphinyl [3; X = $\text{N}(\text{SiMe}_3)_2$].

Addition of sodium naphthalide in THF to $\text{ArP}=\text{PAr}$ gave a signal which we assign to the radical anion $[\text{ArP}=\text{PAr}]^{\cdot-}$.

The stabilisation of metal-centred radicals by Ar is not limited to phosphorus. A 50 G quartet was obtained when AsCl_3 was treated with LiAr and is provisionally assigned to $\dot{\text{A}}\text{sAr}_2$. However, photolysis of $\text{AsCl}(\text{OC}_6\text{H}_2\text{Me-4-Bu}^t\text{-2,6})_2$

Table 1. Hyperfine splittings (G) and $g_{\text{av.}}$ -factors for some phosphorus-centred radicals in PhMe (or in one case THF) at ca. 25 °C (Ar = $\text{C}_6\text{H}_2\text{Bu}_3^t\text{-2,4,6}$).

Radical	X	$a(^{31}\text{P})$	$a(\text{other})$	$g_{\text{av.}}$
(2)	OBu ^t	102	44	2.008
(2)	SPr	100	44	2.009
(3)	OBu ^t	100	—	2.005
(3)	SPr	98	—	2.011
(3)	SBU ^t	99	—	2.012
(3)	Cl	92	—	2.005
(3)	$\text{N}(\text{SiMe}_3)_2$	108	—	2.006
(3)	$\text{CH}(\text{SiMe}_3)_2$	104	13.5	2.008
(3)	Ph	105	—	2.007
(3)	$\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$	103	—	2.007
(3)	Ar	103	—	2.007
(3)	OAr	94	—	2.006
$\dot{\text{P}}(\text{OAr})_2$		82	—	1.999
$\dot{\text{P}}\text{Ar}_2(:\text{O})$		365	—	2.005
$\dot{\text{P}}\text{Ar}[\text{N}(\text{SiMe}_3)_2](:\text{NSiMe}_3)$		336	—	2.004
$[\text{ArP}=\text{PAr}]^{\cdot-}$ ^a		55	—	2.010

^a In tetrahydrofuran (THF).

with the electron-rich olefin (4) in PhMe at ca. 20 °C afforded the persistent aryloxy-radical⁷ [a quartet of triplets: $a(\text{quartet})$, 10.83 G; $a(\text{triplet})$, 1.71 G; $g_{\text{av.}}$, 2.0039].

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