Synthesis and Electron Spin Resonance Study of Stable Dialkyls and Diamides of Phosphorus and Arsenic, $R^1{}_2M\cdot$ and $(R^2{}_2N)_2M\cdot$†

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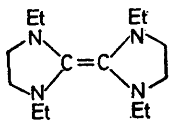
Summary Photolysis of toluene solutions of dialkylphosphorus or -arsenic chlorides $[(Me_3Si)_2CH]_2MCl$ (M = P or As) or bisamido-phosphorus or -arsenic chlorides $[(Me_3Si)_2N]_2MCl$ (M = P or As) in the presence of an electron-rich olefin leads to solutions containing persistent ($t_{\frac{1}{2}} > 1$ month at 20 °C) two-co-ordinate phosphorus or arsenic-centred radicals $[(Me_3Si)_2CH]_2M\cdot$ or $[(Me_3Si)_2N]_2M\cdot$ (M = P or As) characterised by their e.s.r. spectra.

WE have prepared and characterised, by their e.s.r. spectra, the first examples of stable two-co-ordinate phosphorus- and arsenic-centred radicals, (I) and (II). These radicals

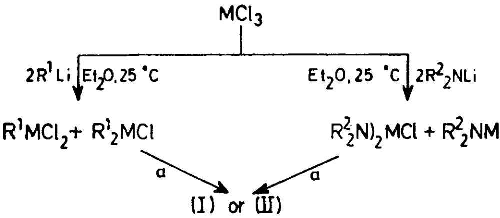
$[(Me_3Si)_2CH]_2M\cdot$ (I)
a, M = P
b, M = As

$[(Me_3Si)_2N]_2M\cdot$ (II)
a, M = P
b, M = As

were prepared by photolysis of degassed toluene solutions of the corresponding three-co-ordinate chlorides in the presence of the electron-rich olefin (III), a method which has been demonstrated previously to be an efficient way of removing a halogen atom from a metal or metalloidal centre.[1]



(III)



SCHEME. $R^1 = (Me_3Si)_2CH$; $R^2 = Me_3Si$; M = P or As; a = *in situ* irradiation with u.v. light of a PhMe solution of the olefin (III).

The precursors $[(Me_3Si)_2CH]_2MCl$ (M = P or As) to (Ia) and (Ib) (see Scheme and footnotes to Table) were prepared by reactions between the element trichlorides and $(Me_3Si)_2CHLi$ in ether. The compound, $[(Me_3Si)_2N]_2PCl$, has been previously described,[2] and is thermally unstable; it was therefore used in a crude state. The arsenic analogue, $[(Me_3Si)_2N]_2AsCl$, was prepared by a similar reaction, but was thermally stable and distillable at reduced pressure. The radical (Ia) was also produced by reduction of $[(Me_3Si)_2CH]_2PCl$ with 1 equiv. of sodium in light petroleum.

The solution e.s.r. spectra at 300 K of the P-centred radicals consist (Table) of a large ^{31}P doublet similar in

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magnitude to values reported for phosphino-radicals in the solid state[3] and in solution.[4] The spectrum of (Ia) (Figure) also exhibits coupling to two equivalent protons. The decrease in splitting observed on going from (Ia) to (IIa) is similar to that found on comparing $Ph_2P\cdot$ and $(PhHN)_2P\cdot$.[5] The solid state spectra of (Ia) and (IIa) recorded in toluene at 120 K show anisotropic hyperfine features characteristic of phosphino-radicals with $A_{\parallel}$ *ca.* 30 mT and $A_{\perp}$ *ca.* 0 [(Ia), $A_{\parallel} = 29{\cdot}4$, $A_{\perp} = -0{\cdot}3$; (IIa), $A_{\parallel} = 28{\cdot}9$, $A_{\perp} = -0{\cdot}7$ mT]. The *g*-values are close to free spin values.

TABLE. Hyperfine splittings (mT) and *g*-factors.

Radical	*a*(M)	*a*(H)	*g*
(Ia)[a,b]	9·63	0·64	2·009
(IIa)[b]	9·18	—	2·008
(Ib)[b,c]	3·72	—	2·04
(IIb)[b,d]	3·18	—	2·007

[a] $[(Me_3Si)_2CH]_2PCl$, m.p. 62—64 °C. [b] $[(Me_3Si)_2CH]_2MCl$ or $[(Me_3Si)_2N]_2MCl$ (M = P or As), τ 9·5—9·6. [c] $[(Me_3Si)_2CH]_2AsCl$, m.p. 70—72 °C. [d] $[(Me_3Si)_2N]_2AsCl$, b.p. 140—142 °C at 3 mmHg.

The room temperature spectra of (Ib) and (IIb) consist of quartets due to hyperfine coupling with ^{75}As ($I = {}^3/_2$). On lowering the temperature, the spectra exhibit, in addition to the normal asymmetric line-width effect, a further line-broadening followed by collapse of the hyperfine structure which we attribute to quadrupolar relaxation[6] of the ^{75}As nuclear spin. From the solid state spectrum of (Ib), we find $A_{\parallel} = 24{\cdot}5$ mT, which combined with our isotropic value from the solution spectrum gives $A_{\perp} = -6{\cdot}7$ mT. The value of $A_{\parallel}$ is close to those reported for $Me_2As\cdot$ and $Ph_2As\cdot$ in solid matrices,[7] but we feel the value of $A_{\perp}$ (*ca.* 0) quoted for these species is in error. A more detailed account of the solid state spectrum, the perpendicular region of which is complicated by quadrupole effects, will be given elsewhere. The similarity of the hyperfine parameters obtained for the P-centred species to those of other phosphino-radicals indicates that they have comparable structures, with the odd electron essentially in a $3p\pi$-orbital on phosphorus and bond angles in the range 95—100°. Similar considerations apply to the arsenic radicals, with the unpaired electron largely in a $4p$-orbital.

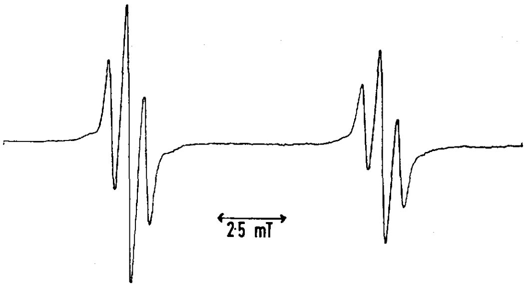

FIGURE. E.s.r. spectrum of $[(Me_3Si)_2CH]_2P\cdot$ at 300 K in PhMe.

The e.s.r. signals observed for (Ia,b) and (IIa,b) are unchanged in intensity over extended periods (> 15 days) at room temperature, and are even unaffected by short-term heating in solution to 360 K. These radicals are unexpectedly and surprisingly stable, in view of earlier observations and discussion of phosphino-radicals.[4] The persistence of these radicals must be attributed to the steric effect of the bulky ligands and the absence of β-hydrogen atoms which, as has previously been noted for group 4 radicals,[8] bestows kinetic stability. In the present case, the π-electron nature of the radical may also be a contributory factor. The normal fate of, *e.g.*, dialkylphosphino radicals produced by reaction of the chloride with an alkali metal, would be a coupling reaction to give a diphosphine as shown in equation (1). In the present systems the

$$R_2PCl \longrightarrow R_2P\cdot \longrightarrow 2R_4P_2 \qquad (1)$$

bulkiness of the R groups reduces the rate of radical coupling to such an extent that the two-co-ordinate radicals become persistent species.

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[1] M. J. S. Gynane and M. F. Lappert, *J. Organometallic Chem.*, 1976, **114**, C4.
[2] O. J. Scherer and N. Kuhn, *Chem. Ber.*, 1974, **107**, 2123.
[3] B. W. Fullam, S. P. Mishra, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 2145.
[4] D. Griller, B. P. Roberts, A. G. Davies, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 554.
[5] L. Ginet and M. Geoffroy, *Helv. chim. Acta*, 1974, **57**, 1761.
[6] A. Hudson and R. F. Treweek, *J.C.S. Faraday II*, 1976, 855.
[7] J. R. Preer, F-D. Tsay and H. B. Gray, *J. Amer. Chem. Soc.*, 1972, **94**, 1875; A. R. Lyons and M. C. R. Symons, *J. Amer. Chem. Soc.*, 1973, **95**, 3483.
[8] J. D. Cotton, C. S. Cundy, D. H. Harris, A. Hudson, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1974, 651.