Bulky Alkyls, Amides, and Aryloxides of Main Group 5 Elements. Part 1. Persistent Phosphinyl and Arsinyl Radicals ·MRR′ and their Chloro-precursors MRR′Cl and Related Compounds

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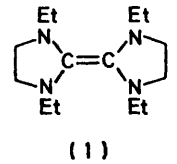
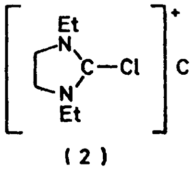
Interaction of LiR [R = $CH(SiMe_3)_2$ or $N(SiMe_3)_2$] and MCl_3 in appropriate stoicheiometry affords the following new compounds: $M[CH(SiMe_3)_2]Cl_2$ or $M[CH(SiMe_3)_2]_2Cl$ (M = P, As, or Sb), $M[N(SiMe_3)_2]Cl_2$ or $M[N(SiMe_3)_2]_2Cl$ (M = As or Sb), or $Bi[N(SiMe_3)_2]_3$. Reaction of $P(NPr^i_2)Cl_2$ with $Li[N(SiMe_3)_2]{\cdot}OEt_2$, $Li[N(CMe_3)(SiMe_3)]$, $Li[CH(SiMe_3)_2]$, $MgBu^tBr$, or $NHPr^i_2$ yields the corresponding new compound $P(NPr^i_2)RCl$, while $Li[CH(SiMe_3)_2]$ with $P(NMe_2)Cl_2$ affords $P[CH(SiMe_3)_2](NMe_2)Cl$. Reduction of the appropriate phosphorus(III) or arsenic(III) monochloride in toluene by photolysis with the olefin $[Et\overline{N(CH_2)_2N(Et)C}{=}\overline{CN(Et)(CH_2)_2N}Et$ gives the persistent ($t_{\frac{1}{2}}$ = 3 days to > 1 year in PhMe at 300 K) phosphorus(II) or arsenic(II) alkyl or amide: $\cdot M[CH(SiMe_3)_2]_2$ (M = P or As), $\cdot M[N(SiMe_3)_2]_2$, $\cdot P[CH(SiMe_3)_2](NR_2)$ (R = Pr^i or $SiMe_3$), $\cdot P(NPr^i_2)[N(SiMe_3)_2]$, $\cdot P[N(CMe_3)(SiMe_3)]_2$, or $\cdot P(NPr^i_2)[N(CMe_3)(SiMe_3)]$. Electron spin resonance parameters are discussed.

THE principal objective of this series is to explore the scope of bulky alkyl, amido-, aryloxy-, and related ligands (generally free from a β-hydrogen atom) in the context of the compounds which they form with the main Group 5 elements.

The Sussex workers have previously published on the following: $Me_3SiCH_2^-$, $Me_3CCH_2^-$, $(Me_3Si)_2CH^-$, Ph_2CH^-, $o\text{-}C_6H_4(CH_2^-)_2$, $(R_3Si)_2N^-$ (R = Me or Et), $(Me_3Si)(Me_3C)N^-$, $(R_3Ge)_2N^-$, $(Ph_3Ge)_2N^-$, $Me_2\overline{C(CH_2)_3CMe_2N}^-$, $(Me_3C)_2N^-$, $2,6\text{-}Bu^t_2C_6H_3O^-$, $4\text{-}Me\text{-}2,6\text{-}Bu^t_2C_6H_2O^-$, and $2,4,6\text{-}Bu^t_3C_6H_2O^-$ (see refs. 1—3). A feature of these ligands is that they often confer kinetic stability on unusual compounds which, when containing numerous methyl groups, are usually conveniently soluble in hydrocarbon solvents. Particularly relevant to the subject matter of the present paper are the subvalent Group 4 metal alkyls and amides, such as the monomeric gaseous (at 100 °C and 10^{-2} atm) † $Sn[N(SiMe_3)_2]_2$,[4] and the σ radicals $\cdot M[CH(SiMe_3)_2]_3$ (M = Si, Ge, or Sn[5]), $\cdot M'[N(SiMe_3)_2]_3$ (M′ = Ge or Sn), $\cdot M'[N(CMe_3)(SiMe_3)]_3$, $\cdot M'[N(GeMe_3)_2]_3$,[6] and $\cdot Sn[N(GeEt_3)_2]_3$, which are indefinitely persistent at *ca.* 25 °C in solution in n-hexane or benzene, except for $\cdot Si[CH(SiMe_3)_2]_3$ for which $t_{\frac{1}{2}}$ is *ca.* 10 min.[5] One of us (H. G.) has a longstanding commitment to phosphorus and arsenic organometallic chemistry.[7] The Sussex–Los Angeles collaboration thus derives from complementary interests, and the initial impetus was provided by a sabbatical year (1975—1976) which H. G. spent in Brighton.

The present paper concerns (*i*) the synthesis of bulky trivalent alkyl- or amido-phosphorus, -arsenic, or -antimony chlorides, (*ii*) their characterisation, and (*iii*) their use as precursors for bivalent alkyl- or amido-metal-centred radicals. A preliminary communication dealing with a few of these compounds has been published.[8] With reference to item (*iii*), the use of an electron-rich olefin, such as (1), as a reducing agent under photolytic conditions was based on the discovery of this procedure for the conversion of a tetravalent trialkyl Group 4 metal chloride to the trivalent metal-centred radical,[9] with the insoluble electron-rich carbonium ion salt, such as (2), as the by-product. The theme of item (*ii*) is taken up again in Part 2, with special emphasis on the problem of the activation energy to rotation about P–N or P–C bonds for some of the phosphorus(III) compounds.[10]


(1)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Although the first aminyl radical, $\cdot NPh_2$, was produced as long ago as 1911, it is only comparatively recently that a large number of these species has been characterised,[11] principally by e.s.r. spectroscopy. Phosphinyl radicals, $\cdot PR_2$, have also attracted interest in recent years [12] but the remaining Group 5 elements have received little attention. The chemical and spectroscopic properties of aminyl [11] and phosphinyl [12] radicals have been the subject of review articles. Since the survey by Bentrude in 1973,[12] several uncertain assignments in the e.s.r. spectra of phosphinyl radicals prepared in polycrystalline matrices have been resolved. In particular, reliable data are now available for $\cdot PF_2$[13] and $\cdot PPh_2$.[14] Perhaps the most detailed information on radicals of this type is provided by single-crystal e.s.r. studies of $\cdot PPh_2$,[14,15] $\cdot AsPh_2$,[16] and, most recently, $\cdot SbPh_2$.[17] The results leave little doubt that all these species have highly bent structures with bond angles in the range 90—100° and the unpaired electron in a p_π valence orbital of the Group 5 element. This conclusion is supported by *ab initio* calculations on simple phosphinyl radicals.[18] The bond angles in aminyl radicals are somewhat larger and lie in the range 110—115°.

However, apart from aminyl radicals, e.s.r. studies

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† Throughout this paper: 1 atm = 101 325 Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

TABLE 1

Some properties of the radical precursors, alkyl- or amido-phosphorus(III) and arsenic(III) chlorides, or antimony(III) analogues, and of Bi[N$(SiMe_3)_2]_3$

Compound	B.p. (°C/mmHg)	^{1}H n.m.r. data in C_6H_6			
		τ(MCH)	τ($SiMe_3$)	*J*(HCP)[a]	*J*(HCSiCP)[a]
P[CH$(SiMe_3)_2$]Cl_2[b]	97—100/5	8.72	9.6	14.0	
P[CH$(SiMe_3)_2]_2$Cl[c]	(m.p. 62—64 °C)	8.6	9.5 (d of d)	7.50	0.8, 1.2
As[CH$(SiMe_3)_2$]Cl_2	94—96/3	8.68	9.48		
As[CH$(SiMe_3)_2]_2$Cl	(m.p. 70—72 °C)	8.75	9.52 (complex)		
As[N$(SiMe_3)_2$]Cl_2	96—98/4		9.69		
As[N$(SiMe_3)_2]_2$Cl	140—142/3		9.58		
Sb[CH$(SiMe_3)_2]_2$Cl	134—136/1	8.80	9.53 (complex)		
Sb[N$(SiMe_3)_2]_2$Cl	124—128/2		9.59		
Bi[Ni$(SiMe_3)_2]_3$	(m.p. *ca.* 90 °C decomp.)		9.58		

[a] *J* values in Hz. [b] ^{31}P chemical shift in 15% C_6D_6–C_6H_6, −225.8 p.p.m. from 85% H_3PO_4 (*i.e.*, downfield from H_3PO_4); ^{13}C n.m.r. in 15% C_6D_6–C_6H_6 relative to $SiMe_4$: 4.43 ($SiMe_3$), 35.2 (CH) p.p.m., *J*(CSiC*P*) = 5.9 Hz and *J*(C*P*) = 79.4 Hz. [c] ^{31}P chemical shift in 15% C_6D_6–C_6H_6, −150.5 p.p.m. from 85% H_3PO_4; ^{13}C n.m.r. in 15% C_6D_6–C_6H_6 relative to $SiMe_4$: 4.08 and 2.47 (diastereotopic $SiMe_3$), 24.07 (CH) p.p.m., *J*(CSiC*P*) = 2.9 and 7.4 Hz, *J*(C*P*) = 73.5 Hz.

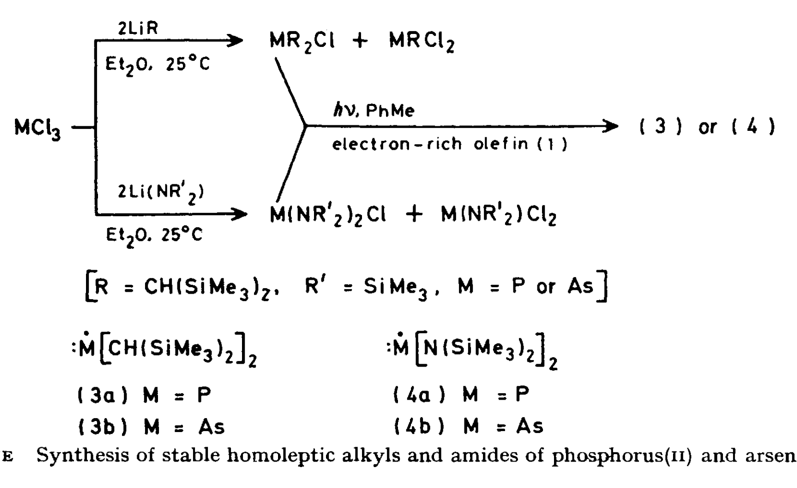
have been almost exclusively confined to the solid state. Only the transient radicals ·P$(OEt)_2$, and ·P$(NMe_2)_2$ have been reported [19] in fluid solution when they were found to recombine at the diffusion controlled limit. It was concluded from this work that ' there does not appear to be much likelihood that an unconjugated, long-lived neutral *P*-centred radical will be prepared '.

In this paper we report the preparation and solution e.s.r. spectra of a series of novel phosphinyl and arsinyl radicals. The main feature of interest lies in the extreme persistence of the radicals, which exhibit half lives as long as 3 months at ambient temperatures. This stability has been achieved, as indicated in a preliminary communication,[8] by the use of bulky alkyl or amido-ligands previously employed in the generation of persistent silyl, germyl, and stannyl radicals.[5,6]

RESULTS AND DISCUSSION

Synthesis and Characterisation of the Alkyl- or Amido-metal(III) *Chlorides* MCl_nR_{3-n}, $MCl_n(NR'_2)_{3-n}$ [M = P, As, *or* Sb; n = 1, 2, *or* 3; R = CH$(SiMe_3)_2$; *and* R' = $SiMe_3$], *and of* Bi[N$(SiMe_3)_2]_3$.—Addition of lithiobis(trimethylsilyl)methane or lithiobis(trimethylsilyl)amide in diethyl ether to the appropriate metal(III) chloride yielded the appropriate mixed alkyl- or amido-metal(III) chloride. In the case of the $BiCl_3$–2Li[N$(SiMe_3)_2$] system, the only identified product was Bi[N$(SiMe_3)_2]_3$. Details are in Table 1. The compound P[N$(SiMe_3)_2]_2$Cl has been reported previously,[20] and the arsenic analogue has been mentioned; [21] the former readily eliminated $SiMe_3$Cl to yield $Me_3SiN{=}PN(SiMe_3)_2$,[20] while the latter upon heating was said to lose N$(SiMe_3)_3$ to afford $[As(NSiMe_3)Cl]_n$.[21] Details on the preparation of other amido-phosphorus(III) chlorides, which were used as precursors to phosphorus-centred radicals, are in the Experimental section, but ^{1}H n.m.r. data on these are in Part 2 [10] together with variable-temperature n.m.r. studies and calculations of P–N rotational barriers; these compounds are P[CH$(SiMe_3)_2$](NMe_2)Cl, P[CH$(SiMe_3)_2$](NPr^i_2)Cl, $PBu^t(NPr^i_2)$Cl, PBu^t[N$(SiMe_3)_2$]Cl, $P(NPr^i_2)_2$Cl, $P(NPr^i_2)$[N$(SiMe_3)_2$]Cl, and $P(NPr^i_2)$[N$(CMe_3)(SiMe_3)$]Cl. The compound ·P$(C_6H_2Me_3$-2,4,6)[N$(SiMe_3)_2$] was prepared by Dr. A. El-Soueni.[22]

The Generation of Phosphorus(II)- *and Arsenic*(II)-*centred Radicals*.—Persistent homoleptic alkyls and amides of phosphorus, (3a) and (4a), and As, (3b) and (4b), were prepared (Scheme) by photolysis of degassed toluene solutions of the corresponding three-co-ordinate chlorides in the presence of an electron-rich olefin.[9] Heteroleptic analogues (5)—(11) were obtained similarly



SCHEME Synthesis of stable homoleptic alkyls and amides of phosphorus(II) and arsenic(II) from the appropriate phosphorus(III) chloride. Electron spin resonance signals were detected, using Varian E3 and E104A spectrometers,[5] except from $PBu^t(NPr_2)Cl$, $PBu^t[N(SiMe_3)_2]Cl$, and $P(NPr^i_2)_2Cl$ The e.s.r. spectrum of $P[CH(SiMe_3)_2]_2$, (3a), has been published previously;[6] the spectrum of the analogous arsinyl radical (3b) is shown in Figure 1. The e.s.r. results are summarised in Table 2. Approximate $g_{av.}$ values were obtained by comparison of the magnetic field at the centre of the spectrum with diphenylpicrylhydrazyl (dpph) ($g =$ 2.003 6) and are uncorrected for second-order hyperfine splitting. The e.s.r. spectra of the phosphinyl radicals (3a) (Figure 2) and (4a) (Figure 3) and the arsinyl radical (3b) (Figure 4) were also recorded in polycrystalline matrices by freezing solutions of the radicals at low temperature (*ca.* −150 °C). The analysis of the phosphinyl spectra was checked by computer simulation.[23] When reduction of $Sb(Cl)R_2$ [$R = CH(SiMe_3)_2$ or $N(SiMe_3)_2$] was attempted, using similar conditions (see Scheme), metallic antimony was deposited.

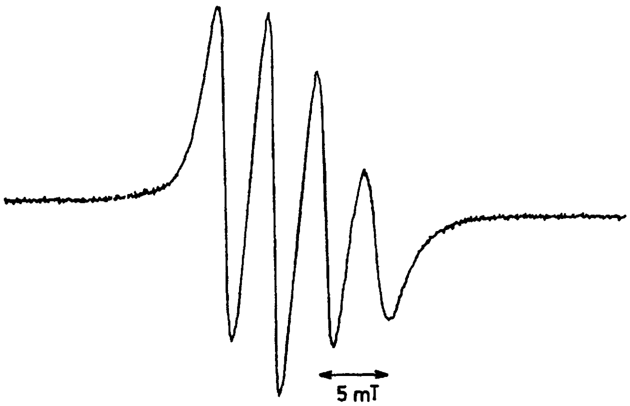


FIGURE 1 E.s.r. spectrum of $\cdot As[CH(SiMe_3)_2]_2$ in PhMe at *ca.* 300 K

TABLE 2

E.s.r. parameters for the phosphorus(II) and arsenic(II) alkyls and amides in toluene solution at *ca.* 300 K

		a(M)/mT	a(H)/mT	$a(^{14}N)$/mT	$g_{av.}$	$t_{\frac{1}{2}}$
(3a)	$:\dot{P}[CH(SiMe_3)_2]_2$	9.63	0.640		2.009	> 1 year
(3b)	$:As[CH(SiMe_3)_2]_2$	3.72			2.04	*ca.* 10 days
(4a)	$:\dot{P}[N(SiMe_3)_2]_2$	9.18			2.008	*ca.* 5 days
(4b)	$:As[N(SiMe_3)_2]_2$	3.18			2.008	*ca.* 15 days
(5)	$:\dot{P}[CH(SiMe_3)_2][N(SiMe_3)_2]$	9.30	0.81		2.008	*ca.* 10 days
(6)	$:\dot{P}[CH(SiMe_3)_2](NPr^i_2)$	6.3		0.37	2.005	*ca.* 1 day
(7)	$:\dot{P}(NPr^i_2)[N(SiMe_3)_2]$	7.72		0.52	2.007	*ca.* 1 day
(8)	$:\dot{P}[N(CMe_3)(SiMe_3)]_2$	10.15			2.007	*ca.* 5 days
(9)	$:\dot{P}(NPr^i_2)[N(CMe_3)(SiMe_3)]$	7.40		0.51	2.007	*ca.* 3 days
(10)	$:\dot{P}[CH(SiMe_3)_2](NMe_2)$	6.5			2.008	
(11)	$:\dot{P}(C_6H_2Me_3\text{-}2,4,6)[N(SiMe_3)_2]$	9.67			2.008	

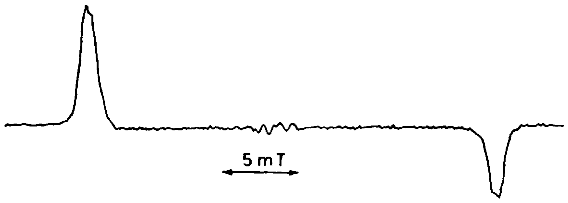


FIGURE 2 E.s.r. spectrum of $\cdot P[CH(SiMe_3)_2]_2$ in frozen PhMe

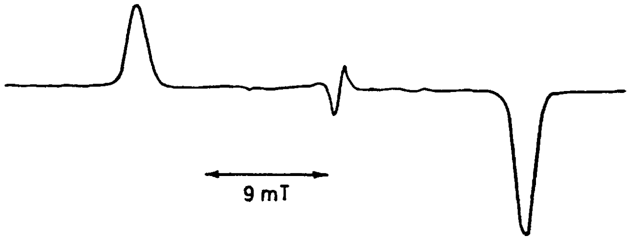


FIGURE 3 E.s.r. spectrum of $\cdot P[N(SiMe_3)_2]_2$ in frozen PhMe

The Phosphinyl Radicals.—The main interest in the two-co-ordinate *P*-centred radicals listed in Table 2 lies in their stability which we attribute to the steric effects of bulky ligands which stabilise the monomeric radicals, relative to the P–P bonded dimers, and which slow down reaction at phosphorus. The solution e.s.r. spectra at 300 K consist of a large ^{31}P doublet similar in magnitude to values found for phosphinyls in the solid state,[12,24] and in solution.[19,25] The structural similarity to other phosphinyls is also reflected in the solid-state spectra of $\cdot P[CH(SiMe_3)_2]_2$, (3a), and $\cdot P[N(SiMe_3)_2]_2$, (4a). The bis(amido)-radical (4a) has a large parallel hyperfine splitting (29.4 mT) and a small perpendicular component (−0.93 mT). The corresponding values for the bis(alkyl) species (3a) are 29.1 mT and −0.10 mT. The perpendicular components have been chosen to give agreement with the isotropic hyperfine splittings observed in fluid solution.

In a number of cases the solution e.s.r. spectra also exhibit coupling to ligand protons or ^{14}N atoms. A noteworthy feature is the contrast between radicals having alkylamido- and silylamido-substituents. The former have lower ^{31}P coupling constants and exhibit coupling to the ^{14}N nucleus. Compare, for example, the data for the radicals (4a), (5), or (6) (Table 2) with $\cdot P(NMe_2)_2$ which has $a(^{31}P) = 7.02$ mT and $a(^{14}N) =$ 0.42 mT.[19] No resolvable coupling is found for nitrogen with silyl substituents. Thus, we presume that the nitrogen coupling observed in $\cdot P(NPr^i_2)[N(SiMe_3)_2]$ (Figure 5) is due to NPr^i_2. The increase in $a(^{31}P)$ suggests a higher spin density on phosphorus in the silylamido-radicals and a decrease in P–N p_π–p_π interaction.

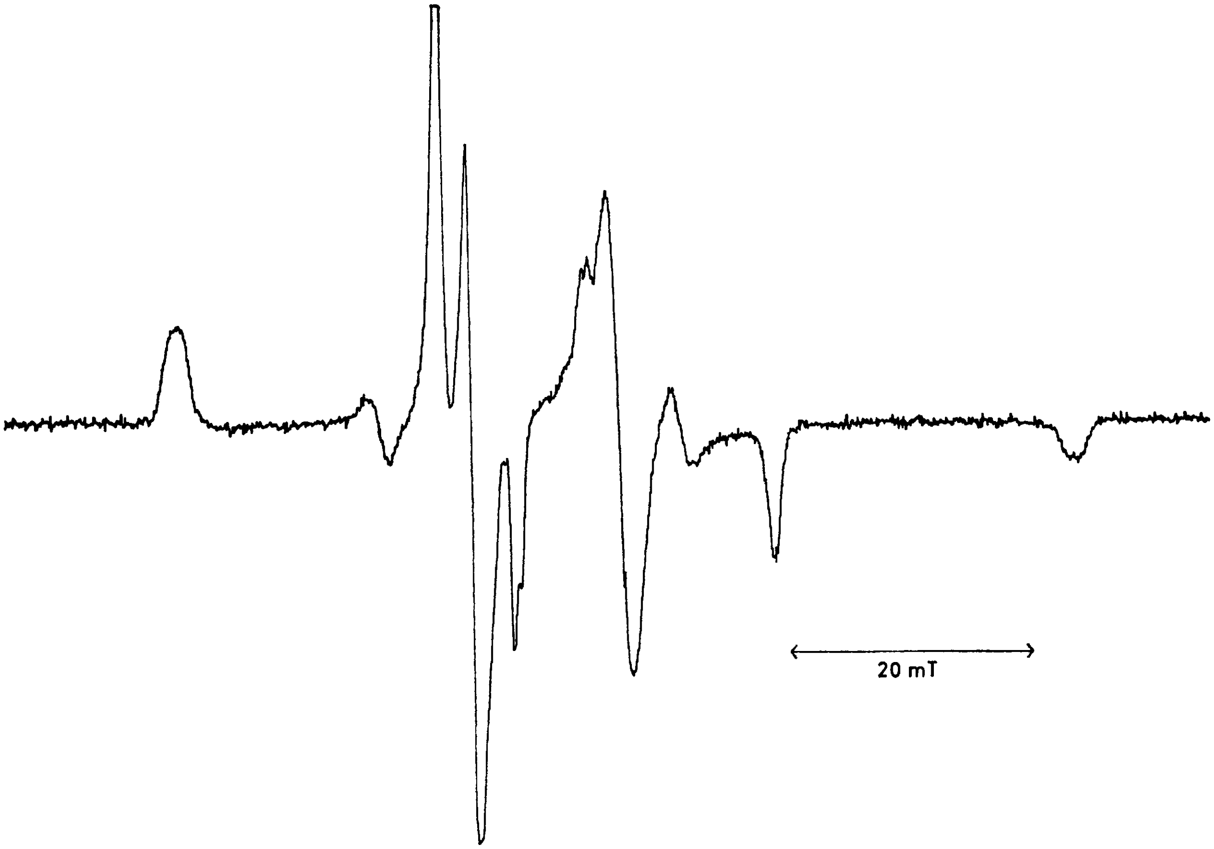


FIGURE 4 E.s.r. spectrum of ·$As[CH(SiMe_3)_2]_2$ in frozen PhMe

The Arsinyl Radicals.—The room-temperature e.s.r. solution spectra of ·$As[CH(SiMe_3)_2]_2$, (3b), and ·$As[N(SiMe_3)_2]_2$, (4b), both consist of a 1 : 1 : 1 : 1 quartet. The lines are quite broad (Figure 1) and no ligand coupling was resolvable. The hyperfine structure collapsed as the temperature was lowered, probably due to quadrupole relaxation of the ^{75}As nuclear spin. However, a strong solid-state spectrum of the bis(alkyl) radical (3b) was obtained from a frozen solution. Previous work on arsinyl radicals has been limited to studies of ·$AsMe_2$ and similar species in irradiated polycrystalline matrices [26,27] and a single-crystal study [16] of ·$AsPh_2$. In the latter investigation the ^{75}As hyperfine interaction had parallel and perpendicular components of 22.5 and −3.8, −4.4 mT respectively. This gives an isotropic component of 4.75 mT comparable in magnitude with our results for radicals (3b) and (4b). The solid-state spectrum of (3b) has strong parallel features separated by 24.5 mT and using our solution result we estimate a perpendicular splitting of −6.7 mT. The perpendicular region of the polycrystalline spectrum is complicated by the presence of quadrupole effects. A complete determination of the ^{75}As nuclear quadrupole interaction was made in the single-crystal study of ·$AsPh_2$ already referred to.[16] Investigations of ·$AsPh_2$ and ·$AsMe_2$ in irradiated frozen solutions [26,27] gave similar values for the parallel hyperfine splittings (22.0 mT) but the assumption of a near-zero value for the perpendicular component is inconsistent both with the results of the single-crystal study of ·$AsPh_2$ and with our own work and would appear to be in error.

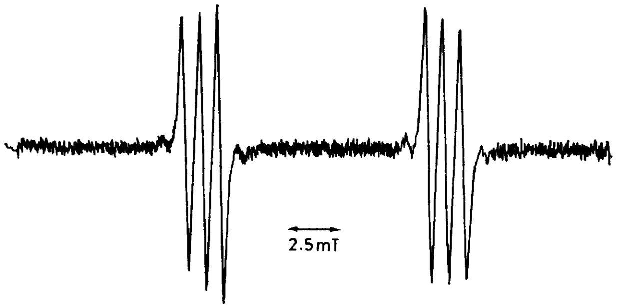


FIGURE 5 E.s.r. spectrum of ·$P(NPr^i_2)[N(SiMe_3)_2]$ in PhMe at 300 K

EXPERIMENTAL

Manipulative techniques relevant to synthetic procedures are described in ref. 6, while those concerned with e.s.r. spectroscopy are considered in ref. 5.

[Bis(trimethylsilyl)methyl]dichlorophosphorus.—A diethyl ether solution of bis(trimethylsilyl)methyl-lithium (15 mmol in 20 cm^3) was added dropwise to an ice-cooled diethyl ether solution (25 cm^3) of phosphorus trichloride (1.35 cm^3, 15 mmol). A white precipitate of lithium chloride was immediately produced and after stirring for 2 h the volatiles were removed *in vacuo*. The residue was extracted with n-pentane and the solution filtered. The pentane was removed by distillation and the residual pale yellow liquid

was distilled under reduced pressure to afford *[bis(trimethylsilyl)methyl]dichlorophosphorus* (2.8 g, 73%) as a colourless liquid, b.p. 98—100 °C (5 mmHg) (Found: C, 32.3; H, 7.1. $C_7H_{19}Cl_2PSi_2$ requires C, 32.2; H, 7.3%).

Bis[bis(trimethylsilyl)methyl]chlorophosphorus.—A diethyl ether solution of bis(trimethylsilyl)methyl-lithium (20 mmol in 25 cm^3) was added dropwise to a stirred ice-cooled solution of phosphorus trichloride (0.9 cm^3, 10 mmol) in diethyl ether (20 cm^3). A white precipitate of lithium chloride was immediately produced and when the addition of the lithium reagent was complete the solution was refluxed for 2 h. The volatiles were removed *in vacuo*. Extraction of the residue with n-pentane, filtration of the solution, and removal of the n-pentane *in vacuo* afforded a pale yellow viscous oil. Distillation under reduced pressure afforded *bis[bis(trimethylsilyl)]chlorophosphorus* (2.3 g, 60%) as a colourless viscous oil which slowly crystallised at 25 °C, b.p. 148—150 °C (4 mmHg), m.p. 62—64 °C (Found: C, 43.2; H, 4.9. $C_{14}H_{38}ClPSi_4$ requires C, 43.7; H, 4.95%).

[Bis(trimethylsilyl)methyl]dichloroarsenic.—A diethyl ether solution of bis(trimethylsilyl)methyl-lithium (10 mmol in 20 cm^3) was added dropwise to a cooled solution of arsenic trichloride (1.81 g, 10 mmol) in diethyl ether (15 cm^3) with stirring. The solution was stirred for a further 2 h and the volatiles were removed *in vacuo*. Extraction of the residue with n-pentane, filtration, and distillation of the solution afforded *[bis(trimethylsilyl)methyl]dichloroarsenic* (2.13 g, 70%) as a colourless liquid, b.p. 96—98 °C (4 mmHg) (Found: C, 28.0; H, 6.10. $C_7H_{19}AsCl_2Si_2$ requires C, 27.6; H, 6.25%).

Bis[bis(trimethylsilyl)methyl]chloroarsenic.—A diethyl ether solution of bis(trimethylsilyl)methyl-lithium (20 mmol in 35 cm^3) was added dropwise to a cooled solution of arsenic trichloride (1.8 g, 10 mmol) in diethyl ether (20 cm^3). The volatiles were removed *in vacuo* after stirring for 2 h. Extraction of the residue with pentane followed by filtration and distillation under reduced pressure afforded *bis[bis(trimethylsilyl)methyl]chloroarsenic* (2.51 g, 61%) as a colourless oil which solidified on cooling, b.p. 142—144 °C (3 mmHg), m.p. 70—72 °C (Found: C, 38.9; H, 8.75. $C_{14}H_{38}AsClSi_4$ requires C, 39.2; H, 8.95%).

Bis[bis(trimethylsilyl)methyl]chloroantimony.—A diethyl ether solution of bis(trimethylsilyl)methyl-lithium (20 mmol in 40 cm^3) was added dropwise to a cooled solution of antimony trichloride (2.25 g, 10 mmol) in diethyl ether (20 cm^3). The solution was stirred for 2 h and refluxed for a further 1 h. The volatiles were removed *in vacuo* and the residue was dissolved in n-pentane, the solution filtered, and distilled under reduced pressure to afford *bis[bis(trimethylsilyl)methyl]chloroantimony* (3.1 g, 65%) as a colourless oil, b.p. 147—149 °C (2 mmHg) (Found: C, 35.3; H, 7.85. $C_{14}H_{38}ClSbSi_4$ requires C, 35.3; H, 8.05%).

[Bis(trimethylsilyl)amido]dichloroarsenic.—Bis(trimethylsilyl)amidolithium monoetherate (2.01 g, 8.3 mmol) was added slowly to a solution of arsenic trichloride (1.5 g, 8.25 mmol) in diethyl ether (20 cm^3) and stirred for 2 h. Removal of volatiles *in vacuo*, extraction with n-pentane, filtration, and distillation under reduced pressure afforded *[bis(trimethylsilyl)amido]dichloroarsenic* (2.1 g, 84%) as a colourless liquid, b.p. 95—97 °C (4 mmHg) (Found: C, 23.4; H, 5.6; N, 4.60. $C_6H_{18}AsCl_2NSi_2$ requires C, 23.5; H, 5.90; N, 4.55%).

Bis[bis(trimethylsilyl)amido]chloroarsenic.—Bis(trimethylsilyl)amidolithium monoetherate (6.59 g, 27 mmol) was added slowly to a cooled diethyl ether (40 cm^3) solution of arsenic trichloride (1.44 cm^3, 13.5 mmol) with stirring. After 2 h the volatiles were removed, the residue extracted with n-pentane, and filtered. Distillation of the filtrate afforded *bis[bis(trimethylsilyl)amido]chloroarsenic* (4.3 g, 76%), b.p. 138—142 °C (3 mmHg) (Found: C, 34.8; H, 8.15; N, 6.40. $C_{12}H_{36}AsClN_2Si_4$ requires C, 34.5; H, 8.4; N, 6.50%).

Bis[bis(trimethylsilyl)amido]chloroantimony.—Bis(trimethylsilyl)amidolithium monoetherate (4.82 g, 17.7 mmol) was added slowly to a diethyl ether solution of antimony trichloride (2.02 g, 8.8 mmol) and stirred for 2 h. The volatiles were removed *in vacuo* and the residue extracted with n-pentane and filtered. The n-pentane was removed from the filtrate *in vacuo* and the remaining pale yellow oil was distilled to afford *bis[bis(trimethylsilyl)amido]chloroantimony* (2.86 g, 68%) as a viscous colourless oil, b.p. 145—147 °C (1 mmHg) (Found: C, 32.0; H, 7.3; N, 5.45. $C_{12}H_{36}ClN_2SbSi_4$ requires C, 31.5; H, 7.60; N, 5.85%).

Reaction between $BiCl_3$ *and* $Li[N(SiMe_3)_2]{\cdot}Et_2O$.—Bis(trimethylsilyl)amidolithium monoetherate (3.2 g, 13.25 mmol) was added slowly to a cooled solution of $BiCl_3$ (2.1 g, 6.6 mmol) in diethyl ether (25 cm^3) and stirred for 2 h. The volatiles were removed *in vacuo* from the orange solution, the residue extracted with n-pentane, and filtered. The filtrate was reduced in volume to *ca.* 4 cm^3 and cooled to −78 °C, affording pale yellow crystals. The supernatant solution, on removal of volatiles, afforded an orange oil which gave a complex ^1H n.m.r. spectrum in the $SiMe_3$ region. The pale yellow crystals gave a singlet (τ 9.58) in the $SiMe_3$ region. The analysis indicated that these crystals were probably $Bi[N(SiMe_3)_2]_3$ (1.38 g, 30%), m.p. 90 °C (decomp.) (Found: C, 29.6; H, 7.65; N, 5.80. $C_{18}H_{54}BiN_3Si_6$ requires C, 30.3; H, 7.90; N, 6.10%).

[Bis(trimethylsilyl)amido]chloro(di-isopropylamido)phosphorus.—Bis(trimethylsilyl)amidolithium monoetherate (1.0 g, 4.14 mmol) was added slowly to a diethyl ether solution (25 cm^3) of dichloro(di-isopropylamido)phosphorus (0.828 g, 4.15 mmol) and stirred for 2 h. The volatiles were removed *in vacuo* and n-pentane (20 cm^3) was added; the solution was filtered and the volume of the filtrate reduced to *ca.* 7 cm^3 *in vacuo*. Cooling to −78 °C afforded colourless crystals of *the title compound* (0.98 g, 72%), b.p. 85—86 °C (1 mmHg) (Found: C, 43.9; H, 9.65; N, 8.50. $C_{12}H_{32}ClN_2PSi_2$ requires C, 44.1; H, 9.85; N, 8.55%).

[Bis(trimethylsilyl)methyl]chloro(di-isopropylamido)phosphorus.—Bis(trimethylsilyl)methyl-lithium (3 mmol) in diethyl ether (10 cm^3) was added dropwise to a stirred solution of dichloro(di-isopropylamido)phosphorus (0.6 g, 3 mmol) in diethyl ether (20 cm^3). After stirring for 2 h the volatiles were removed *in vacuo* and the residue was extracted with pentane (20 cm^3) and filtered. The volume of the filtrate was reduced *in vacuo* to afford a pale yellow oily residue which was distilled under reduced pressure to afford *the title compound* (0.62 g, 63%) as a colourless oil, b.p. 98—101 °C (1 mmHg) (Found: C, 48.0; H, 10.3; N, 4.25. $C_{13}H_{33}ClNPSi_2$ requires C, 47.9; H, 10.15; N, 4.3%).

Chloro(di-isopropylamido)(t-butyl)phosphorus.—t-Butylmagnesium bromide (3.5 mmol) in diethyl ether (25 cm^3) was added dropwise to a stirred solution of dichloro(di-isopropylamido)phosphorus (0.7 g, 3.5 mmol) in diethyl ether (10 cm^3). After stirring for 2 h the volatiles were removed *in vacuo* and the residue extracted with pentane (20 cm^3) and filtered. The volatiles were removed *in vacuo* and the residue was distilled under reduced pressure to afford *the product* (0.56 g, 71%) as a colourless oil, b.p. 68—70 °C (1 mmHg) (Found: C, 53.1; H, 10.2; N, 6.4. $C_{10}H_{23}ClNP$ requires C, 53.7; H, 10.35; N, 6.25%).

Chloro(*di-isopropylamido*)[(*t-butyl*)*trimethylsilylamido*]-*phosphorus*.—t-Butyl(trimethylsilylamido)lithium (2 mmol) (synthesised by treatment of the amine with n-butyllithium) in diethyl ether (20 cm^3) was added dropwise to a stirred solution of dichloro(di-isopropylamido)phosphorus (0.4 g, 2 mmol) in diethyl ether (10 cm^3). The solution was stirred for a further 2 h and the volatiles removed *in vacuo*. The residue was extracted with pentane (15 cm^3) and filtered. The pentane was removed *in vacuo* and the residual pale yellow oil was distilled under reduced pressure to afford *the title compound* (0.373 g, 60%) as a colourless liquid, b.p. 80—81 °C (1 mmHg) (Found: C, 50.6; H, 10.1; N, 8.9. $C_{13}H_{32}ClN_2PSi$ requires C, 50.2; H, 10.3; N, 9.0%).

[*Bis*(*trimethylsilyl*)*amido*]*chloro*(*t-butyl*)*phosphorus*.—t-Butylmagnesium bromide (3 mmol) in diethyl ether (10 cm^3) was added dropwise to a stirred solution of [bis(trimethylsilyl)amido]dichlorophosphorus (0.786 g, 3 mmol) in diethyl ether (10 cm^3). The solution was stirred for a further 2 h and the volatiles removed *in vacuo* and the residue extracted with n-pentane (20 cm^3) and filtered. The pentane was removed *in vacuo* and the pale yellow residue was distilled under reduced pressure to afford *the product* (0.55 g, 65%), b.p. 74—76 °C (1 mmHg) (Found: C, 43.0; H, 9.4; N, 5.1. $C_{10}H_{27}ClNPSi$ requires C, 42.3; H, 9.50; N, 4.95%).

[*Bis*(*trimethylsilyl*)*methyl*]*chloro*(*dimethylamido*)*phosphorus*.—Bis(trimethylsilyl)methyl-lithium (4.5 mmol) in diethyl ether (10 cm^3) was added dropwise to a stirred solution of dichloro(dimethylamido)phosphorus (0.657 g, 4.5 mmol) in diethyl ether (10 cm^3). The solution was stirred for a further 2 h and the volatiles were removed *in vacuo*. The residue was extracted with pentane (15 cm^3) and filtered. The pentane was removed *in vacuo*, and the residual pale yellow oil was distilled under reduced pressure to afford *the product* (0.86 g, 70%), b.p. 86—88 °C (1 mmHg) (Found: C, 39.3; H, 9.1; N, 5.0. $C_9H_{25}ClNPSi_2$ requires C, 39.9; H, 9.25; N, 5.2%).

Chlorobis(*di-isopropylamido*)*phosphorus*.—Di-isopropylamine (4.04 g, 40 mmol) in diethyl ether (20 cm^3) was added dropwise to a cooled, stirred solution of dichloro(di-isopropylamido)phosphorus (4.0 g, 20 mmol) in diethyl ether (20 cm^3). The volatiles were removed and pentane (50 cm^3) was added. The pentane solution was cooled to 0 °C and filtered. The volume of the filtrate was reduced *in vacuo* to *ca.* 20 cm^3 and cooling of the residual solution afforded white crystals of *the product* (2.1 g, 40%), m.p. 96—98 °C (Found: C, 54.1; H, 10.4; N, 10.45. $C_{12}H_{28}ClN_2P$ requires C, 54.0; H, 10.6; N, 10.5%).

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