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Radical Ions Derived from Hydrides and Methyls of Aluminium, Silicon and Phosphorus: a Semi-Empirical SCF–MO Study

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Abstract

Semi-empirical SCF–MO calculations were made of the energies, and geometric and electronic structures of a range of radical ions of type $MR_3^{\pm}$ and $M_2R_6^{\pm}$ where M = Al, Si or P, and R = H or CH_3. In each of the MH_3 radicals, methylation effects an increase in the HMH angle: the structure of $Al_2Me_6^-$, formed by γ-irradiation of Al_2Me_6, is found to have C_s symmetry and to resemble a weak complex of $AlMe_2$ and $AlMe_4^-$. Possible identities for the radical, other than AlH_3^-, formed on γ-irradiation of $LiAlH_4$ are suggested, and a considerable number of plausible identities are firmly ruled out.

Introduction

It has been deduced [1] from electron spin resonance data [2–5], that the isoelectronic hydride radicals AlH_3^-, $SiH_3^{\cdot}$, and PH_3^+ have very similar 3s character in the SOMO, and hence very similar geometric structures. On the other hand, the corresponding methyl radicals $AlMe_3^-$, $SiMe_3^{\cdot}$, and PMe_3^+ appear to exhibit a variation in structure [1, 6, 7], indicative of considerable flattening upon methylation from PH_3^+ to PMe_3^+, but rather little geometric change from $SiH_3^{\cdot}$ to $SiMe_3^{\cdot}$: the original [5] assignment for $AlMe_3^-$ has recently been questioned [3], and it is now suggested [3] that the species originally described as $AlMe_3^-$ was in fact a bridged dimer $Al_2Me_6^-$ having the SOMO in some way concentrated on just one of the aluminium centres, since hyperfine coupling to just one ^{27}Al nucleus was observed [3, 5]. On the basis of the earlier assignment [5] for $AlMe_3^-$, it was deduced that methylation at aluminium caused an increase in pyramidality, from AlH_3^- to $AlMe_3^-$, that is the opposite of the change found in the phosphorus cation radicals.

Here we report semi-empirical calculations relevant to the questions of the structural variations between MH_3 and MMe_3 radicals (M = Al, Si, P); the geometric and electronic structure of $AlMe_3^-$ and $Al_2Me_6^-$; the impurity-derived radical, denoted X [3], formed from γ-irradiation of $Bu_4N^+AlH_4^-$; and possible structures of the dinuclear hydride and methyl radicals $Al_2R_6^-$, $Si_2R_6^{\pm}$, and $P_2R_6^+$ (R = H, Me).

Calculations

All calculations were carried out using the MNDO method [8–10] implemented on a VAX 11/780 computer, with the published parameterization, and UHF wavefunctions for all open-shell species: we have demonstrated previously [11–13] that this semi-empirical SCF method yields entirely satisfactory results for free radicals containing heteroatoms.

In general, all internal geometric variables were optimised independently and simultaneously, without constraints: additionally, the effect of applying specific symmetry constraints was also investigated in a number of cases.

Results and Discussion

The Structures of MH_3 and MMe_3

The optimised values of the angles <(HMH) in the hydride radicals MH_3 (M = Al^-, $Si^{\cdot}$, and P^+) and <(CMC) in the corresponding methyl radicals MMe_3 are recorded in Table I, along with values deduced [3, 5] from e.s.r. data, where these are known. The calculated value of the angle in $SiH_3^{\cdot}$ may be compared with the results of *ab initio* calculations [14]: using a basis set of double-zeta quality, the calculated value of <(HSiH) was 112.4°, while when polarisation functions were added on all atoms, the calculated value of the angle was 111.3°.

The calculated values of the angles <(HMH) and <(CMC) show that (i) the bond angle in each example MH_3 is increased upon methylation, as expected for the substitution of a ligand of lower electronegativity [15]; (ii) the change upon methylation is least for silicon and most for phosphorus, although the range spanned by Al^-, $Si^{\cdot}$, and P^+ is not large; (iii) the range of bond angles spanned by the hydrides, 3.1° is smaller than that spanned by the

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TABLE I. Optimised Molecular Parameters for MH_3 and MMe_3 Radicals.

M	MH_3			MMe_3		
	ΔH_f°/kJ mol^{-1}	<(HMH)/° (calc)	<(HMH)/° (e.s.r.)	ΔH_f°/kJ mol^{-1}	<(CMC)/° (calc)	<(CMC)/° (e.s.r.)
Al^-	+76.6	110.5	[a]	−221.7	115.1	107.9[b,c]
$Si^\bullet$	+156.6	110.0	112.8[b]	−182.1	113.5	113.3
P^+	+1029.9	113.1	113.9[b]	+664.0	118.1	115.5[d]

[a] Not reported. [b] Ref. 5. [c] Assignment doubtful (ref. 3): see text. [d] Value for PEt_3^+ (ref.5): calculated value for PEt_3^+ is 118.4°.

TABLE II. Calculated Spin-Densities and Observed Central-Atom Hyperfine Couplings in MH_3 and MMe_3.

M[a]	MH_3			MMe_3		
	ρ(M)	*A*(M)/G[b]	[A/ρ]/G	ρ(M)	*A*(M)/G	[*A*/ρ]/G
Al^-	0.2673	154[c]	576	0.1757	324[f]	1844
$Si^\bullet$	0.2162	190[d]	879	0.2050	191[g]	932
P^+	0.1396	517[e]	3703	0.0774	385[h]	4974

[a] M = ^{27}Al, ^{29}Si, ^{31}P. [b] G = 10^{-4} T. [c] Ref. 2. [d] G. S. Jackel and W. Gordy, *Phys. Rev., 176,* 443 (1968). [e] Ref. 5. [f] Assignment doubtful (ref. 3): see text. [g] Ref. 6. [h] M. C. R. Symons and G. D. G. McConnachie, *J. Chem. Soc., Chem. Commun.*, 851 (1982). See also ref. 1.

methyls, 4.6°. So far as these angles are known from e.s.r. data [3, 5], the trends in the calculated angles mirror those in the experimental values. Of the data in Table I, only the observed value for $AlMe_3^-$ is seriously out of line with the other angles.

A further indication that the original assignment [5] for $AlMe_3^-$ may be incorrect [3] is given by a comparison of the calculated ρ(M) values with the observed isotropic *A*(M) values in the two series of radicals MH_3 and MMe_3. These data are recorded in Table II. Because there are, as yet, no reliable scale factors relating ρ(M) to *A*(M) available in the MNDO parameterization for M = ^{27}Al, ^{29}Si or ^{31}P, Table II is based upon a comparison of the ratio A/ρ for corresponding radicals MH_3 and MMe_3. For each of M = ^{29}Si and ^{31}P, the values of A/ρ are adequately similar for MH_3 and MMe_3: however when M = ^{27}Al the ratio A/ρ is quite different for AlH_3^- and for $AlMe_3^-$. Since the assignment for AlH_3^- appears to be entirely secure [2, 3], this result is consistent with the geometrical data in Table I in casting further doubt [3] upon the original assignment [5] for $AlMe_3^-$. The question of the exact nature of the species described earlier as $AlMe_3^-$ will be returned to below.

The Anion Radical $Al_2Me_6^-$

The radical originally assigned [5] as $AlMe_3^-$ was produced by γ-irradiation of aluminium trimethyl. This compound is dimeric both in the solid state and in solution in non-coordinating solvents [16–18], having a bridged structure, $Me_2Al(\mu_2\text{-}Me)_2AlMe_2$, of overall D_{2h} symmetry. Consequently, plausible formulations for the radical species produced by electron attachment include not only $AlMe_3^-$ but also $Al_2Me_6^-$ for which either an unbridged ethane-type σ radical (iso-electronic with $Me_6C_2^+$) or a bridged diborane-type structure is possible. Optimisations of the structure of $Al_2Me_6^-$ were therefore made based upon starting connectivities for the heavy atoms of both ethane-type and diborane-type: at the same time, optimisations were made for a series of methyl–aluminium fragments: $AlMe_3$, $AlMe_3^-$, $AlMe_2^\bullet$, $AlMe_4^\bullet$ and $AlMe_4^-$, and data for all these species are given in Tables III and IV.

The global energy minimum for $Al_2Me_6^-$ is calculated to occur for the ethane-type radical structure which optimises to D_{3d} symmetry: formation of this σ radical from $AlMe_3$ and $AlMe_3^-$ is calculated to be exothermic by *ca.* 37 kJ mol^{-1}. It is a genuine σ radical, analogous to $(Me_3O)_3B\cdot B(OMe)_3^-$ [19], and has the same $^{27}Al(3s)$ spin density at each aluminium: consequently this isomer cannot be responsible for the six-line spectrum arising from γ-irradiation of Al_2Me_6, since in that radical only one ^{27}Al nucleus (I = 5/2) is coupled to the unpaired electron.

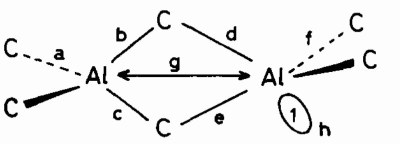
Free optimisation of the $Me_2Al(\mu_2\text{-}Me)_2AlMe_2^-$ isomer yielded a structure of precise C_s symmetry

TABLE III. Optimised Parameters for Aluminium Methyl Species.

	ΔH_f°/kJ mol^{-1}	Point group	$\rho[^{27}Al(3s)]$	Geometry
$AlMe_3$	−167.9	C_{3h}	–	d(Al–C), 1.828 A
$AlMe_3^-$	−221.7	C_{3v}	0.1757	d(Al–C), 1.849 A; <(C–Al–C), 115.1°
$AlMe_2^\bullet$	+25.5	C_{2v}	0.3679	d(Al–C), 1.818 A; <(C–Al–C), 124.2°
$AlMe_4^\bullet$ [a]	–	–	–	–
$AlMe_4$	−393.6	T_d	–	d(Al–C), 1.882 A
$Al_2Me_6^-$	−426.4	D_{3d}	0.0540(2Al)	d(Al–Al), 2.993 A; d(Al–C), 1.851 A; <(Al–Al–C), 102.6°
$Al_2Me_6^-$ [b]	−376.9	C_s	0.3844(1Al) 0.0000(1Al)	See Table IV

[a] Dissociates to $CH_3^\bullet$ and $AlMe_3$. [b] Bridged structures with imposed D_{2h} or C_{2v} symmetry have ΔH_f° of −298.4 or −369.4 kJ mol^{-1} respectively: $\rho[^{27}Al(3s)]$ of 0.261 (×2) or 0.422 (×1) and 0.000 (×1) respectively.

TABLE IV. Optimised Geometric Parameters for the C_s, Bridged, Isomer of $Al_2Me_6^-$.[a]



Distances/A		Angles/°	
a	1.880 (×2)	$a^\wedge a'$	109.7
b	1.880	$a^\wedge b$	109.4 (×2)
c	1.881	$a^\wedge c$	109.4 (×2)
d	4.449	$b^\wedge c$	109.5
e	4.491	$b^\wedge d$	105.9
f	1.822 (×2)	$c^\wedge e$	104.4
g	5.281	$d^\wedge e$	40.2
		$d^\wedge f$	92.2 (×2)
		$e^\wedge f$	109.7 (×2)
		$f^\wedge f'$	122.9
		$d^\wedge h$	126.5
		$e^\wedge h$	86.3
		$f^\wedge h$	118.3 (×2)

[a] The vector h represents the orientation of the aluminium contribution to the SOMO.

whose geometric and electronic structure indicated that it should be regarded as a weak complex of the radical $AlMe_2$ with the closed-shell anion $AlMe_4^-$ (see Tables III and IV). Not only are the geometries of the two fragments in $Al_2Me_6^-$ almost identical with those of the isolated components, but the $^{27}Al(3s)$ spin density in $Al_2Me_6^-$ is confined entirely to one aluminium atom, having a magnitude very similar to that in $AlMe_2^\bullet$. This complex, whose formation from $AlMe_2^\bullet$ and $AlMe_4^-$ is calculated to be exothermic by only 8.8 kJ mol^{-1}, has a SOMO which is concentrated largely on the aluminium of the $AlMe_2^\bullet$ fragment. The orientation of the SOMO (Table IV) indicates that this aluminium can be regarded as a very highly distorted 5-coordinate fragment, in which the singly-occupied orbital is regarded as occupying one coordination site, in the symmetry plane. To this extent, the structure is consistent with that suggested earlier [3] by analogy with phosphoranyl radicals: we note that this isomer of $Al_2Me_6^-$ has an aluminium 3s spin density (and hence isotropic hyperfine coupling) more than double that of monomeric $AlMe_3^-$.

When the symmetry of $Al_2Me_6^-$ was constrained to be C_{2v}, instead of the C_s found in the unconstrained optimisation, the energy rose only to −369.4 kJ mol^{-1}, only marginally more stable than ($AlMe_2^\bullet$ + $AlMe_4^-$). The basic structure of the complex remained similar to the C_s structure, with a, 1.882 Å; b(≡c), 1.880 Å; d(≡e), 4.178 Å; f, 1.825 Å; and g, 4.949 Å: the angles around the strictly 4-coordinate aluminium were very close to tetrahedral, with, in addition, $d^\wedge e$, 43.5°; $d^\wedge f$ (≡$e^\wedge f$), 116.8°; and $f^\wedge f$, 122.0°. The principal difference lies in the orientation of the SOMO which in this constrained structure points at the other aluminium *i.e.* $g^\wedge h$ is zero, rather than 106.5° as in the freely optimised structure. Associated with this rotation of the SOMO is a change in $\rho[^{27}Al(3s)]$ from 0.384 to 0.422. On the other hand, when the symmetry was constrained to D_{2h} the energy rose by some 80 kJ mol^{-1} to give a σ^* radical.

Although the present calculations have defined the structure of the radical anion $Al_2Me_6^-$, they show also that no distinction is likely to be possible, on the grounds of hyperfine couplings alone, between $Al_2Me_6^-$ and $AlMe_2^\bullet$. Distinctions between $AlMe_3^-$, and $Al_2Me_6^-/AlMe_2^\bullet$, based, upon hyperfine couplings, require at least a rough estimate of the MNDO scale factor between ρ and A for ^{27}Al. Values of A/ρ are: for AlH_3^-, 577; for $Al(OH)_3^-$ (see below), 584;

TABLE V. Possible Identity of Radical X.

Radical	$\rho[^{27}Al(3s)]$	Sum of angles at Al/°
(i) Three-coordinate radicals		
AlH_3^-	0.267	331.5
$[AlH_2(OH)]^-$	0.296	331.6
$[AlH(OH)_2]^-$	0.338	329.9
$[Al(OH)_3]^-$	0.401	327.0
$[H_2Al(HAlH_3)]^-$	0.363	327.0
(ii) *Four-coordinate radicals*		
$AlH_4^{\bullet}$	−0.007	
$[AlH_4]^{-2}$	0.524	
$[AlH_3(OH)]$	−0.025	
$[AlH_3(OH)]^{-2}$	0.340	
$[AlH_2(OH)_2]$	0.611	
$[AlH_2(OH)_2]^{-2}$	0.344	
$[AlH(OH)_3]$	a	
$[AlH(OH)_3]^{-2}$	0.329	
$[Al(OH)_4]$	−0.004	
$[Al(OH)_4]^{-2}$	0.422	

[a] Dissociates to H• and $Al(OH)_3$.

for Me_2AlCl^- [20], 841; and for $Al(OR)_3^-$ (R = alkyl) [2-, 625. The observed [5] *A* value for γ-irradiated aluminium trimethyl of 324 G then implies an $\rho[Al(3s)]$ value in the range 0.38 to 0.56: this clearly rules out $AlMe_3^-$ (ρ = 0.176), but is consistent with $AlMe_2^{\bullet}$ (ρ = 0.368), or $Al_2Me_6^-$ (ρ = 0.384). The possibility of $AlMe_4^{\bullet}$ as the 324 G species is probably ruled out by its calculated dissociation to $CH_3^{\bullet}$ and $AlMe_3$.

The Identity of the Radical X Derived from $LiAlH_4$

When $LiAlH_4$ is subjected to γ-irradiation a radical is formed characterised by A_{iso} (^{27}Al) of 234 G [3, 21], and denoted by X: this radical is not the expected AlH_3^- as this has A_{iso} (^{27}Al) of 154 G both in THF solution [2] and in the solid state [3]. Whereas AlH_3^- is unambiguously identified by the observation [2, 3] of proton hyperfine coupling, no such information is available for the radical X.

The plausible precursors for X include AlH_4^- itself and various hydroxylated analogues $[AlH_x(OH)_{4-x}]^-$, formed by hydrolysis and/or oxidation of the initial AlH_4^- ions. Consequently, the plausible identities for X are considerable in number, and the mononuclear examples include: $AlH_4^{\bullet}$ and AlH_4^{-2} formed by electron-loss and -capture by AlH_4^-; $[AlH_x(OH)_{3-x}]^-$ formed by hydrogen atom loss from $[AlH_x(OH)_{4-x}]^-$ species (x = 0–3); and species $[AlH_x(OH)_{4-x}]^{\circ}$ and $[AlH_x(OH)_{4-x}]^{-2}$, formed from $[AlH_x(OH)_{4-x}]^-$. In addition, there is the possibility [3] that X is in fact an isomeric form of AlH_3^- whose structure has been perturbed, in the sense of becoming more pyramidal, by interaction with neighbouring counter-ions. In any event, any candidate for identification as X requires a calculated value of $\rho[^{27}Al(3s)]$ some 50% greater than that, 0.267, in AlH_3^-, in order to accommodate the observed value of $A(^{27}Al)$.

Hydroxylation of AlH_3^- to yield the radicals $[AlH_x(OH)_{3-x}]^-$ causes a steady increase in $\rho(Al)$ (Table V), associated with a decrease in the sum of the interbond angles at aluminium. In a similar way the calculated value of $\rho(Al)$ in $Al(OBu^t)_3^-$ is 0.481, associated with an angle sum of 329.9°. This is entirely consistent with the observation [2] of $A(Al)$ = 300.7 G in $Al(OBu^t)_3^-$: the ratio of *A* values observed for $Al(OBu^t)_3^-$ and AlH_3^- is 1.95, while the ratio of $\rho(Al)$ values calculated for $Al(OBu^t)_3^-$ and AlH_3^- is 1.80. Hence a possible identity for the radical X is $[Al(OH)_3]^-$, although $[AlH(OH)_2]^-$ and $[AlH_2(OH)]^-$ are unlikely identities. The data of Table VI also rule out definitively the following four-coordinate species as possible radicals X: $AlH_4^{\bullet}$, $[AlH_3(OH)]$, $[AlH_2(OH)_2]$, $[AlH(OH)_3]$ and $[Al(OH)_4]$. The corresponding dinegative radical anions are possible candidates, although overall less likely than $[Al(OH)_3]^-$. In the neutral fragment $AlH_2^{\bullet}$, $\rho[^{27}Al(3s)]$ is calculated to be 0.115, thereby effectively ruling out this radical as a possible X. There remains also the open chain isomer of $Al_2H_6^-$ (see below): in this the 3s spin densities calculated at the aluminium are 0.363 at the three-coordinate metal and only 0.003 at the four-coordinate metal.

To increase $\rho(Al)$ in AlH_3^- radical, distorted by inter-ionic interactions, to the required value needs a decrease in the angle <(HAlH) from the minimum-energy value of 110.5° to *ca.* 83°, with a corresponding increase in ΔH_f° of some 54 kJ mol^{-1}.

Dinuclear Ion Radicals $M_2H_6^+$ (M = Al, Si, P)

In view of the known [1, 22, 23] propensity of radicals such as Me_3P^+ and Me_2S^+ to form dinuclear σ* radicals $Me_nM\dot{-}MMe_n$, allied to the formation of both $Me_3M^{\bullet}$ and the dinuclear σ radicals $(Me_3M)_2^+$ for M = Si, Ge, and Sn [6, 24–28], we have also investigated dimer formation by the radicals AlH_3^-, $SiH_3^{\bullet}$ and PH_3^+. For each of $Al_2H_6^-$, $Si_2H_6^+$, $Si_2H_6^-$, and $P_2H_6^+$ (representing two iso-electronic pairs), distinct minima were found for atom connectivities corresponding to D_{3d}, C_{2v} $H_2M(\mu_2\text{-}H)_2MH_2$, and C_s $H_2M{-}H{-}MH_3$ configurations (Table VI): in addition, the doubly-bridged isomer was also constrained to D_{2h} symmetry. Minima were found for all configurations of each ion radical, with the exceptions of the D_{2h} isomers of $Si_2H_6^-$ and $P_2H_6^+$. The lowest-energy isomer of $Al_2H_6^-$ is calculated to be the open chain form $[H_2Al{-}H{-}AlH_3]^-$ while for the isoelectronic ion $Si_2H_6^+$, the most stable isomer is

TABLE VI. Optimised Properties for Dinuclear Ion Radicals of Type MH (M = A, Si, P).[a]

	Ethane-type, D_{3d}	Bridged, C_{2v}	Bridged, D_{2h}	$H_2M{-}H{-}MH_3$, C_s
(i) $\Delta H_f^{\ominus}$/kJ mol^{-1}				
$Al_2H_6^{-}$ [b]	+96.2	+100.3	+102.2	+44.1
$Si_2H_6^{+}$ [c]	+1047.5	+919.1	+919.9	+922.3
$Si_2H_6^{-}$ [d]	−102.4	+59.8	[f]	−60.6
$P_2H_6^{+}$ [e]	+792.6	+982.4	[f]	+960.0
(ii) SOMO types				
$Al_2H_6^{-}$	σ(Al–Al)	σ^*(Al···Al)	σ^*(Al···Al)	$n\sigma$(Al), A′
$Si_2H_6^{+}$	σ(Si–Si)	σ^*(Si···Si)	σ^*(Si···Si)	$n\sigma$(Si), A′
$Si_2H_6^{-}$	σ^*(Si–Si)	σ(Si···Si)	[f]	$n\sigma$(Si), A′
$P_2H_6^{+}$	σ^*(P–P)	$p\pi$(P), B_2	[f]	$n\sigma$(P), A′
(iii) ρ[M(3s)]				
$Al_2H_6^{-}$	0.053 (×2)	0.464 (×1)	0.294 (×2)	0.363 (×1)
		0.098 (×1)		0.003 (×1)
$Si_2H_6^{+}$	0.003 (×2)	0.203 (×1)	0.138 (×2)	0.212 (×1)
		0.060 (×1)		0.000 (×1)
$Si_2H_6^{-}$	0.238 (×2)	0.279 (×1)	[f]	0.321 (×1)
		0.014 (×1)		−0.005 (×1)
$P_2H_6^{+}$	0.174 (×2)	0.023 (×1)	[f]	0.052 (×1)
		0.000 (×1)		−0.007 (×1)

[a] D_{3d}, C_{2v} and C_s minima result from unconstrained optimisations: D_{2h} symmetry was imposed. [b] $\Delta H_f^{\ominus}$ (AlH_3 + AlH_3^{-}), +177.8 kJ mol^{-1}. [c] $\Delta H_f^{\ominus}$ (SiH_3^{+} + $SiH_3^{\bullet}$) + 1111.0 kJ mol^{-1}. [d] $\Delta H_f^{\ominus}$ (SiH_3^{-} + $SiH_3^{\bullet}$), +104.5 kJ mol^{-1}. [e] $\Delta H_f^{\ominus}$ (PH_3 + PH_3^{+}), +1046.4 kJ mol^{-1}. [f] No D_{2h} minimum located.

the doubly bridged form $H_2Si(\mu_2\text{-}H)_2SiH_2^{+}$: the C_{2v} and D_{2h} isomers are very close in energy, although quite different in terms of bonded distances. The SOMO in these two ions are of $n\sigma$ and σ^* type respectively. In the isoelectronic pair of ions $Si_2H_6^{-}$ and $P_2H_6^{+}$, the D_{3d} isomer, a σ^* radical, is the most stable isomer in each case.

None of these di-nuclear ions appears so far to have been identified: we note however that $B_2H_6^{-}$, formally isoelectronic with $Al_2H_6^{-}$, appears [29] to have a structure very similar to that of $C_2H_6^{+}$ [30], which may be regarded as a half-way house between the D_{3d} ethane structure and the D_{2h} diborane structure.

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