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PM3 study of organometallic radicals formed by elements in periodic Groups 13–16

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Abstract

Calculations have been made by the PM3 SCF method of the molecular and electronic structures of a range of neutral, cationic and anionic organometallic radicals derived from permethyl derivatives of elements from Groups 13–16. In Group 13, the planar methyls $M(CH_3)_3$ all yield pyramidal mononuclear radical-anions $[M(CH_3)_3]^-$, but only for M = Al was a stable dinuclear radical-anion $[Al_2(CH_3)_6]^-$ found; this is a weak complex of $[Al(CH_3)_2]^\cdot$ and $[Al(CH_3)_4]^-$. In Group 14, dinuclear σ radical-cations $[M_2(CH_3)_6]^+$ of D_{3d} symmetry are found for M = Si–Pb, and analogous σ^* radical-cations are found for M = P–Bi in Group 15. The dinuclear $[M_2(CH_3)_4]^+$ formed by sulphur and selenium both have C_{2h} symmetry.

1. Introduction

Recent papers have demonstrated that MNDO calculations can make a significant contribution to the interpretation of the ESR spectra observed for Main Group organometallic radicals [1–5]. The principal constraint upon the development of this work has hitherto been the availability of appropriate atomic parameter sets for the calculation. The recent development of the PM3 computational method [6,7], and its parameterization for a wide range of elements [8,9], has opened up most of the post-transition elements for study in this manner, and here we report on the mononuclear and dinuclear radicals (neutral, cationic and anionic) formed by the simplest organometallics, $M(CH_3)_x$, where M represents one of the elements of Groups 13–16 inclusive.

2. Calculations

All calculations were undertaken by use of published atomic parameters [8,9] with Version 5.0 of the MOPAC system implemented on a network of SUN workstations; in all calculations, all independent geometric parameters were allowed to vary independently (a total of 72 variables for $M_2(CH_3)_6$ species). The convergence criterion adopted throughout was GNORM = 0.01.

3. Results and Discussion

3.1. Organometallic radicals in Group 13

In Group 13, the neutral monomeric species $M(CH_3)_3$ all optimized to structures having C_{3h} molecular symmetry (Table 1), with planar MC_3 cores, as found experimentally for $Al(CH_3)_3$ [10], $Ga(CH_3)_3$ [11] and $In(CH_3)_3$ [12], and a conformation with all the methyl groups geared together with a single hydrogen atom from each group in the MC_3 plane. For M = Al, Ga or In, the LUMO was calculated to be almost entirely composed of the metal p orbital perpendicular to the MC_3 plane, but for M = Tl, the calculated LUMO was an antibonding thallium–carbon orbital of A' symmetry.

Electron attachment to form monomeric $[M(CH_3)_3]^-$ species leads in every case to anions in which the SOMO is bound typically by *ca.* 4 eV. and which optimize to C_{3v} symmetry (Table 1) with a methyl group conformation having one C–H bond parallel to the molecular symmetry axis, pointing away from the SOMO. For all M, the SOMO was calculated

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TABLE 1. Calculated properties for the Group 13 species $M(CH_3)_3$ and their radical-anions $[M(CH_3)_3]^-$

	ΔH_f^θ (kJ mol^{-1})	d(M–C) (Å[a])	C–M–C (°)	ρ[H(1s)]
$Al(CH_3)_3$	−23.9	1.892(1.957)[b]	120.0	–
$[Al(CH_3)_3]^-$	−260.5	1.976	112.0	0.0140
$Ga(CH_3)_3$	+99.6	1.832(1.967)[c]	120.0	–
$[Ga(CH_3)_3]^-$	−372.7	1.734	118.3	−0.0195
$In(CH_3)_3$	−9.0	2.159(2.093)[d]	120.0	–
$[In(CH_3)_3]^-$	−308.7	2.198	114.7	0.0296
$Tl(CH_3)_3$	+509.9	2.386[e]	120.0	–
$[Tl(CH_3)_3]^-$	+99.4	2.397	99.0	0.0111

[a] Experimental values in parentheses. [b] Ref. 10. [c] Ref. 11. [d] Ref. 12. [e] Average Tl–C short bonds in crystalline $[Tl(CH_3)_3]_4$, 2.29(9) Å [13].

to have A_1 symmetry, but to be a metal (s, p) combination for M = Al, Ga and In, and a M–C antibonding orbital when M = Tl.

Only for M = Al was a minimum located corresponding to a neutral dimeric species of D_{2h} symmetry. Only aluminium forms such a dimer in the vapour phase [10], while in the solid state both indium [14] and thallium [13] trimethyls form tetrameric aggregates of overall S_4 symmetry. Extensive exploration of the potential energy surfaces for $[M_2(CH_3)_6]^-$ revealed a minimum corresponding to a bridged structure only for M = Al. This structure, of overall C_s molecular symmetry, is rather similar to that found earlier [1] from MNDO calculations, namely a weak complex of the radical $[Al(CH_3)_2]^{\cdot}$ with the anion $[Al(CH_3)_4]^-$. In the PM3 structure, the calculated Al $\cdots$ Al distance. 3.36 Å is considerably shorter than that calculated earlier [1] by use of MNDO, namely 5.281 Å, reflecting the rather greater stability of this complex over its components by 52.6 kJ mol^{-1} as calculated by PM3 compared with only 8.8 kJ mol^{-1} from MNDO calculation. However, despite the rather stronger aggregation between $[Al(CH_3)_2]^{\cdot}$ and $[Al(CH_3)_4]^-$ indicated by the PM3 calculations, the electronic structure is virtually identical with that found by MNDO, having the ^{27}Al(3s) spin density H confined solely to one aluminium atom, and that in the $[Al(CH_3)_2]^{\cdot}$ like fragment, with a magnitude within 2% of that calculated for the isolated mononuclear radical $[Al(CH_3)_2]^{\cdot}$.

A rather similar minimum was found for the indium species $[In_2(CH_3)_6]^-$, best represented as a complex of the diamagnetic anion $[In(CH_3)_4]^-$ with the neutral radical $[In(CH_3)_2]^{\cdot}$. For both aluminium and indium, these complexes are calculated to be significantly more stable, by *ca.* 137 and 76 kJ mol^{-1}, respectively, than the isomeric ethane-type σ radical-anions of overall C_{3v} symmetry for M = Al and D_{3d} for M = In. By contrast, no minima corresponding to $[M_2(CH_3)_6]^-$ were found for either M = Ga or M = Tl.

3.2. *Organometallic radicals in Group 14*

In Group 14, each of the neutral radicals $[M(CH_3)_3]^{\cdot}$ (for M = Si, Ge, Sn, Pb) was calculated by the PM method to have C_{3v} symmetry (Table 2) with a SOMO of A_1 symmetry localized on the heavy atom M and a single C–H bond in each methyl group directed parallel to but away from the SOMO. In a similar way, all of the corresponding cations $[M(CH_3)_3]^+$ were calculated to have C_{3h} symmetry, with a single C–H bond of each methyl group lying in the MC_3 plane. The dimeric radical-cation $[M_2(CH_3)_6]^+$ for each of M = Si, Ge, Sn or Pb was calculated (Table 2) to have D_{3d} molecular symmetry, and to be a σ radical with the SOMO of A_{1g} symmetry strongly localized between the pair of M atoms.

The above PM3 results for Group 14 $[M(CH_3)_3]^{\cdot}$ and $[M_2(CH_3)_6]^+$ species are broadly in accord with

TABLE 2. Calculated properties for Group 14 species

	ΔH_f^θ (kJ mol^{-1})	d(M–C) (Å)	d(M–M) (Å)	C–M–C (°)	C–M–M (°)	ρ[H(1s)]
(a) Mononuclear						
$[Si(CH_3)_3]^+$	+591.5	1.799		120.0		–
$Si(CH_3)_3$	−67.3	1.847		116.4		0.0193
$[Ge(CH_3)_3]^+$	+738.2	1.913		120.0		–
$Ge(CH_3)_3$	−57.2	1.911		120.0		0.0189
$[Sn(CH_3)_3]^+$	+773.2	2.053		120.0		–
$Sn(CH_3)_3$	+28.0	2.141		110.2		0.0054
$[Pb(CH_3)_3]^+$	+878.3	2.127		120.0		–
$Pb(CH_3)_3$	+139.9	2.179		110.6		0.0050
(b) Binuclear						
$[Si_2(CH_3)_6]^+$	+394.2	1.834	2.650	117.6	98.9	0.0124
$[Ge_2(CH_3)_6]^+$	+632.8	1.924	2.569	117.0	100.0	0.0106
$[Sn_2(CH_3)_6]^+$	+792.0	2.124	3.418	116.6	100.8	0.0059
$[Pb_2(CH_3)_6]^+$	+1022.2	2.169	3.051	114.1	104.2	0.0032

TABLE 3. Calculated values of D(M–M) (kJ mol^{-1}) for the Group 14 species $[M_2(CH_3)_6]^+$

M	MNDO value	PM3 value
Si	101.3	130.0
Ge	−18.4	48.2
Sn	39.8	9.2
Pb	27.0	−5.0

TABLE 4. Calculated values of ρ[H(1s)] in Group 14 radicals and radical cations

	MNDO value	PM3 value	A(^{1}H)/G
$Si(CH_3)_3$	−0.0014	+0.0193	6.4 [a]
$Ge(CH_3)_3$	+0.0065	+0.0189	5.3 [b]
$Sn(CH_3)_3$	+0.0024	+0.0054	2.7 [c]
$Pb(CH_3)_3$	−0.0073	+0.0050	–
$[Si_2(CH_3)_6]^+$	+0.0055	+0.0124	5.6 [d]
$[Ge_2(CH_3)_6]^+$	+0.0031	+0.0106	5.3 [d]
$[Sn_2(CH_3)_6]^+$	−0.0044	+0.0059	3.4 [e]
$[Pb_2(CH_3)_6]^+$	+0.0018	+0.0031	–

[a] Ref. 17. [b] Ref. 18. [c] Ref. 19. [d] Ref. 20. [e] Ref. 21.

those calculated earlier [2–4,15] by use of the MNDO approximation [16]; however, detailed examination of both the molecular energies and the spin-density distributions for the open-shell systems suggests that the PM3 treatment for some of these Group 14 elements is markedly superior to the earlier MNDO version. Firstly (Table 3), the dissociation energies of D(M–M) in the dinuclear cations $[M_2(CH_3)_6]^+$ when calculated by the PM3 method show a monotonic decrease down the group, whereas those calculated by the MNDO method show a clear discontinuity between silicon and tin. Although $[Pb_2(CH_3)_6]^+$ is calculated to be less stable than the pair of mononuclear fragment $[Pb(CH_3)_3]^{\cdot}$ and $[Pb(CH_3)_3]^+$ by some 5 kJ mol^{-1}, there is a small energy barrier, 11.6 kJ mol^{-1} at a Pb ··· Pb distance of 3.57 Å, which opposes spontaneous dissociation of the dinuclear radical-cation into mononuclear fragments. At the equilibrium configuration of $[Pb_2(CH_3)_6]^+$, the molecular and electronic structure conform to D_{3d} symmetry; this symmetry of the electronic structure is preserved up to the transition state for dissociation, but at Pb ··· Pb distances longer than the 3.57 Å found in this transition state the symmetry is reduced to C_{3v}, with two distinguishable $Pb(CH_3)_3$ fragments as the dissociation proceeds towards one pyramidal neutral fragment and the planar cationic fragment. Secondly (Table 4), the mean spin densities at hydrogen, appropriate to freely rotating CH_3 groups, as observed experimentally for both $[M(CH_3)_3]^{\cdot}$ and $[M_2(CH_3)_6]^+$ [17–21], show monotonic variation with M for both series, as found for the experimental A(^{1}H) values, when calculated by the PM3 method, but there is no correlation between the MNDO spin densities and the A values as M varies; this has led to the idea that the MNDO method may require different scale factors to relate calculated spin density with A(^{1}H) for different heavy atoms M. The PM3 method, by contrast, shows more prospect of being able to put such data on to a common scale.

3.3. *Organometallic radicals in Group 15*

The neutral Group 15 permethyls $M(CH_3)_3$ for M = P, As, Sb and Bi all optimized to C_{3v} structures, each having a single C–H bond in each methyl group parallel to the three-fold molecular axis and *trans* to the lone pair. The calculated M–C distances and C–M–C angles (Table 5) are in satisfactory agreement with the experimentally determined values [22–24]. For each neutral species, the HOMO was calculated to be on A_1 orbital localized primarily on the central M, in effect the M lone pair orbital. In keeping with the stereochemical role of this lone pair, ionization to form the

TABLE 5. Calculated properties for Group 15 species

	ΔH_f^θ (kJ mol^{-1})	d(M–C) (Å) [a]	d(M–M) (Å)	C–M–C (°) [a]	C–M–M (°)	ρ[H(1s)]
(a) Mononuclear						
$P(CH_3)_3$	−124.8	1.872(1.839) [b]		100.6(98.8) [b]		–
$[P(CH_3)_3]^+$	+644.8	1.761		113.9		+0.0090
$As(CH_3)_3$	−62.2	1.975(1.979) [c]		99.7(96.2) [c]		–
$[As(CH_3)_3]^+$	+755.5	1.883		113.4		+0.0093
$Sb(CH_3)_3$	−1.4	2.163(2.169) [c]		95.0(94.2) [c]		–
$[Sb(CH_3)_3]^+$	+893.8	2.173		109.3		−0.0087
$Bi(CH_3)_3$	+180.2	2.266(2.263) [c]		97.0(97.1) [c]		–
$[Bi(CH_3)_3]^+$	+987.7	2.301		107.9		−0.0304
(b) Binuclear						
$[P_2(CH_3)_6]^+$	+389.2	1.847	2.258	104.1	114.4	−0.0011
$[As_2(CH_3)_6]^+$	+580.8	1.956	2.498	103.7	114.8	−0.0025
$[Sb_2(CH_3)_6]^+$	+755.4	2.180	2.762	102.2	116.0	−0.0087
$[Bi_2(CH_3)_6]^+$	+1067.7	2.292	3.113	104.4	114.2	−0.0260

[a] Experimental values in parentheses. [b] Ref. 22. [3] Ref. 23.

TABLE 6. Calculated properties for Group 16 species

	ΔH_f° (kJ mol^{-1})	d(M–C) (Å) [a]	d(M–M) (Å)	C–M–C (°) [a]	C–M–M (°)	ρ[H(1s)]
(a) Mononuclear						
$S(CH_3)_2$	−45.8	1.801(1.807) [b]		102.5(99.1) [b]		–
$[S(CH_3)_2]^+$	+783.6	1.754		105.9		0.0282
$Se(CH_3)_2$	−77.4	1.948(1.943) [c]		100.8(96.2) [c]		–
$[Se(CH_3)_2]^+$	+757.8	1.959		103.5		0.0183
(b) Binuclear						
$[S_2(CH_3)_4]^+$	+556.9	1.817	2.112	103.5	108.5	0.0062
$[Se_2(CH_3)_4]^+$	+345.8	1.977	2.272	102.4	98.6	0.0111

[a] Experimental values in parentheses. [b] Ref. 32. [c] Ref. 33.

radical-cations $[M(CH_3)_3]^+$ was calculated in every case to cause a significant increase in the CMC angle (Table 5).

An important feature of the behaviour of $[P(CH_3)_3]^+$ is the formation of the dimeric species $[P_2(CH_3)_6]^+$ [25,26], a σ^* radical having three electrons effectively localized in the P–P interaction with configuration $(a_{1g})^2(a_{2u})^1$ in D_{3d} symmetry. The present PM3 calculations indicate that similar dimeric species, all of D_{3d} molecular symmetry and all σ^* radicals, are formed for all the elements P–Bi, with bond dissociation energies D(M–M) in the dimers varying from 130.6 kJ mol^{-1} in $[P_2(CH_3)_6]^+$ down to +100.2 kJ mol^{-1} in $[Bi(CH_3)_6]^+$ (Table 5). For the phosphorus radical-cations, the ratio of the mean spin-density at hydrogen, A(^{1}H), $[P(CH_3)_3]^+$ to that in $[P_2(CH_3)_6]^+$ is calculated by PM3 to be 8.2 (*cf.* MNDO 9.9 [15], experimental 1.9 [25,26]). This calculated ratio decreases to 3.7 (As), 1.0 (Sb) and 1.2 (Bi); however, for all of the dimeric radical-cations $[M_2(CH_3)_6]^+$, the calculated CMC angles are intermediate in magnitude between those calculated for $M(CH_3)_3$ and $[M(CH_3)_3]^+$. A similar geometric pattern is observed for the dinuclear radical-cations $M_2(CH_3)_6]^+$ formed by the Group 14 elements (Table 2) but with a significant electronic difference. In Group 14, the paramagnetic neutral species $[M(CH_3)_3]^\cdot$ are all more pyramidal than the diamagnetic cations $[M(CH_3)_3]^+$, which are planar, wheras in Group 15 the paramagnetic radical-cations $[M(CH_3)_3]^+$ are all less pyramidal than the diamagnetic neutral species $M(CH_3)_3$; hence in Group 15, the dinuclear radical-cations $[M_2(CH_3)_6]^-$ show greater pyramidal character at M than the mononuclear radical-cations, whereas in Group 14 it is the mononuclear radical-cations which are the more pyramidal at M.

3.4. *Organometallic radicals in Group 16*

The formation of dinuclear cations $(M_2R_4)^+$ for M = S [27–29], Se [30] and Te [31] is an important property of Group 16 organometallic radical-cations. The present PM3 calculations on sulphur and selenium permethyl species (Table 6) show: (i) excellent agreement with experimental data [32,33] for the neutral species, with both $S(CH_3)_2$ and $Se(CH_3)_2$ calculated to have, as HOMO, a p orbital on the central atom M, perpendicular to the CMC plane; and (ii) a rather modest change in the C–M–C angle upon ionization to $[M(CH_3)_2]^+$, which has a SOMO the same p orbital normal to the CMC plane; and (iii) a very high stability for the dinuclear species $[M_2(CH_3)_4]^+$ of C_{2h} symmetry and containing a three-electron σ^* M–M bond. In contrast to those for $S(CH_3)_2$ and $Se(CH_3)_2$ (as well as other simple dialkyls of sulphur and selenium) whose HOMO is a p orbital normal to the CMC plane, PM3 calculations for a series of teurium alkyls TeR_2 (R = Me, Et, ^{n}Pr, ^{n}Bu, $^nC_5H_{11}$, $^nC_6H_{13}$ as well as allyl and $C(CH_3)_3$) consistently predict that the HOMO is the Te-based lone-pair orbital in the CTeC plane, and that the corresponding radical cations $(TeR_2)^+$ are all σ-radicals, whereas experimental evidence $[Te(CH_3)_2]^+$ and $[Te(C_2H_5)_2]^+$ indicates clearly that they are both π-radicals [31]. This discrepancy is probably a consequence of an inadequate parameterization for tellurium within the PM3 model [9], which itself is almost certainly a reflection of the inadequate range of structural and particularly thermochemical data available for the construction of the tellurium parameter set.

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