2908 *Organometallics* 1991, *10*, 2908-2913

Attempted Synthesis of 1,3,5-Triphenyl-2,4,9-trithia-1,3,5-triplumbaadamantane. Decomposition of Organolead Iodides

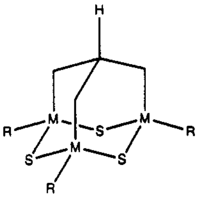
Michio Kobayashi, Stéphan Latour, and James D. Wuest*

Département de Chimie, Université de Montréal, Montréal, Québec, H3C 3J7 Canada

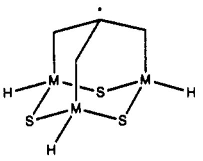
Received January 25, 1991

MNDO calculations suggest that the strength of the bridgehead carbon–hydrogen bond in 2,4,9-trithia-1,3,5-triplumbaadamantane (**2a**) should be only 54 kcal/mol and the hydride affinity of the corresponding bridgehead cation **2a**$^+$ should be only 215 kcal/mol. As a donor of hydrogen atoms or hydride, plumbaadamantane **2a** should therefore be even more reactive than the analogous stannaadamantane **1a**. Unfortunately, substituted derivative **2b** could not be prepared from $(Ph_3PbCH_2)_3CH$ by controlled iodinolysis followed by treatment of the intermediate hexaiodide $(PhI_2PbCH_2)_3CH$ with $Ph_3SnSSnPh_3$. This failure results in part from the tendency of organolead diiodides R_2PbI_2 to undergo redistribution reactions that produce unstable triiodides $RPbI_3$. Diiodides capable of intramolecular redistributions are particularly reactive. The resulting triiodides then decompose by a formal reductive elimination of RI and PbI_2. Since the iodinolysis of (cyclopropylmethyl)triphenylplumbane (**11**) yields mainly (iodomethyl)cyclopropane instead of ring-opened products derived from cyclopropylmethyl cations or radicals, we suggest that the reductive elimination of RI and PbI_2 from $RPbI_3$ is concerted.

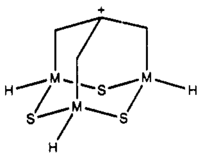
Carbon–hydrogen bonds antiperiplanar to several lone pairs or carbon–metal bonds are unusually reactive donors of hydride or hydrogen atoms.[1] For example, the bridgehead carbon–hydrogen bond in hypothetical stannaadamantane **1a** is activated as a donor of hydrogen by three antiperiplanar carbon–tin bonds. MNDO calculations suggest that this arrangement reduces the strength of the carbon–hydrogen bond to 61 kcal/mol by stabilizing the bridgehead radical **1a**$^\bullet$.[2] As a result, substituted derivative **1b** acts like a tin hydride and reduces activated alkyl halides to hydrocarbons by donating hydrogen atoms to the corresponding alkyl radicals.[1b] Similarly, the unique orientation of carbon–tin bonds in stannaadamantane **1a** should also promote direct transfers of hydride by stabilizing the bridgehead cation **1a**$^+$, which has a calculated hydride affinity of only 228 kcal/mol.[2] Since carbon–lead bonds are weaker than carbon–tin bonds,[3] since lead is more electropositive than tin, and since carbon–lead bonds participate more effectively than carbon–tin bonds in hyperconjugation,[4] we expected the bridgehead radical **2a**$^\bullet$ and cation **2a**$^+$ derived from the analogous plumbaadamantane **2a** to be even more dramatically stabilized. In this paper, we estimate the strength of the activated bridgehead carbon–hydrogen bond of plumbaadamantane **2a** and the hydride affinity of cation **2a**$^+$, and we describe the novel behavior of organolead iodides observed during unsuccessful attempts to synthesize substituted plumbaadamantane **2b**.



1a (M = Sn, R = H)
1b (M = Sn, R = Ph)
2a (M = Pb, R = H)
2b (M = Pb, R = Ph)



1a• (M = Sn)
2a• (M = Pb)



1a$^+$ (M = Sn)
2a$^+$ (M = Pb)

Table I. Heats of Formation (kcal/mol) Calculated for Stannaadamantanes 1a, 1a$^\bullet$, and 1a$^+$[8] and for Plumbaadamantanes 2a, 2a$^\bullet$, and 2a$^+$ by Using the MNDO Procedure[5,6]

1a	1a$^\bullet$	1a$^+$	2a	2a$^\bullet$	2a$^+$
37.0	46.8	230.2	144.7	146.6	325.1

Using the MNDO procedure,[5,6] we calculated the heats of formation of simple plumbaadamantane **2a** and the corresponding bridgehead radical **2a**$^\bullet$ and cation **2a**$^+$. These values are listed in Table I along with those calculated for the analogous stannaadamantanes **1a**, **1a**$^\bullet$, and **1a**$^+$.[8] Combined with the heats of formation of $H^\bullet$ (52.1 kcal/mol) and H^- (34.7 kcal/mol),[10] the values in Table

---

[1] (a) Kobayashi, M.; Wuest, J. D. *Organometallics* **1989**, *8*, 2843–2850. (b) Ducharme, Y.; Latour, S.; Wuest, J. D. *J. Am. Chem. Soc.* **1984**, *106*, 1499–1500. (c) Beauchamp, A. L.; Latour, S.; Olivier, M. J.; Wuest, J. D. *Ibid.* **1983**, *105*, 7778–7780. (d) Erhardt, J. M.; Grover, E. R.; Wuest, J. D. *Ibid.* **1980**, *102*, 6365–6369. Erhardt, J. M.; Wuest, J. D. *Ibid.* **1980**, *102*, 6363–6364.

[2] Dewar, M. J. S.; Grady, G. L. *Organometallics* **1985**, *4*, 1327–1329.

[3] (a) Smith, G. P.; Patrick, R. *Int. J. Chem. Kinet.* **1983**, *15*, 167–185. (b) Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17–19. (c) Steele, W. V. *J. Chem. Thermodyn.* **1978**, *10*, 445–452. (d) Kana'an, A. S.; Morrison, T. I. *Ibid.* **1977**, *9*, 423–429. (e) Butler, R. S.; Carson, A. S.; Laye, P. G.; Steele, W. V., *Ibid.* **1976**, *8*, 1153–1158. (f) Carson, A. S.; Laye, P. G.; Spencer, J. A.; Steele, W. V. *Ibid.* **1972**, *4*, 783–787.

[4] For references, see: Lambert, J. B.; Wang, G.-t.; Teramura, D. H. *J. Org. Chem.* **1988**, *53*, 5422–5428. Wilt, J. W.; Lusztyk, J.; Peeran, M.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 281–287. Egorochkin, A. N.; Razuvaev, G. A. *Uspekh. Khim.* **1987**, *56*, 1480–1503. Traylor, T. G.; Koermer, G. S. *J. Org. Chem.* **1981**, *46*, 3651–3657. Hannon, S. J.; Traylor, T. G. *Ibid.* **1981**, *46*, 3645–3650. Eaborn, C.; Pande, K. C. *J. Chem. Soc.* **1960**, 1566–1571.

[5] Dewar, M. J. S.; Holloway, M. K.; Grady, G. L.; Stewart, J. J. P. *Organometallics* **1985**, *4*, 1973–1980.

[6] Heats of formation were calculated by the standard MNDO procedure, as implemented in the AMPAC Version 2.10 package of computer programs.[7] Geometries were optimized by the Davidon–Fletcher–Powell method. Open-shell systems were calculated by using the UHF version of MNDO.

[7] Quantum Chemistry Program Exchange (QCPE), Publication 506, Department of Chemistry, Indiana University, Bloomington, IN 47405.

[8] The parameters reported for stannaadamantanes **1a**, **1a**$^\bullet$, and **1a**$^+$ differ slightly from those published earlier by Dewar and Grady[2] because we have used an improved set of MNDO parameters for sulfur.[9]

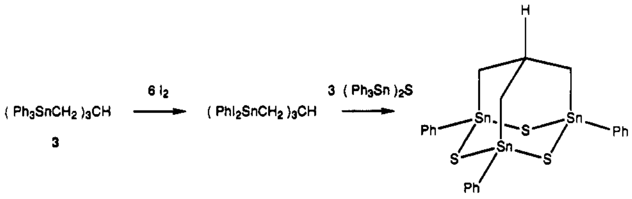
[9] Dewar, M. J. S.; Reynolds, C. H. *J. Comput. Chem.* **1986**, *7*, 140–143.

[10] Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2162–2169. Doering, W. v. E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279–5283. Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. J. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1.

Table II. Average Bond Lengths (Å) and Bond Angles (deg) Measured for Stannaadamantane 1b and Calculated for Stannaadamantanes 1a, 1a$^\bullet$, and 1a^{+}[8] and for Plumbaadamantanes 2a, 2a$^\bullet$, and 2a^{+} by Using the MNDO Procedure[5,6]

parameter	**1b** (M = Sn)	**1a** (M = Sn)	**2a** (M = Pb)	**1a**$^\bullet$ (M = Sn)	**2a**$^\bullet$ (M = Pb)	**1a**$^+$ (M = Sn)	**2a**$^+$ (M = Pb)
M-S	2.408	2.279	2.374	2.281	2.374	2.282	2.375
M-CH_2	2.153	2.096	2.210	2.122	2.284	2.141	2.261
CH_2-C	1.529	1.546	1.542	1.486	1.467	1.472	1.465
S-M-S	108.7	109.1	108.8	108.6	109.0	111.1	110.5
S-M-CH_2	109.3	108.2	108.1	106.9	106.0	104.8	104.4
M-CH_2-C	119.3	118.2	118.7	107.7	108.2	108.0	108.4
CH_2-C-CH_2	114.1	113.9	114.4	119.7	119.9	119.8	119.9
M-S-M	94.3	98.1	97.3	100.1	100.0	101.5	101.3

Scheme I



I indicate that the strength of the activated carbon–hydrogen bond in plumbaadamantane **2a** is only 54 kcal/mol and that the hydride affinity of cation **2a**$^+$ is only 215 kcal/mol. These low values confirmed our expectation that the bridgehead radical **2a**$^\bullet$ and cation **2a**$^+$ derived from plumbaadamantane **2a** would be strongly stabilized by three antiperiplanar carbon–lead bonds and that substituted plumbaadamantane **2b** would be a donor of hydrogen even more reactive than the analogous stannaadamantane **1b**.

We also used the MNDO procedure[5,6] to calculate the geometries of simple plumbaadamantane **2a** and the corresponding bridgehead radical **2a**$^\bullet$ and cation **2a**$^+$. The estimated bond lengths and bond angles are listed in Table II along with those calculated for the analogous stannaadamantanes **1a**, **1a**$^\bullet$, and **1a**$^+$[8] and those measured for substituted stannaadamantane **1b** by X-ray crystallography.[1c] Although the carbon–lead and sulfur–lead bond lengths calculated for plumbaadamantane **2a** are somewhat shorter than those observed in other organolead sulfides,[11] the calculations nevertheless provide qualitatively reasonable results. They indicate that the carbon bridgeheads of adamantanes **1a** and **2a** should both be markedly flattened and that the CH_2–C–CH_2 angles should open to approximately 114°. In addition, both compounds should have similarly opened M–CH_2–C angles and closed M–S–M angles. Furthermore, the calculations indicate that the corresponding radicals and cations should also have similar geometries and that the carbon bridgeheads should be essential planar. The conspicuous geometrical similarity of these plumba- and stannaadamantanes is not surprising, since plumbanes and stannanes are known to be nearly isostructural.[12] This similarity was reassuring, since it suggested that the increased reactivity predicted for plumbaadamantane **2b** as a donor of hydrogen would not necessarily be associated with increased strain and thermodynamic instability.

We have shown that substituted stannaadamantane **1b** can be prepared efficiently by controlled iodinolysis of tristannane **3**,[13] followed by the addition of bis(triphenyltin) sulfide (Scheme I).[1b,14,15] The success of this strategy depends critically on two features of the halogenolysis of main-group carbon–metal bonds: aryl–metal bonds are typically cleaved much faster than alkyl–metal bonds, and halogenolysis becomes progressively slower as carbon–metal bonds are replaced by halogen–metal bonds.[16] Unfortunately, an analogous sequence failed to convert triplumbane **4**[17] into detectable amounts of plumbaadamantane **2b**.

$$(\mathrm{Ph}_n\mathrm{I}_{3-n}\mathrm{PbCH}_2)_3\mathrm{CH}$$

4 (n = 3)

5 (n = 2)

6 (n = 1)

We suspected that this setback might be due to the known instability of organolead dihalides R_2PbX_2.[18] The rate of thermolysis of these compounds in solution is concentration-dependent, so decomposition is presumably preceded by a redistribution reaction that generates small amounts of the corresponding organolead trihalide $RPbX_3$ (eq 1).[18b] This reactive intermediate then decomposes

$$2\ R_2PbX_2 \rightleftharpoons R_3PbX + RPbX_3 \qquad (1)$$

$$RPbX_3 \longrightarrow RX + PbX_2 \qquad (2)$$

irreversibly by a formal reductive elimination of PbX_2 (eq 2),[19] a process facilitated by the stability of Pb(II). By using ^1H NMR spectroscopy to follow the decomposition of simple organolead mono- and diiodides in solution, we have established that the redistribution reaction of eq 1 takes place, and we have obtained evidence that the reductive elimination occurs in a single step.

The ^1H NMR spectrum of triphenylpropylplumbane (**7**)[20] in $CDCl_3$ shows aliphatic signals at δ 1.03 (t, 3 H), 2.02 (m, 2 H), and 2.23 (t, 2 H), as well as an aromatic multiplet at 7.2–7.7 (15 H). Treatment of 0.033 M solution in $CDCl_3$ with 1 equiv of I_2 at 0 °C yielded primarily iodobenzene and the expected monoiodide **8**, with corresponding aliphatic multiplets at δ 1.02, 2.22, and 2.75. In addition, small amounts of unreacted plumbane **7** could be detected, along with equivalent amounts of a second minor product with aliphatic signals at δ 1.16 (t, 3 H), 2.30 (m, 2 H), and

---

[11] (a) Begley, M. G.; Gaffney, C.; Harrison, P. G.; Steel, A. *J. Organomet. Chem.* **1985**, *289*, 281–293. (b) Dräger, M.; Kleiner, N. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 923–924. (c) Furmanova, N. G.; Struchkov, Y. T.; Kravtsov, D. N.; Rokhlina, E. M. *Zh. Strukt. Khim.* **1979**, *20*, 1047–1051.

[12] Chieh, P. C. *J. Chem. Soc., Dalton Trans.* **1972**, 1207–1208.

[13] Ducharme, Y.; Latour, S.; Wuest, J. D. *Organometallics* **1984**, *3*, 208–211.

[14] For a similar procedure, see: Gallant, M.; Kobayashi, M.; Latour, S.; Wuest, J. D. *Organometallics* **1988**, *7*, 736–739.

[15] Bis(triphenyltin) sulfide was prepared from chlorotriphenylstannane and sodium sulfide by a procedure similar to one used to synthesize the corresponding selenide: Schmidt, M.; Ruf, H. *Chem. Ber.* **1963**, *96*, 784–785.

[16] For references, see: Abraham, M. H.; Grellier, P. L. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley & Sons: New York, 1985; Vol. 2, pp 25–149.

[17] Chandrasekhar, S. C.; Gallant, M.; Kobayashi, M.; Latour, S.; Wuest, J. D., submitted for publication.

[18] (a) Bhattacharya, S. N.; Raj, P. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1699–1700. (b) Stafford, S.; Haupt, H.-J.; Huber, F. *Inorg. Chim. Acta* **1974**, *11*, 207–216. Lindemann, H.; Huber, F. *Z. Anorg. Allg. Chem.* **1972**, *394*, 101–110. Gmehling, J.; Huber, F. *Ibid.* **1972**, *393*, 131–135. Haupt, H. J.; Huber, F.; Gmehling, J. *Ibid.* **1972**, *390*, 31–40. (c) Potts, D.; Walker, A. *Can. J. Chem.* **1969**, *47*, 1621–1626.

$Ph_nI_{3-n}PbCH_2CH_2CH_3$

7 (n = 3)

8 (n = 2)

9 (n = 1)

10 (n = 0)

3.39 (t, 2 H). We propose that this compound is diiodide **9**, which presumably arises because further iodinolysis of monoiodide **8** is fast enough to compete inefficiently with iodinolysis of unreacted plumbane **7**. As this assignment requires, direct treatment of plumbane **7** with 2 equiv of I_2 at 0 °C produced only diiodide **9**. No 1-iodopropane could be detected initially, confirming that aryl-lead bonds are cleaved faster than alkyl-lead bonds by iodine.

Solutions of monoiodide **8** ($CDCl_3$, 0.033 M) proved to be stable at 25 °C, and no decomposition or redistribution to give plumbane **7** and diiodide **9** could be observed after 24 h. In contrast, solutions of diiodide **9** decomposed completely under similar conditions, giving an approximately equimolar mixture of monoiodide **8**, 1-iodopropane, and PbI_2, which precipitated from solution and could be isolated in 100% yield. These observations support the hypothesis that the decomposition of diiodide **9** is triggered by redistribution (eq 1) and that the putative triiodide **10** undergoes rapid reductive elimination (eq 2). Triiodide **10** could not be detected even when plumbane **7** was treated directly with 3 equiv of I_2 ($CDCl_3$, 0.021 M, 0 °C). Under these conditions, further iodinolysis of diiodide **9** is faster than redistribution, but decomposition of triiodide **10** is faster still, and detectable concentrations are never present. Iodobenzene and 1-iodopropane are formed quantitatively in a 3:1 ratio, and PbI_2 could be isolated in 94% yield by filtration. Earlier reports that simple organolead triiodides can be isolated should therefore be regarded skeptically.[19]

In principle, reductive elimination of RX from organolead trihalides $RPbX_3$ can occur by the four plausible mechanisms summarized in Scheme II. One (path a) occurs in a single step. Another (path b) involves initial heterolysis of the carbon-lead bond, followed by transfer of halide. A third (path c) postulates homolysis of the carbon-lead bond and subsequent transfer of $X^\bullet$. It is also conceivable that $R^\bullet$ transfers an electron to $PbX_3^\bullet$ or $X^\bullet$, thereby producing the ion pairs formed by direct heterolysis.[21] A fourth alternative (path d) is homolysis of the halogen-lead bond followed by transfer of $R^\bullet$. Related possibilities include radical-chain mechanisms in which the radical pairs separate and $R^\bullet$ or $X^\bullet$ then react with $RPbX_3$ or other organolead halides.[22,23] However, the addition of chain terminators like $^3O_2$ failed to retard the decomposition of diiodide **9**, so we doubt that radical chains are involved.

Scheme II

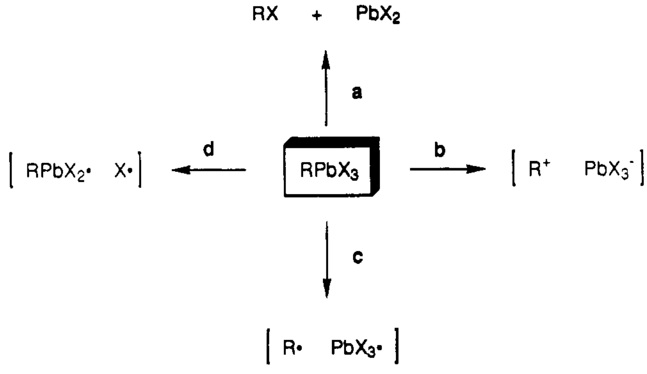


Table III. Heats of Formation (kcal/mol) Calculated by Using the MNDO Procedure[a,5,6]

compound	ΔH_f	compound	ΔH_f
H_4Pb	63.1 (59.7)[b]	$H_3Pb^\bullet$	64.8
$(CH_3)_4Pb$	26.1 (32.6)[c]	$(CH_3)_3Pb^\bullet$	32.5 (46.7)[c]
H_3PbI	57.9	$H_2PbI^\bullet$	46.8
$(CH_3)_3PbI$	27.7	$(CH_3)_2PbI^\bullet$	25.9
H_2PbI_2	52.6	$HPbI_2^\bullet$	33.7
$(CH_3)_2PbI_2$	30.8	$CH_3PbI_2^\bullet$	22.9
$HPbI_3$	47.1	$PbI_3^\bullet$	21.6
CH_3PbI_3	35.2	H_2PbI^-	−35.8
PbI_4	41.2	$HPbI_2^-$	−57.9
PbI_2	9.0 (−0.8)[d]	$(CH_3)_2PbI^-$	−54.2
		$CH_3PbI_2^-$	−66.5
		PbI_3^-	−76.5

[a] Experimental values, where available, appear in parentheses. [b] Saalfeld, F. E.; Svec, H. J. *Inorg. Chem.* **1963**, *2*, 46–50. [c] Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 4329–4332. Lappert, M. F.; Pedley, J. B.; Simpson, J.; Spalding, T. R. *J. Organomet. Chem.* **1971**, *29*, 195–208. [d] Chase, M. W.; Curnutt, J. L.; Prophet, H.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1975**, *4*, 1–175.

To permit a detailed thermodynamic comparison of paths a–d, we calculated the heats of formation of $R_{4-n}PbI_n$ (R = H and CH_3, n = 0–4), radicals $R_{3-n}PbI_n^\bullet$ (R = H and CH_3, n = 0–3), and anions $R_{3-n}PbI_n^-$ (R = H and CH_3, n = 1–3) by using the MNDO procedure.[5,6] The results are listed in Table III.[24] These values can be used to calculate that the redistribution of eq 1 (X = I) should be nearly thermoneutral for R = H and R = CH_3. However, a large driving force propels the reductive elimination of RI and PbI_2 from $RPbI_3$, which should be exothermic by 22.7 kcal/mol when R = CH_3.[25] The values in Table III, when combined with the standard heats of formation of H^+ (367.2 kcal/mol)[27a] and CH_3^+ (260.0 kcal/mol),[27b] indicate that the heterolytic cleavage of H^+ from H_3PbI, H_2PbI_2, and $HPbI_3$ should require 273.5, 256.7, and 243.6 kcal/mol, respectively, and that heterolytic cleavage of CH_3^+ from $(CH_3)_3PbI$, $(CH_3)_2PbI_2$, and CH_3PbI_3 should require 178.1, 162.7, and 148.3 kcal/mol. These estimates are consistent with our observation that organolead iodides become less stable as the number of iodines increases.[3e] Although the

---

[19] For a brief report of an implausible synthesis of organolead triiodides by the direct reaction of PbI_2 and RI at high temperatures, see: Chobert, G.; Devaud, M. *J. Organomet. Chem.* **1978**, *153*, C23–C24.

[20] Gilman, H.; Summers, L.; Leeper, R. W. *J. Org. Chem.* **1952**, *17*, 630–640.

[21] A similar electron transfer occurs in radical pairs formed by the photolysis of alkyl iodides. Kurz, M. E.; Noreuil, T.; Seebauer, J.; Cook, S.; Geier, D.; Leeds, A.; Stronach, C.; Barnickel, B.; Kerkemeyer, M.; Yandrasits, M.; Witherspoon, J.; Frank, F. J. *J. Org. Chem.* **1988**, *53*, 172–177. Bhalerao, V. K.; Nanjundiah, B. S.; Sonawane, H. R.; Nair, P. M. *Tetrahedron* **1986**, *42*, 1487–1496. Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131–137. Kropp, P. J.; Sawyer, J. A.; Snyder, J. J. *J. Org. Chem.* **1984**, *49*, 1583–1589.

[22] Generation of $PbX_3^\bullet$ in $CHCl_3$ would not necessarily lead to abstraction of chlorine atoms. Davies, A. G.; Hawari, J. A.-A.; Gaffney, C.; Harrison, P. G. *J. Chem. Soc., Perkin Trans. 2* **1982**, 631–635. Cooper, J.; Hudson, A.; Jackson, R. A. *Ibid.* **1973**, 1056–1060.

[23] Related abstractions of halogen atoms from alkyl halides by alkyl radicals are fast. Newcomb, M.; Sanchez, R. M.; Kaplan, J. *J. Am. Chem. Soc.* **1987**, *109*, 1195–1199.

[24] (a) These MNDO calculations[5,6] indicate that radicals $R_{3-n}PbI_n^\bullet$ should be nearly planar when $n \geq 2$ and pyramidal when $n < 2$ and that anions $R_{3-n}PbI_n^-$ should be pyramidal in all cases. (b) For recent related work, see: Glidewell, C. *J. Organomet. Chem.* **1990**, *398*, 241–249.

[25] This value is estimated by using the measured heat of formation of CH_3I (3.5 kcal/mol).[26]

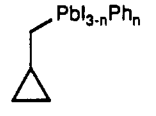
[26] Luo, Y.-R.; Benson, S. W. *J. Phys. Chem.* **1988**, *92*, 5255–5257.

[27] (a) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046–6056. (b) Anicich, V. G.; Blake, G. A.; Kim, J. K.; McEwan, M. J.; Huntress, W. T., Jr. *J. Phys. Chem.* **1984**, *88*, 4608–4617. (c) Russell, J. J.; Seetula, J. A.; Gutman, D. *J. Am. Chem. Soc.* **1988**, *110*, 3092–3099.

calculations indicate that organolead triiodides $RPbI_3$ cannot decompose readily in the gas phase by heterolysis of the carbon–lead bond (path b), the formation of ions may nevertheless be fast in condensed phases.

Our calculations also support the alternative hypothesis that organolead triiodides decompose by homolysis of carbon–lead or iodine–lead bonds (paths c and d). The values in Table III, when combined with the standard heats of formation of $H^{\bullet}$ (52.1 kcal/mol), $I^{\bullet}$ (25.5 kcal/mol), and $CH_3^{\bullet}$ (34.8 kcal/mol),[27c] indicate that the hydrogen–lead bond strengths in H_4Pb, H_3PbI, H_2PbI_2, and $HPbI_3$ are 53.8, 41.0, 33.2, and 26.6 kcal/mol, respectively, while the carbon–lead bond strengths in $(CH_3)_4Pb$, $(CH_3)_3PbI$, $(CH_3)_2PbI_2$, and CH_3PbI_3 are 41.5, 33.3, 27.2, and 21.5 kcal/mol, respectively. Similarly, the iodine–lead bond strengths in H_3PbI, H_2PbI_2, $HPbI_3$, and PbI_4 are 32.4, 19.7, 12.1, and 5.9 kcal/mol, respectively, while those in $(CH_3)_3PbI$, $(CH_3)_2PbI_2$, and CH_3PbI_3 are 30.3, 20.6, and 13.2 kcal/mol, respectively. The rather large discrepancy between the calculated carbon–lead bond strength in $(CH_3)_4Pb$ (41.5 kcal/mol) and the best measured value (55–58 kcal/mol)[3a] suggests that the calculated values should be used cautiously. Nevertheless, they are qualitatively consistent with our observation that bonds to lead weaken significantly as the number of iodines increases,[3e] and they suggest that organolead triiodides $RPbI_3$ can decompose homolytically with half-lives of less than approximately 12 s at 0 °C.

To distinguish paths a–d experimentally, we studied the iodinolysis of (cyclopropylmethyl)triphenylplumbane (11).[17] In $CDCl_3$, the ^1H NMR spectrum of compound 11 shows a characteristic doublet at δ 2.18 (2 H) for the exocyclic methylene. Treatment of a 0.020 M solution in $CDCl_3$ with 1 equiv of I_2 at 0 °C yielded primarily iodobenzene and the expected monoiodide 12, with a corresponding doublet at δ 2.80 (2 H). Only small amounts of (iodomethyl)cyclopropane[28] could be detected, confirming that aryl–lead bonds are cleaved faster than cyclopropylmethyl–lead bonds by iodine. Solutions of monoiodide 12 proved to be stable at 25 °C, and no decomposition or redistribution could be observed after 48 h. Treatment of a 0.024 M solution of plumbane 11 in $CDCl_3$ with 2 equiv of I_2 at 0 °C yielded iodobenzene, monoiodide 12, (iodomethyl)cyclopropane, and PbI_2 as the major products in an approximate ratio of 2:1:1:1. These observations suggest that iodinolysis produces intermediate diiodide 13, which then yields monoiodide 12 and putative triiodide 14 by normal redistribution. Decomposition of triiodide 14 by reductive elimination finally provides (iodomethyl)cyclopropane and PbI_2.



11 (n = 3)

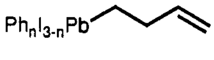
12 (n = 2)

13 (n = 1)

14 (n = 0)

The nearly complete absence of 4-iodobutene[29] and iodocyclobutane[30] among the products of reductive elimination is a noteworthy observation, since it helps distinguish paths a–d in Scheme II. Initial heterolysis (path b) would generate the cyclopropylmethyl cation, which would react with iodide to form a highly characteristic manifold of products including (iodomethyl)cyclopropane, 4-iodobutene, and iodocyclobutane.[31] Alternatively, initial homolysis (paths c and d) would produce the cyclopropylmethyl radical.[32] Rapid rearrangement of the radical and subsequent iodine transfer would then yield significant amounts of 4-iodobutene, which were not observed. Our evidence therefore supports the hypothesis that reductive elimination of RI and PbI_2 from $RPbI_3$ occurs in a single step (step a) or that it occurs by homolysis (paths c or d) followed by steps in which the cyclopropylmethyl radical combines with iodine atoms much more rapidly than it rearranges.[33] As expected, direct treatment of plumbane 11 with 3 equiv of I_2 ($CDCl_3$, 0.020 M, 0 °C) yielded iodobenzene, (iodomethyl)cyclopropane, and PbI_2 as the only initial products. After 48 h at 25 °C, however, the (iodomethyl)cyclopropane was converted almost quantitatively into 4-iodobutene and traces of iodocyclobutane. These products are characteristic of a cationic rearrangement of (iodomethyl)cyclopropane, presumably induced by PbI_2. As this hypothesis requires, no subsequent rearrangement of (iodomethyl)cyclopropane occurred when PbI_2 was removed from the initial reaction mixture by filtration.

In a related experiment, we treated 3-butenyltriphenylplumbane (15)[17,34] with 3 equiv of I_2 ($CDCl_3$, 0.10 M, 25 °C). The only products were iodobenzene (96%), 4-iodobutene (85%), and PbI_2 (93%), which are presumably derived from unstable triiodide 16 by reductive elimination. Since the 3-butenyl radical is not normally a precursor of derivatives of methylcyclopropane, the products derived from triiodide 16 do not distinguish a concerted reductive elimination from a stepwise homolytic pathway.



15 (n = 3)

16 (n = 0)

Since the decomposition of simple organolead diiodides R_2PbI_2 is triggered by intermolecular redistribution reactions, we suspected that more complex organolead diiodides capable of rapid intramolecular redistributions would be particularly unstable. To test this hypothesis, we followed the iodinolysis of 1,3-propanediylbis[triphenylplumbane] (17)[17,35] by ^1H NMR spectroscopy. Treatment of compound 17 with 2 equiv of I_2 ($CDCl_3$, 0.033 M, 0 °C) initially yielded the symmetric diiodide 18. Unlike simple analogues 8 and 12, organolead iodide 18 decomposed completely within 24 h at 25 °C, giving cyclopropane as the only product derived from the 1,3-propanediyl group. This observation suggests that organolead iodide 18 undergoes a direct 1,3-elimination[36] or

---

(28) (a) San Filippo, J., Jr.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834–4842. (b) Lansbury, P. T.; Pattison, V. A.; Clement, W. A.; Sidler, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 2247–2251.

(29) Kaplan, L. *J. Chem. Soc., Chem. Commun.* **1968**, 754–755.

(30) Wiberg, K. B.; Barth, D. E.; Pratt, W. E. *J. Am. Chem. Soc.* **1977**, *99*, 4286–4289.

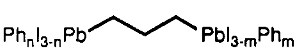
(31) For a recent reference, see: Moss, R. A.; Ho, G. J.; Wilk, B. K. *Tetrahedron Lett.* **1989**, *30*, 2473–2476.

(32) For recent references, see: Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275–277.

(33) For recent efforts to devise substituted cyclopropylmethyl radicals that rearrange more rapidly than the parent and can therefore be used as more sensitive mechanistic probes, see: Lemieux, R. P.; Beak, P. *J. Org. Chem.* **1990**, *55*, 5454–5460.

(34) Gilman, H.; Towne, E. B.; Jones, H. L. *J. Am. Chem. Soc.* **1933**, *55*, 4689–4693.

(35) Gilman, H.; Summers, L. *J. Am. Chem. Soc.* **1952**, *74*, 5924–5927.



17 (m = n = 3)

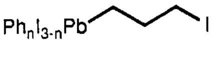
18 (m = n = 2)

19 (m = n = 1)

20 (m = 2, n = 0)

an indirect 1,3-elimination preceded by intra- or intermolecular redistribution reactions.

Treatment of diplumbane **17** with 4 equiv of I_2 ($CDCl_3$, 0.016 M, 0 °C) initially yielded a complex mixture in which significant amounts of the expected symmetric tetraiodide **19** could not be detected. We therefore propose that compound **19** undergoes a rapid intramolecular redistribution reaction and that the resulting unsymmetric tetraiodide **20** then decomposes by reductive elimination. This would produce iodo(3-iodopropyl)diphenylplumbane (**22**), which would be converted into diiodo(3-iodopropyl)phenylplumbane (**23**) by further iodinolysis.



21 (n = 3)

22 (n = 2)

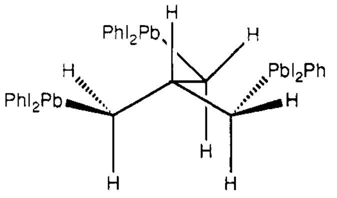
23 (n = 1)

24 (n = 0)

In fact, both compounds **22** and **23** are major components of the mixture initially formed by treating diplumbane **17** with 4 equiv of I_2. This was established by using controlled iodinolyses of (3-iodopropyl)triphenylplumbane (**21**) to prepare solutions of authentic samples of compounds **22** and **23**. The ^1H NMR spectrum of compound **21** in $CDCl_3$ shows characteristic aliphatic signals at δ 2.16 (t, 2 H), 2.38 (m, 2 H), and 3.20 (t, 2 H). Treatment of a 0.015 M solution in $CDCl_3$ with 1 equiv of I_2 at 0 °C yielded primarily iodobenzene and the expected iodide **22**, with aliphatic signals at δ 2.65 (m, 4 H) and 3.26 (t, 2 H). Like other organolead monoiodides, this compound proved to be stable in solution at 25 °C, and no decomposition or redistribution occurred after 24 h. Addition of 2 equiv of I_2 to a solution of plumbane **21** ($CDCl_3$, 0.015 M, 0 °C) produced the expected iodide **23**, which showed characteristic aliphatic signals at δ 2.72 (quint, 2 H), 3.29 (t, 2 H), and 3.35 (t, 2 H). Like other organolead diiodides, compound **23** proved to be unstable in solution at 25 °C, and its decomposition generated an approximately equimolar mixture of iodide **22**, 1,3-diiodopropane,[37] and PbI_2, which could be isolated in 83% yield. These observations support the hypothesis that compound **23** decomposes by normal intermolecular redistribution to give organolead monoiodide **22** and triiodide **24**, which then yields 1,3-diiodopropane and PbI_2 by rapid reductive elimination. The absence of significant amounts of cyclopropane and propene indicates that the reductive elimination cannot involve long-lived 3-iodopropyl radicals.[38] As expected, addition of 6 equiv of I_2 to diplumbane **17** ($CDCl_3$, 0.059 M, 25 °C) produced only iodobenzene, 1,3-diiodopropane, and PbI_2, which were formed in 87%, 72%, and 90% yields, respectively.

Our studies of the iodinolyses of monoplumbanes **7**, **11**, **15**, and **21** and of diplumbane **17** demonstrate that (1) phenyl–lead bonds are cleaved selectively, (2) simple organolead monoiodides are stable in solution, (3) organolead diiodides are susceptible to redistribution reactions that produce the corresponding organolead monoiodides and triiodides, and intramolecular versions of these redistributions are particularly rapid, and (4) organolead triiodides undergo reductive eliminations in a single rapid step. With these simple generalizations as a guide, we examined the iodinolysis of triplumbane **4**. Treatment of a 0.0025 M solution in $CDCl_3$ with 3 equiv of I_2 at 0 °C caused the characteristic methylene doublet at δ 2.42 to be replaced by a new doublet at δ 2.99. This indicated that the initial product of iodinolysis retains an axis of effective C_{3v} symmetry and must therefore be the expected symmetric triiodide **5**. Like analogue **18**, compound **5** decomposed slowly by 1,3-elimination, and after 96 h at 25 °C it was converted into significant amounts of (cyclopropylmethyl)iodoplumbane **12**.

Treatment of triplumbane **4** with 6 equiv of I_2 under similar conditions yielded a single product with a doublet at δ 3.70. This is convincing evidence for formation of the symmetric hexaiodide **6**, the precursor required for the synthesis of plumbaadamantane **2b**. Although hexaiodide **6** is unstable in solution at 25 °C, it does not undergo intramolecular redistributions as rapidly as the analogous tetraiodide **19**. We attribute the unexpected stability of hexaiodide **6** to a preference for C_3 conformation **6a**,[39] in which bridging by iodide or phenyl is disfavored.[41] As expected, treatment of triplumbane **4** with 9 equiv of I_2 ($CDCl_3$, 0.0095 M, 25 °C) produced primarily iodobenzene, 1,3-diiodo-2-(iodomethyl)propane (**25**),[44] and PbI_2, as well as minor amounts of other organic iodides.[45]



6a

$(ICH_2)_3CH$

25

The relatively slow redistribution of hexaiodide **6** gave us hope that it could be trapped at low temperatures by donors of sulfide and converted into plumbaadamantane **2b**. We therefore added 3 equiv of bis(triphenyltin) sulfide to freshly prepared solutions of hexaiodide **6** in CH_2Cl_2 at −78 °C. An unexpected black solid precipitated immediately, and no signals attributable to plumbaadamantane **2b** could be detected in the ^1H NMR spectrum of the

---

(36) For a similar 1,3-elimination, see: Seetz, J. W. F. L.; Hartog, F. A.; Böhm, H. P.; Blomberg, C., Akkerman, O. S.; Bickelhaupt, F. *Tetrahedron Lett.* **1982**, *23*, 1497–1500.

(37) Collman, J. P.; Brauman, J. I.; Madonik, A. M. *Organometallics* **1986**, *5*, 218–222.

(38) Conlin, R. T.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 7637–7638. Drury, R. F.; Kaplan, L. *Ibid.* **1973**, *95*, 2217–2221. Drury, R. F.; Kaplan, L. *Ibid.* **1972**, *94*, 3982–3986.

(39) Similar C_3 conformations are adopted by triplumbane **4**[17] and tristannane **3**.[40]

(40) Beauchamp, A. L.; Latour, S.; Olivier, M. J.; Wuest, J. D. *J. Organomet. Chem.* **1983**, *254*, 283–291.

(41) In the solid state, bromide bridging occurs in organolead bromides,[42] but intramolecular iodide bridges are not found in similar compounds of tin.[43]

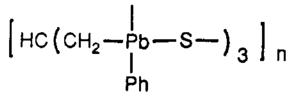
(42) Kroon, J.; Hulscher, J. B.; Peerdeman, A. F. *J. Organomet. Chem.* **1970**, *23*, 477–485.

(43) Cody, V.; Corey, E. R. *J. Organomet. Chem.* **1969**, *19*, 359–365.

(44) Latour, S.; Wuest, J. D. *Synthesis* **1987**, 742–745.

(45) The ultimate products of the iodinolysis of triplumbane **4** depend critically on the number of equivalents of I_2 and the concentration, which determine the initial product and the rate of subsequent intermolecular redistributions. Under the influence of PbI_2, the intermediate organolead iodides can undergo a complex variety of 1,3-eliminations and rearrangements characteristic of derivatives of triplumbane **4** and related compounds.[1a,17]

supernatant solution. The solid was isolated by filtration and identified as PbS by IR spectroscopy and elemental analysis. These observations are consistent with the transient formation of plumbaadamantane **2b** or oligomer **26**, followed by rapid decomposition leading to PbS and unidentified organic fragments. Simple organolead disulfides are known to be unstable,[11b,46] but some have nevertheless been isolated and characterized at room temperature. We attribute the unusually high reactivity of plumbaadamantane **2b** or oligomer **26** to strain or to the possible intramolecularity of their redistribution reactions. The intrinsic weakness of bonds to lead in organolead dihalides and disulfides and the tendency of these compounds to undergo redistribution reactions make the synthesis, detection, and isolation of plumbaadamantane **2b** and its analogues an extremely difficult objective.



$$\left[HC(CH_2-\underset{Ph}{\overset{|}{Pb}}-S-)_3 \right]_n$$

26

Experimental Section

Infrared (IR) spectra were recorded on Perkin-Elmer Model 710B and 783 spectrometers. A Varian VXR-300 spectrometer was used to obtain ^1H nuclear magnetic resonance (NMR) spectra at 300 MHz. ^1H NMR chemical shifts are reported in parts per million downfield from internal tetramethylsilane (δ). Mass spectra were recorded on a V. G. Micromass 12-12 quadrupole spectrometer using chemical ionization mass spectrometry. Capillary vapor-phase chromatographic (GC) separations were accomplished on an SE-54 column (15 m × 0.25 mm) using a Hewlett-Packard 5890 instrument. Melting points were recorded on a Thomas-Hoover capillary apparatus. Galbraith Laboratories, Knoxville, TN, performed all elemental analyses.

$CDCl_3$ was dried by passage through activity I basic Al_2O_3, and tetrahydrofuran (THF) was dried by distillation from the sodium ketyl of benzophenone. Triphenylpropylplumbane (**7**),[20] (cyclopropylmethyl)triphenylplumbane (**11**),[17] (iodomethyl)cyclopropane,[28a] 4-iodobutene,[29] iodocyclobutane,[30] 3-butenyltriphenylplumbane (**15**),[17,34] 1,3-propanediylbis[triphenylplumbane] (**17**),[17,35] 1,3-diiodopropane,[37] [2-[(triphenylplumbyl)methyl]-1,3-propanediyl]bis[triphenylplumbane] (**4**),[17] 1,3-diiodo-2-(iodomethyl)propane (**25**),[44] and bis(triphenyltin) sulfide[15] were prepared by published procedures. The lithium wire used to generate solutions of (triphenylplumbyl)lithium[47] in THF was 3.2 mm in diameter and contained approximately 0.01% sodium. All other reagents were commercial products of the highest purity available.

Iodinolyses of Organoplumbanes 4, 7, 11, 15, 17, and 21. Under dry N_2, weighed amounts of the organoplumbane and 1,2-diphenylethane, added as an internal standard, were dissolved in a specific volume of $CDCl_3$. The solution was stirred and treated dropwise with a solution containing an appropriate number of equivalents of I_2 dissolved in a specific volume of $CDCl_3$. ^1H NMR spectra of aliquots were recorded at suitable intervals. Organic products were identified by their characteristic ^1H NMR signals and GC retention times, and yields were determined by comparing the measured integrals with those of the internal standard. PbI_2 was isolated by filtration and identified by IR and mass spectroscopy.

(3-Iodopropyl)triphenylplumbane (21). A solution of (triphenylplumbyl)lithium[47] in THF was prepared under dry Ar by agitating a large excess of Li wire (601 mg, 86.6 mmol), freshly cut into small pieces, with hexaphenyldiplumbane (955 mg, 1.09 mmol) in THF (10 mL) at 25 °C for 45 min. The mixture was centrifuged, and then the supernatant solution was transferred by syringe to a second flask, stirred, and treated dropwise at 0 °C with neat 1,3-diiodopropane (644 mg, 2.18 mmol).[37] The mixture was stirred at 0 °C for 24 h, treated with deoxygenated H_2O (10 mL), stirred briefly at 25 °C, treated in air with additional H_2O (20 mL), and then extracted with CH_2Cl_2. The extracts were dried ($MgSO_4$), and solvent was removed by evaporation under reduced pressure. Column chromatography of the residue (activity III basic Al_2O_3, hexane (99%)/ethyl acetate (1%)) yielded (3-iodopropyl)triphenylplumbane (**21**) as a white solid (591 mg, 0.973 mmol, 44.6%). Recrystallization from 95% ethanol provided an analytically pure sample in the form of fine colorless needles: mp 175–177 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.16 (t, 2 H), 2.38 (m, 2 H), 3.20 (t, 2 H), 7.2–7.7 (m, 15 H). Anal. Calcd for $C_{21}H_{21}IPb$: C, 41.51; H, 3.46. Found: C, 41.79; H, 3.48.

Acknowledgment. This work was funded by the Natural Sciences and Engineering Research Council of Canada and by the Ministère de l'Éducation du Québec. We also thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support. In addition, we thank the Centre de Calcul, Université de Montréal, for a generous gift of computer time. We are grateful to Michael Evans and Christine Johnson of the Regional Mass Spectrometry Laboratory for recording our mass spectra.

---

(46) Gaffney, C.; Harrison, P. G. *J. Chem. Soc., Dalton Trans.* **1982**, 1055–1060. Wieber, M.; Baudis, U. *J. Organomet. Chem.* **1977**, *125*, 199–207. Davidson, W. E.; Hills, K.; Henry, M. C. *Ibid.* **1965**, *3*, 285–294.

(47) Willemsens, L. C.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1968**, *15*, 117–124. Gorth, H.; Henry, M. C. *Ibid.* **1967**, *9*, 117–123. Tamborski, C.; Ford, F. E.; Lehn, W. L.; Moore, G. J.; Soloski, E. J. *J. Org. Chem.* **1962**, *27*, 619–621.