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Electron-Transfer Mechanisms in Organometallic Chemistry. Alkyl Transfer from Organolead Compounds with Hexachloroiridate(IV)[1]

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Abstract: The importance of electron-transfer processes as viable routes for reactions of organometals is shown in the facile transfer of alkyl groups in the reaction between alkyllead compounds and hexachloroiridate(IV) as a model system. The rates of reaction for a series of methyl/ethyllead compounds ($Et_{4-n}PbMe_n$, $4 \geq n \geq 0$) with hexachloroiridate(IV) follow second-order kinetics. The rate constants k_2 increase progressively as methyl is replaced by ethyl groups, and a given ethyl group is cleaved more than 20 times faster than a methyl group. Both of these reactivity trends are diametrically opposed to known patterns of electrophilic cleavage. A rate-limiting step involving electron transfer from a series of organolead compounds to hexachloroiridate (i.e., log k_2) correlates with the energetics of other electron-detachment processes including: electrochemical oxidation, He I photoelectron spectroscopy, and charge-transfer bands of tetracyanoethylene complexes. Mass spectral studies indicate that selectivity in the scission of CH_3–Pb and CH_3CH_2–Pb bond arises during spontaneous fragmentation of the organolead cation radicals. Alkyl radicals are shown to be intermediates by spin trapping and the observation of the ESR spectra of nitroxide adducts. Separate experiments demonstrate that alkyl chloride arises as a product from the highly efficient scavenging of alkyl radicals by hexachloroiridate(IV). The reduced chloroiridium(III) species are partially characterized.

The formation and cleavage of carbon–metal bonds play important roles in the chemistry of organometallic intermediates involved in catalytic processes of organic as well as biochemical substrates. Transfer of alkyl groups from one metal to another can constitute the route by which alkyl groups are transported, a particularly relevant example being the cobalamin-dependent transfer of methyl groups to metals such as mercury and other heavy elements.[2]

Electrophilic processes represent by far the most common pathway by which carbon–metal bonds are cleaved, as indicated schematically in eq 1.[3] However, most organometallic

$$CH_3{-}M + E^+ \longrightarrow CH_3{-}E + M^+ \qquad (1)$$

intermediates have relatively low ionization potentials, and electron-transfer processes in eq 2, as well as other efficient free-radical chain processes, are possible.

$$CH_3{-}M + E^+ \longrightarrow [CH_3{-}M\cdot^+E\cdot] \longrightarrow CH_3\cdot + M^+ + E\cdot, \text{etc.} \qquad (2)$$

There are several reports relating to the possible importance of charge transfer in the reactions of organometallic compounds. Thus, methyl transfer in eq 3 is rapid in dimethyl sulfoxide and accompanied by electron transfer between cobalt(III) and cobalt(II).[4] The large number of oxidation states available to cobalt unfortunately complicates the mechanistic interpretation of alkyl transfer between those organocobalt species. Similar ambiguities are inherent in the alkyl-transfer reactions between alkylcobalt(III) and chromium(II).[5]

$$CH_3{-}Co^{III}(acen) + Co^{II}(tfacen) \longrightarrow Co^{II}(acen) + CH_3Co^{III}(tfacen) \qquad (3)$$

The oxidative cleavage of benzylbis(dimethylglyoximato)cobalt(III) by hexachloroiridate(IV) proceeds according to eq 4,[6] but it is unlikely that a benzyl radical is an intermediate arising from the homolysis of the cobalt–carbon bond. For example, a related oxidative cleavage of optically active *sec*-octyl-$Co^{III}(DH)_2$ by hexachloroiridate(IV) in the presence of added bromide ion afforded *sec*-octyl bromide of inverted configuration, and nucleophilic displacement from an alkylcobalt(IV) intermediate was proposed.[7,8]

$$RCo^{III}(DH)_2 + 2IrCl_6^{2-} \xrightarrow[H_2O]{} Co^{III}(DH)^+ + 2IrCl_6^{3-} + ROH \qquad (4)$$

$$RCo^{III}(DH)_2 + IrCl_6^{2-} \longrightarrow RCo^{IV}(DH)_2^+ + IrCl_6^{3-} \qquad (5)$$

$$RCo^{IV}(DH)_2^+ + Br^- \longrightarrow RBr + Co^{II}(DH)_2 \qquad (6)$$

$$Co^{II}(DH)_2 + IrCl_6^{2-} \longrightarrow Co^{III}(DH)_2^+ + IrCl_6^{3-} \qquad (7)$$

Finally, the observation of an ESR spectrum assigned to a complex between mercury and semiquinone radical was recently reported during the addition of diethylmercury to 3,5-di-*tert*-butyl-1,2-benzoquinone at 40°.[9] Homolytic cleavage of the Hg-Et bond subsequent to electron transfer was postulated, but no experimental details have appeared as yet.

We have chosen organolead compounds as models for the study of alkyl-transfer reactions, because they incorporate the best features of organometallic systems; i.e., they are reactive but sufficiently substitution stable and well behaved in solution to allow for meaningful quantitative study.[10] The intra- and intermolecular competitive cleavage of CH_3-Pb vs. CH_3CH_2-Pb bonds in a series of methyl/ethyllead compounds $(CH_3)_{4-n}Pb(CH_2CH_3)_n$ provides a useful diagnostic test for various cleavage mechanisms.[11a,b] Hexachloroiridate(IV) was chosen for its well-known properties

Table I. The Stoichiometry of Oxidative Cleavage of Methyl/Ethyllead Compounds by Hexachloroiridate(IV)[a]

$Et_{4-n}PbMe_n$ (mmol)	$IrCl_6^{-2}$, mmol	Solvent	RCl, mmol EtCl	RCl, mmol MeCl	$\frac{EtCl^b}{MeCl}$	$\frac{2RCl^c}{Ir(IV)}$
Et_4Pb (0.100)	0.200	CH_3CN	0.101	0		1.0
Et_4Pb (0.255)	0.0635	HOAc	0.030	0		0.95
Et_4Pb (0.100)	0.200	HOAc	0.100	0		1.0
Et_4Pb (0.050)	0.198	HOAc	0.094	0		0.95
Et_4Pb (0.025)	0.199	HOAc	0.49	0		0.49
Et_3PbMe (0.100)	0.200	CH_3CN	0.104	0.0015	24	1.1
Et_3PbMe (0.100)	0.200	HOAc	0.102	0.0033	11	1.0
Et_2PbMe_2 (0.100)	0.200	CH_3CN	0.101	0.0040	25	1.1
Et_2PbMe_2 (0.067)	0.200	CH_3CN	0.095	0.010		1.0
Et_2PbMe_2 (0.100)	0.200	HOAc	0.092	0.0060	15	1.0
$EtPbMe_3$ (0.100)	0.200	CH_3CN	0.092	0.012	23	1.0
$EtPbMe_3$ (0.100)	0.200	HOAc	0.087	0.0095	27	0.97
Me_4Pb (0.100)	0.200	CH_3CN	0	0.105		1.0
Me_4Pb (0.100)	0.200	HOAc	0	0.098		0.98

[a] At 25° using $Na_2IrCl_6 \cdot 6H_2O$. [b] Normalized. [c] Relative to Ir(IV) consumed.

as a one-electron oxidant capable of participating in both outer-sphere and inner-sphere processes.[12] We wish to demonstrate in this report the importance of electron-transfer processes as viable routes for reactions of alkyl metals since charge transfer and other homolytic processes are little known in contrast to the usual electrophilic mechanisms.

Results

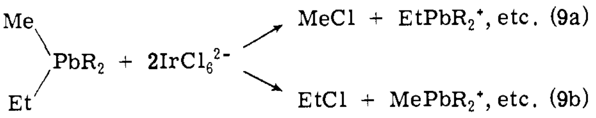
Tetraalkyllead compounds react rapidly with hexachloroiridate(IV) at 25° in acetonitrile or acetic acid solution. For example, the addition of tetramethyllead to a solution of $IrCl_6^{2-}$ in acetic acid results in the immediate discharge of the dark red-brown color, followed by the partial precipitation of the reduced iridium(III) species from solution.

Products and Stoichiometry. Methyl chloride and trimethyllead acetate are formed from tetramethyllead and hexachloroiridate(IV) in acetic acid solutions according to the stoichiometry in eq 8. Methyl chloride was determined

$$(CH_3)_4Pb + 2IrCl_6^{2-} \xrightarrow{HOAc} (CH_3)_3PbOAc + CH_3Cl + IrCl_6^{3-} + (IrCl_5^{2-}) \quad (8)$$

by quantitative gas chromatography. The formation of trimethyllead acetate was examined by its ^1H NMR spectrum in acetic-d_4 acid using nitrobenzene as an internal standard.

Only one alkyl group is readily cleaved from each tetraalkyllead compound. The mixed methyl/ethyllead derivatives afford mixtures of methyl and ethyl chlorides, the yields of which depend on the organolead compound as listed in



$$\begin{tikzcd}[column sep=small] & MeCl + EtPbR_2^{+}, \text{etc.} \quad (9a) \\ \begin{matrix}Me\\ \\ Et\end{matrix}\!\!>PbR_2 + 2IrCl_6^{2-} \arrow[ur] \arrow[dr] & \\ & EtCl + MePbR_2^{+}, \text{etc.} \quad (9b)\end{tikzcd}$$

Table I. After normalization for each type of alkyl group in the reactant, the relative yields of ethyl chloride and methyl chloride are rather constant at about 25:1 in acetonitrile but vary somewhat in acetic acid.

If more than a stoichiometric amount of tetraalkyllead is charged relative to hexachloroiridate(IV), the production of alkyl chlorides is rapid but ceases abruptly, when two $IrCl_6^{2-}$ are consumed as indicated by the loss of color. If a large excess of hexachloroiridate(IV) is employed, two alkyl groups can be cleaved from each tetraalkyllead, but the rate of cleavage of the first alkyl group is much faster than that of the second (vide infra). Furthermore, the selectivity in the oxidative cleavage of Me-Pb vs. Et-Pb bonds shows only a slight dependence on solvent, whether it is acetonitrile or acetic acid.

The characterization of the reduced iridium(III) species was more difficult since the absorption spectrum of the material isolated from acetonitrile was almost featureless between 320 and 700 nm as shown in Figure 1a. However, oxidation of the light-brown product with either chlorine or lead dioxide afforded a highly colored solution which could be separated into two components by silica gel chromatography. The spectrum of the first component shown in Figure 1b is clearly associated with hexachloroiridate(IV),[12d] but the spectrum of the second component (Figure 1c) does not correspond to any known iridium(IV) compound. We presume that this species is pentachloro(acetonitrile)iridate(IV) since separate experiments show that the same product is obtained (after treatment with chlorine) from the reduction of hexachloroiridate(IV) by ethyl radicals produced by the thermolysis of propionyl peroxide (vide infra). Similar results were obtained with iridium(III) products isolated from reactions carried out in acetic acid.

We infer from these results that the iridium-containing products formed in nonaqueous solutions consist of an equimolar mixture of hexachloroiridate (III) and pentachloroiridate(III). The latter probably exists as dimers and oligomers,[13] which are difficult to manipulate owing to the generally greater substitution lability of iridium(III) compounds compared with the iridium(IV) counterparts. However, these oligomers are quantitatively converted on oxidation to monomeric iridium(IV) species which are more readily characterized.

Essentially all previous studies on the chemistry of hexachloroiridate(IV) have been carried out in aqueous solutions.[12,14] In those cases where reduction of iridium(IV) occurs by abstraction of a chlorine atom, water is available to fill the vacant coordination site in the metastable pentachloroiridate(III) species. Unfortunately, $Ir^{III}Cl_5(OH_2)^{2-}$ is not readily distinguished from $Ir^{III}Cl_6^{3-}$ due to their similar absorption spectra, but oxidation affords a mixture of $Ir^{IV}Cl_5(OH_2)^-$ and $Ir^{IV}Cl_6^{2-}$, which are readily distinguished.[12d] For these ions, isosbestic points occur at 438, 476, and 524 nm, where ϵ = 3060, 2750, and 1260 M^{-1} cm^{-1}, respectively. Indeed, the reaction of Me_3PbEt and hexachloroiridate(IV) in 30% aqueous acetic acid remains homogeneous, and spectrophotometric analysis of the oxidized reaction mixture showed the presence of $IrCl_6^{2-}$ and $IrCl_5(OH_2)^-$ in 42 and 58% yields, respectively. The same reaction in a wholly aqueous medium was slow due to the insolubility of the organolead compound. Nonetheless, the visible absorption spectrum of the solution after a prolonged period indicated a maximum at 410 nm and a shoulder at

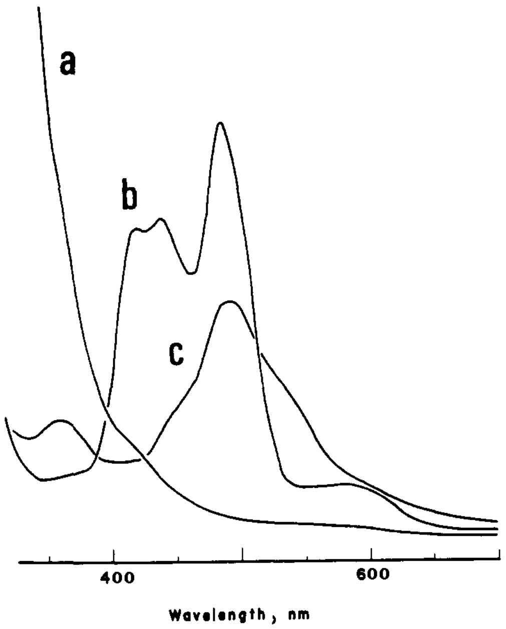


Figure 1. Visible absorption spectra of iridium products from the reaction of tetraethyllead and hexachloroiridate(IV) in acetonitrile. Absorption units are arbitrary. (a) Reduced iridium(III) products in methanol. Oxidation of Ir(III) product with chlorine: (b) fraction 1, hexachloroiridate(IV); and (c) fraction 2, pentachloro(acetonitrile)iridium(IV).

Table II. Kinetics of the Reaction between Tetraalkyllead and Hexachloroiridate(IV)[a]

$Et_{4-n}PbMe_n$	Concn,[b] $10^4 M$	$IrCl_6^{2-}$,[b] $10^4 M$	Solvent	Rate[c] constant, M^{-1} sec^{-1}	Detn[d]
Et_4Pb	0.16	1.2	CH_3CN	$2.6 \pm 0.25 \times 10$	18
	6.5	20.9			
Et_4Pb	1.0	0.18	HOAc	$1.2 \pm 0.17 \times 10^4$	8
	10.0	4.7			
Et_3PbMe	0.67	1.0	CH_3CN	$1.1 \pm 0.12 \times 10$	10
	5.8	21.0			
Et_3PbMe	0.28	0.29	HOAc	$7.0 \pm 0.6 \times 10^3$	7
	3.3	6.5			
Et_2PbMe_2	1.5	2.2	CH_3CN	3.3 ± 0.2	7
	12.5	21.4			
Et_2PbMe_2	0.30	0.30	HOAc	$1.1 \pm 0.16 \times 10^3$	5
	12.0	4.7			
$EtPbMe_3$	2.0	1.2	CH_3CN	$5.7 \pm 0.3 \times 10^{-1}$	5
	11.9	20.8			
$EtPbMe_3$	0.33	0.50	HOAc	$1.1 \pm 0.11 \times 10^2$	5
	3.3	4.3			
Me_4Pb	18.2	1.6	CH_3CN	$2.0 \pm 0.5 \times 10^{-2}$	7
	124	19.4			
Me_4Pb	1.3	0.62	HOAc	4.7 ± 0.3[e]	4
	6.5	9.2			

[a] Reactions in CH_3CN contain 1.0 *F* $LiClO_4$, under nitrogen atmosphere at 36°. Reactions in HOAc at 25.4°. [b] Upper and lower limits in concentrations of reactants. [c] Error limits correspond to one standard deviation. [d] Number of determinations. [e] By conventional methods.

Table III. Temperature Dependence of the Reaction of Hexachloroiridate(IV) and Tetraalkyllead[a]

$Et_{4-n}PbMe_n$	Solvent	Temp, °C	Rate constant, M^{-1} sec^{-1}
Et_4Pb	CH_3CN[b]	18.8	11.5 ± 1.0
		25.0	17 ± 1.5
		36.0	26 ± 2.5
		42.2	38 ± 4.0
Et_4Pb	HOAc	25.4	$1.2 \pm 0.2 \times 10^4$
		36.0	$2.0 \pm 0.2 \times 10^4$
		46.0	$2.9 \pm 0.3 \times 10^4$
Me_4Pb	HOAc	8.0	1.8 ± 0.2
		19.0	3.6 ± 0.5
		25.4	4.7 ± 0.3
		36.0	9.3 ± 0.6

[a] In solutions containing 1.0×10^{-4} *M* R_4Pb and 2.0×10^{-4} *M* $IrCl_6^{2-}$. [b] Containing 1.0 *F* $LiClO_4$.

340 nm, suggesting that $IrCl_6^{3-}$ and $IrCl_5(OH_2)^{2-}$ are the only important iridium(III) products. Spectrophotometric examination of the iridium(IV) products after oxidation indicated that $IrCl_6^{2-}$ and $IrCl_5(OH_2)^-$ were present in a ratio of 49:51.

Kinetics. Tetraalkyllead compounds react with hexachloroiridate(IV) at differing rates, which were followed spectrophotometrically by the disappearance of the absorption bands at 490 and 585 nm. The kinetics showed a first-order dependence on tetraalkyllead and hexachloroiridate(IV) in both acetonitrile and acetic acid solution. The second-order

$$-\frac{d(IrCl_6^{2-})}{dt} = k(R_4Pb)(IrCl_6^{2-}) \qquad (10)$$

rate constants determined in acetonitrile solutions were obtained by conventional methods and found to increase progressively from Me_4Pb, Me_3PbEt, Me_2PbEt_2, $MePbEt_3$, to Et_4Pb as listed in Table II. The facile reaction of Et_4Pb represented the upper limit by this technique, and its rate constant was thus subject to the largest error. Lithium perchlorate was added to maintain constant ionic strength of the medium. Under these conditions, the second-order rate constant was invariant over a tenfold concentration range in each reactant. Since the reaction in acetic acid was roughly three orders of magnitude faster than that in acetonitrile, the rates were determined with a stopped-flow spectrophotometer. The reduced iridium(III) products exerted no effect on the rate of reaction.

The rate of disappearance of hexachloroiridate(IV) was reduced by roughly 20–30%, when the reaction with tetraethyllead was carried out in an atmosphere of oxygen. This rate decrease could be accounted for by the partial scavenging of ethyl radicals (vide infra). Thus, the oxidative cleavage of 0.4 mmol of Et_4Pb with 0.2 mmol of $IrCl_6^{2-}$ afforded 0.02 mmol of acetaldehyde in addition to the expected

$$CH_3CH_2\cdot + O_2 \longrightarrow CH_3CH_2O_2\cdot \longrightarrow CH_2CHO \qquad (11)^{15}$$

ethyl chloride (0.085 mmol). Finally, the addition of other nucleophiles such as bromide ion (0.1 *M*) and water (up to 30 vol %) had little or no effect on the production of alkyl chlorides.

The temperature dependence of the rate constants for the reactions of hexachloroiridate(IV) with tetraethyllead and tetramethyllead in acetic acid and acetonitrile are listed in Table III.

Studies of Electron Detachment from Tetraalkyllead Compounds. In order to measure the energetics of oxidative cleavages of tetraalkyllead compounds, we examined several electron-detachment processes including: (1) electro-

$$R_4Pb \longrightarrow R_4Pb^{\cdot+} + e \qquad (12)$$

chemical oxidation; (2) ionization potential by photoelectron spectroscopy; (3) charge-transfer complexes; and (4) mass-spectral cracking patterns.

1. Electrochemical Oxidation of Tetraalkyllead Compounds. The anodic oxidation of methyl/ethyllead compounds was examined in acetonitrile solutions with lithium fluoroborate as a supporting electrolyte. The value of *n*, the number or electrons involved in the anodic process, was determined by thin-layer chronopotentiometry using a platinum electrode.[16] For thin-layer chronopotentiometry, eq 13

$$i\tau = nFC^{\circ}V \qquad (13)$$

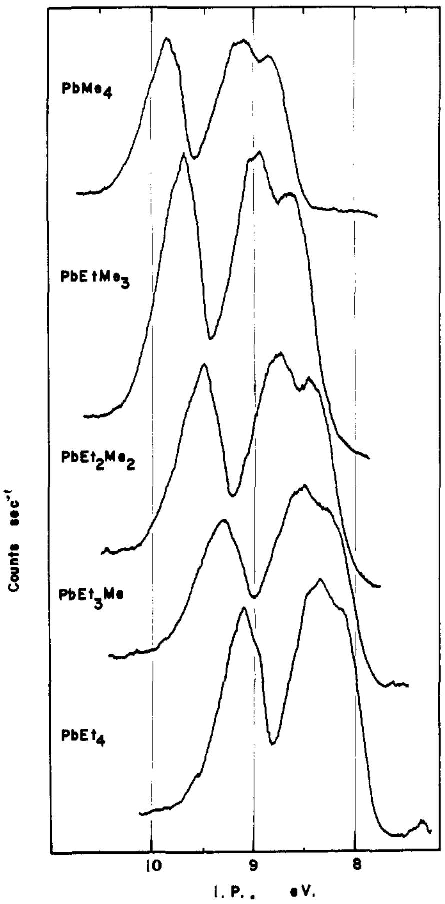


Figure 2. He I photoelectron spectra of methyl/ethyllead compounds, $Et_{4-n}PbMe_n$ in 8–10 eV region. Counts per second units are arbitrary.

Table IV. Thin-Layer Chronopotentiometric Determination of n^a

Compd	Current range, μA	$i\tau$,^{b} μA sec	Detn^c
$Fe(phen)_3(ClO_4)_2$	4.0 15.5	120 ± 7	10
Et_4Pb	4.9 8.7	116 ± 12	9
Et_3PbMe	5.0 8.3	121 ± 10	8
Et_2PbMe_2	4.9 7.9	124 ± 10	5
$EtPbMe_3$	5.0 7.9	124 ± 10	5
Me_4Pb	4.9 7.9	130 ± 12	6

[a] In 5 × 10^{-3} M acetonitrile solutions containing 0.23 F $LiClO_4$ at 22.5° (the value of V is 0.23 μl). [b] Error limits are one standard deviation. [c] Number of determinations.

Table V. Potentials for Anodic Oxidation of Methyl/Ethyllead Compounds at Constant Current Density^a

	Potential, V^b		
$Et_{4-n}PbMe_n$	i/A = 1.0^c	i/A = 0.4^c	i/A = 0^{c,d}
Et_4Pb	1.67	1.58	1.52
Et_3PbMe	1.75	1.67	1.62
Et_2PbMe_2	1.84	1.74	1.68
$EtPbMe_3$	2.01	1.88	1.80
Me_4Pb	2.13	2.00	1.90

[a] In 2.0 × 10^{-3} M R_4Pb in acetonitrile containing 0.25 F lithium fluoroborate at 25°. [b] Versus Ag|AgCl. [c] mA cm^{-2}. [d] Extrapolated to zero current density from measurements taken at 0.1 intervals between 0.3 and 1.2 mA cm^{-2}.

applies, where i is the constant current, τ is the transition time, F is the Faraday, $C°$ is the bulk concentration of R_4Pb, and V is the volume of the thin-layer cavity. The apparatus was calibrated under standard conditions with tris(1,10-phenanthroline)iron(II) perchlorate for which n = 1.0 has been previously established.[17] We deduce from the $i\tau$ products listed in Table IV that n = 1.0 for all of the tetraalkyllead compounds examined.

A chronopotentiometric cell of standard design was equipped with platinum wire working and auxiliary electrodes and a silver–silver chloride reference electrode. The anodic oxidation of each of the tetraalkyllead compounds was found to be irreversible by current-reversal chronopotentiometry, suggesting that the alkyllead cation radical is unstable. Equation 14 represents a probable mode of decomposition.

$$R_4Pb^{\cdot +} \longrightarrow R_3Pb^+ + R\cdot \qquad (14)$$

The potential in a magnetically stirred solution of tetraalkyllead depended on the identity of the lead compound. Since each of these oxidative processes is irreversible, the observed potentials shifted to more positive values as the current density increased, and no theoretical significance can be placed on the absolute values of the measured potentials. At a given current density, however, the potentials listed in Table V reflect the relative ease of removal of a single electron from the series of methyl/ethyllead compounds examined in this study. The latter rests on the presumption that anodic oxidation of these closely related compounds proceeds via a common mechanism.

2. Ionization Potentials from Photoelectron Spectra. We examined the He I photoelectron spectra of the same series of methyl/ethyllead compounds in order to determine if there is a correlation between the ease of anodic oxidation of tetraalkylleads in solution and their ionization potentials.

The vapor-phase photoelectron spectra (PES) of the group 4B tetramethyls, i.e., neopentane, tetramethylsilane, tetramethylgermane, tetramethylstannane, and tetramethylplumbane, have been previously scrutinized by several research groups.[19-22] With the exception of neopentane, the spectra are all similar, each showing two broad bands. The higher energy band occurs at about 14 eV, and comparison with simple compounds suggests that this band is associated with ionization from the σ_{C-H} bonding molecular orbital mainly localized on the methyl fragment.

The threshold or adiabatic ionization energy of the lower energy band decreases in the order: $(CH_3)_4Si$ > $(CH_3)_4Ge$ > $(CH_3)_4Sn$ > $(CH_3)_4Pb$ from 10.25, 9.42, 9.38, 8.85, to 8.38 eV, respectively, indicating that ionization is associated with electrons localized relatively close to the metal atom. The lower band has been assigned to ionization from the $3t_2$ orbital derived principally from the σ_{M-C} bonding orbitals.[20] In tetramethylplumbane, it is split into two well-resolved bands as shown in Figure 2. Examination of the PES for the series of methyl/ethyllead compounds in Figure 2 reveals that the ionization potentials decrease monotonically with increasing substitution of ethyl for methyl groups around the lead nucleus.[23,24] Moreover, the regular trend noted over the entire series of methyl/ethyllead compounds suggests that substitution of an ethyl group for a methyl group is largely an electronic effect, and that steric interactions between these alkyl groups around the lead atom are not large.

The vertical ionization potential corresponds to a Franck-Condon allowed process. Electron detachment from tetraalkyllead in eq 12 under those conditions shows a striking relationship to the electrochemical oxidation potentials in acetonitrile solution,[25,26] as shown in Figure 3.

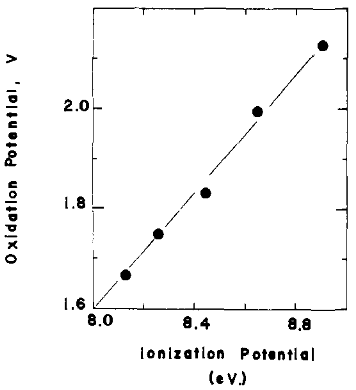


Figure 3. Correlation of the electrochemical oxidation potential of methyl/ethyllead compounds in acetonitrile solution with the vertical ionization potentials determined by He I photoelectron spectroscopy.

3. Charge-Transfer Complexes of Tetraalkyllead Compounds. The addition of tetraalkyllead to tetracyanoethylene (TCNE) in chloroform or methylene chloride at room temperature results in a transient color characteristic of the lead compound added. The solution rapidly turns yellow as the intense absorption due to the pentacyanopropenide product [$(NC)_2CC(CN){=}C(CN)_2^-$, ϵ(417 nm) = 22,800 M^{-1} cm^{-1}] dominates the spectrum.[27] Of the organolead compounds examined in this study, Me_4Pb produces the most stable charge-transfer species with TCNE, and the band shown in Figure 4 may persist for as long as 50 min in chloroform solutions at −10°.

$$(CH_3)_4Pb + (NC)_2C{=\!=}C(CN)_2 \overset{K}{\rightleftharpoons} [(CH_3)_4Pb(NC)_2C{=\!=}C(CN)_2]$$

The large donor concentration (0.1-0.5 M) necessary to produce the charge-transfer band suggests that the formation constant K and the extinction coefficient ϵ of the charge-transfer complex are small.[28,29,32] These values suggest that this σ-donor-π-acceptor pair is only weakly associated, and that the new absorption bands involve contact charge transfer resulting from random encounters between donors and acceptors.[30] Similar conclusions were drawn by Hammond from studies of π-aromatic donors and σ acceptors,[31,32] and weak σ-donor-π-acceptor complexes have only recently been observed with permethylated polysilanes.[33,34]

The stabilities of the charge-transfer complexes of TCNE with the other tetraalkylleads decreased in the order $Me_4Pb > Me_3PbEt > Me_2PbEt_2 > MePbEt_3 > Et_4Pb$. A Pyrex cell suitable for low-temperature spectroscopy[35] was constructed for measurements in 1,2-dichloropropane, chosen as a solvent of low nucleophilicity, dielectric constant, and freezing point. The charge-transfer band obtained under these conditions is reported in Table VI. Unfortunately, the band from tetraethyllead could not be obtained since it disappeared within a minute even at −50°. The limited solubility of TCNE precluded observation of this band at lower temperatures.

Measurement of the frequencies of the charge-transfer bands formed by a series of donors with a common acceptor reflects the relative ease of oxidation of each member of the series.[29,36] The trend in the frequencies of the charge-transfer bands for tetraalkylleads with TCNE correlates with the data obtained by He I photoelectron spectroscopy and electrochemical studies. All of these processes relate, in measure, to the relative ease of electron detachment from various methyl/ethyllead compounds.

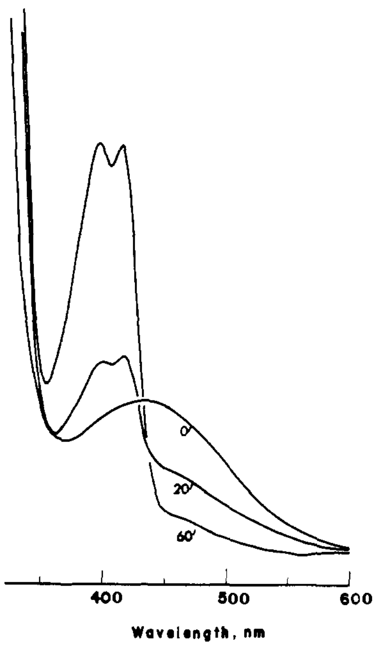


Figure 4. Changes in the visible absorption spectrum during the reaction of 0.3 M tetramethyllead and 0.01 M tetracyanoethylene in chloroform at −10°. Disappearance of the charge-transfer band after 0, 20, and 60 min.

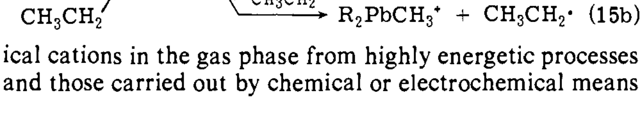
Table VI. Charge-Transfer Frequencies for Tetraalkyllead–Tetracyanoethylene Complexes[a]

$Et_{4-n}PbMe_n$	Charge-transfer band λ_{max}, nm	ν_{max}, cm^{-1}	Vertical[b] IP, eV	Color
Et_4Pb	*c*	*c*	8.13	Violet
Et_3PbMe	491	20,400	8.26	Red-violet
Et_2PbMe_2	454	22,000	8.45	Red
$EtPbMe_3$	430	23,300	8.65	Gold
Me_4Pb	412	24,300	8.90	Yellow-gold

[a] In 1,2-dichloropropane solutions containing 0.1–0.4 M R_4Pb and 0.008 M TCNE at −35 to −52°. [b] By He I PES. [c] Charge-transfer band too unstable.

4. Mass-Spectral Cracking Pattern of Methyl/Ethyllead Compounds. The examination of the mass spectra of tetraalkyllead compounds was undertaken in order to obtain information on the relative bond dissociation processes involving CH_3-Pb and CH_3CH_2-Pb scission in eq 14.[11b] The formation of the radical cation $R_4Pb\cdot^+$ in the step preceding fragmentation[37] allows mass spectroscopy to be a useful diagnostic tool for studying the oxidative cleavage of tetraalkyllead compounds. The relative rates of cleavage of methyl and ethyl groups, for example, can be compared with the intensities of the peaks for $P - CH_2CH_3$ (i.e., the parent molecule ion minus ethyl). The intensities of the peaks corresponding to trialkyllead resulting from the loss of one methyl group and the loss of one ethyl group are compared in Table VII for three unsymmetrical tetraalkyllead compounds as a function of the electron energy, in which the relative abundance of $P - CH_3$ and $P - CH_2CH_3$ is almost constant over the range of electron energies.

We attribute the competitive cleavage to arise from selectivity in the fragmentation of the parent molecule ion (eq 15). The inherent differences between the formation of radical cations in the gas phase from highly energetic processes and those carried out by chemical or electrochemical means



$$(CH_3)(CH_3CH_2)PbR_2\cdot^+ \xrightarrow{k'_{CH_3}} R_2PbCH_2CH_3^+ + CH_3\cdot \quad (15a)$$

$$(CH_3)(CH_3CH_2)PbR_2\cdot^+ \xrightarrow{k'_{CH_3CH_2}} R_2PbCH_3^+ + CH_3CH_2\cdot \quad (15b)$$

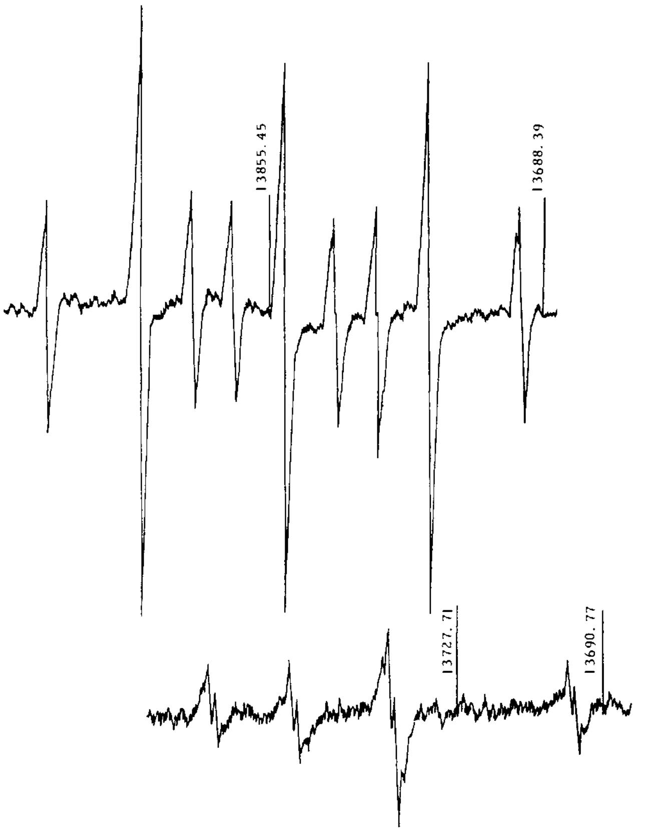


Figure 5. The ESR spectrum of the spin adduct of ethyl radical to NB from the reaction of $PbEt_4$ and $IrCl_6^{2-}$ in acetic acid at room temperature. The inset is the lowfield portion of the spectrum at higher resolution showing resolved γ-proton splittings ($a_N = 16.52$ G, $a_{\beta H} = 10.67$ G, $a_{\gamma H} = 0.37$ G). NMR field markers are in kHz.

Table VII. Variations in the Relative Abundances of Ions in the Mass Spectra of Tetraalkyllead Compounds at Different Ionizing Voltages

$Et_{4-n}Pb(CH_3)_n$	Relative abundance $(P - CH_3)/(P - CH_2CH_3)$[a] Ionizing Voltage, eV[b] 70	45	25	20	15
$CH_3Pb(CH_2CH_3)_3$	0.21	0.21	0.12	0.08	0.05[c]
$(CH_3)_2Pb(CH_2CH_3)_2$	0.17	0.16	0.15	0.14	0.07
$(CH_3)_3Pb(CH_2CH_3)$	0.19	0.19	0.18	0.16	0.12[c]

[a] Ratio of methyl cleavage vs. ethyl cleavage from parent molecular ion (P). Normalized for number of alkyl groups present. [b] Nominal values (uncalibrated). [c] At 17.5 eV.

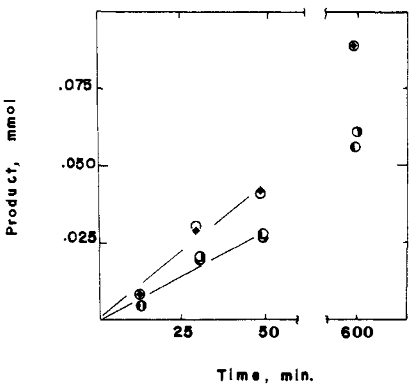


Figure 6. Thermal decomposition of 0.06 mmol of propionyl peroxide in acetonitrile at 83°: (○) carbon dioxide, (◑) ethane. Effect of 0.09 mmol of sodium hexachloroiridate(IV): ◆ carbon dioxide, ◐ ethyl chloride.

Table VIII. Production of Ethyl Radicals from the Thermal Decomposition of Propionyl Peroxide. Reaction with Hexachloroiridate(IV)[a]

$IrCl_6^{2-}$	CO_2,[b] %	mmol C_2H_4	C_2H_6	C_4H_{10}[c]	EtCl	ΣC_2,[b] %
0	73	0.006	0.062	0.018	0	72
0.119	74	0.006	0.002	0.017	0.059	70
0.084	74	0.006	0.002	0.016	0.055	66
0.042	75	0.006	0.022	0.018	0.039	71
0.033	72	0.006	0.029	0.017	0.030	69
0[d]	44	0.003	0.028	0.008	0.040	30

[a] In 3 ml of CH_3CN containing 0.060 mmol of propionyl peroxide at 83° for 6 half-lives. [b] Based on $2CO_2$ and $2C_2H_5\cdot$ per peroxide. [c] 2 × *n*-butane. [d] With 0.99 mmol of tetraethylammonium chloride added; 0.072 mmol of peroxide.

in solution, however, make the quantitative treatment of competitive cleavage processes somewhat tenuous. Nonetheless, the qualitative trends in the data are clear; that is, ethyl cleavage of the parent molecule ion predominates over methyl cleavage. A more complete discussion of the mass spectra has been presented elsewhere.[11b]

Alkyl Radicals During Oxidative Cleavage of Tetraalkyllead. 1. Spin Trapping. The intermediacy of radicals during the oxidative cleavage of tetraalkyllead compounds was investigated by electron spin resonance using spin-trapping techniques.[38] Solutions of various tetraalkylleads and hexachloroiridate(IV) in the presence of nitrosoisobutane (NB) or phenyl-*tert*-butylnitrone produced only spin adducts of alkyl radicals. The most intense ESR spectra were produced from tetraethyllead in acetic acid solutions, but spin adducts of ethyl radical were also detected in those reactions with Et_3PbMe and Et_2PbMe_2. The ESR spectrum of the spin adduct of ethyl radical to nitrosoisobutane is shown in Figure 5. No ESR spectrum was observed in the absence of spin trap, even at temperatures as low as −20°. These studies together with the chronopotentiometric results described above further indicate that cation radicals of tetraalkyllead are short-lived.

2. Scavenging of Alkyl Radicals by Hexachloroiridate(IV). Ethyl radicals were generated in independent experiments in order to examine their fate in the presence of hexachloroiridate(IV). The thermolysis of dipropionyl peroxide provides an unambiguous method for the production of ethyl radicals.[39] The rates of formation of carbon dioxide and ethane in acetonitrile at 83° are illustrated in Figure 6. The

$$(CH_3CH_2CO_2)_2 \xrightarrow{\Delta} 2CH_3CH_2\cdot + 2CO_2 \qquad (16)$$

$$CH_3CH_2\cdot + CH_3CN \longrightarrow CH_3CH_3 + \cdot CH_2CN, \text{etc.} \qquad (17)$$

addition of hexachloroiridate(IV) has no affect on the rate of carbon dioxide evolution, but only limited amounts of ethane are formed under these conditions. Significantly, ethyl chloride is produced in amounts approximately equal to the ethane formed in the absence of hexachloroiridate(IV). These results indicate that ethyl chloride is derived from ethyl radical and hexachloroiridate(IV) in a facile process such as

$$CH_3CH_2\cdot + Ir^{IV}Cl_6^{2-} \longrightarrow CH_3CH_2Cl + Ir^{III}Cl_5^{2-}, \text{etc.} \qquad (18)$$

subsequent to the rate-limiting homolysis in eq 16.[40]

In order to assess the ability of hexachloroiridate(IV) to scavenge ethyl radicals, we examined the yield of ethyl chloride at various concentrations of reactants. The results in Table VIII clearly show that only one ethyl chloride is formed from each hexachloroiridate(IV). When less than a stoichiometric amount of hexachloroiridate(IV) is present,

Table IX. The Correlation of Selectivities and Rates of Oxidative Cleavage of Tetraalkylleads by Hexachloroiridate(IV) with the Energetics of Electron-Detachment Processes

$PbMe_nEt_{4-n}$	k,[a] l./mol sec	EtCl[b]/MeCl	IP,[c] eV	E,[d] V	CT,[e] cm^{-1}
$PbEt_4$	26		8.13	1.67	
$PbEt_3Me$	11	24	8.26	1.75	20,400
$PbEt_2Me_2$	3.3	25	8.45	1.80	22,000
$PbEtMe_3$	0.57	24	8.65	2.01	23,300
$PbMe_4$	0.02		8.90	2.13	24,300

[a] Second-order rate constant in acetonitrile at 36°. [b] Statistically corrected. [c] By He(I) PES. [d] Potential vs. Ag|AgCl reference at I = 1.0 mA cm^{-2}. [e] Charge-transfer band of TCNE complex in 1,2-dichloropropane.

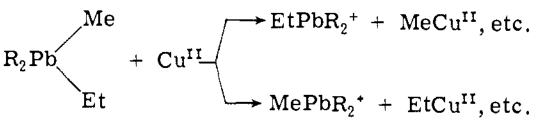
the remaining ethyl radicals are converted to ethane. Two important conclusions can be reached from these results: (1) hexachloroiridate(IV), and not one of its reduction products, is responsible for the production of ethyl chloride; and (2) the rate of scavenging of ethyl radicals by hexachloroiridate must be at least a factor of 10^3 faster than reaction with acetonitrile.

The reduced iridium(III) species, presumably $IrCl_5(CH_3CN)^{2-}$, can be isolated from acetonitrile as a light-brown solid. The infrared spectrum (KBr) shows a stretching frequency at 2250 cm^{-1}, shifted slightly from that of free acetonitrile (2257 cm^{-1}).[41] The visible absorption spectrum in methanol solution has maxima at 320 and 370 nm compared with 358 and 415 nm for hexachloroiridate(III). Oxidation with chlorine or lead dioxide in methanol affords a purple solution (357, 493 nm) of $IrCl_5(CH_3CN)^-$, which can be isolated after chromatography on silica gel (infrared: 2303 cm^{-1} for coordinated CH_3CN).[41]

Ethyl chloride is still the predominant product when the thermal decomposition of propionyl peroxide is carried out in acetic acid with hexachloroiridate(IV). However, the reduced iridium(III) species formed under these conditions show only a featureless end absorption at less than 450 nm, suggesting the presence of oligomeric species (vide supra).[13]

Discussion

Two important criteria can be used to distinguish the reaction of tetraalkyllead with hexachloroiridate(IV) from the more conventional electrophilic processes, e.g., those involving Brønsted acids, silver(I), copper(I), or copper(II) complexes, etc.[10,11] First, the rate of reaction of $Et_{4-n}PbMe_n$ with hexachloroiridate(IV) increases successively as methyl is replaced by ethyl groups (see n = 4-0 in Table IX, column 2). Second, a given ethyl group is cleaved approximately 25 times faster than a methyl group (column 3). Both of these reactivity trends are diametrically opposed to an electrophilic cleavage such as reaction 19 with copper(II),[11b] in which preferential attack by a copper(II) electrophile occurs directly at the less hindered methyl site by a factor of 44 faster than at an ethyl site under equivalent conditions.



$$R_2Pb(Me)(Et) + Cu^{II} \rightarrow EtPbR_2^+ + MeCu^{II}, \text{etc.} \quad (19a)$$

$$R_2Pb(Me)(Et) + Cu^{II} \rightarrow MePbR_2^+ + EtCu^{II}, \text{etc.} \quad (19b)$$

Scheme I

$$R_4Pb + Ir^{IV}Cl_6^{2-} \xrightarrow{k} R_4Pb\cdot^+ + Ir^{III}Cl_6^{3-} \quad (20)$$

$$R_4Pb\cdot^+ \xrightarrow{\text{fast}} R\cdot + R_3Pb^+ \quad (14)$$

$$R\cdot + Ir^{IV}Cl_6^{2-} \xrightarrow{\text{fast}} RCl + Ir^{III}Cl_5^{2-}, \text{etc.} \quad (18)$$

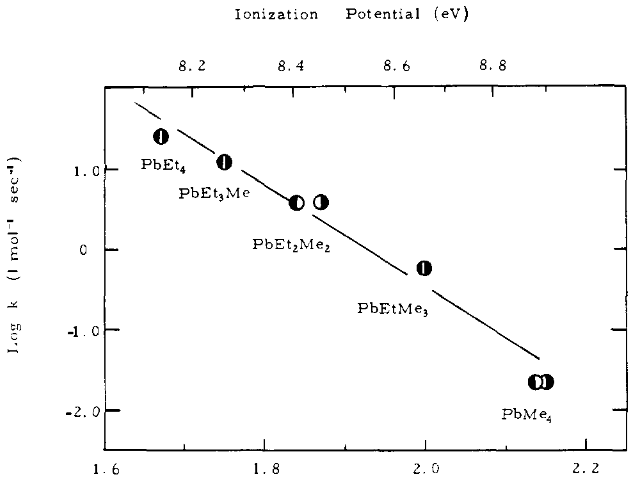


Figure 7. Correlation of the rates of oxidation of $Et_{4-n}PbMe_n$ by $IrCl_6^{2-}$ in acetonitrile with the electrochemical oxidation potential [(◐) lower scale] and the vertical ionization potential [(◑) upper scale].

These results suggest that the rate-limiting step with hexachloroiridate(IV) occurs prior to alkyl transfer. We propose the mechanism given in Scheme I in which the slow step 20 involves charge transfer. Indeed, there is a reasonable linear correlation of the rates (log k) with the one-electron oxidation potentials determined electrochemically as shown in Figure 7. The oxidation potentials of $PbMe_nEt_{4-n}$ are related to the electron-detachment process, $R_4Pb \rightarrow R_4Pb\cdot^+ + e$, since there is also a striking relationship with the vertical ionization potentials determined by He I photoelectron spectroscopy. The latter together with the correlation observed with the energies of the charge-transfer bands of complexes between R_4Pb and TCNE suggests that electron detachment from the tetraalkyllead involves at most a minor structural reorganization of the cation radical.

According to the mechanism in Scheme I, the activation parameters for the reaction of tetramethyl- and tetraethyllead with hexachloroiridate(IV) in Table X are related directly to the energetics of the rate-limiting electron-transfer step 20. Other examples of electron transfer in the oxidation of neutral substrates with hexachloroiridate(IV) are also included in Table X, although protonated species may be involved in aqueous perchloric acid. It is interesting to note that the enhancement in rate by a factor of roughly 10^3 for the reaction of tetraethyllead in acetic acid relative to acetonitrile is largely due to entropic factors. The importance of the solvent structure on electron-transfer rates has been discussed, but the limited experimental studies available heretofore preclude a quantitative assessment as yet.[42]

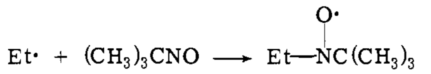
Selectivity in the cleavage of alkyl groups from organolead according to Scheme I occurs during fragmentation of the cation radical in a fast subsequent step 14, which is consistent with the mass-spectral study. Thus, a quantitative determination of the cracking patterns of the series of $PbMe_nEt_{4-n}$ showed that scission of the Et-Pb bond is favored over that of the Me-Pb bond in the parent molecular ions, largely because of bond energy differences, as discussed above in eq 15.

Examination of the electron spin resonance spectrum during the reaction with hexachloroiridate(IV) did not reveal the presence of the cation radical $PbEt_4\cdot^+$, which must be highly unstable even at temperatures as low as −20°. Nonetheless, the formation of ethyl radicals in high yields was evident from spin-trapping experiments with nitrosoisobutane and phenyl-*tert*-butylnitrone. The well-resolved

Table X. Activation Parameters for Hexachloroiridate(IV) Oxidations of Uncharged Substrates

Substrate	Solvent	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J deg^{-1} mol^{-1}	Ref
Me_4Pb	HOAc	38 ± 2	−106 ± 8	This work
Et_4Pb	HOAc	31 ± 4	−63 ± 11	This work
Et_4Pb	CH_3CN	35 ± 3	−101 ± 9	This work
$RCo(DMG)_2$[a]	$HClO_4$–HOAc			b
Phenol	$HClO_4$–H_2O	ca. 39	ca. −117	c
2,6-Dimethylphenol	$HClO_4$–H_2O	42	−75	c
Cyclohexanone	$HClO_4$–H_2O	67 ± 2	−50 ± 4	c

[a] R = benzyl and *sec*-octyl. [b] From ref 6 and 7. [c] From ref 14.



$$Et\cdot + (CH_3)_3CNO \longrightarrow Et\text{—}\overset{O\cdot}{\overset{|}{N}}C(CH_3)_3 \qquad (21)$$

spectrum in Figure 5 of the ethyl adduct to nitrosoisobutane is a relevant example.

The use of hexachloroiridate(IV) as an efficient scavenger for alkyl radicals is implied in Scheme I by the isolation of alkyl chlorides in high yields. In support, separate experiments do indeed show that ethyl radicals generated unambiguously from the thermolysis of propionyl peroxide are quantitatively converted by hexachloroiridate(IV) to ethyl chloride in eq 18. There is an alternative possibility that alkyl halide is formed directly from the cation radical by a reaction such as 22, without the intermediacy of an alkyl

$$R_4Pb\cdot^{+} + Ir^{IV}Cl_6^{2-} \longrightarrow R_3Pb^{+} + RCl + Ir^{III}Cl_5^{2-}, \text{etc.} \qquad (22)$$

radical. The difference between this formulation and that presented by eq 14 and 18 in Scheme I rests on the degree of metastability of the cation radical toward fragmentation. Our inability to observe the ESR spectra of $R_4Pb\cdot^{+}$ and the irreversibility of the oxidation wave in chronopotentiometry suggests that its lifetime is short. Furthermore, the lack of participation by foreign nucleophiles, such as bromide and water, preclude the participation of a substitution process

$$R_4Pb\cdot^{+} + Br^{-} \longrightarrow RBr + R_3Pb\cdot, \text{etc.} \qquad (23)$$

similar to that observed with alkylcobalt complexes (compare eq 6).

Finally, we wish to emphasize that the distinction between alkyl transfers which proceed by electrophilic pathways and those that involve electron-transfer routes is subtle and must be scrutinized in individual cases. For example, products and stoichiometry of the reaction between tetraalkyllead and hexachloroiridate(IV) in eq 8 are similar to those for chlorocuprate(II) in eq 24,[11b] each forming

$$(CH_3)_4Pb + 2Cu^{II}Cl_3^{-} \longrightarrow (CH_3)_3PbCl + CH_3Cl + 2Cu^{I}Cl_2^{-} \qquad (24)$$

alkyl chloride and requiring 2 equiv of metal complex. Nonetheless, it is clear from these studies that they proceed by distinctly different mechanisms.

Conclusions

Alkyllead compounds used as models for the study of alkyl transfer in organometals are shown to react with hexachloroiridate(IV) by an electron-transfer mechanism described in Scheme I. The energetics of the rate-limiting step correlate with other electron-detachment processes including the electrochemical oxidation, vertical ionization potential, and charge-transfer bands of the organolead compounds. Evidence for the formation of metastable cation radicals and alkyl radical is adduced from selectivity, spin-trapping, and chemical-scavenging studies. In view of the abilities of other organometallic compounds to act as electron donors[43] and electrophiles to be oxidants,[36] other alkyl-transfer reactions assumed to proceed by electrophilic mechanisms may have important charge-transfer components.

Experimental Section

Materials. The series of methyl/ethyllead compounds were described previously.[11] Analysis by gas chromatography on a propylene glycol-Quadrol column[44] indicated a minimum purity of more than 97%. Sodium hexachloroiridate(IV) ($Na_2IrCl_6{\cdot}6H_2O$) and potassium hexachloroiridate(III) ($K_3IrCl_6{\cdot}3H_2O$) were obtained from Varlacoid Chemical Co. and Alfa Inorganics, respectively. The visible spectra agreed with literature values,[12d] e.g., ϵ_{487} 4070 M^{-1} cm^{-1} for $IrCl_6^{-2}$ in 1 *N* $HClO_4$. Lithium perchlorate was recrystallized from acetonitrile and dried in vacuo at 130°. Lithium fluoroborate (Ozark-Mahoning Co.) was twice recrystallized from tetrahydrofuran-ether mixtures and dried in vacuo at 150°. Tetra-*n*-butylammonium bromide was prepared by the method of Sadler and Fuoss[45] and recrystallized from tetrahydrofuran. Tris(1,10-phenanthroline)iron(II) perchlorate $[Fe(phen)_3(ClO_4)_2{\cdot}4H_2O]$ was prepared by the method of Dwyer and McKenzie.[46]

Acetonitrile (Mallinckrodt, analytical reagent) was stirred over calcium hydride for 2 days and distilled under argon from phosphorus pentoxide. Acetic acid was refluxed with acetic anhydride and redistilled. Silica gel (80–200 mesh) was obtained from G. F. Smith Chemical Co. and used for all chromatographic separations. Di-*n*-propionyl peroxide was prepared by the method of Sheldon and Kochi.[47]

Reaction of Tetraalkyllead with Hexachloroiridate(IV). Formation of Akyl Chlorides. Typically 0.200 mmol of $Na_2IrCl_6{\cdot}6H_2O$ was weighed into a 25-ml round-bottomed flask containing a magnetic stirring bar. The flask was sealed with a rubber serum cap and the gas in the flask removed by means of a hypodermic needle attached to a vacuum line. After an atmosphere of nitrogen was added to the flask, 3 ml of deoxygenated solvent was added with a hypodermic syringe. Internal standards (isobutane and *n*-propyl chloride) were then added. The flask was transferred to a constant-temperature bath (±0.1°), and a 0.100-mmol sample of a tetraalkyllead compound was added with a syringe to the magnetically stirred solution. Samples of gas (<0.1%) were periodically removed from the flask to monitor the progress of the reaction. Analyses generally reproducible to ±3% were carried out on a Varian Aerograph 204B chromatograph, using a tandem column consisting of 15 ft of 20% Apiezon L on Chromosorb P and 21 ft of 20% FFAP on Chromosorb P. Ratios of ethyl chloride–methyl chloride were determined on a 14-ft column of 10% FFAP on Chromosorb P.

Procedures were also developed to minimize the possibility of trace-metal catalysis. The all-glass reaction vessel consisted of a 10-ml flask (containing $Na_2IrCl_6{\cdot}6H_2O$ and solvent) and a two-necked 15-ml round-bottomed flask (containing tetraalkyllead and solvent) connected by a 105° connecting tube. The other opening in the 15-ml flask was covered with a serum cap for carrying out the operations as in the normal procedure. For these experiments, the solvent was added with a glass pipet to the nitrogen-flushed apparatus containing $Na_2IrCl_6{\cdot}6H_2O$. The ratios of ethyl and methyl chlorides determined with this apparatus were the same as those found using the normal procedure. The presence of ethyl chloride as the principal (alkyl chloride) product from the reaction of $IrCl_6^{2-}$ and $PbMe_3Et$ was established by gas chromatography-mass spectrometry.

The Reaction of Tetraethyllead and Hexachloroiridate(IV) under Oxygen. An atmosphere of oxygen was established in a 25-ml flask containing 0.198 mmol of $IrCl_6^{2-}$ in 3 ml of acetic acid. Analysis of the volatile reaction products after addition of 0.396 mmol of $PbEt_4$ indicated the presence of 0.085 mmol of ethyl chloride and 0.02 mmol of acetaldelyde. Acetaldehyde was tentatively identified on the basis of its retention times on two separate columns (Apiezon L and FFAP).

The Reaction of Tetraethyllead and Hexachloroiridate(IV) in the Presence of Bromide Ion. A 25-ml round-bottomed flask containing 0.198 mmol of $IrCl_6^{2-}$ was sealed with a serum cap, evacuated, and then filled with a nitrogen atmosphere. Air-free acetonitrile (3 ml) containing 1.5 mmol of tetrabutylammonium bromide was added with a hypodermic syringe. After addition of 0.100 ml of isobutane as the internal standard 0.099 mmol of $PbEt_4$ was added to the heterogeneous reaction mixture. In 14.5 min, 0.101 mmol of ethyl chloride was formed.

The Reaction of Tetraalkyllead with Hexachloroiridate(III). A heterogeneous mixture resulted when 0.100 mmol of $K_3IrCl_6\cdot 3H_2O$ was added to 4 ml of deoxygenated acetic acid in a round-bottomed flask sealed with a serum cap. (The potassium salt is much less soluble than the sodium salt.) Methyl chloride was detected in the reaction mixture after the addition of 0.100 mmol of $PbMe_4$. After 12 min, 0.001 mmol of methyl chloride was produced.

Kinetics. The decay in the absorbance due to $IrCl_6^{2-}$ was followed spectrophotometrically at 487 (ϵ 4060 M^{-1} cm^{-1}) and 585 nm (ϵ 586 M^{-1} cm^{-1}) in acetic acid and at 490 (ϵ 5250 M^{-1} cm^{-1}) and 585 nm (ϵ 434 M^{-1}) in 1.0 *F* $LiClO_4$ in acetonitrile. Beer's law was followed at all wavelengths in the concentration range studied. Only the initial rates of disappearance of hexachloroiridate(IV) could be determined due to a precipitate which formed during the latter stages of the reaction.

In acetonitrile and for the reaction of $PbMe_4$ in acetic acid, kinetic measurements were made under nitrogen in evacuable cells constructed from 1.0 cm i.d. square Pyrex tubing attached to a 25-ml flask having two openings. In a typical procedure, the cells were evacuated and then filled with an atmosphere of nitrogen. A sample (3 ml) of $IrCl_6^{2-}$ solution was added to the cell with a hypodermic syringe. The cell was placed in a constant-temperature bath held at the same temperature as the cell block of the spectrophotometer. Immediately before a determination, the cell was removed from the bath, and a solution of tetraalkyllead was added with a syringe. Within 10 sec, the contents of the cell was mixed and the cell replaced in the spectrophotometer.

Rate constants for the reaction of $IrCl_6^{2-}$ with $PbMe_2Et$, $PbMe_2Et_2$, $PbMeEt_2$, and $PbEt_4$ in acetic acid were determined using a Durrum-Gibson stopped-flow spectrophotometer. Temperature control was maintained by a Neslab RTE-3 circulator. The disappearance of $IrCl_6^{2-}$ was monitored at 487 and 585 nm with a spectral slit width of 1.0 μm.

In a typical procedure, solutions of air-free reagents were prepared immediately before use in 25-ml round-bottomed flasks which were sealed with a serum cap. The solution was stirred for about 2 min while the air in the flask was removed by means of a syringe needle attached to a vacuum line. The contents of the flasks were transferred to the reservoir syringes with a minimum of agitation immediately before a determination was made. The observed percent transmittance of the $IrCl_6^{2-}$ solution was checked against a similar reading using a Beckman DB-G spectrophotometer. Reproducible measurements were obtained only from freshly prepared solutions of PbR_4.

The rate of disappearance of $IrCl_6^{2-}$ in the presence of $PbEt_4$ in acetonitrile was also measured by the incremental addition of $PbEt_4$ to the equilibrated reaction mixture. The rate constants obtained from reactions carried out in this manner were the same as those measured in the usual way.

Electrochemical Measurements. A standard chronopotentiometric cell containing 85 ml of 2.0×10^{-3} *M* PbR_4 (and 0.23 *F* $LiBF_4$ supporting electrolyte) in acetonitrile was used for all measurements. The potential in the nitrogen-flushed magnetically stirred solution was measured by a calibrated Houston Omnigraphic 2000 x-t recorder for various current densities at the platinum wire working anode. Because of high cell resistance, a Keithley Model 610B electrometer was placed on series in the cell-recorder circuit. At a current density of 1.0 mA cm^{-2}, the reproducibility of potential measurements was $<\pm 0.03$ V for a given tetraalkyllead compound. The *n* values for the oxidation of each PbR_4 were measured using a thin-layer electrode of the design of Sheaffer and Peters.[16] The volume of the TLE cavity was found by studying the oxidation of tris(1,10-phenanthroline)iron(II) perchlorate under the same solvent-supporting electrolyte conditions as were used for the tetraalkyllead compounds. Solutions of PbR_4 (5.0×10^{-3} *M*) and 0.23 *F* $LiBF_4$ in acetonitrile were studied over the current range of 4–8 μA. The potential of the Ag|AgCl reference electrode was -0.165 ± 0.015 V vs. SCE in a saturated aqueous KCl solution for all measurements.[48]

Analysis of Inorganic Reaction Products. Reactions in Acetonitrile. After analysis of the volatile reaction products was completed, the reaction flask was transferred to a vacuum line to remove the solvent. Portions of the solid residue were dissolved in methanol, and the visible spectrum of the solution was recorded. Methanolic solutions were then oxidized with chlorine and chromatographed on a 0.5 × 12 in. silica gel column. The first fraction to elute was identified as $IrCl_6^{2-}$ by comparison of the spectrum with an authentic sample (ϵ_{487} 3700 M^{-1} cm^{-1} for $IrCl_6^{2-}$ in methanol). The second fraction did not correspond to any known iridium complex, but its visible spectrum showed maxima at 493 and 357 nm. Oxidation of the residue in 1 *N* $HClO_4$ with PbO_2 gave the same spectrum. Errors in the determination of $IrCl_6^{2-}$ in the oxidized residue were caused by the metastability of $IrCl_6^{2-}$ in methanol and the difficulty in separating the iridium(IV) products. The amount of $IrCl_6^{2-}$ is also probably affected by a slow reaction with the chloroiridium(III) residue which evolves alkyl chloride.

Reaction in Water. $Na_2IrCl_6\cdot 6H_2O$ (0.0174 mmol) was dissolved in 4 ml of water in an evacuable Pyrex cell. After the air in the cell was removed and an atmosphere of nitrogen added, 0.0087 mmol of $PbEt_4$ was added by means of a hypodermic syringe. The red-brown solution became pale yellow in about 20 min. The visible absorption spectrum of the solution showed a peak at 410 nm and a shoulder at about 340 nm. Oxidation of this solution with chlorine followed by removal of the excess chlorine in vacuo yielded an intensely colored solution which was shown to consist of $IrCl_6^{2-}$ and $IrCl_5(OH_2)^-$. The absolute yields of $IrCl_6^{2-}$ and $IrCl_5(OH_2)^-$ were determined to be 0.091 and 0.093 mmol, respectively, by spectrophotometric analysis of the solution at 487 and 438 nm.

Reactions in Acetic Acid–Water Mixtures. The residue from the reaction of 0.092 mmol of $PbMe_3Et$ and 0.165 mmol of $IrCl_6^{2-}$ in 70:30 (vol) $HOAc{:}H_2O$ was dissolved in 1 *N* $HClO_4$ and oxidized with chlorine. The presence of only two species in the oxidized solution was confirmed by the observation of isosbestic points for $IrCl_6^{2-}$ and $IrCl_5(OH_2)^-$ at 438, 476, and 524 nm, where the molar extinction coefficients are 3060, 2750, and 1260 M^{-1} cm^{-1}, respectively.[12d] The absolute yields of $IrCl_6^{2-}$ and $IrCl_5(OH_2)^-$ were determined to be 0.066 and 0.080 mmol, respectively, by spectrophotometric analysis of the solutions.

Determination of Trialkyllead Acetate. The residue from the reaction of $PbMe_4$ (0.084 mmol) and $IrCl_6^{2-}$ (0.168 mmol) in acetic-d_4 acid was partially dissolved in CD_3OD and transferred to an NMR tube. Nitrobenzene was added as an internal standard. The yield of the trimethyllead ion was 0.079 mmol and identified by its chemical shift (δ = 1.52 ppm vs. external Me_4Si) and characteristic $^{207}Pb-CH_3$ splitting (J $^{207}Pb-CH_3$ = 80 Hz in CD_3OD).[49] Addition of a known sample of trimethyllead acetate enhanced the signal assigned to the trimethyllead ion. The reaction was repeated, and after the residue was dissolved in D_2O, a quantitative yield of trimethyllead ion was determined by the internal standard method.

Spin-Trapping Experiments. Solutions of 2.5×10^{-2} *M* $IrCl_6^{2-}$ and PbR_4 were added to separate arms of a tube attached to an ESR sample tube. After a few milligrams of spin trap (nitrosoisobutane or phenyl-*tert*-butylnitrone) was added, and the solutions were degassed, the tube was inverted and placed in the cavity of an ESR spectrometer.[50] No ESR signal was detected unless $IrCl_6^{2-}$, PbR_4, and the spin trap were all present.

Scavenging of Alkyl Radicals by $IrCl_6^{2-}$ in Acetonitrile. A 3-ml sample of propionyl peroxide in acetonitrile was pipetted into a 25-ml glass tube containing a known amount of $Na_2IrCl_6\cdot 6H_2O$. The solution was subjected to at least five freeze–pump–thaw cycles on a vacuum line before being sealed. The tubes were placed in a thermostated bath at 83° and removed periodically for analysis.

A small piece of rubber tubing was slipped over the thin end of the tube and the tube cracked to introduce the internal standards (methane and isobutane). A 1.5 ft × 0.25 in. Porapak Q column was used for CO_2 and C_2H_6 analyses. Ethyl chloride and *n*-butane were analyzed on the Apiezon L-FFAP tandem column previously mentioned. Similar product distributions were obtained when the peroxide decompositions were carried out in 25-ml round-bottomed flasks filled with rubber serum caps.

At the end of the reaction, a tan solid was present which was separated by filtration and chromatographed on silica gel with methanol. The visible spectrum of the methanolic solution of the tan solid showed maxima at 370 and 320 nm. Oxidation of this solution with chlorine yielded an intense purple solution having absorption maxima at 493 and 357 nm and a shoulder at 525 nm. The same spectrum remained after chromatography of the purple solution on silica gel.

The infrared spectrum of the tan solid was obtained from a KBr pellet. Since the purple solid isolated from the oxidized solution reacted with KBr, the infrared spectrum of this solid was determined in a Fluorolube mull. The frequency assigned to a coordinated nitrile stretch in each compound was compared with the 1944.0 cm^{-1} band in polystyrene. The estimated reproducibility of ν_{CN} measurements is ± 3 cm^{-1}.

Photoelectron Spectra. The He I photoelectron spectra were kindly recorded for us by Drs. Charles W. McFarland and Gheorghe D. Mateescu on a Varian VIEE-15 spectrometer.

Charge-Transfer Spectra. A cell based on the design of Nakane and coworkers[35] was used in the determination of charge-transfer spectra at low temperatures. The optical path length of this cell was 1.0 cm. By means of pipet, 5 ml of 0.008 *M* TCNE in 1,2-dichloropropane was added to the sample compartment which was sealed by a serum cap. The air was evacuated and replaced with nitrogen. Diethyl carbitol (mp −52.9°) was added to the cooling chamber of the cell and was partially frozen by addition of liquid nitrogen. The cell contents was allowed to reach thermal equilibrium during a period of 10–15 min and was transferred to the sample compartment of the Cary 14 spectrophotometer. Reproducible alignment of the cell with the spectrophotometer optics was effected by matching the marks on the base of the cell with those on a specially marked wooden block within the spectrophotometer. The spectrum of the TCNE solution was recorded at a scan rate of 300 nm/min in the region of 700–300 nm. A known amount of alkyllead compound was added by syringe to the cell, and the new spectrum was recorded periodically.

The following procedure was used for the $PbMe_4$–TCNE charge-transfer spectra in chloroform. A 4.5-ml portion of 0.01 *m* TCNE solution was pipetted into a Pyrex evacuable cell (1.0-cm path length). The cell was sealed with serum cap, the air was evacuated, and a nitrogen atmosphere was established. The cell was cooled to −10° in an ethanol-water bath. The bath and the cell block of the Beckmann DB-G spectrophotometer were maintained at −10° by a Neslab RTE-3 circulator. Immediately before a spectrum was recorded, the cell was removed from the bath and placed in the spectrophotometer. A known amount of alkyllead compound was then added by syringe.

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Electrical Discharge Mechanisms. Stereochemistry of Electrocyclic Reactions of *cis*- and *trans*-1,2,3,4-Tetramethylcyclobutene and *cis,cis,cis*-, *cis,cis,trans*-, and *trans,cis,trans*-2,4,6-Octatriene. Hot Ground States as Probable Reactive Species[1]

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Abstract: The electrical discharge reactions of *cis*- and *trans*-1,2,3,4-tetramethylcyclobutene, *cis,cis,cis*-, *trans,cis,trans*-, and *cis,cis,trans*-2,4,6-octatriene, and *trans*-5,6-dimethylcyclohexadiene were studied, the products being isolated and identified for comparison with products formed in thermal and photochemical electrocyclic reactions. The major liquid products from the cyclobutenes were *cis,trans*-3,4-dimethyl-2,4-hexadiene (27%) and *trans,trans*-3,4-dimethyl-2,4-hexadiene (53%), respectively. The electrocyclic product from 99% isomerically pure *cis,cis,trans*-2,4,6-octatriene was *trans*-5,6-dimethyl-1,3-cyclohexadiene (5.4%), and studies of isomeric mixtures established that the other isomers give *cis*-5,6-dimethyl-1,3-cyclohexadiene. The products are the same as the products of thermal electrocyclic ring opening, and the reactions occur with essentially complete stereospecificity. Orbital-symmetry correlations and experimental analogies appear to rule out electronically excited molecules, as well as ground-state and excited-state molecular cations and anions, and to suggest that electrocyclic reactions in the electrical discharge proceed from vibrationally excited, but thermally nonequilibrated, ground states of the neutral molecules.

Although the reaction of an organic molecule in an electrical discharge typically leads to a complex mixture of products,[2] including a considerable quantity of one, two, and three carbon fragments, various rather specific reactions can occur. Under high-energy conditions, whether thermal, photochemical, or electron impact (mass spectrum or electrical discharge), entropy control—favoring smaller molecules through the resulting increase in translational degrees of freedom—drains off reactant molecules in fragmentations. However, the mechanistic pathways for the specific electrical discharge reactions are conceptually very interesting, because they are caused by electron impact, an energy source different from the more widely studied and understood sources, heat and light.

Since the stereochemistry of many reactions is controlled by orbital-symmetry effects,[3] it appeared that a search for stereochemical specificity in electrocyclic reactions, which have been studied under thermal and photochemical reaction conditions, would, if successful, be a valuable tool. Applying symmetry considerations, we could predict the stereochemistry of our reactions for the set of mechanistic possibilities (electronically excited and vibrationally excited neutral molecules, and molecular cations and anions) and then rule out those which disagreed with the observed stereochemistry. While such evidence would apply only to the electrocyclic component of the reaction(s) investigated, it might begin to provide a key to the elusive mechanistic features of electrical discharge and related electron-impact reactions.[4-11]

In addition to its present application to the production of ozone, direct industrial use of electrical energy for chemical transformations is being explored, both for possible commercial value and for possible conservation of fossil fuels as environmentally acceptable alternative sources of electricity are developed.[12] Studies of reaction pathways and intermediates may provide useful guidelines for such developments as well.

In view of the extensive recent investigations on thermolysis[13] and photolysis[14] of derivatives of cyclobutene, conjugated acyclic dienes, cyclohexadiene, and conjugated acyclic trienes, we examined the products of the electrocyclic reactions of *cis*- and *trans*-1,2,3,4-tetramethylcyclobutene, *cis*- and *trans*-5,6-dimethyl-1,3-cyclohexadiene, and *cis,cis,cis*-, *cis,cis,trans*-, and *trans,cis,trans*-2,4,6-octatriene in an ac electrical discharge, using platinum electrodes in a flow system, and quenching the products on a liquid nitrogen-filled cold finger placed 9 cm from the second electrode. We found substantial yields of electrocyclic ring-opening products in the case of the cyclobutenes, and they were formed with complete stereospecificity in the conrotatory mode. The cyclohexadienes did not undergo electrocyclic ring opening, but the octatrienes gave substantial amounts of ring-closure products (cyclohexadienes), and these were formed with complete stereospecificity in the disrotatory mode.

These results agree with experiment for thermal rearrangements, do not agree with experiment for photochemical rearrangements, and thus rule out a photochemical analogy for electrical discharge in this case. Thermocouple measurements lead us to believe that the electrical discharge is not hot enough (translationally) to account for the results by a simple pyrolysis mechanism. We present arguments which make reaction through molecular cations or anions appear unlikely and conclude that the most reasonable interpretation involves reaction through vibrationally excited electronic ground states.