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$$CuO_2^+ + H^+ \rightarrow \cdot Cu^{2+} + HO_2$$

The reverse of this was not considered. Recently this has been shown to occur with k = ca. $10^8\ M^{-1}\ s^{-1}$.[39]
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Alkyl Cleavages from Organomercurials. 2. Electron Transfer Process with Hexachloroiridate(IV)

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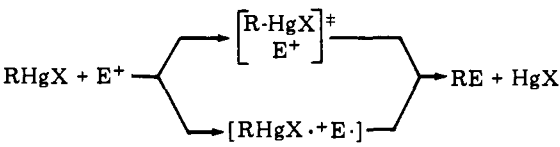
Abstract: Alkyl transfer from organomercury by hexachloroiridate(IV) proceeds by a rate-determining electron transfer process, followed by the facile homolysis of the mercury–alkyl bond. The alkyl radicals so formed are trapped by a second $IrCl_6^{2-}$, either as alkyl chloride via chlorine transfer or alkene via alkyl carbonium ions. All of the mercury products as well as the reduced iridium(III) species are characterized, and the stoichiometry of the cleavage is fully delineated. Alkyl radicals are established as prime intermediates through the ESR observation of nitroxide adducts formed by spin traps and the quantitative scavenging by oxygen. The second-order rate constants k for cleavage of R–HgMe increase in the order: R = Me (1.5×10^{-3}), Et (2.0), *i*-Pr (2.2×10^2), *t*-Bu ($1.6 \times 10^3\ M^{-1}\ s^{-1}$). The values of log k correlate well with the energetics of other electron detachment processes, i.e., $R_2Hg \rightarrow R_2Hg\cdot^+ + \epsilon$, such as the vertical ionization potentials and the frequency of the charge transfer bands of tetracyanoethylene complexes. Inner and outer-sphere mechanisms for electron transfer processes in organomercurials are discussed.

Organomercury compounds are involved as reactants or intermediates in a variety of synthetic organic procedures.[1] In a majority of these transformations, the cleavage of the carbon–mercury bond proceeds via an electrophilic mechanism.[2] However, a variety of electrophilic processes have recently been shown to involve prior electron transfer.[3] The mechanistic distinction between an electrophilic cleavage of a carbon-mercury bond and one proceeding via electron transfer is outlined in eq 1 and 2, respectively.



$$RHgX + E^+ \rightarrow \begin{bmatrix} R\text{-}HgX \\ E^+ \end{bmatrix}^{\ddagger} \rightarrow RE + HgX^+ \qquad (1)$$

$$RHgX + E^+ \rightarrow [RHgX\cdot^+ E\cdot] \rightarrow RE + HgX^+ \qquad (2)$$

The electrophilic cleavage in eq 1 is a one-step process in which no intermediates are generated. The electronic factors involved in the *transition state* of electrophilic cleavage of organomercurials are discussed in the foregoing study.[4] In contrast, the electron transfer process in eq 2 proceeds by a two-step mechanism in which the transfer of an electron from the mercurial to the electrophile constitutes the rate-limiting reaction. The difference between the two mechanisms lies in the ability of electrophiles to function as one-electron acceptors, i.e., $E^+ + \epsilon \rightarrow E\cdot$. Since many electrophiles are indeed oxidants, the distinction between electrophilic and electron transfer processes is not easily made. Thus, it is not surprising that only a limited number of authenticated examples are extant.[5]

We wish to examine the cleavage of the carbon–mercury bond by an electron transfer process in order to develop diagnostic patterns for such mechanisms in organomercurials. Moreover, it is important to differentiate electron transfer from electrophilic mechanisms in the cleavage of organometals in general, and organomercurials are excellent models for study since they are not commonly considered to participate in electron transfer processes as are their transition metal counterparts. In this study, hexachloroiridate(IV) was chosen for its well-known properties as a one-electron oxidant capable of participating in both outer-sphere and inner-sphere processes.[6] Criteria are developed to distinguish the reaction of organomercurials with hexachloroiridate(IV) from the more conventional electrophilic cleavages.

Results

A complete series of symmetrical as well as unsymmetrical dialkylmercury compounds, that is, R_2Hg and $RHgCH_3$, in which R is methyl, ethyl, isopropyl, and *tert*-butyl, were investigated in this study. All of these organomercurials reacted readily with a solution of hexachloroiridate(IV) in acetic acid or acetonitrile under an inert atmosphere. For example, the addition of diethylmercury to a solution of hexachloroiridate(IV) resulted in the immediate discharge of the red-brown color, followed by partial precipitation of reduced iridium(III) salts.

Products and Stoichiometry. The organic and the mercurial products of the reaction were identified and analyzed quantitatively by NMR spectroscopy and gas liquid chromatography.

Table I. The Stoichiometry of Oxidative Cleavage of Dialkylmercury by Hexachloroiridate(IV)[a]

HgRR′	(mmol)	Solvent	RCl (mmol)	R′Cl (mmol)	R′(−H) (mmol)	Others (mmol)	$\sum R_{ox}/\frac{1}{2}[IrCl_6^{2-}]$[b]
$HgMe_2$	(0.084)	CH_3CN	0.080				0.95
$HgMe_2$	(0.087)	HOAc	0.085				0.97
$HgEt_2$	(0.086)	CH_3CN	0.088				1.02
$Hg(i\text{-}Pr)_2$	(0.087)	CH_3CN	0.081		0.012	0	1.07
$Hg(i\text{-}Pr)_2$	(0.043)[c]	CH_3CN	0.074		0.013	0	1.02
$Hg(t\text{-}Bu)_2$	(0.084)	CH_3CN	0.046		0.047	0	1.10
$Hg(t\text{-}Bu)_2$	(0.094)	HOAc	0.018		0.059	0.034[d]	1.05
HgMe(Et)	(0.086)	CH_3CN	0.001	0.088	Trace	0	1.03
HgMe(Et)	(0.169)[e]	CH_3CN	0.001	0.085	Trace	0	1.02
HgMe(*i*-Pr)	(0.085)	CH_3CN	0	0.078	0.011	0	1.05
HgMe(*i*-Pr)	(0.085)	HOAc	0.003	0.054	0.025	0.001[f]	0.97
HgMe(*t*-Bu)	(0.084)	CH_3CN	0	0.039	0.050	0	1.05
HgMe(*t*-Bu)	(0.087)	HOAc	0.003	0.009	0.059	0.017[d]	1.01

[a] In 3 ml of solvent at 37 °C, with 2 equiv of $IrCl_6^{2-}$ under a nitrogen atmosphere. [b] $IrCl_6^{2-}$ completely consumed. [c] Four equivalents of $IrCl_6^{2-}$. [d] *tert*-Butyl acetate. [e] One equivalent of $IrCl_6^{2-}$. [f] Isopropyl acetate.

Table II. Quantitative Analysis of Mercury- and Iridium-Containing Products in the Reaction of Dialkylmercury with Hexachloroiridate(IV)

HgRR′	(mmol)	$IrCl_6^{2-}$[a] (mmol)	Solvent[b]	HgR^+[c] (mmol)	$IrCl_5(CH_3CN)^{2-}$[d] (mmol)	$IrCl_6^{3-}$[d] (mmol)
$HgMe_2$	(0.124)	0.097	CD_3CN	0.051[e]	0.056	0.042
$HgMe_2$	(0.124)	0.107	CH_3CN	0.048[e]	0.054 (0.056)[f]	0.040
$HgEt_2$	(0.089)	0.098	CH_3CN	0.05[g]	0.058 (0.059)[f]	0.040
$Hg(i\text{-}Pr)_2$	(0.063)	0.100	CH_3CN	0.044[h]	0.054 (0.060)[f]	0.038
$Hg(t\text{-}Bu)_2$	(0.053)	0.088	CH_3CN		0.029	0.060
$Hg(t\text{-}Bu)_2$	(0.051)	0.102	CH_3CN	0.044[i]	(0.034)[f]	
$Hg(t\text{-}Bu)_2$	(0.056)	0.090	CH_3CO_2H		0.021[j]	0.068
HgMeEt	(0.091)	0.182	CD_3OD	0.091[k]		
HgMe(*t*-Bu)	(0.094)	0.188	CD_3OD	0.091[k]		

[a] No unreacted $IrCl_6^{2-}$. [b] Solvent. [c] By NMR, CH_3CN replaced by pyridine. [d] By spectrophotometric measurements, as $IrCl_5(CH_3CN)^-$ and $IrCl_6^{2-}$. [e] δ 0.97 (s), $J_{Hg\text{-}H}$ = 217 Hz. [f] By NMR, δ 2.39 (s) in pyridine. [g] δ 0.8–2.2, multiplets. [h] δ_{Me} = 1.42 (d), $J_{H_\alpha\text{-}Me}$ = 7 Hz. [i] δ 1.43 (s), $J_{Hg\text{-}C\text{-}CH_3}$ = 256 Hz. [j] See text. [k] δ 0.96 (s), $J_{Hg\text{-}H}$ = 216 Hz.

The reduced iridium(III) products were separated by thin layer chromatography and determined spectrophotometrically as described in the Experimental Section.

Symmetrical dialkylmercury compounds such as dimethyl- and diethylmercury reacted with hexachloroiridate(IV) in acetonitrile solution according to the stoichiometry in eq 3 as shown in Tables I and II.

$$R_2Hg + 2Ir^{IV}Cl_6^{2-} \xrightarrow[CH_3CN]{} RCl + RHg^+ + Ir^{III}Cl_6^{3-} + Ir^{III}Cl_5(CH_3CN)^{2-} \quad (3)$$
$$\text{where } R = CH_3,\ CH_3CH_2$$

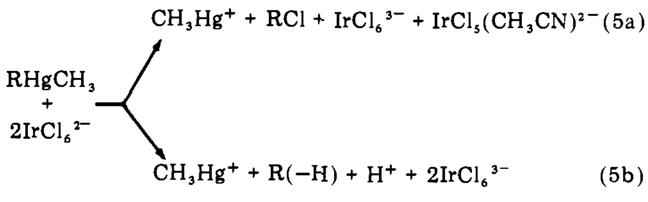
On the other hand, the same reaction with either diisopropyl- or di-*tert*-butylmercury afforded propylene or isobutylene, respectively, in addition to alkyl chloride. The formation of olefins is accompanied by a corresponding increase in the production of $IrCl_6^{3-}$ at the expense of $IrCl_5(CH_3CN)^{2-}$. Since alkyl chlorides do not afford olefins under reaction conditions, eq 4 must be considered (vide infra) in addition to eq 3 to account for the formation of some olefins in the reactions of diisopropyl- and di-*tert*-butylmercury.

$$R_2Hg + 2Ir^{IV}Cl_6^{2-} \longrightarrow R(-H) + H^+ + RHg^+ + 2Ir^{III}Cl_6^{3-} \quad (4)$$
$$\text{where } R = (CH_3)_2CH,\ (CH_3)_3C$$

The last column in Table I shows that 2 equiv of hexachloroiridate(IV) are always consumed for each mole of organic products, irrespective of the fate of the cleaved alkyl group (i.e., as alkyl chloride or olefin). Furthermore, the results in Table II show that one RHg^+ was found for every 2 mol of hexachloroiridate(IV) consumed.

Essentially the same results were obtained for reactions carried out in glacial acetic acid. The exception was di-*tert*-butylmercury, in which a considerable amount of *tert*-butyl acetate was found in addition to *tert*-butyl chloride and isobutylene. Similarly, small but discrete amounts of isopropyl acetate were detected in addition to the major products, isopropyl chloride and propylene, when diisopropylmercury was treated with hexachloroiridate(IV) in acetic acid. No esters were formed from reactions of methyl- and ethylmercury compounds.

Unsymmetrical dialkylmercury compounds, $RHgCH_3$, behave in the same way toward hexachloroiridate(IV) as their symmetrical counterparts, but an opportunity is presented here to observe the cleavage of either the methyl or the alkyl group. Indeed, the reaction of hexachloroiridate(IV) with the series of methyl(alkyl)mercury compounds leads to the preponderant cleavage of the alkyl-mercury bond since alkene, alkyl chloride, and CH_3Hg^+ are the principal products, i.e.,



$$RHgCH_3 + 2IrCl_6^{2-} \longrightarrow CH_3Hg^+ + RCl + IrCl_6^{3-} + IrCl_5(CH_3CN)^{2-} \quad (5a)$$
$$RHgCH_3 + 2IrCl_6^{2-} \longrightarrow CH_3Hg^+ + R(-H) + H^+ + 2IrCl_6^{3-} \quad (5b)$$

Table III. NMR Parameters for CH_3HgX in Various Solvents

Solvent	X	δ (ppm)	$J_{\text{Hg-H}}$ (Hz)
CH_3CN	Cl	0.98	218
	AcO	0.92	220
	CF_3SO_3	1.04	267
	$IrCl_x$	1.00	216
Pyridine	Cl	0.95	216
	$IrCl_x$	0.97	217

Thus, CH_3Hg^+ was found as the only organomercury product when stoichiometric amounts of $RHgCH_3$ and hexachloroiridate(IV) were mixed.[7] It was necessary to employ a 1:2 stoichiometric ratio of reactants in these studies, since the alkyl exchange in eq 6 occurs in the presence of excess dialkylmercury under reaction conditions.

$$CH_3Hg^+ + i\text{-}PrHgCH_3 \rightleftharpoons CH_3HgCH_3 + i\text{-}PrHg^+ \qquad (6)$$

Iridium(II) Products. It is noteworthy that the reduced iridium(III) products were usually found in acetonitrile to be almost equally partitioned between $IrCl_6^{3-}$ and $IrCl_5(CH_3CN)^{2-}$ as required by eq 1. The slightly higher values of $IrCl_5(CH_3CN)^{2-}$ may be attributed to partial solvolysis of $IrCl_6^{3-}$ during reaction since increasing amounts were found when solutions were allowed to age. The significantly *lower* values of $IrCl_5(CH_3CN)^{2-}$ observed in the reactions of di-*tert*-butylmercury are accountable by the incursion of eq 4 leading to the formation of isobutylene. This relationship between the yields of iridium(III) and organic products is supported by the results in Table I, which predict that 25% of the Ir(III) products should be $IrCl_5(CH_3CN)^{2-}$ compared to the 33% actually reported in Table II. (For the details of the Ir(III) products in acetic acid see the Experimental Section.)

RHg⁺ Products. The reactions described in eq 3-5 imply that a lone alkyl group is cleaved from dialkylmercury. Indeed, only a single alkyl group is removed from dimethyl-, diethyl-, and methyl(alkyl)mercury compounds, since they all afford RHg^+ species which are stable to further cleavage. However, both alkyl groups are cleaved in diisopropyl- and di-*tert*-butylmercury if more than 4 equiv of hexachloroiridate(IV) are allowed to react with each mole of dialkylmercury. The fifth entry in Table I suggests that hexachloroiridate(IV) is capable of effecting cleavage of $i\text{-}PrHg^+$. However, the rate of this cleavage must be slower than that of $(i\text{-}Pr)_2Hg$ since the cleavage of the latter can be interrupted at the intermediate stage by spectrally titrating a solution of $IrCl_6^{2-}$ with $(i\text{-}Pr)_2Hg$ rapidly. A similar titration with di-*tert*-butylmercury affords no distinct "end-point" until a stoichiometry of 4:1 is reached. Thus, the intermediate, $t\text{-}BuHg^+$, is very readily cleaved by $IrCl_6^{2-}$. The rate of the latter, however, is not as fast as the cleavage of the parent $(t\text{-}Bu)_2Hg$, since $t\text{-}BuHg^+$ can be observed in high yield if only a stoichiometric (i.e., 2:1) amount of $IrCl_6^{2-}$ is employed in the cleavage of $(t\text{-}Bu)_2Hg$. It is interesting to note that the same relative amounts of isopropyl chloride and propylene are obtained from the primary cleavage of $(i\text{-}Pr)_2Hg$ and the secondary cleavage of $i\text{-}PrHg^+$ (compare fourth and fifth entries in Table I). The same isopropyl moiety must be formed in both cases in the process of cleavage.

There is evidence that the species, designated as RHg^+ above, is covalently bound to the reduced chloroiridium(III) species. Petrosyan and Reutov[8] have shown that the NMR chemical shift δ and the $^{199}Hg\text{-}H$ coupling constant ($J_{\text{Hg-H}}$) of the α- and β-protons in a series of alkylmercury derivatives, RHgX, is quite sensitive to the bonding of X to mercury. Inspection of the parameters listed in Table III shows that the closest comparison of the species formed in our reaction is to one in which CH_3Hg^+ is bound to chloride. However, there are only two anions in solution, viz., $IrCl_6^{3-}$ and $IrCl_5(CH_3CN)^{2-}$. Since $IrCl_3^{3-}$ as the sodium salt is almost completely insoluble in the reaction medium (by spectrophotometric analysis), CH_3Hg^+ is left with only $IrCl_5(CH_3CN)^{2-}$ to bind. Indeed, equimolar amounts of CH_3Hg^+ and $IrCl_5(CH_3CN)^{2-}$ are found in solution by NMR analysis (see Table II), and we conclude that the binuclear complex, $CH_3HgClIrCl_4(CH_3CN)^{-1}$, is the dominant form in solution.

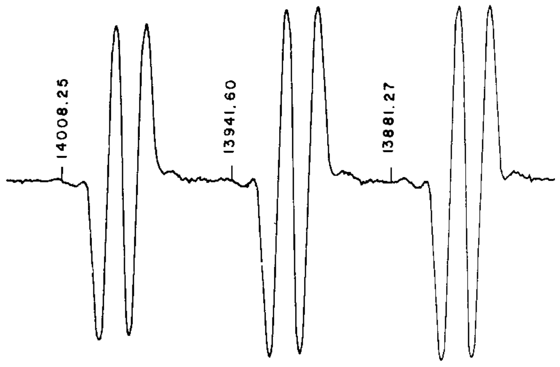


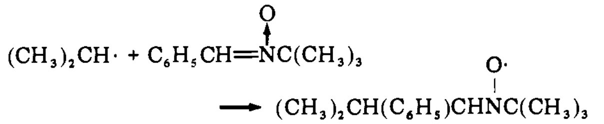
Figure 1. The ESR spectrum of the spin adduct of isopropyl radical to phenyl *tert*-butyl nitrone during the reaction of methylisopropylmercury with hexachloroiridate(IV) in acetic acid solution at room temperature. NMR field markers are in kHz.

Table IV. ESR Parameters of the Spin Adducts of Alkyl Radicals with NB and PBN during the Reaction of Dialkylmercury with Hexachloroiridate(IV) in Acetic Acid at Room Temperature

RHgR′	Spin[a] trap	Hyperfine splitting (G)	
		a_N	a_H
$HgEt_2$	NB	16.5	10.6
$HgMe(i\text{-}Pr)$	PBN	15.4	2.73
$Hg(t\text{-}Bu)_2$	NB	16.3	

[a] NB = nitrosoisobutane, PBN = phenyl *tert*-butyl nitrone.

Trapping of Reactive Intermediates. 1. Spin Trapping of Radicals. Electron spin resonance (ESR) studies were undertaken to probe for paramagnetic intermediates formed in these reactions. The intense ESR spectrum shown in Figure 1 was obtained during the reaction of methyl(isopropyl)mercury and hexachloroiridate(IV) in the presence of phenyl *tert*-butyl nitrone (PBN). The spectrum can be clearly assigned to the isopropyl adduct of PBN.[9] Furthermore, there is no evidence of the methyl adduct in the spectrum.



$$(CH_3)_2CH\cdot + C_6H_5CH{=}\overset{\overset{\displaystyle O}{\uparrow}}{N}C(CH_3)_3 \longrightarrow (CH_3)_2CH(C_6H_5)CH\overset{\overset{\displaystyle O\cdot}{|}}{N}C(CH_3)_3 \qquad (7)$$

Ethyl and *tert*-butyl radicals were also successfully trapped by nitrosoisobutane (NB) or phenyl *tert*-butyl nitrone. The spin adducts listed in Table IV were identified by the nitrogen and β-proton hyperfine splittings. The methyl adduct to neither NB nor PBN could be observed when dimethylmercury was cleaved with hexachloroiridate(IV).

2. Molecular Oxygen as a Scavenger for Alkyl Radicals. Alkyl radicals are known to react with molecular oxygen at

Table V. The Stoichiometry of the Cleavage of Dialkylmercury of Hexachloroiridate(IV) in the Presence of Oxygen[a]

HgRR′	(mmol)	$IrCl_6^{2-}$ (mmol)	R′Cl (mmol)	R′OH (mmol)	CH_3COCH_3 (mmol)	Others (mmol)	$\sum R_{ox}$
$HgMe_2$	(0.062)	0.054	0.002				
$HgMe_2$	(0.124)	0.069	0.010[b]	0.019[b]			
$HgEt_2$	(0.054)	0.054	<0.0005	0.014		0.040[c]	0.054
$HgEt_2$	(0.054)	0.054	<0.0005	0.012		0.037[c]	0.049
$Hg(i\text{-}Pr)_2$	(0.054)	0.054	0.001	0.018	0.032		0.050
	(0.054)	0.054	0.0005	0.019	0.029		0.048
HgMe(*t*-Bu)	(0.046)	0.054[f]	0.0004	0.035	0.0052	0.0041[d] 0.0032[e]	0.048
HgMe(*t*-Bu)	(0.054)	0.054	0.0006	0.041	0.0068	0.0052[d] 0.0031[e]	0.057

[a] One atmosphere of oxygen, in acetonitrile solutions. [b] In CD_3CN, by NMR. 0.069 mmol of unreacted $HgMe_2$ and 0.063 mmol of $HgMe^+$ found in product solution. 0.034 mmol of methyl group unaccounted for, which is most likely converted to H_2CO. [c] CH_3CHO. [d] Isobutylene. [e] Di-*tert*-butyl peroxide. [f] 0.08 mmol of $IrCl_6^{2-}$ unconsumed.

Table VI. Effect of Bromide Salts on the Cleavage of Dialkylmercury by Hexachloroiridate(IV) in Acetonitrile[a]

RR′Hg	(mmol)	$IrCl_6^{2-}$ (mmol)	RCl (mmol)	R′Cl (mmol)	RBr (mmol)	R′Br (mmol)	R′(−H) (mmol)
$HgMe_2$	(0.175)	0.175	0.061		0.037		
HgMe(Et)	(0.178)	0.174	0.002	0.087	0	Trace	0
HgMe(*i*-Pr)	(0.087)	0.173	0	0.082	0	0	0.003

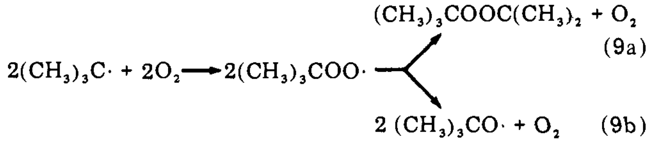
[a] At 37 °C, $[n\text{-}Bu_4NBr]$ = 1.5 M in 3.0 ml of solvent.

diffusion-controlled rates to produce a mixture of alcohols, ketones, and peroxides, depending on their structure.[10] When the reaction of dialkylmercury and $IrCl_6^{2-}$ was carried out in the presence of oxygen, the products (alkyl chlorides, olefins, etc.), usually formed under a nitrogen atmosphere, were largely eliminated as shown in Table V; and ethyl alcohol together with acetaldehyde were found in high yields from diethylmercury, and isopropyl alcohol and acetone from diisopropylmercury. These products are expected from the self-reaction of ethylperoxy and isopropylperoxy radicals, respectively.[10]

$$2R_2CH\cdot + 2O_2 \longrightarrow 2R_2CHOO\cdot \longrightarrow R_2CO + R_2CHOH + O_2 \qquad (8)$$

$$\text{where } R = CH_3, H$$

Oxygen also effectively quenches the formation of *tert*-butyl chloride and isobutylene during the cleavage of *tert*-butylmercury compounds. *tert*-Butylperoxy radicals with no α-hydrogens can only form di-*tert*-butyl peroxide and *tert*-butoxy radicals by self-reaction. Excellent yields of *tert*-butyl



$$2(CH_3)_3C\cdot + 2O_2 \longrightarrow 2(CH_3)_3COO\cdot \begin{cases} \longrightarrow (CH_3)_3COOC(CH_3)_3 + O_2 & (9a) \\ \longrightarrow 2\,(CH_3)_3CO\cdot + O_2 & (9b) \end{cases}$$

alcohol andd acetone reported in Table V can be produced from *tert*-butoxy radical.[10]

The highly efficient interception of the alkyl group by molecular oxygen indicates that alkyl radicals are important intermediates during the cleavage of dialkylmercury by $IrCl_6^{2-}$. Direct autoxidation of dialkylmercury can be dismissed, since no reaction is observed in the absence of $IrCl_6^{2-}$ under these conditions. (The quantitative accounting of all the oxidation products is discussed further in the Experimental Section.)

3. Bromide as a Nucleophilic Trap. Cationic (carbonium ion) intermediates in the cleavage reaction were sought in the presence of bromide ion as a nucleophilic trap. However, no incorporation of bromide in the products was observed during the reactions of ethyl- and isopropyl(methyl)mercury (Table VI). Thus, we conclude that the cleavages of ethyl and isopropyl groups during the reactions with $IrCl_6^{2-}$ do not proceed via the corresponding carbonium ions or other cationic analogues.

Methyl bromide is observed in the reaction of dimethylmercury with $IrCl_6^{2-}$ in the presence of bromide salts. However, control experiments show that it arose from a facile halide exchange (eq 10) of methyl chloride subsequent to its formation.

$$CH_3Cl + Bu_4N^+Br^- \longrightarrow CH_3Br + Bu_4N^+Cl^- \qquad (10)$$

The quantitative scavenging of the methyl group by oxygen as a methyl radical (vide supra) also argues against any trapping of methyl cations or a precursor.

Kinetics. The rate of the cleavage of dialkylmercury was followed spectrophotometrically by the disappearance of hexachloroiridate(IV). The reaction obeyed second-order kinetics, being first order in each reactant.

$$-d[IrCl_6^{2-}]/dt = 2k[IrCl_6^{2-}][R_2Hg] \qquad (11)$$

The kinetic experiments were carried out with $IrCl_6^{2-}$ in the concentration range, 10^{-4}–10^{-5} M, and with at least a tenfold excess of R_2Hg to approximate pseudo-first-order conditions.

The rate of cleavage of diethylmercury by $IrCl_6^{2-}$ (10^{-4} M) in acetonitrile is not affected by water up to 0.2 M. The addition of salts such as tetrakis-*n*-butylammonium bromide (7×10^{-3} m) and perchlorate (1.9×10^{-2} M) retarded the reaction by a factor of 2 and 6, respectively. On the other hand, alkali metal perchlorates such as lithium (1.6×10^{-2} M) and sodium (1.4×10^{-2} M) increased the rate by factors of 1.6 and 5.0, respectively. These variations in salt effects are probably due to a subtle balance in ion-pair equilibria in these nonaqueous media.[11] We could find no evidence for specific complexation of diethylmercury by salts under these conditions. To obviate salt effects, the kinetic experiments in Table II were carried out at constant ionic strength.

Table VII. Kinetics of the Reaction of Dialkylmercury with Hexachloroiridate(IV) in Acetonitrile at 25 °C[a]

R_2Hg	$IrCl_6^{2-}$ (10^4 M)	R_2Hg (M)	k ($M^{-1}\ s^{-1}$)	Deter.[b]
$HgMe_2$	2.0	0.05–0.23	$(1.5 \pm 0.1) \times 10^{-3}$	5
HgMeEt	0.6–2.4	1.8×10^{-3}–2.0×10^{-2}	2.0 ± 0.1	10
$HgEt_2$	0.6–3.4	6.3×10^{-4}–1.8×10^{-3}	48 ± 1	10
HgMe(*i*-Pr)	0.22	1.1×10^{-3}–2.0×10^{-2}	$(2.2 \pm 0.1) \times 10^{2}$	6
$Hg(i\text{-}Pr)_2$	0.22	6.8×10^{-5}–4.8×10^{-4}	$(3.3 \pm 0.1) \times 10^{4}$	6
HgMe(*t*-Bu)	0.22	2.6×10^{-4}–3.8×10^{-3}	$(1.6 \pm 0.1) \times 10^{3}$	4
$Hg(t\text{-}Bu)_2$	0.22	6.2×10^{-5}–2.5×10^{-4}	$(9.0 \times 0.5) \times 10^{4}$	5

[a] Containing 5.0×10^{-3} M $NaClO_4$. [b] Number of determinations.

Table VIII. Charge Transfer Spectra of the Tetracyanoethylene Complexes and Ionization Potentials of Dialkylmercury Compounds[a]

HgRR′	Charge transfer band		Log k	Vertical[b] IP, eV	Stability at 25 °C[c]
	λ_{max}, nm	ν_{max}, cm^{-1}			
$HgMe_2$	395	25 300	−2.82	9.33	Very stable
HgMeEt	445	22 500	0.30	8.84	~24 h
HgMe(*i*-Pr)	490	20 400	2.34	8.47	10 min
HgMe(*t*-Bu)	505 ± 5	19 800	3.20	8.32	2 min
$HgEt_2$	500	20 000	1.68	8.45	1 h
$Hg(i\text{-}Pr)_2$	570 ± 20	17 500	4.52	8.03	20 min[d]
$Hg(t\text{-}Bu)_2$	655 ± 20	15 300	4.96	7.57	3 min[d]

[a] In 1,2-dichloropropane solutions containing 0.1–0.4 M R_2Hg and 0.035 M TCNE at 25 °C except HgMe(*t*-Bu) (at 0 °C), $Hg(i\text{-}Pr)_2$ (at −77 °C), and $Hg(t\text{-}Bu)_2$ (at −77 °C). [b] By He(I) photoelectron spectroscopy, ref 14. [c] Approximate time for half disappearance. [d] At −77 °C.

No retardation of the cleavage of dimethylmercury by $IrCl_6^{2-}$ (6×10^{-5} M) was detected when the reaction was carried out at 50 °C in the presence of added iridium(III) products (3×10^{-4} M each of $IrCl_6^{3-}$ and $IrCl_5(CH_3CN)^{2-}$). Unfortunately the low solubility of Na_3IrCl_6 in acetonitrile limited the extension of the study to higher concentrations of iridium(III) complexes.

It is noteworthy that the second-order rate constant decreased by a factor of precisely 2.0 when the cleavage of diethylmercury was carried out in an oxygen atmosphere.

The second-order rate constants for the cleavage of a series of dialkylmercury compounds by hexachloroiridate(IV) are listed in Table VII. There is a factor of more than 10^7 which separates the least reactive dimethylmercury from di-*tert*-butylmercury, and there is a monotonic trend for the cleavage rate to increase progressively with the addition of each α-methyl group, i.e., $CH_3 < CH_3CH_2 < (CH_3)_2CH < (CH_3)_3C$.

Charge Transfer Complexes of Dialkylmercury with Tetracyanoethylene. The addition of dialkylmercury to a solution of tetracyanoethylene (TCNE) in 1,2-dichloropropane results in weak but distinct colors (Table VIII), characteristic of the mercurial added. The stability of the band also varies (last column, Table VIII), being the most stable with dimethylmercury. The transient bands from diisopropyl and di-*tert*-butylmercury were recorded at −77 °C, but even at this temperature the solution turns yellow as the charge transfer complexes rapidly undergo further thermal reactions.[5b,12] The broadness of the bands coupled with their fleeting existence precluded accurate determinations of $\lambda_{max(CT)}$ for these compounds.

The high concentrations (0.1–0.4 M) of dialkylmercury required to produce a charge transfer band suggest that the formation constants K and/or the extinction coefficients of the charge transfer complexes are small, which is generally expected for the interaction of a σ donor with a π acceptor.[12,13]

$$R_2Hg + TCNE \overset{K}{\rightleftharpoons} [R_2Hg\ TCNE] \qquad (12)$$

Discussion

The cleavage of dialkylmercury by hexachloroiridate(IV) is highly dependent on the structure of the alkyl groups. Thus, in the homologous series of $RHgCH_3$, the relative rates of cleavage increase from R = methyl:ethyl:isopropyl;*tert*-butyl, roughly in the order of 10^0:10^3:10^5:10^6. These results run counter to expectations based on increasing steric hindrance, and suggest that the rate-limiting step occurs prior to alkyl transfer. We wish to show that the cleavage of the alkylmercury bond is preceded by an electron transfer process described in Scheme I. R_{ox} in eq 15 represents products of oxidation of the alkyl radical such as alkyl chloride, alkene + H^+ or alkyl acetate + H^+, and X may be solvent ($n = 2$) or chloride ($n = 3$). The activation process in Scheme I is represented by the electron transfer step 13, followed by the spontaneous fragmentation of the dialkylmercury radical-cation in eq 14 to yield an alkyl radical which is efficiently intercepted by hexachloroiridate(IV) in eq 15. Scheme I accords with the extensive observations we have made in this system, including (1) the energetics and kinetics in the electron transfer step, (2) the prime importance of alkyl radicals as intermediates, and (3) the selectivity in the cleavage of unsymmetrical dialkylmercury. Each point will be discussed individually in the following discussion.

Scheme I

$$R_2Hg + Ir^{IV}Cl_6{}^{2-} \xrightarrow{k} R_2Hg^{\cdot +} + Ir^{III}Cl_6{}^{3-} \qquad (13)$$

$$R_2Hg^{\cdot +} \xrightarrow{fast} RHg^+ + R\cdot \qquad (14)$$

$$R\cdot + Ir^{IV}Cl_6{}^{2-} \xrightarrow{fast} R_{ox} + Ir^{III}Cl_5X^{n-} \qquad (15)$$

Electron Transfer as the Rate-Determining Step. The second-order kinetics for cleavage indicate that R_2Hg and only one $IrCl_6^{2-}$ are involved in the rate-limiting transition state.

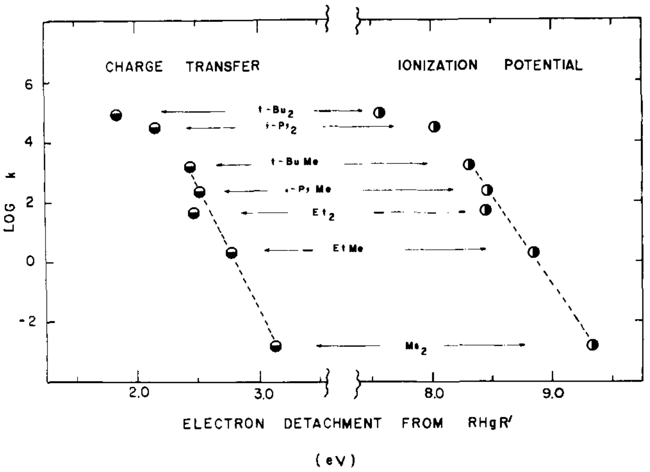


Figure 2. Correlation of the logarithms of the second-order rate constants for cleavage of dialkylmercury RHgR′ by hexachloroiridate(IV) in acetonitrile solutions with the energetics of electron detachment from RHgR′ involving ◒ the frequencies of the charge transfer complexes RHgR′–TCNE and ◑ the vertical ionization potential of RHgR′.

The other $IrCl_6^{2-}$ required by the stoichiometry must be involved in a fast subsequent step. For an electron transfer process between R_2Hg and $IrCl_6^{2-}$, the second-order rate constant k in eq 13 should increase with increasing ease of electron detachment from R_2Hg. The energetics of electron detachment from R_2Hg are represented as,

$$\mathrm{R_2Hg} \longrightarrow \mathrm{R_2Hg}^{\cdot+} + \epsilon \tag{16}$$

and measured independently by the ionization potential.[14] Indeed, Figure 2 shows the linear correlation between log k for cleavage and the vertical ionization potential of a series of related $RHgCH_3$. A similar correlation is also observed with the energies ($h\nu_{CT}$) of the charge transfer bands of R_2Hg–TCNE complexes,

$$[\mathrm{R_2Hg\ TCNE}] \xrightarrow{h\nu_{\mathrm{CT}}} [\mathrm{R_2Hg}^{\cdot+}\ \mathrm{TCNE}^{\cdot-}] \tag{17}$$

Electron transfer as presented above is an outer-sphere process.[15] The relationship of log k for cleavage with the ionization potentials of R_2Hg and with the charge transfer interactions in R_2Hg–TCNE complexes suggests that electron detachment from R_2Hg involves only a minor structural reorganization of the organomercury cation–radical. However, both correlations suffer somewhat when the more sterically hindered di-*tert*-butyl, diisopropyl, and diethyl analogues are included. Further discussion of steric effects will be postponed until the last section, involving inner and outer-sphere mechanisms in electron transfer from R_2Hg.

The electron transfer between R_2Hg and $IrCl_6^{2-}$ in eq 15 is essentially irreversible, since the rate of cleavage is unaffected by added iridium(III) products. The irreversibility derives in part from the metastable nature of the dialkylmercury cation–radical which we treat hereafter as an intermediate for convenience. (The same conclusions are reached if the electron transfer proceeds through an inner-sphere complex (see last section)). Our inability to observe directly the electron spin resonance spectrum of $R_2Hg^{\cdot+}$ suggests that its lifetime is very short. It is present as one of the principle species during electron impact of R_2Hg in the gas phase.[16]

Alkyl Radicals as Prime Intermediates. The observation of paramagnetic intermediates by spin trapping indicates that alkyl radicals are formed during the cleavage of R_2Hg by $IrCl_6^{2-}$. In fact, the quantitative accounting of the alkyl fragments as alkylperoxy products, when the reaction is carried out in the presence of oxygen, shows that *all* of the alkyl groups must depart from mercury as free radicals according to eq 14. The latter is strongly supported by the observation that $IrCl_6^{2-}$ disappears under these conditions at just one-half the rate observed in an inert atmosphere, as predicted by Scheme I.

Furthermore, the lack of incorporation of foreign nucleophiles such as bromide and water, precludes the participation of competing substitution processes similar to those previously observed with alkylcobalt complexes,[17] e.g.,

$$\mathrm{R_2Hg}^{\cdot+} + \mathrm{Br}^- \longrightarrow \mathrm{R\,Br} + \mathrm{RHg}\cdot \ \text{etc.} \tag{18}$$

A similar situation exists with organolead cation-radicals.[5]

According to Scheme I, the isolation of alkyl chlorides in high yields implies that hexachloroiridate(IV) is an efficient scavenger of alkyl radicals in eq 15. Indeed, separate experiments have confirmed that ethyl radicals (unambiguously generated from the thermolysis of dipropionyl peroxide in acetonitrile) are quantitatively converted to ethyl chloride by $IrCl_6^{2-}$ under these conditions.[5] Furthermore, transfer of chlorine in this manner must leave one-half of the reduced iridium(III) product as $IrCl_5(CH_3CN)^{2-}$, as found experimentally.

Redox transfer of chlorine from hexachloroiridate(IV) to alkyl radical according to eq 15 is akin to other ligand transfer processes previously described with copper(II) complexes.[18] Extending the analogy, the observation of isobuutylene and *tert*-butyl acetate from *tert*-butyl radicals and hexachloroiridate(IV) is analogous to electron transfer oxidation of alkyl radicals.[19]

$$\mathrm{(CH_3)_3C}\cdot + \mathrm{Ir^{IV}Cl_6}^{2-} \longrightarrow \mathrm{Ir^{III}Cl_6}^{3-} + \mathrm{(CH_3)_3C^+}\ \text{etc.} \tag{19}$$

The *tert*-butyl cation formed under such circumstances will undergo solvation, for example to *tert*-butyl acetate, or loss of a β-proton to isobutylene. The resultant iridium(III) product must then maintain its coordination sphere intact as $IrCl_6^{3-}$. Indeed, the distribution of $IrCl_6^{3-}$ and $IrCl_5(CH_3CN)^{2-}$ among reduced iridium(III) products formed from various alkylmercurials is precisely in accord with this formulation. Thus, the results in Table I clearly indicate that methyl and ethyl radicals react with $IrCl_6^{2-}$ in acetonitrile, exclusively by chlorine transfer. For isopropyl and *tert*-butyl radicals, approximately 85 and 50%, respectively, of the reaction proceeds by chlorine transfer and the remainder by electron transfer. The latter becomes more important in acetic acid solutions. The decreasing trend of alkyl radicals to react with $IrCl_6^{2-}$ by electron transfer in the order *t*-Bu > *i*-Pr ≫ Et > Me, follows the ease of ionization of the radical (I.P. (eV): *t*-Bu (6.93), *i*-Pr (7.55), Et (8.38), Me (9.84)).[20] Furthermore, the opposed trend in the yields of alkyl chlorides is consistent with the generally decreasing alkyl–chlorine bond energies from MeCl through *t*-BuCl. Whether chlorine transfer and carbonium ion formation represent inner- and outer-sphere redox processes, respectively, forms an interesting speculation.[21] Studies are in progress to delineate this formulation for various alkyl radicals generated by independent methods.

Selectivity during Fragmentation of Alkylmercury Ion–Radical. Selectivity in the cleavage of alkyl groups from unsummetrical dialkylmercury by $IrCl_6^{2-}$ according to Scheme I occurs during fragmentation of $R_2Hg^{\cdot+}$ radical-cation or its equivalent (vide infra). Indeed, the *exclusive* cleavage of R = *t*-Bu and *i*-Pr and *preferential* cleavage of R = Et in the homologous series of $RHgCH_3$ in Table I is in accord with a weaker alkyl-mercury compared to a methyl-mercury bond. Similar selectivities are observed in the mass spectral cracking patterns of these mercurials examined by Spielmann and Delaunois.[16]

$$\mathrm{RHgCH_3}^{\cdot+} \begin{cases} \longrightarrow \mathrm{R}\cdot + \mathrm{CH_3Hg^+} & \text{(20a)} \\ \longrightarrow \mathrm{CH_3}\cdot + \mathrm{RHg^+} & \text{(20b)} \end{cases}$$

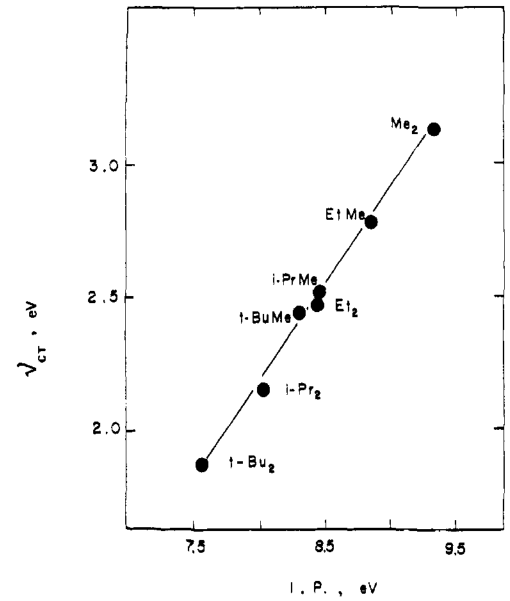


Figure 3. Correlation of the charge transfer frequencies of dialkylmercury-tetracyanoethylene complexes with the vertical ionization potentials of dialkylmercury measured by He(I) photoelectron spectroscopy.

Although quantitative comparisons of the behavior of highly energetic species formed in the mass spectrometer with those radical-cations formed in solution are tenuous, the qualitative trends in the two systems are unmistakable. The predominant factor which determines alkyl vs. methyl cleavage are the strengths of the relevant C-Hg bonds. These values can be evaluated from the average bond energies for Me_2Hg, Et_2Hg, and i-Pr_2Hg which are 58, 48, and 42 kcal mol^{-1}, respectively.[22]

An alternative mode of fragmentation of $R_2Hg^{\cdot+}$ may be represented by eq 21,

$$R_2Hg^{\cdot+} \longrightarrow R^+ + RHg\cdot \qquad (21)$$

particularly when R is a t-Bu group. However, the observation of t-$BuHg^+$ by its NMR spectrum after cleavage by $IrCl_6^{2-}$ and the complete scavenging of *tert*-butyl radicals by oxygen strongly disfavor such a formulation.

Finally, it is conceivable that $R_2Hg^{\cdot+}$ or an equivalent (vide infra) is not an intermediate, but cleavage by $IrCl_6^{2-}$ occurs by an electrophilic reaction such as that represented in eq 22.

$$R_2Hg + IrCl_6^{2-} \longrightarrow RHg^+ + RClIrCl_5^{3-} \text{ etc.} \qquad (22)$$

The observed selectivity is not consistent with direct attack on the alkyl-mercury bond, e.g., on protonolysis. Thus, proton transfer takes place at least 10^2 times more slowly at the sterically encumbered *tert*-butyl-mercury bond in *tert*-$BuHgCH_3$ than an equivalent methyl-mercury bond in CH_3HgCH_3 during acetolysis.[4,23] This pattern of selectivity in electrophilic cleavage contrasts strongly with a factor of 10^6 in *favor* of t-Bu in a comparative cleavage of t-$BuHgCH_3$ and CH_3HgCH_3 by $IrCl_6^{2-}$. A difference in the mechanisms of these two processes is clearly implicated, since steric restraints for hexachloroiridate cleavage, if it were to proceed by an electrophilic mechanism, would be even more dominant than that observed in protonolysis, due to the differences in the sizes of the electrophiles. Indeed, the relative reactivities of dialkylmercury compounds can be employed in this manner as a diagnostic criterion to differentiate electron transfer from electrophilic process in cleavages by various reagents.

Charge Transfer Spectra for Inner- and Outer-Sphere Mechanisms in Electron Transfer Involving R_2Hg. Inner- and outer-sphere mechanisms merit consideration for the process by which electron transfer occurs from R_2Hg to $IrCl_6^{2-}$ in the rate-limiting step in eq 13. A linear free energy relationship between log k of reaction and I.P. of R_2Hg is expected for this system if electron transfer occurs by an outer-sphere process.[15,24] However, the negative deviation of di-*tert*-butyl-, diisopropyl-, and diethylmercury from the linear plot in Figure 2 suggests that steric factors are important in the electron transfer to $IrCl_6^{2-}$.

In order to study steric effects of R_2Hg, we examined their donor properties in outer-sphere complexes, viz., charge transfer (CT) interactions with tetracyanoethylene (TCNE).

$$R_2Hg + TCNE \rightleftharpoons [R_2Hg\ TCNE] \qquad (12)$$

According to the valence-bond description,[25] the frequency of the CT band corresponds roughly to the energy required to transfer an electron from R_2Hg to TCNE.

$$[R_2Hg\ TCNE] \xrightarrow{h\nu_{CT}} [R_2Hg^{\cdot+}\ TCNE^{\cdot-}] \qquad (17)$$

For weakly associating systems, such as these are, $h\nu_{CT}$ is approximated by eq 23,[26]

$$h\nu_{CT} = I_D - E_A - [G_1 - G_0] \qquad (23)$$

where I_D and E_A refer to the vertical ionization potential of R_2Hg and the electron affinity of TCNE, respectively, and G_1, the dominant term in the brackets, involves Coulombic interaction in the excited state. Since G_1 is inversely related to the encounter distance, $h\nu_{CT}$ is expected to shift to higher energies with increasing bulkiness of R_2Hg.[12] With TCNE as the common acceptor, Figure 3 shows the linear relationship between $h\nu_{CT}$ and the vertical ionization potential for the complete series of R_2Hg examined in this study. It is important to note that di-*tert*-butyl-, diisopropyl-, and diethylmercury are included in the same correlation with the other mercurials. The extent to which there is a small monotonic increase in steric hindrance in going from Me, Et, i-Pr, to t-Bu is shown in Figure 3 by a change in the slope of the line from the 1.0 expected[26] to the 0.79 observed. Thus, minor differences in steric interactions represent perturbations in the charge transfer interactions between R_2Hg and TCNE.[27] The point for di-*tert*-butylmercury is particularly noteworthy since large steric interactions of this compound with TCNE would actually represent a deviation from the linearity shown in Figure 3.

By using CT interactions with TCNE as models for steric hindrance in outer-sphere complexes of R_2Hg, we infer that the pronounced negative deviation for di-*tert*-butylmercury in the linear free energy relationship in Figure 2 indicates the presence of sizable steric interactions between R_2Hg and $IrCl_6^{2-}$ in the transition state for electron transfer. Furthermore, the steric effects would be more pronounced in R-Hg-Me when homologation occurs on Me rather than R. It is not surprising therefore to observe linearity only among the series of $RHgCH_3$ in Figure 2, which does not include diethyl-, diisopropyl-, and di-*tert*-butylmercury. An inner-sphere mechanism for electron transfer is suggested but our experiments do not distinguish between a process in which a binuclear complex is a transition state or an intermediate.[28] Electron transfer from R_2Hg to $IrCl_6^{2-}$ by an inner-sphere complex is analogous to the binuclear complex $[(NC)_5CoClIrCl_5^{5-}]$ detected during electron transfer between pentacyanocobaltate(II) and hexachloroiridate(IV).[29] Three-coordinate

$$R_2Hg + IrCl_6^{2-} \rightleftharpoons R_2HgClIrCl_5^{2-}$$

complexes, R_2HgX^-, between dialkylmercury and halide ions have been reported.[30]

Electron transfer by an inner-sphere mechanism, thus, may lead directly to $R_2Hg^{\cdot+}$ or, if a precursor complex is formed, by cleavage as shown in eq 24.

$$R_2HgClIrCl_5^{2-} \rightarrow R_2Hg^{\cdot+} + IrCl_6^{3-} \qquad (24)$$
$$\hookrightarrow R\cdot + RHg^+ \qquad (14)$$

It is also possible, however, that alkyl radical is liberated directly from the complex, i.e.,

$$R_2HgClIrCl_5{}^{2-} \longrightarrow R\cdot + RHgClIrCl_5{}^{2-} \text{ etc.}$$

Unfortunately, these mechanisms are not readily distinguishable simply by trapping RHg^+ before it combines with $IrCl_6{}^{3-}$, owing to the substitution lability of $RHgClIrCl_5{}^{2-}$.

$$RHgClIrCl_5{}^{2-} + IrCl_5(CH_3CN)^{2-} \rightleftharpoons RHgClIrCl_4(CH_3CN)^{-} + IrCl_6{}^{3-}$$

The differences are largely a matter of timing in the bond-breaking processes involved in the formation of alkyl radicals, but they do not materially affect the principal mechanistic conclusions embodied in Scheme I.

Experimental Section

Materials. The series of dialkylmercury compounds used in this study was described previously.[4] Sodium hexachloroiridate(IV) $Na_2IrCl_6{\cdot}6H_2O$ was obtained from Varlacoid Chemical Co. and Apache Chemicals, and was used without purification since the visible spectra (e.g., ϵ_{487} 4060 M^{-1} in 1 M $HClO_4$) of these samples agreed with that in the literature.[6d] Tetracyanoethylene from E. I DuPont Co. was sublimed before use. Acetonitrile (Mallinkrodt, analytical reagent) was stirred with calcium hydride overnight, filtered, and then distilled from P_2O_5 under a nitrogen atmosphere. Acetic acid (Eastman Kodak Co.) and 1,2-dichloropropane (Matheson, Coleman and Bell) were both redistilled before use. Nitrosoisobutane and phenyl *tert*-butyl nitrone (Aldrich reagent grades) were used as received. Sodium perchlorate was prepared by careful neutralization of concentrated $HClO_4$ with Na_2CO_3, and recrystallized twice from water. Tetra-*n*-butylammonium bromide was prepared by the method of Sadek and Fuoss,[31] and recrystallized from tetrahydrofuran. Tetra-*n*-butylammonium perchlorate (Southwestern Chemicals) was recrystallized from 1,2-dimethoxyethane. Lithium perchlorate (G. F. Smith Chemical Co.) was recrystallized from acetonitrile.

Reactions of Dialkylmercury with Hexachloroiridate(IV). A. Analyses of Olefins, Alkyl Chlorides, and Alkyl Acetates. Typically, 0.160 mmol of $Na_2IrCl_6{\cdot}6H_2O$ was weighed into a 25-ml round-bottom flask containing a magnetic stirring bar. The flask was sealed with a gas-tight rubber serum cap, and the atmosphere removed by means of a hypodermic syringe while attached to a vacuum line. After an atmosphere of pure nitrogen was added, 3 ml of deoxygenated solvent was added by means of a hypodermic syringe. A Teflon cannula attached to a glass-tipped syringe was used to transfer acetic acid. Internal standards (isobutylene, ethyl chloride, etc.) were added, and the flask was transferred to a constant temperature bath, regulated at 37 °C. The reaction was initiated by 0.080 mmol of a dialykylmercury compound added by means of a syringe to the magnetically stirred solution. Samples of gas were periodically removed from the flask to monitor the yields of olefins and alkyl chlorides by gas chromatography on a column consisting of 15 ft 20% Apiezon L plus 15 ft 20% FFAP at 90 °C.

Reactions with the solid di-*tert*-butylmercury were carried out in two-necked 25-ml round-bottom flasks. One neck was sealed with a gas-tight rubber serum cap and the other was sealed with a solids addition tube containing the di-*tert*-butylmercury. The reaction was initiated by mixing the contents of the solids addition tube with the hexachloroiridate(IV) solution in the flask.

Many dialkylmercury compounds react rapidly with hexachloroiridate(IV). The possibility that the observed selectivity was caused by a surface reaction on the droplets of the added dialkylmercury was examined. A solution of 0.085 mmol of methylisopropylmercury in 2 ml of CH_3CN was added with a syringe to a solution of 0.170 mmol of $Na_2IrCl_6{\cdot}6H_2O$ in 1 ml of CH_3CN under a nitrogen atmosphere at 37 °C. The distribution of products (propene, methyl chloride, and isopropyl chloride) was the same as that observed when 0.085 mmol of neat methylisopropylmercury was added to 0.170 mmol of Na_2IrCl_6 in 3 ml of CH_3CN.

B. Analyses of Alkylmercury and Iridium Products by NMR. In a typical experiment, 0.10 mmol of $Na_2IrCl_6{\cdot}6H_2O$ was dissolved in 0.50 ml of deuterated acetonitrile in an NMR tube under nitrogen atmosphere. Neat dialkylmercury (0.10 mmol) was then added by means of a hypodermic syringe. The NMR spectrum of the solution for alkylmercury products was recorded after the addition of Me_4Si and CH_2Cl_2 as internal standards. For the quantitative determination of $IrCl_5(CH_3CN)^{2-}$ the reaction was carried out in non-deuterated acetonitrile. The product solution was pumped to dryness and 0.5 ml of pyridine was then added in order to digest the solid residue. The NMR spectrum of the solution (in which the insoluble Na_3IrCl_6 had settled to the bottom) was then recorded. The good analytical agreement between $IrCl_5(CH_3CN)^{2-}$ found by NMR and that determined by spectrophotometric analysis (vide infra) suggests that almost all of the $IrCl_5(CH_3CN)^{2-}$ was dissolved in pyridine. The amount of $HgMe^+$ found in pyridine solutions also agrees with that found in reactions carried out in the deuterated solvent. For di-*tert*-butylmercury, both $Na_2IrCl_6{\cdot}6H_2O$ and the mercurial were weighed into an NMR tube. The contents were deoxygenated, and the reaction was initiated by injecting 0.5 ml of the deoxygenated solvent.

C. Analyses of Ir(III) Products by Spectrophotometry. The reactions were carried out under conditions similar to that described in section A above. Immediately after the reaction was complete, the product solution was pumped to dryness and the solid residue digested with 5.0 ml of CH_3CN. Gaseous chlorine was passed through the solution in order to oxidize all of the Ir(III) products. A 100 μl aliquot of the oxidized solution was subjected to silica gel thin-layer chromatographic separation using Cl_2/CH_3CN. Additional chlorine was added in order to reoxidize any Ir(IV) that was reduced on the column. The pink $IrCl_5(CH_3CN)^-$ moved with the solvent front, and the gold-colored $IrCl_6{}^{2-}$ lagged behind the solvent front. Effective separation was achieved on a silica gel plate 2 in. long. The spots on the silica gel plate containing iridium products were removed with a spatula, and the iridium products were then leached off with a solution of chlorine in CH_3CN. Roughly 20% of $IrCl_6{}^{2-}$ was not washed off by Cl_2/CH_3CN, and water (1.0 M in $HClO_4$) was then used to remove the remaining $IrCl_6{}^{2-}$. Ultraviolet spectra of these solutions were recorded and the amounts of $IrCl_5(CH_3CN)^-$ and $IrCl_6{}^{2-}$ were calculated from the extinction coefficients of these complexes: for $IrCl_6{}^{2-}$, ϵ_{489} 4630 in CH_3CN[5a] and ϵ_{487} 4060 in 1.0 M aqueous $HClO_4$;[6d] for $IrCl_5(CH_3CN)^-$, ϵ_{500} 3130 in CH_3CN.[5a] In general, 85–95% of the Ir(III) products were recovered from the TLC separation.

The analysis of the reduced iridium(III) products from the reaction of dialkylmercury and hexachloroiridate(IV) in glacial acetic acid afforded unusual results. Thus, the solution obtained by dissolving the product residue in acetonitrile saturated with chlorine gave only $IrCl_6{}^{2-}$ and $IrCl_5(CH_3CN)^-$. Similarly, the oxidation of the product residue in methanol with chlorine afforded a new species (λ_{max} 455, 366 nm) possibly $IrCl_5(CH_3OH)^-$, together with $IrCl_6{}^{2-}$. Separate experiments showed that reduction of hexachloroiridate(IV) by ethyl radical (generated by thermolysis of dipropionyl peroxide[5]) in methanol gave the same new species after treatment with chlorine. These observations can be explained if $IrCl_5(OAc)^{3-}$ is the reduced Ir(III) species. Oxidation with chlorine is expected to produce $IrCl_5(OAc)^{2-}$ which is unstable. Decarboxylation may proceed by an intramolecular redox reaction to generate methyl radical together with the coordinatively unsaturated $IrCl_5{}^{2-}$ and subsequently produce $IrCl_5(CH_3CN)^{2-}$ or $IrCl_5(CH_3OH)^{2-}$ by reaction with the solvent.

Spin-Trapping Experiments. An ESR tube containing 0.02 mmol of $Na_2IrCl_6{\cdot}6H_2O$ and 0.1 mmol of spin trap (nitrosoisobutane or phenyl *tert*-butyl nitrone) was sealed with a gas-tight serum cap and purged with a stream of nitrogen. Deoxygenated acetic acid (0.5 ml) was then added by means of a Teflon cannula attached to a glass-tipped syringe, followed by the addition of 0.1 mmol of dialkylmercury. The ESR spectrum of the solution was recorded at room temperature on a Varian V4502 spectrometer.[5] Control experiments indicated that a very small amount of di-*tert*-butyl nitroxide was present after a solution of di-*tert*-butylmercury was mixed with nitrosoisobutane. On the addition of $Na_2IrCl_6{\cdot}6H_2O$, the ESR signal due to di-*tert*-butyl nitroxide increased by a factor of more than ten. However, no spin adduct was detected in solutions containing only nitrosoisobutane and any other dialkylmercury compounds used in this study. Furthermore, radical adducts were not detected in solutions containing phenyl *tert*-butyl nitrone and dialkylmercury compounds, nor in solutions containing only Na_2IrCl_6 and either phenyl *tert*-butyl nitrone or nitrosoisobutane.

Reactions of Dialkylmercury with Hexachloroiridate(IV) in the Presence of Oxygen. A solution of oxygen-saturated acetonitrile (1.0 ml) containing a known amount of dialkylmercury was added to a sealed vial (serum cap) under an oxygen atmosphere. The solution was transferred to a constant-temperature bath regulated at 37 °C, and

3.0 ml of a solution of Na_2IrCl_6, also saturated with oxygen, was added dropwise over a period of a few minutes while the solution was vigorously stirred. Instantaneous decoloration of hexachloroiridate(IV) was observed with every dialkylmercury compound with the exception of dimethylmercury. After the reaction was complete, the products of the reactions were analyzed by gas-liquid chromatography. A sample of the gas was analyzed for olefins and alkyl chlorides with a column consisting of 15 ft 20% Apiezon L plus 15 ft 20% FFAP. The liquid was analyzed for aldehydes, ketones, alcohols, and peroxides with either a 15 ft or a 20 ft 10% FFAP column at 30–60 °C.

It is noteworthy that the relative amounts of alcohol and carbonyl products from ethyl- and isopropylmercury compounds are not equal, as required by eq 8. The further radical-chain autoxidation of alcohol to carbonyl compound is a strong possibility. Since their combined yields are roughly equal to the $IrCl_6^{2-}$ consumed, it is unlikely that the latter is involved in the oxidation of the alcohol. Furthermore, the combined yields of the oxidation products from *tert*-butylmercury is 1.2 times the amount of $IrCl_6^{2-}$ consumed.[32] Since the deviation from 1.0 is too large to dismiss, an induced decomposition of the mercurial by *tert*-butoxy radical may be involved, e.g.,

$$(CH_3)_3CHgCH_3 + (CH_3)_3CO\cdot$$
$$\longrightarrow (CH_3)_3COH + (CH_3)_2C{=}CH_2 + CH_3Hg\cdot \text{ etc.}$$

Kinetic Measurements. All the reactions were followed spectrophotometrically with either a Beckman DBG spectrophotometer or a Durrum-Gibson stopped-flow spectrophotometer. The reactions were carried out in an argon atmosphere, and the temperature was regulated at 25.0 ± 0.2 °C.

The reactions were followed by the disappearance of the band due to hexachloroiridate(IV) at λ_{max} 489 nm. Dialkylmercury compounds were generally employed in at least 20-fold excess to ensure that their concentrations remained essentially constant throughout the reaction. The pseudo-first-order plots were linear for more than three half-lives.

The reactions of $HgMe_2$, HgMeEt, and $HgEt_2$ with hexachloroiridate(IV) were studied in a Beckman DBG spectrophotometer. In a typical experiment, a cell containing 1.0×10^{-4} M Na_2IrCl_6 and 5.0×10^{-3} M $NaClO_4$ in 2.5 ml of acetonitrile was thermostated for 15 min. and either a concentrated stock solution or a neat sample of dialkylmercury in the amount of 20–100 µl was added with a microsyringe to initiate the reaction.

The much faster reactions of HgMe(*i*-Pr), $Hg(i\text{-}Pr)_2$, HgMe(*t*-Bu), and $Hg(t\text{-}Bu)_2$ were studied in a Durrum-Gibson stopped-flow spectrophotometer. In a typical experiment, the two reactant solutions, prior to mixing in the stopped-flow apparatus, contained the following reagents: solution A, 4.0×10^{-5} M Na_2IrCl_6 and 5.0×10^{-3} M $NaClO_4$; solution B, dialkylmercury (the concentration of which is equal to or greater than five times the concentration of Na_2IrCl_6 in solution A) and 5.0×10^{-3} M $NaClO_4$. Both solutions were deoxygenated with argon and were allowed to reach thermal equilibrium for 10–15 min prior to mixing.

Charge-Transfer Spectra. Most of the charge-transfer complexes of dialkylmercurials with tetracyanoethylene (TCNE) are sufficiently stable to enable their charge-transfer spectra to be recorded at room temperature or at 0 °C without special precaution. In general, the solution was prepared by the addition of a 20 µl neat sample of dialkylmercury to a cell containing 2.0 ml of a 1,2-dichloropropane solution of TCNE (3.5×10^{-2} M) in a nitrogen atmosphere. The solution was vigorously shaken, and the spectra were then recorded on a Cary 14 spectrophotometer. For spectra recorded at 0 °C, nitrogen was used to purge the cell compartment of the spectrometer to prevent frosting on the wall of the cell.

The charge-transfer complexes of $Hg(i\text{-}Pr)_2$ and $Hg(i\text{-}Bu)_2$ showed only transient existence at room temperature, but their spectra were successfully recorded at −77 °C. Even at this temperature, the complex of $Hg(t\text{-}Bu)_2$ was stable for only a few minutes. The cell used in the determination of charge-transfer spectra at low temperature was previously described.[5a] In general, 1.4 ml of a 1,2-dichloropropane solution of 5.0×10^{-1} M $Hg(i\text{-}Pr)_2$ or $Hg(t\text{-}Bu)_2$ was added to the sample compartment which was sealed with a serum cap (previously purged with nitrogen). Acetone was added to the cooling chamber of the cell and it was partially frozen by the addition of dry ice. The cell contents were allowed to reach thermal equilibrium for 15 min, and the cell was transferred to the spectrophotometer. A solution of 3.5×10^{-2} M TCNE (1 ml) was then added by rapid injection from a syringe (to ensure good mixing) and the spectrum was recorded immediately.

The absorption maxima of the charge-transfer complexes of $Hg(i\text{-}Pr)_2$ and $Hg(t\text{-}Bu)_2$ with TCN could not be determined accurately. In addition to the broadness of the band (characteristic of charge-transfer complexes), the intensity of the absorption bands were very weak even in solutions in which TCNE and HgR_2 were almost saturated. Furthermore, the complexes are not stable even at −77 °C, and interference (overlap) of the charge-transfer bands by absorption due to products formed in subsequent reactions[12] made the determination of the charge-transfer band even more difficult. Therefore, the maxima of these two complexes were determined with an accuracy of ±20 nm.

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Metallointercalation Reagents. Synthesis, Characterization, and Structural Properties of Thiolato(2,2′,2″-terpyridine)platinum(II) Complexes

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Abstract: The synthesis, characterization, and x-ray crystal structure analysis of 2-hydroxyethanethiolato(2,2′,2″-terpyridine)-platinum(II) nitrate, $[Pt(terpy)(SCH_2CH_2OH)]NO_3$, are reported. Solution studies reveal the presence of both monomers and stacked dimers in aqueous media above 10^{-4} M. The red complex crystallizes in the triclinic space group $P\overline{1}$ with two formula units per unit cell of dimensions a = 10.487 (2) Å, b = 10.718 (2) Å, c = 9.131 (2) Å, α = 82.72 (1)°, β = 111.96 (1)°, and γ = 112.53 (1)°. From 3224 unique observed reflections collected on an automated four-circle diffractometer, the structure was solved and refined to final values for the discrepancy indices of R_1 = 0.028, R_2 = 0.033. The platinum in the slightly distorted square planar complex is bound to the three nitrogen atoms of terpyridine and to the sulfur atom of mercaptoethanol with N–Pt–N angles of 80.6 (2) and 80.8 (2)° and N–Pt–S angles of 100.4 (1) and 98.1 (2)°. The Pt–N bond to the middle nitrogen atom of the terpyridine ligand is shorter, 1.968 (5) Å, than those to the other nitrogen atoms, 2.023 (5) and 2.030 (5) Å. The two methylene carbon atoms of the mercaptoethanol ligand are disordered. There is a hydrogen bond between the hydroxyl proton on the mercaptoethanol ligand and an oxygen atom of the nitrate anion. Two types of stacking interactions are seen in the crystal, a direct head-to-tail overlap, and an overlap involving only two of the three aromatic rings of the terpyridine ligand. A comparison is made of the stacking properties of $[Pt(terpy)(SCH_2CH_2OH)]NO_3$ with those of ethidium bromide. Both compounds are known to bind to double stranded DNA by intercalation. The syntheses and preliminary characterization of several related metallointercalation reagents in the class $[Pt(terpy)(SCH_2R)]^{n+}$ are reported.

The use of electron dense metal ions or complexes as probes for elucidating biological structure and function is of great interest.[1-4] We recently found that the heavy metal complex 2-hydroxyethanethiolato(2,2′,2″-terpyridine)-platinum(II), $[Pt(terpy)(HET)]^+$, binds strongly to DNA by intercalation.[5] This metallointercalation reagent is an example of an "addition probe"[1] that facilitates the study of the intercalator–nucleic acid complex.

The intercalation mechanism for binding of planar aromatic dyes to DNA was first suggested by Lerman.[6] He proposed that the flat portion of a dye molecule inserts between adjacent base pairs in the DNA double helix. The base pairs, which remain perpendicular to the helix axis, move apart 3.4 Å to accommodate the intercalator. The DNA–dye intercalation complex is stabilized by hydrophobic, polar, and dipolar interactions, and by the electrostatic forces of the cationic dye with the polyanionic nucleic acid. X-Ray fiber diffraction patterns[6-8] of intercalation complexes of various acridines and ethidium with DNA show loss of regular helical structure, a decrease in the helix diameter, and retention of the 3.4 Å spacing of the base pairs. The strong intercalative binding of many dyes is restricted to one binding site per 2–2.5 base pairs. Cairns[9] measured an approximate 44% lengthening of T2 DNA containing bound proflavine and suggested that only every second site between base pairs is available for intercalation. This nearest "neighbor exclusion" binding model proposes that intercalation of a dye at a given site prevents binding at an adjacent site,[10] giving rise to bound intercalator at every other interbase pair site at saturation. Among the types of drug molecules known to intercalate are antibiotics, antibacterials, trypanocides, antimalarials, schistosomicides, antitumor substances, and mutagens.[11]

Platinum and palladium terpyridine compounds were first synthesized by Morgan and Burstall[12] and later investigated by several workers.[13-15] Initial studies of the binding of $[Pt(terpy)Cl]^+$ to calf thymus DNA revealed covalent interactions with the bases, as well as intercalation.[5] In order to prevent binding to the bases, derivatives of $[Pt(terpy)Cl]^+$ were synthesized by substituting the relatively labile chloride with a sulfur donor ligand. The rate of substitution of the Pt–S bond is expected to be several orders of magnitude slower than the Pt–Cl bond.[16] This approach proved to be satisfactory, and extensive studies of the interaction of 2-hydroxyethanethiolato(2,2′,2″-terpyridine)platinum(II), $[Pt(terpy)(HET)]^+$ (Figure 1), with DNA showed that it binds strongly by intercalation.[5]

The utility of this electron dense metallointercalation reagent was subsequently demonstrated in x-ray fiber diffraction studies of $[Pt(terpy)(HET)]^+$ bound to DNA.[17] The fiber patterns retain the strong 3.4 Å meridional reflection from the stacked base pairs. The equatorial reflections revealed the effective molecular diameter, d_{eff}, to be 24 Å at 92% relative humidity. This value is smaller than that of B-DNA, 25 Å, and is remarkably similar to the d_{eff} of DNA containing bound ethidium bromide, Etd Br, 23.9 Å. In addition, near-meridional reflections appeared on 10.2 and 5.1 Å layer lines. These re-