Electron Transfer with Organometals. Steric Effects as Probes for Outer-Sphere and Inner-Sphere Oxidations of Homoleptic Alkylmetals with Iron(III) and Iridate(IV) Complexes

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Abstract: An outer-sphere mechanism is shown for electron transfer to iron(III) complexes from a variety of substitution-stable alkylmetals, particularly tetraalkyltin compounds. In accord with Marcus theory, the second-order rate constant (log k) is linearly related to the reduction potentials E^0 of a series of substituted trisphenanthroline complexes of iron(III), with a theoretical slope of 8.5. For a given iron(III) oxidant, the ionization potentials I_D of a wide variety of homoleptic alkylmetals of four-coordinate tin and lead as well as two-coordinate mercury are also linearly related to log k over more than 10^8. Electron transfer to iron(III) is not subject to steric effects, and even the highly hindered tetraneopentyltin is included in this correlation. On the other hand, the rates of electron transfer from the same alkylmetals to hexachloroiridate(IV) can be from 10 to 10^5 times faster than those expected on the basis of $E^0_{IrCl_6^{2-}}$ alone. The contribution from an inner-sphere pathway is also indicated by the high susceptibility to steric effects. Thus, a plot of log k for hexachloroiridate(IV) oxidation shows strong, systematic deviations of those tetraalkyltin compounds with α- or β-branched alkyl groups. An inner-sphere mechanism proposed for electron transfer to hexachloroiridate(IV) involves a precursor or activated complex in which the configuration of tetraalkyltin is partially distorted to a quasi-five-coordinate structure. Outer-sphere and inner-sphere processes described in this manner probably represent the extremes of a continuum of mechanisms for electron transfer from alkylmetals. Finally, the products of oxidation are derived by a sequence of fast subsequent steps in which the unstable alkylmetal cation radical undergoes fragmentation, and the resultant alkyl radical is oxidized by a second equivalent of iron(III). Selectivity studies with methylethyltin compounds indicate that electron transfer with iron(III) and iridate(IV) produces structurally related cation radicals which are distinct from those generated in the gas phase by electron impact.

Introduction

The mechanisms of oxidation–reduction of transition-metal complexes have received widespread attention.[1-3] However, the concepts are much less developed in organometallic chemistry despite the fact that many organometals are known to be electron donors. Indeed, the alkyl group is an excellent σ-donor ligand.[4,5] Consequently, the ionization potential of a given alkylmetal is always lower than that of most other metal derivatives (e.g., tetramethyllead is a reducing agent whereas tetrachlorolead is an oxidant). This property of alkyl ligands confers upon organometals RM a unique role as electron donors in their facile *charge transfer* interactions with many types of organic and inorganic electrophiles, E, i.e.,[5,6]

$$RM + E \underset{}{\overset{K_{CT}}{\rightleftharpoons}} [RM\ E] \xrightarrow{k_{et}} [RM^+\ E^-], \text{ etc.} \tag{1}$$
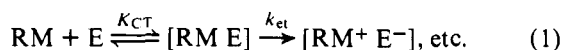
In a similar vein, a number of alkylmetals readily undergo *electron transfer* with the familiar outer-sphere oxidant, hexachloroiridate(IV).[7-9]

$$RM + IrCl_6^{2-} \xrightarrow{k} RM^+ + IrCl_6^{3-} \tag{2}$$
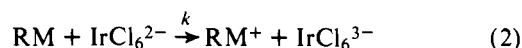
For alkylmetals derived from the main-group elements (e.g., M = Sn, Pb, Hg, etc.), electron transfer as described in eq 1 and 2 differs from that usually encountered with other metal complexes since the electron is lost from a carbon–metal *bonding* orbital (HOMO).[10] Indeed, the second-order rate constants (log k) in eq 2 are found to be linearly related to the ionization potentials of RM for a series of four-coordinate methylethyllead ($Me_{4-n}Et_nPb$) and two-coordinate methylalkylmercury (MeHgR).[8] However, the correlation breaks down when it is extended to higher and more branched alkyl homologues, suggesting that steric effects must be taken into account in these apparently outer-sphere processes. The latter is perhaps understandable if one considers that electron transfer from alkylmetals, particularly those with tetrahedral

configurations, must occur through a lipophilic sheath enveloping the metal center.

The question thus arises as to whether alkylmetals can participate as electron donors in outer-sphere processes. If so, how bulky can the alkyl ligands be, and what are the limits of the ionization potentials which can be spanned? To probe these points we examined the iron(III) oxidation of an extensive series of alkylmetals of the group 4A elements and mercury. We focused our attention on the oxidation of organotin compounds as described in the equation

$$R_4Sn + FeL_3^{3+} \xrightarrow{k} R_4Sn^+ + FeL_3^{2+} \tag{3}$$
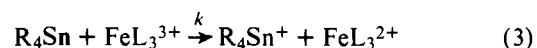
since they are tetrahedral and occupy an intermediate position, both with regard to reactivity as well as metal size. Furthermore, as oxidants the iron(III) complexes of L = 2,2'-bipyridine and various substituted 1,10-phenanthrolines are only known to react by outer-sphere mechanisms,[11] and the accessibility of a variety of substituted phenanthrolines allows the systematic variation in the standard reduction potentials E^0 of these iron(III) complexes with prescribed structural changes.[12]

The theoretical basis for outer-sphere electron transfer processes is well provided by the Marcus theory,[13] which has been successfully applied to many wholly inorganic systems.[14] According to Marcus, the activation barrier to electron transfer can be represented by

$$\Delta G^{\ddagger} = \frac{\Delta G^0}{2} + \frac{\lambda}{4} + \omega \tag{4}$$

where ΔG^0 is the free-energy change within the ion pair upon electron transfer and proportional to the difference in standard reduction potentials of the reactants (i.e., $E^0_{RM} - E^0_{Fe(III)}$). In the activated complex, the effective radii of the reactants are included both in the reorganizational parameter λ, as well as in the work term ω, which is the energy required to bring them together. If electron transfer in eq 3 proceeds via an

Table I. Ionization Potentials of Homoleptic Alkylmetals[a]

	R₄Sn			Tin[15] RSnMe₃			R₂SnMe₂	
3	Me	(9.69)	3	Me	(9.69)	3	Me	(9.69)
6	Et	(8.93)	4	Et	(9.1)	5	Et	(9.06)
7	n-Pr	(8.82)	13	n-Pr	(9.1)	20	n-Pr	(8.8)
8	i-Pr	(8.46)	14	i-Pr	(8.9)	17	i-Pr	(8.56)
9	n-Bu	(8.76)	15	n-Bu		21	n-Bu	(8.8)
10	sec-Bu	(8.45)	16	t-Bu	(8.6)	19	i-Bu	
11	i-Bu	(8.68)				18	t-Bu	(8.22)
12	neo-Pent	(8.67)						

|	R₄Pb			RPbR₃′			R₂PbMe₂	
				Lead[9a]				
22	Me	(8.90)	23	Et Me₃	(8.65)	24	Et	(8.45)
26	Et	(8.13)	25	Me Et₃	(8.26)			
				Silicon and Germanium[16]				
1	Et₄Si	(9.78)	2	Et₄Ge	(9.41)			
				Mercury[9b]				
27	Me₂Hg	(9.33)	28	EtHgMe	(8.84)			
29	Et₂Hg	(8.45)	30	i-PrHgMe	(8.47)			
31	i-Pr₂Hg	(8.03)	32	t-BuHg- Me	(8.32)			

[a] Ionization potentials in parentheses given in eV, references as superscripts.

outer-sphere mechanism, we expect the second-order rate constant (log k) for a series of iron(III) complexes with a given alkyltin to be linearly related to $E^0_{Fe(III)}$. Similarly, log k for a series of alkyltin compounds with a particular iron(III) complex should be proportional to $E^0_{R_4Sn}$, independent of the steric bulk of the alkyl groups. We wish to show how the latter provides the basis for describing outer-sphere mechanisms for a variety of other homoleptic organometals.

Results

Three series of symmetrical and unsymmetrical tetraalkyltin compounds were examined in this study, viz., R₄Sn, RSnMe₃, and R₂SnMe₂. Each alkyltin compound is identified in Table I with a boldface numeral. In addition, a selected number of alkylmetals derived from silicon, germanium, lead, and mercury are also included in the table.

Ionization Potentials of Alkylmetals. The ionization potentials I_D of the various alkylmetals in the gas phase are listed in Table I.

$$R_4M \rightarrow R_4M^+ + \epsilon \tag{5}$$
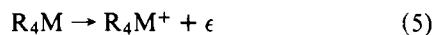
Attempts to measure the reversible oxidation potentials E^0 by cyclic voltammetry were unsuccessful since the voltammograms were irreversible even at scan rates as high as 10 V s⁻¹ and temperatures as low as −35 °C in acetonitrile solutions. In this study we wish to utilize the linear relationship observed between the ionization potential I_D and half-wave potentials $E_{1/2}$ for similarly constituted reducing agents.[17] In an analogous manner, eq 6 which relates E^0 and I_D can be obtained from the theoretical relationship between $E_{1/2}$ and the highest occupied molecular orbital of the donor RM.[18]

$$I_D + \Delta E_{solv} \propto E^0 + \frac{T\sum \Delta S_i^0}{F} + \frac{RT}{F} \ln \frac{\gamma_{RM^+}D_{RM}}{\gamma_{RM}D_{RM^+}} \tag{6}$$

ΔE_{solv} is the difference in the heats of solvation of RM⁺ and RM; $\sum \Delta S_i^0$ is the sum of the entropy changes of solvation during electron transfer; F is the Faraday constant; γ_i and D_i are the activity coefficients and diffusion constants, respectively. For reactions involving a series of analogous complexes, it is expected that terms containing ΔS^0, γ, and D would be

Table II. Cyclic Voltammetry of Iron(III) Complexes in Acetonitrile

FeL₃(ClO₄)₃ L	E^0, V vs. SHE	i_c/i_a[a]	Δ,[b] mV
4,7-diphenyl-1,10-phenanthroline	1.15₅ ± 0.001	1.01	65
2,2′-bipyridine	1.21₂ ± 0.003	1.02	70
1,10-phenanthroline	1.22₀ ± 0.001	1.00	68
5-chloro-1,10-phenanthroline	1.31₇ ± 0.001	1.01	67
5-nitro-1,10-phenanthroline	1.41₇ ± 0.006	1.02	72
Other Oxidants			
[Fe(phen)₂(CN)₂][ClO₄]	0.63₁ ± 0.001	1.01	70
ferrocenium	0.55₆[c]	1.00	65
hexachloroiridate(IV)	0.67 ± 0.01[d]		

[a] Ratio of the peak currents for the cathodic (i_c) and anodic (i_a) waves. [b] Separation of anodic and cathodic peaks at 50 mV s⁻¹ scan rate. [c] Calibrant, from ref 19. [d] Measured by the equilibrium method relative to Fe(phen)₂(CN)₂ClO₄ as described in the Experimental Section.

small relative to I_D and ΔE_{solv}, i.e.

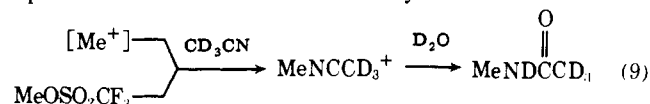$$I_D + \Delta E_{solv} = \alpha E^0 + \text{constant} \tag{7}$$

Reduction Potentials of Iron(III) Complexes. The reduction potentials of low-spin tris-2,2′-bipyridine and 1,10-phenanthroline complexes of iron(III) perchlorate were measured in acetonitrile solutions by cyclic voltammetry. All the iron(III,II) redox couples were completely reversible in this medium as indicated by the separation of the cathodic and anodic peaks and the same magnitudes of their peak currents as listed in Table II. The values are calibrated relative to ferrocene which is well behaved in this medium.[19]

Products and Stoichiometry for the Oxidative Cleavage of Tetraalkyltin by Iron(III) Complexes. The organic and the tin products of the reaction were identified and analyzed quantitatively by NMR spectroscopy and gas–liquid chromatography. The reduced iron(II) products were determined spectrophotometrically as described in the Experimental Section. Spectral titration with excess Fe(bpy)₃³⁺, Fe(phen)₃³⁺, or Fe(Ph₂phen)₃³⁺ in the absence of air indicated a stoichiometric requirement of 2Fe(III) for each mol of alkylmetal (see Experimental Section). The presence of oxygen lowered the usage of iron(III) (vide infra). On the other hand, the higher Fe(III) requirements shown by the chloro- and nitrophenanthroline complexes are probably due to further oxidation of the products, consistent with the higher electrode potentials of these complexes.

The oxidation of tetramethyltin by tris(phenanthroline)-iron(III) produced trimethyltin perchlorate quantitatively according to the stoichiometry

$$Me_4Sn + 2Fe(phen)_3(ClO_4)_3 \xrightarrow{CH_3CN} Me_3Sn(ClO_4)$$
$$+ [Me^+]ClO_4 + 2Fe(phen)_3(ClO_4)_2 \tag{8}$$
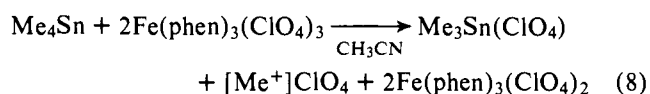
Trimethyltin perchlorate was identified by its proton NMR spectrum showing a sharp singlet at δ 0.67 ppm, which upon the addition of 1 M lithium chloride was completely shifted to δ 1.20, assigned to trimethyltin chloride by comparison with that of an authentic sample. The cleaved methyl group, designated as [Me⁺] in eq 8, was quantitatively identified as *N*-methylacetamide after hydrolysis. The methylnitrilium ion is the immediate precursor to the latter, since its ¹H NMR spectrum can be observed in rigorously anhydrous CD₃CN and corresponds to that obtained independently from the solvolysis[22] of methyl trifluoromethanesulfonate in this medium, e.g., eq 9. The same reaction with tetraethyltin afforded the anal-

$$[Me^+] \begin{array}{c} \\ \end{array} \xrightarrow{CD_3CN} MeNCCD_3^+ \xrightarrow{D_2O} MeN\overset{\overset{\displaystyle O}{\parallel}}{D}CCD_3 \tag{9}$$
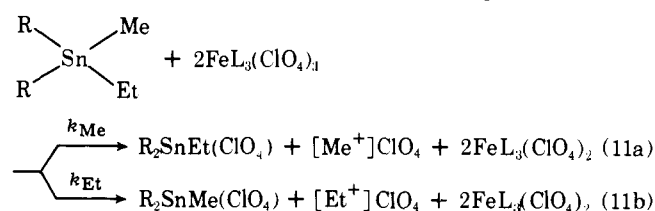$$MeOSO_2CF_3$$

ogous product triethyltin perchlorate in quantitative yields. Furthermore, the oxidized ethyl group was observed as the ethylnitrilium ion, $EtNCCD_3^+$, and N-ethylacetamide, as described in more detail in the Experimental Section.

Kinetics of Oxidative Cleavage of Tetraalkyltin by Iron(III) Complexes. The rates of oxidative cleavage of tetraalkyltin were followed spectrophotometrically at 25 °C in acetonitrile solutions by the appearance of the iron(II) bands, using either a conventional (Cary) or a stopped flow (Durrum-Gibson) spectrophotometer. The degassed solutions were maintained at constant ionic strength with either lithium or tetraethylammonium perchlorate. The reactions obeyed second-order kinetics, being first-order in each reactant.

$$- \frac{d[FeL_3^{3+}]}{dt} = 2k[R_4Sn][FeL_3^{3+}] \qquad (10)$$

The kinetic experiments were carried out with either the iron-(III) complex or the alkylmetal in excess to approximate pseudo-first-order conditions for at least 2.5 half-lives. The second-order rate constants under both circumstances were the same. The rates were unaffected by changes in ionic strength from 0.01 to 0.1, and by the addition of the iron(II) complex in an equimolar amount. The second-order rate constants listed in Table III were carried out in at least duplicate.

Selectivity Studies in the Oxidative Cleavage of Methylethyltin Compounds. Selectivity in the oxidation of alkyltin compounds is represented by the products of cleavage, as illustrated for methylethyltin compounds in eq 11 (where R =

$$\begin{array}{c} R \\ \diagdown \\ Sn \\ \diagup \quad \diagdown \\ R \qquad Et \end{array} \begin{array}{c} Me \end{array} + \ 2FeL_3(ClO_4)_3$$

$$\xrightarrow{k_{Me}} R_2SnEt(ClO_4) + [Me^+]ClO_4 + 2FeL_3(ClO_4)_2 \quad (11a)$$

$$\xrightarrow{k_{Et}} R_2SnMe(ClO_4) + [Et^+]ClO_4 + 2FeL_3(ClO_4)_2 \quad (11b)$$

Me, Et). The selectivity $[S(Et/Me)]$ represents the ratio of rate constants k_{Et}/k_{Me}, and it is obtained directly from the analysis of the alkyltin perchlorates as products described in the Experimental Section. The same result was obtained from the quantitative analysis of the alkyl products, viz., alkylnitrilium ions and/or amides.

The ethyl/methyl selectivities shown in Table IV were obtained by reacting either Me_2Et_2Sn or Me_3EtSn with 2 equiv of $Fe(phen)_3^{3+}$. The normalized values of $S(Et/Me) = 27 \pm 2$ are the same for both methylethyltin compounds. Interestingly, this selectivity is slightly higher than that (11 ± 2) obtained with $IrCl_6^{2-}$.

Mass Spectral Cracking Patterns of Methylethyltin Compounds. The examination of the mass spectral cracking patterns of methylethyltin compounds was undertaken to obtain information on the relative bond dissociation processes involving Me and Et to Sn scissions. In these intramolecular processes, the competitive rates of methyl and ethyl cleavage can be obtained from the relative intensities of the peaks for P − Me and P − Et (i.e., the parent molecular ion minus Me and Et, respectively).

The relative abundances of P − Me and P − Et are relatively constant over the range of instrumental readings of electron energies employed as shown in Figure 1. From the ratios of the intensities of the peaks corresponding to these trialkyltin cations (including normalization), we conclude that fragmentation in eq 12b is approximately eight to ten times greater than that in eq 12a.
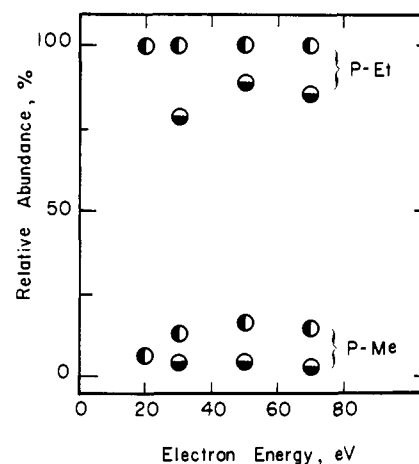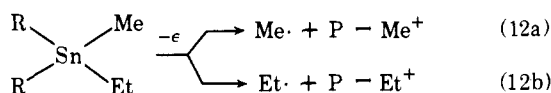
$$\begin{array}{c} R \\ \diagdown \\ Sn \\ \diagup \quad \diagdown \\ R \qquad Et \end{array} \begin{array}{c} Me \end{array} \xrightarrow{-e} \begin{array}{c} \longrightarrow Me\cdot + P - Me^+ \quad (12a) \\ \\ \longrightarrow Et\cdot + P - Et^+ \quad (12b) \end{array}$$

Figure 1. Mass spectral cracking patterns of (○) Me_2Et_2Sn and (◑) Me_3EtSn showing the P − Et and P − Me fragment ions at various ionizing energies (nominal).
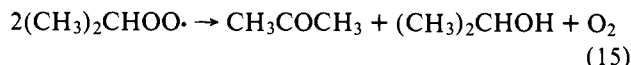
Paramagnetic Species as Intermediates. 1. Spin Trapping of Alkyl Radicals. To establish alkyl radicals as intermediates in the oxidative cleavage of alkylmetals, nitroso-*tert*-butane was added as a spin trap as described in the Experimental Section. No ESR signal was detected unless $Fe(bpy)_3(ClO_4)_3$, Et_4Pb, and nitroso-*tert*-butane were all three present simultaneously. The spectrum centered at $g = 2.0058$ showed hyperfine splittings ($a_N = 16.38$ G, $a_{\beta H} = 10.56$ G, and $a_{\gamma H} = 0.35$ G) characteristic of the ethyl adduct.[9a] No other paramagnetic species was observed.

2. Molecular Oxygen as a Scavenger for Alkyl Radicals. The oxidative cleavage of tetraisopropyltin with $Fe(phen)_3^{3+}$ was carried out in acetonitrile solutions at 25 °C under 2 atm pressure of oxygen. Analysis of the reaction mixture by gas chromatography showed that acetone and isopropyl alcohol were produced in equimolar amounts. The yields of acetone and isopropyl alcohol in Table V are based on the partial stoichiometry in the equation

$$2i\text{-}Pr_4Sn + 2Fe^{III} \xrightarrow{O_2} CH_3COCH_3$$

$$+ (CH_3)_2CHOH + 2[i\text{-}Pr_3Sn^+] + 2Fe^{II} \quad (13)$$
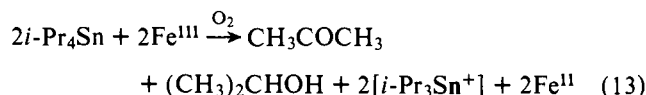
No acetone or isopropyl alcohol could be detected when the same reaction was carried out in argon in the absence of oxygen.

Isopropyl radicals are known to react with molecular oxygen at diffusion-controlled rates to produce an equimolar mixture of acetone and isopropyl alcohol.[24]

$$(CH_3)_2CH\cdot + O_2 \rightarrow (CH_3)_2CHOO\cdot \quad (14)$$

$$2(CH_3)_2CHOO\cdot \rightarrow CH_3COCH_3 + (CH_3)_2CHOH + O_2 \quad (15)$$

Oxidative Cleavage of Tetraalkyltin by Hexachloroiridate(IV). The tetraalkyltin compounds listed in Table I react readily with hexachloroiridate(IV) at 25 °C in acetonitrile solutions. Methyl chloride is formed from tetramethyltin and hexachloroiridate(IV) in acetonitrile solutions according to the stoichiometry[25]

$$Me_4Sn + 2IrCl_6^{2-} \underset{S}{\rightarrow} MeCl + Me_3Sn^+$$

$$+ IrCl_6^{3-} + IrCl_5(S)^{2-} \quad (16)$$
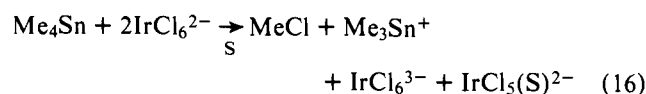
The kinetics of the oxidative cleavage showed a first-order dependence on tetraalkyltin and hexachloroiridate(IV).

$$- \frac{d[IrCl_6^{2-}]}{dt} = 2k[R_4Sn][IrCl_6^{2-}] \quad (17)$$

Table III. Kinetics of Electron Transfer from Homoleptic Alkylmetals to Iron(III) and Iridate(IV) Complexes[a]

no.	R_nM	$k_{Fe(4,7\text{-}di\text{-}Ph\text{-}phen)_3{}^{3+}}$	$k_{Fe(bpy)_3{}^{3+}}$	$k_{Fe(phen)_3{}^{3+}}$	$k_{Fe(5\text{-}Cl\text{-}phen)_3{}^{3+}}$	$k_{Fe(5\text{-}NO_2\text{-}phen)_3{}^{3+}}$	$k_{IrCl_6{}^{2-}}$
1	Et_4Si	1.66×10^{-4} (−3.78)		3.25×10^{-4} (−3.49)	3.57×10^{-3} (−2.45)	4.91×10^{-2} (−1.31)	5.16×10^{-5} (−4.29)
2	Et_4Ge			2.82×10^{-2} (−1.55)	0.311 (−0.508)	3.62 (0.559)	1.35×10^{-4} (−3.87)
3	Me_4Sn		5.15×10^{-4} (−3.29)	1.54×10^{-3} (−2.81)	1.72×10^{-2} (−1.76)	0.256 (−0.592)	
4	$EtMe_3Sn$						
5	Et_2Me_2Sn	1.23 (0.090)	2.24 (0.35)	5.68 (0.754)	48.3 (1.68)	449 (2.65)	6.9×10^{-4} (−3.16)
6	Et_4Sn	3.45 (0.538)	5.17 (0.71)	13.2 (1.12)	99.5 (2.00)	774 (2.89)	6.25×10^{-4} (−3.20)
7	$n\text{-}Pr_4Sn$	10.7 (1.03)	19.3 (1.28)	46.1 (1.66)	290 (2.46)	3.2×10^3 (3.5)	4.62×10^{-4} (−3.34)
8	$i\text{-}Pr_4Sn$						9.9×10^{-4} (−3.0)
9	$n\text{-}Bu_4Sn$						3.2×10^{-3} (−2.5)
10	$sec\text{-}Bu_4Sn$	867 (2.94)	1.15×10^3 (3.06)	4.50×10^3 (3.65)	3.52×10^4 (4.55)	1.62×10^5 (5.21)	5.89×10^{-4} (−3.23)
11	$i\text{-}Bu_4Sn$	43.0 (1.63)	79.3 (1.90)	257 (2.41)	1.58×10^3 (3.20)	9.22×10^3 (3.96)	1.40×10^{-4} (−3.86)
12	$neo\text{-}Pent_4Sn$	52.4 (1.72)	111 (2.04)	353 (2.55)	2.66×10^3 (3.42)	1.78×10^4 (4.25)	
13	$n\text{-}PrMe_3Sn$						5.3×10^{-5} (−4.28)
14	$i\text{-}PrMe_3Sn$						6.5×10^{-3} (−2.19)
15	$n\text{-}BuMe_3Sn$						3.0×10^{-5} (−4.52)
16	$t\text{-}BuMe_3Sn$			7.6×10^2 (2.88)			7.8×10^{-2} (−1.11)
17	$i\text{-}Pr_2Me_2Sn$						6.4×10^{-3} (−2.19)
18	$t\text{-}Bu_2Me_2Sn$			7.8×10^4 (4.89)			9.4×10^{-4} (−3.02)
19	$i\text{-}Bu_2Et_2Sn$						1.6×10^{-4} (−3.8)
20	$n\text{-}Pr_2Me_2Sn$						1.3×10^{-3} (−2.89)
21	$n\text{-}Bu_2Me_2Sn$						3.6×10^{-4} (−3.4)
22	Me_4Pb	5.06 (0.704)	9.09 (0.96)	25.5 (1.41)	166 (2.22)	1.49×10^3 (3.17)	0.02 (−1.70)
23	$EtMe_3Pb$						0.57 (−0.24)
24	Et_2Me_2Pb	566 (2.75)	1.41×10^3 (3.15)	3.53×10^3 (3.55)	2.76×10^4 (4.44)	1.96×10^5 (5.29)	3.3 (0.52)
25	Et_3MePb						1.1 (1.04)
26	Et_4Pb	1.19×10^4 (4.07)	3.19×10^4 (4.50)	1.07×10^5 (5.03)	9.3×10^5 (5.97)		25 (1.40)
27	Me_2Hg						
28	$EtMeHg$	20.1 (1.30)	43.5 (1.64)	115 (2.06)	1.11×10^3 (3.04)	7.4×10^3 (3.87)	
29	Et_2Hg	2.31×10^3 (3.36)	4.13×10^3 (3.62)	1.10×10^4 (4.04)	8.1×10^4 (4.91)	5.05×10^5 (5.70)	

[a] Second-order rate constants listed as $M^{-1} s^{-1}$ at 25 °C; log k in parentheses.

The second-order rate constants at 25 °C are listed in Table III.

Discussion

The ease of oxidative cleavage of tetraalkyltin by iron(III) complexes is highly dependent on the donor properties of the alkyl groups as measured by the ionization potentials. Thus, in the homologous series of symmetrical tetraalkyltin compounds R_4Sn, the rates progressively increase with α-methyl substitut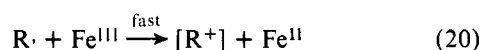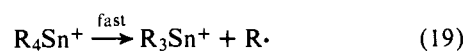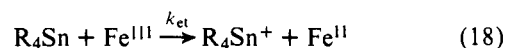ion from R = methyl < ethyl < isopropyl, roughly in the order of $10^0:10^4:10^7$. This trend, reflecting an *inverse* steric effect, is counter to any expectation based on a direct bimolecular scission, and it suggests that the activation process does not involve cleavage of the alkyl–tin bond itself. Instead, we propose that electron transfer occurs in a prior, rate-limiting step during oxidative cleavage of organometals. This formulation is in basic accord with the well-established property of tris(phenanthroline) and related iron(III) cations to function as oxidants in many inorganic systems.[11] According to the general mechanism presented in Scheme I, the activation

Table IV. Selectivity Studies in the Oxidative Cleavage of Methylethyltin Compounds by Fe(phen)$_3^{3+}$ and IrCl$_6^{2-}$ [a]

alkyltin (M)	oxidant	S(Et/Me)[b]
	Me$_2$Et$_2$Sn	
3.8×10^{-2}	Fe(phen)$_3$(ClO$_4$)$_3$	26
4.3×10^{-2}	Fe(phen)$_3$(ClO$_4$)$_3$	27
5.8×10^{-2}	Fe(phen)$_3$(ClO$_4$)$_3$	29
5.3×10^{-2}	Na$_2$IrCl$_6$	10 (12)[c]
6.1×10^{-2}	Na$_2$IrCl$_6$	11 (11)
6.2×10^{-2}	Na$_2$IrCl$_6$	10 (11)[d]
	Me$_3$EtSn	
5.1×10^{-2}	Fe(phen)$_3$(ClO$_4$)$_3$	25
5.7×10^{-2}	Fe(phen)$_3$(ClO$_4$)$_3$	26
6.3×10^{-2}	Fe(phen)$_3$(ClO$_4$)$_3$	25
5.4×10^{-2}	Na$_2$IrCl$_6$	10 (10)
5.9×10^{-2}	Na$_2$IrCl$_6$	12 (10)[c]
6.1×10^{-2}	Na$_2$IrCl$_6$	11 (12)[d]
	MeEt$_3$Sn	
0.10	Na$_2$IrCl$_6$	−(10)[c]
7.0×10^{-2}	Na$_2$IrCl$_6$	−(11)[d]

[a] In acetonitrile solutions at 25 °C with 2 equiv of oxidant. [b] Selectivity (±4) is statistically corrected in Me$_3$EtSn and MeEt$_3$Sn. Numbers in parentheses refer to selectivities (±3) determined from the analysis of MeCl and EtCl. [c] 0.10 M and [d] 7.0 × 10^{-2} M tetraalkyltin.

process for oxidative cleavage is represented by the electron transfer step 18, which is rapidly followed by homolytic fragmentation of the alkyltin cation radical [*formally* an alkyltin(V) species] in eq 19, and further oxidation of the alkyl radical by a second Fe(III) in eq 20.

Scheme I

$$R_4Sn + Fe^{III} \xrightarrow{k_{et}} R_4Sn^+ + Fe^{II} \qquad (18)$$

$$R_4Sn^+ \xrightarrow{fast} R_3Sn^+ + R\cdot \qquad (19)$$

$$R\cdot + Fe^{III} \xrightarrow{fast} [R^+] + Fe^{II} \qquad (20)$$

The mechanism in Scheme I accords with all the observations we have made in this system, including (1) the stoichiometry, energetics, and kinetics of the electron transfer step, (2) the observation of alkyl radicals during oxidative cleavage, and (3) the selectivity observed in the oxidative cleavage of methylethyltin compounds. Each of these will be described more fully in the following discussion.

1. Electron Transfer as the Rate-Determining Step. The second-order kinetics for cleavage in eq 10 indicate that alkyltin and only one iron(III) are represented in the rate-determining transition state. The other iron(III) required by the stoichiometry must be involved in a fast subsequent step (vide infra). For an electron transfer process to occur between alkyltin and iron(III), the second-order rate constant k_{et} in eq 18 should reflect the ease of electron detachment from alkyltin, as measured independently by the ionization potential in eq 5. Indeed, Figure 2 shows the smooth correlation between the vertical ionization potentials of a series of alkyltin compounds and the log k_{et} for oxidative cleavage. The linearity observed for each of the three oxidants, viz., tris(2,2'-bipyridine), 1,10-phenanthroline, and 5-chloro-1,10-phenanthrolineiron-(III), spans a range of more than 10^8 in rates.

The electron transfer between alkyltin and iron(III) in eq 18 is essentially irreversible since the rate of oxidative cleavage is unaffected by the added iron(II) product. The irreversibility derives in part from the metastable nature of the tetraalkyltin cation radical (vide infra). Indeed, our inability to observe the
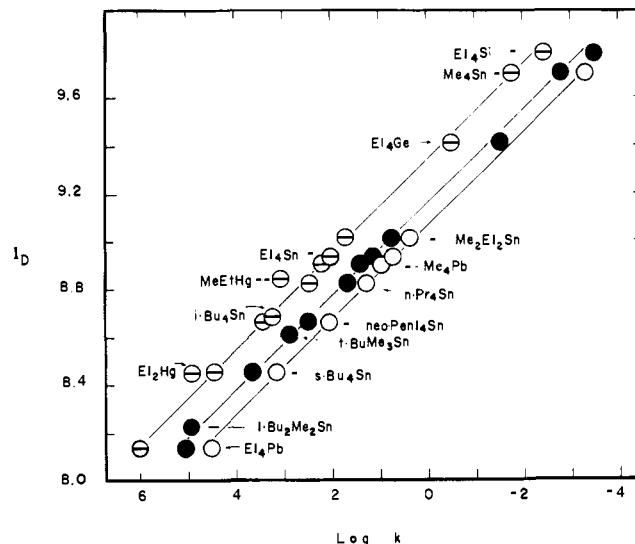

Figure 2. Correlation of the rates (log k) of electron transfer with the ionization potentials I_D for a series of alkylmetals as indicated, using (⊖) tris-5-chloro-1,10-phenanthrolineiron(III), (●) tris-1,10-phenanthrolineiron(III), and (○) tris-2,2-bipyridineiron(III) as oxidants.

Table V. Oxygen Scavenging of Isopropyl Radicals from Tetraisopropyltin and Iron(III)[a]

| i-Pr$_4$Sn, mmol	Fe(phen)$_3^{3+}$ mequiv	CH$_3$COCH$_3$, mmol (%)[b]	(CH$_3$)$_2$CHOH, mmol (%)[b]
1.0×10^{-2}	1.0×10^{-2}	2.1×10^{-3} (21)	1.9×10^{-3} (19)
1.0×10^{-2}	1.4×10^{-2}	2.8×10^{-3} (20)	2.9×10^{-3} (21)
8.0×10^{-3}	6.0×10^{-3}	1.7×10^{-3} (28)	1.6×10^{-3} (27)

[a] In 3 mL of CH$_3$CN at 25 °C with 2 atm of O$_2$. [b] Yields in parentheses based on the stoichiometry in eq 13.

ESR spectrum of the alkyltin cation radical and the irreversibility of the cyclic voltammetry indicate that its lifetime is very short. Analogous cation radicals derived from tetraalkyllead, dialkylmercury, and dialkylbis(phosphine)platinum are also unstable.[8]

2. Alkyl Radicals as Prime Intermediates—Oxidation by Iron(III). The observation of paramagnetic intermediates by spin trapping indicates that alkyl radicals are formed during the oxidative cleavage of alkyltin by iron(III). Furthermore, the scavenging of the alkyl fragments in the presence of molecular oxygen as alkylperoxy products show that they must depart from tin as the alkyl radicals indicated in eq 19. Accordingly, the oxidation of alkyl radicals in excellent yields implies that iron(III) is an efficient scavenger in eq 20. Indeed, the absence of alkane indicates that hydrogen abstraction from solvent is unable to compete with oxidation (eq 20 and 21) even

$$R\cdot \begin{cases} \xrightarrow{Fe^{III}} [R^+] + Fe^{II} & (20) \\ \xrightarrow{CH_3CN} RH + \cdot CH_2CN & (21) \end{cases}$$
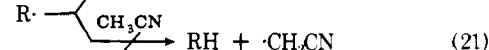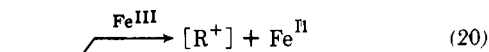
when oxidative cleavage is carried out with a stoichiometrically limited supply of iron(III), i.e., in the presence of excess alkyltin. Moreover, our inability to scavenge all the isopropyl radicals from the oxidative cleavage of i-Pr$_4$Sn in the presence of excess oxygen (eq 20 and 22) suggests that the oxidation by

$$R\cdot \begin{cases} \xrightarrow{Fe^{III}} [R^+] + Fe^{II} & (20) \\ \xrightarrow{O_2} ROO\cdot & (22) \end{cases}$$
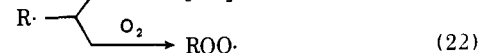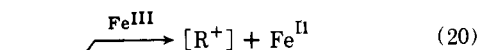
iron(III) may approach the diffusion-controlled rates known for eq 22.[24] This conclusion is consistent with the second-order

rate constant $k \geqslant 4 \times 10^8$ M^{-1} s^{-1} estimated by Walling and Johnson[26] for the oxidation of hydroxymethyl radical by Fe_{aq}^{3+}, which is a significantly weaker oxidant ($E^0 = 0.77$ V) than $Fe(phen)_3^{3+}$ ($E^0 = 1.22$ V) in water.[27] Significantly, the facile oxidations associated with these paramagnetic iron(III) complexes are reminiscent of similar high rates of interaction of alkyl radicals with various copper(II), iridium(IV), and chromium(II) complexes.[9c,28]
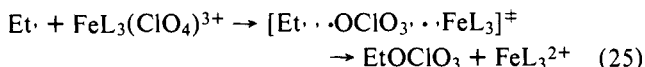
Oxidation of alkyl radicals by iron(III) can be an outer-sphere process, i.e.

$$R\cdot + FeL_3^{3+} \rightarrow R^+ + FeL_3^{2+} \qquad (23)$$
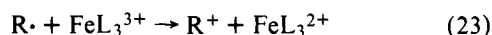
although an inner-sphere mechanism involving an alkyliron-(IV) intermediate

$$R\cdot + FeL_3^{3+} \rightarrow RFeL_3^{3+} \qquad (24)$$

is possible. The alternative, inner-sphere process involving perchlorate as a bridging ligand, i.e.

$$Et\cdot + FeL_3(ClO_4)^{3+} \rightarrow [Et\cdot\cdot\cdot OClO_3\cdot\cdot\cdot FeL_3]^{\ddagger}$$
$$\rightarrow EtOClO_3 + FeL_3^{2+} \qquad (25)$$

is unlikely owing to its limited ability to ligate,[29] coupled with the coordinative saturation of the iron center.

The distinction between the mechanisms in eq 23 and 24 lies in whether an alkylnitrilium ion is the initial product or whether it is derived subsequently from the solvolysis of an alkyl perchlorate. Thus, an alkyliron(IV) intermediate is expected to solvolyze rather than react with perchlorate (which is less nucleophilic than acetonitrile).

$$EtFeL_3^+ \quad \begin{array}{c} \xrightarrow{\ CD_3CN\ } CD_3CNEt^+ + FeL_3^{2+} \qquad (26) \\ \xrightarrow{\ ClO_4^-\ } Et(ClO_4) + FeL_3^{2+} \qquad (27) \end{array}$$
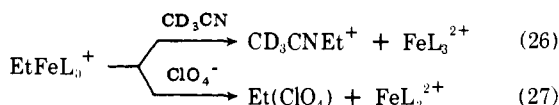
At this juncture we are unable to distinguish the outer-sphere and inner-sphere processes for the oxidation of alkyl radicals by iron(III) owing to the enhanced solvolytic reactivity of alkyl perchlorates in this medium.

The possibility of simple alkyl cations as actual intermediates in the oxidation of alkyl radicals by iron(III) under these mild, neutral conditions raises a number of interesting possibilities to be explored, since these species have hitherto only been observed in highly acidic media.[30] However, the postulation of an outer-sphere mechanism for the oxidation of alkyl radicals by iron(III) is not without its attendant difficulties. For example, the ionization potential of methyl radical is 9.84 eV,[31] and, even if a high solvation energy for the methyl cation is taken into account, it is unlikely to be of sufficient magnitude as to render a reasonable driving force for the process in eq 20 (R = CH_3). Clearly this problem merits further study.[32]
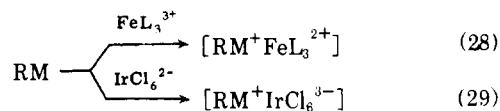
3. Selectivity during Fragmentation of Alkyltin Cation Radicals. Selectivity in the cleavage of alkyl groups from unsymmetrical alkyltin compounds by iron(III), according to Scheme I, occurs subsequent to the rate-determining electron transfer. During fragmentation of the cation radical in eq 19, the preference for ethyl cleavage indicated by $S(Et/Me) = 27$ and 11 for FeL_3^{3+} and $IrCl_6^{2-}$, respectively in the mixed methylethyltin compounds in Table IV, is roughly the same as that previously observed[9a] in the related oxidative cleavage of methylethyllead compounds by $IrCl_6^{2-}$ with $S(Et/Me) = 25$. Similar selectivities are observed in the mass spectral cracking patterns of methylethyltin compounds in Figure 1, although reduced in magnitude. The latter doubtlessly reflects the loss in selectivity of highly energetic species formed by electron impact relative to those cation radicals formed in solution.[33] The effect of solvation cannot be assessed quantitatively, but the qualitative trends in selectivity, both in solution and in the gas phase, are unmistakable. The prevailing factor

which determines the predominance of ethyl over methyl cleavage is the strength of the relevant alkyl–metal bonds. These values can be evaluated from the mean bond energies for Et_4Sn and Me_4Sn, which are 46 and 54 kcal mol^{-1}, respectively, and for Et_4Pb and Me_4Pb, which are 33 and 40 kcal mol^{-1}, respectively.[34]

It is noteworthy that all of these *unimolecular* selectivities are inverted relative to those observed in other *bimolecular* processes. For example, the electrophilic cleavage of methylethyllead compounds by acid [$S(Et/Me) = 0.11$ and 0.021 for HOAc and H_2OAc^+, respectively] and metal ions [$S(Et/Me) = 0.018$ and 0.022 for CuOAc and $CuCl_2$, respectively] all involve the direct scission of the alkyl–metal bond by the electrophile.[35] As such, the inverted order in selectivity in each of these processes (i.e., methyl cleaved in preference to ethyl) reflects the dominance of steric constraints over electronic effects in bimolecular transition states.[36]

Indeed, differences in selectivity patterns provide one of the best diagnostic methods for distinguishing electrophilic (two-equivalent) from electron transfer (one-equivalent) mechanisms for the cleavage of alkylmetals.[4,9c,37] More relevant to the issue here, the similar patterns of selectivity observed for the oxidative cleavage of methylethyltin compounds induced by FeL_3^{3+} and by $IrCl_6^{2-}$ are only consistent with the cation radical as the common intermediate leading directly to cleavage.

Mechanisms of Electron Transfer from Alkylmetals. It is conceivable that the cation radical $R_4Sn^{+\cdot}$ formed in eq 18 is not free, and the degree to which it is still associated with the reduced iron(II) species would affect its subsequent reactivity. In order to evaluate this problem, we first consider whether the electron-transfer step itself conforms to the Marcus criterion for an outer-sphere mechanism. We next compare the oxidation of an alkylmetal RM by iron(III) with that effected by hexachloroiridate(IV) (eq 28 and 29). Such a comparison also focuses on the ion-pairing energies, since the electrostatic potential in the ion pair derived from iron(III) in eq 28 is repul-

$$RM \quad \begin{array}{c} \xrightarrow{\ FeL_3^{3+}\ } [RM^+ FeL_3^{2+}] \qquad (28) \\ \xrightarrow{\ IrCl_6^{2-}\ } [RM^+ IrCl_6^{3-}] \qquad (29) \end{array}$$

sive, whereas it clearly changes to an attractive energy in the ion pair derived from iridate(IV) in eq 29.

1. Outer-Sphere Processes for Electron Transfer from Alkylmetals to Iron(III) Complexes. In the outer-sphere reaction of alkylmetals with iron(III), Marcus theory predicts a slope of 0.5 in the correlation of the rates of electron transfer (log k) with the difference in standard free energy changes of RM and FeL_3^{3+}.

a. Structural Effects of Iron(III). For a particular alkylmetal, we find that log k for electron transfer is linear with the standard reduction potential of the five iron(III) complexes employed in this study. The slope of the correlation in the equation

$$\log k = 8.5E^0 + \text{constant} \qquad (30)$$

is equivalent to that of a linear free energy plot in the equation

$$\Delta G^{\ddagger} = 0.50\Delta G^0 + \text{constant} \qquad (31)$$

predicted by the Marcus theory for outer-sphere electron transfer. It is noteworthy that the family of lines in Figure 3 for all 11 alkylmetals passes through the experimental points with slopes (8.9 ± 0.4) close to this value.[38] Both two-coordinate dialkylmercury compounds and four-coordinate tetraalkyltin as well as lead compounds are generally included in this correlation. Furthermore, the points for the iron(III) complex with the most sterically hindered ligand, L = 4,7-

diphenyl-1,10-phenanthroline, also fall close to the lines. If the alkylmetal must penetrate the octahedral, tris ligand sphere around iron(III) before electron transfer can take place, we would expect the substantial difference in steric effects between 4,7-diphenyl-1,10-phenanthroline and 1,10-phenanthroline to be manifested most either with the linear mercury alkyls or with the highly congested tetraneopentyltin. Thus, the linear relationships generally observed suggest a transition state in which the alkylmetal is located along the periphery of the iron(III) complex. Electron transfer probably could occur via the π orbitals of the phenanthroline ligand.[39] Indeed, the negative deviations consistently observed with the analogous bipyridine iron(III) complex in Figure 3 accord with the less extensive π conjugation in this ligand.

b. Structural Effects of the Alkylmetal—HOMO and Steric Effects. For a particular iron(III) complex, we find that log k for electron transfer is also linear with the ionization potential of the alkylmetal. The smooth correlation in Figure 2 includes the tetraalkylmetals of silicon, germanium, tin, and lead as well as the two-coordinate dialkylmercury compounds. The linearity spans a range of almost 10^8 in the rates of electron transfer. Furthermore, the correlation

$$\log k = -4.9 I_D + \text{constant} \tag{32}$$

accords with the relationship between I_D and E^0 in eq 7, and provides additional support for the outer-sphere mechanism. Our failure to measure the electrode potential E^0 due to the extreme instability of the cation radical unfortunately precludes an estimation of the self-exchange rates and the reorganizational barriers for the RM/RM^+ couples.

If only tetraalkyltin and -lead compounds are considered, the linear correlation in Figure 2 is excellent. It suggests that the solvation terms are essentially constant throughout the series of tin and lead compounds.[40] This is not unreasonable since the effective size of the cation radical from lead(V) is probably not much larger than that of tin(V) due to the lanthanide contraction. However, differences in solvation terms as a result of changes in size may be responsible for the slight negative deviations observed with the germanium and silicon derivatives in Figure 2.

It is noteworthy that the mercury alkyls are slightly more reactive than expected from their value of I_D. Indeed, changes in solvation may actually be *less* for mercury than for either tin or lead, since the two coordination would allow more solvation of the reactant itself. Furthermore, the rate enhancement observed could also be due to an increase in adiabaticity for electron transfer (i.e., a slightly more effective orbital overlap) allowed by the closer approach of the linear dialkylmercury to the iron(III) complex.

The most important feature of the correlation in Figure 2 is the striking absence of steric effects with changes in the structures of the alkyl ligands. In particular, increasing the branching of the alkyl ligand at the β carbon with methyl groups in the homologous series CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CHCH_2$, and $(CH_3)_3CCH_2$ leads to no deviation from the linear free energy correlation. Even the oxidative cleavage of the sterically hindered tetraneopentyltin[41] is included precisely in the correlations with all three iron(III) complexes. The same applies to α branching in the series CH_3, CH_3CH_2, $(CH_3)_2CH$, and $(CH_3)_3C$. Tetra-*tert*-butyltin is unknown, but the most hindered compounds we had available, *t*-BuSnMe$_3$ and $(t$-Bu$)_2$SnMe$_2$, are both nicely correlated.

Steric effects of alkyl groups can be quantitatively evaluated as ligands with the steric parameter E_s' listed in Table VI.[4,37] A recent reevaluation and extension of Taft's values suggest that very hindered ligands such as *t*-Bu$_2$CH and Et$_3$C (with $E_s' = -6.97$ and -5.29, respectively[42]) may be helpful in determining the steric limits to which the correlation is applicable. Indeed it is reasonable to expect the correlation to fail with
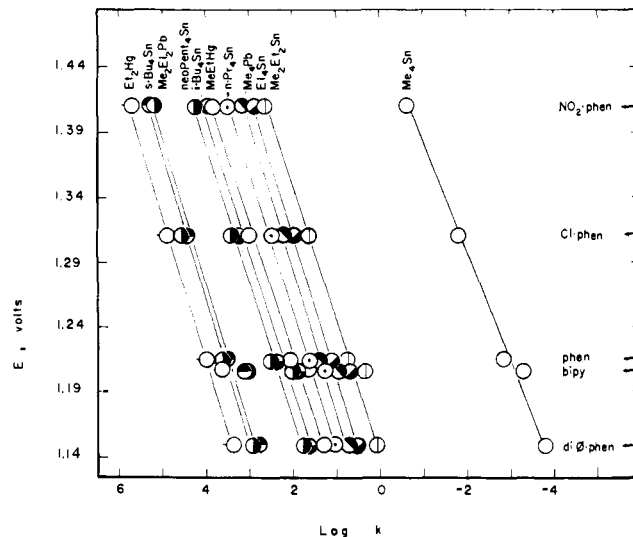

Figure 3. The Marcus plot of standard reduction potentials (E^0 vs. SHE) for various iron(III) complexes with the second-order rate constant (log k) for electron transfer from the alkylmetals listed at the top.

Table VI. Taft Steric Parameter for Alkyl Ligands[a]

α branching		β branching	
alkyl	E_s'	alkyl	E_s'
methyl	0	ethyl	−0.08
ethyl	−0.08	*n*-propyl	−0.31
isopropyl	−0.48	isobutyl	−0.93
tert-butyl	−1.43	neopentyl	−1.63

[a] From ref 42.

highly hindered alkyl derivatives, since the concept of an outer-sphere mechanism itself can lose its operational validity in the nonadiabatic limit.[43]
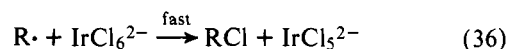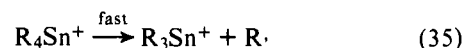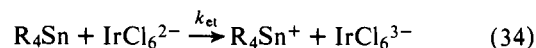
2. Inner-Sphere Processes for Electron Transfer from Alkylmetals to Hexachloroiridate(IV). Alkylmetals are oxidatively cleaved by hexachloroiridate(IV) by essentially the same mechanism as that described in Scheme I for iron(III). For example, the facile reaction with the homoleptic alkylmetals of mercury and lead has been shown to proceed via a rate-limiting electron transfer.[8]

$$RM + IrCl_6{}^{2-} \xrightarrow{k} RM^+\cdot + IrCl_6{}^{3-} \tag{33}$$
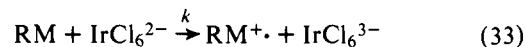
The products, stoichiometry, and kinetics indicate that the tin derivatives in this study also react by the same mechanism, as shown in Scheme II.

The reduction potential of hexachloroiridate(IV) in acetonitrile solution is 0.67 V, which is less than the E^0 of the iron(III) complexes. However, the second-order rate constants for electron transfer from both tetramethyltin and -lead to hexachloroiridate(IV) are significantly larger than those predicted from an extrapolation of the correlations in Figure 3.[44] Indeed, tetramethyltin reacts about 10^5 times faster than expected, as indicated by the value of $\Delta \log k$ in Table VII. Thus in contrast to iron(III), an inner-sphere contribution[47] to electron transfer is indicated in the case of hexachloroiridate(IV), and it suggests

Scheme II

$$R_4Sn + IrCl_6{}^{2-} \xrightarrow{k_{et}} R_4Sn^+ + IrCl_6{}^{3-} \tag{34}$$

$$R_4Sn^+ \xrightarrow{\text{fast}} R_3Sn^+ + R\cdot \tag{35}$$

$$R\cdot + IrCl_6{}^{2-} \xrightarrow{\text{fast}} RCl + IrCl_5{}^{2-} \tag{36}$$
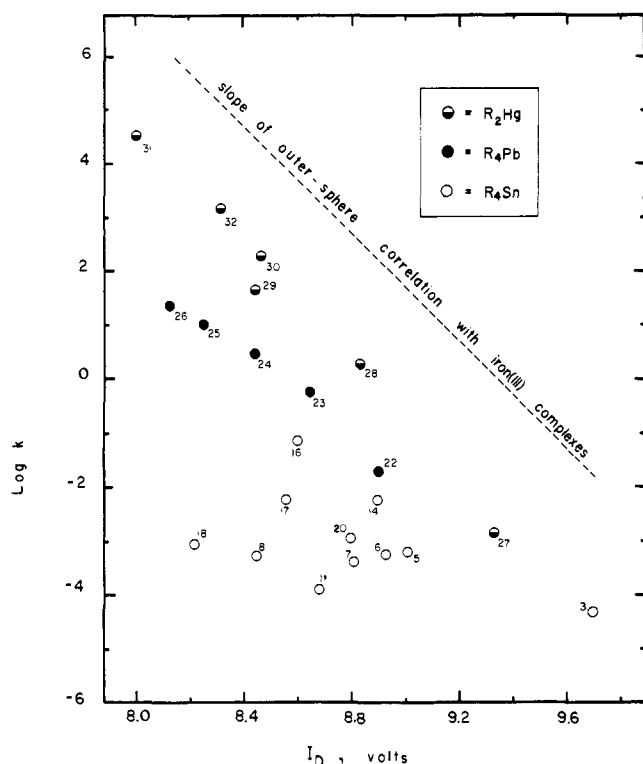
Figure 4. The relationship between the rates of electron transfer (log k) to hexachloroiridate(IV) and the ionization potentials I_D of a series of tetraalkyltin compounds indicated by open circles (O). Comparison with (●) methylethyllead and (◒) dialkylmercury compounds. The numbers refer to compounds designated in Table I. The outer-sphere slope is indicated by the dashed line taken from Figure 2 for tris-5-chloro-1,10-phenanthrolineiron(III).

Table VII. Comparison between the Calculated and Experimental Rate Constants for the Reaction with Hexachloroiridate(IV) in CH_3CN

alkylmetal	log k_{calcd}[a]	log k_{exptl}	Δ log k[b]
Me_4Sn	−9.5	−4.29	+5.2
Et_2Me_2Sn	−4.7	−3.2	+1.5
Et_4Sn	−3.9	−3.20	+0.7
n-Pr_4Sn	−3.5	−3.34	+0.2
sec-Bu_4Sn	−1.6	−3.23	−1.6
i-Bu_4Sn	−2.6	−3.86	−1.3
Me_4Pb	−3.8	−1.7[c]	+2.1
Et_2Me_2Pb	−1.8	+0.52[c]	+2.3
Et_4Pb	+0.02	+1.40[c]	+1.4
EtMeHg	−3.2	+0.30[d]	+3.5
Et_2Hg	−0.7	+1.68[d]	+2.4

[a] From extrapolation of the curves in Figure 2 to $E^0_{IrCl_6^{2-}/3-} \equiv 0.67_1$ V in acetonitrile solutions. [b] Difference between log k_{calcd} and log k_{exptl}. [c] From ref 9a. [d] From ref 9b.

that the alkylmetal can be approached by hexachloroiridate(IV) closer than by iron(III) in the transition state for electron transfer. In other words, steric effects are more important in electron-transfer reactions with hexachloroiridate(IV) than those with iron(III). Indeed, the smooth correlation shown in Figure 2 between I_D and log k_{et} for outer-sphere electron transfer with iron(III) is no longer valid. Instead, the rates of oxidative cleavage of the same alkylmetals by hexachloroiridate(IV) are depicted in Figure 4. However, despite the random, "buckshot" appearance of the plot, a closer scrutiny of the data shows a systematic trend among a limited number of related compounds. For purposes of calibration, the dashed line in Figure 4 is the correlation with iron(III), for which we judge the slope to be representative of outer-sphere electron transfer from these alkylmetals (vide supra). If so, the correlations of hexachloroiridate(IV) with the methylethyl derivatives of both mercury and lead are fairly linear, with approximately this slope, but not on the same line. Apparently, with these less hindered alkylmetals, the rates of electron transfer to hexachloroiridate(IV) are determined more by electronic effects (i.e., the HOMOs) rather than by steric effects. A greater variety of alkyl structures are included among the tetraalkyltin derivatives and the points in Figure 4 show considerable, but accountable, scatter. Thus, the negative deviation from the outer-sphere slope is most pronounced with the α- and β-branched alkyl groups, i.e., the isopropyl, isobutyl, and *tert*-butyl derivatives. Clearly, the hindered alkyltin compounds are cleaved by hexachloroiridate(IV) much more slowly than their values of I_D alone would indicate. A similar conclusion may be reached from the varying magnitudes of Δ log k for different alkylmetals in Table VII.[48] Such a steric effect must reflect the perturbation of the inner sphere of the alkylmetal in the transition state for electron transfer. Indeed

this conclusion can be used as an operational criterion for an inner-sphere mechanism of electron transfer from alkylmetals to hexachloroiridate(IV).

3. A Continuum of Outer- and Inner-Sphere Processes for Electron Transfer from Alkylmetals—A Proposal. The concepts of outer-sphere and inner-sphere electron transfer as we have employed here depend on the availability of various alkyl groups as highly "tunable" probes for steric effects. As such, we might ask how these processes basically differ since we have shown that alkylmetal cation radical is an intermediate which is common to both iron(III) and iridate(IV). Thus, selectivity studies demonstrate that there is no direct, covalent bond formed between the alkylmetal and hexachloroiridate(IV) during inner-sphere electron transfer.[49]

We propose as a working hypothesis for further development that outer- and inner-sphere processes with alkylmetals are distinguished by the magnitudes of the intermolecular separation between the alkylmetal and the oxidant in the transition states for electron transfer. The driving force as well as electrostatic forces are expected to contribute to the "tightness" of these transition states. In the inner-sphere activated complex, changes in the steric properties of alkyl ligands indicate that the alkylmetal is geometrically perturbed, and we tentatively suggest that a precursor complex is formed in which the tetraalkyltin achieves a quasi-five-coordinate configuration reminiscent of a variety of trigonal bipyramidal structures known for tin(IV) derivatives.[50,51]

According to our proposal, substitution-inert organometals can undergo outer-sphere as well as inner-sphere electron transfer. For tetraalkylmetals the inner-sphere process is subject to steric hindrance by the alkyl groups which may be relieved by partial distortion of the configuration at the metal center.[52] This formulation implies that a continuum of outer-sphere and inner-sphere processes is possible for electron transfer which differ principally in geometrical constraints. Charge-transfer interactions with electron acceptors such as tetracyanoethylene will provide a further development as described in the following paper.[25] Finally, we hope that these quantitative studies of steric effects will provide a helpful guide to more theoretical studies of electron-transfer mechanisms.[13,54]

Experimental Section

Materials. 2,2'-Bipyridine and 1,10-phenanthroline (monohydrate) were obtained from J. T. Baker Chemical Co. and Fisher Scientific Co., respectively. All the substituted 1,10-phenanthroline ligands were obtained from G. F. Smith Chemical Co. The iron(II) complexes were prepared by adding an equivalent amount of the appropriate ligand to an aqueous solution of ferrous sulfate. The perchlorate salts of the

Table VIII. Absorption Spectra of Iron Complexes in Acetonitrile Solutions

iron(II,III) complex	λ_{max}, nm (ϵ)	λ used to monitor reaction, nm (ϵ)	alternate λ for product analysis, nm (ϵ)
Fe(4,7-di-Ph-1,10-phen)$_3$(ClO$_4$)$_2$	530 (1.42 × 10^4)	510 (1.26 × 10^4)	450 (8.65 × 10^3)
Fe(4,7-di-Ph-1,10-phen)$_3$(ClO$_4$)$_3$	600 (1.12 × 10^2)	510 (4.75 × 10^1)	450 (7.41 × 10^1)
Fe(bpy)$_3$(ClO$_4$)$_2$	520 (8.24 × 10^3)	520 (8.24 × 10^3)	550 (4.05 × 10^3)
Fe(bpy)$_3$(ClO$_4$)$_3$	608 (2.61 × 10^2)	520 (1.54 × 10^2)	550 (1.80 × 10^2)
Fe(phen)$_3$(ClO$_4$)$_2$	507 (1.31 × 10^4)	510 (1.30 × 10^4)	550 (3.43 × 10^3)
Fe(phen)$_3$(ClO$_4$)$_3$	592 (5.79 × 10^2)	510 (1.90 × 10^2)	550 (4.12 × 10^2)
Fe(5-Cl-1,10-phen)$_3$(ClO$_4$)$_2$	510 (9.33 × 10^3)	510 (9.33 × 10^3)	550 (2.73 × 10^3)
Fe(5-Cl-1,10-phen)$_3$(ClO$_4$)$_3$	585 (3.38 × 10^2)	510 (1.89 × 10^2)	550 (2.87 × 10^2)

iron(II) complexes were precipitated with sodium perchlorate.[14b] The iron(III) complexes of 2,2'-bipyridine and 1,10-phenanthroline were prepared by chlorine oxidation of an acidic aqueous solution of the sulfate salt of the corresponding iron(II) complexes.[55] After complete oxidation, sodium perchlorate was added and the blue solution was subsequently cooled to allow precipitation of the blue solid. The iron(III) complex of 5-chloro-1,10-phenanthroline was prepared by oxidation of the perchlorate salt of the corresponding iron(II) complex in concentrated sulfuric acid with ceric ammonium sulfate. The perchlorate salt of the iron(III) complex was precipitated by careful addition of 0.1 M perchloric acid to the resulting blue solution.[14b] The iron(III) complexes of 4,7-diphenyl-1,10-phenanthroline and 5-nitro-1,10-phenanthroline were generated in situ by electrolytic oxidation of the corresponding iron(II) complexes in acetonitrile using 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. Disodium hexachloroiridate(IV) hexahydrate was obtained from Varlacoid Chemical Co. (99.5%) and used without purification.

Tetraethyllead was a gift from Ethyl Corp. and was purified by steam distillation followed by fractional vacuum distillation. Tetramethyllead was prepared according to Gilman and Jones.[56] Diethyldimethyllead was synthesized from diethyllead diacetate and methylmagnesium iodide in tetrahydrofuran.[9a] The methylethyllead compounds were analyzed by gas–liquid chromatography, being resolved on a 4-ft column containing 10% polyethylene glycol 600/1% Quadrol supported on Chromosorb W.[57]

All the symmetrical tetraalkyltin compounds (i.e., R$_4$Sn) were prepared by the standard reaction between anhydrous stannic chloride and the corresponding alkyl Grignard reagent in either diethyl ether or di-*n*-butyl ether as solvent.[56] The unsymmetrical tetraalkyltin compounds (SnR$_n$R'$_4$ − n) were prepared from the appropriate alkylchlorotin compound (SnR$_n$Cl$_4$ − n) and the alkyl Grignard reagent (R'MgX) or vice versa.[56] Tetraethylsilane and tetraethylgermane were prepared by an analogous procedure from ethylmagnesium bromide and tetrachlorosilane and tetrachlorogermane, respectively. Dimethyl-, diethyl-, and methylethylmercury were obtained from a previous study.[9c]

Tetraethylammonium perchlorate was obtained from G. F. Smith Chemical Co. and recrystallized three times from distilled water. Both tetraethylammonium perchlorate and lithium perchlorate were dried in vacuo at 78 °C overnight before use. Analytical grade acetonitrile from Mallinckrodt, Inc., was purified and dried by the standard procedure,[58] followed by redistillation from phosphorus pentoxide.

Kinetic Measurements. Solutions of alkylmetal in acetonitrile were purged with argon and used within 2 days of preparation. Solutions of iron(III) complexes were freshly prepared in deaerated acetonitrile. Whenever possible, the reactions were carried out under pseudo-first-order conditions with either the alkylmetal or the iron(III) complex in excess. For the slower reactions, the appropriate concentrations of alkylmetal and iron(III) complex were made up in pre-deaerated acetonitrile and subsequently transferred to a gas-tight Pyrex cuvette in a thermostated cell compartment of a Cary-14 spectrophotometer. The rate of disappearance of hexachloroiridate(IV) was followed at 489 nm. For oxidations with iron(III), the rate of appearance of the band due to the corresponding iron(II) complex was followed, the spectral characteristics of which are summarized in Table VIII. The ionic strength of the reaction medium was adjusted to 0.1 with either lithium perchlorate or tetraethylammonium perchlorate. For reactions which were too fast to be followed by this procedure, separate solutions of the alkylmetal and the iron(III) complex were sealed in conical flasks with serum caps and purged

with argon. The resulting reagents were transferred by means of glass syringes to a Durrum-Gibson stopped-flow spectrophotometer.

Cyclic Voltammetry. The standard reduction potentials of all the Fe(II)/Fe(III) couples were measured by cyclic voltammetry on a Princeton Applied Research Model 173 potentiostat/galvanostat equipped with a Houston Instrument Series 2000 Omnigraphic X–Y recorder. The experiments were carried out in acetonitrile with 0.1 M tetraethylammonium perchlorate as supporting electrolyte, using a platinum working electrode and a saturated NaCl calomel reference electrode. The scan rates were varied between 50 and 600 mV s^{-1}. Although the separation of cathodic and anodic peaks in Table II was slightly higher than the theoretical separation of 59 mV, the unit ratio of the peak currents i_c/i_a supports a reversible one-electron process. At the fastest scan rate of 600 mV s^{-1}, all the iron(III)/iron(II) couples become irreversible.

Attempts to measure the E^0 for the IrCl$_6{}^{2-/3-}$ couple as the sodium salt dissolved in anhydrous acetonitrile by cyclic voltammetry using either a platinum or graphite electrode were unsuccessful. The cyclic voltammograms do not show the peaks corresponding to the reoxidation of the Ir(III)Cl$_6{}^{3-}$. The same behavior was observed using the PPN salt of the hexachloroiridate(IV).

Owing to the irreversibility of the cyclic voltammogram of IrCl$_6{}^{2-/3-}$ in acetonitrile, the reversible redox couple was measured by the equilibrium method described as follows. A solution containing a known concentration of both IrCl$_6{}^{2-}$ (0.83–1.8 × 10^{-4} M) and Fe(phen)$_2$(CN)$_2$ (1.4–2.1 × 10^{-4} M) was made up in acetonitrile, and the final absorbance of the solution measured on a Cary-14 spectrophotometer. From the molar absorptivity of the reactants and products [$\epsilon^{490}_{\text{IrCl}_6{}^{3-}} \simeq 10$;[59] $\epsilon^{490}_{\text{IrCl}_6{}^{2-}} = 4085$; $\epsilon^{490}_{\text{Fe(phen)}_2(\text{CN})_2{}^+} = 560$; $\epsilon^{490}_{\text{Fe(phen)}_2(\text{CN})_2} = 5757$], the equilibrium constant of the equilibrium in eq 37 could be calculated.

$$\text{IrCl}_6{}^{2-} + \text{Fe(phen)}_2(\text{CN})_2 \overset{K}{\rightleftharpoons} \text{IrCl}_6{}^{3-} + \text{Fe(phen)}_2(\text{CN})_2{}^+ \quad (37)$$
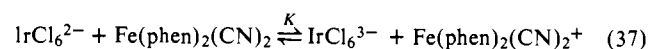
The results obtained in acetonitrile at an ionic strength $\mu = 0.1$ using NaClO$_4$ were as follows (equilibrium constant, $K/\Delta E^0$ vs. SHE): 5.2/0.042; 7.3/0.051; 4.7/0.040; 4.9/0.041; 4.6/0.039; 5.9/0.045 (average $\Delta E^0 = 0.043 \pm 0.004$). Based on the value of $E^0_{\text{Fe(phen)}_2(\text{CN})_2} = 0.63$ V, measured by cyclic voltammetry (see Table II), the $E^0_{\text{IrCl}_6{}^{2-/3-}}$ was found to be 0.67 V.

The E^0 for hexachloroiridate(IV) in water was previously reported as 1.017 V by Nyholm et al.[60] and 0.904 V at $\mu = 0.1$ by George.[61] The discrepancy has been attributed by Kravtsov[62] to hydrolyses of the iridium species. Indeed, if a solution of hexachloroiridate(IV) in 0.1 M aqueous NaClO$_4$ solution is allowed to stand for approximately 90 min, the apparent E^0 increases from 0.826 to 0.941 V. Jackson[63] redetermined the E^0 and found a value of 0.899 V at $\mu = 0.1$ using a Norbide (boron carbide) electrode. Margerum et al.[64] also reported a lower value of 0.892 V using a carbon (paste) electrode. We have reproduced the latter value using a platinum electrode.

The anodic oxidations of alkyltin, lead, and mercury compounds were irreversible.[9] Sweeping of the voltage from zero to beyond the anodic peak potential led to no reduction wave even at sweep rates as fast as 10 V s^{-1}. No measurements were made beyond this upper limit for the platinum electrode since the charging current increased steadily at higher sweep rates.

Mass Spectroscopy. The mass spectra were measured on a Varian-MAT CH7 mass spectrometer as described previously for the methylethyllead analogues.[35b]

Table IX. Stoichiometric Consumption of Iron(III) Measured as the Amount of Iron(II) Complexes Formed per Mole of Alkylmetal in Deoxygenated and Air-Saturated Acetonitrile[a]

R_nM	Fe(4,7-di-Ph-1,10-phen)$_3$$^{3+}$	Fe(bpy)$_3$$^{3+}$	Fe(phen)$_3$$^{3+}$	Fe(5-Cl-1,10-phen)$_3$$^{3+}$	Fe(5-nitro-1,10-phen)$_3$$^{3+}$
Me$_4$Pb	2.06	1.98 ± 0.09	1.98 ± 0.11	2.47 ± 0.04	
		1.43 ± 0.02[b]	1.43 ± 0.01[b]	1.62 ± 0.02[b]	
Et$_4$Pb	2.09	1.96 ± 0.09	2.03 ± 0.15	4.02 ± 0.22	
		1.59 ± 0.03[b]	1.60 ± 0.04[b]	3.00 ± 0.08[b]	
Et$_4$Sn	2.04	2.08 ± 0.03	1.98 ± 0.07	3.24 ± 0.08	
n-Pr$_4$Sn	2.08	2.01	2.01	3.0	3.13
i-Bu$_4$Sn	1.99	2.05	2.08	3.01	3.09
sec-Bu$_4$Sn	2.02	2.07	2.02	3.03	3.13

[a] Standard deviations only indicated whenever four or more independent experiments were performed. All others are an average of two determinations. [b] Experiments in air-saturated acetonitrile.

Spectral Titration of Iron(III). The stoichiometric requirement of iron(III) in the oxidative cleavage of alkylmetals was determined spectrophotometrically in the presence of excess FeL$_3$(ClO$_4$)$_3$. After reaction, the absorption spectrum due to the resulting reduced iron(II) was the same as that of the authentic iron(II) complex. Thus, the stoichiometries in Table IX were calculated from the amount of iron(II) formed per mol of alkylmetal employed, assuming complete reaction (vide infra).

Analysis of Products Derived from the Oxidative Cleavage of Alkyltin Compounds by Iron(III). Tetramethyltin. A suspension of Fe(phen)$_3$(ClO$_4$)$_3$ (0.15 mmol) in 0.5 mL of CD$_3$CN was purged with argon and treated with tetramethyltin (0.075 mmol) in the absence of air. The ^{1}H NMR spectrum showed the gradual disappearance of the resonance at δ 0.05 ppm due to Me$_4$Sn, and its concomitant replacement with two sharp singlets at δ 0.67 and 2.9 ppm due to Me$_3$Sn(ClO$_4$) and CD$_3$CONDCH$_3$, respectively. When the reaction was complete, 1 M LiCl was added, and the resonance at δ 0.67 due to Me$_3$Sn(ClO$_4$) was completely replaced by a new singlet at δ 1.2 ppm assigned to Me$_3$SnCl in comparison with that of an authentic sample. Integration using either methylene chloride or toluene as an internal standard indicated that both Me$_3$Sn(ClO$_4$) and Me$_3$SnCl were formed in essentially quantitative yields. The amide was also identified by comparing its ^{1}H NMR spectrum with that of an authentic sample. Integration of the signal indicated that CD$_3$CONDCH$_3$ was quantitatively formed, based on the intial concentration of Me$_4$Sn. However, when the experiments were carried out in carefully dehydrated CD$_3$CN using P$_2$O$_5$, a broad signal centered at δ ~3.55–3.70 ppm emerged. The signal at ~3.55–3.70 ppm was due to CD$_3$CNMe(ClO$_4$), since this nitrilium ion, when it was generated by an independent method from MeO$_3$SCF$_3$ in CD$_3$CN, showed a resonance at δ 3.76 ppm, which could be shifted upfield to ~3.59 ppm by the addition of Fe(phen)$_3$(ClO$_4$)$_2$ and LiClO$_4$. Integration of the signal indicated that CD$_3$CNMe$^+$ was formed in 40–70% yields, based on the initial concentration of Me$_4$Sn. The formation of CD$_3$CONDCH$_3$ may be due to hydrolysis of the initially formed CD$_3$CNMe$^+$ by adventitious water in the reaction mixture. However, addition of approximately 50 μL of D$_2$O after reaction afforded CD$_3$CONDCH$_3$ in quantitative yield, based on the initial concentration of Me$_4$Sn.

The NMR spectral changes of the phenanthroline ligand on the iron species could also be followed. Thus, the broad, unresolved resonance at δ 6.4 ppm due to Fe(phen)$_3$$^{3+}$ gradually shifted downfield and decreased in intensity as the reaction progressed. On completion, the spectrum consisted of two sharp singlets at 7.72 and 8.30 ppm together with an unresolved multiplet at 8.68 ppm due to Fe(phen)$_3$(ClO$_4$)$_2$ in comparison with an authentic sample. The gradual shift in the phenanthroline resonances during the course of reaction is due to electron exchange processes occurring in the Fe(III)/Fe(II) couple.[65]

Tetraethyltin reacts with Fe(phen)$_3$$^{3+}$ on mixing, but the shifting of the NMR spectrum of the phenanthroline ligand occurs too rapidly to follow. In the presence of excess iron(III), Et$_4$Sn disappeared completely and its NMR spectrum [δ 0.32–1.45 (multiplet)] was replaced by a new spectrum consisting of the superposition of the spectrum of Et$_3$Sn(ClO$_4$) consisting of a sharp singlet (δ 1.32 ppm) and the spectrum of CD$_3$CONDC$_2$H$_5$ [δ 1.10–1.16 (t, J = 7.2 Hz), 3.24–3.28 (q, J = 7.2 Hz)]. The latter was identified by comparison with an authentic sample of N-ethylacetamide introduced into the reaction mixture and also by IR spectroscopy. Integration of the

quartet at 3.24–3.28 ppm indicated that CD$_3$CONDC$_2$H$_5$ was quantitatively formed, based on the initial concentration of Et$_4$Sn. Again, if the reaction was carried out in carefully dried CD$_3$CN, a broad signal at 3.86–3.94 ppm due to CD$_3$CNC$_2$H$_5$(ClO$_4$) also appeared, together with that of CD$_3$CONDC$_2$H$_5$. The nitrilium ion, generated independently from EtO$_3$SCF$_3$ and CH$_3$CN, showed resonances at δ ~1.4 and ~3.92 ppm. Integration of the signal at 3.86–3.94 ppm indicated that only 35–60% yield of the CD$_3$CNC$_2$H$_5$$^+$ was formed. The remaining product could be accounted for by CD$_3$CONDC$_2$H$_5$, based on the initial concentration of Et$_4$Sn. Addition of D$_2$O quantitatively converted CD$_3$CNC$_2$H$_5$(ClO$_4$) to CD$_3$CONDC$_2$H$_5$. The reaction product was also shown to be N-ethylacetamide by IR spectroscopy. The carbonyl stretching frequency ($\nu_{C=O}$ 1675) was compared with that of an authentic sample of N-ethylacetamide introduced into the reaction product mixture. The amount of N-ethylacetamide generated was quantitatively analyzed using ethyl acetate as the internal standard. Thus from 0.36 mmol of tetraethyltin, 0.29 mmol of N-ethylacetamide was analyzed by this technique. Similarly, 0.47 mmol of Me$_3$EtSn yielded 0.36 mmol of N-ethylacetamide. The inaccuracy of this method arises from the uncertainty in drawing the base line due to the intense absorptions arising from the phenanthroline ligands.

Selectivity Studies of the Reaction between SnMe$_n$Et$_{4-n}$ with IrCl$_6$$^{2-}$ and Fe(III) Complex. Methylethyltin compounds, Me$_2$Et$_2$Sn and Me$_3$EtSn, used in the selectivity studies have characteristic NMR spectra in which the methyl groups attached to tin absorb at 0.03 ppm, and the multiplet resonances of the ethyl groups consistently lie at δ 0.28–1.48 ppm, akin to those of Me$_4$Sn and Et$_4$Sn, respectively. Furthermore, the methylethyltin perchlorates obtained on oxidative cleavage show characteristic sharp singlet resonances at 0.62 and 1.32 ppm due to Me and Et groups, respectively. The latter allows the relative concentrations of the methylethyltin cations to be determined quantitatively simply by measuring the relative intensities of these peaks and solving the two simultaneous equations. Essentially, the same method was used for the reaction with hexachloroiridate(IV). The validity of this method is shown separately by analysis of the mixtures of ethyl chloride and methyl chloride formed in the reaction with hexachloroiridate(IV) by gas–liquid chromatography using a 15-ft 20% FFAP on 60/80 mesh Chromosorb P column with isobutene as the internal standard, and by ^{1}H NMR [CH$_3$Cl, δ 3.05 (s); CH$_3$CH$_2$Cl, δ 3.60 (q), J = 7 Hz].

Scavenging of Isopropyl Radicals by O$_2$ in CH$_3$CN. Tetraisopropyltin (~0.01 M) in acetonitrile was placed in a Schlenk flask equipped with a side arm containing an aliquot of Fe(phen)$_3$(ClO$_4$)$_3$ (~0.01 M). The two solutions were equilibrated under 2 atm of oxygen pressure for about 15 min. After the reaction vessel was sealed off, the two solutions were allowed to mix. The reaction mixture was analyzed by gas chromatography using a 14-ft column filled with 10% FFAP on 60/80 mesh Chromosorb b at 85 °C for acetone and isopropyl alcohol. Quantitative analysis was effected with ethyl acetate as the internal standard.

Spin-Trapping Experiments. Solutions of tetraethyllead (2 × 10^{-2} M) containing 2-methyl-2-nitrosopropane (5 × 10^{-2} M) and Fe(bpy)$_3$(ClO$_4$)$_3$ (5 × 10^{-3} M) in acetic acid were added to separate arms of a tube attached to an ESR sample tube. The two separate solutions were degassed by three successive freeze–thaw–pump cycles before mixing. No ESR signal was detected unless Fe(bpy)$_3$(ClO$_4$)$_3$, PbEt$_4$, and 2-methyl-2-nitrosopropane were all present. The ESR spectrum centered at g = 2.0058 with the hyperfine splittings a_N =

16.38 G, $a_{\beta H}$ = 10.56 G, and $a_{\gamma H}$ = 0.35 G accords with that of *t*-BuN(Et)O· reported previously.[9a]

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