

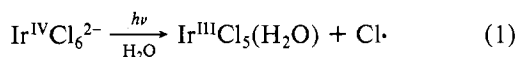
Charge-Transfer Photochemistry in the Cleavage of Alkylmetals by Hexachloroiridate(IV). ESR Studies of Paramagnetic Intermediates

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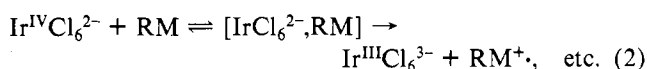
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The photochemical cleavage of various tin alkyls by hexachloroiridate(IV) is examined by broad-band irradiation at low temperatures where the thermal reaction is too slow to compete. The formation of transient paramagnetic intermediates is examined by ESR spectroscopy in rigid media. Evidence is presented for the formation of chlorine atom complexes and alkyl radicals. A photochemical charge-transfer process is compared to an earlier study of the thermal reaction.

Photochemical reactions of transition-metal complexes, particularly charge-transfer transitions leading to redox decompositions in both intra- and intermolecular processes, are of recent interest.^{1,2} In this study we have focused on the photochemical cleavage reactions of hexachloroiridate(IV). The electronic spectrum of hexachloroiridate(IV) in aqueous solutions consists of two sets of strong absorption bands—the low-energy absorption consisting of twin maxima at 490 and 433 (410) nm has been assigned to a $\pi_L \rightarrow \pi_M^*$ charge-transfer to metal (CTTM) transition and the very intense band at 232 nm assigned to a $\pi_L \rightarrow \sigma_M^*$ CTTM transition.³ Consistent with these spectral assignments, Moggi and co-workers⁴ found that no reaction occurred when aqueous solutions of hexachloroiridate(IV) were irradiated at 433 and 495 nm, but they observed a photoredox process upon irradiation at 254 nm, i.e., eq 1. Our interest in the photo-



chemistry of hexachloroiridate(IV) stems from the charge-transfer interaction observed with a variety of alkylmetals RM in eq 2.⁵ We have found that there is also a facile photo-



chemical reaction between hexachloroiridate(IV) and tetraalkyltin in acetonitrile solutions under low-temperature conditions, in which the thermal reaction in eq 2 is negligible. In this study we have focused on the photoreduction of hexachloroiridate(IV) with alkylmetals, by probing for the paramagnetic intermediates by ESR spectroscopy.

Experimental Section

Materials. Tetramethyltin was prepared from methylmagnesium bromide and stannic chloride as previously described (bp 78 °C (758 mm)).⁶ The alkyltrimethyltin compounds were prepared from trimethyltin chloride and the appropriate Grignard reagent in either

diethyl ether or di-*n*-butyl ether: EtSnMe₃, bp 105 °C (760 mm); *n*-BuSnMe₃, bp 150 °C (760 mm). Trimethyltin chloride was prepared by syn proportionation of 3 mol of Me₄Sn with SnCl₄, and dimethyltin dichloride was prepared by a similar procedure using equimolar amounts of each reagent. The unsymmetrical *t*-Bu₂SnMe₂ was prepared from Me₂SnCl₂ and *tert*-butylmagnesium bromide; bp 75 °C (30 mm). Tri-*n*-butylgermane and triethylsilane were prepared by the lithium aluminum hydride reduction of *n*-Bu₃GeCl and Et₃SiCl, respectively: *n*-Bu₃GeH, bp 124 °C (20 mm);⁷ Et₃SiH, bp 110 °C (75 mm).⁸ Sodium hexachloroiridate(IV), Na₂IrCl₆·6H₂O, was obtained from Varlacoid Chemical Co. (99.5%) and used without further purification. Acetonitrile (Mallinckrodt Analytical Reagent) was purified by stirring it over calcium hydride overnight. After filtration, it was followed by treatment with potassium permanganate and then distillation from P₂O₅ through a 20-plate bubble-cap column under a nitrogen atmosphere. Potassium ferrioxalate was synthesized according to the literature procedure⁹ and recrystallized three times from hot water.

ESR Spectral Measurements. The appropriate alkylmetal (20 μL) was added to a Pyrex sample tube containing 0.5 mL of an acetonitrile solution of 0.10 M hexachloroiridate(IV). The contents were thoroughly degassed by successive freeze-pump-thaw cycles prior to sealing. The tubes were then placed in the ESR cavity at -170 °C, and the frozen sample was irradiated with a 1-kW high-pressure mercury lamp. The ESR spectrum was recorded on a Varian E112 X-band spectrometer, employing 100-kHz modulation, and calibrated with a proton NMR field marker. The yield of radicals was determined by double integration of the first-derivative mode of the spectrum, by using DPPH as the standard.¹⁰ The experimental errors in the determination of the absolute and relative concentrations of radicals by this method are ±20% and 5%, respectively.

Alkylmetal Cleavage by Hexachloroiridate(IV). Thermal. In a typical procedure, sufficient tetramethyltin was added to a solution of 0.1 M sodium hexachloroiridate(IV) in acetonitrile to make a ~0.08 M solution. The vessel was flushed with argon, sealed, and heated in a constant-temperature bath at 40 °C. After 16 h, the extensive color of IrCl₆²⁻ was bleached and the reaction complete.

Photochemical. A similar solution of tetramethyltin and hexachloroiridate(IV) was placed in a cooled quartz tube. The sample was thoroughly degassed by successive freeze-pump-thaw cycles and sealed. The sample was placed in a transparent Dewar cooled to -30 °C with a stream of nitrogen. After irradiation for 5 h, the solution was bleached, and the contents of the tube were analyzed.

Analysis. The alkylmetal products, alkyl halide, and trialkyltin derivatives were analyzed by the procedures described previously.^{5,11} The iridium(III) products, IrCl₅(NCCH₃)₂²⁻ and IrCl₆³⁻, were analyzed by pumping off the solvent in vacuo and digesting the solid residue in pyridine.^{5b} The soluble IrCl₅(NCCH₃)₂²⁻ was analyzed by ¹H NMR spectroscopy and chlorine oxidation as previously described.⁵ The insoluble hexachloroiridate(III) was also analyzed spectroscopically following chlorine oxidation.

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Table I. Selectivities in the Thermal and Photochemical Cleavage of Tetraalkyltin by Hexachloroiridate^a

R ₄ SnMe ₃ (M)	mode ^b (Φ)	time, h	[products], M		
			RCl	MeCl	S(R/Me)
EtSnMe ₃ (0.061) ^c (0.057) ^c (0.088) ^d (0.068) ^d (0.067) ^d (0.039) ^d	$h\nu$ (1.0)	6 ^f	0.061	0.017	11
	$h\nu$ (0.8)	8	0.064	0.019	10
	Δ	1 ^g	0.026	0.008	9.8
	Δ	2	0.044	0.012	11
	Δ	3	0.048	0.015	9.6
	Δ ^h	1	0.061	0.018	10.5
<i>n</i> -BuSnMe ₃ (0.089) ^e (0.083) ^e (0.099) ^d (0.073) ^d (0.068) ^d (0.051) ^d	$h\nu$ (0.7)	4	0.027	0.008	10
	$h\nu$ (i)	8	0.035	0.011	10
	Δ	1.5	0.026	0.008	9.8
	Δ	3	0.039	0.013	9.0
	Δ	9	0.048	0.015	9.6
	Δ ^h	1	0.074	0.023	9.7

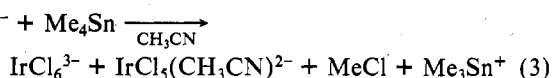
^a In acetonitrile solutions at -20°C . ^b $h\nu$ = photochemical at -20°C ; Δ = thermal at 30°C unless stated otherwise. Quantum yield $\Phi = [\text{RCl} + \text{MeCl}] \times \text{time} / 0.013 \text{ einstein L}^{-1} \text{ h}^{-1}$. ^c $[\text{IrCl}_6^{2-}] = 0.20 \text{ M}$. ^d $[\text{IrCl}_6^{2-}] = 0.12 \text{ M}$. ^e $[\text{IrCl}_6^{2-}] = 0.10 \text{ M}$. ^f Time of irradiation. ^g Time of heating. ^h At 50°C . ⁱ Reaction complete.

Since our primary interest in the redox photochemistry of hexachloroiridate(IV) lies in the nature of the transient paramagnetic intermediates, no extensive efforts were made to monitor the wavelength dependence of the cleavage reactions. Photochemical experiments were carried out with broad-band irradiation from either a tungsten lamp or a high-pressure mercury lamp (Hanovia 777B-1) with a Pyrex filter.

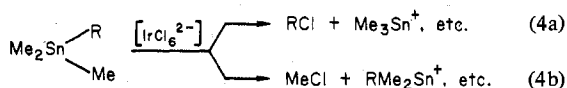
Selectivity Studies of the Photochemical Reactions. Typically, twin tubes, each containing the same amounts of hexachloroiridate(IV) in acetonitrile-*d*₃ (0.4 mL of 0.10 M) and an internal standard (0.067 mmol CH_2Cl_2), were sealed with gastight rubber serum caps under argon and placed in a transparent Pyrex Dewar maintained at either -30 or -20°C with a cold stream of nitrogen. One of the tubes was used as a reference and completely sheltered from light with an aluminum foil. The same amount of EtSnMe₃ (10 μL) was added to each tube, and the contents were mixed thoroughly. The tubes were placed in the Dewar so as to allow exposure to equivalent amounts of light from a 100-W tungsten lamp. The yields of alkyl chlorides were determined by ¹H NMR spectroscopy as described previously.¹¹ The selectivities, determined from the ratios of products after statistical correction, were reproducible to $\pm 5\%$. The light intensities for all the photochemical experiments were determined ($\pm 10\%$) by ferrioxalate actinometry⁹ and repeatedly calibrated, before and after reaction, for the experimental configuration employed. No reaction was observed in the tube sheltered from light.

Results and Discussion

Photochemical Cleavage of Alkylmetals with Hexachloroiridate(IV). When sodium hexachloroiridate(IV) is treated with tetramethyltin in acetonitrile solutions, reduction takes place thermally according to the stoichiometry in eq 3.^{5,11} The



same reaction can be induced photochemically at -30°C , a temperature at which the thermal reaction is too slow to compete effectively. With use of a slight excess of alkyltin compound, the quantum yield based on the appearance of alkyl chloride is close to unity under these conditions (see Table I). When an unsymmetrical tetraalkyltin compound such as RSnMe₃ (R = alkyl ligand) is used, two modes of cleavage are possible (see eq 4). The selectivity for alkylmetal cleavage



$S(\text{R}/\text{Me})$ is obtained from the relative amounts of products

Table II. Quantum Yield for the Disappearance of Hexachloroiridate(IV) and the Effect of Alkylmetals^a

$10^2 [\text{IrCl}_6^{2-}]$, M	[tetra- methyltin], M	time, min	Φ
3.0 ^b	0	0	
2.6	0	20	0.6
2.0	0	40	0.7
1.6	0	63	0.6
3.0 ^b	0.12	0	
1.9	0.12	20	1.6
1.0	0.12	40	1.5
2.9 ^b	0.24	0	
2.2	0.24	10	2.1
1.4	0.24	20	2.2
0.72	0.24	40	1.6
2.9 ^b	0.35	0	
2.2	0.35	10	2.1

^a In acetonitrile solution at -30°C . Light intensity = $(3.4 \pm 0.3) \times 10^{-4} \text{ einstein L}^{-1} \text{ min}^{-1}$. ^b Initial concentration; others determined from the spectra by using ϵ 4630 at 490 nm.

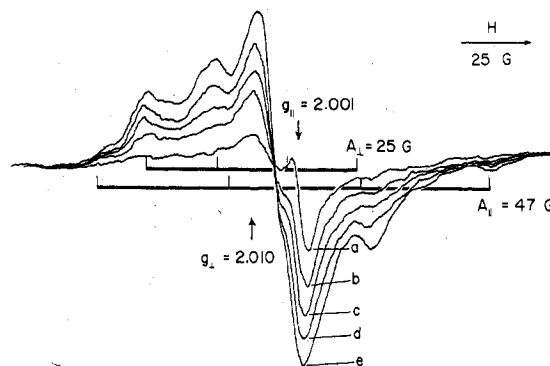


Figure 1. The ESR spectrum obtained during the photolysis of 0.01 M hexachloroiridate(IV) in acetonitrile at -170°C after irradiation for (a) 1, (b) 3, (c) 5, (d) 7.5, and (e) 11.5 min. The stick diagrams show the anisotropic ESR parameters $g_{\perp} = 2.010$, $g_{\parallel} = 2.001$, $A_{\perp} = 25 \text{ G}$, and $A_{\parallel} = 47 \text{ G}$ for $I = 3/2$.

(e.g., 3/1 RCl/MeCl), and it provides a measure of the reactivities of the various alkyl-tin bonds. The selectivities in the thermal and the photochemical cleavages of ethyltrimethyltin and *n*-butyltrimethyltin are compared in Table I.

If a solution of only sodium hexachloroiridate(IV) in acetonitrile is irradiated through a Pyrex filter, the intensities of the absorptions centered at 490 and 433 (410) nm both diminish monotonically with time. The quantum yield of 0.6 obtained from ferrioxalate actinometry⁹ is listed in Table II. It is noteworthy that this measured quantum yield increases to 2, i.e., twice the value based on the formation of alkyl chloride (vide supra), when the photolysis is carried out under the same conditions, but with the exception of various amounts of added tetramethyltin (which is optically transparent in this region).

Detection of Paramagnetic Intermediates. In order to probe for reactive intermediates in the photochemically induced cleavage of alkylmetals by hexachloroiridate(IV), we employed ESR spectroscopy for studies in solution and in frozen matrices.

1. Chlorine Atoms from the Photolysis of Hexachloroiridate(IV). The steady irradiation of a 0.10 M solution of sodium hexachloroiridate(IV) in acetonitrile produced no ESR signal between -40°C and room temperature. However, if the solution is frozen at -170°C , the persistent anisotropic spectrum in Figure 1a is obtained. The signal intensity increased monotonically with exposure time, as shown in Figure 1b-e. The hyperfine features of the spectrum can be analyzed as $g_{\perp} = 2.010$, $A_{\perp} = 25 \text{ G}$ ($I = 3/2$) and $g_{\parallel} = 2.001$, $A_{\parallel} =$

47 G ($I = 3/2$) as shown by the accompanying stick spectrum. The ESR spectrum disappeared immediately if the matrix was subsequently allowed to anneal at slightly higher temperatures (-163°C).

Two reasonable structural assignments can be made for the paramagnetic species, giving rise to the ESR spectrum in Figure 1, viz., either a chloroiridate or chlorine atom. Hexachloroiridate(IV) itself is a paramagnetic ion (defined in a low-spin d^5 state), but its ESR spectrum is usually very broad and unresolved owing to the short relaxation time from the large spin-orbit coupling of the heavy atom. Indeed a very broad ESR signal can be observed prior to irradiation at -170°C , and the ESR parameters ($g \approx 1.97$, $\Delta H_{pp} \approx 450$ G) are consistent with those previously reported for IrCl_6^{2-} at 20 K by Griffiths and Owen.¹² The other possible paramagnetic iridate species would be derived from the d^7 , low-spin iridium(II) intermediates, which have been reported as transient hot ions in the γ irradiation of iridium(III) complexes.¹³ Although the splitting patterns are similar to those in Figure 1, the ESR parameters ($g_{\perp} = 2.811$, $A(\text{Ir}) = 72.5$ G) for the iridium(II) species are quite different from those obtained from Figure 1.

The nuclear spins of the iridium isotopes ^{191}Ir and ^{193}Ir in 38.5% and 61.5% natural abundances, respectively, are both $I = 3/2$, which is the same $I = 3/2$ as that of the alternative possibility, chlorine atoms, with isotopes ^{35}Cl and ^{37}Cl in 75% and 25% natural abundances, respectively. Unfortunately there is no clear indication that the ESR spectrum of chlorine atoms, either in solution or in the solid state, has been experimentally observed.¹⁴⁻¹⁶ Since halogen atoms are orbitally degenerate, it is likely that the unpaired spin will be strongly coupled to the environment, resulting in the broadening of the resonance lines beyond recognition.¹⁷ However, the degeneracy of the 3p atomic orbitals would be removed in a strong crystal field of, for example, tetragonal or orthorhombic symmetry.¹⁸ Under these conditions the theoretical spectrum of the chlorine atom will depend on the splitting ΔE of the 3p energy levels, since the principal components of the g tensor are given by eq 5 and 6,¹⁸ where g_e is the g value of the free tetragonal:

$$g_{zz} = g_{\parallel} = g_e \quad g_{xx} = g_{yy} = g_{\perp} \approx g_e + 2\lambda/\Delta E \quad (5)$$

orthorhombic:

$$\begin{aligned} g_{zz} &\approx g_e & g_{xx} &= g_e + 2\lambda/\Delta E_1 \\ g_{yy} &= g_e + 2\lambda/\Delta E_2 \end{aligned} \quad (6)$$

electron and $\lambda = 586 \text{ cm}^{-1}$ is the spin-orbit coupling constant of the chlorine atom.¹⁶ Both sets of equations yield anisotropic g values in which two principal components g_{xx} and g_{yy} are greater than g_e and the other (g_{zz}) is almost equal to g_e , consistent with the results in Figure 1. The experimental g

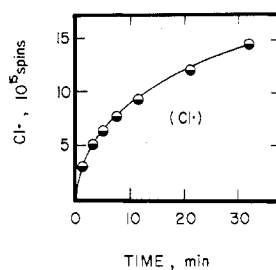


Figure 2. The time dependence of the growth of the ESR spectrum of the chlorine atom during the steady irradiation of hexachloroiridate(IV) in acetonitrile at -170°C .

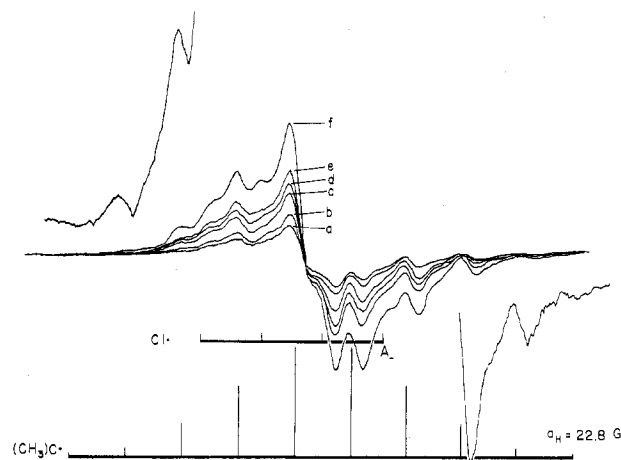


Figure 3. ESR spectrum obtained during the photolysis of a mixture of hexachloroiridate(IV) and $t\text{-Bu}_3\text{SnMe}_2$ in acetonitrile at -170°C for (a) 3, (b) 4.5, (c) 11, (d) 17, (e) 25, and (f) 40 min. The insets show the $m_I = \pm 9/2, 7/2,$ and $5/2$ lines at higher gain. The accompanying stick diagrams are for the isotropic spectrum of *tert*-butyl radicals ($\langle g \rangle = 2.0026$, $\langle a_H \rangle = 22.8$ G) and the anisotropic spectrum of chlorine atom ($g_{\perp} = 2.010$, $A_{\perp} = 25$ G) from Figure 1.

values appear to have axial symmetry which accords better with the formulation in eq 5 for tetragonal splitting. With regard to the hyperfine tensor, the values in eq 7 are derived

$$|A_{\text{iso}}| \approx 1 \text{ G} \quad |B| \approx 23 \text{ G} \quad (7)$$

for $I = 3/2$ from the experimental values of A_{\parallel} and A_{\perp} ,¹⁹ where A_{iso} is the isotropic hyperfine constant, B is an anisotropic hyperfine constant, and the sign of A is taken to be the same as that of B .²⁰ The small value of A_{iso} indicates that most of the unpaired spin density is in a p orbital, as expected for a chlorine atom. However, when the value of $\langle 1/r^3 \rangle_{3p}$ for chlorine is taken from the calculations of Sternheimer,²¹ the value of B is estimated to be 62 G²² which is larger than that in eq 7. The discrepancy may be attributable to the distortion of the p orbital as a result of a strong crystal field sufficient to resolve the degeneracy of the 3p orbitals.²³ In either case, the anisotropic ESR parameters point to atomic chlorine

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- (13) Fujiwara, S.; Watanabe, T.; Inoue, T. *Chem. Lett.* **1974**, 755. Compare also: Stock, J. R.; Rogers, M. T. *J. Chem. Phys.* **1975**, *62*, 2640.
- (14) (a) The report of chlorine atoms adsorbed on silica gel surfaces (Gardner, C. L. *J. Chem. Phys.* **1967**, *46*, 2991) has been disputed (Bennett, J. E.; Mile, B.; Ward, B. *Ibid.* **1968**, *49*, 5556) and subsequently retracted (Gardner, C. *Ibid.* **1968**, *49*, 5558). The paramagnetic species has been assigned to $\text{Cl}_2^{\cdot -}$. (b) See also: Edward, C. *J. Chem. Phys.* **1973**, *59*, 1599.
- (15) The ESR spectrum of a chlorine-containing species formed on the surface of MgO has been analyzed in detail and assigned to the chlorine atom (Tench, A. J.; Kibblewhite, J. F. *J. Chem. Soc. A* **1971**, 2282).
- (16) For the ESR spectrum of chlorine atoms in the gas phase see: Vanderkooi, N., Jr.; Mackenzie, J. S. *Adv. Chem. Ser.* **1962**, *No. 36*, 98.
- (17) Atkins, P. W.; Symons, M. C. R. "The Structure of Inorganic Radicals"; Elsevier: Amsterdam, 1967.
- (18) Lunsford, J. H. *Adv. Catal.* **1972**, *22*, 265.

- (19) These values compare with $|A_{\text{iso}}| = 35$ G and $|B| = 28$ G from the data in ref 15. There is a better agreement between $g_{\perp} = 2.025$ and $g_{\parallel} = 2.002$ in ref 15 with the values in Figure 1.
- (20) The alternative possibility, i.e., that the signs of A_{iso} and B are opposite, yields $|A_{\text{iso}}| = 32$ G and $|B| = 7$ G. Such large isotropic hyperfine splittings are unlikely in this case.
- (21) Sternheimer gives $\langle 1/r^3 \rangle_{3p} = 55.6 \times 10^{24} \text{ cm}^{-3}$. Sternheimer, R. *Phys. Rev.* **1951**, *84*, 244.
- (22) From $B = 2/5 g\beta g_n \beta_n \langle 1/r^3 \rangle$.
- (23) For example using Tench's data,¹⁵ Gardner and Casey (*Catal. Rev.* **1974**, *9*, 1) obtained ΔE in eq 5 as $5.1 \times 10^4 \text{ cm}^{-1}$ by assuming $g_{\perp} = g_e + 2\lambda/\Delta E$ and $g_{\parallel} = g_e$. The splitting is expressed as $\Delta E = (3e/5)(\partial^2 V/\partial v^2)_0 \langle r^2 \rangle_{3p}$, from which the field gradient $(\partial^2 V/\partial v^2)_0$ is obtained as $1.1 \times 10^{17} \text{ V cm}^{-2}$ where $\langle r^2 \rangle = 0.95 \times 10^{-10} \text{ cm}^2$ on the basis of Slater orbitals.

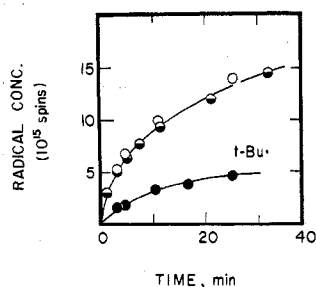
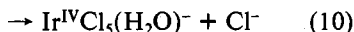
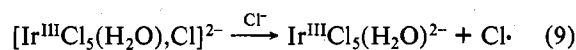
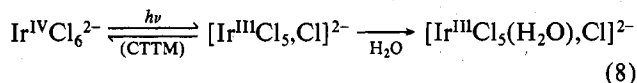


Figure 4. The competition between the formation of chlorine atoms and *tert*-butyl radicals during the photolysis of 0.10 M hexachloroiridate(IV) and 0.24 M *t*-Bu₂SnMe₂ in 0.5 mL of acetonitrile at -170 °C: ●, *t*-Bu·; ○, *t*-Bu· plus Cl·. Light intensity = 2.0×10^{16} quanta min^{-1} . ○ = Cl· from IrCl_6^{2-} alone taken from Figure 2.

species interacting with its environment as the most likely source of the ESR signal. The latter also accords with the photochemical studies in aqueous solutions of Moggi and co-workers,⁴ who described the excitation of hexachloroiridate(IV) at 254 nm as a charge-transfer to metal (CTTM) transition $\pi_L \rightarrow \sigma_M^*$ (e_g) in the following manner:



Thus, we tentatively ascribe the ESR spectrum in Figure 1 to a chlorine atom still associated with iridium, e.g., $[\text{IrCl}_5, \text{Cl}]^{2-}$, which we refer to hereafter as a chlorine atom, for simplicity.

The yield of chlorine atoms, obtained by double integration of the ESR spectrum in Figure 1, is plotted against the irradiation time in Figure 2. The quantum yield for the formation of chlorine atom, obtained from the initial slope in Figure 2 and the light intensity (2.0×10^{16} quanta min^{-1}), is estimated to be 0.14.²⁴ This quantum yield is significantly larger than that reported in aqueous solution ($\Phi = 0.029$),⁴ indicating an important difference in solvent effects.²⁵

2. *tert*-Butyl Radicals from *tert*-Butyltin Compounds and Hexachloroiridate(IV). The irradiation of hexachloroiridate(IV) in the presence of the tetraalkyltin *t*-Bu₂SnMe₂ at -170 °C affords the ESR spectrum shown in Figure 3. The series of time-lapse spectra in Figure 3 were recorded under steady irradiation at constant temperature. Each spectrum consists of the superposition of the somewhat broadened, but clearly resolved, spectrum of the *tert*-butyl radical ($g = 2.0026$, $a_{\text{H}} = 22.8 \text{ G}^{26}$) superimposed on that of the chlorine atom described in the foregoing section. All 10 lines of the *tert*-butyl radical are discernible, the $m_I = \pm 9/2, 7/2$, and $5/2$ being shown at higher gain in the insets. No ESR spectra of the *tert*-butyl radicals are observed in the absence of hexachloroiridate(IV).

Since the spectrum of the *tert*-butyl radical was somewhat obscured by the overlapping lines of the chlorine atom, the photochemical yield of *tert*-butyl radicals was determined by calibrating it relative to that of an authentic spectrum²⁷ formed

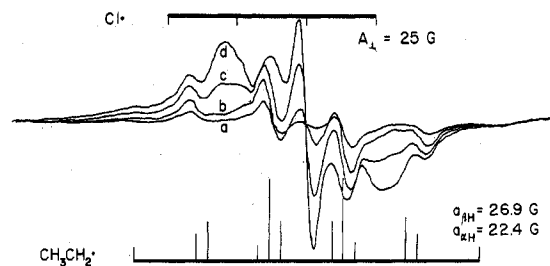


Figure 5. ESR spectrum obtained during the photolysis of a mixture of hexachloroiridate(IV) and Et₄Ge in acetonitrile at -180 °C for (a) 4, (b) 18, (c) 65, and (d) 140 min. The stick diagrams represent the isotropic spectrum of ethyl radicals (lower, $a_{\beta\text{H}} = 26.9 \text{ G}$ and $a_{\alpha\text{H}} = 22.4 \text{ G}$) and the anisotropic spectrum of chlorine atom ($A_1 = 25 \text{ G}$).

under the same conditions. The yield of *tert*-butyl radicals determined in this way is plotted in Figure 4 against the irradiation time. The total yield of radicals, including both *t*-Bu· and Cl·, is also compared in Figure 4 with the yield of chlorine atom formed in the absence of tetraalkyltin (see Figure 2). As clearly seen in Figure 4, the total yield of radicals (i.e., *t*-Bu· plus Cl·) formed during the photolysis of hexachloroiridate(IV) in the presence of *t*-Bu₂SnMe₂ is the same as the yield of chlorine atoms formed by the photolysis of hexachloroiridate(IV) alone, under the same photochemical conditions. The yield of *tert*-butyl radicals, which is lower than the chlorine atom yield, increases with the irradiation time parallel with the formation of chlorine atom in the absence of *t*-Bu₂SnMe₂.

3. Formation of Other Paramagnetic Species. The photolysis of hexachloroiridate(IV) was also studied in the presence of tetraethylgermane, tri-*n*-butylgermane, and triethylsilane. The irradiation of IrCl_6^{2-} and Et₄Ge at -180 °C afforded the series of ESR spectra shown in Figure 5 taken after various irradiation times. Each spectrum consists of the spectrum of chlorine atom (previously shown in Figure 1, the A_1 component is drawn at the top), together with the ESR spectrum of the ethyl radical (the isotropic hyperfine splittings of Et· in solution²⁶ are indicated by the stick spectrum). The yield of ethyl radicals appears to reach a steady state, and at longer irradiation times the chlorine atom spectrum becomes dominant. The quantum yield of Cl· and Et· together is estimated to be 0.18, which is in reasonable agreement with the results reported for *t*-Bu₂SnMe₂ above. The formation of ethyl radicals thus appears to arise by a similar process.

The irradiation of hexachloroiridate(IV) in the presence of the metal hydrides, *n*-Bu₃GeH and Et₃SiH, produces hydrogen atoms as clearly shown by the characteristic doublet splitting of 505 G in the ESR spectra in Figure 6.²⁸ Hydrogen atoms are not formed in the absence of hexachloroiridate(IV). Hydrogen atoms are also formed during the photolysis of a mixture of iodine and *n*-Bu₃GeH at -180 °C in the absence of chloroiridate species. In both cases, the disappearance of hydrogen atoms follows first-order kinetics as shown in Figure 7. Interestingly, the rate constant $k = 1.5 \times 10^{-3} \text{ s}^{-1}$ at -163 °C obtained for hydrogen atoms from hexachloroiridate(IV) photolysis is the same as that derived for H· from iodine. Under these conditions, the disappearance of hydrogen atoms appears to be a diffusion-controlled process.

Mechanisms of Alkylmetal Cleavage by Hexachloroiridate(IV). Thermal and Photochemical Processes. The stoichiometry and selectivity for alkylmetal cleavage by hexachloroiridate(IV) in eq 3 and 4, respectively, are the same regardless of whether the reaction is induced thermally or photochemically. Indeed, our earlier studies⁵ of the mechanism of the thermal cleavage of alkylmetals can provide insight into

(24) This value is smaller than that obtained in solution (Table I), since it does not include the facile recombination processes resulting from restraints imposed by the matrix, as well as light loss owing to reflection from the frozen surface.

(25) Differences in solvation and viscosity are likely to be factors affecting the extent of cage recombination in various solvents.

(26) (a) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147. (b) See also: Ayscough, P. B.; Thomson, C. *Trans. Faraday Soc.* **1962**, *58*, 1477.

(27) Fukuzumi, S.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5961.

(28) Beringer, R.; Heald, M. A. *Phys. Rev.* **1954**, *95*, 1474.

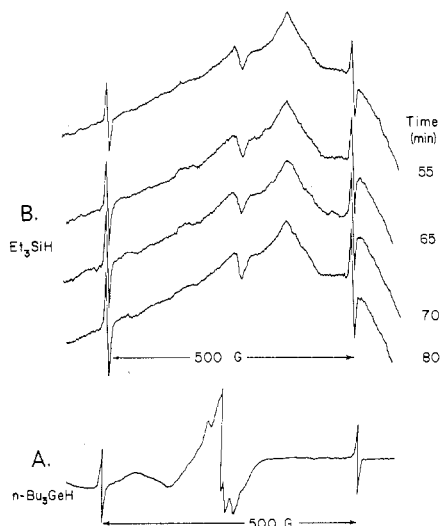


Figure 6. The formation of hydrogen atoms during the photolysis of hexachloroiridate(IV) in the presence of the metal hydrides, (A) $n\text{-Bu}_3\text{GeH}$ and (B) Et_3SiH , in acetonitrile at -170°C . The features in the center of the spectrum in part A are mainly due to chlorine atom (see A_{\perp} in Figure 1) and those in part B are due to the Pyrex vessel.

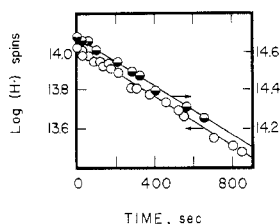
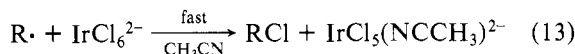
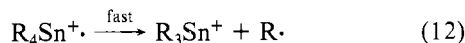
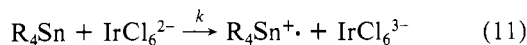


Figure 7. The first-order disappearance at -163°C of hydrogen atoms produced by the photolysis of $n\text{-Bu}_3\text{GeH}$ with IrCl_6^{2-} (●) and I_2 (○) in acetonitrile.

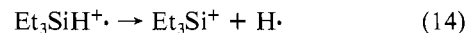
the nature of the photochemical process. Thus, the thermal cleavage of alkylmetals by hexachloroiridate(IV) in acetonitrile solutions has been shown to proceed by the multistep mechanism described in Scheme I for tetraalkyltin compounds.⁵ The activation process in Scheme I is represented by the electron-transfer step in eq 11, followed by the facile fragmentation of the cation radical R_4Sn^+ to yield an alkyl radical which is efficiently intercepted by a second equivalent of hexachloroiridate in the last step.

Scheme I



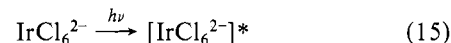
In Scheme I, the formation of the alkylmetal products (i.e., RCl and R_3Sn^+) occurs subsequent to the rate-limiting step, being determined solely by the spontaneous fragmentation of the alkylmetal cation in eq 12. Consequently, the selectivity in the cleavage of unsymmetrical tetraalkyltin compounds such as RSnMe_3 is inherent to the property of the alkylmetal cation and independent of its mode of formation. Thus, the similar selectivities observed in the thermal and photochemical cleavages by hexachloroiridate(IV) strongly suggest that the same alkylmetal cation is an intermediate common to both processes. Indeed, the ESR observation of alkyl radicals from the fragmentation of R_4Sn^+ (eq 12) in Figures 3 and 5 con-

stitutes independent support for alkylmetal cations as metastable intermediates in photochemical processes. Moreover, the cleavage of hydrogen atoms in Figure 6 is also a characteristic mode of decay of the metastable cations of alkylmetal hydrides,²⁹ i.e., eq 14.



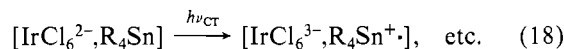
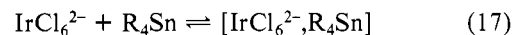
Alkylmetal cations may arise during the (exciplex) quenching of a photoexcited hexachloroiridate(IV) (Scheme II) since alkylmetals are known to be effective electron do-

Scheme II

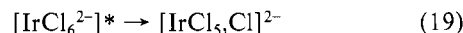


nors.^{30,31} Photoexcitation of the intermolecular charge-transfer band ($h\nu_{\text{CT}}$) represents an alternative route by which an electron transfer can be effected from alkylmetal to hexachloroiridate(IV)^{32,33} (Scheme III).

Scheme III



It is noteworthy that neither of these mechanisms explicitly includes the chlorine atom as a key intermediate in the photochemical cleavage of alkylmetals by hexachloroiridate(IV). Since there is independent spectroscopic evidence (Figure 1) in rigid media for the formation of a chlorine atom complex from the photolysis of hexachloroiridate(IV), it might be included in an electron-transfer scheme such as³⁴



Alternatively, the photochemical process leading to chlorine atoms could be a side reaction (in rigid media), unrelated to the alkylmetal cleavage itself. In either case, a cleavage process stemming directly from chlorine atom displacement on alkylmetals, i.e., eq 21, is not important since it does not accord with the stoichiometry in eq 3.³⁵



Acknowledgment. We wish to thank the National Science Foundation for financial support.

Registry No. IrCl_6^{2-} , 16918-91-5; EtSnMe_3 , 3531-44-0; $n\text{-BuSnMe}_2$, 1527-99-7; $t\text{-Bu}_2\text{SnMe}_2$, 3531-47-3; Et_4Ge , 597-63-7; Et_3SiH , 617-86-7; $n\text{-Bu}_3\text{GeH}$, 998-39-0; EtCl , 75-00-3; $n\text{-BuCl}$, 109-69-3; MeCl , 74-87-3; I_2 , 7553-56-2.

- (29) Klingler, R. J.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6626.
- (30) For the excited states $[\text{IrCl}_6^{2-}]^*$ possibly involved in the quenching, see ref 3.
- (31) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; see Part III.
- (32) For photochemically excited charge-transfer states, see the study with tetracyanoethylene (TCNE) in ref 27. [There is a strikingly parallel behavior between IrCl_6^{2-} and TCNE toward alkylmetal cleavage (Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928).]
- (33) For a comparison between exciplex quenching of excited states and photoactivation of charge transfer, see: Davidson, R. S. "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1975; p 215 ff.
- (34) Since the excited state $[\text{IrCl}_6^{2-}]^*$ is as yet undefined, eq 19 is qualitatively intended to convey (one or more) intersystem crossings leading to the photoredox process described by Moggi⁴ in eq 8.
- (35) (a) Homolytic displacement in eq 21 is known to be facile (see: Davies, A. G. *Adv. Chem. Ser.* **1977**, No. 157, 26). (b) The involvement of eq 21 leads to the stoichiometry $2\text{IrCl}_6^{2-} + \text{R}_4\text{Sn} \xrightarrow{\text{h}\nu} \text{R}_3\text{SnCl} + \text{RCl} + 2\text{IrCl}_5(\text{NCCH}_3)^{2-}$. Since roughly half of the hexachloroiridate(IV) is converted to hexachloroiridate(III), this process cannot be important. [Note that the conversion of $\text{IrCl}_5(\text{NCCH}_3)^{2-}$ to IrCl_6^{3-} is especially slow under these conditions.]