Notes

conjugate base, can be used to estimate two other quantities of interest. For the lowest energy d-d transition of the conjugate base, one gets an estimated wavelength shift of 3 nm, based on the well-known correlation between ^{59}Co nmr frequencies and d-d transition wavelengths.[8,9] The fact that wavelength shifts have not been observed for $Co(en)_3^{3+}$ in strongly basic solutions[3,10] is consistent with this estimated value. An approximate upper limit for the mean lifetime for exchange (presumably due to proton transfer) between $Co(en)_3^{3+}$ and its conjugate base can be estimated from $\Delta \nu_0$: $\tau \ll 5 \times 10^{-4}$ sec for 0.39^{-1} M OH$^-$ solutions of $Co(en)_3^{3+}$.

We found the ^{59}Co frequency of $Co(en)_3^{3+}$ to vary with DMSO concentration in mixed DMSO–water solutions. Although the behavior was qualitatively similar to that observed for basic solutions, the maximum observed shift with DMSO was about one-eighth as large as that at comparable OH$^-$ concentrations and the reciprocal relation given in eq 1 was not obeyed. Since hydrogen bonding between DMSO and the amine protons probably occurs, one would expect a ^{59}Co frequency variation with increased DMSO concentration similar to that observed for the deprotonation reaction, although not as great in magnitude. The result that the ^{59}Co frequency change with DMSO concentration does not obey the reciprocal relation (eq 1) suggests that more than one amine group on a given complex may be hydrogen bonded to DMSO; accordingly, it would be necessary to invoke several equilibria in order to interpret quantitatively the variation of the ^{59}Co frequency change with DMSO concentration.

Registry No. Cobalt-59, 7440-48-4; $Co(en)_3^{3+}$, 14878-41-2.

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Contribution from the Chemistry Department, University of Malaya, Kuala Lumpur, Malaysia

Proton Magnetic Resonance Study of [(n-C₄H₉)₃NCH₃][(C₆H₅)₃PCoBr₃]

Tong-Chiew Tan[1] and Yau-Yan Lim*

Recently, proton magnetic resonance spectroscopy has been widely used in the study of ion association in solution.[2] The property that is being observed is the isotropic shift of the cationic protons in the presence of the paramagnetic anion. The interpretation of the isotropic nmr shift of the cation has stirred considerable interest for quite some time and it was only recently that it was established that the iso-

(1) Abstracted in part from the M.Sc. thesis of T.-C. Tan, University of Malaya, Kuala Lumpur, Malaysia, 1973.
(2) L. Rosenthal and I. M. Walker, *Inorg. Chem.*, **11**, 2444 (1972), and references therein.

tropic nmr shift, $\Delta \nu_p$, is the sum of two terms:[3,4] the Fermi contact shift, $\Delta \nu_c$, and the dipolar or "pseudocontact" shift, $\Delta \nu_{dip}$. Information such as ion-pair geometries and concentration association constants in various solvents can usually be determined from such a study.[5]

In this article, we report some additional findings obtained from the study of $[(C_4H_9)_3NCH_3][(C_6H_5)_3PCoBr_3]$ in nitrobenzene, propylene carbonate, and chloroform. A special feature of this compound is that in contrast to the one studied earlier,[5] the cation is unsymmetrical and smaller in size. It would therefore be of interest to examine how these changes in the properties of the cation would affect the ion-pair geometry and association constant for the 1:1 electrolyte in nonaqueous solvents.

Experimental Section

The nmr spectra were obtained on a Hitachi Perkin-Elmer R-20B spectrometer at 34 (± 0.5)°. Tetramethylsilane was used as the internal reference. The visible spectra were obtained with a Beckman DB-G spectrophotometer.

Preparation of Complexes. $[(n\text{-}C_4H_9)_3NCH_3]Br$ was prepared[6] by treating $(n\text{-}C_4H_9)_3N$ (Merck, for synthesis LAB) with CH_3Br (Fluka, Purum) using cyclohexane as solvent in the dark.

$[(n\text{-}C_4H_9)_3NCH_3][(C_6H_5)_3PCoBr_3]$ was prepared by the method reported by Rettig and Drago.[7] The crude product was recrystallized from 2-butanol and dried over silica gel under vacuum. The melting point was 155–157° (uncorrected).

Anal. Calcd for $C_{31}H_{45}Br_3CoNP$: C, 48.91; H, 5.92; N, 1.84; Br, 31.51. Found: C, 48.69; H, 6.05; N, 1.70; Br, 31.7.

$[(n\text{-}C_4H_9)_3NCH_3][(C_6H_5)_3PZnBr_3]$ was prepared in the same way as the Co(II) analog. The melting point (uncorrected) was 139–141°.

Anal. Calcd for $C_{31}H_{45}Br_3ZnNP$: C, 48.5; H, 5.87. Found: C, 48.18, H, 5.93.

Analyses were performed by the Australian Microanalytical Service, Division of Applied Chemistry, CSIRO, and University of Melbourne.

Solvents. It was necessary to remove all traces of ethanol in the chloroform used (Merck; zur analyse) by column chromatography[7] because the complex was found to be decomposed by chloroform containing about 0.6–1.0% of ethanol as a preservative.[5] Nitrobenzene (H & W; Analar Standard) was fractionally distilled at reduced pressure and stored over molecular sieves 4A. Propylene carbonate (Fluka; Purum) was dried over molecular sieves and distilled under reduced pressure. The distillate was stored over molecular sieves for at least 24 hr before use.

Treatment of Nmr Data. As shown previously,[5] for the equilibrium $C + A \rightleftharpoons CA$, where C represents the cation, A the anion, and CA the ion pair, the association constant K_{as} is defined as

$$K_{as} = [CA]/[C][A] \qquad (1)$$

where brackets denote concentration in terms of moles per liter of solution, and K_{as}^{-1} is given by

$$K_{as}^{-1} = \frac{[A_0]\Delta \nu_{pi}}{\Delta \nu_{oi}} - [A_0] - [C_0] + \frac{[C_0]\Delta \nu_{oi}}{\Delta \nu_{pi}} \qquad (2)$$

where $[A_0]$ and $[C_0]$ denote the initial concentration of anion and cation, respectively, $\Delta \nu_{pi} = \nu_{pi} - \nu_{di}$ is the isotropic shift of the ith set of protons, and $\Delta \nu_{oi} = \nu_{oi} - \nu_{di}$ is the observed isotropic shift of the ith set of protons.

In this article, for the solvent nitrobenzene the set of equivalent methylene protons next to the nitrogen atom as well as the methyl protons next to the nitrogen atom is used for calculation. It is found that the K_{as} values obtained by both methods agree within the limit of experimental error. The observed isotropic shifts for the N-methyl protons are used for the calculation of K_{as} in the solvent

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Table I. Association of $[(C_4H_9)_3NCH_3][(C_6H_5)_3PCoBr_3]$ and $[(C_4H_9)_4N][(C_6H_5)_3PCoBr_3]^a$ in Various Nonaqueous Solvents

Solvent	Dielectric const, ϵ (at 34°)	$[(C_4H_9)_3NCH_3][(C_6H_5)_3PCoBr_3]^b$		$[(C_4H_9)_4N][(C_6H_5)_3PCoBr_3]^a$	
		$\Delta\nu_p$, Hz	K_{as}, M^{-1}	$\Delta\nu_p,^d$ Hz	K_{as}, M^{-1}
Propylene carbonate	63.0	167 ± 4^c	1.00 ± 0.05		
		174 ± 6^e		170 ± 25	0.85 ± 0.15
Nitrobenzene	33.3	257 ± 7^c	38.1 ± 2.3		
		226 ± 4^d	36.0 ± 1.6	265 ± 15	17.9 ± 1.4

^{a} Results taken from ref 5. ^{b} Results obtained from this work; errors estimated statistically from a plot of $\Delta\nu_p$ *vs.* K_{as}^{-1} (95% confidence level). ^{c} $\Delta\nu_p$ for N-CH$_3$ protons. ^{d} $\Delta\nu_p$ for N-CH$_2$ protons. ^{e} $\Delta\nu_p$ for N-CH$_2$ protons obtained by substituting K_{as} and observed $\Delta\nu_o$ for N-CH$_2$ protons in eq 2.

Table II. Equilibrium Constant Data in Various Solvents

| Solvent	Concn, M	$\Delta\nu_H$, Hz Obsd^a (±2.0 Hz)	Calcd	Solvent	Concn, M	$\Delta\nu_H$, Hz Obsd^a (±2.0 Hz)	Calcd
Nitrobenzene	0.010	59.0^b	58.3	Propylene carbonate	0.061	9.0^b	9.1
	0.014	71.5	71.3		0.101	14.0	14.1
	0.020	84.5	86.2		0.199	24.0	24.2
	0.030	105.0	103.9		0.347	35.5	35.7
	0.040	116.0	116.5		0.499	47.5	44.6
	0.059	132.0	133.2	Chloroform	0.060	745^b	
	0.693	230 (±20)^c	212		0.100	669	
Nitrobenzene	0.010	50.0^d	49.6		0.150	587	
	0.014	61.5	60.8		0.300	433	
	0.020	74.0	73.8		0.500	341	
	0.030	87.5	89.3	Chloroform	0.060	450^d	
	0.040	99.5	100.4		0.100	400	
	0.059	115.0	115.2		0.150	365	
	0.081	127.0	126.8		0.300	296	
	0.101	137.0	134.5		0.500	243	
	0.148	145.0	147.0				

^{a} The diamagnetic reference compound used is $[(C_4H_9)_3NCH_3][(C_6H_5)_3PZnBr_3]$. ^{b} For the N-CH$_3$ group. ^{c} Estimated from the shoulder of the broad peak and was not used in the calculation of K_{as}. ^{d} For the N-CH$_2$ group.

propylene carbonate. Equation 2 has two unknowns, K_{as}^{-1} and $\Delta\nu_p$, which are determined by the method of Rose–Drago plots.[8]

Results and Discussion

The visible spectra of the various solutions were recorded to show that the complex anion remains intact in solution. Since a similar system has already been fully reported,[5] there is no need to discuss it further here.

The nmr spectra of the paramagnetic Co(II) complex were obtained at various concentrations in chloroform, nitrobenzene, and propylene carbonate and the N-methyl and N-methylene proton frequencies measured relative to tetramethylsilane. The spectral assignments were made according to methods previously described[9-11] and the numbering system

$$C\overset{+}{-}N-(C-C-C-C)_3$$
$$\qquad 1\ 2\ 3\ 4$$
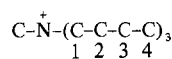
is used.

In the diamagnetic Zn(II) complex, we found that the relative position of the N-methyl and N-methylene peaks is independent of the nature of the solvents; *viz.* ν_{CH_2} is further downfield than ν_{CH_3} for all three solvents (compare with reference 9). For the paramagnetic Co(II) complex, the observed isotropic shifts at various concentrations for N-methyl and N-methylene protons were as shown in Figure 1. The trend is the same as that reported previously.[5]

The results of the calculation of K_{as} and $\Delta\nu_p$ are tabulated in Table I. It can be seen that the K_{as} values for nitrobenzene using either N-CH$_2$ or N-CH$_3$ shifts gave K_{as} values which
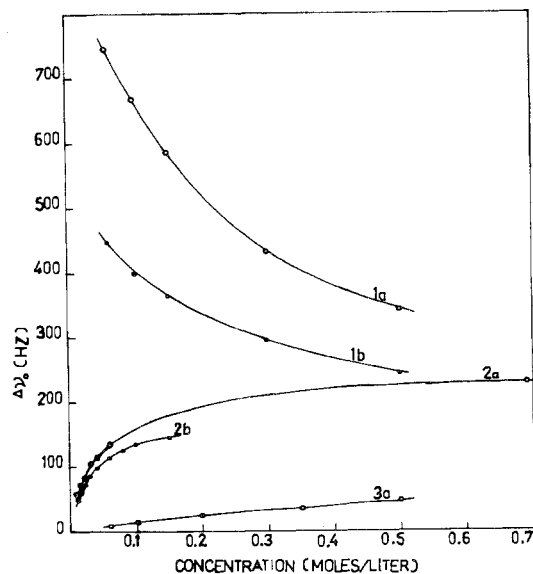

Figure 1. Concentration dependence of the observed shift $(\Delta\nu_o)$ of $[(n\text{-}C_4H_9)_3NCH_3][(C_6H_5)_3PCoBr_3]$ in various solvents: 1, chloroform; 2, nitrobenzene; 3, propylene carbonate; a and b stand for the N-CH$_3$ and N-CH$_2$ shifts, respectively.

agree within the limit of experimental error.[12] Therefore, the observed N-CH$_3$ shifts were used for the evaluation of K_{as} in propylene carbonate as its peak was much sharper. The reliability of the $\Delta\nu_p$ and K_{as} values was tested by comparing the observed values of $\Delta\nu_o$ with those calculated from $\Delta\nu_p$ and K_{as} (Table II). No attempt was made to fit the equilibrium constant data to a 1:1 expression in chloroform as in

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this low dielectric constant solvent, extensive ionic clustering occurs and the 1:1 equilibrium no longer exists as was found previously.[5]

Comparing the K_{as} and $\Delta\nu_p$ values of our unsymmetrical methyltributylammonium cation with those of the symmetrical tetrabutylammonium cation in nitrobenzene and propylene carbonate (see Table I), we find that although $\Delta\nu_p$ values are comparable for the N-methylene protons, the value of K_{as} of the former complex is twice the latter in nitrobenzene. This shows that the association constant increases with the decrease in size of the cation. This is in agreement with the results reported by Evans, *et al.*,[13] based on their conductance measurements of the symmetrical tetraalkylammonium halides and picrates in acetonitrile.

In the interpretation of the isotropic shift $\Delta\nu_p$ for ion-paired systems, it is now established that $\Delta\nu_p$ arises from the contact and pseudocontact interactions. Thus, for a given proton i

$$(\Delta\nu_p)_i = (\Delta\nu_c)_i + (\Delta\nu_{dip})_i \tag{3}$$

where

$$(\Delta\nu_c/\nu_o)_i = -Ag_{av}\beta_e S(S+1)/3g_n\beta_n kT \tag{4}$$

and

$$(\Delta\nu_{dip}/\nu_o)_i = DF(\chi_{\parallel}, \chi_{\perp})[(3\cos^2\theta_i - 1)/R_i^3] \tag{5}$$

Here, $\Delta\nu$ is the shift in hertz, ν_o is the probe frequency, g_{av} is the average g value for the complex being considered, g_n is the nuclear g value, A is the electron–nuclear hyperfine coupling constant, $\chi_{\parallel}$ and $\chi_{\perp}$ are the parallel and perpendicular components of the magnetic susceptibility tensor, D is a function of temperature, θ is the angle between the C_3 axis and the radius vector from the metal to the resonating proton, and R_i is the length of this radius vector. Walker, *et al.*,[14] on the basis of La Mar's model,[10] have shown that for the H_i proton in an axially symmetric system

$$\langle(3\cos^2\theta - 1)/R^3\rangle_{av} = 2/a^3 \tag{6}$$

where a is the distance between centers in the ion pair, and that this value is independent of the proton considered; *i.e.*, it is the same for H(1), H(2), H(3), and H(4). Though in nitrobenzene the H(4) chemical shift is found to shift by as much as 10% of the observed isotropic shift for H(1), we cannot use the H(4) shift as an estimate of pseudocontact shift as one might have thought, simply because the estimate is made possible only with the following assumptions: (1) La Mar's model of ion pairing is valid, (2) the hydrogen bonding to the anion occurs *via* N-methylene protons, and (3) spin delocalization in σ systems proceeds with attenuation as the number of bonds separating the spin center from the resonating protons increases. Though the second assumption seems plausible and the third has been verified experimentally to be true,[15] the first is questionable because of its over-simplified assumption of free rotation of the carbon–carbon bond of the butyl chains.[16] In short, we do not have any means of estimating the relative contribution of pseudocontact and contact shift to the total isotropic shift.

In spite of the shortcoming discussed above, the conclusion

on the relative interionic distance in various solvents is not affected. From eq 6, the pseudocontact contribution should decrease with increase in interionic distance, and the contact contribution is also expected to fall off as the interionic distance increases because of the decrease in the overlap integral. Therefore, as shown in Table I since $\Delta\nu_p$ in propylene carbonate is smaller than that in nitrobenzene, the interionic distance of the ion pair is larger in propylene carbonate than in nitrobenzene. In chloroform, clusters or micelles are formed, and as the solution is diluted, the clusters become smaller.[17] At infinite dilution, simple ion pairs are expected to be the predominant species in the solution. Thus, the observed isotropic shift, $\Delta\nu_o$, at infinitely low concentrations, should give a good estimate of the relative interionic distance of the ion pair in chloroform. The very large $\Delta\nu_o$ values obtained show that in chloroform, the interionic distance is smaller than that in nitrobenzene which therefore agrees with the general trend of increasing interionic distance as the dielectric constant of the solvent increases.[5]

The resonance signals of the paramagnetic Co(II) complex in chloroform were well resolved. For 0.150 M solution, the peaks at -40, -3, 61, 165, 196, and 398 Hz were assigned to H(4), H(3), H(2), H(1), ortho H, and N-CH$_3$, respectively, by varying the ratio of the paramagnetic anion to the diamagnetic anion while keeping the overall cation concentration constant. It is of interest to note that the observed N-CH$_3$ shift (with reference to the diamagnetic analog) is much greater than that of the N-CH$_2$ shift, the difference being as much as 222 Hz at 0.15 M concentration. The nmr signal is also much broader for the N-methyl protons. Now, in a low dielectric constant solvent such as chloroform, it is expected that micelle formation occurs to a considerable extent and our nmr result indicates that in the clusters, the methyl group is situated in a position where the methyl protons are under greater influence of the paramagnetic anion than the other three sets of N-methylene protons. It can therefore be concluded that in the ionic clusters, the quaternary ammonium ion orients itself in such a way that the N-CH$_3$ group is nearer to the anion than the other three sets of N-CH$_2$ protons. This kind of configuration is sterically favored. In nitrobenzene and *o*-dichlorobenzene (this solvent, with a dielectric constant of 9.74 at 29°, was used to confirm the trend further) it was also found that the N-CH$_3$ peak shifts more than the N-CH$_2$ peak though the difference is not as great as in chloroform. This result is in conflict with that reported recently by Walker, *et al.*,[2] on the study of some unsymmetrically substituted quaternary ammonium salts (2:1 electrolytes). We attribute this discrepancy to the difference in the geometrical configuration of the ion pairs. It should be noted that the shift difference between the observed isotropic shifts of N-CH$_3$ and N-CH$_2$ protons increases with decrease in the dielectric constant of the solvent and that in propylene carbonate, a relatively high dielectric constant solvent, the shift difference is no longer detectable. This is reasonable in view of the earlier conclusion that the interionic distance increases with increase in dielectric constant of the solvent. In low dielectric constant solvent, such as chloroform, the interionic distance is so short (relative to that in propylene carbonate) that it hinders free rotation of the cation, and as a result, there is a preferred orientation of the N-CH$_3$ group toward the complex anion. As dielectric constant increases, interionic distance increases and the cation becomes freer until finally there is a complete free

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tumbling of the cation with respect to the anion, as might have occurred in propylene carbonate.

Recently, there has been considerable controversy[18,19] over the necessity of using activity coefficients in the evaluation of equilibrium constants by spectrophotometric means for 1:1 association. For our system, we have attempted to introduce activity coefficients in the evaluation of K_{as} by a detailed analysis analogous to that reported by Larson.[20] By using activity terms instead of concentration units, eq 2 would become

$$K_{as}^{-1} = \left(\frac{\Delta\nu_p}{\Delta\nu_o} + \frac{\Delta\nu_o}{\Delta\nu_p} - 2 \right) C\gamma_{\pm}^2 \qquad (7)$$

where $\gamma_{\pm}$, the mean activity coefficient, can be estimated by the extended Debye-Huckel equation, *i.e.*

$$\log\gamma_{\pm} = \frac{-A\sqrt{(1-\alpha)C}}{1 + aB\sqrt{(1-\alpha)C}} + b(1-\alpha)C \qquad (8)$$

where $A = (1.824 \times 10^6)[1/(\epsilon T)^{3/2}]$, $B = (50.29 \times 10^8)[1/(\epsilon T)^{1/2}]$, α is the degree of association, and C is the molar concentration. By varying a from 3.8 to 10.0 Å and b from 0.1 to 0.4, K_{as} and $\Delta\nu_p$ can be obtained by the method of Rose-Drago plots. From the plots, we find that the introduction of activity coefficients did not give a better fit to the data as compared to the fit obtained by using concentration units. Our result which, in effect, shows that $\gamma_{\pm}$ is a constant or unity at various concentrations, gives further support to the findings of Drago, *et al.*,[5,18,21] that one should not indiscriminantly correct any one of the species in the equilibrium with activity coefficients.

Registry No. [(*n*-C₄H₉)₃NCH₃][(C₆H₅)₃PCoBr₃], 40544-51-2; [(*n*-C₄H₉)₃NCH₃][(C₆H₅)₃PZnBr₃], 40544-52-3.

Acknowledgment. The authors wish to thank Mr. Richard Quah Boon Hock for technical assistance.

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## Intramolecular Oxidation-Reduction Isomerism in (P(C₆H₅)₃)₂(CO)ClIr(SnCl₄)

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Many types of isomerism are known for metal coordination complexes,[1] but intramolecular oxidation-reduction isomerisms involving formal oxidation state changes at the metal are unusual. High-energy redox isomers are often accessible by photochemical, thermal, or chemical means, but they are usually short-lived and often reactive (*e.g.*, transient metal-ligand charge-transfer excited states). Ex-
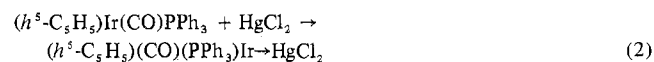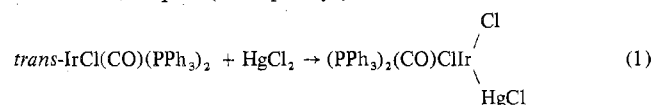
(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 13.

amples where two formal oxidation states are in measurable equilibrium under mild conditions are most uncommon. Collman, Farnham, and Dolcetti have reported such a case in cobalt-nitrosyl chemistry, wherein an equilibrium apparently exists between a trigonal-bipyramidal cobalt(I) complex with a linear nitrosyl (NO⁺) and a square-pyramidal cobalt(III) complex with a bent nitrosyl (NO⁻).[2]
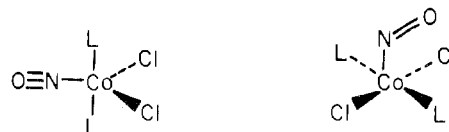
L = tertiary alky or aryl phosphine

An equally promising area in which to search for redox isomerism is in the reactions between d⁸ complexes and HgX₂ or SnX₄ (X is a halogen). Two limiting kinds of products are obtained from these reactions, arising either from oxidative addition,[3] eq 1,[4] or from donor-adduct formation,[5] eq 2[6] (Ph = phenyl).

$$\text{trans-IrCl(CO)(PPh}_3)_2 + \text{HgCl}_2 \rightarrow (\text{PPh}_3)_2(\text{CO})\text{ClIr}\begin{smallmatrix}\text{Cl}\\ \diagup\\ \diagdown\\ \text{HgCl}\end{smallmatrix} \qquad (1)$$

$$(h^5\text{-C}_5\text{H}_5)\text{Ir(CO)PPh}_3 + \text{HgCl}_2 \rightarrow$$
$$(h^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{Ir}\rightarrow\text{HgCl}_2 \qquad (2)$$

We find that both SnCl₄ and CH₃SnCl₃ react rapidly with *trans*-IrCl(CO)(PPh₃)₂ giving well-defined samples of (PPh₃)₂(CO)ClIr(SnCl₄) and (PPh₃)₂(CO)ClIr(CH₃SnCl₃). From the available infrared and pmr data, both samples consist of two rapidly interconverting isomers, and the most likely form of isomerism is an oxidation-reduction isomerism.

Experimental Section

Materials. Reagent grade methylene chloride and benzene were dried over molecular sieves before use. All other solvents were reagent or spectral grade and were used without further purification. Stannic chloride (J. T. Baker) was distilled under a dry nitrogen atmosphere prior to use. Crystalline trichloromethyltin(IV) was obtained from Alfa Inorganics and was used without further purification. Tetraethylammonium chloride (Aldrich) was dried over P₄O₁₀, *in vacuo*. Commercial iridium trichloride was obtained from Engelhard Industries. Other chemicals were readily available commercially. The following complexes were prepared by literature methods: *trans*-IrCl(CO)(PPh₃)₂,[7] IrCl₂(CO)(HgCl)(PPh₃)₂,[4] and IrCl₂(SnCl₃)(CO)(PPh₃).[8]

Preparation of Complexes. All complexes were prepared in a dry (over P₄O₁₀) glove bag, under an atmosphere of nitrogen. This was done as a safety factor. The two tin complexes are basically very stable in the solid state. In solution, there is little, if any, danger of aerial oxidation. However, these complexes are water sensitive in solution and may be subject to photolysis. Therefore, they were handled for only short periods of time in solution in the open air.

[P(C₆H₅)₃]₂(CO)ClIr(SnCl₄). Stannic chloride (2 ml, 18 mmol) was added to *trans*-IrCl(CO)(PPh₃)₂ (0.5 g, 0.64 mmol) in a 25-ml erlenmeyer flask. The mixture was stirred at room temperature for 20 min, during which time the color changed from bright yellow to

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