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. $[(n\text{-}C_4H_9)_3NCH_3][(C_6H_5)_3PCoBr_3]$, 40544-51-2; $[(n\text{-}C_4H_9)_3NCH_3][(C_6H_5)_3PZnBr_3]$, 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 $(P(C_6H_5)_3)_2(CO)ClIr(SnCl_4)$

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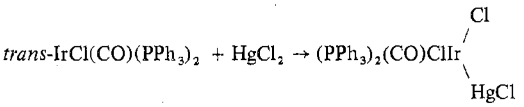
Many types of isomerism are known for metal coordination complexes,[1] but intramolecular oxidation–reduction isomerisms involving formal oxidation state changes at the metal are unusual. High-energy redox isomers are often accessible by photochemical, thermal, or chemical means, but they are usually short-lived and often reactive (*e.g.*, transient metal–ligand charge-transfer excited states). Examples 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 d^8 complexes and HgX_2 or SnX_4 (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).



$$trans\text{-}IrCl(CO)(PPh_3)_2 + HgCl_2 \rightarrow (PPh_3)_2(CO)ClIr\begin{smallmatrix}\diagup Cl\\ \diagdown HgCl\end{smallmatrix} \qquad (1)$$

$$(h^5\text{-}C_5H_5)Ir(CO)PPh_3 + HgCl_2 \rightarrow (h^5\text{-}C_5H_5)(CO)(PPh_3)Ir\rightarrow HgCl_2 \qquad (2)$$

We find that both $SnCl_4$ and CH_3SnCl_3 react rapidly with *trans*-$IrCl(CO)(PPh_3)_2$ giving well-defined samples of $(PPh_3)_2(CO)ClIr(SnCl_4)$ and $(PPh_3)_2(CO)ClIr(CH_3SnCl_3)$. 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 P_4O_{10}, *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*-$IrCl(CO)(PPh_3)_2$,[7] $IrCl_2(CO)(HgCl)(PPh_3)_2$,[4] and $IrCl_2(SnCl_3)(CO)(PPh_3)$.[8]

Preparation of Complexes. All complexes were prepared in a dry (over P_4O_{10}) 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.

$[P(C_6H_5)_3]_2(CO)ClIr(SnCl_4)$. Stannic chloride (2 ml, 18 mmol) was added to *trans*-$IrCl(CO)(PPh_3)_2$ (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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pale yellow. The crude yellow product which separated was washed onto a frit with several portions of pentane and dried by suction. Recrystallization from methylene chloride-pentane and drying, *in vacuo*, for 12 hr gave a pale yellow powder (64% yield), mp 234-236°. *Anal.* Calcd for $IrC_{37}H_{30}P_2SnCl_5O$: C, 42.67; H, 2.88; Cl, 17.06; Sn, 11.44; mol wt 1040.5. Found: C, 41.92; H, 2.96; Cl, 17.61; Sn, 12.18; mol wt (1% in CH_2Cl_2) 975.

$[P(C_6H_5)_3]_2(CO)ClIr[Sn(CH_3)Cl_3]$. A CCl_4 solution of excess trichloromethyltin(IV) was added to solid $IrCl(CO)(PPh_3)_2$ (0.3 g, 0.38 mmol). The solution was stirred at room temperature until the bright yellow solution had become nearly colorless (20 min). The off-white solid was collected by suction filtration, washed with CCl_4 and pentane, and dried, *in vacuo*, for 16 hr. *Anal.* Calcd for $IrC_{38}H_{33}P_2SnCl_4O$: C, 44.71; H, 3.24; Cl, 13.92. Found: C, 45.08; H, 3.35; Cl, 14.04.

Reactions of Complexes. Solutions of both tin complexes in methylene chloride were treated with chlorine gas, hydrogen chloride gas, solid tetraethylammonium chloride, and dilute sodium bicarbonate in water. These reactions were carried out at room temperature, and their progress was followed by solution ir spectra. The solvent was removed and non-iridium-containing compounds were extracted with warm ethanol. All solid products were isolated and identified by melting point and ir and pmr spectra.

Physical Measurements. Infrared spectra (4000–550 cm^{-1}) were obtained using a Perkin-Elmer Model 421 dual grating spectrophotometer and a Digilab FTS-14 fourier transform infrared spectrometer. Far-infrared spectra (600–200 cm^{-1}) were run as Nujol mulls on a Beckman IR-12 spectrometer. Nuclear magnetic resonance spectra were recorded on a Jeolco C-60 HL high-resolution spectrometer. Melting points were determined using a Fisher-Johns melting point apparatus. Molecular weights were determined in methylene chloride using a Hewlett-Packard Model 302B vapor pressure osmometer. Conductivities were measured in acetone using an Industrial Instruments Inc. conductivity bridge, Model RC-16B1.

Analyses. Carbon, hydrogen, and chlorine analyses were determined by Galbraith Laboratories Inc., Knoxville, Tenn. 37921. Tin analyses were determined by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, N. Y. 11377.

Results and Discussion

Physical Properties. The complex $(PPh_3)_2(CO)ClIr(SnCl_4)$ forms rapidly when *trans*-$IrCl(CO)(PPh_3)_2$ and $SnCl_4$ are mixed, either neat or in benzene or CCl_4 solution, eq 3.

$$\textit{trans}\text{-}IrCl(CO)(PPh_3)_2 + SnCl_4 \rightarrow \underset{\text{I}}{(PPh_3)_2(CO)ClIr(SnCl_4)} \qquad (3)$$

From molecular weight and conductivity studies, in dichloromethane and acetone, respectively, the complex is monomeric and nonionic in solution. The infrared spectrum of this complex shows two carbonyl stretching vibrations, both in the solid state and in solution (Table I). The relative intensities of the two bands are independent of concentration in methylene chloride over the concentration range 1.6×10^{-2} to 1.1×10^{-3} *M*. There is no evidence for the appearance of *trans*-$IrCl(CO)(PPh_3)_2$ (ν(CO) 1967 cm^{-1} in $CHCl_3$) in acetone, tetrahydrofuran, chloroform, dichloromethane, or 1,2-dichloroethane.

The infrared and molecular weight data demonstrate that neither dimerization nor loss of $SnCl_4$ occurs to an appreciable extent in solution and that the origin of the two ν(CO) bands is an isomerism. The complexity of the far-ir spectrum in the M-Cl stretching region also supports the presence of more than one isomer of I.

The relative intensities of the two ν(CO) bands vary with solvent (see Figure 1). Attempts to separate isomers by fractional crystallization or column chromatography have been unsuccessful, and all indications are that the isomers are rapidly interconverted, even in the solid state. The solid-state infrared spectrum (in Nujol) of a sample which had been melted (at ~240°) and rapidly cooled was identical with the initial spectrum. Also, the relative intensities of the two ν(CO) bands in the solid state are independent of the solvent from which I is precipitated, even though the relative intensities are solvent dependent.

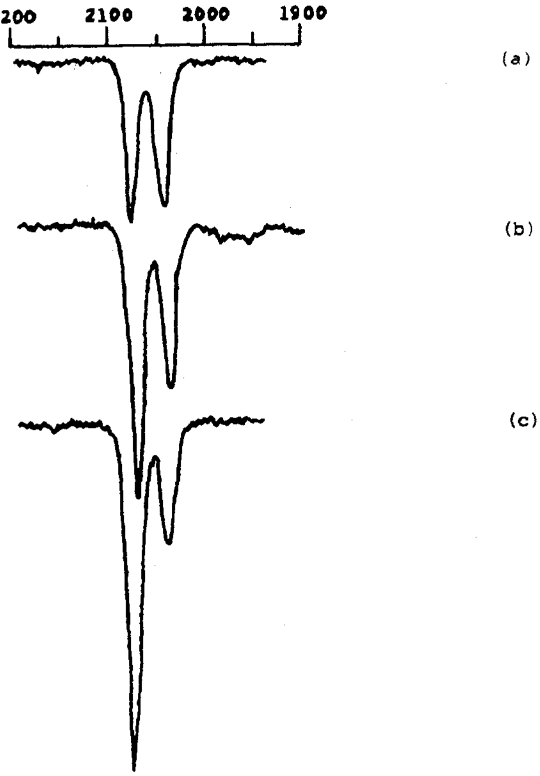


Figure 1. Infrared spectra in carbonyl stretching region for $(Ph_3P)_2(CO)ClIr(SnCl_4)$ in (a) $ClCH_2CH_2Cl$, (b) CH_2Cl_2, and (c) $CHCl_3$. Carbonyl stretching frequencies (cm^{-1}): (a) 2078, 2041; (b) 2079, 2040; (c) 2080, 2041.

In an attempt to measure the rate of interconversion of the isomers, we have prepared the complex $(PPh_3)_2(CO)ClIr[Sn(CH_3)Cl_3]$, eq 4. Complex II also has two carbonyl

$$\textit{trans}\text{-}IrCl(CO)(PPh_3)_2 + CH_3SnCl_3 \rightarrow \underset{\text{II}}{(PPh_3)_2(CO)ClIr[Sn(CH_3)Cl_3]} \qquad (4)$$

stretching vibrations both in the solid state and in solution (Table I) in approximately the same positions as for I. However, the exact positions of these two bands and their relative intensities are different from the values found for I.

The pmr spectrum of II has a single methyl resonance (τ 8.90 in $CDCl_3$ at 25°) from +25 to −50°. Assuming that the two isomeric forms of II are equally populated and have a difference in intrinsic $\tau(CH_3)$ values of 0.2 ppm and that the interconversion between isomers is an intramolecular process, we estimate that, for the isomerization in $CDCl_3$ solution, $t_{1/2} < 1 \times 10^{-3}$ sec at −50°.

If free CH_3SnCl_3 is added to solutions of II in $CDCl_3$, distinct methyl resonances are observed for bound ($\tau(CH_3)$ 8.90) and free ($\tau(CH_3)$ 8.33) CH_3SnCl_3, at temperatures up to 60°. Assuming that intermolecular exchange between bound and free CH_3SnCl_3 is first order in both CH_3SnCl_3 and II, eq 5, we estimate that, for exchange, $t_{1/2} \gg 5 \times 10^{-2}$

$$CH_3{}^*SnCl_3 + (PPh_3)_2(CO)ClIr(CH_3SnCl_3) \rightarrow (PPh_3)_2(CO)ClIr(CH_3{}^*SnCl_3) + CH_3SnCl_3 \qquad (5)$$

sec at 60°.

Solutions of CH_3SnCl_3 in CCl_4 and $CDCl_3$ exhibit $^{117,119}Sn-CH_3$ coupling constants ($J_{Sn^{117}-CH_3} = 94$ Hz, $J_{Sn^{119}-CH_3} =$

Table I. Characteristic Infrared Bands[a]

Complex	ν(CO), cm^{-1}	ν(M-Cl),[b] cm^{-1}
trans-IrCl(CO)-(PPh$_3$)$_2$	1967[c]	316 m
(PPh$_3$)$_2$(CO)-ClIr(SnCl$_4$)	2080, 2020[b]	355 s, 343 s, 332 m, 316 m,
	2080, 2041[c]	294 m
(PPh$_3$)$_2$(CO)-ClIr(CH$_3$SnCl$_3$)	2074, 2034[c]	
IrCl(SnCl$_3$)-(CO)(PPh$_3$)	2077, 2072[b]	357 sh, 355 vs, 351 sh, 308 vw
(PPh$_3$)$_2$(CO)-Cl$_2$Ir(HgCl)	2030[b]	320 m, 295 m, 270 s, 229 w

[a] Abbreviations: very strong, vs; strong, s; medium, m; weak, w; very weak, vw; shoulder, sh. [b] As Nujol mulls. [c] In CHCl$_3$ solution.

98 Hz) in agreement with the values reported in the literature.[9] Compound II in CDCl$_3$ displays tin satellites for the methyl resonance with $J_{\mathrm{Sn}^{117}-\mathrm{CH}_3} = 55$ Hz and $J_{\mathrm{Sn}^{119}-\mathrm{CH}_3} = 58$ Hz. No change is observed in the satellite resonances with changes in temperature or upon mixing solutions of II with excess CH$_3$SnCl$_3$. The tin-methyl coupling constant of CH$_3$SnCl$_3$ is reduced approximately 40% upon complexation with *trans*-IrCl(CO)(PPh$_3$)$_2$. The structural implications of this change are not clear since tin-proton coupling constants for organotin halides are not easily correlated with the % s character in tin-carbon bonds.[10]

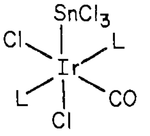
Chemical Properties. Tetrachlorotin(IV) is firmly bound in (PPh$_3$)$_2$(CO)ClIr(SnCl$_4$). A solid sample was heated at 100° under high vacuum for 12 hr with no noticeable loss of SnCl$_4$. In methylene chloride at room temperature, the complex does not react with chlorine or gaseous HCl. This is strong evidence for the fact that there is very little, if any, dissociation of I into free Vaska's compound and SnCl$_4$. However, addition of chloride ion or slightly basic water to methylene chloride solutions of I causes decomposition of I into *trans*-IrCl(CO)(PPh$_3$)$_2$ and coordinately saturated tin(IV) compounds, eq 6 and 7. The CH$_3$SnCl$_3$ complex,

$$\mathrm{(PPh_3)_2(CO)ClIr(SnCl_4)} + 2[\mathrm{(C_2H_5)_4N}]\mathrm{Cl} \rightarrow \textit{trans}\text{-}\mathrm{IrCl(CO)(PPh_3)_2} + [\mathrm{N(C_2H_5)_4}]_2\mathrm{(SnCl_6)} \qquad (6)$$

$$\mathrm{(PPh_3)_2(CO)ClIr(SnCl_4)} \xrightarrow{\mathrm{H_2O}} \textit{trans}\text{-}\mathrm{IrCl(CO)(PPh_3)_2} + \mathrm{SnO_2 \cdot \mathit{x}H_2O} + 4\mathrm{Cl^-} \qquad (7)$$

II, undergoes similar reactions, but at a noticeably slower rate.

Nature of the Isomerism. Because of the nature of the products of reactions like (1) and (2), there are several possible explanations for the isomerism observed in (PPh$_3$)$_2$(CO)-ClIr(SnCl$_4$), as discussed below. Of the various possibilities, most are unlikely when the physical and chemical properties of I are considered.



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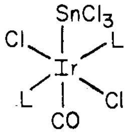

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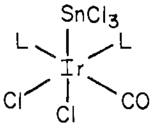

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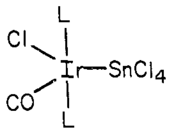

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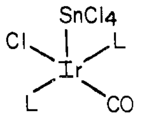

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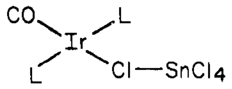

VIII

1. Oxidative Addition Isomers with SnCl$_3$ Cis or Trans to CO. This type of isomerism (*e.g.*, III ⇄ IV) is unlikely for several reasons. Iridium(III) complexes are known to be substitution inert, and yet the isomers observed here undergo rapid interconversion and react rapidly with Cl$^-$ giving SnCl$_6{}^{2-}$, eq 6. The trans isomer, IV, should give the higher frequency ν(CO), because of π-bonding effects, and should not be the dominant isomer, because of the thermodynamic trans effect. However, in I the high-frequency band always has the greatest relative intensity; see Figure 1. The observed difference in ν(CO) values ($\Delta\nu$(CO) = 60 cm^{-1}) is higher than might be expected for a cis-trans isomerism.[11] The far-ir spectrum of IrCl$_2$(CO)(SnCl$_3$)-(PPh$_3$), prepared by heating *trans*-IrCl(CO)(PPh$_3$)$_2$ at reflux in SnCl$_4$ for 16 hr,[8] has a strong ν(Sn-Cl) stretch at 355 cm^{-1}, with shoulders at 357 and 351 cm^{-1}. The far-ir spectrum of I is much more complex.

Cis-trans isomerisms with regard to the phosphine groups (III ⇄ V) are even less likely, in light of the chemical and infrared properties of I, and the known tendency of bis(triphenylphosphine) complexes of iridium to adopt structures in which the PPh$_3$ groups are mutually trans.[12]

2. Five-Coordinate Donor-Adduct Isomers. An isomerism involving trigonal-bipyramidal and square-pyramidal isomers (VI ⇄ VII) is improbable because of the high ν(CO) value for one of the isomers, indicative of oxidative addition,[13] the large $\Delta\nu$(CO) value, and the complexity of the far-ir spectrum of I.

3. SnCl$_4$ Bound to Iridium or to a Ligand. Stannic chloride is not bound to CO, because the shifts in ν(CO) upon complexation are in the wrong direction.[14] There is precedence, in other systems, for Lewis acids bound to complexed CO[14] or complexed Cl$^-$,[15] but the large positive shifts in ν(CO) indicate clearly that there is a direct interaction between tin and iridium in both isomers of I.[13]

4. Oxidative Addition or Donor-Adduct Formation. All of the available data are consistent with an isomerism arising from rapidly equilibrating oxidative addition and donor-adduct isomers (III ⇄ VII). For the oxidative addition isomer, the ν(CO) stretch at 2080 cm^{-1} is consistent with values found for related complexes of iridium(III) including IrCl$_3$(CO)(PPh$_3$)$_2$ (2079 cm^{-1} in CHCl$_3$)[13] and IrCl$_2$(SnCl$_3$)-(CO)(PPh$_3$) (2077, 2072 cm^{-1} in Nujol mull).[8] The assignment of the ν(CO) band at 2020 cm^{-1} to a donor-adduct isomer is consistent with values found for other adducts including the SO$_2$ complex, (PPh$_3$)$_2$(CO)ClIr(SO$_2$) (2021 cm^{-1} in CHCl$_3$).[13] The complexity of the far-ir spectrum of I in the Sn-Cl stretching region (Table I) is also consistent with the presence of isomers in which SnCl$_4$ is present in more than one chemical form. For comparison, Table I gives ν(Sn-Cl) bands for IrCl$_2$(CO)(SnCl$_3$)(PPh$_3$) which apparently

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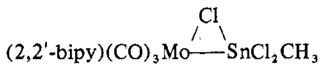
contains $SnCl_3^-$. A donor-adduct complex of $SnCl_4$, ((1,5-cyclooctadiene)RhCl)$_2$·2$SnCl_4$, has been prepared and found to have a strong ν(Sn–Cl) band at 313 cm^{-1} (Nujol mull).[16]

There is precedence for the reaction between I and Cl^-, eq 6, if it is assumed that the donor-adduct isomer is the reactive form.[5,16,17] Although an oxidative addition isomer is not expected to react with Cl^-, it will participate in the net reaction if it is in rapid equilibrium with a reactive, donor-adduct isomer. The evidence for a rapid interconversion between isomers had been given above. It should also be noted that if less than stoichiometric amounts of Cl^- are added to solutions of I in dichloromethane, ν(CO) for *trans*-IrCl(CO)(PPh$_3$)$_2$ appears and the intensities of *both* ν(CO) bands for I decrease.

The structural details of the donor-adduct isomer may resemble the simple metal–metal interaction found in (h^5-C_5H_5)(CO)$_2$Co·HgCl$_2$[18] or the halide-bridged structure found, for example, in[19]



$$(2,2'\text{-bipy})(CO)_3Mo\overset{Cl}{\frown}SnCl_2CH_3$$

Unfortunately, we have been unable to grow suitable crystals for an X-ray diffraction study.

Discussion of the Isomerism. Kinetic[20,21] and synthetic[5,22,23] evidence is available which indicates that reactions between metal complexes and HgX_2 or SnX_4 may proceed in a stepwise fashion, with the first step involving donor-adduct formation and the second, oxidation, *e.g.*, eq 8.[24] In

$$(h^5\text{-}C_5H_5)Rh(CO)_2 + SnCl_4 \rightarrow (h^5\text{-}C_5H_5)(CO)_2Rh(SnCl_4) \rightarrow (h^5\text{-}C_5H_5)(CO)ClRh(SnCl_3) + CO \quad (8)$$

most reactions, either the donor-adduct or the oxidized form is favored energetically, and a single product is obtained. In net oxidation reactions, it appears that either step can be rate limiting.[20,21,25]

The case reported here is unusual in that donor–adduct and oxidative addition isomers appear to be in measurable equilibrium both in solution and in the solid state. The energetics relating the two isomers are clearly closely balanced, as evidenced by the solvent dependence of the equilibrium. A closely related isomerism may exist in complexes like (bipy)(CO)$_3$Mo(SnCl$_4$), where the likely isomers are chloride bridged, previously shown, and nonbridged (bipy)(CO)$_3$ClMo(SnCl$_3$) oxidative elimination products.[19,25]

The existence of rapidly equilibrating intramolecular redox isomers in (PPh$_3$)$_2$(CO)ClIr(SnCl$_4$) may have important implications for the formulation of the products of reactions between metal complexes and HgX_2 and SnX_4 and for an understanding of the factors important in the microscopic reverse of oxidative addition, reductive elimination.

Registry No. *trans*-IrCl(CO)(PPh$_3$)$_2$, 15318-31-7; (PPh$_3$)$_2$(CO)ClIr(SnCl$_4$), 40813-53-4; (PPh$_3$)$_2$(CO)ClIr(SnCl$_4$), 39310-35-5; (PPh$_3$)$_2$(CO)ClIr(CH$_3$SnCl$_3$), 39310-36-6; IrCl(SnCl$_3$)(CO)(PPh$_3$), 40903-18-2; (PPh$_3$)$_2$(CO)Cl$_2$Ir(HgCl), 14515-76-

Acknowledgments. Acknowledgments are made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Materials Research Center, University of North Carolina, under Grant GH 33632 for support of this research.

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Preparation and Properties of Nonaborane(13) Carbonyl[1]

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In the thermal decomposition of borane carbonyls such as BH_3CO and B_4H_8CO, carbon monoxide and the parent borane fragments are formed initially.[2-7] Carbon monoxide is a weak nucleophile and has little effect on subsequent reactions. This fact makes borane carbonyls useful precursors to study the chemistry of reactive borane fragments such as ligand exchange reactions, hydrogenation, and hydroboration.[8-13] In addition, they may be precursors of some less stable boranes.

As a promising source of a B_9H_{13} fragment we wish to report the preparation of $B_9H_{13}CO$. This compound is formed when *i*-B_9H_{15} is decomposed at −30° in pentane solution under 25 atm of CO. In a typical reaction *i*-B_9H_{15} was prepared by refluxing 2.26 g of KB_9H_{14} with liquid hydrogen chloride in a 200-ml heavy-walled flask equipped with a break-off tip.[14,15] Unreacted hydrogen chloride was distilled from the flask at −78° and the last traces were pumped off under high vacuum. Dried *n*-pentane, 100 ml, and about a tenfold excess of CO were condensed into the reaction flask at −196°. The amount of CO was controlled such that 30 atm of pressure would not be exceeded if the sample was accidently warmed to room temperature. The

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