The Reaction of $Cl_3SnCo(CO)_4$ with Group 5 Donor Ligands; Evidence for a Novel Radical Chain Process[1]

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Abstract: The reaction of $Cl_3SnCo(CO)_4$ with tributylphosphine, triphenylphosphine, or triphenylarsine, B, results in the formation of the ionic compound, $[Co(CO)_3B_2][SnCl_3]$, as product. The reaction was found to be sensitized by light and inhibited by oxygen or other inhibitors of free radical chain processes. The reaction rate shows a three-halves order dependence on $Cl_3SnCo(CO)_4$ concentration. The reaction rate clearly increases with base concentration, but the reaction order in base could not be unambiguously determined. A free radical chain mechanism is proposed to account for both the chemical products and the kinetics observations. The mechanism involves a homolytic cleavage of the Sn–Co bond to produce a 17-electron $Co(CO)_4$ species which is highly labile with respect to CO substitution. An outer-sphere electron transfer process is proposed as a subsequent step in the mechanism that results in the formation of the observed ionic product. The proposed mechanism can be plausibly extended to account for several reactions of binuclear carbonyl compounds with bases.

During the past 20 years a substantial body of data relating to reactions of transition metal carbonyl compounds has accumulated. The substitution reactions of six-coordinate carbonyl complexes have been extensively investigated, and several possible reaction pathways for substitution have been identified. By contrast, kinetic studies of analogous five-coordinate complexes have not been numerous. Yet, a comparison of the kinetics behaviors of analogous five- and six-coordinate species suggests many interesting and important questions. For example, what are the relative importances of CO dissociation or an associative pathway for substitution, in analogous $M(CO)_6$ as compared with $M(CO)_5$ species, or in $XM(CO)_5$ as compared with $XM(CO)_4$ species? With this and similar questions in mind we have begun to study the substitution reactions of $XCo(CO)_4$ compounds, in which X is a group such as $SnCl_3$, $Si(C_6H_5)_3$, and so forth.

The number of known cobalt carbonyl compounds that contain a group 4 metal bonded directly to cobalt, of general formula $R_3MCo(CO)_4$, has increased considerably during the past 10 years.[2,3] The structures of $H_3SiCo(CO)_4$,[4] $F_3SiCo(CO)_4$,[5] $Cl_3SiCo(CO)_4$,[6] and $Cl_3GeCo(CO)_4$[7] have been reported. In all four compounds, the molecule possesses approximate C_{3v} symmetry, and the configuration around the cobalt atom is approximately trigonal bipyramidal. In these four cases the angles between the equatorial and axial metal-carbon vectors are 98°, 94°, 95°, and 93°, respectively.

The type of bonding between cobalt and the group 4 metal is of relevance to the question of the reactivity of these compounds. The group 4 metals have empty d orbitals of appropriate symmetry to overlap with the filled d orbitals of the cobalt center; thus, the R_3M group may act as a π-acceptor when bonded to $Co(CO)_4$. Several physical studies, including ^{59}Co NQR[8,9] and NMR,[10,11] vibrational spectroscopic studies and force field calculations,[12-21] ^{119}Sn Mössbauer spectra,[22-24] molecular orbital calculations,[25] measurements of metal–metal bond energies,[26,27] and bond length observations,[4-7] have been related to the contribution of π-bonding in the M–Co bond. However, the importance of this interaction in a given compound is still largely undetermined.

The reactivities of various $R_3MCo(CO)_4$ complexes with respect to CO substitution by group 5 bases, and the nature of the product obtained, vary with the R_3M group.[28,29] For example, when $R_3M = (C_6H_5)_3Sn$,[28] the reactions with phosphines at high temperatures are relatively slow and the products have the general formula $(C_6H_5)_3SnCo(CO)_3B$. By contrast, for $R_3M = Cl_3Sn$[29] the reaction is very fast at room temperature and the ionic products, $[Co(CO)_3B_2][Cl_3Sn]$, form. This large change in reactivity is unexpected. It suggests that more than one mode of reaction is possible, but the effect of various structural perturbations on reaction pathway is not clear.

Basolo and Breitshaft[30] investigated the ^{14}CO exchange reactions of $(C_6H_5)_3SnCo(CO)_4$ and $(CH_3)_3SnCo(CO)_4$. The process was found to be slow and first order in complex at 20 °C, in $(\eta\text{-}C_4H_9)_2O$ as solvent. No mechanism was proposed, but substitution and ^{14}CO exchange were thought to proceed via different paths. Reaction of $Cl_3SnCo(CO)_4$ with $P(OC_2H_5)_3$ results[29] in formation of $Cl_2Sn[Co(CO)_4]_2$ and $SnCl_4[P(OC_2H_5)_3]_n$. A kinetic study of the reaction in hexane in the dark showed that it is first order each in complex and phosphite. A mechanism involving base-induced Sn–Co bond heterolysis was proposed:

$$Cl_3SnCo(CO)_4 + P(OR)_3 \rightleftarrows Cl_3SnCo(CO)_4P(OR)_3$$

$$Cl_3SnCo(CO)_4P(OR)_3 \rightarrow [Cl_3SnP(OR)_3][Co(CO)_4]$$

$$Cl_3SnCo(CO)_4 + [Cl_3SnP(OR)_3][Co(CO)_4] \rightarrow Cl_2Sn[Co(CO)_4]_2 + SnCl_4P(OR)_3$$

$$SnCl_4P(OR)_3 + P(OR)_3 \rightarrow SnCl_4[P(OR)_3]_2$$

Reactions of acyl and hydrido cobalt tetracarbonyl compounds with $P(C_6H_5)_3$ were reported by Heck.[31-33] A CO dissociative pathway was proposed for the reactions. However, Bor and co-workers[34] suggested alkyl migration to explain their observations regarding ^{13}CO exchange with benzylcobalt tetracarbonyl.

The compound of interest in this study, $Cl_3SnCo(CO)_4$, involving a metal–metal bond between a group 4 metal and cobalt, bears a close resemblance to those structural isomers of $Co_2(CO)_8$ that involve a Co–Co bond, with no bridging carbonyl groups.[35,36] The general course of the reaction with group 5 bases is similar in the two cases, suggesting the likelihood of a similar reaction pathway.

We report here the results of our study of the reactions of $Cl_3SnCo(CO)_4$ with $As(C_6H_5)_3$, $P(C_6H_5)_3$, and $P(n\text{-}C_4H_9)_3$. We have found that the reactions proceed via a free radical chain process. A mechanism is proposed to account for the results observed.

Experimental Section

$Cl_3SnCo(CO)_4$[29] and $Cl_3SnCo(CO)_3P(C_6H_5)_3$[37] were prepared in accordance with literature descriptions. The compounds were stored in a freezer. Triphenylphosphine (PPh_3) and triphenylarsine ($AsPh_3$) (Aldrich Chemical) were recrystallized from ethanol and then from hexane prior to use. Tributylphosphine (PBu_3) (Aldrich Chemical) was distilled from $LiAlH_4$ under a 40 mm pressure of N_2. Spectrograde hexane (Fisher Scientific) was washed with concentrated H_2SO_4, $NaHCO_3$ solution, and distilled water, dried over anhydrous $MgSO_4$, distilled over P_2O_5, and stored over sodium wire and under nitrogen. Prior to its use in the kinetic studies with $AsPh_3$, the hexane was vacuum-distilled after thorough degassing. Before use in kinetic studies with PPh_3 and PBu_3 it was redistilled in a N_2-atmosphere box.

Reaction between $Cl_3SnCo(CO)_4$ and $AsPh_3$. The product of the reaction of $Cl_3SnCo(CO)_4$ with excess $AsPh_3$ at room temperature in hexane is the ionic product $[Co(CO)_3(AsPh_3)_2][Cl_3Sn]$, which precipitates as a finely divided yellow solid. The product was identified on the basis of its IR spectrum as compared with that of $[Co(CO)_3(PPh_3)_2][Cl_3Sn]$,[29] and from elemental analysis. Anal. Calcd for $C_{39}H_{30}As_2Cl_3CoO_3Sn$: C, 47.75; H, 3.06; Cl, 10.87. Found: C, 47.75; H, 3.11; Cl, 13.41. As it forms in the course of the reaction in hexane it exhibits a broad absorption at 2001 cm^{-1}. In chloroform solution the yellow product exhibits three bands, at 2003 (s), 2010 (s), and 2071 (vw) cm^{-1}.

The kinetics behavior of the reaction was studied under various conditions. In particular, the effects of light, oxygen, concentration of $AsPh_3$, galvinoxyl, tetracyanoethylene, and trichlorobromomethane on the rate of the reaction were examined.

In a typical run, the complex and the $AsPh_3$ are weighed and then transferred to an N_2-atmosphere box, where hexane and other reagents are added. The kinetics run is carried out in a jacketed flask fitted with a stopcock and a rubber serum cap. The flask is left to equilibrate at the temperature desired after loading and transferring it to the outside of the box and keeping it always in the dark. For the reactions carried out in light, the flask was kept at a fixed position with respect to a fluorescent lamp (Westinghouse, 15 W). Portions of the solution were withdrawn at appropriate time intervals using syringes and needles flushed with N_2. IR spectra were recorded immediately using 1-mm path length NaCl cells.

Reaction between $Cl_3SnCo(CO)_4$ and PPh_3. The reaction between $Cl_3SnCo(CO)_4$ and PPh_3[29] was reported earlier; the ionic compound, $[Co(CO)_3(PPh_3)_2][Cl_3Sn]$, forms as product.

The reaction occurred too rapidly to be followed by the technique used for the $AsPh_3$ reaction. A simple stopped-flow apparatus, illustrated in Figure 1, was designed. This apparatus is more than adequate for mixing solutions for study using a conventional IR spectrometer, in which the instrument response time is limited by detector response and beam chopping rate to times on the order of 0.5 s or longer. Special care was taken in design of the experiments to protect the solutions from air. The mixing chamber and the IR cell are housed in compartment A, kept at the desired temperature by a stream of dry thermostated air. During operation, compartment A is mounted in the spectrometer cell compartment. Radiation from the instrument source (a Nernst Glower) passes through an IR-pass filter ($\lambda > 1\ \mu$), the IR cell, and an AgCl window, respectively.

In a typical series of experiments, the reservoirs are loaded in an N_2-atmosphere box in the dark with the hexane solutions of PPh_3 and $Cl_3SnCo(CO)_4$, and closed with rubber serum caps. The stopped-flow apparatus is thoroughly flushed with N_2 while the reservoirs and compartments A and B are brought to a common desired temperature. For each run, around 5 mL of each solution is drawn and quickly pushed from the syringes into the IR cell. Disappearance of the $Cl_3SnCo(CO)_4$ is followed by monitoring the disappearance of the band at 2046 cm^{-1}.

Reaction between $Cl_3SnCo(CO)_4$ and PBu_3. The reaction between $Cl_3SnCo(CO)_4$ and excess PBu_3 has been reported;[29] the ionic compound, $[Co(CO)_3(PBu_3)_2][Cl_3Sn]$, forms as product.

A study of the kinetics of this reaction was attempted using the stopped-flow apparatus described above. However, reaction was too rapid to be followed, even at temperatures below −6 °C.

Photolysis of $Cl_3SnCo(CO)_4$ Solution in Hexane. The photolysis of a $Cl_3SnCo(CO)_4$ solution (4×10^{-3} M) was carried out using a Xenon 1000-W high-pressure arc lamp (PEK 1000B) and a 254-nm interference filter. The solution was placed in a quartz flask fitted with a rubber serum cap. Samples were withdrawn at suitable time intervals and the IR spectra for the region 1800–2150 cm^{-1} were recorded immediately. A similar procedure was followed for the photolysis of a hexane solution of $Cl_3SnCo(CO)_4$ (3.5×10^{-3} M) and $Re_2(CO)_{10}$ (7×10^{-3} M) except a 350-nm interference filter was used in this case.

All IR spectra were recorded on a Beckman IR 7 spectrophotometer, frequency-calibrated using water vapor bands. The UV spectra were recorded on a Cary 14 spectrophotometer using 1-cm quartz cells.

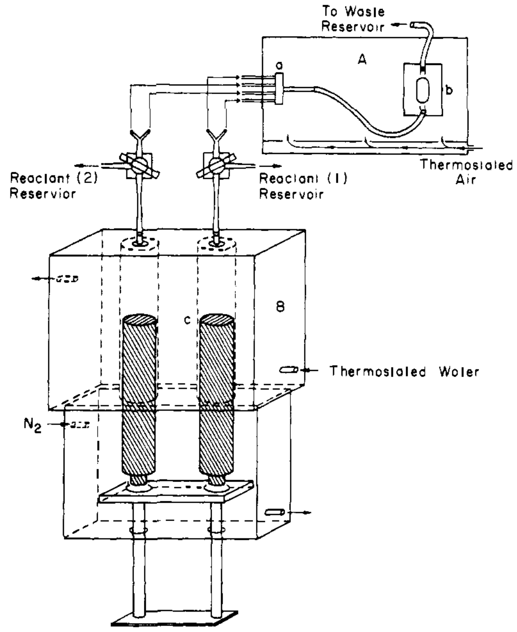

Figure 1. Diagram of the stopped-flow apparatus showing the thermostated compartments A and B, the mixing chamber (a), the 1-mm NaCl IR cell, and the 30-mL syringes.

Results and Discussion

Effects of Oxygen and Light. Our preliminary investigations of the reactions of $Cl_3SnCo(CO)_4$ with PPh_3 or $AsPh_3$ indicated that the system is complex. Both oxygen and light proved to have important effects on the observed kinetic behavior.

The effect of oxygen was very obvious in the $AsPh_3$ reactions. In experiments conducted under the fluorescent lamps, in which no special precautions were taken to exclude oxygen, the rate of disappearance of $Cl_3SnCo(CO)_4$ from solutions containing excess $AsPh_3$ was observed to be pseudo-first-order in carbonyl, with an observed rate constant of the order of $1 \times 10^{-6}\ s^{-1}$ at 25 °C. On the other hand for reactions in which the hexane was degassed thoroughly and used immediately the reaction was around 100 times faster. The rate law was found to be three-halves order with respect to carbonyl, and the observed rate constant was of the order of $5 \times 10^{-3}\ M^{-1/2}\ s^{-1}$. Furthermore, the ionic product, $[Co(CO)_3(AsPh_3)_2][Cl_3Sn]$, was not observed in the runs in which oxygen was present. Rather, an unidentified bluish white solid formed. In reaction solutions in which every effort has been made to exclude oxygen, and in which reaction is proceeding satisfactorily, admission of air causes immediate quenching of the reaction. Thus, the reaction of $AsPh_3$ with $Cl_3SnCo(CO)_4$ to form $[Co(CO)_3(AsPh_3)_2][Cl_3Sn]$ is strongly inhibited by the presence of oxygen.

Similar observations were also made for the reaction of the carbonyl with PPh_3. In a series of kinetic runs using a given pair of stock solutions, a sharp decrease in the rate of disappearance of $Cl_3SnCo(CO)_4$ is observed in the runs following the injection of oxygen into the solutions.

Reactions of $SnCl_3Co(CO)_4$ with PPh_3 or $AsPh_3$ were found to be affected by visible light. The reaction of $Cl_3SnCo(CO)_4$ with $AsPh_3$ in the dark starts with an induction period whose duration depends on the level of the trace oxygen content and on temperature (Figure 2). The induction period is followed by a rapid reaction that results in formation of the ionic product. However, the reactions carried under the light of the fluorescent lamp exhibit shorter induction periods and proceed

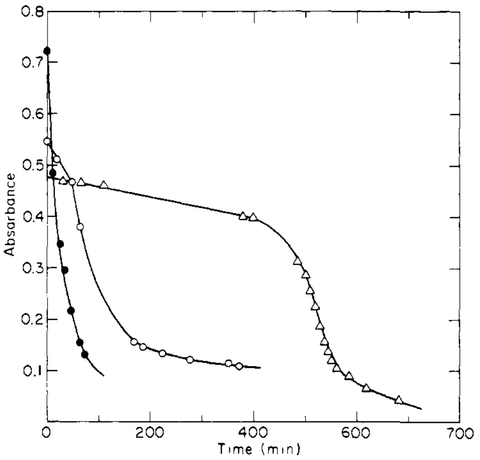

Figure 2. The absorption at 2046 cm^{-1} of $Cl_3SnCo(CO)_4$ as a function of time during the reaction with $AsPh_3$ under fluorescent light (●), in the dark (○), and in the presence of galvinoxyl (1×10^{-5} M) (△). Approximately equal concentrations of $AsPh_3$ were used in the three cases.

to give the ionic product at a much faster rate than reactions occurring in the dark (Figure 2).

The emission spectrum of the fluorescent lamp used in the study shows sharp bands at 313 and 365 nm and two broad bands at 450 and 560 nm. A $Cl_3SnCo(CO)_4$ solution in hexane exhibits an absorption maximum at 271 nm. For solutions of $Cl_3SnCo(CO)_4$ of 1 to 7×10^{-3} M, the range of concentrations employed in the kinetics runs, the tail of the 271-nm band showed considerable intensity at 300 nm, decreasing to near zero at 450–500 nm (Figure 3).

Under the fluorescent light, reaction of $Cl_3SnCo(CO)_4$ (1.02×10^{-3} M) with $AsPh_3$ (4.56×10^{-2} M) in hexane at 25 °C and in the presence of galvinoxyl ($\sim 1 \times 10^{-5}$ M) shows a long induction period with slow disappearance of the carbonyl, as shown in Figure 2. Following the induction period, a fast reaction occurs and the ionic product forms. The initial disappearance of $Cl_3SnCo(CO)_4$ has a pseudo-first-order rate constant of 5×10^{-6} s^{-1}. The reaction that follows was observed to be three-halves order with respect to $Cl_3SnCo(CO)_4$, with an observed rate constant of 3×10^{-4} s^{-1} M$^{-1/2}$.

Furthermore, under fixed experimental conditions the duration of the induction period is directly proportional to the concentration of galvinoxyl in solution. The reaction was also monitored by observing the ESR absorption of galvinoxyl in a sealed ESR tube. The intensity of the ESR signal due to galvinoxyl decreased slowly; the ionic product was observed to form at a rapid rate just at the time when the galvinoxyl signal had nearly vanished.

Mechanism of the Reaction. These results are suggestive of a free radical chain pathway for the reaction. Inhibition of the reaction by oxygen and galvinoxyl is indicative of a process involving free radicals. The chain nature of the pathway is indicated by the slow rate of disappearance of the complex when an inhibitor such as oxygen or galvinoxyl is present, in comparison with the rate of reaction after the inhibitor is consumed.

The following free radical chain mechanism is in agreement with the observed chemistry and the kinetics behavior observed for the reactions:

$$Cl_3SnCo(CO)_4 + B \overset{K}{\rightleftharpoons} Cl_3(B)SnCo(CO)_4 \tag{1}$$

$$Cl_3(B)SnCo(CO)_4 \xrightarrow[\text{and/or } h\nu]{k_1} Cl_3SnB\cdot + Co(CO)_4 \tag{2}$$

$$Co(CO)_4\cdot + B \xrightarrow{k_2} Co(CO)_3B\cdot + CO \tag{3}$$

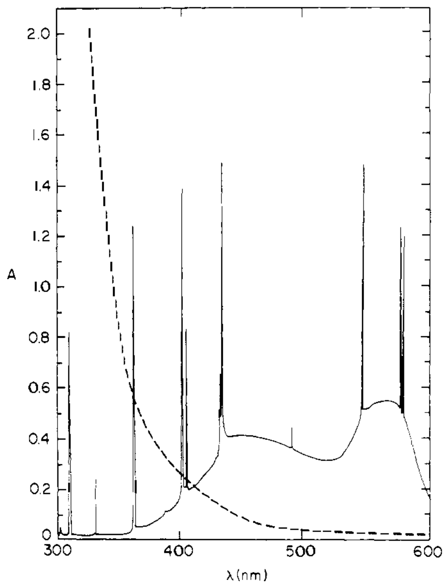

Figure 3. The emission spectrum of the fluorescent lamp used in the study of the reaction with $AsPh_3$ (—) and the absorption spectrum in the visible region of a $Cl_3SnCo(CO)_4$ solution (2×10^{-3} M) in hexane (- - -).

$$Co(CO)_3B\cdot + Cl_3(B)SnCo(CO)_4 \xrightarrow{k_{31}} Co(CO)_3B^+ + Cl_3(B)SnCo(CO)_4^{-}\cdot \tag{4}$$

$$Co(CO)_3B\cdot + Cl_3SnCo(CO)_4 \xrightarrow{k_{32}} Co(CO)_3B^+ + Cl_3SnCo(CO)_4^{-}\cdot \tag{5}$$

$$Cl_3(B)SnCo(CO)_4^{-}\cdot \xrightarrow{k_{41}} Co(CO)_4\cdot + SnCl_3^- + B \tag{6}$$

$$Cl_3SnCo(CO)_4^{-}\cdot \xrightarrow{k_{42}} Co(CO)_4 + SnCl_3^- \tag{7}$$

$$Co(CO)_3B^+ + B \xrightarrow{\text{fast}} Co(CO)_3B_2^+ \tag{8}$$

$$2Co(CO)_4\cdot \xrightarrow{k_5} Co_2(CO)_8 \tag{9}$$

$$2Co(CO)_3B\cdot \xrightarrow{k_6} Co_2(CO)_6B_2 \tag{10}$$

$$Co(CO)_4\cdot + Co(CO)_3B\cdot \xrightarrow{k_7} Co_2(CO)_7B \tag{11}$$

$$SnCl_3B\cdot + Co(CO)_3B\cdot \xrightarrow{k_8} SnCl_3Co(CO)_3B + B \tag{12}$$

$$SnCl_3B\cdot + Co(CO)_4\cdot \xrightarrow{k_9} SnCl_3Co(CO)_4 + B \tag{13}$$

$$2SnCl_3B\cdot \xrightarrow{k_{10}} Sn_2Cl_6 + 2B \tag{14}$$

In these equations B is either $AsPh_3$, PPh_3, or PBu_3. The process represented in eq 2 is that which leads to solvent-separated radicals. To derive a rate law from the above mechanism, several simplifying assumptions can be made. The first is that substitution of $Co(CO)_4$, once formed, by B is rapid relative to all other pathways for reaction of $Co(CO)_4$. Consequently, steps 9, 11, and 13 of the mechanism become unimportant as termination steps. This assumption is rendered reasonable by observations that other 17-electron carbonyl intermediates have been found[38,39] very reactive toward substitution.

Two additional assumptions, which are in fact generalizations for all free radical chain processes,[40] are also made. Assuming a steady state concentration of each radical intermediate, the rate of initiation must be equal to the rate of termi-

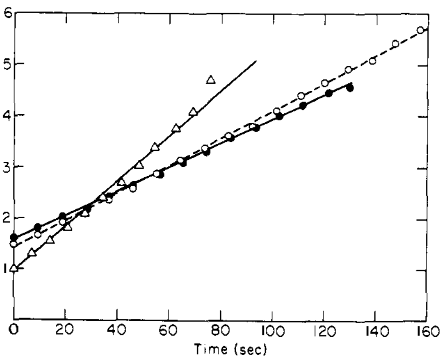

Figure 4. Pseudo-three-halves-order plots of the absorption (A) at 2046 cm^{-1} for the reaction of $Cl_3SnCo(CO)_4$ with PPh_3. The concentrations of the base are 2.87×10^{-2} M (○), 3.00×10^{-2} M (●), and 3.47×10^{-2} M (△).

Table I. Observed Pseudo-Three-Halves-Order Rate Constants of the Reaction with PPh_3 in Hexane at 21 °C

$10^3[Cl_3SnCo(CO)_4]$, M	$10^2[PPh_3]$, M	k, $M^{-1/2}s^{-1}$
1.01	1.49	0.47 ± 0.16
1.37	1.98	0.70 ± 0.11
1.23	2.87	0.99 ± 0.07
1.27	3.00	0.54 ± 0.01
1.97	3.47	1.36 ± 0.16
1.44	4.01	0.99 ± 0.22

nation for any free radical of the chain. A second assumption is that all propagation steps in the chain have the same rate. Finally, reaction 10 is assumed to be more important for the termination of the $Co(CO)_3B\cdot$ radical than eq 12.

By using these assumptions, the derived rate law is (see Appendix):

$$\frac{-d[Cl_3SnCo(CO)_4]}{dt} = \left(\frac{k_1K}{k_6}\right)^{1/2}[Cl_3SnCo(CO)_4]^{3/2} \times [k_{31}K[B]^{3/2} + k_{32}[B]^{1/2}] \quad (15)$$

If termination step 12 is assumed more important than step 10, the same rate law will result except for a different combination of rate constants.

Figures 4 and 5 show graphs of $(A - A_\infty)^{-1/2}$ vs. time for several kinetics experiments with varying concentration of either PPh_3 or $AsPh_3$, with base present in large excess. The data fit linear plots very well, indicating that the reaction is three-halves order in $Cl_3SnCo(CO)_4$. However, it is evident that the slopes of the linear plots do not vary uniformly with base concentration. A few results relating to the dependence of k on base concentration are shown in Tables I and II. In a radical chain process of the type proposed, it is exceedingly difficult to determine the order of reaction in the excess reagent by comparisons of data from different kinetics runs. The chain process is very sensitive to trace impurities, such as oxygen, which may trap one or more species involved in the chain. The levels of such trace impurities inevitably vary from one kinetics run to another. Nevertheless, we carried out several experiments in an attempt to determine the reaction order in base. Conditions were maintained as nearly identical as possible, with changing concentration of excess base the only variable from one run to another. Figure 6 shows graphs of the pseudo-three-halves-order rate constant observed vs. various powers of base concentration, for reactions with both PPh_3 and $AsPh_3$. Each data point represents the averaged results of several kinetics runs at that base concentration. The error bars represent the 95% confidence limit of the value obtained for k in each case. Although a fairly regular increase in observed rate constant was seen with increasing base concentration, the quality of the data do not permit assigning a specific order to the base dependence.

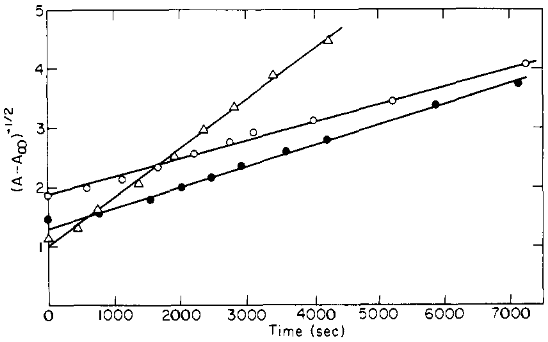

Figure 5. Pseudo-three-halves-order plots of the absorption (A) at 2046 cm^{-1} for the reaction of $Cl_3SnCo(CO)_4$ with $AsPh_3$. The concentrations of the base are 2.25×10^{-2} M (●), 4.56×10^{-2} M (○), and 6.78×10^{-2} M (△).

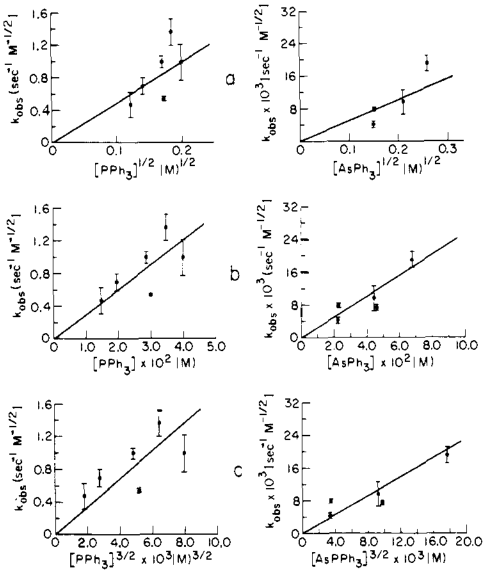

Figure 6. Plots of the observed rate constants vs. base concentration raised to various possible powers. The order of dependence on base is assumed to be ½ in (a), 1 in (b), and $\frac{3}{2}$ in (c). The range of k_{obsd} shown for each concentration is the 95% confidence limit.

Table II. Observed Pseudo-Three-Halves-Order Rate Constants of the Reaction with $AsPh_3$ in Hexane at 25 °C[a]

$10^2[AsPh_3]$, M	10^3k, $M^{-1/2}s^{-1}$
2.2	4.12 ± 0.73
2.25	7.84 ± 0.07
4.4	9.60 ± 2.84
4.56	7.28 ± 0.04
6.78	19.03 ± 1.86

[a] $Cl_3SnCo(CO)_4$ concentrations $1.2\text{-}1.6 \times 10^{-3}$ M.

The dependence of the rate on base concentration arises from preequilibrium 1 in the proposed mechanism. An acid-base interaction between the base and the tin center is expected. Stable complexes of $(C_6H_5)SnCl_3$ with PBu_3 have been reported;[41] $Cl_3SnCo(CO)_4$ might be expected to be of comparable acidity. The order of the dependence is determined by the value of K; a large K will result in making $k_{32}[Cl_3SnCo(CO)_4] \ll k_{31}[Cl_3(B)SnCo(CO)_4]$ and the order in base is three-halves. On the other hand, for a small K the order becomes one-half. For some intermediate values of K, the order in base will be intermediate between three-halves and one-half.

Formation of the complex in preequilibrium 1 could promote homolytic cleavage of the Sn–Co bond, possibly by reducing the π-acidity of the Cl_3Sn group. This could result in a weakening of the Sn–Co bond, making it more susceptible to homolytic cleavage, either thermally or photochemically. However, there is as yet no direct evidence on this point. The overall character of the mechanism is not dependent on the importance of the preequilibrium to the initial homolysis.

When $Cl_3SnCo(CO)_4$ alone in hexane was photolysed using 254-nm irradiation, $Cl_2Sn[Co(CO)_4]_2$ and a dark red solid product with no IR absorptions in the carbonyl region formed. These results can be viewed in terms of the following processes:

$$Cl_3SnCo(CO)_4 \xrightarrow{h\nu} Cl_3Sn\cdot + Co(CO)_4\cdot \qquad (16)$$

$$Co(CO)_4\cdot + Cl_3SnCo(CO)_4 \rightarrow Co(CO)_4Cl + Cl_2SnCo(CO)_4\cdot \qquad (17)$$

$$SnCl_3\cdot + Cl_3SnCo(CO)_4 \rightarrow SnCl_4 + Cl_2SnCo(CO)_4\cdot \qquad (18)$$

$$Co(CO)_4\cdot + Cl_2SnCo(CO)_4\cdot \rightarrow Cl_2Sn[Co(CO)_4]_2 \qquad (19)$$

$$Co(CO)_4Cl \rightarrow \text{decomposition products} \qquad (20)$$

Additional support for the above reactions, in particular the abstraction of chlorine atom by the carbonyl free radical was obtained from the photolysis at 350 nm of $Cl_3SnCo(CO)_4$ in the presence of $Re_2(CO)_{10}$, which is already known to undergo homolytic cleavage of the Re–Re bond to form $Re(CO)_5$ radicals.[38] From the IR spectra recorded during the photolysis, it was clear that $Re(CO)_5Cl$ was produced, in addition to either $Cl_2Sn[Re(CO)_5][Co(CO)_4]$ or a mixture of $Cl_2Sn[Co(CO)_4]_2$ and $Cl_2Sn[Re(CO)_5]_2$. Photolysis at 350 nm presumably results mainly in formation of $Re(CO)_5$ radicals, with subsequent abstraction of Cl from $SnCl_3Co(CO)_4$.

Under the conditions normally employed to observe the reaction of $Cl_3SnCo(CO)_4$ and $AsPh_3$, the reaction was inhibited by the presence of CCl_3Br, which is known to undergo Br abstraction by free radicals. Elemental analysis of the hygroscopic precipitate formed after 5 h showed a high percentage of bromine, indicating that bromine abstraction did take place. $Co(CO)_4Br$ must have formed during the reaction and decomposed to some cobalt-bromine product. The carbonyl halides of cobalt have been prepared and found to be unstable at room temperature.[42]

Steps 4 and 5 of the mechanism are electron-transfer processes producing the very short-lived intermediates $Cl_3SnCo(CO)_4^-\cdot$ and $Cl_3(B)SnCo(CO)_4^-\cdot$. Recently Symons and co-workers[43] reported the detection by ESR of a similar species, $Ph_3PbCo(CO)_4^-\cdot$, produced by γ-irradiation of $Ph_3PbCo(CO)_4$. Further evidence for an electron-transfer process was obtained by carrying out the reaction of $Cl_3SnCo(CO)_4$ with $AsPh_3$ under the fluorescent light and in the presence of tetracyanoethylene, TCNE ($\sim 1 \times 10^{-4}$ M), which readily undergoes one-electron reduction to form $TCNE^-$.[44] The chain process was inhibited and the parent carbonyl disappeared slowly, with an observed first-order rate constant of 4×10^{-6} s^{-1}. The inhibition is presumably the result of the reaction:

$$Co(CO)_3B\cdot + TCNE \rightarrow [Co(CO)_3B^+TCNE^-]$$

In electrochemical studies carried out on various $[Co(CO)_3B]_2$[45] and other substituted carbonyl compounds[46] it has been shown that the reduction potential becomes more negative as the σ-donor ability of B increases. These observations can be explained in terms of an increased energy of the metal orbitals. Such an increase, which results in making the reduction potential more negative, would also be expected to result in making the oxidation potential more positive. Thus the potential for the oxidation:

$$Co(CO)_3B\cdot \rightarrow Co(CO)_3B^+ + e^-$$

would be expected to increase in the order CO < $AsPh_3$ < PPh_3 < PBu_3. The rate constants for reactions 4 and 5 should also increase in the same order,[47-49] resulting in an overall increase in reaction rate. This conclusion is in agreement with our observations regarding the relative rates of the reaction with $AsPh_3$, PPh_3, and PBu_3.

The character of the overall reaction scheme suggests that it should be possible to initiate the radical chain process by introducing a substance capable of electron transfer to $Cl_3SnCo(CO)_4$:

$$A + Cl_3SnCo(CO)_4 \rightarrow A^+ + Cl_3SnCo(CO)_4^-\cdot$$

We were not successful in finding a suitable hexane-soluble reducing agent, but two interesting results were obtained. When the reaction between $AsPh_3$ and $Cl_3SnCo(CO)_4$ was carried out in the dark and in the presence of a small piece of sodium metal, reaction was four to five times faster. Similarly, reaction in the presence of a small quantity of bisacetylacetonatochromium(II) was also considerably faster than a comparable reaction without the reducing agent.

From the experimental data for the initial stage of the reaction with $AsPh_3$ under the fluorescent light in the presence of O_2, galvinoxyl, or TCNE, it is possible to calculate a pseudo-first-order rate constant for disappearance of $Cl_3SnCo(CO)_4$. For all three cases, the value of the rate constant so calculated is on the order of 10^{-6} s^{-1}. In the absence of a chain propagation step, and assuming that the dissociation products of reaction 1 are efficiently consumed, the overall rate of homolysis of the Sn–Co bond is the sum of the rates of thermal and photochemical bond cleavage. The latter is determined by the flux of photons effective in causing dissociation. Since the flux of photons from the fluorescent lamp used as light source is constant in all the experiments, and since temperature is maintained constant, the rate of loss of starting material via nonchain processes should be the same in all three systems, as observed.

Parts of the overall reaction scheme presented here, in particular the key steps 4 and 6, are strikingly similar to those which operate in the radical anion chain mechanism for substitution at carbon, as delineated by Kornblum.[50] It is especially significant that our observations on the effects of light, electron acceptors, or oxygen or other radicals correspond closely to those of Kornblum and co-workers.

The possibilities for a pathway other than the proposed radical chain mechanism were considered and tested. The dissociative, associative, and ligand migration pathways usually proposed for carbonyl substitution reactions[51-53] can be excluded in our study on the basis of the observed effects of oxygen and light and the observed reaction orders. Furthermore, any pathway that involves the monosubstituted carbonyl, $Cl_3SnCo(CO)_3B$, as an intermediate, can be excluded; the reaction of $Cl_3SnCo(CO)_3PPh_3$ with PPh_3 in hexane and under light was found to be very slow.

The prevalence of radical species as intermediates in the reactions of transition metal carbonyl compounds has only recently been recognized.[38,54-58] Since radical chain processes can in many instances be inhibited by the presence of oxygen or other impurity, it is likely that many other examples have been overlooked as a result of the experimental conditions employed. Two aspects of the mechanism proposed here are worthy of special note. The first is that the $Co(CO)_4\cdot$ radical intermediate, with 17 electrons in the valence shell of the central metal, is presumed to be subject to facile substitution. Behavior of this kind has been documented for $Mn(CO)_5$ and $Re(CO)_5$,[38,39] both of which involve 17 electrons in the valence shell of the metal. The supposition that $Co(CO)_4$ behaves similarly is not unreasonable. Secondly, a very important step in the chain is the outer- sphere electron transfer from a substituted radical species, $Co(CO)_3B\cdot$, to the parent carbonyl compound, $Cl_3SnCo(CO)_4$. While this a reasonable hypothesis, there is yet little direct evidence for it. Electrochemical measurements under appropriate conditions of solvent might eventually provide more direct evidence for such a step.

The mechanism outlined here is, with some slight modifications, applicable to several other reactions of metal carbonyl compounds with bases, particularly to the disportionation reactions of binuclear carbonyl compounds such as $Co_2(CO)_8$,[59,60] $Mn_2(CO)_{10}$,[61-65] and $Re_2(CO)_{10}$[65] in basic solvents.

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Appendix

On the basis of the assumption that all propagation steps in a free radical chain process have the same rate, the rate of disappearance of $Cl_3SnCo(CO)_4$ can be derived from the parallel reactions 4 and 5 of the proposed mechanism:

$$\frac{-d[Cl_3SnCo(CO)_4]}{dt} = k_{31}[Cl_3(B)SnCo(CO)_4][Co(CO)_3B\cdot] + k_{32}[Cl_3SnCo(CO)_4][Co(CO)_3B\cdot]$$

Since $[Cl_3(B)SnCo(CO)_4] = K[B][Cl_3SnCo(CO)_4]$ from preequilibrium 1 then:

$$\frac{-d[Cl_3SnCo(CO)_4]}{dt} = [k_{31}K[B] + k_{32}][Cl_3SnCo(CO)_4][Co(CO)_3B\cdot] \quad (1A)$$

The steady state concentration of $Co(CO)_3B$ can be derived by applying the steady-state assumption to all transient species.

$$\frac{d[Co(CO)_3B\cdot]}{dt} = k_2[Co(CO)_4\cdot][B] - k_{31}[Co(CO)_3B\cdot][Cl_3(B)SnCo(CO)_4] - k_{32}[Co(CO)_3B\cdot][Cl_3SnCo(CO)_4] - k_6[Co(CO)_3B\cdot]^2 - k_7[Co(CO)_4\cdot][Co(CO)_3B\cdot] - k_8[Co(CO)_3B\cdot][SnCl_3\cdot] = 0 \quad (2A)$$

$$\frac{d[Co(CO)_4\cdot]}{dt} = k_1[Cl_3(B)SnCo(CO)_4] - k_2[Co(CO)_4\cdot][B] + k_{41}[Cl_3(B)SnCo(CO)_4{}^-\cdot] + k_{42}[Cl_3SnCo(CO)_4{}^-\cdot] - k_5[Co(CO)_4\cdot]^2 - k_7[Co(CO)_4\cdot][Co(CO)_3B\cdot] - k_9[Co(CO)_4\cdot][SnCl_3\cdot] = 0 \quad (3A)$$

$$\frac{d[Cl_3SnCo(CO)_4{}^-\cdot]}{dt} = k_{32}[Co(CO)_3B\cdot][Cl_3SnCo(CO)_4] - k_{42}[Cl_3SnCo(CO)_4{}^-\cdot] = 0 \quad (4A)$$

$$\frac{d[Cl_3SnBCo(CO)_4{}^-\cdot]}{dt} = k_{31}[Co(CO)_3B\cdot][Cl_3(B)SnCo(CO)_4] - k_{41}[Cl_3(B)SnCo(CO)_4{}^-\cdot] = 0 \quad (5A)$$

Substituting eq 4A and 5A in 3A and adding the result to eq 2A to get

$$k_1[Cl_3(B)SnCo(CO)_4] - k_5[Co(CO)_4\cdot]^2 - 2k_7[Co(CO)_4\cdot][Co(CO)_3B\cdot] - k_9[Co(CO)_4\cdot][SnCl_3\cdot] - k_6[Co(CO)_3B\cdot]^2 - k_8[Co(CO)_3B\cdot][SnCl_3\cdot] = 0 \quad (6A)$$

The assumption that the substitution of $Co(CO)_4\cdot$ by B is very rapid relative to all other pathways for reactions of $Co(CO)_4\cdot$ and that reaction 10 is more important than reaction 12, will simplify eq 6A to:

$$k_1[Cl_3(B)SnCo(CO)_4] = k_6[Co(CO)_3B\cdot]^2 \quad (7A)$$

Using the steady state concentration of $Co(CO)_3B$ of eq 7A the rate law for disappearance of $Cl_3SnCo(CO)_4$ will finally become:

$$\frac{-d[Cl_3SnCo(CO)_4]}{dt} = \left(\frac{k_1K}{k_6}\right)^{1/2}[k_{31}K[B]^{3/2} + k_{32}[B]^{1/2}][Cl_3SnCo(CO)_4]^{3/2}$$

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Intramolecular Metalation with Methylmanganese and Methylrhenium Carbonyl Complexes. 9. The Crystal and Molecular Structure of Tetracarbonyl-2-(bis-*p*-tolylphosphino)-5-methylphenylmanganese, $(CH_3C_6H_4)_2\overline{PC_6H_3(CH_3)M}n(CO)_4$, an Internal Aromatic Metalation Product Involving a Four-Membered Metallocycle[1]

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Abstract: The structure of $(p\text{-tolyl})_2\overline{PC_6H_3(CH_3)M}n(CO)_4$ has been determined from data collected on an automated diffractometer with monochromatized Mo $K\alpha$ radiation. The compound crystallizes in the monoclinic space group $P2_1/c$ with a = 10.865 (3) Å, b = 13.508 (3) Å, c = 16.571 (3) Å, β = 100.63 (2)°, and V = 2390.3 (10) Å^3. The density of 1.30 g cm^{-3} calculated on the basis of four molecules per unit cell agrees with the flotation value of 1.29 g cm^{-3}. The structure was solved by use of Patterson and Fourier summations and refined by use of full-matrix least-squares methods to a conventional R index of 6.0% based on 1459 independent observed reflections. Four carbonyl groups and a bidentate tris-*p*-tolylphosphine bound to manganese through the phosphorus atom and an ortho atom of one of the tolyl groups occupy essentially octahedral coordination sites on manganese. The carbon atoms of the metalated tolyl group are coplanar with manganese and phosphorus. The greatest distance to any of these atoms from the least-squares plane through them is 0.027 Å. Variations from standard bond lengths in the four-membered ring fused to the aromatic ring are found to be in the direction of electron delocalization in the metallocycle.

The cyclometalation reaction has been the subject of increasing attention[2] owing first to interest in its intrinsic properties, secondly to its relation to the activation of carbon-hydrogen bonds,[3] and thirdly to possibilities for organic synthesis.[4] This body of work of course has included a proportional number of crystallographic studies[5] on derivatives in which metals are bonded to a variety of aromatic rings or to a side chain of an aromatic ring also connected through a donor atom to the same metal. There have been only two communications, of structures for iridium compounds, in which the metal is part of a four-membered ring.[6] This type of system has proven to be somewhat elusive from the crystallographic point of view although compounds containing four-membered rings were among the earliest known examples of cyclometalation, e.g., $Ph_2\overline{PC_6H_4I}r(H)(Cl)(PPh_3)_2$,[7] and $Ph_2\overline{PC_6H_4M}(PPh_3)_2$ M = Rh,[8a] Ir.[8b] For manganese, we observed a four-membered metallocyclic product in the complex tetracarbonyl-2-(bisphenylphosphino)phenylmanganese, $Ph_2\overline{PC_6H_4M}n(CO)_4$[9] (OPMn).[10] Both we[11a] and other groups[11b,c] had earlier tried without success to obtain suitable single crystals of OPMn and we therefore turned to the title compound (TOPMn)[9,10] in hopes that the factors leading to twinning or other crystal growth problems would be overcome. This proved to be the case and we here report the first crystallographic study in full of an internal metalation product in which the metal is part of a four-membered ring.