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The Mechanism of Substitution of Dicobalt Octacarbonyl[1]

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Abstract: The kinetics of the substitution of dicobalt octacarbonyl, $Co_2(CO)_8$, by triphenylarsine, $AsPh_3$, tributylphosphine, PBu_3, triphenylphosphine, PPh_3, and ^{13}C-enriched CO in hexane solution has been observed at temperatures in the range of +30 to −15 °C. Reaction with $AsPh_3$ leads first to $Co_2(CO)_7AsPh_3$ and then to $Co_2(CO)_6[AsPh_3]_2$. The rate is first order in $Co_2(CO)_8$ and zero order in $AsPh_3$ and is reduced by added CO. The rate-determining step is presumably CO loss. At 25 °C, $k_1 = 2.0 \times 10^{-2}\ s^{-1}$. From variation in k with temperature, $\Delta H^{\ddagger} = 93 \pm 4$ kJ mol^{-1} and $\Delta S^{\ddagger} = +42 \pm 10$ J K^{-1} mol^{-1}. The exchange reaction of $Co_2(CO)_8$ with ^{13}CO proceeds at 0 °C with pseudo-first-order rate constant at 0 °C of about $3 \times 10^{-4}\ s^{-1}$, in good agreement with the extrapolated rate constant for reaction with $AsPh_3$. Reaction with PBu_3 is very fast; it leads to $[Co(CO)_3(PBu_3)_2]Co(CO)_4$ as the product. Reaction with PPh_3 leads to an analogous product but the reaction is slower. The kinetic behavior is complex; the apparent order in $Co_2(CO)_8$ varies from values near 1.5 at the lowest temperatures studied to values of about 1.0 at the higher temperatures. The reactions are markedly inhibited by traces of oxygen. A radical chain mechanism fits the observations very well. Key steps in the radical chain involve an electron-transfer process of the form $Co(CO)_3L\cdot + Co_2(CO)_8 \rightarrow Co(CO)_3L^+ + Co_2(CO)_8^-\cdot$, rapid dissociation of the radical anion to form $Co(CO)_4^-$ and $Co(CO)_4\cdot$, and then rapid substitution of $Co(CO)_4\cdot$ by L to form $Co(CO)_3L\cdot$. Numerical integration of the rate equations, using reasonable values for the various rate constants, leads to computed behavior that closely approximates the observations.

Since its discovery in 1910, dicobalt octacarbonyl, $Co_2(CO)_8$, has been a challenging subject of study. It is one of the more reactive of the simple binary carbonyls of the transition metals. Interest in the substance has been all the greater for the fact that it is itself a catalyst or the precursor for a catalyst in several reactions,[2] most notably the oxo process in which olefins are hydroformylated.[3]

From IR studies of solutions of $Co_2(CO)_8$[4] and from matrix isolation spectroscopic studies,[5] three isomeric forms differing only slightly in energy have been identified. In the solid state only one of these isomers, the one form that involves bridging CO groups, is observed.[6] There is uncertainty about the strength of the metal–metal bond in $Co_2(CO)_8$. Thermochemical data are most consistent with a relatively low value, perhaps as low as 48 kJ mol^{-1}, obtained from mass spectral measurements.[7] However, activation enthalpies for reactions thought to involve rupture of the Co–Co bond in advance of the rate-determining step lead to a higher estimated value.[8]

Quantitative studies of the kinetics of reactions of $Co_2(CO)_8$ are not numerous. The compound undergoes reaction with Lewis bases to give various products, depending on the nature of the base and reaction conditions. Reaction with alcohols or piperidine is reported to yield unstable $[Co(CO)_4L][Co(CO)_4]$ salts;[9,10] the evidence for a product of this formulation is in fact weak, and there is good reason to suppose that it is not obtained as a primary product of the reaction of $Co_2(CO)_8$ with the base. With phosphines or phosphites the usual initial product is $[Co(CO)_3L_2]$-$[Co(CO)_4]$.[11] With arsines first $Co_2(CO)_7L$[12] and then $Co_2(CO)_6L_2$[13] are obtained. The salts obtained with phosphines can be converted to $Co_2(CO)_6L_2$ compounds by heating to about the boiling point of benzene for a time. Treatment of $Co_2(CO)_8$ with aqueous base, e.g., amines, can lead to $[CoL_6][Co(CO)_4]_2$ salts.[14] Reaction with hydrogen leads to $HCo(CO)_4$ in an equilibrium reaction;[15,16] treatment with acetylenes, RCCR′, leads to $Co_2(CO)_6RCCR'$.[17] Controlled thermal decomposition of $Co_2(CO)_8$ yields $Co_4(CO)_{12}$ as the initial product.[18,19]

In these reactions the reactivity of $Co_2(CO)_8$ appears to vary greatly. Reaction with acetylenes[17] or H_2,[16] exchange of labeled CO,[20,21] or conversion to $Co_4(CO)_{12}$[19] have been the subject of kinetic studies. All proceed with half-lives at room temperature on the order of perhaps 10 min or longer. By contrast, reactions with amines,[22] phosphines,[23,24] or phosphites are very rapid. The reported kinetics studies do not permit a unified interpretation of the reactivity of $Co_2(CO)_8$ toward Lewis bases, neither in accounting for the wide range of observed reaction rates nor in explaining the diversity of products obtained. To this end we have studied the kinetics of reaction of $Co_2(CO)_8$ with triphenylarsine, $AsPh_3$, ^{13}CO, triphenylphosphine, PPh_3, and tributylphosphine, PBu_3.

Experimental Section

Dicobalt octacarbonyl (Pressure Chemical) was recrystallized twice from hexane in an N_2 atmosphere box prior to its use in the kinetic

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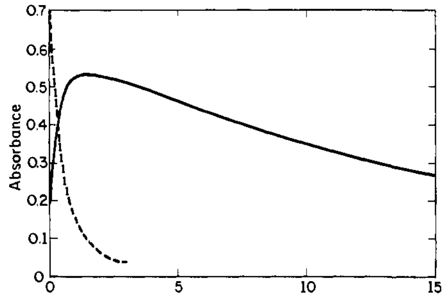

Figure 1. Absorbance vs. time for IR bands due to $Co_2(CO)_8$ (2042 cm^{-1}, dotted line) and $Co_2(CO)_7AsPh_3$ (1996 cm^{-1} solid line) in reaction of $AsPh_3$ with $Co_2(CO)_8$ in hexane at 30 °C.

studies. $AsPh_3$ and PPh_3 (Aldrich Chemical) were recrystallized twice from ethanol and then from hexane prior to use. PBu_3 (Aldrich Chemical) was distilled from $LiAlH_4$ under a 40-mm pressure of nitrogen at 139 °C. Isotopically enriched ^{13}CO (>90%) was purchased from Merck, Sharpe and Dohme. Spectrograde hexane (Fisher Scientific) was stirred over concentrated H_2SO_4, washed with dilute $NaHCO_3$ solution and distilled water, and dried over anhydrous $MgSO_4$. The solvent was then distilled over P_2O_5 and stored over sodium wire under nitrogen. Prior to its use, hexane was redistilled over P_2O_5 in an N_2 atmosphere box.

Reaction Products. The product of reaction of $Co_2(CO)_8$ with $AsPh_3$ is the monosubstituted carbonyl $Co_2(CO)_7AsPh_3$,[12] which subsequently undergoes further reaction to form the symmetrically disubstituted binuclear compound $Co_2(CO)_6(AsPh_3)_2$. The monosubstituted compound was identified by the growth of IR bands at 1965, 1999, 2015, and 2080 cm^{-1} during reaction. The disubstituted compound was obtained as a solid after disappearance of $Co_2(CO)_8$; it was identified by a satisfactory elemental analysis and from the IR spectrum (IR bands in $CHCl_3$: 1958 (s), 1985 (m), 2010 (m), 2035 (m), 2080 (m) cm^{-1}) as compared with those of the analogous compound $Co_2(CO)_6(As(C_2H_5)_3)_2$.[25]

The reaction products of $Co_2(CO)_8$ with PPh_3 and PBu_3 in hexane are the ionic compounds $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ and $[Co(CO)_3(PBu_3)_2][Co(CO)_4]$, respectively. Both products were identified by elemental analysis and IR spectra. (IR bands for $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ in $CHCl_3$: 1890 (s), 2005 (m), 2013 (m) cm^{-1}. Bands for $[Co(CO)_3(PBu_3)_2][Co(CO)_4]$ in $CHCl_3$: 1889(s), 1990(m), 1997(s) cm^{-1}.)

Kinetics Techniques. Most of the kinetics studies of the reactions reported here were carried out by using a simple stopped-flow technique with a Beckman IR-7 spectrometer.[26] However, any reference to the reaction of PBu_3 with $Co_2(CO)_8$ at 25 °C is based on data obtained on a fast-response IR stopped-flow instrument.[24] For a typical series of runs, solutions of the reactants were prepared in a glovebox with N_2 atmosphere, loaded in the reservoirs of the stopped-flow apparatus, and kept under a positive pressure of N_2. Utmost precautions were taken to protect the system from contamination with atmospheric oxygen during the runs. Concentrations of $Co_2(CO)_8$ in the range $(1-2.5) \times 10^{-3}$ M were employed. The absorbance of the band at 2042 cm^{-1} due to $Co_2(CO)_8$ was used to monitor progress of the reactions.

The exchange of ^{13}CO with $Co_2(CO)_8$ at 0 °C in hexane was studied by using techniques previously described.[27] The apparatus was modified to permit withdrawal of small samples of solution by direct transfer through a fritted-glass tube, via stainless-steel tubing, directly into the IR cell for observation. The incorporation of ^{13}CO into $Co_2(CO)_8$ was monitored by observation of the absorptions due to bridging CO in the 1900–1780-cm^{-1} region. Because intramolecular exchange of CO groups in $Co_2(CO)_8$ is rapid,[28,29] the extent of ^{13}CO incorporation as measured in the bridging CO IR bands reflects the overall level of incorporation. The concentration of CO in solution was varied by dilution with prepurified N_2. At lower CO concentrations the total number of moles of CO in the gas phase is sufficiently low so that the abundance of ^{13}CO in the gas sample changes appreciably during the exchange process. It was necessary in these cases to correct the apparent pseudo-first-order rate constant, k_{obsd}, as

$$k = k_{obsd}(F(M)_\infty - F(M)_0)/(F(G)_0 - F(M)_0)$$

where $F(M)_\infty$ represents the extent of ^{13}CO enrichment in the metal carbonyl at equilibrium, $F(M)_0$ the enrichment at the start of the exchange reaction, and $F(G)_0$ the enrichment in the gas phase at the beginning of the reaction.

Table I. Observed Pseudo-First-Order Rate Constants of $Co_2(CO)_8$[a] Reaction with $AsPh_3$

$10^2[AsPh_3]$, M	T, °C	$10^3 k$,[b] s^{-1}
4.04	15	5.09 ± 0.04
4.04[c]	15	3.39 ± 0.08
2.50	15	5.16 ± 0.09
1.99	15	5.2 ± 0.8
1.88	15	5.3 ± 0.3
1.48	15	5.5 ± 0.4
1.11	15	5.08 ± 0.3
1.11	20	10.6 ± 0.3
1.11	25	20.0 ± 0.8
1.11	30	34.1 ± 2.2
1.11[d]	30	38.0 ± 3.0

[a] $Co_2(CO)_8$ concentration on the order of 1.3×10^{-3} M. [b] Averages and standard deviations of constants based upon several kinetic runs. [c] CO-saturated solution, 1 atm. [d] Oxygen-saturated solution.

Table II. Rate Constants for ^{13}CO Exchange with $Co_2(CO)_8$ in Hexane Solution at 0 °C

rel CO concn	$10^4 k$,[a] s^{-1}	rel CO concn	$10^4 k$,[a] s^{-1}
1.0	2.3 (1.1)	5.8	2.6 (1.5)
2.0	3.0 (2.4)	17.4	3.5 (0.5)
2.0	2.6 (0.3)	17.4	4.1 (0.8)

[a] Uncertainties, listed in parentheses, represent 99% confidence limit on the basis of the IR data for individual runs.

Results

Reaction with $AsPh_3$. The reaction of $Co_2(CO)_8$ with $AsPh_3$ results in formation of the monosubstituted intermediate $Co_2(CO)_7AsPh_3$, which reacts further at a much slower rate to form the disubstituted product $Co_2(CO)_6(AsPh_3)_2$. Figure 1 shows plots of absorbance vs. time for the bands at 2042 cm^{-1} of $Co_2(CO)_8$ and 1996 cm^{-1} of $Co_2(CO)_7AsPh_3$ during the reaction of $Co_2(CO)_8$ with $AsPh_3$ at 30 °C.

The rate of $Co_2(CO)_8$ reaction with $AsPh_3$ showed first-order dependence on carbonyl and no dependence on base over a fourfold range of base concentrations employed in the study. Excellent first-order kinetic plots over several half-lives were obtained in all cases. Observed first-order rate constants for various concentrations of $AsPh_3$ and for reaction at several temperatures are listed in Table I.

From an Arrhenius plot of the rate constant at differing temperatures, an estimated activation energy of 93 ± 4 kJ mol^{-1} was obtained over the temperature range 15–30 °C, with $\Delta S^\ddagger = +42 \pm 10$ J K^{-1} mol^{-1}.

As can be seen from observed rate constants at 30 °C in the presence and absence of oxygen (Table I), oxygen has no effect on the reaction. On the other hand, the reaction proceeded more slowly when carried out in a CO-saturated solution (Table I).

Exchange with ^{13}CO. The exchange of ^{13}CO with $Co_2(CO)_8$ was carried out at several different partial pressures of CO of 90% ^{13}C isotopic abundance. The actual concentration of CO in the solutions is not accurately known, but the relative concentrations are known, as listed in Table II. The values listed for k show some variation with CO concentration; however, the uncertainties in the values for each k are rather large. We conclude that any concentration dependence that exists is not large and may be null within our experimental uncertainties.

Reactions with PPh_3 and PBu_3. The study of the kinetics of $Co_2(CO)_8$ reaction with PPh_3 and PBu_3 was considerably complicated by the observation that the apparent order with respect to $Co_2(CO)_8$ varied within the range 1.0–1.5, depending on the conditions of the reaction. It was found that the order in $Co_2(CO)_8$ is higher at lower temperatures for a given base and for a given temperature is higher for the less nucleophilic base. For example,

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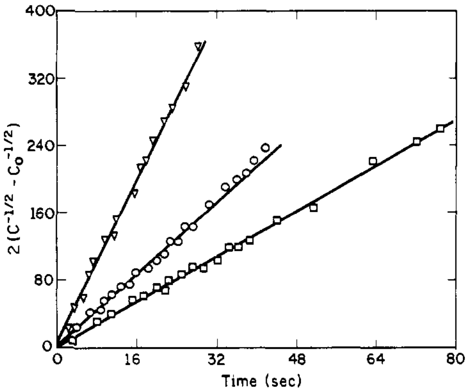

Figure 2. Pseudo-3/2-order graphs for reaction of 1.5 × 10^{-3} M $Co_2(CO)_8$ with 4.0 × 10^{-2} M PPh_3 at 0 °C in hexane: △, no added O_2 (k_{obsd}) = 14.3 ± 0.4 $M^{-1/2}$ s^{-1}; ○, 5 mL of O_2 injected into a 0.200-L $Co_2(CO)_8$ solution (k_{obsd} = 5.3 ± 0.3 $M^{-1/2}$ s^{-1}); □, 15 mL of O_2 injected into a 0.200 L $Co_2(CO)_8$ solution (k_{obsd} = 3.7 ± 0.6 $M^{-1/2}$ s^{-1}).

Table III. Observed Rate Constants for Reaction of 1.5 × 10^{-3} M $Co_2(CO)_8$ with PPh_3 in Hexane at 15 °C

$10^2[PPh_3]$, M	k,[a] $M^{-0.35}$ s^{-1}	$10^2[PPh_3]$, M	k,[a] $M^{-0.35}$ s^{-1}
4.75	47.4 ± 3.2	2.00	23.6 ± 2.8
3.56	36.8 ± 3.8	1.50	19.1 ± 2.4
2.67	28.6 ± 3.0		

[a] Averages and standard deviations of constants from several kinetic runs using the same stock solutions.

the orders of the reaction with respect to carbonyl for the reactions with PPh_3 and PBu_3 at 0 °C are 1.5 and 1.3, respectively; in contrast, at 10 °C the orders are 1.33 and 1.00, respectively.

It was observed that addition of O_2 to the reaction system resulted in a slowing of the rate. For those reactions in which the order of the reaction in $Co_2(CO)_8$ is less than $^3/_2$, introduction of O_2 also had the effect of increasing the reaction order. Thus the presence of residual impurities of oxygen in reaction solutions, which vary from one set of kinetic runs to another, results in a varying order in carbonyl, depending on the temperature of the reaction and the base. Injection of oxygen into reaction solutions, when the reactions are carried out under conditions that result in $^3/_2$ order in carbonyl, slows down the reaction rate. Pseudo-$^3/_2$ order plots for the reaction of $Co_2(CO)_8$ with PPh_3 at 0 °C, in the presence and absence of oxygen, are shown in Figure 2.

The reaction of $Co_2(CO)_8$ with PPh_3, at varying concentrations at 0 °C, was studied by using the same hexane stock solutions in all the runs. The reactions followed good pseudo-$^3/_2$ order rate behavior up to at least 95% completion. However, the pseudo-$^3/_2$-order rate constants did not vary uniformly with PPh_3 concentration. We have already noted the marked effect of traces of O_2 on the reaction rate, as depicted in Figure 2. The effects of traces of O_2 on reaction rate seemed most marked for PPh_3 at this lowest temperature studied. Possible reasons for this will be more conveniently discussed when we consider the mechanism (vide infra).

The reaction of $Co_2(CO)_8$ with PPh_3 was also studied at 15 °C. At this temperature the apparent order of the reaction in $Co_2(CO)_8$ is 1.35. The observed rate constants in these kinetic runs are listed for various PPh_3 concentrations in Table III.

Reaction of $Co_2(CO)_8$ with PBu_3 was studied at −15, −10, 5, and 10 °C. The order of the reaction in $Co_2(CO)_8$ was observed to be 1.40, 1.35, 1.20, and 1.0, respectively. A graph of the kinetic data at −15 °C, based on an assumed 1.40 order in $Co_2(CO)_8$, is shown in Figure 3. Graphs of some results at 10 °C, based on an assumed pseudo-first-order dependence on $[Co_2(CO)_8]$, are shown in Figure 4. Pseudo-1.40-order observed rate constants for the reaction at −15 °C and pseudo-first-order rate constants for the reaction at 10 °C are listed in Table IV.

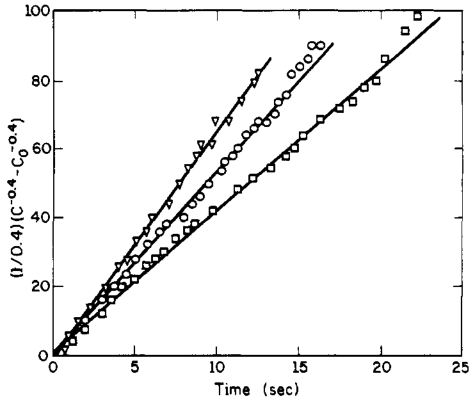

Figure 3. Pseudo-1.40-order plots for reaction of 1.5 × 10^{-3} M $Co_2(CO)_8$ with PBu_3 at −15 °C. Base concentrations are as follows: ▽, 6.00 × 10^{-2} M; ○, 4.50 × 10^{-2} M; □, 2.53 × 10^{-2} M.

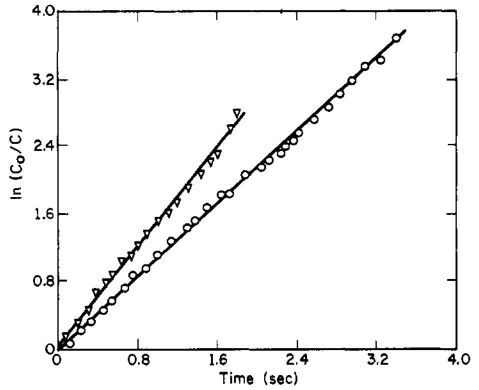

Figure 4. Pseudo-first-order plots for reaction of 1.5 × 10^{-3} M $Co_2(CO)_8$ with PBu_3 at 10 °C. Base concentrations are as follows: ▽, 5.63 × 10^{-2} M; ○, 2.51 × 10^{-2} M.

Table IV. Rate Constants for Reaction of 1.5 × 10^{-3} M $Co_2(CO)_8$ with PBu_3 in Hexane

$10^2[PBu_3]$, M	T, °C	k[a]
8.00	−15	5.0 ± 1.6[b]
6.00	−15	6.4 ± 0.6[b]
4.50	−15	5.6 ± 0.9[b]
3.38	−15	4.4 ± 0.4[b]
2.53	−15	4.1 ± 0.4[b]
5.63	10	1.5 ± 0.1[c]
3.75	10	1.4 ± 0.1[c]
2.51	10	1.2 ± 0.1[c]

[a] Averages and standard deviations based on several kinetic runs using the same stock solutions. [b] Units of k are $M^{-0.4}$ s^{-1}. [c] Units of k are s^{-1}.

It is evident from the data presented that the rate of reaction of $Co_2(CO)_8$ with PPh_3 or PBu_3 varies with the particular base and, for a given base, with base concentration. However, the order of the dependence on phosphine concentration in the range (1.0–5.0) × 10^{-2} M is difficult to ascertain. The order in phosphine appears to be about 0.3 for reaction with PBu_3 at 10 °C, 0.6 for reaction with PBu_3 at −15 °C, and 0.8 for reaction with PPh_3 at 15 °C. (We have previously reported an apparent order in phosphine of 0.6 for reaction with PBu_3 in hexane at 25 °C.[24]) These values have relatively high uncertainty due to the marked inhibiting effects of traces of oxygen and other impurities on the reaction rates.

Discussion

The three major possibilities for reaction pathways in the initial reaction of $Co_2(CO)_8$ with a base L are as follows.

(a) Homolytic dissociation via rupture of the Co–Co bond:

$$Co_2(CO)_8 \rightarrow 2Co(CO)_4\cdot \quad (1)$$

$$Co(CO)_4\cdot + L \rightarrow Co(CO)_3L\cdot + CO \quad \text{fast} \quad (2)$$

This pathway is rendered plausible by the reputed weakness of the Co–Co bond. A rapid substitution into the $Co(CO)_4\cdot$ radical is expected on the basis of other studies of metal carbonyl substitution reactions proceeding via radical intermediates.[26,30–32]

(b) Dissociative loss of CO:

$$\mathrm{Co_2(CO)_8 \rightarrow Co_2(CO)_7 + CO} \tag{3}$$

$$\mathrm{Co_2(CO)_7 + L \rightarrow Co_2(CO)_7L}\quad \text{fast} \tag{4}$$

This pathway has been suggested as a first step in reactions of $Co_2(CO)_8$ in several contexts. It is noteworthy in comparing processes a and b that matrix isolation IR spectra of $Co_2(CO)_8$ deposited into inert matrices from the gas phase at about 30 °C show evidence of small amounts of $Co_2(CO)_7$ but no evidence of the mononuclear $Co(CO)_n$ fragments that might result from an initial Co–Co bond rupture.[5] On the other hand, there is ESR evidence for homolytic rupture of the Co–Co bond under these conditions.[33,34]

(c) Associative interaction of L with $Co_2(CO)_8$:

$$\mathrm{Co_2(CO)_8 + L \rightarrow Co_2(CO)_8L} \tag{5}$$

The product $Co_2(CO)_8L$ might be supposed to lose CO to form $Co_2(CO)_7L$ and undergo rupture of the metal–metal bond or some other process. An associative interaction of this type was suggested by Heck to account for a limited set of kinetic observations of the reaction of $Co_2(CO)_8$ with PPh_3.[23] A species of the form $Co_2(CO)_9$ was also proposed to account for certain IR absorptions in solutions of $Co_2(CO)_8$ under high CO pressures.[35] However, the results of more recent work[36] provide no evidence for such a species. Two reports of $Co_2(CO)_8L$ substances actually refer to ionic formulations, $Co(CO)_4L\ Co(CO)_4$, where L is an alcohol,[9] or piperidine.[10] However, in neither case was the product isolated and thoroughly characterized.

Reaction of $Co_2(CO)_8$ with $AsPh_3$ or ^{13}CO. The kinetics of reaction of $Co_2(CO)_8$ with $AsPh_3$ is most clearly consistent with pathway b. The first-order rate law, containing no term in the entering ligand, is consistent with a rate-determining loss of CO, followed by rapid reaction to form $Co_2(CO)_7AsPh_3$. It is consistent also with the observed inhibition of reaction upon addition of CO.

An alternative process (eq 6) involving Co–Co bond rupture,

$$\mathrm{Co_2(CO)_8 \rightleftarrows \langle 2Co(CO)_4\rangle \rightleftarrows \langle Co(CO)_3,Co(CO)_4\rangle \rightleftarrows Co_2(CO)_7} \tag{6}$$

$$\mathrm{Co_2(CO)_7 + AsPh_3 \rightarrow Co_2(CO)_7AsPh_3}$$

with CO loss and recombination occurring in a cage (indicated by $\langle\ \rangle$) to form $Co_2(CO)_7$, might be formulated. To account for the observed kinetics, it is necessary to assume that a large fraction of $Co(CO)_4$ radicals react as indicated, whereas it seems more reasonable that a fairly large fraction would diffuse from the cage and separately undergo substitution, in which case $Co(CO)_6(AsPh_3)_2$ would be a major initial product. By contrast, the disubstituted product appears only as a secondary product, in the subsequent reaction of the initially formed $Co_2(CO)_7AsPh_3$. Furthermore, the absence of any effect of added O_2 on the reaction rate is not consistent with the presence of radicals. We thus conclude that Co–Co bond breaking it not rate determining in this simple substitution process. This conclusion in turn suggests that the estimate of only about 50 kJ mol^{-1} for the Co–Co bond dissociation energy must be low. Since the entropy of activation accompanying Co–Co bond rupture is likely to be positive for CO dissociation (e.g., $\Delta S^\ddagger$ for metal–metal bond rupture in reactions of $Mn_2(CO)_{10}$ is on the order of 70–90 J K^{-1} mol^{-1}),[37] the free-energy barrier for this homolytic cleavage should be much lower than the observed free energy of activation if the enthalpy change were only about 50 kJ mol^{-1}.[8] On the basis of these considerations, we suggest that the Co–Co bond dissociation energy must be 100 kJ mol^{-1} or larger.

The observed kinetics for the reaction with $AsPh_3$ is in good agreement with results obtained by others for processes in which the loss of CO is postulated as an initial step. For example, reaction with $AsPh_3$ is rapid in comparison with the rate of reaction of $Co_2(CO)_8$ with H_2,[16] as required by the assumption that reaction with H_2 is preceded by a preequilibrium involving loss of CO. For the equilibrium process

$$\mathrm{Co_2(CO)_8 \rightleftarrows Co_2(CO)_7 + CO} \tag{7}$$

Ungvary reports a ΔH of 88 kJ mol^{-1}. This compares favorably with the value of 93 kJ mol^{-1} estimated for $\Delta H^\ddagger$ from our kinetics. It is reasonable to expect that the activation enthalpy for a dissociative process should be just slightly larger than the overall enthalpy change, assuming that the transition state is well advanced toward dissociation.[38]

The rate constant for exchange of ^{13}CO at 0 °C, about 3.0×10^{-4} s^{-1}, is in reasonable agreement with the rate constant for reaction with $AsPh_3$ extrapolated to 0 °C (5.4×10^{-4} s^{-1}), given the difficulties in measurement of the exchange rate constant. We conclude that both processes proceed via the same rate-determining dissociative loss of CO.

Reaction of $Co_2(CO)_8$ with Phosphines. It is evident that the reaction of phosphines cannot be proceeding by the same overall mechanism as the reaction with $AsPh_3$ or ^{13}CO; the phosphine reactions are much faster and the products differ. The form of the observed rate law, dependence on trace concentrations of oxygen, and the formation of disproportionation products all suggest a radical chain mechanism involving electron transfer, analogous to that invoked in accounting for the reactions of $SnCl_3Co(CO)_4$.[26] The suggested mechanism is seen in eq 8–17.[24,39]

$$\mathrm{Co_2(CO)_8 + L \underset{k_2}{\overset{k_1}{\rightleftarrows}} Co_2(CO)_8L} \tag{8}$$

$$\mathrm{Co_2(CO)_8L \xrightarrow{k_3} Co(CO)_3L\cdot + Co(CO)_4\cdot + CO} \tag{9}$$

$$\mathrm{Co(CO)_3L\cdot + Co_2(CO)_8 \xrightarrow{k_4} Co(CO)_3L^+ + Co_2(CO)_8{}^-\cdot} \tag{10}$$

$$\mathrm{Co_2(CO)_8{}^-\cdot \xrightarrow{k_5} Co(CO)_4\cdot + Co(CO)_4{}^-} \tag{11}$$

$$\mathrm{Co(CO)_3L^+ + L \xrightarrow{k_6} Co(CO)_3L_2{}^+} \tag{12}$$

$$\mathrm{Co(CO)_4\cdot \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} Co(CO)_3 + CO} \tag{13}$$

$$\mathrm{Co(CO)_3 + L \xrightarrow{k_8} Co(CO)_3L\cdot} \tag{14}$$

$$\mathrm{Co(CO)_4\cdot + Co(CO)_3L\cdot \xrightarrow{k_9} Co_2(CO)_7L} \tag{15}$$

$$\mathrm{Co(CO)_3L\cdot + Co(CO)_3L\cdot \xrightarrow{k_{10}} Co_2(CO)_6L_2} \tag{16}$$

$$\mathrm{Co(CO)_4\cdot + Co(CO)_4\cdot \xrightarrow{k_{11}} Co_2(CO)_8} \tag{17}$$

The initial formation of a ligand–carbonyl adduct can be assumed to occur rapidly and to be reversible. The adduct might go on to a further reaction as shown in eq 9, but other possibilities exist, notably the formation of $Co_2(CO)_7L$ with expulsion of CO. In separate experiments we determined that PBu_3 reacts with $Co_2(CO)_7PBu_3$ at a much slower rate than with $Co_2(CO)_8$. Furthermore, the products of the reaction are a mixture of

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$Co_2(CO)_6(PBu_3)_2$ and the ionic product $[Co(CO)_3(PBu_3)_2]Co(CO)_4$. These results do not unequivocally rule out a role as intermediate for $Co_2(CO)_7PBu_3$ in a reaction system containing both $Co_2(CO)_8$ and PBu_3 but it seems very unlikely.

The fact that no significant quantity of $Co_2(CO)_7PBu_3$ nor $Co_2(CO)_6(PBu_3)_2$ is formed during reaction suggests also that the chain process, involving eq 10–14, is rapid relative to the bimolecular recombination processes eq 15 and 16.

It is assumed that decomposition of $Co_2(CO)_8^{-}\cdot$ to $Co(CO)_4\cdot$ and $Co(CO)_4^-$ is rapid. This is a reasonable assumption; the highest energy electron in the radical anion doubtlessly resides in the antibonding orbital of the metal–metal bond. Experimental evidence that such processes are fast is found in the results of a pulse radiolysis study involving $Mn_2(CO)_{10}$ and $Mn(CO)_5Br$,[40] in which fast Mn–Mn or Mn–Br bond dissociations were observed from the respective radical anions.

The electron-transfer step eq 10 should vary in rate with the energy of the highest occupied level in the radical. This in turn should be a function of the donor characteristics of the ligand L. A ligand such as $AsPh_3$, of relatively low nucleophilicity, fails to give rise to the radical chain mechanism either because the preequilibrium with $Co_2(CO)_8$ does not lead to Co–Co bond rupture (eq 8), or because reaction 10 does not proceed at a rate that is rapid with respect to chain termination steps.

It is possible to obtain an idea of the sort of kinetic behavior that follows from such a mechanism by assuming the simplest set of conditions: a steady state in which the rate of initiation (eq 9) equals the rate of termination for the intermediate $Co(CO)_6L\cdot$ radical. We assume also for simplicity that the most important termination process for $Co(CO)_3L\cdot$ is eq 16. Thus we have

$$-d[Co_2(CO)_8]/dt = k_4[Co(CO)_3L\cdot][Co_2(CO)_8] \tag{18}$$

$$k_{10}[Co(CO)_3L\cdot]^2 = k_3[Co_2(CO)_8L] \tag{19}$$

$$k_{10}[Co(CO)_3L\cdot]^2 = (k_3k_1/k_2)[Co_2(CO)_8][L] \tag{20}$$

$$-d[Co_2(CO)_8]/dt = k_4(k_3k_1/k_{10}k_2)^{1/2}[Co_2(CO)_8]^{3/2}[L]^{1/2} \tag{21}$$

This idealized model for the reaction predicts a $^3/_2$ order dependence on $Co_2(CO)_8$ and $^1/_2$ order dependence on L. The observed kinetics may differ considerably from these predictions, for a variety of reasons. The most important is that the steady-state assumptions are likely to fail when the radical chain loop is very fast. Orders in substrate which depart from the values derived from the idealized steady-state treatment are not uncommon in the kinetics of free-radical chain reactions. For example, observed and derived rate laws for the photolytic reaction of toluene (RH) with *tert*-butyl hypochlorite (*t*-BuOCl) are[41]

$$\text{observed rate} = k'[RH]^{0.92}[t\text{-BuOCl}]^{0.65}$$

$$\text{derived rate} = k[RH][t\text{-BuOCl}]^{0.5}$$

For the photolytic reaction of $CHCl_3$ with *t*-BuOCl

$$\text{observed rate} = k'[t\text{-BuOCl}]^{1.30}$$

$$\text{derived rate} = k[t\text{-BuOCl}]^{1.5}$$

It is noteworthy that addition of O_2 causes a general decrease in overall rate and shift in reaction order in $Co_2(CO)_8$ to the value 1.5 expected from the derived rate law. The origin of this effect is probably the formation of a dioxygen adduct with the radical species, e.g.

$$Co(CO)_3L\cdot + O_2 \rightleftarrows (CO)_3LCo{-}O{-}O \tag{22}$$

Reversible dioxygen adduct formation is well-known for several five-coordinate Co(II) species possessing 17 electrons in the metal valence orbitals.[42] The formation of dioxygen adducts with $Co(CN)_5^{3-}$ and carbonyl radicals, including $Co(CO)_4\cdot$, has been established from matrix isolation ESR measurements.[34,43] It is not unreasonable that a dioxygen adduct of $Co(CO)_4\cdot$ should form reversibly in solution. With the assumption that the dioxygen complex does not undergo electron transfer to $Co_2(CO)_8$, the effect of added O_2 would be to reduce the overall rate and in particular to slow the chain propagation step in relation to the initiation process. Under such conditions a closer approach to the derived rate law might be realized.

Although added O_2 markedly reduces reaction rates, it does not have the dramatic effect in these reactions that we have observed in some other cases, notably in the substitution of $Cl_3SnCo(CO)_4\cdot$.[26] The reasons for this are not clear; additional study of the character of dioxygen interaction with the metal carbonyl radicals will be required before much progress can be made on this question. In addition, there is a need for more information regarding oxidation and reduction potentials of the carbonyl radicals, especially with respect to how these are affected by substitution.

We have chosen to represent the substitution of the $Co(CO)_4\cdot$ radical as proceeding by a dissociative process, followed by rapid uptake of ligand L. It has been argued that such a process is more likely to occur by an associative displacement by L.[44] The analysis of the present reaction system is not significantly different for this alternative view regarding the substitution process. What is important is that the carbonyl radical is very labile.

Numerical Testing of the Reaction Scheme. As a means of further testing the proposed reaction scheme we have numerically integrated the rate equation for reactions 8 through 17, by using an efficient algorithm for numerical integration of "stiff" differential equations.[45] The purposes of this procedure have been to determine whether there is a physically reasonable set of rate constants k_1 through k_{11} that can reproduce the observed behavior for a given phosphine, PBu_3 in particular. The requirements are that the overall apparent rate constant and reaction order in $Co_2(CO)_8$ must be fitted. Furthermore, the apparent order in L that results from calculating the overall rate constant as a function of initial L (present in excess) should resemble that observed. The rate constants must lead to the correct product (note that *several* products are possible), and the absence of observable concentrations of intermediates during reaction must also be accounted for.

The rate constants k_{10} and k_{11} have recently been measured in flash photolysis experiments in our laboratory and found to have values of $k_{10} = 9.1 \times 10^7$ M^{-1} s^{-1} and $k_{11} = 4.1 \times 10^8$ M^{-1} s^{-1}.[46] These results are qualitatively consistent with those observed for other metal carbonyl radical recombinations.[47] We assume that k_9 is intermediate in value between k_{10} and k_{11}; $k_9 = 1.9 \times 10^8$ M^{-1} s^{-1}.

Once past the induction period the overall rate of reaction is determined by the cycling time for the loop in the chain process. To account for the observed overall rates of reaction with PBu_3, it is necessary to assign k_7 a value of about 10^6 s^{-1} or greater. This is not unreasonable in light of the observed characteristics of the 17-electron carbonyl radicals, several of which exhibit extraordinary lability toward substitution for CO.[32,48] For example, the *lower bound* on the first-order rate constant for dissociative loss of CO from $Mn(CO)_5\cdot$ is >10 s^{-1}.[32]

Outer-sphere electron-transfer processes have been invoked before in mechanisms involving organometallic compounds.[49,51]

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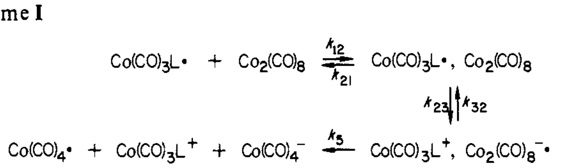
Scheme I



The outer-sphere electron-transfer process represented by eq 10 is a key step in the chain process we proposed. The rate constant k_4 is likely to be very sensitive to the nature of L. Unfortunately, we do not know the energetics of this proposed electron transfer. The potentials for reversible oxidation or reduction of neither the radical $Co(CO)_3L\cdot$ nor $Co_2(CO)_8$ are known. However, it is known that $Co_2(CO)_8$ is irreversibly reduced to $Co(CO)_4^-$ in a 2-electron process, at relatively low potential.[52] Further, the replacement of CO by L to afford $Co_2(CO)_6L_2$ compounds results in a substantial negative shift in reduction potential.[53] We may thus reason that when L is a strongly electron-donating ligand such as PBu_3, the potential for oxidation of $Co(CO)_3L\cdot$ may be quite high. To fit the observed orders of reaction in $Co_2(CO)_8$ at the temperatures 25 and −15 °C and to fit the overall reaction rate at each temperature, we found the optimal values of k_4 to be 2.1×10^8 and 1.7×10^7 M^{-1} s^{-1} for 25[24] and −15 °C, respectively.

Electron-transfer processes of a kind related to that under consideration here have recently been discussed.[54,55] The overall process may be described as in Scheme I. The rate constant k_4 in our reaction scheme embraces several preequilibrium rate constants and incorporates the reverse electron-transfer process (k_{32}), if it is of importance in relation to dissociation of $Co_2(CO)_8^{-}\cdot$. Dissociation of the dinuclear radical anion may be expected to be prompt following the electron attachment. Although the cobalt system has not been studied, Waltz and co-workers have noted that the rate constant for dissociation of $Mn_2(CO)_{10}^-$ following electron attachment in pulsed radiolysis is 10^7 M^{-1} s^{-1} and possibly much faster.[40] It is to be noted also that the Co–Co bond in $Co_2(CO)_8$ is not notably strong. Addition of an electron to the metal–metal σ^* orbital should result in a substantial weakening of an already weak bond. We may guess that $\Delta H^{\ddagger}$ for the dissociation of $Co_2(CO)_8^{-}\cdot$ is not more than perhaps 50 kJ mol^{-1}. Scheme I may represent an example of the third class of electron-transfer situations recently described by Schuster,[55] in which the electron-transfer step is endergonic, i.e., $\Delta G > 0$, but substantially irreversible because $k_5 \gg k_{32}$. The value required for our overall electron-transfer rate constant k_4 to obtain a fit with the PBu_3 data at room temperature (2.1×10^8 M^{-1} s^{-1}) is sufficiently high to suggest that ΔG is small. At the same time, the temperature dependence of the rate constant (vide infra) suggests an activated process.

We can ignore the reverse reaction in eq 13 in the absence of added CO. The rate constants k_6 and k_8 should both be large because they refer to reactions of a base with a coordinatively unsaturated, electrophilic species. We assume $k_6 = 1 \times 10^5$ M^{-1} s^{-1} and $k_8 = 1 \times 10^7$ M^{-1} s^{-1}. (Note by way of analogy that recombination of $Cr(CO)_5$ with ligands occurs in cyclohexane with a rate constant of 3×10^6 M^{-1} s^{-1}.[56])

Table V. Values of Rate Constants for Equations 8-17 Employed in Numerical Analysis

	I, °C	
	25	−15
k_1	6.1 (3)	7.0 (1)
k_2	1.7 (7)	6.8 (5)
k_3	7.0 (1)	5.0 (0)
k_4	2.1 (8)	1.5 (7)
k_5	1.0 (8)	1.0 (8)
k_6	1.0 (5)	1.0 (5)
k_7	1.0 (6)	1.0 (6)
k_8	1.0 (7)	1.0 (7)
k_9	1.9 (8)	1.0 (8)
k_{10}	9.1 (7)	2.5 (7)
k_{11}	4.1 (8)	4.1 (8)

[a] Values for k are written in the form $a(b)$, which represents $a \times 10^b$. Units are s^{-1} or M^{-1} s^{-1} as appropriate.

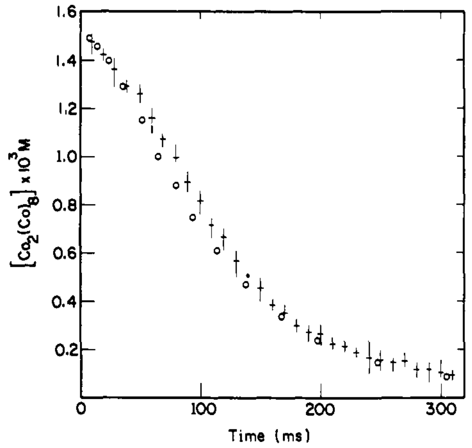


Figure 5. Variation in $[Co_2(CO)_8]$ with time in reaction of 1.5×10^{-3} M $Co_2(CO)_8$ with 3.0×10^{-2} M PBu_3 in CH_2Cl_2 at 25 °C. The daggers represent experimental data (average of three separate runs);[24] the circles represent calculated results using the rate constants in Table V.

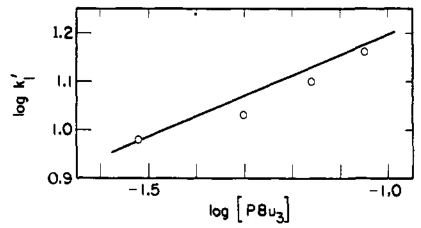


Figure 6. Log pseudo-first-order rate constant at 25 °C for reaction of $Co_2(CO)_8$ with excess PBu_3 in CH_2Cl_2 vs. log $[PBu_3]$. The circles refer to experimental data[24] and the line to calculated results.

The preequilibria involving rate constants k_1, k_2, and k_3 are important because they determine the time dependence of the reaction at short times. In addition, for a given value of k_4, chosen to yield the correct reaction order in $Co_2(CO)_8$, the values for the rate constants k_1, k_2, and k_3, involving the preequilibrium, are important in determining the overall rate of reaction. Furthermore, the course of the reaction in the very early stages is a sensitive function of the values for these rate constants. However, we do not in any case see large and prominent induction periods. In fact, induction periods were not noted at all when the reaction was studied on the conventional IR spectrophotometer used to obtain the data described in this paper. Only when an IR stopped-flow instrument with exceptional short-time response capability was used could induction periods be seen in the PBu_3 reactions. To achieve a reasonable fit to the PBu_3 data at 25 °C, we required values of $k_1 = 6.1 \times 10^3$ M^{-1} s^{-1}, $k_2 = 1.7 \times 10^7$ s^{-1}, and $k_3 = 70$ s^{-1}.[24]

With the set of rate constants at 25 °C just discussed and listed in Table V, it is possible to obtain an excellent fit to the $[Co_2(CO)_8]$ vs. time data for reaction with PBu_3,[24] as illustrated in

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Figure 5. The apparent order of the reaction in $Co_2(CO)_8$ was determined from these results by calculating the value for n that gives the best fit with data in the integrated rate expression for the pseudo-nth-order rate expression eq 23. A best fit for the

$$d[Co_2(CO)_8]/dt = k'[Co_2(CO)_8]^n \qquad (23)$$

25 °C data was obtained for $n = 1.0$, whether or not the data for the induction period were retained in the fitting procedure, for data covering the first 5 half-lines.

To test the apparent order in the concentration of ligand L, the pseudo-first-order rate constants based on the calculated $Co_2(CO)_8$ concentration vs. time data were computed for varying assumed initial PBu_3 concentrations. Figure 6 shows a log of the pseudo-first-order rate constants k'_1 based on the experimental data at 25 °C in CH_2Cl_2 solvent as a function of log $[PBu_3]$. The experimental data are represented by circles; the line represents the calculated variation in log k'_1 vs. log $[PBu_3]$. The agreement is quite good.

As temperature is lowered, all of the rate constants estimated in the reaction scheme should decrease. However, the relative rates of decrease should vary greatly; k_5, k_9, k_{10}, k_{11}, k_6, and k_8 should undergo relatively small changes, because the enthalpies of activation in the processes involved are likely to be low. The model calculations show that the major factor in determining the apparent order of the reaction is the rate constant k_4 in relation to the recombination rate constants k_9 and k_{10}.

The temperature coefficients of rate constants k_9 and k_{10} should be quite small; we assume an Arrhenius energy for reaction 15 of 12 kJ mol^{-1} and for reaction 16 of 21 kJ mol^{-1}. Having values for k_9 and k_{10} at 25 °C, it is thus possible to estimate values for these two constants in the temperature range +25 to -15 °C. With these values for k_9 and k_{10}, values for k_1, k_2 k_3, and k_4 that give an order in $Co_2(CO)_8$ in agreement with that of experimental values can be found. The values of the rate constants employed to fit the experimental observations are listed in Table V.

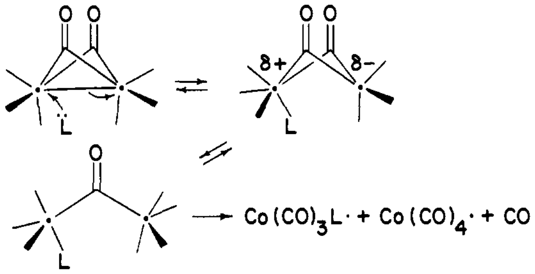
It is encouraging that the temperature dependencies of the rate constants that need to be varied to obtain a fit with the data are all reasonable. The apparent Arrhenius energies calculated from the temperature variations of k_1, k_2, k_3, and k_4 are about 75, 55, 45, and 40 kJ mol^{-1}, respectively. The value of E_a of eq 10 seems rather high considering the value of k_4, near the diffusion-controlled limit. The estimate of E_a is, of course, quite rough; it might be as low as half this value. In general, however, the results suggest a relatively positive value for $\Delta S^\ddagger$. This is a reasonable result, because there is little contribution from solvent rearrangement and there may be only a small contribution from ligand reorganization in oxidant or reductant.

The calculations described have not been carried out with the intention of accurately determining any of the rate constants in the reaction scheme. The system contains too many disposable parameters for this to be feasible. However, it is important that for a reasonable set of rate constants the proposed reaction scheme is in excellent accord with experiment. Furthermore, for certain critical rate constants such as k_4 the range of values that gives acceptable agreement with experiment is not large and not strongly influenced by changes that can reasonably be made in the other parameters. The agreement with experimental values extends to reproducing the observed apparent orders in both reactants and to reproducing the observed variations in order with temperature by making credible assumptions about the temperature variations in the rate constants.

It is evident that the experimental results for PPh_3 as ligand are analogous to those for PBu_3. The reaction is slower, probably because the initial equilibrium formation of $Co_2(CO)_8L$ lies further to the left and because the electron-transfer rate with $Co(CO)_3PPh_3\cdot$ is not as high as for $Co(CO)_3PBu_3\cdot$. We speculate that the sensitivity of the reaction rates to traces of O_2 is greater for the PPh_3 reactions at lower temperatures because the average lifetime of the $Co(CO)_3PPh_3\cdot$ radical is longer due to a lower value for k_4. This longer lifetime permits a greater extent of reaction with any agent that can act to block the chain. However, to make further detailed distinctions, we must have more data regarding key individual steps in the reaction scheme.

By way of summary we have in the present work demonstrated the existence of two distinct mechanisms for substitution of CO in $Co_2(CO)_8$ in aprotic solvent media. One of these involves a rate-determining dissociation of CO. The first-order rate constant for CO loss is comparable to that for loss of CO from $Ni(CO)_4$.[57] As CO loss rates from binary carbonyls go, this is a relatively fast process. Presumably the coordinatively unsaturated intermediate $Co_2(CO)_7$ is the same moiety that has been observed in matrix isolation studies.[5]

The second and more extraordinary pathway for substitution involves an associative attack at $Co_2(CO)_8$, forming an intermediate $Co_2(CO)_8L$ species. The form of the dinuclear metal compound that contains bridging CO groups should be particularly susceptible to such an attack, which can be pictured as



Through an outer-sphere electron-transfer reaction, the $Co(CO)_3L\cdot$ species thus formed initiates a radical chain process leading to formation of the observed ionic product. For the radical chain pathway to be important the ligand must be sufficiently nucleophilic to form an adduct with $Co_2(CO)_8$ and for $Co(CO)_3L\cdot$ to undergo the electron-transfer reaction with $Co_2(CO)_8$. In a following paper we will show the manner in which the reaction course is influenced by both the nucleophilicity and steric requirements of the ligand L.

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(57) Day, P. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 6927–6933.