Title
Nucleophilic Activation of Carbon Monoxide. A Kinetics Investigation of the Reaction of Chloride with Triruthenium Dodecacarbonyl

Permalink
https://escholarship.org/uc/item/8pz232kr

Journal
Inorganic Chemistry, 32(23)

ISSN
0020-1669

Authors
Lillis, J
Rokicki, A
Chin, T
et al.

Publication Date
1993

DOI
10.1021/ic00075a016

Peer reviewed
Nucleophilic Activation of Carbon Monoxide. A Kinetics Investigation of the Reaction of Chloride with Triruthenium Dodecacarbonyl

Jerome Lillis, Andrzej Rokicki, Tyrena Chin, and Peter C. Ford

Department of Chemistry, University of California, Santa Barbara, California 93106

Received May 27, 1993

Kinetics studies of the reaction of the triruthenium cluster Ru₃(CO)₁₂, with the "highly dissociated" chloride salt [PPN][Cl] to give the Ru₃(CO)₁₁Cl⁻ anion in THF/CH₂Cl₂ solutions show a rate law first order in [Cl⁻] and in [Ru₃(CO)₁₂]. Rates are significantly higher in 90/10 than in 80/10 (v/v) THF/CH₂Cl₂ solutions, and the reactivity order is qualitatively the inverse of that of solvent acceptor properties. No intermediates were observed in the reactions. For P_CO > 0.1 atm, the rates appeared nearly CO independent although systematic small rate increases were observed at lower P_CO. It is suggested that the reaction with Cl⁻ may involve competitive nucleophilic attack at both metal and carbonyl centers.

Introduction

Reactions of Lewis base nucleophiles with metal carbonyl complexes have been well documented, and adducts formed by attack at the coordinated CO (eq 1) have been characterized for a number of oxygen and nitrogen bases. Such species play important roles in the homogeneous catalytic activation of CO via reactions such as the water gas shift, reductive carbonylation of nitroaromatics, oxidations and reductions of CO, and Reppe hydrogenation and hydroformylations of alkenes. Adduct formation also strongly influences the subsequent reactions of the complex; e.g., the methoxycarbonyl cluster Ru₃(CO)₁₁(COCH₃)⁻ is orders of magnitude more reactive toward ligand substitution (eq 2) and hydrogen activation (eq 3) than is the parent cluster Ru₃(CO)₁₂ under comparable conditions.

\[
\text{M-CO + Nu} \rightarrow \text{M-CO} - \text{Nu} \quad (1)
\]

\[
\text{Ru₃(CO)₁₁(COCH₃)⁻ + L} \rightarrow \text{Ru₃(CO)₁₀(L(CO₂CH₃)⁻) + CO} \quad (2)
\]

\[
\text{Ru₃(CO)₁₁(CO₂CH₃)⁻ + H₂} \rightarrow \text{HRu₃(CO)₁₀ + HCO₂CH₃} \quad (3)
\]

Among nucleophiles also known to activate metal carbonyls are the simple halide and pseudohalide anions X⁻ in relatively nonpolar solvents. For example, "highly dissociated" halide salts are the simple halide and pseudohalide anions nonpolar solvents. For example, "highly dissociated" halide salts have been characterized for eqs 2 and 5, the final product being the anion cluster Ru₃(CO)₁₂Cl⁻. For example, the direct reaction of Cl⁻ with Ru₃(CO)₁₂ in tetrahydrofuran follows the sequence outlined in eqs 4 and 5, the final product being the anion cluster Ru₃(CO)₁₂Cl⁻.

\[
\text{Ru₃(CO)₁₂ + Cl⁻} \rightarrow \text{Ru₃(CO)₁₁Cl⁻ + CO} \quad (4)
\]

\[
\text{Ru₃(CO)₁₁Cl⁻} \rightarrow \text{Ru₃(CO)₁₀(μ-Cl)⁻ + CO} \quad (5)
\]

Ru₃(CO)₁₀(μ-Cl)⁻ (A) with two CO's replaced by a bridging chloride. One intermediate is the monosubstituted anion Ru₃(CO)₁₁Cl⁻ (B), which we have isolated as the PPN⁺ salt ([PPN][Cl] (97%), and characterized crystallographically. The present kinetics investigation was initiated with the goal of providing a more quantitative characterization of this reaction.

Experimental Section

Materials. Gases, CO (CP grade), CO/Ar mixtures, argon, and nitrogen, were purchased from Liquid Carbones Inc. The CO and CO/Ar mixtures were purified by passing through a heated column of BASF Deox catalyst and then a Drierite column. Argon and nitrogen were treated in the same way.

Solvents were distilled under argon or nitrogen. Tetrahydrofuran (THF) was from freshly opened bottles, and for kinetics studies this was purified by distilling first from sodium and then from lithium aluminum hydride immediately before use. Methylene chloride and hexanes were distilled from calcium hydride. Triphenylphosphine oxide, 2,6-di-tert-butyl-4-methylphenol (BHT), and bis(triphenylphosphoranylidine)ammonium chloride, ([PPN][Cl] (97%), were purchased from Aldrich. Trimethyl phosphite was distilled from sodium and stored in a Schlenk type flask under nitrogen. Ru₃(CO)₁₂ was prepared by a high-pressure reaction of RuCl₃ with CO as described previously or was purchased from Strem Chemicals. The solid ([PPN][Cl] was recrystallized from 9/1 THF/CH₂Cl₂ ground to a fine powder.
dried overnight in a Schlenk tube under vacuum, and then stored under an inert atmosphere until use. The [PPN]Cl purified in this manner had a melting point of 237 °C (lit. 271 °C).

**Instrumentation.** Infrared spectra were collected on a Bio-Rad Digilab FT-60 FTIR in NaCl liquid samples cells. UV/vis spectra were collected on a Cary 118, an OLIS computerized Cary 118, or a Hewlett Packard 8452A diode array spectrophotometer interfaced to a HP 9000 computer, each equipped with thermostated cell compartments. The UV/vis cells were used in 1.0-cm quartz cells adapted for Schlenk techniques. Teflon stopcocks were used in order to minimize potential contact with vacuum grease. Rate data analyses were done on an IBM compatible 286 computer using Asystar (Macmillan Software), MINSQ software (Micromath Scientific Software), or the OLIS kinetic fitting routines.

**Synthesis and Characterization.** (a) [PPN][Ru(CO)3Cl2]. A solution of [PPN][Cl] (0.062 g, 0.10 mmol) and Ru3(CO)12 (0.058 g, 0.09 mmol) was prepared by placing the solids together in a Schlenk tube and evacuating for 1 h before introducing CO (1 atm) and deaerated THF (10 mL). After reaction at room temperature for 1 h, the solution had turned from orange to dark red and displayed an IR spectrum corresponding to Ru3(CO)11Cl-. The solvent was then removed under vacuum to leave a red residue. A CO atmosphere was reintroduced, and a minimum volume of THF was added by syringe to a clean Schlenk tube. The product was precipitated by adding hexanes (yield ~80%). For UV/vis spectra, the solutions were transferred by syringe to a Schlenk-adapted 1-cm quartz cell. For FTIR spectra, solutions were transferred by syringe to a deaerated IR solution cell. The IR spectrum displayed ν(CO) bands at 2066 (vs), 2034 (sh), 2030 (s), 2065 (m), 1975 (m), 1862 (m), and 1838 (s, br) cm⁻¹, in agreement with literature values for [PPN][Ru3(CO)11Cl2].

The optical spectrum displayed a λmax at 404 nm (ε = 6600 M⁻¹ cm⁻¹) in THF solution, and the ambient temperature 1H NMR spectrum showed a singlet at 211 ppm in both THF solution and in the solid state (as measured by CMAS spectroscopy).

(b) [PPN][Ru3(CO)10(μ-Cl)]. An equimolar solution of [PPN][Cl] (0.062 g, 0.10 mmol) and Ru3(CO)12 (0.058 g, 0.09 mmol) was prepared by placing the solids together in a Schlenk tube and evacuating for 1 h before introducing N2 (1 atm) and THF (10 mL). Once again, the solution changed from orange to red, and the initial product was identified by the FTIR spectrum to be Ru3(CO)10Cl-. Excess CO was removed by eight successive freeze–pump–thaw cycles, each with 0.5-h equilibration periods at ambient T. The product was identified by its FTIR spectrum to the Ru3(CO)10(μ-Cl). The solvent was then removed under vacuum. A N2 atmosphere was reintroduced, and a minimum volume of THF was added to redissolve the solid. The resulting solution was transferred by syringe to a clean Schlenk tube, and [PPN][Ru3(CO)10(μ-Cl)] was precipitated by the addition of hexanes. The FTIR spectrum gave ν(CO) bands at 2113 (vw), 2077 (w), 2070 (s), 2034 (sh), 2030 (vs), and 1997 (w) cm⁻¹, in agreement with the literature. The optical spectrum gave maxima at 520 nm (2300 M⁻¹ cm⁻¹) and 370 nm (7900 M⁻¹ cm⁻¹).

**Kinetics Studies.** Solutions of Ru3(CO)12 and [PPN][Cl] were prepared in various THF/CH2Cl2 mixtures from freshly distilled solvents under the appropriate atmosphere using Schlenk techniques. CH2Cl2 was required in order to obtain sufficient solubility of [PPN][Cl]. Prior to use, the solvents were subjected to four freeze–pump–thaw degassing cycles. Quantitative amounts of the respective solids were weighed into small volumetric flasks which were then sealed with white Suba-Septa. The flasks were evacuated for a minimum of 1 h, solvent mixtures equilibrated with the appropriate gases were added, and then the flasks were weighed to determine the amounts of solvent added. The [PPN][Cl] stock solution was briefly sonicated to ensure complete dissolution. A 3.0–3.5-mL aliquot of the degassed [PPN][Cl] stock solution was then added to a Schlenk-adapted cuvette and allowed to equilibrate to the experimental T. A 0.5-mL volume of the Ru3(CO)12 stock solution was added by syringe, and the cell was then shaken vigorously. The mixing time before the start of measurements was approximately 10 s. The progress of the reaction was monitored by absorbance vs time at a single λmax on the Cary 118 spectrophotometers or as spectral changes between 300 and 500 nm using the HP diode array spectrophotometer.

**Initial kinetics studies** were plagued by serious irreproducibility problems, eventually traced to solvent impurities. Solutions prepared from THF not rigorously purified immediately before use gave relatively poor reproducibility of the rates and isosbestic points lasting only a few half-lives. (See ref 1 for more details.) The possible role of phosphine oxide impurities in the [PPN][Cl] was examined by adding Ph3PO equivalent to 6% of the [PPN][Cl], but these solutions showed no differences in the kinetic behavior from those with no added Ph3PO. Another possible impurity is a 2,6-di-tert-butyl-4-methylphenol (BHT) (present as a radical inhibitor in commercial THF), but addition of 9 × 10⁻² M BHT led to no differences in the rate behavior.

The reaction of Ru3(CO)12 with P(OMe)3 was studied by adding the neat ligand via microliter syringes to solutions of the cluster in the appropriate solvent. Absorbance changes were followed at 390 nm.

**Results**

The electronic spectrum of Ru3(CO)12 in 90/10 (v/v) THF/CH2Cl2 displays an absorbance maximum (λmax) at 390 nm (εmax = 7900 M⁻¹ cm⁻¹) and a minimum (λmin) at 350 nm (εmin = 3500 M⁻¹ cm⁻¹). Addition of [PPN][Cl] (1.0 × 10⁻³ M) to Ru3(CO)12 (1.0 × 10⁻⁴ M) in THF under CO (PCO = 1.0 atm) led to the spectral changes illustrated in Figure 1. As the reaction progressed, the absorption increased at 350 nm and decreased at 390 nm to give a final spectrum with a λmax at 404 nm (εmax = 6600 M⁻¹ cm⁻¹), consistent with that of Ru3(CO)11Cl-. Thus, the reaction is that indicated by eq 4, and the persistence of isosbestic points at 374, 412, and 446 nm for 5 half-lives suggests that no intermediates of spectrally significant concentrations accumulated under these conditions. A similar experiment carried out at higher concentrations (equimolar [PPN][Cl] and Ru3(CO)12 at 1 × 10⁻² M) in THF under 1 atm of CO demonstrated IR spectral changes consistent with eq 4. There was no indication of other products, e.g., A, in either experiment. When the reaction was carried out at the higher concentration under N2 or Ar, the spectral changes were experimentally indistinguishable from those carried out under added CO.

The enhanced reactivity of B relative to Ru3(CO)12 was demonstrated by an experiment where H2 was bubbled through an ambient-temperature solution of B prepared in situ by reaction of Ru3(CO)12 plus [PPN][Cl] in THF. Over a period of minutes the IR and UV/vis spectra changed in a manner indicating the quantitative conversion of B to the hydride cluster anion HRu3(CO)11. Although the other product was not determined, simple stoichiometry would suggest this to be HCl. Bubbling H2 through an analogous solution of Ru3(CO)12 led to no obvious reaction, although it is well-known that if such solutions are heated, the ruthenium cluster is hydrogenated to give H2Ru4(CO)12. As noted above, the somewhat different nucophile adduct Ru3(CO)11(CO2CH3)2 also reacts readily with H2 at ambient temperature (eq 3) and the enhanced reactivity can in large part be attributed to the enhanced lability of the anionic adduct. The reaction kinetics of eq 4 were studied under conditions where [Cl⁻] ≫ [Ru3(CO)12] by following the absorbance decrease at 390 nm.

---


---

Figure 1. Changes in the absorption spectrum as a function of time for the reaction of [PPN][Cl] (1.0 × 10⁻³ M) with Ru3(CO)12 (1.0 × 10⁻⁴ M) in 90/10 THF/CH2Cl2 (v/v) as a function of time (PCO = 1.0 atm; T = 25 °C).

---

The effect of varying PCO on the reaction kinetics was also probed in 90/10 CH3Cl/THF (v/v) with [Ru3(CO)12Cl] = 1 × 10⁻⁴ M and [Cl⁻] = 1 × 10⁻³ M. Solutions were equilibrated with different CO/Ar mixtures with PCO varied from 0.0011 to 1.0 atm and PAr = 1.0 atm. This gave a [CO] range from 1.1 × 10⁻⁴ to 1.0 × 10⁻² M (assuming CO solubility identical to that in pure THF, 0.011 M atm⁻¹). For PCO > 0.01 atm, the observed reaction proceeded cleanly to Ru3(CO)11Cl⁻ and displayed isosbestic points at 374, 412, and 446 nm for ~3 half-lives. The kobs values obtained at λmax = 390 nm agreed with those obtained for λmax = 350 nm and exhibited modest, but systematic, increases in kobs as PCO was decreased to 0.01 atm (Table I). At lower PCO, the kinetics continued to exhibit first-order behavior, but the temporal absorbance data failed to maintain isosbestic points.

The dependence of the rates on the chloride ion concentration was studied in 90/10 THF/CH3Cl (v/v) under PCO = 1 atm. Solutions were equilibrated with [Cl⁻] ranging from 90/10 atm to 80/20 atm (v/v) in various THF/CH3Cl (v/v) under 0.1 atm (390 nm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[Cl⁻] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.

The dependence of the rates on the CO pressure was studied using THF/CH3Cl (v/v) under 0.1 atm (½ atm). The observed rates at 390 nm agreed with those obtained in Table I. The second-order rate constant was determined to be kobs/[CO] = 0.2 s⁻¹ atm⁻¹, virtually independent of temperature.
acterizable species, the reaction of $\text{Ru}_3(\text{CO})_{12}$ with chloride leads to CO displacement to give a species B with a terminally bound Cl-. The facile reaction in tetrahydrofuran solutions can be attributed to the low acceptor number of THF. Thus, the relative inability of this medium to solvate the halide anion leads to strongly enhanced nucleophilicity of that species. In the mixed THF/dichloromethane solutions, the presence of the CH$_2$Cl$_2$ enhances the solubility of [PPN]Cl but at the same time must suppress the anion's nucleophilicity owing to specific solvation by the better acceptor cosolvent.

A similar solvent effect has been noted by Gross et al.$^{14}$ who showed that the reactions of $\text{Ru}_3(\text{CO})_{12}$ and of Fe(CO)$_5$ with methoxide ion are dramatically faster in mixed THF/MeOH solutions than in neat MeOH. Furthermore, it should be noted that earlier observations of cluster carbonyl activation by "highly dissociated" halide salts such as PPN$^+$Cl$^-$ have generally been made for reactions in poor acceptor solvents, principally THF.

A kinetic solvent effect is of course the result of medium dependent changes in the free energy of activation. In the present case, it is likely that the rate of eq 4 is slower in media with higher AN because these would stabilize the smaller chloride anion relative to the transition state formed by association of Cl$^-$ and $\text{Ru}_3(\text{CO})_{12}$ (see below).

One can envision two limiting mechanisms for the formation of B. The simplest of these would be the direct attack of Cl$^-$ at one of the metal centers of $\text{Ru}_3(\text{CO})_{12}$. Since the metal center is already saturated (i.e., it satisfies the 18-electron rule), one might expect such a process to be accompanied by concerted loss of CO. Alternatively, it would be possible to keep the electron count at a lower value if Cl$^-$ attack were accompanied by scission of a metal-metal bond of the triangular Ru$_3$ cluster, although there is no evidence in the present case of cluster fragmentation accompanying the formation of B. Quantitative studies$^{15}$ of the reactions of $\text{Ru}_3(\text{CO})_{12}$ and various trialkyl- or triarylphosphines and trialkyl phosphites at elevated temperatures have argued that the resulting ligand substitutions occur via competitive dissociative and associative mechanisms; however, the dissociative pathway is too slow to play a significant role at ambient temperature.

An alternative mechanism would involve the attack of Cl$^-$ first on one of the carbonyls to form a chlorocarbonyl adduct as a reactive intermediate. This would be followed by reversible loss of CO to give an unsaturated intermediate C, which could rapidly isomerize to form the chloride complex B (eqs 8–10). The observation of well-behaved isosbestic points in Figure 1 indicates that there is no significant buildup of reactive intermediates such as C and D, although this certainly does not preclude the formation of such species in small steady-state concentrations. Ample analogy exists for eqs 8 and 9 in the form of the known reactivity of $\text{Ru}_3(\text{CO})_{12}$ with strong Brønsted bases such as alkoxides and hydroxides plus the lability of the resulting nucleophile-carbonyl adducts toward CO dissociation and subsequent capture of the resulting unsaturated cluster by various ligands.$^{2,3}$ Indeed such a mechanism was proposed in 1968 by Basolo and Morris$^{16}$ to explain halide ion catalysis of $\text{Fe(CO)}_5(\text{NO})_2$ substitution reactions. An analogous mechanism has been invoked to explain the catalysis of metal carbonyl substitutions by other Lewis bases.$^{17}$

In principle, one should be able to differentiate these mechanisms from the kinetics behavior. If the reaction were proceeding via direct displacement of CO by Cl$^-$, then a simple second-order rate law should be in effect, and there should be no effect of changing $P_{\text{CO}}$, i.e.

$$\frac{d[R_u(\text{CO})_{12}]}{dt} = k_5[\text{Cl}^-][R_u(\text{CO})_{12}]$$  \hspace{1cm} (11)$$

Thus, the modest but systematic increase in $k_{\text{obs}}$ values at lower $P_{\text{CO}}$ would argue against a simple, concerted associative mechanism. On the other hand, the second mechanism might suggest CO effects on the rate of product formation. Application of the steady-state approximation to eqs 8–10 would give the following rate law:$^{18}$

$$\frac{d[R_u(\text{CO})_{12}]}{dt} = \left(\frac{a}{b + c[\text{CO}]}ight)[\text{Cl}^-][R_u(\text{CO})_{12}]$$  \hspace{1cm} (12)$$

However, examination of this rate law in detail shows that CO dependence will become a factor when $c[\text{CO}] \sim b$, but at higher [CO], the reaction should become inversely proportional to [CO] instead of essentially independent of [CO] as observed experimentally (Table I).

Thus, it is clear that neither of the two limiting pathways alone can satisfactorily serve to explain the modest acceleration of the reaction at low $P_{\text{CO}}$ and unresponsiveness of $k_{\text{obs}}$ to this parameter at higher $P_{\text{CO}}$. However, one rationalization might be that both mechanisms, i.e., competitive Cl$^-$ attack either at a Ru site or at a CO, are operational. This would give a rate law of the form

$$\frac{d[R_u(\text{CO})_{12}]}{dt} = \left(\frac{a}{b + c[\text{CO}]} + k_4[\text{Cl}^-]\right)[R_u(\text{CO})_{12}]$$  \hspace{1cm} (13)$$

where $k_4$ would have a value of about $2 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}$ under the conditions of the experiments while a modest contribution from eqs 8–10 may be measurable at the lower $P_{\text{CO}}$ values studied here.

Acknowledgment. This research was sponsored by a grant (DE-FG03-85ER13317) to P.C.F. from the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.

---

(18) $a = k_3k_4k_5; b = k_6(k_+ + k_5) - k_6k_4; c = k_4(k_+ + k_5).$