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

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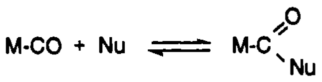
Kinetics studies of the reaction of the triruthenium cluster $Ru_3(CO)_{12}$ with the "highly dissociated" chloride salt [PPN]Cl to give the $Ru_3(CO)_{11}Cl^-$ anion in THF/CH_2Cl_2 solutions show a rate law first order in $[Cl^-]$ and in $[Ru_3(CO)_{12}]$. Rates are significantly higher in 90/10 than in 80/10 (v/v) THF/CH_2Cl_2 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



$$\mathrm{M{-}CO + Nu \rightleftharpoons M{-}C(=O)Nu} \qquad (1)$$

a number of oxygen and nitrogen bases.[2] 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.[2] Adduct formation also strongly influences the subsequent reactions of the complex; e.g., the methoxycarbonyl cluster $Ru_3(CO)_{11}(COCH_3)^-$ is orders of magnitude more reactive toward ligand substitution (eq 2) and hydrogen activation (eq 3) than is the parent cluster $Ru_3(CO)_{12}$ under comparable conditions.[3]

$$\mathrm{Ru_3(CO)_{11}(CO_2CH_3)^- + L \rightleftharpoons Ru_3(CO)_{10}L(CO_2CH_3)^- + CO} \qquad (2)$$

$$\mathrm{Ru_3(CO)_{11}(CO_2CH_3)^- + H_2 \rightarrow HRu_3(CO)_{11^-} + HCO_2CH_3} \qquad (3)$$

Among nucleophiles also known to activate metal carbonyls are the simple halide and pseudohalide anions X^- in relatively nonpolar solvents.[2] For example, "highly dissociated" halide salts have been found to accelerate the substitution reactions of various metal carbonyls, including those of $Ru_3(CO)_{12}$ with a variety of ligands,[4] and various halides have been shown to be effective promoters for certain catalysts for CO and H_2 activation based on ruthenium carbonyls.[5] While the roles of these promoters are not fully delineated, several workers have shown facile reactions of halides with $Ru_3(CO)_{12}$ to give anionic clusters of the type $Ru_3(CO)_mX_n^{n-}$.[6] For example, the direct reaction of Cl^- with $Ru_3(CO)_{12}$ in tetrahydrofuran follows the sequence outlined in eqs 4 and 5, the final product being the anion cluster

$$\mathrm{Ru_3(CO)_{12} + Cl^- \rightleftharpoons \underset{\mathbf{B}}{Ru_3(CO)_{11}Cl^-} + CO} \qquad (4)$$

$$\mathrm{Ru_3(CO)_{11}Cl^- \rightleftharpoons \underset{\mathbf{A}}{Ru_3(CO)_{10}(\mu\text{-}Cl)^-} + CO} \qquad (5)$$

$Ru_3(CO)_{10}(\mu\text{-}Cl)^-$ (**A**) with two CO's replaced by a bridging chloride.[6] One intermediate is the monosubstituted anion $Ru_3(CO)_{11}Cl^-$ (**B**), which we have isolated as the PPN^+ salt ($PPN^+ = (Ph_3P)_2N^+$) and characterized crystallographically.[7] 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 Carbonics 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(triphenylphosphoranylidene)ammonium chloride, [PPN]Cl (97%), were purchased from Aldrich. Trimethyl phosphite was distilled from sodium and stored in a Schlenk type flask under nitrogen. $Ru_3(CO)_{12}$ was prepared by a high-pressure reaction of $RuCl_3$ with CO as described previously[8] or was purchased from Strem Chemicals. The solid [PPN]Cl was recrystallized from 9/1 THF/CH_2Cl_2, ground to a fine powder,

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(1) Taken in part from the Ph.D. dissertation of J.L., UC Santa Barbara, 1992.

(2) Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988,** *28,* 139–217 and references therein.

(3) (a) Anstock, M.; Taube, D.; Gross, D.; Ford, P. C. *J. Am. Chem. Soc.* **1984,** *106,* 3696–3697. (b) Taube, D.; Rokicki, A.; Anstock, M.; Ford, P. C. *Inorg. Chem.* **1987,** *26,* 526–530.

(4) (a) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984,** *106,* 4647–4648. (b) Stevens, R. E.; Gladfelter, W. L. *Inorg. Chem.* **1983,** *22,* 2034–2042.

(5) (a) Dombeck, B. D. *Organometallics* **1985,** *4,* 1707–1712. (b) Knifton, J. F. *J. Mol. Catal.* **1987,** *40,* 243–254. (c) Zuffa, J. L.; Blohm, M. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986,** *108,* 552–553. (d) Yoshida, S. I.; Mori, S.; Kinoshita, H.; Watanabe, Y. *J. Mol. Catal.* **1987,** *42,* 215–227. (e) Kaesz, H. D. *J. Organomet. Chem.* **1990,** *383,* 413–420. (f) Lavigne, G.; Lugan, N.; Rivomanana, S.; Mulla, F.; Soulie, J.-M.; Kalck, P. *J. Cluster Sci.* **1993,** *4,* 49–58. (g) Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F.; La Monica, G. *J. Chem. Soc., Chem. Commun.* **1984,** 1286.

(6) Han, S.-H.; Geoffroy, G. L.; Dombeck, B. D.; Rheingold, A. L. *Inorg. Chem.* **1988,** *27,* 4355–4361.

(7) Chin-Choy, T.; Harrison, W. T. A.; Stucky, G. D.; Keder, N.; Ford, P. C. *Inorg. Chem.* **1989,** *28,* 2028–2029.

(8) Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Dalton Trans.* **1980,** 383.

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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[9]).

Instrumentation. Infrared spectra were collected on a Bio-Rad Digilab FTS-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 used were 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 Asystant (Macmillan Software), MINSQ software (Micromath Scientific Software), or the OLIS kinetic fitting routines.

Synthesis and Characterization. (a) [PPN][$Ru_3(CO)_{11}Cl$]. A solution of [PPN]Cl (0.062 g, 0.10 mmol) and $Ru_3(CO)_{12}$ (0.058 g, 0.09 mmol) was prepared by placing the solids together in 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 $Ru_3(CO)_{11}Cl^-$. The solvent was then removed under vacuum to leave a red residue. A CO atmosphere was reintroduced, a minimum of THF was added to redissolve the solid, and the resulting solution was transferred 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 2060 (s), 2066 (vs), 2009 (s), 1975 (m), 1962 (m), and 1828 (s, br) cm^{-1}, in agreement with literature values for [PPN][$Ru_3(CO)_{11}Cl$].[6,7] The optical spectrum displayed a λ_{max} at 404 nm (ϵ = 6600 M^{-1} cm^{-1}) in THF solution, and the ambient temperature ^{13}C NMR spectrum showed a singlet at 211 ppm both in THF solution and in the solid state (as measured by CMAS spectroscopy).

(b) [PPN][$Ru_3(CO)_{10}(\mu\text{-}Cl)$]. An equimolar solution of [PPN]Cl (0.062 g, 0.10 mmol) and $Ru_3(CO)_{12}$ (0.058 g, 0.09 mmol) was prepared by placing the solids together in a Schlenk tube and evacuating for 1 h before introducing N_2 (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 $Ru_3(CO)_{11}Cl^-$. 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 $Ru_3(CO)_{10}(\mu\text{-}Cl)^-$. The solvent was then removed under vacuum. A N_2 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][$Ru_3(CO)_{10}(\mu\text{-}Cl)$] 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.[6] The optical spectrum gave maxima at 520 nm (2300 M^{-1} cm^{-1}) and 370 nm (7900 M^{-1} cm^{-1}).

Kinetics Studies. Stock solutions of $Ru_3(CO)_{12}$ and [PPN]Cl were prepared in various THF/CH_2Cl_2 mixtures from freshly distilled solvents under the appropriate atmosphere using Schlenk techniques. (CH_2Cl_2 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-Seal 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 $Ru_3(CO)_{12}$ 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 as absorbance vs time at a single λ_{mon} 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[10] was examined by adding Ph_3PO equivalent to 6% of the [PPN]Cl, but these solutions showed no differences in the kinetic behavior from those with no added Ph_3PO. Another possible impurity is 2,6-di-*tert*-butyl-4-methylphenol (BHT) (present as a radical inhibitor in commercial THF), but addition of 9 × 10^{-3} M BHT led to no differences in the rate behavior.

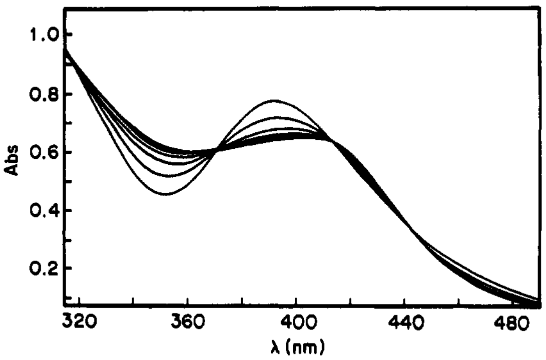

Figure 1. Changes in the absorption spectrum as a function of time for the reaction of [PPN]Cl (1.0 × 10^{-3} M) with $Ru_3(CO)_{12}$ (1.0 × 10^{-4} M) in 90/10 THF/CH_2Cl_2 (v/v) as a function of time (P_{CO} = 1.0 atm; *T* = 25 °C).

The reaction of $Ru_3(CO)_{12}$ with $P(OMe)_3$ was studied by adding the neat ligand via microliter syringe to solutions of the cluster in the appropriate solution. Absorbance changes were followed at 390 nm.

Results

The electronic spectrum of $Ru_3(CO)_{12}$ in 90/10 (v/v) THF/CH_2Cl_2 displays an absorbance maximum (λ_{max}) at 390 nm (ϵ_{max} = 7900 M^{-1} cm^{-1}) and a minimum (λ_{min}) at 350 nm (ϵ_{min} = 3500 M^{-1} cm^{-1}). Addition of [PPN]Cl (1.0 × 10^{-3} M) to $Ru_3(CO)_{12}$ (1.0 × 10^{-4} M) in THF under CO (P_{CO} = 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 λ_{max} at 404 nm (ϵ_{max} = 6600 M^{-1} cm^{-1}), consistent with that of $Ru_3(CO)_{11}Cl^-$. 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 $Ru_3(CO)_{12}$ 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 N_2 or Ar, the spectral changes were experimentally indistinguishable from those carried out under added CO.

The enhanced reactivity of **B** relative to $Ru_3(CO)_{12}$ was demonstrated by an experiment where H_2 was bubbled through an ambient-temperature solution of **B** prepared *in situ* by reaction of $Ru_3(CO)_{12}$ 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 $HRu_3(CO)_{11}^-$. Although the other product was not determined, simple stoichiometry would suggest this to be HCl. Bubbling H_2 through an analogous solution of $Ru_3(CO)_{12}$ led to no obvious reaction, although it is well-known that if such solutions are heated, the ruthenium cluster is hydrogenated to give $H_4Ru_4(CO)_{12}$.[8] As noted above, the somewhat different nucleophile adduct $Ru_3(CO)_{11}(CO_2CH_3)^-$ also reacts readily with H_2 at ambient temperature (eq 3) and the enhanced reactivity can in large part be attributed to the enhanced lability of the anionic adduct.[3b]

The reaction kinetics of eq 4 were studied under conditions where $[Cl^-] \gg [Ru_3(CO)_{12}]$ by following the absorbance decrease

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(9) Martinsen, A.; Songstad, J. *Acta Chem. Scand.* **1977**, *A31*, 645.

(10) (a) Darensbourg, D. J.; Darensbourg, M. Y.; Walker, N. *J. Am. Chem. Soc.* **1980**, *102*, 1213. (b) Darensbourg, D. J.; Darensbourg, M. Y.; Walker, N. *Inorg. Chem.* **1981**, *20*, 1918.

Table I. Rate Data for the Formation of $Ru_3(CO)_{11}Cl^-$ as a Function of $[Cl^-]$, P_{CO}, and Different Solvent Compositions (λ_{mon} = 350 or 390 nm; $[Ru_3(CO)_{12}]_{init} = 1 \times 10^{-4}$ M; T = 25 °C; Cl^- Added as [PPN]Cl)

$$Ru_3(CO)_{12} + Cl^- \rightarrow Ru_3(CO)_{11}Cl^- + CO$$

$[Cl^-]$, M	solvent THF/CH_2Cl_2 (v/v)	P_{CO}, atm	k_{obs}, 10^{-3} s^{-1} (no. of runs)	$k_{obs}/[Cl^-]$, M^{-1} s^{-1}
1.1×10^{-3}	90/10	1.00	2.3 ± 0.1 (5)	2.1
1.0×10^{-3}	95/5	1.00	3.5 ± 0.1 (5)	3.5
	90/10	1.00	1.8 ± 0.1 (15)	1.8
		1.00	1.8 ± 0.1 (9)[a]	1.8
		0.50	1.9 ± 0.1 (8)	1.9
		0.25	2.1 ± 0.1 (9)	2.1
		0.10	2.2 ± 0.1 (8)	2.2
		0.01	2.4 ± 0.1 (15)	2.4
	85/15	1.00	0.78 ± 0.05 (8)	0.78
	80/20	1.00	0.25 ± 0.08 (14)	0.25
7.0×10^{-4}	90/10	1.00	1.3 ± 0.1 (3)	1.9
5.0×10^{-4}	90/10	1.00	1.1 ± 0.2 (5)	2.2

[a] With added BHT (9×10^{-3} M).

at 390 nm due to the disappearance of $Ru_3(CO)_{12}$. Temporal absorbance data gave good fits both to linear (ln(Abs(t) − Abs(∞)) vs t, correlation coefficient >0.995 over 3 half-lives) and exponential (Abs = $A \pm B\exp(-k_{obs}t)$ vs t, correlation coefficient >0.999 95) expressions. Thus, the reaction rate appears first order in $[Ru_3(CO)_{12}]$, i.e.

$$-\frac{d[Ru_3(CO)_{12}]}{dt} = k_{obs}[Ru_3(CO)_{12}] \qquad (6)$$

Following formation of $Ru_3(CO)_{11}Cl^-$ at 350 nm gave k_{obs} values identical to those obtained by monitoring $Ru_3(CO)_{12}$ depletion at 390 nm.

The dependence of the rates on the chloride ion concentration was studied in 90/10 THF/CH_2Cl_2 (v/v) under P_{CO} = 1.0 atm with $[Ru_3(CO)_{12}]_{init} = 1.0 \times 10^{-4}$ M and $[PPN^+Cl^-]$ varied from 5.0×10^{-4} to 1.1×10^{-3} M. The narrow $[Cl^-]$ range was determined by the limited solubility of [PPN]Cl. Numerous runs at each concentration were carried out to ensure reproducibility. Solutions with high $[Cl^-]$ were sonicated to ensure the dissolution of the solid. Notably, the overall changes in the FTIR and the UV/vis spectra were the same for different $[Cl^-]$. The $Ru_3(CO)_{11}Cl^-$ product formed cleanly, and the temporal absorption data showed isosbestic points at 374, 412, and 446 nm. The k_{obs} values determined for different $[Cl^-]$ are listed in Table I. The plot of k_{obs} versus $[Cl^-]$ proved to be linear with a slope of $k_2 = 2.0 \pm 0.2$ M^{-1} s^{-1} (Figure 2); thus, under these conditions the reaction appears first order in chloride, i.e.

$$k_{obs} = k_2[Cl^-] \qquad (7)$$

The effect of varying P_{CO} on the reaction kinetics was also probed in 90/10 CH_2Cl_2/THF (v/v) with $[Ru_3(CO)_{12}] = 1 \times 10^{-4}$ M and $[Cl^-] = 1 \times 10^{-3}$ M. Solutions were equilibrated with different CO/Ar mixtures with P_{CO} varied from 0.0011 to 1.0 atm and P_{tot} = 1.0 atm. This gave a [CO] range from 1.1×10^{-5} to 1.0×10^{-2} M (assuming CO solubility identical to that in pure THF, 0.011 M atm^{-1}).[11] For $P_{CO} > 0.01$ atm, the observed reaction proceeded cleanly to $Ru_3(CO)_{11}Cl^-$ and displayed isosbestic points at 374, 412, and 446 nm for ~3 half-lives. The k_{obs} values obtained at λ_{mon} = 390 nm agreed with those obtained for λ_{mon} = 350 nm and exhibited modest, but systematic, increases in k_{obs} as P_{CO} was decreased to 0.01 atm (Table I). At lower P_{CO}, the kinetics continued to exhibit first-order behavior, but the temporal absorbance data failed to maintain isosbestic points and appeared to give some $Ru_3(CO)_{10}(\mu\text{-}Cl)^-$ product. Under Ar, N_2, or P_{CO} = 0.0011 atm, the respective k_{obs} values were $(3.0 \pm 0.2) \times 10^{-3}$, 2.9×10^{-3}, and $(2.9 \pm 0.2) \times 10^{-3}$ s^{-1}, and the kinetics displayed extreme sensitivity to contamination.

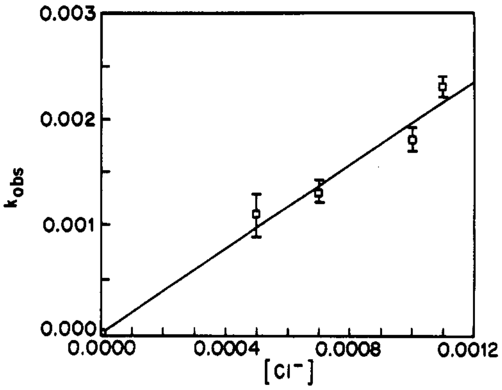

Figure 2. Plot of k_{obs} vs $[Cl^-]$ for the reaction of [PPN]Cl with $Ru_3(CO)_{12}$ (1.0×10^{-4} M) in 90/10 THF/CH_2Cl_2 (v/v) (P_{CO} = 1.0 atm; T = 25 °C).

Mixed solvents were required for the kinetics studies described here owing to the poor solubility of [PPN]Cl in pure THF. The effects resulting from varying solvent composition were examined for THF/CH_2Cl_2 mixtures ranging from 95/5 to 80/20 (v/v) with $[Ru_3(CO)_{12}] = 1.0 \times 10^{-4}$ M, $[Cl^-] = 1.0 \times 10^{-3}$ M, 25 °C, and P_{CO} = 1 atm. For each solvent mixture, spectral changes exhibited isosbestic points at 374, 412, and 446 nm, and temporal absorbance data fit first-order equations. As the concentration of the methylene chloride in the solvent was raised, the rates dropped sharply, the range in k_{obs} values being more than an order of magnitude. In related, semiquantitative studies, it was demonstrated that the formation of an adduct in the reaction between [PPN]Cl and $Ru_3(CO)_{12}$ was quite solvent dependent with reactivities falling in the order THF (seconds) ≫ acetone > acetonitrile > dichloromethane ≫ methanol (no reaction over period of many hours). This order is the inverse of that of the solvent "acceptor number" as defined by Guttmann.[12]

For the sake of comparison to an uncharged ligand in THF solution at 25 °C, the reaction of $Ru_3(CO)_{12}$ with $P(OMe)_3$ was examined by following the disappearance of the parent cluster at 390 nm. The reaction leads to formation of the monosubstituted complex $Ru_3(CO)_{11}L$ (λ_{max} 406 nm), although subsequent substitutions of the product with additional L and cluster fragmentation lead to a mixture of eventual products. The disappearance rate of $Ru_3(CO)_{12}$ is first order in $P(OMe)_3$ over the range 0.008–0.08 M and virtually independent of P_{CO} (0.1–1 atm). The second-order rate constant was determined to be $(6.4 \pm 0.6) \times 10^{-4}$ M^{-1} s^{-1}, more than 3 orders of magnitude smaller than that seen for the comparable reaction with Cl^-. Notably, this rate is comparable to those (estimated for 25 °C from activation parameters) previously reported for comparable ligands in decalin solutions.[13] By contrast, substitution rates were much faster in methanol, but the kinetics were highly irreproducible. Since the reaction was largely suppressed by addition of small concentrations of triflic acid (~10^{-3} M), it appears that adventitious base may be acting as catalyst.

Discussion

Unlike the reaction of CH_3O^- with $Ru_3(CO)_{12}$, which gives the methoxycarbonyl adduct $Ru_3(CO)_{11}(CO_2CH_3)^-$ as a char-

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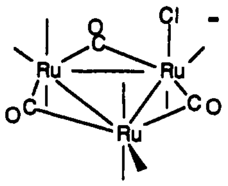
[11] Payne, M. W.; Leussing, D. L.; Shore, S. G. *Organometallics* **1991**, *10*, 574.

[12] (a) Guttmann, V. *The Donor Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978; p 29. (b) Values of AN given in ref 12a: THF, 8.0; acetone, 12.5; acetonitrile, 19.3; dichloromethane, 20.4; methanol, 41.3.

[13] Keeton, D. P.; Malik, S. K.; Poe, A. *J. Chem. Soc., Dalton Trans.* **1977**, 233.

acterizable species, the reaction of $Ru_3(CO)_{12}$ with chloride leads to CO displacement to give a species **B** with a terminally bound



B

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_2Cl_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 $Ru_3(CO)_{12}$ 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 $Ru_3(CO)_{12}$ (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 $Ru_3(CO)_{12}$. 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 between $Ru_3(CO)_{12}$ and various trialkyl- or triarylphosphines and trialkyl or triaryl 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 $Ru_3(CO)_{12}$ with strong Brønsted bases such as alkoxides and

$$Ru_3(CO)_{12} + Cl^- \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \underset{\mathbf{C}}{Ru_3(CO)_{11}(COCl)^-} \tag{8}$$

$$Ru_3(CO)_{11}(COCl)^- \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} \underset{\mathbf{D}}{Ru_3(CO)_{10}(COCl)^-} + CO \tag{9}$$

$$Ru_3(CO)_{10}(COCl)^- \xrightarrow{k_p} Ru_3(CO)_{11}Cl^- \tag{10}$$

hydroxide 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 $Fe(CO)_2(NO)_2$ 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_{CO}, i.e.

$$-\frac{d[Ru_3(CO)_{12}]}{dt} = k_s[Cl^-][Ru_3(CO)_{12}] \tag{11}$$

Thus, the modest but systematic increase in k_{obs} values at lower P_{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]

$$-\frac{d[Ru_3(CO)_{12}]}{dt} = \left(\frac{a}{b + c[CO]}\right)[Cl^-][Ru_3(CO)_{12}] \tag{12}$$

However, examination of this rate law in detail shows that CO dependence will become a factor when $c[CO] \sim b$, 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_{CO} and unresponsiveness of k_{obs} to this parameter at higher P_{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

$$-\frac{d[Ru_3(CO)_{12}]}{dt} = \left(\frac{a}{b + c[CO]} + k_s\right)[Cl^-][Ru_3(CO)_{12}] \tag{13}$$

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

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[14] (a) Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 585–593. (b) Trautman, R. J.; Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 2355–2362.

[15] Poe, A.; Twigg, M. *J. Chem. Soc., Dalton Trans.* **1974**, *1860*–1866.

[16] Basolo, F.; Morris, D. E. *J. Am. Chem. Soc.* **1968**, *90*, 2535.

[17] (a) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160. (b) Bellus, P. A.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 3726. (c) Darensbourg, D. J.; Walker, N.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1980**, *102*, 1212.

[18] $a = k_a k_d k_p$; $b = k_p(k_{-a} + k_d) - k_d k_{-d}$; $c = k_{-d}(k_{-a} + k_d)$.