of all methyl groups. They were included as fixed-atom contributions in the refinement. Refinement of 4 was severely hampered by excessive disorder of the ethyl groups. Final refinement was done with isotropic thermal parameters for the ethyl carbons and one ethyl group of each independent molecule in two different conformations. H atoms were not included in the refinement. A final difference synthesis still gave indications for further partially occupied ethyl group alternatives.

The function minimized was $\sum w(|F_o| - |F_c|)^2$, with unit weights for 2 and 4, while statistical weights were used for 3 (SHELX76). Corrections for $\Delta f'$ and $\Delta f''$ were applied to all atoms. Reference 41 gives the sources of the scattering curves as well as references to the programs used. Table II contains important bond distances and angles; Tables V-VII contain the atomic parameters. Figure 7 gives perspective views of 3 and 4.

Other Physical Measurements. The IR data were obtained from KBr disks with a Perkin-Elmer 577 spectrometer and the MS data from a Varian MAT 311A spectrometer (EI, 70 eV). The molecular weights were determined cryoscopically in benzene with a homemade glassware apparatus equipped for inert-gas manipulation. The temperature was determined with a Knaur low-temperature measuring device with type F 22 sensor. We thank M. Barth for these measurements.

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Registry No. 1, 92421-50-6; 2, 92421-53-9; 3, 92421-54-0; 4, 92421-55-1; 5, 105335-44-2; 6, 105335-45-3; 7, 105335-46-4; 8, 105335-47-5; 9, 105335-48-6; 10, 105335-49-7; 11, 105335-50-0; 12, 92421-56-2; 1,1′-dimethylmanganocene, 32985-17-4; 1,1′-(trimethylsilyl)manganocene, 101932-73-4; bis(1,2-dimethoxyethane)manganese diiodide, 105335-52-2; bis(1,2-dimethylcyclopentadienyl)manganese, 101932-74-5.

Supplementary Material Available: Tables of experimental NMR shifts including variable-temperature data, variable-temperature magnetic susceptibilities, and magnetic moments at different field strengths, crystal data, fractional coordinates, and anisotropic temperature factors (26 pages); listings of observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

Activation Volumes for the Substitution Reactions of the Triruthenium Cluster Anions $HRu_3(CO)_{11}^-$ and $Ru_3(CO)_{11}(CO_2CH_3)^-$

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Pressure effects on the stopped-flow kinetics for the reaction $HRu_3(CO)_{11}^- + PPh_3 \rightarrow HRu_3(CO)_{10}(PPh_3)^- + CO$ in tetrahydrofuran have been used to calculate the activation volume $\Delta V^* = +21.2 \pm 1.4$ cm^3/mol. This result is interpreted as confirming the dissociative mechanism previously proposed for this reaction. Analogous studies on the reaction of $P(OCH_3)_3$ with the methoxycarbonyl adduct $Ru_3(CO)_{11}(CO_2CH_3)^-$ in 90/10 THF/CH_3OH gives a similarly large positive ΔV^* (+16 ± 2 cm^3/mol) also consistent with a previously proposed dissociative mechanism for this reaction. However in the more protic solvent mixture 10/90 THF/CH_3OH, ΔV^* for the latter reaction is nearly zero, a result which suggests a markedly greater role of solvation changes in the rate-limiting step in this medium.

Introduction

The trinuclear ruthenium hydride ion $HRu_3(CO)_{11}^-$ has drawn considerable recent attention as a prominent species in homogeneous catalysts for the water-gas shift reaction[3] and for the hydrogenation, hydroformylation, and hydrosilation of alkenes.[4] In the course of investigating the reactivity of $HRu_3(CO)_{11}^-$ and its potential roles in such catalytic cycles, this ion was found to be remarkably more labile toward ligand substitution (eq 1) than the parent

$$HRu_3(CO)_{11}^- + PPh_3 \rightleftharpoons HRu_3(CO)_{10}(PPh_3)^- + CO \quad (1)$$

neutral carbonyl $Ru_3(CO)_{12}$ under comparable conditions.[5] A similarly enhanced substitution lability (eq 2) has also

$$Ru_3(CO)_{11}(CO_2CH_3)^- + P(OCH_3)_3 \rightarrow Ru_3(CO)_{10}(CO_2CH_3)(P(OCH_3)_3)^- + CO \quad (2)$$

been described[6] for the methoxide adduct $Ru_3(CO)_{11}(CO_2CH_3)^-$, which is a likely intermediate in reactions such as the $Ru_3(CO)_{12}$/$NaOCH_3$ cocatalyzed reductive carbonylation of nitroarenes.[7] Previous kinetics studies have concluded that both reactions 1 and 2 are likely to proceed via dissociative mechanisms[5,6] and that it is this dissociative process which makes the latter anion particularly reactive toward dihydrogen (eq 3).[6] However, not only

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

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are these cluster substitutions unusually facile, but they display low activation enthalpies (16.0 kcal/mol for eq 1 in THF, 12 kcal/mol for eq 2 in 10/90 THF/CH_3OH, and 10.5 kcal/mol for eq 2 in 90/10 THF/CH_3OH, as well as negative activation entropies (-2, -13 and -20 cal/(mol deg), respectively). These are atypical of carbonyl dissociative substitution mechanisms[8] and lend some ambiguity to the above interpretations.

Described here are extensions of these kinetics investigations using pressure effects[9-11] to probe more intimately the nature of the substitution mechanisms. To our knowledge, these results represent the first use of such pressure effects to study the substitution reactions of metal cluster complexes.

Experimental Section

All manipulations were conducted under dry N_2, CO, or CO/N_2 mixtures by using Schlenk techniques. Methanolic solutions of $NaOCH_3$ were prepared by the addition of small amounts of sodium metal to freshly distilled methanol and were standardized by titration against oxalic acid with phenolphthalein as the indicator. The solutions were freeze-pump-thaw degassed and stored under N_2. Solvents were dried by using standard methods[5] and distilled under N_2. Triruthenium dodecacarbonyl and the hydride salt $[PPN][HRu_3(CO)_{11}]$ were prepared by literature procedures.[5,12]

Kinetics studies were carried out by using the high-pressure stopped-flow apparatus developed at the University of Frankfurt and described previously.[13] Reactions in THF mixtures required replacement of the Kel-F syringes with glass syringes, since the Viton sealing rings used in the original design swelled in these solvents. The drive syringes, receiving syringes, and block were flushed and then loaded with the appropriate solution. The stopped-flow unit was then lowered into the high-pressure chamber and pressurized with *n*-heptane as the pressure-transmitting medium. Subsequent to each pressure increase, the system was thermally equilibrated for 15 min before collecting data.

Reaction solutions were prepared by using Schlenk techniques and then transferred to the stopped-flow syringes without exposure to air. Reactions of $HRu_3(CO)_{11}^-$ were investigated under a dinitrogen atmosphere while reactions of $Ru_3(CO)_{11}(CO_2CH_3)^-$ were studied under a 10/90 CO/N_2 atmosphere owing to the latter ion's instability under pure N_2. Care was taken to ensure that the stopped-flow syringes were filled with no gas bubbles present. Solutions of the methoxide adduct were prepared under 10/90 CO/N_2 in situ by addition of excess methanolic $NaOCH_3$ to THF solutions of $Ru_3(CO)_{12}$ (4×10^{-4} mol L^{-1}). The excess methoxide was added to ensure complete formation of the adduct. For the 10/90 THF/CH_3OH (v/v) system, the total methoxide concentration in solution was 5×10^{-3} mol L^{-1}, while in 90/10 THF/CH_3OH a lower concentration (1.8×10^{-3} mol L^{-1}) was used owing to the larger equilibrium constant for the adduct formation under these conditions. THF solutions of the hydride complex $HRu_3(CO)_{11}^-$ (1.0×10^{-4} mol L^{-1}) were prepared for kinetics studies from the PPN^+ salt under a N_2 atmosphere.

Table I. First-Order Rate Constants (k_{obsd}) for the Reaction of $(PPN)[HRu_3(CO)_{11}]$ with Excess PPh_3 in THF Solution as a Function of Pressure[a]

run I ([PPh_3] = 0.053 M)		run II ([PPh_3] = 0.086 M)	
P, MPa	k_{obsd}, s^{-1}	*P*, MPa	k_{obsd}, s^{-1}
5.0	1.73 ± 0.02	5.3	1.66 ± 0.01
24.0	1.43 ± 0.01	24.6	1.41 ± 0.02
50.2	1.11 ± 0.01	50.6	1.15 ± 0.04
74.4	0.90 ± 0.01	74.6	0.97 ± 0.02
98.6	0.67 ± 0.01	98.7	0.76 ± 0.01

[a] Each run consists of a series of kinetics experiments using the same solutions. For each pressure the k_{obsd} value reported is an average of two or more independent rate determinations. [b] *T* = 25.0 °C, under N_2; $[HRu_3(CO)_{11}^-] = 1 \times 10^{-4}$ M.

Results and Discussion

The systems studied here by using pressure effects were specifically chosen to duplicate those for which the kinetics were reasonably well characterized under ambient conditions.[5,6]

A. $HRu_3(CO)_{11}^-$ plus PPh_3 in THF. Table I summarizes data for two pressure runs representing the observed first-order rate constants for the formation of $HRu_3(CO)_{10}(PPh_3)^-$ via the reaction of $HRu_3(CO)_{11}^-$ in THF with two different concentrations of excess PPh_3 at 25 °C under a dinitrogen atmosphere. Notably, the k_{obsd} values for eq 1 are essentially independent of $[PPh_3]$ in the two cases but decrease with increasing hydrostatic pressure. For example, at an applied pressure of about 98 MPa (980 bar), k_{obsd} in each run is less than half that at about 5 MPa (50 bar).

For the $HRu_3(CO)_{11}^-$ anion, recent studies have shown the kinetics for the reaction with PPh_3 in THF (eq 1) to be consistent with the following scheme:[5]

$$HRu_3(CO)_{11}^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \underset{I_i}{HRu_3(CO)_{10}^-} + CO \qquad (4)$$

$$I_i + PPh_3 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} HRu_3(CO)_{10}(PPh_3)^- \qquad (5)$$

Under conditions of excess $[PPh_3]$ and low [CO], this leads to the predicted rate law for the forward reaction

$$-\frac{d[HRu_3(CO)_{11}^-]}{dt} = \left(\frac{k_4k_5[PPh_3]}{k_{-4}[CO] + k_5[PPh_3]}\right)[HRu_3(CO)_{11}^-] \qquad (6)$$

Equation 6 predicts that at low [CO] a plot of k_{obsd} vs. $[PPh_3]$ will approach the condition where $k_5[PPh_3] >> k_{-4}[CO]$ and k_{obsd} reaches a limiting value equal to k_4, the rate of CO dissociation from $HRu_3(CO)_{11}^-$. This has been shown to be the case for several different [CO], and k_{obsd}(limiting) = 2.1 s^{-1} ± 0.1 (i.e., k_4) has been determined at 25 °C and ambient pressure.[5] Equation 6 also predicts that, at constant $[PPh_3]$, increasing [CO] will slow the reaction, as indeed was shown.[5] Thus, the rate data reported are consistent with this model and argue against an alternative mechanism whereby PPh_3 reacts with $HRu_3(CO)_{11}^-$ in an associative or interchange pathway to displace CO. However, another alternative by which CO is displaced by the nucleophilic attack of solvent (eq 7) cannot be as easily excluded. If the resulting solvated intermediate is susceptible to competitive trapping by reaction with either CO or PPh_3, the same kinetics be-

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(8) (a) For example, the substitution kinetics for the triruthenium clusters $Ru_3(CO)_{12}$ (ref 8b) and $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ (ref 8c) have been studied. For reaction of the former cluster with PPh_3, both first-order and second-order substitution pathways were observed, the "dissociative" pathway displaying the ΔH^* and ΔS^* values 31.8 kcal mol^{-1} and +20.2 cal mol^{-1} deg^{-1}, respectively, the "associative" pathway giving $\Delta H^* = 15.1$ kcal mol^{-1} and $\Delta S^* = -23.8$ cal mol^{-1} deg^{-1}. Reaction of the latter cluster with $AsPh_3$ occurs via a first-order pathway with $\Delta H^* = 26.6$ kcal mol^{-1} and $\Delta S^* = +8$ cal mol^{-1} deg^{-1}. Notably, each of these triruthenium clusters are many orders of magnitude less substitution labile than are either $HRu_3(CO)_{11}^-$ or $Ru_3(CO)_{11}(CO_2CH_3)^-$. (b) Poë, A.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1860–1866. (c) Dalton, D. M.; Barnett, D. J.; Duggan, T. P.; Keister, J. B.; Malik, P. T.; Modi, S. P.; Shaffer, M. R.; Smesko, S. A. *Organometallics* **1985**, *4*, 1854–1866.

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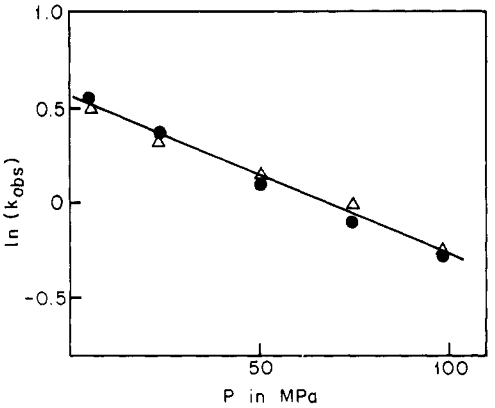

Figure 1. Plot of data from Table I as ln k_{obsd} vs. pressure for the reaction $HRu_3(CO)_{11}^- + PPh_3 \rightleftharpoons HRu_3(CO)_{10}(PPh_3)^- + CO$: (dots) run I; (triangles) run II.

havior toward variation of [CO] or [PPh_3] would be expected.

$$HRu_3(CO)_{11}^- + S \rightleftharpoons HRu_3(CO)_{11}S^- \rightleftharpoons HRu_3(CO)_{10}S^- + CO \quad (7)$$

$$HRu_3(CO)_{10}S^- + L \rightleftharpoons HRu_3(CO)_{10}L^- + S \quad (8)$$

In this context, it is interesting that the activation parameters $\Delta H^\ddagger = 16.0 \pm 1.7$ kcal/mol and $\Delta S^\ddagger = -1.9 \pm 3.0$ cal/(mol deg), determined from the temperature dependence of k_{obsd}(limiting),[5] would indeed appear to be more consistent with an associative type mechanism than with the dissociative path described in eq 4.

The k_{obsd} values of Table I were determined under limiting conditions, i.e. low [CO] and high [PPh_3]. Thus, the activation volume for k_{obsd}(limiting) can be determined from a plot of ln k_{obsd} vs. P according to[10]

$$\Delta V^\ddagger = -RT\left(\frac{d \ln k_{obsd}}{dP}\right)_T \quad (9)$$

From such plots of the data in Table I (Figure 1), the $\Delta V^\ddagger$ values $+22.0 \pm 0.9$ cm³/mol and 20.3 ± 0.7 cm³/mol were determined for the reaction of $HRu_3(CO)_{11}^-$ with PPh_3 at the latter's concentrations 0.053 and 0.086 mol/L, respectively. These $\Delta V^\ddagger$'s are essentially indistinguishable ($\Delta V^\ddagger_{av} = +21.2 \pm 1.4$ cm³/mol), as would be expected since both concentrations fall in the range where k_{obsd} is effectively limiting under N_2.

In order to interpret this $\Delta V^\ddagger$, it is valuable to examine the expected volume changes between the reactant species and the transition states in the rate-determining steps of various model mechanisms. For an interchange or associative mechanism involving solvent attack upon the unsubstituted cluster, it is probable that the volume change between the reactant and transition states would be negative, as proposed previously for other metal complex substitution reactions.[10] In contrast, the limiting dissociation of a neutral, nonpolar ligand from the cluster should have a positive $\Delta V^\ddagger$ given that the unsaturated cluster intermediate would not be expected to be enough smaller to compensate for the volume of the new species (the dissociated ligand) formed in solution. Given that THF is a rather poor solvent for anions,[14] both $HRu_3(CO)_{11}^-$ and the proposed intermediate $HRu_3(CO)_{10}^-$ should have similar partial molar volumes in this solvent and the major contribution to $\Delta V^\ddagger$ should be the partial molar volume $\bar{V}$(CO) for the labilized CO.

Quantitative prediction of the expected $\Delta V^\ddagger$'s for these models is restricted by the absence of partial molar volume data in THF for the various reactants and intermediates. However, if one assumes that $HRu_3(CO)_{11}^-$ and the dissociated intermediate I_i have similar $\bar{V}$'s, then the dissociation noted in eq 4 could have a $\Delta V^\ddagger$ value as large as the partial molar volume of CO in THF. Again $\bar{V}$(CO) in this solvent is unknown, but it can be estimated from the specific gravity of liquid CO (0.81 g/cm³ at 79 K)[15] to have a value of about 23 cm³/mol. Thus, the measured $\Delta V^\ddagger$ value of $+21.2 \pm 1.2$ cm³/mol for k_{obsd}(limiting) provides powerful evidence for the operation of a limiting dissociative mechanism for the rapid substitution reaction of $HRu_3(CO)_{11}^-$ and is consistent with the previous observation[5] that k_{obsd} is essentially independent of whether the solvent is THF or the more sterically demanding 2,5-dimethyltetrahydrofuran.

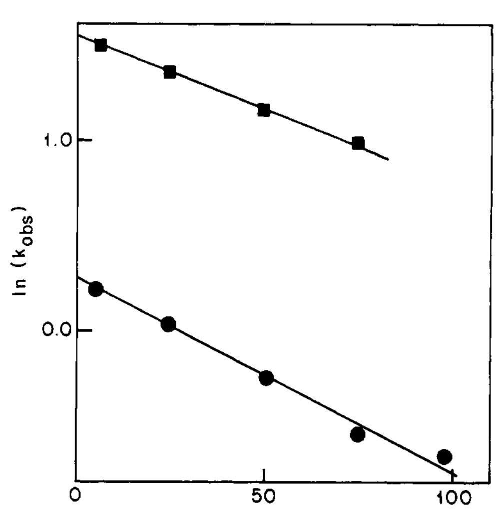

Figure 2. Plot of ln k_{obsd} vs. pressure for the reactions of methoxycarbonyl cluster anions with L = $P(OCH_3)_3$ in 90/10 v/v THF/CH_3OH: (squares) $Ru_3(CO)_{11}(CO_2CH_3)^- + L \rightarrow Ru_3(CO)_{10}L(CO_2CH_3)^- + CO$; (dots) $Ru_3(CO)_{10}L(CO_2CH_3)^- + L \rightarrow Ru_3(CO)_{10}L_2 + CH_3O^- + CO$.

B. $Ru_3(CO)_{11}(CO_2CH_3)^-$ plus $P(OCH_3)_3$. This anion was prepared by adding methanolic $NaOCH_3$ to $Ru_3(CO)_{12}$ in THF.[3b]

$$Ru_3(CO)_{12} + CH_3O^- \rightleftharpoons Ru_3(CO)_{11}(CO_2CH_3)^- \quad (10)$$

Therefore, the rates for reaction of the methoxycarbonyl anion with $P(OCH_3)_3$ were determined in the mixed solvent 90/10 (v/v) THF/CH_3OH. Under these conditions, accurate determination of rates was complicated by the sequential formation first of the monosubstituted anionic cluster $Ru_3(CO)_{10}(P(OCH_3)_3)(CO_2CH_3)^-$ and then of the disubstituted neutral cluster $Ru_3(CO)_{10}(P(OCH_3)_3)_2$. These reactions can be rationalized by the substitution reaction depicted in eq 2 followed by a second substitution to give the disubstituted methoxycarbonyl cluster (eq 11). The product of the latter reaction apparently then loses the methoxide (eq 12) owing to the decreased stability of the methoxycarbonyl adduct when the second CO is replaced by the more electron-donating $P(OCH_3)_3$. First-order rate

$$Ru_3(CO)_{10}(P(OCH_3)_3)(CO_2CH_3)^- + P(OCH_3)_3 \rightleftharpoons Ru_3(CO)_9(P(OCH_3)_3)_2(CO_2CH_3)^- + CO \quad (11)$$

$$Ru_3(CO)_9(P(OCH_3)_3)_2(CO_2CH_3)^- \rightleftharpoons Ru_3(CO)_{10}(P(OCH_3)_3)_2 + CH_3O^- \quad (12)$$

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constants for the formation of the monosubstituted and disubstituted methoxycarbonyl complexes (eqs 2 and 11, respectively) in the presence of a large excess of $P(OCH_3)_3$ as a function of pressure are plotted according to eq 9 in Figure 2.

Earlier investigations of eq 2 in this laboratory[6a] have demonstrated rate dependences on P_{CO} and on [L] consistent with the dissociative mechanism described in the following scheme:

$$Ru_3(CO)_{11}(CO_2CH_3)^- \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} \underset{I_{ii}}{Ru_3(CO)_{10}(CO_2CH_3)^-} + CO \quad (13)$$

$$I_{ii} + P(OCH_3)_3 \xrightarrow{k_{14}} Ru_3(CO)_{10}(P(OCH_3)_3)(CO_2CH_3)^- \quad (14)$$

This type of mechanism leads to a rate law of the form analogous to that seen for the hydride anion.

$$-\frac{d[Ru_3(CO)_{11}(CO_2CH_3)^-]}{dt} = \left(\frac{k_{13}k_{14}[P(OCH_3)_3]}{k_{-13}[CO] + k_{14}[P(OCH_3)_3]}\right)[Ru_3(CO)_{11}(CO_2CH_3)^-] \quad (15)$$

A similar analysis applies to the second substitution pathway (eq 11).[6a]

Under conditions where $k_{14}[P(OCH_3)_3] >> k_{-13}[CO]$, k_{obsd}(limiting) = k_{13}. For the $Ru_3(CO)_{11}(CO_2CH_3)^-$ ion, it was necessary to carry out the experiments in solutions which had been equilibrated with a 10/90 CO/N_2 gas mixture ([CO] ~0.001 M)[16] owing to the instability of $Ru_3(CO)_{11}(CO_2CH_3)^-$. Under these conditions the k_{obsd} data recorded in Figure 2 are close to, but not quite, limiting. Slopes of these plots give $\Delta V^{\ddagger}$ values of +16 ± 2 and +24.5 ± 2 cm^3/mol for the k_{obsd} values measured under these conditions for the first and second substitutions, respectively, in the 90/10 THF/methanol solutions. Although the uncertainties are larger than for the analogous reactions of the hydride cluster, it is clear that these $\Delta V^{\ddagger}$'s are large and positive and are comparable in magnitude to that found for the substitution reactions of $HRu_3(CO)_{11}^-$ in THF. Thus, we conclude that in 90/10 THF/CH_3OH, both of these sequential substitutions occur via a near limiting dissociative mechanism.

The situation in a predominantly methanol solution (10/90 THF/CH_3OH) proved to be markedly different. In this solvent, only monosubstitution was observed, since $Ru_3(CO)_{10}(P(OCH_3)_3)(CO_2CH_3)^-$ once formed undergoes CH_3O^- loss to give the neutral $Ru_3(CO)_{11}(P(OCH_3)_3)$;[6a] i.e., the equilibrium constant for formation of the methoxycarbonyl adduct is much smaller in this case.[3b] Furthermore, the rate constants measured under the conditions P_{CO} = 0.1 atm, $[P(OCH_3)_3]$ = 0.2–0.4 M, where k_{obsd} is approximately limiting showed little pressure dependence over the 5–98-MPa range. Treatment of these data according to eq 9 gave a $\Delta V^{\ddagger}$ value of 2.5 ± 2.5 cm^3/mol; thus, it is apparent that $\Delta V^{\ddagger}$ is remarkably different in a predominantly methanol solution than it is in a predominantly THF solution.

Table II. Summary of $\Delta V^{\ddagger}$ Values Measured at 25.0 °C

reaction	medium	$\Delta V^{\ddagger}$, in $cm^3\ mol^{-1}$
$HRu_3(CO)_{11}^-$ + PPh_3	THF	21.2 ± 1.4
$Ru_3(CO)_{11}(CO_2CH_3)^-$ + $P(OCH_3)_3$	90/10 THF/CH_3OH	16 ± 2
$Ru_3(CO)_{10}(P(OCH_3)_3)$-$(CO_2CH_3)^-$ + $P(OCH_3)_3$	90/10 THF/CH_3OH	24.5 ± 2
$Ru_3(CO)_{11}(CO_2CH_3)^-$ + $P(OCH_3)_3$	10/90 THF/CH_3OH	2.5 ± 2.5

The most puzzling aspect of the $\Delta V^{\ddagger}$ differences between the two solvents for this reaction is that the reaction kinetics are closely similar.[6a] The two solutions display analogous k_{obsd} vs. [L] curves at constant [CO] and the difference between the measured k_{obsd}(limiting) values is small (10.4 ± 1.1 s^{-1} and 5.8 ± 0.5 s^{-1} in 10/90 and 90/10 THF/CH_3OH, respectively). Thus, we have previously concluded that the reaction proceeds via a dissociative mechanism in both solutions.[6a] An alternative explanation may simply be that, despite the apparent similarity of the kinetics behaviors, there is a change in mechanism to one occurring via CO displacement by interchange with solvent to give the labile intermediate $Ru_3(CO)_{10}(S)(CO_2CH_3)^-$ in a predominantly methanol solvent. However, given that the Gutmann donor numbers (measures of Lewis basicity) for THF (DN = 20) and for CH_3OH (DN = 19) are nearly identical,[14] it is difficult to understand why the mechanism would change from apparently limiting dissociative paths for both the first and second substitutions for $Ru_3(CO)_{11}(CO_2CH_3)^-$ in THF to an interchange or associative mechanism for substitution in a predominantly methanol solution.

An alternative possibility which should be considered would be for the markedly smaller value of $\Delta V^{\ddagger}$ in methanol to be the result of a large, negative contribution ($\Delta V^{\ddagger}_{sol}$) to the overall activation volume owing to solvation changes between the reactants and the transition state. Similar negative $\Delta V^{\ddagger}_{sol}$ contributions are certainly evident in cases where the departing ligand is an anion;[10] hence there is charge creation in the transition state. However, in this case, the departing ligand is uncharged; thus a large, negative $\Delta V^{\ddagger}_{sol}$ value would have to result from a charge redistribution between $Ru_3(CO)_{11}(CO_2CH_3)^-$ and the intermediate I_{ii}. This could perhaps be due to greater localization of the negative charge on the methoxycarbonyl group leading to enhanced solvation via hydrogen bonding from solvent methanol to that site, e.g.,

That such charge redistribution would be much more strongly stabilized by methanol, hence leading to negative solvation contributions to $\Delta V^{\ddagger}$, is consistent with the very large Gutmann acceptor number value for methanol (AN = 41.3) compared to that of THF (8.0).[14]

Concluding Remarks

The activation volumes measured here are summarized in Table II. There have been several fragmentary studies of the pressure effects on carbonyl substitutions of mononuclear complexes,[17] but the present work represents the first such investigations for metal carbonyl clusters. The large, positive $\Delta V^{\ddagger}$ values found for the reaction of PPh_3 with $HRu_3(CO)_{11}^-$ in THF solution and for the first and second substitutions of $P(OCH_3)_3$ into the coordination

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(16) See footnote 10 in ref 5.

(17) (a) Brower, K. R.; Chen, T. *Inorg. Chem.* **1973**, *12*, 2198–2199. In this case $\Delta V^{\ddagger}$ values of +10 and +15 $cm^3\ mol^{-1}$ were measured for the high-temperature (>100 °C), "first-order" reactions of PPh_3 with $Mo(CO)_6$ and $Cr(CO)_6$, respectively, in hydrocarbon solutions. (b) Schmidt et al. (Schmidt, G.; Elias, H.; van Eldik, R., unpublished results) have found $\Delta V^{\ddagger}$ = +20.6 ± 0.4 $cm^3\ mol^{-1}$ for the rate-determining loss of CO in the reaction $Mn(CO)_5Cl$ + dab → $Mn(CO)_3Cl(dab)$ + 2CO (dab = biacetyl bis(phenylimine)).

sphere of $Ru_3(CO)_{11}(CO_2CH_3)^-$ in 90/10 THF/CH_3OH provide a strong support for the limiting dissociative pathway proposed previously on the basis of kinetics behavior.[5,6a] However, the $\Delta V^{\ddagger}$ values measured for the first substitution reaction of $Ru_3(CO)_{11}(CO_2CH_3)^-$ (eq 2) displayed a remarkable dependence on the solvent not paralleled by changes in the apparent rate law. A logical explanation would be a shift in mechanism for limiting dissociation in THF to a solvent-assisted displacement of CO in methanol, but the similarity of the donor numbers for the two solvents leads one to question why such a mechanism change would occur. An alternative proposal is that the dissociation of CO from $Ru_3(CO)_{11}(CO_2CH_3)^-$ would be accompanied by charge redistribution on the cluster leading to negative solvation contributions to $\Delta V^{\ddagger}$ owing to the much greater tendency of methanol to act as an acceptor. These and similar effects of solvent character on the reaction dynamics of metal cluster reactions are the subject of continuing investigation in these laboratories.

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Electroreduction of Carbonylmanganese(I) Cations. Mechanism of Ligand Substitution and Hydride Formation via Manganese(0) Intermediates

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Hydridomanganese(I) complexes $(OC)_3MnL_2H$ are the principal products from a series of acetonitrile derivatives of carbonylmanganese cations, i.e., $(OC)_3Mn(NCMe)_nL_{3-n}{}^+$ (I), when the reductions are carried out electrochemically in the presence of added phosphines L. Cyclic voltammetric studies show that the conversion to the hydride can be formulated in three discrete stages. First, the carbonylmanganese cation such as $(OC)_3Mn(NCMe)_3{}^+$ with $n = 3$ undergoes an electrocatalytic ligand substitution with added L to form the bis(phosphine) complex $(OC)_3Mn(NCMe)L_2{}^+$ via labile 19-electron Mn(0) intermediates as in Scheme V. Second, the substitution product $(OC)_3Mn(NCMe)L_2{}^+$ is reduced to the Mn(0) radical $(OC)_3Mn(NCMe)L_2\cdot$ which is common to all cationic precursors irrespective of the degree of prior phosphine coordination in the precursor I (i.e., $n = 1, 2$). Third, the hydridomanganese product is derived by hydrogen atom transfer to the carbonyl ligand of the 19-electron intermediate $(OC)_3Mn(NCMe)L_2\cdot$ to form the formyl complex $(OC)_2Mn(NCMe)L_2CHO$, followed by the electrocatalytic extrusion of the coordinated ligand (MeCN) as in Scheme III. The third stage is established in the reductive conversion of the cationic $(OC)_4Mn(PPh_3)_2{}^+$ to the hydride $(OC)_3Mn(PPh_3)_2H$ by the observation of the intermediate $(OC)_3Mn(PPh_3)_2CHO$ during cyclic voltammetry. A competition to form the carbonylmanganate $(OC)_3MnL_2{}^-$ as a byproduct of reduction is also delineated.

Introduction

Electrochemistry offers a potentially useful method for the preparation of various types of transition metal hydrides, especially by exploiting the reduction of various types of carbonylmetal cations.[2,3] In a preliminary report,[4] we described the successful electrosynthesis of hydridomanganese carbonyls and the unusual observation of facile, multiple ligand substitutions which accompany the reduction of cationic manganese(I) carbonyls. As a part of our continuing studies of the electrocatalytic phenomena associated with metal carbonyls,[5] we wish to describe the use of transient electrochemical techniques, particularly cyclic voltammetry, to show how such reductive processes can occur via reactive paramagnetic intermediates.

Results

We have focussed our attention in this study on the reduction of a series of acetonitrile derivatives of tricarbonylmanganese(I) cations $(OC)_3Mn(NCMe)_nL_{3-n}{}^+$ (I), where L is a phosphine ligand and $n = 1$–3.

I. Electroreduction of Carbonylmanganese(I) Cations. A solution of the mono(acetonitrile) cation Ia ($n = 1$), $(OC)_3Mn(NCMe)(PMe_2Ph)_2{}^+$, as the $PF_6{}^-$ or $BF_4{}^-$ salt[6] in acetonitrile containing 0.1 M tetraethylammonium perchlorate (TEAP) is electroactive at a potential of −1.5 to −1.8 V vs. SCE. When a cathodic current of 20 mA was passed through the 4.2×10^{-2} M solution under galvanostatic conditions, a total charge of 1.3 coulombs was taken up per mole of I. Workup of the catholyte afforded

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