Metal Cluster Catalysis: A Kinetic and Mechanistic Study of the Carbonylation of Methanol to Give Methyl Formate as Catalyzed by $[Et_4N]_2[Fe_3(CO)_9E]$ ($E = S, Se, Te$)

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The cluster compounds $[Et_4N]_2[Fe_3(CO)_9E]$ ($E = S$, Se, Te) catalyze the homogeneous carbonylation of methanol to form methyl formate under moderate CO pressures (600−1200 psi) between 50 and 90 °C. A detailed kinetic analysis of this system shows that the reaction is first order with respect to cluster concentration and quasi-second order with respect to the pressure of CO. All three cluster compounds show similar behavior. The reaction appears to be almost independent of the $[CH_3O^-]_{total}$ at values of $[CH_3O^-]_{total} \leq 3 \times 10^{-3}$ M, but at higher concentrations it appears to be first-order dependent on $[CH_3O^-]_{total}$. This system affords the opportunity to compare the effects of different main group heteroatoms in a homologous series. The rates of the reaction were found to lie in the following order: Te (6×10^{-4} M·min^{-1}) > S (4×10^{-4} M·min^{-1}) > Se (2×10^{-4} M·min^{-1}) at 1200 psi and 90 °C. The activation energies were found to be 43 ± 11 kJ·mol^{-1} ($E = S$), 76 ± 8 kJ·mol^{-1} ($E = Se$), and 72 ± 7 kJ·mol^{-1} ($E = Te$). The rate dependence upon CO pressure suggests a mechanism in which metal−metal bond opening is important.

Introduction

Catalysis by metal cluster complexes is attractive since they may be viewed as fragments of a metal surface surrounded by a layer of adsorbed ligand molecules.[1−4] Well-defined metal cluster complexes afford the possibility of performing complex transformations in homogeneous solution similar to those observed for conventional heterogeneous catalysts that may be complex and difficult to control.[5] Cluster compounds potentially offer a variety of binding sites and modes that can lead to regio- and stereoselectivity. Further opportunities are available in heterometallic systems where differences in metal reactivity may lead to site-specific processes and synergistic affects not observed in homonuclear systems. Small molecules such as alkenes, alkynes, CO, and H_2 are known to be activated on metal clusters, but they may bind in far more complex ways than those afforded by a single metal center.[6−10] Cluster compounds facilitate a number of organic transformations, as exemplified by the layer-segregated platinum−ruthenium cluster complexes that Adams and Barnard have reported to catalyze the hydrosilylation of diarylalkynes.[11] Kinetic and labeling studies support intact cluster catalysis in that system. Similarly, Meilleur and co-workers have recently reported that $[Pd_4(dppm)_4(H_4)_2][X]_2$ ($X = Cl^-$, Br^-) homogeneously electrocatalyze formate decomposition with no evidence of cluster decomposition.[12] There are other examples of cluster-catalyzed reactions that can be carried out without cluster degradation. Cabeza and co-workers have reported kinetic evidence for catalysis by intact clusters in the hydrogenation of diphenylacetylene by triruthenium cluster complexes,[13−15] while Süss-Fink and Herrmann have provided indirect evidence for $[HRu_3(CO)_{11}]^-$ as a hydroformylation catalyst[16] and the hydrogenation of benzene on a triruthenium cluster.[17] Catalysis by cluster systems has been reviewed recently.[18,19]

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Our interest in the chalcogenide-containing clusters stemmed from a desire to understand how the incorporation of main group elements into transition metal clusters would affect their stability, structure, and reactivity patterns.[20−22] These hybrid systems often violate the electron-counting formalisms established for homonuclear clusters. We have examined these hybrid systems in order to build upon the existing activity for transition metal-only clusters.[23−26] In this report, we describe our discovery that the carbonylation of methanol to produce methyl formate is catalyzed by $[Et_4N]_2[Fe_3(CO)_9E]$ ($[Et_4N]_2$[**Ia**], E = S; Se, $[Et_4N]_2$[**Ib**]; Te, $[Et_4N]_2$[**Ic**]). (Throughout the text structure labels will use “a” to designate S, “b” to designate Se, and “c” to designate Te.) This cluster system affords the opportunity of studying the catalytic cycle as a function of main group element in a homologous series.

Experimental Section

Materials and General Methods. All manipulations were performed using standard techniques on a Schlenk line or in a Vacuum Atmospheres inert atmosphere box.[27] Solvents were distilled from the appropriate drying agent under nitrogen prior to use. The complexes $[Et_4N]_2$[**Ia**],[28] $[Et_4N]_2$[**Ib**],[29] $[Et_4N]_2$[**Ic**],[29] and $[Et_4N][HFe_3(CO)_{11}]$[30] were prepared according to the indicated literature methods using Et_4N^+ salt. $[Et_4N][HFe(CO)_4]$ was prepared as follows. Solid potassium hydroxide (8.0 g, 0.14 mol) was dissolved in methanol in an ice bath, after which $Fe(CO)_5$ (6.32 mL, 0.048 mol) was added by syringe. The reaction mixture was stirred 30 min and then allowed to warm to room temperature. The solvent was removed under vacuum, and the residue was dissolved in water. While stirring, an aqueous solution of 12 g (0.057 mol) of $[Et_4N]Br$ was added dropwise. The resulting precipitate was filtered, washed with water, and dried under vacuum. Yield: 11 g (80%). $[Et_4N][OCH_3]$ was prepared by cation exchange in $NaOCH_3$ using $[Et_4N]Br$ (Acros). The following materials were used as received from their commercial sources: $Fe_3(CO)_{12}$ and $Fe(CO)_5$ from Strem Chemicals; $NaOCH_3$, $[Et_4N]OH$, $[Et_4N]I$, and CH_3I from Acros.

Kinetic Studies. The progress of the catalytic reactions was followed by a ReactIR 1000 system with a ZrComp probe manufactured by Applied Systems Inc. (ASI) for in situ infrared characterization utilizing a 250 mL Parr stainless steel vessel equipped with a magnetic drive for stirring (~80 rpm). The spectra were collected over 128 scans at a spectral resolution of 8 cm^{-1}. Reaction rates were obtained by measuring the concentration of methyl formate as a function of time using $\nu_{(C-O)}$ at 1723 cm^{-1}. Solutions of appropriate cluster concentration were prepared inside the drybox and placed in a stainless steel pipet attached to the Parr reactor containing 20 mL of methanol. Typically the vessel was purged with CO three times before it was pressurized to 200 psi below the desired final pressure. It was then heated to the desired temperature, whereupon 5 mL of the cluster solution was introduced into the Parr vessel and the pressure was adjusted to the desired value. This produced a total volume of 25 mL of the solution at the target temperature and pressure. Data were collected over a period of 6 h for all reactions unless otherwise stated. The reactions were performed at 90 °C and varying pressures between 600 and 1200 psi of CO with constant cluster concentration (1.0 mM) for the pressure dependence studies. To measure the concentration dependency, concentrations of the cluster were varied from 0.5 to 1.0 mM, with constant temperature at 90 °C and constant pressure of 1200 psi. Finally, temperature was varied between 50 and 90 °C, with a constant cluster concentration (1.0 mM) and constant pressure of 1200 psi for the activation energy studies. Each experiment was performed at least 10 times under a given set of conditions to establish the reproducibility of the reaction. The data were analyzed using the least-squares fitting routines in the program Origin.[31]

Results and Discussion

Carbonylation Catalysis. Many early studies of carbonylation reactions, reactions in which carbon monoxide along with other small molecules are added to organic substrates, were performed by W. Reppe, who discovered in 1941 that the reaction of CO with methanol to yield acetic acid could be catalyzed by carbonyl compounds of Fe, Co, and Ni in the presence of iodide ions at 210 °C and 7500 psi.[32] Since then, many other reactions involving carbonylation of methanol have been reported. Reaction products range from methyl formate and methyl acetate to acetaldehyde and acetic anhydride.[23−25,33−41]

Methyl formate production is greater than 150 kt/a in 2001 worldwide annually,[25,42,43] and the compound finds use as a curing agent, a larvicide for tobacco, and a fumigant for edible fruit and can be used as a starting reagent for the production of other useful organic derivatives such as formic acid, acetic acid, formamide, dimethylformamide, dimethyl carbonate, and ethylene glycol. Although methyl formate can be produced in a variety of catalytic processes,[24,25,38,39] the commercial process has not changed significantly since BASF first patented it in 1925.[44] That process is based on sodium methoxide as catalyst and is carried out at about 80 °C and 675 psi of CO. The BASF process is thought to involve the direct nucleophilic attack on the carbon monoxide by methoxide anion. Subsequent protonation by a methanol molecule would then produce methyl

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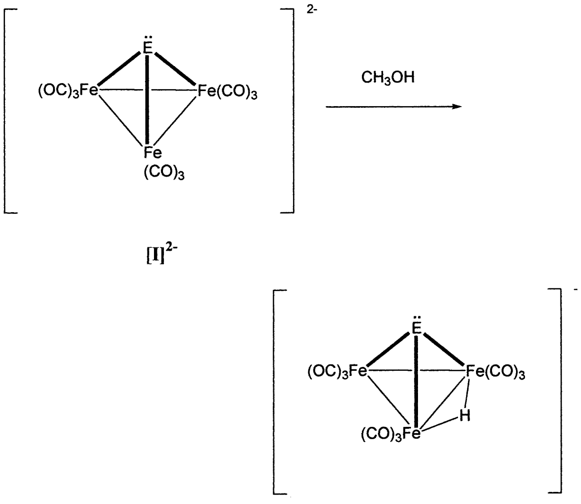
formate and regenerate methoxide anion. One disadvantage of this process is the need to maintain strictly anhydrous conditions to prevent the formation of insoluble sodium formate.[25]

Catalysis by Metal Cluster Compounds. To achieve a catalytic reaction with a cluster compound, vacant coordination sites have to be present or created during the course of the reaction. Cluster catalysis requires the additional caveat that this must occur without fragmenting the cluster. There are a couple of pathways by which a cluster might achieve this end. The simplest ways are similar to those observed in mononuclear systems and involve the loss of a bound ligand or a change in a ligand's hapticity to create a vacant coordination site,[45] but other routes are also available for cluster compounds. A few clusters are known that are formally coordinatively unsaturated. The best example of this is $H_2Os_3(CO)_{10}$, a compound that possesses only 46 cluster electrons as compared to the more usual 48-electron count consistent with the 18-electron rule. It adds ligands readily, a process similar to that widely observed for 16-electron mononuclear species. Another pathway is the breakage of an M−M bond upon addition of substrate. Formally the addition of a ligand is equivalent to the addition of two electrons to the cluster electron count, and this addition may be viewed as a formal reduction of a metal−metal bond. In the absence of some additional bridging framework to hold the metals together, the result may be cluster fragmentation,[46−48] but where bridging ligands or stabilizing heteroatoms are present the metal stoichiometry may be conserved. Alternatively, higher nuclearity cluster compounds can undergo more complex skeletal rearrangements upon addition of a ligand. These new cluster core geometries are often consistent with predictions based upon the Wade/Mingos rules. For example, the addition of a two-electron donor ligand to a *closo* N-vertex cluster with $N+1$ skeletal electron pairs (SEPs) could result in the formation of a *nido* N-vertex cluster with $N+2$ SEPs. Some bridging groups can stabilize the cluster composition throughout a M−M bond cleavage process or a core structural rearrangement.[49]

There are several strategies to circumvent the problem of cluster fragmentation during catalysis. One can simply avoid carbonylation reactions, focusing on hydrogenations or other reactions such as hydrosilylation that avoid the fragmentation difficulty. Another approach is to use second-row transition metals where the metal−metal bond strengths are known to be more robust than for those of the first transition series. Multidentate ligands based on P- and N-donors serve to hold multimetallic units together and allow the tailoring of stability and reactivity patterns by variations in the geometrical and electronic properties of the ligand substituents.[12,50−52] Supported metal clusters are reported to have increased stability compared to the unsupported starting compounds. Various impregnation methods are available to immobilize homo- and heterometallic clusters onto surfaces, and methods for the synthesis of clusters in zeolites and other supports have also been reported.[53] In these cases, the clusters appear to remain intact or convert to another well-defined cluster compound on the support surface. Incorporation of main-group heteroatoms into the cluster framework appears to increase dramatically the stability of the clusters and is the method chosen for this study.[54,55]

The $[EFe_3(CO)_9]^{2-}$ Cluster System. The cluster compounds $[\mathbf{I}]^{2-}$ chosen for this study contain a tetrahedral EFe_3 framework where the main group element is easily varied to be S, Se, or Te. The synthetic reactions to produce these compounds are straightforward, producing multigram quantities cleanly and in good yields. The clusters are soluble in a variety of organic solvents. Upon dissolution in methanol, they are immediately and quantitatively converted to $[HFe_3(CO)_9E]^-$ ($[\mathbf{II}]^-$), in which the hydride ligand bridges an Fe−Fe bond.[56,57] It proved easier to perform the reactions starting with the dianions because of their ease of synthesis, isolation, and purification. The monohydrides are readily prepared in solution but are more difficult to isolate in pure form. For simplicity of discussion, we will refer to the individual catalytic trials using the starting cluster dianion $[\mathbf{I}]^{2-}$, except in those cases where we explicitly wish to denote the structural form $[\mathbf{II}]^-$.



$[\mathbf{I}]^{2-}$

$[\mathbf{II}]^-$

(1)

Rate Data and Determination of the Rate Law. A representative conversion of methanol and carbon monoxide into methyl formate is shown in Figure 1. Details of the kinetic measurements represented in Figures 1−7 and Table 1 are given in the Supporting

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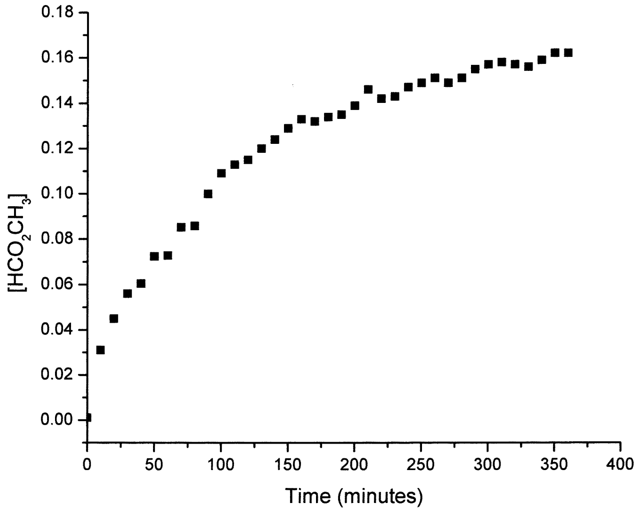

Figure 1. Representative plot for the conversion of methanol and CO into methyl formate with $[Et_4N]_2$[**Ib**] (1.0 mM) at 1200 psi pressure of CO and 90 °C.

Table 1. Comparison of Reaction Rates for Different Iron Carbonyl Species and Bases at 1200 psi CO and 90 °C[a]

compound	concentration (mM)	rate ([methyl formate]/min)
$[Et_4N]_2[Fe_3(CO)_9S]$	1.0	4×10^{-4}
$[Et_4N]_2[Fe_3(CO)_9Se]$	1.0	2×10^{-4}
$[Et_4N]_2[Fe_3(CO)_9Te]$	1.0	6×10^{-4}
$[Et_4N][HFe_3(CO)_9Te]$	1.0	4×10^{-4}
$[Et_4N][HFe_3(CO)_{11}]$	1.0	9×10^{-6}
$Fe_3(CO)_{12}$	1.0	NR
$Fe(CO)_5$	3.0	9×10^{-6}
$[Et_4N][HFe(CO)_4]$	3.0	1×10^{-4}
$NaOCH_3$	3.0	5×10^{-5}
$[Et_4N]OH$	1.0	1×10^{-4}
$[Et_4N]I$	1.0	7×10^{-5}
$[Et_4N][CH_3O]$	1.0	8×10^{-5}
CH_3I	1.0	1×10^{-4}

[a] Under these conditions the concentration of CO in MeOH is approximately 0.70 M.[59]

Information. The data were examined in the range of 60−90 °C and 600−1000 psi CO unless otherwise indicated. Note that these conditions place these experiments in the supercritical region for CO ($T_c = -140$ °C; $P_c = 34.5$ atm or 507 psi) but well below that region for methanol ($T_c = 240$ °C; $P_c = 78.5$ atm). Dissolution of carbon monoxide in methanol shows linear behavior for Henry's law plots over the temperature and pressure range studied here with the molar concentration ranges on the order of 0.2−0.8 m. The solubility of CO at a given pressure does not vary much with temperature in the region under study.[59] Equilibrium is apparently achieved in the reaction after approximately 6 h, when the concentration of methyl formate reaches a plateau. The equilibrium constant calculated is 8×10^{-5} using the calculated molar concentration for CO dissolved in methanol at the reaction conditions obtained from the literature.[58]

Rates were determined as initial rates from the time versus conversion curves. The rate dependence on the catalyst was determined by measuring the rates of several runs at different concentrations of the catalyst, while the pressure and temperature were kept constant. Plots of rate versus cluster concentration afforded straight lines with slopes of 3.32, 1.96, and 6.13 for $[Et_4N]_2[Fe_3(CO)_9S]$ ($[Et_4N]_2$[**Ia**]), $[Et_4N]_2[Fe_3(CO)_9Se]$ ($[Et_4N]_2$[**Ib**]), and $[Et_4N]_2[Fe_3(CO)_9Te]$ ($[Et_4N]_2$[**Ic**]), respectively (Figure 2). The catalytic reaction is therefore first-order with respect to $[Et_4N]_2$[**I**]. The first-order dependence on cluster concentration supports the contention that each cluster produces only one catalytic species. Plots of ln(rate) versus ln(P_{CO}) with temperature and cluster concentration kept constant afforded straight lines (Figure 3) with slopes that are the same within experimental error: 1.70 for $[Et_4N]_2$[**Ia**], 1.62 for $Et_4N]_2$[**Ib**], and 1.70 for $[Et_4N]_2$[**Ic**]. To determine the temperature dependence, data were obtained at different temperatures while holding cluster concentration and P_{CO} constant. These are graphed in the form of an Arrhenius plot (Figure 4). The slopes are -5.13×10^3,

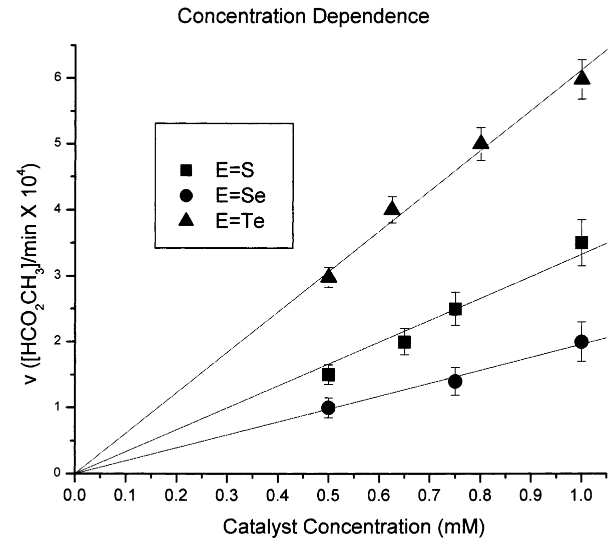

Figure 2. Rate of formation of methyl formate as a function of catalyst concentration. Catalyst used was [**I**]$^{2-}$, pressure was 1200 psi at 90 °C. Correlation factors were 1.00, 0.99, and 0.99 for $[Et_4N]_2$[**Ia**], $[Et_4N]_2$[**Ib**], and $[Et_4N]_2$[**Ic**], respectively.

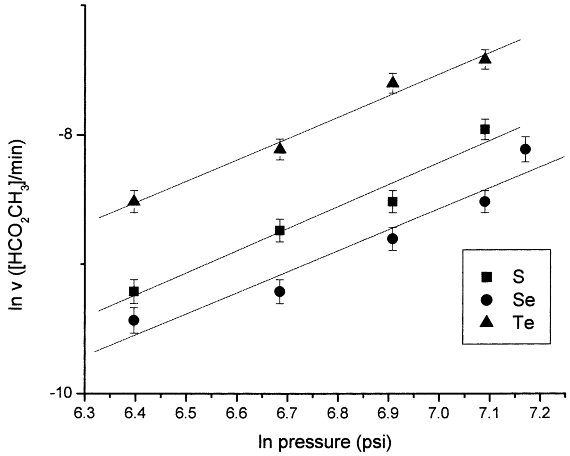

Figure 3. Rates of formation of methyl formate as a function of CO pressure. Catalyst used was [**I**]$^{2-}$, concentration was 1 mM psi at 90 °C. Correlation factors were 0.98, 0.97, and 0.99 for $[Et_4N]_2$[**Ia**], $[Et_4N]_2$[**Ib**], and $[Et_4N]_2$[**Ic**], respectively.

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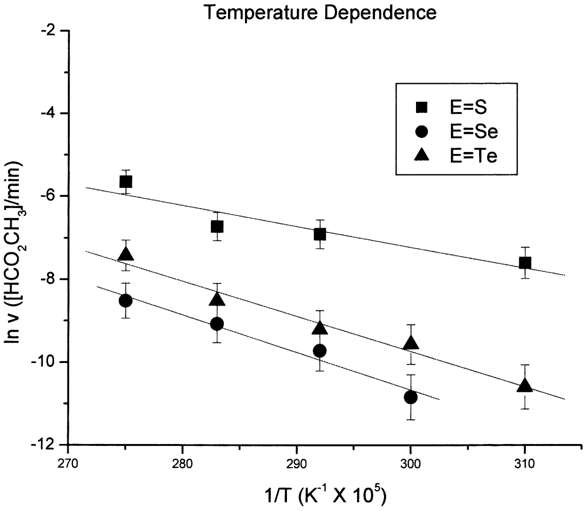

Figure 4. Temperature dependence of the rates for the formation of methyl formate. The catalyst used was $[\mathbf{I}]^{2-}$, concentration was 1 mM at 1200 psi pressure of CO. Correlation factors were 0.93, 0.98, and 0.99 for $[Et_4N]_2[\mathbf{Ia}]$, $[Et_4N]_2[\mathbf{Ib}]$, and $[Et_4N]_2[\mathbf{Ic}]$, respectively.

-8.65×10^3, and -9.25×10^3 for $[Et_4N]_2[\mathbf{Ia}]$, $[Et_4N]_2[\mathbf{Ib}]$, and $[Et_4N]_2[\mathbf{Ic}]$, respectively. These data yield activation energies of 43 ± 11, 76 ± 8, and 72 ± 7 kJ·mol^{-1} for $[Et_4N]_2[\mathbf{Ia}]$, $[Et_4N]_2[\mathbf{Ib}]$, and $[Et_4N]_2[\mathbf{Ic}]$, respectively. The corresponding intercepts were 8.17, 17.1, and 16.2, giving for *A*, the preexponential factor in the Arrhenius equation, values of 3.5×10^3, 2.6×10^7, and 1.1×10^7. The activation energies for the E = Se and Te clusters are comparable in magnitude, while for E = S the cluster exhibits both a much lower activation energy and also the least favorable preexponential parameter. Based upon the initial rates for the E = S, Se, and Te cluster, the turnover numbers for methyl formate formation are approximately 24 (S), 12 (Se), and 36 h^{-1} (Te). Atomic radius, ionization potential, electronegativity, and the Fe−E bond distances did not show an obvious correlation to the activation energy, but the effective nuclear charge of the chalcogen atom does seem to correlate (S, 5.45; Se 6.95; Te, 6.95) and suggests an electronic role for the main group element.

Since $[CH_3O]^-$ is a known catalyst for carbonylation of methanol and since it is produced when clusters $[\mathbf{I}]^{2-}$ are dissolved in methanol, the formation of methyl formate was studied additionally as a function of $[Et_4N][CH_3O]$ concentration in the absence of cluster as shown in Figure 5. The linearity of this plot (slope = 1.02, correlation factor = 0.99) indicates a first-order dependence on methoxide ion concentration as expected. Several runs were performed with constant $[CH_3O^-]$ concentration and temperature to determine the CO pressure dependence of the production of methyl formate for this pathway. We observed that the rate was the same, i.e., independent of the CO pressure, using only methoxide ion as the catalyst over the range 600−1200 psi.

The effect on the rate of cluster-catalyzed carbonylation was also examined in the presence of added CH_3O^- (as $[Et_4N][CH_3O]$). The rate data for the case of $[Et_4N]_2[\mathbf{Ic}]$ were plotted as a function of $[CH_3O^-]_{total}$ (Figure 6). The total concentration of methoxide ion equals added methoxide concentration plus the concentration of methoxide produced from dissolution of the cluster dianion in methanol (1 mmol of cluster produces 1 mmol of methoxide ion in solution). The total rate (rate$_{total}$) of methyl formate production is thus a combination of the rates of the methoxide-catalyzed pathway and the cluster-catalyzed pathways (rate$_{methoxide}$ + rate$_{cluster\ pathways}$). Subtracting the rate due to the methoxide-only pathway from the total rate yields the rate of reaction deriving from the cluster pathways alone. A plot of ln(rate$_{cluster\ pathways}$) versus ln($[CH_3O^-]_{total}$) is shown in Figure 7. The slope of the straight lines in such a plot gives the order of reaction with respect to the particular reagent being examined. This plot shows that the rate is virtually independent of the $[CH_3O^-]_{total}$ at values of $[CH_3O^-]_{total} \leq 3 \times 10^{-3}$ M (slope ≅ 0, correlation factor of 1.00), while at higher concentrations it appears to be first-order dependent on $[CH_3O^-]_{total}$ (slope = 1.12, correlation factor of 0.96). From these observations, we arrive at eq 1, in which the rate of the reaction depends on three terms: the rate due to methoxide ion catalysis

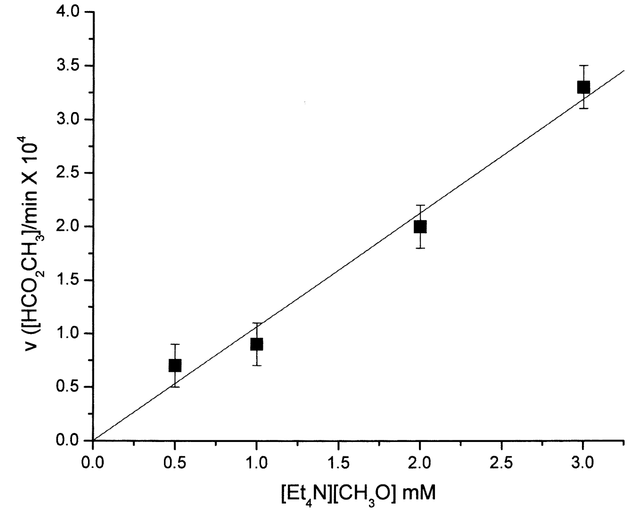

Figure 5. Rate for the formation of methyl formate as a function of $[Et_4N][CH_3O]$ in the absence of cluster (correlation factor of 0.99).

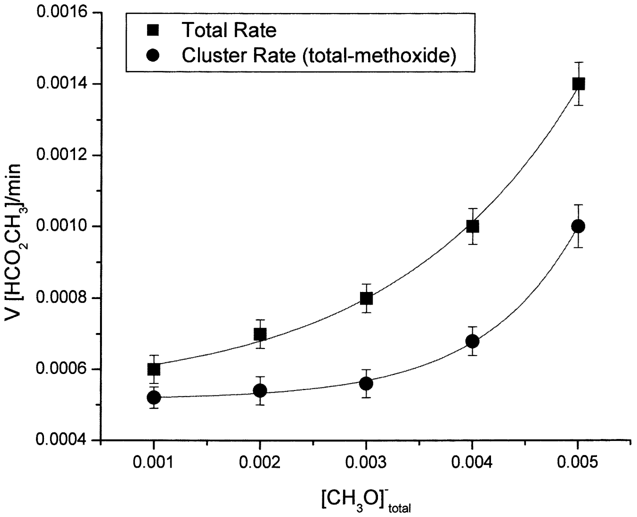

Figure 6. Dependence of the ratio of the rates for the formation of methyl formate on the amount of $[CH_3O]^-_{total}$ as $[Et_4N][CH_3O]$. Catalyst used was $[Et_4N]_2[\mathbf{Ic}]$, concentration was 1.0 mM psi at 90 °C.

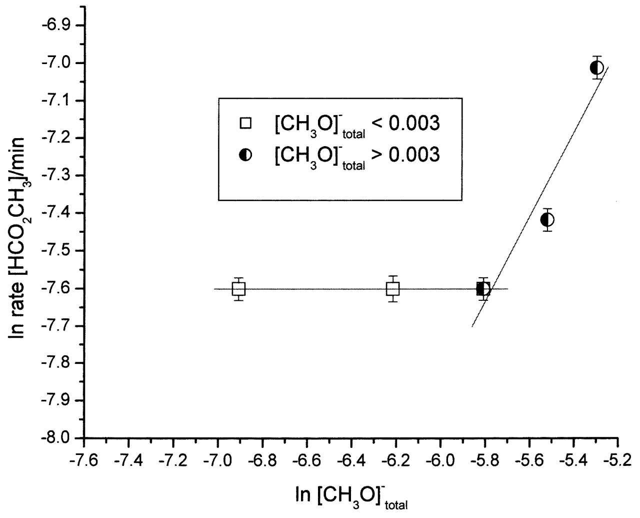

Figure 7. Rates of formation of methyl formate as a function of $[CH_3O]^-_{total}$. Catalyst used was $[Et_4N]_2$[**Ic**], concentration was 1.0 mM psi at 90 °C.

and the rate due to the cluster pathways, one of which is independent of methoxide ion concentration and the other has a first-order dependence on CH_3O^-.

$$\frac{d[HCO_2CH_3]}{dt} = k_{cluster1}[HFe_3(CO)_9E^-]P_{CO}{}^{1.7} + k_{cluster2}[HFe_3(CO)_9E^-][CH_3O^-]P_{CO}{}^{1.7} + k_{methoxide}[CH_3O^-] \quad (1)$$

$$k_{cluster1} = 3.5 \times 10^{-13}\ \text{min}^{-1}\cdot\text{psi}^{-1.7}$$

$$k_{cluster2} = 2.3 \times 10^{-10}\ \text{min}^{-1}\cdot\text{psi}^{-1.7}\cdot\mathbf{M}^{-1}$$

$$k_{methoxide} = 1.1 \times 10^{-4}\ \text{min}^{-1}$$

Tests for Lower Nuclearity Complexes Being the Catalytically Active Species. One of the most difficult aspects of cluster catalysis is to establish that the catalysis is not taking place using mononuclear fragments.[61-65] Selected lower-nuclearity species that could possibly arise from cluster fragmentation were examined for comparison to the cluster-catalyzed processes. The results for runs at 1200 psi CO and 90 °C are summarized in Table 1. The concentration chosen for $Fe(CO)_5$ or $[HFe(CO)_4]^-$ was 3 mM because 1 equiv of the cluster could produce 3 equiv of these mononuclear species upon fragmentation. The compounds $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $[HFe(CO)_4]^-$, and $[HFe_3(CO)_{11}]^-$ have previously been reported as modest catalysts for the production of methyl formate.[26,60] The rate of catalysis by $NaOCH_3$ was measured, as it is a known catalyst for the reaction, and we wished to compare its activity under identical conditions to those using the cluster systems. The concentration of 3 mM NaOMe gave the most consistently reproducible results. The rates at lower concentrations of NaOMe were so slow that little methyl formate was observed in the same time periods as for the clusters. Since methoxide ion is also produced when the dianionic clusters are dissolved in methanol, the cluster systems were also examined with added methoxide or hydroxide ion and these ions were examined in the absence of cluster.

It is clear that the lower nuclearity species listed in Table 1 cannot be responsible for the catalysis exhibited by $[Et_4N]_2$[**I**], since the activity of each is below that of the cluster. Using the ASI ReactIR system, we were able to observe the ν_{CO} bands characteristic of the cluster compound at 2041, 1981, and 1950 cm^{-1} during the entire course of the reaction with no evidence of cluster degradation or formation of other metal carbonyl species of lower nuclearity. If mononuclear species were present, they would have had to be present at far lower concentrations than those reported in Table 1 since they were not detectable by IR spectroscopy. Complete decomposition of the cluster to $[HFe(CO)_4]^-$ would result in three of the mononuclear complexes being produced per mol of cluster, so the 3 mmol concentration employed represents a limiting condition. The well-behaved kinetic data and excellent first-order dependence on the cluster concentration are indicative of a process that does not involve fragmentation of the cluster.[11,61-65] If mononuclear species deriving from cluster breakdown were involved, then one would expect the dependence on cluster concentration to be greater than first-order and perhaps not well-behaved, as the decomposition of the cluster would lead to an increasing number of mononuclear fragments with time.

Tests for Heterogeneous Catalysis. It is also necessary to address the question of whether the catalysis is occurring via *heterogeneous* metal particles generated in situ from decomposition of the cluster.[61-65] To test the homogeneous character of the reaction, a trial was undertaken in which the cluster catalysis was halted after 3 h, cooled, and then filtered. The 3 h time was chosen because the methyl formate achieves an equilibrium value at approximately 6 h. The reaction solution was returned to the reaction vessel and allowed to run for three more hours. Although the rate was slightly lower after filtration (4×10^{-4} [methyl formate]/min), this was believed to occur because of the inability to obtain a fresh background spectrum for the reaction already in progress. Once the reaction solution was filtered and returned to the reaction vessel, it was not possible to take a background spectrum and the same one used at the beginning of the data collection was used. The use of added mercury as the conventional poison test for heterogeneously catalyzed reactions was not possible because the clusters react with mercury under the experimental conditions to give insoluble species with no carbonyl-containing compound remaining in solution.[66]

Mechanistic Considerations. An important aspect of the cluster compounds under examination is the

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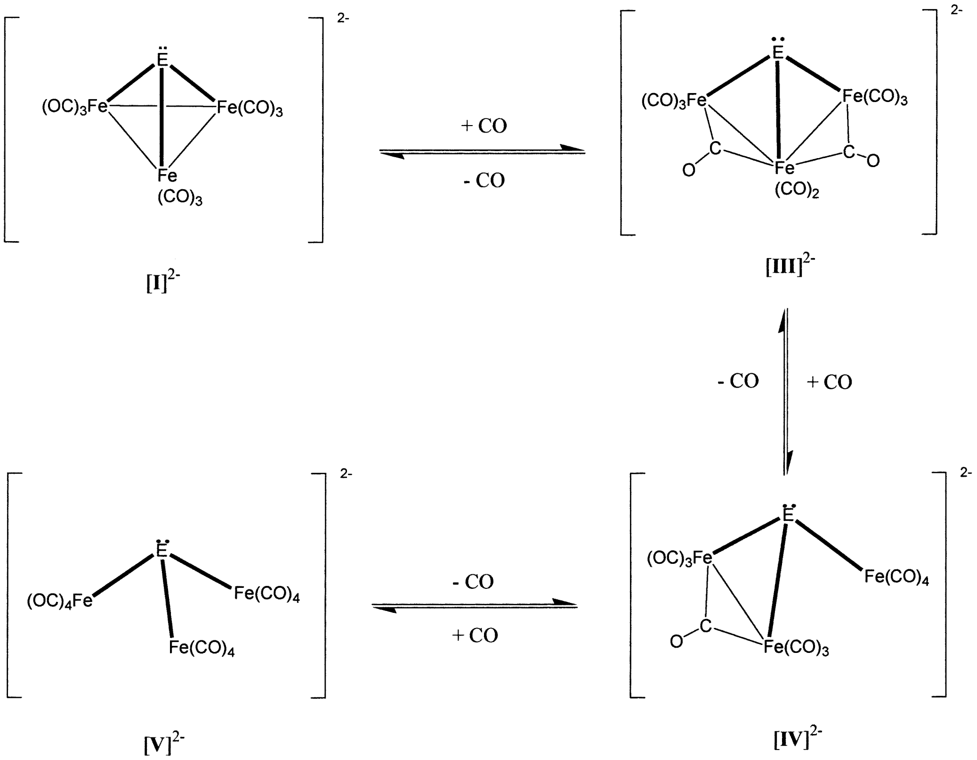
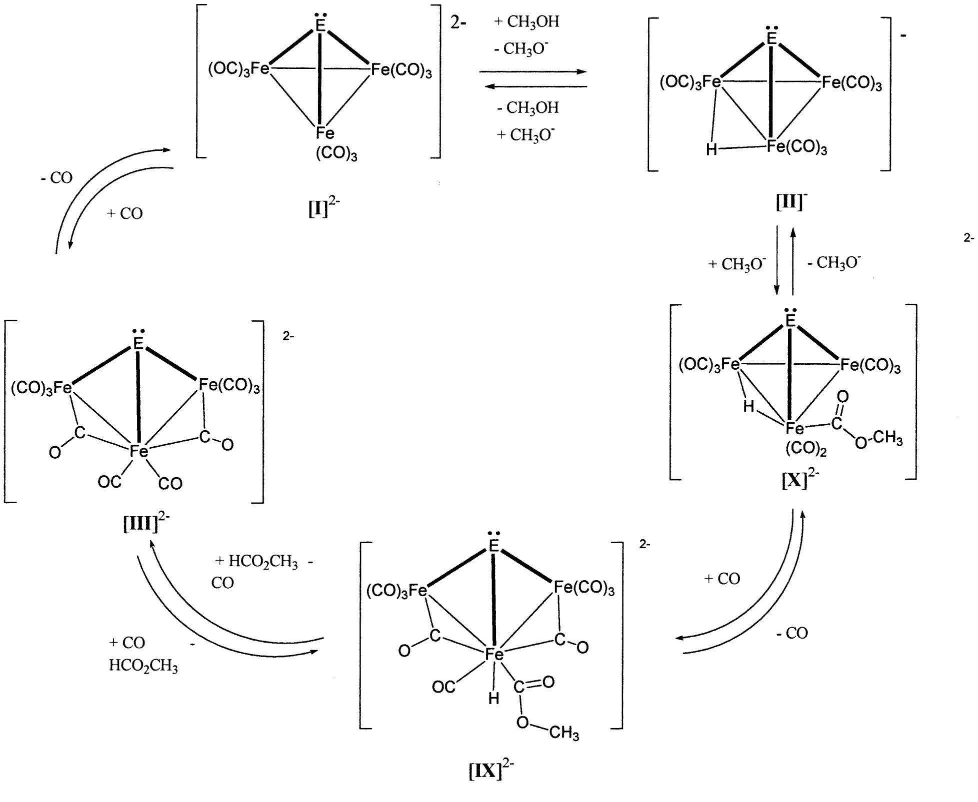
Scheme 1. M−M Bond Opening Processes for $[Et_4N]_2[I]$



Scheme 2. Proposed Mechanism for the Carbonylation of Methanol Catalyzed by $[Et_4N]_2[I]$ with the Catalytically Active Species Being an Open Cluster in Which Two Metal−Metal Bonds Have Been Broken



potential for undergoing reversible M−M bond cleavage upon the addition of CO as shown in Scheme 1. The open trigonal-pyramidal iron carbonyl species $[\mathbf{Vc}]^{2-}$ has been prepared and isolated previously in our group, and the Se analogue has been observed briefly in solution.[67] The intermediate species $[\mathbf{III}]^{2-}$ and $[\mathbf{IV}]^{2-}$ have not been observed but are plausible based upon electron-counting considerations. The processes written in Scheme 1 should all be reversible processes. Even though $[\mathbf{I}]^{2-}$ is apparently the dominant species present in solution

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under the conditions employed (as evidenced by the in situ IR data), the catalytically active species could be any of the forms of the cluster shown. An added complication is the ability of the clusters to undergo protonation by methanol, so that catalytically active species could be protonated forms of any of these species. We know that [**I**]$^{2-}$ is quantitatively protonated upon dissolution in MeOH; however, the open structure [**V**]$^{2-}$ is not protonated upon exposure to MeOH. We cannot, therefore, be certain where these equilibria would lie for the intermediate forms of the cluster. Furthermore, the reaction could proceed via reaction of either methanol or methoxide ion on whichever intermediate species is the active catalyst.

Given the sheer number of possible variations of the pathways involved, which in many cases cannot be determined by the experimental data available, we will simplify the discussion and base our comments on the use of the dianionic forms given in Scheme 1, acknowledging that fast, reversible acid−base equilibria are likely involved. Since proton transfer reactions are generally very fast, especially in protic solvents, it would be difficult to ascertain whether a protonation step preceded or followed the rate-determining step of the reaction.

There are two general scenarios for the mechanism starting from any of the possible cluster intermediates presented in Scheme 1. The rate-determining step of the reaction is likely to be either (1) direct attack of methoxide ion or MeOH on the cluster compound or (2) CO addition to a cluster after formation of a bound methoxyformyl ligand. Reversible opening of metal−metal bonding upon addition of a ligand[68] and the attack at coordinated carbon monoxide in a carbonyl cluster by methoxide ion have been previously reported.[69] Sample derivations of the kinetic rate expressions based upon fast equilibrium and/or steady state approximations are given in the Supporting Information starting with each of the possible cluster forms as active catalyst. From these simple considerations, we can rule out [**I**]$^{2-}$ and [**V**]$^{2-}$ as the active cluster. In the case of [**I**]$^{2-}$, if the rate-determining step is initial attack of MeOH or MeO$^-$ on the cluster, no pressure dependence for CO would be observed. If the rate-determining step were the displacement of the methoxy carbonyl ligand from the tetrahedral framework after MeOH/MeO$^-$ attack, then the pressure dependence expected would be only first-order in CO. Likewise, the preequilibrium processes leading to [**V**]$^{2-}$ would predict either $P_{CO}{}^3$ or $P_{CO}{}^4$ dependencies if the completely open form were the catalytically active species. This leaves the two cluster forms [**III**]$^{2-}$ and [**IV**]$^{2-}$ for consideration. If the attack of MeOH/MeO$^-$ on these forms is rate-determining, then the pressure dependency (fast equilibrium approximation) on CO would be first-order for [**III**]$^{2-}$ and second-order of [**IV**]$^{2-}$. Similarly, if the rate-determining process is CO displacement after MeOH/MeO$^-$ addition, then the orders anticipated would be second-order for [**III**]$^{2-}$ and third-order for [**IV**]$^{2-}$. From the observed rate dependency (order 1.7) for CO pressure, we can narrow our consideration to the second-order processes, which would be CO displacement of a preformed methoxycarbonyl ligand from [**III**]$^{2-}$ or CO addition to give the open species [**IV**]$^{2-}$. That the order of pressure dependency is somewhat less than CO implies that the fast equilibrium model is not completely accurate.

The quasi-second-order rate dependence on CO indicates involvement of equilibrium processes involving CO. Kinetic derivations often show nonintegral dependencies when equilibria are involved. This situation arises because the reversible steady state creation of intermediates gives rise to counterproductive terms in the denominator of the rate expression. Increased pressure of CO is expected to promote the elimination of methyl formate. The rate may also be enhanced if the catalytically active form of the cluster is one of the forms in which CO has been added with metal−metal bond cleavage (e.g., [**III**]$^{2-}$, [**IV**]$^{2-}$, or [**V**]$^{2-}$) but could also act as an inhibitor if the further reaction with CO reduces the concentration of active compound. For example, if the catalytically active species is [**III**]$^{2-}$ (or [**IV**]$^{2-}$), the formation of [**IV**]$^{2-}$ (or [**V**]$^{2-}$) would decrease the rate of the reaction in the case where the rate at which the intermediate is lost due to further reaction with CO is significant compared to the rate of formation of that complex. In the productive cycle, the intermediate active complex would undergo elimination upon addition of CO, producing methyl formate and regenerating the initial cluster catalyst [**I**]$^{2-}$ or one of the other cluster forms. The derived rate expressions given in the Supporting Information show that the pressure dependencies for either of these processes are complex and mathematically could give the observed CO pressure dependency given an appropriate set of forward and reverse equilibrium constants for each of the processes involved. Unfortunately, we have no means of measuring the rates of these intermediate processes and cannot distinguish between the two.

At low methoxide ion concentration, the rate could be determined by either CO addition alone or, perhaps more likely, the attack of MeOH instead of MeO$^-$. As indicated previously, this dependency is masked by the use of that reagent as the solvent. At larger methoxide ion concentrations a dependency upon that ion is observed. The methoxide ion-independent pathway has a rate that is comparable to the methoxide-dependent pathway when the latter's concentration is included: k_{cluster1} (3.5×10^{-13} min^{-1}·psi$^{-1.7}$) is comparable to $k_{\text{cluster2}}[\text{MeO}^-] = (2.3 \times 10^{-10}\ \text{min}^{-1}\cdot\text{psi}^{-1.7}\cdot\text{M}^{-1})(1 \times 10^{-3}\ \text{M}) = 2.3 \times 10^{-13}\ \text{min}^{-1}\cdot\text{psi}^{-1.7}$), making it plausible that a slight shift in the mechanism occurs that alters the dependency on the concentration of MeO$^-$.

Finally we comment on the observations as a function of main group element. The activation energy for the E = S compound is considerably lower than that for E = Se or Te (S, 43 ± 11 kJ (E = S), vs Se, 76 ± 8 kJ, and Te, 72 ± 7 kJ). The preexponential factor is also significantly different. For S, the value is 3.5×10^3, while the values for Se and Te are much more comparable at 2.6×10^7 and 1.1×10^7, respectively. Thus, while the E = S compound has a lower activation energy, it also has a less favorable preexponential constant, making its rate fall between that of Se and Te under the conditions employed. These dramatic differences suggest a fundamental difference between

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the lighter S atom-containing compound and the heavier Se- and Te-containing species. Considering the chemistry of the clusters themselves, we would expect it to be much more difficult to open the metal−metal bonds for the lightest element. The open complex $[Te\{Fe(CO)_4\}_3]^{2-}$ is easily isolated and converted to the closed compound under mild heating.[29] The corresponding open selenium compound is observable but difficult to isolate because it spontaneously closes to the tetrahedral structure at room temperature, and the open sulfur analogue has not been observed. We would, therefore, expect the sulfur compound to be the least favorable catalyst for a mechanism where metal−metal bond breaking was the key step. The fact that the activation parameter for the sulfur compound is considerably lower suggests a different mechanism for that cluster, probably one in which the slow step is not the cluster-opening process. Since the overall rate law appears the same for all three chalcogens, our postulate is that the mechanistic steps are similar but that the rate-determining process is slightly different, most probably being the direct attack of methoxide on the E = S cluster followed by metal−metal bond opening upon the addition of CO, as opposed to prior addition of CO followed by methoxide ion attack. We note also one other example where the chemistry of the E = S compound differs notably from that of the E = Se and Te species. Alkylation of the dianionic clusters $[\mathbf{I}]^{2-}$ results in attachment of the alkyl group to the chalcogen atom in the case of sulfur but to the metal framework in the case of selenium and tellurium. This charge redistribution in the cluster compound brought about by the smaller, more highly electronegative character of the sulfur atom coupled with the greater availability of the s-electrons for bonding may well be the origin of the less favorable preexponential factor.

Conclusions

The cluster compounds $[Et_4N]_2[\mathbf{I}]$ serve as catalysts that selectively and homogeneously carbonylate methanol to methyl formate. While the mechanism of the reaction is clearly complex and some details cannot be ascertained, the rate of the reaction appears to depend on three pathways: the rate due to methoxide ion catalysis, the rate due cluster catalysis that is dependent on P_{CO} and methoxide, and the rate due to cluster catalysis that is dependent upon CO concentration but independent of methoxide ion concentration. The rate is first-order with respect to cluster concentration and quasi-second order with respect to CO pressure. At $[CH_3O^-]_{total}$ less than approximately 3×10^{-3} M, the reaction is independent of methoxide ion concentration, but at higher concentrations it shows first-order dependence on $[CH_3O]^-_{total}$. These results can be explained in terms of the catalytically active species being an intact cluster that has added CO with the concomitant breakage of one or more M−M bonds.

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Supporting Information Available: Details of the kinetics data found in Figures 1−7 and Table 1, Schemes 1S and 2S showing alternate mechanisms, various derivations of kinetic rate laws based upon different catalytically active species, and a graph showing the temperature and pressure dependence on the solubility of CO in methanol. This information is available free of charge via the Internet at http://pubs.acs.org.

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