in isolating the unstable *cis*-$[PtCl_2(HL^1)_2]$ is clearly the result of the unusual synthetic approaches provided by the ready protonation–deprotonation equilibrium associated with the presence of the fluorinated alcohol function in the molecule.

Conclusions. This study has significantly extended the range of known platinum(II) complexes of P–O hybrid ligands to include a phosphino alcohol in both monodentate and bidentate modes of coordination. We have shown the value of a soft phosphine ligand in stabilizing the Pt–O bond, and we have again demonstrated that steric, electronic, and kinetic factors may all be significant in determining the geometry of a platinum(II) complex formed in any particular situation.

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Supplementary Material Available: For the structure determinations of compounds **2** and **5**, tables of hydrogen atom positional parameters (Table S-I), anisotropic thermal parameters (Tables S-II and S-III), supplementary bond distances and angles (Tables S-VI and S-VII), and weighted least-squares planes (Tables S-IX and S-X), and for **2**, a table of selected torsion angles (Table S-VIII) (10 pages); tables of calculated and observed structure factors (Tables S-IV and S-V) (51 pages). Ordering information is given on any current masthead page.

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Nucleophilic Activation of Carbon Monoxide. 4. Dihydrogen Reduction of the Methoxycarbonyl Adduct $Ru_3(CO)_{11}(CO_2CH_3)^-$

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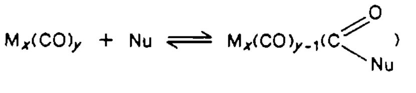
The anionic triruthenium cluster $Ru_3(CO)_{11}(CO_2CH_3)^-$ reacts with dihydrogen in dry THF to give methyl formate plus the hydride cluster $HRu_3(CO)_{11}^-$. Use of D_2 instead leads to the formation of DCO_2CH_3 plus $DRu_3(CO)_{11}^-$ as shown by ^2H NMR. The rate of the hydrogenation is demonstrated to be first order in $[H_2]$ but inhibited by CO. These observations are interpreted in terms of a mechanism by which the principal pathway for reduction of the cluster involves the reversible dissociation of coordinated CO followed by rate-limiting H_2 addition to the unsaturated intermediate. Details of the synthesis and spectroscopic properties of the $Ru_3(CO)_{11}(CO_2CH_3)^-$ anion are also described.

Introduction

Investigations in this laboratory have been concerned with the activation of coordinated carbon monoxide by oxygen nucleophiles such as hydroxide or methoxide ion.[3,4] Such reactions with OH^- are key to CO activation in mechanisms for homogeneous catalysis of the water gas shift reaction in alkaline solution,[5–8] while CH_3O^- activation is involved in certain methoxide cocatalyzed processes such as the carbonylation of methanol[9] and the reductive carbonylation of nitroarenes.[10] Methoxycarbonyl adducts, such as $M_x(CO)_{y-1}(CO_2CH_3)^-$, are likely intermediates in the latter catalysis cycles, while other adducts (e.g., eq 1) are proposed to be the labilized species in nucleophile-catalyzed CO exchange and other substitution reactions of metal carbonyl complexes.[11] However, few such adducts have been subjected to direct kinetics investigation.


$$M_x(CO)_y + Nu \rightleftharpoons M_x(CO)_{y-1}(C(=O)Nu) \quad (1)$$

In this context, we have undertaken a quantitative investigation of certain reactions of the triruthenium methoxycarbonyl anion $Ru_3(CO)_{11}(CO_2CH_3)^-$ (I), which can be prepared via the reaction of methoxide salts with the neutral cluster $Ru_3(CO)_{12}$.[3,4a] In previous reports[3] from this laboratory, it was shown that I is dramatically activated toward ligand substitution reactions relative to $Ru_3(CO)_{12}$ and that this enhanced lability apparently also leads to a markedly greater reactivity toward dihydrogen:[3]

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

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

A similar reaction of the mononuclear (ethoxycarbonyl)cobalt carbonyl species $Co(CO)_4(CO_2C_2H_5)$ (to give ethyl formate plus $Co_2(CO)_8$) has also been reported and investigated mechanistically by Ungváry and Markó.[12] In that case the parent carbonyl would be the unstable cation $Co(CO)_5^+$.

Described here is a kinetics investigation of the reaction of $Ru_3(CO)_{11}(CO_2CH_3)^-$ with dihydrogen. Also summarized are the details of the synthesis procedure and spectroscopic properties of this anionic cluster, parts of which have been described earlier.

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Experimental Section

All manipulations were conducted under dry dinitrogen or CO using Schlenk techniques. Solvents were dried by using standard methods[13] and distilled under N_2. The parent cluster $Ru_3(CO)_{12}$ was prepared by literature procedures.[14] Methanolic solutions of $NaOCH_3$ were prepared by the addition of small amounts of sodium metal to freshly distilled methanol. The solutions were freeze–pump–thaw degassed and stored under N_2. Tetrabutylammonium methoxide was prepared from $[NBu_4]OH$ (1.0 M in methanol, Aldrich) as described.[4] The methoxide solutions were standardized by titration against oxalic acid using phenolphthalein as the indicator. Bis(triphenylphosphoranylidene)ammonium chloride ([PPN]Cl) was placed in vacuo at 100 °C for 3 h to remove traces of water.

The PPN^+ salt of I was prepared from $Ru_3(CO)_{12}$ as follows. Equimolar amounts of $Na[OCH_3]$ (2.0 M in CH_3OH, 0.15 mmol) and dry [PPN]Cl, dissolved in the minimum volume of anhydrous methanol (about 2 mL), were successively added to a stirring solution of $Ru_3(CO)_{12}$ (50 mg, 0.078 mmol) in CO-saturated tetrahydrofuran (THF, 12.5 mL). The bright red solution was then syringed dropwise (over a period of 30 min) to stirred, CO-saturated hexanes (about 100 mL) cooled to −78 °C. The resulting orange solid was collected by filtration under CO. This product was subsequently dissolved in a minimum amount of CO-saturated THF, passed through a fine glass frit to remove the insoluble NaCl impurity, and then recrystallized by slow addition of the filtrate solution to hexanes at −78 °C. The yields for this reaction approached 90%. Anal. Calcd for $[PPN][Ru_3(CO)_{11}(CO_2CH_3)]$ ($C_{43}H_{39}O_{13}NP_2Ru_3$): C, 48.67; H, 2.73; N, 1.16; P, 5.13. Found: C, 48.56; H, 2.79; N, 1.18; P, 5.23.

Electronic spectra were recorded on a Cary 118 spectrophotometer, infrared spectra on Perkin-Elmer 683 and Digilab FTS 60 spectrometers, and ^1H and ^{13}C NMR spectra on a Nicolet 300-MHz NMR spectrometer operating in the pulsed FT mode with deuterium lock. The ^2H NMR spectra were recorded in THF without lock. Some NMR spectra were obtained by using the 500-MHz instrument of the NSF Regional NMR Facility at the California Institute of Technology.

Kinetics studies were carried out using $Ru_3(CO)_{11}(CO_2CH_3)^-$ solutions prepared in situ by the addition of concentrated $[NBu_4][OCH_3]$ or $Na[OCH_3]$ solutions in methanol to THF solutions of $Ru_3(CO)_{12}$ (1.3×10^{-4} M). A stock solution of $Ru_3(CO)_{12}$ (5 mL) under H_2 was syringed into UV/vis cells with a gas reservoir filled with the appropriate gas and the solution was thermally equilibrated (10 min). The dihydrogen partial pressures for different runs were varied by the use of manometer techniques. A Schlenk-fitted quartz cuvette was used for total pressures less than 1.0 atm, but a thick-walled glass cell was used for pressures greater than 1.0 atm. The reaction was then initiated by adding the methoxide solution (25 μL, 0.112 M) by microliter syringe, and the resulting optical density changes were followed at 460 nm by using a Cary 118 spectrophotometer fitted with a thermostated cell compartment. The dependence of the reaction rates on the partial pressure of CO was determined by using a similar technique. In a quartz cuvette attached to a glass reservoir of 139.3 mL total volume, a THF solution of $Ru_3(CO)_{12}$ was equilibrated with a gas mixture consisting of 1.0 atm of H_2 to which various volumes of CO (0.33–20 mL) were added via a gastight syringe. With this technique, partial pressures of CO over the range 0.0025–0.15 atm were achieved.

Results and Discussion

Properties of $Ru_3(CO)_{11}(CO_2CH_3)^-$. The electronic spectrum of this anion in methanol solution has previously been described.[4] In the presence of excess $Na[OCH_3]$, I displays two absorption bands, a maximum at 460 nm ($\epsilon = 4.0 \times 10^3$ M^{-1} cm^{-1}) and a shoulder at 370 nm ($\epsilon = 5.8 \times 10^3$ M^{-1} cm^{-1}). In 90/10 THF/CH_3OH solution, only a small excess of methoxide is required to give an equivalent spectrum, in agreement with the larger equilibrium constant for formation of $Ru_3(CO)_{11}(CO_2CH_3)^-$ in the less polar solvent.[4]

Solutions of the $[PPN][Ru_3(CO)_{11}(CO_2CH_3)]$ salt in CO-saturated THF displayed infrared bands at 2014 s (sometimes split into two equally intense bands at 2017 and 2010 cm^{-1}), 1995 s, 1962 m, and 1637 m cm^{-1}. The first three bands can be attributed to terminal carbonyls but occur at frequencies lower than those for the terminal CO's of $Ru_3(CO)_{12}$ owing to the negative charge on I. The fourth band is attributed to the $CO_2CH_3^-$ group. Notably, the Na^+ salt of I prepared in situ by the addition of $Na[OCH_3]$ to $Ru_3(CO)_{12}$ (about 0.005 M) in CO-saturated THF shows a slightly different spectrum with ν_{CO}'s at 2017 s, 1995 s, 1966 m, and 1596 m cm^{-1}. The lower frequency of the band for the $-CO_2CH_3$ functionality as well as the slightly higher frequencies of the terminal CO stretches can be attributed to intimate ion pairing between Na^+ and the CO_2CH_3 group drawing charge from the cluster. (Such ion pairing was not seen under the dilute conditions used for the kinetics studies.) A similar phenomenon has been described for the mononuclear $M(CO)_4CO_2CH_3^-$ anions (M = Fe, Ru or Os)[3] as well as other metal carbonyl anions.[15] (It is notable that some of the frequencies listed above are slightly different than those reported from this laboratory previously.[4a] These differences can possibly be attributed to the use of a different IR spectrometer or, more likely, to the fact that the carbonyl frequencies of the methoxycarbonyl adduct are sensitive to small perturbations of the solvent medium.)

When the $[PNN][Ru_3(CO)_{11}(CO_2CH_3)]$ salt was dissolved in THF under 1.5 atm of ^{13}CO (99% ^{13}C), exchange of coordinated and free CO was rapid as would be expected from the proposed dissociative mechanism for the ligand substitution reactions of $Ru_3(CO)_{11}(CO_2CH_3)^-$.[3] Exchange at room temperature was complete within minutes as monitored by the IR spectra. The formation of the methoxycarbonyl adduct is undoubtedly responsible for the methoxide catalysis of CO exchange between $Ru_3(CO)_{12}$ and free CO as described previously.[12e] The spectrum of the ^{13}CO-exchanged cluster showed the expected shifts of the ν_{CO} bands to lower frequencies, displaying bands at 1960 s, 1951 s, 1920 m, and 1600 m cm^{-1}.

The ^1H NMR spectrum (300 MHz) of $[PPN][Ru_3(CO)_{11}(CO_2CH_3)]$ in CD_2Cl_2 displayed a singlet at 3.36 ppm and a multiplet at 7.5 ppm with relative integrated areas of 1:10. These can be assigned to methoxycarbonyl methyl hydrogens (3) and the PPN^+ phenyl hydrogens (30), respectively.

The room-temperature ^{13}C NMR spectrum of ^{13}CO 99% enriched $[PPN][Ru_3(CO)_{11}(CO_2CH_3)]$ (3.2×10^{-2} M) in THF-d_8 recorded under a 50 kPa excess pressure of ^{13}CO, displayed a very broad, weak resonance centered at $\delta_C = 185.3$ and two sharp singlets at 207.9 and 188.9 ppm, the latter two in an approximate intensity ratio 22:1. At −95 °C, the low-temperature limit of the 300-MHz instrument, the spectrum consists of two sharp peaks of roughly equal intensity at δ_C 185.3 and 189.0 and a much stronger, broad resonance at 208.1 ppm. These spectral properties are in qualitative agreement with those reported for the $Ru_3(CO)_{11}(CO_2CH_3)^-$ ion prepared and studied in situ in 2/1 THF/CH_3OH (v/v) by Darensbourg et al.[12e] These spectra can be interpreted[12e] in terms of the absorption at 185.3 ppm being the carbon of free CO, the peak at 189 ppm being the carbon of the methoxycarbonyl group, and the much more intense peak at 208.1 ppm being the remaining carbonyls of the cluster. This implies that site exchange among the 11 terminal CO's remains rapid even at −95 °C. The same result was obtained when the ^{13}C spectrum was recorded on the Caltech 500-MHz (125.7 MHz for ^{13}C) instrument at −105 °C. For comparison, it is notable that the ^{13}C NMR spectrum of $Ru_3(CO)_{12}$ in THF is also a singlet at −100 °C, implying similar low-temperature fluxionality,[16] while the ^{13}C NMR spectrum of the hydride ion $HRu_3(CO)_{11}^-$ in methanol-d_4 gives a singlet at room temperature but a structured spectrum at −85 °C.[8,17] The increased intensity for the resonance of the dissolved free carbon monoxide at the lower temperature is probably the result of a decreased rate of exchange between free CO and CO coordinated to this very labile cluster. (Free CO is observable as a sharp signal at 185.0 ppm at room temperature

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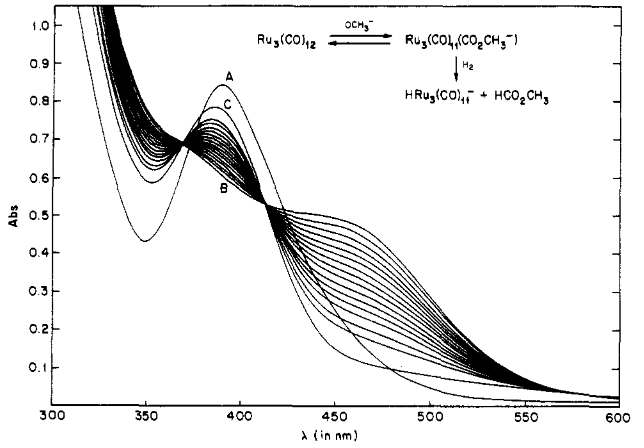

Figure 1. Temporal absorbance changes resulting from the reaction of H_2 with $Ru_3(CO)_{11}(CO_2CH_3)^-$ *in THF. Spectrum A is that of* $Ru_3(CO)_{12}$ in THF under H_2. Spectrum B is that of the methoxycarbonyl adduct immediately after adding $[NBu_4][CH_3O]$. Spectrum C is that of $HRu_3(CO)_{11}^-$ after 2-h reaction.

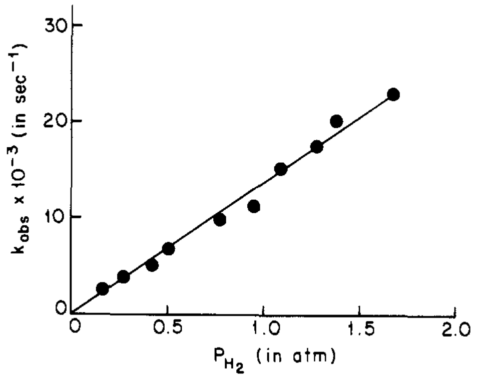

Figure 2. Plot of k_{obsd} vs. P_{H_2} for the reactions of methoxycarbonyl cluster anions with H_2 in THF. $Ru_3(CO)_{11}(CO_2CH_3)^- + H_2 \rightarrow HRu_3(CO)_{11}^- + HCO_2CH_3$.

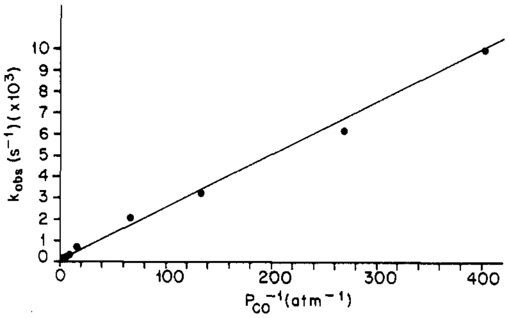

Figure 3. Plot of k_{obsd} vs. $(P_{CO})^{-1}$ for reaction of $Ru_3(CO)_{11}(CO_2CH_3)^-$ with H_2 (1.0 atm) in THF (25 °C).

under analogous conditions in the absence of the cluster.)

Reaction with Dihydrogen. THF solutions of $Ru_3(CO)_{12}$ (1.1×10^{-4} M) under CO display a strong absorption band in the electronic spectrum centered at 390 nm ($\epsilon = 7.9 \times 10^3$ M^{-1} cm^{-1}) and a minimum at 350 nm ($\epsilon = 4.0 \times 10^3$ M^{-1} cm^{-1}). The identical spectrum was observed under a H_2/Co atmosphere, and no spectral changes occurred over an extended period. However, when a 2-fold excess of $[NBu_4][OCH_3]$ was added to THF solutions of $Ru_3(CO)_{12}$, the bright yellow solution immediately turned red and new absorption bands appeared at 460 nm ($\epsilon = 4.0 \times 10^3$ M^{-1} cm^{-1}) and 360 nm ($\epsilon = 5.8 \times 10^3$ M^{-1} cm^{-1}), indicating formation of $Ru_3(CO)_{11}(CO_2CH_3)^-$. Under CO the spectrum did not change further, but under H_2 or H_2/CO atmospheres, there was a slow decrease in the 460-nm band and the growth of a new one at 386 nm (Figure 1). Throughout the reaction with H_2, isosbestic points at 575, 413, and 369 nm were maintained; thus no intermediates of detectable concentrations were observable.

The product spectrum in Figure 1 displayed λ_{max} at 387 nm, consistent with the formation of $HRu_3(CO)_{11}^-$ in >95% yield according to expected optical density changes.[13] This product was also confirmed by infrared and ^1H NMR spectral changes. A THF solution of $[NBu_4][Ru_3(CO)_{11}(CO_2CH_3)]$ (prepared in situ from 0.002 M $Ru_3(CO)_{12}$ plus 0.004 M $[NBu_4][OCH_3]$) displayed ν_{CO} bands at 2010 s, 1990 s, 1962 m, 1637 w, and 1596 w cm^{-1}. When H_2 was bubbled through this solution, these disappeared and new bands at 2064 w, 2006 s, 1983 s, and 1962 m cm^{-1} characteristic of $[HRu_3(CO)_{11}^-]$ appeared. A strong band at 1712 cm^{-1}, assigned to the carbonyl stretch of methyl formate, also appeared. (The ν_{CO} expected at 1725 cm^{-1} for the bridging carbonyl of $HRu_3(CO)_{11}^-$ was apparently obscured by the much stronger band due to methyl formate under these conditions.)

For the NMR experiment, the reaction of $[NBu_4][Ru_3(CO)_{11}(CO_2CH_3)]$ (0.013 M) with H_2 was carried out in THF-d_8 solution. After the mixture was bubbled with H_2 new resonances appeared at δ −12.67, 3.74 and 8.05 ppm, which can be assigned to the hydride of $HRu_3(CO)_{11}^-$ plus the methyl and formyl hydrogens of HCO_2CH_3, respectively. Traces of methanol as evidenced by the methyl hydrogens at δ 3.40 were also observed. The analogous reaction of D_2 plus $Ru_3(CO)_{11}(CO_2CH_3)^-$ in THF gave resonances at −12.5 ppm ($DRu_3(CO)_{11}^-$) and 8.02 ppm (DCO_2CH_3) in the ^2H NMR spectrum. Stoichiometries under conditions where the H_2 was introduced by bubbling through the solution (as determined from the integrated ^1H intensities) gave less than a one-to-one methyl formate to ruthenium hydride ratio; however, this discrepancy can be attributed to the high volatility of the methyl formate (bp 31.5 °C). When the reaction of $[PPN][Ru_3(CO)_{11}(CO_2CH_3)]$ with H_2 was instead investigated in situ in a closed system (in this case, using CD_2Cl_2 as solvent and a 5-mm NMR tube fitted with a Young valve), the resonances at −12.67, 3.74, and 8.05 ppm appeared with the integrated ratios 1.0:3.0:∼1, the integration of the formyl hydrogen being somewhat perturbed by the close resonances of the PPN^+ hydrogens. Thus, the stoichiometry of eq 3 is confirmed. However, in each case, a small amount of methanol was detected in the product mixtures as evidenced by a resonance at 3.40 ppm. A probable explanation for this is hydrolysis of the methoxycarbonyl adduct by traces of water in the system.

A brief ^1H NMR investigation of the reaction of $[PPN][Ru_3(CO)_{11}(CO_2CH_3)]$ in THF-d_8 with H_2 was carried out over the range −80 to +10 °C. Over this temperature range, the reaction was quite slow and no intermediates or other interactions between the substrates were detected. Above 10 °C, reaction to form products was relatively rapid on the time scale of the NMR data collection and again no intermediates were observed.

Kinetics Studies. The reactions of I with excess H_2 were followed on a Cary 118 spectrophotometer. Plots of ln $(A - A_\infty)$ are linear, indicating a first-order dependence on $Ru_3(CO)_{11}(CO_2CH_3)^-$ concentration. A plot of the resulting k_{obsd} values vs. P_{H_2} is linear with a slope of 0.014 s^{-1} atm^{-1} over the range 0.17–1.7 atm (Figure 2). Thus, one may conclude that the rate of this reaction is first order with respect to P_{H_2}. The reaction of I with D_2 proved to be slower than that with H_2, an observation which suggests that the dihydrogen in some form is directly involved in the rate-limiting step. When the reaction was carried out under a dihydrogen pressure of 0.79 atm, the measured k_{obsd} value was 0.0098 s^{-1} for H_2 and 0.0071 s^{-1} for D_2. The ratio gives a kinetic isotope effect k_H/k_D of 1.4.

Kinetics runs carried out under a pure H_2 atmosphere showed some long term deviations in the reaction end points, presumably owing to further reaction of $HRu_3(CO)_{11}^-$ with H_2 to give $H_3Ru_4(CO)_{12}^-$.[8,18] However, reactions carried out under H_2/CO mixtures gave stable end points consistent with the formation of $HRu_3(CO)_{11}^-$ as the only ruthenium product. Given that the reaction solutions of $Ru_3(CO)_{11}(CO_2CH_3)^-$ prepared in situ

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contained excess [NBu$_4$][OCH$_3$] or Na[OCH$_3$], the effect of the methoxide concentration was examined briefly, but no rate differences were noted over the 3-fold range, $(0.4-1.2) \times 10^{-3}$ M.[19]

The P_{CO} dependence of the reaction rate was determined for sets of runs using a fixed P_{H_2} (1.0 atm) but CO partial pressures ranging from 0.0025 to 0.15 atm. The reaction is dramatically suppressed by CO, and the plot of k_{obsd} vs. P_{CO}^{-1} was linear with a zero intercept (within experimental uncertainty) (Figure 3). Thus, the kinetics for the reaction of I with H_2 follow the rate equation

$$-\frac{d[I]}{dt} = k_H[Ru_3(CO)_{11}(CO_2CH_3)^-](P_{H_2})(P_{CO})^{-1} \quad (4)$$

Equation 4 would be consistent with the following mechanistic scheme:

$$Ru_3(CO)_{11}(CO_2CH_3)^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Ru_3(CO)_{10}(CO_2CH_3)^- + CO \quad (5)$$

$$Ru_3(CO)_{10}(CO_2CH_3)^- + H_2 \xrightarrow{k_6} HRu_3(CO)_{11}^- + HCO_2CH_3 \quad (6)$$

This is a mechanism involving reversible dissociation of CO from I to give an unsaturated (or solvento) intermediate A followed by a rate-limiting reaction with H_2. Such a mechanism would display the rate law

$$-\frac{d[I]}{dt} = \frac{k_5k_6[H_2][I]}{k_{-5}[CO] + k_6[H_2]} \quad (7)$$

For the condition where $k_{-5}[CO] > k_6[H_2]$, this simplifies to

$$-\frac{d[I]}{dt} = \frac{k_5k_6[H_2][I]}{k_{-5}[CO]} \quad (8)$$

consistent with the behavior described by eq 4. On the other hand, if $k_6[H_2] >> k_{-5}[CO]$, then k_{obsd} should simplify to $k_5[I]$; i.e., the rate should be independent of P_{H_2}. Such limiting behavior was not observed even in the absence of added CO; thus, the magnitude of k_{-5} may be such that CO labilized in eq 5 is sufficient to prevent this type of limiting behavior. While there have been no direct measurements of the reactivities of unsaturated cluster anions such as A with CO or similar ligands, the reaction of CO with $Ru_3(CO)_{11}$ produced by flash photolysis in THF has an estimated limiting rate constant of $>10^3$ s^{-1}.[20] The first-order limiting rate behavior apparently reflects the dissociation of THF from $Ru_3(CO)_{11}(THF)$; the methoxide adduct of this species should be much more labile.

According to the above scheme, the ultimately limiting rate would be that of CO dissociation from I. Previous investigations of the reactions of I with $P(OCH_3)_3$ (eq 2) concluded that k_5 has a value of 5.8 s^{-1} (25 °C) in 90/10 THF/CH$_3$OH[3] and 4.0 ± 0.2 s^{-1} (25 °C) in THF.[1] In contrast, the first-order rate constant k_{obsd} for $HRu_3(CO)_{11}^-$ formation (eq 3) under the highest P_{H_2} investigated (1.7 atm) was 2.3×10^{-2} s^{-1}, several orders of magnitude below the above limit.

If eq 8 were valid, the k_{obsd} values plotted in Figure 3 would equal $k_5k_6[H_2]/k_{-5}[CO]$. The slope of the plot is $(2.5 \pm 0.1) \times 10^{-5}$ atm s^{-1}, which can be translated to $(2.1 \pm 0.1) \times 10^{-7}$ L mol^{-1} s^{-1} by taking into account the estimated solubility of CO is THF (8.4×10^{-3} mol L^{-1} atm^{-1} at 25 °C).[21] The concentration of H_2 under these conditions (P_{H_2} = 1.0 atm) would be 6.0×10^{-3} given an estimated solubility of H_2 in THF;[21] accordingly, the rate constant ratio k_5k_6/k_{-5} would be 3.5×10^{-5} s^{-1}. Given the value of 4.0 s^{-1} determined for k_5 (above),[3] the ratio $k_6/k_{-5} = 8.8 \times 10^{-6}$ can be calculated. This ratio represents the competitive reactivities of H_2 (k_6) and CO (k_{-5}) for the proported unsaturated intermediate $Ru_3(CO)_{10}(CO_2CH_3)^-$ and indicates that A is more than 5 orders of magnitude more reactive toward CO to re-form I than it is toward H_2 to give $HRu_3(CO)_{11}^-$. For comparison, the tricoordinate 14-electron intermediate $RhCl(PPh_3)_2$ in benzene has been shown to be only 700 times as reactive toward CO than toward H_2; the less reactive tetracoordinate species $RhCl(PPh_3)_3$ displays a reactivity ratio of about 4×10^4.[22]

The failure to detect measurable concentrations of intermediates along the reaction coordinate of eq 6 restricts interpretation of the detailed mechanism of this complicated transformation. However, a logical sequence would be for dihydrogen to add to the dissociated intermediate $Ru_3(CO)_{10}(CO_2CH_3)^-$ or its solvento analogue to give a dihydride species $H_2Ru_3(CO)_{10}(CO_2CH_3)^-$ (C), perhaps via the equilibrium precoordination of dihydrogen to give $(H_2)Ru_3(CO)_{10}(CO_2CH_3)^-$ (B) followed by H–H bond cleavage (e.g., eq 9). The dihydride C may then undergo rapid reductive elimination of HCO_2CH_3 to give $HRu_3(CO)_{10}^-$, which subsequently would scavenge CO to give $HRu_3(CO)_{11}^-$. The kinetic isotope effect $k_H/k_D = 1.4$ is consistent with the values noted for various oxidative additions of dihydrogen[23] and indicates that the transition state of eq 6 probably involves partial breaking of the dihydrogen single bond. This plus the observation of the first-order dependence on P_{H_2} would indicate that the hypothetical dihydrogen species B could only be formed in small equilibrium concentrations under these conditions (i.e. $K_s[H_2] << 1$), so that $k_6 = K_sk_{oa}[H_2]$. If so, the low reactivity of H_2 relative to CO may be attributed either to a small value of K_s or of k_{oa}.

$$Ru_3(CO)_{10}(CO_2CH_3)^- + H_2 \overset{K_s}{\rightleftharpoons} (H_2)Ru_3(CO)_{10}(CO_2CH_3)^- \xrightarrow{k_{oa}} H_2Ru_3(CO)_{10}(CO_2CH_3)^- \quad (9)$$

The results of the present studies on the triruthenium system show a strong similarity with those observed for the reaction of the mononuclear cobalt analogue $Co(CO)_4(CO_2C_2H_5)$ with dihydrogen in hydrocarbon solutions of Unvâry and Markó.[12] The rate of the latter reaction also proved first order in P_{H_2} and inversely proportional to P_{CO}, and reversible CO dissociation to form the unsaturated intermediate $Co(CO)_3(CO_2C_2H_5)$ was proposed as the first step. Although the CO dissociation rate constant (0.0017 s^{-1}) was found to be much smaller than that for I, the overall reactivity with H_2 under H_2/CO mixtures was comparable given that the back-reaction of the unsaturated cobalt intermediate with CO proved to be only 150 times as fast as the reaction of this species with H_2. Two other features of the cobalt ethoxycarbonyl complex should also be noted. Unlike the ruthenium complex, there was no kinetic isotope effect when D_2 was used instead of H_2. Also, $Co(CO)_4(CO_2C_2H_5)$ was reduced about 1 order of magnitude more rapidly by the hydride $HCo(CO)_4$ than by H_2. Attempts in this laboratory to carry out an analogous reaction of I with the ruthenium hydride $HRu(CO)_4^-$ gave no reaction in THF at ambient temperature, the electrostatic repulsion of the two anions probably reducing the reactivity.

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[19] It is notable that IR spectra of the $Ru_3(CO)_{11}(CO_2CH_3)^-$ adduct at higher concentrations of Na[OCH$_3$] in THF displayed weak bands indicating the presence of low concentrations of another species, namely the proposed diadduct $Ru_3(CO)_{10}(CO_2CH_3)_2^{2-}$.[4c] The independence of the hydrogenation rates to methoxide concentration indicates that this species did not have particular kinetics significance under the conditions investigated.

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[21] (a) Solubilities in the THF of H_2 and CO are estimated to be 0.0034 and 0.0084 mol L^{-1} atm^{-1}, respectively, according to solution theory[21b] and published parameters.[21c] (b) Prausnitz, J. M. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1969; Chapter 8. (c) *Encyclopedia of Chemical Technology*, 3rd ed.; Wiley: New York, 1978; Vol. 21, p 377. (d) **Note added in proof**: A recent measurement by Shore and co-workers indicates the CO solubility in THF to be about 4-fold higher than the above estimate (Payne, M. W.; Leussing, D. L.; Shore, S. G., submitted for publication; private communication from S. Shore). This would increase the calculated k_6/k_{-5} ratio by the same factor to about 4×10^{-5} but does not change the conclusion that the dissociated intermediate A is dramatically more reactive with CO than with H_2.

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In summary, the key feature of these studies is that the $Ru_3(CO)_{11}(CO_2CH_3)^-$ anion is dramatically activated toward reduction by H_2 relative to the neutral parent $Ru_3(CO)_{12}$. Although kinetics studies have not been reported for the H_2 reduction of the latter cluster, this reaction is generally accomplished under conditions such as refluxing octane (bp 125 °C),[24] the ruthenium product being the tetranuclear tetrahydride $H_4Ru_4(CO)_{12}$. The likely reason for this activation toward H_2 is the markedly greater lability of the anionic cluster toward ligand substitution reactions in comparison to that of the relatively inert parent cluster. The similarity of these results to those for the mononuclear cobalt complexes suggests some generality to this aspect of nucleophilic activation of metal carbonyl complexes.

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Photochemical Formation of Mononuclear Bis- and Tris(ethylene) Complexes from Irradiation of Iron Pentacarbonyl or Triruthenium Dodecacarbonyl: Species Involved in Catalytic Alkene Isomerization

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In alkane or $CF_3C_6F_{11}$ solutions that contain excess C_2H_4, near-UV irradiation of $Ru(CO)_4(C_2H_4)$, formed quantitatively in situ from visible light ($\lambda > 420$ nm) irradiation of $Ru_3(CO)_{12}$, yields $Ru(CO)_3(C_2H_4)_2$ at 298 K. At temperatures below 253 K further substitution can be effected photochemically to give *trans*-$Ru(CO)_2(C_2H_4)_3$. Near-UV irradiation of $Ru(CO)_4(C_2H_4)$ in rigid, C_2H_4-saturated, 3-methylpentane glasses at 90 K yields $Ru(CO)_3(C_2H_4)_2$, but further CO loss to give *cis*-$Ru(CO)_2(C_2H_4)_3$ is observed after only ~5% consumption of $Ru(CO)_4(C_2H_4)$. Isomerization of photogenerated *cis*-$Ru(CO)_2(C_2H_4)_3$ to *trans*-$Ru(CO)_2(C_2H_4)_3$ is only observed on warming the glass above 210 K. Prolonged irradiation of photogenerated *cis*-$Ru(CO)_2(C_2H_4)_3$ at 90 K yields loss of additional CO to give a monocarbonyl complex, formulated as $Ru(CO)(C_2H_4)_4$, which reacts on warming with photoreleased CO to initially regenerate *cis*-$Ru(CO)_2(C_2H_4)_3$. The photochemistry of $Fe(CO)_4(C_2H_4)$ is the same as that of the $Ru(CO)_4(C_2H_4)$ except that *trans*-$Fe(CO)_2(C_2H_4)_3$ could only be detected by IR spectroscopy at temperatures below 210 K. The new results show that species previously formulated as $Fe_2(CO)_6(\text{alkene})_2$ are in fact $Fe(CO)_3(\text{alkene})_2$. In solution, $M(CO)_3(C_2H_4)_2$ (M = Fe, Ru) and $Ru(CO)_2(C_2H_4)_3$ are substitutionally labile and may serve as versatile reagents in preparative chemistry. Addition of deoxygenated 1-pentene to solutions of the bis- and tris(ethylene) complexes results in rapid catalytic isomerization at 293 K to a mixture of 2-pentenes, thus establishing the viability of both $M(CO)_3$ and $M(CO)_2$ species as repeating units in the catalytic alkene isomerization. Deactivation of $M(CO)_3(\text{alkene})_2$ as a 1-pentene isomerization catalyst, in the absence of excess CO, proceeds, at least in part, by dehydrogenation of 1-pentene to form the stable, catalytically inactive (at 298 K) $M(CO)_3(\eta^4\text{-}1,3\text{-pentadiene})$ complexes.

Research in this group and elsewhere has established that an extraordinarily active alkene isomerization catalyst results from photolysis of $Fe(CO)_5$ in the presence of alkenes.[1-3] A carbonyl-bridged diiron complex[4] and, alternatively, a mononuclear tricarbonyl iron unit[1b,3] have been proposed to carry the catalytic cycle. A report from this group[5] establishes that iron carbonyl intermediates in the photocatalytic systems could be observed spectroscopically at subambient temperatures, including $HFe(CO)_3(\eta^3\text{-}C_3H_5)$ from photolysis of $Fe(CO)_4(C_3H_6)$ in a rigid alkane glass at 77 K. In neat 1-pentene, warmup of photogenerated $HFe(CO)_3(\eta^3\text{-}C_5H_9)$ (from $Fe(CO)_5$/1-pentene at 77 K) result in significant catalytic isomerization of 1-pentene above 243 K in the dark. Eventual regeneration of $Fe(CO)_4(\text{alkene})$ is accompanied by decline of catalytic activity. $Fe(CO)_3(\eta^3\text{-allyl})$ radical species, also detected at 143 K in 1-3% yield as photoproducts of $Fe(CO)_5$ and olefins, have been implicated in catalytic reactions of olefins.[6]

New findings reported here reveal the nature of the dominant species resulting from near-UV irradiation of $Fe(CO)_5$/alkene solutions. Species previously formulated as $Fe_2(CO)_6(\text{alkene})_2$[5] are in fact mononuclear $Fe(CO)_3(\text{alkene})_2$ complexes, consistent with a report by Fleckner, Grevels, and Hess.[7] Other important mononuclear Fe species are reported herein including *di*- and monocarbonyl complexes. We have also extended the low-temperature photochemistry to $Ru(CO)_4(\text{alkene})$ systems and find that mononuclear bis- and tris(ethylene) complexes can be generated photochemically via sequential photochemical reactions represented by eq 1-3 for the case of alkene = C_2H_4. Photochemistry according to eq 1 is known[8-10] and provides an excellent

$$Ru_3(CO)_{12} + 3C_2H_4 \xrightarrow[\text{alkane, 298 K}]{h\nu\ (\lambda > 420\ \text{nm})} 3Ru(CO)_4(C_2H_4) \quad (1)$$

$$Ru(CO)_4(C_2H_4) + C_2H_4 \xrightarrow[\text{alkane, 298 K}]{h\nu\ (\lambda < 400\ \text{nm})} Ru(CO)_3(C_2H_4)_2 + CO \quad (2)$$

$$Ru(CO)_3(C_2H_4)_2 + C_2H_4 \xrightarrow[\text{alkane, 243 K}]{h\nu\ (\lambda < 400\ \text{nm})} trans\text{-}Ru(CO)_2(C_2H_4)_3 + CO \quad (3)$$

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