Table III. Free-Energy Functions in J mol^{-1} K^{-1} and Heat-Content Functions in kJ mol^{-1} for $Mo_2(g)^a$

T, K	$-(G^\circ_T - H^\circ_{298})/T$	$H^\circ_T - H^\circ_{298}$
298.15	247.98	0.00
2400	292.67	78.24
2500	294.01	81.98
2600	295.30	85.72
2700	296.54	89.46
2800	297.75	93.20
2900	298.92	96.94
3000	300.06	100.68

^{a} $H^\circ_{298} - H^\circ_0 = 9.73$ kJ mol^{-1}.

in the bond energies of Cr_2 and Mo_2 is, however, surprising, especially since their optical spectra suggest that the electronic configurations and bonding interactions in Cr_2 and Mo_2 are similar.[3] Moreover, the three known dissociation energies, $D(V_2)$, $D(Cr_2)$, and $D(Mo_2)$, are in nonconformity with the trend indicated by MO calculations[3] that $D(Mo_2) > D(Cr_2) > D(Nb_2) > D(V_2)$. It is clear that an experimental determination of the dissociation energy of Nb_2 is needed in order to gain insight into the bonding properties of these diatomic molecules.

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Registry No. Mo^+, 16727-12-1; Mo_2^+, 67891-04-7; Mo_2, 12596-54-2; Mo, 7439-98-7.

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Contribution from the Department of Chemical Engineering,
University of Waterloo, Waterloo, Ontario, Canada

Hydrogen Reduction of μ_3-Oxo-triruthenium(III) Acetate in Dimethylformamide

S. A. FOUDA, B. C. Y. HUI, and G. L. REMPEL*

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μ_3-Oxo-triruthenium(III) acetate exists in dimethylformamide as a weakly dissociated 1:1 electrolyte, $[Ru_3O(OCOCH_3)_6(DMF)_3][OCOCH_3]$, with $K_{diss} = 8 \times 10^{-4}$ M at 30 °C. $[Ru_3O(OCOCH_3)_6(DMF)_3][OCOCH_3]$ undergoes three sequential reduction reactions with molecular hydrogen in DMF at 80 °C. The first reduction reaction involves consumption of 1 mol of hydrogen/mol of oxotriruthenium(III) acetate and results in the formation of 1 mol of an intermediate ruthenium hydride and 1 mol of acetic acid. A detailed mechanistic study for this first stage of reduction indicates that a monohydridic triruthenium species, $[HRu_3O(OCOCH_3)_5(DMF)_3][OCOCH_3]$, is formed via a heterolytic splitting of hydrogen by $[Ru_3O(OCOCH_3)_6(DMF)_3][OCOCH_3]$. The monohydride species undergoes a subsequent intramolecular reduction to produce the species $[Ru_3O(OCOCH_3)_4(DMF)_n][OCOCH_3]$ and an additional mole of acetic acid per mole of intramolecular reduction product. This intramolecular reduction product activates hydrogen in the second reduction reaction which involved consumption of 2 mol of H_2/mol of $[Ru_3O(OCOCH_3)_4(DMF)_n][OCOCH_3]$ and results in the production of an additional 2 mol of acetic acid and dimeric ruthenium(I) species. The activation appears to involve the formation of a three-centered intermediate between molecular hydrogen and one of the ruthenium centers of $[Ru_3O(OCOCH_3)_4(DMF)_n][OCOCH_3]$. This three-centered species gives rise to a heterolytic splitting of hydrogen. The consumption of the second mole of hydrogen during the second stage of reduction occurs rapidly and results in the formation of ruthenium(I) products. Decarbonylation of DMF occurs during the second stage of reduction and/or isolation of the solid ruthenium(I) products. The dimeric ruthenium(I) species are isolated from the DMF solution as a mixture of $Ru_2(OCOCH_3)_2(CO)_4L_2$ ($L = P(C_6H_5)_3$, $P(C_6H_5)_2(C_2H_5)$, $Sb(C_6H_5)_3$, C_5H_5N) and the novel compound $Ru_2(OCOCH_3)_2(HOCOCH_3)(CH_3OH)$. The DMF solution containing the dimeric ruthenium(I) species is found to undergo further reaction with hydrogen. The final products of the overall reaction are isolated as a mixture of $Ru_2(OCOCH_3)_2(CO)_4L_2$ and the polymeric hydridoruthenium carbonyl $[HRu(CO)_3]_n$.

Introduction

Although the chemistry of oxotriruthenium(III) acetate, $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$, in aqueous and methanolic media has been extensively investigated,[1-3] no information on its behavior or reduction chemistry in dimethylformamide has previously been reported. Previous investigations[1-3] indicate that trimeric complexes resulting from the hydrogen or electrochemical reduction of $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$ in water or methanol were not active as hydrogenation catalysts. Since $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$, when treated with H_2 in dimethylformamide, has been found to be effective in providing homogeneous catalysts for a variety of unsaturated substrates,[4] we have carried out a detailed study of its solution chemistry and hydrogen reduction in dimethylformamide. The objective of this study was primarily aimed at gaining further insight into the nature of oxotriruthenium acetate and the hydrogenation catalysts or catalyst precursors in DMF.

Experimental Section

Ruthenium trichloride trihydrate was obtained from Engelhard Industries Ltd. Reagent grade chemicals and solvents were used throughout. Dimethylformamide was purified by storing over CaH_2 under N_2 for at least 40 h followed by distillation under reduced pressure; the constant-boiling fraction was collected onto Linde 4A

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Table I. Hydrogen Reduction of μ_3-Oxo-triruthenium Acetate in Dimethylformamide: Summary of Kinetic Data for the First and Second Stages of Reduction

$10^3[Ru_3]$, M	$10^3[H_2]$, M	T, °C	$10^4 k_1'$, s^{-1}	$10^4 k_2'$, s^{-1}
7.68	2.75	80	1.25	0.80
10.18	2.75	80	1.38	1.02
10.18	2.75	80	1.75	
13.36	2.75	80	1.50	1.00
13.36[a]	2.75	80	1.35	0.99
13.36[b]	2.75	80	1.12	
13.36[c]	2.75	80	0.52	
13.73	2.75	80	1.70	
18.40	2.75	80	1.63	0.92
21.49	2.75	80	1.58	
24.49	2.75	80	1.59	
25.93	2.75	80	1.40	0.80
31.40	2.75	80	1.50	0.80
13.36	2.15	80	1.20	0.70
13.36	1.32	80	0.67	0.37
13.36	0.92	80	0.49	0.28
13.36	2.78	85	1.65	1.60
6.36	2.71	76	1.10	0.75
13.36	2.69	74	0.90	0.60
13.36	2.55	64	0.42	0.22
13.36[d]	2.75	80	0.94	0.78
13.36[e]	2.75	80		[f]

[a] $LiOCOCH_3$ (0.003 M) was added. [b] 0.013 M $HOOCCH_3$ was added. [c] 0.60 M $HOOCCH_3$ was added. [d] D_2 was used in place of H_2. [e] 0.026 M $HClO_4$ was added. [f] Very slow reaction.

molecular sieve and stored under Linde ultrahigh-purity nitrogen. Linde ultrahigh-purity hydrogen was passed through an Engelhard Deoxo Purifier before use.

UV–visible spectra were recorded on a Beckman DK2; IR on a Perkin-Elmer 337. NMR were obtained on a Varian HR100 spectrometer as well as a Bruker 60-MHz Spectrospin. ESR measurements were obtained on a Varian V-4502-19 spectrometer. GLC analysis was carried out using a Hewlett-Packard F & M Scientific 700 laboratory chromatograph. A 12 ft column of Union Carbide 10% UC-W98 at 90 °C was used for analysis of isomerized olefins. Emf measurements as well as potentiometric titrations were carried out using a Radiometer pH meter, Model 26, and an oxygen-free thermostated cell equipped with glass and calomel electrodes. Conductometric measurements were carried out in the complete absence of air using a Yellow-Springs Model Y51-31 conductivity bridge and a thermostated conductivity cell (cell constant = 0.1).

Hydrogen stoichiometry and kinetic measurements were made by following the consumption of hydrogen at constant pressure using the apparatus and procedure described earlier.[5] The solubility of H_2 in dimethylformamide was determined as 2.75×10^{-3} M at a total pressure of 760 mmHg and at 80 °C, Henry's law being obeyed up to at least 1 atm. The solubility of H_2 was also determined over the temperature range of 64–85 °C (see Table I).

Air-sensitive compounds and solutions were handled inside a Dri-Lab glovebox equipped with a Dri-Train, both obtained from Vacuum Atmospheres Co. Elemental analyses and molecular weight measurements were by Galbraith Laboratories, Inc., Knoxville, Tenn. Mass spectra were by the Brock University Mass Spectrometry Laboratory on a AEI MS-30 mass spectrometer.

μ_3-Oxo-triruthenium Acetate. $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$ was prepared from commercially available ruthenium trichloride trihydrate according to a procedure based on that given by Wilkinson and co-workers.[1] Thus, 4 g of "$RuCl_3{\cdot}3H_2O$" together with 7 g of sodium acetate trihydrate was dissolved in a mixture of 75 mL of glacial acetic acid and 75 mL of ethanol. The solution was refluxed under nitrogen for approximately 2 h, during which time the initial reddish brown color of the solution changed to dark green. The solution was cooled to −30 °C and decanted to separate precipitated sodium chloride and sodium acetate. The decanted solution was then filtered and the filtrate was taken to dryness. The solid thus obtained is the crude oxotriruthenium(III) acetate complex. The purification procedure described by Wilkinson and co-workers,[1] namely, the recrystallization of the crude complex from a methanol–acetone mixture, resulted in very low yields of the pure compound. In the present work the purification of the complex was accomplished as follows: The resulting crude acetate complex was dissolved in a minimum amount of ethanol and cooled to −30 °C overnight. Excess sodium acetate and sodium chloride precipitated and were separated by filtration. The filtrate was taken to dryness and the solid was washed with benzene to remove excess acetic acid. Several extractions with ethanol (ca. four to six) were performed until no more precipitate was apparent on filtration. This final filtrate was taken to dryness, and after a final benzene wash, the product was dried in vacuo over sodium hydroxide pellets at 60 °C overnight. The yield was 3.2 g (80% on the basis of Ru content of $RuCl_3{\cdot}3H_2O$). Anal. Calcd for $C_{14}H_{27}O_{18}Ru_3$: C, 21.30; H, 3.44; Cl, 0.00. Found: C, 20.97; H, 3.36; Cl, 0.00. The electronic spectra and infrared spectra agreed with those reported previously.[1]

A. Second-Stage Hydrogen Reduction Products of μ_3-Oxo-triruthenium Acetate. One gram of $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$ was dissolved in ca. 75 mL of H_2-degassed DMF. The solution was heated under a reflux condenser at 80 °C under an atmosphere of H_2 for ca. 10 h at which time the solution was dark brown and the visible absorption spectra of the solution corresponded to that obtained when the molar H_2 consumption to initial oxotriruthenium acetate was 3:1. The solvent was completely removed under vacuum at 70 °C. An extremely air-sensitive dark brown residue was obtained, ca. 300 mg of which was completely insoluble in oxygen-free methanol.

B. Di-μ-acetato-tetracarbonyldiruthenium Adducts. The methanol-soluble brown residue described in A was made up to 25 mL with oxygen-free methanol and then filtered into a methanol solution containing L (=$P(C_6H_5)_3$, $P(C_6H_5)_2(C_2H_5)$, $Sb(C_6H_5)_3$, $P(C_6H_5O)_3$, or (C_5H_5N)). The crystalline materials which separated were washed with oxygen-free methanol, dried, recrystallized from benzene, and dried at 25 °C under vacuum. All of these products provided satisfactory analyses for the respective $[Ru(OCOCH_3)CO_2L]_2$ adducts.

C. $Ru_2(OCOCH_3)_2(HOCOCH_3)(CH_3OH)$. The methanol-insoluble residue of A was recrystallized from a minimum of DMF at room temperature. On cooling of the mixture to ca. −30 °C, brown microcrystals separated. The recrystallized material was dried under vacuum at 25 °C for 24 h. Anal. Calcd for $Ru_2C_7H_{14}O_7$: C, 20.39; H, 3.42; Ru, 49.03. Found: C, 20.84 (23.13); H, 2.77 (3.90); Ru, 49.27 (48.94).

Results and Discussion

Solution Chemistry of $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$. When aqueous solutions of $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$ were treated with the anionic exchange resin Dowex 1-X8 (Cl^- form) in the presence of sufficient KOH to raise the pH value of the solution to 10.5, the green oxotriruthenium species present in solution was readily absorbed. This result was in accord with the report[1] that ionization of two of the terminally coordinated water molecules to form an anionic oxotriruthenium species occurs when the pH is greater than 9. In neat DMF, however, treatment with the anionic exchange resin resulted in no detectable absorption of the oxotriruthenium species in 24 h at room temperature. Thus it was concluded that no anionic form of the complex existed in neat DMF solutions. However, when DMF solutions of the complex were treated with the cationic exchange resin Dowex 50 W-X8 (Na^+ form), a slow absorption did occur. Treatment of an aqueous solution of the complex with the cationic resin, in the presence of sufficient acid to drop the pH value of the solution to 2, resulted in ready absorption of the complex, again in accord with the report[1] that at pH <2 the formation of a cationic oxotriruthenium species is favored. These results indicate that oxotriruthenium acetate in DMF is present in both cationic (i.e., dissociated) and neutral (i.e., undissociated) form.

The conductivity of oxotriruthenium acetate in DMF and in deionized water was measured at 30 °C over a small range of concentration (0.08–0.30 mM). Kohlrausch plots for the results obtained are shown in Figure 1. For 0.1 mM $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$, the molar conductivity of the complex was estimated as 44 and 199 $ohm^{-1}\ cm^2\ mol^{-1}$ in DMF and deionized water, respectively. Strong 1:1 electrolytes in DMF exhibit molar conductivities in the range of 70–100 $ohm^{-1}\ cm^2\ mol^{-1}$ at this concentration level.[6,7] A

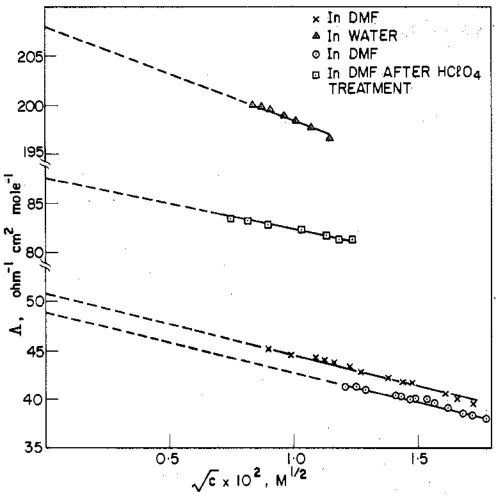

Figure 1. Kholrausch plots for μ_3-oxo-triruthenium(III) acetate at 30 °C.

solution of oxotriruthenium acetate in DMF was treated with $HClO_4$ (mole ratio of $HClO_4$ to complex was 0.7:1) at 80 °C for about 7 h to obtain essentially the perchlorate salt of the oxotriruthenium acetate complex. Substoichiometric concentration of the acid was used to eliminate protonation of an acetate bridge. Emf measurements on the solution after 7 h indicated that the free protons from the added $HClO_4$ were consumed (i.e., acetic acid formed is essentially undissociated in neat DMF[8]). The molar conductivity of the solution containing primarily the perchlorate salt of the oxotriruthenium species (see Figure 1) was found to be 82 ohm^{-1} cm^2 mol^{-1} at 0.1 mM. This value is close to those normally found for strong 1:1 electrolytes in DMF.[7] These conductivity measurements for the oxotriruthenium acetate complex suggest that the complex exhibits ionic character but is not fully dissociated in DMF and that the equilibrium given by eq 1 (L = H_2O or DMF) is present in DMF.

$$[Ru_3O(OCOCH_3)_6L_3][OCOCH_3] \rightleftarrows [Ru_3O(OCOCH_3)_6L_3]^+ + OCOCH_3^- \quad (1)$$

The above mentioned conductivity measurements were carried out primarily for the purposes of obtaining values at a given concentration for comparative purposes. Only a relatively small concentration range was covered and high accuracy in determining the slopes of the Kohlraush lines or the limiting conductances shown in Figure 1 is by no means claimed. Nevertheless, an attempt was made to use these data to estimate the approximate value of the dissociation constant of the oxotriruthenium acetate complex in DMF as defined by eq 1. Since the slope of the Kohlrausch plot was found to be more negative than the theoretical slope of the Onsager equation, the method of Shedlovsky[9] was used to estimate the dissociation constant. The value thus obtained was 8 × 10^{-4} M at 30 °C.

In view of the coordinating power of DMF, it is expected that the terminal water molecules of the initial $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$ complex would be displaced by DMF when the complex is placed in neat DMF solution. It appears that the displacement of the terminal water ligands by DMF is a fast process. The water molecules coordinated to the oxotriruthenium complex were removed by heating the solid complex for 12 h at 105 °C under vacuum; the IR spectra of the resulting solid showed no bands in the 3500-cm^{-1} region, thus indicating the removal of coordinated water from the complex. The visible spectrum of a DMF solution of this water free complex, however, was identical with that obtained immediately after dissolution of the solid aquated oxotriruthenium acetate complex in DMF (i.e., λ, nm (ϵ_{Ru_3}): 720 (3750), 630 (3600), 420 sh (5000)). Further evidence for displaced water molecules was obtained from the low-field NMR spectra of $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$ in DMF-d_7 which showed a resonance at τ 5.2.

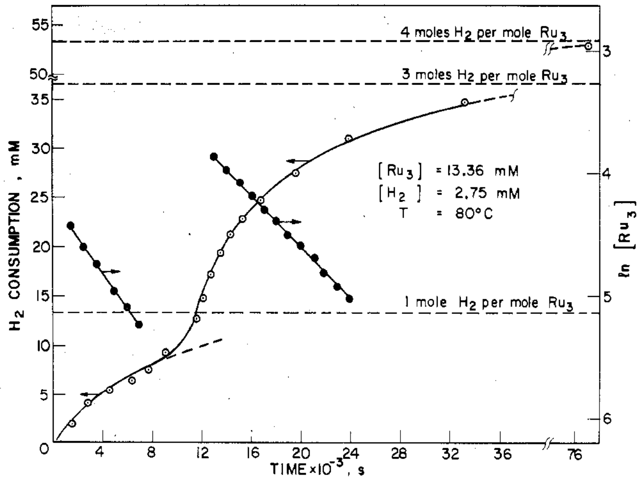

Figure 2. Representative hydrogen consumption plot for the H_2 reduction of oxotriruthenium(III) acetate in DMF.

Interaction of $[Ru_3O(OCOCH_3)_6(DMF)_3][OCOCH_3]$ with Molecular Hydrogen in DMF. Solutions of $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$ in DMF were found to undergo reaction with hydrogen at atmospheric pressure and 80 °C. A representative hydrogen consumption plot is shown in Figure 2. Such uptake plots obtained indicate essentially three rather distinct stages of reaction. The first stage corresponds to almost 1 mol of the initial oxotriruthenium acetate compound, the second stage corresponds to an additional 2 mol of hydrogen consumption, and the third stage was found to involve close to 1-mol consumption. Figure 2 also shows that both the first and second stages of the reduction reaction have a hydrogen uptake plot that follows a first-order dependence on Ru_3 concentration. Data points at the end of the first stage and those at the start of the second stage were not used in kinetic analyses, since in these regions there is a considerable overlap of one stage with the other.

First Stage of Hydrogen Reduction. The effect of the reagent variables and temperature on the slopes of ln $[Ru_3]$ vs. time plots (i.e., k_1' values) for the first stage of hydrogen reduction was studied. The pseudo-first-order rate constant k_1' is defined by eq 2. In Table I a summary of the kinetic

$$-d[Ru_3]/dt = k_1'[Ru_3] \quad (2)$$

results is given. Table I shows that the pseudo-first-order rate constants at different $[Ru_3]$ agree within ±11.5%. When the hydrogen concentration was varied from 0.92 to 2.75 mM, a first-order dependence of the rate on the hydrogen concentration was observed.

The kinetic data presented above are in accord with the rate law

$$\frac{-d[Ru_3]}{dt} = \frac{-d[H_2]}{dt} = k_1[H_2][Ru_3] = k_1'[Ru_3] \quad (3)$$

From Table I, the average value obtained for k_1' at 80 °C is 1.31 × 10^{-4} s^{-1} which gives a value for the second-order rate constant k_1 of 4.75 × 10^{-2} M^{-1} s^{-1} at 80 °C. k_1 can also be obtained from the slope of the line obtained from a plot of k_1' vs. $[H_2]$. The computed k_1 from the least-squares fitting of this plot is 5.32 × 10^{-2} M^{-1} s^{-1} which is in fair agreement with the value obtained from the average k_1' values.

Measurements on the temperature dependence of k_1', defined by eq 1 over the range 64–85 °C (see Table I), yielded a good Arrhenius rate plot. The activation parameters for the first stage of hydrogen reduction are $\Delta H^* = 15.0 \pm 1.2$ kcal mol^{-1} and $\Delta S^* = -22.3 \pm 3.4$ eu.

When the reaction was stopped at the end of the first stage (the reaction was run at a temperature of 65 °C in order to suppress the contribution of the second stage), the solution had a brownish coloration. The electronic absorption spectra of the solution at this stage of reaction exhibited λ_{max} (ϵ) of 400 sh (2800), 760 sh (2000), and 920 nm (2350). At this stage the solution was extremely sensitive to air and a number of attempts at the isolation of products, even in the complete absence of air, proved unsuccessful. Addition of triphenylphosphine (molar ratio of $P(C_6H_5)_3:Ru_3 = 3:1$), under nitrogen atmosphere, to the first stage solution resulted in formation of $Ru_3O(OCOCH_3)_6(P(C_6H_5)_3)_3$. However, it is known that oxotriruthenium acetate complexes having ruthenium oxidation states of III or II yield the complex $[Ru_3O(OCOMe)_6(PPh_3)_3]$ on the addition of triphenylphosphine.[1] In the present case, a conversion of the product of the first stage of reduction to the above mentioned complex probably occurred on the addition of triphenylphosphine.

When the product solutions of the first stage of hydrogen reduction were titrated with sodium methoxide in benzene–ethanol, the formation of 1 equiv of acid/equiv of the starting oxotriruthenium compound was indicated. Consequently, 1 mol of acetic acid results from each mole of hydrogen consumed during the first stage and suggests the formation of a monohydridic ruthenium product as shown in eq 4.

$$[Ru_3O(OCOCH_3)_6(DMF)_3][OCOCH_3] + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [HRu_3O(OCOCH_3)_5(DMF)_3][OCOCH_3] + HOCOCH_3 \quad (4)$$

High-field NMR measurements of DMF solutions of the first-stage solution provided no signals which could be assigned to a metal hydride. Although fully deuterated DMF (i.e., $(CD_3)_2NCOD$) solutions of the first-stage ruthenium species also did not show any high-field NMR signals, examination of the low-field region showed, in addition to resonances at τ 8.1 and 5.2 which were assigned to the protons of the acetate groups and displaced water molecules, respectively, a definite signal at τ 2.0 which is due to the formation of $(CD_3)_2NCOH$ via exchange of $(CD_3)_2NCOD$ with the metal hydride. The solvent DMF has a signal at ca. τ 2.0 which is assigned to the hydrogen bonded to the carbonyl group.[10] No exchange of the metal hydride with the deuterated methyl groups of the DMF-d_7 was apparent. Failure to detect the metal hydride in the high-field NMR is not unexpected, as the species $[HRu_3O(OCOCH_3)_5(DMF)_3][OCOCH_3]$ is formally a Ru^{III}_3 complex, the unpaired spins of which would prevent observation of any hydride. In this complex the hydride is likely to be a bridging ligand. The cleavage of a bridging carboxylate ligand between rhodium nuclei with the formation of a hydride bridge has previously been reported.[11]

Solution infrared spectra were noninformative since complete compensation for DMF bands, which are strong in the region in which a metal hydride frequency would be expected, could not be achieved.

Further evidence for the formation of a hydride species during the first stage of reduction was obtained from experiments in which the addition of protons (i.e., $HClO_4$) in the absence of air caused re-formation of the starting oxotriruthenium(III) complex and quantitative evolution of hydrogen as shown in eq 5.

$$[HRu_3O(OCOCH_3)_5(DMF)_3][OCOCH_3] + HClO_4 \rightarrow [Ru_3O(OCOCH_3)_6(DMF)_3][ClO_4] + H_2 \quad (5)$$

The cleavage of metal hydride bonds by reaction with dissociated acids is well documented.[12] Such reactions with acid usually result in complete displacement of the hydride ligand by the anion of the acid or by another complexing agent present in solution. For example, the hydridochlororuthenium(II) carbonyl complex, $HRuCl(CO)(Me_2PPh)_3$, reacts with nitric acid in ethanol as shown in reaction 6.[13]

$$HRuCl(CO)((CH_3)_2P(C_6H_5))_3 + HNO_3 \rightarrow RuCl(NO_3)(CO)((CH_3)_2P(C_6H_5))_3 + H_2 \quad (6)$$

In the present system, the oxotriruthenium(III) complex probably re-forms via the nonbridging acetate becoming a bridging ligand and the perchlorate species functioning as the anion for the oxotriruthenium species. Addition of perchloric acid to the initial oxotriruthenium(III) acetate compound results in formation of $[Ru_3O(OCOCH_3)_6(DMF)_3][ClO_4]$ as does such addition for the analogous oxotrirhodium(III) acetate.[14]

The above results suggest that the mechanism for the first stage of hydrogen reduction involves a heterolytic splitting of hydrogen as indicated in eq 4. The initial step in reaction 4 likely involves substitution of a terminal DMF molecule by hydrogen in order for the activation of the hydrogen molecule to occur at a metal center. Displacement of a DMF molecule is necessary since the metal centers exist in octahedral environments with the axial positions (i.e., positions trans to the central oxygen) being available for ligand substitution. Aquo, pyridine, and triphenylphosphine adducts of this complex have previously been isolated.[1]

Complete coordination of the hydrogen molecule to form an intermediate ruthenium(V) dihydride prior to splitting of the hydrogen molecule as shown in reaction 7 cannot be ruled out.

$$Ru^{III} + H_2 \rightleftarrows [Ru^{V}H_2] \rightleftarrows Ru^{III}H^- + H^+ \quad (7)$$

However, besides requiring a high valency state for the ruthenium atom, a seven-coordinate species would have to be postulated. A ruthenium(V) dihydride species was previously suggested in the hydrogen reduction of ruthenium(III) chloride species in dimethyl sulfoxide,[15] although the postulation of a seven-coordinate species was not necessary.

The relatively high dielectric constant and the basic nature of DMF could assist in polarization of the hydrogen molecule by the ruthenium center in order to bring about an overall heterolytic splitting of hydrogen as shown in reaction 4. Heterolytic splitting of hydrogen by Ru(III) has previously been demonstrated in both aqueous acid and dimethylacetamide solutions.[16,17] The heterolytic splitting mechanism has been regarded as involving a four-center transition state in which the released proton is stabilized by the coincident release of a coordinated basic ligand.[18] Thus, in the present system this transition state is obtained by polarization of hydrogen by a Ru(III) center such that the positive end of the hydrogen molecule interacts with a bridging acetate ligand, giving rise to the formation of acetic acid and Ru(III)–H^- bond formation.

A deuterium isotope effect of $k_H/k_D = 1.52$ was observed for the first-stage reduction process. Isotope effects of unity are almost invariably obtained for systems that definitely involve dihydride formation or oxidative addition to square-planar d^8 systems.[19] Small isotope effects observed in systems involving a direct heterolytic splitting of hydrogen may be rationalized in terms of metal–hydride bond formation and hydrogen–hydrogen bond breaking occurring in a concerted process. In the present case the value obtained for the isotope effect suggests that the H–H bond breaking could be of some importance in the rate-determining step.[20]

The value of the molar conductance of the first-stage solution (57 ohm^{-1} cm^2 mol^{-1} for $[Ru_3] = 0.1$ mM) indicates that the resultant species exhibits electrolytic properties similar to those of the starting oxotriruthenium(III) acetate. This observation provides further support for the above suggestion, that the proton resulting from the heterolytic splitting of hydrogen is accepted by bridging acetate ligand. If the nonbridging acetate group were to accept the released proton, a neutral species (i.e., $HRu_3O(OCOCH_3)_6(DMF)_2$) with six bridging acetates would be formed which would not be consistent with the observed molar conductance.

The product of the first stage reduction was also found to catalyze the isomerization of dec-1-ene to a mixture of *cis*- and *trans*-dec-2-ene in the absence of hydrogen. When a DMF solution of the hydride, which was 7.68 mM in Ru_3, was mixed with dec-1-ene (0.3 M) and kept at 75 °C under N_2 for 30 min, 40% of the dec-1-ene was converted to a mixture of the *cis*- and *trans*-dec-2-ene (3:1 ratio respectively). Double-bond isomerization in the absence of hydrogen is generally regarded as good evidence for the presence of a metal hydride complex. Although not all transition-metal hydrides are active as isomerization catalysts, a metal hydride appears to be necessary for olefin isomerization to take place in the absence of hydrogen.[21]

Although there seems to be little doubt that the species $[HRu_3O(OCOCH_3)_5(DMF)_3][OCOCH_3]$ is the initial reduction product for the first stage of hydrogen reduction, this species decays with time under nitrogen or hydrogen. The species which results from this decay process is stable to the presence of perchloric acid. Titration of acetic acid of first-stage solutions in which the new species is believed to be appreciably formed results in close to 2 mol of acetic acid/mol of trimeric ruthenium complex being indicated. Thus, a decay process as shown in eq 8 follows the initial hydrogen consumption of reaction 4.

$$[HRu_3O(OCOCH_3)_5(DMF)_3][OCOCH_3] \xrightarrow{k_1} [Ru_3O(OCOCH_3)_4(DMF)_n][OCOCH_3] + HOCOCH_3 \quad (8)$$

The molar conductance for a 0.1 mM solution of the nonhydridic ruthenium product had a value of 73 $ohm^{-1}\ cm^2\ mol^{-1}$ indicating that the acetate involved in acetic acid formation originates from an acetate bridge as shown in eq 8. It is also of interest to note here that the nonhydridic decay product resulting from reaction 8 does not catalyze the isomerization of olefins in the absence of hydrogen.

Precedents for the capability of ruthenium hydrides to reduce other ruthenium species has been demonstrated in the case of ruthenium–chloro complexes in dimethylacetamide[17] as shown in reactions 9 and 10. If such a process were to

$$Ru^{III}H^- + Ru(III) \rightarrow 2Ru(II) + H^+ \quad (9)$$

$$Ru^{II}H^- + Ru(II) \rightarrow 2Ru(I) + H^+ \quad (10)$$

occur intramolecularly, as in the present triruthenium reduction, the product of reaction 8 is best described as a ruthenium species with an average oxidation state of 7/3 for each Ru center.

On the basis of the kinetics observed for the first mole of hydrogen consumption by oxotriruthenium(III) acetate and the products of the reaction, a mechanism comprised of reactions 4 and 8, respectively, is presented for the first stage of hydrogen reduction.

In the absence of added acid, the k_{-1} path of reaction 4 is not significant since acetic acid is a very weak acid in DMF (pK_a = 11.2 at 25 °C).[22] Experiments carried out in the presence of perchloric acid or relatively high concentrations of added acetic acid (see Table I) substantiate the k_{-1} step. The occurrence of the k_1 path of reaction 8 does not require the presence of hydrogen. Consequently, the kinetics obtained from hydrogen consumption measurements are for the heterolytic splitting of hydrogen as defined by the k_1 path of reaction 4. This mechanism predicts a first-order dependence on $[H_2]$ and on the initial $[Ru_3]$ as found experimentally.

The second-order rate constant k_1 at 80 °C was found to have a value of $5.04 \times 10^{-2}\ M^{-1}\ s^{-1}$; $\Delta H^* = 15.0 \pm 1.2$ kcal mol^{-1}; $\Delta S^* = -22.3 \pm 3.4$ eu. The hydrogen reduction of chlororuthenium(III) complexes in dimethylacetamide[17] was reported to have $\Delta H^* = 15.5 \pm 1.5$ kcal/mol^{-1} and $\Delta S^* = -16.4 \pm 3.0$ eu. In this case a heterolytic splitting of hydrogen by a ruthenium(III) complex was also established. The negative entropy of activation is in agreement with the general observations for reactions involving the consumption of neutral entities and the production of ionic species.[23]

Second Stage of Hydrogen Reduction. The computation procedure followed in the analysis of the kinetic data of the first stage of reduction was also followed in the analysis of the kinetic data for the second stage. In Table I a summary of the kinetic data obtained for this stage is provided. The slopes of ln $[Ru_3]$ vs. time plots (k_2' values) are given as a function of the different variables in the system. The fairly constant value obtained for k_2' (i.e., ±14.6% for $[Ru_3]$ of 7.68–31.4 mM at constant $[H_2]$ and temperature) confirms the first-order dependence of the reaction rate on $[Ru_3]$ over this range (see Table I). A straight line obtained for a plot of k_2' vs. $[H_2]$ indicates a first-order dependence on $[H_2]$ for the second reduction stage. Thus, the rate law that governs the second stage of reduction is

$$\frac{-d[Ru_3]}{dt} = -\frac{1}{2}\frac{d[H_2]}{dt} = k_2[H_2][Ru_3] = k_2'[Ru_3] \quad (11)$$

The second stage of the hydrogen reduction was complete when the hydrogen consumption was equivalent to 3 mol of hydrogen/mol of oxotriruthenium acetate. At this point the solution was dark brown. The solution was extremely air sensitive becoming greenish on exposure to air. The visible absorption spectrum of this greenish solution indicated that the original $[Ru_3O(OCOCH_3)_6(DMF)_3][OCOCH_3]$ complex cannot be restored on simply treating the second-stage reduction product with oxygen. ESR spectra run on such solutions gave no signals for paramagnetic ruthenium species. These spectral results together with the hydrogen consumption strongly suggested that the solution contained a dimeric ruthenium(I) entity or entities.

In an attempt to obtain solid products, the solutions at the end of the second stage of reduction were carefully concentrated, protected from air, and cooled to <−30 °C; this yielded no solid products. Addition of oxygen-free benzene to such solutions followed by cooling also did not cause any solid precipitation. This method has been previously used to obtain a solid ruthenium(I) product from the hydrogen reduction of "$RuCl_3 \cdot 3H_2O$" in dimethylacetamide.[24]

The addition of donor ligands such as phosphines, amines, and various chelating ligands to the DMF solution at the end of the second stage, followed by cooling to <−30 °C, also failed to result in compound precipitation. Since no simple method could be found to precipitate the suggested dimeric ruthenium(I) complex from solution, the solution was carefully taken to dryness by applying vacuum and heat (ca. 70 °C). A dark brown solid residue was obtained which was very sensitive to oxygen. Consequently, all manipulations with the solid were carried out with oxygen-free materials in a glovebox. On examination of the solubility properties of the solid, it was noticed that only part of it (containing ca. 50% of the initial ruthenium present) could be dissolved in methanol.

Although the methanol-soluble part could not be crystallized on cooling a concentrated methanol solution or by the addition of a cosolvent, addition of triphenylphosphine did yield a bright, yellow, crystalline solid which was easily recrystallized from benzene. Solids were also readily obtained on the addition of the donor ligands: ethyldiphenylphosphine, triphenylstibene, triphenyl phosphite, and pyridine. In all cases the solids can be formulated on the basis of their elemental analyses as $[Ru(OCOCH_3)(CO)_2L]_2$ where L is the added donor ligand. These compounds were also prepared by re-

Table II. Infrared Spectra of $[Ru_2(OCOCH_3)_2(HOCOCH_3)(CH_3OH)]$

band, cm^{-1}	assignments[a]
3370 s	OH str (CH_3OH and/or $HOCOCH_3$)
2950, 3020 m	CH str (CH_3OH and $OCOCH_3$)
1650 sh	OCO asym str ($HOCOCH_3$)
1550 s	OCO asym ($OCOCH_3$)[b]
1410 s	OCO sym str ($OCOCH_3$)[b]
1345	CH_3 def
1110	OH bend (CH_3OH)
1050	CH_3 rock ($OCOCH_3$)
1020	CH_3 rock (CH_3OH)
680	OCO def
620	π(CH) or π(OCO)

[a] Proposed on basis of information in ref 28 and 29. [b] Δ(asym OCO-sym OCO) = 140 cm^{-1}.

ducing $RuCl_3 \cdot 3H_2O$ in DMF with hydrogen followed by addition of sodium acetate and acetic acid under nitrogen. Workup of the brown solutions obtained in this case was as for the brown solutions obtained via hydrogen reduction of oxotriruthenium acetate in DMF. The analytical data obtained for these compounds as well as their infrared spectra indicate that these compounds are undoubtedly the dimeric ruthenium(I) carbonyl acetates which were previously prepared and characterized by Lewis et al.[25] These workers prepared these compounds via the oxidative addition of acetic acid to triruthenium dodecacarbonyl ($Ru_3(CO)_{12}$). This class of compounds can also be obtained on treating a 1-propanol solution of oxotriruthenium acetate with carbon monoxide in the presence of some acetic acid.[26] In the present synthesis, the CO groups of the carbonyl dimer probably result from decarbonylation of DMF.[27]

The methanol-insoluble part of the second-stage solid was recrystallized from a minimum of DMF on cooling to −30 °C. The recrystallized material was dried under vacuum at 25 °C for 24 h. Although this compound was found to be air sensitive, it appears to be stable when stored under nitrogen. The elemental analysis obtained for this material together with the observed hydrogen consumption is in fair agreement with the formulation $Ru_2(OCOCH_3)_2(HOCOCH_3)(CH_3OH)$. Although the analysis certainly does not enable the distinction to be made between three acetate groups per Ru_2 or two acetates and one acetic acid group per Ru_2, the latter formulation is preferred in view of the observed hydrogen consumption stoichiometry. A molecular weight of 410 was obtained for the compound in DMF. This again lends support for the above dimeric formulation which requires a molecular weight of 412. The mass spectrum of the compound showed signals at 412, 352, and 249 which could be assigned to the species $[Ru_2(OCOCH_3)_2(HOCOCH_3)(CH_3OH)]$, $[Ru_2(OCOCH_3)_2(CH_3OH)]$, and perhaps $[Ru(OCOCH_3)_2(CH_3OH)]$, respectively.

The infrared spectrum of the methanol-insoluble material showed no bands which could be attributed to a metal carbonyl, a metal hydride, or coordinated DMF. However, bands attributable to coordinated acetate are seen in the 1600–1300 cm^{-1} region. In addition a strong broad band indicative of an OH grouping is seen at about 3370 cm^{-1}. A summary of the infrared spectrum of the second-stage methanol-insoluble product together with possible band assignments is shown in Table II. The value obtained for the difference in the asymmetric and symmetric stretching modes for the OCO groups (i.e., 140 cm^{-1}) suggests that the ruthenium atoms are linked through bridging acetate groups. The shoulder observed at 1650 cm^{-1} is assigned to the asymmetric OCO stretch of a coordinated acetic acid molecule.

$Ru_2(OCOCH_3)_2(HOCOCH_3)(CH_3OH)$ is fairly soluble in DMF (a 0.23 M solution in DMF is obtainable) and a number of other solvents. For a series of solvents examined, the order of solubility provided was DMF > DMSO > $CDCl_3$ > $HOCOCH_3$ > $H_2O \simeq C_6H_6$.

High-field NMR spectra for the compound in DMF, DMF-d_7, and $CDCl_3$ showed no signals for a metal hydride.

The electronic absorption spectrum of $Ru_2(OCOCH_3)_2(HOCOCH_3)(CH_3OH)$ in DMF showed one distinct band at λ 440 nm (ϵ_{Ru_2} 1060). The molar conductance, Λ_M, of the compound in DMF at 30 °C was immeasurably low (<0.1 $ohm^{-1}\ cm^2\ mol^{-1}$ at 0.1 mM) suggesting that $Ru_2(OCOCH_3)_2(HOCOCH_3)(CH_3OH)$ is a nonelectrolyte. In the solvent dimethylacetamide, which is similar in a number of its solvent properties to DMF, nonelectrolytes have been classified as exhibiting Λ_M values below 15.[24,30]

Since the “$Ru^{III}H^{-}$” species formed in the first stage of the reduction, i.e., $[HRu_3O(OCOCH_3)_5(DMF)_3][OCOCH_3]$, undergoes an intramolecular two-electron reduction reaction to give $[Ru_3O(OCOCH_3)_4(DMF)_n][OCOCH_3]$ in a time which is relatively short at 80 °C compared to that required for the second-stage process, it appears that this latter species is the species which activates hydrogen in the second stage. Consequently, the hydrogen reduction process of the second stage can be represented by the overall reaction shown in eq 12, as defined by the observed H_2 consumption, the

$$\begin{array}{l} \mathrm{[Ru_3O(OCOCH_3)_4(DMF)_{\mathit{n}}][OCOCH_3] + 2H_2 \rightarrow} \\ \qquad\qquad \mathrm{3Ru(OCOCH_3) + H_2O + 2HOCOCH_3} \\ \qquad\qquad\qquad \downarrow \\ \qquad\qquad \mathrm{{}^3/_2\,Ru_2(OCOCH_3)_2L_{\mathit{n}}} \\ \qquad\qquad \mathrm{L = DMF,\ HOCOCH_3} \end{array} \tag{12}$$

$HOCOCH_3$ product stoichiometry, and the spectral and analytical data presented above which indicate the formation of dimeric ruthenium(I) acetate species. The species $Ru_2(OCOCH_3)_2L_n$, when in DMF, can react further via decarbonylation of DMF to yield $Ru_2(OCOCH_3)_2(CO)_4L_2$, where L is probably DMF. Further attention to this decarbonylation process will be given below.

The observed kinetics for the second-stage reduction process (i.e., first order with respect to both $[Ru_3]$ and $[H_2]$, as well as a strong inhibition by protons when $[H^+]$:$[Ru_3]$ is greater than 1 (see Table I)) suggests a rate-determining step in which heterolytic splitting of molecular hydrogen is involved. It should be noted that the addition of acetate to the reaction solution caused no rate enhancement or inhibition (see Table I), and therefore the release of a bridged acetate is favored during the heterolytic splitting of hydrogen. The possibility of the released proton being accepted by the central O^{2-} anion to yield a OH^- group remains. This cannot be ruled out on the basis of the information presently available. The hydrogen activation process could alternatively be represented by a sequence of reactions in which initial dihydride formation is postulated prior to the heterolytic splitting.

These alternatives for the hydrogen activation are kinetically indistinguishable; however, the behavior of the reactive complex $[Ru_3O(OCOCH_3)_4][OCOCH_3]$ in catalyzing the hydrogenation of olefins[4] suggests that the sequence of reactions 13 and 14 is the most likely. The value obtained for

$$\mathrm{[Ru_3O(OCOCH_3)_4][OCOCH_3] + H_2} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \mathrm{[H_2Ru_3O(OCOCH_3)_4][OCOCH_3]} \tag{13}$$

$$\mathrm{[H_2Ru_3O(OCOCH_3)_4][OCOCH_3]} \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} \mathrm{[HRu_3O(OCOCH_3)_{\mathit{x}}][OCOCH_3]_{\mathit{y}}} + \begin{array}{c} \mathrm{HOCOCH_3} \\ \downarrow\uparrow \\ \mathrm{H^+ + HOCOCH_3^-} \end{array} \tag{14}$$

$x + y = 4$; DMF ligands omitted

the isotope effect ($k_H/k_D = 1.3$) does not favor one mechanism over the other although the possibility of a hydrogen molecule being oriented as a dihydride prior to the heterolytic splitting is not necessarily inconsistent with such a value as pointed out previously.

On the basis of the mechanism represented by eq 13 and 14, the rate law shown in eq 15 is obtained when no added

$$\frac{-d[H_2]}{dt} = \frac{k_b k_a}{k_{-a} + k_b}[Ru_3][H_2] = k_2[Ru_3][H_2] \quad (15)$$

protons are present. In the absence of added protons the amount of free protons will be very small[22] and consequently the k_{-b} path is insignificant. The composite rate constant k_2 was evaluated at 3.31×10^{-2} M^{-1} s^{-1}.[31] The enthalpy of activation was evaluated as 20.9 ± 0.6 kcal/mol and the entropy of activation as −6.4 ± 1.7 eu.

Since the 2-mol hydrogen consumptions for the second-stage reduction process as defined by reaction 12 occur simultaneously, reaction 14 must be followed by processes which are rapid in the absence of added acid (e.g., reactions 16 and 17) which result in the formation of the dimeric ruthenium(I) acetate species, $Ru_2(OCOCH_3)_2L_n$.

$$[HRu_3O(OCOCH_3)_x][OCOCH_3]_y \rightarrow Ru_3O(OCOCH_3)_3 + HOCOCH_3 \quad (16)$$

$$Ru_3O(OCOCH_3)_3 + H_2 \rightarrow {}^3/_2 Ru_2(OCOCH_3)_2 + H_2O \quad (17)$$

$$x + y = 4;\ \text{DMF or HOCOCH}_3 \text{ ligands omitted}$$

The mechanism discussed above accounts for how the dimeric ruthenium(I) acetate species may be formed via hydrogen reduction of $[Ru_3O(OCOCH_3)_4(DMF)_n]^+$ in DMF. However, this ruthenium(I) species appears to undergo further reaction(s), which does (do) not consume hydrogen, to yield a carbonylated reaction product, namely, $[Ru(OCOCH_3)(CO)_2(L)]_2$. The hydrogen consumption and rate measurements do not provide much information about the mechanism of the formation of the carbonylated product. The fact that two different products are obtained at the end of the second stage of the hydrogen reduction indicates that the decarbonylation process is not fast enough for all the ruthenium(I) species to form the carbonyl product under the reaction conditions used. The formation of the carbonyl product could occur via the decarbonylation of either the solvent DMF or of the acetic acid present in solution.

Ruthenium(I) chlorides have been found to abstract CO from dimethylacetamide and from ether to give ruthenium(I) carbonyl complexes,[27] and DMF has previously been found to be a good carbonylating agent for rhodium(I) complexes.[32]

With respect to the possibility of decarbonylating the acetic acid formed during the reduction of the present study, it appears that this process, if it occurs at all, does not contribute significantly to the decarbonylation reaction. Titration of the reduction solution at this stage showed the presence of 3.8 mol of acetic acid/mol of starting compound.

It is important to note that the starting compound $[Ru_3O(OCOCH_3)_6][OCOCH_3]$ did not cause decarbonylation of DMF in the absence of hydrogen. When DMF solutions of μ_3-oxo-triruthenium acetate were refluxed overnight under nitrogen, the IR spectra of the solid, obtained upon removal of DMF and washing with benzene, did not contain any carbonyl bands.

When $(HOCOCH_3)Ru_2(OCOCH_3)_2(CH_3OH)$ was refluxed with neat DMF under N_2 overnight, the solid obtained after drying did show weak carbonyl bands in the IR spectra. Isolation of the carbonyl product as the phosphine adduct resulted in a small amount of $Ru_2(OCOCH_3)_2(CO)_4(PPh_3)_2$. Thus, it appears that the decarbonylation under the reaction conditions is much faster; this could be due to the presence of acetic acid in solution. Interactions between DMF and acetic acid have been reported.[33,34] Such an interaction between a DMF and an $HOCOCH_3$ molecule coordinated to a Ru atom may be a precursor for the carbonyl abstraction from DMF.

Table III. Products of the Hydrogen Reduction of μ_3-Oxo-triruthenium(III) Acetate in DMF at 80 °C

hydrogen consumption[a]	ruthenium product	amt of acetic acid product[b]
1	$[HRu_3O(OCOCH_3)_5(DMF)_3][OCOCH_3]$	ca. 1
	or	
	$[Ru_3O(OCOCH_3)_4(DMF)_n][OCOCH_3]$	ca. 2
3	$[Ru(OCOCH_3)(CO)_2L]_2$ and $[Ru_2(OCOCH_3)_2(HOCOCH_3)(CH_3OH)]$	ca. 4
ca. 4	$[Ru(OCOCH_3)(CO)_2L]_2$ and $[HRu(CO)_3]_n$	ca. 4

[a] mol of H_2/mol of Ru_3. [b] mol of CH_3COOH/mol of Ru_3.

Third Stage of Hydrogen Reduction. When the hydrogen uptake ceased, a total of approximately 4 mol of hydrogen/mol of oxotriruthenium acetate complex was consumed. The randomness observed in the measurement of the hydrogen consumption stoichiometry at this stage could be due to competitive reactions which may or may not consume hydrogen; the relative rates and consequently the extent of those reactions could be dependent on the ruthenium concentration.

When dimethylformamide was removed from the reaction mixture at the end of the third stage, addition of methanol again yielded two products. The methanol-soluble products could again be obtained as $[Ru(OCOCH_3)(CO)_2L]_2$ adducts. The methanol-insoluble part which was black was washed several times with methanol, and the IR spectrum was recorded over the range 4000–600 cm^{-1}. No strong bands which could be attributed to acetate groups were apparent. However, a broad band appeared at ca. 1980 cm^{-1}, and no bands were observed below 1300 cm^{-1}.

The complex was not reactive toward hydrogenation and was insoluble in common organic solvents such as benzene, ethanol, carbon tetrachloride, and chloroform. It was also insoluble in water. A ruthenium(I) complex having elemental analyses, IR spectra, and solubility properties very similar to those of the present compound was previously prepared in this laboratory on treating aqueous solutions of "$RuCl_3 \cdot 3H_2O$" with CO.[26] This compound was characterized as a polymeric ruthenium(I) carbonyl complex, $[HRu(CO)_3]_n$, and was used as a catalyst for the carbonylation of amines,[35,36] although it was not found to be reactive for the hydrogenation of olefins. The products of the reaction of μ_3-oxo-triruthenium acetate with hydrogen in DMF can be summarized as shown in Table III.

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Registry No. $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$, 38998-79-7; $[Ru_3O(OCOCH_3)_6(DMF)_3][OCOCH_3]$, 67662-44-6; $[HRu_3O(OCOCH_3)_5(DMF)_3][OCOCH_3]$, 67662-46-8; $Ru_2(OCOCH_3)_2(HOCOCH_3)(CH_3OH)$, 67662-47-9; $[Ru(OCOCH_3)(CO)_2(P(C_6H_5)_3)]_2$, 24846-24-0; $[Ru(OCOCH_3)(CO)_2(P(C_6H_5)_2(C_2H_5))]_2$, 67662-48-0; $[Ru(OCOCH_3)(CO)_2(Sb(C_6H_5)_3)]_2$, 67662-49-1; $[Ru(OCOCH_3)(CO)_2(P(C_6H_5O)_3)]_2$, 67662-50-4; $[Ru(OCOCH_3)(CO)_2(C_5H_5N)]_2$, 35397-92-3.

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Contribution from the U.E.R. de Chimie and Ecole Nationale Superieure de Chimie de Lille,
Université de Lille I, 59650 Villeneuve d'Ascq, France

Kinetics and Stereochemistry of the Reversible Nitrosylation of the *fac*-Tris(violurato)ruthenate(II) Anion. Evidence for a Unidentate Violurato Intermediate

CLAUDE BREMARD,*[1a] GUY NOWOGROCKI,[1b] and STEPHANE SUEUR[1b]

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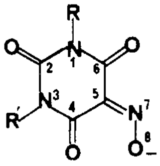
The tris(violurato)ruthenate(II) anion *fac*-$Ru(H_2vi)_3^-$ reacts with acidic solutions of nitrite salts to form a new series of mononitrosylruthenium complexes *cis*-$Ru(H_2vi)_2NOX$ (X is monodentate ligand Cl, Br, OH, or NO_2 or monodentate H_2vi). A nitrosylation mechanism of *fac*-$Ru(H_2vi)_3^-$ is proposed on the basis of kinetic and stereochemical criteria. The introduction of the nitrosonium ion NO^+ into the coordination sphere of ruthenium occurs according to a second-order rate law; however, the mechanism is thought to be dissociative. The rate-determining step is the breaking of the ring chelate, but a strongly coordinating ligand such as NO^+ must be present to prevent the ring chelate reformation. The substitution of the dangling ligand H_2vi by a Cl, Br, OH, or NO_2 anion occurs by an acid-catalyzed process. The proposed mechanism of the overall nitrosylation reaction is checked by the solvolysis of *cis*-$Ru(H_2vi)_3NO$.

The synthesis,[2] structure,[3] and reactivity[4] of nitrosyl complexes have long been of great interest, but the thermodynamic instability and oxidizing power of NO and NO^+ against metal and ligands have motivated the development of new approaches to introducing the nitrosyl functionality into coordination complexes.[2] However, there are relatively few publications which relate the mechanistic data of the substitution reactions. The observed kinetics of a substitution reaction rarely give the mechanism unambiguously[5] and a further criterion of the mechanism that has been widely used is that of stereochemistry. The role of solvents[6,7] and added components such as ionic species[6] is very important and has been extensively investigated.

The synthesis and stereochemistry of the tris chelates of the $Ru(AB)_3^-$ type, where AB represents an unsymmetrical bidentate ligand, have been achieved in previous works.[9,10]



1,3-dihydrogenoviolurate, H_2vi^-; R = R' = H

1,3-dimethylviolurate, dmvi⁻; R = R' = CH_3

These complexes are inert to substitution and do not react with nucleophiles such as Cl^- or H_2O. However, they are very sensitive to acidic nitrite solutions forming nitrosyl complexes of the $Ru(AB)_2NOX$[10] type, where X represents a monodentate ligand. The kinetics and stereochemistry of nitrosylation of *fac*-$Ru(H_2vi)_3^-$ have determined specific pieces of information about the reaction mechanism.

Experimental Section

Starting Materials. $Na[Ru(H_2vi)_3]\cdot 4H_2O$ and $H_3O[Ru(H_2vi)_3]\cdot 3H_2O$ were obtained as described in ref 9 and 10. The compounds gave satisfactory elemental analyses.

Preparation of Ruthenium–Nitrosyl Complexes. All syntheses were performed in darkness under an argon atmosphere.

$Ru(H_2vi)_3NO$, $Ru(H_2vi)_2NOCl$, and $Ru(H_2vi)_2NOBr$ were obtained as described in ref 10. The compounds gave satisfactory elemental analyses.

$Ru(H_2vi)_2(NO)(OH)$ was prepared by adding of 0.14 g of sodium nitrite (2 mmol) to a stirred solution of 0.5 g of $Na[Ru(H_2vi)_3]\cdot 4H_2O$ (0.75 mmol) with perchloric acid (5 mmol) in 25 mL of twice-distilled water. After filtration, the yellow solution was held at 5 °C a few days, during which time small yellow crystals appeared. The product was collected and washed rapidly with 5 mL of ethanol and 5 mL of ether. The yellow crystals were dried in vacuo over P_4O_{10} and then at 100 °C for 3 h under argon yielding 0.29 g (85%) of end product. Anal. Calcd for $RuC_8H_5N_7O_{10}$: Ru, 21.95; C, 20.86; H, 1.08; N, 21.30. Found: Ru, 21.64; C, 20.55; H, 1.2; N, 20.94.

$Ru(H_2vi)_2(NO)(NO_2)$ was prepared using a modification of the former procedure. $Na[Ru(H_2vi)_3]\cdot 4H_2O$, 0.5 g (0.75 mmol), and $NaNO_2$, 1.4 g (20 mmol), were added to 25 mL of twice-distilled water. The solution was stirred and perchloric acid added (10 mmol). After filtration, the yellow solution was held at 5 °C a few days, during

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