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Reactivities of Ruthenium Cluster Anions: Implications for Catalysis of the Water-Gas Shift Reaction

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We find that $[HRu_3(CO)_{11}]^-$ functions as an apparent hydride donor in the presence of CO at atmospheric pressure and room temperature. This observation provides new insights into the chemistry of cluster anions and suggests a previously unanticipated mechanism for catalysis of the water-gas shift reaction by ruthenium clusters in basic solution.

Three separate reactions have been examined, each of which is consistent with and suggests hydridic behavior of $[HRu_3(CO)_{11}]^-$.

1. Reaction with CO. The salt $K[HRu_3(CO)_{11}]$ is stable in THF at room temperature. However, precipitation of $Ru_3(CO)_{12}$ is evident within minutes upon adding CO (1 atm) to the system. Other than $[HRu_3(CO)_{11}]^-$ and $Ru_3(CO)_{12}$, no other ruthenium-containing species is observed by spectroscopic (^{13}C, ^1H NMR, and IR) means. From the system of 4 mL of 0.3 M $K[HRu_3(CO)_{11}]$ in THF and 3.5 mmol of CO at 1 atm, 10% of the ruthenium is isolated as $Ru_3(CO)_{12}$. A reasonable source for the $Ru_3(CO)_{12}$ is reaction 1a expressed as an equilibrium.[1] Evidence

$$K[HRu_3(CO)_{11}] + CO \rightleftharpoons KH + Ru_3(CO)_{12} \tag{1a}$$

for such an equilibrium is given by the following observations: (a) Removal of the CO atmosphere from the above system causes rapid back reaction to give $[HRu_3(CO)_{11}]^-$. (b) The reverse of reaction 1a occurs readily[2] in THF (reaction 1b). An equilibrium

$$KH + Ru_3(CO)_{12} \rightarrow K[HRu_3(CO)_{11}] + CO \tag{1b}$$

system is indicated in that reaction 1b is severely retarded when CO at 1 atm of pressure is above the solution. When the CO is removed, the reaction goes to completion. Similarly, with ^{13}CO at 1 atm, reaction 1b is inhibited to less than a 1% overall conversion (^{13}C NMR spectrometry) to $[HRu_3(CO)_{11}]^-$ in a 48-h period at 25 °C.[3] Yet in this time frame, ^{13}CO–^{12}CO equilibration is achieved between carbon monoxide and triruthenium dodecarbonyl. However, when KH is absent from the system, no detectable ^{13}CO–^{12}CO equilibration occurs for the same time period and temperature.

2. Reaction with $[Ph_3C][BF_4]$ and CO. The following reaction was complete within 30 min at room temperature, with 1 atm of CO pressure, and in THF solution 0.3 M in $K[HRu_3(CO)_{11}]$ and $[Ph_3C][BF_4]$:

$$K[HRu_3(CO)_{11}] + [Ph_3C][BF_4] + CO \rightarrow KBF_4 + Ru_3(CO)_{12} + Ph_3CH \tag{2}$$

No byproducts were detected. In the absence of CO, evidence of a reaction (trace of $Ru_3(CO)_{12}$) is apparent only after several days. Reaction 2 probably proceeds through a hydride pathway. A possible radical pathway seems to be less favorable. We generated[4] $[HRu_3(CO)_{11}\cdot]$ in the presence and absence of CO and found it to be extremely unstable. Above −20 °C no ESR signal was detected and a number of decomposition products, insoluble in THF, were very rapidly formed.

3. Reaction with H_2O and CO. The reaction of $[DRu_3(CO)_{11}]^-$ with H_2O in the presence of CO is of interest due to its possible relationship to catalysis of the water-gas shift reaction. At room temperature and 1 atm of CO, HD gas (95% pure) is rapidly evolved from 0.01 M $K[DRu_3(CO)_{11}]$.

$$K[DRu_3(CO)_{11}] + CO + H_2O \xrightarrow{H_2O} HD + Ru_3(CO)_{12} + KOH \tag{3}$$

The solvent water eliminates possible back reaction of $Ru_3(CO)_{12}$ with KOH. In the absence of CO, $K[DRu_3(CO)_{11}]$ reacts slowly with water producing only traces of HD. Similarly, with $K[HRu_3(CO)_{11}]$ in H_2O in the absence of CO, only trace H_2 is formed and no $Ru_3(CO)_{12}$. Thus the anion is not significantly protonated by H_2O since the resulting $H_2Ru_3(CO)_{11}$ is known to decompose at room temperature to give H_2 and $Ru_3(CO)_{12}$ (90% conversion).[5] We believe reaction 3 reflects a hydridic character of $K[HRu_3(CO)_{11}]$ in the presence of CO.

Although kinetically indistinguishable, two possibilities for CO participation in these reactions are considered: (1) a concerted process in which H^- is eliminated as CO is added;[6] (2) an associative process. The latter case requires that an intermediate $[HRu_3(CO)_{12}]^-$ be formed, an electron-rich complex containing hydridic hydrogen bound to either a metal or to a carbon atom of a formyl group[7] which could function as a hydride transfer agent.[8]

Therefore, we propose a cycle (reactions 4–6) for catalysis of the water-gas shift reaction that differs from previously proposed[9] cycles involving $[HRu_3(CO)_{11}]^-$ because it emphasizes hydridic properties of this ion in the presence of CO. At present under the mild conditions of CO pressure and temperature chosen, there is no evidence for the reaction proceeding through mononuclear species.

$$Ru_3(CO)_{12} + [OH]^- \rightarrow [HRu_3(CO)_{11}]^- + CO_2 \tag{4}$$

$$[HRu_3(CO)_{11}]^- + CO \rightarrow Ru_3(CO)_{12} + H^- \tag{5a}$$

$$H^- + H_2O \rightarrow H_2 + [OH]^- \tag{6a}$$

or reaction 4 followed by

$$[HRu_3(CO)_{11}]^- + CO \rightarrow [HRu_3(CO)_{12}]^- \tag{5b}$$

$$[HRu_3(CO)_{12}]^- + H_2O \rightarrow Ru_3(CO)_{12} + H_2 + [OH]^- \tag{6b}$$

Examination of the anions[10,11] $[H_3Ru_4(CO)_{12}]^-$ and $[HRu_4(CO)_{13}]^-$ in the presence of CO and H_2 provides insight into the

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[1] We have not yet been able to obtain X-ray powder pattern evidence for KH, most likely because it is a poor X-ray scatterer compared to $Ru_3(CO)_{12}$ and $K[HRu_3(CO)_{11}]$. Furthermore, any KH formed must be in an active state since removal of CO pressure results in rapid back reaction according to eq 1a.

[2] Our preparation of $K[HRu_3(CO)_{11}]$ is the first preparation of this anion from a simple saltlike hydride. The standard method for preparing $[HRu_3(CO)_{11}]^-$ involves reaction of a complex borohydride with $Ru_3(CO)_{12}$ and has been shown to proceed through a formyl intermediate, which then loses CO: Schoening, R. C.; Vidal, J. L.; Fiato, R. A. *J. Organomet. Chem.* **1981**, *206*, C43. Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Suss, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1356.

[3] Experimental conditions: 95% ^{13}CO, 5.68 mmol of CO, 0.149 mmol of KH, 0.150 mmol of $Ru_3(CO)_{12}$. All gas samples were determined by mass spectrometry.

[4] This cluster radical may be prepared from $K[HRu_3(CO)_{11}]$ and $AgBF_4$ at −78 °C in THF, analogous to the recently reported preparation of $[HFe_3(CO)_{11}\cdot]$: Krusic, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 2131–33.

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[6] Hydride elimination promoted by an incoming CO ligand has been observed for $[PPN^+][HFe(CO)_4]$ but requires 140 atm of CO: King, R. B.; Frazier, C. C.; Hanes, R. M.; King, A. D., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 2925. We find a trace of $Fe(CO)_5$ produced from $K[HFe(CO)_4]$ at 1 atm of CO. Possible hydride elimination promoted by an incoming ligand has been suggested in the reactions of binuclear $(\mu\text{-}H)[M(CO)_5]_2^-$ (M = Cr, Mo, W) complexes with group 5A incoming ligands: Darensbourg, M. Y.; Walker, N.; Burch, R. R. *Inorg. Chem.* **1978**, *17*, 52.

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relative contributions of trinuclear vs. tetranuclear ruthenium carbonylates in the catalysis of the water–gas shift reaction. Our results are described below.

Reactions with H_2 and CO were carried out on 3-mL quantities of 0.01 M THF or ethoxyethanol solutions of potassium salts at 0.9 atm (5.7 mmol of CO or H_2). Solutions were analyzed by ^1H NMR and IR spectroscopy and mass spectrometry of initial and final gas mixtures. Chemical reactions were established through isolation of products and a determination of mass balances as well as spectroscopic identification. Although inert to H_2, $[H_3Ru_4(CO)_{12}]^-$ reacts with CO according to equation 7. Forward and reverse steps have been independently established by using either $[H_3Ru_4(CO)_{12}]^-$ or a 3:1 ratio of $[HRu_3(CO)_{11}]^-$ to $Ru_3(CO)_{12}$ as the starting point. Studies conducted under varying CO/H_2 ratios at a total gas pressure of 1 atm indicate an equilibrium constant of 2×10^{-2} at 60 °C in glyme.

$$3[H_3Ru_4(CO)_{12}]^- + 9CO \rightleftharpoons 3[HRu_3(CO)_{11}]^- + Ru_3(CO)_{12} + 3H_2 \quad (7)$$

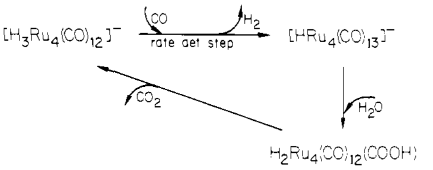
The forward reaction of equation 7 was examined under 1 atm of CO as a function of time at 60 and 80 °C in glyme. At 60 °C no intermediate species could be detected. However, at 80 °C this reaction proceeds through the intermediate $[HRu_4(CO)_{13}]^-$, the concentration of which never exceeds 12% of all ruthenium species since it is rapidly consumed by CO to give $[HRu_3(CO)_{11}]^-$ and $Ru_3(CO)_{12}$. Reaction 7 probably proceeds through the following sequence.

$$[H_3Ru_4(CO)_{12}]^- + CO \rightleftharpoons [HRu_4(CO)_{13}]^- + H_2 \quad (8)$$

$$[HRu_4(CO)_{13}]^- + 2CO \rightleftharpoons [HRu_3(CO)_{11}]^- + {}^1/_3Ru_3(CO)_{12} \quad (9)$$

Forward and reverse steps of eq 8 and 9 were observed at 80 °C in separate reactions.

A current view[9] that tetranuclear ruthenium clusters catalyze the water–gas shift reaction assumes the equivalent of reaction 8 as the rate determining step in the catalytic cycle (see eq 10).



(10)

This cycle is presumed to be operative whether the starting point is $H_4Ru_4(CO)_{12}$[12] or $Ru_3(CO)_{12}$ in basic solution since the "mature" catalytic system in each case has the same activity, and the same tetranuclear ionic species, $[H_3Ru_4(CO)_{12}]^-$, is observed in solution.[9] No $[HRu_4(CO)_{13}]^-$, a component of the cycle in eq 10, is observed. This is not unexpected since we see a rapid reaction of $[HRu_4(CO)_{13}]^-$ with base to give mixtures of $[H_3Ru_4(CO)_{12}]^-$ and $[H_2Ru_4(CO)_{12}]^{2-}$.[13] However, since we also observe reaction 9, in which $[HRu_4(CO)_{13}]^-$ is converted to $Ru_3(CO)_{12}$ and $[HRu_3(CO)_{11}]^-$ by CO, it is possible that over a period of time the effectiveness of the above cycle would be diminished and catalytic activity would be due primarily to trinuclear species.

If H_2 could be removed as it is formed in the water–gas shift reaction, then according to equilibrium 7 the concentration and subsequent contribution of $[H_3Ru_4(CO)_{12}]^-$ to the catalysis could be minimized. This point was tested by setting up a water–gas shift experiment in which H_2 was continuously removed from the apparatus by diffusion through a palladium thimble while CO remained behind. As expected, only $[HRu_3(CO)_{11}]^-$ was observed in solution even though $H_4Ru_4(CO)_{12}$ was the starting cluster. In this effectively H_2-free environment the turnover was approximately 4 times that observed in an earlier report[9] in which H_2 was allowed to accumulate in the catalytic system. The presence of H_2 shifts equilibrium 7 toward $[H_3Ru_4(CO)_{12}]^-$, but the presence of H_2 also inhibits the reductive elimination step according to equilibrium 8.

Thus it is clear that the trinuclear combination $[HRu_3(CO)_{11}]^-$–$Ru_3(CO)_{12}$ plays the major role in catalysis of the water–gas shift reaction in basic media, irrespective of whether the reaction is initiated by tetranuclear or trinuclear ruthenium carbonylates.

Furthermore, it seems reasonable that participation of trinuclear species in the catalysis of the water–gas shift reaction proceeds through a mechanism that involves a hydridic character of $[HRu_3(CO)_{11}]^-$ in the presence of CO.

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Registry No. CO, 630-08-0; $K[HRu_3(CO)_{11}]$, 80662-65-3; $Ru_3(CO)_{12}$, 15243-33-1; $[HRu_3(CO)_{11}]^-$, 60496-59-5; $[Ph_3C][BF_4]$, 341-02-6; $[H_3Ru_4(CO)_{12}]^-$, 70073-18-6; $[HRu_4(CO)_{13}]^-$, 76917-52-7; $K[H_3Ru_4(CO)_{12}]$, 80662-68-6; $K[HRu_4(CO)_{13}]$, 76917-54-9.

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[12] $H_4Ru_4(CO)_{12}$ is rapidly deprotonated (ref 10) under these basic catalytic conditions to yield $[H_3Ru_4(CO)_{12}]^-$, which has been presumed to be one of the active species in the water–gas shift catalysis.

[13] In an earlier report (ref 9) the isolation of $H_2Ru_4(CO)_{13}$ from neutralized basic solutions that catalyze the water–gas shift was taken as evidence for the presence of $[HRu_4(CO)_{13}]^-$ in the active solutions. However, our results indicate that $[HRu_4(CO)_{13}]^-$ will not exist in basic solutions.

Dienophilic Thioaldehydes

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Thioaldehydes have been virtually ignored in synthesis, probably due to their reported tendency to polymerize. Isolated reports mention carbon bond-forming reactions of transient thioaldehydes with 1,3-dienes[1] or with butyllithium,[2] but other publications that postulate thioaldehyde formation include little systematic information on their potential for intermolecular reactions other than polymerization.[3-5]

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