

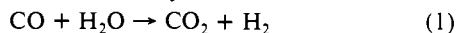
Hydride Donating Properties of $[\text{HRu}_3(\text{CO})_{11}]^-$ in the Presence of CO; Chemistry of Ruthenium Carbonyl Anions Relevant to the Catalysis of the Water Gas Shift Reaction

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Abstract: The chemistry of selected ruthenium carbonyl anions was studied with respect to the catalysis of the water gas shift reaction (WGSR: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$). Sodium and potassium salts of $[\text{HRu}_3(\text{CO})_{11}]^-$ in THF reacted with CO (1 atm) to precipitate $\text{Ru}_3(\text{CO})_{12}$ and probably metal hydride. In the presence of CO, $[\text{HRu}_3(\text{CO})_{11}]^-$ functioned as an apparent hydride donor to $\text{B}(\text{OCH}_3)_3$ and reacted with H_2O to give H_2 . The effect of counterion (K^+ , Na^+ , Li^+ , $\text{N}(\text{CH}_3)_4^+$, $\text{N}(\text{C}_2\text{H}_5)_4^+$) on the hydride donating reactions of $[\text{HRu}_3(\text{CO})_{11}]^-$ was studied. For catalysis of the WGSR, a catalytic cycle was proposed which involves $[\text{HRu}_3(\text{CO})_{11}]^-$ and $\text{Ru}_3(\text{CO})_{12}$ and emphasizes the apparent hydridic nature of $[\text{HRu}_3(\text{CO})_{11}]^-$ in the presence of CO. An equilibrium between tetranuclear and trinuclear clusters under CO/H_2 (1 atm) gas was shown to exist in aprotic media: $\text{K}[\text{H}_3\text{Ru}_4(\text{CO})_{12}] (\text{soln}) + 3\text{CO}(\text{g}) \rightleftharpoons \text{K}[\text{HRu}_3(\text{CO})_{11}] (\text{soln}) + \frac{1}{3}\text{Ru}_3(\text{CO})_{12}(\text{s}) + \text{H}_2(\text{g})$. Consistent with this equilibrium, in basic catalytic solutions derived from either $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ or $\text{Ru}_3(\text{CO})_{12}$ as catalyst precursors, activity decreased when H_2 was allowed to accumulate in the system and the equilibrium shifted toward the formation of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$. However, when H_2 was continuously removed from the system by diffusion through a Pd thimble while CO remained behind, the equilibrium shifted toward $[\text{HRu}_3(\text{CO})_{11}]^-$ and the activity increased with increasing $[\text{HRu}_3(\text{CO})_{11}]^-$ concentration. The trinuclear combination $[\text{HRu}_3(\text{CO})_{11}]^- - \text{Ru}_3(\text{CO})_{12}$ plays the dominant role in catalysis of the WGSR in this system, irrespective of whether the reaction is initiated by a tetranuclear or trinuclear ruthenium carbonyl. The effect of counterion (K^+ , Na^+ , Li^+ , $\text{N}(\text{CH}_3)_4^+$, $\text{HN}(\text{C}_2\text{H}_5)_3^+$) and the effect of phosphine (DPPE = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$; DPPM = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) substitution on $[\text{HRu}_3(\text{CO})_{11}]^-$ were examined. Although the counterion had little effect on catalysis, the degree of phosphine substitution had a significant effect on catalytic activity.

Catalysis of the water gas shift reaction [WGSR: reaction 1] by mononuclear catalyst precursors such as $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ is well-known and has been studied in detail.¹ While the nature of catalytic WGS solutions initiated



by transition-metal clusters has received less attention,^{2,3} it is known that basic solutions employing ruthenium cluster carbonyl catalyst precursors are capable of catalyzing the WGSR.^{10,23} Two ruthenium cluster anions, $[\text{HRu}_3(\text{CO})_{11}]^-$ and $[\text{HRu}_4(\text{CO})_{12}]^-$, have been identified in active WGS catalysis solutions.^{2b}

The systematic synthesis and chemistry of ruthenium cluster anions has been of continuing interest in these laboratories.⁴⁻⁹ In the process of studying the chemistry of the cluster anions $[\text{H}-$

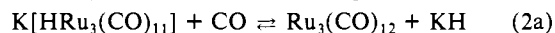
$\text{Ru}_3(\text{CO})_{11}]^-$, $[\text{HRu}_4(\text{CO})_{13}]^-$, $[\text{HRu}_4(\text{CO})_{12}]^{2-}$, and $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ with CO and H_2 , a number of reactions pertinent to WGS catalysis were observed. We found that such studies aided in determining the role that ruthenium cluster anions play in the homogeneous catalysis of the water gas shift reaction. A preliminary account of the reactivity of ruthenium cluster anions and implications for catalysis of the WGS reaction has been reported.³ Reported here are new results which include the effect of counterions on anion reactivity and reactivities of phosphine-substituted carbonylate ions and details of the earlier report.

Results and Discussion

A. Hydride Donating Reactions of $[\text{HRu}_3(\text{CO})_{11}]^-$. The following results show that $[\text{HRu}_3(\text{CO})_{11}]^-$ can function as an apparent hydride donor in the presence of CO. Under aprotic conditions counterion effects are observed. In addition to the reactions given below other examples have been observed.^{3,10}

1. Reactions with CO. The salt $\text{K}[\text{HRu}_3(\text{CO})_{11}]$ is stable in aprotic media such as THF. However, when a THF solution of $\text{K}[\text{HRu}_3(\text{CO})_{11}]$ (0.3 M) was exposed to CO (1 atm) at 25 °C, a precipitate of $\text{Ru}_3(\text{CO})_{12}$ formed. This system was cycled between -78 and 60 °C in THF and -78 and 85 °C in glyme. $\text{Ru}_3(\text{CO})_{12}$ was not observed above 25 °C. The optimum temperature for obtaining a maximum yield of $\text{Ru}_3(\text{CO})_{12}$ appeared to be -10 °C. Carbon-13 and proton NMR spectra taken in the range -80 to +25 °C indicated that the only ruthenium containing species present were $[\text{HRu}_3(\text{CO})_{11}]^-$ and $\text{Ru}_3(\text{CO})_{12}$. No proton signal attributable to the known¹¹ formyl $[\text{HRu}_3(\text{CO})_{11}\text{CHO}]^-$, a potential intermediate, was observed. Also, no signal due to a terminal metal hydride intermediate such as $[\text{HRu}(\text{CO})_4]^-$ (τ 18.8) was observed.¹²

The following equilibrium (reaction 2a) is considered to be the most reasonable source of $\text{Ru}_3(\text{CO})_{12}$, based upon the following observations: (1) Removal of the CO atmosphere from the above



system caused a back reaction which gave $[\text{HRu}_3(\text{CO})_{11}]^-$ and

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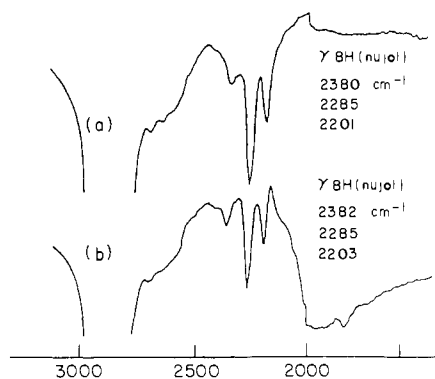


Figure 1. Infrared spectra: (a) reaction of KH with B(OMe)₃ in THF; (b) reaction between [HRu₃(CO)₁₁]⁻ and B(OMe)₃ in THF under CO (1 atm).

CO. (2) Starting with KH and Ru₃(CO)₁₂, the reverse of reaction 2a, reaction 2b, occurred in THF at 25 °C and is consistent with observation 1. (3) Reaction 2b was inhibited, proceeding very

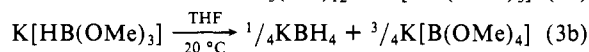
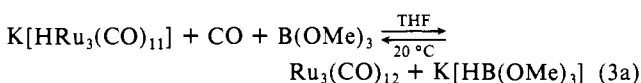


slowly to [HRu₃(CO)₁₁]⁻ when CO at 1 atm was above the solution.

Attempts to separate KH from Ru₃(CO)₁₂ were unsuccessful, in part because removal of CO led to the back reaction between KH and Ru₃(CO)₁₂. Identification of KH by an X-ray powder pattern of the mixture was not definitive, most likely because KH is a poor X-ray scatterer compared to Ru₃(CO)₁₂ and K[HRu₃(CO)₁₁]. Attempts to identify the KH spectroscopically by solubilizing it with cryptate were unsuccessful because equilibrium 2a was shifted rapidly to the left when the KH was solubilized. Thus, if Kryptofix222 was added to a 1:1 molar mixture of KH and Ru₃(CO)₁₂ under 1 atm of CO, K[HRu₃(CO)₁₁] and CO were formed quantitatively in minutes at 25 °C.

It was of interest to determine the effect of the counterion on the extent of reaction of CO with [HRu₃(CO)₁₁]⁻. In THF, no Ru₃(CO)₁₂ appeared to form from Li[HRu₃(CO)₁₁] while yields of 2 mol % from Na[HRu₃(CO)₁₁] and 10 mol % from K[HRu₃(CO)₁₁] were obtained under comparable conditions (1 atm of CO (5 mmol); 3.0 mL of 0.3 M [HRu₃(CO)₁₁]⁻). Since the other product of the reaction with CO is most likely an alkali metal hydride which is only slightly soluble in THF, the trend toward decreasing extent of reaction might be due to increased ion pairing of the alkali metal cation with [HRu₃(CO)₁₁]⁻, thereby inhibiting the extent of reaction with CO. Spectroscopic evidence for ion pairing of alkali metal salts of the [HRu₃(CO)₁₁]⁻ ion is available.^{13,14} The effect of ion pairing on the hydride-donating reactions of mononuclear hydrido(phosphine)ruthenate complexes has been reported.¹⁵

2. Hydride Transfer to B(OCH₃)₃ in the Presence of CO. Hydride transfer to boron was demonstrated in the reaction of K[HRu₃(CO)₁₁] with B(OCH₃)₃ under CO, according to reaction sequence 3a to 3b. This reaction sequence was complete after 48 h under CO (1 atm) at 20 °C. Disproportionation of the



[HB(OMe)₃]⁻ ion in ether solvents is well-known,^{16,17} and we found that when KH reacted with B(OMe)₃ the intermediate K[HB(OMe)₃] disproportionated according to reaction 3b. The infrared spectrum in the B-H stretching region of the product from se-

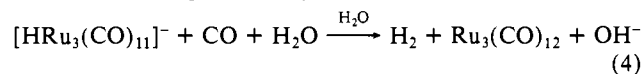
Table I. Reactions of K[HRu₃(CO)₁₁] and K[DRu₃(CO)₁₁] with H₂O

A. In the Presence of CO (1 atm)				
complex	concn, M	temp, °C	time, h	% yield of H
K[HRu ₃ (CO) ₁₁]	0.01	25	48	80
K[HRu ₃ (CO) ₁₁]	0.01	60	8	100
K[DRu ₃ (CO) ₁₁]	0.01	50	48	90 (95% HD, 5% H ₂)
B. In the Absence of CO				
complex	concn, M	temp, °C	time, h	moles of gas/ moles of cluster
K[HRu ₃ (CO) ₁₁]	0.01	25	48	0.080 (95% CO, 5% O ₂ , ^a trace H ₂)
K[HRu ₃ (CO) ₁₁]	0.01	60	8	2.5 (94% CO, 3% O ₂ , ^a 3% H ₂)
K[DRu ₃ (CO) ₁₁]	0.01	50	32	0.068 (98% CO, 2% O ₂ , ^a trace HD, H ₂)

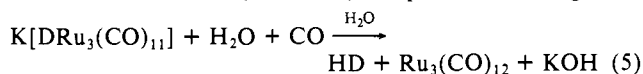
^a The O₂ product was not due to a leak in the reaction vessel.

quence 3a to 3b was identical with the infrared spectrum of the product from the reaction of KH with B(OMe)₃, shown in Figure 1. When CO was absent from the system, there was no apparent reaction between B(OMe)₃ and K[HRu₃(CO)₁₁]. The key to observing borohydride in this system is the limited solubilities of KBH₄ and K[B(OMe)₄] in THF, which drives the reaction to the right. However, when CO is removed the KBH₄ and Ru₃(CO)₁₂ react. When Na[HRu₃(CO)₁₁] was employed under identical conditions, no apparent reaction occurred because of the favorable solubility of NaBH₄ in THF which, in turn, favored the reverse reaction.

3. Reaction with H₂O in the Presence of CO. The reaction of H[Ru₃(CO)₁₁]⁻ with H₂O in the presence of CO (1 atm) is of interest because of its relationship to the catalysis of the water gas shift reaction. The K⁺, Na⁺, and Li⁺ salts of [HRu₃(CO)₁₁]⁻ (0.01 M) all reacted with H₂O in the presence of CO at similar rates (reaction 4). Thus in an ionizing solvent there was no counterion effect produced by alkali metal cations. Since the



solutions were dilute (0.01 M) and since the CO reacts with OH⁻ ion to lower the pH of the system to an observed value of about 8, possible back reaction was minimized.¹⁸ When the reaction was carried out at 60 °C, Ru₃(CO)₁₂ was formed quantitatively over a period of 8 h. The reaction was 80% complete after 48 h at 25 °C. In the absence of CO, only a trace of H₂ and no Ru₃(CO)₁₂ was formed at 25 and 60 °C in the reaction periods cited above. Results obtained from K[HRu₃(CO)₁₁] are summarized in Table I. The fact that Ru₃(CO)₁₂ was not formed in the absence of CO suggested that [HRu₃(CO)₁₁]⁻ was not significantly protonated by H₂O. This is consistent with the observations that [HRu₃(CO)₁₁]⁻ is a very weak base,^{2c} plus the fact that protonation of [HRu₃(CO)₁₁]⁻ has been shown to proceed through the unstable intermediate H₂Ru₃(CO)₁₁,¹⁹ which decomposes giving H₂ and CO in a 1:1 ratio and Ru₃(CO)₁₂ as the major decomposition products.⁷ An experiment with a deuterium label and 1 atm of CO (reaction 5) was performed analogous to



reaction 4; it employed K[DRu₃(CO)₁₁] instead of K[HRu₃(CO)₁₁]. The noncondensable gaseous products were analyzed (Table

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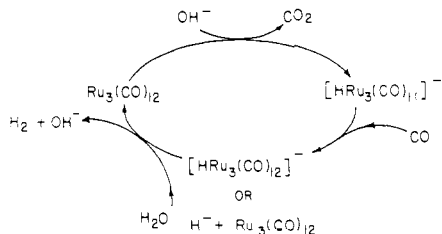
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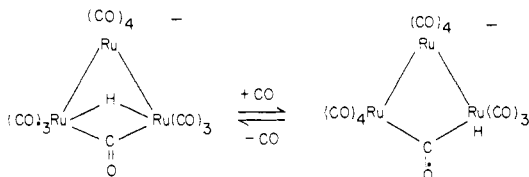
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Scheme I



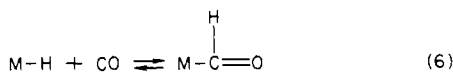
Scheme II



I) by mass spectrometry. The results of reactions 4 and 5 are consistent with hydrogen derived from the cluster having negative character and reacting with protons in water. The purity of the HD evolved in reaction 5 militates against a process in which $\text{Ru}_3(\text{CO})_{12}$ is formed by an electron-transfer³³ reaction or by a radical process.²¹

B. Catalysis of the Water Gas Shift Reaction by the $[\text{HRu}_3(\text{CO})_{11}]^-$ - $\text{Ru}_3(\text{CO})_{12}$ System. In view of the above observations, we propose a cycle (Scheme I) for catalysis of the water gas shift reaction which differs from previously proposed cycles^{2c} involving $[\text{HRu}_3(\text{CO})_{11}]^-$. We prefer to emphasize the apparent hydridic and hydride transfer properties of this ion in the presence of CO. Two possibilities for CO participation are considered: a concerted²⁰ process in which H^- is eliminated as CO is added to $[\text{HRu}_3(\text{C}-\text{O})_{11}]^-$; or an associative mechanism. The latter case is probably more realistic. It requires that an electron-rich intermediate, $[\text{HRu}_3(\text{CO})_{12}]^-$, be formed. Such a complex could function as a hydride transfer agent containing hydridic terminal hydrogen bound to either a metal²¹ or a carbon atom of a formyl group.^{22,23}

The formation of a formyl intermediate would require the migratory insertion of CO into a metal-hydrogen bond (reaction 6). Such a migration has only been observed in two instances



and does not appear to be a favorable process.^{22,24} Nevertheless, if such an intermediate were formed in the reaction of $[\text{HRu}_3(\text{CO})_{11}]^-$ with CO, it would be the known¹¹ formyl $[(\text{CO})_{11}^-\text{Ru}_3\text{CHO}]^-$. This formyl has been shown to be extremely unstable, decomposing to $[\text{HRu}_3(\text{CO})_{11}]^-$ and CO at temperatures above -50°C . Thus, although it might be the active species it is unlikely that $[\text{HRu}_3(\text{CO})_{11}]^-$ could be observed in the reactions discussed

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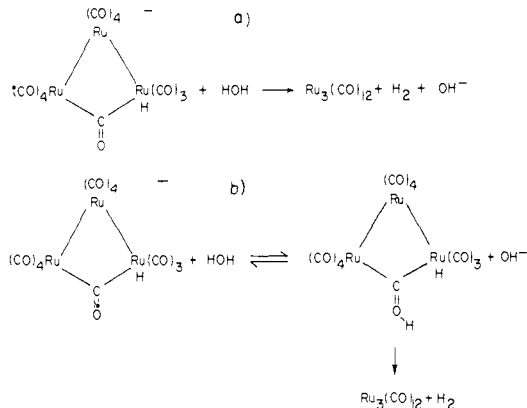
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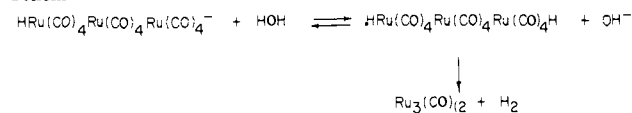
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Scheme III



Scheme IV



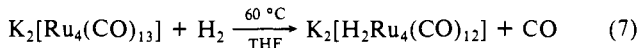
above. Another type of intermediate which might be formed would contain hydridic hydrogen bound terminally to ruthenium. The donation of two electrons by the incoming CO ligand could induce the opening of the 3-center, 2-electron bridge bond to a 2-center, 2-electron terminally bound hydrogen (Scheme II).

If the intermediate $[\text{HRu}_3(\text{CO})_{12}]^-$ in Scheme II is formed, the hydrogen is presumed to be hydridic in the sense that it would react with the protonic hydrogen in water through an intermolecular reaction as in Scheme IIIa. On the other hand perhaps $[\text{HRu}_3(\text{CO})_{12}]^-$ would be sufficiently basic to be protonated in basic solution even though $[\text{HRu}_3(\text{CO})_{11}]^-$ is not. A possible sequence involving protonation is shown in Scheme IIIb. The proton is presumed to add initially to the oxygen of the bridging CO^{19,32} and thus retains its positive character. It could then interact intramolecularly with the hydridic hydrogen on ruthenium to give H_2 . This scheme is consistent with our observation that HD (95%) is formed.

Another scheme for the reaction of $[\text{HRu}_3(\text{CO})_{12}]^-$ with H_2O has been proposed by other investigators.^{2b} In this case the intermediate $[\text{HRu}_3(\text{CO})_{12}]^-$ is believed to be an open chain (Scheme IV). Since we obtain high-purity HD in reaction 5, Table I, significant exchange in the prior equilibrium step of this scheme is unlikely, but the succeeding step is reasonable. In view of the purity of the HD given off in reaction 5, if Scheme IV is operative, elimination of H_2 from $\text{H}_2\text{Ru}_3(\text{CO})_{12}$ has to be primarily intramolecular.

C. Reactivities of Tetranuclear Ruthenium Cluster Anions. Under water gas shift conditions, a variety of ruthenium carbonyl cluster precursors are capable of giving a catalytically active system. Catalytic systems have been initiated by $\text{H}_2\text{Ru}_4(\text{CO})_{13}$, $\text{H}_4\text{Ru}_4(\text{CO})_{12}$, or $\text{Ru}_3(\text{CO})_{12}$, giving solutions which were spectroscopically indistinguishable after an initial "maturing" period of 24 h.^{2b} Two species of different nuclearity, $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ and $[\text{HRu}_3(\text{CO})_{11}]^-$, have been observed in the ¹H NMR spectra of active catalytic solutions.^{2b} However, we found that $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ was present only when H_2 was allowed to accumulate in the catalytic system. This result combined with earlier proposals of catalytic cycles based on tetranuclear clusters^{2b} suggested to us that examination of the reactivities of the tetranuclear anions $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$, $[\text{H}_2\text{Ru}_4(\text{CO})_{12}]^{2-}$, $[\text{HRu}_4(\text{CO})_{13}]^-$, and $[\text{Ru}_4(\text{CO})_{13}]^{2-}$ with CO and H_2 was in order.

The anion $[\text{Ru}_4(\text{CO})_{13}]^{2-}$ reacted with H_2 according to reaction 7. The reverse of this reaction could not be achieved with CO



(1 atm) was placed over $\text{K}_2[\text{H}_2\text{Ru}_4(\text{CO})_{12}]$ in THF. Neither of these anions is believed to play a significant role in the catalysis of the WGS under conditions employed in the present study.³⁴

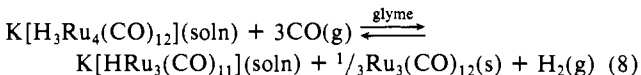
Table II. Relative Equilibrium Concentrations in Reaction 8^a

H ₂ /CO	$\frac{[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-}{[\text{HRu}_3(\text{CO})_{11}]^-}$	$K_{\text{eq(atm)}}^b$
0.040	2.3	0.019
0.087	3.3	0.031
0.13	6.3	0.026
		0.025 av
100% H ₂	only $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ observed	

^a60 °C in glyme. ^b $K_{\text{eq(atm)}} = \{[\text{HRu}_3(\text{CO})_{11}]^- P_{\text{H}_2}\} / \{[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^- P_{\text{CO}}\}$.

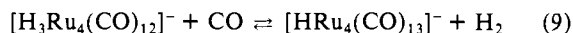
We found that $[\text{H}_2\text{Ru}_4(\text{CO})_{12}]^{2-}$ can exist only at basicities higher than that of the formate-CO buffer present in mature catalytic solutions.

Although inert to H₂ at 1 atm, $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ reacted with CO (1 atm) according to reaction 8. When reaction 8 was



performed at 80 °C, the equilibrium was driven to the right and to completion by the sublimation of $\text{Ru}_3(\text{CO})_{12}$ from the solution. $[\text{HRu}_3(\text{CO})_{11}]^-$ and $\text{Ru}_3(\text{CO})_{12}$ were isolated in a 3:1 mol ratio and 1 mol of H₂ was given off per mol of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ consumed. That reaction 8 is an equilibrium was established by the following observations. If the reaction of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ with CO was carried out at lower temperatures (≤ 60 °C), where $\text{Ru}_3(\text{CO})_{12}$ did not sublime from solution, complete consumption of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ did not occur. Instead, a mixture of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$, $[\text{HRu}_3(\text{CO})_{11}]^-$, and $\text{Ru}_3(\text{CO})_{12}$ was observed. If the gas above this mixture was removed and replaced by pure H₂ (1 atm), quantitative regeneration of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ occurred. Subsequent experiments showed that the ratio of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ occurred. Subsequent experiments showed that the ratio of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ to $[\text{HRu}_3(\text{CO})_{11}]^-$ was dependent on the H₂-to-CO ratio in the system. Under 1 atm of H₂ pressure, a 3:1 molar ratio of $[\text{HRu}_3(\text{CO})_{11}]^-$ to $\text{Ru}_3(\text{CO})_{12}$ reacted at 60 °C to give $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ and CO in accord with the back reaction of eq 8. In order to determine the equilibrium constant for reaction 8, the equilibrium was established from both directions. $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ was reacted with varying H₂/CO ratios in separate experiments at 60 °C and a total gas pressure of 1 atm. In a second set of separate experiments, a 3:1 molar ratio of $[\text{HRu}_3(\text{CO})_{11}]^-$ to $\text{Ru}_3(\text{CO})_{12}$ was reacted with varying H₂/CO ratios under identical conditions (60 °C, 1 atm). The reactions were followed with time by ¹H NMR spectroscopy, and the equilibrium H₂/CO ratio was determined by mass spectrometry. For a given H₂/CO ratio at 1 atm of total pressure, a constant molar ratio of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ to $[\text{HRu}_3(\text{CO})_{11}]^-$ was observed, irrespective of whether the starting point was $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ or a 3:1 molar ratio of $[\text{HRu}_3(\text{CO})_{11}]^-$ to $\text{Ru}_3(\text{CO})_{12}$. Results are summarized in Table II and indicate that small partial pressures of H₂ were capable of producing a significant concentration of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$. From the data in Table II, the equilibrium constant at 60 °C in glyme was estimated ($K_{\text{p(atm)}} = 0.025$).

It was also of interest to determine the pathway by which $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ and $[\text{HRu}_3(\text{CO})_{11}]^-$ interconvert. The forward reaction of eq 8, in which $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ reacts with CO, was examined by ¹H NMR spectroscopy as a function of time at 60 and 80 °C in glyme. Although no intermediate was observed at 60 °C, the cluster anion $[\text{HRu}_4(\text{CO})_{13}]^-$ was observed as an intermediate at 80 °C, but its concentration never exceeded 14% of the total ruthenium species in solution. Thus, the initial step in the reaction of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ with CO involves H₂ displacement by CO according to reaction 9. The reverse step of reaction 9 was observed at 60 and 80 °C; it occurred more rapidly



than the forward step and went to apparent completion at low H₂ partial pressure. That the concentration of $[\text{HRu}_4(\text{CO})_{13}]^-$ was low throughout the course of the reaction between $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$

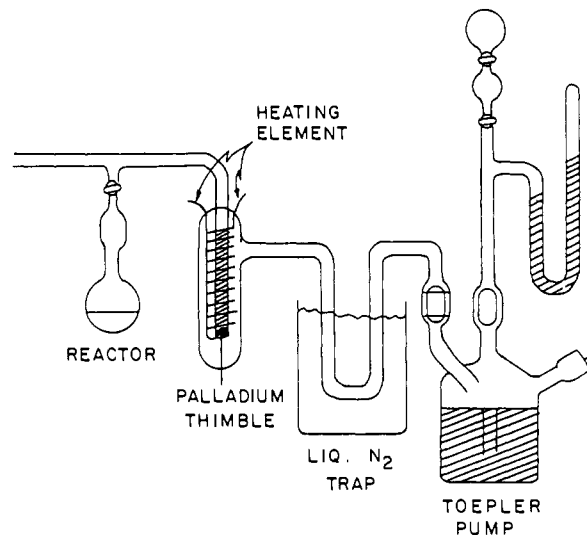
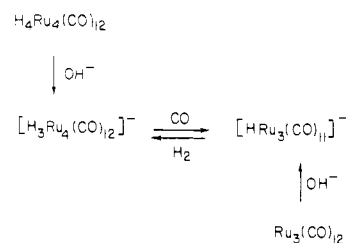
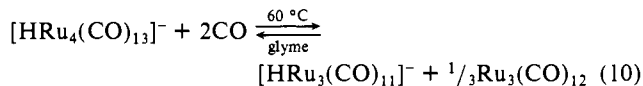


Figure 2. Palladium thimble experiment for continuous removal of H₂ from active catalysis system.

Scheme V



$[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ and CO was due, in part, to the ease with which CO was found to react with $[\text{HRu}_4(\text{CO})_{13}]^-$ according to reaction 10.



We found that at relatively low CO partial pressures (20 torr), reaction 10 went to apparent completion. Reaction 10 could be reversed only if CO was continually removed from the system. Thus, equilibrium 8 can be represented as the sum of equilibria 9 and 10. Clearly, the presence of H₂ favors the formation of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ while the presence of CO favors the formation of $[\text{HRu}_3(\text{CO})_{11}]^-$.

D. Active Catalysis Solutions. Although equilibrium 8 was determined in neutral solutions the possibility was considered that a similar relationship applies to WGS catalysis solutions under basic conditions.^{25,26} Indeed, from ¹H NMR spectra of active catalysis solutions it was found that when the H₂ partial pressure (H₂/CO mixture at 1 atm of total pressure) was increased, $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ was favored. On the other hand, $[\text{HRu}_3(\text{CO})_{11}]^-$ was favored when the CO partial pressure was increased. Scheme V accounts for the relative concentration dependence of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ and $[\text{HRu}_3(\text{CO})_{11}]^-$ on the H₂/CO ratio in the system. The possibility of such a relationship was suggested by Ford.^{2b} It also accounts for the fact that similar catalytic activities are observed irrespective of whether the starting point is a tetranuclear or trinuclear cluster.

Scheme V suggests that if H₂ could be removed as it is formed in the water gas shift reaction, then the concentration and subsequent contribution of $[\text{HRu}_3(\text{CO})_{11}]^-$ to catalysis would be maximized. This was demonstrated by setting up a water gas shift

(25) Both $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ and $[\text{HRu}_3(\text{CO})_{11}]^-$ are relatively stable in basic media as evidenced by their preparation under such conditions.^{2b,27}

(26) We found that the anion $[\text{HRu}_4(\text{CO})_{13}]^-$ was unstable in basic solution:

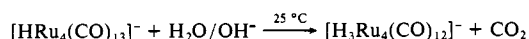


Table III. Catalysis of the Water Gas Shift Reaction

expt no.	base	cluster	conditions ^a	turnovers ^b after day =						mol % of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$	mol % of $[\text{HRu}_3(\text{CO})_{11}]^-$
				1	2	3	4	5	6		
1	KOH	$\text{H}_4\text{Ru}_4(\text{CO})_{12}$	H_2 removed ^c	3.4	2.7	2.6	2.8	2.8		0	100
2	KOH	$\text{H}_4\text{Ru}_4(\text{CO})_{12}$	H_2 accumulated ^d	3.1	2.2	2.0	2.2	2.0		10	90
3	KOH	$\text{Ru}_3(\text{CO})_{12}$	H_2 removed ^c	3.8	2.8	2.8	2.8			0	100
4	KOH	$\text{Ru}_3(\text{CO})_{12}$	H_2 accumulated ^d	3.0	2.2	1.9	2.3	2.1		15	85
5	NaOH	$\text{Ru}_3(\text{CO})_2$	H_2 removed ^c	2.8	2.8	2.7	2.9			19	90
6	NaOH	$\text{Ru}_3(\text{CO})_{12}$	H_2 accumulated ^d	2.1	2.1	2.2	2.2			10	100
7	LiOH	$\text{Ru}_3(\text{CO})_{12}$	H_2 removed ^c	2.7	2.6	2.6	2.8			0	90
8	LiOH	$\text{Ru}_3(\text{CO})_{12}$	H_2 accumulated ^d	1.9	2.0	2.0	2.1			10	90
9	NMe_4OH	$\text{Ru}_3(\text{CO})_{12}$	H_2 removed ^c	2.4	2.5	2.4	2.4			0	100
10	NMe_4OH	$\text{Ru}_3(\text{CO})_{12}$	H_2 accumulated ^d	1.8	1.5	1.9	2.0			10	90
11	MHEt_3OH	$\text{Ru}_3(\text{CO})_{12}$	H_2 removed ^c	3.1	3.0	3.1				0	100
								2.2 ^f		10	90
12	NHEt_3OH	$\text{Ru}_3(\text{CO})_{12}$	H_2 accumulated ^d	1.9	2.1	2.3	2.1	2.4		10	90
13	KOH	$\text{Ru}_3(\text{CO})_{10}(\text{DPPE})$	H_2 accumulated ^d	4.7	3.7	3.9	4.1	3.9	4.2	$[\text{HRu}_3(\text{CO})_9(\text{DPPE})]^-$ (100%)	
14	KOH	$\text{Ru}_3(\text{CO})_8(\text{DPPM})_2$	H_2 accumulated ^d	non catalytic						$\text{Ru}_3(\text{CO})_8(\text{DPPM})_2$ (100%)	

^a Conditions: 100 °C; 0.9 atm of CO; ethoxyethanol (3 mL); H_2O (0.36 mL), MOH (2.0 mol), cluster (0.04 mol). ^b Turnovers = nmol H_2 /(nmol Ru)(day). ^c H_2 removed continuously through Pd thimble. ^d H_2 removed every 24 h. ^e H_2 was added after day 4 and H_2 was allowed to accumulate through day 5. ^f H_2 was allowed to accumulate for day 4.

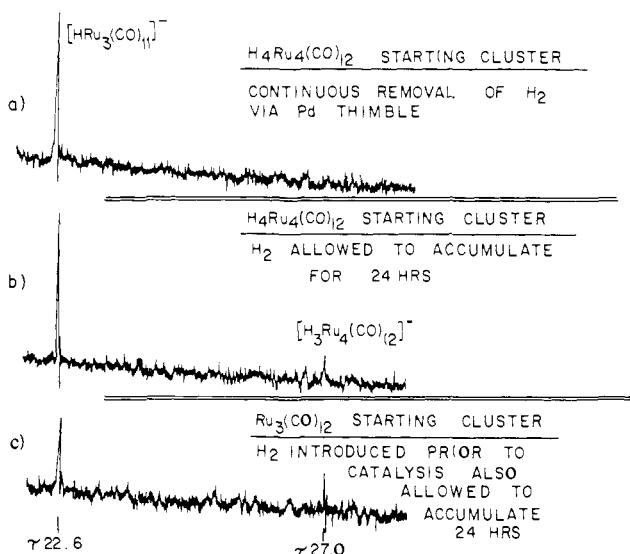
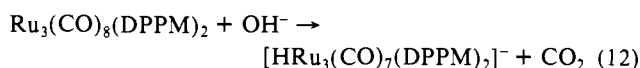
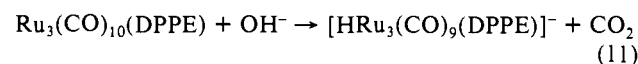


Figure 3. Proton NMR spectra of active WGS catalysis solutions: (a) continuous removal of H_2 with a Pd thimble; (b) H_2 allowed to accumulate in the system; (c) H_2 introduced prior to catalysis.

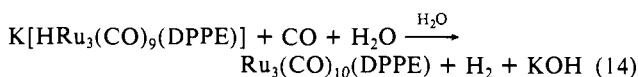
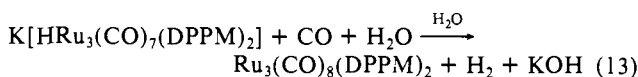
experiment in which H_2 was continuously removed from the apparatus by diffusion through a palladium thimble (Figure 2) while CO remained behind. As expected, only $[\text{HRu}_3(\text{CO})_{11}]^-$ was observed in solution even though $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ was the starting cluster (Figure 3a). When H_2 was allowed to accumulate in the system, the resulting solution contained $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ and $[\text{HRu}_3(\text{CO})_{11}]^-$ (Figure 3b,c). When we reduced the amount of H_2 allowed to accumulate in the catalytic system, the number of turnovers per ruthenium atom in solution increased with the increased $[\text{HRu}_3(\text{CO})_{11}]^-$ concentration. The maximum number of turnovers observed per ruthenium atom in solution occurred when the H_2 was continuously removed and $[\text{HRu}_3(\text{CO})_{11}]^-$ was the only observed ruthenium species in solution. Results are summarized in Table III. The effect of H_2 inhibition is clear from the results given here. Thus $[\text{HRu}_3(\text{CO})_{11}]^-$ plays the dominant role in the catalysis rather than, as previously supposed,^{2b} the $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ ion. Indeed, in an earlier study in which the concentration of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ (63 mol %) exceeded that of $[\text{HRu}_3(\text{CO})_{11}]^-$ (37 mol %) in the catalytic solution, the number of turnovers was only 0.9.^{2b} Although $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ can give hydrogen through a reductive elimination step (reaction 9), an equilibrium is involved. By allowing H_2 to accumulate in the system this reductive elimination step is inhibited thereby minimizing the effectiveness of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ in the catalysis.

Another point which is clear from Table III is that although a variety of bases were used to generate the catalytic system (KOH, LiOH, NaOH, NMe_4OH , and NHEt_3OH), the counterion did not have a significant effect on catalytic activity. Thus, under ionizing conditions, the counterion effect is minimized. Only when the possibility of intimate ion pairs exists, as in reactions 2a,b and 3a,b in THF, does the counterion effect become significant.

E. Phosphine-Substituted Clusters. The phosphine-substituted clusters $\text{Ru}_3(\text{CO})_{10}(\text{DPPE})$ ($\text{DPPE} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) and $\text{Ru}_3(\text{CO})_8(\text{DPPM})_2$ ($\text{DPPM} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) were tested as catalyst precursors for catalysis of the water gas shift reaction. Under WGS conditions $\text{Ru}_3(\text{CO})_{10}(\text{DPPE})$ and $\text{Ru}_3(\text{CO})_8(\text{DPPM})_2$ would be expected to react with hydroxide ion to produce $\text{K}[\text{HRu}_3(\text{CO})_9(\text{DPPE})]^-$ and $\text{K}[\text{HRu}_3(\text{CO})_7(\text{DPPM})_2]^-$, respectively (reactions 11 and 12). Since the phosphine ligands



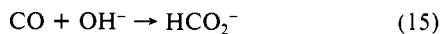
are better σ donors than CO, it was thought that an increase in electron density on the metal atoms might give a more hydridic intermediate upon reaction with CO. Thus the reaction of H_2O with $\text{K}[\text{HRu}_3(\text{CO})_9(\text{DPPE})]^-$ and $\text{K}[\text{HRu}_3(\text{CO})_7(\text{DPPM})_2]^-$ in the presence of CO was examined. Reactions 13 and 14 were approximately 5–7 times faster at 25 °C and 60 °C than reaction 4 under identical conditions.



Under WGS conditions (Table III), the catalyst precursor $\text{Ru}_3(\text{CO})_{10}(\text{DPPE})$ produced a catalytic system which was ~30% more active than the system produced by $\text{Ru}_3(\text{CO})_{12}$. On the other hand, the catalyst precursor $\text{Ru}_3(\text{CO})_8(\text{DPPM})_2$ produced a catalytically inactive system. This apparent contradiction can be interpreted in the following manner. There are two factors which vary as the degree of phosphine substitution on the ruthenium cluster increases. First, the increase in electron density on the metal atoms results in a more electron-rich intermediate upon reaction with CO which in turn reacts more rapidly with H_2O . However, a second consequence of increased electron density on the metal is to increase back-bonding to the remaining carbonyls, rendering them less susceptible to attack by hydroxide ion, thereby accounting for the fact that $\text{Ru}_3(\text{CO})_{10}(\text{DPPE})$ was only 30% more

active in WGS catalysis than $\text{Ru}_3(\text{CO})_{12}$. The system remained homogeneous and only $[\text{HRu}_3(\text{CO})_9(\text{DPPE})]^-$ was found to be present in solution. This system showed no tendency to form the tetranuclear cluster anion $[\text{H}_3\text{Ru}_4(\text{CO})_{10}\text{DPPE}]^-$ in the presence of H_2 .

In the case of the catalyst precursor $\text{Ru}_3(\text{CO})_8(\text{DPPM})_2$, $[\text{HRu}_3(\text{O})_7(\text{DPPM})_2]^-$ was formed initially because of the initial high pH of the catalytic solution. However, as the pH of the solution was lowered by a buffering^{1h,2b} of the system through the reaction of CO with hydroxide ion^{1h,2b} (reaction 15), Ru_3 -



$(\text{CO})_8(\text{DPPM})_2$ precipitated from the solution. $\text{Ru}_3(\text{CO})_8(\text{DPPM})_2$ was recovered from the catalysis solution in quantitative yield. A similar result was obtained with $\text{K}[\text{HRu}_3(\text{CO})_7(\text{DPPM})_2]$ as the starting material; within 3 h $\text{Ru}_3(\text{CO})_8(\text{DPPM})_2$ had precipitated from solution and was recovered quantitatively. Thus, reaction 12 does not appear to occur at the hydroxide ion concentration present under WGS conditions, thereby preventing formation of a catalytic system.

Experimental Section

I. Materials. $\text{Ru}_3(\text{CO})_{12}$ and $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2$ were used as received from Strem Chemical Co. $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (Strem Chemical Co.) was recrystallized from hot ethanol (95%) prior to use. CO, 99.9% was obtained from Matheson Scientific and passed through a -196°C trap prior to use. ^{13}CO , 99% ^{13}C , was obtained from Monsanto Co. (Mound Laboratory) and used as received. Tetrahydrofuran (THF) and monoglyme were distilled from and stored over sodium benzophenone ketyl. Ethoxyethanol (Aldrich) was purified by distillation from Mg turnings and was stored under N_2 . Deionized, triply distilled water was degassed by several freeze, pump, thaw cycles on the vacuum line. $\text{B}(\text{OCH}_3)_3$ (Metal Hydrides, Inc.) was purified by being stirred over KH at 25°C followed by fractionation on a vacuum line. The hydrides KH, KD, and NaH (Alpha-Ventron) were washed repeatedly with dry hexane until free-flowing powders were obtained, which were then stored under N_2 . LiH (Alpha-Ventron) was used as received and stored under N_2 . NaOH and KOH were obtained from MCB Manufacturing Chemists in pellet form, ground to a fine powder, and dried at 130°C at 10^{-5} mmHg prior to use. A standard solution of LiOH was prepared from the reaction of LiH with water. $\text{N}(\text{C}_2\text{H}_5)_3$ and $[\text{N}(\text{CH}_3)_4]\text{OH}$ were used as received from Aldrich Chemical Co. The metal carbonyls $\text{H}_4\text{Ru}_4(\text{C}-\text{O})_{12}$,²⁸ $\text{Ru}_3(\text{CO})_8(\text{DPPM})_2$,²⁹ $\text{K}[\text{H}_3\text{Ru}_4(\text{CO})_{12}]$,⁴ $\text{K}_2[\text{H}_2\text{Ru}_4(\text{CO})_{12}]$,⁴ $\text{K}[\text{HRu}_4(\text{CO})_{13}]$,⁷ and $[\text{Na}[\text{HRu}_3(\text{CO})_{11}]]^{13}$ were prepared by standard literature procedures. The salt $[\text{Li}[\text{HRu}_3(\text{CO})_{11}]]$ was prepared by slight modification of the literature method.¹³

The salt $[\text{K}[\text{HRu}_3(\text{CO})_{11}]]$ was prepared by reduction of $\text{Ru}_3(\text{CO})_{12}$ by $[\text{K}[\text{HB}(\text{CH}_3)_3]]$.^{7,14} In the drybox, 686 mg (1.07 mmol) of $\text{Ru}_3(\text{CO})_{12}$ and 45.2 mg (1.12 mmol) of KH (93.5% active) were weighed into the reaction vessel. THF, 10 mL, was distilled onto the reactants at -78°C followed by approximately 0.5 mmol of $\text{B}(\text{CH}_3)_3$ at -196°C . When the reaction was warmed to 25°C , CO gas was rapidly given off and the solution turned bright red in color. After 2 h, 1.00 mmol of CO had been given off, and the THF and $\text{B}(\text{CH}_3)_3$ were removed under vacuum. The salt $[\text{K}[\text{HRu}_3(\text{CO})_{11}]]$ was precipitated by dissolving the product in a minimum volume of CH_2Cl_2 (2 mL) and adding hexane (7 mL). The $[\text{K}[\text{HRu}_3(\text{CO})_{11}]]$ was filtered in a vacuum extractor and washed off with fresh hexane to remove unreacted $\text{Ru}_3(\text{CO})_{12}$. The yield of $[\text{K}[\text{HRu}_3(\text{C}-\text{O})_{11}]]$ was 580 mg (83%). ^1H NMR; τ 22.6 (THF, 25°C). IR (THF): 2075 (vw); 2018 (s); 1985 (s); 1948 (m); 1730 (w); 1680 cm^{-1} (w). The salt $[\text{K}[\text{DRu}_3(\text{CO})_{11}]]$ was prepared in an identical manner with the exception that KD (99% deuterium) was employed in place of KH. The infrared spectrum of $[\text{K}[\text{DRu}_3(\text{CO})_{11}]]$ in THF was indistinguishable from that of $[\text{K}[\text{HRu}_3(\text{CO})_{11}]]$ in the C-O stretching region.

The salts $[\text{Et}_4\text{N}][\text{HRu}_3(\text{CO})_{11}]$ and $[\text{Me}_4\text{N}][\text{HRu}_3(\text{CO})_{11}]$ were prepared by metathesis of the $[\text{K}[\text{HRu}_3(\text{CO})_{11}]]$ salt with $[\text{Et}_4\text{N}]\text{Br}$ and $[\text{Me}_4\text{N}]\text{Cl}$, respectively, in a $\text{THF}:\text{CH}_2\text{Cl}_2$ (3:1) solvent mixture. The infrared spectra of these salts were in agreement with those in previous reports.^{28,13}

The phosphine-substituted compound $\text{Ru}_3(\text{CO})_{10}(\text{DPPE})$ was prepared by the following method. A two-neck bulk, equipped with a stirrer and an adapter, was loaded with 0.80 g (1.25 mmol) of $\text{Ru}_3(\text{CO})_{12}$.

A tip tube containing 0.498 g (1.25 mmol) of bis(diphenylphosphino)ethane (DPPE) was attached to the sidearm of the two-necked vessel. The vessel was evacuated, and 6 mL of CH_3CN was condensed into it at -78°C . The mixture was allowed to stir for 2 h. DPPE was then added while the mixture was stirred at room temperature. The stirring was continued for another 2 h, the solvent CH_3CN removed by distillation, and THF added. The mixture was then stirred for additional 8 h or overnight, or until about 90% of theoretical amount of CO had evolved. The vessel was opened to air. The THF solution was taken to dryness and CH_2Cl_2 was added. The CH_2Cl_2 solution was taken to dryness leaving solid $\text{Ru}_3(\text{CO})_{10}(\text{DPPE})$. This crude $\text{Ru}_3(\text{CO})_{10}(\text{DPPE})$ was purified by washing the solid with dry hexane several times. The yield was 1.0 g, 80%. The product was characterized by infrared spectroscopy.³⁰

The phosphine-substituted cluster anion $[\text{K}[\text{HRu}_3(\text{CO})_9(\text{DPPE})]]$ was prepared in a similar manner to that described for $[\text{K}[\text{HRu}_3(\text{CO})_{11}]]$. The reaction of $\text{Ru}_3(\text{CO})_{10}(\text{DPPE})$ (0.036 mmol) with $[\text{K}[(\text{CH}_3)_3\text{BH}]]$ (0.036 mmol) in THF at 25°C produced quantitative CO gas (0.036 mmol) in 1 h. The THF and $\text{B}(\text{CH}_3)_3$ were removed under vacuum, and the product was precipitated from CH_2Cl_2 (1 mL) and hexane (3 mL). The salt $[\text{K}[\text{HRu}_3(\text{CO})_9(\text{DPPE})]]$ was filtered in a vacuum extractor and washed with fresh hexane. Yield: 26 mg (75%). IR (THF): 2041 (m); 2005 (sh); 1958 (s); 1938 (sh); 1718 (w); 1651 (w). ^1H NMR: triplet at τ 21.9 (THF, 25°C).

II. Apparatus. All manipulations were carried out on a standard high-vacuum line or in a glovebox under an atmosphere of dry, pure nitrogen.³⁰ Analyses of all gas mixtures were carried out on an AEI MSIO mass spectrometer calibrated for H_2/CO mixtures. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer with matched 0.1-mm KBr liquid cells. Proton, boron-11, and carbon-13 NMR spectra were recorded on either Bruker WM-300, Bruker HX-90, and Bruker HX-80 spectrometers operating in the FT mode or a Varian EL390 spectrometer. Chemical shifts for ^{13}C and ^1H NMR spectra were referenced to $\text{Me}_4\text{Si} = 0.00$ ppm. A palladium thimble (General Electric), which was employed in WGS catalysis studies, was attached to the vacuum line and operated in conjunction with a Toepler pump.^{10,31}

III. Water Gas Shift Catalysis Studies. A. Preparation of Catalyst Solutions. Water gas shift catalysis studies employing $\text{Ru}_3(\text{CO})_{12}$, $\text{H}_4\text{Ru}_4(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{10}(\text{DPPE})$, and $\text{Ru}_3(\text{CO})_8(\text{DPPM})_2$ as catalyst precursors were all carried out with use of the same procedure. In a 120-mL reaction vessel, 0.04 mmol of metal carbonyl was weighed out and 3.0 mL of ethoxyethanol was added under a flow of N_2 . The ethoxyethanol-metal carbonyl mixture was cooled to -78°C and 0.36 mL of a H_2O solution which contained 2.0 mmol of the appropriate base (KOH, NaOH, LiOH, NEt_3 , Me_4NOH) was added. The N_2 flow was stopped, the vessel evacuated, and the catalytic solution thoroughly degassed at -78°C . A known amount of CO pressure (~ 0.9 atm) was expanded through a -196°C U-trap into the catalysis vessel and into a sample bulb simultaneously at -78°C . The sample bulb was analyzed by mass spectrometry for background H_2 in the carbon monoxide. At this stage, the system was prepared for the catalytic study, which was performed in two different ways which are described below.

B. Methods of Performing Catalytic Studies. 1. Hydrogen Accumulation in a Closed System. The closed reaction system was heated to 100°C and stirred for 24 h. During this time, the H_2 produced catalytically by the water gas shift reaction accumulated in the reaction vessel. After 24 h, the catalysis solution was quenched by cooling the reaction to -78°C and the gas was collected by a Toepler pump. The gas was analyzed for CO/H_2 content by a mass spectrometer calibrated with known CO/H_2 mixtures.

2. Continuous Removal of H_2 through a Pd Thimble. The reaction vessel was attached to a Pd thimble (Figure 3). The contents of the reaction vessel was stirred at 100°C , and the Pd thimble was operated at 400°C .¹⁰ Leaving CO behind, hydrogen continuously diffused through the Pd thimble and was collected with a Toepler pump, which operated continuously. The gas which diffused through the Pd thimble was 99 + % H_2 (mass spectrum). The gas over the catalysis solution was

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collected by a Toepler pump and analyzed for CO/H₂ content by mass spectrometry.

If the catalytic reaction was to proceed for several days, new CO was expanded into the system and the entire process repeated every 24 h. The catalytic solution was analyzed by ¹H NMR spectrometry. The solution was tipped into an NMR tube which was connected to the catalysis vessel, and the NMR tube was then sealed.

IV. Reactions of $[\text{HRu}_3(\text{CO})_{11}]^-$. **A. With CO.** In the drybox, 0.9 mmol of the K⁺, Na⁺, and Li⁺ salts of $[\text{HRu}_3(\text{CO})_{11}]^-$ were weighed into 100-mL vessels. THF, 3 mL, was distilled onto the K⁺, Na⁺, and Li⁺ salts at -78 °C. CO (1 atm) was expanded over the three solutions at -78 °C, and the solutions were stirred over the temperature range -15 to 25 °C. The K⁺ salt was stirred over the temperature range -78 to 60 °C in THF and -78 to 85 °C in glyme. Ru₃(CO)₁₂ precipitated from the THF solutions of the K⁺ and Na⁺ salts at 25 °C, and the maximum Ru₃(CO)₁₂ production occurred at -10 °C. These solutions were filtered in a vacuum extractor in the presence of CO (1 atm). Ru₃(CO)₁₂ was identified by infrared spectroscopy and X-ray powder diffraction. If the CO gas was removed from the solutions of Na $[\text{HRu}_3(\text{CO})_{11}]^-$ and K $[\text{HRu}_3(\text{CO})_{11}]^-$ in which Ru₃(CO)₁₂ had precipitated, a rapid reaction (~2 min) occurred which consumed the Ru₃(CO)₁₂ precipitate and evolved CO gas.

The reaction of K $[\text{HRu}_3(\text{CO})_{11}]^-$ with CO (1 atm) in THF was followed by ¹³C and ¹H NMR spectroscopy. Only signals due to K $[\text{HRu}_3(\text{CO})_{11}]^-$ and Ru₃(CO)₁₂, at 206 and 199.6 ppm, respectively, were observed in the carbon-13 NMR spectrum of the reaction mixture in the temperature range -25 to +25 °C. The ¹H NMR spectrum of this mixture revealed a single resonance at τ 22.6 in the temperature range -80 to +25 °C.

B. With CO and B(OCH₃)₃. In the drybox, 300 mg (0.461 mmol) of K $[\text{HRu}_3(\text{CO})_{11}]^-$ was weighed into a 120-mL reaction vessel. THF, 4 mL, and 0.8 mmol of B(OCH₃)₃ were distilled onto the salt at -78 °C. CO (1 atm) was expanded over the solution at -78 °C, and the reaction was stirred at 25 °C. Considerable Ru₃(CO)₁₂ precipitated from the solution over a period of 90 h. The precipitate was filtered and dried at 27 °C and 10⁻⁵ mmHg. An infrared spectrum of the precipitate as a Nujol mull revealed that KBH₄ and K[B(OCH₃)₄] were present. The infrared spectrum obtained was identical with that obtained for the products in the reaction of KH with B(OCH₃)₃ in THF (Figure 1). Additional infrared spectra (THF, hexane) indicated that Ru₃(CO)₁₂ was also present.

The salt Na $[\text{HRu}_3(\text{CO})_{11}]^-$ (0.5 mmol) did not produce a precipitate when reacted with B(OCH₃)₃ (0.8 mmole) in the presence of CO (1 atm) in THF. A ¹H NMR spectrum of the reaction mixture indicated only the presence of unreacted Na $[\text{HRu}_3(\text{CO})_{11}]^-$ and B(OCH₃)₃.

C. With B(OCH₃)₃. B(OCH₃)₃, 0.8 mmol, and 4 mL of THF were distilled into a 100-mL reaction bulb containing 303 mg (0.465 mmol) of K $[\text{HRu}_3(\text{CO})_{11}]^-$. Stirring for 90 h at 25 °C did not produce a precipitate, and a ¹H NMR spectrum of the reaction mixture indicated only the presence of unreacted B(OCH₃)₃ and K $[\text{HRu}_3(\text{CO})_{11}]^-$.

D. With CO and H₂O. A 0.030-mmol quantity of the K⁺, Na⁺, and Li⁺ salts of $[\text{HRu}_3(\text{CO})_{11}]^-$ was weighed into 100-mL vessels which were equipped with an addition tube containing 3.0 mL of triply distilled, deionized H₂O. CO, 1 atm, was expanded into the vessels, and the H₂O (pH 7) was added at -78 °C. The three reactions were warmed to 25 °C, and Ru₃(CO)₁₂ precipitated from the solutions over a period of 48 h. The Ru₃(CO)₁₂ was recovered (16 mg) in 80% yield and identified by its infrared spectrum. The gas over each solution was collected, and mass spectral analysis revealed that H₂ (~0.03 mmol) had been given off. When the reaction was performed with K $[\text{HRu}_3(\text{CO})_{11}]^-$ at 60 °C under otherwise identical conditions, quantitative precipitation at Ru₃(CO)₁₂ occurred with concurrent H₂ production over a period of 8 h. A pH of 8 was observed in the solution.

E. With H₂O. The blank reactions between H₂O and the Li⁺, Na⁺, and K⁺ salts of $[\text{HRu}_3(\text{CO})_{11}]^-$ were performed as described above with the exception that CO was not present. Water solutions of the Li⁺, Na⁺, and K⁺ salts (0.030 mmol in 3.0 mL) were stirred at 25 °C for a period of 8 h. A Ru₃(CO)₁₂ precipitate was not observed in these reactions. Approximately 0.002 mmol of noncondensable gas was given off which analyzed for 95% CO, 5% O₂, and only a trace of H₂. When the reaction was performed at 60 °C, 0.074 mmol of noncondensable gas was given off which analyzed for 94% CO, 3% O₂, and 3% H₂. The IR spectrum in H₂O of the products of the reaction at 60 °C revealed a single broad and strong absorption centered at 1966 cm⁻¹. Ru₃(CO)₁₂ was not observed (IR) as a product when the reaction was performed at 25 or 60 °C. No Ru₃(CO)₁₂ or H₂ products were observed in the reactions of the NMe₄⁺ and NEt₄⁺ salts with H₂O at 28 °C in CH₃OH:H₂O (9:1) solvent mixtures.

V. Reactions of K $[\text{DRu}_3(\text{CO})_{11}]^-$. **A. With CO and H₂O.** In the drybox, 17 mg (0.026 mmole) of K $[\text{DRu}_3(\text{CO})_{11}]^-$ was weighed into a

Table IV. Reaction of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ with CO^a

reaction time, h	mol % $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$	mol % $[\text{HRu}_4(\text{CO})_{13}]^-$	mol % $[\text{HRu}_3(\text{CO})_{11}]^-$
0	100		
4.5	65	10	25
12.0	38	14	48
22.0	14	14	72
59	2	0	98

^a 80 °C in glyme. Ru₃(CO)₁₂ sublimed from the system, thereby driving reaction 8 to completion.

100-mL reaction vessel. Pure H₂O, 3.3 mL, was tipped onto the salt at -78 °C and CO (1 atm) was expanded into the system. The reaction was stirred at 50 °C and Ru₃(CO)₁₂ precipitated from solution. After 32 h, the gas over the solution was analyzed mass spectrometrically. It consisted of CO and hydrogen gas which was essentially pure HD. The system was then charged with fresh CO and maintained at 50 °C for an additional 16 h by which time the reaction was about 90% complete. The gas over the solution consisted of CO and hydrogen (90% HD and 10% H₂). The average composition of hydrogen gas given off in reaction 5 was about 95% HD and 5% H₂. That the gas appears to be enriched in protium as reaction 5 nears completion is probably due to some back-reaction of Ru₃(CO)₁₂ with OH⁻ to give $[\text{HRu}_3(\text{CO})_{11}]^-$ which then reacts with H₂O in the presence of CO to give H₂.

B. With H₂O. The blank reaction was performed with 20 mg (0.031 mmol) of K $[\text{DRu}_3(\text{CO})_{11}]^-$ and 4.0 mL of H₂O. Stirring at 50 °C for 32 h produced 0.002 mmol of noncondensable gas which analyzed for 98% CO, 2% O₂, and a trace of HD and H₂. No Ru₃(CO)₁₂ was observed.

VI. Reaction of Ru₃(CO)₁₂ with KH. In the drybox, 91.6 mg (0.143 mmole) of Ru₃(CO)₁₂ and 5.7 mg (0.14 mmol) of KH (93% active) were weighed into a reaction vessel. THF, 3 mL, was distilled onto the reactants at -78 °C and the reaction performed at 25 °C. The solution turned deep red, and 0.139 mmol of CO gas was given off over a period of 14 h. An infrared spectrum of the reaction solution indicated that K $[\text{HRu}_3(\text{CO})_{11}]^-$ had been formed cleanly.

VII. Reactions of K $[\text{HRu}_3(\text{CO})_9(\text{DPPE})]$ and K $[\text{HRu}_3(\text{CO})_7(\text{DPPM})_2]$. **A. With CO and H₂O.** In the drybox, 45 mg (0.045 mmol) of K $[\text{HRu}_3(\text{CO})_9(\text{DPPE})]$ and 55 mg (0.050 mmol) of K $[\text{HRu}_3(\text{CO})_7(\text{DPPM})_2]$ were weighed into 100-mL reaction vessels. A 0.1-mL quantity of THF and 4 mL of H₂O were added to the salts at -78 °C. CO (1 atm) was expanded into each system, and the reactions were allowed to proceed at 25 °C. Ru₃(CO)₁₀(DPPE) and Ru₃(DPPM)₂ precipitated from the respective solutions over a period of 6 h. The gas over the solutions was collected with a Toepler pump, and mass spectrometric analysis indicated that H₂ (~0.05 mmol) had been given off. The Ru₃(CO)₁₀(DPPE) and Ru₃(CO)₈(DPPM)₂ precipitates were isolated (39 and 46 mg, respectively) and identified by infrared spectroscopy. A pH of 8 was observed in the solution. When the reactions were performed at 60 °C under otherwise identical conditions, quantitative precipitation of Ru₃(CO)₁₀(DPPE) and Ru₃(CO)₈(DPPM)₂ occurred with concurrent H₂ production over a period of 1.5 h.

B. With H₂O. The blank reactions were performed as described above with the exception that no CO was added. Stirring for 6 h did not produce a precipitate of Ru₃(CO)₈(DPPM)₂ or Ru₃(CO)₁₀(DPPE). Mass spectra of the gasses given off in the reactions (0.002 < mmol) indicated that CO was present. No H₂ was observed.

VIII. Reactions of $[\text{HRu}_4(\text{CO})_{13}]^-$. **A. With H₂.** In the drybox, 30 mg (0.037 mmol) of K $[\text{HRu}_4(\text{CO})_{13}]^-$ was weighed into a 100 mL reaction vessel. Glyme, 4 mL, was added at -78 °C, and 1 atm of H₂ was expanded over the solution. Stirring at 80 °C for 25 min resulted in quantitative formation of K $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ (¹H NMR) and evolution of 0.04 mmol of CO gas (mass spectrum). A similar result was obtained at 60 °C.

B. With CO. When 40 mg (0.050 mmol) of K $[\text{HRu}_4(\text{CO})_{13}]^-$ in glyme (4 mL) was reacted with CO at 1 atm at 80 °C, complete consumption of the K $[\text{HRu}_4(\text{CO})_{13}]^-$ occurred in 1 h. No H₂ gas was produced, and K $[\text{HRu}_3(\text{CO})_{11}]^-$ and Ru₃(CO)₁₂ were the only metal carbonyl products. If the reaction products were heated to 80 °C in the absence of CO, K $[\text{HRu}_4(\text{CO})_{13}]^-$ was formed quantitatively and 2 equiv (0.10 mmol) of CO were evolved when the CO was removed continuously.

IX. Reactions of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ with CO. In the drybox, 68 mg (0.086 mmol) of K $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ was weighed into a 120-mL reaction vessel. Glyme, 3 mL, was condensed into the vessel at -78 °C, and 1 atm of CO (5.5 mmole) was expanded over the solution. The reaction was stirred at 80 °C and monitored with time by ¹H NMR spectroscopy. Results (Table IV) indicate that this reaction produces $[\text{HRu}_3(\text{CO})_{11}]^-$ as a final product. Infrared spectra indicated that Ru₃(CO)₁₂ was also a product of the reaction. The mass spectrum of the gas over the solution in a parallel experiment revealed that H₂ (0.08 mmol) was also produced.

This reaction went to completion because $\text{Ru}_3(\text{CO})_{12}$ sublimed from the system at 80 °C. Equilibrium experiments at 60 °C are described below.

X. Tetranuclear/Trinuclear Cluster Equilibrium Studies. A. Reaction of $[\text{HRu}_3(\text{CO})_{11}]^-$ with $\text{Ru}_3(\text{CO})_{12}$. In the drybox, 78.8 mg (0.121 mmol) of $\text{K}[\text{HRu}_3(\text{CO})_{11}]$ and 26.0 (0.0407 mmol) of $\text{Ru}_3(\text{CO})_{12}$ were weighed into a 50-mL reaction vessel. Glyme, 4 mL, was distilled onto the reactants at -78 °C, and the system was warmed to 80 °C. Noncondensable gases were removed from time to time as the reaction progressed. After 4 h, 0.24 mmol of CO gas had been evolved and a ^1H NMR spectrum of the reaction solution showed only $\text{K}[\text{HRu}_4(\text{CO})_{13}]$. An infrared spectrum confirmed that $\text{K}[\text{HRu}_4(\text{CO})_{13}]$ had been formed and $\text{K}[\text{HRu}_3(\text{CO})_{11}]$ and $\text{Ru}_3(\text{CO})_{12}$ had been completely consumed.

B. Reaction of $[\text{HRu}_3(\text{CO})_{11}]^-$ with $\text{Ru}_3(\text{CO})_{12}$ under H_2 . In the drybox, 45.0 mg (0.069 mmol) of $\text{K}[\text{HRu}_3(\text{CO})_{11}]$ and 15.0 mg (0.023 mmol) of $\text{Ru}_3(\text{CO})_{12}$ were weighed into a 100-mL reaction vessel. Glyme, 3 mL was distilled into the vessel at -78 °C and H_2 (1 atm), was expanded over the solution. Stirring at 80 °C resulted in quantitative formation of $\text{K}[\text{H}_3\text{Ru}_4(\text{CO})_{12}]$ after 16 h as evidenced by ^1H NMR. Mass spectral analysis of the gas over the solution indicated that CO had been evolved (~ 0.14 mmol).

C. Reaction of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ with CO/H_2 Mixtures. The reaction of $\text{K}[\text{H}_3\text{Ru}_4(\text{CO})_{12}]$ with CO/H_2 mixtures was performed in a 120-mL reaction vessel at 60 °C under a total gas pressure of 1 atm. The species present in solution were determined by ^1H NMR spectroscopy taken as a function of time. In the drybox, 91.5 mg (0.117 mmol) of $\text{K}[\text{H}_3\text{Ru}_4(\text{CO})_{12}]$ was weighed into the reaction vessel adapted with a NMR tube

as a sidearm. Glyme, 3 mL, was condensed onto the solid at -78 °C and a CO/H_2 mixture of known composition was expanded over the solution. The reaction vessel was stirred at 60 °C for at least 24-h periods and the gas above the solution was analyzed by mass spectrometry. Proton NMR spectra of the reaction solution were recorded under the CO/H_2 atmosphere. This process was repeated to ensure that equilibrium had been achieved during the time frame of the experiment. The results are given in Table II for reaction in glyme. Similar results were obtained in THF and ethoxyethanol. The equilibrium was tested by also examining the reverse reaction, starting with a 3:1 ratio of $[\text{HRu}_3(\text{CO})_{11}]^-:\text{Ru}_3(\text{CO})_{12}$ under CO/H_2 mixtures as described below.

D. Reaction of $[\text{HRu}_3(\text{CO})_{11}]^-:\text{Ru}_3(\text{CO})_{12}$ (3:1) with CO/H_2 Mixtures. The reaction of a 3:1 mixture of $\text{K}[\text{HRu}_3(\text{CO})_{11}]:\text{Ru}_3(\text{CO})_{12}$ with CO/H_2 mixtures was performed identically with those of $\text{K}[\text{H}_3\text{Ru}_4(\text{CO})_{12}]$ as described above. For the experiments performed in this manner, 75.1 mg (0.117 mmol) of $\text{K}[\text{HRu}_3(\text{CO})_{11}]$ and 24.9 mg (0.039 mmol) of $\text{Ru}_3(\text{CO})_{12}$ were employed. Results are given in Table II. Irrespective of the starting point, the same ratio of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ to $[\text{HRu}_3(\text{CO})_{11}]^-$ was achieved at a given CO/H_2 ratio.

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Examination of Rhodium Carboxylate Antitumor Agents Complexed with Nucleosides by Extended X-ray Absorption Fine Structure Spectroscopy

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Abstract: Extended X-ray absorption fine structure spectra have been measured of rhodium carboxylates and their complexes with five adenine nucleoside systems in order to elucidate the structural basis of the antineoplastic activity of such complexes. The analysis reveals several structural features. The Rh-Rh bond lengths of $[\text{Rh}_2\text{Ac}_4(\text{adenosine})]\cdot\text{H}_2\text{O}$, $[\text{Rh}_2\text{Ac}_4(\text{cordycepin})]\cdot\text{H}_2\text{O}$, $[\text{Rh}_2\text{Ac}_4(\text{ara-A})]\cdot\text{H}_2\text{O}$, and $[\text{Rh}_2\text{Ac}_4(8\text{-Br-adenosine})]\cdot\text{H}_2\text{O}$ are the same, within experimental uncertainty, as that of $[\text{Rh}_2\text{Ac}_4(\text{caffeine})_2]$, 2.395 Å (Ac is used for acetate rather than acetyl). The Rh-Rh bond length of $[\text{Rh}_2\text{Bu}_4\text{2MeOH}]$, however, is 0.026 Å shorter than in the rhodium acetate complexes. Substituting 8-bromoadenosine in $[\text{Rh}_2\text{Ac}_4(\text{adenosine})]$ results in a significant change in the disorder parameters of the first coordination shell around Rh. Furthermore, the complexation of rhodium acetate to 8-bromoadenosine elicits a syn to anti conformation change at the nucleoside. It is concluded that rhodium probably binds the purine at N_7 in the adenosine complex and at N_1 in the 8-bromoadenosine complex.

The interaction of metal complexes with nucleic acids is of current interest.^{1,2} We report here structural studies on rhodium carboxylate adenine nucleoside systems by extended X-ray absorption fine structure (EXAFS) spectroscopy. These species are active antitumor agents^{3,4} and bind specifically to adenine and its nucleotides and nucleosides.⁵

The factors which affect specificity in metal-purine binding are now well delineated^{6,7} and of particular interest is the dictation of this specificity in the absence or presence of intramolecular hydrogen bonding between exocyclic groups and ligand donor atoms.⁸

The binding site of purines to rhodium carboxylates has been assigned to N_7 , due to favorable H-bonding interaction between the exocyclic amino group and the acetate oxygens of the lig-

ands,^{9,10} by analogy with the structure elucidated for $[\text{Co}(\text{acac})_2(\text{NO}_2)](2'\text{-deoxyadenosine})$.³ While the exact mechanism of action of the rhodium carboxylates is not clear,¹¹ rhodium-purine binding may still be important. Thus, the possibility that

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