Condensation of mononuclear [HM(CO)4]- to trinuclear [HM3(CO)11]- metal hydridocarbonyl anions (M = Fe, Ru, Os) under protic and water gas shift conditions

Jeffery C. Bricker, and Sheldon G. Shore

Organometallics, **1984**, 3 (2), 201-204• DOI: 10.1021/om00080a005 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

3 hydride probably will not be a useful route for the preparation of a low oxidation state group 3 derivative. Reductive elimination reactions of group 4 hydrides (R_3MH, M = Ge, Sn, Pb) are not synthetically useful routes to low oxidation state group 4 compounds[11] either.

Experimental Section

General Comments. All compounds described in this investigation were extremely oxygen and moisture sensitive and were manipulated in a vacuum line or in a purified argon atmosphere. All solvents were rigorously dried and vacuum distilled just prior to use. Infrared spectra were obtained by using a Perkin-Elmer 683 infrared spectrometer. The spectra were recorded as Nujol mulls by using CsI plates. (Bands due to Nujol have been omitted from data.) Proton NMR spectra were recorded by using a Varian EM-390 spectrometer. Proton chemical shifts are reported in δ units, parts per million downfield from tetramethylsilane, with benzene as an internal reference (δ 7.13). The solvent was vacuum distilled onto samples at −196 °C. Spectra were recorded immediately upon warming samples to room temperature unless stated otherwise.

$SiMe_4$ formed during synthetic, hydrolysis, and thermal decomposition reactions was separated by vacuum distillation with passage through two −78 °C traps and into a −196 °C trap and was measured by PVT or mass measurements. The purity of the $SiMe_4$ was determined by its ^1H NMR spectrum. Hydrogen was isolated and measured with a Toepler pump–gas burette assembly.

Synthesis and Characterization of $KGa(CH_2SiMe_3)_2H_2$. The reagents, 3.000 g (9.265 mmol) of $Ga(CH_2SiMe_3)_2Br$[4] and 1.115 g (27.80 mmol) of KH, were combined in a reaction tube equipped with a Teflon valve in the drybox. Then, 20 mL of dry dimethoxyethane was vacuum distilled into the tube. After 4-h reaction time at room temperature, the dimethoxyethane and a trace of noncondensable gas were removed on the vacuum line. Then, the mixture was extracted with dry benzene. The filtrate, a white paste, was pumped on overnight at 65 °C to remove all dimethoxyethane. Since the product was gray, the mixture was extracted with benzene a second time and then washed twice with cold *n*-pentane. The resulting colorless solid (1.21 g, 4.25 mmol) $KGa(CH_2SiMe_3)_2H_2$, which was slightly soluble in cold C_5H_{12}, was isolated in 45.8% yield based on $Ga(CH_2SiMe_3)_2Br$. $KGa(CH_2SiMe_3)_2H_2$: mp 147–153 °C, bubbles and turns gray 212 °C; hydrolysis (6 M HCl, 110 °C, 7 days) of 0.288 g (1.01 mmol) yields 1.99 mmol of H_2 and 1.98 mmol of $SiMe_4$ (by PVT measurements); ^1H NMR (C_6H_6, ppm, reference C_6H_6 7.13); spectrum immediately upon dissolution, +0.34 (s, 4.3, Me), −0.80 (s, 1.0, CH_2), spectrum after 4 months +0.33 (s, 10.2, Me), +0.26 (s, 4.0, Me), −0.81 (s, 1.9, CH_2), −0.91 (s, 1.0, CH_2). IR (Nujol Mull): 1620 (vs, br), 1290 (w), 1253 (m), 1239 (s), 960 (s), 850 (vs), 820 (vs), 775 (s), 746 (s), 715 (m), 700 (m), 679 (m), 604 (w), 575 (m), 511 (m), 479 (vw), 442 (w), 250 (vw) cm^{-1}. $KGa(CH_2SiMe_3)_2D_2$: ^1H NMR (C_6H_6, ppm, reference C_6H_6 7.13) spectrum immediately upon dissolution, +0.33 (s, 4.0, Me), −0.82 (s, 1.0, CH_2), after 24 h, +0.33 (s, 11.1, Me), +0.26 (s, 3.9, Me), −0.82 (s, 2.1, CH_2), −0.92 (s, 1.0, CH_2); IR (Nujol mull) 1650 (w, br), 1290 (vw), 1251 (m), 1238 (s), 1170 (m, br), 955 (vs), 849 (vs), 819 (vs), 742 (m), 714 (m), 677 (w), 600 (m), 585 (w, sh), 514 (m), 482 (vw) cm^{-1}.

Reaction of $KGa(CH_2SiMe_3)_2H_2$ with $Ga(CH_2SiMe_3)_2Br$. An Attempted Synthesis of $Ga(CH_2SiMe_3)_2H$. To 0.381 g (1.34 mmol) of $KGa(CH_2SiMe_3)_2H_2$ in 5 mL of C_6H_6 was added 0.433 g (1.34 mmol) of $Ga(CH_2SiMe_3)_2Br$ in 5 mL of C_6H_6 at room temperature. A white precipitate formed immediately but turned gray after several hours. After being stirred for 24 h, the mixture was cooled to −196 °C and 1.10 mmol of H_2 were measured with a Toepler pump–gas burette assembly. Fractionation of the volatile components throught two −78 °C traps and into a −196 °C trap produced less than 0.01 mmol of $SiMe_4$ (PVT measurements). The mixture was then filtered to separate 0.210 g of a gray insoluble solid (KBr plus Ga). The removal of all benzene from the filtrate left a yellow paste. Vacuum distillation of this paste at a bath temperature of 110 °C produced 0.41 g (1.2 mmol) of $Ga(CH_2SiMe_3)_3$ which was identified by ^1H NMR (+0.13, C_6H_6) and IR.

Acknowledgment. This work was generously supported by the National Science Foundation through Grant CHE-81-3316.

Registry No. $KGa(CH_2SiMe_3)_2H_2$, 87828-71-5; $Ga(CH_2SiMe_3)_2Br$, 74251-17-5; $Ga(CH_2SiMe_3)_2H$, 87801-07-8.

---

[11] Coates, G. E.; Aylett, B. J.; Green, M. L. H.; Mingos, D. M. P.; Wade, K. "Organometallic Compounds"; Halstead Press: New York, 1979; Vol. 1, Part II.

Condensation of Mononuclear $[HM(CO)_4]^-$ to Trinuclear $[HM_3(CO)_{11}]^-$ Metal Hydrido Carbonyl Anions (M = Fe, Ru, Os) under Protic and Water Gas Shift Conditions

Jeffery C. Bricker, Nripendra Bhattacharyya, and Sheldon G. Shore*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received August 9, 1983

Stoichiometries and conditions for the condensation of $[HM(CO)_4]^-$ to $[HM_3(CO)_{11}]^-$ for M = Fe, Ru, and Os have been determined. Under protic and water gas shift conditions, the $[HRu(CO)_4]^-$ anion is rapidly converted to the trinuclear cluster anion $[HRu_3(CO)_{11}{}^-]$. In protic media the $[HFe(CO)_4]^-$ anion condenses to $[HFe_3(CO)_{11}]^-$, but at a markedly slower rate. Under water gas shift conditions, $[HFe(CO)_4]^-$ does not form ($[HFe_3(CO)_{11}]^-$. Instead, within a period of 24 h a catalytically inactive material is formed. In protic media $[HOs(CO)_4]^-$ slowly forms $[HOs_3(CO)_{11}]^-$. The $[HOs(CO)_4]^-$ anion is more active than $[HOs_3(CO)_{11}]^-$ for the catalysis of the water gas shift reaction.

Introduction

Minimal details have been reported concerning the abilities of mononuclear anions of the type $[HM(CO)_4]^-$ (M = Fe, Ru, Os) to form higher nuclearity cluster anions through self-condensation.[1-3] It is known, however, that these anions are stable in aprotic media and that $[HRu(CO)_4]^-$ is converted to $[HRu_3(CO)_{11}]^-$ in CH_3OH at 60 °C.[2] It is also known that the anion $[HFe(CO)_4]^-$ interconverts with $[HFe_3(CO)_{11}]^-$ in aqueous amine solutions in the

---

[1] Pearson, R. G.; Walker, H. W.; Mauermann, H.; Ford, P. C. *Inorg. Chem.* **1981**, *20*, 2741.

[2] Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179.

[3] Wada, F.; Matsuda, T. *J. Organomet. Chem.* **1973**, *61*, 365.

Table I. Conversion of $[HM(CO)_4]^-$ to $[HM_3(CO)_{11}]^-$ in Protic Media

solvent	metal	$([HM(CO)_4^-])^a$	temp, °C	min^b	products
HCl/THF	Ru	0.08	25	1.0	$[HRu_3(CO)_{11}]^-$, CO, H_2
	Fe	0.06	25	1800	$[HFe_3(CO)_{11}]^-$, CO, H_2
CH_3OH	Ru	0.16	25	1200	$[HRu_3(CO)_{11}]^-$, CO, H_2
CH_3OH/H_2O	Ru	0.13	25	0.3	$[HRu_3(CO)_{11}]^-$, CO, H_2
H_2O	Ru	0.10	0 → 5	0.3	$[HRu_3(CO)_{11}]^-$, CO, H_2
	Fe	0.15	25	600	$[HFe_3(CO)_{11}]^-$, CO, H_2
	Os	0.13	25	>5000	$H_2Os(CO)_4$, $[HOs_3(CO)_{11}]^-$, CO, H_2
H_2O/KOH	Ru	0.10	25	1.0	$[HRu_3(CO)_{11}^-]$, $[H_2Ru_4(CO)_{12}]^{2-}$, CO, H_2
water gas shift^c	Ru^d	0.03	0 → 100	2.0	$[HRu_3(CO)_{11}]^{-g}$
	Fe^e	0.03	0 → 100	800	Fe^{2+} species
	Os^f	0.03	0 → 100	1400	$[HOs_3(CO)_{11}]^-$

[a] mol/L. [b] Time for complete consumption of $[HM(CO)_4]^-$ to occur. [c] H_2O (0.35 mL); ethoxyethanol (3.0 mL); KOH (2.0 mmol); CO (5.0 mmol) 1 atm; 100 °C. [d] $[HRu(CO)_4]^-$ catalyst precursor. [e] $Fe_3(CO)_{12}$ catalyst precursor. [f] $[HOs(CO)_4]^-$ catalyst precursor. [g] If H_2 is removed continuously as it forms from the water gas shift reaction.[6]

presence of CO.[3] The stoichiometries of these reaction systems have not been reported. In the present study, we have determined the relative tendencies of the title mononuclear anions to self-condense in protic media and under water gas shift conditions. The stoichiometries of the condensation reactions have been determined. Since the possibility of mononuclear species existing in protic and in water gas shift catalytic systems[3-19] is a current consideration,[4,7] it was of interest to determine the likelihood of their survival under such conditions.

Results and Discussion

Ruthenium Anions. In the presence of protic media, $K[HRu(CO)_4]$ was converted to $K[HRu_3(CO)_{11}]$.[1,2] Results are summarized in Table I. A mixture of anhydrous HCl and $K[HRu(CO)_4]$ in THF in the molar ratio of 2:3 reacted within minutes according to eq 1.[20] Hydrogen and carbon

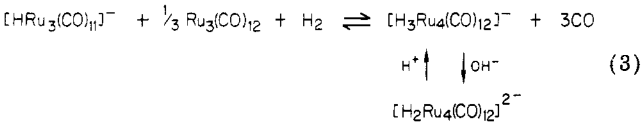
$$3K[HRu(CO)_4] + 2HCl \xrightarrow{25\ °C} K[HRu_3(CO)_{11}] + 2H_2 + CO + 2KCl \quad (1)$$

monoxide were produced quantitatively in a 2:1 molar ratio, and the reaction solution yielded spectroscopically pure $K[HRu_3(CO)_{11}]$ which was isolated in 92% yield. Two protons were required for the quantitative conversion of $K[HRu(CO)_4]$ to $K[HRu_3(CO)_{11}]$. When the molar ratio of reactants employed was less than 2:3 HCl/$K[HRu(CO)_4]$, incomplete reaction was observed.

In H_2O, the condensation reaction proceeded to completion in 20 s according to eq 2. The reaction was slightly retarded in basic KOH (5.6 M) solution. In anhydrous methanol at 25 °C, the reaction proceeded very slowly but in an alcohol/water (3:2) mixture it proceeded nearly as rapidly as in pure H_2O.

$$3K[HRu(CO)_4] + 2H_2O \rightarrow K[HRu_3(CO)_{11}] + CO + 2H_2 + 2KOH \quad (2)$$

Under water gas shift conditions (Table I) $K[HRu(CO)_4]$ did not survive in detectable concentration in the temperature range studied (0–100 °C). It was rapidly transformed into $K[HRu_3(CO)_{11}]$. In the presence of the H_2 that was formed in the reaction, this $K[HRu_3(CO)_{11}]$ was slowly converted[6] to the tetranuclear anion $K_2[H_2Ru_4(CO)_{12}]$ (eq 3).



$$\begin{tikzcd}[HRu_3(CO)_{11}]^- + \frac{1}{3}Ru_3(CO)_{12} + H_2 \arrow[r, shift left, ""] & \arrow[l, shift left] [H_3Ru_4(CO)_{12}]^- + 3CO \arrow[d, shift left, "OH^-"] \\ & {[H_2Ru_4(CO)_{12}]^{2-}} \arrow[u, shift left, "H^+"] \end{tikzcd} \quad (3)$$

These results show that under a variety of conditions in protic media, $[HRu(CO)_4]^-$ is unstable with respect to forming $[HRu_3(CO)_{11}]^-$. Clearly, this makes difficult the observation of $[HRu(CO)_4]^-$ in aqueous catalytic systems. The only hope of observing it would be if a sufficiently high CO pressure could be achieved to force significant fragmentation of $[HRu_3(CO)_{11}^-]$. Two types of fragmentation can be envisioned. One would be the reverse of reaction 2. This would require H_2 as well as CO plus a base to absorb the protons formed. However, as pointed out above, $[HRu_3(CO)_{11}]^-$ forms tetranuclear clusters when H_2 is present.[6] Thus, in the presence of H_2, a competing process could minimize the possibility of forming $[HRu(CO)_4]^-$. A second type of fragmentation that might occur in the presence of CO would produce $[HRu(CO)_4]^-$ and $Ru(CO)_5$ as products (reaction 4). This second type of

$$[HRu_3(CO)_{11}]^- + 3CO \rightarrow [HRu(CO)_4^-] + 2Ru(CO)_5 \quad (4)$$

fragmentation could occur in aprotic media and has been observed for the analogous iron system.[4] However, attempts to fragment $[HRu_3(CO)_{11}]^-$ in protic or aprotic media under high CO pressures have been unsuccessful.[4,33] Therefore, under the conditions employed in the low-pressure catalysis of the water gas shift reaction (100 °C, 1 atm CO), it is unlikely that $[HRu(CO)_4]^-$ is an important intermediate.[6,18,25]

Reaction 2 probably occurs through the following sequence of steps:[2]

$$[HRu(CO)_4]^- + H_2O \rightleftarrows H_2Ru(CO)_4 + OH^- \quad (5a)$$

$$2H_2Ru(CO)_4 + [HRu(CO)_4]^- \rightleftarrows [HRu_3(CO)_{11}]^- + CO + 2H_2 \quad (5b)$$

In the first step (5a) $[HRu(CO)_4]^-$ is protonated to give $H_2Ru(CO)_4$. As the $H_2Ru(CO)_4$ is formed, it undergoes rapid reaction (5b) with remaining $[HRu(CO)_4]^-$ to yield

---

(4) Dombek, B. D.; Harrison, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 2485.
(5) Dombek, B. D. *J. Am. Chem. Soc.* **1981**, *103*, 6508.
(6) Bricker, J. C.; Nagel, C. C.; Shore, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1444.
(7) Dombek, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855.
(8) Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419.
(9) King, R. B.; King, A. D.; Tanaka, K. *J. Mol. Catal.* **1981**, *10*, 75.
(10) Suss-Fink, G.; Reiner, J. *J. Mol. Catal.* **1982**, *16*, 231.
(11) Markó, L.; Palagyi, J. *J. Organomet. Chem.* **1982**, *236*, 343.
(12) Kang, H.; Maudlin, C. H.; Cole, T.; Sleigeir, W.; Cann, K.; Pettit, R. *J. Am. Chem. Soc.* **1977**, *99*, 8323.
(13) Pettit, R.; Maudlin, C.; Cole, T.; Kang, H. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 151.
(14) Laine, R. M. *J. Am. Chem. Soc.* **1978**, *100*, 6451.
(15) Cann, K.; Cole, T.; Slegeir, W.; Pettit, R. *J. Am. Chem. Soc.* **1978**, *100*, 3968.
(16) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685.
(17) Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959.
(18) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31 and references therein.
(19) Whyman, R. "Abstract", Report on the Anglo-American Seminar, "The Chemistry of the Reaction of Carbon Monoxide with Hydrogen"; Robinson College: Cambridge, Sept 9–12, 1981.
(20) Reaction 1 fully supports the proposed stoichiometry for the reaction between $[HRu(CO)_4]^-$ and $[CpRe(CO)_2(NO)]^+$ discussed in ref 4.

$[HRu_3(CO)_{11}]^-$. Each step in the proposed sequence has been demonstrated. The protonation of $[HRu(CO)_4]^-$ to generate $H_2Ru(CO)_4$ was demonstrated earlier.[21] We have shown the second step to be feasible by adding $H_2Ru(CO)_4$ to $K[HRu(CO)_4]$ in THF. This resulted in the rapid formation of $[HRu_3(CO)_{11}]^-$ and CO and H_2. The combination of steps 5a and 5b gives the stoichiometry observed in eq 2.

A less likely pathway for the formation of $[HRu_3(CO)_{11}]^-$ in reaction 2 would involve formation of $H_2Ru(CO)_4$ (eq 5a) followed by thermal decomposition of $H_2Ru(CO)_4$ to form $H_2Ru_3(CO)_{12}$ (reaction 6).[22] The $H_2Ru_3(CO)_{12}$ formed in this manner could be deprotonated by the hydroxide ion generated in (5a) to form $[HRu_3(CO)_{11}]^-$ (reaction 7).[23] Although we find that $H_2Ru(CO)_4$ will form $H_2Ru_3(CO)_{12}$, according to reaction 6, $H_2Ru_3(CO)_{12}$ is not deprotonated sufficiently rapidly by hydroxide ion (studied in the range of 0.07–5.6 M $[OH^-]$) to contribute significantly to the formation of $[HRu_3(CO)_{11}]^-$ in the condensation reactions considered above.

$$3H_2Ru(CO)_4 \rightarrow H_2Ru_3(CO)_{12} + 2H_2 \qquad (6)$$

$$H_2Ru_3(CO)_{12} + OH^- \rightarrow [HRu_3(CO)_{11}]^- + CO + H_2O \qquad (7)$$

Iron Anions. Reactions of $K[HFe(CO)_4]$ with anhydrous HCl in THF and H_2O (equations 8 and 9) are analogous to the reactions of $K[HRu(CO)_4]$ (eq 1 and 2). Results are summarized in Table I. However, the rate of transformation of $K[HFe(CO)_4]$ to $K[HFe_3(CO)_{11}]$ is markedly slower than in the ruthenium system (Table I). This is probably due to the fact that $K[HRu(CO)_4]$ is much more basic[2] than $K[HFe(CO)_4]$. Furthermore, $K[HFe_3(CO)_{11}]$ is very susceptible to fragmentation under CO pressure compared to $K[HRu_3(CO)_{11}]$.[3,4] We find that in the presence of a large excess (12:1) of CO (1 atm) in THF at 25 °C, $K[HFe_3(CO)_{11}]$ (0.1 M) is converted quantitatively to $K[HFe(CO)_4]$ and $Fe(CO)_5$ over a period of 10 h. This result shows that fragmentation of $K[HFe_3(CO)_{11}]$ will occur even under much less severe conditions than previously reported.[3,4]

$$3K[HFe(CO)_4] + 2HCl \xrightarrow[25\ ^\circ C]{THF} K[HFe_3(CO)_{11}] + 2H_2 + CO + 2KCl \qquad (8)$$

$$3K[HFe(CO)_4] + 2H_2O \xrightarrow{25\ ^\circ C} K[HFe_3(CO)_{11}] + 2H_2 + CO + 2KOH \qquad (9)$$

Under water gas shift conditions (Table I) at 100 °C and 1 atm CO pressure, $K[HFe_3(CO)_{11}]$ is completely converted to $K[HFe(CO)_4]$ (~6 h) which, in accord with earlier observations,[24] decomposes to insoluble, inactive Fe^{II} species. Thus we find that after a period of 1 day, catalytic activity for the water gas shift has ceased. Even under very mild conditions, the trinuclear iron system is converted to mononuclear species which, in turn, are not active at low CO pressures. A previous report[25] for water gas shift catalysis using $Fe_3(CO)_{12}$ as a catalyst precursor under relatively high CO pressure (75 atm) undoubtedly involved formation of the mononuclear anion $[HFe(CO)_4^-]$. In this case, the system showed activity because of the high CO pressure. It has been shown[24] that $[HFe(CO)_4]^-$ is active at high CO pressures but deactivates at low CO pressure as indicated above.

Osmium Anions. The reaction of $K[HOs(CO)_4]$ with H_2O (25 °C) resulted in evolution of only 0.01 equiv of noncondensable gas (Table I), suggesting that conversion to higher nuclearity species had not occurred. This was confirmed by ^1H NMR spectra which indicated that $H_2Os(CO)_4$ (86%) and $K[HOs(CO)_4]$ (14%) were in solution after 3 days at 25 °C. Only after extended periods of time (~7 days) was $[HOs_3(CO)_{11}]^-$ present in detectable concentration (~10%). Under water gas shift conditions (Table I) employing $Os_3(CO)_{12}$ as a catalyst precursor, $[HOs_3(CO)_{11}]^-$ was the only species detectable by ^1H NMR spectra.

When $[HOs(CO)_4]^-$ was employed as a water gas shift catalyst precursor, the activity observed after 24 h was 4 times greater than that observed when $Os_3(CO)_{12}$ was used as the catalyst precursor under identical conditions. In either case, however, the major species present after 1 day was the $[HOs_3(CO)_{11}]^-$ anion. Once formed under water gas shift conditions, the $[HOs_3(CO)_{11}]^-$ is apparently stable. It has not been observed to fragment to $[HOs(CO)_4]^-$ under 1 atm CO pressure in THF or under water gas shift conditions.

Experimental Section

Materials. $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ were used as obtained from Strem. Chemical Co. $Fe(CO)_5$ (Alpha-Ventron) was purified prior to use by trap to trap distillation on a vacuum line. Potassium (Mallinckrodt) was washed with hexane in a N_2 filled glovebox and stored under N_2. Potassium hydride (Alfa-Ventron) in a 50% mineral oil suspension was washed repeatedly with dry hexane to remove the oil and then stored under dry nitrogen. 2-Ethoxyethanol (Aldrich) was distilled from and stored over Mg turnings. Anhydrous HCl (gas) (Matheson) was purified by fractionation through successive U traps at −111 and −126 °C and stored in a bulb with a Kontes stopcock at −196 °C. Reagent grade methanol (MCB) was dried over molecular sieve 3A and then distilled from Mg turnings. Tetrahydrofuran was distilled from sodium benzophenone ketyl prior to use. $K[HFe(CO)_4]$,[26] $K[HRu(CO)_4]$,[27] $K[HOs(CO)_4]$,[28,29] $K[HRu_3(CO)_{11}]$,[30] and $K[HOs_3(CO)_{11}]$[31] were prepared by minor modification of literature procedures.

Apparatus. All manipulations were carried out on a standard high vacuum line or in a glovebox under an atmosphere of dry, pure nitrogen.[32] Analyses of all gas mixtures were carried out

---

(21) Cotton, J. D.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2162.

(22) The thermal decomposition of $H_2Ru(CO)_4$ has been suggested[21] to yield $H_2Ru_3(CO)_{12}$. We have found this to be the case. An improved preparation of $H_2Ru_3(CO)_{12}$ and its properties are described by: Bricker, J. C. Ph.D. Thesis, The Ohio State University, 1983.

(23) Reaction 7 was considered based on the stoichiometry of the following deprotonation reaction which has been observed.

$$H_2Ru_3(CO)_{12} + KH \xrightarrow[25 ^\circ C]{THF} K[HRu_3(CO)_{11}] + CO + H_2$$

(24) King, A. D.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 1028.

(25) Ford, P. C.; Ungermann, C.; Landis, V.; Moya, S. A.; Rinker, R. G; Laine, R. M. *Adv. Chem. Ser.* **1979**, *No. 173*, 81.

(26) Medford, G. Ph.D. dissertation, The Ohio State University, Columbus, OH, 1978.

(27) Walker, H. W.; Ford, P. C. *J. Organomet. Chem.* **1981**, *214*, C43.

(28) George, R. D.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 972.

(29) Collman, J. P.; Murphy, D. W.; Fleischer, E. B.; Swift, D. *Inorg. Chem.* **1974**, *13*, 1.

(30) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Süss, G. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1356.

(31) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C. *J. Chem. Soc., Dalton Trans.* **1978**, 1358.

(32) Shriver, D. F. "The Manipulation of Air Sensitive Compounds"; McGraw-Hill: New York, 1969.

on an AEI MS10 mass spectrometer calibrated for H_2/CO mixtures. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer using matched 0.1-mm KBr liquid cells. Proton NMR were recorded on a Varian EL 390 NMR spectrometer. Chemical shifts for ^{1}H NMR were referenced to Me_4Si, 0.00 ppm.

Conversion of $[HM(CO)_4]^-$ to $[HM_3(CO)_{11}]^-$ (M = Fe, Ru, Os). The following procedures for the ruthenium system are essentially identical with those used for the iron and osmium systems. Therefore, these two are not described here. Differences in reactivity patterns are discussed in the text.

$K[HRu(CO)_4]$ to $K[HRu_3(CO)_{11}]$ Using (a) HCl. In a nitrogen glovebox, 63.3 mg (0.250 mmol) of $K[HRu(CO)_4]$ was weighed in a reaction vessel. After it was degassed, 3–4 mL of THF was distilled onto the solid at −78 °C. The vessel was kept at −196 °C, and 0.418 mmol of anhydrous HCl was condensed into the vessel. Upon slow warming of the mixture to room temperature, a rapid (~1 min) reaction took place. The THF solution turned deep red, and H_2 and CO gas were evolved. After 1.0 min at 25 °C, 0.254 mmol of noncondensable gas was given off (Anal. 66% H_2, 34% CO). This result corresponded to 2.0 equiv of hydrogen and 1.0 equiv of carbon monoxide evolved per 3.0 equiv of $K[HRu(CO)_4]$ consumed. The infrared spectrum of the reaction solution indicated that $K[HRu_3(CO)_{11}]$ of very high purity was formed. [IR (THF): 2075 (vw), 2018 (vs), 1985 (vs), 1948 (m), 1730 (w), 1680 (w) cm^{-1}]. Isolation of $K[HRu_3(CO)_{11}]$ yielded 50 mg (92%) of product. In a second experiment, 97.5 mg (0.385 mmol) of $K[HRu(CO)_4]$ and 0.571 mmol of anhydrous HCl were reacted under less than stoichiometric conditions in which insufficient HCl was available (3:1.76). Gas evolution was less than stoichiometric according to eq 1, and the solution consisted of a mixture of $K[HRu(CO)_4]$ and $K[HRu_3(CO)_{11}]$.

(b) CH_3OH. In a nitrogen-filled glovebox, 63.4 mg (0.251 mmol) of $K[HRu(CO)_4]$ was weighed and placed in an NMR tube. Approximately 1.5 mL of dry CH_3OH was condensed onto the $K[HRu(CO)_4]$ at −78 °C, and the NMR tube was sealed off under vacuum at −196 °C. The sample was allowed to warm to room temperature, and proton NMR spectra were observed as a function of time. Initially the major component (>95%) was $K[HRu(CO)_4]$ (18.5 τ). With time, the solution changed from yellow to red in color and the signal due to $K[HRu(CO)_{11}]$ grew in intensity while that for $K[HRu(CO)_4]$ decreased. After 14 h at 25 °C, the ratio of $K[HRu(CO)_4]$ to $K[HRu_3(CO)_{11}]$ was 1:2.

(c) CH_3OH/H_2O. The above reaction was repeated identically with the exception that 1.0 mL of H_2O (pH 7.0) was added to the methanol solution of $K[HRu(CO)_4]$. A rapid (~20 s) conversion to $K[HRu_3(CO)_{11}]$ occurred. One atmosphere of CO pressure had no observable effect on the conversion of $K[HRu(CO)_4]$ to $K[HRu_3(CO)_{11}]$ in anhydrous methanol or in a methanol/water (3:2) mixture.

In a number of experiments, H_2O was added directly to $K[HRu(CO)_4]$. The reaction was so vigorous that substantial $H_2Ru(CO)_4$ was formed which underwent some thermal decomposition to produce $H_2Ru_3(CO)_{12}$. Consequently, gas evolution was somewhat less than expected (88%). $K[HRu_3(CO)_{11}]$ was the only soluble metal carbonyl product. No $K[HRu(CO)_4]$ was detected by ^{1}H NMR in any of the above reactions which contained H_2O.

(d) Ethoxyethanol/H_2O/KOH. In a N_2 filled glovebox, 63.3 mg (0.250 mmol) of $K[HRu(CO)_4]$ was weighed into an NMR tube. An adapter containing 2 mL of 5.6 M aqueous KOH solution and 1 mL of ethoxyethanol was attached. The solution was tipped into the NMR tube at −78 °C which was sealed off at −196 °C. The NMR spectra were recorded as a function of time at 25 °C. These proton spectra showed that the $K[HRu(CO)_4]$ was transformed into $K[HRu_3(CO)_{11}]$ over a period of less than 2 min. After 5 min at 25 °C, the ^{1}H NMR spectrum indicated that the solution consisted of primarily $[HRu_3(CO)_{11}^-]$ (80%), and $[H_2Ru_4(CO)_{12}]^{2-}$ (20%). No $K[HRu(CO)_4^-]$ was observed. This experiment was repeated under 1 atm CO pressure (0.41 mmol) under otherwise identical conditions. No observable difference in the rate of conversion from mononuclear to trinuclear species was observed by ^{1}H NMR.

Water Gas Shift Catalysis. Reactions employing $Fe_3(CO)_{12}$, $K[HOs(CO)_4]$, $Ru_3(CO)_{12}$, $K[HRu(CO)_4]$, and $Os_3(CO)_{12}$ as catalyst precursors were all carried out by using the same procedure. In a 120-mL reaction vessel, 0.04 mmol of metal carbonyl was weighed and 3.0 mL of ethoxyethanol was added. The mixture was cooled to −78 °C, and under a flow of N_2, 2.0 mmol of KOH and 0.36 mL of H_2O were added. The resulting mixture was degassed, and CO pressure (~1 atm) was added at −78 °C. The solution was stirred at 100 °C and was monitored by ^{1}H NMR samples taken at regular intervals (every 4 h for the first 24 h and, thereafter, once every 24 h). The activity of the system was monitored by mass spectral analysis of the gas collected on a vacuum line by use of a Toepler pump. In a number of experiments, continuous removal of H_2 as it formed in the water gas shift reaction was achieved with a Pd thimble.[6]

Acknowledgment. This work was supported by the National Science Foundation through Grant No. CHE 79-18148.

Registry No. $K[HFe(CO)_4]$, 17857-24-8; $K[HRu(CO)_4]$, 87869-41-8; $K[HOs(CO)_4]$, 80462-68-6; $K[HFe_3(CO)_{11}]$, 87145-35-5; $K[HRu_3(CO)_{11}]$, 80662-65-3; $K[HOs_3(CO)_{11}]$, 87869-42-9; $H_2Os(CO)_4$, 22372-70-9; $[H_2Ru_4(CO)_{12}]^{2-}$, 67430-39-1; $Fe_3(CO)_{12}$, 17685-52-8; $Os_3(CO)_{12}$, 15696-40-9.

---

(33) We attempted to study the reaction

$$[HM(CO)_4]^- + 2M(CO)_5 \xrightarrow[25\,°C]{THF} [HM_3(CO)_{11}]^- + 3CO$$

the reverse of reaction 4. With M = Fe, an equilibrium was observed that could be shifted to the right or left by removing or adding CO. With M = Ru, the reaction was complex, giving $[HRu_3(CO)_{11}]^-$ and $[H_2Ru_4(CO)_{12}]^-$ as major products plus small amounts of $[HRu_4(CO)_{13}]^-$ plus $[H_3Ru_4(CO)_{12}]^-$. With M = Os, $[HOs(CO)_4]^-$ was presented after 48 h plus small amounts of unidentified products.