CHEMISTRY LETTERS, pp. 39-42, 1986.

IN SITU GENERATION AND CHEMICAL REACTIVITIES OF $HRu(CO)_4^-$ RELEVANT TO THE REDUCTION OF CARBON MONOXIDE

Masato TANAKA,* Toshiyasu SAKAKURA, Teruyuki HAYASHI,
and Toshi-aki KOBAYASHI
National Chemical Laboratory for Industry,
Yatabe, Tsukuba, Ibaraki 305

$HRu(CO)_4^-$ could be *in situ* generated from $Ru_3(CO)_{12}$ in the presence of basic salts in amide solvents when exposed to syn gas. In the reduction of carbon monoxide, $HRu(CO)_4^-$ generating catalyst systems selectively gave methanol. $HRu(CO)_4^-$ exerted higher reactivities in the reduction of acetaldehyde and in the bimolecular reductive elimination with $CH_3COCo(CO)_3PPh_3$, as compared to $HRu_3(CO)_{11}^-$.

In view of the chemical feedstocks in the future, the methodologies for the reduction of carbon monoxide into fundamental oxygenated chemicals like acetaldehyde, ethanol, acetic acid, and/or ethylene glycol are highly desired, since syn gas can be produced from essentially any carbon source. Toward this goal, a number of homogeneous catalyst systems have been described, and ruthenium catalysts with halide promoters have received great attention.1) Although some of ruthenium-halide systems can efficiently reduce carbon monoxide, non-selective formation of a wide spectrum of products usually occurs. Dombek *et al.* have observed the presence of $Ru(CO)_3I_3^-$ and $HRu_3(CO)_{11}^-$ in the ruthenium-potassium iodide catalyzed reaction mixture,2) and proposed that the initial step of the CO reduction is the formation of a ruthenium-formyl species by a nucleophilic attack of $HRu(CO)_4^-$, derivable from $HRu_3(CO)_{11}^-$, to $Ru(CO)_4I_2$, which is in equilibrium with $Ru(CO)_3I_3^-$.3) However, $HRu(CO)_4^-$ has never been detected in the syn gas reaction. Moreover, although $HRu(CO)_4^-$ has been synthesized recently,4) its reactivity has been little studied due to the difficulty with which it is *in situ* generated.

In our research program for the synthesis of oxygenated compounds from syn gas, we have learned that $HRu(CO)_4^-$ is selectively generated *in situ* from $Ru_3(CO)_{12}$ and basic promoters under the CO reduction conditions, and that it possesses high reactivities in the reduction of aldehydes and in the bimolecular reductive elimination. Very recently, Hidai *et al.* have reported the bimolecular reductive elimination of an acylcobalt carbonyl complex with $HRu(CO)_4^-$, albeit without any comparison with the reduction of the former with molecular hydrogen.5) This paper prompted us to report our own results observed in the relevant area.

When a N-methylpyrrolidone solution of $Ru_3(CO)_{12}$ (0.1 mg-atom) and bis(triphenylphosphine)iminium acetate (PPNOAc, 0.5 mmol) was exposed to syn gas (500 atm) at 230 °C for 3 h, the resulting mixture exhibited two sets of IR absorption bands characteristic to $HRu_3(CO)_{11}^-$ (2018s, 1995s, and 1959m cm^{-1}) and $HRu(CO)_4^-$ (1934m and 1892s cm^{-1}). The latter was selectively generated in the presence of other basic additives such as alkali metal hydroxides, acetates, and carbonates. Fluorides of rubidium and cesium, which are known to be strongly basic, also cleanly afforded the complex, although potassium fluoride gave a mixture of the tri- and mononuclear hydride anions. The transformation into $HRu(CO)_4^-$ occurred in other amide solvents like N,N-dimethylformamide, N,N-dimethylacetamide, and N-isopropylpyrrolidone as well.

The outcome of the syn gas conversion in the presence of these $HRu(CO)_4^-$ generating catalyst systems is featured by the observation that methanol is formed as almost the sole product at the rate ca. 10 mol/g-atom(Ru)/h. Moreover, the activity for the methanol formation by other complex catalyst systems could be enhanced by combining the $HRu(CO)_4^-$ generating systems. For example, when $Ru_3(CO)_{12}$ (0.1 mg-atom) coupled with benzyl chloride (0.1 mmol) was treated with syn gas under the conditions of 500 atm and 230 °C for 3 h, the resulting mixture showed the $HRu_3(CO)_{11}^-$ formation, and methanol was formed at the rate 10.0 mol/g-atom(Ru)/h.6) On the other hand, when the reaction catalyzed by the Ru-$PhCH_2Cl$ system was effected in the presence of PPNOAc (0.5 mmol) as a second additive, methanol formation was greatly accelerated (41.6 mol/g-atom(Ru)/h).7) Both $HRu(CO)_4^-$ and $HRu_3(CO)_{11}^-$ were detected in the resulting mixture.

Dombek *et al.* have, based on the model reaction between $CpRe(NO)(CO)_2^+$ and $HRu(CO)_4^-$,8) pointed out the importance of $HRu(CO)_4^-$ as a reductant at the step of the formation of metal formyl species. In order to estimate the reduction ability

Table 1. Reduction of $CH_3COCo(CO)_3PPh_3$ at 35 °C in THF[a)]

$HRu(CO)_4^-$ or $HRu_3(CO)_{11}^-$	Atmosphere	Reaction time/h	Yield/% CH_3CHO	Yield/% CH_3CH_2OH
-	H_2 (150 atm)	3	20[b)]	56[b)]
-	H_2 + CO (1/1, 300 atm)	3	0	0
-	H_2 + CO (1/1, 300 atm)	21	3[c)]	0
PPN[$HRu(CO)_4$]	H_2 + CO (1/1, 300 atm)	3	4[c)]	0
PPN[$HRu(CO)_4$]	H_2 + CO (1/1, 300 atm)	21	32[c)]	0
PPN[$HRu(CO)_4$][d)]	N_2 (1 atm)	3	80[e)]	0
PPN[$HRu_3(CO)_{11}$][d)]	N_2 (1 atm)	3	0	0

a) $CH_3COCo(CO)_3PPh_3$ (0.2 mmol) was treated with 1.5 equiv. of the ruthenium hydrides in THF (6 cm^3). b) Estimated by GLC. c) Estimated by IR. d) CH_3CO-$Co(CO)_3PPh_3$ (0.075 mmol) was treated with 1.5 equiv. of the ruthenium hydride in THF (0.5 cm^3). e) Estimated by PMR.

of $HRu(CO)_4^-$ at the subsequent steps of the syn gas conversion, its reactivity in bimolecular reductive elimination with an acetylcobalt carbonyl complex, as a model for metal-formyl species, was compared with those of $HRu_3(CO)_{11}^-$ and molecular hydrogen. The results are summarized in Table 1. The reduction, which was fast under pure hydrogen, was heavily suppressed by carbon monoxide. However, the reduction did proceed even under pressurized syn gas when effected in the presence of $HRu(CO)_4^-$. As was also observed by Hidai *et al.*, $HRu_3(CO)_{11}^-$ exhibited much lower reactivity than $HRu(CO)_4^-$ in the bimolecular reductive elimination.[9)]

$HRu(CO)_4^-$ showed a high reactivity also in the reduction of aldehydes: acetaldehyde (20 mmol) in N-isopropylpyrrolidone (10 cm^3) was heated at 180 °C under 445 atm of syn gas (H_2/CO = 1/1) for 3 h. The reaction in the presence of PPN[$HRu(CO)_4$] (0.1 mmol) afforded ethanol (9.4 mmol), butyraldehyde (0.7 mmol), and butanol (0.9 mmol), while more than 90% of acetaldehyde was recovered when PPN[$HRu_3(CO)_{11}$] (0.1 mmol) was used as the catalyst.

These results described above seem to indicate the high reduction ability also at the steps subsequent to the formyl species formation. The main path of the methanol formation from syn gas in the presence of $HRu(CO)_4^-$ generating systems could be:

$$\mathrm{Ru\text{-}CO} \xrightarrow{\mathrm{HRu(CO)_4^-}} \mathrm{Ru\text{-}CHO} \xrightarrow{\mathrm{HRu(CO)_4^-}} \mathrm{HCHO} \xrightarrow{\mathrm{HRu(CO)_4^-}} \mathrm{CH_3OH}$$

The high methanol selectivity may be due to the high reduction ability of $HRu(CO)_4^-$ toward formaldehyde which could have been transformed into other oxygenates when the reaction was effected in the presence of other type of catalyst systems.

Studies on the reductive reactivities of $HRu(CO)_4^-$ and on the bimolecular reductive elimination are further in progress.

This work is a part of "C_1 Chemistry Project", a National Research and Development Program of Agency of Industrial Science and Technology, Ministry of International Trade and Industry (M.I.T.I.), Japan.

References

1) B. D. Dombek, Adv. Catal., 32, 325 (1983).
2) B. K. Warren and B. D. Dombek, J. Catal., 79, 334 (1983).
3) B. D. Dombek, J. Organomet. Chem., 250, 467 (1983).
4) H. W. Walker and P. C. Ford, J. Organomet. Chem., 214, C43 (1981).
5) Y. Koyasu, A. Fukuoka, Y. Uchida, and M. Hidai, Chem. Lett., 1985, 1083.
6) M. Tanaka, T. Hayashi, T. Kobayashi, T. Sakakura, and Y. Kawabata, Jpn. Pat. Appl., Jpn. 59-127216.
7) Similar acceleration of methanol formation was also observed by Dr. K. Wada and his coworkers (Mitsubishi Chemical Industries, Ltd.). We thank them for sharing their results with us prior to publication and for stimulative discussions.
8) B. D. Dombek and A. M. Harrison, J. Am. Chem. Soc., 105, 2485 (1983).
9) PPN[$HRu(CO)_4$] and PPN[$HRu_3(CO)_{11}$] were prepared according to the literatures (refs. 4 and 10). Found for the former: C, 63.81; H, 4.08; N, 1.86%. Calcd for $C_{40}H_{31}NO_4P_2Ru$: C, 63.83; H, 4.15; N, 1.86%. Found for the latter: C, 48.95; H, 2.87; N, 1.20%. Calcd for $C_{47}H_{31}NO_{11}P_2Ru_3$: C, 49.05; H, 2.71; N, 1.22%.
10) B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. Süss, J. Chem. Soc., Dalton Trans., 1979, 1356.

(Received October 12, 1985)