August, 1989] © 1989 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 62, 2709—2710 (1989) 2709

Cluster Chemistry. Catalytic Behavior of $[H_2Ru_4(CO)_{12}]^{2-}$ in Reduction of Benzaldehyde and Nitrobenzene

Fumio WADA,* Masanori SHIMUTA, and Tsutomu MATSUDA
Department of Organic Syntheses, Faculty of Engineering,
Kyushu University, Hakozaki, Fukuoka 812

(Received January 26, 1989)

Synopsis. The dianion, $[H_2Ru_4(CO)_{12}]^{2-}$, showed excellent catalytic activity for the reduction of nitrobenzene, but not of benzaldehyde. In the presence of benzaldehyde under H_2 pressure, the dianion was converted to a new species of good catalytic activity, which is closely similar to a complex obtained from the reaction of $[H_2Ru_6(CO)_{18}]$ with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene).

We previously reported that the reaction of $[HRu_3(CO)_{11}]^-$ (**I**) with DBU under H_2 pressure gave $[H_2Ru_4(CO)_{12}]^{2-}$ (**II**), which can act as a catalyst for the water gas shift reaction.[1a)] Although the catalytic behavior of **I** has been studied in various reactions,[2)] very little is known about that of **II**. In this paper we report on the catalytic activity of the dianion **II** in the reduction of benzaldehyde and nitrobenzene, compared with those of monoanionic hydrido ruthenium clusters, such as **I** and $[H_3Ru_4(CO)_{12}]^-$ (**III**). We also describe the formation of a new active catalyst from **II** (or $[H_2Ru_6(CO)_{18}]$ with DBU) in the benzaldehyde reduction.

Results and Discussion

The hydrido clusters (**I**, **II**, and **III**) used in this study are interconvertible, depending upon both the ratio of CO/H_2 under pressure of 10—30 kg cm^{-2} and the type of base used.[1b)] Thus, reduction using these clusters must be carried out under conditions where only a desired anionic cluster acts as the main catalyst, as shown in Table 1.

Moreover, the substrates were shown to affect the interconversion. In the presence of benzaldehyde (or nitrobenzene), **II** was transformed into species **IV**, which can be prepared by a reaction of $[H_2Ru_6(CO)_{18}]$ with DBU; however, **II** in the presence of nitrobenzene was converted to an insoluble higher unclear cluster(s) under pure hydrogen pressure (20 kg cm^{-2}). Runs 2, 6, and 7 in Table 1, therefore, were carried out under hydrogen containing 10% of CO in order to prevent any transformation of **II** during reduction.

The complex **III** prepared from $[H_4Ru_4(CO)_{12}]$ and NEt_3 was stable, even in the presence of benzaldehyde under pure H_2 pressure.

Table 1 shows the results of the reduction together with the anionic hydrido clusters existing in each reaction system before and after reaction. The structures of these clusters were confirmed by a comparison of their IR spectra with those of authentic samples.[1)] As can be seen in Table 1, the catalytic activity of **I** for benzaldehyde reduction was low (comparable to the result reported by Laine[2)]), whereas **II** and **III** showed moderate activity (Runs 2 and 3, respectively). When benzaldehyde reduction with **II** was carried out under pure H_2 pressure (Run 1), **II** was easily changed to another species **IV** during the reduction, and a much higher conversion of benzaldehyde was observed, suggesting the increased catalytic activity of **IV**. Figure 1a shows the IR spectra of **IV** and complex **V** prepared in situ from $[H_2Ru_6(CO)_{18}]$ and DBU in methanol. Complex **V** is not the same as the known complex $[HRu_6(CO)_{18}]^-$ prepared by protonation of $[Ru_6(CO)_{18}]^{2-}$.[4)] The ^{1}H NMR spectrum of **V** in CD_3OD shows two kinds of proton resonances at τ=29.3 (H_a) and 29.5 (H_b), and the intensity ratio of H_a/H_b is almost 1 : 1. At present, it is not yet clear whether species **V** is a single species or a mixture of two complexes. In view of the close similarity of complexes **IV** to **V** regarding their IR spectra, the catalytic activity of **V** was examined for benzaldehyde reduction. As expected, the result was comparable

Table 1. Hydrogenation of Organic Compounds Catalyzed by Anionic Hydrido Ruthenium Clusters[a)]

Run	Reactant	$P_{H_2}:P_{CO}$ (kg cm^{-2})	Convn. (%)	Prod.	Selectivity (%)	Anionic species[b)] (by IR)
	C_6H_5CHO			$C_6H_5CH_2OH$		
1		20/0	91		89	IV[c)]
2		18/2	37		80	$[H_2Ru_4(CO)_{12}]^{2-}$
3		0/20[d)]	7		6	$[HRu_3(CO)_{11}]^-$
4		20/0[e)]	27		75	$[H_3Ru_4(CO)_{12}]^-$
5		20/0[f)]	100		89	V
	$C_6H_5NO_2$			$C_6H_5NH_2$		
6		19/1	93		100	$[H_2Ru_4(CO)_{12}]^{2-}$
7		18/2	92		94	$[H_2Ru_4(CO)_{12}]^{2-}$

a) Catalyst, 0.05 mmol; DBU, 0.5 ml; MeOH, 4.0 ml; substrate, 5.0 mmol; total pressure=20 kg cm^{-2}; 120±1 °C, 3 h. b) The existence of these anionic clusters was confirmed by IR except Run 1. c) The starting complex was **II**. d) NEt_3 and H_2O were used instead of DBU. e) NEt_3 instead of DBU was used. f) The starting complex was **V**.

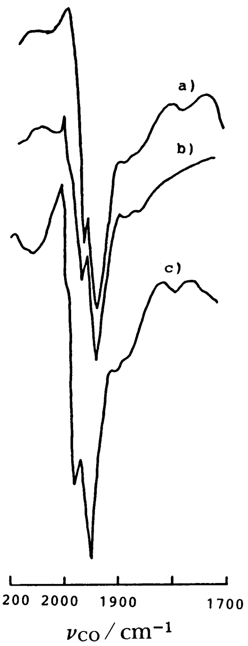

Fig. 1. IR spectrum in ν_{CO} region of the catalyst components after hydrogenation of benzaldehyde. a) **II** was used as a precursor under H_2 presure; b) the species **V** before reduction; c) after the reduction with **V**.

to that of **IV** (see Run 5), and the IR spectrum of the catalyst component in the ν_{CO} region shows that the starting complex **V** remains unchanged after reduction (see Fig. 1b and c). Unfortunately, many attempts to isolate **IV** have not yet been successful.

At present it is difficult to explain why species **IV** (or **V**) is so active for benzaldehyde reduction compared with other hydrido clusters, since the reactivity of the hydrogen atom in hydrido clusters does not always correspond to the hydridic character predicted from ^{1}H NMR.[5] A more detailed study is necessary in order to clarify the reactivity of **IV** (or **V**).

As mentioned above, the known anionic hydrido clusters (**I**, **II**, and **III**) are not good catalysts for benzaldehyde. The dianion **II**, however, acts as an excellent catalyst for nitrobenzene (Runs 6 and 7) under the same conditions (Run 2).[6] In the case of nitrobenzene reduction under pure H_2 pressure, **II** was readily converted not to **IV** but to higher nuclear cluster(s) which can be changed to **I** under CO pressure. This result suggests that the catalytic behavior of **II** in nitrobenzene reduction would be different from that of **II** in benzaldehyde reduction.

Experimental

The solvents and reagents used in this study were purified by distillation or recrystallization before use under N_2. All operations were carried out under a nitrogen atmosphere.

The typical reaction procedure was as follows. A catalyst solution (MeOH, 4 ml) containing only the desired anionic hydrido cluster (0.05 mmol) was previously prepared according to the methods described in the literature.[1] The catalyst solution (4 ml), benzaldehyde (or nitrobenzene) (5.0 mmol), and cyclohexanol (15 mmol) as an internal standard were placed in a 30 ml autoclave. Nitrogen in the autoclave was flushed three times with H_2, and then 20 kg cm^{-2} of H_2 (or a mixture of H_2 and CO) was charged. After the reaction at 120±1 °C for 3 h, the products were analyzed by GLC and the anionic clusters in the reaction mixture were identified by comparison of their IR spectra with those of authentic samples.[1]

References

1) a) F. Wada, M. Shimuta, and T. Matsuda, *Nippon Kagaku Kaishi*, **1985**, 503, and references cited therein; b) F. Wada, M. Shimuta, T. Goto, T. Ikeda, K. Kikukawa, and T. Matsuda, *Chem. Lett.*, **1983**, 1987; c) C. Ungerman, V. Landis, S. A. Moya, H. Cohen, M. Walker, R. G. Pearson, R. G. Rinker, and P. C. Ford, *J. Am. Chem. Soc.*, **101**, 5922 (1979) and references cited therein.

2) a) W. J. Thomson and R. M. Laine, "Catalytic Activation of Carbon Monoxide—ACS Symposium Series 152," ed by P. C. Ford, ACS, Washington (1981), p. 133. Turnover frequency moles of product/(mole of catalyst)(h) of $[HRu_3(CO)_{11}]^-$ is 9 at 125 °C for 1 h. b) R. A. Sheldon, "Chemicals from synthesis gas," D. Reidel Publishing Company, Holland (1983), p. 167.

3) C. C. Nagel and S. G. Shore, *J. Chem. Soc., Chem. Commun.*, **1980**, 530: ^{1}H NMR data for anionic hydrido ruthenium carbonyl clusters used here are as follows $[HRu_3(CO)_{11}]^-$, τ=25.8 ppm; $[H_3Ru_4(CO)_{12}]^-$, τ=27.0 ppm; $[H_2Ru_4(CO)_{12}]^{2-}$, τ=29.3 ppm.

4) C. R. Eady, B. F. G. Johnson, J. Leuies, M. C. Malatesta, P. Machis, and M. Mcpartlin, *J. Chem. Soc., Chem. Commun.*, **1976**, 945.

5) P. Chini, S. Martinengo, and G. Giordano, *Gazz. Chim. Ital.*, **102**, 330 (1972), For example, ^{1}H NMR of $[HRh_6(CO)_{15}]^-$ shows at τ=22.3 ppm, but the complex is active for benzaldehyde reduction (turnover frequency$^{2a)}$= 105±10 at 125 °C, for 1 h).

6) $[HRu_3(CO)_{11}]^-$ and $[H_3Ru_4(CO)_{12}]^-$ were less effective, compared with $[H_2Ru_4(CO)_{12}]^-$. $[HRu_3(CO)_{11}]^-$: conv. 94%, Select. 84%.; $[H_3Ru_4(CO)_{12}]^-$: conv. 89%, Select. 82%.