Direct Observation of Unusual CO Insertion on a New SiO_2-attached Rh Dimer Catalyst by FTIR

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The behaviour of a new surface Rh dimer, prepared by attachment of *trans*-[{Rh(C_5Me_5)Me}$_2$(μ-CH_2)$_2$] on SiO_2 in three elementary reaction steps related to ethene hydroformylation, was observed by FTIR which revealed metal-assisted reversible insertion of adsorbed CO into an alkyl group, unlike Rh monomers.

Silica-supported rhodium catalysts are known to be good catalysts for selective production of C_2-oxygenated compounds from syngas at high pressures,[1] while Rh-monomer complexes have been used as hydroformylation catalysts in homogeneous systems.[2] The CO insertion reaction is a key step in these reactions, but there are few reports of its direct observation by spectroscopic methods in heterogeneous systems,[3] although there are several instances of spectroscopically detected CO insertion reactions in homogeneous systems.[4—8] We report a new aspect of reversible CO insertion on a new Rh dimer catalyst which showed good catalytic activity for ethene hydroformylation.

The SiO_2-attached Rh dimers (1—2 wt%) were prepared by the reaction of *trans*-[{Rh(C_5Me_5)Me}$_2$(μ-CH_2)$_2$][9] with surface OH groups of SiO_2 (Aerosil 300) pretreated at 673 K. Distilled pentane or deuteriated benzene (Aldrich 99.5 D-atom%) was used as a solvent for the Rh dimer. All procedures were carried out *in vacuo* because the attached sample was sensitive to air, unlike the original Rh dimer complex. IR spectra were recorded on a double-beam transmission FTIR spectrometer (JEOL JIR-100).

Table 1. TOF and selectivity of hydroformylation of ethene at 413 K.[a]

Catalyst	TOF (10^{-4} molecules Rh^{-1} min^{-1}) Total	Ethane	Propanal	Selectivity (%)
Impregnated catalyst	10.9	9.9	0.96	8.8
Rh dimer/SiO_2	11.9	8.8	3.1	26.1

[a] C_2H_4 : CO : H_2 = 1 : 1 : 1 (total pressure = 40.0 kPa).

Figure 1(a) shows the IR spectrum of the Rh dimer complex, which is complicated in the ν(CH) region. In order to separate the methyl and carbene in the ν(CH) stretching vibration region, the deuteriated-C_5Me_5 (C_5Me_5*) Rh complex was used to prepare the incipient surface Rh dimers [Figure 1(d)]. From comparison with the spectra of the deuteriated complexes [Figure 1(b) and (c)] the bands at 2935 and 2879 cm^{-1} in Figure 1(d) were assigned to μ-carbene groups, while the bands at 2879 and 2790 cm^{-1} were attributed to methyl groups. On attaching the Rh complex to the SiO_2 surface at 313 K, one methane per Rh dimer was evolved. The temperature programmed decomposition analysis of the surface Rh dimers revealed that about one C_5Me_5 ligand per Rh dimer was lost on attachment. Furthermore, the intensity of surface OH groups decreased. These results show that the Rh-dimer complexes react with the surface OH groups, losing one Me ligand and one C_5Me_5 ligand per Rh dimer. The Rh–Rh bond distance was observed to be 0.262 nm by EXAFS, indicating retention of the dimer framework on SiO_2.[10]

The intensity of the peak at 2790 cm^{-1} decreased on heating

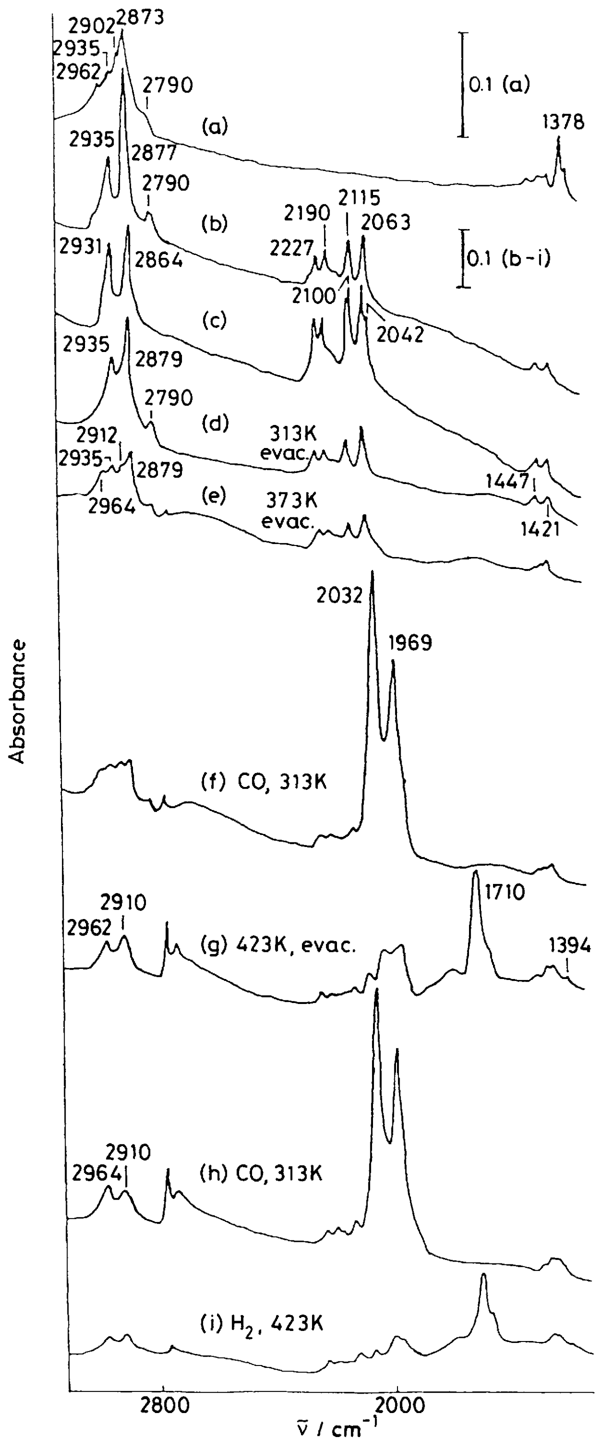
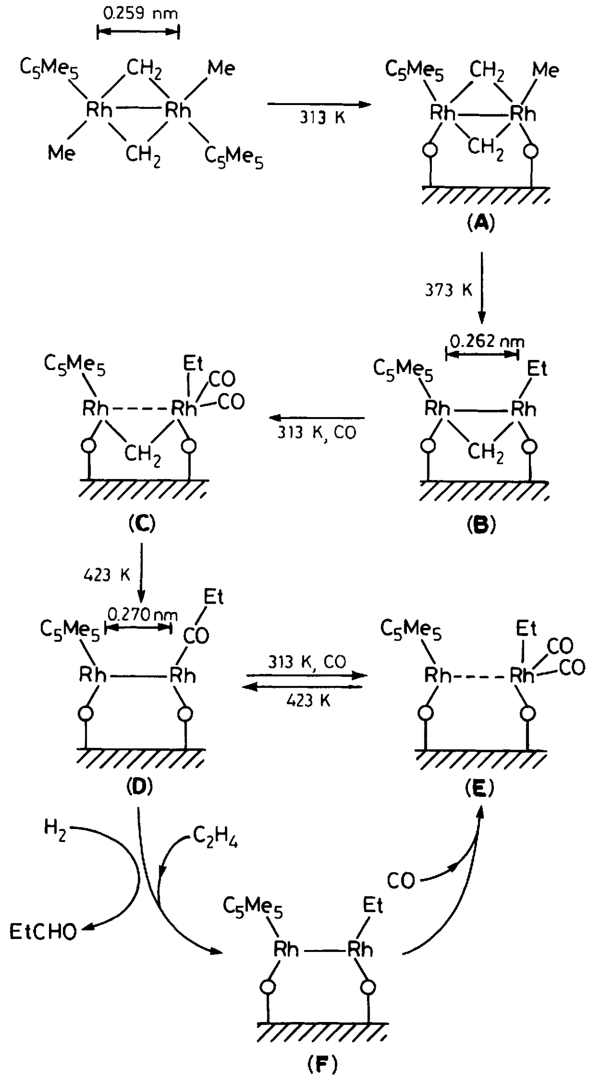


Figure 1. IR spectra of unsupported Rh dimers and the attached Rh dimers under various conditions. (a) Rh dimer/KBr; (b) Rh dimer (C_5Me_5*)/KBr; (c) Rh dimer (C_5Me_5*, CD_3)/KBr; (d)—(i) Rh dimer (C_5Me_5*)/SiO_2.



Scheme 1. Surface structures and transformations of the SiO_2-attached Rh dimers, and a catalytic cycle for ethene hydroformylation.

the sample *in vacuo* and disappeared at 373 K as shown in Figure 1(e). Simultaneously, the bands at 2935 and 2879 cm^{-1} were markedly reduced in intensity and new peaks at 2964 and 2912 cm^{-1} developed. In order to examine these changes in the ν(CH) region, *trans*-[(Rh(C_5Me_5*)CD_3)$_2$(μ-CH_2)$_2$] was attached to SiO_2, followed by evacuation at 373 K. The peaks at 2935 and 2874 cm^{-1} (μ-CH_2 groups) decreased to half intensity and new peaks appeared at 2964 and 2908 cm^{-1}, which were assigned to the CH_2 group of the ethyl (CH_2CD_3) ligand on Rh. Thus, the methyl ligand reacted with one μ-CH_2 group (carbene insertion) to form an ethyl group as shown in Scheme 1.

The Rh dimers (**B**) were exposed to CO at 313 K. New bands observed at 2032 and 1969 cm^{-1} are shown in Figure 1(f). The adsorbed CO on the surface Rh dimers (**C**) is of twin type (two CO groups bound to one Rh) on the basis of the observation of peaks at 2019—1943 cm^{-1} for the ^{12}CO –^{13}CO pair and 1986—1922 cm^{-1} for the ^{13}CO–^{13}CO pair. The amount of adsorbed CO was two molecules per Rh dimer. The unsupported Rh dimer complex did not adsorb any CO, which implies that a large C_5Me_5 ligand blocks CO adsorption on the Rh atom. Heating at 423—473 K *in vacuo* produced a new band at 1710 cm^{-1} with concomitant disappearance of the twin CO [Figure 1(g)]. At this stage the carbene signals almost disappeared. When CO was admitted to the system at 313 K, the band at 1710 cm^{-1} completely disappeared and the twin CO peaks were regenerated [Figure 1(h)]. The spectral change between Figure 1(g) and (h) was completely reversible and was accompanied by the reversible change of the relative intensities of the two ν(CH) peaks. Heating *in vacuo* also produced a peak at 1394 cm^{-1}, assigned to δ(CH), which disappeared with the peak at 1710 cm^{-1} on CO adsorption. The band at 1710 cm^{-1} shifted to 1672 cm^{-1} on ^{13}CO substitution. From these results we can assign the band at 1710 cm^{-1} to ν(CO) of the acyl (propanoyl) group on the Rh atom. In fact, the acyl peak at 1710 cm^{-1} decreased on reaction with H_2 at 423 K, as shown in Figure 1(i), producing propanal with a turnover frequency (TOF) of 1.0×10^{-2} molecules Rh^{-1} min^{-1}.

It is noted that the acyl peak disappeared on CO admission and reappeared on heating *in vacuo*. This behaviour is entirely different from usual mononuclear metal-complex chemistry in which the acyl ligand (CO insertion) can be formed in the presence of ambient CO and the reverse decarbonylation of the acyl group takes place on evacuation. An *in situ* EXAFS study revealed that the Rh–Rh bond of the attached Rh dimer was cleaved by twin-CO formation, and was regenerated (0.270 nm, Scheme 1) when the acyl group was formed.[10] Thus the phenomenon reported here is explained by the contribution of metal–metal bonding to the CO insertion; adsorbed twin CO cleaved the Rh–Rh bond and subsequent heating at 423 K *in vacuo* resulted in Rh–Rh bond-promoted CO insertion to the ethyl ligand as shown in Scheme 1. A similar observation for metal-promoted CO insertion has been reported with an Fe dimer in homogeneous systems,[11] although neither reversibility in the CO insertion–decarbonylation reaction nor reaction of the acyl group with H_2 were found.

The new Rh dimer catalyst has been found to have catalytic activity for ethene hydroformylation. Typical results are given in Table 1. The attached Rh dimer catalyst showed a higher activity and selectivity for propanal formation from a mixture of CO : H_2 : C_2H_4, 1 : 1 : 1 (total pressure 40.0 kPa), compared with an impregnated Rh catalyst which was obtained by the usual impregnation method using an aqueous $Rh(NO_3)_3$ solution. The catalytic reaction mechanism is suggested to involve metal-assisted CO insertion as shown in Scheme 1 (**D**), (**E**), and (**F**).

Received, 18th September 1989; Com. 9/03980E

References

1 M. M. Bashin, W. J. Bartly, P. C. Ellgen, and T. P. Wilson, *J. Catal.*, 1978, **54**, 120.

2 D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1968, 3133.

3 F. Correa, R. Nakamura, R. E. Stimson, R. L. Burwell, Jr., and D. F. Shriver, *J. Am. Chem. Soc.*, 1980, **102**, 5112.

4 R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, 1964, **86**, 3994.

5 G. Fachinetti, S. D. Nero, and C. Floriani, *J. Chem. Soc., Dalton Trans.*, 1976, 203.

6 M. L. H. Green, L. C. Mitshard, and M. G. Swanwick, *J. Chem. Soc. A*, 1971, 794.

7 Z. Nagy-Magos, G. Bor, and L. Marko, *J. Organomet. Chem.*, 1968, **14**, 205.

8 S. B. Butts, E. M. Holt, S. H. Strauss, N. W. Alcock, R. E. Stimson, and D. F. Shriver, *J. Am. Chem. Soc.*, 1979, **101**, 5864.

9 K. Isobe, A. Vazquez de Miguel, P. M. Bailey, S. Okeya, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1983, 1441.

10 K. Asakura, K. Kitamura-Bando, K. Isobe, H. Arakawa, and Y. Iwasawa, to be published.

11 J. P. Collman, R. K. Rothrock, R. G. Finke, E. J. Moore, and F. Rose-Munch, *Inorg. Chem.*, 1982, **21**, 146.