

## XAFS analysis of Wilkinson's complex in solutions

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Wilkinson's complex,  $[\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3]$ , is a hydrogenation catalyst for alkenes, alkynes, and aromatic compounds[1]. It is one of the most important homogeneous catalysts in organic synthesis. Though the mechanism of its catalytic cycle has been known well, chemical species which truly give catalytic action are still unknown in solutions. As the first step to confirm species in the catalytic cycle, XAFS analyses for the species correspond to **2** and **4** without  $\text{H}_2$  in Fig. 1 were attempted in tetrahydrofuran (THF) and benzene.

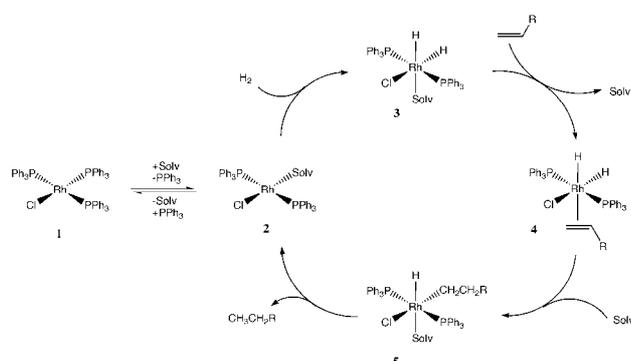


Fig. 1. Catalytic cycle of alkene hydrogenation involving Wilkinson's complex.

**Experimental**

Wilkinson's complex was purchased from Wako Pure Chemical, which was revealed as the red allotrope[2] by X-ray diffraction. Solvents used were dehydrated grade for organic synthesis. Solutions were prepared just before their X-ray absorption measurements in the sample cell made of fluorohydrocarbon resin. At first, 0.1 mol/L solutions were prepared but after the measurements precipitates were found in the solutions. Then, 0.01 mol/L solutions were measured. Later study on the precipitation revealed the crystallization much depended on various conditions such as temperature.

X-Ray absorption spectra of Rh K-edge were measured for simple solutions in THF and benzene, octene-added solution in THF, and the powder of the complex in transmission mode with Si(311) monochromator. XAFS data were analyzed by a laboratory-made system and FEFF 6L. Fourier transformations in Fig. 2 performed over the  $k$ -range of  $3.0 \text{ \AA}^{-1}$  —  $9.5 \text{ \AA}^{-1}$  with the phase shift and amplitude correction to phosphorous.

**Results and discussion**

Figure 2 shows Fourier transforms for Wilkinson's complex powder, its simple solutions, and octene-added mixed THF solution. Three independent transforms for the powder show good reproducibility of the measurements and analysis. Peaks for the solutions appear at shorter distances and are higher, but not narrower, than those for the powder, indicating that the solvents can coordinate to the additive sites of Rh rather than substitute for a triphenylphosphane group as shown complex **2** in Fig. 1. THF and benzene will coordinate through their oxygen and aromatic ring carbons, respectively, and be closer to Rh than the chlorine and the phosphorous. Complex coordinated by benzene will have more coordination atoms, *viz.* six carbons, and gives larger peak than by THF. Octene-added THF solution of the complex gives not so different transform from the simple THF solution does. That shows octene may not be added to Rh but substitute for coordinated THF. Fourier transforms alone are inadequate for these discussions. Further analysis have been tried but not succeeded yet.

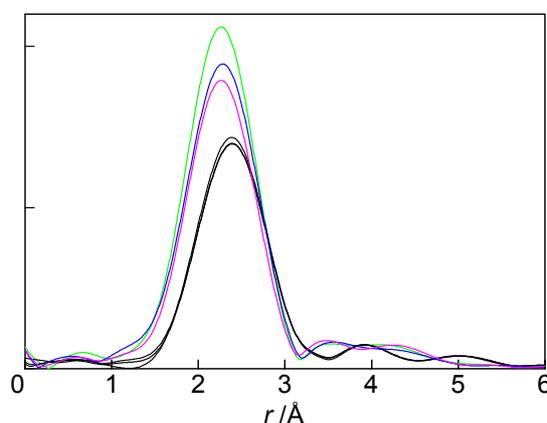


Fig. 2. Rh K-edge EXAFS Fourier transforms for Wilkinson's complex powder (three black lines), its benzene solution (green), THF solution (blue), and octene-added THF solution (magenta).

**References**

- [1] F. H. Jardine, *Prog. Inorg. Chem.* 28, 63 (1981).
- [2] M. J. Bennett, P. B. Donaldson, *Inorg. Chem.* 16, 655, (1977).

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