EXAFS investigations on diamine(diphosphine) and diamine(ether-phosphine) ruthenium(II) complexes

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Interphase catalysis is gaining great importance in recent years due to the ability to combine the merits of homogeneous and heterogeneous catalysis with a remarkable reduction of drawbacks like leaching and reduced catalytic activity of the reactive center. Noyori et al. recently discovered a new ruthenium(II) complex system containing diphosphine and 1,2-diamine ligands which, in the presence of a base and 2-propanol, proved to be excellent catalysts for the hydrogenation of ketones with excellent yield and selectivities under mild conditions [1]. Subsequently several chiral ruthenium(II) complexes were developed for the asymmetric hydrogenation of functionalised ketones [2]. Supporting of these complexes in polysiloxane matrices avoids leaching, whereas the activity and enantioselectivity remains constant [3]. The catalytic activity is traced back to the electronic properties of the coordination center and that the stereoselectivity is controlled by the chiral ligand [4]. Here in this report, the EXAFS investigations on the diamine(diphosphine) and diamine(ether-phosphine) ruthenium(II) complexes are presented.
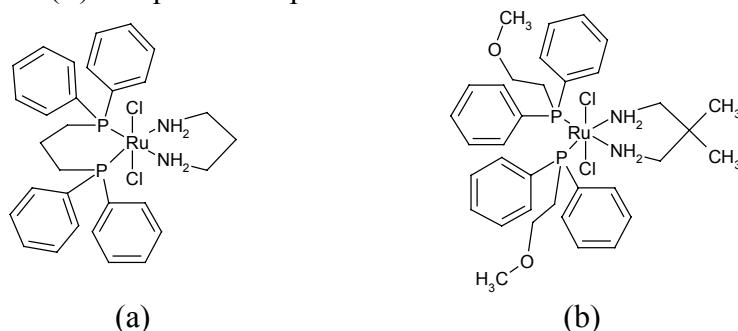

(a) (b)

Figure 1: (a) Structure of diamine(diphosphine) ruthenium(II) complex
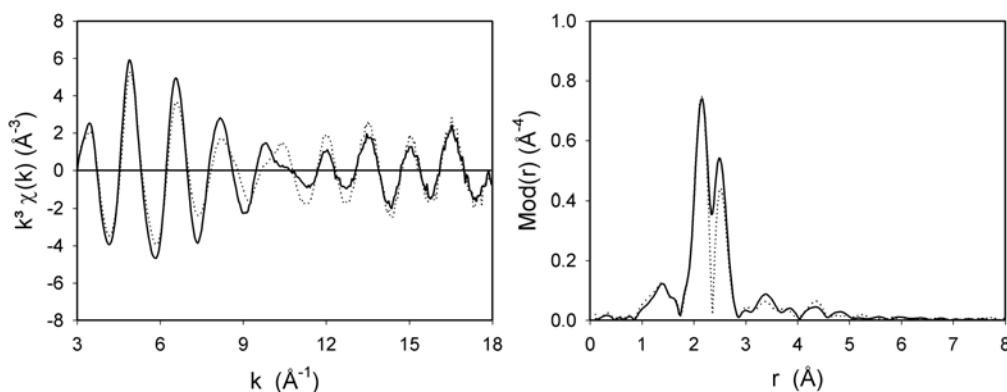(b) Structure of diamine(ether-phosphine) ruthenium (II) complex

Figure 2: Experimental k^3 $\chi(k)$ functions and their Fourier transforms of diamine(diphosphine) ruthenium(II) complex (dotted line) and diamine(ether-phosphine) ruthenium(II) complex (solid line).

Table 1: Structural parameters of diamine(diphosphine) and diamine(ether-phosphine) ruthenium(II) complexes, determined from the Ru K-edge EXAFS spectrum (Beamline X1, HASYLAB at DESY). Underground correction was performed with AUTOBK 2.61. EXAFS Simulation was done with the EXCURV92 module of CERIUS².

	A-Bs[a]	N[b]	r[c] [Å]	σ[d] [Å]	ΔE_0[e] [eV]	k-range [Å^{-1}]	Fit-Index
Diamine(diphosphine) ruthenium(II) complex	Ru-N	2	2.19 ± 0.02	0.050 ± 0.005	21.99	3.0-18.0	22.47
	Ru-P	2	2.26 ± 0.02	0.056 ± 0.006			
	Ru-Cl	2	2.41 ± 0.02	0.065 ± 0.007			
Diamine(ether-phosphine) ruthenium(II) complex	Ru-N	2	2.18 ± 0.02	0.050 ± 0.005	21.57	3.0-18.0	21.88
	Ru-P	2	2.29 ± 0.02	0.069 ± 0.007			
	Ru-Cl	2	2.42 ± 0.02	0.061 ± 0.006			

[a] absorber (A) – backscatterers (Bs), [b] coordination number N, [c] interatomic distance r, [d] Debye-Waller factor σ with its calculated deviation and [e] shift of the threshold energy ΔE_0.

The results of the EXAFS analysis are shown in Table 1. In the analysis of the experimental k^3 weighed $\chi(k)$ function, a three shell model can be fitted for both the complexes. The coordination numbers were set to the known values and the other parameter were determined by iterations. In the diamine(diphosphine) ruthenium(II) complex, two ruthenium-nitrogen backscatterers at 2.19 Å, two ruthenium-phosphorous backscatterers at 2.26 Å and two ruthenium-chlorine backscatterers at 2.41 Å were found whereas in the diamine(ether-phosphine) ruthenium(II) complex, two ruthenium-nitrogen distances at 2.18 Å, two ruthenium-phosphorous distances at 2.29 Å and two ruthenium-chlorine distances at 2.42 Å were observed. The diamine(ether-phosphine) ruthenium(II) complex has the same backbone structure like the diamine(diphosphine) ruthenium(II) complex, with the difference that the two phosphorous atoms are not rigidly bonded through the carbon atoms, but bonded freely to the oxygen atom through carbon atoms. Due to this fact, a slight lengthening of the ruthenium-phosphorous bond was observed in the case of diamine(ether-phosphine) ruthenium(II) complex, which is clearly evident from the EXAFS spectra (Figure 2). The differences in the other distances is within the order of magnitude and not obviously noticeable from the spectra.

References
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