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EXAFS STUDIES OF LEWIS ACID PROMOTED HOMOGENEOUS CATALYSTS

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Resumé. Les structures des complexes $\text{NiX}_2(\text{PR}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{Ph}, \text{Et}$) précurseurs de catalyseurs l'oligomérisation des alcènes ont été déterminées par l'étude des spectres EXAFS (seuil K de Ni). Les longueurs des liaisons mesurées pour les échantillons polycristallins diffèrent de 3% des résultats obtenus par diffraction X. La précision des paramètres mesurés sur $\text{NiBr}_2(\text{PPh}_3)_2$ est nettement meilleure que pour le dérivé chlore $\text{NiCl}_2(\text{PPh}_3)_2$. L'étude des spectres EXAFS de $\text{NiBr}_2(\text{PR}_3)_2$ ($\text{R} = \text{Et}, \text{Ph}$) en solution du toluène ne montre aucun changement dans les liaisons interatomiques. Les données de transmittance des spectres EXAFS (seuil K de Ti) du catalyseur de métathèse des alcènes $\text{Ti}(\text{CH}_2\text{AlMe}_2\text{Cl})(\eta\text{-C}_5\text{H}_5)_2$ en solution du toluène gélé et à l'état solide ont la structure attendue: Ti-CH₂ 1.95 Å, Ti-Cl 2.40 Å and Ti...Al 3.05 Å.

Abstract. The complexes $\text{NiX}_2(\text{PR}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{Ph}, \text{Et}$), which are precursors to alkene oligomerisation catalysts, have been investigated by Ni K-edge EXAFS. Bond lengths on polycrystalline samples were within 3% of those derived by X-ray diffraction. The precision of the parameters obtained on $\text{NiCl}_2(\text{PPh}_3)_2$ is substantially less than that relating to the bromo analogue. EXAFS spectra of $\text{NiBr}_2(\text{PR}_3)_2$ ($\text{R} = \text{Et}, \text{Ph}$) in toluene solution indicate no change in bond lengths on dissolution. Transmittance Ti K-edge EXAFS data on an alkene metathesis catalyst $\text{Ti}(\text{CH}_2\text{AlMe}_2\text{Cl})(\eta\text{-C}_5\text{H}_5)_2$ in frozen toluene solution and as a solid indicate the expected structure with Ti-CH₂ 1.95 Å, Ti-Cl 2.40 Å and Ti...Al 3.05 Å.

1. Introduction

The oligomerisation and metathesis of olefins can be catalysed in solution by transition metal complexes with aluminium co-catalysts. For example, oligomerisation of alkenes can be effected by the presence of many nickel compounds [1]. However rates and product distributions are extremely sensitive to the addition of phosphines. The Tebbe complex (1) (Figure 1) is active in methylene transfer to organic carbonyls and the catalytic degenerate metathesis of terminal alkenes [2]. Its structure, however, has largely been inferred from spectroscopic data and subsequent products with alkynes [3].

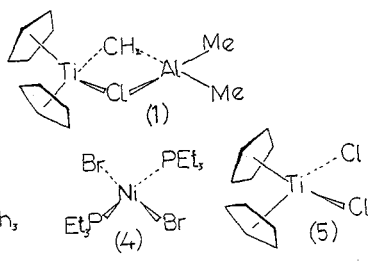


FIGURE 1.

We report initial EXAFS work on two systems. Firstly nickel catalyst precursors $\text{NiX}_2(\text{PR}_3)_2$, $\text{X} = \text{Cl}$, $\text{R} = \text{Ph}$ (2), $\text{X} = \text{Br}$, $\text{R} = \text{Ph}$ (3) and $\text{X} = \text{Br}$, $\text{R} = \text{Et}$ (4) (Figure 1), are investigated to determine the precision to which structural data can be derived in solution with mixed halo-phosphine ligand sets. Secondly, the Tebbe complex provides an example of a heterometallic species to establish the possibility of detecting a non-bonded aluminium atom from the transition metal edge EXAFS.

2. Experimental

The X-ray spectra were recorded on Station 7.1 of the SRS at the Daresbury Laboratory using a silicon(111) crystal monochromator. The solid and solution Ni-K edge samples were recorded in transmission and fluorescence modes respectively, whilst all Ti-K edge data was in transmission mode. Calibration and background subtraction routines using EXCALIB and EXBACK programmes [4] were carried out. An EXCURVE program [5] using spherical wave methods and *ab initio* phase shifts was employed.

3. Results and Discussion

The *ab initio* phase shifts used in the analysis of the Ni K-edge EXAFS were calibrated successfully against the metal and simple halo-species: $[\text{NiCl}_4]^{2-}$ and NiX_2 , $\text{X} = \text{Cl}$ and Br . The catalyst precursors (2) and (3) were also investigated as solids to check the phosphorus phase shifts.

On attempting to fit the theoretical and experimental data for (2) the Ni-Cl and Ni-P bond distances given were not well defined. The similar phase shifts of the phosphorus and chlorine make them difficult to distinguish by EXAFS analysis. Indeed a model with 4P coordinated produced a fit with the experimental data, comparable to that for the 2P,2Cl system (Fit Index 1.25 compared to 1.09). The bond length given for the 4P system was 2.24 \AA , which is an approximate average of the two bond lengths. With (3) the stronger backscattering bromine should make the Ni-halide distance better defined than that for the chlorine analogue (2).

Figure 2 shows the contour maps of the fit index for a range of values of the Ni-halide and Ni-P bond distances for (2) and (3). In the latter case the bond distances are much better defined. The standard deviations of the bond distances for (3) are approximately one order of magnitude smaller than those for (2), the values being Ni-P(2) 0.05 \AA , (3) 0.006 \AA ; Ni-halide (2) 0.03 \AA , (3) 0.005 \AA . The Debye Waller factors are also better defined for (3) than for (2) as can be seen in Figure 3. The standard deviations are Ni-P(2), 0.007 \AA^2 , (3) 0.001 \AA^2 ; Ni-halide (2) 0.014 \AA^2 , (3) 0.0004 \AA^2 . The oval and circular character of the contours for (3) and (2) are expected from the nature of the phase shifts files of the phosphorus and respective halides.

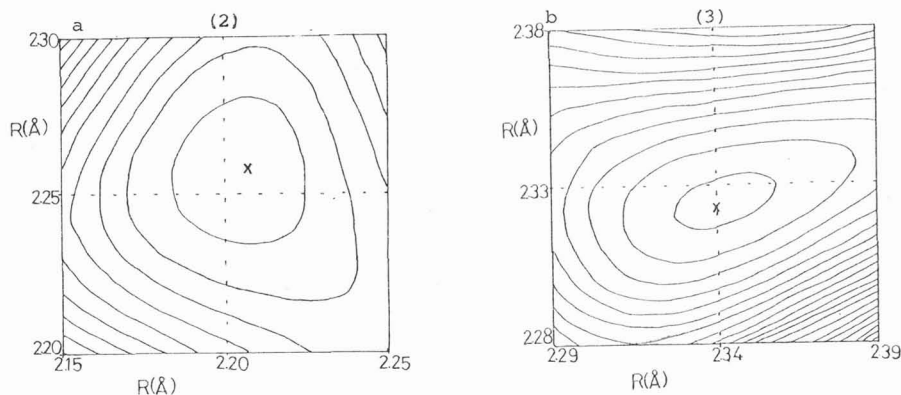


FIGURE 2. Contour maps of the fit indices for the Ni-halide versus Ni-P bond lengths of (a) minimum 1.1, lower contour 1.8, increment 1.31, upper contour 13.6. (b) (2) minimum 0.75, lower contour 1.08, increment 1.31, upper contour 26.0.

Saturated toluene solutions of the bromo complexes (3) and (4) were studied at room and liquid nitrogen temperatures. These complexes are tetrahedral and square planar respectively, in both solution and the solid state [6]. EXAFS analysis of the solutions at room temperatures gave bond lengths that differed by less than 1% from those determined from X-ray data. The frozen solutions however showed significant derivatives from those of the solid state structures.

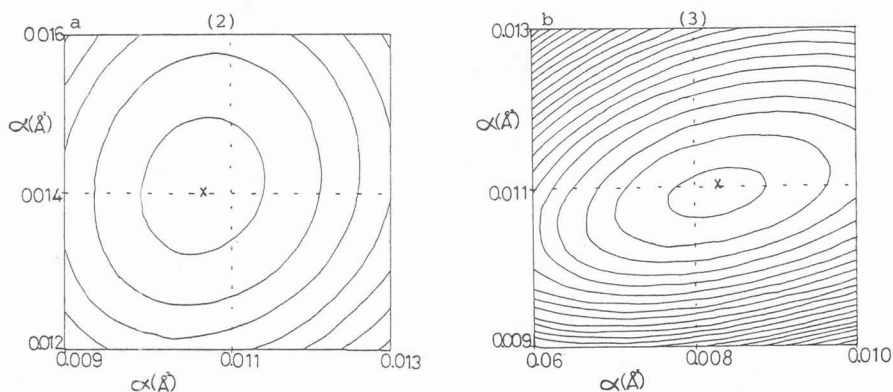


FIGURE 3. Contour maps of the fit indices for the Ni-halide versus Ni-P Debye Waller factors for (a) minimum 1.07, lower contour 1.09, increment 0.054, upper contour 1.41. (b) minimum 0.73, lower contour 0.74, increment 0.054, upper contour 1.77.

A decrease in bond length would be expected at lower temperatures resulting from a decrease in thermal motion of the bonds. With (3) the Ni-P and Ni-Br bond lengths decreased on cooling (by 0.08 Å and 0.03 Å respectively). With (4), however, the Ni-Br bond length did not change and the Ni-P bond increased by 0.04 Å. This unexpected change in bond length may result from the isomerisation of the square planar $\text{NiBr}_2(\text{PET}_3)_2$ to tetrahedral at these low temperatures. Though some low temperature ^1H nmr work has been carried out on (4) [6] establishing the square planar arrangement in solution, analysis at liquid nitrogen temperature has not been reported.

Though the changes in bond lengths of the PET_3 and PPh_3 systems appear to be in opposite directions they become more defined at lower temperatures. Maps of Ni-Br and Ni-P bond lengths show distinctly steeper minima for the spectra run at liquid nitrogen temperatures than those at room temperatures. The standard deviations of the bond lengths were approximately half those run at room temperature. The Debye Waller factors for the Ni-P and Ni-Br bonds, however, did not differ significantly at the different temperatures. These seemed equally defined from the gradients of the maps, and their standard deviations.

The structure of the Tebbe complex (1) has been provisionally assigned by analysis of the Ti K-edge EXAFS data, with the current fit of the k^2 weighted EXAFS and the Fourier transforms presented in Figure 4, and the interatomic distances listed in Table 1. The standard deviation of the Debye Waller factor for the chlorine atom is large. However, this is also evident in the refinement on the crystallographically characterised compound $\text{TiCl}_2(\eta\text{-C}_5\text{H}_5)_2$ (5). This appears to be a consequence of being at a similar distance to the ten carbon atom shell of the cyclopentadienyl rings. There is no significant difference in the interatomic distances between the solid and in frozen solution. In each case a peak attributable to the aluminium atom is evident in the Fourier transform and such a shell is refinable.

This complex has not been characterised by X-ray diffraction, with the only suggested interatomic distances resulting from molecular orbital calculations on the hypothetical compound $\text{H}_2\text{Ti}(\text{CH}_2\text{AlH}_2\text{Cl})$ [7]. These indicated an essentially planar four membered ring with the following bond lengths: Ti-CH₂ 2.01 and Ti-Cl 2.24 Å. The EXAFS derived Ti-Cl distance is closer to that observed in complex (5) than that of this theoretical study. However the Ti-CH₂ distance is probably shorter than anticipated and would incite some double bond character.

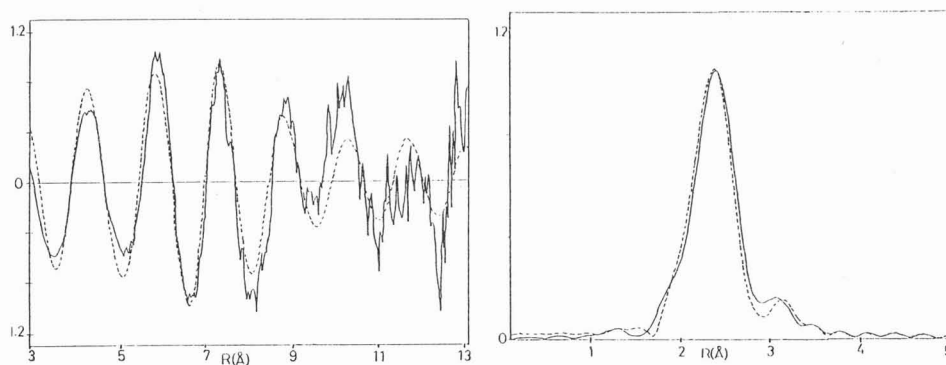


FIGURE 4. Fits of the k^2 weighted Ti K-edge EXAFS and the Fourier transform for the Tebbe complex (1).

Compound	Atom	X-ray	Solid	EXAFS	
				toluene solution	Frozen solution
NiCl ₂ (PPh ₃) ₂ (2)	P	2.28	2.20(5)		
	Cl	2.27	2.26(3)		
NiBr ₂ (PPh ₃) ₂ (3)	P	2.33	2.33(1)	2.33(1)	2.25(1)
	Br	2.34	2.34(0)	2.32(0)	2.29(0)
NiBr ₂ (PEt ₃) ₂ (4)	P	2.26		2.26(1)	2.30(0)
	Br	2.30		2.29(0)	2.30(0)
(η-C ₅ H ₅) ₂ TiCl ₂ (5)	C	2.37	2.37(2)		
	Cl	2.36	2.34(2)		
Ti(CH ₂ AlMe ₂ Cl)(η-C ₅ H ₅) ₂ (1)	CH		1.90(1)		1.94(1)
	C(C ₅ H ₅)		2.40(6)		2.41(1)
	Cl		2.34(2)		2.41(2)
	Al		3.09(1)		3.05(1)

TABLE 1. EXAFS derived interatomic distances, R (Å), from the data associated with the transition metal K-edge.

Acknowledgements

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