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Structure−Performance Relations in Homogeneous Pd Catalysis by In Situ EXAFS Spectroscopy

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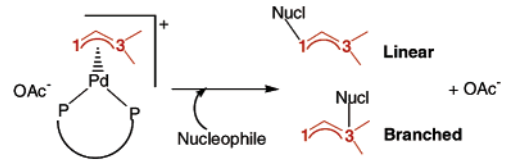
Palladium is one of the most widely used metals in transition-metal-catalyzed organic synthesis, as it is capable of catalyzing a wide variety of commercially important reactions.[1] Ligands are attached to palladium to increase the performance and stability of the catalysts, and they are used to fine-tune the steric and electronic properties of the catalyst and thereby the activity and selectivity obtained with these catalysts. The missing link in explaining structure−activity and −selectivity relationships in homogeneous catalysis is the detailed structural information about the catalysts in their active phase, in solution.

We have therefore applied extended X-ray absorption fine structure (EXAFS) spectroscopy to elucidate the origin of the regioselectivity in the Pd-catalyzed allylic substitution reaction. EXAFS spectroscopy provides both structural and electronic information about a specific element in a compound in any state of aggregation.[2] Only a few EXAFS studies on homogeneous organometallic Pd complexes have been reported in the literature so far.[3] This can partly be explained by the complexity of the EXAFS data-analysis, especially as overlapping coordination shells hamper data-analysis severely. Recent developments in EXAFS data-analysis methods,[4] using the so-called difference file technique,[2] allow the reliable separation of the different contributions resulting in a proper analysis.

The use of bidentate diphosphine (P−P) ligand Pd catalysts in the allylic substitution reaction of a nonsymmetrically substituted dimethylallyl moiety results in either linear or branched products as shown in Scheme 1. For bidentate ligand complexes, it has been suggested that the bonding of the allyl moiety determines the regioselectivity.[5,6] Moreover, the regioselectivity was found to be influenced by the P−Pd−P angle, that is, bite angle of the bidentate phosphine ligands.[7] Isolated (ligand)Pd(allyl) complexes are studied in detail by molecular modeling, X-ray crystallography, and (solution-) NMR techniques.[6−10] It was proposed that the selectivity in the allylic alkylation reaction is a tradeoff between electronic and steric contributions. A larger bite angle of the ligand enhances the electronic preference for nucleophilic attack at the branched position, but also increases the steric hindrance at this position.[6,7] Because these studies are mainly based on characterization of solid samples, they fail in providing a detailed structural analysis of the catalytic complexes in solution, the actual active phase of homogeneous catalytic intermediates in the active phase differs from that in the solid state. This can lead to a direct explanation of the regioselectivity of the different catalysts in the allylic alkylation reaction.

Scheme 1. Regioselectivity in the Pd-Catalyzed Allylic Substitution Reaction



Reaction.

EXAFS Pd K-edge data are collected for two cationic (ligand)-Pd(allyl) complexes: (dppe)Pd(C_5H_9) (dppe 1,2-bis(diphenylphosphino)ethane) and (DPEphos)Pd(C_5H_9) (DPEphos 2,2-bis(diphenylphosphino(diphenyl ether)) with, respectively, a narrow and wide bite angle and, consequently, a different product selectivity in the allylic alkylation reaction.[6,7] The complexes were synthesized as described in the literature[7,11,12] and characterized with both X-ray crystallography and solution NMR.[6] EXAFS measurements were performed on the solid-state complexes (at room temperature) and in THF solution at room temperature. NMR spectra taken before and after EXAFS data collection showed that no changes had occurred in the complexes.

The crystal structure of the (dppe)Pd(C_5H_9) complex is shown in Figure 1 (left). The different carbon neighbors of Pd up to a distance of 3.5 Å are denoted as C^{yellow}, C^{red}, and C^{white}. The XRD values for the coordination numbers and distances of the Pd−C^{yellow}, Pd−P^{blue}, Pd−C^{red}, and Pd−C^{white} coordination shells are given in Table 1. EXAFS data of excellent quality are obtained. Theoretical reference data were generated in the commercially available program XDAP[13] using FEFF8.0.[14] The results of the EXAFS data-analysis are given in Table 1. The total fits are of good quality in all weightings applied as can be concluded from the low variances found between both the imaginary and the absolute parts of the Fourier transforms of the fits and the spectra.[2]

The structural parameters for the solid samples obtained with EXAFS are in good agreement with the XRD results. Thus, EXAFS confirms that the orientation of the allyl moiety toward the Pd is similar for both solid-state complexes as was found with XRD.[6] However, major structural differences (Table 1) are found for the (dppe)Pd(C_5H_9) complex between the solid state and in THF. The coordination number of the Pd−C^{red} contribution increases from one to two, whereas at the same time the coordination number of the Pd−C^{yellow} contribution changes from three to two. The increase in the Debye−Waller factor for the Pd−C^{red} shell is consistent with both the increase in coordination number and the increase in disorder going from the solid state to solution. The decrease in the

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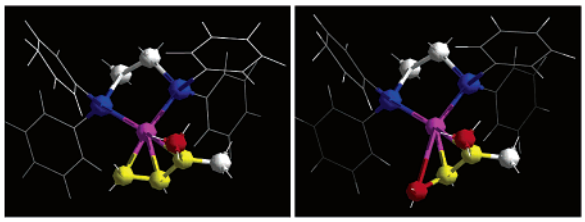

Figure 1. (left) The crystal structure of the (dppe)Pd(C_5H_9) complex as determined with single-crystal XRD (omitting the counterion). (right) Possible representation of the structure of the (dppe)Pd(C_5H_9) complex in solution as determined with EXAFS (distances correlate with the found values; the angles between the different atoms are not determined and can be slightly different).

Table 1. EXAFS Analysis

shell	aggregation	*N*	*R* (Å)	$\Delta\sigma^2$ (Å^2)	ΔE_0 (eV)
		(dppe)Pd(C_5H_9)[a]			
	solid (XRD)	2	2.30 (±0.02)		
Pd−P^{blue}	solid	1.9	2.28	0.004	11.5
	solution	1.8	2.28	0.011	4.8
	solid (XRD)	3	2.20 (±0.05)		
Pd−C^{yellow}	solid	3.0	2.27	0.015	13.4
	solution	2.1	2.15	0.001	13.3
	solid (XRD)	1	2.94		
Pd−C^{red}	solid	0.9	3.00	0.004	−3.7
	solution	1.8	2.95	0.007	5.5
	solid (XRD)	3	3.32 (±0.02)		
Pd−C^{white}	solid	3.0	3.34	0.017	4.3
	solution	3.1	3.29	0.023	6.7
		(DPEphos)Pd(C_5H_9)[b]			
	solid (XRD)	2	2.36 (±0.02)		
Pd−P^{blue}	solid	1.7	2.33	0.005	5.4
	solution	1.7	2.33	0.005	6.2
	solid (XRD)	3	2.25 (±0.02)		
Pd−C^{yellow}	solid	3.1	2.24	0.009	10.2
	solution	2.8	2.23	0.009	11.8
	solid (XRD)	1	3.16		
Pd−C^{red}	solid	1.2	3.18	0.009	−4.3
	solution	1.3	3.08	0.012	1.7
	solid (XRD)	1	3.50		
Pd−O	solid	1.0	3.50	0.017	2.5
	solution	1.3	3.50	0.022	5.6

[a] Fit: *R*-space, 2.8 < *k* < 17.0, 1.0 < *R* < 3.5; solid k^0-weighted V.I. = 0.03, V.A. = 0.02 and k^3-weighted V.I. = 0.59, V.A. = 0.22; solution k^0-weighted V.I. = 0.01, V.A. = 0.01 and k^3-weighted V.I. = 0.06, V.A. = 0.01 (V.I. = variance in imaginary part, V.A. = variance in absolute part). [b] Fit: *R*-space, 2.8 < *k* < 15.0, 1.0 < *R* < 3.5; solid k^0-weighted V.I. = 0.06, V.A. = 0.03 and k^3-weighted V.I. = 0.76, V.A. = 0.35; solution k^0-weighted V.I. = 0.05, V.A. = 0.02 and k^3-weighted V.I. = 1.43, V.A. = 0.73.

Debye−Waller factor for the Pd−C^{yellow} contribution agrees with a coordination number of two instead of three. In the solid state, three carbon atoms contribute to this shell with a rather high deviation in distances, whereas in THF only two carbon atoms remain present at a somewhat smaller distance with a smaller deviation. The Pd−P^{blue} and Pd−C^{white} distances are not changing significantly when dissolving the complex, indicating that the Pd-ligand itself is hardly influenced by dissolving the complex. The Debye−Waller factor increases due to a higher disorder in solution.

Comparing these structural results in solution with the solid structure of this Pd complex (Figure 1 (left)), a simple, but for catalysis very essential, explanation for the EXAFS results can be given. The Pd-ligand complex remains unchanged, whereas the Pd-allyl coordination and binding in solution are altered.

One C^{yellow} atom bends away from the Pd, possibly as displayed in Figure 1 (right). This leads to a decrease in the Pd−C^{yellow} coordination with a simultaneous increase in the coordination number of the Pd−C^{red} shell. As a consequence of this distortion, the two remaining C^{yellow} atoms approach the Pd, and the C^{red} atoms are also positioned at a smaller distance toward the palladium. Because the distances of the methyl groups attached to the allyl (C^{red} and C^{white}) hardly change, most likely the unsubstituted allylic carbon atom changes its conformation. A referee suggested that this change might find its origin in a change in conformation of the dppe ligand relative to the allyl moiety, which cannot be deducted from EXAFS.

The (DPEphos)Pd(C_5H_9) complex displays almost no structural changes upon dissolution in THF (Table 1). Dissolving the complex only results in a slight increase in Debye−Waller factors for all contributions, reflecting an increase in static disorder, as expected.

The unsubstituted carbon atom of the allyl moiety changes its conformation in THF and therefore becomes more accessible for a nucleophile to be attacked. In addition, when this carbon atom bends away from the palladium atom, the allyl−Pd binding distorts, decreasing the electron density on this carbon atom so the atom becomes electronically activated. A direct explanation for the favorable formation of linear products using Pd-complexes with a narrow bite angle enforcing ligand[6,10,15] as in dppe is thus proven in this study.

The results of these studies directly establish structure−selectivity relationships in important catalytic reactions and therefore are of great importance in revealing the actual reaction mechanisms. Therefore, we are convinced that the displayed strength of EXAFS techniques of measuring samples in all aggregation states, and thus in their active phase, will be extremely important in revealing structure−selectivity/activity relationships in homogeneous catalysis.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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