

Carbonylation chemistry in detail

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A series of catalytically highly capable hydrido rhodium complexes containing mono-, bi- and hemilabile tridentate phosphite ligands has been investigated within the context of olefin hydroformylation. High pressure NMR as well as in situ HP FTIR spectroscopy, DFT calculations and isotopic labeling were applied to characterize and to quantify catalytically relevant intermediates at a low total rhodium concentration of 0.3 mM. Results show that both, monophosphite rhodium hydrido and rhodium acyl complexes do coexist nearly over the entire conversion range. A combination of spectroscopy and NBO analysis gave the proof that the monophosphite coordination mode changes within the catalytic cycle, thus going from equatorial in the hydride $[\text{HRh}(\text{CO})_3\text{L}]$, to axial in the acyl complex $[\text{RC}(\text{O})\text{Rh}(\text{CO})_3\text{L}]$. The molar ratio of these complexes shifts with the olefin concentration. Precise concentration profiles were derived for the organometallic components from superposed experimental spectra with a new mathematical algorithm which, together with the data obtained for the olefin and the aldehyde, fit perfectly to a model derived for Michaelis-Menten type kinetics.¹ In contrast, a rhodium(I) acyl is usually not seen for active rhodium catalysts formed from bidentate ligands. We have found conditions where respective complexes indeed dominate in solution and where hydroformylation activity is unusually high compared to the well known catalysts formed with bulky monophosphites. A catalytically relevant species of the type $[\text{HRh}(\text{CO})_2(\text{diphosphite})]$ surprisingly was stable enough to be isolated and has been studied by X-ray diffraction.²

With triphosphites, a new catalyst lead structure has been found. Industrially relevant activities and *n*-regioselectivities were measured for the isomerizing hydroformylation of internal olefins as a result of ligand hemilability. Combined in situ spectroscopic and theoretical studies were performed to elucidate the solution structures of the equilibrating rhodium hydrides involved, during the catalytic reaction.³

1. a) C. Kubis, D. Selent, M. Sawall, R. Ludwig, K. Neymeyr, W. Baumann, R. Franke, A. Börner, *Chemistry-A European Journal* **2012**, *18*, 8780-8794. b) C. Kubis, M. Sawall, A. Block, K. Neymeyr, R. Ludwig, A. Börner, D. Selent, *Chemistry - A European Journal* **2014**, *20*, 11921-11931.

2. C. Kubis, R. Ludwig, M. Sawall, K. Neymeyr, A. Börner, K.-D. Wiese, D. Hess, R. Franke, D. Selent, *ChemCatChem* **2010**, *2*, 287-295.

3. to be published.