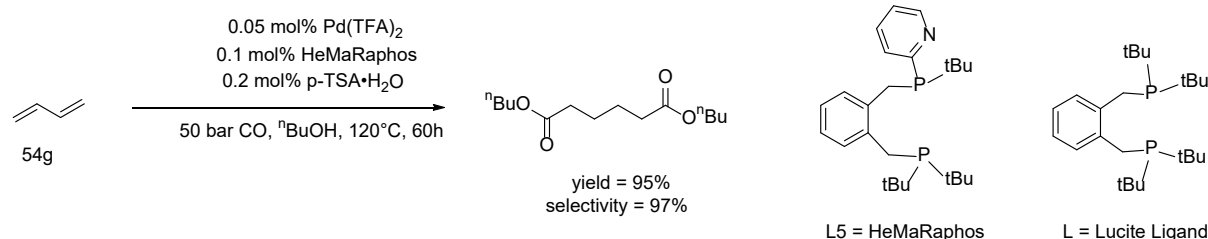


## Palladium Catalyzed Carbonylation of Challenging Olefins to Esters and Acids

H. Neumann, J. Yang, K. Dong, R. Sang, R. Jackstell, M. Beller  
Leibniz-Institute for Catalysis, Rostock, Germany

### Abstract

In 1953, Walter Reppe published in "Justus Liebigs Annalen der Chemie" a seminal carbonylation of acetylene with carbon monoxide and a nucleophile using nickel salts as catalysts. [1] The formed methyl acrylates are belonging to an important class of buildings blocks and are synthesized in ton scales. Since this discovery there was a perennial interest both from the industry and academia in Reppe carbonylations. In the late 1980's a big jump ahead was contributed by Drent from Shell AG, who developed highly efficient palladium catalysts in homogenous phase, which surpassed the former catalysts.[2] Based on his results the so called Alpha-Lucite process [3] was set up, where tons of ethylene are converted to methyl propionate in a palladium catalyzed reaction using 1,2-bis((di-*tert*-butylphosphino)methyl)-benzene (Lucite Ligand, L) as an outstanding ligand. Inspired by this success, we developed in cooperation with Evonik AG a ligand system where we modified the Lucite Ligand (L) by replacing one *t*-butyl group on each side with a pyridyl unit. This catalyst system becomes much more active than the Lucite system and is even able to carbonylate internal and tetrasubstituted olefins.[4] Recently, we prepared the unsymmetrical Lucite analogous (L5 = HeMaRaphos) by replacing only one *t*-butyl group with a pyridyl unit. This catalyst is very active for the double carbonylation of 1,3-butadiene to adipinates. [5] Adipinates are important building blocks for many industrial products especially for the Nylon 66 production and have a big economical prominence.



[1] W. Reppe, Liebigs Ann. Chem., 582, 1 (1953).

[2] G. Kiss, Chem. Rev., 101, 3435 (2001).

[3] (a) G. R. Eastham et al. World Patent. WO2004014552A1 (2004).

[4] K. Dong, X. Fang, S. Gülak, R. Franke, A. Spannenberg, H. Neumann, R. Jackstell, M. Beller, Nature Communications, 8, 14117 (2017).

[5] J. Yang, J. Liu, H. Neumann, R. Franke, R. Jackstell, M. Beller, Science, 366, 1514 (2019).