

Professor David Cole-Hamilton

Irvine Professor of Chemistry

e-mail: djc@st-and.ac.uk

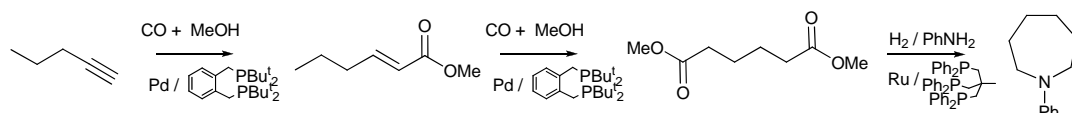
tel: 01334-463805

Research Interests: Applications of organometallic compounds in homogeneous catalysis.



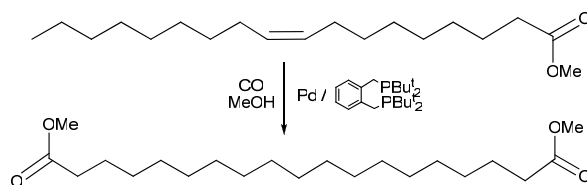
Homogeneous Catalysis

We are studying catalysts which will give very high selectivity to desirable products often via cascade reactions. In Scheme 1, α,ω -diesters are formed in a single cascade reaction by the methoxycarbonylation of alkynes. The same catalyst catalyses the methoxycarbonylation to the α,β -unsaturated ester (the reaction can be stopped here), the double bond isomerisation and the second methoxycarbonylation, which only occurs when the double bond is in the least thermodynamically favoured terminal position. In a

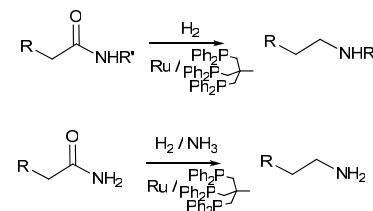


Scheme 1 Formation of dimethyl adipate from 1-butyne by a methoxycarbonylation – isomerisation – isomerisation Cascade sequence; also shown is the reductive amination of dimethyl adipate to N-phenylazacycloheptane.

separate reaction, also shown in Scheme 1, α,ω -diesters can be converted by reductive amination to heterocycles. Related reactions are the formation of long chain α,ω -diesters from natural feedstocks (Scheme 2) and the catalytic hydrogenation of amides to amines (Scheme 3).



Scheme 2 Upgrading of methyl oleate to a polymer precursor



Scheme 3 Hydrogenation of amides to amines

In addition, we have a major programme on new approaches to separating products from the catalyst in homogeneous reactions using biphasic systems involving aqueous, ionic liquid and supercritical fluid solvents. Recent studies have included additives to aqueous biphasic systems which give rate enhancements of 100 times without catalyst leaching or emulsion formation, catalysts which can be switched between water and organic phases by bubbling or removing CO_2 (Figure 1) and supported ionic liquid phase catalysts with supercritical flow.

Related reactions are the formation of long chain α,ω -diesters from natural feedstocks (Scheme 2) and the catalytic hydrogenation of amides to amines (Scheme 3).

SELECTED RECENT PUBLICATIONS

- 1) Highly selective formation of unsaturated esters or cascade reactions to α,ω -diesters by the methoxycarbonylation of alkynes, A. A. Núñez Magro, L. M. Robb, P. J. Pogorzelec, A. M. Z. Slawin, G. R. Eastham and D. J. Cole-Hamilton, *Chem. Sci.* 2010, accepted
- 2) The synthesis of amines by the homogeneous hydrogenation of secondary and primary amides, A. A. Nunez Magro, G. R. Eastham and D. J. Cole-Hamilton, *Chem. Commun.*, 2007, 3154-3156.
- 3) Continuous Flow Hydroformylation of Alkenes in Supercritical Fluid – Ionic Liquid Biphasic Systems, P. B. Webb, M. F. Sellin, T. E. Kunene, S. Williamson, A. M. Z. Slawin and D. J. Cole-Hamilton, *J. Am. Chem. Soc.*, 2003, **125**, 15577
- 4) Supported ionic liquid phase catalysis with supercritical flow, U. Hintermair, G. Y. Zhao, C. C. Santini, M. J. Muldoon and D. J. Cole-Hamilton, *Chem. Commun.*, 2007, 1462-1464.
- 5) Aqueous-biphasic hydroformylation of alkenes promoted by "weak" surfactants, S. L. Desset, S. W. Reader and D. J. Cole-Hamilton, *Green Chem.*, 2009, **11**, 630-637
- 6) Carbon Dioxide Induced Phase Switching for Homogeneous-Catalyst Recycling, S. L. Desset and D. J. Cole-Hamilton, *Angew. Chem. Int. Ed.*, 2009, **48**, 1472-1474.

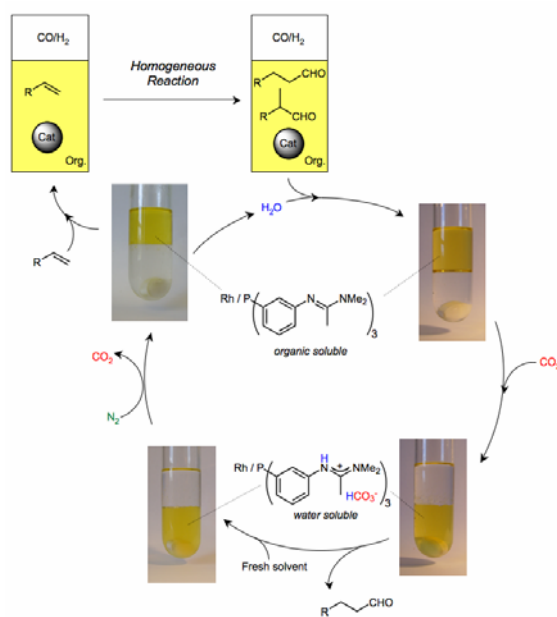


Figure 1 Catalyst separation by transfer into and from water using CO_2