**FINAL REPORT**

**New Tools for CO$_2$ Fixation by Homogeneous Catalysis**

**Philip G. Jessop (P.I.)**

**1 Nov. 2002 to 30 October 2005**

# ABSTRACT

**Project Title:**    New Tools for $CO_2$ Fixation by Homogeneous Catalysis

**DOE Grant No.:**    DE-FG03-99ER14986

**PI Name:**    Philip G. Jessop    (Note: Dr. Mark Kurth, UCDavis, served as temporary PI for the last part of the funded period while the work was subcontracted to Dr. Jessop at Queen's University)

**Student names:**    Christopher Ablan, David Heldebrant, Chih-Cheng Tai, David Heldebrant, Li Xiaowang

**Collaborators:**    John Linehan (Pacific Northwest National Lab), April Getty (Pacific Northwest National Lab), Charles Eckert (Georgia Institute of Technology, School of Chemical Engineering), Charles Liotta (Georgia Institute of Technology, School of Chemistry), Eric Beckman (University of Pittsburgh, Chemical Engineering).

**Contact Information:** (current address) Philip G. Jessop, Dept. of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6. Tel. (613) 533-3212. Fax (613) 533-6669. email: jessop@chem.queensu.ca

**Yearly budget:**    $125,000

**Current period:**    1 November 2002 to 31 October 2004. No-cost extension was approved to 31 October 2005.

**Project started:**    1999

**Overall goals:**

The overall goal is the development of new or more efficient methods for the conversion of $CO_2$ into useful organic products, via the design or discovery of new catalysts, ligands, solvents, and methods.

**Specific objectives for this funded period:**

1. To develop a high-throughput screening technique and use it to develop an efficient catalyst/reagent/solvent system for the synthesis of ureas or carboxylic acids.

2. To use in-situ spectroscopic and kinetic methods to study the mechanism of the synthesis of ureas or carboxylic acids.

3. To develop bifunctional ligands capable of secondary interactions with $CO_2$, to detect the interactions, and to demonstrate applications to catalysis,

**Significant results:**

The PI and his team have achieved the following related to each of the three specific objectives.

1. Two separate apparati for high pressure high-throughput screening of catalysts have been built, one allowing a 6 x 6 array to be tested, and the other an 8 x 12 array. A new method for rapid assay of the results from such experiments was also developed. The new apparatus and method were tested in a successful search for an active catalyst for $CO_2$ hydrogenation without the use of expensive platinum-group metals. The method was also used in an unsuccesful search for catalysts for the insertion of $CO_2$ into C-H bonds. Nevertheless, new reactions of $CO_2$ were found, including a synthesis of β–hydroxycarboxylic acids, a synthesis of acylureas, and reactions of $CO_2$ that can be

incorporated into switchable solvents.  The last discovery was published in the journal *Nature*[1] and obtained world-wide press coverage.[2-7]

   New solvents were also tested.  Results with a biphasic mixture of liquid poly(ethylene glycol) (PEG) and supercritical $CO_2$ (sc$CO_2$), with catalyst recovery and reuse, were excellent for two test reactions, the hydrogenation of styrene and the asymmetric hydrogenation of tiglic acid.  PEG and other liquid polymers were also found to be effective solvents for other reactions including the hydrogenation of $CO_2$ and yeast-catalyzed reductions of organics.  The results with PEG were covered as news items in the journal *Nature*[8] and the magazine *Chemical and Engineering News*.[9]

   2.  In-situ spectroscopic work on the insertion of $CO_2$ into C-H bonds was not performed, beyond a simple study of the uncatalyzed insertion, because a catalyst was not identified for this reaction in the work under objective 1.  However, the spectroscopic study of the uncatalyzed reaction revealed that the literature understanding of the role of the amidine in the carboxylation reaction and indeed in $CO_2$-fixation in general was incorrectly understood.  Amidines do not form very stable zwitterionic adducts with $CO_2$; the species that had been identified in that way in the literature was in fact a bicarbonate salt of the protonated amidine.  In our work on the preparation of acylureas from $CO_2$, spectroscopic detection of phenylisocyanate lead us to a proposed mechanism for that reaction.

   3.  The proposal for the development of bifunctional phosphine ligands was divided into two portions.  a) Triphenylphosphine analogues containing Lewis basic functional groups within or attached to the aromatic rings were developed in order to find substitutes for $PPh_3$ that have greater solubility in $CO_2$.  Many phosphines were prepared and two of these were indeed found to have greater solubility.  b) Triphenylphosphine analogues containing Brønsted-acidic functional groups attached to the aromatic rings were developed in order to find substitutes for $PPh_3$ that would kinetically or thermodynamically promote the insertion of $CO_2$ into metal-hydrogen bonds.  The most effective such phosphine, in terms of the rate of $CO_2$ hydrogenation, was para-diphenylphosphinobenzoic acid, very surprising in that its geometry prevents, rather than allows, intramolecular interaction between the Brønsted-acidic functional group and either the metal, the hydride ligand, or a formate ligand on the metal.

**Potential impact:**

   Development of new catalysts for hydrogenation of $CO_2$ and the discovery of new reactions of $CO_2$ during this work could result in wider use of waste $CO_2$ as an inexpensive feedstock that does not rely on the availability of oil.  The products of $CO_2$ fixation already include aspirin and urea, but given further work of this kind a much wider range of products could be prepared.

   The invention of the entirely nontoxic and benign solvent system of PEG and sc$CO_2$ makes it possible to use, recover and recycle homogeneous catalysts without the use of volatile organic solvents and without significant heavy metal contamination of the product.  The method has the potential to increase the usage of homogeneous catalysis in industry, not only for $CO_2$ fixation but for many reactions, by eliminating the usual weakness of homogeneous catalysts – the separation problem.

   Switchable solvents, which are an entirely new discovery arising, somewhat unexpectedly, from this work, may become an entirely new field of research and lead to

significant changes in industrial practice in fine chemical production. Subsequent work, under other funding, is showing that the impact may reach even further, to oil production, nanoparticle synthesis, and the production of polymers.


## RESULTS IN DETAIL


### Bifunctional phosphines – Lewis basic

In the search for an aromatic phosphine that is more $CO_2$-soluble than $PPh_3$, the Jessop group prepared several new phosphines and several known phosphines. We sought to determine whether nonhalogenated groups could be used to increase the solubility of triphenylphosphine or other phosphines with similar electronic and steric properties. In particular, we chose to evaluate three strategies for making halogen-free $CO_2$-soluble phosphine ligands. The solubility of the ligands prepared by the Jessop group was measured in $CO_2$ by the group of Dr. Eric Beckman at the University of Pittsburgh.

For the first strategy, the working hypothesis was that triarylphosphines which have para-substituents incorporating Lewis basic secondary functional groups such as esters would be more soluble than triarylphosphines without such substituents. Despite literature[10] speculation, the ligand $Ph_2PC_6H_4pCO_2Me$, one of those that we prepared and tested, is not more soluble in $CO_2$ than is $PPh_3$; in fact the solubility of the former is very low indeed. In fact, only one of the ester-containing phosphines showed greater solubility than $PPh_3$, and that was a peracetylated sugar-containing phosphine (structure 1).



| 1 | 2 | 3 |
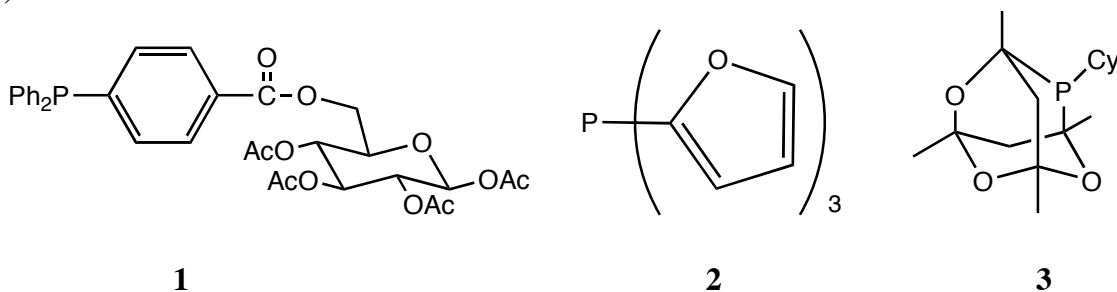
The second strategy was the incorporation of Lewis basic groups into the aromatic ring; this could lead to favorable ligand-$CO_2$ interactions without the penalty of increased molar mass that is encountered in the first strategy. While (2-pyridyl)diphenylphosphine was not more soluble than $PPh_3$, tri(2-furyl)phosphine (structure **2**) was indeed more soluble.

The third strategy was to evaluate a phospha-adamantyl ligand (structure **3**) that has similar electronic and steric properties to triphenylphosphine; under the assumption that the aryl rings in triarylphosphines are a major contributor to stabilization of the solid state by π-π stacking effects and that the substitution of two of these aryl rings by an adamantyl cage would eliminate such stacking effects and thereby increase solubility in $CO_2$. Unfortunately, it was found to be completely insoluble in $CO_2$ up to the limits of the equipment (660 bar, 25 °C).

## Bifunctional phosphines – Brønsted acidic

Current theory in the fields of ketone[11] and $CO_2$[12, 13] hydrogenation suggest that the presence of Brønsted-acidic or hydrogen bond-donating groups proximate to a metal hydride site assists in the hydrogenation of C=O double bonds. While this has been substantially established in the ketone hydrogenation literature, it has remained speculation in the $CO_2$ fixation literature. Phosphines (compounds **4**-**7**) containing hydrogen bond-donating ancillary groups were prepared or purchased and then evaluated as ligands for the catalytic hydrogenation of $CO_2$ to formic acid (equation 1, "catalyst" = $RuCl_3/4PR_3$). Of these, the most active for catalysis, and the only one of the four to generate a more active catalyst than did $PPh_3$, was ligand **7**. This result was surprising because it is the only one of the four incapable of an intramolecular hydrogen-bonding interaction with Lewis-basic ligands on the metal, such as hydride or formate.



$$CO_2 + H_2 \xrightarrow[\text{50°C, NR}_3]{\text{catalyst}} HCO_2H \qquad (1)$$
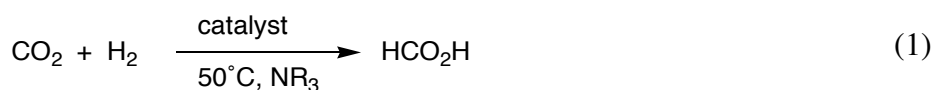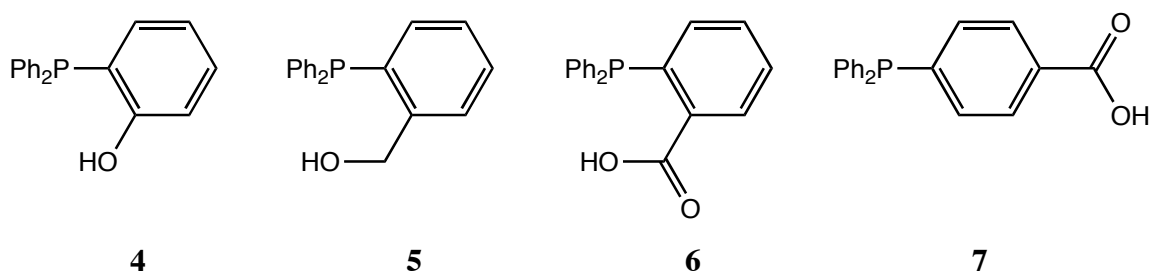
An unusual reaction was found during the (still on-going) studies of the coordination chemistry of these ligands. An aldehyde-phosphine, which was used as a precursor of ligand **5**, was reacted with $RuCl_3$ to give a complex containing an ester-phosphine and a decarbonylated phosphine (equation 2).



$$(2)$$
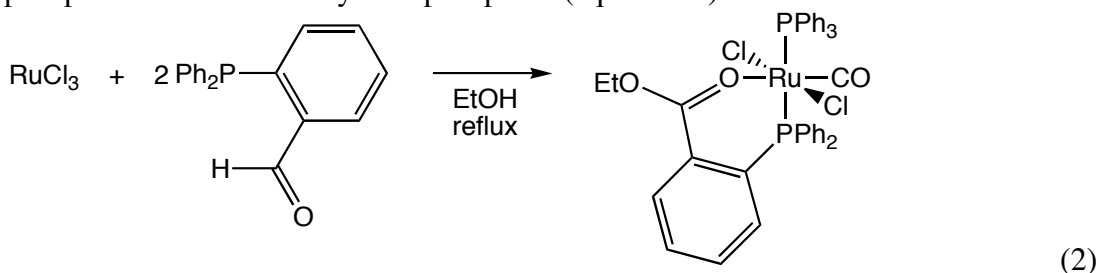
## Development of new $CO_2$-hydrogenation catalysts

The application of homogeneous catalysis is hampered, at least partly, by the over-reliance on complexes of the extremely expensive platinum-group metals. A combinatorial study[14] of the catalytic activity of combinations of phosphine and amine ligands with other transition metal salts as potential $CO_2$ hydrogenation catalysts (cf. equation 1) has found many that have at least moderate catalytic activity and a few, including $NiCl_2$/dcpe and $FeCl_3$/dcpe that have fairly high activity (dcpe = 1,2-bis(dicyclohexylphosphino)ethane). The isolated complex $NiCl_2$(dcpe) was then found to

catalyze the hydrogenation of $CO_2$ to formic acid in 4,400 turnovers (mol product per mol catalyst). This activity is three orders of magnitude greater than the activity of the only previously-known catalyst[15] outside of the platinum group metals.

The combinatorial method for identifying catalysts used equipment designed and built in-house (Figure 1). A colorimetric assay method was also developed so that catalysts could be screened more rapidly than normal NMR or chromatographic assays would permit.
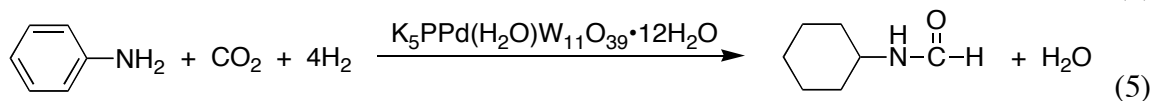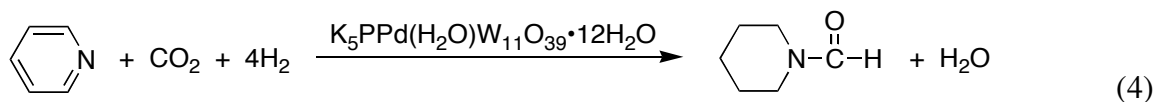


Figure 1. High-pressure vessels for combinatorial testing of catalysts, capable of testing a 6x6 array at 200 bar (left) and an 8x12 array at 100 bar (centre). The colorimetric assay method is illustrated at right, where catalytically active metal/ligand combinations appear yellow while inactive combinations appear blue.

Catalysts for the hydrogenation of $CO_2$ to oxalic acid or oxalate salts proved to be much more elusive. At first, assay method development was necessary because oxalate anion is notoriously difficult to detect spectroscopically and distinguish from formate. The student researcher was able to identify conditions suitable for the in-situ methylation of oxalate anion by dimethylsulfate to dimethyloxalate, which was then detectable by gas chromatography. With this assay method, it was possible to show, for the first time, that catalysts having high activity for the hydrogenation of $CO_2$ to formate anion do not simultaneously produce detectable quantities of oxalate anion. However, the catalyst prepared in-situ from tricyclohexylphosphine and either $PdCl_2(MeCN)_2$ or tris(dibenzylideneacetone)-dipalladium(0) was found to be capable of producing small quantities of oxalate anion at 100 °C (equation 3). Any variation of the ligand choice suppressed the activity. Denise and Sneeden reported the detection of traces of diethyloxalate in a similar reaction in ethanol solvent at 120 °C.[16]

$$2CO_2 + H_2 \xrightarrow[\text{base}]{PdCl_2(MeCN)_2 / PCy_3} HO_2CCO_2H \xrightarrow{MeOSO_3Me} MeO_2CCO_2Me \quad (3)$$
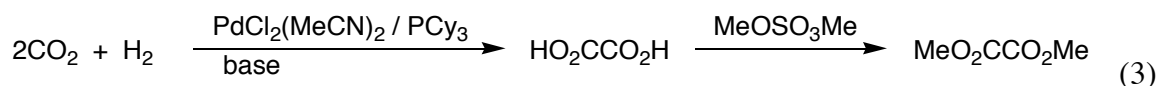
The co-hydrogenation of $CO_2$ and aromatic amines catalyzed by a Pd/W cluster was found to give alkylformamides via simultaneous hydrogenation of C=C, C=N and C=O double bonds (equations 4 and 5).

$$\text{(pyridine)} + CO_2 + 4H_2 \xrightarrow{K_5PPd(H_2O)W_{11}O_{39}\cdot12H_2O} \text{(piperidine-N-C(O)-H)} + H_2O \qquad (4)$$

$$\text{(C}_6\text{H}_5\text{)}-NH_2 + CO_2 + 4H_2 \xrightarrow{K_5PPd(H_2O)W_{11}O_{39}\cdot12H_2O} \text{(cyclohexyl-NH-C(O)-H)} + H_2O \qquad (5)$$

**Development of new catalysts for $CO_2$ insertion reactions**

      The research group also investigated the insertion of $CO_2$ into C-O, C-N and C-H bonds.

     a) Insertion into C-H bonds: Screening of catalysts for the amidine-promoted carboxylation of C-H bonds was ultimately unsuccessful. The uncatalyzed reaction[17, 18] only works for particularly activated C-H bonds such as those adjacent to keto groups. However, the work did result in useful information that has spawned several new projects. First, we explored the reaction between amidines and $CO_2$, which is central to the carboxylation chemistry. This lead to a correction of the literature and to an entirely new field of switchable solvents. Second, we explored a combination of the amidine-promoted ketone carboxylation (the product of which is very prone to decarboxylation) and an asymmetric hydrogenation, with the result that isolation of the unstable carboxylation product became unnecessary and a new transformation, a net 1,3-hydrocarboxylation, was discovered. These discoveries will be described in more detail below. Future work on the original project, catalytic carboxylation of unactivated C-H bonds, may continue but it must be recognized that the kinetic problems of the reaction do not seem conducive to a ready solution.

     We showed[19] that the reaction between amidines and $CO_2$ (equation 5), which has been widely published in the literature,[20-28] is incorrect. Amidines have been reported to react with $CO_2$ to form a zwitterionic adduct but the literature studies were performed in the presence of at least some water. However, our spectroscopic study of the reaction between DBU and $CO_2$ in the presence of water detected the rapid formation of the bicarbonate salt of DBU when wet DBU is exposed to $CO_2$ (equation 7). Adduct formation (reaction 6) was not detected in dry acetonitrile, the solvent used in the literature, or in dry neat DBU. If water was present in the acetonitrile or DBU, then bicarbonate formed. The NMR and IR spectra of the bicarbonate product matched exactly the reported spectra for the zwitterionic adduct.



DBU     + $CO_2$ ⇌

$$\qquad (6)$$

$$(7)$$
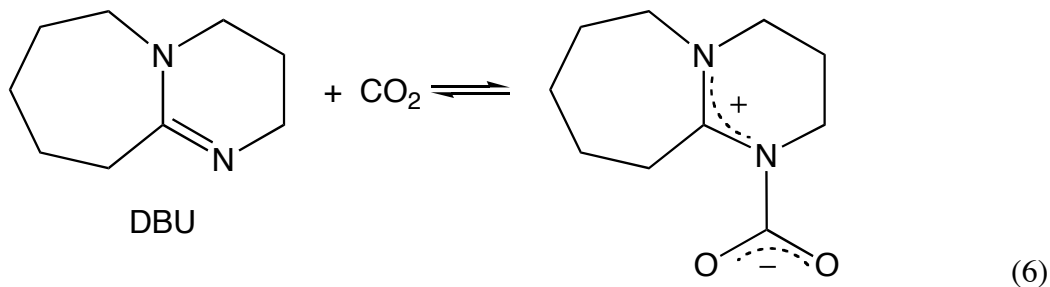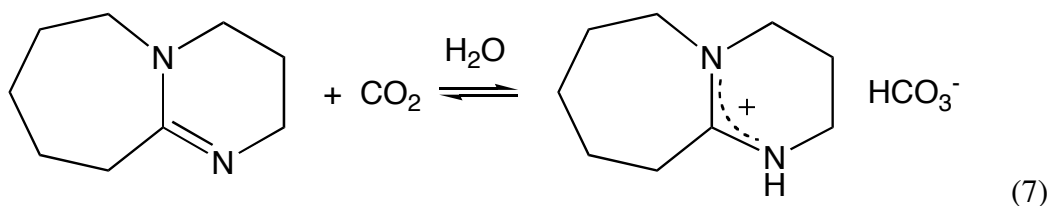
We found that the amidine-promoted carboxylation of ketones can be combined in one pot with asymmetric hydrogenation to give a β–hydroxycarboxylic acid via a net 1,3-hydrocarboxylation of ketones (reaction 8). This unprecedented transformation may more easily be achieved via this one-pot double reaction than via a two-pot process of carboxylation followed by asymmetric hydrogenation of the resulting β–ketocarboxylic acid because that intermediate too readily decarboxylates.



$$(8)$$
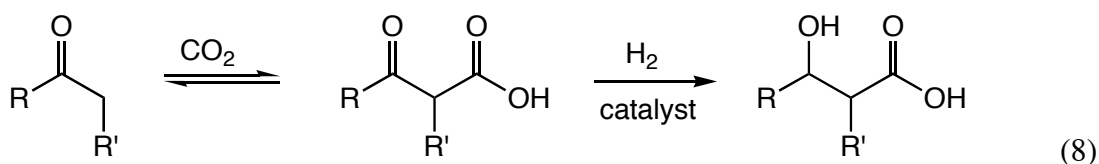
Hydrocarboxylations of alkenes are known,[29,][30] but are always 1,2-hydrocarboxylations and always use toxic CO rather than nontoxic $CO_2$. Hydrocarboxylation of ketones is unknown in the literature, as is any hydrocarboxylation using $CO_2$.

The net hydrocarboxylation has been achieved in the conversion of acetophenone to 3-phenyl-3-hydroxypropanoic acid (reaction 9). The optimization of the yield is currently underway and the optimization of enantioselectivity will follow shortly. At present, the enantioselectivity (entirely unoptimized) is 42%.



$$(9)$$
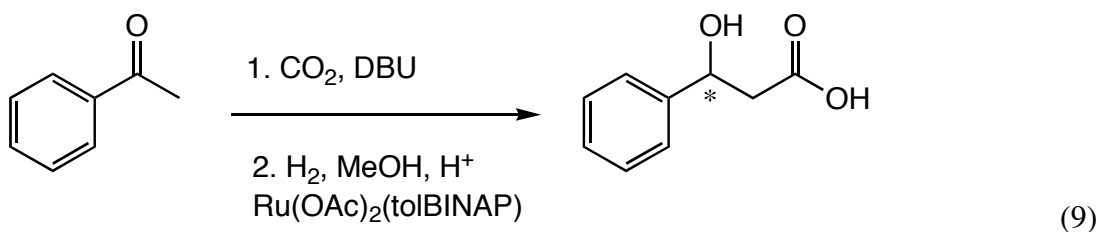
Work is currently underway (under different funding) to improve the enantioselectivity and evaluate the scope of this exciting new transformation. It is anticipated that the reaction can be made into a kinetic resolution for substrates that give two chiral centres in the β–hydroxycarboxylic acid product. It is also hoped that the reaction can be used with alkenes to give chiral carboxylic acids (reaction 10, postulated) and potentially, if decarboxylation can be induced, chiral alkanes!



$$(10)$$
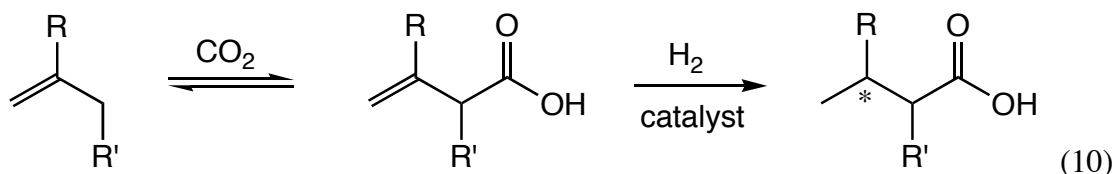
b) Insertion into C-O bonds: If DBU and $CO_2$ were reacted together in the presence of alcohol rather than water, an alkylcarbonate salt was obtained instead (reaction 11). This reversible formation of an alkylcarbonate salt lead to an unexpected discovery; switchable solvents.[1, 31] These are solvents that can reversibly switch from being nonpolar to being polar, upon command. There are no prior literature reports of such a solvent, so our initial communication, published in the journal *Nature*,[1] was the first of what we hope will be a new field of endeavour. Switchable solvents should find use in fine chemical production, where processes require sequences of reaction and/or separation steps. Each step usually requires a certain kind of solvent, and it is very commonly found that the solvent which is optimum for any one step is an unsatisfactory solvent for the very next step. As a result, solvents are usually removed from the system and discarded after every single step in the process. This generates a very large amount of waste and consumes an unnecessarily large amount of energy. The use of switchable solvents should allow solvents to change themselves to match the requirements of each succesive step and reduce the need to remove and replace solvents. The switchable solvents are based upon reaction 11; an equimolar mixture of DBU and 1-hexanol under nitrogen gas serves as a nonpolar liquid solvent. However, when $CO_2$ is bubbled through the mixture, the reaction produces an alkylcarbonate salt that is an ionic liquid and therefore a very polar solvent. Bubbling $N_2$ or argon through the ionic liquid reverses the process.



(11)
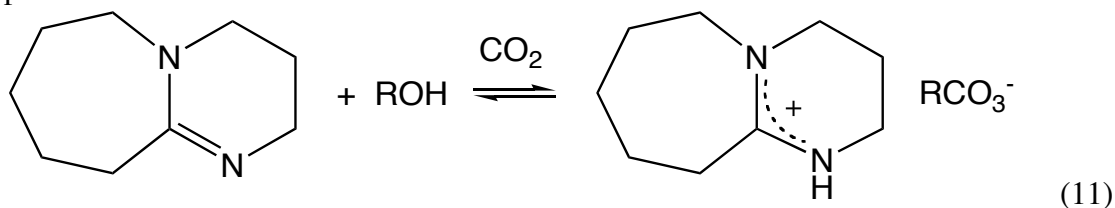
c) Insertion into C-N bonds: If DBU is exposed to $CO_2$ in wet MeCN, then the bicarbonate salt is obtained. However, if an amine such as aniline is present, then an entirely different product can be obtained; at slightly elevated temperatures, an acylurea formed (reaction 12). This is a new reaction for $CO_2$, the closest literature precedent being an intramolecular cyclization of a cyanoaniline.[32, 33] The product can be isolated in high yield. Initial investigations showed that the mechanism is likely to be a dehydrative coupling of aniline and $CO_2$ to give phenylisocyanate, followed by hydration of the acetonitrile to give acetamide (Scheme 1). Acetamide and phenylisocyanate are known to couple to give the acylurea.[34] We spectroscopically observed the presence of phenylisocyanate.



(12)
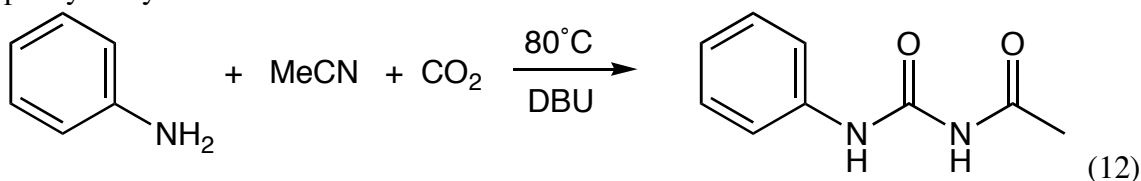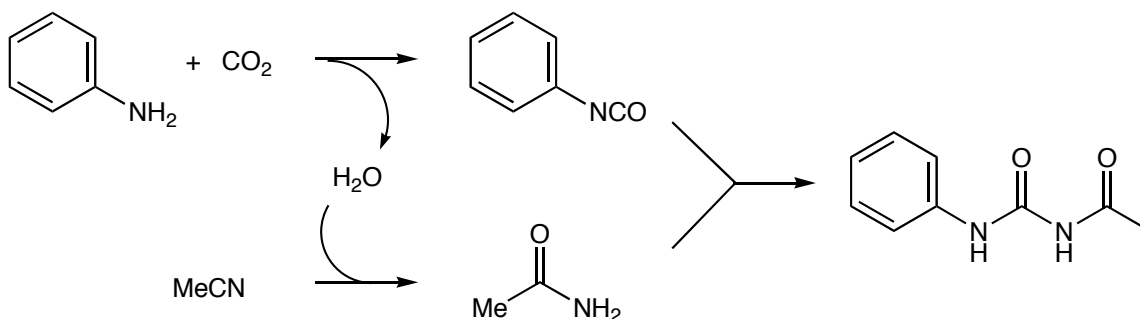
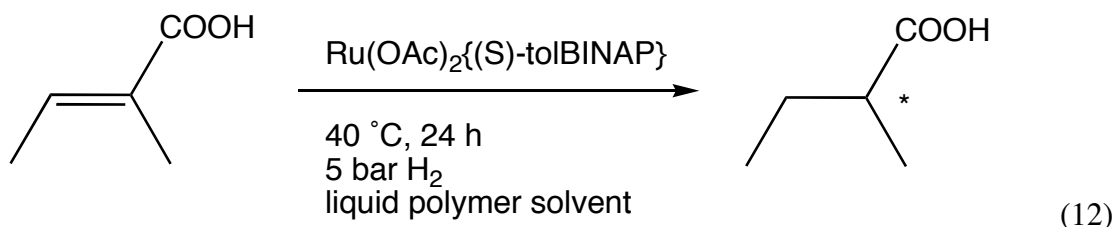Scheme 1. Proposed mechanism for formation of the acylurea.

**Utilization of $CO_2$ in combination with new solvents**

In work partly funded by this grant, the group discovered a new method for recovering and recycling homogeneous catalysts without the use of volatile or halogenated organic solvents. The combination of supercritical $CO_2$ and a liquid polymer such as PEG (poly(ethylene glycol)) gives a biphasic solvent system which is environmentally benign, nontoxic, extremely inexpensive in materials, and very efficient for catalyst recycling. Several hydrogenation and reduction reactions were tested in liquid polymers and polymer/$CO_2$ mixtures, and the solvent polarity of the liquid polymers was also measured.[35, 36] The initial communication[37] received press coverage in *Chemical and Engineering News*[38] and a full page news commentary in *Nature*.[8] The full paper is now in completed draft form and will be submitted for publication in January or February 2006. A summary of the results is presented below.
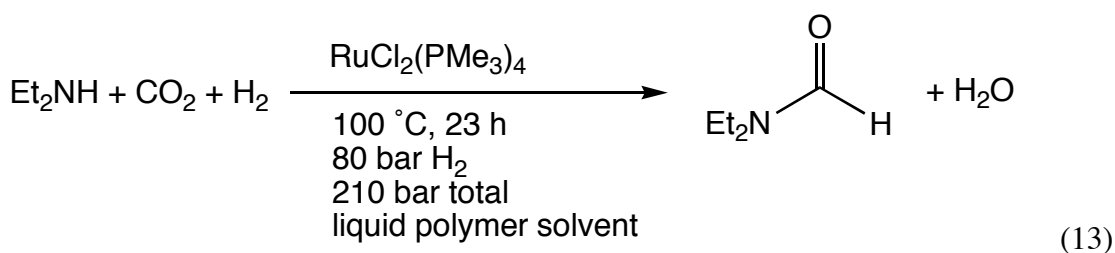
The reactions evaluated in various liquid polymers and, for comparison, some ionic liquids, were the hydrogenation of styrene (equation not shown) and the asymmetric hydrogenation of tiglic acid (equation 12), the hydrogenation of $CO_2$ in the presence of diethylamine to give diethylformamide (equation 13), and the yeast-catalysed reduction of ethyl pyruvate (equation 14). The conclusions were as follows:

Homogeneously-catalyzed hydrogenation of styrene was performed in the molten PEG, followed by extraction of the product by scCO₂. The catalyst-containing PEG phase which remains in the vessel can be reused repeatedly for hydrogenation without addition of further catalyst or PEG. The conversion remained high and steady for all 5 cycles. The extraction of PEG along with the product could be largely avoided by the use of polymer molecular weights of over 1000 and preferably over 1500 g/mol.

The hydrogenation of tiglic acid (equation 12) gave excellent conversion (>99%) and good enantioselectivity (81-83%) in several liquid polymers, including poly(ethyleneglycol) (PEG), poly(tetrahydrofuran) (PTHF), and poly(methylphenylsiloxane) (PMPS). The enantioselectivity was comparable to that obtained in the ionic liquid tri(hexyl)(tetradecyl)phosphonium dicyanamide, better than that obtained in poly(propylene glycol) (PPG) or poly(dimethylsiloxane) (PDMS), and slightly inferior to that obtained in methanol or the ionic liquid 3-butyl-1-methylimidazolium hexafluorophosphate ([bmim]PF₆). The hydrogenation catalyst in PEG could be used over and over again, for at least 5 times, with >90% conversion and >80% ee every time. This proved that the catalyst remained active and selective for multiple uses, which was the desired result.

$$\text{(structure)} \xrightarrow[\substack{\text{40 °C, 24 h} \\ \text{5 bar } H_2 \\ \text{liquid polymer solvent}}]{\text{Ru(OAc)}_2\{\text{(S)-tolBINAP}\}} \text{(structure)} \qquad (12)$$

The synthesis of diethylformamide by $CO_2$ hydrogenation (equation 13) has now been tested in varied liquid polymers. The yield of amide from the reaction performed in PPG was superior to that obtained in any other polymer tested or that obtained in the absence of any added solvent. Surprisingly, the other polyethers (PEG and PTHF) were inferior for this application.

$$Et_2NH + CO_2 + H_2 \xrightarrow[\substack{\text{100 °C, 23 h} \\ \text{80 bar } H_2 \\ \text{210 bar total} \\ \text{liquid polymer solvent}}]{\text{RuCl}_2(\text{PMe}_3)_4} \quad \underset{Et_2N\phantom{xx}H}{\overset{O}{\|}} \quad + H_2O \qquad (13)$$

The yeast-promoted asymmetric reduction of ethyl pyruvate (equation 14) proceeded readily and in high enantioselectivity in PMPS but failed entirely in PPG. Extraction of the product from PMPS by $scCO_2$ was found to be impractical because of the resulting destruction of the yeast cells and coextraction of cell residues.

$$\text{(structure)} \xrightarrow[\substack{\text{liquid polymer solvent} \\ \text{1\% } H_2O \text{ v/v,} \\ \text{room temp, 23 h}}]{\text{Baker's Yeast}} \text{(structure)} \qquad (14)$$
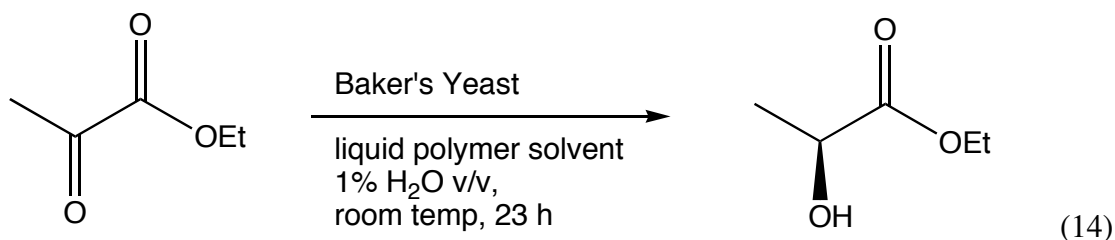
Encapsulation of air-sensitive homogeneous catalysts in polymers is a strategy for protecting the catalyst from air while the catalyst is not being used. It is important, of course, that the polymer coating be removed before the catalyst is used. However, physically blocking the access of $O_2$ molecules to the catalyst also prevents the access of substrate molecules. The melting of PEG by $CO_2$ offers us a new way of protecting the catalyst between runs without preventing catalyst/substrate interactions during runs. We showed that encapsulating homogeneous catalysts in polyethers such as PEG is generate a superior catalyst recycling method for air-sensitive catalysts. PEG-1500 and $RhCl(PPh_3)_3$ were stirred together for 30 min at 50 °C under 50 bar of $CO_2$. The sample was cooled and bled to atmospheric pressure. The residual "puck" of catalyst solidified in PEG-1500 was exposed to air for 1 month, following which it was tested for catalytic activity for the hydrogenation of styrene at 40 °C under 30 bar $H_2$ and 50 bar $CO_2$; the conversion was >99%. For comparison, solid $RhCl(PPh_3)_3$ and a THF solution of

RhCl(PPh$_3$)$_3$ were similarly exposed to air for 1 month and then tested for activity; they were completely inactive. This demonstrates that PEG, frozen around the catalyst when the CO$_2$ pressure is released, protects air-sensitive catalysts from air.

In conclusion, four reductions have been succesfully performed in liquid polymer solvents, showing that these solvents have the potential to be more widely used as media for reactions and catalysis. Notably, the best liquid polymer solvent was different from reaction to reaction (PEG or PMPS for tiglic acid, PPG for CO$_2$ hydrogenation and PMPS for the yeast catalysed reduction). Extraction of the product by scCO$_2$ followed by recycling of the catalyst was demonstrated for styrene hydrogenation and tiglic acid asymmetric hydrogenation but was found to be impossible for the yeast-catalyzed reduction. The full paper describing these results in detail will be submitted shortly.[36]

**Journal articles citing this grant and published since the start of this funding period**

1.  P. Munshi, D. J. Heldebrant, E. P. McKoon, Patrick A. Kelly, C.-C. Tai, P. G. Jessop, "Formanilide and Carbanilide from Aniline and Carbon Dioxide" *Tetrahedron Letters* (2003) *44*, 2725-2727.

2.  P. G. Jessop, "Homogeneous Catalysis and Catalyst Recovery using Supercritical Carbon Dioxide and Ionic Liquids" *J. Synth. Org. Chem.* (2003), *61*, 484-488.

3.  D. J. Heldebrant, P. G. Jessop, "Poly(Ethylene Glycol) and Supercritical Carbon Dioxide: A Benign Biphasic Solvent System for Recycling of Homogeneous Catalysts" *J. Am. Chem. Soc.* (2003) *125*, 5600-5601.

4.  C.-C. Tai, T. Chang, B. Roller, P. G. Jessop, "High Pressure Combinatorial Screening of Homogeneous Catalysts: Hydrogenation of Carbon Dioxide" *Inorg. Chem.* (2003), *42,* 7340-7341.

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1. P. G. Jessop, "Asymmetric Catalysis in Supercritical Fluids" in *Supercritical Fluid Technology for Drug Product Development*, P. York, B. Kompella, B. Y. Shekunov (eds.), Marcel Dekker, New York, 2004, pp. 461-495.

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3. P. G. Jessop and D. J. Heldebrant, "Green Biphasic Homogeneous Catalysis" in *Environmental Catalysis*, V. Grassian (ed.), Marcel Dekker, NY, 2005, pp. 627-648.

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**Articles in "submitted" status**

1. A. D. Getty, C.-C. Tai, J. C. Linehan, P. G. Jessop, M. M. Olmstead, A. L. Rheingold, "Hydrogenation of Carbon Dioxide Catalyzed by Ruthenium Trimethylphosphine Complexes: A Mechanistic Investigation using High-Pressure NMR Spectroscopy" *submitted*.

**Special Recognitions Received by the PI**

The PI was awarded a Canada Research Chair (endowed chair) position by the federal government of Canada (the PI's home country) in June 2003 in recognition of his contributions to the field of green chemistry. He was also given the 2004 Canadian Catalysis Lectureship Award for his contributions to the field of catalysis.

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