

**Carbon dioxide as a green carbon source in transition metal catalyzed  
syntheses**

**Project no. 121171**

**Acronym: CO2Green**

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# Consortium

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## Abstract

The primary objective of the project is to produce new catalytically active transition metal systems for reduction and utilization of CO<sub>2</sub>. In this project two catalysis concepts are considered. The first one is straightforward reduction of CO<sub>2</sub> either *via* reversed water-gas shift reaction or *via* electro and photo chemical methods. The second approach consists of a one-pot reaction, which combines CO<sub>2</sub> reduction to CO with secondary catalysis reaction, hydroformylation of alkenes to aldehydes and alcohols. Additional goals are:

- Design of sustainable synthesis methods and catalytic processes
- Improving sustainability of catalysis reactions
- To understand properties and phenomena underlying the activities of studied compounds

To meet these goals the project is divided into three main tasks: 1) Design, synthesis and characterization of ligands and new transition metal compounds. 2) Catalytic testing of the new compounds. 3) Computational studies to shed light on the factors behind the catalytic activity.

### Allocation of the tasks:

- Joensuu group
  - o Conventional synthesis of ligands and metal complexes
  - o Structural characterization of new compounds
  - o CO<sub>2</sub> reduction *via* reversed water-gas shift reaction, hydroformylation utilizing CO<sub>2</sub> as feedstock

- Molecular modeling
- Grenoble group
  - Synthesis of new ligands and complexes by conventional, electrochemical and photochemical methods.
  - Electrochemical and photochemical characterizations of the new compounds
  - Electrochemical and photochemical reduction of CO<sub>2</sub>

## Results of the project and related work

1. Oresmaa, L., Moreno, M.A., Jakonen, M., Suvanto, S., and Haukka, M. "Catalytic activity of linear chain ruthenium carbonyl polymer [Ru(CO)<sub>4</sub>]<sub>n</sub> in 1-hexene hydroformylation" *Appl.Catal.A* 353(1) (2009) 113-116.
2. Niskanen, M., Hirva, P., and Haukka, M. "Computational DFT Study of Ruthenium Tetracarbonyl Polymer" *J.Chem.Theor.Comput.* 5(4) (2009) 1084-1090.
3. Kontkanen, M-L., Oresmaa, L., Moreno, M.A., Jänis, J., Laurila, E., and Haukka, M. "One-dimensional Metal Atom Chain [Ru(CO)<sub>4</sub>]<sub>n</sub> as a Catalyst Precursor - Hydroformylation of 1-hexene Using Carbon Dioxide as a Reactant" *Appl.Catal A.* 365(1) (2009) 130-134.
4. Hartl, F., Renfrew, A.K., Lafalet, F., Mahabiersing, T., Calhorda, M.J., Chardon-Noblat, S., Haukka, M., and Deronzier, A. "Soluble Redox-Active Polymetallic Chains [{Ru<sup>0</sup>(CO)(L)(bpy)}<sup>m</sup>]<sub>n</sub> (bpy = 2,2'-bipyridine, L = PrCN, Cl<sup>-</sup>, m = 0, -1): Electrosynthesis and Characterization" *Inorg.Chem.* 48(17) (2009) 8233-8244.
5. Jänis, J., Jakonen, M., Oresmaa, M., Hirva, P., Laurila, E., Vlasova, L., Vainiotalo, P., and Matti Haukka "Fragmentation pathways of [MX<sub>2</sub>(CO)<sub>2</sub>(dcbpy)] (M = Ru, Os; X = Cl, Br, I; dcbpy = 4,4'-dicarboxylic acid-2,2'-bipyridine) complexes" *Submitted to Organometallics.*
6. "Photo-induced oxidation and reduction vs CO dissociation in [Os(L)(CO)<sub>2</sub>Cl<sub>2</sub>] complexes ; L = 2,2'-bipyridine, 4,4'-dimethyl 2,2'-bipyridine" *join paper in preparation*
7. Gerbaud, G., Mouesca, J.M., Hediger, S., Chardon-Noblat, S. Lafalet, F., Deronzier, A., and Bardet, M. "Structural characterization of metal-metal bonded polymer [Ru(L)(CO)<sub>2</sub>]<sub>n</sub> (L= 2,2'-bipyridine ) in the solid state using high-resolution NMR and DFT chemical shift calculations" *to be submitted to J. Am. Chem. Soc.*

## Activities

1. CO<sub>2</sub>Green Kick-off meeting, Département de Chimie Moléculaire (DCM) Université Joseph Fourier, Grenoble, France, January 29, 2009.

2. KETJU annual seminar, Helsinki Suomenlinna Sea Fortress, Helsinki, Finland, February 10-11, 2009.
3. 18th International Symposium on the Photochemistry and Photophysics of Coordination Compounds (18th ISPPCC), Sapporo, Japan, July 4-9, 2009 "Photoredox reaction vs. CO dissociation in [Os(diimine)(CO)<sub>2</sub>Cl<sub>2</sub>]"
4. CO<sub>2</sub>-SUSE –seminar, Åbo Akademi Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering, Åbo, Finland, October 8-9.10, 2009.
5. CO<sub>2</sub>Green 1<sup>st</sup> Follow-up meeting, 13-15.1.2010, University of Eastern Finland, Department of Chemistry, Joensuu, Finland, January 13 -14, 2010.

## Progress of the project

As originally planned, the focus of the research during the first year of the project has been on synthesis of new nitrogen donor ligands and metal carbonyl complexes of late transition metals. A series of new carbonyl containing complexes of Fe, Ru, Os, Ir and Rh with nitrogen donor ligands, such as polypyridines, oximes, imidazole derivatives, and N,N'-(isopropyl)<sub>2</sub>-1,4-diaza-1,3-butadiene have been synthesized and characterized.

Catalytic testing as well as computational studies has been started. Polymeric [Ru(CO)<sub>4</sub>]<sub>n</sub> synthesized via reductive carbonylation from RuCl<sub>3</sub>, has found to be active both in conventional hydroformylation and in RWGS-hydroformylation. In the latter case, conventionally used CO is replaced with CO<sub>2</sub> feedstock.

Series of Ru, Os complexes have been preliminarily tested in electrocatalytic CO<sub>2</sub> reduction at the analytical level. Some of the new complexes show promising results and this work is in ongoing.

Computational work has started with the analysis of the properties of [Ru(CO)<sub>4</sub>]<sub>n</sub> and [Ru(L)(CO)<sub>2</sub>]<sub>n</sub> (L= 2,2'-bipyridine ).

The synthesis task has been carried out in collaboration between the participating groups. New complexes synthesized in Joensuu have been sent to Grenoble for electrochemical analysis, photochemical studies and electrocatalytic testing. Similarly, ligands and complexes synthesized in Grenoble, have been sent to Joensuu for further synthesis, structural characterization and catalytic testing in reversed water-gas shift.

During the second and third year the role of the project catalysis will be emphasized. In the field on synthesis, the selection of new complexes is planned to be extended with multinuclear systems. Also, search for new active and environmentally more benign iron complexes will continue.