

Organometallic Chemistry for Enabling Carbon Dioxide Utilization

In photosynthesis, carbon dioxide is used as the carbon source; indeed, most carbon atoms in the structure of a massive tree—the trunk, the branches, the leaves—originate from CO₂. This insight has profound implications for chemical synthesis: complex molecular structures are built from something as simple and inert as CO₂. Scientists have long been fascinated by this concept, and chemists have tried to reproduce it by generating artificial systems for the transformation of CO₂ into more valuable products.

Over the past two decades, chemical conversion of CO₂ has developed into a major research field. Several comprehensive reviews have summarized advances on coupling CO₂ with nucleophiles to form carboxylic acids, carbonates, or carbamates or on reducing CO₂ to C1 species such as formate and methanol.¹ The reviews of this field also emphasize an important point: chemical utilization of CO₂ is not a strategy for helping mitigate climate change.^{1b} CO₂ is, however, a renewable carbon feedstock that can replace nonrenewable fossil-fuel-based starting materials. Therefore, methods for the efficient conversion of CO₂ should be viewed as an integral part in the development of sustainable chemical processes.

The 22 articles in this Special Issue highlight the many ways in which organometallic chemistry can help solve challenges related to CO₂ utilization: Organometallic complexes can be used in thermal, electrochemical, or photochemical conversion of CO₂ to various products such as formate, carbon monoxide, carboxylic acids, acrylates, and polycarbonates. Remarkably, the work presented here involves the activation of CO₂ with 15 different metals, including the first-row transition metals titanium, manganese, iron, cobalt, nickel, and copper; the second-row elements ruthenium, and rhodium; the third-row species rhenium, platinum, and iridium, the actinide uranium; and the main-group metals cesium, magnesium and aluminum (see Figure 1 for a selection of metal complexes featured in this Special Issue). One may think, there are many roads to Rome; however, an important point is that the various metals have distinct strengths in terms of selectivity and activity for chemical CO₂ utilization. The behaviour of these different metals in CO₂ conversion can further be modulated through introduction of different ligands.

The effect of the metal on the product selectivity is highlighted by Skrydstrup, Daasbjerg, and coworkers from

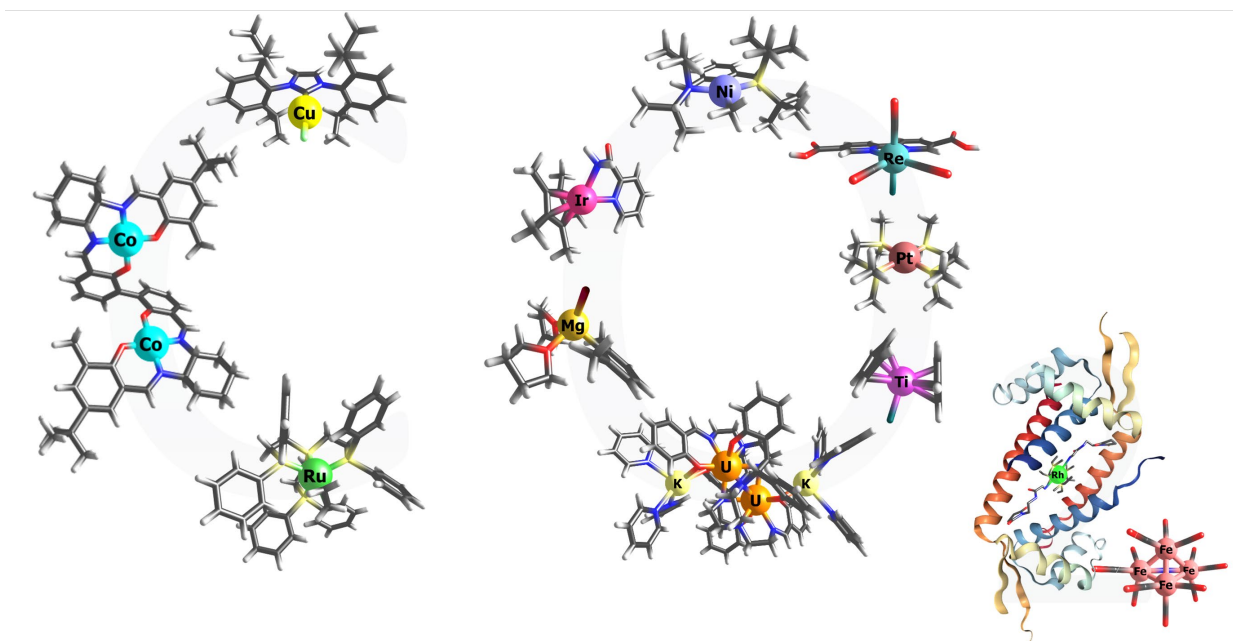


Figure 1. Selected metal complexes featured in the Special Issue, *Organometallic Chemistry for Enabling Carbon Dioxide Utilization*.²

Aarhus University. They report on electrocatalytic reduction of CO₂ with rhenium(I) and ruthenium(II) bipyridine complexes bearing pendant amines. For both systems, the major product is CO, in contrast to a related manganese(I) complex that mainly gives formic acid (DOI: [10.1021/acs.organomet.9b00815](https://doi.org/10.1021/acs.organomet.9b00815)). Yang and her group from the University of California – Irvine report a series of electrochemical and NMR experiments, from which the thermodynamic parameters and rate constants for conversion of CO₂ with [Pt(dmpcpe)₂]²⁺ are determined. They conclude that both thermodynamic and kinetic factors are responsible for the high selectivity for formate production over undesired alternative pathways, such as hydrogen evolution (DOI: [10.1021/acs.organomet.9b00720](https://doi.org/10.1021/acs.organomet.9b00720)). Apfel from the Ruhr-University Bochum and Ray from the Humboldt University of Berlin with their coworkers report that an exchange of a nitrogen donor atom by a chalcogen (O, S, Se) in a series of isocyclam-based nickel complexes alters the product selectivity in electrochemical CO₂ reductions. With increasing electron density of the chalcogen, the selectivity for CO generation is lost and instead, hydrogen evolution becomes favoured (DOI: [10.1021/acs.organomet.0c00129](https://doi.org/10.1021/acs.organomet.0c00129)).

Efficient CO₂ reduction to C1 species is a prominent goal in the field of CO₂ utilization. Ishitani, Fabry, and coworkers from Tokyo Institute of Technology report a novel supramolecular photocatalyst composed of a ruthenium(II) photosensitizer and a manganese(I) catalyst. The photocatalytic efficiency for formic acid formation from CO₂ is higher for the dinuclear system than for the mononuclear species (DOI: [10.1021/acs.organomet.9b00755](https://doi.org/10.1021/acs.organomet.9b00755)). Himeda and coworkers from Japan's National Institute of Advanced Industrial Science & Technology and Fushita and Ertem from the U.S.'s Brookhaven National Laboratory together with their coworkers report a combined experimental and computational study of CO₂ hydrogenation using a series of pentamethyl-cyclopentadienyl-iridium(III) complexes with amide ligands. Good activity is observed under ambient conditions in basic aqueous solutions (DOI: [10.1021/acs.organomet.9b00809](https://doi.org/10.1021/acs.organomet.9b00809)). A fascinating hybrid of a protein scaffold with a covalently linked rhodium(I) catalyst is studied in the work of Shaw and her group from the Pacific Northwest National Laboratory and their coworkers from Washington State University. The team evaluates the effect of amino acid mutations in the scaffold on the CO₂ reduction activity and shows that a positive charge near the active site is beneficial for catalysis (DOI: [10.1021/acs.organomet.9b00843](https://doi.org/10.1021/acs.organomet.9b00843)).

Coupling of carbon nucleophiles with CO₂ generates carbon-carbon bonds. Xi and coworkers from Tsinghua University and Nankai University have focused their attention on aryl carboxylic acids and report a novel protocol for titanium(II)-catalyzed carboxylation of aryl chlorides with CO₂ under mild conditions (DOI: [10.1021/acs.organomet.9b00712](https://doi.org/10.1021/acs.organomet.9b00712)).

[10.1021/acs.organomet.9b00712](https://doi.org/10.1021/acs.organomet.9b00712)). Hopmann, Bayer, and coworkers from UiT The Arctic University of Norway report a combined experimental and computational study exploring copper(I)-catalyzed formation of alkyl and benzyl carboxylic acids in the presence of cesium fluoride as a base. They show that the cesium additive by itself is able to carboxylate benzylic carbons with CO₂, whereas carboxylation of nonbenzylic carbons requires the copper catalyst (DOI: [10.1021/acs.organomet.9b00710](https://doi.org/10.1021/acs.organomet.9b00710)). The usefulness of copper in carbon-CO₂ coupling is emphasized by He and coworkers from Nankai University, who provide a comprehensive review of recent advances in carboxylation reactions based on carbocuprate species (DOI: [10.1021/acs.organomet.9b00642](https://doi.org/10.1021/acs.organomet.9b00642)). In contrast to copper systems, nickel(II) is known to be notoriously poor for CO₂ insertion into metal-alkyl bonds. However, the group of Wendt from the University of Lund reports a novel nickel(II) complex with an unsymmetric PCN pincer ligand that can insert CO₂ into a nickel-methyl bond under similar conditions to those used for palladium PCP pincer complexes (DOI: [10.1021/acs.organomet.9b00817](https://doi.org/10.1021/acs.organomet.9b00817)).

The possibility to form acrylates from CO₂ and olefins has long intrigued chemists. However, a major challenge is the cleavage of the formed metalalactones. Iwasawa and his group from Tokyo Institute of Technology describe a detailed analysis of the formation of acrylate salt from ethylene and CO₂ using ruthenium complexes. The studied systems are remarkable as they allow cleavage of the formed metallalactones through heating. Further, the group reports isolation of key catalytic intermediates, Ru(0)-ethylene, ruthenialactone, and Ru(II)-hydridoacrylate, and studies the effect of different tetrasubstituted phosphine ligands on individual reaction steps (DOI: [10.1021/acs.organomet.9b00659](https://doi.org/10.1021/acs.organomet.9b00659)). The group of Bernskoetter from the University of Missouri and their coworkers from Sekisui Chemical Co. have analyzed nickel-catalyzed coupling of CO₂ and ethylene to acrylate. By testing a series of 1,2-bis(dialkylphosphino)benzene and related diphosphine ligands and bases, important insights are gained into how structure affects activity in the studied systems (DOI: [10.1021/acs.organomet.9b000708](https://doi.org/10.1021/acs.organomet.9b000708)). Analogous to the coupling of CO₂ with alkenes, the oxidative coupling with alkynyl substrates is also of great interest. Field and coworkers from the University of New South Wales and their collaborators from Heriot-Watt University describe the formation of metalalactones from CO₂ and acetylido iron hydride complexes. Depending on the acetylene, diverse reactivity is observed, including an unprecedented insertion of CO₂ into the C-H bond of a σ -bound acetylide (DOI: [10.1021/acs.organomet.9b00830](https://doi.org/10.1021/acs.organomet.9b00830)).

Coupling of CO₂ with oxygen-based nucleophiles can provide carbonates and polycarbonates. The group of Mazzanti from Ecole Polytechnique Fédérale de Lausanne, reports a new dinuclear macrocyclic uranium complex that

promotes reductive disproportionation of CO₂ to carbonate. The new complex is more reactive than previously reported uranium(IV) species of reduced Schiff bases (DOI: [10.1021/acs.organomet.9b000792](https://doi.org/10.1021/acs.organomet.9b000792)). Meyer and his group from Friedrich-Alexander-University of Erlangen-Nürnberg describe the successful design of a closed synthetic cycle for the transformation of CO₂ to carbonate with a tris-aryloxide-ligated uranium(IV) complex. Carbonate is formed through insertion of CO₂ into the uranium-aryloxide bond and is subsequently eliminated from the metal with trimethylsilyl halide (DOI: [10.1021/acs.organomet.9b00786](https://doi.org/10.1021/acs.organomet.9b00786)). A conceptually intriguing approach is the insertion of a metal complex into a polycarbonate. Darensbourg and coworkers from Texas A&M University report a one-pot, two-step synthesis for forming triblock ABA polycarbonates, where the B block contains a rhenium complex. The resulting anionic polymers self-assemble to micelles, paving the way for the design of micellar catalysts that can promote organometallic transformations in water (DOI: [10.1021/acs.organomet.9b00704](https://doi.org/10.1021/acs.organomet.9b00704)). The group of Williams from the University of Oxford and their coworkers from the University of Bath report on the performance of titanium-amino-tris(phenolate) systems for copolymerization of cyclohexene oxide and CO₂. Notable features of their titanium(IV) complexes include thermal and redox stability, earth-abundance, low toxicity, and a lack of color. The studied complexes show moderate activity but excellent selectivity for forming carbonate linkages (DOI: [10.1021/acs.organomet.9b00845](https://doi.org/10.1021/acs.organomet.9b00845)). Lu and his group from the Dalian University of Technology report on enantioselective terpolymerization of CO₂, cyclohexene oxide, and racemic β -butyrolactone in a one-pot reaction utilizing an enantiopure bimetallic cobalt(III) catalyst. The products are optically active polymers that have adjustable properties (DOI: [10.1021/acs.organomet.9b000782](https://doi.org/10.1021/acs.organomet.9b000782)).

Mechanistic studies are crucial to understand the activity and selectivity of catalytic CO₂ conversion. The group of Ahlquist from KTH Royal Institute of Technology and their coworkers from the University of Aarhus have investigated why the adhesion of cobalt(I) porphyrin to a carbon nanotube enhances the electrochemical conversion of CO₂ to CO. Computational studies indicate that the main effect comes from the stabilization of intermediates by the solvent, water, which only can be used for the heterogeneous but not the homogeneous system (DOI: [10.1021/acs.organomet.9b000726](https://doi.org/10.1021/acs.organomet.9b000726)). The group of Kleij from Institute of Chemical Research of Catalonia and their coworkers from Universitat Rovira i Virgili and Catalan Institute of Research & Advanced Studies, have studied how an aluminium(III) aminotriphenolate complex affects the regio- and stereochemistry of the coupling of CO₂ with a cyclic epoxy alcohol. The study shows how a change in reaction conditions can control conversion of the same starting material to three distinct bicyclic carbonates, two

of them with unusual *trans*-configurations, with selectivities of around 90% (DOI: [10.1021/acs.organomet.9b00773](https://doi.org/10.1021/acs.organomet.9b00773)). Lee and coworkers from the University of Copenhagen and Bae and coworkers at Sungkyunkwan University performed kinetic analyses and in-situ infrared spectroscopy to study the effect of catalytic amounts of nucleophilic bases on insertion of CO₂ into magnesium-carbon bonds. They conclude that nucleophilic base additives can affect the CO₂ solubility and the carboxylation yields (DOI: [10.1021/acs.organomet.9b00838](https://doi.org/10.1021/acs.organomet.9b00838)). Berben and her group from the University of California, Davis, show that [Fe₄N(CO)₁₂]⁻ is a much better electrocatalyst for CO₂ reduction to formate than [Fe₃MnO(CO)₁₂]⁻, although the cluster with manganese has the same butterfly structure and electron count as the four-center iron system. However, the cluster containing manganese is several kcal/mol less hydridic, preventing hydride transfer to CO₂ in acetonitrile solution (DOI: [10.1021/acs.organomet.9b00848](https://doi.org/10.1021/acs.organomet.9b00848)).

The 22 contributions in this Special Issue highlight the remarkable versatility and progress of organometallic CO₂ utilization. We believe that the reported results will inspire researchers in this field to devise new and exciting experiments, which we hope to read about in *Organometallics*.

Nilay Hazari,[†]

Nobuharu Iwasawa,[‡]

Kathrin H. Hopmann, Associate Editor*,&

[†]The Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520, United States.

[‡]Department of Chemistry, School of Science, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan.

[&]Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, UiT The Arctic University of Norway, N- 9037 Tromsø, Norway.

AUTHOR INFORMATION

Corresponding Author*

E-mail for K.H.H: kathrin.hopmann@uit.no

ORCID

Nilay Hazari: 0000-0001-8337-198X

Nobuharu Iwasawa: 0000-0001-6323-6588

Kathrin H. Hopmann: 0000-0003-2798-716X

Notes

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Biographies



Nilay Hazari (Ph.D. 2006) is a Professor of Chemistry at Yale University. His research focuses on the rational design of homogeneous transition metal complexes using mechanistic studies. In particular, his group has developed a number of highly active catalysts for the transformation of CO₂ into C1 species and performed fundamental studies exploring the pathway for CO₂ insertion into metal-element s-bonds.



Nobuharu Iwasawa (Ph.D. 1984) is a Professor in the Department of Chemistry at Tokyo Institute of Technology. His research focuses on the development of transition metal-catalyzed reactions such as carboxylations and the synthesis of natural and nonnatural compounds of unique functionality.



Kathrin H. Hopmann (Ph.D. 2008) is an Associate Professor in Computational Chemistry at UiT The Arctic University of Norway. Her research focuses on the mechanistic analysis and design of organometallic catalysts, especially for hydrogenation and carboxylation reactions.

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(2) Complexes are either solid state structures (from X-ray crystallography) or predicted structures (from DFT): Ir complex from DOI: [10.1021/acs.organomet.9b00809](https://doi.org/10.1021/acs.organomet.9b00809), Cu complex from DOI: [10.1021/as.organomet.9b00710](https://doi.org/10.1021/as.organomet.9b00710), Ni complex from DOI: [10.1021/acs.organomet.00817](https://doi.org/10.1021/acs.organomet.00817), U complex from DOI: [10.1021/acs.organomet9b00792](https://doi.org/10.1021/acs.organomet9b00792), Re complex from DOI: [10.1021/acs.organomet.9b00704](https://doi.org/10.1021/acs.organomet.9b00704), Ru complex from Cambridge Crystallographic Data Centre (CCDC) 1876653, Ti complex from CCDC 1121676, Fe complex based on CDCC 89607, Pt complex adapted from CDCC 187325, Mg complex adapted from CCDC 738501 by replacing ligands, Co complex adapted from CDCC 1001988, Rh complex adapted from PDB 6D00.