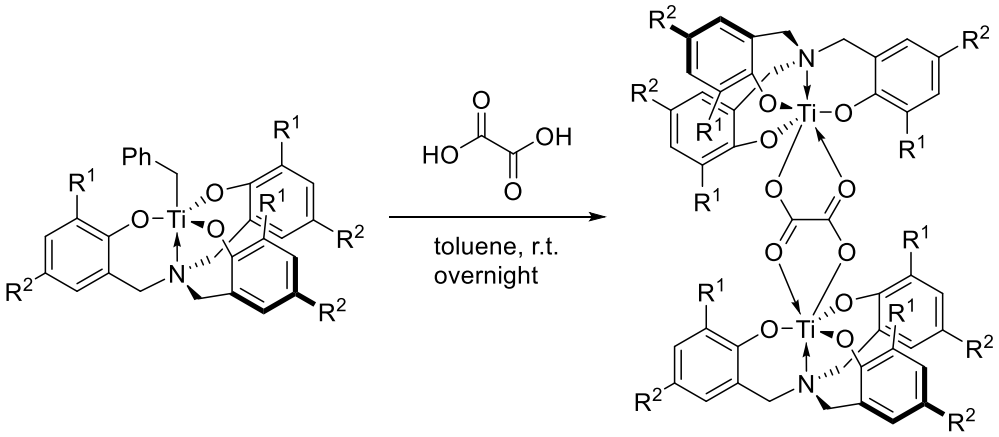
Synthesis of Dinuclear Titanium Oxalate Complexes Supported by a Tris(phenolato)amine Ligand

(*RWTH Aachen Univ.*) ○Akira Okumura, Florentine Mohr, Thomas Paul Spaniol, Jun Okuda
Keywords: Titanium Complex, Oxalate, Reduction, Carbon Dioxide, Phenolate Ligand

Carbon dioxide (CO_2) could become an attractive C1 building block for synthetic chemistry to produce sustainable chemicals and polymers.[1] However, because of the high thermodynamically stability and inertness of CO_2, catalytic transformation of CO_2 remains challenging. It is known that CO_2 can be catalytically transformed by organometallic complexes, heterogeneous catalysts, and electrocatalysts. Especially, the electrochemical reduction of CO_2 to formate and oxalate can offer C1 and C2 key intermediates.[2] As model compounds, metal formate and oxalate complexes are important to understand the coordination and reaction mode of CO_2 at metal centers. We have recently reported that titanium(IV) chlorido complex, which bears a sterically bulky tris(phenolato)amine(O_3N) ligand, can be transformed to titanium(IV) formate complexes.[3] Here, we report that dinuclear titanium(IV) oxalate complex can be synthesized by protonolysis of the titanium(IV) benzyl precursor.

When titanium(IV) benzyl complex ([(O_3N)TiBn]) was treated with 0.5 equiv. of oxalic acid in toluene at room temperature overnight, dinuclear titanium(IV) oxalate complex ([(O_3N)Ti(C_2O_4)Ti(O_3N)]) was obtained as dark orange powder in 75% yield. Single-crystal X-ray diffraction analysis revealed that two titanium(IV) centers are bridged by an oxalate dianion with μ,κ*O*-coordination mode. This dinuclear titanium(IV) oxalate complex was reduced by potassium metal to give a yellow complex, whose two titanium(IV) atoms are reduced to titanium(III).



1) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.*, **2014**, *114*, 1709. 2) a) E. Schuler, M. Demetriou, N. R. Shiju, G.-J. M. Gruter, *ChemSusChem*, **2021**, *14*, 3636. b) E. E. Benson, C. P. Kubiak, A. J. Sathrum, J. M. Smieja, *Chem. Soc. Rev.*, **2009**, *38*, 89. 3) A. Okumura, P. Ghana, F. Fink, R. Schmidt, A. Hoffmann, T. P. Spaniol, S. Herres-Pawlis, J. Okuda, *Dalton Trans.*, **2022**, *51*, 14345.