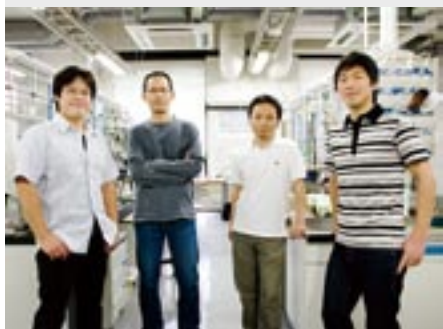


Synthesis and Reactions of Transition Metal Complexes Having Aryloxy-Based Ligands, Especially with Regard to Activation of Small Molecules

Department of Life and Coordination-Complex Molecular Science
Division of Functional Coordination Chemistry



KAWAGUCHI, Hiroyuki
MATSUO, Tsukasa
WATANABE, Takahito
AKAGI, Fumio
ARII, Hidekazu
FUKAWA, Tomohide
ISHIDA, Yutaka

Associate Professor
Assistant Professor*
IMS Fellow
Post-Doctoral Fellow
Post-Doctoral Fellow
Post-Doctoral Fellow
Post-Doctoral Fellow

This project is focused on the design and synthesis of new ligands that are capable of supporting novel structural features and reactivity. Currently, we are investigating multidentate ligands based on aryloxy and thiolate. In addition, we set out to study metal complexes with sterically hindered aryloxy and arylthiolate ligands. Our recent efforts have been directed toward activation of small molecules.

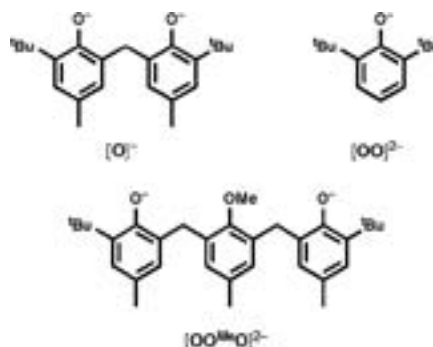
Development of ligands that play important roles in coordination chemistry has been the subject of intense interest. The chemistry of metal aryloxy complexes has shown that aryloxy ligands can promote various important transformations at metal centers. Therefore, aryloxy ligands complement the well-studied cyclopentadienyl-based systems, with the major difference being the greater reactivity of the aryloxy complexes due to their relatively higher unsaturation and lower coordination numbers for a $(\text{ArO})_n\text{M}$ fragment. However, coordinatively unsaturated metal complexes undergo facile ligand redistribution reactions, which are occasionally a severe obstacle to synthetic efforts.

One of strategies for overcoming this problem is the use of covalently linked ancillary ligands, thereby limiting ligand mobility and leaving little possibility to reorganize the molecule. This feature has led to the isolation and structural characterization of a number of metal complexes that are difficult to obtain with aryloxy monodentate ligands. In this context, we set out to investigate aryloxy-based multidentate ligands as new ancillary ligands.

1. Reduction of Carbon Dioxide with Hydrosilanes Catalyzed by Zirconium-Borane Complexes¹⁾

Carbon dioxide is the stable carbon end product of metabolism and other combustions, and it is an abundant yet low-value carbon source. This molecule would be very valuable as

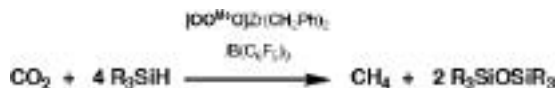
a renewable source if it were to be effectively transformed into reduced organic compounds under mild conditions. However, thermodynamic stability of CO_2 has prevented its utilization in industrial chemical processes, and thus this represents a continuing scientific challenge. In this study, we found that CO_2 is catalytically converted into CH_4 and siloxanes via bis(silyl)acetals with a mixture of a zirconium benzyl phenoxide complex and tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$).



Scheme 1.

In a first set of experiments, we studied the catalytic activity of cationic zirconium benzyl complexes bearing phenoxide ligands (Scheme 1) in the course of reducing CO_2 with PhMe_2SiH as the test substrate. The catalysts used in this study were synthesized by treatment of the dibenzyl complexes with $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene. The reaction of CO_2 with PhMe_2SiH proceeded exothermically to form $(\text{PhMe}_2\text{Si})_2\text{O}$ (Scheme 2). Performing the analogous reaction in benzene- d_6 in a NMR tube revealed the release of CH_4 as the byproduct. The resonance due to CH_4 was observed as singlet at 0.15 ppm in the ^1H NMR spectrum. Mono- and bis-phenoxide ligands $[\text{O}]^-$ and $[\text{OO}]^{2-}$ gave zirconium complexes that preformed with low activity relative to the tridentate ligand $[\text{OO}^{\text{Me}}\text{O}]^{2-}$. The combination of a zirconium complex with $\text{B}(\text{C}_6\text{F}_5)_3$ is responsible

for this result, because the analogous reaction using $[(\text{O}^{\text{Me}}\text{O})\text{Zr}(\text{CH}_2\text{Ph})][\text{B}(\text{C}_6\text{F}_5)_4]$ did not give CH_4 but led to formation of $\text{Ph}_2\text{Me}_2\text{Si}$ and Me_2SiH_2 . Thus, neither zirconium cationic species nor $\text{B}(\text{C}_6\text{F}_5)_3$ alone provided an active catalyst.



Scheme 2.

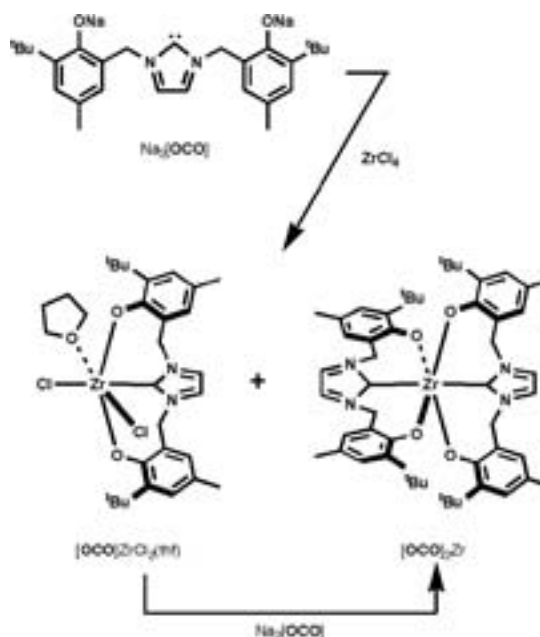
In order to obtain insight into the intervening processes in the reaction, isotopically enriched $^{13}\text{CO}_2$ (99 atom% ^{13}C) was admitted into a resealable NMR tube containing a solution of $(\text{O}^{\text{Me}}\text{O})\text{Zr}(\text{CH}_2\text{Ph})_2$, $\text{B}(\text{C}_6\text{F}_5)_3$, and Et_3SiH in benzene- d_6 at room temperature. The reaction requires approximately one week for completion and is monitored by NMR spectroscopy. The reaction proceeded cleanly, during which time $^{13}\text{CO}_2$ and Et_3SiH were fully consumed. Monitoring the reaction by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy indicates the presence of bis(silyl)acetal $^{13}\text{CH}_2(\text{OSiEt}_3)_2$ as a detectable intermediate. The resonance at 84.5 ppm due to $^{13}\text{CH}_2(\text{OSiEt}_3)_2$ grew to a maximum relative intensity over a period of about 7 h and then decreased as that at -4.4 ppm due to $^{13}\text{CH}_4$ continued to grow until, after about 1 week, it was the only resonance attributable to a ^{13}C -labeled product. Additionally, in the absence of proton decoupling, the resonances due to $^{13}\text{CH}_2(\text{OSiEt}_3)_2$ and $^{13}\text{CH}_4$ split into a triplet and a quintet with a coupling constant of 161.5 and 125.6 Hz, respectively. This observation unambiguously confirms that the carbon atom of CH_4 originates from CO_2 , and the source of its hydrogen atoms is added Et_3SiH .

The method for catalytic reduction of CO_2 presented here offers some significant advantages, since it proceeds under mild conditions and permits complete reduction of CO_2 to CH_4 . Another curious aspect of this system is the formation of polysiloxane from CO_2 and hydrosilane in chemical CO_2 fixation. The present results are promising, but we note that catalytic activity will need to be improved and the long-term stability and performance of the catalyst demonstrated.

2. Zirconium Complexes of a Tridentate Bis(aryloxide)-NHC Ligand²⁾

The chemistry and application of *N*-heterocyclic carbenes (NHCs) have been extensively explored. They can bind as two-electron donors to a wide range of transition metal, main group, and *f*-block derivatives. Especially, NHCs have been found extensive use as ancillary ligands in late transition metal complexes, in which they have shown enhanced catalytic activity compared to their phosphine analogues. In contrast, NHC complexes of early transition metals are considerably less developed despite the great potential of this class of molecules. This is mainly due to the ease of dissociation of the NHC ligand from the electron deficient metal center, which

makes it difficult to study the chemistry of NHCs in early transition metals and *f*-elements. A potential means of directing metal–NHC interactions is the covalent tethering of the anionic functional groups to the NHC ligand system, where the NHC moiety is held in proximity of the metal center by a covalent tether and should affect reactivity in a specific way. In this study, we show the synthesis of zirconium complexes having a bis(aryloxide)-NHC ligand ($[\text{OCO}]^{2-}$, Scheme 3)



Scheme 3.

The disodium salt of a ligand $\text{Na}_2[\text{OCO}]$, was prepared by reaction of $\text{H}_3[\text{OCO}]\text{Br}$ with 3 equiv of $\text{NaN}(\text{SiMe}_3)_2$. Reaction of $\text{ZrCl}_4(\text{thf})_2$ with 1 equiv of $\text{Na}_2[\text{OCO}]$ gave a mixture of $[\text{OCO}]\text{ZrCl}_2(\text{thf})$ and $[\text{OCO}]_2\text{Zr}$. When the amount of $\text{Na}_2[\text{OCO}]$ was increased to 2 equiv, $[\text{OCO}]_2\text{Zr}$ was obtained in good yield. The complex $[\text{OCO}]\text{ZrCl}_2(\text{thf})$ is a precursor to organometallic derivatives, and treatment with PhCH_2MgCl or $\text{Me}_3\text{SiCH}_2\text{Li}$ yielded $[\text{OCO}]\text{ZrR}_2$ ($\text{R} = \text{CH}_2\text{Ph}$, CH_2SiMe_3). The disodium salt $\text{Na}_2[\text{OCO}]$ is unstable and undergoes 1,2-benzyl migration, while zirconium complexes of the $[\text{OCO}]^{2-}$ ligand are found to be thermally stable in solid and solution.

Compounds $[\text{OCO}]\text{ZrCl}_2(\text{thf})$ and $[\text{OCO}]\text{ZrR}_2$ should provide excellent starting materials for investigation of the reactivity of this class of group 4 metal complexes. We expect it to demonstrate a rich and varied chemistry.

References

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* Present Address; RIKEN Wako Institute, Frontier Research System