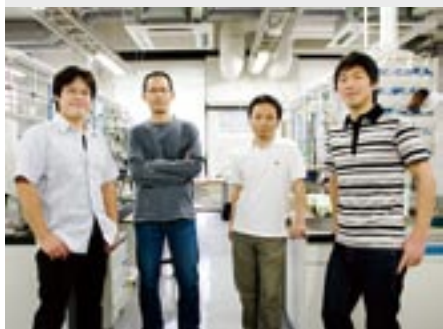


Synthesis and Reactions of Transition Metal Complexes Having Aryloxy-Based Ligands, Especially with Regard to Activation of Small Molecules

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



KAWAGUCHI, Hiroyuki
ISHIDA, Yutaka
WATANABE, Takahito
AKAGI, Fumio

Associate Professor*
Assistant Professor†
IMS 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 might lead to the isolation and structural characterization of a number of metal complexes that are difficult to obtain with aryloxy monodentate ligands.

1. Diniobium Tetrahydride Complex Bearing a Tripodal Triaryloxy Ligand¹⁾

We previously reported the synthesis of early transition metal hydride complexes supported by a linear triaryloxy ligand. As part of our studies of ancillary ligand effects, we recently began to study transition metal complexes with a tripodal triaryloxy ligand $[\text{O}_3]^{3-}$. The $[\text{O}_3]$ ligand provides a

rigid and facial donor environment. Herein, we were interested in extending this chemistry to niobium.

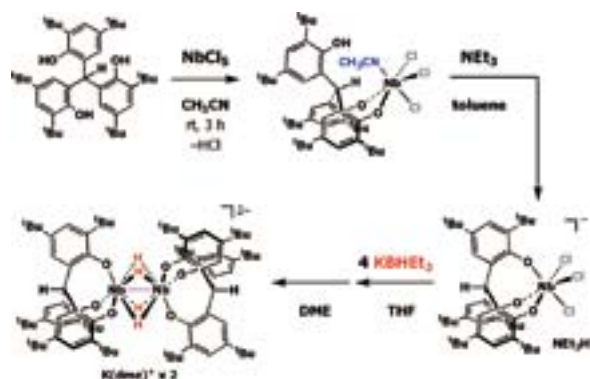


Figure 1. Synthesis of the hydride complex.

Treatment of NbCl_5 with the pro-ligand $\text{H}_3[\text{O}_3]$ in CH_3CN to give $\text{H}[\text{O}_3]\text{NbCl}_3(\text{CH}_3\text{CN})$ in 77% yield. The remaining hydroxy group in the nitrile adduct was deprotonated by NEt_3 in toluene at 80°C , yielding $[\text{NEt}_3\text{H}][(\text{O}_3)\text{NbCl}_3]$ as a red powder in 92%. An X-ray structure analysis of the trichloride complex reveals that the triaryloxy ligand coordinates to Nb facially.

Reaction of the trichloride complex with 4 equivalents of KBHET_3 in toluene/THF followed by recrystallization from DME gave yellow crystals of $[\text{K}(\text{dme})]_2\{[(\text{O}_3)\text{Nb}]_2(\mu\text{-H})_4\}$ in 66% yield along with evolution of H_2 . During the reaction, KBHET_3 partially acts as a reductant, and the metal center is reduced from Nb(V) to Nb(IV). The deuterated analogue was quantitatively prepared by treatment of the hydride complex under D_2 gas for three days at room temperature and was characterized by NMR spectroscopy.

An X-ray crystal structure determination of the hydride complex reveals a dimeric structure with two $[(\text{O}_3)\text{Nb}]$ frag-

ments bridged by four hydride ligands. The short Nb–Nb distance of 2.5690(5) Å indicates metal–metal bonding, thus accounting for the observed diamagnetism. The NMR spectra of the hydride complex are consistent with its solid-state structure if a fluxional process is invoked to explain the observed equivalence of the aryloxy groups on the NMR timescale at 25 °C. The bridging hydrides are observed as a broad signal at 6.29 ppm in the ^1H NMR spectrum. Upon cooling the sample, we did not detect any significant change in the hydride region.

2. Dinitrogen Activation by the Hydride Complex

Activation of molecular nitrogen by soluble metal complexes has attracted widespread attention from both fundamental and practical points of view. Dinitrogen cleavage by metal hydride complexes could be important in a catalytic system and is relevant to the Haber-Bosch process and a biological nitrogen-fixing system constituted by the metalloenzyme nitrogenase. Although late-transition-metal hydride complexes are often found to weakly bind dinitrogen with concomitant elimination of H_2 , conversion of an early-transition-metal hydride to a dinitrogen complex is a rarely documented phenomenon.

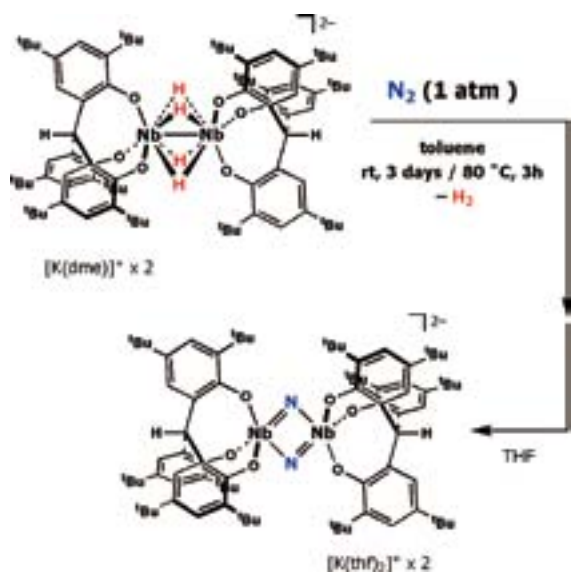


Figure 2. Reaction of the hydride complex with N_2 .

The dinioium tetrahydride complex appears to be thermally stable in solution under argon, while exposure of its toluene solution to an atmosphere of N_2 at room temperature resulted in a gradual color change from maroon to yellow brown for 3 days. Recrystallization from THF/pentane gave $[\text{K}(\text{thf})_2]_2\{[(\text{O}_3)\text{Nb}]_2(\mu\text{-N})_2\}$ as yellow crystals in 37% yield.

The isotopically labeled complex was prepared analogously under $^{15}\text{N}_2$ and exhibits a single resonance at 311 ppm in the ^{15}N NMR spectrum. This result confirms that the origin of the nitride ligands is added N_2 . In the ^1H NMR spectrum, the nitride complex possesses high symmetry in solution, as equivalent aryloxy groups are observed.

An X-ray crystal structure determination of the nitride complex has shown it to be dimeric, constructed around a planar Nb_2N_2 four-membered ring that resides on a pseudo-two-fold axis. Reduction of dinitrogen by the hydride complex results in cleavage of the $\text{N}\equiv\text{N}$ bond, as evidenced by the N–N separation of 2.589(5) Å. Each niobium center displays five-coordinate, distorted trigonal-bipyramidal coordination.

The nucleophilic behavior of the nitride groups was observed in the reaction with methyl iodide. The nitride complex was treated with excess of methyl iodide at room temperature to afford $[\text{K}(\text{thf})]_2\{[(\text{O}_3)\text{Nb}]_2(\mu\text{-N})(\mu\text{-NMe})\}$. When the reaction mixture was carried out at 60 °C for 5 days, the remaining nitride was methylated, giving a bis-imide complex $[\{(\text{O}_3)\text{Nb}\}_2(\mu\text{-NMe})_2]$.

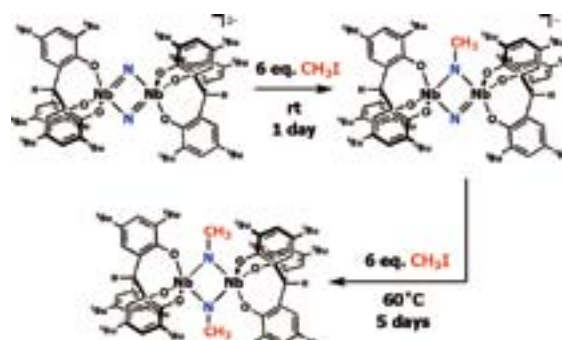


Figure 3. Reaction of the nitride complex with MeI.

Reduction of N_2 utilizing the hydride complex as described here is closely related to work by Fryzuk *et al.*, who used the tantalum(IV) hydride complex $[\{(\text{NPN})\text{Ta}\}_2(\mu\text{-H})_4]$ ($[\text{NPN}] = \text{PhP}(\text{CH}_2\text{SiMe}_2\text{NPh})_2$). This complex was found to react with N_2 through partial loss of H_2 to give the dinitrogen complex $[\{(\text{NPN})\text{Ta}\}_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-N}_2)(\mu\text{-H})_2]$, in which two hydride ligands remain coordinated. Subsequent treatment with boranes, silanes, and zirconium hydrides resulted in N_2 triple bond cleavage of the coordinated N_2 molecule. In our case, the cleavage proceeded spontaneously and did not require external reducing agent. This process corresponds to an overall six-electron reduction of N_2 , in which two electrons are initially stored in a metal–metal bond, and four additional electrons are provided by H_2 elimination.

Reference

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* Present Position; Professor, Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8551

† Present Address; Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8551

‡ Present Address; Department of Materials Science and Environmental Engineering, Tokyo University of Science, Yamaguchi, Sanyo-onodashi, Yamaguchi 756-0884