

VIII-B Coordination Chemistry of Sterically Hindered Ligands and Multidentate Ligands, and Activation of Small Molecules

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.

VIII-B-1 Complexes of Tantalum with Triaryloxides: Ligand and Solvent Effects on Formation of Hydride Derivatives

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A family of tantalum compounds supported by the triaryloxyde $[R-L]^{3-}$ ligands are reported $[H_3(R-L) = 2,6\text{-bis}(4\text{-methyl-6-}R\text{-salicyl})\text{-4-}tert\text{-butylphenol}$, where $R = \text{Me}$ or Bu^t]. The reaction of $H_3[Me-L]$ with $TaCl_5$ in toluene gave $[(Me-L)TaCl_2]_2$ (**1**). The $[Bu^t-L]$ analogue $[(Bu^t-L)TaCl_2]_2$ (**2**) was synthesized *via* treatment of $TaCl_5$ with $Li_3[Bu^t-L]$. A THF solution of $LiBHET_3$ was added to **1** in toluene to provide $[(Me-L)TaCl(THF)]_2$ (**3**), while treatment of **2** with 2 equiv of $LiBHET_3$ or potassium in toluene followed by recrystallization from DME resulted in formation of $[M(DME)_3][\{(Bu^t-L)TaCl\}_2(\mu-Cl)]$ [$M = \text{Li}$ (**4a**), K (**4b**)]. When the amount of $MBHET_3$ ($M = \text{Li}, \text{Na}, \text{K}$) was increased to 5 equiv, the analogous reactions in toluene afforded $[\{(bit-Bu^t-L)Ta\}_2(\mu-H)_3M]$ [$M = \text{Li(THF)}_2$ (**5a**), Na(DME)_2 (**5b**), K(DME)_2 (**5c**)]. During the course of the reaction, the methylene CH activation of the ligand took place. Dissolution of **5a** in DME produced $[\{(bit-Bu^t-L)Ta\}_2(\mu-H)_3Li(DME)_2]$ (**6**), indicating that the coordinated THF molecules are labile. When the **2**/ $LiBHET_3$ reaction was carried out in THF, the ring opening of THF occurred to yield $[(Bu^t-L)Ta(OBu^t)]_2$ (**7**) along with a trace amount of $[Li(THF)_4][\{(Bu^t-L)TaCl\}_2(\mu-OBu^t)]$ (**8**). Treatment of **2** with potassium hydride in DME yielded $[\{(Bu^t-L)TaCl_2K(DME)_2\}_2(\mu-OCH_2CH_2O)]$ (**9**), in which the ethane-1,2-diolate ligand arose from partial C–O bond rupture of DME.

VIII-B-2 A Synthetic Cycle for H_2/CO Activation and Allene Synthesis Using Recyclable Zirconium Complexes

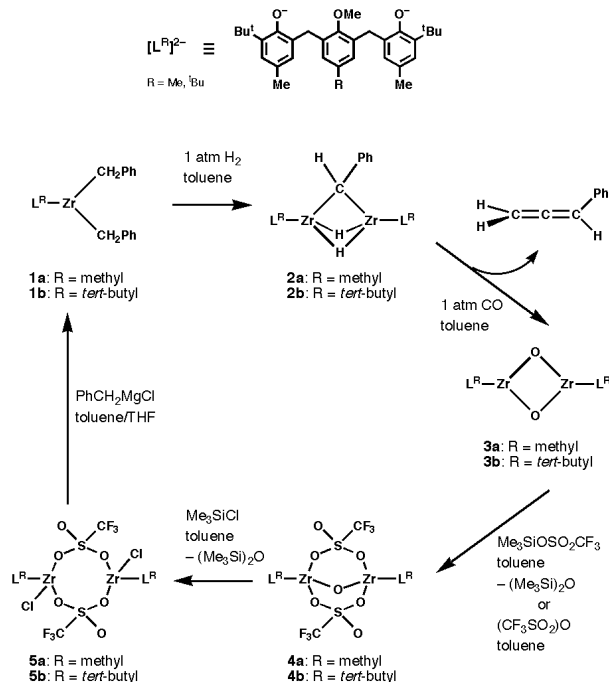
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Fischer–Tropsch (F–T) synthesis is an important chemical reaction to convert H_2 and CO to hydrocarbons along with water, thereby giving access to organic chemistry on the basis of simple inorganic molecules. The impressive F–T chemical transformation has elicited extensive synthetic efforts to reach chemical understanding of the heterogeneous F–T reaction and to produce soluble metal complexes that can react with H_2 and CO to form hydrocarbons with high product selec-

tivity. Although many soluble metal compounds and reactions relevant to surface species in the heterogeneous F–T process are known, well-characterized synthetic systems capable of converting H_2/CO into hydrocarbons have been limited. To explore the transformation of H_2 and CO with metal complexes, we have sought to use zirconium complexes supported by 2,6-bis(3-*tert*-butyl-5-methyl-2-oxybenzyl)-4-*R*-anisole ligands ($[L^R]^{2-}$).

This study demonstrated a synthetic cycle having relevance to F–T chemistry, wherein zirconium alkyl complexes of the $[L^R]$ ligands serves to transform H_2 and CO into corresponding allenes *via* alkylidene intermediates. The synthetic cycle is outlined in Scheme 1. This transformation involves the activation of H_2 , and C–C, C–H bond formation, C–O bond cleavage, and deoxygenative recycling of the oxo-bridging zirconium complexes. All of the preceding reactions are spectroscopically quantitative under mild conditions. Thus there is much potential for yield optimization, including the combination of consecutive steps.



Scheme 1.

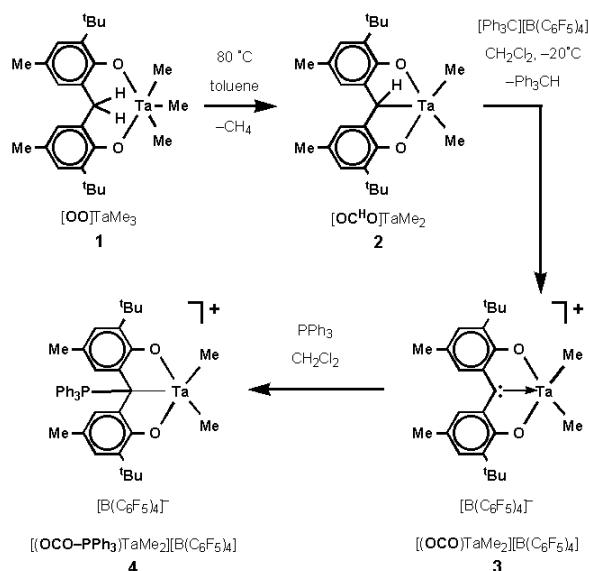
VIII-B-3 A Tantalum(V) Carbene Complex: Formation of a Carbene-Bis(phenoxy) Ligand by Sequential Proton and Hydride Abstraction

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Bis(phenoxides), in which the two phenoxide rings are linked to a donor atom (X) such as sulfur and phosphorous in the *ortho* positions, have been useful dianionic ancillary ligands in coordination chemistry and homogeneous catalysis. In this type of [OXO] ligands that combine the hard phenoxide donors with the soft X donor into a chelating array, electronic and stereochemical parameters can be manipulated by modifications of X donor groups so as to accommodate many transition metals in a variety of oxidation states and induce interesting transformations. With this in mind, we have begun to study the chemistry of carbene–phenoxide hybrid ligands, where a carbene functionality is introduced at the X donor site. The strong two-electron donor ability of the carbene group was appealing to us. In addition, this ligand system would provide the opportunity to study the effect of the σ -donor carbene functionality on the properties of electron deficient metal complexes.

The present work has demonstrated the synthesis and structure of the cationic tantalum(V) dimethyl complex with the [OCO] ligand. The dianionic tridentate [OCO] ligand is formed by the sequential proton and hydride abstraction from the backbone of the [OO] ligand (Scheme 1). The carbene moiety of **3** is stabilized *via* π -bonding to the oxyphenyl groups. This kind of carbene in this circumstance could be viewed as a neutral σ -donor carbene bound to Ta(V). This is a rare example of early transition metal complexes with σ -donor carbene ligands except N-heterocyclic carbenes. The electrophilic nature of carbene **3** has been shown in the reaction with PPh₃. Extension of this work to include other transition metal complexes and reactivity studies of **3** are in progress.



Scheme 1.