

Synthesis and Characterization of Organometal Oxide Complexes

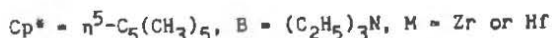
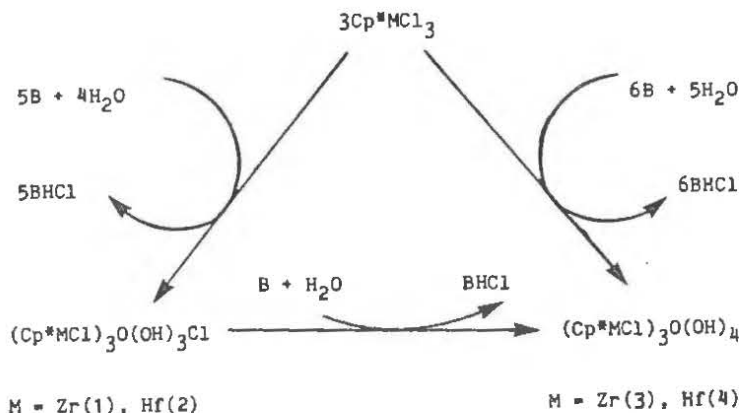
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Organometallic oxide complexes can be prepared by addition of an organometallic fragment to an inorganic oxide or by addition of oxygen atoms to an organometallic complex [1]. The latter route has been investigated to prepare ligand stabilized metal oxide fragments. Knowledge of fundamental geometries and reactivities of these stabilized oxide fragments may give insight concerning the formation of larger molecular units and solid state metal oxide structures. The base assisted hydrolysis of $[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{MCl}_3$ where $\text{M} = \text{Zr}$ and Hf has formed several new organometal oxohydroxide complexes.

The reactions of $[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{MCl}_3$, where $\text{M} = \text{Zr}$ and Hf , shown in Scheme 1 form trimeric oxohydroxide complexes $\{[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{MCl}\}_3\text{O}(\text{OH})_3\text{Cl}$, $\text{M} = \text{Zr}$, 1; Hf , 2, and $\{[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{MCl}\}_3\text{O}(\text{OH})_4$, $\text{M} = \text{Zr}$, 3; Hf , 4 [2,3]. The X-ray crystal



Scheme 1

structure of 3, $\{[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{ZrCl}\}_3\text{O}(\text{OH})_4$, as a THF solvate was determined by Dr. Victor Day. The structure consists of a triangle of Zr atoms capped by a triply bridged oxygen atom and a triply bridged hydroxide ligand. The edges of the trimer are bridged by hydroxide ligands. The $[\eta^5\text{-C}_5(\text{CH}_3)_5]$ and chloride ligands are arranged as seen in Figure 1. The structure for this zirconium complex is not retained in solution, however, the hafnium complex, 4, appears to have this structure both in solution and in the solid state. The structure proposed for 1 and 2, $\{[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{MCl}\}_3\text{O}(\text{OH})_3\text{Cl}$, is similar to 3 except the triply bridging hydroxide ligand is missing and one edge is doubly bridged by a chloride and a hydroxide ligand. Hydrolysis of 1 and 2 with one equivalent each of base and water forms 3 and 4, respectively.

Very little is known about the formation and reactivity of organotitanium oxide cages, $(\text{RTiO}_{3/2})_n$, although the organosiloxane cage complexes with $(\text{RSiO}_{3/2})_n$ frameworks are well established [4]. Oligomeric titanium oxide complexes containing chloride ligands have been prepared by hydrolysis of cyclopentadiene substituted titanium starting materials [1]. Hydrolysis in the presence of base has been found to replace all the chloride ligands with bridging oxygen atoms.

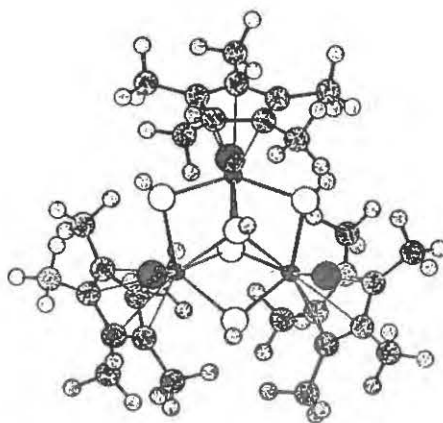


Figure 1

Base hydrolysis of $[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{TiCl}_3$ results in the formation of the organotitanoxane cage $\{[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{Ti}\}_4\text{O}_6$, 5. This complex has an adamantane-like M-O cage surrounded by $[\eta^5\text{-C}_5(\text{CH}_3)_5]$ ligands, Figure 2 [5]. Reaction of 5 with TiCl_4 results in the stepwise chlorination of the cage yielding several

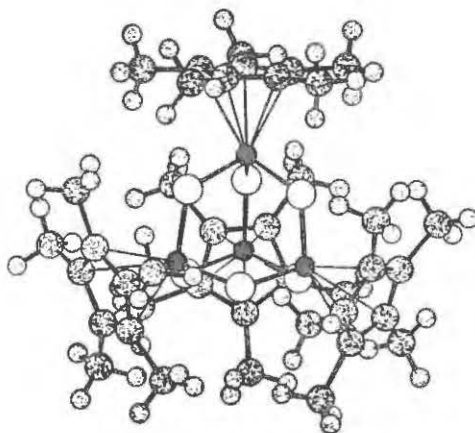
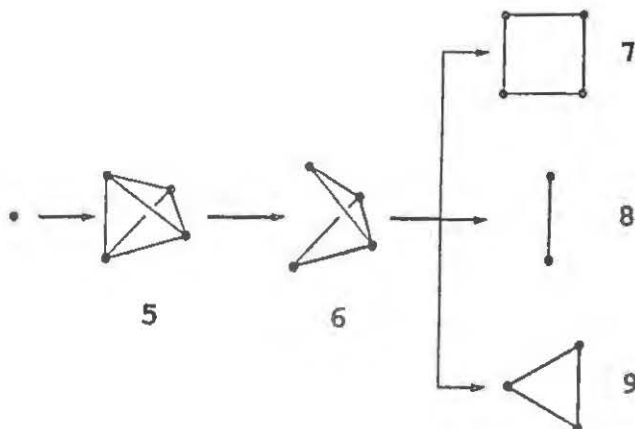


Figure 2

new organotitanium oxide complexes. The first step of these reactions involves cleavage of one edge of the $\{[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{Ti}\}_4\text{O}_6$ cage to give $\{[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{Ti}\}_4\text{O}_5\text{Cl}_2$, 6. The next step results in the formation of several products, a cyclic tetramer, $\{[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{TiClO}\}_4$, 7, a dimer, $\{[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{TiCl}_2\}_2\text{O}$, 8, and a cyclic trimer, $\{[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{TiClO}\}_3$, 9. The products of these reactions are summarized in Scheme 2.



Scheme 2

References

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