DOE/ER/13514 -- T1

SYNTHESIS AND CHEMISTRY OF YTTRIUM AND LANTHANIDE METAL COMPLEXES

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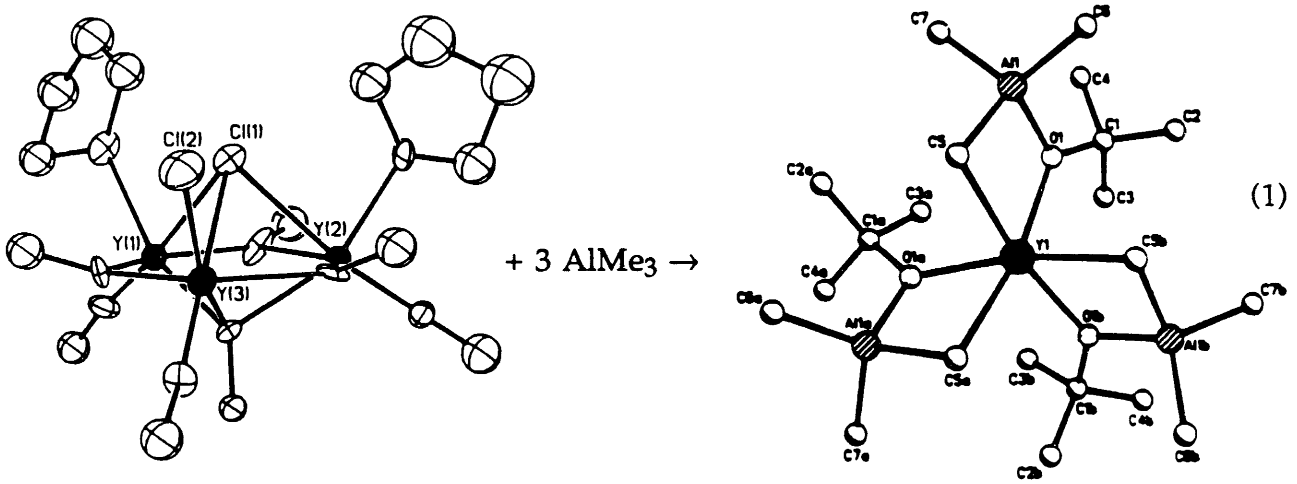
The objective of this research project is to determine the special features of complexes of yttrium and the lanthanide metals which will allow the design and synthesis of materials with unique chemical, physical, and catalytic properties. Past studies of yttrium and lanthanide metal alkyl and hydride complexes stabilized by cyclopentadienyl co-ligands have shown that a substantial, often singular, organometallic chemistry is available via these metals.[1] More extensive utilization of the chemical opportunities available through yttrium and the lanthanides would be possible, however, if stabilizing ancillary ligand systems less sensitive to oxidation and protonolysis than cyclopentadienides could be developed. Alkoxide ligands are attractive in this regard and our recent research has focused on alkoxides and the special opportunities they can provide to these metals. Results on several systems are described below.

Reactivity of Trimetallic Tert-Butoxide Complexes. Synthetic studies of lanthanide and yttrium complexes of simple alkoxides such as $OCMe_3$, $OCHMe_2$, and OMe have demonstrated a strong preference for the formation of polymetallic complexes containing from three to as many as fourteen metals in complexes such as $La_3(OCMe_3)_9(THF)_2$,[2] $Y_3(OCMe_3)_8Cl(THF)_2$,[2] $(C_5H_5)_5Y_5(OMe)_8O$,[3] $Ln_6(O^iPr)_{17}Cl$,[4] and $Y_{14}(OCMe_3)_{28}Cl_{10}O_2(THF)_4$.[5] These complexes are comprised of trimetallic units of general formula $Ln_3(\mu\text{-}OR)_3(\mu_3\text{-}OR)(\mu_3\text{-}X)$ where X = Cl, O, OR and Ln = yttrium or a lanthanide metal. The propensity of these trimetallic complexes to self-assemble suggested that their polymetallic framework would be pervasive in their reaction chemistry. However, in our last report, we described a remarkable result in which major disruption of the trimetallic unit occurred to give a product containing three new metallic components, reaction 1.



+ 3 $AlMe_3$ →

(1)

$Y_3(OR)_7Cl_2(THF)_2$

$Y(\mu\text{-}OR)_3(\mu\text{-}Me)_3Al_3Me_6$

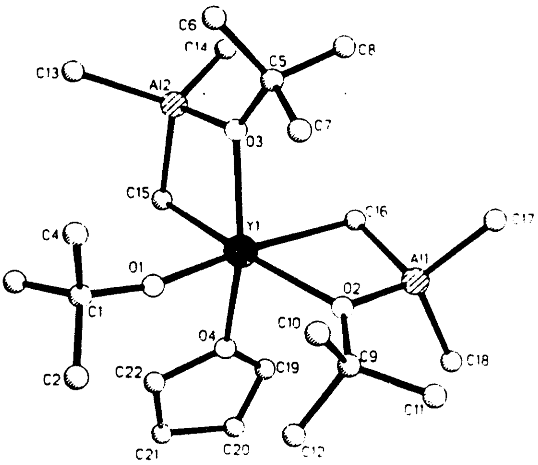
$R = OCMe_3$

We recently have discovered a series of reactions which indicates that this fragmentation reactivity has some generality. Reaction 2 shows a second product isolated from the $AlMe_3$ reaction system. This di-aluminum complex may be an intermediate on the pathway to the tri-aluminum product in reaction 1. The $Y(OR)_3Al_2Me_6(THF)$ complex appears to be well-suited for further derivatization due to the terminal alkoxide ligand and the coordinated THF, which could be removed to provide an open coordination site.

$Y_3(OR)_7Cl_2(THF)_2$ + 3 $AlMe_3$ →

$(RO)(THF)Y(\mu\text{-}OR)_2(\mu\text{-}Me)_2(AlMe_2)_2$

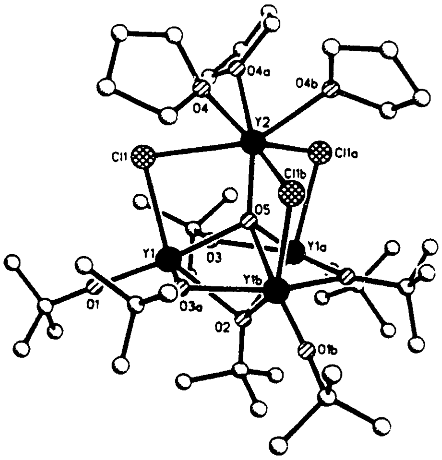
$R = OCMe_3$



(2)

$Y_3(OR)_7Cl_2(THF)_2$ is also fragmented by $LiAlMe_4$, reaction 3. In this case, the

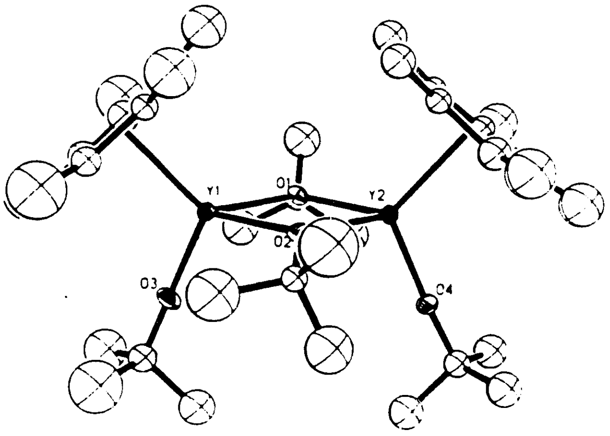
$$Y_3(OCMe_3)_7Cl_2(THF)_2 + LiAlMe_4 \rightarrow Y_4(OCMe_3)_7Cl_3O(THF)_3 \qquad (3)$$



product contains a mono-yttrium fragment combined with one of the original trimetallic units. This species can be viewed as a solvated $YCl_3(THF)_3$ species which has been solubilized by one of the $Ln_3(\mu\text{-}OR)_3(\mu_3\text{-}OR)(\mu_3\text{-}X)$ moieties.

The reaction of $Y_3(OR)_7Cl_2(THF)_2$ with NaC_5Me_5 also causes trimetallic fragmentation, reaction 4. The overall structure of the product is remarkably

$$2\,Y_3(OCMe_3)_7Cl_2(THF)_2 + 6\,NaC_5Me_5 \rightarrow 3\,[(C_5Me_5)(Me_3CO)Y(\mu\text{-}OCMe_3)]_2 + 4\,NaCl + 2\,NaOCMe_3 \qquad (4)$$

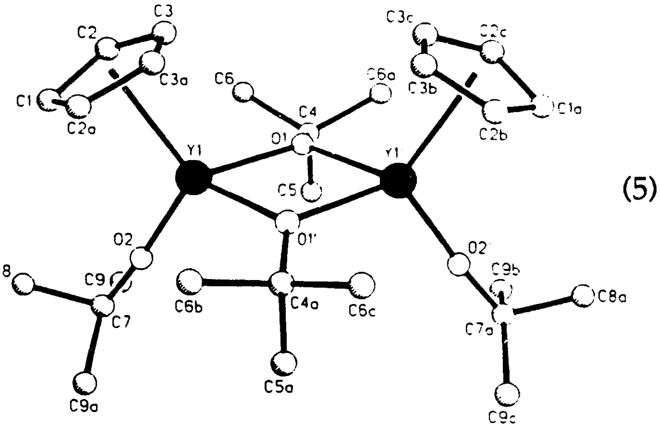


similar to that of the simple bridged bent metallocenes, $[(C_5R_5)_2M(\mu\text{-}Z)]_2$, and suggests that the tert-butoxide ligand is sterically equivalent to a cyclopentadienyl ring in these systems. Surprisingly, an analog to reaction 4 is also obtainable with the un-methylated cyclopentadienyl reagent, NaC_5H_5, reaction 5. Given the difference in size of C_5Me_5 and C_5H_5, the similarity in the structures in reactions 4 and 5 was unexpected.

$2\ Y_3(OCMe_3)_7Cl_2(THF)_2 + 6\ NaC_5H_5 \rightarrow$

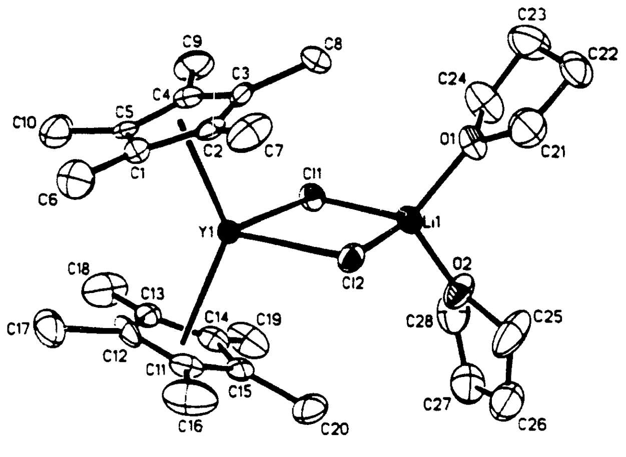
$3\ [(C_5H_5)(Me_3CO)Y(\mu\text{-}OCMe_3)]_2 +$

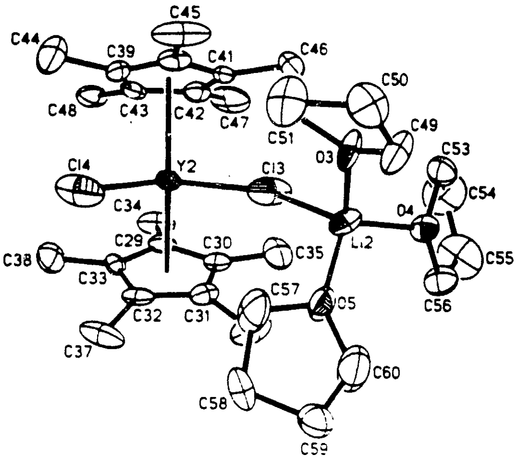
$4\ NaCl + 2\ NaOCMe_3$



(5)

Structural Effects of Ether Solvation. In the course of studying the synthesis of mixed cyclopentadienyl tert-butoxide complexes, single crystals of $[(C_5Me_5)_2Y(\mu\text{-}Cl)_2Li(THF)_2][(C_5Me_5)_2YCl(\mu\text{-}Cl)Li(THF)_3]$ were obtained. Many complexes of the type $(C_5Me_5)_2LnZ_2M(ether)_x$ (Z = monodentate monoanionic ligand such as halide, hydride, alkyl; M = alkali metal) have been reported in the past and it is generally assumed that $x = 2$ and the two Z ligands are doubly bridging. This new system is unique in that two $(C_5Me_5)_2YCl_2Li(THF)_x$ complexes, which differ only in the amount of THF solvation, $x = 2$ vs 3, co-crystallized in the same unit cell. This



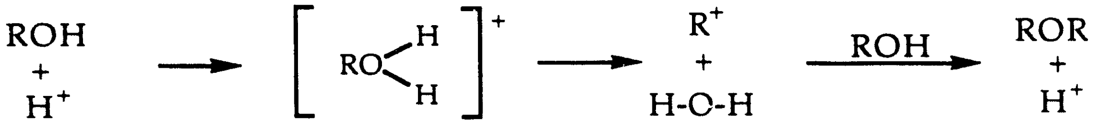


suggests that the two forms are closer in energy than might be expected. Given the differences in reactivity between terminal and bridging ligands in organolanthanide complexes,[1] this could have significant implications in reaction chemistry if both forms are available in solution. Specifically, the presence of a small amount of coordinating solvent, which might be expected to reduce reactivity by occupying a vacant coordination site on a lanthanide metal center, may actually enhance reactivity by generating a terminal ligand via a $(C_5Me_5)_2Ln(\mu\text{-}Z)_2M(ether)_2$ to $(C_5Me_5)_2LnZ(\mu\text{-}Z)M(ether)_3$ process. In such a case, a small amount of an ether in an arene or alkene solvent could substantially change the reactivity from that found in a rigorously ether-free solvent.

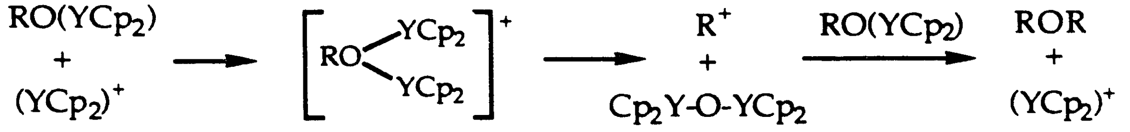
On the Origin of Oxide Ligands in Alkoxide Reactions. Numerous metal alkoxide syntheses produce complexes containing oxide as well as alkoxide ligands (e.g., equation 3). The source of the oxide is difficult to determine and "adventitious" moisture is often suspected. In the reaction 6 (M = Na, K), we

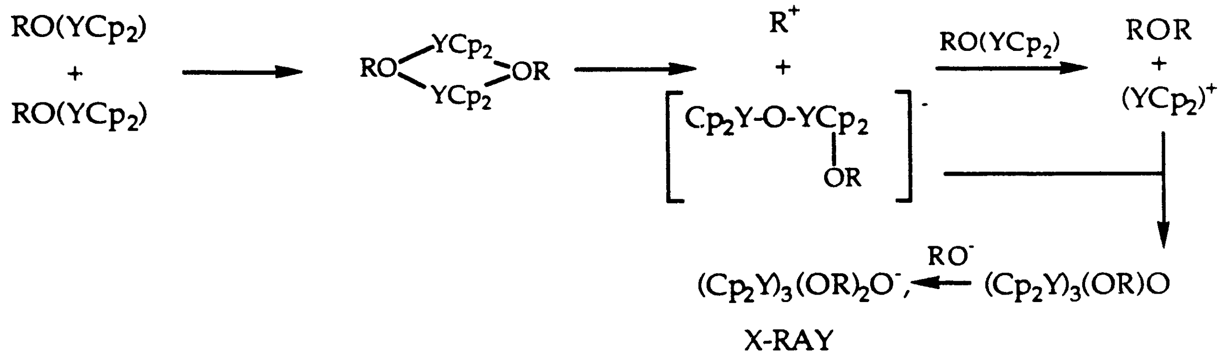
$$Cp_2YCl(THF) + MOMe \xrightarrow{-MCl} [Cp_2Y(OMe)]_2 + Cp_5Y_5(OMe)_8O + [(Cp_2Y)_3(OMe)_2O]^- + \text{other products} \qquad (6)$$

thought we had an ideal system for the investigation of this problem: moisture could be excluded as the source of oxide ligands since the cyclopentadienyl co-ligands did not hydrolyze. On the other hand, there was no evidence that the oxide was generated from methoxide. We now have such evidence. We have found conditions in which the oxide product, $[(Cp_2Y)_3(OMe)_2O]^-$ is formed in good yield and from these reactions we have isolated Me_2O. This suggests that a sequence of the type shown below could explain the formation of oxide from methoxide ligands. Equation 7 is known alcohol chemistry. If we consider a transient Cp_2Y^+ unit[6] to act


(7)

like a proton, Me_2O and oxide formation follow, equation 8. Equation 9 is equation


(8)

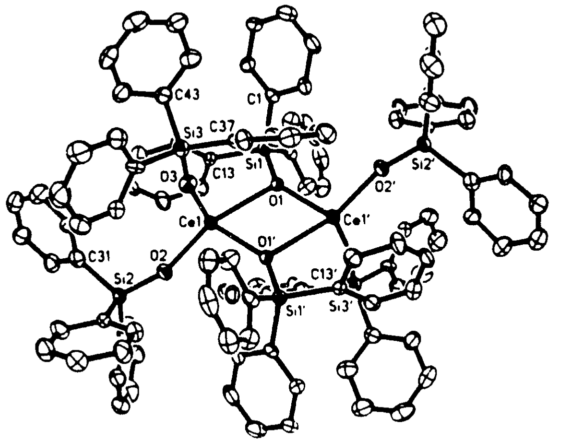

(9)

8 rewritten by adding one alkoxide ligand throughout. The result leads to the observed oxide complex and Me_2O (R = Me).

Tetravalent Chemistry. Using the knowledge gained by studying Ce(IV) alkoxide chemistry, we have attempted to make soluble, isolable complexes of Pr(IV). Reactions of the hexametallic complex, $Pr_6(O^iPr)_{17}Cl$ with quinones generates highly colored materials which indicate that oxidation has occurred. To date the systems studied have not been stable at temperatures over -10°C, however.

Alkoxide/Siloxide Comparisons. We have been able to obtain an unsolvated bimetallic siloxide, equation 10, for comparison with an analogous alkoxide which

$$2\ \mathrm{Ln[N(SiMe_3)_2]_3} + 6\ \mathrm{HOSiPh_3} \rightarrow \mathrm{Ln_2(OSiPh_3)_6} + 6\ \mathrm{HN(SiMe_3)_2} \qquad (10)$$



we reported last year. The triphenylsilanol complexes, $[\mathrm{Ln(OSiPh_3)_2(\mu\text{-}OSiPh_3)}]_2$, (Ln = La, Ce) were found to be considerably more soluble than their alkoxide analogs, $[\mathrm{Ln(OCPh_3)_2(\mu\text{-}OCPh_3)}]_2$, (Ln = La, Ce). In addition, $[\mathrm{Ce(OSiPh_3)_2(\mu\text{-}OSiPh_3)}]_2$ (shown above) was found to have a metal-C(ipso phenyl) orientation (Ce(1)-C(13)) suggestive of interaction not found in the crystal structure of the lanthanum alkoxide analog. The longer Si-O bond compared to the C-O distance may give greater flexibility to the siloxide ligand and enhance solubility and secondary ligand interactions.

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