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HOR* Ligated Metal Alkoxides

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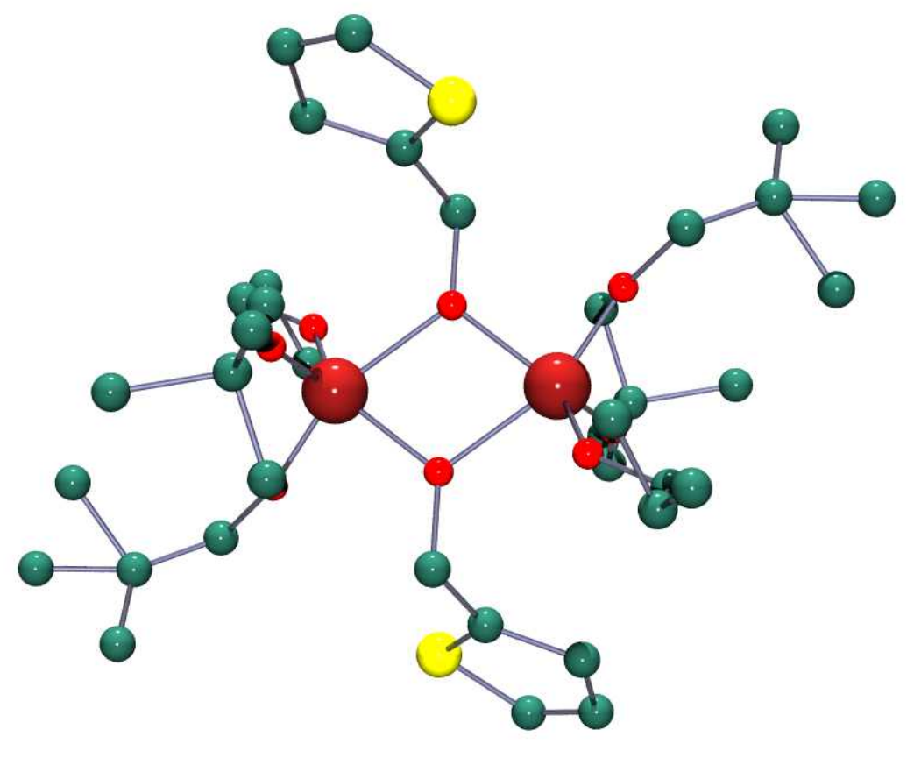
INTRODUCTION

We are investigating a series of bidentate ligands for the controlled construction of metal alkoxides for use in sol-gel, metalorganic chemical vapor deposition and nanoparticle production. Previously we have found that the 4,6-Dihydroxypyrimidine (DHP-H_2) ligand will act exclusively as a bridging ligand. In furthering our studies, we have selected a series of heterocyclic methanol derivatives due to their bidentate nature and similarity to typical solvents used in our laboratory. A schematic digram of the ligands selected are shown in the center hexagon. Several of our results are shown below.

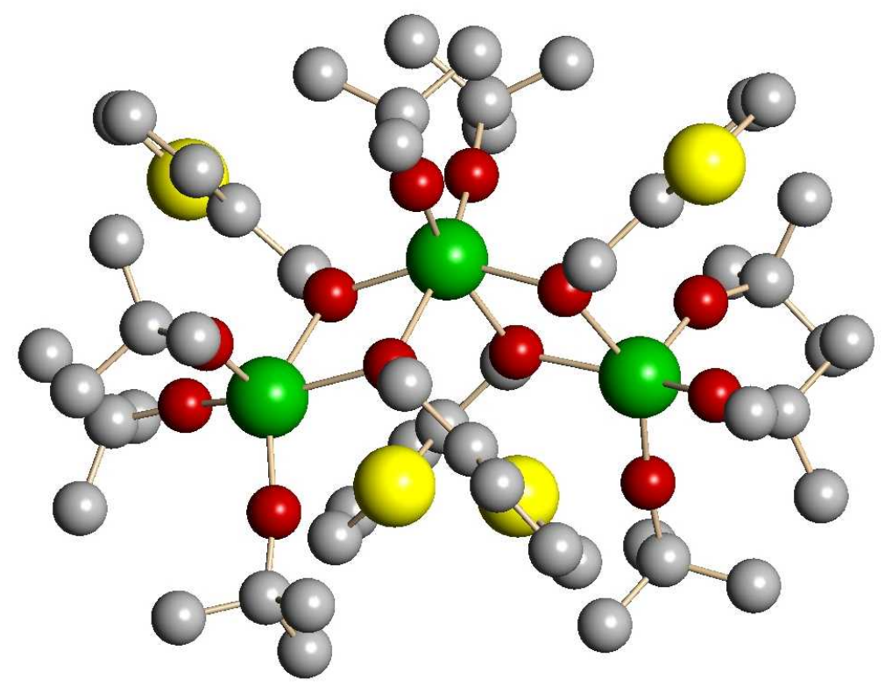
OTPM

The OTPM ligand does not interact with the early transition metals most likely due to the hard soft nature of the early transition metal and hetero atom.

$M(OR)_4$ + H-OTPM ⟶ "$M(OTPM)(OR)_3$"



$[Ti(\mu\text{-}OTPM)(ONep)_3]_2$

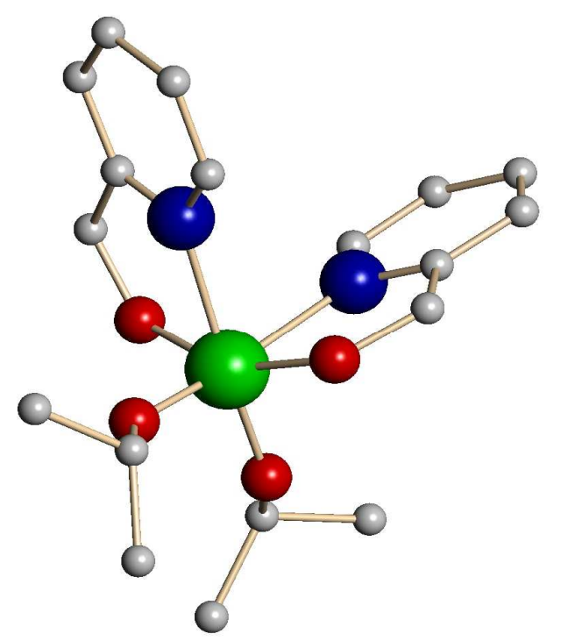


$Zr[(\mu\text{-}OTPM)_2Zr(OBu^t)_3]_2$

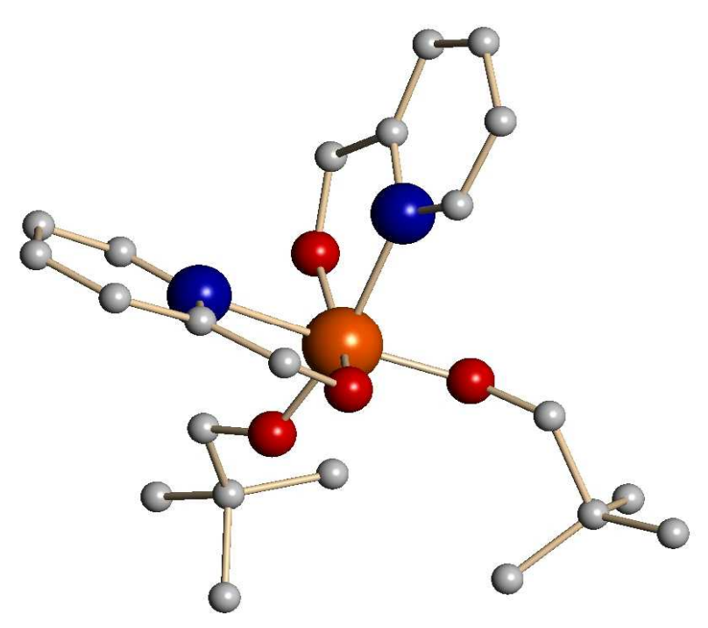
OPy

The Opy ligand was found in all cases to act as a bidenate ligand. This is as epected due to the well-known Lewis basic nature of the py moiety. The OPy acts as a sterically hindering ligand blocking one side of the metal center. This occurs independent of the alkoxide pendant chain and allows for controlled modification around the metal center.

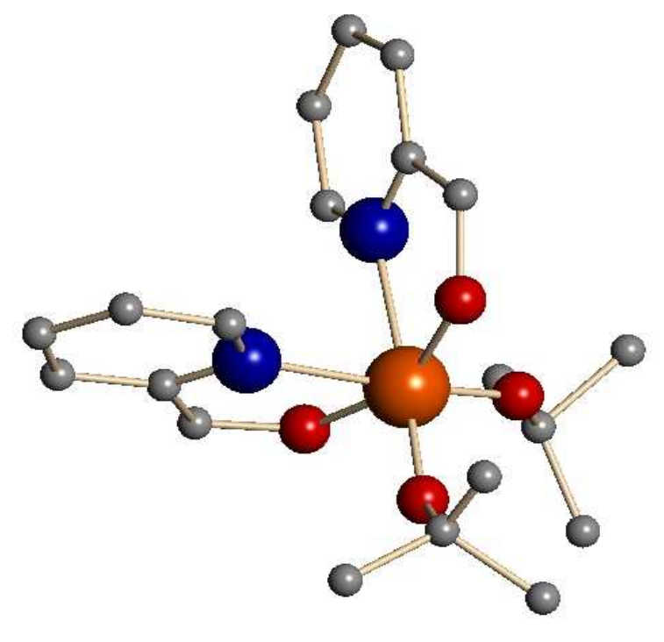
$Ti(OR)_4$ + x HOPy ⟶ $Ti(OPy)_x(OR)_{4-x}$



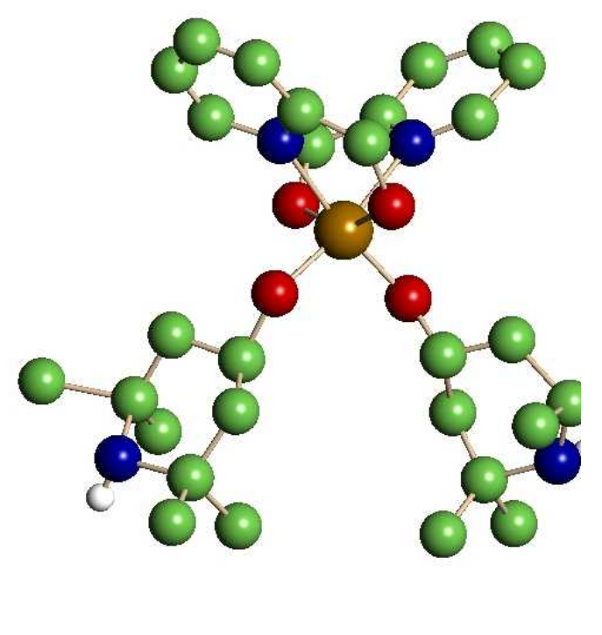
$(OPy)_2Ti(OPr^i)_2$



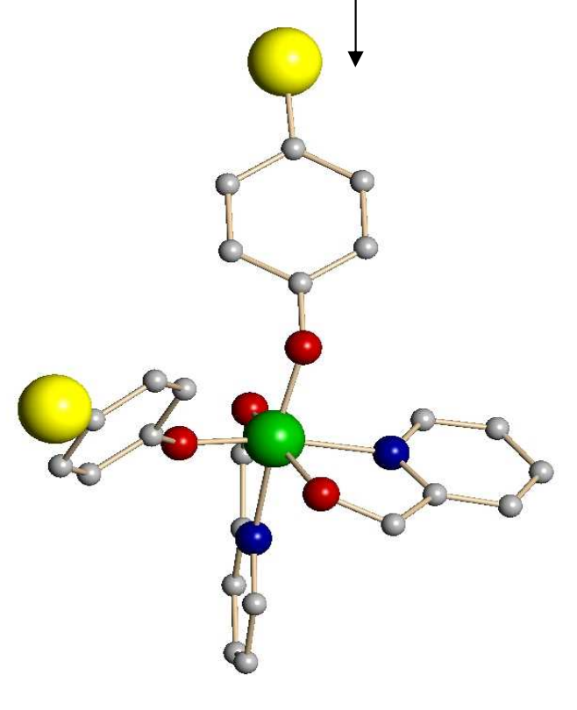
$(OPy)_2Ti(ONep)_2$



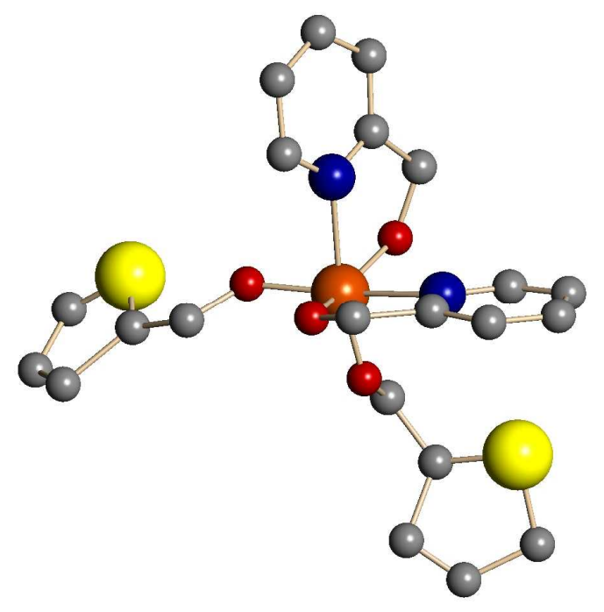
$(OPy)_2Ti(OBu^t)_2$



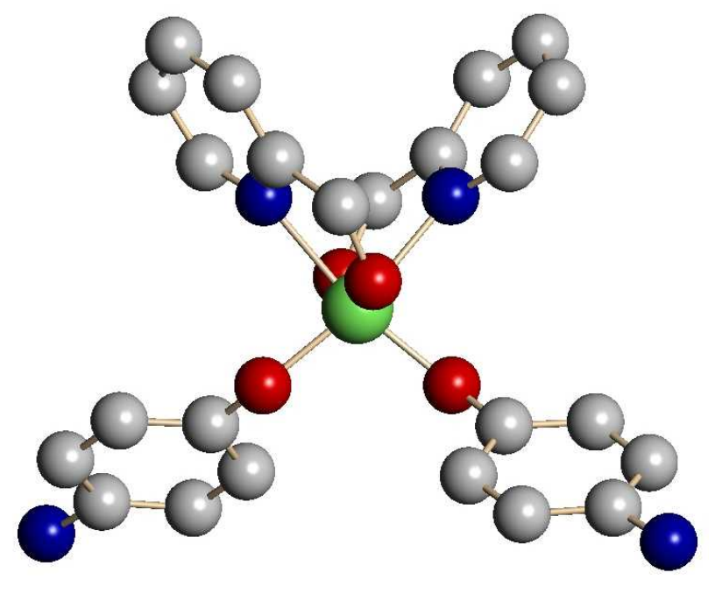
$(OPy)_2Ti(OTMA)_2$



$(OPy)_2Ti(4MP)_2$

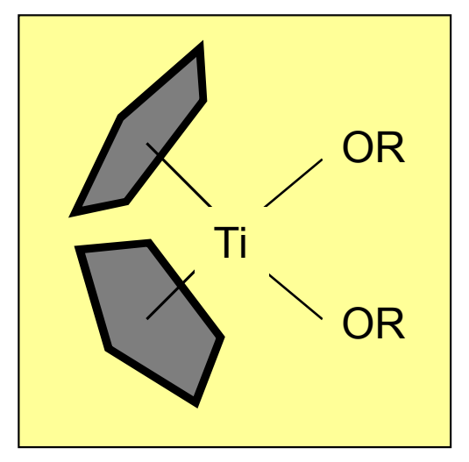


$(OPy)_2Ti(OTPM)_2$

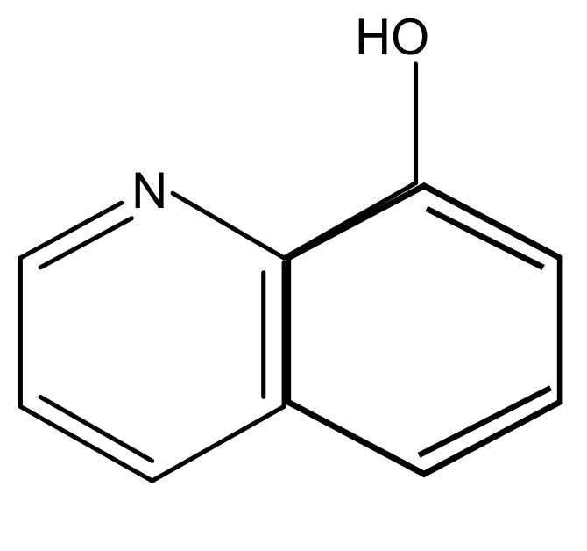


$(OPy)_2Ti(4AP)_2$

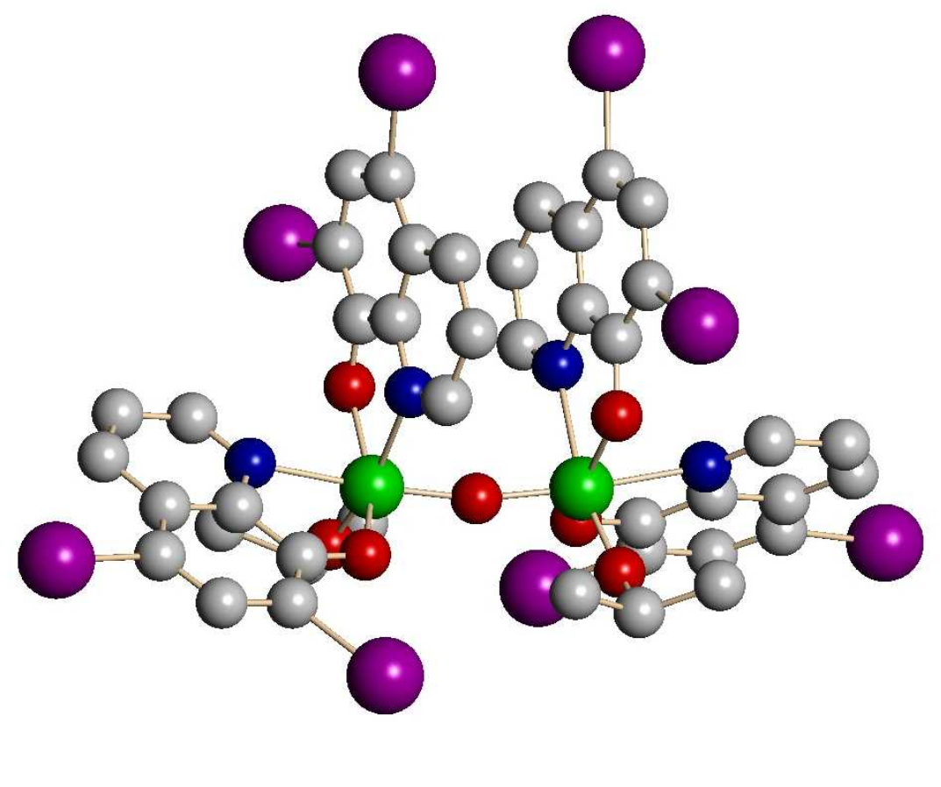
The modified OPy derivatives structurally resemble existing early transition metal species that have proven to be cancer therapuetic agents (see $Cp_2Ti(OR)_2$). The flexibility of the substituents on the phenol ligands allow for biofunctionalization necessary to optimize the utility of these compounds. Studies are underway with the UNM SoM to study the properties of these and other appropriate species.



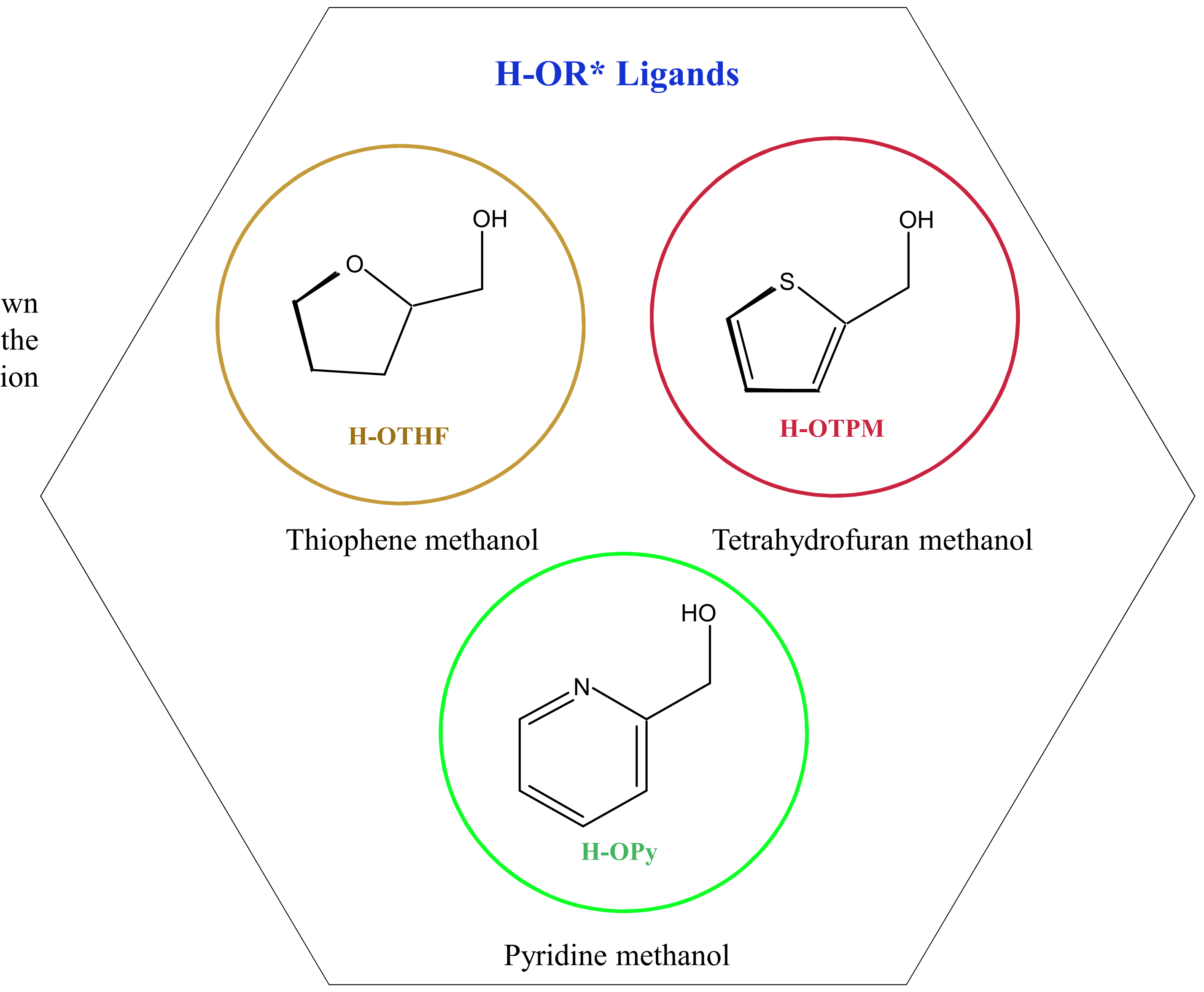
Bioactive species have similar constructs to OPy but usually have addiitonal backbone carbon matrices. The quinolates and their derivatives look ideal for further refinement of the precursors for cancer remediation and possess derivatives that allow for further functionalization.



Hydroxy quinalone (HQ)



$[Ti_2(O)(IHQ)_4(O^iPr)_2]$



H-OR* Ligands

H-OTHF

Thiophene methanol

H-OTPM

Tetrahydrofuran methanol

H-OPy

Pyridine methanol

OTHF

The OTHF ligand displays several modes of coordination chelating, chelating-bridging, terminal. The majority use a chelate bridge as observed for the alkyl aluminum species shown below. Further controlled substitution of these frameworks is possible since the reactivity of the AlR_3 species, through the introduction of the OTHF ligand, is reduced. For most a disubstituted species is achieved but for the DBP derivative more control was observed.
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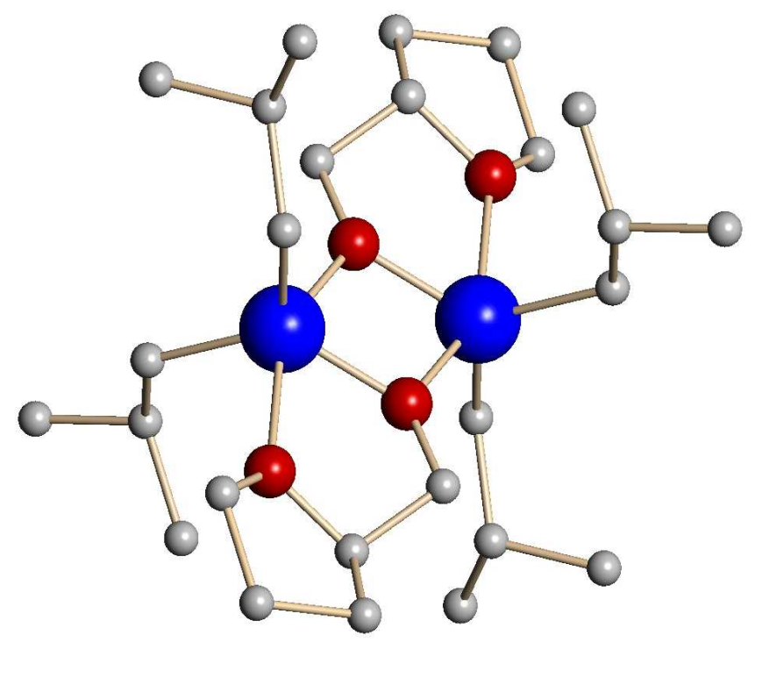
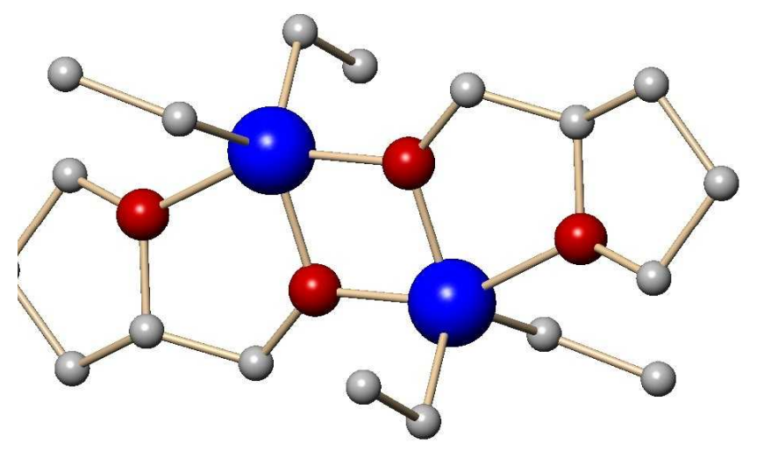
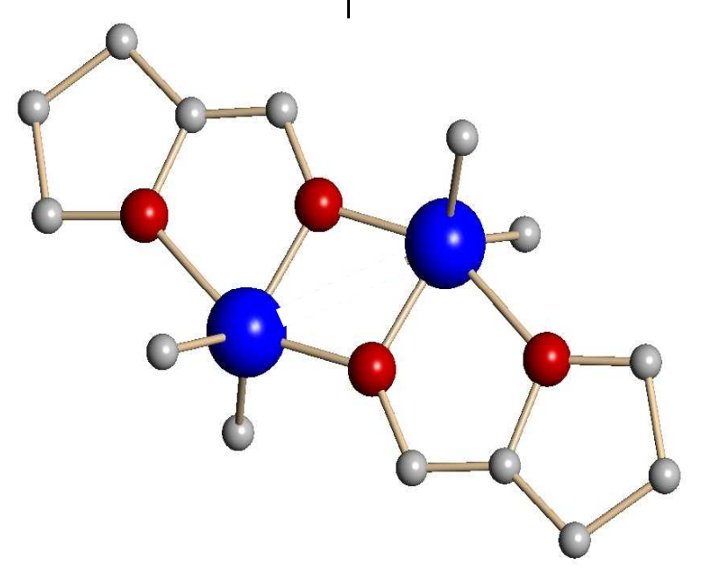
AlR_3 + H-OTHF ⟶ $AlR_2(\mu\text{-}OTHF)$



Iso-butyl



Ethyl



Methyl

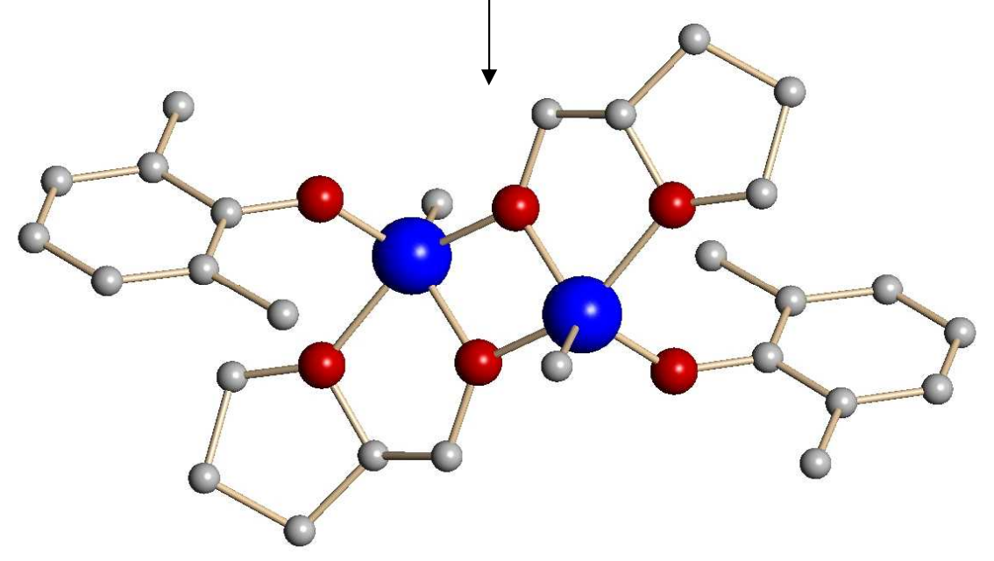
TPS-H

H-DMP

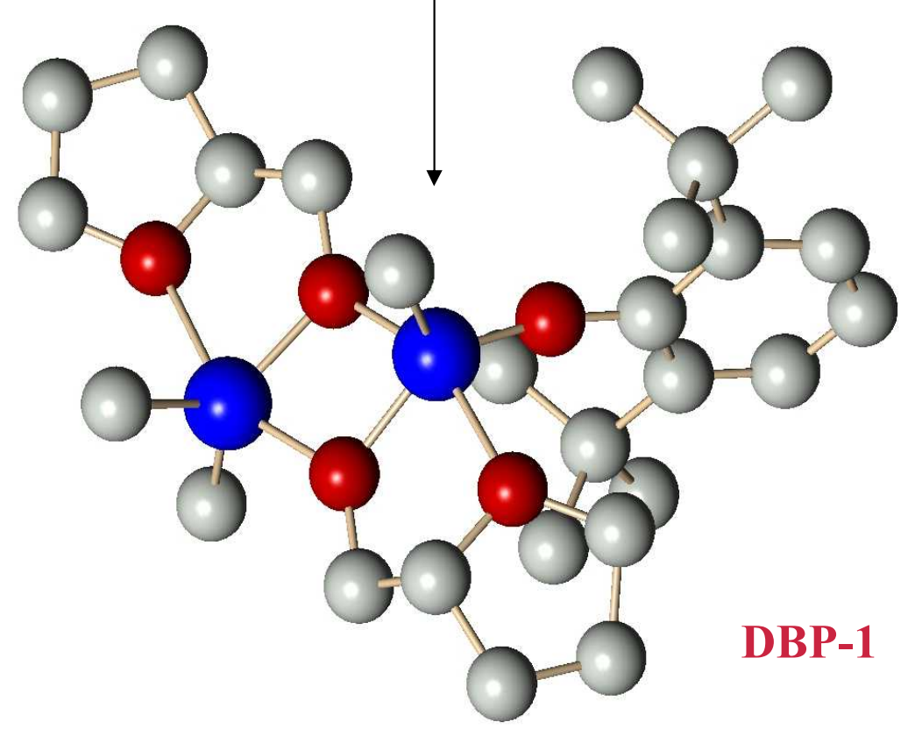
2 H-DBP

Δ

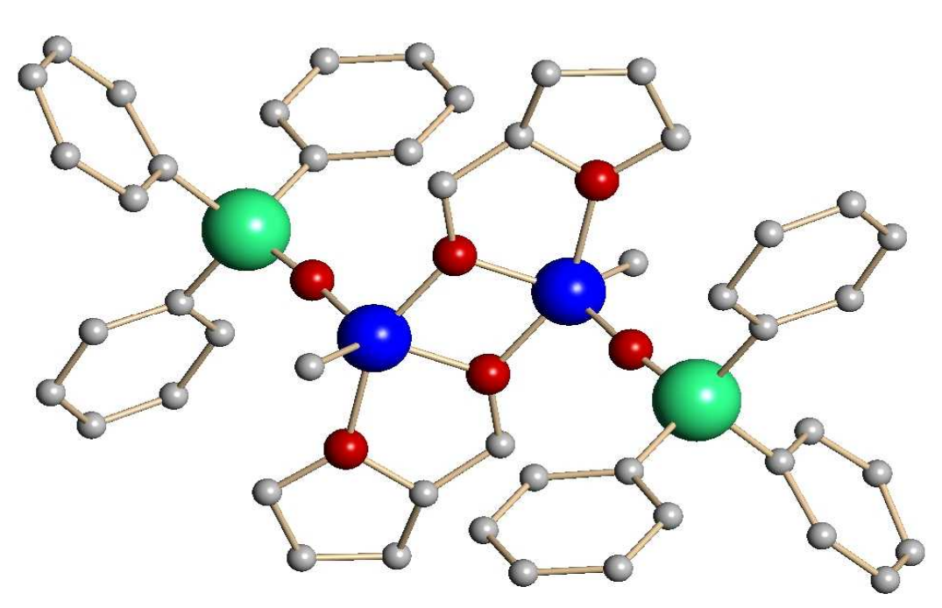
H-DBP



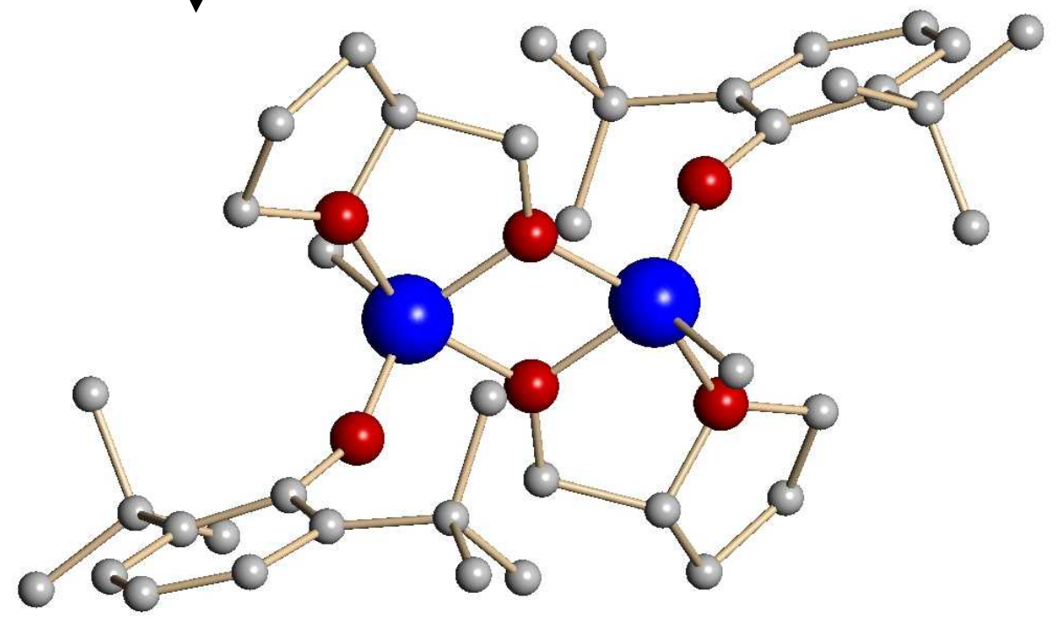
DMP-2



DBP-1



TPS-2

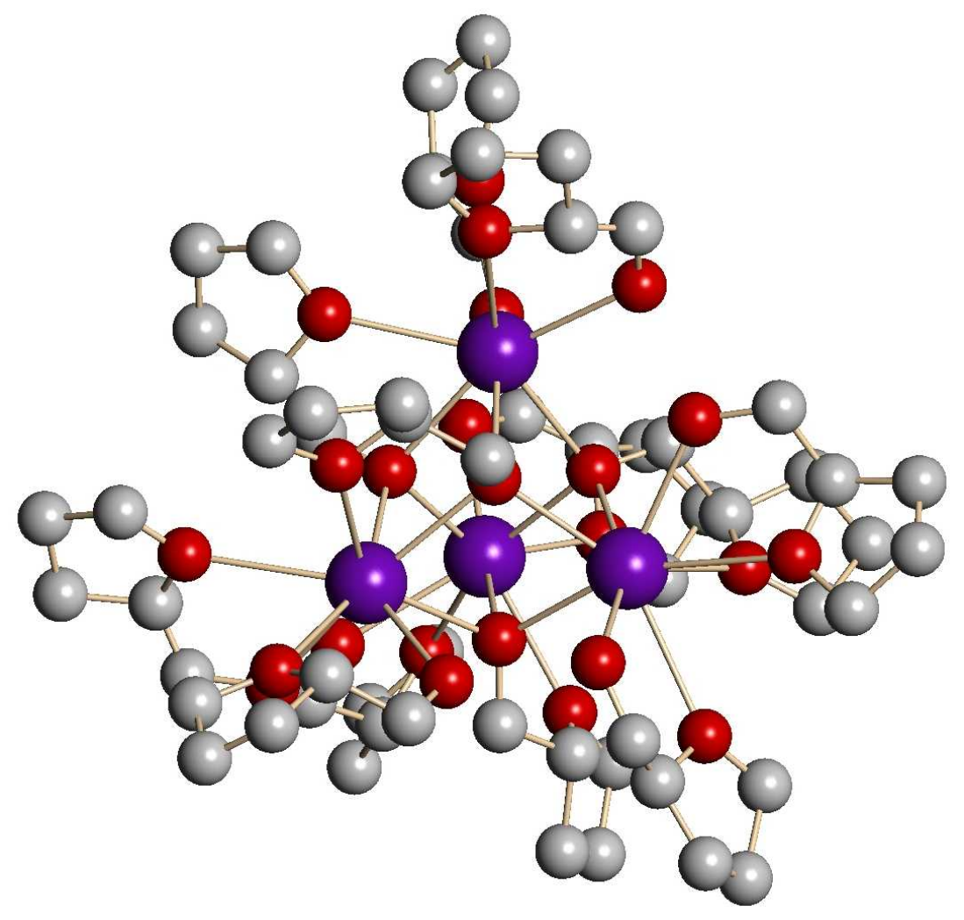


DBP-2

The OTHF derivatives of AlR_3 all adopt identical dinuclear cores. Solution and solid state 27Al NMR studies revealed very little dynamic behavior but due to the chiral carbon on the OTHF moiety, *cis* and *trans* adducts are observed in solution

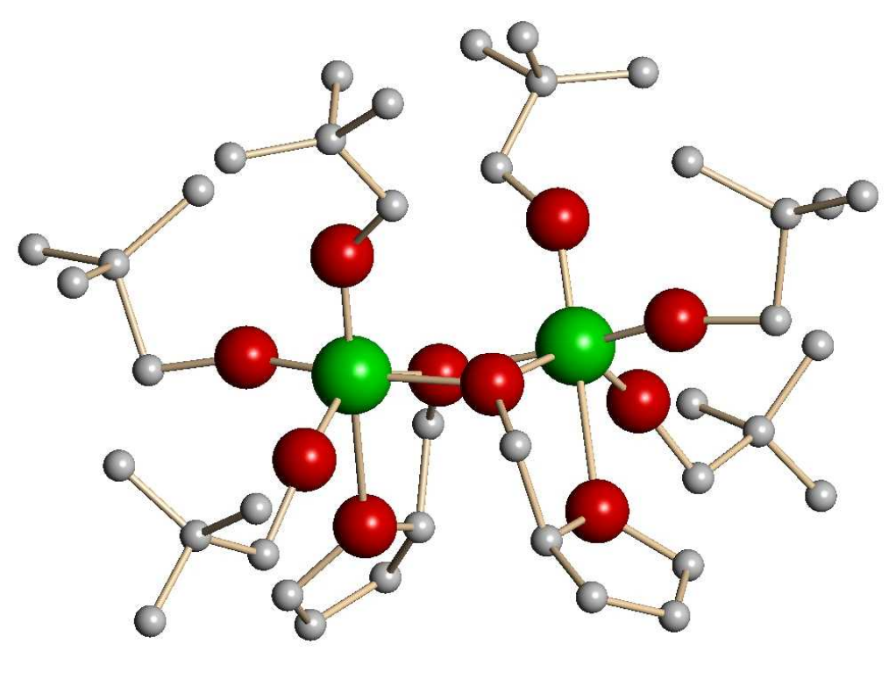
Switching to other metals, a variety of strucutres have been obtained. Again, the OTHF ligand is flexible in its binding mode and clusters are often seen due to the bridging aspect of this ligad. Below are some examples of the complexes generated and the reaction schemes used to synthesize them.

Ba^o + (xs) H-OTHF ⟶

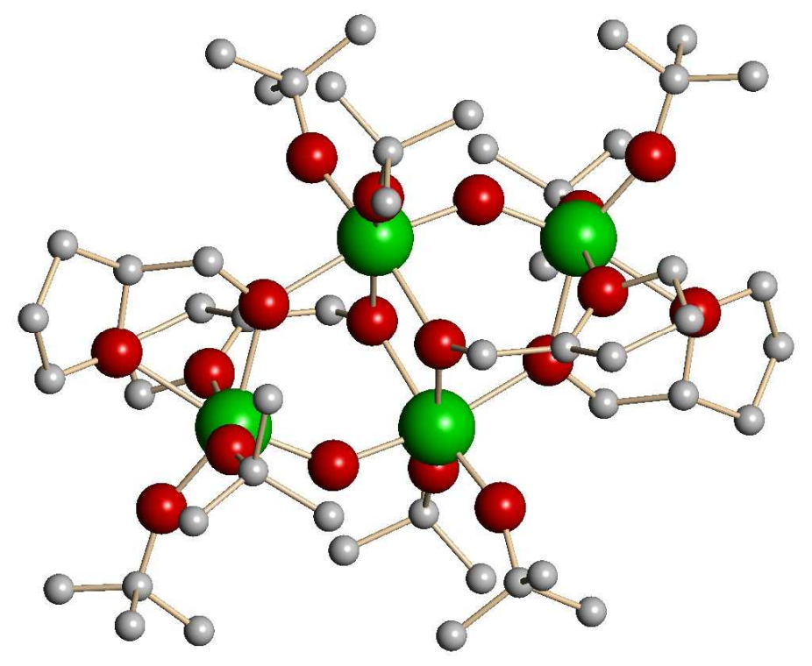


$Ba_4(\mu\text{-}OTHF)_{12}$

$M(OR)_4$ + H-OTHF ⟶ "$M(OTHF)(OR)_3$"

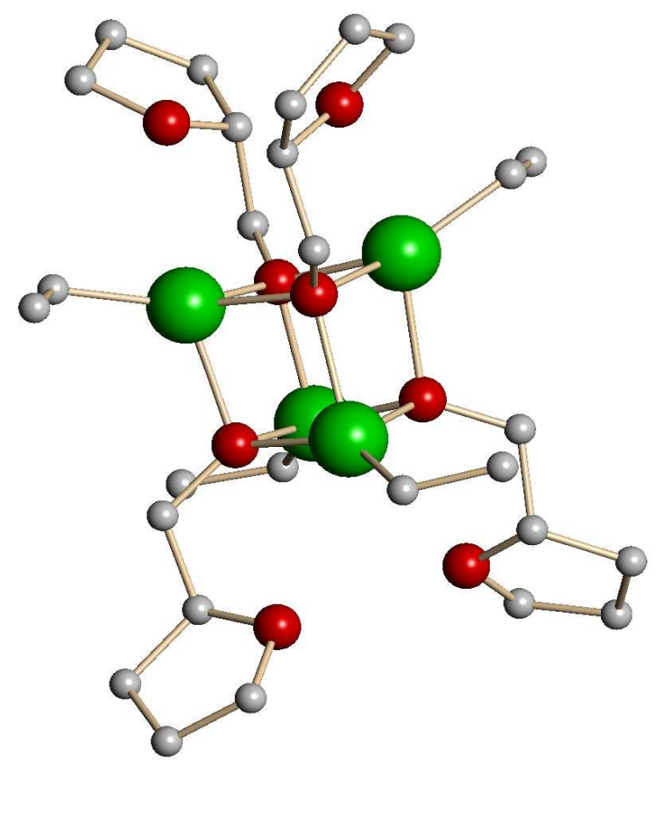


$[Ti(\mu\text{-}OTHF)_2(ONep)_3]_2$



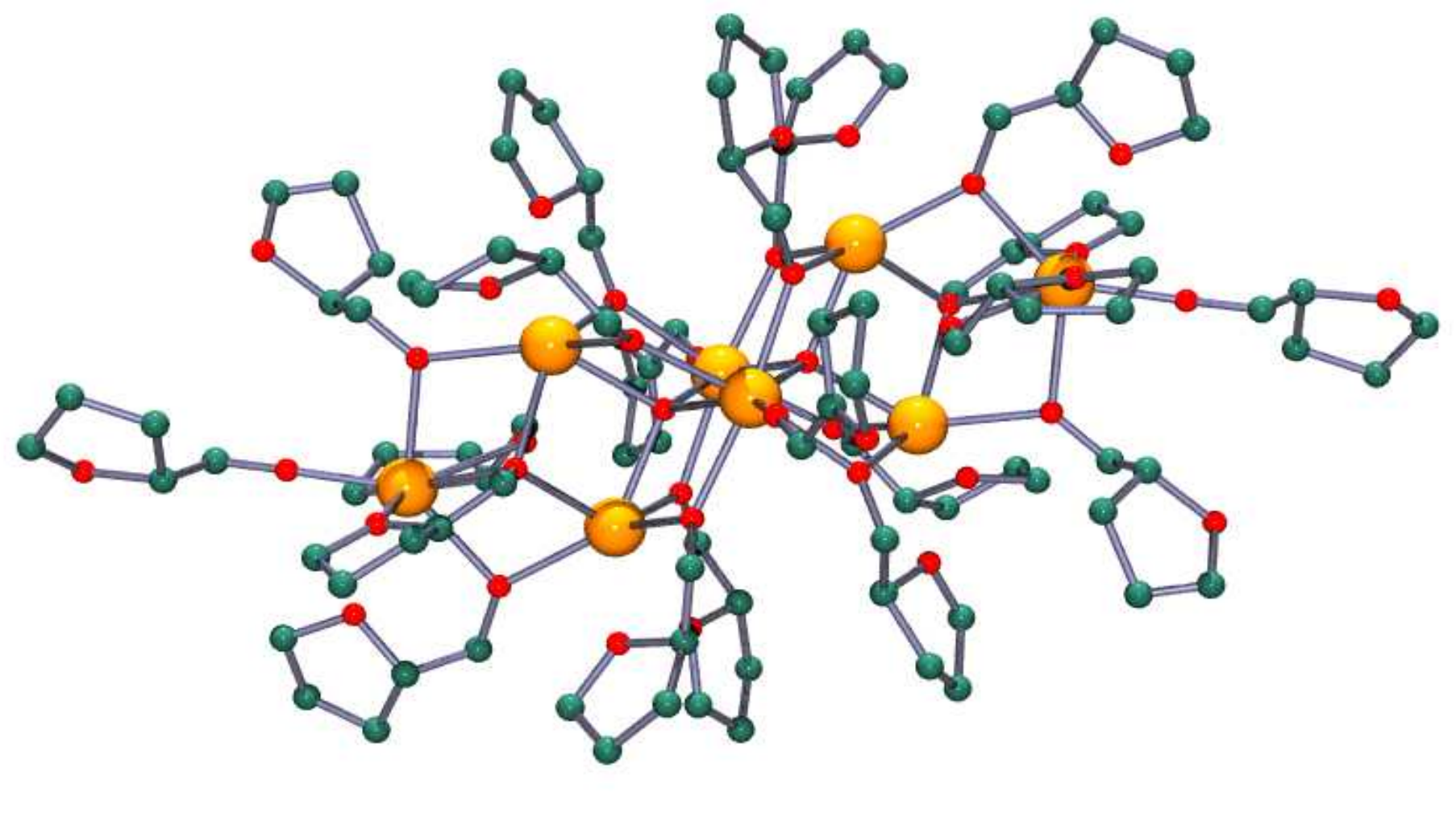
$[Zr_2(\mu\text{-}OTHF)_2(ONep)_4(\mu\text{-}O)]_2$

$Zn(Et)_2$ + H-OTHF ⟶



$[Zn(OTHF)(Et)]_4$

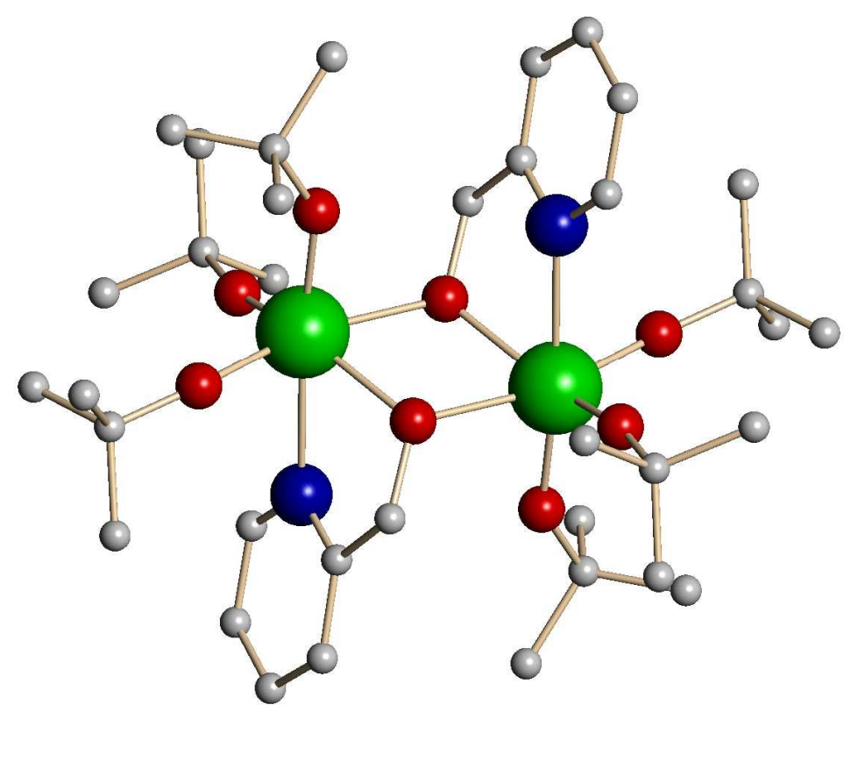
$Ce(NR_2)_3$ + 3H-OTHF ⟶



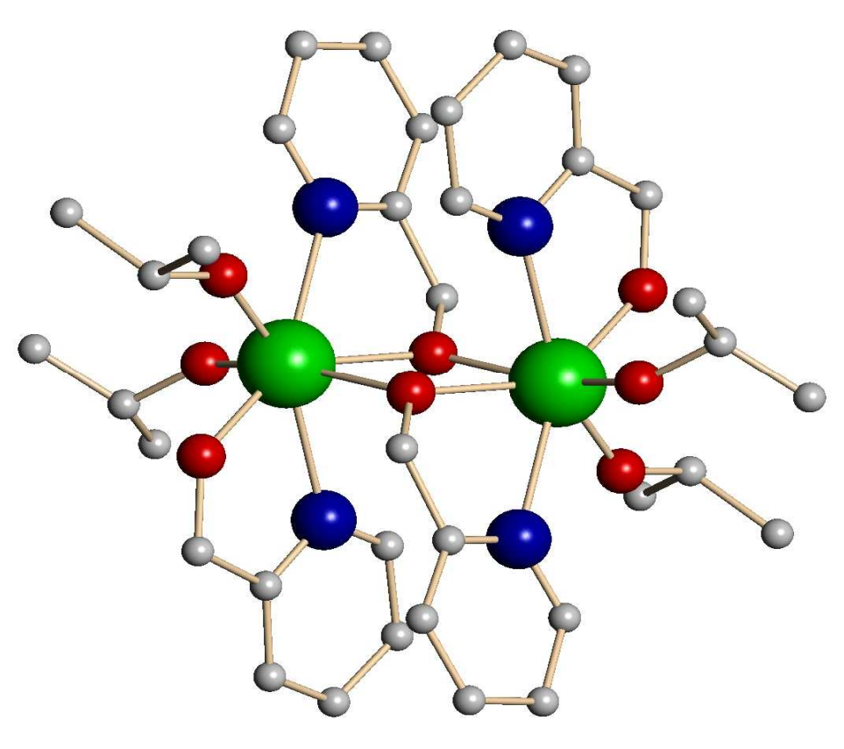
$Ce_8(\mu\text{-}OTHF)_{20}(\mu\text{-}O)_2$

The controlled construciton of metal alkoxides with the OPy and othe rmetals is not readily apparent since in most of these cases the chelating mode is accompanied by bridging mode as well or the coordination sphere of the metal is completely shut down by the bidentate nature of the OPy ligand.

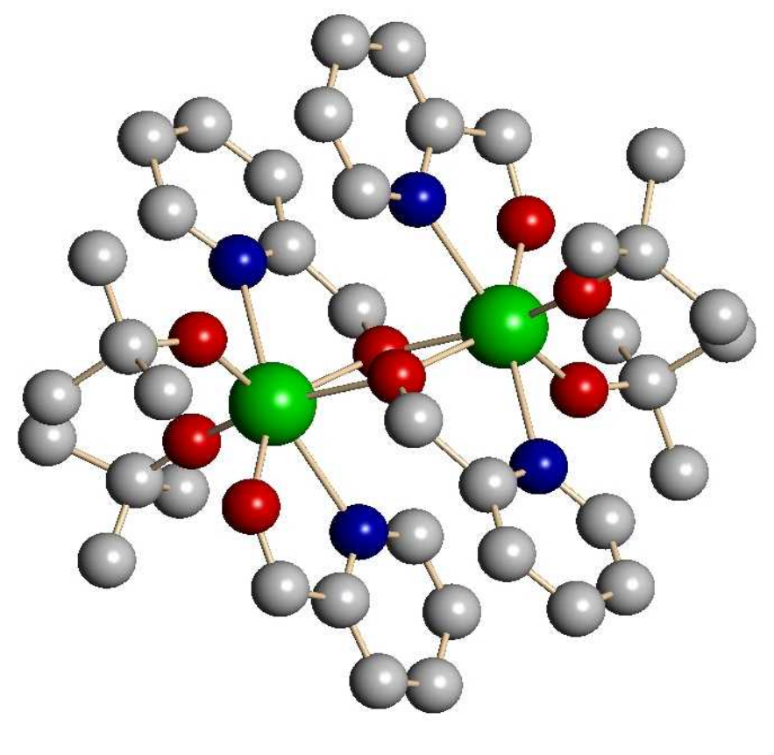
$Zr(OR)_4$ + *n* H-OPy ⟶ "$Zr(OPy)_x(OR)_{4-x}$"



$[Zr(\mu\text{-}OPy)(OBu^t)_3]_2$

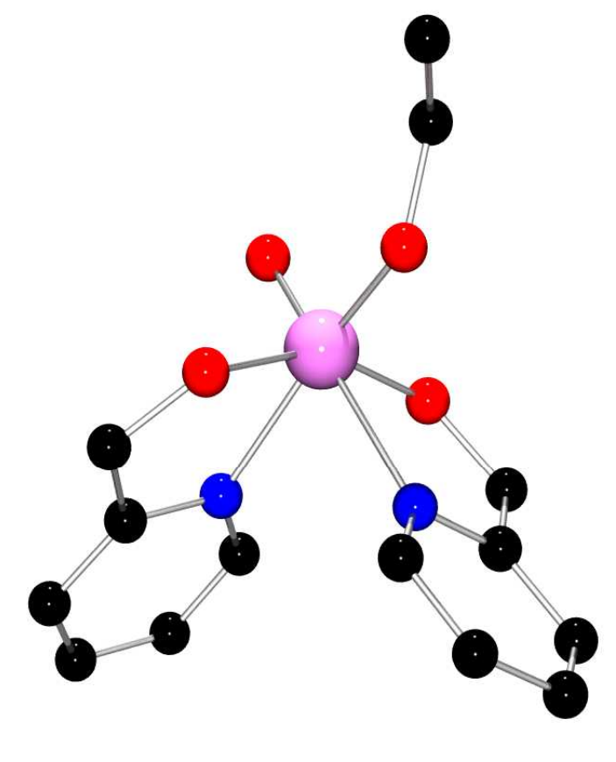


$[Zr(\mu\text{-}OPy)_2(OPr^i)_2]_2$



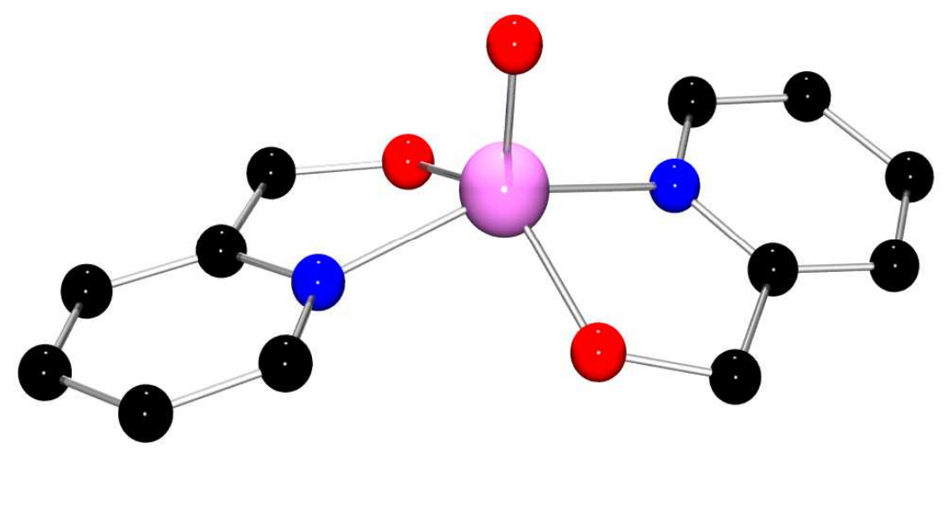
$[Zr(\mu\text{-}OPy)\ _2(OBu^t)_2]_2$

$V(O)(OEt)_3$ + 2 H-OPy ⟶



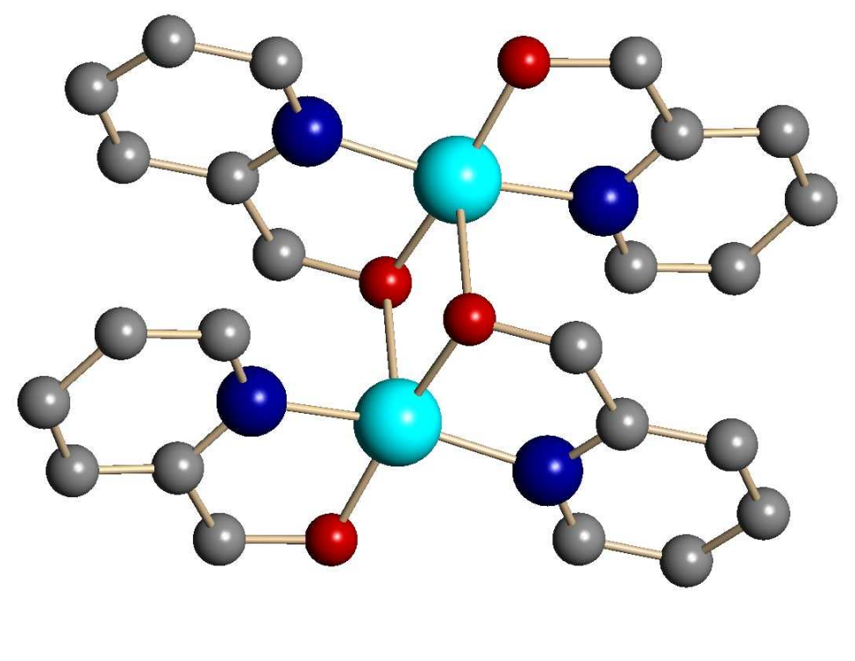
$V(O)(OEt)(OPy)_2$

$V(O)(NR_2)_3$ + 2 H-OPy ⟶



$V(O)(OPy)_2$

$Cu(OEt)_2$ + 2 H-OPy ⟶



$[Cu(OPy)]_2$

Summary and Conclusion

We have synthesized and characterized metal alkoxides from across the periodic table using these bidentate H-OR* ligands. The heteroatom in the ring coupled with the metal used determines the nature of the binding. For the **OTPM** and early transition metals, a monodentate nature was observed. This ligand offers the ability to generate single source non-oxide based materials. For the **OTHF** ligand, a variety of binding modes was observed. For the alkyl aluminum derivatives, a systematic framework was developed to build controlled constructed metal alkoxides. Other metals show some promise for the same systematic synthesis. The **OPy** ligand was always found in a chelating mode and often the oxygen was bridging. This ligand was exploited in the $Ti(OR)_4$ systems for the controlled construction of several potential cancer remediation candidates. Additional work on the **HQ** ligand and its derivatives, is being explored as well.