

## Chiral Organometallic Osmium(VI) Nitrido Complexes

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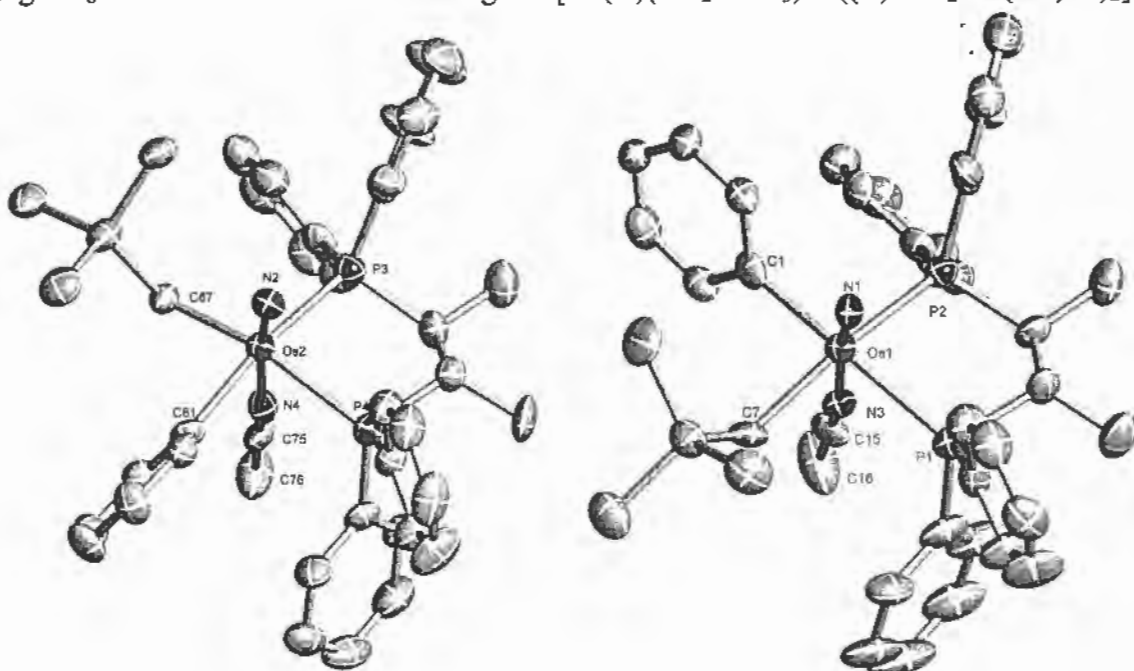
The chirality of a metal complex depends on the make up of the ligands. Many chiral metal complexes derive chirality from chiral ligands such as phosphines, amines, salens, alkoxides, and combinations of these types of these ligand types. Chiral-at-metal complexes derive chirality from the configuration of ligands around the metal center. Werner synthesized the first optically active octahedral complex  $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]\text{Cl}_2$ . The bidentate ethylenediamine ligands form propeller like configurations around the metal similar to complexes of  $[\text{Co}(\text{en})_3]\text{Cl}_3$  that have  $\Delta$  and  $\Lambda$  configurations. Many recent examples of chiral-at-metal complexes have a half sandwich piano stool orientation.

Varying the ligands on an osmium(VI) nitrido complex generates chiral-at-metal complexes. The chiral racemic complexes  $[\text{PPh}_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{MeCl}_2]$  and  $[\text{N}(\text{n-Bu})_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{PhCl}_2]$  form in the protonolysis of achiral  $[\text{PPh}_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{Me}_3]$  and *trans*- $[\text{N}(\text{n-Bu})_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2\text{Ph}_2]$  respectively. These complexes are the starting material for other chiral osmium(VI) complexes.

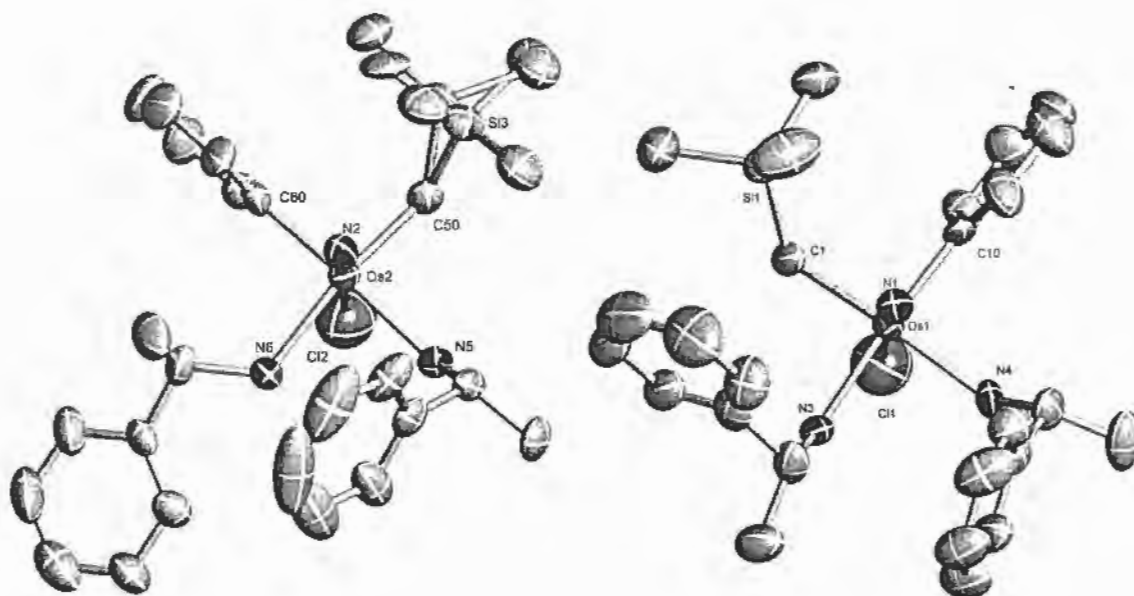
The addition of (2*S*,3*S*)-bis(diphenylphosphino)butane, (*S,S*)-CHIRAPHOS, to  $[\text{N}(\text{n-Bu})_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{PhCl}_2]$  generates a pair of neutral diastereomers,  $\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{PhCl}((\text{S,S})\text{-CHIRAPHOS})$ . The chloride ligand undergoes a fluxional disassociation process that is affected by temperature and the presence of free chloride in solution. The rate of disassociation is different for the two isomers. Careful addition of 0.5 equivalents of  $\text{AgSbF}_6$  to the mixture of neutral diastereomers selectively gives a reaction with only one diastereomer generating the five coordinate cationic complex  $[\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{Ph}((\text{S,S})\text{-CHIRAPHOS})][\text{SbF}_6]$  allowing for chemical separation. Treatment of a mixture of the neutral complex with one equivalent of  $\text{AgSbF}_6$  generates a mixture of cationic diastereomers. Acetonitrile coordinates with the cationic complexes giving diastereomers of the six coordinate complex  $[\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{Ph}((\text{S,S})\text{-CHIRAPHOS})][\text{SbF}_6]$ . X-ray diffraction provides the molecular structure for both diastereomers (Figure 1).

The addition of (*R*)-methylbenzylamine to  $[\text{N}(\text{n-Bu})_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{PhCl}_2]$  generates a pair of neutral diastereomers,  $\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{PhCl}((\text{R})\text{-NH}_2\text{CH}(\text{Me})\text{Ph})_2$ . The amine ligands are labile resulting in broad resonances for the  $^1\text{H}$  NMR spectrum of the mixture. Heating the NMR sample to 100 degrees C results in sharp resonances for one set of time averaged amine resonances. X-ray diffraction provides the molecular structure for both diastereomers (Figure 2). Treatment of an acetonitrile solution of the neutral diastereomers with  $\text{AgBF}_4$  gives a mixture of products. One isolated product is the structurally determined amidine complex  $\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{Ph}(\text{F})\{\text{NHC}(\text{Me})((\text{R})\text{-NHCH}(\text{Me})\text{Ph})\}((\text{R})\text{-NH}_2\text{CH}(\text{Me})\text{Ph})$  resulting from the nucleophilic addition of amine to bound acetonitrile. Similar reactions occur for other transition metal complexes.

Treatment of  $\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{PhCl}((\text{R})\text{-NH}_2\text{CH}(\text{Me})\text{Ph})_2$  with one equivalent of  $\text{AgSbF}_6$  in the absence of acetonitrile gives  $[\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{Ph}((\text{R})\text{-NH}_2\text{CH}(\text{Me})\text{Ph})_2]$ .

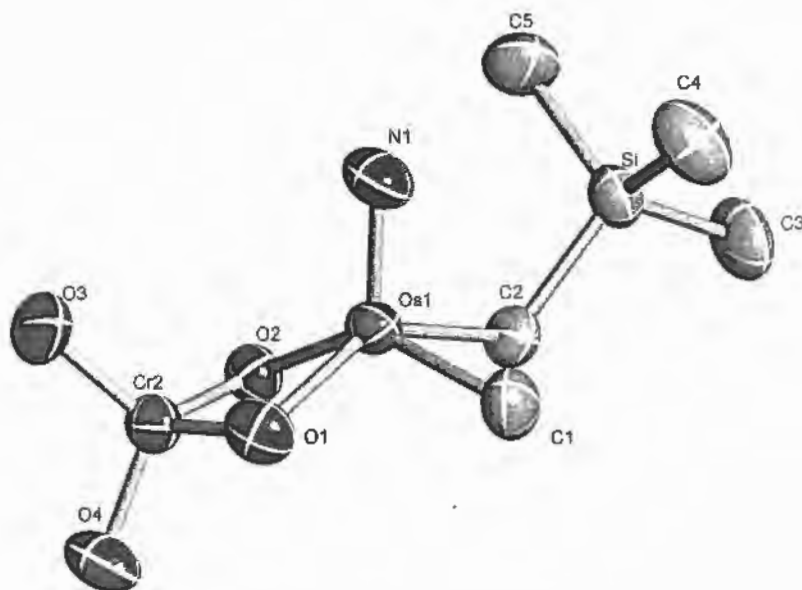


**Figure 1.** Molecular structure for diastereomers of  $[\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{Ph}(\text{NCMe})((\text{S},\text{S})\text{-CHIRAPHOS})][\text{SbF}_6]$ .



**Figure 2.** Molecular structure for diastereomers of  $\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{PhCl}((\text{R})\text{-NH}_2\text{CH}(\text{Me})\text{Ph})_2$ .

The chiral complexes  $[\text{PPh}_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{MeCl}_2]$  and  $[\text{N}(\text{n-Bu})_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{PhCl}_2]$  react with  $\text{Ag}_2\text{CrO}_4$  to make chiral heterobimetallic complexes  $[\text{PPh}_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{Me}(\square\square\square\text{CrO}_2)]$  and  $[\text{N}(\text{n-Bu})_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{Ph}(\square\square\square\text{CrO}_2)]$  that are similar to other OsCr heterobimetallic complexes. Structural determination by X-ray diffraction of  $[\text{PPh}_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{Me}(\square\square\square\text{CrO}_2)]$  (figure 3) gave a molecular structure useful for modeling. The modeling studies demonstrated the selectivity possible in heterometallic complexes using the chiral  $(\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{Ph})$  fragment.



**Figure 3.** Molecular structure of  $[\text{PPh}_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)\text{Me}(\square\square\square\text{CrO}_2)]$ .

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