

Controlling the Reactivity of Metalloenediynes via Metal Ion Coordination: Development of Salen-Like Enediynes

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The ability of enediynes to abstract hydrogen atoms from biological substrates, most notably DNA, via 1,4-phenyl diradicals formed upon Bergman cyclization has driven research into tuning the reactivity of these materials to create compounds which will be reactive under biological conditions. Recent studies have shown that the Bergman cyclization temperatures of enediyne ligands can be controlled through metal ion coordination and the geometry of the resulting complexes. In many cases, ligands can be designed to be thermally quite labile and will generate Bergman cyclized products at modest temperatures. To expand the variety of metal ions which can be used to modulate the reactivity of these ligands, several enediyne ligands based on diimine, bis-phenoxy binding motifs have been synthesized to retain the flexibility and electronic properties of ligands that have proven to be reactive upon metal coordination. Through judicious choice of metal ion, the geometric and electronic properties of these enediyne ligands can be modulated, varying the activation energy required to initiate enediyne cyclization via either a Bergman or Myers-Sato mechanism. The synthesis of these ligands and the corresponding metal compounds will be presented along with structural analysis and discussions of their thermal reactivities.