CHARACTERIZATION OF A NEW CLASS OF TUNABLE RADICAL METAL-CARBENE CATALYSTS. Christian R. Cioce, Jonathan L. Belof, X. Peter Zhang, Brian Space, and H. Lee Woodcock, Department of chemistry, University of South Florida, 4202 E. Fowler Ave CHE205, Tampa, FL 33620.

A new class of radical metal-carbene complex has been characterized as having Fischer-like orbital interactions and adjacent π acceptor stabilization. Density functional theory along with natural bond order analysis and charge decomposition analysis has given insight into the electronics of this catalytic intermediate in an open-shell cobalt-porphyrin, [Co(Por)], system. The complex has a single bond from the metal to the carbene and has radical character with localized spin density on the carbene carbon. In addition, the carbene carbon is found to be nucleophilic and “tunable” through the introduction of different α-carbon substituents. Finally, based on these findings, rational design strategies are proposed that should lead to the enhancement of catalytic activity.