

AUTOCATALYTIC O₂ ACTIVATION BY AN OCO³⁻ TRIANIONIC Pincer Cr^{III} COMPLEX: ISOLATION AND CHARACTERIZATION OF THE AUTOCATALYTIC INTERMEDIATE [Cr^{IV}]₂(μ-O) DIMER. Matthew E. O'Reilly,[‡] Trevor J. Del Castillo,[‡] Joseph M. Falkowski,[‡] Vasanth Ramanchandran,[¶] Mekhela Pati,[¶] Marie C. Correia,[‡] Khalil A. Abboud,[‡] Naresh S. Dalal[¶] David E. Richardson,[‡] and Adam S. Veige.^{‡*}

Kinetic experiments designed to probe the mechanism of O₂ activation by [^tBuOCO]Cr^{III}(THF)₃ (**1**) reveal that the product [^tBuOCO]Cr^V(O)(THF) (**2**) catalyzes the oxidation of [^tBuOCO]Cr^{III}(THF)₃ (**1**) via formation of the μ-O dimer {[^tBuOCO]Cr^{IV}(THF)}₂(μ-O) (**3**). Simulations of the kinetic data confirm an autocatalytic O₂ activation mechanism. In addition to an unprecedented O₂ activation mechanism, single crystals of a rare μ-O dimer **3** were attained. Complex **1** catalyzes the aerobic oxidation of PPh₃ with a turnover number =200. Formation of product (OPPh₃) is known to prevent re-oxidation of the catalysts but the presence of OPPh₃ accelerates O₂ activation by forming the five-coordinate complex *trans*-[^tBuOCO]Cr^{III}(OPPh₃)₂ (**4**).