Structural Characterization of Reactive Metal Nitrenoid Intermediates

Anuvab Das, Joseph H. Reibenspies, Yu-Sheng Chen, and David C. Powers

Department of Chemistry, Texas A&M University, College Station, TX.

Introduction

Photochemically generating reactive intermediates from a stable photo-precursor provides new opportunities to characterize these species with transient absorption or cryogenic methods.

Development of New Tools to Structurally Characterize Reactive Intermediates

Crystal matrix isolation of photoprecursors has enabled direct structural characterization of the reactive Ru3 nitrido intermediate.

Single-crystal-to-single-crystal transformation of Ru3 azide to Ru3 nitrido. (a) Photolysis of a single-crystal of Ru3 azide results in N2 extrusion and the formation of Ru3 nitride. (b) Comparison of EPR spectra obtained at 4 K of solid-state photolysis (--) and solution-phase photolysis (---) confirming the formation of the same reactive intermediate in both habits.


Structural Characterization of Rh2 Nitrenoid Intermediate

Synthesis and steady-state photochemistry of Rh2(espn)(NNTsCl). (a) X-ray crystal structure of the RhN-chloroamide complex. (b) UV-Vis spectra collected during photolysis of the RhN-chloroamide in THF. (c) MALDI-TOF at high laser flux indicates the isotopically-sensitive peak expected for a RhN nitrenoid. (d) Transient absorption (TA) spectra obtained from flash laser photolysis of the RhN-chloroamide.


Acknowledgements