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Exploration of a Unique Uranium Mediated Carbon-Carbon Radical Coupling Reaction

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ABSTRACT

Designing an efficient nuclear fuel cycle has motivated decades of research on aqueous phase uranium chemistry. As such, studies are often limited by the formation of unreactive uranium oxides and/or solubility issues. Carrying out reactions in non-aqueous solvents addresses said problems and enables explorations into previously unattainable reactivity and fundamental properties of uranium. One such feat is the syntheses of uranium alkyls, as they permit research into bond interactions between uranium and carbon. Considering uranium's oxophilicity, we investigated the relatively understudied uranium(III) alkyls-both their reactivity and reaction mechanismtowards oxygen-containing reagents. In an inert atmosphere, various uranium alkyl complexes were treated with substituted phosphine oxides, which provide electronic and steric modularity. Products were characterized via nuclear magnetic resonance (NMR), electronic absorption, and infrared spectroscopies. X-ray crystallographic data were obtained whenever possible. We observed the formation of a new carbon-carbon bond between the alkyl unit and phosphine oxide in a one-electron mechanism, while maintaining the U(III) oxidation state. This radical coupling was favored by electron-poor phosphine oxide and impeded by electron-rich analogs. The ability for the alkyl to form stable radicals drives the reaction forward. All attempts to capture the radical were unsuccessful, as the formation of the new uranium complexes appears to occur in concert with the homolytic cleavage of the U-C bond. To the best of our knowledge, such reactivity with phosphine oxides is unprecedented in the field of coordination chemistry.

KEYWORDS

Uranium Alkyls, Radical Chemistry, Organometallics