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Stable cyclic (alkyl)(amino)carbene (cAAC) radicals with main group substituents

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Isolation and characterization of stable radicals has been a long-pursued quest. While there has been some progress in this field particularly with respect to carbon, radicals involving heavier p-block elements are still considerably sparse. In this review we describe our recent successful efforts on the isolation of stable p-block element radicals particularly those involving aluminum, silicon, and phosphorus.

Introduction

Radical chemistry has long been of interest both from academic and practical points of view.¹ Among the most widely used radical chemistry in industrial processes is the low-density polyethylene manufacture. In addition, radical chemistry is widely utilized in organic synthesis and has implications in many biological processes including cell damage.^{2,3} Indeed, scavenging radicals from cells forms an important aspect of the cell machinery in biological systems.⁴ In view of this ubiquity and importance of radicals there has naturally been an interest in studying radicals both in their transient and isolated forms. While spectroscopic tools such as electron paramagnetic

resonance have been of considerable utility in throwing light on the nature of the radicals, isolating the latter and characterizing them, particularly in the solid-state, has been fraught with considerable challenges in view of the reactivity of these systems. While metal-based radical systems involving coordination complexes have been far more amenable for isolation and characterization similar examples involving carbon and other main-group elements, although known, are still rare. Surprisingly, however, nature stabilizes molecular oxygen in its biradical form, quite readily. Open-shell main-group element compounds containing unpaired electrons are unstable for several reasons including the fact that many of these prefer to adopt closed-shell configurations and they readily react with any available chemical entity.⁵ Considering this propensity for reactivity, typical methods for stabilizing main group element-based radicals mainly involve delocalizing the unpaired electron on the overall molecular scaffold to achieve thermodynamic stability and/or by employing sterically encumbered groups around the main-group element such that the

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