For the past five years we have been exploring the chemistry of electrophilic, or more appropriately π - acidic, carbenes as ligands toward p-block elements. Our initial efforts were in the realm of structure and bonding of low-valent main group species supported by carbonyl-decorated carbenes, specifically diamidocarbenes (DACs) and mono(amido)amino carbenes (MAACs) as ligands. 1-4 More recently, our work has focused on the photochemistry of electrophilic carbenes, and main group fragments supported by these ligands. This presentation will describe our development of the chemistry of electrophilic carbenes and will highlight the following topics: i) the synthesis of the first examples of P8 allotropes, stibinidenes (Sb-R), and borylene (B-R) supported by DACs and MAACs, ii) the redox chemistry of a-acyl amidinium cations,5 iii) the photochemistry of organic radicals and biradicals derived from electrophilic carbenes, iv) the photochemistry of DACs. In addition to describing the synthesis of these compounds, their potential application as novel emissive and energy storing materials will also be discussed.