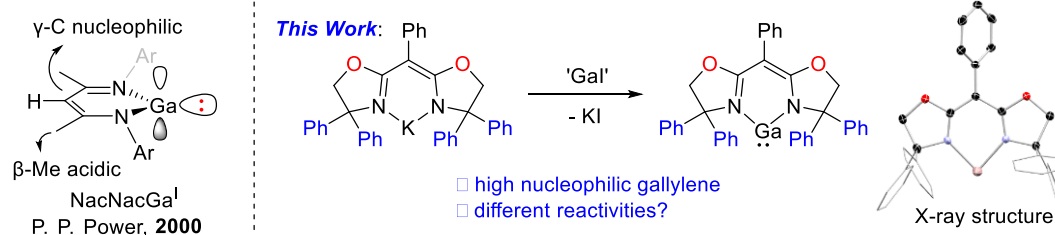


A Monomeric Gallylene Supported by a Bis(oxazolinyl)methanide Ligand

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The synthesis of group-13 species such as aluminum and gallium in the +1 oxidation state is experimentally challenging and consistently hampered by their high reactivity and pronounced tendency towards disproportionation.¹ NacNacGa(I), the first isolable monomeric Ga^I species supported by a β -diketiminate (NacNac) ligand, has widely been studied over the last two decades due to its electrophilic and nucleophilic reactivity.² Though conventionally regarded as a robust ancillary ligand, NacNac lacks electronic tunability and does not behave as a spectator ligand in numerous occurrences.³ For example, the unsubstituted γ -carbon often shows nucleophilicity, while the β -methyl groups are susceptible to deprotonation. Herein, we report the synthesis of gallylene supported by a new bis(oxazolinyl)methanide (boxm) ligand,⁴ which possesses a better π -donating nature due to the introduction of the extra oxygen atoms and is immune from the side reactions originating from the backbone.



The targeted boxmGa was synthesized by a salt metathesis reaction of a potassium salt boxmK with 'GaI'. The resulting boxmGa was unambiguously characterized by NMR spectroscopic and single-crystal X-ray structural analyses. The observed N-Ga-N angle [82.3(8)°] was smaller than that of NacNacGa [87.53(5)°], suggesting higher s-character of the lone pair on the gallium center. To clarify the electronic difference between boxmGa and NacNacGa, DFT studies at the PBE0/def2-TZVP level of theory were performed. As expected, HOMO-LUMO gap of boxmGa (4.56 eV) was slightly larger than that of NacNacGa (4.50 eV). Further details of the boxmGa including its reactivities will be reported in the presentation.

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