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Title:	Highly Active Carbene Potassium Complexes for the Ring-Opening Polymerization of Ïµ-Caprolactone
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Abstract:	Herein we report the synthesis of two complexes of potassium employing strongly nucleophilic carbenes, such as cyclic “(alkyl)(amino)carbene (cAAC) and abnormal N-heterocyclic carbene (aNHC). Both complexes are dimeric in the solid state and the two potassium centers are bridged by trimethylsilylamide. In these complexes, the carbene- - -K interaction is predominantly electrostatic in character, which has been probed thoroughly by NBO and AIM analyses. Indeed, the delocalization energy of the cAAC lone pair calculated from the second-order perturbation theory was only 5.21 kcal mol–1, supporting a very weak interaction. The solution-state behavior of these molecules, as inferred from NOESY spectra, hints that the weak carbene- - -K interaction is retained in nonpolar solvents, and the bond is not dissociated at least on the NMR time scale. We took advantage of such a weak interaction to develop highly effective ring-opening polymerization catalysts for ε-caprolactone and rac-lactide. The efficacy of these catalysts is prominent from a very high substrate/metal-initiator ratio as well as very low dispersity index of the obtained polymer chains, reflecting significant control over polymerization.
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