

Catalyzed Dimerization of Bicyclo[2.2.1]
hepta-2,5-diene by Fe-Containing Ionic Liquids

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Fe-containing imidazolium-based ionic liquids (ILs) were highly effective for the dimerization of bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene, NBD) in the presence of diethylaluminum chloride (DEAC). Fe-containing ILs produced hexacyclic endo-endo NBD dimer (Hnn) in high yield and selectivity, whereas FeCl₃ yielded large amounts of side products. By employing these catalysts, the use of expensive phosphanes was avoided and the required amount of reducing agent (DEAC) was greatly reduced. The yield and selectivity of Hnn were affected by the degree of reduction of Fe(III) compounds by DEAC to Fe(II) species as determined by X-ray photoelectron spectroscopy. Higher yield of Hnn was obtained with the catalytic system producing larger amounts of Fe(II) species. Theoretical calculation and experimental results support that Fe(II) is the active species for the dimerization. The roles of [BMIm]Cl are believed to promote the generation of the active species through the formation of easily reducible [BMIm]FexCl_{3x+1} (x = 1 or 2) or [BMIm]₂FeCl₄, and to stabilize the resulting active species.