

LOW-VALENT $\text{Bi}^{\text{I}} \rightleftharpoons \text{Bi}^{\text{III}}$ REDOX CATALYSIS

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A catalytic transfer-hydrogenation utilizing a well-defined $\text{Bi}(\text{I})$ complex as catalyst and ammonia-borane as transfer agent has been developed. This transformation represents a unique example of low-valent pnictogen catalysis cycling between oxidation states I and III, and proved useful for the hydrogenation of azoarenes and the partial reduction of nitroarenes. Interestingly, the bismuthinidene catalyst performs well in presence of low-valent transition-metal sensitive functional groups and presents orthogonal reactivity compared to analogous phosphorous-based catalysis. Mechanistic investigations suggest the intermediacy of an elusive bismuthine species, which is proposed to be responsible for the hydrogenation and the formation of hydrogen

