

Accelerating role of deaggregation agents in lithium-catalysed hydrosilylation of carbonyl compounds

Ignacio Fernández

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Abstract

A combined computational and experimental approach demonstrates the accelerating role of deaggregation agents, especially HMPA, in the Li-catalysed hydrosilylation of acetophenone in THF solution under very mild conditions.

1 Introduction

The reduction of carbonyl groups into alcohols is of wide interest in synthetic chemistry and therefore, constant efforts are put into developing new efficient methodologies and perfecting the existing ones. Catalytic hydrosilylation¹ has emerged as a convenient method as it operates under mild conditions and combines an exceptional reducing capability with a high selectivity that can be finely tuned via catalyst design. Many Earth-abundant first-row transition metals, specially iron,^{2,3} have been tested in catalytic hydrosilylation of carbonyl compounds, as they are usually more environmentally-friendly and less toxic than their second- and third-row counterparts. Alkali metal salts have also been explored as alternative catalysts, initially by the groups of Corriu⁴ and Hosomi,⁵ and later by Beller⁶ and Nikonov,⁷ among others. Such compounds have been employed to promote hydrosilylation due to their basic character via formation of a pentacoordinated hydridosilicate,^{6–8} usually neglecting any relevant role of the alkali cation in the reaction mechanism. We recently reported the hydrosilylation of carbonyl compounds catalysed by lithiated hydrazones.⁹ However, full understanding at atomic level of detail is still needed for the rational design of catalysts and reaction conditions. Herein we join computational and experimental efforts to understand and optimise processes catalysed by alkali-metal amides.¹⁰ Following theoretical guidance, we demonstrate how deaggregation agents (DAs) can efficiently accelerate hydrosilylation of carbonyl compounds in the presence of readily available lithium amides (Scheme 1) under very mild conditions such as room temperature and very low catalyst loading.