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# Nickel phosphinite pincer complexes as catalysts for deoxygenative hydroboration of amides to amines

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## Abstract

Deoxygenative reduction of readily available carboxamides is considered as an attractive approach for preparation of a variety of primary, secondary and tertiary amines. However, significantly reduced electrophilic character of amides, compared to other carbonyl compounds, makes their reduction a challenging task. Herein we report the preparation of a series of iminophosphinite  $\text{POCN}^{\text{R}}$ , aminophosphinite  $\text{POCN}^{\text{R}2}$  and bis(phosphinite)  $\text{POCOP}$  pincer complexes of Ni(II) and evaluation of their catalytic activity in deoxygenative hydroboration of amides with HBPIn to give the corresponding amines. Among all primary, secondary and tertiary amides, superior reactivity in hydroboration reactions was demonstrated for secondary substrates. Bis(phosphinite) hydride complex  $(\text{POCOP})\text{NiH}$  proved the most active in the reduction of secondary amides, tolerating internal alkene, ester, nitrile, heteroaromatic and tertiary amide functionalities. Preferable hydroboration of secondary amides was also demonstrated in the presence of primary amide groups. The reactions were conducted at 40-80 °C, representing a rare example of a base-metal catalytic system for selective deoxygenation of secondary amides to the corresponding amines under mild conditions. Whereas  $(\text{POCOP})\text{NiH}$  catalyzed selective deoxygenation of secondary amides, primary amide substrates were hydroborated to the corresponding N,N-diborylamines using an iminophosphinite derivative  $(\text{POCN}^{\text{Dmp}})\text{Ni}(\text{CH}_2\text{SiMe}_3)$  (Dmp = 2,6-dimethylphenyl) as a catalyst. Our mechanistic and kinetic studies suggested that deoxygenative hydroboration reactions proceed via a direct C-O bond cleavage route, which is triggered by dehydrogenative N-borylation to access more electrophilic N-borylamides amenable to addition of HBPIn to the carbonyl group.

## Discussion

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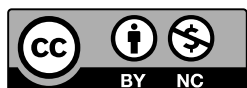
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