Copper–cobalt double metal cyanides as green catalysts for phosphoramidate synthesis

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 $K_3[Co(CN)_6]$

CuCl₂

 H_2O

Phosphoramidate synthesis

*t*BuOH



Phosphoramidates are common and widespread backbones of a great variety of fine chemicals, pharmaceuticals, additives and natural products. Conventional approaches to their synthesis make use of toxic chlorinated reagents and intermediates, which are sought to be avoided at an industrial scale. Here we report the coupling of phosphites and amines promoted by a $Cu_3[Co(CN)_6]_2$ -based double metal cyanide heterogeneous catalyst using I_2 as additive for the synthesis of phosphoramidates.

Catalyst preparation







- Linear Co-N-C-Cu disposition
- Co octahedral geometry
- No free vacancies around Co atoms
- Cu octahedral geometry
- Vacancies exist around Cu atoms!
- Co atoms electronic and spatial structure are not changed
- Co-Cu long distance coordination is partially lost
- Cu exchange ligands, O and N atoms in direct coordination
- Cu adopts a newly square planar geometry



Local structure of the catalyst metal centers



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Abstract

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