

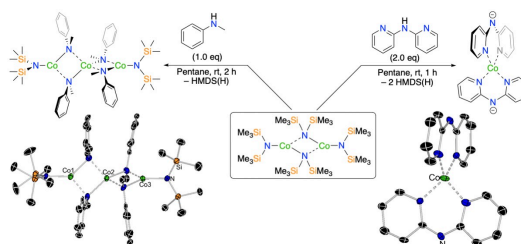
Exploring Trans(amination) Reactions in Co(II) Chemistry

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Pioneered over 60 years ago,^[1] cobalt (II) amide $\text{Co}(\text{HMDS})_2$ ($\text{HMDS} = \text{N}(\text{SiMe}_3)_2$) has found widespread applications in synthesis and catalysis as a precursor of Co(II) complexes.^[2] Previous studies have reported the ability of this complex to undergo trans(amination) reactions with primary amines in the presence of sterically demanding N-heterocyclic carbenes although harsh reaction conditions are required in order to promote the activation of both HMDS groups.^[3]

Breaking new ground in this field, here we systematically study the reactivity of $\text{Co}(\text{HMDS})_2$ towards a range of different amines uncovering its polybasic behaviour when reacted with 2,2'-dipyridylamine (DPA(H)) (see Figure) whereas with other amines like piperidine and *N*-methylaniline it can only undergo hemi(transamination) reactions even under forcing reaction conditions. Isolation and structural characterisation of key reactive intermediates has revealed the remarkable structural diversity of Co(II) amide complexes. Initial reactivity studies have also shown that while $\text{Co}(\text{HMDS})_2$ can react with two equivalents of mesitylacetophenone to form a novel Co(II) enolate complex via deprotonative metalation, $\text{Co}(\text{DPA})_2$ is completely inert towards this substrate.



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