

## Electronic effects in the insertion reaction of copper(I) aryloxides

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Heterocumulenes undergo an insertion reaction with copper(I) aryloxides leading to polynuclear copper complexes. Earlier work has shown that the nuclearities of clusters formed in these reactions are determined purely by steric effects. However, no insight could be gained about the insertion reaction itself. In this study, we report how electronic effects in the insertion reaction could be studied using MeNCS instead of PhNCS. The heterocumulene PhNCS undergoes the insertion reaction in the presence of  $P(OMe)_3$  and results in oligomeric products. However, with MeNCS, the reaction proceeds even in the absence of an ancillary ligand. Since MeNCS is less electrophilic, the insertion reaction results in lower yields of the insertion products. Similarly, the insertion reaction is less favourable when the aryloxide has electron withdrawing substituents. In the case of PhNCS, the insertion reaction proceeds even in the presence of  $PPh_3$  and monomeric or dimeric insertion products are formed. However, with MeNCS, the insertion reaction becomes reversible when  $PPh_3$  is present. The deinsertion reaction can be slowed down by introducing ortho substituents in the aryloxide. Further proof for the reversible nature of the insertion is the exchange of the heterocumulenes present in the clusters, provided  $PPh_3$  is present. The exchange is either with a heterocumulene which has a more electrophilic carbon centre or one that has more sulfur atoms. Exchange also occurs with a more nucleophilic phenol.

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