

## Substituent effects on the insertion of heterocumulenes into copper(I) aryloxides

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The reaction of metal alkoxides with heterocumulenes inevitably leads to an insertion of the heterocumulene into the M–OR bond. However, what happens after the insertion is dependent on the metal, the heterocumulene, the alkoxide and the presence of ancillary ligands. We have found that copper(I) and copper(II) aryloxides undergo insertion followed by rearrangement and oligomerization. The oligomerization is controlled by the steric bulk of the aryloxide, and the nature of the ancillary ligands present. We have investigated the effect of changing the substituent on the heterocumulene and the results are reported in this poster. Surprisingly, a minor change in the heterocumulene led to the formation of oligomers with differences in structure and reactivity. A hexameric complex is formed in the insertion reaction with MeNCS just as in the case of the reaction of PhNCS with copper(I)cresolate. The molecular structure of the complex formed with MeNCS is more symmetrical than that formed with PhNCS. The Cu–Cu distances are also different. The insertion reaction with PhNCS requires the presence of a ligand. MeNCS however undergoes insertion without the aid of ancillary ligands. The insertion reaction is reversible in the case of MeNCS. More drastic conditions like high temperatures are required in the case of the PhNCS inserted product to reverse the reaction. The oligomeric structure of the MeNCS hexamer is broken down readily with ancillary ligands and free MeNCS is formed. However the PhNCS inserted complex takes a longer time to break down and a product which still has the inserted PhNCS is formed. MeNCS insertions do not occur with all aryloxides.

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