

Название публикации:

High-Cluster (Cu-9) Cage Silsesquioxanes: Synthesis, Structure, and Catalytic Activity

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Аннотация:

Unusual high-cluster (Cu-9) cage phenylsilsesquioxanes were obtained via complexation of in situ Cu-11,Na-silsesquioxane species formed with phenanthroline and neocuproine. In the first case, phenanthroline, acting as "a silent ligand" (not participating in the composition of the final product), favors the formation of an unprecedented cagelike phenylsilsesquioxane of Cu₉Na₆ nuclearity, 1. In the second case, neocuproine ligands withdraws two Cu ions from the metallasilsesquioxane matrix, producing two cationic fragments Cu+(neocuproine)₂. The remaining metallasilsesquioxane is rearranged into an anionic cage of Cu₉Na₄ nuclearity, finalizing the formation of a specific ionic complex, 2. The impressive molecular architecture of both types of complexes, e.g., the presence of different (cyclic/acyclic) types of silsesquioxane ligands, was established by single-crystal X-ray diffraction studies. Compound 1 was revealed to be highly active in the oxidative amidation of benzylic alcohol and the catalyst loading could be reduced down to 100 ppm of Cu. Catalytic studies of compound 1 demonstrated its high activity in hydroperoxidation of alkanes with H₂O₂ and oxidation of alcohols to ketones with tert-BuOOH.

Ключевые слова:

Transition-metal catalysts; hybrid materials; chemistry; metallasiloxanes; silanetriols; complexes; alcohols; siloxane