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The activation of molecular oxygen by boron, aluminium and gallium dialkyl complexes

The first part of the thesis concerns investigation on the reactions of boron, aluminium and gallium alkyl compounds with selected bifunctional *O,O'*-, *O,S*- and *O,N*-ligands. The use of wide range of ligands and alkyl compounds of 13^{th} group elements allowed a comprehensive analysis of the influence of the electron and steric factors on the formation and structure of the studied complexes. Isolated and characterized reaction products appeared to be monomers and dimmers. Moreover, the four obtained and rentgenographically analyzed complexes exhibit interesting supramolecular structures.

The second part of the thesis describes the studies of reactivity towards molecular oxygen of previously synthesized complexes of 13^{th} group elements of type $[RM(O,X)]_n$ (where M = B, Al, Ga and *X* = *O'*, *S* or *N*). A unique diversity of the oxygenation products was achieved, ranging from peroxo, alkoxy to oxide system. The most important achievement of the presented thesis is the thorough investigation of alkylgallium methyl ester of 2-thiobenzoic acid (*tiobenz*-H) complexes oxidation reactions. On the basis of the analysis of the final products and ^{1}H NMR kinetic studies of the oxygenation reactions the mechanisms explaining the diversity of the reaction paths of alkylgallium complexes oxygenation were proposed. Moreover, the interesting results have been received for the oxygenation reactions of alkylaluminum derivatives with methyl ester of 2-pyrrolocarboxylic acid (*metpyrrol*-H) ligand. The final product of the oxidation reaction of $(^t\text{Bu})_2$Al(*metpyrrol*) was isolated and characterized. The obtained complex has an unusual structure with the presence of bridging *tert*-butylperoxide groups. Additionally, in comparison to the oxygenation reaction, reactivity of earlier characterized complexes with ethanol and TEMPO has been investigated. The most interesting achievement in this part is the synthesis of the fully characterized complex $[\text{MeAl}(mesal)\text{TEMPO}]_2$.

In the next step of the work the correlation of electrochemical oxidation of the studied complexes with their reaction with O_2 has been investigated. To this end, electrochemical properties of the previously characterized complexes of the 13^{th} group elements of $R_2M(O,X)$ type have been studied. The obtained results show that in the wide range of potentials there is no such correlation and all observed redox properties are linked with the used ligand.

The results allow to significantly extend the knowledge of the chemistry of alkyl, alkoxyl and alkylperoxide boron, aluminum and gallium complexes with *O,X*-ligands and to open the new ways for the further investigation on the activation of molecular oxygen with metal alkyl complexes.