Towards New Metal Alkoxides and Alkylperoxides:

Contrasting Oxygenation vs Protonolysis Reactions of the Respective Organometallics

Continues interest in main group metal alkoxide and alkylperoxide compounds and the related zinc derivatives last for decades. The reason for that is their rich structural diversity, resulting from their nature to exist in different coordination or bridging modes, and possible applications in various areas of chemistry and material science. However, knowledge on the chemistry of metal alkoxides and alkylperoxides with non-redox-active metal center is still limited despite long history of these investigations. Particularly synthesis and reactivity of well-defined metal alkoxides and alkylperoxides supported by chelating ligands remains largely undeveloped field. These species have commonly been generated *in situ* in equimolar protonolysis reactions between $R_nM(L)$-type complexes and alcohols or organic hydroperoxides, respectively. Nevertheless, many reports mention synthetic troubles in specific cases, with the inability to isolate pure compounds and/or formation of complicated mixtures of unidentified compounds and in fact no clear evidence of actual generation of the respective species was gained**.** In turn, in the course of our long-lasting studies on the O_2 reactivity of organometallics with non-redox-active metal center, we clearly demonstrated that the controlled oxygenation of $R_nM(L)$-type complexes might lead to metal alkoxides or alkylperoxides possessing unprecedented structural motifs.

The proposed project is focused around oxygenation and protonolysis reactions of organometallic compounds as various synthetic pathways for metal alkoxides and alkylperoxides incorporating X,Y-bifunctional ligands. The particular emphasis will be paid to contrast this two transformations and their influence on the final products. The search for new ligand systems possessing the desired electronic and steric properties and the investigation of factors influencing the structure and reactivity of the resulting organometallic complexes represents a challenging task for organic and organometallic chemists. Planned studies will provide valuable information about the critical factors controlling the stability and structure of metal alkoxide and alkylperoxide complexes. The obtain compounds will serve afterwards as a platform for investigation on the further controlled transformations of metal alkylperoxides, which leads to variety of products, including metal alkoxide, oxo, hydroxide and carboxylate species. The gathered knowledge will be used for development of new stoichiometric and catalytic reaction systems (e.g. epoxidation of enones and polymerization of) based on metal alkoxides and alkylperoxides.

The proposed investigations should provide more in-depth understanding of the intimate steps of protonolysis and oxygenation reactions, and pave the way to both structurally well-defined metal alkoxides and alkylperoxides, and desired reactivity. **We believe that the results of these studies will catch the imagination of many inorganic/organic/polymer chemists as advances in metal alkoxides and alkylperoxides fabrication with dedicated chemical properties can lead to new classes of reagents and catalysts.**