Manipulating Radicals: Using Cobalt to Steer Radical Reactions.
A. Chirila
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This thesis describes research aimed at understanding and exploiting metallo-radical reactivity and explores reactions mediated by square planar, low-spin cobalt(II) complexes. A primary goal was to uncover novel reactivity of discrete cobalt(III)-bound carbene radicals generated upon reaction of the cobalt(II) catalysts with carbene precursors. Another important goal was to replace cobalt(II)-porphyrin catalysts with cheaper and easier to prepare metallo-radical analogues. Therefore the catalytic activity of planar, low-spin cobalt(II) complexes based on the dibenzotetraaza[14]annulene (MeTAA) ligand scaffold was investigated. Besides the easier synthetic procedure, these complexes are also more active in catalysis than the corresponding cobalt(II)-porphyrins in a variety of ‘carbene transfer’ reactions. The work described in this thesis shows that, like in enzymes, controlled metal-catalysed reactions proceeding via radical-type pathways are certainly possible using well-defined metallo-radical complexes of cobalt(II). Generating ‘carbene-radicals’ upon activation of carbene precursors with these catalysts leads to fascinating new reactivities, taking advantage of the preferred one-electron reactivity of cobalt. The intrinsic reactivity of these species can be controlled by changing the ligand, and the reactions lead to interesting products such as cyclopropanes, ketenes and indenes.