
Summary

Open shell nitrene- and carbene-complexes of cobalt: characterisation and reactivity.

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Nitrene- and carbene-complexes of cobalt(II) porphyrins that are best described as porphyrin cobalt(III)-nitrene and carbene-radicals, respectively, are the key players in this thesis. Discrete spin transfer from the cobalt(II) metalloradical to the nitrene and carbene moiety induces interesting reactivity in these systems; especially for application in catalytic systems. Starting from rigorous characterisation to application in catalysis, this thesis shows that in the coordination sphere of metals, radicals are tamed and their reactivities can be attuned for applications in challenging and new chemical transformations.

Combined, the work described in this thesis shows enzyme-like controlled radical-type reactions with metallo-radical complexes of cobalt(II) provide interesting, new synthetic routes to useful organic products. Formation of nitrene-radical and carbene-radical species upon activation of nitrene and carbene precursors with these catalysis, respectively, leads to fascinating follow-up reactivity involving controlled radical-type reaction steps, made possible by the intrinsic one-electron reactivity of cobalt. The reactivity can be controlled by changing the ligands, and the reactions lead to interesting products such as phenoxazines, benzoxazines, azobenzenes, indolines and difluorocyclopropanes. Future studies in the field of cobalt(II) metalloradical catalysis are expected to uncover many more exciting and novel reactions proceeding via one-electron pathways. This will not only be of synthetic use, but also provides an inspiration for additional fundamental research in molecular catalysis, stimulating additional mechanistic studies and encouraging many thought-provoking synthetic shortcut explorations.