

Summary

Radicals are often considered to be *too reactive to be selective*. For free radicals this might be true, but in the coordination sphere of a transition metal highly chemo-, regio-, diastereo- and enantioselective radical-type reactions become feasible, with many bio-enzymatic radical-type biosynthetic transformations serving as illustrative examples. The main objective of this Thesis is to show that also in organometallic chemistry radical reactions are synthetically useful, and can even lead to selective catalytic reactions. The explorative nature of the investigations that led to these conclusions further led to a number of interesting closed-shell reactivity patterns (Chapter 2 and 3).

Selective radical-type atom transfer reactions of open-shell organometallic compounds often require the presence of unpaired electron (radical) density at a reactive ligand site, and hence the so-called “ligand redox non-innocence” is an important feature in these reactions. This concept is explained in **Chapter 1** on the basis of a literature survey of the intriguing open-shell organometallic chemistry of paramagnetic group 9 (Co, Rh, Ir) complexes bearing carbonyl, carbene and alkene ligands (and alike). One-electron activation of alkene, carbonyl and carbene ligands reveal a remarkable variety of selective radical-type reactions. These ligands have low lying empty orbitals that easily accept an unpaired electron from the metal in open-shell complexes. This triggers radical-type reactivity on their carbon atoms (Figure 1), which leads (among others) to formation of new C–H or C–C bonds by hydrogen atom transfer or reductive coupling to form products that cannot be obtained via closed-shell pathways.

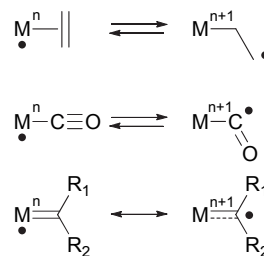


Figure 1. Redox non-innocent behavior of alkene, CO and carbene ligands.

Chapter 2 describes the synthesis and redox properties of rhodium and iridium carbonyl complexes $[M^I(\text{CO})_n(\text{Me}_3\text{tpa})]^+$ ($M = \text{Rh}, \text{Ir}, n = 1, 2$) supported by the Me_3tpa ligand. The iridium bis-carbonyl complex undergoes a selective, irreversible one-electron oxidation which leads to an iridium mono-carbonyl hydride complex (Figure 2). In the investigated systems the CO moiety behaves as a redox

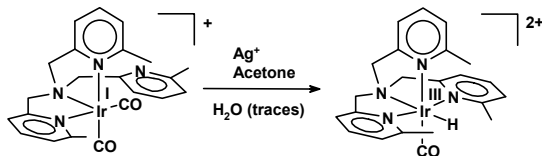


Figure 2. Metal centered reactivity of $[\text{Ir}(\text{CO})_2(\text{Me}_3\text{tpa})]$ triggered by one electron oxidation.

innocent ligand, and oxidation of the complexes leads to selective *metal centered* radical-type reactivity in the case of iridium (Figure 2). This contrasts with previous investigations of Wayland, wherein carbonyl adducts of $\text{Rh}^{\text{II}}(\text{por})$ were clearly shown to behave as carbon-centered radicals. Furthermore, two electron carbonyl ligand activation pathways were revealed for the *closed-shell* $[M^I(\text{CO})_n(\text{Me}_3\text{tpa})]$ systems. Reaction of the iridium bis-carbonyl complex with water (or methanol) results in formation of hydroxycarbonyl-hydride (or methoxycarbonyl-hydride) complexes, which allows the isolation of iridium analogs of all subsequent intermediates relevant in the water gas shift reaction (Figure 3). Reaction of the closed-shell rhodium carbonyl

complex with dioxygen in the presence of water leads to selective formation of a carbonate complex.

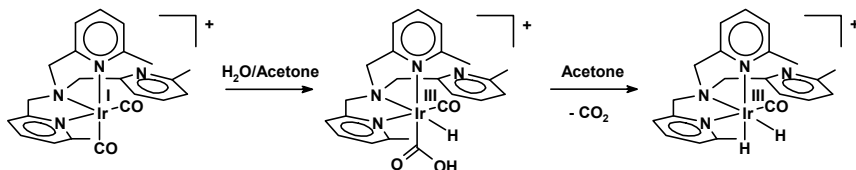


Figure 3. Isolated iridium analogs of intermediates relevant in the water gas shift reaction.

In **Chapter 3** we investigated the impact of the donor strength of tri- and tetradentate bispicolylamine type ligands on the structure of rhodium carbonyls. For more electron donating bpa ligand binuclear triscarbonyl bridged species are favored over terminal carbonyls which are formed with weaker donating alkyl-bpa ligands. Interestingly, rhodium carbonyl complexes with the tetradentate trispicolyl-amine ligand exist in a dynamic equilibrium between the terminal and biscarbonyl bridged dinuclear species (Figure 4).

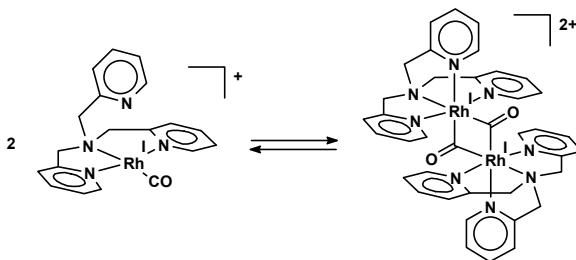


Figure 4. Dynamic equilibrium between mononuclear $[\text{Rh}(\kappa^2\text{-tpa})(\text{CO})]^+$ and dinuclear $[\text{Rh}(\kappa^4\text{-tpa})(\mu\text{-CO})]_2^{2+}$.

In **Chapter 4** we investigated the possible role of aminyl radicals in the reactivity of open-shell rhodium and iridium complexes. Unexpected one-electron reduction of $[\text{M}^{\text{II}}(\text{dbcot})(\text{bla})]^{2+}$ complexes (dbcot = dibenzocyclooctadiene, bla = bislutidylamine), is observed in the presence of a base (Figure 5). Control experiments with $[\text{Rh}^{\text{II}}(\text{dbcot})(\text{Bz-bla})]^{2+}$ (Bn-bla = N-benzyl-bislutidylamine) show that these reactions can also proceed without the involvement of aminyl radicals, but rapid hydrogen atom abstraction from the solvent by an aminyl radical ligand cannot be fully excluded. In any case, these complexes did not allow the formation of detectable aminyl radical ligands upon deprotonation, thus complicating a study of their reactivity. This behavior is in marked contrast with the reported easy formation of Rh-stabilized aminyl radical ligands for structurally similar complexes, as reported by Grützmacher and coworkers. Possible reduction pathways involving base assisted oxidation of solvent or water are discussed.

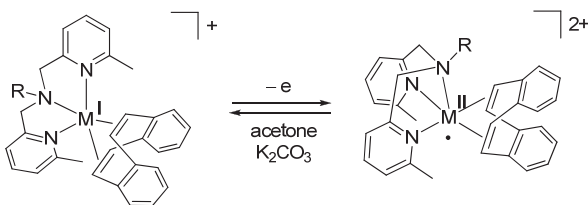


Figure 5. Electrochemical behavior of rhodium and iridium dbcot complexes of bislutidine type ligands.

Chapter 5 describes the reactivity of the paramagnetic complex $[\text{Ir}^{\text{II}}(\text{ethene})(\text{Me}_3\text{tpa})]^{2+}$ with diazo compounds (used as carbene precursors). Here, the carbene ligand, generated at the open-shell Ir^{II} metal, clearly behaves as a redox active

ligand, and to the best of our knowledge the ‘redox non-innocent’ behavior of (Fischer-type) carbenes of group 9 transition metals was demonstrated for the first time with these investigations. Radical-type C–C and C–H bond forming reactions occurring at the ‘carbene radical’ ligand and DFT investigations on their mechanism are presented in this Chapter. Based on these results we give a description of the electronic structure of one-electron activated carbenes. The ‘carbene radicals’ are best described as carbon centered radicals bound to a closed-shell transition metal centre (Figure 6).

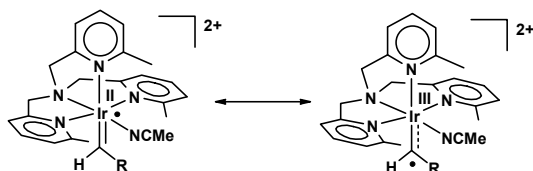
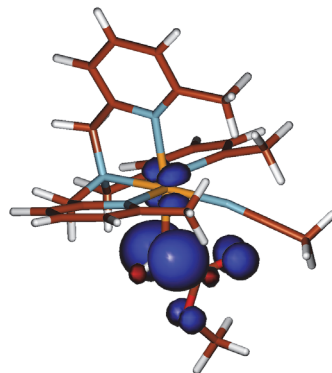
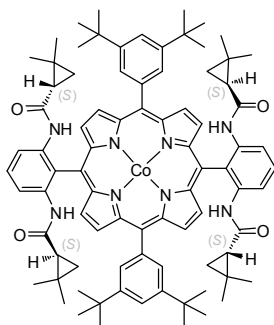


Figure 6. Redox non-innocent behavior of the carbene bound to $[\text{Ir}(\text{Me}_3\text{tpa})(\text{NCMe})]^{2+}$. Resonance structures (top) and the DFT calculated spin density (right).



In **Chapter 6** we show that ‘carbene radicals’ are not just some chemical curiosity, but actually play an *important, previously unknown role* in existing catalytic cyclopropanation reactions mediated by cobalt-porphyrin complexes. Paramagnetic $\text{Co}^{\text{II}}(\text{por})$ complexes are effective catalysts for olefin cyclopropanation, and the most successful cobalt-based cyclopropanation catalyst is the chiral cobalt-porphyrin $\text{Co}^{\text{II}}(3,5\text{-Di}^t\text{Bu-ChenPhyrin})$ complex developed by Zhang and coworkers (Figure 7). It is unprecedented in its reactivity, stereocontrol, and the ability to affect cyclopropanation with (near) stoichiometric amounts of alkenes avoiding carbene dimer formation. Another intriguing feature of this Co^{II} porphyrin system is its effectiveness in cyclopropanation of electron-deficient olefins like methyl acrylate or acrylonitrile. This reactivity is remarkable, and very different from the typical electrophilic Fischer-type carbene intermediate associated with Cu^{I} and Doyle-type Rh_2 -based systems, thus



$\text{Co}(3,5\text{-Di}^t\text{Bu-ChenPhyrin})$

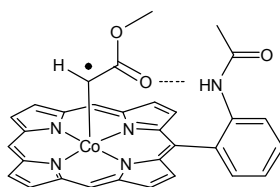


Figure 7. $\text{Co}^{\text{II}}(3,5\text{-Di}^t\text{Bu-ChenPhyrin})$ (left) and its H-bond donation to the ‘carbene radical’ ligand in the key catalytic intermediate (top).

pointing to a very different character of the carbene transfer intermediate for $\text{Co}^{\text{II}}(\text{por})$ -based systems.

In this chapter we investigated the reaction mechanism of this catalyst through EPR spectroscopic and DFT computational investigations.

The cyclopropanation mechanism clearly proceeds

via a radical-type mechanism, which involves the formation of reactive carbon-centered radicals within the coordination sphere of cobalt. We show that the key cobalt-carbene intermediate has a strong carbon radical character, and is in fact a ‘carbene radical’

similar to the iridium-carbene radicals described in Chapter 5 (Figure 8). Its nucleophilic and radical character facilitates the cyclopropanation of electron poor olefins, and suppresses carbene dimerization activity. To our knowledge this is the first and only documented example in which ligand redox-non innocence plays a key role in an organometallic catalytic transformation. Addition of the ‘carbene radical’ to the olefin is followed by a low-barrier transition state for cyclopropane ring closure. The latter process is best described as a radical-type C–C bond coupling with simultaneous homolytic splitting of the cobalt–carbon bond. Hence, besides the ‘redox non-innocence’ of the carbene, also the intrinsic relative weakness of the Co–C bond plays a crucial role in this reaction.

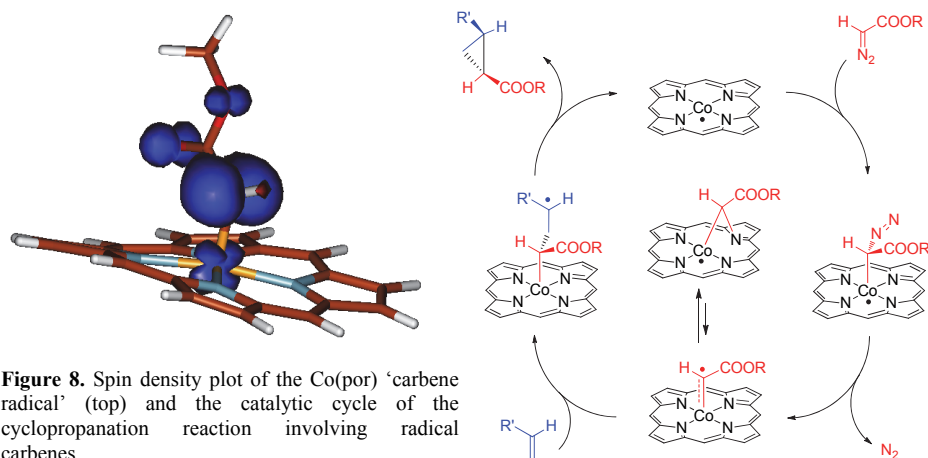


Figure 8. Spin density plot of the Co(por) ‘carbene radical’ (top) and the catalytic cycle of the cyclopropanation reaction involving radical carbenes.

A further interesting feature of this catalyst is that the aryl-dicyclopropane-carboxamido functionalities of the 3,5-Di^tBu-ChenPyrin ligand (Figure 7) are potent H-bond donors. This lowers the activation barrier for formation of the carbene radicals from the diazo ester substrate, thus leading to faster reactions and higher selectivities. With this radical-type mechanism being firmly established, Co^{II}(por)-catalyzed olefin cyclopropanation provides an illustrative example of a synthetic catalytic reaction that operates via a radical-coupling process, but still allows highly selective turnover.

In Chapter 7 we computationally investigated the role of cobalt metallo-radicals in catalytic chain transfer (CCT) in cobalt mediated radical polymerization reactions. The computational study focuses on the reversible hydrogen atom transfer reactions between cobalt porphyrins and organic radicals (Figure 9). The calculations give insight into the CCT mechanism. Results from this study further suggest that the hydrogen atom transfer pathway could be important in numerous reactions in which an olefin is inserted into a weak M–H bond.

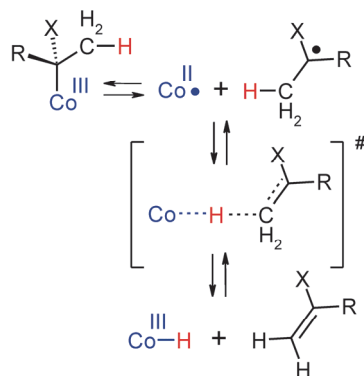


Figure 9. Reversible hydrogen atom transfer between Co^{II} and organic radicals.

Summary

The main finding of this Thesis is that the concept of ligand redox non-innocence can be utilized not only in stoichiometric, but also in catalytic reactions. We showed that one-electron activation of the coordinated ligand results in a dramatic change in the reactivity pathways, which may also allow for reactions with otherwise unreactive substrates. We also claim that a better understanding of the behavior of unsaturated ligands bound to paramagnetic (Group 9) metals can lead to useful, new (catalytic) transformations. Thus, in the **Perspective** we speculate on the possible involvement of carbene radical complexes in new (catalytic) reactions, which might potentially lead to valuable new products via unprecedented catalytic pathways. We propose that reactions of radical carbenes with conjugated dienes or reactions of radical vinylcarbenes with olefins could lead to functionalized cyclopentenes. We also postulate that nitrene ligands should be redox active and thus react via radical type mechanisms.