

File ID 200096
Filename Chapter 1: General introduction: redox non-innocent behavior of alkene,
carbonyl and carbene ligands

SOURCE (OR PART OF THE FOLLOWING SOURCE):

Type Dissertation
Title Group 9 open-shell organometallics: reactivity at the ligand
Author W.I. Dzik
Faculty Faculty of Science
Year 2011
Pages 165

FULL BIBLIOGRAPHIC DETAILS:

<http://dare.uva.nl/record/362994>

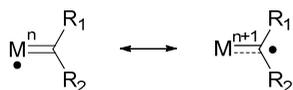
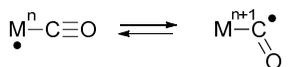
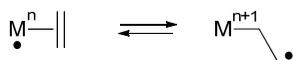
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Chapter 1

General Introduction:

Redox Non-Innocent Behavior of Alkene, Carbonyl and Carbene Ligands



1.1 Introduction

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. Selectivity is primarily a matter of *relative* rather than *absolute rates*, and hence also fast radical-type reactions can be (made) selective using the steric and electronic influence of ligand surroundings in transition metal controlled reactions.¹

Nature is teaching us clearly that *selective radical reactions are certainly possible* and radical-type reactions are actually quite common in several biochemical processes. Many metallo-enzyme catalyzed transformations proceed via radical-type reactions involving open-shell intermediates. They are essential in mediating *difficult reactions* such as C–C or C–O bond formations or transformations, and despite their radical nature these reactions still proceed in the highly selective manner typical for enzymatic reactions.²

Selective radical-type atom transfer reactions most frequently require the presence of unpaired electron (radical) density at a reactive ligand site (*e.g.* oxo / oxyl radical ligands),³ as is clear from mechanistic studies of bio-catalytic processes mediated by among others cytochrome P₄₅₀,⁴ methane monooxygenases,⁵ class I ribonucleotide reductase⁶ or galactose oxidase.

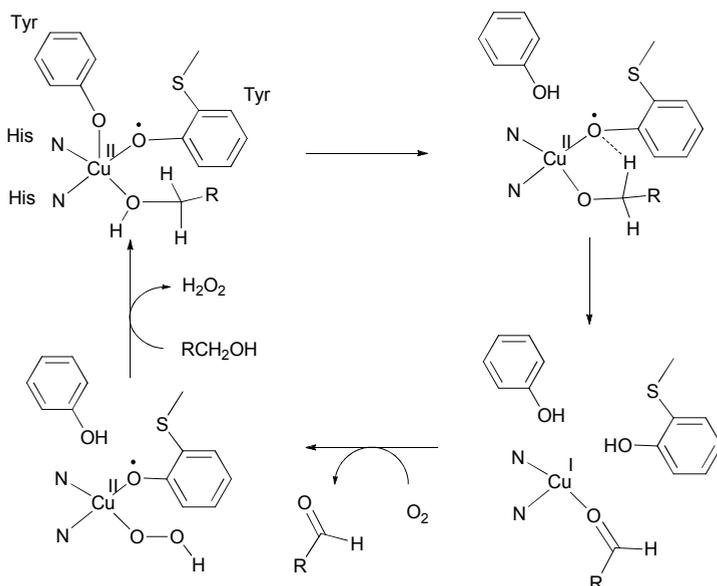


Figure 1. Cooperative ligand radical in the mechanism of alcohol oxidation by galactose oxidase.

The mechanism of Galactose Oxidase (GOase) is perhaps one of the most illustrative examples in showing how radicals can be controlled in the coordination sphere of a transition metal to achieve selectivity (Figure 1).⁷ This fungal enzyme chemo-selectively converts primary alcohols with O₂ into aldehydes and hydrogen peroxide with impressive second order rate constants ($\sim 1.59 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$).⁸ The active site of GOase consists of a redox active Cu^I ion in proximity to a redox active cysteine modified tyrosine. Oxidation of the active site by dioxygen produces a

tyrosinyl radical coordinated to Cu^{II} and a hydroperoxo ligand. In the key subsequent steps of the catalytic cycle the thus obtained hydroperoxo ligand deprotonates the alcohol to form free hydrogen peroxide and an alcoholate ligand. The tyrosinyl radical ligand subsequently abstracts a hydrogen atom from the α -CH functionality of the alcoholate to produce the aldehyde. Remarkably, the tyrosinyl radical is a reactive fragment in the catalytic cycle and functions as a cooperative ligand, assisting copper in the turn-over process. The ligand redox activity allows removal of the second electron from the substrate, and thereby a two-electron oxidation using a copper ion that is normally only capable of one-electron transformations. It is the interplay of the one-electron reactivity of the ligand radical and the one-electron reactivity of the metal which makes the overall two-electron oxidation process possible. The cooperative radical-type process makes the reaction fast and selective.

Metal-ligand bond homolysis within an enzyme pocket is another frequently observed pathway to start selective radical-type transformations. The typical radical-type reactions mediated by cobalamine⁹ (coenzyme B_{12}) based dependent mutases (allowing carbon skeleton rearrangements)¹⁰ and diol dehydrase or ethanolamine deaminase¹¹ are initiated by homolytic splitting of a weak cobalt(III)-carbon bond (Figure 2).¹² The thus formed carbon radical serves as a hydrogen atom acceptor from the substrate CH group. After the first hydrogen atom transfer (HAT) step the open shell substrate rearranges through the migration of a functional group to the radical carbon followed by the second HAT to form the closed-shell rearranged product. The $\cdot\text{CH}_2\text{Ad}$ radical remains in close proximity to the cobalt(II) centre reforming the cobalt-carbon bond after the catalytic turnover.

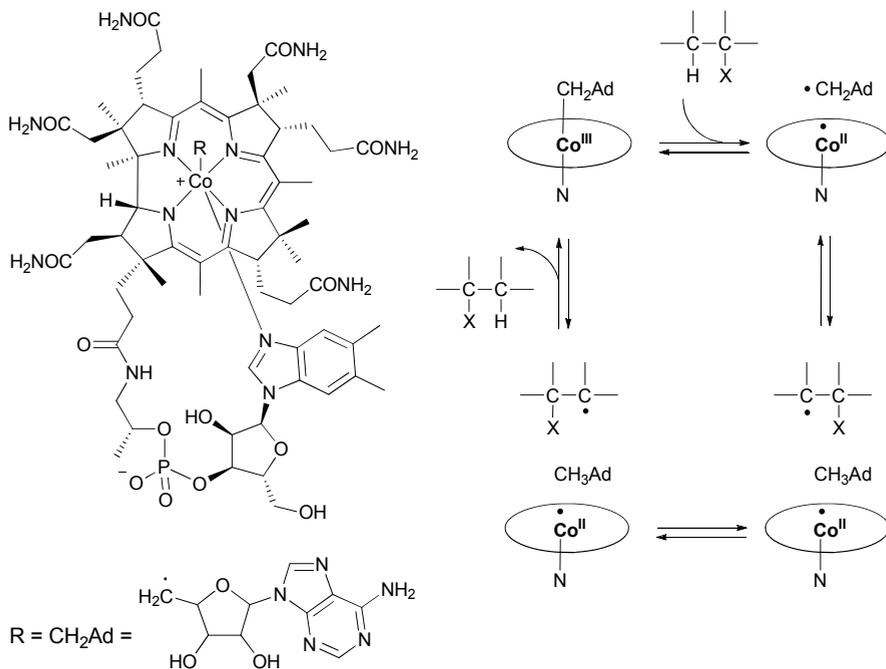


Figure 2. Structure of coenzyme B_{12} and the generic mechanism for AdoCbl-dependent rearrangement reactions.

The mechanisms of reactions catalyzed by galactose oxidase or coenzyme B₁₂ are excellent examples of how radical-type reactions can be controlled in the coordination sphere of a transition metal, and serve as a clear inspiration for synthetic chemists. Interesting bio-mimetic approaches to GOase have already shown synthetic power in alcohol oxidation reactions,¹³ but future studies are likely to uncover a wide field of new opportunities. The ease of reversible generation of a carbon centered radical by the cleavage of the weak Co–C bond (used by Nature in the coenzyme B₁₂) has found wide application in transition metal controlled radical polymerization.¹⁴ The latter example shows elegantly that the same phenomena (*i.e.* homolytic cleavage of a weak metal-carbon bond) that are used in enzymes for certain transformation *in vivo* can be successfully applied to mediate reactions (like polymerization of olefins) that occur only in chemical laboratories. Some other important examples of synthetic (catalytic) reactions that proceed via open-shell intermediates are atom transfer radical polymerization,^{14a} atom transfer radical addition,¹⁵ and oxygenation reactions.¹⁶ For most of these reactions, atom or group transfer to a reactive metal-centered radical (metallo-radical) occurs at some stage of the catalytic reaction, but properly designed synthetic transition metal complexes should allow us to activate substrates in a similar (cooperative) way as Nature does. Especially in the field of organometallic chemistry, the playground of *catalytic* synthetic-organic transformations, controlling the radical-type reactivity of open-shell organometallic compounds can offer vast opportunities to achieve a wide variety of new, fast and selective catalytic transformations proceeding via radical-type rearrangements, and open-shell coupling, abstraction, addition, (single or multi-component) cyclization, and/or disproportionation reactions.

Due to the ligand redox non-innocence of many π -accepting ligands, organometallic complexes offer many possibilities to form ligand radicals, which can play a dominant role in directing the open-shell reactivity of the compounds. Such behavior offers further interesting and new opportunities to achieve selectivity and new reactivity in the field of *open-shell organometallic catalysis*.

In further sections the concept of ligand redox non-innocence will be described, followed by an overview of one-electron reactivity of olefins, carbonyls and carbenes where redox non-innocence plays a crucial role.

1.2 Ligand redox non-innocence

When considering the properties and reactivity of paramagnetic species the location of the unpaired electron(s) is an important issue to address. For many open-shell compounds the atoms or groups bearing the largest unpaired spin density are also the most reactive sites of the molecule. In this Chapter we are primarily considering low-spin complexes containing only a single unpaired electron ($S = \frac{1}{2}$ systems). This does not mean that their electronic structure is always as simple as it seems, because the unpaired electron can be located at the metal, at the ligand, or in-between. Some species should be regarded as distinct metal or ligand radicals, whereas in other species the ligand and metal radical descriptions are limiting resonance structures of the real electronic structure (Figure 3).

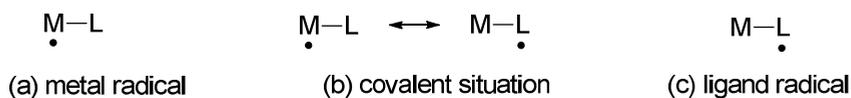


Figure 3. Possible electronic structures of an open-shell complex: (a) metal radical; (b) covalent situation; (c) ligand radical.

In formal oxidation state counting, redox processes of transition metal complexes are always assumed to occur at the metal. Such formal oxidation states are appropriate for ‘classical’ Werner-type coordination compounds, and in combination with convenient ligand-field approximations the thus obtained d-electron configuration is a quite useful concept, applicable for spectroscopic interpretations or predictions of the magnetic behavior of these complexes. However, for complexes bearing redox active ligands, formal oxidation state changes do not always reflect true changes in the d-electron configuration of the metal. Such redox active ligands are usually ligands which undergo π -bonding with the metal and/or have an extended π -system enabling them to delocalize accumulated charges and unpaired spin density upon oxidation or reduction of the complex. In other words, the actual redox process may occur at a ligand site rather than the metal, hence leaving the metal d-electron count unchanged. For such complexes determining the true (spectroscopic) oxidation states of the metal (d-electron configuration) and/or the ligands (ligand electron configuration) requires a detailed spectroscopic study, and the thus obtained ‘spectroscopic oxidation state’ can differ markedly from the formal oxidation state. In such situations the term ‘ligand redox non-innocence’ is used to underline the oxidation state ambiguity.¹⁷

The involvement of ligand redox non-innocence in the mechanisms of several enzymes is meanwhile well established. Redox non-innocent ligands play an active and important role in many (bio)catalytic substrate activation mechanisms, often in cooperation with the transition metal to which they are coordinated.¹⁸ Galactose Oxidase (see section 1.1) provides a seminal example for the involvement of a *cooperative and reactive redox non-innocent ligand playing an active role in the bio-catalytic turnover process* of this enzyme (Figure 1).⁷

Many organometallic complexes bear ligands which undergo π -bonding with the metal (*e.g.* CO, olefins and carbenes) some of which even have an extended π -delocalized system (*e.g.* Cp-derivatives, multi-enes and multi-enyls) and are thus capable of easy charge and spin delocalization upon oxidation or reduction of the complex. Such ligands are by definition suspect, and can easily get oxidized or reduced instead of the metal to which they coordinate. Ligand redox non-innocence indeed plays an important role in the reactivity of open-shell organometallic compounds, although this is not yet so broadly recognized within the organometallic community.

The concept of ligand redox non-innocence in organometallic compounds can be easily understood by looking at the simplified orbital interaction schemes shown in Figure 4.

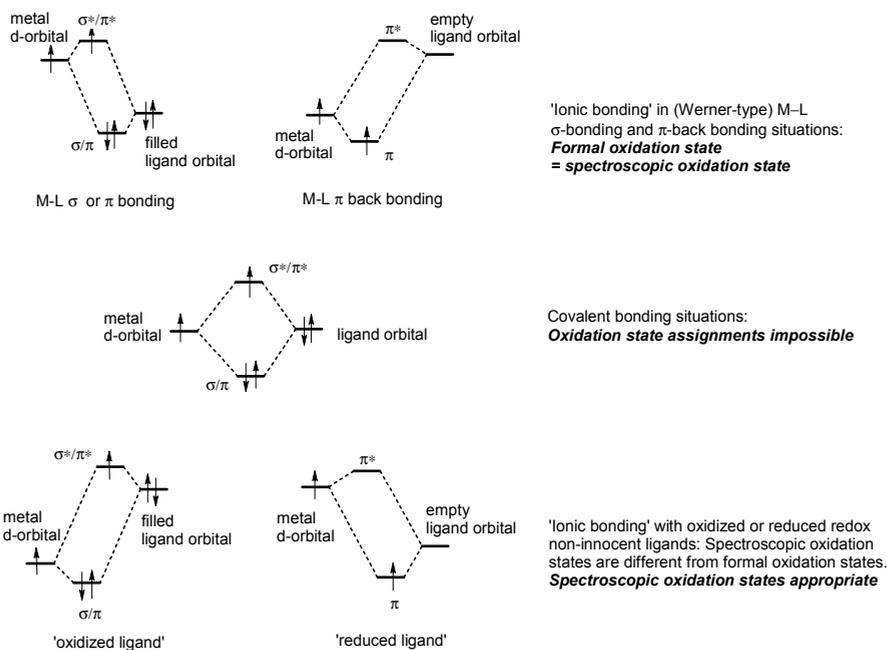


Figure 4. Top: common ionic M–L binding; Middle: covalent M–L binding; Bottom: ionic M–L binding with ‘redox non-innocent’ ligands.

In common Werner-type coordination compounds, the metal d-orbitals are generally substantially higher in energy than the σ -donor type filled ligand orbitals, while their energy is commonly lower than that of the empty ligand π^* -orbitals. Therefore the unpaired electrons are typically (primarily) localized at the metal. Radical reactions initiated by or occurring at such complexes are usually metal-centred. The essential assumption in formal oxidation state counting is that all σ -type metal-ligand interactions are mainly ionic with only small covalent contributions. This means that in using MO descriptions the (filled) valence ligand orbitals used for ligand-to-metal bonding (either σ -bonding or π -bonding) must always be substantially lower in energy than the metal d-orbitals (see Figure 4, top left). Most organometallic complexes also contain π -acceptor ligands. These ligand types contain relatively low-lying empty π^* -orbitals capable of accepting electron density from (the appropriate π -type) metal d-orbitals. Textbook examples of such ligands are CO, NO, and olefinic ligands. The essential assumption made when regarding binding of π -acceptor ligands in formal oxidation state counting is again a large ionic character of the metal-ligand π -interactions, meaning that the ligand valence orbitals involved in the M–L π -back bonding interaction must always be substantially higher in energy than the metal d-orbitals (Figure 4, top right).

Formal oxidation states that go along with these ionic bonding interactions are quite appropriate for ‘classical’ Werner-type complexes, but do not hold for those compounds having more covalent character of the metal-carbon bonds. With strong mixing of more closely energetic metal and ligand orbitals (increasing covalency), formal oxidation

states become quite misleading, and no longer represent the true ‘d-electron’ configurations as the bonding and anti-bonding combinations can no longer be assigned being either of mainly ligand or mainly metal character (Figure 4, middle). The ‘real’ or spectroscopic oxidation state of such complexes is best described as in-between the two limiting metal radical and ligand radical ‘resonance structures’ (Figure 3b).

In certain complexes with redox non-innocent ligands the relative metal and ligand orbital energies can be reversed (Figure 4, bottom). For complexes containing oxidizable ligands, the metal d-orbitals can end-up lower in energy than the ligand orbitals, thus effectively leading to reduction of the metal and oxidation of the ligand. This situation typically involves (but is not restricted to) complexes in high formal oxidation states. In such cases we speak of ‘ligand redox non-innocent’ behavior. For $S = \frac{1}{2}$ systems this has important consequences, as the ligand(s) now contain(s) unpaired spin-density (corresponding to x electrons), and the filling of the metal ‘d-orbitals’ (d^{n+x}) is in reality higher than predicted by the formal oxidation state (d^n). Obviously, ‘redox non-innocent’ behavior of ligands is also possible when π -acceptor type orbitals lie lower in energy than the metal d-orbitals. This situation typically involves (but is not restricted to) complexes in low formal oxidation states, and effectively leads to reduction of the ligands. Also in these cases, the ligand(s) end-up containing unpaired spin-density, and the actual filling of the metal ‘d-orbitals’ (d^{n-x}) is now lower than predicted by the formal oxidation state of the metal.¹⁹

Ligand redox non-innocence (Figure 4, bottom) leading to formation of ligand radicals (Figure 3c) is an important aspect because in many cases the presence of discrete and substantial spin density at a ligand fragment leads to completely different reactivity patterns than commonly observed for these ligands in diamagnetic, closed-shell complexes. The ligand often becomes the most reactive site of the complex in such situations. Nonetheless, such reactive ligand radicals can undergo selective reactions, very different from the uncontrolled reactivity of free radicals. This is possible because the spin density is always shared between the metal and the ligand to some extent (Figure 4, bottom), which leads to higher stabilization of the ligand centered radicals. Moreover, besides their electronic influence, the transition metal and its ligand surroundings can have a profound steric influence on the radical-type reactivity of the substrate. Ligand redox non-innocence can thus be exploited in selective one-electron activation of substrates that usually undergo two-electron transformations, which significantly changes their reactivity patterns and gives access to fast, controlled and selective radical-type organometallic reactions.²⁰

1.3.1 Open-shell reactivity of alkene and alkyne ligands

The π^* -orbitals of alkenes coordinated to paramagnetic transition metals can accept (part of) the unpaired electron(s) from the transition metal, thus forming carbon centered radicals. Hence, the π -accepting alkene fragment is potentially ‘redox non-innocent’, and ‘metallo-radical’ and ‘alkene radical’ descriptions should both be taken into consideration for paramagnetic M(alkene) complexes (Figure 5). A similar behavior can be expected for M(alkyne) complexes. For paramagnetic Rh^{II} and Ir^{II} species this has become quite clear from their unusual ligand based reactivities.

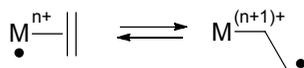


Figure 5. Redox non-innocence of alkene ligands.

Recently, a quite detailed overview concerning the properties and ligand centered radical-type reactivity of open-shell paramagnetic Rh(alkene) and Ir(alkene) species has been presented.²¹ Here only the most illustrative examples will be summarized.

Rhodium(II)- and iridium(II)-porphyrin (por) complexes tend to react with alkenes and alkynes to form hydrocarbon bridged dinuclear M^{III}(por) species. Ogoshi *et al.* reported that Rh(OEP) (OEP = octaethylporphyrinato) generated *in situ* from the Rh(OEP) dimer reacts with acetylenes to form vinylidene bridged species²² (Figure 6). Several M(por) systems (M = Rh, Ir) react with a variety of different olefins to form (por)M–CH₂–CHR–M(por) bridged species.^{23–27} Reacting Rh(por) species with olefins containing allylic hydrogens can also result in allylic radical-type H-atom transfer, pointing to radical-type disproportionation of the proposed β-alkyl radical intermediates (por)Rh–CH₂CHR• (Figure 5).

With more bulky porphyrins, two of such β-alkyl radical intermediates (por)M–CH₂CRH• can couple to form four-carbon –CH₂–CHR–CHR–CH₂– bridged species.^{27,28} Binuclear rhodium complexes with tethered porphyrins react faster with ethene forming the –CH₂–CH₂– bridged species due to lowering the unfavorable entropic term associated with these tri-molecular reactions. With 1,3-butadiene the unsaturated 2-butenone C4 bridged species are formed.²⁹

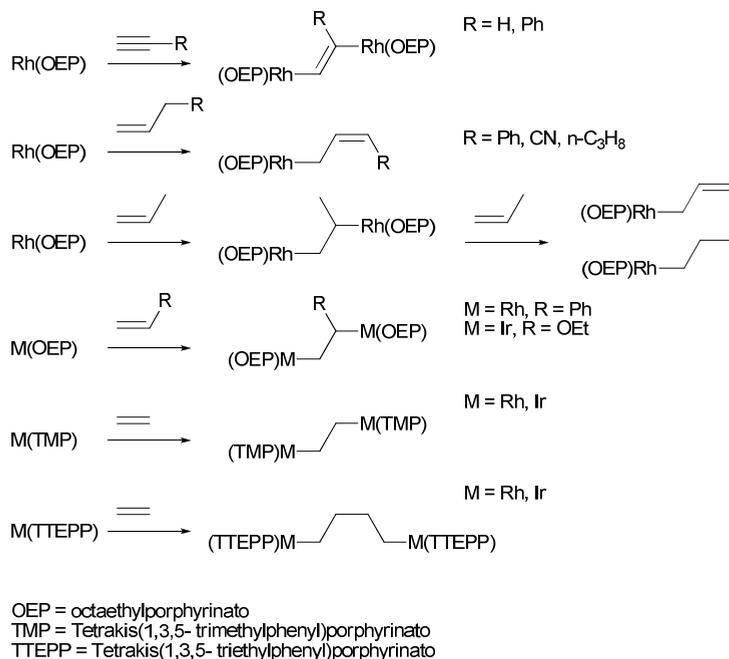


Figure 6. Reactivity of open-shell Rh^{II}(Por) species with alkenes and alkynes.

The reactions of olefins with diamagnetic binuclear $\text{Rh}_2(\text{OEP})_2$ complexes containing a (relatively weak) Rh–Rh bond likely proceed via radical chain processes (Figure 7), and the intermediacy of the proposed $(\text{OEP})\text{Rh}-\text{CH}_2-\text{CHR}\cdot$ ligand centered radicals was evidenced by radical trapping.²³ More recent studies revealed that $(\text{por})\text{Rh}-\text{CH}_2-\text{CHR}\cdot$ ligand centered radicals are likely in equilibrium with metallo-radical $(\text{por})\text{Rh}(\eta^2\text{-alkene})$ species.^{27,28,30}

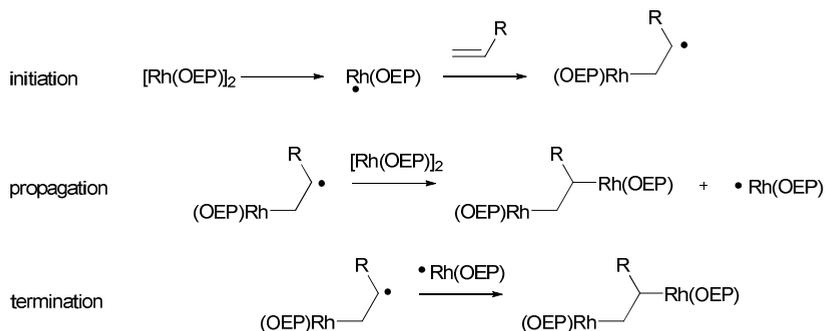


Figure 7. Radical-chain mechanism operative in the reaction of $\text{Rh}_2(\text{OEP})_2$ with olefins.

The chemistry of one-electron activated cot (cot = cyclooctatetraene) coordinated to Fe ,³¹ Ru ,³² Co ³³ or Rh ³⁴ has been systematically studied by the group of Connelly, revealing their ability for radical-type C–C bond forming reactions resulting in binuclear complexes with interesting structures (Figure 8). The η^5 -allyl structure of $\text{Co}_2(\eta^5:\eta^5\text{-C}_{16}\text{H}_{16})(\text{Cp}^*)_2$ is a likely structure of an intermediate in the formation of the Fe, Ru and Rh dimeric complexes.^{20c}

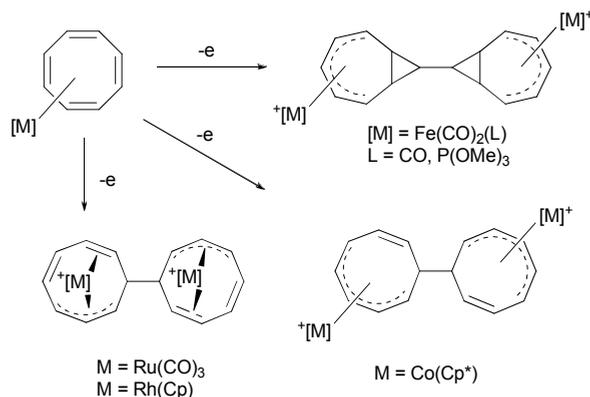


Figure 8. Ligand-ligand radical-coupling of cot ligands upon one-electron oxidation of $\text{Fe}(\text{cot})$ complexes.

The above reactions clearly show that radical-type coupling reactions can proceed in a very selective manner within the coordination sphere of transition metals, and provide interesting synthetic opportunities. For most of these reactions the mechanistic details are not well understood, but more information about the involvement of ligand radicals in ligand-to-metal radical coupling reactions is available from recent studies of open-shell iridium-ethene complexes employing

bulky tetradentate Me_ntpa nitrogen ligands ($n = 3$: Me_3tpa = tris(6-methyl(2-picolyl))amine and $n = 2$: Me_2tpa = bis(6-methyl(2-picolyl))(2-picolyl)amine). These $[\text{Ir}^{\text{II}}(\text{Me}_n\text{tpa})(\text{ethene})]^{2+}$ complexes are relatively stable in weakly coordinating solvents, but undergo selective radical-type reactions at the coordinated ethene moiety in MeCN (Figure 9). This has been illustrated by selective formation of $[\text{Ir}^{\text{III}}(\text{CH}_2\text{CHO})(\text{Me}_n\text{tpa})(\text{MeCN})]^{2+}$ in reaction with dioxygen³⁵ or C2-bridged $[(\text{Me}_n\text{tpa})(\text{MeCN})\text{Ir}^{\text{III}}-\text{CH}_2\text{CH}_2-\text{Ir}^{\text{III}}(\text{Me}_n\text{tpa})(\text{MeCN})]^{4+}$ dinuclear species in pure MeCN.³⁶ Kinetic studies, radical trapping experiments and supporting DFT calculations reveal that the reactions must proceed via $\text{M}-\text{CH}_2\text{CH}_2\cdot$ ligand radical intermediates formed upon MeCN coordination.

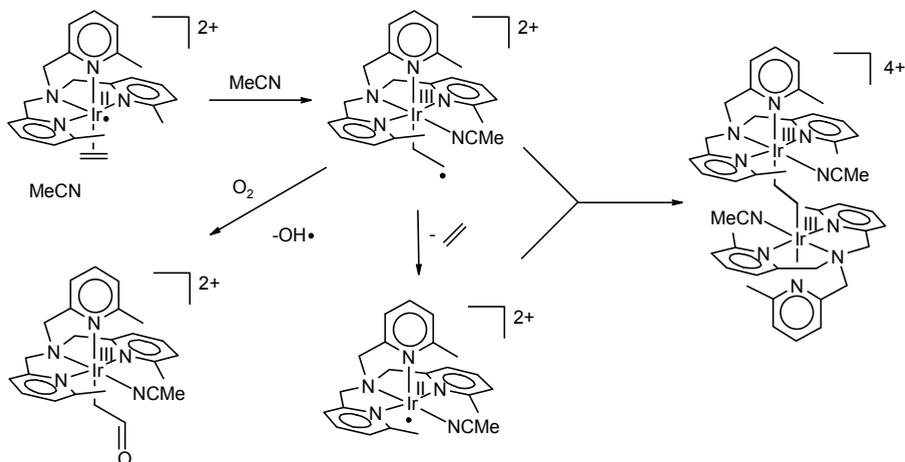


Figure 9. Involvement of $\text{Ir}-\text{CH}_2-\text{CH}_2\cdot$ ligand radicals in the open-shell organometallic chemistry of $\text{Ir}^{\text{II}}(\text{ethene})$ complexes.

The analogous complex with propene does not undergo coupling reactions. Instead hydrogen atom transfer from the allylic position leads to formation of a 1:1 mixture of an iridium allyl and an iridium hydride complex.³⁷ Similar activation of the allylic C–H bond on paramagnetic compounds was also reported for a series of cod complexes (cod = 1,5-cyclooctadiene). One-electron oxidation of the $\text{Rh}(\text{Cp-derivative})\text{Rh}^{\text{I}}(\text{cod})$ complex shown in Figure 10, for example, leads to formation of an η^3 -allyl complex.³⁸

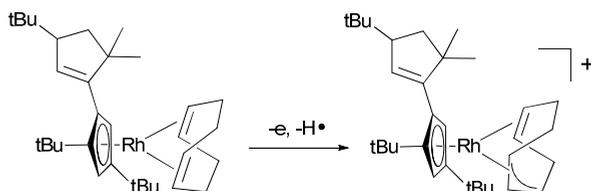


Figure 10. Radical-type activation of allylic C–H bonds of the cod ligand.

The mechanism of this type of transformations was studied further with a series of $[(\text{N}_3\text{-ligand})\text{M}^{\text{II}}(\text{cod})]^{2+}$ complexes ($\text{M} = \text{Rh}, \text{Ir}$). These paramagnetic cod rhodium and iridium complexes, supported with bis-picolylamine type of ligands, easily transform into 1:1 mixtures of η^3 -allyl complexes and $\text{M}-\text{H}$ species (Figure 11). For

iridium the latter hydride species are stable, but for rhodium the hydride undergoes reductive deprotonation by the ligand to form a $[\text{Rh}^{\text{I}}(\text{cod})(\text{N}_3\text{ligandH})]^{2+}$ species.^{37,39} Kinetic measurements showed a second order rate dependency on the concentration of the complex. The proposed mechanism involves hydrogen atom transfer from an allylic position of the olefin to the metal of another complex. The rate of the reaction decreases with increasing steric shielding of the metal, in the order $\text{bpa} > \text{pla} > \text{bla} > \text{Bn-bla}$ (see Figure 11). Involvement of aminyl radicals formed by deprotonation of the NH moiety of the ligand could also play a role in this reaction.³⁷

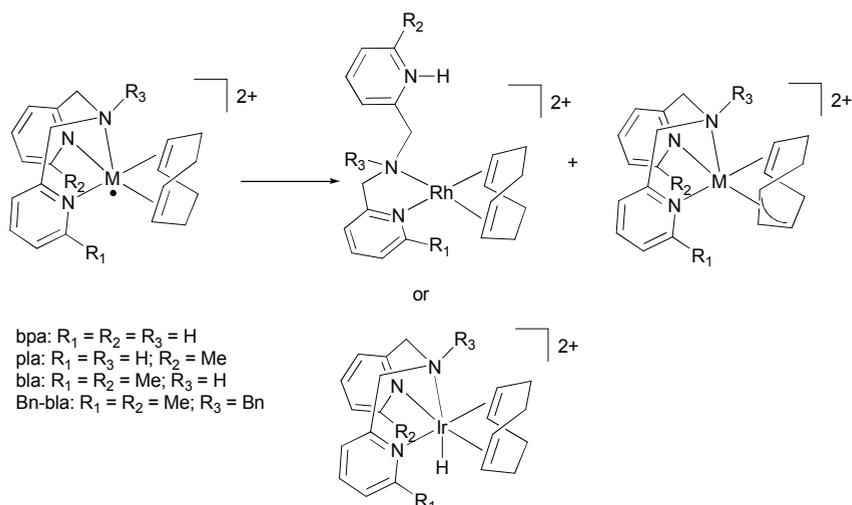


Figure 11. Binuclear radical-type activation of allylic C–H bonds.

Formation of equimolar amounts of cod-allyl and hydride species were also reported for binuclear iridium-2,2-dimethylaziridine-cod radicals (Figure 12).⁴⁰

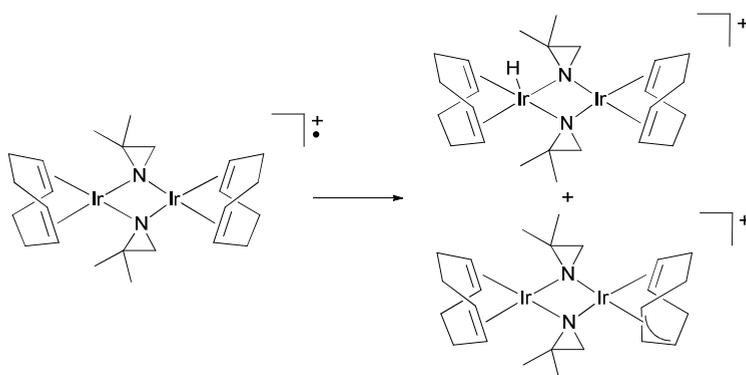


Figure 12. Allylic activation of binuclear iridium-2,2-dimethylaziridine-cod species.

Relevant to the above examples, formation of the rhodium allyl complex $\text{Rh}^{\text{I}}(\text{cod})(\eta^3\text{-C}_8\text{H}_{13})$ by hydrogen atom transfer from the solvent or water to the electrochemically generated $[\text{Rh}^0(\text{cod})_2]$ radical has been postulated, but the exact mechanism of this process is not clear.⁴¹

1.3.2 Open-shell reactivity of the carbonyl ligand

One-electron activation of carbon monoxide is a potentially attractive route for formation of new C–C bonds.⁴² Coordination of CO to rhodium(II) porphyrins (but not Co or Ir)⁴³ results in one electron activation of the carbon atom of the carbonyl group (Figure 13). Similarly to one-electron activation of olefins, the unpaired electron is transferred from the metal into the π^* -orbital of the ligand. Hence, the carbonyl ligand is clearly behaving as a redox non-innocent ligand.

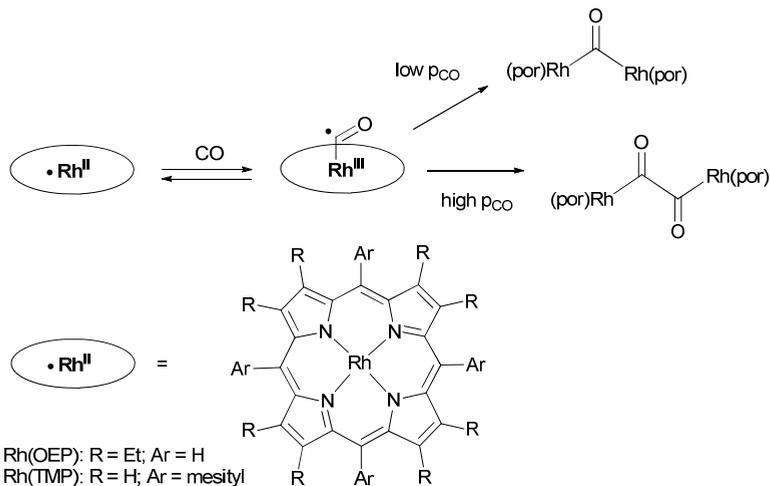


Figure 13. Binding of CO to open-shell $\text{Rh}^{\text{II}}(\text{por})$ species to form a reactive formyl radical.

The follow-up reactivity of thus formed formyl radicals depends on the steric bulk of the porphyrinato ligand and the applied CO pressure. In case of reaction of $\text{Rh}(\text{OEP})$ (OEP = octaethylporphyrinato) with 1 atm CO a metalloketone ($\text{Rh}-\text{C}(\text{O})-\text{Rh}$) is formed and at higher CO pressures a dimetal diketone complex ($\text{Rh}-(\text{O})\text{C}-\text{C}(\text{O})-\text{Rh}$).⁴⁴ Slight increase of the steric bulk allows for selective reversible formation of the diketones for $\text{Rh}(\text{TXP})$ ⁴⁵ and $\text{Rh}(\text{TMP})$ ²⁶ (TXP = tetra-(3,5-dimethylphenyl)porphyrinato; TMP = tetra-(2,4,6-trimethylphenyl)porphyrinato). For the very bulky $\text{Rh}(\text{TTiPP})$ the reductive C–C coupling cannot proceed, thus allowing the EPR detection of the formyl radical.⁴⁶ Further evidence for ligand centered radical reactivity are the reactions of $\text{Rh}(\text{TMP})(\text{CO})$ with the hydrogen atom donor $\text{HSn}(\text{CH}_3)_3$ to form a formyl complex $\text{Rh}(\text{TMP})(\text{CHO})$. Reaction of the carbonyl complex with styrene results in formation of a C4 bridged species $\text{Rh}(\text{TMP})-\text{C}(\text{O})-\text{CH}_2-\text{CH}(\text{Ph})-\text{C}(\text{O})-\text{Rh}(\text{TMP})$ (analogous to the one-electron activation of olefins, as described in section 3.1).²⁶ Tethered dirhodium porphyrin complexes have more favorable thermodynamics for reductive coupling of CO and readily form the 1,2-ethanodione complex (Figure 14).²⁹ Moreover the formyl radicals react with H_2O , $\text{C}_2\text{H}_5\text{OH}$ and H_2 . In case of reaction with H_2 , formyl groups on both rhodium centres are formed by reaction of the carbonyl radical with hydrogen atoms from homolytic cleavage of the dihydrogen molecules. When water or ethanol are the substrates the hydrogen atom of the ROH group is transferred to the formyl radical to form a formyl ligand at one of the metal centres whereas the second formyl radical couples with the thus generated $\text{RO}\bullet$ radical to form a formyl

ester (Rh–C(O)–OEt) or formyl acid (Rh–C(O)–OH). The formyl acid easily collapses to form the rhodium hydride with extrusion of CO₂.

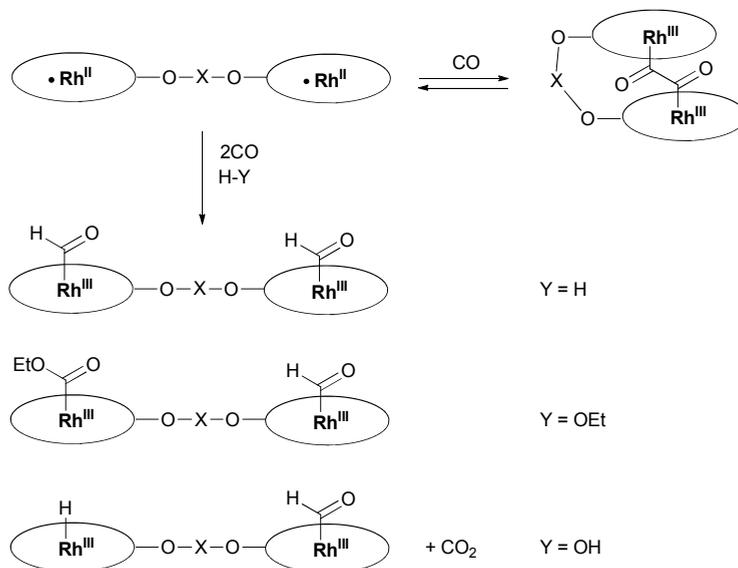


Figure 14. Reactivity of tethered Rh^{II}(por) complexes with CO.

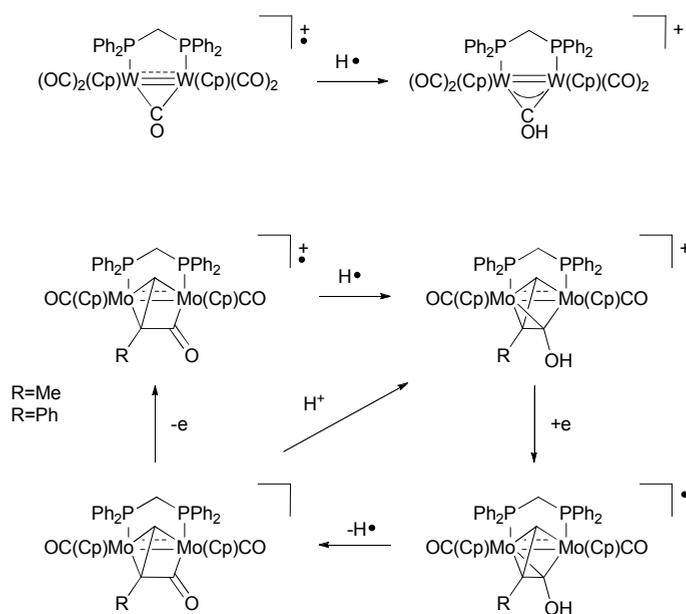


Figure 15. Oxygen-centered radical reactivity of bridging carbonyls.

One-electron activation of carbonyl ligands can also result in reactivity on its oxygen atom instead of its carbon in case of carbonyl bridged binuclear complexes (Figure 15). Radical binuclear tungsten complexes with a bridging carbonyl were

found to react with water to form bridging hydroxyl-carbene species (Figure 15). The proposed mechanism involves hydrogen atom transfer from water to the oxygen atom of the bridging CO ligand, although the radical complex did not react with hydrogen atom donors such as R_3SnH or diphenylsilane.⁴⁷ A related hydrogen atom transfer reaction was also reported for the acyl dinuclear molybdenum complex.⁴⁸ The resulting hydroxy complex can extrude a hydrogen atom when reduced by one electron (Figure 15).

1.3.3 Open-shell reactivity of carbene ligands

One-electron reduction of group 6 transition metal Fischer-type carbene complexes with external reducing agents has been reviewed recently by Sierra *et al.*⁴⁹ The main conclusion of that paper is that Fischer-type carbene ligands are redox active, and can be easily reduced by external reducing agents. Although not mentioned as such in this review, it also implies that Fischer-type carbene ligands are potentially ‘redox non-innocent’, meaning that the metal to which they coordinate may function as an internal reducing agent to generate carbene radicals. Such ‘redox non-innocent’ behavior of Fischer-type carbenes has only very recently been disclosed in a couple of papers, and is so far restricted to the open-shell organometallic chemistry of oxidation state +II group 9 transition metals. Carbene formation at low-spin Rh^{II} and Co^{II} species is clearly associated with radical reactivity. In this section we will shortly summarize some of the most illustrative examples dealing with the reactivity of one-electron reduced group 6 Fischer-type carbenes obtained by employing external reducing agents (for a more detailed overview we refer to the review of Sierra⁴⁹), after which we focus on the typical ‘redox non-innocent’ behavior and reactivity of Fischer-type carbenes coordinated to (low-spin) Rh^{II} and Co^{II} complexes.

1.3.3.1 Reactivity of group 6 transition metal ‘carbene radical’ complexes

The LUMO of Fischer-type carbene complexes is carbene carbon centered, which gives the ligands their typical electrophilic character. This property also makes it possible to form carbon-centered ‘carbene radicals’ upon one-electron reduction of these complexes.⁵⁰ The redox activity of Fischer-type carbene ligands was first demonstrated by Casey *et al.*, who showed that one-electron reduction of group 6 pentacarbonyl alkoxyaryl complexes with Na/K alloy leads to formation of carbon centered radical anions (Figure 16), which are persistent in solution at low temperatures (-50 °C and below), as evidenced by EPR spectroscopy.⁵¹

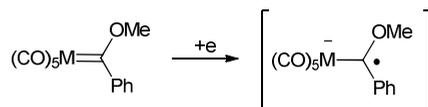


Figure 16. Formation of a carbon centered radical by one electron reduction of a group 6 transition metal carbene complexes (M= Cr, Mo, W).

These carbon-centered radicals could be employed in carbon-carbon bond forming reactions. Iwasawa and Fuchibe reported that tungsten aryl- or silylcarbene complexes dimerize (Figure 17) or undergo radical addition to electron poor olefins (Figure 18) after one-electron reductions with SmI_2 .⁵² The nature of the para-substituent on the aryl group of the alkoxy-carbene influences the outcome of the

reaction with ethyl acrylate. Electron-withdrawing groups lead to subsequent protonolysis, whereas electron-donating groups affect loss of MeO^- , with formation of a tungsten-carbene species. Similar results were obtained with a tungsten diphenylmethylsilyl methoxycarbene complex.

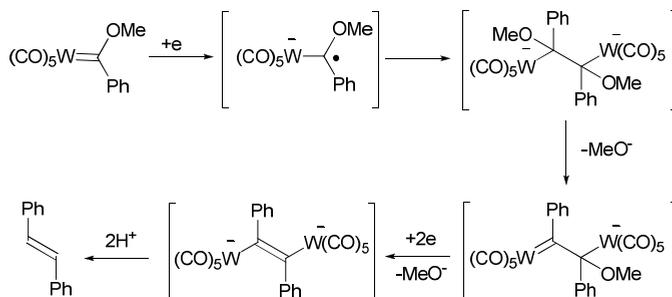


Figure 17. Formation of trans-stilbene via dimerization of one-electron reduced Fischer-type tungsten carbenes.

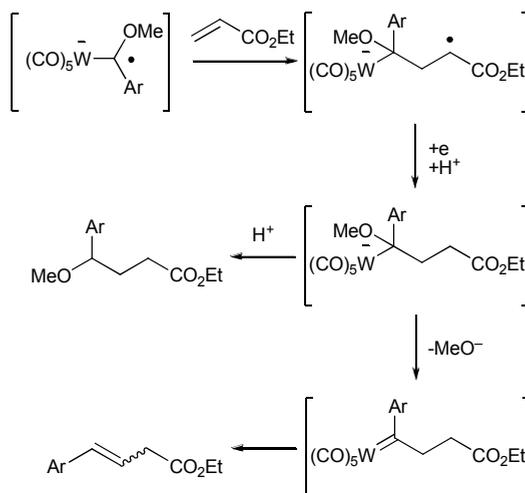


Figure 18. Reaction of one-electron reduced Fischer-type carbenes with ethyl acrylate.

The reactivity of one-electron reduced carbenes conjugated with olefinic bonds leads to radical-type ligand-ligand coupling reactions at more remote distances from the metal, presumably for steric reasons. One-electron reduction of chromium or tungsten α,β -unsaturated carbene complexes results in formation of dinuclear bis-carbene species by radical coupling between the γ -carbon atoms, followed by protonation (protic media) or quenching with another electrophile.^{52,53} Reduction of tungsten dienylcarbene complexes results in radical-type C–C coupling at the terminal olefinic carbon atoms most distant from the metal. Stabilization of the intermediate ligand radical density by the phenyl substituent at this carbon likely also plays a role in directing the reaction towards this remote ligand-coupling (Figure 19).⁵²

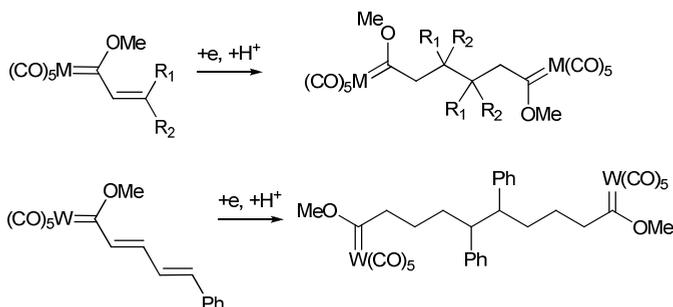


Figure 19. Remote reductive ligand-ligand coupling of unsaturated carbene complexes ($M = \text{Cr}, \text{W}$, $R_1 = \text{Me}, \text{Ph}$; $R_2 = \text{Me}, \text{H}$).

Somewhat related ligand radicals were obtained by deprotonation of Fischer-type carbene complexes bearing β -hydrogen containing substituents, followed by one-electron oxidation of the resulting anionic intermediates. Deprotonation of the chromium(0)-pentacarbonyl-methoxymethylcarbene complex, for example, led to an anionic carbene complex that underwent radical-type C–C coupling after one-electron oxidation (Figure 20).^{54,55} Related manganese carbene complexes show a similar reactivity.⁵⁶ However, this type of reactivity is perhaps not characteristic for Fischer-type carbenes, as similar deprotonation/oxidation induced radical-type reactivity is also known for the methyl group of acetylferrocene.⁵⁵

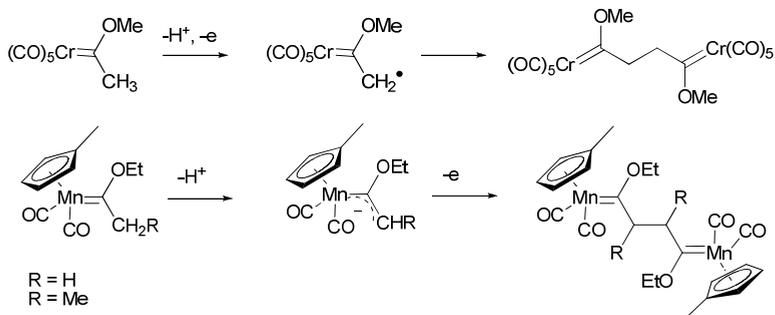


Figure 20. Deprotonation/oxidation induced radical-type reactivity of β -hydrogen containing carbene complexes.

1.3.3.2 Possible involvement of carbene radicals in Rh^{II} and Co^{II} mediated cyclopropanation of olefins

Carbene ligands generated from diazo compounds at open-shell low-spin Rh^{II} and Co^{II} porphyrin complexes seem to have a carbon-radical (carbene radical) character, even without one-electron reduction by an external reducing agent. These ‘carbene radical’ intermediates are capable of hydrogen atom abstraction from the reaction medium to form diamagnetic M^{III} -alkyl complexes, for example. This has been observed for $\text{Co}^{\text{II}}(\text{TPP})$ (TPP = tetraphenylporphyrinato), which forms the diamagnetic alkyl species $\text{Co}^{\text{III}}(\text{TPP})(\text{CH}_2\text{COOEt})$ upon prolonged exposure to ethyl diazoacetate.⁵⁷ A similar hydrogen atom abstraction reactivity was disclosed for $\text{Rh}^{\text{II}}(\text{TMP})$ (TMP = tetramesitylporphyrinato) (Figure 21).⁵⁸

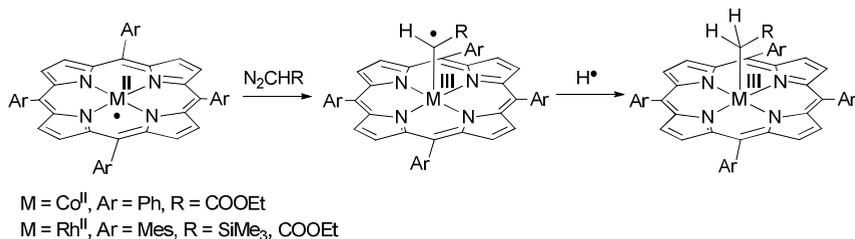


Figure 21. Formation of ‘carbene radicals’ upon reaction of diazo compounds with Co^{II} (por) and Rh^{II} (por) complexes with subsequent hydrogen atom transfer to the carbon-centered radical.

Paramagnetic Co^{II} salen⁵⁹ and in particular Co^{II} porphyrin complexes,^{57,60} are also effective catalysts for (electron poor) olefin cyclopropanation. The groups of Yamada⁶¹ and Zhang^{60a} proposed that the active species may actually be a carbon-centered radical species. Paramagnetic mononuclear Rh^{II} cyclopropanation catalysts developed by the group of Bergman may also operate via comparable carbene radicals.⁶² So far, no direct evidence for the electronic structure of any of these active species has been presented. The intriguing activity of the cobalt porphyrin system, however, suggests a very different electronic structure of the active carbene transfer reagent in case of open-shell group 9 systems as compared to common Fischer-type carbene intermediates commonly observed with other cyclopropanation catalysts. Rationalization of the observed reactivity on the basis of the non-innocent character of the metal-carbene remains however an open issue.

1.4 Outline of the Thesis

As is evident from the above examples, group 9 transition metal (cobalt, rhodium and iridium) complexes with tri- or tetradentate nitrogen ligands (picolylamines and porphyrins) reveal unique redox non-innocent behavior of olefins and carbonyls. More detailed studies on the redox non-innocence of carbenes are however lacking. Considering their possible involvement in important catalytic transformations, we were triggered to investigate further the possible non-innocent behavior of CO, carbenes and olefins in group 9 complexes supported with nitrogen donor ligands. As a result, several aspects of one-electron activation of different ligands by organometallic complexes will be described in the following chapters.

In Chapter 2 we will describe the synthesis and redox properties of rhodium and iridium carbonyls supported by the Me_3tpa ligand. Although this ligand allowed for studies of one-electron activation of ethene, we will see that the iridium carbonyl complex reveals selective metal-centered reactivity after one electron oxidation. In the investigated systems the CO moiety behaves as a redox innocent ligand. However, its two electron transformations occur easily with water or methanol for iridium complexes allowing the isolation of subsequent intermediates in the water gas shift reaction, whereas reaction of the rhodium carbonyl with dioxygen leads to selective formation of a carbonate complex.

In Chapter 3 we digress from radical reactivity to show how even tiny electronic changes can have an impact on the structure of rhodium carbonyls with N-donor ligands, and how can we selectively form terminal *versus* bridging carbonyl complexes.

We will return to the topic of ligand radicals in Chapter 4, in which we investigated the reactivity of open-shell rhodium and iridium complexes bearing an N–H moiety and

suspected the involvement of aminyl radicals. Unexpected one-electron reduction is observed in the presence of bases and the possible reduction pathways are discussed.

Chapter 5 describes the reactivity of the paramagnetic Me₃tpa iridium ethene complex with diazo compounds (used as carbene precursors). Here the ligand system proved to be appropriate to study the redox non-innocence of the carbene. Radical C–C and C–H bond forming reactions of the ‘carbene radical’ are presented and the electronic structure of one electron activated carbenes is discussed.

In Chapter 6 we show that the scope of reactions of ‘radical carbenes’ is expandable from Ir to Co and from stoichiometric (Chapter 5) to catalytic reactions. In a combined theoretical and experimental study we pin down the (radical) active species in cobalt porphyrin catalyzed cyclopropanation of alkenes and show the implications of the carbene redox non-innocence on the reactivity with alkenes having different electronic properties.

In Chapter 7 we investigate reversible hydrogen atom transfer between cobalt porphyrins and organic radicals. We show that HAT has pronounced consequences in the activity of Co(por) as mediators in metal-mediated radical polymerization of olefins.

The Thesis ends with a Perspective on possible applications of the ligand non-innocent complexes, and the resulting new (catalytic) reaction pathways disclosed in this Thesis, potentially leading to valuable new products via unprecedented catalytic pathways.

1.5 Notes and References

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Chapter 1

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