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Photo- and redox activation of homo-and heteronuclear transition metal clusters: experiment and theory

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Chapter 1

Introduction

The chemistry of transition metal clusters has been a rapidly developing research area in the last four decades, providing a shining example of fruitful interactions and subsequent cross-fertilization between frontier disciplines such as molecular and surface chemistry. The highly diversified structures of cluster compounds often involve unprecedented bonds between different chemical elements and unique bonding situations for atoms or (in)organic molecules. A number of their extraordinary properties aroused the interest of physicists (*e.g.* superconductivity), biochemists (*e.g.* multimetallic redox centres), academic and industrial researchers studying new materials and catalysts and, of course, coordination chemists themselves. This Thesis deals in particular with the rather unexplored but challenging photochemical and electrochemical activation of transition metal clusters. The following sections introduce specific features of cluster chemistry and conclude with a detailed scope of this Thesis.

1.1 Homonuclear clusters: structure, physicochemical properties and reactivity

Considering several different definitions of a cluster compound introduced in the literature, a transition metal cluster is defined here as a polynuclear complex containing at least three metal atoms held together by direct metal-metal bonds.[1, 2] In addition, clusters are discrete molecular entities with a well-defined structure that show characteristics intermediate between mononuclear metal complexes and metal surfaces (or bulk metal). Based on the oxidation state of the metal centres and the nature of the ligand shell surrounding the metal framework, transition metal clusters are usually classified in two main groups. To the first group belong group 5 to 7 metals in high formal oxidation states that are stabilized by π-donor ligands, such as halides, S^{2-}, O^{2-} and OR^-. Most important in this group are the halide clusters with general formulas $[M_3X_9]$ (*e.g.* $[(Re_3Cl_9)Cl_3])$,[3] $[M_6X_8]$ (*e.g.* $[W_6Br_8]^{4+})$[4] and $[M_6X_{12}]$ (*e.g.* $[Nb_6Cl_{12}]^{4+})$.[5] Late transition metals in low oxidation states preferentially form clusters stabilized by π-acceptor ligands, such as phosphines and isocyanides. The transition metal *carbonyl* clusters presented in this Thesis belong to this second, most common group. Although molecular clusters exhibit a large variety of structures and nuclearities, the vast majority of the structures reported in the literature correspond to small clusters containing less than ten atoms. To document the structural diversity among the low nuclearity clusters, some frequently encountered geometries are depicted in Figure 1. The stabilizing role of the ligand sphere for the different geometries is of utmost importance, the arrangement of the metal atoms being governed by the type of attached ligands, the cluster nuclearity and the number of cluster valence electrons.
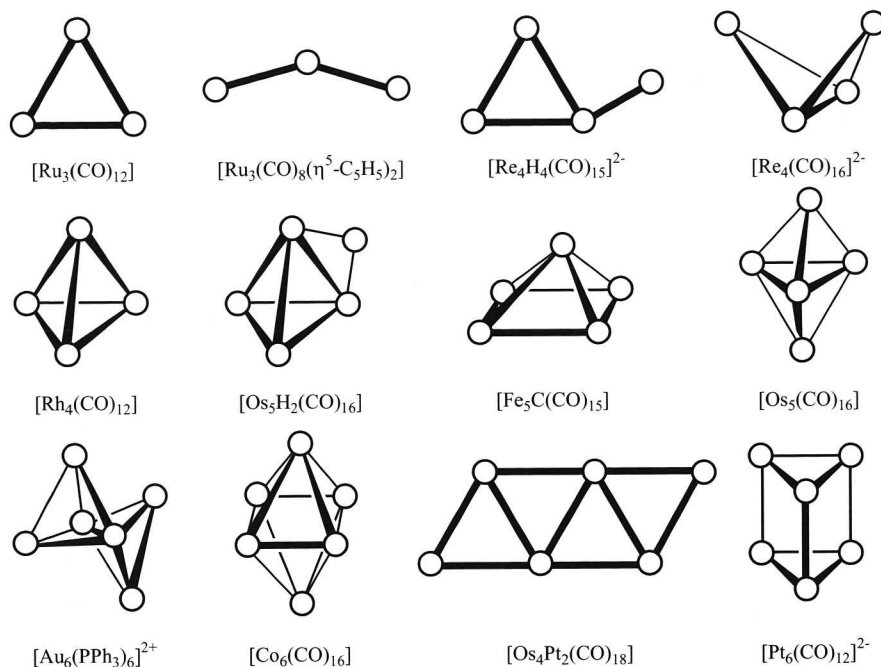
Figure 1. Frequently encountered metal framework geometries of carbonyl transition metal clusters, with corresponding examples.

In general, the structure of the cluster core is derived from polyhedra with triangular faces, the metals being located at the vertices and the metal-metal bonds forming the edges. In accordance with the chosen definition of cluster compounds (*vide supra*), the smallest possible clusters consist of three metal atoms in either chain-like (*e.g.* $[Ru_3(CO)_8(\eta^5-C_5H_5)_2])$[6] or triangular (*e.g.* $[Ru_3(CO)_{12}]$)[7] arrangements. On increasing the cluster nuclearity, a variety of metal core geometries are observed. For example, whereas $[Re_4H_4(CO)_{12}]$[8] has a tetrahedral arrangement, the metal atoms in $[Re_4(CO)_{16}]^{2-}$ define a parallelogram or 'butterfly' structure.[9] The structure of $[Re_4H_4(CO)_{15}]^{2-}$ may be derived from the latter cluster by breaking a Re-Re bond to leave a triangle of rhenium atoms, with the fourth Re atom terminally bound as a 'spike'.[9] Examples of higher nuclearity clusters are $[Os_5(CO)_{16}]$ (trigonal bipyramid),[10] $[Co_6(CO)_{16}]$ (octahedron),[11] $[Au_6(PPh_3)_6]^{2+}$ (edge-sharing tetrahedrons)[12] and $[Pt_6(CO)_{12}]^{2-}$ (trigonal prism).[13] In order to rationalize the great variety of cluster structures and their electronic requirements, a number of different electron-counting rules, based either on empirical observations or on theoretical considerations, have been developed. The fairly simple older theories concern the *18-electron rule*,[14] which holds for clusters with strong π-accepting ligands and metals in low oxidations states, and the *Effective Atomic Number (EAN) rule*.[15] Both theories are essentially valence-bond approaches, where

each edge of the polyhedral cluster is considered as a localized two-centre/two-electron bond, and are adequate for many of the smaller clusters (N ≤ 4). The *Polyhedral Skeleton Electron Pair (PSEP) theory*[16-21] was originally developed for borane and carborane clusters. It describes the bonding in cluster compounds as being delocalized over the whole molecule and allows to predict the shape and the number of filled molecular orbitals of small and medium-sized clusters (N ≤ 5-12), as well as their mode of transformation upon electrochemical oxidation or reduction. The electronic structure of the latter group of clusters can also be rationalized by the *Topological Electron Count (TEC) approach*,[22, 23] which combines Euler's theorem[†] with the EAN rule. Whereas the PSEP theory is easily applicable to metal clusters derived from triangulated polyhedra, the TEC approach can be used to correlate known geometries as well as to predict the yet unresolved or non-existing (virtual) structures of a wide range of metal clusters with unusual polyhedral frameworks having no borane analogue. High-nuclearity clusters (N ≥ 12) are usually treated by an *extended PSEP approach*[24] or *semi-empirical Extended Hückel Molecular Orbital (EHMO) calculations*, often performed on the bare metal cluster framework.[25, 26] The latter approach, which is based on quantum chemical principles, suffers from a number of limitations. The most serious one is that the core levels (orbitals) of the bare clusters are considerably modified upon coordination of the ligands, regarding both their energies and composition.

Although the ordered arrays of metal atoms in medium- and high-nuclearity clusters may be regarded as submicroscopic fragments of a metal surface, the physical properties of a molecular cluster are distinctly different from those of the bulk metal. Low-nuclearity molecular clusters have a discrete energy level structure with well-defined bonding and antibonding orbitals separated by a relatively large HOMO-LUMO[‡] gap. As a result of the energy level quantization, the visible absorption spectra of such clusters display just a limited number of fairly well separated absorption bands. Further, the electron affinities (EA) and ionization potentials (IP) of molecular clusters differ appreciably from those of the metal bulk, IP typically rising by 2-3 eV and EA decreasing in about the same extent.[27] In addition, due to the relatively large HOMO-LUMO gap, small even-electron clusters are normally diamagnetic, while bulk metals exhibit temperature-independent (Pauli) paramagnetism.[28] As a result of these distinct differences, extensive studies of the physical properties of transition metal clusters have been performed in order to investigate the transition from molecular to bulk metallic behaviour which should ensue upon increasing the cluster size.[29-31] EPR and magnetic susceptibility studies in combination with calculations of IP and EA values have shown that the rate at which a cluster can evolve towards the metallic limit is strongly dependent on the physical property under study and most likely proceeds *via* an intermediate

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[†] For a polyhedron with V vertices, F faces and E edges, Euler's theorem states that $E = V + F - 2$.
[‡] The HOMO and LUMO stand for the Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital, respectively.

'mesometallic' regime,[30] possessing properties different from those of the molecular and bulk domains.

Cluster-surface analogy

One of the most important motives for the research in cluster chemistry has been the idea that discrete molecular metal clusters may serve as good models for metallic catalysts and the chemisorption of ligands on metal surfaces. The similarity between clusters and surfaces with respect to the bonding of molecules or molecular fragments has been defined by Muetterties as the 'cluster-surface analogy'.[32, 33] Metal surfaces as heterogeneous catalysts are indispensable for many important industrial processes. However, due to the fact that characterization techniques, such as X-ray diffraction and NMR spectroscopy, are generally not applicable to these highly ordered surfaces, the associated basic surface chemistry is poorly understood on a molecular level.[34] As clusters are amendable to complete characterization by various physical methods, considerable research efforts have been devoted to mimic the binding, migration and reactivity patterns of chemisorbed substrates like CO, hydrides and arenes on transition metal clusters. In addition, the investigation of clusters has provided valuable information about the poisoning of catalytic metal surfaces by undesired irreversible chemisorption of strongly bound ligands[35, 36] and the unique bonding modes of substrates at more than one metal centre (Figure 2a-b).
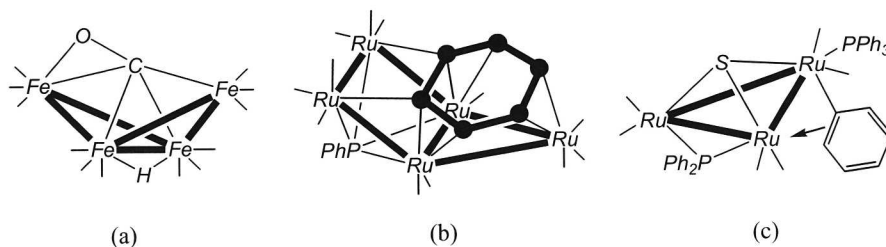

(a) (b) (c)

Figure 2. Unusual bonding- and activation modes of organic substrates on polynuclear metal frameworks.

Clusters as catalysts

The bonding to several metal atoms within the metal framework offers the possibility to stabilize otherwise highly reactive species, such as CCO, BCO, CS and PO, in solution.[2] In contrast, the coordination of small substrate molecules like CO, H_2, thiols, alkenes or carbenes to more than one metal atom at the same time can result in unique activation pathways not encountered in mononuclear complexes.[37] As example may serve the cleavage of a thiophenol molecule into sulfide, phenyl and diphenylphosphanyl ligands on a triruthenium cluster core (Figure 2c).[38] This 'cooperative effect' between the metal centres,

together with the fact that clusters permit the migration of coordinated ligands around the cluster core, underlies the interest in the application of transition metal clusters as homogeneous catalysts.[39, 40] Ideally, a cluster should combine the selectivity of mononuclear homogeneous catalysts with the cooperative nature of the metal network typical for metal surfaces.[2] Over the past three decades numerous examples of cluster-catalyzed reactions have been reported, including isomerization, hydrogenation and hydroformylation of olefins, hydrosilylation, hydrodesulfurization, carbonylation of alcohols and amines and oligomerization of alkynes. Very recently, research into cluster-catalyzed reactions even resulted in the discovery of the mildest and most efficient molecular arene hydrogenation catalyst reported to date.[41] In most cases, however, the cluster catalysts cannot yet fully compete with the conventional catalysts used in industrial processes. As they are usually rather expensive, the potential value of clusters should be sought in unique cluster reactions[42] that cannot easily be performed at a single metal centre (*e.g.* the hydrogenation of the triple bonds in CO, N_2, RCN) or in reactions where the product selectivity significantly differs from the mononuclear case (*e.g.* the cyclooligomerization of thiethane).[43] Besides, a more efficient and/or more selective interaction with substrates may result from introducing a suitable combination of different metals with different chemical properties within the cluster core (*vide infra*).

In recent years, the immobilisation of transition metal clusters on solid supports, such as polymers, zeolites or SiO_2, MgO and Al_2O_3 surfaces, represents a major step in the development of uniform, highly dispersed heterogeneous catalysts. The original motivation for producing such systems was to combine the advantages inherent to homogeneous catalysis (*i.e.* molecular understanding of the mechanism and catalytic cycles, mild reaction conditions, easier tuning of electronic and steric properties) with those characterizing heterogeneous catalysis (*i.e.* higher catalyst stability, ready separation of the reaction products, applicability to a wide range of reactions). Supported cluster catalysts are most commonly prepared *via* decarbonylation of supported metal carbonyl precursors (*e.g.* [$Ir_4(CO)_{12}$] and [$Ir_6(CO)_{16}$])[44] synthesized by reaction of the intact clusters with support surface groups (chemisorption). When the pores of the support (*e.g.* zeolites) are too narrow to allow entry of the precursor carbonyl cluster, the latter may also be efficiently prepared from mononuclear metal carbonyl precursors (ship-in-a-bottle approach).[45] Detailed structural information about the supported metal clusters can be obtained from extended X-ray absorption in fine structure (EXAFS) measurements, transmission electron microscopy (TEM) or scanning tunneling microscopy (STM). Although the associated basic chemistry and the nature of the active species are often not yet completely understood, the cluster size together with the choice of the support are expected to play an important role in the adaptation of such catalysts to a particular process. The recent observation that supported [$Ru_6C(CO)_{17}$][46] exhibits remarkably high activities and selectivities for the hydrogenation of olefins and the transfer hydrogenation of ketones

confirms the catalytic potential of this new class of materials and justifies the search for suitable processes that may be catalyzed with higher activities or selectivies than observed for conventional heterogeneous catalysts.

1.2 Heteronuclear clusters: achievements and challenges

Besides the continued interest in the chemistry and catalytic activity of *homonuclear* cluster compounds, considerable research efforts have also been devoted to explore the intriguing field of *heteronuclear* transition metal cluster chemistry. Just as their homonuclear analogues, heteronuclear (or mixed-metal) clusters, which combine different metal atoms within the cluster framework, may find important applications in homogeneous catalysis. Apart from the fact that multimetallic coordination of organic molecules at clusters facilitates substrate transformations (*vide supra*), the intrinsic polarity of heterometallic bonds together with the different stereochemical and electronic properties of the adjacent metal centres may provide additional activation pathways[47] or increase the selectivity of substrate-cluster interactions. The close proximity of different metal atoms within the cluster core may therefore lead to increased activity and/or selectivity in the overall catalytic transformation, or may initiate novel reactions *via* synergistic interactions. Some illustrative examples of heterodimetallic activation mechanisms are schematically depicted in Figure 3.
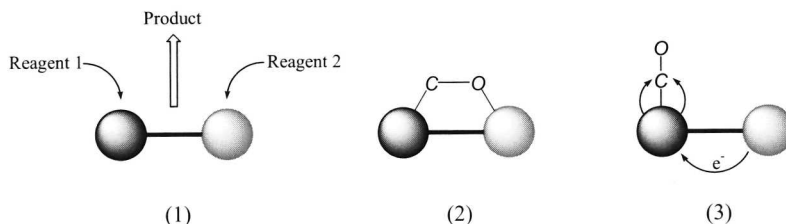

Figure 3. Possible mechanisms for heterobimetallic activation.

Ideally, the metal-specific activation of two different reagents at adjacent metal centres should give rise to the formation of products not observed by conventional homonuclear catalytic systems (mechanism (1)). As an alternative approach, the different atoms of a single substrate molecule may show metal-specific interactions that result in two-site activation pathways different from those observed for monometallic clusters (mechanism (2)). When the chemical transformation of a substrate molecule is taking place at a single metal atom, the presence of a heterometal atom in an adjacent position may result in electronic cooperativity (mechanism (3)). In the latter case, the adjacent metal acts like an 'extended ligand' that may donate or withdraw electron density from the reaction site, thereby influencing the metal-substrate interactions in a beneficial way. The well-defined cluster core of mixed-metal

clusters makes these systems also valuable precursors for the preparation of novel heterogeneous catalysts of high dispersion and known metal stoichiometry. Due to the different temperatures at which homonuclear clusters decompose, such uniform mixed-metal phases would be difficult to produce by coimpregnation of the separate monometallic clusters. In addition, the use of mixed-metal clusters allows systematic variation of the particle stoichiometry by employing precursor complexes of different composition and structure. Finally, the lower symmetry and effective labeling of the heterometallic core make mixed-metal clusters useful for probing various fluxional processes,[48, 49] such as metal-localized ligand scrambling, intermetallic ligand migration or metal framework rearrangement, between which it is difficult to discriminate in homometallic clusters. Obviously, the diversity and complexity of clusters containing more than one metal type is very high. Current research is therefore directed to a better understanding of their syntheses, structures and chemical (stoichiometric and catalytic) properties.

One of the most important factors that determine the usefulness of mixed-metal clusters has been the development of rational synthetic procedures towards the clusters themselves. Since the preparation of the first heteronuclear transition metal cluster $[FeCo_3(CO)_{12}]^-$ by Chini *et al.* in 1959,[50] heterometallic transition metal clusters have been synthesized by a variety of method.[49, 51-53] The most important synthetic procedures can be categorized into four main groups that are schematically depicted in Figure 4: (*i*) ligand substitution reactions (*e.g.* $[M_2Ru_4(\mu-H)_2(CO)_{12}(PPh_3)_2]$ (M = Cu, Au)),[54] (*ii*) condensation reactions (*e.g.* $[OsRe_2(CO)_{13}(MeCN)]$),[55] (*iii*) metal exchange reactions (*e.g.* $[WCo_2(CO)_8(\eta^5-C_5H_5)(\mu_3-CR)]$ (R = Me, Ph))[56] and (*iv*) addition reactions (*e.g.* $[Rh_2Fe(\eta^5-C_5Me_5)_2(\mu-CO)_2(CO)_4]$).[57] Other methods like pyrolysis,[58] radiolysis[59] and CO-induced cluster fragmentation of higher nuclearity clusters[60] are less general and often result in low yields or a less predictable product distribution. This applies for instance to the synthesis of $[Os_2Ru(CO)_{12}]$. A new synthetic approach towards the latter cluster using a ligand substitution reaction (see Figure 4) gives a better result presented hereinafter in Chapter 6. Among all synthetic methods, the most useful procedure for the synthesis of polymetallic complexes is to build up the cluster framework by adding one metal at the time, using mononuclear organometallic complexes as the building blocks. In general, the methods applied to date are not very selective, cumbersome separation schemes being frequently required to obtain the desired products in a pure form. The development of rational synthetic procedures, applicable to the synthesis of a wide range of mixed-metal clusters with different geometries and metal stoicheometries, therefore presents one of the major challenges in the field of heteronuclear cluster chemistry.
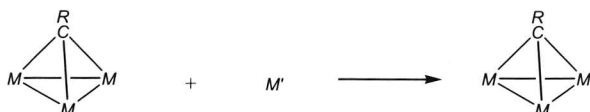
Ligand substitution reaction
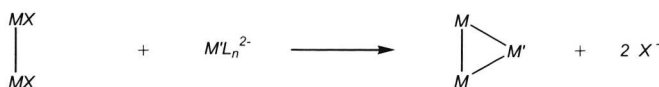
Condensation reaction
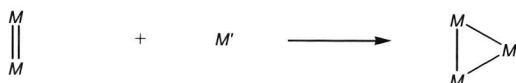

Metal exchange reaction

Addition reactions

Figure 4. General synthetic strategies for the preparation of heteronuclear transition metal clusters.

Mixed-metal clusters in catalysis

The introduction of different transition metals into the cluster framework reduces its effective symmetry, making coordination sites for incoming ligands inequivalent and affording the possibility of site- as well as metal-selective attachment. A number of reactivity studies[49, 61-64] dealt with the metal-specific coordination or bimetallic activation of substrates, such as phosphines, alkynes or H_2, in order to define a 'hierarchy of site reactivities' in mixed-metal clusters.[65] Metal-specific bonding, for example, has been documented for the tetranuclear cluster $[Ru_2Co_2(CO)_{13}]$ where H_2 reacts at the ruthenium sites to give $[Ru(\mu-H)Ru(\mu_3-H)Co_2(CO)_9(\mu-CO)_3]$ whereas alkynes insert between the cobalt centres to form $[Ru_2Co(\mu_4-\eta^2-C_2R_2)Co(CO)_9(\mu-CO)_2]$ (R = Ph, see Figure 5).[66]

$[Ru(\mu-H)Ru(\mu_3-H)Co_2(CO)_9(\mu-CO)_3]$ $[Ru_2Co(\mu_4-\eta^2-C_2Ph_2)Co(CO)_9(\mu-CO)_2]$
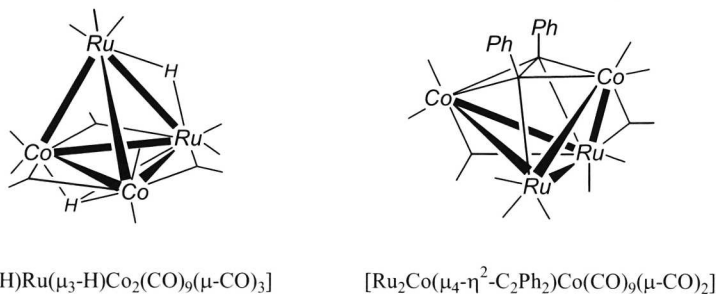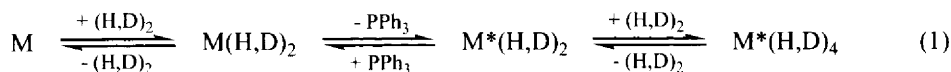
Figure 5. Metal-specific bonding of H_2 and PhC≡CPh to $[Ru_2Co_2(CO)_{13}]$.

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Based on the observed metalloselectivity for a series of reagents, mixed-metal clusters have been applied in a wide range of catalytic transformations in order to search for performances superior to those of their homonuclear counterparts.[39, 40, 67, 68] Probably the best example, where a heterometallic cluster exhibits enhanced catalytic activity compared to its homometallic analogues and where the catalytic process at the same time definitively proved to be homogeneous, is the hydrogenation of diphenylacetylene by the layer-segregated cluster $[Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)]$.[69] The latter catalyst represents an example of metal-specific substrate coordination and documents the importance of substrate migration across the metal framework. Apart from high activity, it also shows increased selectivity for the formation of Z-stilbene. Another illustrative example of increased selectivity and a different product distribution concerns the hydroformylation of N-(2-methyl-2-propenyl)benzamide by a Co/Rh catalysts.[70] Catalysis of the reaction by $[Co_2Rh_2(CO)_{12}]$ afforded 1-benzoyl-4-methylpyrrolidine with $\geq 98\%$ selectivity whereas catalysis by different rhodium complexes like $[RhCl(PPh_3)_3]$ or $[Rh_4(CO)_{12}]$ resulted in mixtures of at least three different pyrrolidines, with ratios depending on the catalyst and experimental conditions. Catalysis of the same reaction by $[Co_2(CO)_8]$ was reported to give a mixture of three amino acids instead of amino aldehydes. In contrast to the variety of examples where catalysis by mixed-metal clusters results in synergistic changes in the activity and/or selectivity, surprisingly little work has been done to reveal the origin of these effects and the role of the different metals in the catalytic cycle. Insight into the mechanistic aspects of mixed-metal cluster catalysis exists therefore only in a few cases. Kinetic studies of the reaction of a series of aromatic and aliphatic thiols with the heteronuclear cluster $[Mo_2Co_2Cp'_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)(CO)_4]$ ($Cp' = \eta^5\text{-}C_5H_4Me$), for example, provided valuable information about the C-S bond cleavage mechanism occurring in hydrodesulfurization (HDS) over heterogeneous Co/Mo/S catalysts.[71] The mechanism for homogeneous, catalytic H_2-D_2 equilibration by mixed platinum- and palladium-gold clusters was studied by Aubart *et al.*[72, 73] Phosphine-stabilized Pt-Au clusters were the first compounds reported to catalyze this reaction, exhibiting turnover frequencies by orders of magnitude higher than those of most monometallic complexes included in homogeneous studies (*e.g.* *trans*-$[IrCl(CO)(PPh_3)_2]$, $[Pt(O_2)(PPh_3)_2]$, $[Pt(C_2H_4)(PPh_3)_2]$, $[RhCl(PPh_3)_3]$, $[RuH_2(PPh_3)_4]$). The H_2-D_2 equilibration proceeds smoothly without any H/D exchange involving the solvent- or ligand hydrogen atoms. Based on kinetic studies upon variable H_2, D_2, and cluster concentrations and addition of uncoordinated PPh_3, a three-step mechanism was proposed, as represented by Eq. (1) where M* denotes the starting cluster M lacking one PPh_3 group. The Pt-Au bonds are assumed to function as the active sites for H_2 activation, which classifies the mixed-metal clusters as suitable models for the activation of H_2 by Pt-Au surfaces.

$$M \underset{-(H,D)_2}{\overset{+(H,D)_2}{\rightleftharpoons}} M(H,D)_2 \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} M^*(H,D)_2 \underset{-(H,D)_2}{\overset{+(H,D)_2}{\rightleftharpoons}} M^*(H,D)_4 \qquad (1)$$

The fundamental importance and industrial relevance of bimetallic, heterogeneous catalysts (especially for key reactions in petrochemistry) have been the driving force for the investigations of the applicability of mixed-metal clusters as single-source precursors in the preparation of novel, highly active and selective heterogeneous catalysts. Heteronuclear clusters offer the possibility of effective design of bimetallic catalytic sites, especially due to the regular distribution of metal atoms already in the cluster precursor. In recent years, numerous examples have appeared in the literature, where catalysts prepared from mixed-metal clusters show higher activities and/or selectivities than obtained on monometallic surfaces or by co-impregnation of the corresponding monometallic precursors.[74] As examples may serve the selective synthesis of methanol from CO_2/H_2 by Pt/W or Pt/Cr bimetallic catalysts,[75] the reductive carbonylation of *o*-nitrophenol to benzoxazol-2(*3H*)-one by Fe/Pd particles[76] and the highly active and selective hydrogenation of alkenes by a Pd/Ru catalyst.[77] In an elaborate study by Ichikawa *et al.*, a series of Rh/Fe, Pt/Fe and Ir/Fe bimetallic catalysts, prepared from different mixed-metal cluster precursors, were shown to exhibit strikingly high activities and improved selectivities in CO hydrogenation and 1-propylene hydroformylation reactions, compared to those obtained by co-impregnation of the homonuclear clusters.[78] EXAFS, TEM and Mössbauer studies on the Fe/Rh catalysts suggest the formation of Rh-Fe^{III}-O heteroatomic sites (Figure 6) that not only play the role of an anchor assembling noble metal atoms (Rh, Ir, Pt) in order to prevent their aggregation, but also provide an active bimetallic site for CO insertion (Figure 3, mechanism 2). The continuing search for new, highly active catalysts very recently resulted in the discovery of Ru/Pt nanoparticle catalysts capable of running the single-step hydrogenation of dimethylterephthalate (DMT) under relatively mild conditions. This process is carried out industrially in two steps using different reactors and separate Pd and Cu catalysts.[79] Although the role of the different metals in this transformation still remains unresolved, there are good prospects to optimize this reaction for industrial applications.
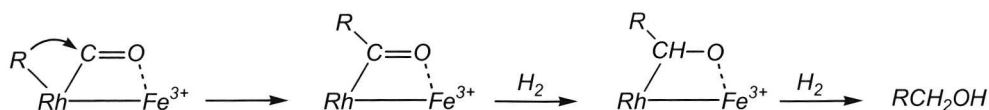
Figure 6. Proposed mechanism for bimetallic activation by a Fe/Rh heterogeneous catalyst in CO hydrogenation and olefin hydroformylation reactions.

Summarizing, the studies of heteronuclear transition metal clusters have focused primarily on their thermal reactivity and application in the field of homo- and heterogeneous catalysis. Even though numerous examples have demonstrated that introduction of a heterometal may induce major changes in the thermal reactivity of a homometallic core, it remains to be investigated why certain metal combinations lead to improved catalytic performance whereas

others decrease the catalytic activity dramatically. A deeper understanding of the role of the separate metal centres in bimetallic systems and their possible synergy therefore still represents a stimulating challenge. Fundamental studies of their frontier orbitals will provide a thorough description of the bonding properties of mixed-metal clusters as the aid to explain their reactivity. The prospects of this promising class of complexes will thereby be put on realistic grounds.

1.3 Electrochemical and photochemical activation of transition metal clusters

As a consequence of the fairly strong metal-metal and metal-carbonyl bonds in transition metal carbonyl clusters, thermally induced ligand loss or metal-metal bond cleavage reactions frequently require elevated temperatures, often resulting in low product selectivity or undesired cluster fragmentation processes. Considerable research efforts have therefore been devoted to the development of novel activation pathways that allow reactions to proceed with high selectivity under mild reaction conditions. Two promising approaches towards cluster activation and selective generation of target compounds are provided by photochemistry and electrochemistry.

By using light as the energy source, photochemical reactions offer the possibility to overcome large enthalpy barriers already at ambient or even low temperatures, which may increase the product selectivity while keeping the cluster core intact. For example, whereas thermal ligand substitution reactions frequently result in random mixtures of polysubstituted products or further transformation of the complexed ligand,[80] photoinduced ligand substitution can be performed in a stepwise fashion, producing the different derivatives in good yields.[81] Electrochemical activation, which implies a change in the number of valence electrons (reduction or oxidation), also provides the advantage to be performed under mild conditions. Similar to photoinduced ligand substitution, a number of electrocatalytic substitution reactions have been reported, where the degree of substitution can be either controlled by the electrode potential applied[82] or the amount of reducing agent added.[80, 83] Interestingly, as the frontier orbitals involved in the electrochemical oxidation or reduction are often identical to those involved in optical excitation, analogies between photochemical and redox reactivity are frequently encountered.[84-86] As example may serve the extrusion of a single mercury atom from the mixed-metal cluster $[Os_{18}Hg_3C_2(CO)_{42}]^2$ upon chemical reduction[87] or irradiation with visible light.[88] Both means induce a slippage of the Os_9 subclusters and are chemically reversible. In general, the activation of clusters by electron-transfer processes (oxidation, reduction or photo-excitation) not only provides a powerful tool to increase the selectivity of existing thermal processes but may also lead to novel reactions (*e.g.* by activation of clusters that are thermally stable) or products different from those

obtained by thermal reactions. Aimed at exploring the possibilities of both activation pathways, a large number of studies have dealt in the past three decades with the photo- and electrochemistry of transition metal clusters.

Electrochemistry

In the literature several examples have been reported where, interestingly, the electrochemical activation of clusters in the presence of substrate molecules resulted in increased product selectivity (*e.g.* substitution reactions, catalytic hydrogenation[89]) and/or generation of novel complexes (electrosynthesis).[90, 91] However, a majority of electrochemical studies have focused on the electrochemical response of the clusters themselves. One of the important stimuli behind the studies was the assumption that, in contrast to dinuclear complexes, the 'robust' metal framework of clusters would be able to act as an 'electron sponge', undergoing several reversible redox steps without destruction of the metal core. Although a number of high-nuclearity clusters are indeed stable in multiple oxidation states (*vide infra*), many redox processes encountered in clusters are of irreversible nature already in the (sub)second time domain.

The degree of reversibility of a redox process is determined by a slow electron transfer, for example induced by a structural change (electrochemical (ir)reversibility), and/or by a coupled fast chemical reaction changing the composition of the primary redox product (chemical (ir)reversibility).[92] These phenomena can conveniently be evaluated by cyclic voltammetry (see Chapter 2). In transition metal clusters, chemically irreversible redox processes often result in the rupture of one or more metal-metal bonds. This process is common for those carbonyl clusters in which the HOMO has predominant metal-metal σ-bonding character while the LUMO is antibonding in this regard. As a result, this group of clusters is subject to a weakening of their metal framework by both electrochemical reduction as well as oxidation. Whereas several approaches have been developed to prevent cluster fragmentation upon reduction (*vide infra*), the removal of electron(s) from a σ(metal-metal) bonding orbital upon oxidation usually results in efficient core opening or fragmentation.[91] Due to their predominantly irreversible nature, the oxidation processes of clusters have been the subject of only a limited number of studies. An example of redox-induced metal-metal bond cleavage without the breakdown of the cluster core is provided by the two-electron reduction of the cluster $[Os_6(CO)_{18}]$.[92] Interestingly, the structural change from the neutral bicapped tetrahedron to the dianionic octahedron is exactly that predicted by the PSEP theory (see Section 1.1). Apart from metal-metal bond splitting, the irreversible nature of a redox process may also result from ligand loss reactions according to EC or ECEC mechanisms (E = electrochemical process, C = chemical process). Illustrative examples include the release of CO upon two-electron reduction of $[M_3(CO)_{12}]$,[93] $[Rh_4(CO)_{12}]$,[94] $[Os_5C(CO)_{15}]$[95] and $[Ru_6C(CO)_{17}]$[96] or the subsequent loss of one or more hydrogen atoms upon reduction of the

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clusters $[Ru_4H_4(CO)_{12}]$,[97] $[Ru_2Rh_2H_2(CO)_{12}]$ or $[RuRh_3H(CO)_{12}]$.[94] Notably, the redox-induced decarbonylation of $[Os_5C(CO)_{15}]$ provides one of the rare examples where the irreversible reduction product was stable enough to allow its crystallographic characterization. Apart from the loss of one carbonyl ligand, the X-ray structure of $[Os_5C(CO)_{13}(\mu\text{-}CO)]^{2-}$ also revealed the presence of a bridging carbonyl group, required to compensate the excess negative charge by increased π-backdonation.

In order to switch the irreversible nature of redox processes and to reinforce the cluster core towards fragmentation, the influence of different ligands on the electrochemical response of clusters has been studied in detail. A useful approach towards reversible redox processes concerns the introduction of bridging ligands, such as diphenylphosphinomethane (dppm),[98-100] and/or the capping of one or more faces of the cluster core by ligands like S, SO, CO, CN, CR, or PML_n (ML_n = $Fe(\eta^5\text{-}C_5H_5)(CO)_2$, $Mn(\eta^5\text{-}C_5H_5)(CO)_2$).[101-104] Numerous examples[91] have shown that reinforcement of the cluster cohesion by bridging or capping ligands usually increases the lifetime of the electrogenerated ionic species compared to the parent clusters. For example, replacement of three carbonyl ligands in $[Co_2Rh_2(CO)_{12}]$ by the basal-clasping tripodal ligand $HC(PPh_2)_3$ significantly prolongs the lifetime of the corresponding radical anion, allowing its characterization by EPR spectroscopy.[105] Interesting examples also exist where fragmentation of the cluster core is prevented, even when reduction induces cleavage of a metal-metal bond.[98, 102] Two-electron reduction of the bicapped clusters $[Fe_3(CO)_9(\mu_3\text{-}PML_n)_2]$, for example, results in the cleavage of an Fe-Fe bond, a process fully reversible upon reoxidation (Figure 7).[102]
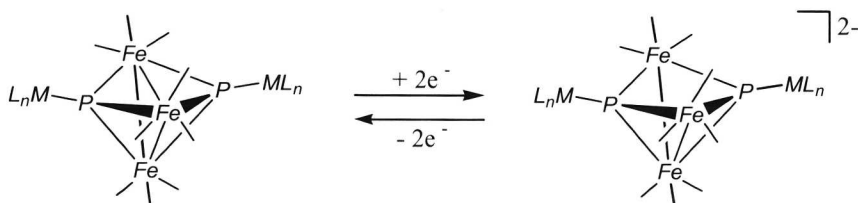
Figure 7. Reversible structural change upon coupled two-electron reduction and oxidation of the bicapped cluster $[Fe_3(CO)_9(\mu_3\text{-}PML_n)_2]$.

As the bridging or capping ligands in the above clusters have been shown to hardly contribute to the largely metal-based LUMO, unsaturated alkyne bridges have been employed to increase the electronic delocalization of the frontier orbitals over the entire molecule and to prevent the labilization of specific bonds upon reduction or oxidation. The LUMO of the clusters $[Fe_3(CO)_9(alkyne)_2]$,[106] in which the linked alkynes interact with the metal framework

in a multicentred σ/π fashion, has, for example, strong contributions from the 'butadiene' fragment, resulting in two subsequent, fully reversible reduction processes.

The coordination of redox-active ligands possessing a low-lying unoccupied π* orbital, provides another approach towards reversible redox processes.[107, 108] Their protecting role as electron reservoirs offers the possibility to stabilize otherwise short-lived radical transients and often prevents fragmentation of the cluster core upon one-electron reduction. Consistent with the dominantly L(π*)-localized LUMO, one-electron reduction of [Ru$_4$(μ-H)$_4$(CO)$_{10}$(α-diimine)] (α-diimine = 2,2'-bipyrimidine, 2,3-bis(pyridin-2-yl)pyrazine), for example, produced stable radical anions that could be characterized by IR, UV-vis and EPR spectroscopies.[109] This behaviour distinctly differs from the unsubstituted cluster [Ru$_4$(μ-H)$_4$(CO)$_{12}$], where the radical anion undergoes a fast disproportionation reaction accompanied by loss of H$_2$.[97] A combination of both strategies is used in the cluster [Os$_3$(μ-H)(CO)$_9$(o-^{i}Pr-PyCa)] (o-^{i}Pr-PyCa = orthometalated pyridine-2-carbaldehyde-N-isopropylimine), possessing an α-diimine ligand bridging an Os-Os bond (see Figure 8).[110]

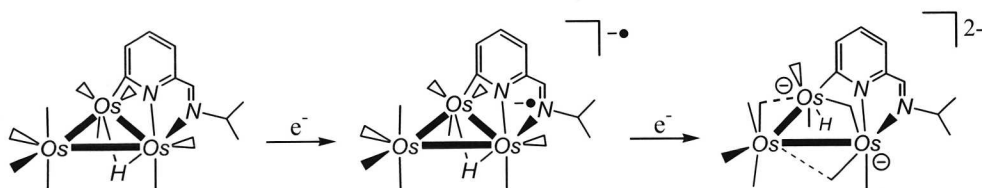**Figure 8**. Reduction path of the cluster [Os$_3$(μ-H)(CO)$_9$(o-^{i}Pr-PyCa)].

Indeed, the presence of a bridging, redox-active ligand resulted in remarkable stabilization with regard to the Os-Os bond cleavage upon one-electron reduction. The latter process is only induced by the second electron transfer. In the dianion, interestingly, the hydride ligand does not dissociate but moves to a terminal position, being replaced by a CO bridge. In general, both approaches towards reversible redox processes have been applied with a reasonable degree of success. It should, however, be noted that most examples include reversible *reduction* processes while examples of reversible cluster *oxidation* remain rare.†

As the (electro)chemical reversibility of redox processes reflects only very small structural changes, they are frequently observed in robust homo- or heteronuclear clusters of higher nuclearity. There is ample proof that these systems, possessing metal cores consisting of 8 to 44 atoms, can behave as electron 'sinks' or electron 'sponges', capable of undergoing multiple redox steps without breakdown of the cluster framework.[111] In the 'smaller' clusters of this group, the observation of multiple oxidation states often results from the presence of a

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† Reversible oxidation processes have, for example, been observed in cubane-type Fe/S or Mo/S clusters.[91, 92] It should, however, be noted that these polymetallic systems do not obey the definition of clusters outlined in Section 1.1.

low-lying highly-delocalized orbital that is either non-bonding or slightly antibonding in character. For example, due to the delocalized nature of its LUMO, the cluster $[Ag_{13}Fe_8(CO)_{32}]^{3-}$ can accept two additional electrons without significant loss of stability.[112] A tightly protecting shell of carbonyl ligands seems necessary to inhibit the formation of high-nuclearity clusters upon oxidation, whereas inclusion of main-group elements in the cluster core can inhibit cluster break-down upon reduction. Electron 'sponge' behaviour seems to arise with the progressive disappearance of a well defined HOMO-LUMO gap. This gradual process is accomplished when the number of metal-metal bonds overtakes the number of metal-CO bonds and the number of bulk to surface metal atoms in the metal core increases. Illustrative examples of electron 'sponge' behaviour in which all redox steps are reversible, are provided by the giant clusters $[Pt_{24}(CO)_{30}]^n$ (n = 0 to 6)[113] and $[Ni_{38}Pt_6(CO)_{48}]^{n-}$ (n = 5 to 10).[114] The reversible redox behaviour of such high-nuclearity clusters enables to model surface electrochemistry and to follow the convergence of charge-dependent cluster properties towards the metallic bulk.

The mixed-metal cluster electrochemistry is a significantly less developed area than that of its homonuclear counterparts. Although electrochemical activation of heteronuclear clusters has been the subject of quite a number of voltammetric studies,[115, 116] the insight into their often complex redox behaviour is still limited. In general, heteronuclear cluster anions were found to be less stable than the homonuclear analogues, their redox activation often resulting in fragmentation of the cluster core. In addition, the electrochemical behaviour of isoelectronic and isostructural homometallic clusters often proved to be unexpectedly different.[116] For example, the electrogenerated 48-CVE (CVE = cluster valence electron) dianions $[Fe_3(CO)_9(RC{\equiv}CR)]^{2-}$ can be reversibly oxidized to the 46-CVE parent clusters,[116] whereas the 48-CVE cluster $[FeCo_2(CO)_9(EtC{\equiv}CEt)]$ does not support electron removal without destruction of the metal framework.[117] A deeper understanding of the redox behaviour of heteronuclear clusters therefore requires investigation of systematically varied cluster series. Such series are aimed to assess trends in redox potentials and the prospects of controlling cluster electronic properties by variation of the metal core.[118] Equally important is the assignment and structural description of the redox products in order to rationalize cluster redox reactivity in the series.

Insight into the electronic and molecular structure of clusters in different oxidation states indeed represents today one of the most stimulating challenges in the field of cluster electrochemistry. In the last decade, considerable research effort has been devoted to characterize their often highly reactive redox products by variable-temperature cyclic voltammetry or *in situ* electrochemistry in combination with spectroscopic techniques.[119-121] In recent years, such spectroelectrochemical studies, sometimes in combination with electronic structure calculations (*e.g.* based on the semi-empirical Extended Hückel Molecular

Orbital (EHMO) approach), have afforded valuable information about the character and relative ordering of the frontier orbitals.[122-124] With the nowadays accessible higher-level quantum chemical calculations (*e.g.* Density Functional Theory (DFT)), capable of correct description of even strongly delocalized bonding in the starting clusters and their redox products, a better understanding of the complex electrochemical behaviour of homo- and heteronuclear clusters has come within the reach.

Photochemistry

Compared to the number of studies dealing with the electrochemical activation of clusters, the area of cluster photochemistry still remains rather unexplored. Pioneering studies of the photochemical reactivity of transition metal clusters often focused on the synthetic and catalytic potential of the reactive intermediates generated upon irradiation. Interesting results have been, for example, obtained in the selective substitution of carbonyl groups in $[M_3(CO)_{12}]$ (M= Ru, Os) and in $[Ru_4(\mu-H)_4(CO)_{12}]$ promoting the photocatalytic isomerization of alkenes.[89, 125] However, most of the observed photoinduced stoichiometric or catalytic reactions have been the result of trial and error attempts. Systematic investigations into the underlying (primary) photoprocesses and the electronic structure of the clusters (*e.g.* the characters of frontier orbitals and reactive excited states) have been scarce.

In contrast to electrochemistry where only the HOMO *or* LUMO are involved in the activation process, photochemical activation may induce more drastic changes in the electronic and molecular structure of a cluster by affecting the population of both orbitals at the same time. In addition, activation by light may also involve other lower- and higher-lying orbitals that are generally not involved in thermal or electrochemical processes. Obviously, the changes in the electronic and molecular structure strongly depend on the character of the excited state that is populated. Therefore, different reactivity patterns can be observed for a single cluster simply by tuning the energy of the photons (*i.e.* irradiation wavelength) supplied to the system, provided prompt chemical reactions take place after photoexcitation. The considerable number of available excited states and their mixed character (in particular in clusters of low symmetry) also brings along significant complications. The structural changes induced upon excitation, for example, can cause (allowed or avoided) crossing of the initially populated excited state with a close-lying state of different character. As a result, the observed photoreactivity may significantly differ from that expected, based on the character of the electronic transition. Thorough mechanistic studies of the photochemical processes of clusters are therefore much more complicated than those of comparable mono- or dinuclear complexes, where the accessible low-lying excited states are less numerous.

The first attempts to correlate the observed photochemical reactivity of clusters with the character of their electronic transitions date back to the late 1970's. Initial photochemical studies of the simple unsubstituted carbonyl clusters $[M_3(CO)_{12}]$ (M = Ru, Os) in the presence

of different substrate molecules revealed that the observed photoreactivity is strongly dependent on M, solvent, irradiation wavelength and the nature of the reacting ligand (*e.g.* phosphines, CO, alkenes).[126-129] Based on the assignment of the substitution- and fragmentation products formed, the primary excited state processes were proposed to include release of CO and cleavage of a metal-metal bond, respectively. Interestingly, these reactions are identical to those underlying most irreversible electrochemical processes (*vide supra*). Different from electrochemical activation, however, photochemistry allows the molecular and electronic structure of reactive intermediates along the reaction pathway to be studied at very low temperatures and/or by fast time-resolved spectroscopic techniques. Irradiation of the clusters $[M_3(CO)_{12}]$ in a low-temperature matrix, for example, resulted in the spectroscopic detection and characterization of coordinatively unsaturated $[M_3(CO)_{11}]$, the primary photoproduct upon short-wavelength irradiation of these clusters.[130, 131] The latter photoproduct could also be detected at room temperature by time-resolved IR spectroscopy on the microsecond time scale.[132] Notably, a similar CO-loss reaction has been established for the tetranuclear cluster $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$.[133] Despite the fact that the use of matrix-isolation techniques and microsecond (μs) time-resolved spectroscopy significantly contributed to the understanding of the initial photoprocess in the above cases, other primary cluster photoproducts are often too short-lived to allow their detection by these techniques. For example, the substitution- and fragmentation products observed upon long-wavelength irradiation of $[M_3(CO)_{12}]$ were proposed to result from a common open-structure intermediate $[M_3(CO)_{11}(\mu\text{-}CO)]$,[134, 135] a photoproduct undetectable with the spectroscopic techniques available at the time (*vide infra*). With the development of (ultra)fast spectroscopic techniques, allowing photochemical reactions to be studied on the femto- to nanosecond time scales, the insight into the nature and reactivity of excited states and primary photoproduct(s) has increased significantly over the past ten years.[136] For example, a combined nanosecond (ns) transient absorption and time-resolved IR study of the substituted clusters $[Os_3(CO)_{10}(\alpha\text{-}diimine)]$ resulted in the detection and characterization of solvent-stabilized biradicals.[137] The latter species were found to be the primary photoproducts of these clusters in non- or weakly coordinating solvents and have lifetimes varying from 5 ns to 10 μs depending on the solvent and α-diimine ligand. As the branching between different reaction pathways in the photochemistry of coordination compounds frequently takes place already in the optically populated, thermally non-relaxed excited state, femto/picosecond time-resolved spectroscopic studies are required to study the primary excited state processes.[138, 139] This also applies for transition metal clusters. Whereas picosecond transient absorption (ps TA) spectra may provide valuable information about the character of the initially populated and/or reactive excited state and its kinetics, picosecond time-resolved IR (ps TRIR) spectroscopy provides a powerful tool to obtain structural information about the cluster in the excited state and/or about the primary photoproduct(s). Very recently, ps TRIR spectroscopy has, for example,

allowed the direct observation and characterization of the CO-bridged primary photoproduct of [Ru$_3$(CO)$_{12}$] (see Chapter 3).[140]

With the oppurtunity to study photochemical reactions on very short time scales, a thorough mechanistic insight into the photochemistry of cluster compounds can now be obtained. However, whereas ps TA and TRIR spectra can contribute significantly to the characterization of the excited state and the nature of the primary photoprocess, the availability of several reaction pathways sometimes prevents unambiguous assignments to be made. Support from high-level theoretical calculations (*e.g.* DFT) is therefore required, not only to clarify the character of the frontier occupied and virtual molecular orbitals but also to understand the mixed nature of the electronic transitions and excited states. At present, general statements about the photochemical reactivity of clusters cannot yet be made. Just as in cluster electrochemistry, small changes in the electronic or molecular structure of a cluster can induce significant changes in its photoreactivity. As example may serve the photoreactivity of the clusters [Os$_3$(CO)$_{10}$(α-diimine)] in strongly coordinating solvents. Whereas for α-diimine = ^{i}Pr-PyCa (^{i}Pr-PyCa = pyridine-2-carbaldehyde-*N*-isopropylimine) or bpy (bpy = 2,2'-bipyridine) zwitterionic photoproducts are formed in pyridine already at room temperature, the latter charge-separated photoproducts can only be observed at low temperatures (253 K) for α-diimine = ^{i}Pr-DAB (^{i}Pr-DAB = *N,N'*-diisopropyl-1,4-diaza-1,3 butadiene), secondary radical coupling reactions dominating at temperatures above 263 K.[141] This difference in photoreactivity has been explained by the theoretically proven strongly delocalized character of the HOMO and the LUMO in [Os$_3$(CO)$_{10}$(^{i}Pr-DAB)], diminishing the charge-transfer character of the lowest-energy excited state.[142] This example demonstrates the intriguing diversity of the photoreactions of clusters and supports the demand for systematic studies, also in the little explored field of heteronuclear cluster photochemistry.

The preceeding paragraphs show that the intriguing field of transition metal cluster chemistry represents a challenging research area with numerous possibilities. Due to the unique bonding modes and activation pathways of organic substrates and the controlable composition of their metal framework, clusters appeared to be useful as homo- and heterogeneous catalysts or catalyst precursors in a number of different transformations. In addition, the study of high-nuclearity clusters has provided valuable information about the transition from molecular to bulk metallic behaviour. It should, however, be noted that despite the present achievements in the different areas, the insight into the electronic structure of clusters and their reactivity is still limited. In order to gain a more detailed understanding of their stoichiometric and catalytic reactions, fundamental studies of the cluster bonding properties are therefore indispensable. A powerful tool to obtain insight into the character of the frontier orbitals is provided by photo- and electrochemistry. In addition, a variety of sophisticated experimental techniques allows the electronic and molecular structure of starting

complexes as well as their photo- or redox products to be studied in great detail. In combination with the support from high-level theoretical calculations (DFT), photo- and electrochemical studies may also facilitate a thorough description of the bonding properties of clusters, stimulating further development in the fields of photochemical, redox and thermal reactivity.

1.4 Scope and contents of this Thesis

The demand for fundamental studies of the electronic structure and reactivity of clusters with the powerful tools provided by photo- and redox chemistry is a clear message for the further development of cluster chemistry in different directions. It is the scope of this Thesis to clarify how the photo- and electrochemistry of transition metal carbonyl clusters are affected by the systematic variation of L or the cluster core composition in selected cluster series, where L represents a non-carbonyl redox-active or innocent ligand. Ultrafast spectroscopic techniques are used to provide insight into the character of the reactive excited states and the nature of the primary photoprocesses (**Chapters 3 - 6**). High-level theoretical calculations are performed in order to gain insight into the bonding properties and the character of the frontier orbitals and low-energy electronic transitions (**Chapters 3, 5 and 6**). The systematic introduction of heterometals into the homometallic cluster core has targetted the establishment of the influence of the cluster core composition on the observed reactivity (**Chapters 6 and 7**). By combining effectively the theoretical results with experimental data and comparing the observed reactivities with those of relevant reference systems, a detailed understanding of the electronic structure, bonding properties and reactivity could be obtained in the majority of the studied systems. The next paragraphs give a more detailed description of the content of the different chapters.

Chapter 2 summarizes the experimental and theoretical research methods used in this Thesis and gives a detailed description of the different experimental set-ups.

Chapter 3 describes the results of mechanistic investigations of the primary photoprocesses of unsubstituted $[Ru_3(CO)_{12}]$ and the substituted cluster $[Os_3(CO)_{10}(s\text{-}cis\text{-}1,3\text{-}cyclohexadiene)]$. Picosecond transient absorption and time-resolved infrared spectroscopy were used to characterize the initially populated and reactive excited states and to study the formation of the primary photoproducts. In order to analyze the frontier orbitals and assign the low-energy electronic transitions, a density functional theoretical (DFT) study was performed on $[Os_3(CO)_{10}(1,3\text{-}butadiene)]$. The results of this study were interpreted in combination with the spectroscopic data and allowed for a detailed understanding of the primary excited state processes.

The introduction of redox-active α-diimine ligands in the clusters $[Os_3(CO)_{10}(\alpha\text{-}diimine)]$ has been reported to influence significantly their photochemical and electrochemical

properties. While the photoproducts of these clusters have been investigated in detail in previous work, the mechanism of their formation has not firmly been established. **Part A** of **Chapter 4** therefore focuses on the primary photoprocesses of these systems. Ultrafast time-resolved techniques were used to investigate the influence of the α-diimine ligand on the lifetime of the $\sigma(Os\text{-}Os)\pi^*$ excited state and to clarify the mechanism of zwitterion formation in strongly coordinating acetonitrile. The short-lived biradical photoproducts, formed by Os-Os bond homolysis in non- or weakly coordinating solvents, are the main topic of **Part B**. Single-wavelength kinetic traces were recorded in order to investigate the stabilization of the biradicals by weakly coordinating solvents and to establish a second pathway for zwitterion formation *via* the conversion of solvent-stabilized biradicals. The thorough understanding of the electron-transfer reactions of the clusters $[Os_3(CO)_{10}(^iPr\text{-}AcPy)]$ has allowed the realization of a purpose-designed $[Os_3(CO)_{10}(^iPr\text{-}AcPy)]$-methylviologen donor-acceptor dyad whose interesting redox-controlled photochemistry is described in **Part C**.

The investigations of the photo- and electrochemistry of the clusters $[Ru_3(CO)_8(\mu\text{-}CO)_2(\alpha\text{-}diimine)]$ are presented in **Chapter 5**. These clusters not only differ from the related compounds in Chapter 4 by the different core composition but also by the presence of two bridging carbonyl groups. The latter ligands are shown to considerably influence the observed photo- and redox reactivity. Density functional theoretical calculations in combination with time-resolved UV-vis and IR spectroscopic studies provide an opportunity to discuss the frontier orbitals and assign the reactive excited state.

Chapter 6 describes a novel synthetic route towards the heteronuclear cluster $[Os_2Ru(CO)_{12}]$ and the synthesis, crystal structures and spectroscopic characterization of the novel derivatives $[Os_2Ru(CO)_{11}(PPh_3)]$ and $[Os_2Ru(CO)_{10}(^iPr\text{-}AcPy)]$. The latter cluster was the subject of a detailed photochemical and electrochemical study. The results together with support from density functional theoretical calculations and results obtained for the homonuclear analogues studied in Chapters 4 and 5, allowed to establish the influence of the heteronuclear cluster core on the observed reactivity.

Explorative studies of the reactivity of several mixed-metal clusters possessing transition metal atoms from different groups of the periodic table are presented in **Chapter 7**. **Part A** reports on the photoreactivity of the heteronuclear clusters $[Os_2Pt(CO)_8(PPh_3)_2]$ and $[Os_2Rh(CO)_9(\eta^5\text{-}C_5Me_5)]$ in the presence or absence of different Lewis bases. The investigations include the characterisation of the different photoproducts, providing valuable information about the nature of the primary photoprocesses. **Part B** deals with the photo- and electrochemically driven conversion of the tetranuclear heterometallic cluster $[Ru_3Ir(\mu_3\text{-}H)(CO)_{13}]$ into $[Ru_3Ir(\mu\text{-}H)_{3\text{-}n}(CO)_{12}]^{n-}$ ($n = 0 - 2$). Both activation pathways provide a promising alternative for the thermal conversion taking place at elevated temperatures.

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