Photochemistry and Electrochemistry of Triosmium Clusters, The Non-Carbonyl Co-Ligand Makes the Difference
Bakker, M.J.

Citation for published version (APA):

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Summary

This Thesis describes the results of a detailed mechanistic investigation into the photo- and electrochemical behaviour of several trisomy carbonyl clusters and of tetraneutral carbonyl clusters of ruthenium and rhodium. In Chapter 1 a general introduction to the field of transition metal carbonyl clusters is followed by a more detailed description of the photo- and electrochemical reactions of the unsubstituted carbonyl clusters \([\text{Os}_3(\text{CO})_{12}]\), \([\text{H}_4\text{Ru}_4(\text{CO})_{12}]\) and \([\text{Rh}_4(\text{CO})_{12}]\), and their substituted derivatives \([\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]\) and \([\text{H}_4\text{Ru}_4(\text{CO})_{10}(\alpha\text{-diimine})]\) (e.g. \(\alpha\text{-diimine} = 2,2'\text{-bipyridine}\)). This chapter concludes with the formulation of the main objectives of this PhD project, which are (i) to establish the influence of variation of \(L\) and the reaction conditions on the photo- and electrochemistry of the clusters \([\text{Os}_3(\text{CO})_{10}(L)]\), \(L\) representing an innocent or a redox-active ligand, and (ii) to determine the influence of the composition of the metal core on the electrochemistry of the tetrahedral clusters \([\text{H}_4x\text{Ru}_{4-x}\text{Rh}_x(\text{CO})_{12}]\) \((x = 0, 2, 3, 4)\). This work is part of a more general investigation into the photochemical and electrochemical activation of transition metal carbonyl clusters.

Chapter 2 and Chapter 3 deal with clusters of the general type \([\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]\). Previous studies had shown that the introduction of the \(\alpha\text{-diimine}\) ligand in \([\text{Os}_3(\text{CO})_{12}]\) results in an intense absorption in the visible region, tentatively attributed to a \(d_d(\text{Os})-\pi^*(\alpha\text{-diimine})\) charge transfer (CT) electronic transition. Upon irradiation into this absorption band homolysis of an Os–Os(\(\alpha\text{-diimine}\)) bond occurs with efficient formation of either a biradical or zwitterionic open-core photoproduct. Depending on the \(\alpha\text{-diimine}\) ligand, the photoproduct reverts to the starting compound or reacts further to a stable isomer.

Chapter 2 presents the results of density functional theoretical (DFT) calculations on model clusters \([\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]\) \((\alpha\text{-diimine} = \text{bpy, H-PyCa and H-DAB})\), providing a theoretical basis for the assignment of the lowest-energy electronic transitions in this type of clusters. The lowest-energy visible absorption band has now been re-assigned to a \(\sigma(\text{Os–Os})-\pi^*(\alpha\text{-diimine})\) CT transition for \(\alpha\text{-diimine} = \text{bpy}\) and \(\text{R-PyCa}\). In contrast to this, the corresponding absorption band for \([\text{Os}_3(\text{CO})_{10}(\text{R-DAB})]\) possesses hardly any CT character and is assigned to a delocalized \(\sigma(\text{Os–Os})\pi^*-\sigma^*(\text{Os–Os})\pi^*\) transition. In this respect, the DFT calculations are in excellent agreement with results of an electronic absorption and resonance Raman spectroscopic study, while they also correctly predict several other experimentally observed trends. On basis of the assignment of the lowest-energy electronic transition, significant weakening of an Os–Os bond is expected upon optical population of the corresponding excited state. Indeed, for \([\text{Os}_3(\text{CO})_{10}(\text{i-Pr-PyCa})]\) in pyridine it was demonstrated for the first time that optical population of this state leads to bond cleavage and zwitterion formation, this reaction being however less efficient than from the higher excited CT states.
Chapter 3 shows how the influence of the solvent, temperature and addition of alkenes or CO on the behaviour of the biradicals [(CO)_4Os^*–Os(CO)_4–Os^+(CO)_2(α-diamoimine)] (α-diimine = i-Pr-AcPy = 2-acetylpypyridine-N-isopropylimine) can be established, using nanosecond time-resolved UV-vis and IR (TRIR) spectroscopy. It has already been known that the coordinating ability of the solvent is of crucial importance in the photochemistry of the clusters [Os_3(CO)_10(α-diimine)]. Whereas in strongly coordinating solvents (acetonitrile, pyridine) very long-lived zwitterions are formed, short-lived biradicals with a lifetime in the nanosecond or even subnanosecond time domain are produced in weakly-coordinating THF or non-coordinating 2-chlorobutane. In this Thesis it is demonstrated that the rate of the fast back reaction of the biradical to the parent cluster depends on the coordinating abilities of the solvent or of an added alkene that stabilize the coordinatively unsaturated Os^+(CO)_2(i-Pr-AcPy^–) moiety, the biradical lifetime increasing in the order 2-chlorobutane < 2-MeTHF < THF < acetone < cyclohexene < 1-octene = styrene. Remarkably long lifetimes, up to even ca. 10 μs for the latter two alkenes, are observed for the biradical adducts. For these alkenes, the back reaction of the biradical is hampered to such an extent that conversion of the Lewis-base-stabilized biradical into the corresponding zwitterion becomes competitive already at room temperature. For less strongly coordinating cyclohexene, acetone and THF this conversion only occurs at sufficiently low temperatures. Interestingly, this pathway for zwitterion formation is intermediate to the instantaneous formation of a zwitterion from the charge transfer excited state in a strongly coordinating solvent and the lack of such a reaction when a biradical is formed in non- or weakly coordinating solvents. The observation of a CO-stabilized zwitterion demonstrates that coordination of a strong two-electron donating Lewis base is not imperative to drive the intramolecular charge separation reaction, provided the back reaction of the biradical is significantly hampered. The TRIR spectra of the open-structure biradical photoproducts reflect the changes in electron density distribution caused by variation of the solvent or alkene.

Chapter 4 reports the syntheses, crystal structures and spectroscopic, photochemical and electrochemical properties of the novel cluster [Os_3(CO)_10(tmbp)] and its PPh_3-derivative [Os_3(CO)_9(tmbp)(PPh_3)], in which tmbp is the redox-active ligand 4,4',5,5'-tetramethyl-2,2'-biphosphinine. The aim of this study was to synthesize a cluster with a similar structure to that of [Os_3(CO)_10(bpy)] (bpy coordinating in a bidentate fashion at a single osmium centre), but with another type of redox-active ligand. Unexpectedly, the crystal structure of [Os_3(CO)_10(tmbp)] (and of its PPh_3-derivative) reveals an unprecedented coordination mode of tmbp with both P atoms bridging between two metal atoms, this result being illustrative for the limited predictability of cluster chemistry. The tmbp ligand in [Os_3(CO)_10(tmbp)] can be considered here as formally doubly reduced by electron transfer from the cluster core, that has consequently lost one metal–metal bond. DFT calculations show that not only the LUMO, but also the HOMO have mainly π*(tmbp) character, implying that the lowest-energy excited state has intraligand instead of metal-to-ligand CT character. This also explains the complete photostability of [Os_3(CO)_10(tmbp)]. The electron-deficiency of the cluster core is responsible
for facile electrocatalytic substitution of CO by more basic PPh₃ producing [Os₃(CO)₆(tmbp)(PPh₃)]. The overall two-electron reduction of [Os₃(CO)₁₀(tmbp)] and [Os₃(CO)₆(tmbp)(PPh₃)] leads to dissociation of CO and PPh₃, respectively, and formation of the dianion [Os₃(CO)₆(tmbp)]²⁻. The initially produced radical anions are sufficiently stable to be observed due to localization of the odd electron on tmbp, which in addition clamps the trisomium core.

Chapter 5 presents a mechanistic photochemical study of the clusters [Os₃(CO)₁₀(1,3-diene)] (diene = cis-1,3-butadiene, 1,3-cyclohexadiene). This study was undertaken to find out if the coordinated 1,3-diene undergoes any reaction at the cluster core, e.g. oxidative addition of a C–H bond, after photochemical metal–metal bond cleavage or CO-loss. No evidence for such a reaction was obtained. However, upon near-UV irradiation the initially formed photoprocess is sufficiently long-lived (ca. 100 ns in hexane) to be characterized by nanosecond time-resolved UV-vis and IR spectroscopy. From the spectroscopic data it was deduced that this primary photoprocess possesses a coordinatively unsaturated open-triangle structure with two bridging carbonyl groups, one bridging the split (CO)₆Os–O₈(CO)₂(diene) bond. This is an important result, as a similar primary photoprocess might play a key role in the diversified photochemistry of unsubstituted [Os₃(CO)₁₂], but has never been directly observed. The primary photoprocess of [Os₃(CO)₁₀(diene)] partially reverts back to the parent cluster and partially undergoes fragmentation to give mononuclear [Os(CO)₉(diene)] and the reactive binuclear fragment [Os₂(CO)₇]. This latter product was trapped by reaction with CO, or with alkenes at low temperatures, to produce the binuclear complexes [Os₂(CO)₇(L")]₂ (L" = CO, ethene, 1-octene).

Chapter 6 deals with the tetrahedral clusters [H₄₋ₓRuₓRh₄(CO)₁₂] (x = 0, 2, 3, 4), aiming at the evaluation of the influence of the metal core composition on the electrochemical and photochemical properties. From this study, it became clear that the reduction pathways in this series are not determined by the metals in the metal core, but by the presence or absence of hydride ligands. If hydride ligands are present, as is the case of [H₄Ru₄(CO)₁₂], [H₂Ru₂Rh₂(CO)₁₂] and [HRuRh₃(CO)₁₂], reduction leads to hydrogen loss in order to preserve the stable electron-precise M₄(CO)₁₂ core. Electrochemical reduction of the hydride-lacking cluster [Rh₄(CO)₁₂] does not result in the formation of a stable tetranuclear anion. Instead, the main reduction products are [Rh₃(CO)₁₅]⁻ and [Rh₄(CO)₁₅]²⁻, proposed to be formed via the initially generated CO-loss product [Rh₄(CO)₁₁]²⁻ by fast redox condensation reactions. Importantly, the results of this detailed study rectify and complete a previously proposed mechanism for the reduction of [Rh₄(CO)₁₂], according to which the radical anion [Rh₄(CO)₁₂]⁻ undergoes cluster fragmentation, one of the products being mononuclear [Rh(CO)₄]⁻. Re-oxidation of the reduction products neatly generates the starting compound together with hexanuclear [Rh₆(CO)₁₆]. Unlike [H₄Ru₄(CO)₁₂] that undergoes photochemical CO-dissociation, [H₂Ru₂Rh₂(CO)₁₂] and [Rh₄(CO)₁₂] appear to be completely photostable, excluding the photochemical activation of these clusters.