Photo- and redox activation of homo-and heteronuclear transition metal clusters: experiment and theory
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Chapter 7

Part A

Exploring the Photoreactivity of the Triangular Mixed-Metal Clusters \([\text{Os}_2\text{Pt(CO)}_8(\text{PPh}_3)_2]\) and \([\text{Os}_2\text{Rh(CO)}_9(\eta^5-\text{C}_5\text{Me}_5)]\)
7A.1 Abstract

In this Chapter the results are presented of a pioneering study of the photochemical reactivity of the heteronuclear transition metal clusters \([\text{Os}_2\text{Pt}(\text{CO})_8(\text{PPh}_3)_2]\) and \([\text{Os}_2\text{Rh}(\text{CO})_9(\text{Cp}^*)]\) \((\text{Cp}^* = \eta^5-\text{C}_5\text{Me}_5)\). Upon irradiation into its lowest-energy absorption band \((\lambda_{\text{irr}} > 420 \text{ nm})\), \([\text{Os}_2\text{Pt}(\text{CO})_8(\text{PPh}_3)_2]\) undergoes efficient photofragmentation into the mononuclear complex \([\text{Os}(\text{CO})_4(\text{PPh}_3)]\) and unsaturated osmium and platinum fragments that are highly reactive. The latter osmium fragments may be stabilized by addition of \(\text{PPh}_3\) or in the presence of \(\text{CO}\) at low temperatures, while otherwise \([\text{Os}_3(\text{CO})_{12}]\) and other unassigned carbonyl products are formed. The photochemical reactivity of \([\text{Os}_2\text{Rh}(\text{CO})_9(\text{Cp}^*)]\) derives from that of the mononuclear complex \([\text{Rh}(\text{CO})_2(\text{Cp}^*)]\). The lowest-lying excited state of \([\text{Os}_2\text{Rh}(\text{CO})_9(\text{Cp}^*)]\) has predominant \(\text{Cp}^*\)-to-Rh/\(\text{CO}\) character. Consistent with this assignment visible excitation \((\lambda_{\text{irr}} = 476 \text{ nm})\) of the cluster does not give rise to efficient bond activation reactions. In contrast, irradiation at 313 \(\text{nm}\) in the presence of \(\text{Et}_3\text{SiH}\) results in the stepwise activation of two substrate molecules by the different metal centres within the heteronuclear cluster core.

7A.2 Introduction

Besides their challenging application as homogeneous catalysts,\(^1\) heteronuclear transition metal clusters, combining the intrinsic properties of different metal centres within the cluster core, will also enter the field of heterogeneous catalysis. The well-defined cluster core of mixed-metal clusters has, for example, proven to be valuable as precursor for the preparation of heterogeneous, multimetallic catalysts of high dispersion and defined metal stoichiometry.\(^2\) Inversely, the anchoring of well-defined heteronuclear clusters to polymeric supports or the study of these compounds in solution may provide a better understanding of the relation between structure and catalytic performance of bimetallic aggregates of non-uniform size and shape.

As an example of the latter approach, the importance of platinum alloy clusters as catalysts in the petroleum reforming process\(^3\)\(^-\)\(^7\) has resulted in an increased interest in the study of the structure, bonding and reactivity of mixed-metal cluster complexes containing platinum. One of the most interesting developments in this field concerns the synthesis of the layer-segregated cluster \([\text{Pt}_3\text{Ru}_6(\text{CO})_{20}(\mu_3-\text{PhC}_2\text{Ph})(\mu_3-\text{H})(\mu-\text{H})]\), exhibiting a higher catalytic activity in the hydrogenation of diphenylacetylene than the homometallic complexes of the separated metals.\(^8\) Importantly, the heterobimetallic catalytic process was proven to be completely homogeneous, the different metals in the cluster core playing a crucial role in the reaction cycle. More recently, the activity of the trinuclear clusters \([\text{MPt}_2(\text{CO})_5(\text{PPh}_3)_2(\text{PhC}_2\text{Ph})]\) \((M = \text{Fe, Ru, Os})\) in the catalytic hydrosilylation of
diphenylacetylene was investigated. Although the formation of (E)-(1,2-diphenyl)ethenyl]triethylsilane was indeed observed for all clusters, there is strong evidence that the catalytic activity in these cases mainly results from fragmentation products.

A rather unexplored type of mixed-metal clusters concerns those combining rhodium and osmium centres within the cluster core. The well-established function of rhodium in several catalytic reactions together with the rich chemistry and kinetic stability of osmium clusters, make these systems promising candidates for the development of efficient homogeneous or heterogeneous catalysts. One of the few examples where a mixed osmium/rhodium cluster is employed in catalysis, concerns the anchoring of [H$_2$RhOs$_3$(CO)$_{10}$(acetylacetonate)] to a polystyrene support in order to investigate the catalytic hydrogenation and isomerization of alkenes. Unfortunately, the active catalysts for the separate reactions were found to form by break-up of the parent bimetallic cluster, segregation of the metals and aggregation of the rhodium centres without significant break-up of the triosmium units.

Combining the demand for systematic investigations into the bonding properties and reactivity of rhodium- and platinum-containing mixed-metal clusters with our continued interest in the photochemistry of triangular clusters, recently with an Os$_2$M core, we report in this Chapter on the photochemical reactivity of the heteronuclear clusters [Os$_2$Pt(CO)$_8$(PPh$_3$)$_2$] (1) and [Os$_2$Rh(CO)$_9$(Cp*)] (Cp* = $\eta^5$-C$_5$Me$_5$) (2), schematically depicted in Figure 1. In order to properly address the influence of the Rh/Cp* moiety on the photoreactivity of the latter cluster, the cluster [Os$_2$Rh(CO)$_9$Cp] (Cp = $\eta^5$-C$_5$H$_5$) (3) was synthesized as a reference. Due to the redistribution of the phosphine ligands during its

Figure 1. Schematic structures of the studied clusters [Os$_2$Pt(CO)$_8$(PPh$_3$)$_2$] (1) and [Os$_2$Rh(CO)$_9$(Cp*)] (2), schematically depicted in Figure 1. In order to properly address the influence of the Rh/Cp* moiety on the photoreactivity of the latter cluster, the cluster [Os$_2$Rh(CO)$_9$Cp] (Cp = $\eta^5$-C$_5$H$_5$) (3) was synthesized as a reference. Due to the redistribution of the phosphine ligands during its
preparation, cluster 1 exists as a mixture of three interconverting isomers in a 4.7:3.4:1.0 ratio (1a:1b:1c, see Figure 1). The presence of the two PPh₃ ligands is required in order to prevent rapid thermal dimerisation of the trinuclear cluster core as observed for the parent decacarbonyl [Os₂Pt(CO)₁₀]. In line with our intention to activate small molecules by transition metal clusters, the interest in clusters 2 and 3 originates from the ability of the mononuclear complexes [Rh(CO)₂(η⁵-C₅R₅)] (R = H, Me) to activate C-H and Si-H bonds upon UV irradiation. In contrast to the previous Chapters, the results described in this Chapter are yet unsupported by density functional theoretical (DFT) calculations or time-resolved IR and UV-vis absorption studies. Although this prevents thorough characterization of the reactive excited states and the primary photoproducts, respectively, a tentative assignment of the primary photoprocesses is made based on the nature of the ultimate photoproducts.

7A.3 Experimental section

Materials and preparations. CO (99.5%, Hock Loos), PPh₃ (Aldrich), 1-octene (Sigma), ferrocene (BDH) and Et₃SiH (Acros) were used as purchased. Solvents of analytical grade (Acros: dichloromethane (CH₂Cl₂), hexane, pentane, tetrahydrofuran (THF)) were freshly distilled from sodium wire (hexane, pentane, THF) or CaH₂ (CH₂Cl₂) under an atmosphere of dry N₂. Silica 60 (70-230 mesh, Merck) for column chromatography was activated by heating in vacuo at 450 K overnight and stored under N₂. Preparative TLC was performed on Silica Gel G plates (20x20 cm, 1.000 μm, Analtech). The supporting electrolyte Bu₄NPF₆ (Aldrich) was recrystallized twice from ethanol and dried in vacuo at 350 K overnight.

Synthetic procedures. All syntheses were performed under an atmosphere of dry N₂, using standard Schlenk techniques. The complexes [Os₂(CO)₆(μ-η¹,η¹-C₅H₅)], [Pt(η²-C₂H₄)(PPh₃)₂] and [Rh(CO)₂(η³-C₅R₅)] (R = H, Me) were prepared according to published procedures. For the synthesis of [Os₂Pt(CO)₆(PPh₃)₂] and [Os₂Rh(CO)₆(C₅R₅)] (R = H, Me) we followed similar procedures as employed by Takats et al.

Synthesis of [Os₂Pt(CO)₆(PPh₃)₂] (1). A solution of [Pt(η²-C₂H₄)(PPh₃)₂] (242.5 mg, 0.32 mmol) in 20 ml THF was added to a stirred solution of [Os₂(CO)₆(μ-η¹,η¹-C₅H₅)] (182 mg, 0.29 mmol) in 20 ml THF. Next, the mixture was stirred overnight (ca. 16 h) at room temperature after which the solvent was removed in vacuo. Purification of the crude product by column chromatography over silica (hexane/CH₂Cl₂ gradient elution) yielded cluster 1 as an orange powder in 30% yield. ¹H NMR (CDCl₃): δ 7.3-7.6 (m, 30H, P(C₆H₅)₃). ³¹P{¹H} NMR (CDCl₃): δ 20.4 (s, br), 3.52 (s, br). IR ν(CO) (hexane): 2074 (w), 2032 (vs), 2025 (sh), 2012 (m), 1990 (s), 1984 (s), 1969 (m), 1957 (m), 1949 (sh), 1943 (sh) cm⁻¹. UV-vis (hexane) λₘₐₓ (εₘₐₓ in M⁻¹ cm⁻¹): 256 (sh), 312 (sh), 361 (sh), 423 (5.2 x 10⁵)
nm. Cyclic voltammetry (10⁻¹ M cluster in THF/10⁻¹ M Bu₄NPF₆, T = 293 K, v = 100 mV s⁻¹): \(E_{pa} = -2.40\) V (irreversible reduction), \(E_{pa} = +0.33\) V (irreversible oxidation) vs Fe/Fe⁺.

**Synthesis of [Os₂Rh(CO)₉(C₅R₅)] (R = Me (2), H (3)).** A solution of [Rh(CO)₉(C₅Me₅)] (77 mg, 0.26 mmol) in 5 ml of hexane was added to a stirred solution of [Os₂(CO)₆(η²-η²-C₅H₄)] (150 mg, 0.24 mmol) in 60 ml hexane. The resulting solution was heated to 45-50°C for 16 h. After this period, the solvent was removed in vacuo. Purification of the crude product by column chromatography over silica (pentane/CH₂Cl₂ gradient elution) and recrystallization from pentane (190 K) yielded cluster 2 as red crystals in 43% yield. Cluster 3 was prepared by the same procedure. [Os₂(CO)₆(η²-η²-C₅H₄)] (180 mg, 0.28 mmol) and [Rh(CO)₉(C₅H₅)] (77 mg, 0.34 mmol) gave red crystals of cluster 3 in 50% yield.

[Os₂Rh(CO)₉(C₅Me₅)] (2): ¹H NMR (CDCl₃): δ 1.87 (s, 15H, C₅Me₅). IR ν(CO) (pentane): 2096 (m), 2049 (s), 2017 (s), 2007 (s), 1998 (m), 1987 (m), 1974 (w), 1953 (vw) cm⁻¹. UV-vis (hexane): 266, 317, 380, 466, 522 (sh) nm. Cyclic voltammetry (10⁻¹ M cluster in THF/10⁻¹ M Bu₄NPF₆, T = 293 K, \(v = 100\) mV s⁻¹): \(E_{pa} = -1.77\) V (irreversible reduction), \(E_{pa} = +0.32\) V (irreversible oxidation) vs Fe/Fe⁺.

[Os₂Rh(CO)₉(C₅H₅)] (3): ¹H NMR (CDCl₃): δ 5.48 (s, 5H, C₅H₅). IR ν(CO) (pentane): 2106 (w), 2060 (s), 2027 (s), 2015 (s), 2009 (sh), 1997 (s), 1984 (w), 1967 (w) cm⁻¹. UV-vis (hexane): 254, 285, 367, 429, 507 (sh) nm. Cyclic voltammetry (10⁻¹ M cluster in THF/10⁻¹ M Bu₄NPF₆, T = 293 K, \(v = 100\) mV s⁻¹): \(E_{pa} = -1.81\) V (irreversible reduction), \(E_{pa} = +0.56\) V (irreversible oxidation) vs Fe/Fe⁺.

**Synthesis of [Os₂Rh(CO)₉(η=C₅Me₅)(Et₃SiH₆)] (n = 1 (2a); n = 2 (2b)).** A solution of cluster 2 (20 mg, 0.023 mmol) in 20 ml 10⁻¹ M Et₃SiH in hexane was irradiated with a 125 W high-pressure Hg lamp using a 313 nm interference filter. The reaction was monitored by IR spectroscopy and irradiation was stopped when no further increase of the ν(CO) bands of 2a was observed (ca. 70% conversion, 7 h). After removal of the solvent, the crude product was purified by preparative TLC (hexane/CH₂Cl₂ 10:1), yielding cluster 2a as a purple solid. Cluster 2b was prepared by a similar procedure. After irradiation of cluster 2 dissolved in hexane/10⁻¹ M Et₃SiH for 30 h, the solvent was removed in vacuo. Purification of the crude product by column chromatography over silica, using hexane as an eluent, yielded cluster 2b as a deep red solid in ca. 90% yield.

[Os₂Rh(CO)₉(η=C₅Me₅)(Et₃SiH₆)] (2a): ¹H NMR (CDCl₃): δ 1.90 (s, 15H, C₅Me₅), 0.96 (m, 15H, Et₃Si), -16.1 (d, \(JṛH₂H = 26.4\) Hz, 1H, Rh-(η-H)-Os). IR ν(CO) (hexane): 2083 (m), 2031 (m), 2012 (vs), 1994 (w), 1986 (m), 1976 (m), 1971 (m) cm⁻¹. FAB⁺ MS: 960.01 [M⁺] (calc. 960.00), 843.9 [M⁻]-Et₃SiH (calc. 843.9), [M⁻]-nCO (n = 1-8).

[Os₂Rh(CO)₉(η=C₅Me₅)(Et₃SiH₆)] (2b): ¹H NMR (CDCl₃): δ 1.92 (s, 15H, C₅Me₅), 0.99 (m, 30H, Et₃Si), -16.0 (d, \(JṛH₂H = 24\) Hz, 1H, Rh-(η-H)-Os), -16.4 (s, 1H, Os-(η-H)-Os). IR ν(CO) (hexane): 2091 (w), 2049 (w), 2009 (vs), 1992 (s), 1969 (m) cm⁻¹. FAB⁺ MS: 1048.13 [M⁺] (calc. 1048.11), 932.0 [M⁻]-Et₃SiH (calc. 932.0), [M-Et₃SiH⁻]-nCO (n = 1-7).

**Spectroscopic measurements.** FT-IR spectra were recorded on Bio-Rad FTS-7 and Bio-Rad FTS-60A spectrometers (16 scans at 2 cm⁻¹ resolution), the latter being equipped with a dual-source Digital
Model 896 interferometer and a nitrogen-cooled MCT detector. The sample compartment of the Bio-Rad FTS-60A spectrometer was modified to allow \textit{in situ} laser irradiation into a thermostated cell. Electronic absorption spectra were recorded on a Hewlett-Packard 8453 diode-array spectrophotometer. $^1$H NMR spectra were recorded on a Bruker AMX 300 (300.13 MHz for $^1$H) spectrometer and mass spectra on a JEOL JMS SX/SX102A four-sector mass spectrometer.

\textbf{Photochemistry.} All photochemical samples were prepared under a nitrogen atmosphere, using standard inert gas techniques, and typically $10^{-3}$-10$^{-4}$ mol dm$^{-3}$ cluster concentrations. As light source for continuous-wave photochemical experiments served a Spectra Physics 2016 argon-ion laser or a Philips HPK 125 W high-pressure Hg lamp equipped with appropriate cut-off or interference filters. Low-temperature IR measurements were performed using an Oxford Instruments DN 1704/54 liquid nitrogen-cooled cryostat with CaF$_2$ windows.

\textbf{Electrochemistry.} Cyclic voltammograms (CV) of approximately $10^{-3}$ M parent clusters in $10^{-1}$ M Bu$_4$NPF$_6$ electrolyte solution were recorded using the set-up described in Chapter 2.

\section*{7A.4 Results and Discussion}

\textbf{Continuous-wave photochemistry of [Os$_2$Pt(CO)$_8$(PPh$_3$)$_2$] (1)}

The electronic absorption spectrum of cluster 1 in hexane is presented in Figure 2. [Os$_2$Pt(CO)$_8$(PPh$_3$)$_2$] possesses a broad, lowest-energy absorption band at 423 nm ($e_{\text{max}} = 5.2 \times 10^3$ M$^{-1}$ cm$^{-1}$), with a negligible solvatochromic shift in solvents of different polarity. In order to initiate photoreactions from the low-lying excited states, solutions of cluster 1 were irradiated with a high-pressure Hg lamp using a cut-off filter transparent at $\lambda_{\text{irr}} > 420$ nm. For comparison, the homonuclear cluster [Os$_6$(CO)$_{12}$] becomes photoreactive only in the presence of Lewis bases (e.g. alkenes, phosphines) upon irradiation into the two lowest-energy bands in hydrocarbon solvents.$^{21,22}$

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{UV-vis spectrum of cluster 1 in hexane at 293 K.}
\end{figure}
In contrast to \([\text{Os}_3(\text{CO})_{12}]\), irradiation of cluster 1 in neat hexane resulted in fragmentation of the cluster. In the course of the irradiation, the IR spectra showed the disappearance of the \(v(\text{CO})\) bands of the parent cluster and the simultaneous appearance of \(v(\text{CO})\) bands due to the mononuclear complex \([\text{Os}(\text{CO})_4(\text{PPh}_3)]\) (4)\(^{23}\) (Table 1). In addition, other new \(v(\text{CO})\) bands belong to \([\text{Os}_3(\text{CO})_{12}]\)\(^{24}\) and one or more unassigned carbonyl compounds. The formation of the mononuclear complex 4 was confirmed by \(^{31}\text{P}\{\text{H}\} NMR spectra recorded before and after \textit{in situ} irradiation of 1 in CD\(_2\)Cl\(_2\) in the NMR tube. A new signal due to 4 was observed at \(8.71\) ppm, in good agreement with the reported literature value.\(^{25}\) Unfortunately, no fragments or clusters of higher nuclearity containing one or more platinum (carbonyl) centres could be detected and characterized.

Analogous to the clusters \([\text{Os}_3(\text{CO})_{16}\text{(diene)}]\) (diene = 1,3-cyclohexadiene, 1,3-butadiene)\(^{26}\) described in Chapter 3, the photofragmentation of cluster 1 presumably involves the formation of mono- and binuclear intermediates that are coordinatively unsaturated and therefore highly reactive. In order to test this hypothesis, we performed the irradiation experiments in the presence of a suitable Lewis base and monitored the reactions with IR spectroscopy. Irradiation of 1 in 1-octene-containing hexane resulted in IR spectral changes similar to those observed in the neat solvent (\textit{vide supra}). Again, the formation of \([\text{Os}_3(\text{CO})_{12}]\) and complex 4 is indicative of the photofragmentation of the starting cluster. No \(v(\text{CO})\) bands due to \([\text{Os}(\text{CO})_4(\text{alkene})]\)\(^{27}\) and/or \([\text{Os}(\text{CO})_3(\text{alkene})_2]\)\(^{28}\) were observed in the course of the experiment, indicating that the coordinatively unsaturated fragments formed shortly after excitation are too reactive to be stabilized by 1-octene at 293 K. Visible irradiation (\(\lambda_{\text{vis}}>420\) nm) of 1 in CO-saturated hexane also yielded complex 4 as the major photoproduct. Surprisingly, the IR spectra in this case did not reveal the formation of \([\text{Os}_3(\text{CO})_{12}]\). Repeating the latter experiment at 213 K resulted in the appearance of new \(v(\text{CO})\) bands at 2036 and 1991 cm\(^{-1}\) that are attributed to the mononuclear complex \([\text{Os}(\text{CO})_5]\).\(^{29}\) The latter photoproduct most likely results from the rapid capture of free CO by the unsaturated \{Os(CO)\}_4^+ moiety, formed upon photodissociation of the cluster core.\(^{30}\) At room temperature, \([\text{Os}(\text{CO})_5]\) is highly unstable and therefore not observed.\(^{29, 31}\) Aimed at stabilizing the platinum(0) carbonyl centre after photodissociation of the cluster core, we irradiated cluster 1 in the presence of excess PPh\(_3\). Besides the formation of complex 4, a new product was observed, possessing a \(v(\text{CO})\) band at 1900 cm\(^{-1}\). In accordance with the literature\(^{32}\) the latter band is ascribed to the mononuclear complex \([\text{Os}(\text{CO})_5(\text{PPh}_3)]\). As complex 4 does not absorb above 420 nm, its photodissociation to give \([\text{Os}(\text{CO})_3(\text{PPh}_3)]\) and CO, followed by rapid capture of PPh\(_3\), is unlikely.\(^{31}\) The observation of \([\text{Os}(\text{CO})_4(\text{PPh}_3)]\) and \([\text{Os}(\text{CO})_3(\text{PPh}_3)_2]\) therefore presumably results from trapping of PPh\(_3\) by the separate, unsaturated \{Os(CO)\}_4^+ and \{Os(CO)_3(PPh)_3\} fragments, respectively, originating from the starting cluster (see Figure 1). Unfortunately, no \(v(\text{CO})\) band of the mononuclear complex
[Pt(CO)(PPh₃)₃] was observed. Attempts to detect the related platinum complexes [Pt(PPh₃)₄]³⁺ and [Pt(PPh₃)₃]⁴⁺ by ³¹P{H} NMR spectroscopy were also unsuccessful.

Summarizing the results described above, the phosphine-substituted cluster 1 undergoes efficient photofragmentation into unsaturated osmium and platinum carbonyl fragments. The osmium fragments, {Os(CO)₃(PPh₃)} and {Os(CO)₄}, could be stabilized by coordination of added PPh₃ or CO at low temperatures. No platinum-containing photoproducts could be detected. In general, platinum carbonyl clusters of higher nuclearity, both with²⁶-²⁸ and without²⁹,³⁰ PPh₃ co-ligands, require stabilization by multiple carbonyl bridges. As no v(CO) bands were detected in the bridging carbonyl region, the efficient reclustering of unsaturated platinum carbonyl centres formed upon fragmentation seems highly improbable. The formation of high-nuclearity platinum clusters without additional CO ligands or the precipitation of Pt(0) from the solution may therefore seem more likely.

In agreement with the observed reactivity and the results reported earlier for [M₃(CO)₁₂] (M = Ru, Os) and [Os₃(CO)₁₀(diene)], the primary photoprocess upon irradiation into the lowest-energy absorption band of 1 most likely concerns cleavage of a metal-metal bond(s). It remains, however, to be investigated which metal-metal bond is initially cleaved (Os-Os or Os-Pt) and whether the bond cleavage reaction takes place from an excited state having, for example, predominant σ(M-M)σ*(M-M) character, as reported for [Ru₃(CO)₁₂],²² or σ(M-M)π*(CO) character, as argued for the clusters [Os₃(CO)₁₀(diene)] (see Chapter 3). In order to address these problems and to unravel the composition of the frontier orbitals, theoretical support from DFT calculations is needed. Time-resolved UV-vis and IR absorption spectroscopic studies should support the DFT results and give more insight into the nature of the primary photoproduct.

**Continuous-wave photochemistry of [Os₂Rh(CO)₉(Cp*)] (2)**

The electronic absorption spectra of clusters 2 and 3 in hexane are presented in Figure 3. Both clusters possess several distinct bands in the region 250-500 nm together with a weak absorption tailing to ca. 600-650 nm. In particular, the lowest-energy band of cluster 2 and the band at 317 nm are slightly shifted to longer wavelengths compared to the corresponding bands of cluster 3. A similar shift of the lowest-energy absorption band to longer wavelengths compared to that of its non-methylated Cp-analogue was observed for the mononuclear complex [Rh(CO)₂(Cp*)].⁴¹ This trend is explained by the increased electron density on the methylated cyclopentadienyl ring that raises the energy of the highest occupied molecular orbitals of the compounds. In order to initiate photoreactions from both the lowest- and higher-lying excited states, solutions of cluster 2 were irradiated with a continuous-wave argon-ion laser (λ irr = 476 nm) and a high-pressure Hg lamp (λ irr = 313 nm), respectively.
In contrast to the cluster $[\text{Os}_2\text{Pt}(\text{CO})_8(\text{PPh}_3)_2]$ (1), irradiation into the lowest-energy absorption band of cluster 2 in neat hexane did not trigger any significant photochemical reaction. In order to decide whether the photostability in this solvent is caused by the inertness of the excited state or by a rapid and complete backreaction of transients to the parent cluster, we performed photoreactivity studies of $[\text{Os}_2\text{Rh}(\text{CO})_9(\text{Cp}^*)]$ in the presence of PPh$_3$ and 1-octene.

### Table 1. IR $\nu$(CO) wavenumbers of the photoproducts of clusters 1 and 2.

<table>
<thead>
<tr>
<th>Cluster$^a$</th>
<th>$T$ [K]</th>
<th>Solvent</th>
<th>Photoproduc t</th>
<th>$\nu$(CO) [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^b$</td>
<td>298</td>
<td>hexane</td>
<td>4$^e$</td>
<td>2062, 1983, 1946</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$[\text{Os}<em>3(\text{CO})</em>{12}]^f$</td>
<td>2070, 2037, 2012, 2003</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>not assigned</td>
<td>2055, 2027, 2019, 1973, 1963</td>
</tr>
<tr>
<td>1$^b$</td>
<td>298</td>
<td>hexane/PPh$_3$</td>
<td>4$^e$</td>
<td>2061, 1982, 1946</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$[\text{Os}(\text{CO})_3(\text{PPh}_3)_2]^h$</td>
<td>1900</td>
</tr>
<tr>
<td>1$^b$</td>
<td>298</td>
<td>hexane/1-octene</td>
<td>4$^e$</td>
<td>2062, 1983, 1946</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$[\text{Os}<em>3(\text{CO})</em>{12}]^f$</td>
<td>2070, 2036, 2011, 2002</td>
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<td></td>
<td></td>
<td>not assigned</td>
<td>2052, 2018, 1975</td>
</tr>
<tr>
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<td>298</td>
<td>hexane/CO</td>
<td>4$^e$</td>
<td>2062, 1983, 1946</td>
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<tr>
<td>1$^b$</td>
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<td>4$^e$</td>
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<td></td>
<td>$[\text{Os}(\text{CO})_3]^i$</td>
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<td>not assigned</td>
<td>2070, 2045, 2024, 2001, 1960, 1807, 1782, 1721</td>
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<td>2$^c$</td>
<td>298</td>
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<td>$[\text{Os}<em>3(\text{CO})</em>{12}]^f$</td>
<td>2070, 2037, 2011, 2002</td>
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<td>not assigned</td>
<td>2020, 1991</td>
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<td>2$^c$</td>
<td>298</td>
<td>hexane/1-octene</td>
<td>$[\text{Os}(\text{CO})_3(\eta^2$-1-octene)]$^e$</td>
<td>2105, 2017, 1991</td>
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<td></td>
<td>$[\text{Rh}(\text{CO})_2(\text{Cp}^*)]^g$</td>
<td>2027, 1964</td>
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<td></td>
<td></td>
<td></td>
<td>$[\text{Rh}(\text{CO})(\text{Cp}^*)(\text{1-octene})]^h$</td>
<td>1964</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>not assigned</td>
<td>2079, 1987, 1971</td>
</tr>
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</table>

$^a$ Assignment given in the main text. $^b$ $\lambda_{\text{irr}} > 420$ nm. $^c$ $\lambda_{\text{irr}} = 476$ nm. $^d$ $\lambda_{\text{irr}} = 313$ nm. $^e$ Ref. 27. $^f$ Ref. 24. $^g$ Ref. 41. $^h$ $[\text{Rh}(\text{CO})(\text{Cp}^*)(\text{cyclooctene})]$ $\nu$(CO) (hexane): 1962 cm$^{-1}$ (Ref. 41).
Prolonged irradiation ($\lambda_{\text{irr}} = 476$ nm) of cluster 2 in the presence of PPh$_3$ resulted in the appearance of weak v(CO) bands at 2070, 2037, 2011 and 2002 cm$^{-1}$ that are attributed to the homonuclear cluster [Os$_3$(CO)$_{12}$]$^{24}$ (see Table 1). The observation of minor amounts of the latter cluster points to an inefficient photofragmentation process, resulting in the formation of unsaturated {Os(CO)$_4$} moieties. Besides [Os$_3$(CO)$_{12}$], the IR spectra also revealed the formation of the mononuclear complexes [Os(CO)$_4$(PPh$_3$)] $^{23}$ [Os(CO)$_3$(PPh$_3$)$_2$]$^{32}$ [Rh(CO)(Cp*)(PPh$_3$)]$^{14}$ and [Rh(CO)$_2$(Cp*)]$^{41}$. Control experiments, however, showed that the latter mononuclear complexes most likely result from a slow thermal reaction of cluster 2 with excess PPh$_3$. When cluster 2 was irradiated in hexane containing 10$^{-3}$ M 1-octene, an inefficient conversion of the starting cluster (15-20% after 1h) into the fragmentation products [Os(CO)$_4$(η$^2$-octene)]$^{27}$ [Rh(CO)$_2$(Cp*)] and [Os$_3$(CO)$_{12}$] was observed. In agreement with the literature value for [Rh(CO)(Cp*)(cyclooctene)],$^{41}$ the lowest-frequency v(CO) band of [Rh(CO)$_2$(Cp*)] at 1964 cm$^{-1}$ may, however, also be attributed to the alkene complex [Rh(CO)(Cp*)(1-octene)]. Both results indicate that irradiation into the lowest-energy absorption band of 2 results in population of an excited state with poorly activated metal-metal and metal-CO bonds (vide infra).

Figure 3. UV-vis spectra of clusters 2 (- -) and 3 (---) in hexane at 293 K.

Photolysis of the mononuclear complexes [Rh(CO)$_2$(η$^5$-C$_5$R$_5$)] (R = H, Me) in the presence of Et$_3$SiH is known to result in the formation of the silyl hydride complexes [Rh(CO)(η$^5$-C$_5$R$_5$)(SiEt$_3$)H] with quantum efficiencies strongly dependent on the irradiation wavelength and the solvent.$^{14, 15}$ In order to explore whether light-induced Si-H bond activation is also feasible when the {Rh(CO)(Cp*)} unit is incorporated in a heteronuclear cluster core, cluster 2 was irradiated at $\lambda_{\text{irr}} = 313$ nm in the presence of excess Et$_3$SiH. In the course of the irradiation, the IR spectra showed a rather slow disappearance of the v(CO) bands of the parent cluster and simultaneous appearance of the v(CO) bands due to a photoproduct 2a. When the conversion reached ca. 60-65 %, photoproduct 2a converted into
a second photoproduct, denoted as 2b. Prolonged irradiation yielded 2b as the final photoproduct in nearly quantitative yield. Both 2a and 2b were obtained in a pure form by preparative photolysis followed by thin-layer or column chromatography, and characterized by IR and NMR spectroscopies and mass spectrometry (see Experimental). Compared to cluster 2, the 1H NMR spectrum of 2a showed two additional resonances at \( \delta 0.96 \) (m, 15H) and \(-16.1\) (d, 1H, J\(^{1H}-H = 26.4\) Hz), which agree with the oxidative addition of one Et\(_3\)SiH molecule to the cluster core. The J\(^{1H}-H\) coupling constant for the high-field doublet is, however, significantly smaller than observed for the terminally bound hydrides in the mononuclear complexes [Rh(CO)(η\(^5\)-C\(_5\)R\(_5\))(SiEt\(_3\))H] (R = H, J\(^{1H}-H = 33.8\) Hz, R = Me, J\(^{1H}-H = 37.4\) Hz\(^{14}\)). In fact, it more closely resembles J\(^{1H}-H\) measured for the mixed-metal cluster [Os\(_2\)Rh\(_2\)(μ-H)\(_2\)(Cp\(^*)(CO)\(_7\)] (J\(^{1H}-H = 26\) Hz\(^{13}\)) in which one of the hydrides is bridging over an Os-Rh bond. The detection of an additional hydride resonance at \(-16.4\) (s, 1H) in the \( ^1H \) NMR spectrum of 2b points to the subsequent activation of a second Et\(_3\)SiH molecule. This is unambiguously confirmed by the increased number of aliphatic protons in the low-field region of the spectrum and by mass spectrometry, where the position of the molecular ion (\( m/z = 1048.13 \)) agrees with the substitution of two CO molecules by Et\(_3\)SiH. The absence of a rhodium coupling to the second hydride resonance strongly suggests that the corresponding hydride is either terminally bound to one of the osmium atoms or occupies a bridging position over the Os-Os bond. In accordance with the proposed structure of [Os\(_3\)(CO)\(_{11}\)(SiEt\(_3\))(μ-H)]\(^{44}\) and the structurally characterized clusters [Os\(_3\)(μ-H)\(_2\)(CO)\(_{10}\)(SiHPh\(_2\))H]\(^{45, 46}\) and [Os\(_3\)(μ-H)\(_3\)(CO)\(_9\)(SiMeCl\(_2\))\(_3\)]\(^{47}\), which all show resonances for the bridging hydrides in the range of \(-16.6\) to \(-18.7\) ppm, oxidative addition of the second Et\(_3\)SiH to the \{Os\(_2\)(CO)\(_8\)\} moiety of 2a most likely results in a bridging hydride between both osmium centres,\(^{48}\) with the silyl group being terminally bound to one of the osmium atoms in an equatorial position. The question remains, however, whether the silyl group in the primary photoproduct 2a is also coordinated to osmium or that it preferably resides at the rhodium centre. In this regard it is important to note that although thermal reactions of [Os\(_3\)(CO)\(_{12}\)] with HSiXCl\(_2\) (X = Me, Cl) resulted in the formation of the trisubstituted clusters [Os\(_3\)(μ-H)\(_3\)(CO)\(_9\)(SiXCl\(_2\))\(_3\)]\(^{47}\) an oxidative addition of two HSiR\(_3\) groups to [Os\(_3\)(CO)\(_{12}\)] with retention of the trisodium core has never been reported. Instead, thermal reactions of the bis(acetonitrile) derivative [Os\(_3\)(CO)\(_{10}\)(MeCN)\(_2\)] with an excess of HSiR\(_3\) (R = Et, (OEt), (OMe)) or HSiHPh\(_2\) in all cases afforded only monosubstituted products [Os\(_3\)(μ-H)(CO)\(_{10}\)(MeCN)(SiR\(_3\))]\(^{44}\). Based on these results, irradiation of cluster 2 in the presence of Et\(_3\)SiH is proposed to result in the cleavage of the Rh-CO bond, followed by rapid oxidative addition of Et\(_3\)SiH to the rhodium centre. Prolonged irradiation of 2a results in the loss of a second CO molecule at one of the osmium sites, leading to the ultimate photoproduct 2b. The proposed structures of both photoproducts are schematically depicted in Figure 3.
Figure 4. Proposed structures for the photoproducts \([\text{Os}_2\text{Rh(Cp*)(CO)}_8(\text{SiEt}_3)(\mu-\text{H})]\) (2a) and \([\text{Os}_2\text{Rh(Cp*)(CO)}_7(\text{SiEt}_3)_2(\mu-\text{H})_2]\) (2b).

The subsequent formation of 2a and 2b provides a nice example of the stepwise activation of the different metal centres within a heteronuclear cluster core. In addition, the formation of 2b is the first example of the light-induced formation of a triangular silyl-substituted osmium cluster. For comparison, irradiation of \([\text{Os}_3(\text{CO})_{12}]\) in the presence of HSiR$_3$ generally results in photofragmentation into mononuclear complexes.$^{49}$ The fact that no significant photochemical reaction was observed upon prolonged irradiation ($\lambda_{\text{in}} = 313$ nm) of cluster 2 in CO-saturated hexane, strongly supports the conclusion that CO loss is most likely the primary photoprocess upon near-UV irradiation.

The wavelength-dependent photochemistry of cluster 2 closely resembles that observed for its separate precursors \([\text{Rh(CO)}_2(\eta^5-C_5R_5)]\) ($R = \text{H}, \text{Me})^{14, 41}$ and \([\text{Os}_3(\text{CO})_{12}]$.\textsuperscript{21} As the latter cluster hardly absorbs above 450 nm, the lowest-energy absorption band of 2 most likely results from the introduction of the \{Rh(CO)(Cp*)\} moiety. This holds in particular for the long-wavelength absorption tailing to 600 nm, which closely resembles the lowest-energy band of \([\text{Rh(CO)}_2(\text{Cp*})].^{41}$ Quantum chemical calculations on the analogous \([\text{Rh(CO)}_2(\text{Cp})]\) complex\textsuperscript{50} have shown that the lowest-energy absorption band of this type of systems belongs to transitions from occupied Rh-Cp bonding and anti-bonding orbitals to Rh-CO non-bonding orbitals with Rh, C and O Rydberg orbital characters. As a result, population of the lowest-lying excited state does not affect the Rh-CO bonds but is proposed to induce a reversible ring-slippage ($\eta^5 \rightarrow \eta^3$) of the cyclopentadieny1 ligand.$^{14}$ Most likely, the lowest excited state of cluster 2 has a character similar to that of \([\text{Rh(CO)}_2(\text{Cp*})]. This is inferred from the inefficient photochemistry observed upon irradiation into the lowest-energy absorption band of 2, even in the presence of suitable Lewis bases. In addition, the oxidation potential of cluster 2 (+ 0.32 V) is clearly less positive compared to that of its Cp analogue 3 (+ 0.56 V), while the reduction potentials of both clusters are almost identical. These results indicate that the Rh/Cp(*) centres indeed contribute significantly to the HOMO of clusters 2 and 3 while their participation in the LUMO is negligible. The shift of the lowest-energy absorption band to longer wavelengths upon methylation of the Cp ring (Figure 3), supports the latter
conclusion. In contrast to the common reactivity pattern observed for the clusters 
[Os3(CO)12], [Os3(CO)10(diene)] and [Os2Pt(CO)8(PPh3)2] (1), the introduction of the 
{Rh(CO)(Cp*)} moiety in the triangular cluster core therefore prevents the efficient cleavage 
of a metal-metal bond upon irradiation into the lowest-energy absorption band.

The primary photoprocess upon short-wavelength photolysis of cluster 2 (λ_\text{irr} = 313 nm) 
most likely involves the cleavage of the Rh-CO bond. A similar photoprocess has been 
oberved upon irradiation into the 314 nm band of [Rh(CO)2(Cp*)], although the quantum 
yield for this reaction is rather low.\textsuperscript{15} The low efficiency in the latter case has been explained 
by the presence of an intense, close-lying Cp*-to-Rh/CO transition that reduces the 
proportion of the metal-to-CO charge transfer transition in the corresponding absorption 
band.\textsuperscript{50} Irradiation into the latter band therefore largely results in a similar non-productive 
ring-slippage reaction as postulated upon irradiation into the lowest-energy band of 
[Rh(CO)2(Cp*)]. Interestingly, the shift of the 317 nm band of cluster 2 to longer wavelength 
compared to the corresponding band of 3 closely resembles that observed for the lowest-
energy band of this cluster. In line with the assignment of the latter band (vide supra), the 317 

nm band of 2 is therefore proposed to have a similar contribution from an intense Cp*-to-
Rh/CO transition as reported for [Rh(CO)2(Cp*)]. This explains the relatively slow 
conversion of 2 into 2a in the presence of Et3SiH and demonstrates that the intrinsic 
photochemical reactivity of the {Rh(CO)(Cp*)} moiety in cluster 2 is still maintained. Apart 
from the contribution from the Rh/Cp* centre, the absorption band at 317 nm is also close in 
energy to the 325 nm band of [Os3(CO)12]. As irradiation into the latter band is also reported 
to result in photodissociation of CO,\textsuperscript{21} the loss of a second CO ligand at one of the osmium 
centres upon prolonged irradiation of 2a is explained accordingly.

Summarizing the above results, the mixed-metal cluster [Os2Rh(CO)9(Cp*)] (2) shows 

wavelength-dependent photochemistry, closely resembling that observed for its separate 
precursors. The lowest-lying excited state of 2 is assumed to be localized on the 
{Rh(CO)(Cp*)} moiety. Its population does not give rise to significant photochemical reactivity but most likely induces a reversible ring-slippage of the Cp* ligand. In line with the 
observed reactivity of [Rh(CO)2(Cp*)] and [Os3(CO)12], near-UV irradiation of 2 in the 
presence of Et3SiH results in the stepwise, Rh- and Os-localized loss of two CO ligands and 
provides a nice example of the separate activation of two different metal centres within a 
heteronuclear cluster core. Likewise for cluster 1, more insight into the nature of the frontier 
orbitals and the character of the lowest- and higher-lying excited states of cluster 2 will no 
doubt be gained from DFT calculations.
7A.5 Conclusions

The experimental results document that the replacement of an \{Os(CO)₄\} moiety in \[[Osₓ(CO)₁₂]\] by \{Pt(CO)(PPh₃)\} or \{Rh(CO)(Cp*)\} results in a different photochemical reactivity than the parent cluster. Cluster 1 undergoes efficient photofragmentation into \[[Os(CO)₄(PPh₃)]\] and unsaturated osmium and platinum fragments that ultimately produce \[[Osₓ(CO)₁₂]\] and other, yet unassigned carbonyl products. The photochemical reactivity of cluster 2 closely resembles that of the mononuclear complex \[[Rh(CO)₂(Cp*)]\], proving that the frontier orbitals are localized on the separate rhodium and osmium moieties within the cluster core. Consistent with the predominant Cp*-to-Rh/CO character of the lowest excited state, long-wavelength irradiation most likely induces a reversible ring-slippage of the Cp* ligand and does not give rise to efficient bond activation reactions. In contrast, irradiation into the 317 nm band of 2 in the presence of Et₃SiH results in the stepwise activation of two substrate molecules by the different metal centres within the heteronuclear cluster core.

In general, the valuable results of this pioneering study into the photochemical reactivity of triangular heteronuclear transition metal clusters can conveniently be combined with theoretical support from DFT calculations in order to obtain more insight into the composition of the frontier orbitals and the nature of the low-lying excited states. This support and a thorough mechanistic understanding of the photoreactivity are indispensable tools for exploring accurately the photoreactivity of purpose-selected series of homo- and heteronuclear transition metal clusters, in particular those with more delocalized bonding within the cluster core.

7A.6 References

Photoreactivity of the Mixed-Metal Clusters \([\text{Os}_2\text{Pt}(\text{CO})_x(\text{PPh}_3)_2]\) and \([\text{Os}_2\text{Rh}(\text{CO})_9(\eta^1-\text{C}_5\text{Me}_5)]\)


[48] In $^1$H NMR spectra of five isomeric $[\text{Os}_5(\text{CO})_{10}H(\mu-H)(\text{PHEt}_2)]$ clusters the proton resonance due to the terminal hydride ligand occurs at ca. -10 ppm while the signal due to the edge-bridging hydride ligand was found at ca. -20 ppm. S. Aime, R. Gobetto, E. Valls, *Inorg. Chim. Acta.* 1998, 275-276, 521.
