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

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CHAPTER 4

Crystal Structures, Bonding Properties and Redox Behaviour of the Novel Clusters [Os₃(CO)₉(tmbp)(L)] (L = CO, PPh₃)

M. J. Bakker, F. W. Vergeer, F. Hartl, K. Goubitz, J. Fraanje, P. Rosa, P. Le Floch

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Abstract

This chapter describes the syntheses, crystal structures, bonding properties and electrochemical behaviour of the novel cluster [Os₃(CO)₁₀(tmbp)] (1) and its PPh₃-derivative [Os₃(CO)₉(tmbp)(PPh₃)] (2), tmbp denoting the redox-active ligand 4,4′,5,5′-tetramethyl-2,2′-biphosphinine. The 50e-clusters 1 and 2 reveal an unexpected and unprecedented bridging coordination mode of tmbp with both P atoms bridging two metal atoms. The tmbp ligand proved to be formally doubly reduced by electron transfer from the triangular cluster core that, as a result, has lost one metal–metal bond. Theoretical (DFT) calculations show that not only the LUMO, but also the HOMO of 1 have mainly π*(tmbp) character, implying that the lowest-energy excited state has intraligand character. This is in agreement with the observed photostability of cluster 1. DFT calculations predict that the experimentally observed structure for 1 is the most stable one in a series of several structural isomers. The overall two-electron reduction of 1 and 2 leads to dissociation of CO and PPh₃, respectively, and formation of the dianion [Os₃(CO)₉(tmbp)]²⁻. The initially produced radical anions are sufficiently stable to be observed at low temperature with cyclic voltammetry and IR spectrotrochhrochemistry, mainly due to localization of the odd electron on tmbp. The electron-deficiency of the cluster core is responsible for facile electrocatalytic substitution of CO in 1 by more basic tertiary phosphines and phosphites.
Introduction

The diverse photochemical and redox behaviour of the triangular clusters [Os₃(CO)₁₀(α-diimine)] (α-diimine = e.g. 2,2'-bipyridine (bpy), 2,2'-bipyrimidine (bpym), pyridine-2-carbaldehyde-ν'-R-imine (R-PyCa, R = alkyl) has extensively been studied (Figure 1).¹-⁴ Visible irradiation in non- and weakly coordinating solvents (toluene, THF) leads to homolytic cleavage of an Os–Os(α-diimine) bond and reversible formation of short-lived biradical photoproducts [(CO)₄Os⁺–Os(CO)₄–Os(CO)₂(α-diimine⁺)].¹,² Electrochemical reduction of [Os₃(CO)₁₀(α-diimine)] initially gives the radical anions [Os₃(CO)₁₀(α-diimine⁻)], which are thermally unstable and convert to several anionic open-structure products in a series of chemical and electron-transfer steps.³,⁴ Both in the biradical photoproduct and in the radical anion there is an unpaired electron localized on the redox-active α-diimine ligand. As a consequence, the electronic properties of the α-diimine play an important role in the photo- and electrochemistry of the clusters. Decreasing the energy of the lowest empty π*(α-diimine) orbital has shown to improve the ability of the α-diimine to accommodate the electron density, hence increasing the lifetime of the biradical photoproducts as well as the stability of the radical anions.

Figure 1. Schematic molecular structures of the clusters [Os₃(CO)₁₀(bpy)] and [Os₃(CO)₄(tmbp)(L)] (1: L = CO; 2: L = PPh₃), and of the ligands tmbp and bpy.
Closely related to the hitherto used α-diimine ligands is the phosphorus derivative of bpy, viz. 4,4',5,5'-tetramethyl-2,2'-biphosphinin (tmbp) (see Figure 1). It was first synthesized in the early 1990s,⁵ and since then its versatile coordination chemistry has been extensively explored.⁶⁻⁷ Compared to bpy, the π⁺ LUMO of tmbp lies significantly lower in energy, as reflected in the strongly positively shifted reduction potential (E°(tmbp) = -1.85 V and E°(bpy) = -2.20 V vs SCE).⁸ As a consequence, coordinated tmbp is a stronger π acceptor and better stabilizes low oxidation states of the metal in the M(σP,σP'-tmbp) chelate ring in a variety of complexes, such as homoletic [Ni(tmbp)₂] and [W(tmbp)₃].⁹,¹⁰ On the contrary, the rather limited σ-donor ability of neutral tmbp prevents, for example, the preparation of [Ru(tmbp)₃]²⁺.⁷

The fairly different electronic properties of tmbp and bpy inspired us to attempt the synthesis of the cluster [Os₃(CO)₁₀(σP,σP'-tmbp)], aimed at performing a comparative spectroscopic, photo- and electrochemical study. However, instead of the intended product a structural isomer was obtained, presenting the first example of the biphosphinin ligand coordinated to three transition metal centres as a doubly bridging ligand (cluster 1 in Figure 1). This chapter deals with the syntheses, crystal structures and spectroscopic characterization of the novel cluster 1 and its PPh₃-derivative 2 (Figure 1). A theoretical (DFT) study has been performed to obtain insight into their bonding properties. The redox behaviour of 1 and 2 has been investigated in detail and will be compared with that of [Os₃(CO)₁₀(bpy)] and unsubstituted [Os₃(CO)₁₂].

Results and Discussion

Crystal Structures and Spectroscopic Properties of [Os₃(CO)₉(tmbp)(L)] (L = CO and PPh₃)

The precursor cluster [Os₃(CO)₁₀(MeCN)₂] reacts with tmbp in THF at room temperature to give purple [Os₃(CO)₁₀(μ₂-P,μ₂-P'-tmbp)], 1 (Figure 1). Alternatively, [Os₃(CO)₁₀(cis-1,3-butadiene)], with the diene ligand chelated at one osmium centre, can be used as a precursor for 1. Cluster 1 was isolated in high yield and characterized by IR and NMR spectroscopy, mass spectrometry and elemental analysis (Experimental Section).

The crystal structure of 1 (Figure 2, Table 1, see also Figure 1) reveals the unusual coordination of tmbp. Similarly to the four-electron donor 2,2'-bipyridine in [Os₃(CO)₁₀(bpy)], the biphosphinin ligand is chelated at Os(1). At the same time, however, each phosphorus atom forms a bridge between Os(1) and one of the other two osmium centres. Cleavage of the Os(1)–Os(2) bond has resulted in an opening of the osmium triangle (∠Os(1)–Os(3)–Os(2) = 85.93(2)°). Interestingly, in 1 the tmbp ligand is strongly distorted and its aromaticity is lifted. In the majority of its mononuclear complexes, tmbp displays a high degree of aromaticity, the phosphininine rings being perfectly (co-)planar with intraring C–C bond lengths between 1.38 and 1.41 Å.⁶,⁷ In contrast, the C–C bond lengths in 1 range from
Chapte rr  4

Figur ee  2.

Crystal structure of the cluster $[\text{Os}_3(\text{CO})_{10}(\text{tmbp})]$ (I).

Table 1. Selected bond lengths (in Å) and bond angles (in degrees) for 1 with standard deviations in parentheses

<table>
<thead>
<tr>
<th></th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
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<tbody>
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<td>Os1-Os3</td>
<td>2.8856(1)</td>
<td>P2-C10</td>
</tr>
<tr>
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<td>2.441(4)</td>
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</tr>
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<td>Os3-P2</td>
<td>2.376(4)</td>
<td>C5-C10</td>
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<tr>
<td>P1-C1</td>
<td>1.77(2)</td>
<td>Os1-Os3-Os2</td>
</tr>
<tr>
<td>P1-C5</td>
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<td>C2-C3</td>
<td>1.46(3)</td>
<td>P1-Os1-P2</td>
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<tr>
<td>C3-C4</td>
<td>1.38(2)</td>
<td>C1-P1-C5</td>
</tr>
<tr>
<td>C4-C5</td>
<td>1.39(2)</td>
<td>C6-P2-C10</td>
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<tr>
<td>P2-C6</td>
<td>1.78(2)</td>
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</tr>
</tbody>
</table>

1.33(2) Å, typical for isolated C=C bonds, to 1.47(2) Å, close to the value for a single C–C bond (ca. 1.53 Å). Importantly, the interring C–C bond length in 1 is rather short (1.41(2) Å) compared to the characteristic values for the non-reduced uncoordinated ligand (1.49 Å, average of two isomers)\(^8\) and for mononuclear complexes of tmbp (ca. 1.47 Å)\(^6,7\). Also the P–C bonds are rather long (1.77(2)–1.80(2) Å) compared to P–C bond lengths of 'aromatic' tmbp.
Crystal Structures, Bonding Properties and Redox Behaviour of $[\text{Os}_3(\text{CO})_9(\text{tmbp})(\text{L})]$

(1.71–1.74 Å)$^{6,7}$ These data point to reduction of the tmbp ligand by intramolecular electron transfer from the triosmium core, which process also caused the cleavage of the Os(1)–Os(2) bond. Indeed, comparison of the structure of tmbp in $[\text{Os}_3(\text{CO})_{16}(\text{tmbp})]^{-}$ with the crystal structures of free neutral tmbp and its radical anion$^{11}$ and dianion$^{12}$, convincingly demonstrates that in the cluster the ligand can only be considered as doubly reduced. In particular, the close correspondence between the bond distances in coordinated tmbp in $[\text{Os}_3(\text{CO})_6(\text{tmbp})(\text{PPh}_3)]^-$ (the PPh$_3$-derivative of 1, *vide infra*) with those in the free dianion $[\text{tmbp}]^{2-}$ is striking (Figure 3). Also in the latter dianion the phosphinine rings are clearly not co-planar anymore. The lowest unoccupied π* orbital (LUMO) of biphosphinines is antibonding with respect to the P–C bonds, and bonding with respect to the interring C–C bond,$^{13}$ explaining why the electron transfer from the triosmium metal core to the LUMO of tmbp results in elongation of the P–C bonds and shortening of the interring C–C distance. A similar situation applies for several electron-rich neutral and anionic metal complexes such as $[\text{W(tmbp)}_3]$, $[\text{M(tmbp)}_3]^{2-}$ (M = Zr, Hf, Ti) and $[\text{Mn(CO)}_3(\text{tmbp})]^{-}$.$^{10,13-15}$ Another remarkable feature of 1 is the large difference between the two Os–P–Os bridge angles: 75.2(1)$^\circ$ for P(2) spanning the intact Os(1)–Os(3) bond, but 110.0(1)$^\circ$ for P(1) spanning the non-bonded Os(1) and Os(2) centres. The very different environments of both phosphorus atoms are reflected in their $^{31}$P NMR chemical shifts ($\delta$ = 146.2 for P(1) and 26.2 for P(2)). Both values significantly deviate from the strongly positive $^{31}$P chemical shifts for non-reduced 'aromatic' tmbp complexes ($\delta$ 178–250).$^6,7$ The loss of aromaticity is also reflected in the shift of the ring proton signals to lower ppm values by ca. 1.5 ppm, compared to those for free tmbp.

![Figure 3](image-url)

**Figure 3.** Schematic molecular structures with relevant bond distances (in Å) of neutral free tmbp,$^8$ the corresponding radical anion$^{11}$ and dianion,$^{12}$ and of coordinated tmbp in the cluster $[\text{Os}_3(\text{CO})_6(\text{tmbp})(\text{PPh}_3)]$ (2).
Figure 4. *IR spectra of the clusters 1 (solid line) and 2 (dashed line).*

Figure 5. *Crystal structure of the cluster [Os₃(CO)₆(tmbp)(PPh₃)] (2).*
Table 2. Selected bond lengths (in Å) and bond angles (in degrees) for 2 with standard deviations in parentheses

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
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<tbody>
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<td>Os1-Os3</td>
<td>2.8741(7)</td>
<td>1.466(8)</td>
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<td>Os2-Os3</td>
<td>3.003(1)</td>
<td>1.361(8)</td>
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<tr>
<td>Os1-P1</td>
<td>2.418(2)</td>
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<td>1.344(8)</td>
</tr>
<tr>
<td>Os2-P1</td>
<td>2.428(2)</td>
<td>1.45(1)</td>
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<tr>
<td>Os2-P3</td>
<td>2.414(2)</td>
<td>1.36(1)</td>
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<tr>
<td>Os3-P2</td>
<td>2.378(2)</td>
<td>1.437(8)</td>
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<tr>
<td>P1-C1</td>
<td>1.789(6)</td>
<td>Os1-Os3-Os2</td>
</tr>
<tr>
<td>P1-C5</td>
<td>1.823(6)</td>
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<td>P2-C6</td>
<td>1.778(7)</td>
<td>Os1-P2-Os3</td>
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<tr>
<td>P2-C10</td>
<td>1.803(6)</td>
<td>P1-Os1-P2</td>
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<td>C5-C10</td>
<td>1.372(8)</td>
<td>C1-P1-C5</td>
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<tr>
<td>C1-C2</td>
<td>1.355(8)</td>
<td>C6-P2-C10</td>
</tr>
</tbody>
</table>

The phosphine-derivative of 1, the cluster \([\text{Os}_3(\text{CO})_9(tmbp)(\text{PPh}_3)])\) (2), was prepared in high yield from 1 via electrocatalytic substitution of CO by PPh_3. The details of this reaction will follow later in this chapter. The IR \(\nu(\text{CO})\) pattern of 2 resembles that of 1, although its bands are shifted to smaller wavenumbers due to replacement of CO by the more basic phosphine (see Figure 4). In combination with the NMR data it can be concluded that the overall structure of the triosmium biphosphinine cluster 2 is the same as that of 1. In particular, the \(^1\text{H}\) and \(^{31}\text{P}\) NMR spectra show that the two rings of tmbp are inequivalent, the two \(^{31}\text{P}\) resonances of tmbp being shifted from 26.2 and -146.2 ppm for 1 to 25.5 and -134.4 ppm for 2. Furthermore, PPh_3 is not coordinated to Os(1), but either to Os(2) or Os(3), as its \(^{31}\text{P}\) resonance is coupled only to one of the resonances of tmbp (δ -134.4). These presumptions were confirmed by the crystal structure of 2 (see Figure 5, Table 2). The PPh_3 ligand is coordinated to Os(2) in a trans-position to P(1) of tmbp, thereby allowing unambiguous assignment of the \(^{31}\text{P}\) NMR resonances of tmbp in 2 (and indirectly in 1 as well).

The clusters 1 and 2 are the first examples of tmbp compounds where each phosphorus atom of tmbp forms a bridge between two metal centres. The bridging ability of the phosphorus atom in ligands containing only one phosphinine ring has already been reported in the literature. In the dimers \([\text{M}_2(\text{COD})_2(\text{NIPHOS})]_2^{2+}\) (M = Ir, Rh; COD = 1,5-cyclooctadiene; NIPHOS = 2-(2'-pyridyl)-4,5-dimethylphosphinine) the metal-metal bond is bridged by the phosphorus atoms of both phosphinine rings, but the aromaticity of the phosphinine ring remains preserved. More interesting in this respect is the cluster \([\text{Os}_3(\mu-\text{H})_2(\mu^3-(t-\text{Bu-C}_5\text{H}_4\text{P}))\text{(CO)}_3])\) synthesized by Arce and co-workers (Figure 6). The aromaticity of the phosphinine ligand is completely disrupted by ortho-metallation, as
indicated by the two localized C=C bonds in the phosphininine ring. Recently, the dimers [Rh(tmbp)\(_2\)]\(_2\) (Figure 6), [Ru(Cp*)\(_2\)(tmbp)]\(_2\) and [Fe(tmbp)\(_2\)]\(_{2}^{2-}\) were synthesized by Le Floch et al.\(^{18}\) In these dimers two tmbp ligands bridge between the two metal centres through one of their phosphorus atoms. Only in the case of the dimer [Fe(tmbp)\(_2\)]\(_{2}^{2-}\) the aromaticity of the bridging phosphininine rings is disrupted, indicating that the negative charge is mainly localized on the bridging rings of tmbp. In general, tmbp seems to favour a bridging coordination mode in polynuclear transition metal complexes.

![Figure 6](image)

**Figure 6.** Examples of metal complexes with bridging (bi)phosphinine ligands. Left: [Os\(_3\)(\(\mu\)-H)\(_2\)(\(\mu\)-\(\mu\)-\(t\)-Bu-\(C_3\)H\(_4\)P))(CO)\(_2\)] (ref 17); right: [Rh(tmbp)\(_2\)]\(_2\) (ref. 18).

![Figure 7](image)

**Figure 7.** Schematic structure of the 50e-cluster [Os\(_3\)(CO)\(_{10}\)(\(\mu\)-ER)]\(_2\) with only two metal–metal bonds (refs 19, 20).

The structure of cluster 1 is reminiscent of that of [Os\(_3\)(CO)\(_{10}\)(ER)\(_2\)] (E = Se, R = Me, Ph; E = Te, R = Ph) where both ER\(^-\) groups bridge between two osmium centres and again one of the bridged metal–metal bonds is broken (see Figure 7).\(^{19,20}\) According to cluster electron-counting rules cluster 1, [Os\(_3\)(CO)\(_{10}\)(ER)\(_2\)] and related clusters with only two metal-metal bonds should be considered as 50e-clusters.\(^{21}\) Each phosphorus atom of the aromatic biphosphininine is normally a 2e-donor. The crystal structure shows that the P atoms in 1 are
formally sp³-hybridized and therefore comparable to 4e-donating phosphido (PR₂⁻) ligands. If one takes into account the 'localized' phosphinine ring C–C and C=C bonds and the short interring C=C bond, the ligand is indeed best described as the dianion [tmbp]²⁻, while the triosmium core is formally doubly oxidized.

**Table 3. Comparison of the calculated bond lengths (in Å) and bond angles (in degrees) in the model cluster \([\text{Os}_3(\text{CO})_{10}(\text{bp})]\) with the experimental values taken from the crystal structure of \([\text{Os}_3(\text{CO})_{10}(\text{tmbp})]\)**

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**Density Functional Study of \([\text{Os}_3(\text{CO})_{10}(\text{biphosphinine})]\)**

Density functional theoretical (DFT) calculations were performed in order to obtain more insight into the bonding properties of 1. As a model system for 1 served the cluster \([\text{Os}_3(\text{CO})_{10}(\text{bp})]\) (bp = 2,2'-biphosphinine), 1A, with the methyl groups in the tmbp ligand replaced by hydrogen atoms. The optimized geometry for 1A is in good agreement with the experimental structure of 1 (Figure 8, Table 3), although the calculated Os–Os, Os–P and P–C bond distances are slightly longer than the experimental ones. This appears to be a general result of DFT calculations and was also observed for the related complexes \([\text{Os}_3(\text{CO})_{12}]^{22}\), \([\text{Os}_3(\text{CO})_{10}(\text{α-diimine})]^{23}\) and \([\text{W}(\text{tmbp})_3]^{13}\). In the optimized geometry of \([\text{Os}_3(\text{CO})_{10}(\text{bp})]\) the alternation of 'single' and 'double' bonds in the biphosphinine is well reproduced.

The composition of the frontier orbitals of 1A is given in Table 4. In contrast to \([\text{Os}_3(\text{CO})_{10}(\text{bpy})]\) (see Chapter 2), not only the LUMO but also the HOMO have dominant biphosphinine character. In agreement with the reduced state of bp in the cluster, the lowest
\( \pi^* \) orbital (unoccupied in the free ligand) most likely contributes strongly to the HOMO of the cluster 1A.

### Table 4. Energies and composition of the frontier orbitals of [Os\(_3\)(CO)\(_{10}\)(bp)] with the experimentally determined\(^a\) and separately optimized structures

<table>
<thead>
<tr>
<th>MO</th>
<th>Experimental structure</th>
<th>Optimized structure</th>
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<tbody>
<tr>
<td></td>
<td>E(EV)</td>
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<tr>
<td>93a</td>
<td>-3.16</td>
<td>8.5%</td>
</tr>
<tr>
<td>92a (LUMO)</td>
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<tr>
<td>91a (HOMO)</td>
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<tr>
<td>90a</td>
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<tr>
<td>89a</td>
<td>-5.92</td>
<td>47.6%</td>
</tr>
</tbody>
</table>

\(^a\) The crystal structure of cluster 1 was used with the methyl groups of tmbp replaced by hydrogen atoms.

**Figure 8.** Optimized geometries and relative energies (in kJ/mol) of the model cluster 1A and its isomers 1B-E.
Cluster 1 was synthesized with the intention to prepare the structural equivalent of \([\text{Os}_3(\text{CO})_{10}(\text{bpy})]\), with tmbp chelated at a single osmium centre. In this regard, it is interesting to learn whether the theoretical calculations indeed predict the model 1A as the most stable isomer. Figure 8 shows 1A together with a few structural isomers, 1B-E, and the calculated relative energies. The isomers 1B-E have in common that each P atom of bp only coordinates to a single osmium atom (no \(\mu\)-P bridges), but they differ in the coordination of the P atoms relative to the triosmium plane (equatorial or axial), either to the same or to different osmium atoms. Most importantly, isomer 1A has indeed been calculated to be more stable by 30.1 kJ/mol than isomer 1B (the structural equivalent of \([\text{Os}_3(\text{CO})_{10}(\text{bpy})]\)). It cannot be excluded that isomer 1B is the kinetic reaction product, rapidly isomerizing to 1A. Isomer 1B, with one phosphorus axial and the other equatorial, is in turn more stable than isomer 1C with both phosphorus atoms bound equatorially to the same osmium centre. This trend has also been found for the corresponding structures of \([\text{Os}_3(\text{CO})_{10}(\text{bpy})]\). The isomers 1D and 1E, with P atoms bound to different metals, are highest in energy.

**Photostability of 1**

The lowest electronic transition of \([\text{Os}_3(\text{CO})_{10}(\text{bpy})]\) has predominant cluster-core-to-ligand charge transfer character (\(\sigma(\text{Os-Os})-\pi^*(\text{bpy})\)), resulting in an intense and strongly solvatochromic absorption band in the visible spectrum.\(^1\)\(^,\)\(^2\)\(^4\) The UV-vis spectrum of deep-purple cluster 1 shows a broad absorption band at 556 nm. In contrast to the corresponding lowest-energy electronic transition of the bpy-cluster, this band exhibits no solvatochromism (\(\lambda_{\text{max}} = 556 \text{ nm (toluene)}, 556 \text{ nm (THF); } \varepsilon_{\text{max}} = 3.6 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}\), 552 nm (acetonitrile), 559 nm (pyridine)) and apparently lacks charge-transfer character. This is in agreement with the results of DFT calculations (vide supra) that point to the intraligand character of the electronic transition, since the HOMO and LUMO are mainly localized on the biphosphinine ligand.

Cluster 1 is completely photostable upon continuous irradiation into the lowest-energy absorption band in CCl₄, THF, acetonitrile and pyridine at room temperature. No UV-vis transient was observed even on a nanosecond time scale (\(\lambda_{\text{tr}} = 532 \text{ nm, } \tau(\text{laser pulse}) = 7 \text{ ns}\)). Indeed, population of the largely tmbp-localized intraligand excited state is not expected to weaken significantly any metal–ligand or metal–metal bond.

**Redox Behaviour of 1 and 2**

The redox potentials and IR \(\nu(\text{CO})\) wavenumbers of cluster 1, its PPh₃-derivative 2, and their reduction products are summarized in Tables 5 and 6, respectively. All (spectro)electrochemical experiments were performed in THF (unless stated otherwise).
Table 5. Redox potentials of the clusters 1 and 2 and their reduction products\(^a\)

<table>
<thead>
<tr>
<th>Cluster</th>
<th>(E_{pc}(R_1))</th>
<th>(\Delta E_p(R_1/O_1))</th>
<th>(E_{pa}(R_2))</th>
<th>(E_{pa}(O_2(B)))</th>
<th>(E_{pa}(O_2(B')))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.75 (irr)</td>
<td></td>
<td></td>
<td>-1.53</td>
<td>-1.27</td>
</tr>
<tr>
<td>1(^b)</td>
<td>-1.80</td>
<td>123 (156)</td>
<td>-2.19</td>
<td>-1.48</td>
<td>-1.23</td>
</tr>
<tr>
<td>1(^c)</td>
<td>-1.80 (rev)</td>
<td>104 (120)</td>
<td>-2.18</td>
<td>-1.49(^d)</td>
<td>-1.27(^d)</td>
</tr>
<tr>
<td>2</td>
<td>-1.93 (irr)</td>
<td></td>
<td></td>
<td>-1.55</td>
<td>-1.29</td>
</tr>
<tr>
<td>2(^e)</td>
<td>-1.92 (rev)</td>
<td>82 (104)</td>
<td>-2.29</td>
<td>-1.51(^d)</td>
<td>-1.26(^d)</td>
</tr>
</tbody>
</table>

\(^a\) Conditions and definitions: 5 \(\times\) 10\(^{-4}\) M solutions in THF (containing 10\(^{-1}\) M Bu\(_4\)NPF\(_6\)) at \(T = 293\) K, unless stated otherwise; Pt disc electrode; \(v = 100\) mV/s; redox potentials given in V vs E\(_{1/2}\)(Fe/Fc\(^+\)); \(E_{pc}(R_1)\), cathodic peak potential for reduction of parent cluster, \(E_{pa}(R_2)\), cathodic peak potential for reduction of the corresponding radical anion; \(E_{pa}\), anodic peak potential for oxidation of the reduction products; \(\Delta E_p\), peak separation for a redox couple (with \(\Delta E_p(Fc/Fc^+\)) in brackets). \(^b\) \(v = 20\) V/s. \(^c\) \(T = 244\) K. \(^d\) Both anodic peaks are associated with the reduction of the radical anion at \(E(R_2)\). \(^e\) \(T = 252\) K.

Cyclic Voltammetry

At room temperature cluster 1 undergoes chemically irreversible reduction (cathodic peak \(R_1(1)\); Figure 9A). The anodic peak \(O_2(B)\) on the reverse scan is associated with this cathodic process and corresponds to oxidation of a secondary reduction product, B. At \(v = 20\) mV/s no other anodic peaks are observed, but at higher scan rates (\(v \geq 100\) mV/s) a second anodic peak \(O_2(B')\) starts to grow in at the expense of \(O_2(B)\). At \(v \geq 10\) V/s re-oxidation of the parent radical anion \(1^{*-}\) becomes observable (anodic peak \(O_1(1)\)), together with its reduction to the dianion \(1^{2-}\) at \(E(R_1(1))\). At \(v = 50\) V/s the formation of \(1^{*-}\) is almost completely chemically reversible. The reduction of 1 becomes fully reversible at lower temperatures (\(T \leq 243\) K; \(v = 100\) mV/s; Figure 9B). The reduction of the radical anion \(1^{*-}\) to \(1^{2-}\) remains irreversible even at 213 K. At the latter temperature the dianion \(1^{2-}\) decomposes to the same product B' that is formed upon reduction of 1 at \(R_1(1)\) at room temperature, as testified by the anodic peak \(O_2(B')\) at 213 K. At higher temperatures also \(O_2(B)\) is observed. Summarizing, the transient species B' (only observable at low temperatures or high scan rates) is formed from 1 in an overall two-electron process\(^{25}\) and rapidly reacts further to give the more stable product B, that could be identified as \([\text{Os}_3(\text{CO})_9(\text{tmbp})]^{2-}\) (\textit{vide infra}). At low temperatures an EEC path is followed according to which first two cathodic steps (E) (subsequent formation \(1^{*-}\) and \(1^{2-}\)) are needed to induce a chemical reaction (C) producing B'. At room temperature and slow scan rates the sequence changes to ECE as the radical anion \(1^{*-}\) readily undergoes a chemical reaction and its product is directly reduced at the cathodic potential \(R_1(1)\) to give B' and B.

The redox behaviour of 2 revealed to be very similar to that of 1 (Figure 9C-D). The reduction of 2 at \(R_1(2)\) at room temperature is chemically irreversible and is shifted negatively (\(\Delta E_{1/2} = 130\) mV; see Table 5) compared to that of 1, in agreement with the substitution of a CO ligand by more basic PPh\(_3\). At sufficiently low temperatures (\(T \leq 253\) K, \(v = 100\) mV/S), the one-electron reduction producing the radical anion \(2^{*-}\) is again fully reversible on the time
scale of cyclic voltammetry. Upon scan reversal beyond \( E(R_1(2)) \) at room temperature, the anodic peaks \( O_2(B) \) and \( O_2(B') \) are observed at exactly the same potentials as for 1. This interesting result implies that the reduction of 1 and 2 yields the same products \( B \) and \( B' \).

\[
\begin{array}{c}
\text{A} \quad \text{R}_1(1) \\
\text{O}_2(B') \quad \text{O}_2(B) \\
-1.2 -1.6 -2.0 -2.4
\end{array}
\]

\[
\begin{array}{c}
\text{B} \quad \text{R}_1(1) \\
\text{O}_2(1) \quad \text{O}_2(1) \\
-1.2 -1.6 -2.0 -2.4
\end{array}
\]

\[
\begin{array}{c}
\text{C} \quad \text{R}_1(2) \\
\text{O}_2(B') \quad \text{O}_2(B) \\
-1.2 -1.6 -2.0 -2.4
\end{array}
\]

\[
\begin{array}{c}
\text{D} \quad \text{R}_1(2) \\
\text{O}_2(B') \quad \text{O}_2(B) \\
-1.2 -1.6 -2.0 -2.4
\end{array}
\]

\[
\begin{array}{c}
\text{E} \quad \text{R}_1(2) \\
\text{O}_2(B) \\
-1.2 -1.6 -2.0 -2.4
\end{array}
\]

\[
\begin{array}{c}
\text{F} \quad \text{R}_1(1) \\
\text{O}_2(B) \\
-1.2 -1.6 -2.0 -2.4
\end{array}
\]

**Figure 9.** Cyclic voltammograms of the clusters 1 and 2 in THF. Conditions: A. 1, \( \nu = 100 \text{ mV/s}, 293 \text{ K} \); B. 1, \( \nu = 100 \text{ mV/s}, 244 \text{ K} \); C. 2, \( \nu = 100 \text{ mV/s}, 293 \text{ K} \); D. 2, \( \nu = 100 \text{ mV/s}, 252 \text{ K} \); E. 1 + excess \( \text{PPh}_3 \), \( \nu = 20 \text{ mV/s}, 293 \text{ K} \); F. 1 + excess \( \text{PPh}_3 \), \( \nu = 100 \text{ mV/s}, 293 \text{ K} \).
IR Spectroelectrochemistry

In order to further characterize the reduction products formed, the reduction pathways of 1 and 2 were studied by IR spectroelectrochemistry and thin-layer cyclic voltammetry on the same time scale (v = 5 mV/s).

At temperatures below 243 K the initial reduction product, the radical anion 1\(^{\bullet-}\), becomes stable on the time scale of cyclic voltammetry (v \(\geq\) 100 mV/s). Its IR spectrum could be recorded in butyronitrile at 213 K (see Figure 10). As expected, the \(\nu\)(CO) pattern of 1\(^{\bullet-}\) is nearly the same as that of 1, with the \(\nu\)(CO) bands shifted to smaller wavenumbers by 30-35 cm\(^{-1}\) and the strongest band (at 2019 cm\(^{-1}\) for 1) split. Therefore, the molecular structure of 1\(^{\bullet-}\) will strongly resemble that of the parent cluster.

According to the cyclic voltammetric experiments, the same secondary reduction product B is formed for the clusters 1 and 2 (vide supra). Indeed, upon reduction of both clusters at room temperature in THF formation of B was observed by IR spectroelectrochemistry (see Figure 10). For 1 an additional side product, denoted as C, is formed. Re-oxidation of product B at E(\(O_2(B)\)) (Table 5) results in regeneration of 1 and 2, respectively, although for the former cluster also the amount of C increased simultaneously.

The sole difference between 1 and 2 is the substitution of a carbonyl by PPh\(_3\). Hence, only dissociation of the 2e-electron donors CO and PPh\(_3\) can explain the formation of the same product upon reduction of 1 and 2, respectively. It is therefore proposed that B is the CO/PPh\(_3\)-loss product [Os\(_3\)(CO)\(_9\)(tmbp)]\(^{2-}\) (see Scheme 1). The dianionic nature of B is in agreement with the cyclic voltammetric data (vide supra). Additional support is given by the IR spectrum of B. Its \(\nu\)(CO) bands are generally shifted by nearly 100 cm\(^{-1}\) to lower wavenumbers compared to those of 1, and two weak bands at 1716 and 1693 cm\(^{-1}\) point to the
presence of bridging CO ligands. Such a large shift of the \( v(\text{CO}) \) wavenumbers is typical for two-electron reduced clusters with the negative charge mainly localized on the triosmium core.\(^{4,26,27}\)

**Table 6. IR spectroscopic data of the clusters 1 and 2 and their reduction products**

<table>
<thead>
<tr>
<th>compound</th>
<th>( v(\text{CO}) ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^a)</td>
<td>2104(m), 2052(s), 2021(sh), 2018(vs), 1982(m), 1966(m), 1941(m)</td>
</tr>
<tr>
<td>1(^b)</td>
<td>2109(m), 2053(s), 2023(sh), 2019(vs), 2007(sh), 1983(m), 1965(m), 1938(m)</td>
</tr>
<tr>
<td>1(^{−−})</td>
<td>2082(m), 2020(vs), 2006(s), 1987(s), 1977(sh), 1947(m), 1932(m), 1905(m)</td>
</tr>
<tr>
<td>2(^a)</td>
<td>2061(m), 2036(s), 2003(vs), 1988(s), 1970(m), 1958(m), 1932(m)</td>
</tr>
<tr>
<td>B(^ac)</td>
<td>2009(m), 1952(s), 1947(sh), 1929(m), 1876(m), 1858(sh), 1716(sh), 1693(w)</td>
</tr>
<tr>
<td>C(^ad)</td>
<td>2033(m), 2006(m), 1981(s), 1952(m), 1922(sh), 1912(m)</td>
</tr>
<tr>
<td>C(^d)</td>
<td>2060(w), 2050(w), 2028(m), 1983(s), 1953(m), 1945(sh), 1916(m)</td>
</tr>
<tr>
<td>C(^aa)</td>
<td>2050(w), 2033(w), 2022(m), 2007(w), 1979(s), 1954(m), 1922(sh), 1911(m)</td>
</tr>
</tbody>
</table>

\( ^a \) In THF at 293 K. \( ^b \) *In situ* reduction in n-PrCN at 213 K in an IR OTTLE cell. \( ^c \) *In situ* reduction at room temperature in an IR OTTLE cell. \( ^d \) Chemical reduction with [Fe\(^{I}(\text{Cp})(\text{C}_6\text{Me}_6)] \) performed in DME. \( ^e \) Chemical reduction with Na/Hg.

**Chemical Reduction of 1**

With the intention to further characterize the reduction products B and C with NMR spectroscopy, their preparation via chemical reduction of cluster 1 was attempted. The IR \( v(\text{CO}) \) spectrum of the product obtained by reduction of 1 with 1% Na/Hg in THF, strongly resembles that of C generated in the IR OTTLE cell (Table 6). Alternatively, product C was formed by addition of two equivalents of [Fe\(^{I}(\text{Cp})(\text{C}_6\text{Me}_6)] \) to a solution of 1 in DME. During these experiments formation of B was not detected, although its initial formation is probable. In the presence of air C decomposed rapidly into unidentified products. The IR spectra of product C produced via the different methods deviate only in the high-frequency \( v(\text{CO}) \) region between 2060-2000 cm\(^{-1}\). Probably, some minor side products are formed upon chemical reduction, that are not observed in the course of the IR spectroelectrochemical experiment. Unfortunately, thermal decomposition of C has prevented its further characterization.

**Electrocatalytic CO Substitution of 1**

Electrocatalytic substitution of CO by more electron-releasing ligands has proven to be a versatile method to synthesize substituted metal carbonyl complexes.\(^{28}\) Electrocatalysis also facilitates the synthesis of substitution products of 1. The cyclic voltammograms of 1 in the presence of an excess of PPh\(_3\) at various temperatures and scan rates are presented in Figures 9E-F. The cyclic voltammogram recorded at room temperature and \( v = 100 \) mV/s shows a decrease of the cathodic peak current at \( E(R_1(1)) \) and the appearance of a new cathodic peak
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(R1(2)) at slightly more negative potential (E(R1(2)) = -1.90 V). At lower scan rate (v = 20 mV/s) the current of this second cathodic peak increases at the expense of R1(1). The new cathodic peak R1(2) arises due to the reduction of the cluster [Os3(CO)9(PPh3)(tmbp)] (2) (vide supra), formed by the reaction of the radical anion 1** with PPh3 (Scheme 2). The increased R1(2) and decreased R1(1) at lower scan rates are indicative for electrocatalysis, since a higher concentration of 2 can then build up at the electrode surface. It is known from the literature that formation of the electrocatalytic substitution product can be so fast that the initial redox process of the starting complex is hardly observable anymore.29 Cyclic voltammetry testified that other PR3 ligands (R = Et, cyclohexyl, OPh) also undergo electrocatalytic substitution reactions with 1.30 Surprisingly, no such reactions were observed with other substrates such as AsPh3, pyridine, 1-octene and diphenylacetylene.

Scheme 1. Reduction pathways for the clusters [Os3(CO)9(tmbp)(L)] (L = CO (1), PPh3 (2)).

As mentioned above, the phosphine-substituted cluster [Os3(CO)9(PPh3)(tmbp)], 2, could also be synthesized on a preparative scale in high yield. Cluster 1 reacts instantaneously in THF at room temperature with a catalytic amount (5%) of sodium biphenyl ketyl in the presence of three equivalents of PPh3 to give 2 as the only product, providing additional evidence for the electrocatalytic mechanism given in Scheme 2.
Crystal Structures, Bonding Properties and Redox Behaviour of $[\text{Os}_3(\text{CO})_9(\text{tmbp})(\text{L})]$}

**Scheme 2.** *Electrocatalytic substitution of CO by PPh$_3$ in cluster 1.*

![Scheme](image)

**Comments on the Redox Behaviour of 1**

The DFT calculations predict that the LUMO of 1 is predominantly localized on tmbp. For this reason, it is assumed that in the radical anion $1^{--}$ the unpaired electron resides on this ligand. Comparison of the reduction potentials of uncoordinated aromatic tmbp and some of its metal complexes with their bpy or 4,4'-dimethyl-2,2'-bipyridine (dmb) derivatives shows that the former complexes are systematically reduced more positively by ca. 0.3-0.35 V, ($E_{1/2}(\text{tmbp}) = -1.85$ V, $E_{1/2}(\text{dmb}) = -2.16$ V vs SCE$^8$; $E_{1/2}([\text{Ni(tmbp)}_2]) = -1.64$ V, $E_{1/2}([\text{Ni(bpy)}_2]) = -1.97$ V vs SCE$^9$). In the case of 1 the reduction potential is raised much closer to that of $[\text{Os}_3(\text{CO})_{10}(\text{dmb})]^2$ ($E_{1/2}([\text{Os}_3(\text{CO})_{10}(\text{tmbp})]) = -1.80$ V (244 K) and $E_{1/2}([\text{Os}_3(\text{CO})_{10}(\text{dmb})]) = -1.89$ V (213 K) vs Fe/F$^{+}$), reflecting the different coordination mode of tmbp in 1 and the loss of its aromaticity. For unsubstituted $[\text{Os}_3(\text{CO})_{12}]$ the corresponding radical anion is too short-lived to be detected, due to fast chemical follow-up reactions.$^{32}$ By contrast, $1^{--}$ is sufficiently stable to allow its observation with both cyclic voltammetry and IR spectrotelectrochemistry at low temperatures. Two factors are thought to have increased the stability of the radical anion. First, the one-electron reduction is not localized on the cluster core, but on the redox-active ligand tmbp, and secondly, tmbp spans the triosmium core. Remarkably stable radical anions were also observed for the clusters $[\text{HOS}_3(\text{CO})_9(o-L)]$ where the redox-active ligand L is an *ortho*-metallated $\alpha$-diimine (o-L) bridging an Os–Os bond.$^4$

At room temperature, the radical anion $1^{--}$ is not stable and undergoes a chemical reaction and a second electron transfer step, ultimately producing the CO-loss product $[\text{Os}_3(\text{CO})_9(\text{tmbp})]^2$.$^2$ Such a 'substitution' of a two-electron donor by two electrons occurs frequently in cluster electrochemistry, e.g. in the clusters $[\text{M}_3(\text{CO})_{12}]$ (M = Ru, Os).$^{32,33}$ The redox behaviour of 1 is quite different from that of $[\text{Os}_3(\text{CO})_{10}(\text{bpy})]$. The latter cluster undergoes metal-metal bond cleavage on reduction instead of CO-loss.$^{31}$ However, in 1 already one Os–Os bond is broken, and the tmbp ligand, spanning the triosmium core, probably prevents cleavage of a second metal–metal bond. Secondly, in 1 the triosmium core has become electron-deficient due to the oxidative addition of tmbp, which facilitates the substitution of a strong $\pi$-acceptor carbonyl group by the more basic PPh$_3$. 

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By contrast, neither via thermal substitution nor via radical-anion-initiated substitution (catalyzed by sodium biphenyl ketyl), a CO ligand could be substituted by PPh$_3$ in [Os$_3$(CO)$_{10}$(bpy)], the σ-donor bpy ligand making the triosmium core rather electron-rich.$^{34}$ Instead, thermal reaction of PPh$_3$ with [Os$_3$(CO)$_{10}$(bpy)] leads to substitution of bpy yielding [Os$_3$(CO)$_{10}$(PPh$_3$)$_2$].$^{34}$

**Conclusions**

The 50e-cluster [Os$_3$(CO)$_{10}$(μ$_2$-P$_2$-μ$_2$-P'-tmpb)], 1, and its PPh$_3$-derivative 2 show an unprecedented bridging coordination mode of tmpb with both P atoms bridging two metal atoms. The tmpb ligand is formally doubly reduced by electron transfer from the cluster core that consequently lost one metal–metal bond. The electron-deficiency of the cluster core accounts for the facile electrocatalytic substitution of CO by more basic PPh$_3$. The overall two-electron reduction of 1 and 2 leads to dissociation of CO and PPh$_3$, respectively, and formation of the dianion [Os$_3$(CO)$_9$(tmpb)]$^2^-$. The initially produced radical anions are fairly stable due to localization of the odd electron on tmpb, which in addition clamps the triosmium core. DFT calculations show that the HOMO and LUMO are localized on tmpb. The lowest-energy electronic transition of 1 therefore possesses intraligand character, thereby explaining the photostability of 1.

**Experimental Section**

**Materials and Preparations**

[Os$_3$(CO)$_{12}$] (ABCR) and PPh$_3$ (Aldrich) were used as purchased. Trimethylamine-N-oxide dihydrate, Me$_3$NO.2H$_2$O (Alfa) was dehydrated before use by vacuum sublimation. Analytical grade solvents (Acros: hexane, dichloromethane, THF, toluene, acetonitrile, dimethoxyethane (DME)) and spectroscopic grade solvents (Aldrich: pyridine; Fluka: butyronitrile; Merck: CCL$_4$) were dried over sodium wire (hexane, THF, toluene, DME) or CaH$_2$ (dichloromethane, CCL$_4$, pyridine, acetonitrile, butyronitrile) and freshly distilled prior to use. The ligand 4,4',5,5'-tetramethyl-2,2'-biphosphinine (tmpb) was synthesized according to a published procedure.$^5$ Silicagel (Kieselgel 60, Merck, 70-230 Mesh), used for column chromatography, was activated by heating overnight in vacuo at 160 °C. Elemental analyses were carried out in the 'Mikroanalytisches Laboratorium' of Dr. H. Kolbe (Müllheim an der Ruhr, Germany). The reducing agent [Fe$^0$(Cp)(C$_6$Me$_5$)]$^+$ was prepared by reduction of [Fe$^{II}$(Cp)(C$_6$Me$_5$)]$^-[PF_6]^{-}$ with 1% Na/Hg in DME according to the procedure described in ref. 35.

**Synthesis of [Os$_3$(CO)$_{10}$(tmpb)] (1)**

[Os$_3$(CO)$_{10}$(MeCN)$_2$] (190 mg, 0.17) and tmpb (45 mg, 0.18 mmol) were dissolved in THF (50 ml). The yellow solution quickly turned red and finally deep purple. The solution was stirred for 1.5 h after
Crystall Structures, Bonding Properties and Redox Behaviour of [Os$_3$(CO)$_9$(tmbp)(L)]

which the solvent was evaporated in vacuo. The crude purple product was purified by column chromatography over silica eluting with hexane/dichloromethane 20:1. Pure 1 was obtained in a 70% yield. Single crystals of 1 suitable for crystal structure determination were grown from hexane at 293 K.

IR ν(CO) (hexane): 2104 (m), 2057 (s), 2036 (m), 2025 (vs), 2007 (w), 1991 (m), 1976 (m), 1959 (w), 1952 (w) cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 6.93 (d, 1H, $^3$J(P(1)-H) = 19.2 Hz), 6.75 (d, 1H, $^3$J(P(2)-H) = 17.4 Hz), 6.39 (d, 1H, $^2$J(P(1)-H) = 28.2 Hz), 6.36 (d, 1H, $^2$J(P(2)-H) = 32.1 Hz), 2.20 (s, Me), 2.15 (s, Me), 1.90 (s, Me) ppm.

Synthesis of [Os$_3$(CO)$_9$(tmbp)(PPh$_3$)] (2)

A solution of [Os$_3$(CO)$_{10}$(tmbp)], 1 (87 mg, 0.079 mmol) and excess PPh$_3$ (62 mg, 0.24 mmol) in THF (60 ml) was stirred for 30 minutes, after which period no thermal reaction was observed. A catalytic amount of sodium diphenyl ketyl (5%), prepared by addition of finely cut sodium metal to a solution of benzophenone (76 mg) in THF (5 ml), was added. The solution was stirred for 5 minutes and the solvent was evaporated in vacuo. The crude product was purified by column chromatography over silica. First a small amount of unreacted 1 and excess PPh$_3$ were eluted with hexane/toluene 5:1, followed by the product in hexane/toluene 4:3. Pure 2 was obtained as a purple powder in 85% yield.

Crystals suitable for X-ray diffraction were grown from a cyclohexane solution of 2.

IR ν(CO) (THF): 2061 (m), 2035 (s), 2025 (vs), 1987 (s), 1970 (m), 1958 (w), 1935(sh), 1930 (w) cm$^{-1}$. $^1$H NMR (CDCl$_3$) δ 7.39 (m, 15 H, PPh$_3$), 6.85 (d, 1H, $^3$J(P(1)-H) = 19.2 Hz), 6.65 (d, 1H, $^3$J(P(2)-H) = 16.5 Hz), 6.39 (d, 1H, $^2$J(P(2)-H) = 31.8 Hz), 6.23 (d, 1H, $^2$J(P(1)-H) = 28.2 Hz), 2.13 (s, 6H), 1.93 (s, 3H), 1.78 (s, 3H). $^3$P{H} NMR (CDCl$_3$) δ 25.5 (P(2), d, IP), -7.64 (P(3) PPh$_3$, d, IP), -134.4 (P(1), dd, 1P) ppm, $^2$J(P(1)-P(2)) = 109 Hz, $^2$J(P(1)-P(3)) = 310 Hz. UV-vis (THF): 347 (sh), 455 (sh), 548, 593 (sh) nm. FAB MS (m/z): M$^+$ 1332.0 (calc. 1332.0). Elemental analysis for C$_{41}$H$_{31}$O$_9$Os$_3$P$_3$ (calculated values in parentheses): C 37.09 (36.99), H 2.36 (2.35), P 7.01 (6.98).

X-ray Analyses

Crystal Structure Determination of 1

C$_{24}$H$_{16}$O$_{10}$Os$_3$P$_2$; M = 1097; monoclinic, space group P2$_1$/a; a = 9.8115(8), b = 16.359(1), c = 18.276(1) Å, β = 98.693(6)°; U = 2899.7(3) Å$^3$; Z = 4; D$_c$ = 2.51 g cm$^{-3}$; λ(CuKα) = 1.5418 Å; μ(CuKα) = 257.9 cm$^{-1}$; T = 253 K; F(000) = 1992, 5954 unique reflections measured, final R = 0.060 for 5264 observed reflections. A wedge-shaped crystal with dimensions 0.20 × 0.20 × 0.40 mm approximately was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated CuKα radiation and ω-2θ scan. A total of 5954 unique reflections were measured within the range -12 ≤ h ≤ 0, 0 ≤ k ≤ 20, -22 ≤ l ≤ 22. Of these, 5264 were above the significance level of 2.5 $σ$(I). The range of (sinθ/λ) was 0.041 - 0.626 Å$^{-1}$ (3.6 < θ < 74.8). Two reference reflections (112, 223) were measured hourly and showed 10% increase during the 73 h collecting time, which was
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Corrected for. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with 80 ≤ 2θ ≤ 82. Corrections for Lorentz and polarisation effects were applied. The structure was solved by the PATTY option of the DIRDIF-96 program system36. Full-matrix least-squares refinement on F, anisotropic for the Os and P atoms and isotropic for the remainder of the atoms, keeping the H-atoms fixed at their calculated positions with U = 0.1 Å², converged to R = 0.060, R_w = 0.072, (Δ/σ)max = 0.03, S = 1.09. A weighting scheme w = [95.0 + 0.01 × (σ(F_obs))^2 + 0.01 / σ(F_obs))] was used. The secondary isotropic extinction coefficient37,38 was refined to Ext = 0.053(3). A final difference Fourier map revealed a residual electron density in the vicinity of the heavy atoms. An empirical absorption correction (DIFABS39) was applied with coefficients in the range 0.69 - 1.88. Scattering factors were taken from the literature40,41. The anomalous scattering of Os and P was taken into account.42 All calculations were performed with XTAL,43 unless stated otherwise. The high residual electron density values and the fact that only the Os and P atoms could be refined anisotropically, reflect the strange behaviour of the crystal during the measurement (increase of the intensity control reflections).

Crystal Structure Determination of 2

C₄₁H₃₁O₉Os₃P₃; M = 1332.0; crystal habit: red plates, crystal dimensions 0.16 × 0.07 × 0.04, triclinic, space group P-1; a = 11.599(5) Å, b = 11.936(5) Å, c = 17.561(5) Å, α = 78.220(5)°, β = 84.330(5)°, γ = 76.830(5)°; U = 2314.0(15) Å³; Z = 2, d = 2.030 g cm⁻³; λ(MoKα) = 0.71069 Å; μ(MoKα) = 8.374 cm⁻¹; T = 150(0) K; F(000) = 1338, Ω(max) = 27.44; hkl ranges: -15 to 13, -15 to 15, -22 to 22; 15390 reflections measured, 10491 independent reflections, 8291 reflections used; refinement type: F², full matrix; hydrogen atoms mixed; 563 parameters refined; reflections/parameters = 14; wR2 = 0.0818; R1 = 0.0411; criterion: I > 2σ(I); Flack's parameter not applicable; GOF = 0.995; difference peak/ hole = 2.260(0.219/-2.452(0.219) e Å³. Data were collected on an Nonius Kappa CCD diffractometer using a MoKα (λ = 0.71073 Å) X-ray source and a graphite monochromator. The crystal structure was solved using maXus44 and finally refined against F² with SHELXL-9745.

Computational Details

All Density Functional Theory calculations were performed using the Amsterdam Density Functional program package (ADF-2.3 and ADF99).46-48 The Local Spin Density (LSD) exchange correlation potential was used49 with the Local Density Approximation of the correlation energy (Vosko-Wilk-Nusair).50 Furthermore, Becke's nonlocal corrections51,52 to the exchange energy and Perdew's nonlocal corrections53,54 to the correlation energy were included in the calculation of the gradients. Relativistic effects were treated by a quasi-relativistic method where Darwin and mass-velocity terms are incorporated.55-57 The inner shells of Os (1s-5p), P (1s-2p), C and O (1s) were frozen. A triple-ζ STO basis set was used for the valence part of Os (5d, 6s, 6p). The 2s and 2p valence shells of C, as well as the 3s, 3p valence shells of P, were described by a triple-ζ STO basis, augmented by one 3d polarization function. For O (2s, 2p) and H (1s) a double-ζ STO basis was used.
Spectroscopic Measurements

FTIR spectra were recorded on Bio-Rad FTS-7 or Bio-Rad FTS-60A spectrometers, the latter equipped with a liquid-nitrogen-cooled MCT detector (16 scans at 2 cm\(^{-1}\) resolution). UV-vis absorption spectra were recorded on a Hewlett Packard 84533 diode-array spectrophotometer. NMR spectra were recorded on a Bruker AMX 300 spectrometer (300.13 MHz). FAB mass spectra were recorded on a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-MP 7000 data system.

Photochemistry

Continuous-wave irradiation was performed with a Spectra Physics 2025 argon-ion laser. Nanosecond time-resolved UV-vis experiments were carried out with 7 ns pulses (fwhm) of a 532 nm line obtained by frequency doubling of the 1064 nm fundamental of a Spectra Physics GCR-3 Nd:YAG laser. Details of the data collection system have been described in Chapter 2.

(Spectro)electrochemistry

Cyclic voltammetry was performed in a gastight cell under an atmosphere of dry argon. The cell was equipped with a Pt disc working (apparent surface area of 0.42 mm\(^2\)), Pt wire auxiliary, and Ag wire pseudo-reference electrodes. The working electrode was carefully polished with a 0.25 µm grain diamond paste. All redox potentials are reported against the ferrocene-ferrocenium (Fc/Fc\(^+\)) redox couple used as an internal standard.\(^{58}\) The solutions for cyclic voltammetric experiments were typically 5 × 10\(^{-4}\) M in the cluster compounds and 0.1 M in NBu\(_4\)PF\(_6\). The potential control was achieved with a PAR Model 283 potentiostat equipped with positive feedback for ohmic-drop compensation. Infrared spectroelectrochemical experiments at variable temperature were performed with optically transparent thin-layer electrochemical (OTTLE) cells,\(^{59,60}\) equipped with a Pt minigrid working electrode (32 wires per cm) and CaF\(_2\) optical windows. The spectroelectrochemical samples were typically 5 × 10\(^{-3}\) M in the cluster compounds. A PAR potentiostat (EKOM, Czech Republic) was


(12) Rosa, P.; Le Floch, P. personal communication.


(18) Le Floch, P. personal communication.


(25) Determination of the apparent number of electrons n_{app} involved in the reduction of 1 at room temperature, using the method described by Amatore (Amatore, C.; Azzabi, M.; Calas, P.; Juttand, A.; Lefrou, C.; Rollin, Y. J. Electroanal. Chem. 1990, 288, 45) gave a too high value of n_{app} = 2.7. However, comparison of the anodic peak current of the one-electron oxidation wave of the internal standard Fe with those of the reduction wave of 1 both at 223 K (one-electron process) and at room temperature, confirm that reduction of 1 at the latter temperature involves transfer of two electrons. This is also in agreement with the formation of B' from the dianion 1²⁻ at low temperature.


Crystal Structures, Bonding Properties and Redox Behaviour of [Os₃(CO)₉(tmbp)(PR₃)]


(30) The substitution products [Os₃(CO)₉(tmbp)(PR₃)] are all reduced at similar potentials: Eₚ,c = -1.90 V (R = Ph); -1.91 V (R = Et); -1.93 V (R = cyclohexyl); -1.89 V (R = OPh) vs Fe/Fe⁺.

(31) Hartl, F., unpublished results.


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