Synthesis, Structure, and Infrared Spectroelectrochemistry of the Cluster [Os₃H(μ-FcCO)(CO)₁₀] (Fc = ferrocenyl), a Product of Oxidative Addition of Formylferrocene to [Os₃(CO)₁₀(MeCN)₂]

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Reaction of the cluster [Os₃(CO)₁₀(MeCN)₂] with formylferrocene gives the oxidative addition product [Os₃H(μ-FcCO)(CO)₁₀] (Fc = ferrocenyl) (structurally characterised by X-ray crystallography), which has been shown by cyclic voltammetry and i.r. spectroelectrochemistry to undergo a reversible one-electron oxidation at iron and an irreversible two-electron reduction at the osmium cluster.

Benzaldehyde reacts with [Os₃(CO)₁₂] (**1**) or [Os₃(CO)₁₀(MeCN)₂] (**2**) to give the benzoyl cluster [Os₃H(μ-PhCO)(CO)₁₀][1,2] which undergoes a double decarbonylation in refluxing nonane (150 °C) to give the benzyne (*ortho*-phenylene) cluster [Os₃H₂(μ₃-C₆H₄)(CO)₉], which may also be formed by direct reaction of benzene with (**1**).[3] We have unsuccessfully attempted to copy this chemistry as a route to the analogous ferrocyne cluster [Os₃H₂(μ₃-C₅H₃FeC₅H₅)(CO)₉]. Direct reactions of ferrocene with [Os₃(CO)₁₂] or [Os₃(CO)₁₀(MeCN)₂] require very high temperatures and give no tractable products; however, cluster (**2**) [or (**1**), less effectively and at higher temperatures] reacts with formylferrocene (FcCHO) in refluxing cyclohexane (45 min) to give the acyl oxidative addition product [Os₃H-
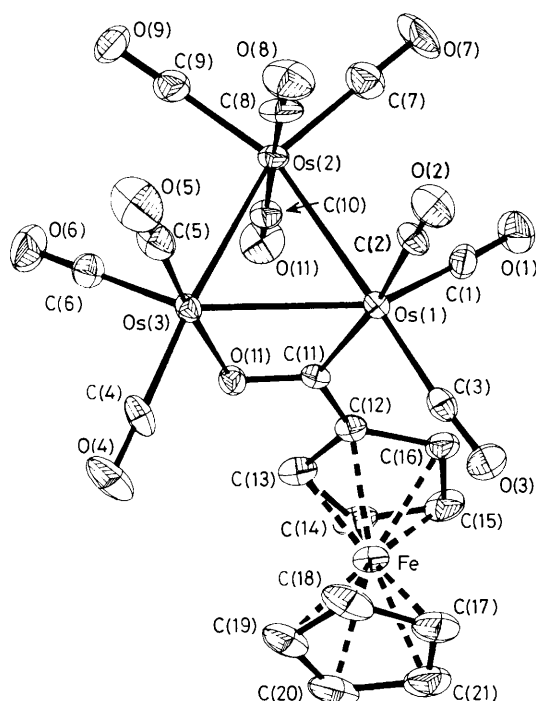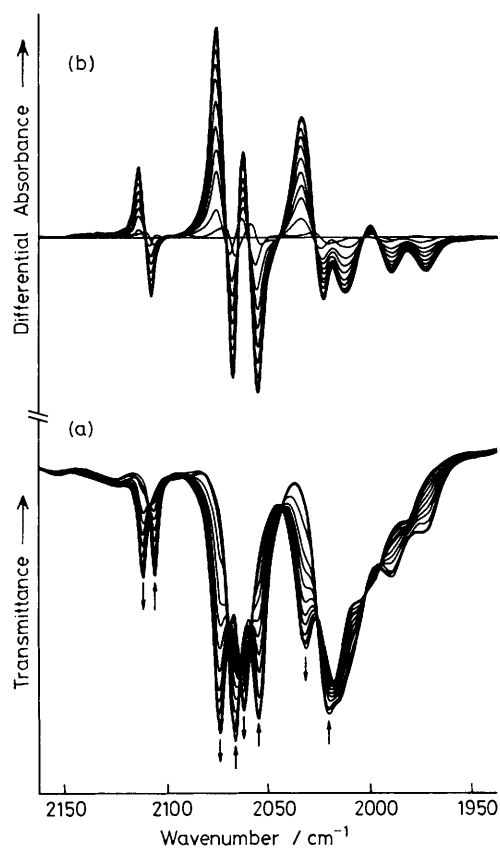
Figure 1. Molecular structure of [Os₃H(FcCO)(CO)₁₀] (**3**). H-atoms were not located but the hydride ligand probably lies close to the intersection of the Os(3)–C(6) and Os(1)–C(1) directions. Bond lengths: Os(1)–Os(2) 2.879(4), Os(2)–Os(3) 2.843(4), Os(1)–Os(3) 2.888(4), Os(1)–C(11) 2.072(11), Os(3)–O(11) 2.093(9), C(11)–O(11) 1.273(11), C(11)–C(12) 1.478(14) Å. Bond angles: Os(3)–O(11)–C(11) 109.9(7), Os(1)–C(11)–O(11) 115.8(8), Os(1)–C(11)–C(12) 131.6(7), C(12)–C(11)–O(11) 112.5(9)°.

(FcCO)(CO)₁₀] (**3**) as red crystals (68% yield) after t.l.c. on silica. The i.r. and n.m.r. spectral data for (**3**),† when compared with those of the corresponding benzoyl complex,[1,2] indicate that these complexes have related structures. To confirm this we have determined the single crystal X-ray structure of (**3**) (Figure 1).‡ The ferrocenyl (Fc) group is linked to the Os₃H(CO)₁₀ group through the carbonyl C(11)O(11). The FcCO ligand relates directly to other μ-acyl ligands such as phenacyl (PhCH₂CO).[2] The strongest contact between the acyl and the metal atoms is through C(11), and the bond *trans* to it [Os(1)–C(2) 1.955(13) Å] is much longer than the bond *trans* to O(11) [Os(3)–C(5) 1.883(14) Å].

Figure 2. (a) Time-resolved i.r. spectra (interval 10 s) and (b) corresponding difference spectra, of a solution of (**3**) in CH₂Cl₂ on changing the applied potential from 0.00 to + 1.00 V. The arrows indicate the directions of intensity changes on oxidation of (**3**) to (**5**).
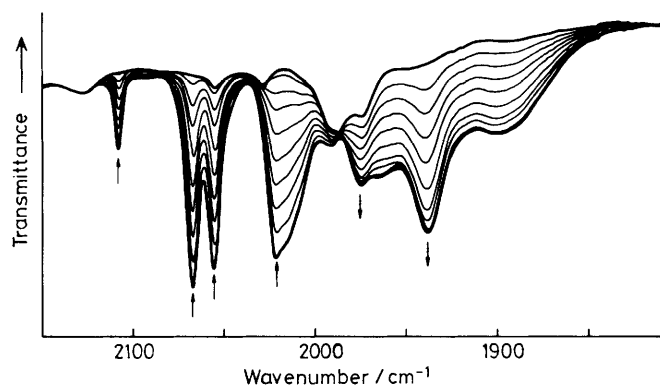
Figure 3. Time-resolved i.r. spectra (interval 10 s) of a solution of (**3**) in CH₂Cl₂ during a two-electron reduction initiated by changing the applied potential from 0.00 to −2.00 V. The arrows indicate the directions of intensity changes on reduction.

In spite of the structural and spectroscopic similarity between the clusters [Os₃H(RCO)(CO)₁₀] (R = Ph, PhCH₂, or Fc), the PhCO complex readily decarbonylates to [Os₃H₂(C₆H₄)(CO)₉] at 150 °C, whereas the FcCO complex is remarkably stable even in refluxing decane (173 °C) and does not decarbonylate on u.v. irradiation. However, it does react with an excess of Me₃NO·2H₂O to give [Os₃H(FcCO)(CO)₉(NMe₃)] (**4**) in moderate yield.† Even though this compound contains weakly co-ordinated NMe₃, there is no observable tendency for Fc transfer from carbon to osmium,

and on being heated (4) decomposes to (3). It is possible that the ferrocyne cluster is stable but that a large kinetic barrier to Fc migration prevents its formation by this route.

Interested in the transmission of electronic effects through complexes,[4] in this case through the linking carbonyl C(11)O(11), we have examined the electrochemistry and spectroelectrochemistry of cluster (3). Cyclic voltammetry (c.v.) studies show that this cluster in dichloromethane solution undergoes reversible one-electron oxidation at +0.80 V,§ close to the oxidation potential for formylferrocene (+0.78 V). Since the benzoyl analogue $[Os_3H(PhCO)(CO)_{10}]$ shows only an irreversible oxidation at +1.36 V, we can be sure that the oxidation of (3) is at the Fc group [to give the ferrocenium cation (5)] and not at the triosmium centre. Figure 2 shows time-resolved i.r. spectra of (3) (and difference spectra) during its oxidation to (5) in an i.r. spectroelectro-chemical cell[5] initiated by switching the applied potential from 0.00 to +1.00 V, i.e. about 0.20 V beyond the oxidation potential. The spectra of (3) and its oxidised form (5) are very similar in shape showing that there is no substantial structural difference between the two compounds. The v(CO) wave-numbers are 6—8 cm^{-1} higher for (5) than for (3) so that, although it is primarily the ferrocene moiety that is oxidised, there is estimated to be a positive charge of ca. 0.15 on the triosmium component of cation (5) relative to that on (3); this is based on an expected wavenumber change of +45 to +50 cm^{-1} on introducing a full positive charge.[6] The spectral changes in Figure 2 are totally reversible on returning the potential to 0.00 V.

An irreversible two-electron reduction of (3) in dichloro-methane occurs at −1.63 V with an associated re-oxidation at

−0.46 V. Time-resolved i.r. spectroelectrochemical results (Figure 2) show that the reduction is cluster based with a build-up of negative charge at the osmium atoms and that on re-oxidation there is about 80% recovery of compound (3). The reduced species has not been fully characterised, but its generation probably involves either loss of CO, the process being substantially reversed on re-oxidation, or a structure change involving Os–Os bond cleavage, or possibly conver-sion of the acyl into a monodentate ligand. We have looked unsuccessfully for spectral changes at lower wavenumbers which might have characterised this structural change.

This work exemplifies the potential of spectroelectro-chemistry in direct characterisation of oxidation and reduction products.

References

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