

Fragmentation pathways of $[\text{Re}_2(\mu\text{-OR})_3(\text{CO})_6]^-$ ($\text{R} = \text{H}, \text{Me}$) and ligand exchange reactions with oxygen donor ligands, investigated by electrospray mass spectrometry

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Probing the chemistry of the dinuclear rhenium carbonyl complexes $[\text{Re}_2(\mu\text{-OR})_3(\text{CO})_6]^-$ ($\text{R} = \text{H}, \text{Me}$) by electrospray mass spectrometry. 1. Fragmentation pathways and ligand exchange reactions with oxygen donor ligands

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Graphical contents entry

Electrospray mass spectrometry is found to be a powerful technique for exploring the fundamental chemistry of the dinuclear hydroxo- and alkoxy-bridged species $[\text{Re}_2(\mu\text{-OR})_3(\text{CO})_6]^-$ ($\text{R} = \text{H}, \text{Me}$); fragmentation processes include dehydration, β -hydride elimination and CO loss, and exchange reactions with alcohols and phenols are also reported.

Abstract

The rhenium hydroxy and methoxy carbonyl complexes $[\text{Re}_2(\mu\text{-OR})_3(\text{CO})_6]^-$ ($\text{R} = \text{H}, \text{Me}$) have been studied by negative-ion electrospray mass spectrometry (ESMS). The complexes $[\text{Re}_2(\mu\text{-OR})_3(\text{CO})_6]^-$ ($\text{R} = \text{H}, \text{OMe}$) undergo facile exchange reactions with protic compounds, including alcohols and phenols. With dimethylmalonate, ester hydrolysis occurs giving carboxylate-containing complexes, and with H_2O_2 or Bu^tOOH , oxidation to ReO_4^- occurs. The feasibility and extent of these reactions can be conveniently, rapidly, and unambiguously determined by electrospray mass spectrometry, and is dependent on the acidity and steric bulk of the protic compound. The results also suggest that the complexes can be used as versatile starting materials for the synthesis of a wide range of analogous $[\text{Re}_2(\mu\text{-OR})_3(\text{CO})_6]^-$ complexes by simple reaction with an excess of the appropriate alcohol. By varying the applied cone voltage, the fragmentation pathways have been investigated; the hydroxy complex undergoes dehydration followed by CO loss, whereas for the methoxy complex, β -hydride elimination (and CO loss) is observed, with confirmation provided by deuterium labelling studies. Under ESMS conditions, the neutral complexes $[\text{Re}_2(\mu\text{-OR})_2(\mu\text{-dppf})(\text{CO})_6]$ [$\text{R} = \text{H}, \text{Me}$; dppf = 1,1'-bis(diphenylphosphino)ferrocene] undergo substantial solvolysis and hydrolysis to give mainly mononuclear species; simple parent ions (e.g. $[M + \text{H}]^+$) are not formed in appreciable abundance, probably due to the lack of an efficient ionisation pathway.

Introduction

Metal carbonyl complexes which also contain ancillary 'hard' ligands such as alkoxides (OR⁻) or hydroxide (OH⁻) are attracting interest¹ since they are likely intermediates in reactions such as the olefin carboalkoxylation reaction² and in the metal-catalysed hydrogenation of CO.³ Water-soluble, low-valent Re⁴ and ^{99m}Tc⁵ carbonyl compounds are also receiving much current attention due to their potential application in radioimmunotherapy and protein labelling. The formation of heterobimetallic aggregates from [Re₃(μ-OH)₄(CO)₉]⁻ has also been recently reported.⁶

The dinuclear species [Re₂(μ-OR)₃(CO)₆]⁻ (**1**, R = H; **2**, R = OMe) have been known for some time,⁷⁻⁹ and **1** has also been the subject of recent studies, which suggest that the chemistry of rhenium-carbonyl-hydroxo/aquo complexes is quite extensive.⁹⁻¹¹ However, to date the ligand-exchange chemistry of these complexes has received little attention, though facile alkoxide exchange and insertion reactions of terminal rhenium alkoxide complexes have been described.^{12,13} It was therefore of interest to investigate the chemistry of analogous exchange reactions of the triply-bridged complexes [Re₂(μ-OR)₃(CO)₆]⁻, which have, in principle, three exchangeable hydroxo or alkoxo ligands. Such exchange reactions have been briefly alluded to in the literature^{7,14} but no systematic study has been carried out.

Here we apply the technique of electrospray mass spectrometry (ESMS) to the study of such exchange reactions. ESMS is a soft ionisation technique, originally developed for the analysis of large, polar, involatile molecules such as polyethers, peptides and proteins, but in recent years the power of the technique for the analysis of inorganic and organometallic complexes has been realised.¹⁵ ESMS is particularly well-suited for the analysis of charged species, where the ionisation process simply involves the transfer of pre-existing solution ions into the gas phase

for analysis. In such cases, the ESMS technique is likely to give an accurate representation of the solution speciation of the various charged species present in the equilibrium mixture, and the technique has been compared to low temperature NMR spectroscopy.¹⁵ In the case of the dinuclear Re complexes considered here, identification of interconverting species by techniques such as IR or NMR spectroscopy is expected to be difficult, especially if the R group (e.g. *n*-octyl) gives a complex NMR spectrum. An additional advantage of the ES technique is that it allows fragmentation processes of ions to be explored; by use of a low (skimmer) cone voltage, 'parent' ions are typically observed, with increasing fragmentation occurring at higher cone voltages.

ESMS has recently been applied to the study of hydrolysis of $[\text{Re}(\text{CO})_3\text{Br}_3]^{2-}$ to the aquo complex $[\text{Re}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ ¹⁰ and to the study of base hydrolysis of CH_3ReO_3 , which proceeds *via* Re-OH species;¹⁶ other Re carbonyl species have also been studied by ESMS.¹⁷ Some of our studies presented in this paper have been reported in a preliminary Communication.¹⁸

Results and discussion

Preliminary ESMS study of complex 1

As expected for a charged species, the negative ion spectra of **1** (as its Et_4N^+ salt) in MeCN solvent show intense ions at all cone voltages. At a low initial cone voltage (5-10 V), the parent anion $[\text{Re}_2(\mu\text{-OH})_3(\text{CO})_6]^-$ is observed at m/z 591, together with a weak signal at m/z 879 corresponding to $[\text{Re}_3(\text{OH})_4(\text{CO})_9]^-$, Figure 1 (bottom spectrum). The latter ion is most probably a side product formed during the synthesis of **1**.⁹ This impurity can be simply and quickly converted into **1** by adding a drop of aqueous 2M NaOH to the ESMS solution, consistent with equation 1.



When the spectrum of **1** is recorded in MeCN- H_2O at a low cone voltage (5 V), the spectrum was very similar to that in pure MeCN, except that a series of low intensity aquated ions $[\text{Re}_2(\mu\text{-OH})_3(\text{CO})_6 + n\text{H}_2\text{O}]^-$ ions were seen, separated by m/z 18, with

n 1 to 15, and decreasing intensity to higher mass. These presumably arise due to strong hydrogen bonding of the water solvent with the OH groups of the complex, and similar observations have been found with other strongly hydrogen-bonded systems.¹⁹

Exchange reactions of complexes 1 and 2 with alcohols

During the course of our studies into **1**, we found that adventitious traces of methanol in the MeCN solvent resulted in observation of a species at m/z 605, indicating that facile replacement of an OH group by an OMe group was occurring. We have therefore undertaken a study of exchange reactions of **1** with various protic compounds, using the simplicity and convenience of ESMS to follow the progress of reactions, using a low cone voltage (typically 5 V, unless otherwise specified) to minimise fragmentation. Increased cone voltages were subsequently used to explore fragmentation routes.

About 1 min. after addition of a few drops of methanol to the ESMS solution of **1** in MeCN, the spectrum showed peaks at m/z 605, 619 and 633, corresponding respectively to the singly-, doubly- and triply-exchanged species $[\text{Re}_2(\mu\text{-OH})_n(\mu\text{-OMe})_{3-n}(\text{CO})_6]^-$ ($n = 0\text{-}2$), Scheme 1. The intensity of the peaks due to the exchanged species rapidly grew in intensity with respect to the parent ion $[\text{Re}_2(\mu\text{-OH})_3(\text{CO})_6]^-$ over 10 min., although the exact relative intensities of the peaks varied between experiments. On standing overnight (16 h) the main ion observed was $[\text{Re}_2(\mu\text{-OMe})_3(\text{CO})_6]^-$ **2**, with the bis- and mono-methoxy ions still present in successively lower abundance, and no parent ion remaining. After two weeks, a clean, intense peak due to the permethoxylated ion $[\text{Re}_2(\mu\text{-OMe})_3(\text{CO})_6]^-$ **2** was observed, together with a trace of the bis-methoxy species remaining. Similar results were obtained using ethanol as the alcohol. The time-dependent exchange reaction of **1** with MeOH is illustrated in Figure 1, and Figure 2 shows the high resolution spectrum of the individual ions after 10 min. It is worth noting that even on prolonged standing, the tri-rhenium species $[\text{Re}_3(\mu\text{-OH})_4(\text{CO})_9]^-$ was unaffected

by methanol, in contrast to the facile replacement of OH groups on **1**. In the Re₃ species the OH groups are spread out between three Re centres, whereas in [Re₂(μ-OH)₃(CO)₆]⁻ all three OH groups bridge the same two Re atoms, so the negative charge in the Re₃ species will be better dissipated, and the OH groups less nucleophilic.

The ES spectrum of a pre-formed sample of complex **2** shows the strong parent ion (*m/z* 633) at low cone voltages. The ES spectra always contain traces of the ion [Re₂(μ-OMe)₂(μ-OH)(CO)₆]⁻, even in a freshly made solution of the complex in MeCN, suggesting facile hydrolysis by adventitious water. On adding two drops of water to the ESMS solution, hydrolysis occurred over a period of minutes to generate a mixture of mono-, di-, and tri-hydroxy complexes, and after 35 min., the dominant species was [Re₂(μ-OH)₃(CO)₆]⁻ **1**. Addition of 4 drops of methanol to this solution quickly (within 1 min.) removed **1** and regenerated [Re₂(μ-OMe)₃(CO)₆]⁻, suggesting that OH → OMe exchange is more facile than OMe → OH exchange, and that the exchange is readily reversible. This is possibly due to the greater steric accessibility of the Re(μ-OH)Re unit compared to Re(μ-OMe)Re.

The exchange reaction of **2** with ethanol has also been investigated by ESMS; addition of excess ethanol to **2** resulted in slow exchange of OMe groups by OEt groups (the exchange was complete after standing overnight). The exchange was noticeably slower than the hydrolysis of **2**, and the reaction of **1** with methanol or ethanol, presumably due to the lower nucleophilicity of coordinated alkoxy groups compared to hydroxy groups, and the greater acidity of water compared to alcohols.

The exchange reaction of **1** with *n*-octanol readily affords analogous species as those from methanol, and the final [Re₂(μ-OR)₃(CO)₆]⁻ product is formed completely after standing overnight. The reaction of **1** with Bu^tOH, however, only affords the singly-exchanged species [Re₂(μ-OH)₂(μ-OBu^t)(CO)₆]⁻ (*m/z* 647), even with excess Bu^tOH and overnight reaction (16 h). Compared with the reaction of

MeOH, it is clear that steric factors are responsible for the difference in reactivity of the two alcohols.

Proton transfer from ROH to the hydroxo ligands of **1** is probably the initial, and critical step for the exchange reaction to proceed; a similar proton transfer mechanism has been proposed for the exchange of *fac*-[Re(η^1 -OR)(L)₂(CO)₃] with alcohols and phenols.^{12,20} Consistent with this, the hydrogen-bonded proton of the complex [Re{(MeO)⋯HOC₆H₄Me}(CO)₃(Et₂PCH₂CH₂PEt₂)] was located in the X-ray crystal structure.¹² In this context, it is noteworthy that the ES spectrum of a 1:1 mixture of **1** and **2** in alcohol-free MeCN showed no OH/OMe scrambled species even after 24 h. It is also worth noting that compounds with very weakly acidic protons do not replace the OH ligands, and complex **1** is unreactive towards the weak carbon acid malononitrile [CH₂(CN)₂], and **2** is unreactive towards acetone and Me₂SO, even after standing overnight. Steric factors also clearly play a role in the exchange reactions, since the sterically bulky *t*-butanol can only exchange one OH group.

The results described in this section parallel the tendency for ligand exchange observed previously, for example, the anion [Re₂(μ -OMe)₃(CO)₆]⁻ was found to convert into [Re₂(μ -OMe)_{*n*}(μ -OEt)_{3-*n*}(CO)₆]⁻ during its crystallisation from ethanol.¹⁴ The proposed mechanism of formation of the mixed-bridge trirhenium anion [Re₃(μ -OH)₂(μ -OMe)(μ_3 -OMe)(CO)₉]⁻ also involves methoxo-hydroxo exchange on the reaction intermediates.²¹

Exchange reactions of 1 and 2 with phenols

A summary of the extent of reaction of complexes **1** and **2** with different oxygen donor ligands is given in Table 1. The singly-, doubly- and triply-exchanged species are all observable from the reaction of **1** and phenol. A similar, slow but complete exchange of OMe groups by OPh groups was observed on addition of excess phenol to **2**. The tris-phenoxy species [Re₂(μ -OPh)₃(CO)₆]⁻ has been prepared previously from the reaction of Re₂(CO)₁₀ and phenol in the presence of

Me₃NO.²¹ or from the reaction of [Re₃(CO)₁₀(μ-H)₄]⁻ with an excess of phenol.²² It is also noteworthy that there is a minor ion at *m/z* 955 which can be assigned to the phenoxo-substituted trinuclear complex [Re₃(OH)₃(OPh)(CO)₉]⁻. However, with 2,4,6-tribromophenol (ROH), the monosubstituted species [Re₂(OH)₂(OR)(CO)₆]⁻ (*m/z* 905) was formed rapidly, but even in the presence of excess 2,4,6-tribromophenol further substitution did not occur on standing.

In a similar fashion, addition of excess hydroquinone (**3**) to **1** resulted in formation of the mono-substituted product [Re₂(OH)₂(OC₆H₄OH)(CO)₆]⁻ (*m/z* 683), and over several days the parent **1** disappeared, the monosubstituted ion was the dominant species, with some bis-substituted [Re₂(OH)(OC₆H₄OH)₂(CO)₆]⁻ (*m/z* 775). With pyrocatechol (**4**), a rapid but different reaction occurred with **1**, presumably due to the chelating nature of the catecholate ligand. The initial species formed were [Re₂(OH)(OC₆H₄O)(CO)₆]⁻ (*m/z* 665) and [Re₂(OH)₂(OC₆H₄OH)(CO)₆]⁻ (*m/z* 683). One possibility for the structure of the *m/z* 665 ion is **5**, with a bridging catecholate ligand. On standing, two new species rapidly grow in intensity: [Re(OC₆H₄O)(CO)₃]⁻ (*m/z* 379), [Re₂(OC₆H₄O)(OC₆H₄OH)(CO)₆]⁻ (*m/z* 757) together with [Re₂(OH)(OC₆H₄OH)₂(CO)₆]⁻ (*m/z* 775). About 25 min. after addition of the catechol, the solution had turned brown (from colourless), and the major species in the ES spectrum was [Re₂(OC₆H₄O)(OC₆H₄OH)(CO)₆]⁻. For a mixture of phloroglucinol (**6**) and **1**, the only major species observed after 3 d was the monosubstituted ion [Re₂(OH)₂{OC₆H₃(OH)₂}(CO)₆]⁻ (*m/z* 699); as with hydroquinone, no chelation is possible. ESMS is thus very useful in exploring the different coordination possibilities of related ligands toward **1**.

Reactions of 1 with carboxylic acids and phenylboronic acid

With a relatively strong acid (methanoic acid), the negative ion ES spectrum of **1** at 5 V shows an intense signal at *m/z* 647, assigned as [Re₂(μ-OH)(O₂CH)₂(CO)₆]⁻, together with a weak ion [Re₂(μ-OH)₂(O₂CH)(CO)₆]⁻ (*m/z*

618). Similarly, the addition of *ortho*-chlorobenzoic acid to **1** rapidly and almost quantitatively gave the mono-substituted species $[\text{Re}_2(\text{OH})_2(\text{O}_2\text{CC}_6\text{H}_4\text{Cl})(\text{CO})_6]^-$ (m/z 729). The positive ion spectrum of **1** with added HCOOH in MeCN at a cone voltage of 20 V showed mono-rhenium species, such as $[\text{Re}(\text{MeCN})_3(\text{CO})_3]^+$ (m/z 394), $[\text{Re}(\text{MeCN})_2(\text{CO})_4]^+$ (m/z 381) and $[\text{Re}(\text{MeCN})_2(\text{CO})_3]^+$ (m/z 353), which presumably result from acid cleavage of the bridging OH groups of **1**, followed by coordination of the solvent. In a related manner, the complex $[\text{Re}(\text{O}_2\text{CMe})(\text{CO})_3(\text{dppf})]$ has also been synthesised from $[\text{Re}_2(\mu\text{-OMe})_2(\mu\text{-dppf})(\text{CO})_6]^-$ and MeCO_2H in thf.²³ This suggests that controlled acidolysis reactions of rhenium carbonyl hydroxides and alkoxides could be a very useful and general preparative route to rhenium carboxylate complexes.

Compounds containing B-OH groups are known to react with hydroxylic compounds (ROH) forming B-OR linkages,²⁴ and so the reactivity of **1** towards phenylboronic acid $[\text{PhB}(\text{OH})_2]$ was studied. After addition of excess $\text{PhB}(\text{OH})_2$, the ES spectrum showed in addition to considerable unreacted **1**, adduct ions formed by condensation, *viz.* $[\text{Re}_2(\text{OH})_2\{\text{OB}(\text{OH})\text{Ph}\}(\text{CO})_6]^-$ (m/z 695) and $[\text{Re}_2(\text{OH})\{\text{OB}(\text{OH})\text{Ph}\}_2(\text{CO})_6]^-$ (m/z 799), but on standing for 1 week, these diminished in intensity, and an intense peak due to $[\text{Re}_3(\text{OH})_4(\text{CO})_9]^-$ was seen. The effect of acid on **1** has been documented previously,⁹ and is the reverse of equation 1.

Reactions of 1 with esters

The reaction of **1** with dimethylmalonate ($\text{MeO}_2\text{CCH}_2\text{CO}_2\text{Me}$) rapidly gives the main species $[\text{Re}_2(\text{OH})_2(\text{O}_2\text{CCH}_2\text{CO}_2\text{Me})(\text{CO})_6]^-$ at m/z 691. Only a small amount of the bis(carboxylate) species $[\text{Re}_2(\text{OH})(\text{O}_2\text{CCH}_2\text{CO}_2\text{Me})_2(\text{CO})_6]^-$ (m/z 791) was observed. On standing overnight, the main ion observed is the monorhenium complex $[\text{Re}(\text{O}_2\text{CCH}_2\text{CO}_2\text{Me})_2(\text{CO})_3]^-$ at m/z 505. These ions are formed by the facile cleavage of an ester bond by a bridging OH group, possibly promoted by the basicity of the $\mu\text{-OH}$ groups of **1** which attack the ester carbonyl

group. The dinuclear carboxylate species may have two possible structures which maintain six-coordination at rhenium, containing either a bridging carboxylate oxygen (7) or a bridging carboxylate group (8); the latter is probably the more likely, this being the most common bridging mode of a carboxylate ligand. The coordination chemistry of carboxylates with rhenium has been recently summarised.²⁵

Reaction of 1 with hydrogen peroxide and t-butylhydroperoxide (Bu^tOOH)

Addition of 2 drops of 27% H₂O₂ to a solution of **1** in MeCN resulted in immediate decomposition of **1**, and the species ReO₄⁻ (*m/z* 251) and a minor unidentified species at *m/z* 285 containing 1 Re. This may be the peroxy-rhenate(V) species [ReO₂(OOH)₂]⁻ and excellent agreement between observed and calculated isotope patterns was obtained. An alternative is the species [ReO₄ + H₂O₂]⁻, but since no [ReO₄ + H₂O]⁻ analogue is observed, we favour the peroxorhenate assignment. This result is not completely unexpected, given that H₂O₂ is a powerful oxidising agent, able to oxidise Re to the 7 oxidation state. However, we were interested to see if any reaction intermediates (oxo-carbonyl complexes, or hydroperoxy analogues of **1**) could be detected in the oxidation process, and therefore investigated the reaction using a smaller quantity of H₂O₂ (1 drop of 6% solution). However, the peak due to **1** slowly decreased in intensity, and that due to ReO₄⁻ grew, and no hydroperoxy analogues of **1**, *viz.* [Re₂(OH)_{*n*}(OOH)_{3-*n*}(CO)₆]⁻, could be observed. The reaction with a less reactive hydroperoxide, *t*-butylhydroperoxide (Bu^tOOH), was therefore investigated. Addition of excess Bu^tOOH to **1** in MeCN resulted in a much slower reaction than with H₂O₂, though the end product of the reaction after *ca.* 20 min. - ReO₄⁻ - was the same. The largest new species observed was at *m/z* 661, and this may be assigned as [Re₂(O₂)(OO^tBu)(CO)₆]⁻ (the anticipated species [Re₂(OH)₂(OO^tBu)(CO)₆]⁻ has *m/z* 663. Several other minor ions at *m/z* 605, 619, and 633 may be the mono OMe, OEt and OPr species, probably formed from adventitious traces of alcohols.

Fragmentation pathways of complexes 1 and 2 investigated by ESMS

Dehydration of **1** begins to occur at a cone voltage of 20 V, when a low abundance peak due to $[\text{Re}_2(\text{O})(\text{OH})(\text{CO})_6]^-$ (m/z 573) occurs. At 40 V, this is the most abundant ion, and very little parent ion **1** remains. When the cone voltage is increased to 60 V, decarbonylation of the dehydrated species occurs, as shown by the formation of the ions $[\text{Re}_2(\text{O})(\text{OH})(\text{CO})_n]^-$ ($n = 3-5$). The dehydration of complex **1** is much more favourable than decarbonylation, since ions $[\text{Re}_2(\mu\text{-OH})_3(\text{CO})_n]^-$ ($n = 3-5$) are not detected. At 60 V, weak ions assigned as dehydrated trirhenium and tetrarhenium species are also observed. The main Re_4 species are assigned as $[\text{Re}_4(\text{O})(\text{OH})_3(\text{CO})_{12}]^-$ (m/z 1149) and $[\text{Re}_4(\text{O})_2(\text{OH})(\text{CO})_{12}]^-$ (m/z 1131), while the ion $[\text{Re}_4(\text{OH})_5(\text{CO})_{12}]^-$ (m/z 1165) is much less abundant, consistent with higher degrees of dehydration at the higher cone voltage. Similarly, for the Re_3 species, $[\text{Re}_3(\text{O})_2(\text{CO})_9]^-$ (m/z 843) is more abundant than $[\text{Re}_3(\text{O})(\text{OH})_2(\text{CO})_9]^-$ (m/z 861), which in turn is more abundant than the ion $[\text{Re}_3(\text{OH})_4(\text{CO})_9]^-$ (m/z 879). It is noteworthy that the Re_4 species are not observed at low cone voltages {unlike the Re_3 species $[\text{Re}_3(\text{OH})_4(\text{CO})_9]^-$ }, and are therefore not likely to represent a charged component of the ESMS solution. Instead, aggregation of Re_2 and/or Re_3 species in the source of the spectrometer, promoted by the higher energy collisions at higher cone voltages, could provide a pathway to formation of small amounts of the Re_4 species.

At even higher cone voltages, e.g. 80 V, monorhenium species are observed due to fragmentation at the high cone voltage, e.g. $[\text{Re}(\text{O})(\text{CO})_3]^-$ (m/z 287) and $[\text{Re}(\text{O})(\text{CO})_2]^-$ (m/z 259), besides the dehydrated and decarbonylated dirhenium species $[\text{Re}_2(\text{O})(\text{OH})(\text{CO})_n]^-$.

Complex **2** fragments initially via β -hydride elimination, at cone voltages of 50 V and higher. The parent ion eliminates formaldehyde ($\text{H}_2\text{C}=\text{O}$) to form $[\text{Re}_2(\text{H})(\text{OMe})_2(\text{CO})_6]^-$ (m/z 603), $[\text{Re}_2(\text{H})_2(\text{OMe})(\text{CO})_6]^-$ (m/z 573) and finally the known species⁷ $[\text{Re}_2(\text{H})_3(\text{CO})_6]^-$ (m/z 543). The proposed mechanism of β -hydride

elimination of **2** is shown in Scheme 2. Decarbonylation of the β -eliminated species also occur at 50 V to give $[\text{Re}_2(\text{H})(\text{OMe})_2(\text{CO})_5]^-$ (m/z 575) and $[\text{Re}_2(\text{H})_2(\text{OMe})(\text{CO})_5]^-$ (m/z 545). The peaks of these decarbonylated ions overlap with the peaks at m/z 573 and 543 respectively (due to the 2 m/z difference between H_2CO and CO), to give characteristic 'quartet' patterns. (Species containing 2 Re atoms give 2 major peaks in the isotope distribution pattern, refer Fig. 2). At a higher cone voltage of 80 V, more decarbonylated species are observed, such as $[\text{Re}_2(\text{H})_3(\text{CO})_5]^-$ and $[\text{Re}_2(\text{H})(\text{CO})_5]^-$ overlapping around m/z 515, $[\text{Re}_2(\text{H})_3(\text{CO})_4]^-$ (m/z 487), $[\text{Re}_2(\text{H})_2(\text{OMe})(\text{CO})_2]^-$ (m/z 461) and some mononuclear species such as $[\text{Re}(\text{H})_2(\text{CO})_3]^-$ (m/z 271), and $[\text{Re}(\text{H})_2(\text{CO})_4]^-$ (m/z 299).

Support for the β -hydride mechanism comes from the elimination of ethanal (acetaldehyde) from the ion $[\text{Re}_2(\mu\text{-OEt})_3(\text{CO})_6]^-$, generated by addition of excess EtOH to **1** in MeCN, and allowing the solution to stand for 5 days. Thus, at a cone voltage of 50 V, β -hydride eliminated species are observed, *viz.* $[\text{Re}_2(\text{H})(\text{OEt})_2(\text{CO})_6]^-$ (m/z 631), $[\text{Re}_2(\text{H})_2(\text{OEt})(\text{CO})_6]^-$ (m/z 587), $[\text{Re}_2(\text{H})_3(\text{CO})_6]^-$ (m/z 543) and $[\text{Re}_2(\text{H})_3(\text{CO})_5]^-$ (m/z 515). Deuterium labelling studies are described in the next section.

There are many reports on β -hydride elimination of metal alkoxides,²⁶ indeed, reduction reactions of late transition metal complexes are often carried out in alcohol as the solvent and reducing agent. However there are few examples of β -hydride elimination of rhenium alkoxo complexes,²⁷ and, as far as we are aware, β -hydride elimination from coordinated alkoxide ligands has not been observed by ESMS, except from the stereoselective β -hydrogen elimination from nickel(II) glycoside complexes.²⁸ The mono-rhenium alkoxide complexes $[\text{Re}(\text{OR})(\text{CO})_3\text{L}_2]$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^i$; $\text{L}_2 =$ bidentate phosphine or arsine) are stable towards decomposition by β -hydride elimination.¹² Other types of C-H activation by organometallic complexes have been observed by ESMS,²⁹ such as the substitution of a Me ligand in $[\text{CpIr}(\text{PMe}_3)\text{Me}]^+$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) by R-H to form $[\text{CpIr}(\text{PMe}_3)(\text{R})]^+$ *via* an elimination-addition or σ -bond metathesis mechanism.³⁰

ESMS studies of β -hydrogen elimination from metal alkoxo carbonyls may help in the understanding of the decomposition of such complexes, and the metal-catalysed mechanisms for the formation of aldehydes and ketones. Here, we demonstrate clear evidence for the elimination using ESMS, and the formation of a bridging hydride ligand from the alkoxide species suggests that such species might also be formed synthetically under suitable conditions.

Ions formed by similar dehydration and decarbonylation processes are also observed in the ES spectra of partly-exchanged phenoxy derivatives at higher cone voltages, but, of course β -hydride elimination is not possible in this system. The fragmentation patterns of partly-substituted species depend on the number of hydroxyl groups, and in the case of phenoxy ligands, on the type of aryl substituent. For example, at 40 V the spectrum of a mixture of **1** and phenol which generates predominantly the monosubstituted $[\text{Re}_2(\text{OH})_2(\text{OPh})(\text{CO})_6]^-$ (m/z 667) shows the ion $[\text{Re}_2(\text{O})(\text{OPh})(\text{CO})_6]^-$ (m/z 649), which is formed by dehydration. On the other hand, the diphenoxo species $[\text{Re}_2(\text{OH})(\text{OPh})_2(\text{CO})_6]^-$ (m/z 743) does not undergo dehydration and is much more stable at higher cone voltages, since it contains only one OH group. At 60 V, besides the above species, a series of decarbonylated species appear, e.g. $[\text{Re}_2(\text{O})(\text{OPh})(\text{CO})_n]^-$ ($n = 3-5$), together with mononuclear fragments, e.g. $[\text{Re}(\text{O})(\text{CO})_3]^-$ (m/z 287). For the monosubstituted species $[\text{Re}_2(\text{OH})_2(\text{OR})(\text{CO})_6]^-$ ($R = 2,4,6$ -tribromophenol) at a cone voltage of 60 V, the ion $[\text{Re}_2(\text{O})(\text{OR})(\text{CO})_6]^-$ (m/z 887) was observed, together with $[\text{Re}_2(\text{O})(\text{OH})(\text{CO})_6]^-$. Since $[\text{Re}_2(\text{OH})_2(\text{OR})(\text{CO})_6]^-$ was essentially the only species observed at the lower cone voltage (20 V) in the sample used, elimination of the bulky phenol ROH (instead of H_2O) may provide the most likely pathway to $[\text{Re}_2(\text{O})(\text{OH})(\text{CO})_6]^-$.

Deuterium labelling studies of 2

Confirmation of the β -hydride elimination mechanism discussed above was achieved by deuterium labelling of **2**. The species $[\text{Re}_2(\mu\text{-OCD}_3)_3(\text{CO})_6]^-$ was

conveniently generated by addition of excess CD₃OD to complex **1** (as described earlier for CH₃OH exchange) and investigated at high cone voltages. Several minutes after addition of three drops of CD₃OD to a solution of **1** in MeCN the ES spectrum showed groups of peaks centred at *m/z* 594, 610, 626 and 642, corresponding to [Re₂(OH/OD)₃(CO)₆]⁻ and its singly, doubly and triply (OH/OD → OCD₃) exchanged species respectively, Figure 3. Overlap of species occurred in the spectrum, due to the exchange of H atoms for D atoms (from the exchangeable protons of CD₃OD), which occurs more rapidly than the exchange of OH/OD groups by OCD₃ groups, and to a lesser extent due to the isotopic impurity of the CD₃OD (i.e. the presence of e.g. some CD₂HOD). The peaks of higher (OH/OD → OCD₃) exchanged species grew in intensity with time. On standing, the main species is [Re₂(OCD₃)(CO)₆]⁻, with bis- and singly-exchanged species in successively lower abundance, and the parent ions [Re₂(OH/OD)₃(CO)₆]⁻ had disappeared. Since the byproduct of the (OH/OD → OCD₃) exchange reaction, water, can reverse the reaction, it is difficult to get the pure [Re₂(OCD₃)₃(CO)₆]⁻ at equilibrium. The equilibrated solution of **1** with excess CD₃OD was evaporated, the residue dissolved in fresh CD₃OD and monitored by ESMS. After 4 days, the solution contained predominantly [Re₂(OCD₃)₃(CO)₆]⁻. This species can also be cleanly obtained by the exchange reaction of [Re₂(OMe)₃(CO)₆]⁻ **2** with excess CD₃OD for 4 days.

At a cone voltage of 50 V, the ES spectrum of [Re₂(OCD₃)₃(CO)₆]⁻ (Figure 4) showed the ions [Re₂(D)_n(OCD₃)_{3-n}(CO)₆]⁻ (*n* = 0-3) at the expected *m/z* values: 642, 610, 580 and 546, consistent with β-deuteride elimination. Further decarbonylation of these ions was also observed. The overlapping of peaks of [Re₂(D)(OCD₃)₂(CO)₅]⁻ and [Re₂(D)₂(OCD₃)(CO)₅]⁻ with the above species was observed around *m/z* 580 and 546. The ion [Re₂(D)₃(CO)₅]⁻ was also detected in low intensity.

Fragmentation and ionisation of the neutral complexes [Re₂(μ-OR)₂(μ-dppf)(CO)₆] (R = H, Me)

The complexes [Re₂(μ-OR)₂(μ-dppf)(CO)₆] (R = H, Me) can be prepared by controlled acidolysis of [Re₂(μ-OR)₃(CO)₆]⁻ (R = H, Me) in the presence of dppf.⁹ The ESMS behaviour of the neutral complexes has been investigated to make a comparison between the properties of the two groups of complexes. The detected ions for [Re₂(μ-OR)₂(μ-dppf)(CO)₆] (R = H, Me) are largely common. In positive-ion mode at a cone voltage of 20 V the solvated fragments [Re(O)(MeCN)(dppf)(CO)₃]⁺ (*m/z* 882), [Re(MeCN)(dppf)(CO)₃]⁺ (*m/z* 866) together with the minor ion [Re(O)(MeCN)(dppfO)(CO)₃]⁺ (*m/z* 898) are all observed in the spectra of the complexes. In negative-ion mode (cone voltage 20 V), ReO₄⁻ is the common anion observed for both complexes, besides their correspondingly hydrolysed species.

For the hydroxy complex [Re₂(μ-OH)₂(μ-dppf)(CO)₆], in addition to the common ions discussed above, minor ions [Re₂(OH)(MeCN)₂(dppf)(CO)₆]⁺ (*m/z* 1194), [*M* + H]⁺ (*m/z* 1129) and [dppfO₂ + H]⁺ (*m/z* 587) were also observed. The observation of [*M* + H]⁺ indicates that the species can be protonated, presumably at one of the OH groups. Even at a low cone voltage of 5 V, the oxo and non-oxo 'parent' ions [Re(O)(MeCN)(dppf)(CO)₃]⁺ (*m/z* 882) and [Re(MeCN)(dppf)(CO)₃]⁺ (*m/z* 866) are observed. At a higher cone voltage of 50 V, new species appear such as [Re(O)(dppf)(CO)₃]⁺ (*m/z* 841), [Re(O)(MeCN)(dppf)(CO)₂]⁺ (*m/z* 854), [Re(O)(MeCN)(dppf)(CO)]⁺ (*m/z* 826), [Re(O)(dppf)(CO)₂]⁺ (*m/z* 813) and [Re₂(OH)(dppf)(CO)₆]⁺ (*m/z* 1111). The latter ion can be formed from the parent compound [Re₂(μ-OH)₂(μ-dppf)(CO)₆] by loss of an OH⁻ group, an ionisation process reminiscent of the halide-loss ionisation pathway commonly observed for a wide range of neutral transition metal halide complexes.³¹ The negative-ion spectrum at 20 V shows (in addition to ReO₄⁻) the trinuclear species [Re₃(OH)₄(CO)₉]⁻ (*m/z* 878).

Conclusions

Electrospray mass spectrometry has been shown to be a powerful technique for studying ligand exchange reactions and fragmentation processes of the anionic rhenium carbonyl complexes $[\text{Re}_2(\mu\text{-OR})_3(\text{CO})_6]^-$. The strength of the technique lies with its convenience, and ability to provide information on exchanging systems; this would be of particular use when relatively complex ligands are under investigation. The results of this study suggest that it should be possible to synthesise novel alkoxo-bridged rhenium complexes based on this simple exchange reaction, which is experimentally easy to carry out, and which can be rapidly and simply monitored by ESMS. In the subsequent paper, we describe the use of ESMS in monitoring the chemistry of complexes $[\text{Re}_2(\mu\text{-OR})_3(\text{CO})_6]^-$ with S, Se, N and P-based ligands.

Experimental

The complexes $[\text{Et}_4\text{N}][\text{Re}_2(\mu\text{-OH})_3(\text{CO})_6]$, $[\text{Et}_4\text{N}][\text{Re}_2(\mu\text{-OMe})_3(\text{CO})_6]$ and $[\text{Re}_2(\mu\text{-OR})_2(\mu\text{-dppf})(\text{CO})_6]$ ($\text{R} = \text{H}, \text{Me}$) were synthesised by the literature procedures.⁹ Alcohols used were at least of LR grade, and were used as supplied. Dimethylmalonate (BDH), phenylboronic acid (Aldrich), pyrocatechol (BDH), hydroquinone (Aldrich), phloroglucinol (Aldrich) and *t*-butylhydroperoxide (Sigma, 70% aqueous solution) were used as supplied.

Electrospray mass spectrometry

ES spectra were recorded in negative-ion mode on a VG Platform II quadrupole instrument (m/z range 0 - 3000), using CH_3CN [or occasionally $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (1:1 v/v)] as the mobile phase. The CH_3CN was of hplc grade, and the water was double distilled prior to use. The sample solutions (2 mL), of approximate concentration (of **1** or **2**) of 0.1 mg mL^{-1} (in some cases with several added drops of

a liquid reagent, or several small crystals of a solid reagent) were introduced *via* a microlitre syringe and a 10 μL sample loop fitted to a Rheodyne injector. The mobile phase was delivered to the mass spectrometer by a SpectraSystem P1000 LC pump, at a flow rate of 0.02 mL min^{-1} . Nitrogen was employed both as the nebulising and drying gas. The capillary voltage was 3.5 kV. Fragmentation was investigated by varying the skimmer cone voltage, typically from 5 to 80 V. Spectra were typically acquired as 10 to 12 scans, subsequently averaged.

Identification of all major ions was achieved by comparison of experimental and calculated isotope distribution patterns; the latter were obtained using the *Isotope* simulation program.³²

Before each series of experiments, the spectrum of complex **1** was recorded as a measure of instrument cleanliness, in particular to identify any trace contamination of alcohols (ROH) in the CH_3CN or $\text{CH}_3\text{CN-H}_2\text{O}$ mobile phase, which leads to the *in situ* formation of the species $[\text{Re}_2(\mu\text{-OH})_n(\mu\text{-OR})_{3-n}(\text{CO})_6]^-$ ($n = 1\text{-}3$).

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Electronic supplementary information available: Table of ESMS data for the complexes $[\text{Re}_2(\mu\text{-OR})_2(\mu\text{-dppf})(\text{CO})_6]$ (R = H, Me).

Table 1. Ions resulting from the exchange reactions (16 h duration) of complexes **1** and **2** with selected simple protic reagents in MeCN

Complex	Reagent	Major observed ions (<i>m/z</i> , intensity)
1	-	$[\text{Re}_2(\text{OH})_3(\text{CO})_6]^-$ (591, s)
1	Methanol	$[\text{Re}_2(\text{OH})_n(\text{OMe})_{3-n}(\text{CO})_6]^-$ n = 2(605, w), 1(619, m), 0(633, s)
1	Ethanol	$[\text{Re}_2(\text{OH})_n(\text{OEt})_{3-n}(\text{CO})_6]^-$ n = 2(619, w), 1(647, w), 0(675, s)
1	<i>n</i> -Octanol	$[\text{Re}_2(\text{OH})_n(\text{OOct})_{3-n}(\text{CO})_6]^-$ n = 2(703, m), 1(815, s), 0(927, m)
1	Phenol	$[\text{Re}_2(\text{OH})_n(\text{OPh})_{3-n}(\text{CO})_6]^-$ n = 2(667, m), 1(743, s), 0(819, w)
1	<i>tert</i> -Butanol	$[\text{Re}_2(\text{OH})_2(\text{OPh})(\text{CO})_6]^-$ (647, s)
1	Formic acid	$[\text{Re}_2(\text{OH})_n(\text{HCOO})_{3-n}(\text{CO})_6]^-$ n = 2(619, w), 1(647, s)
1	R-CO ₂ Me (R= CH ₂ CO ₂ Me)	$[\text{Re}_2(\text{OH})_n(\text{RCO}_2)_{3-n}(\text{CO})_6]^-$ n = 2 (691, s), 1(791, w) after 15 min. $[\text{Re}(\text{RCO}_2)_2(\text{CO})_3]^-$ (505, s) overnight
2	-	$[\text{Re}_2(\text{OMe})_3(\text{CO})_6]^-$ (633, s)
2	Water	$[\text{Re}_2(\text{OMe})_n(\text{OH})_{3-n}(\text{CO})_6]^-$ n = 0(591, s), 1(605, w), 2(619, w)
2	Ethanol	$[\text{Re}_2(\text{OMe})_n(\text{OEt})_{3-n}(\text{CO})_6]^-$ n = 0(675, s), 1(661, w), 2(647, w)
2	Phenol	$[\text{Re}_2(\text{OMe})_n(\text{OPh})_{3-n}(\text{CO})_6]^-$ n = 0(819, w), 1(757, m), 2(695, s)

Captions for Figures

Figure 1. Negative ion ES spectra (cone voltage 5 V) of $[\text{Re}_2(\mu\text{-OH})_3(\text{CO})_6]^-$ in MeCN at various times after addition of excess MeOH.

Figure 2. High-resolution negative ion ES spectrum (cone voltage 5 V) of a solution of $[\text{Re}_2(\mu\text{-OH})_3(\text{CO})_6]^-$ **1** in MeCN, 10 min. after addition of excess MeOH, showing the presence of the individual ions $[\text{Re}_2(\text{OH})_n(\text{OMe})_{3-n}(\text{CO})_6]^-$ ($n = 0\text{-}3$). The inset shows the calculated isotope distribution pattern for the $n = 2$ ion.

Figure 3. Negative ion ES spectra (cone voltage 20 V) of $[\text{Re}_2(\mu\text{-OH})_3(\text{CO})_6]^-$ **1** in MeCN, 10 min. after adding CD_3OD , showing the presence of OH/OD and OCD_3 exchanged species.

Figure 4. Negative ion ES spectrum of $[\text{Re}_2(\mu\text{-OCD}_3)_3(\text{CO})_6]^-$ in MeCN at a cone voltage of 50 V, showing the formation of Re-D species by β -deuteride elimination.