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Ligand exchange reactions of $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ (R = H, Me) with sulfur, selenium, phosphorus and nitrogen donor ligands, investigated by electrospray mass spectrometry †

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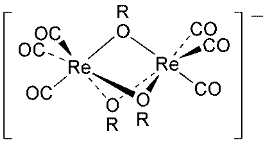
Negative-ion electrospray mass spectrometry has been used to investigate the reactions of the dinuclear rhenium aggregates $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ **1** and $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$ **2** with a range of thiols, benzeneselenol, and some other sulfur-, phosphorus- and nitrogen-based ligands. Typically up to three of the hydroxo ligands are replaced by simple thiolates, giving the series of species $[Re_2(OH)_2(SR)(CO)_6]^-$, $[Re_2(OH)(SR)_2(CO)_6]^-$, and $[Re_2(SR)_3(CO)_6]^-$. Similarly, reaction of **1** with H_2S gives the species $[Re_2(\mu\text{-}SH)_3(CO)_6]^-$, which undergoes an analogous fragmentation process to $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$, at high cone voltages, by loss of H_2S and formation of $[Re_2(S)(SH)(CO)_6]^-$. With ligands which are good chelating agents (such as dithiocarbamates $R_2NCS_2^-$, and thiosalicylic acid, $HSC_6H_4CO_2H$) initial substitution of one or two OH groups readily occurs, but on standing the dimer is cleaved giving $[Re(S_2CNR_2)_2(CO)_3]^-$ and $[Re(SC_6H_4CO_2)(CO)_3]^-$. The different reactivities of the dithiol reagents benzene-1,2- and benzene-1,4-dimethanethiol towards **1** are also described. Complex **1** also reacts with aniline, and with primary (but not secondary) amides $RC(O)NH_2$, giving monosubstituted species $[Re_2(OH)_2(NHPh)(CO)_6]^-$ and $[Re_2(OH)_2\{NHC(O)R\}(CO)_6]^-$ respectively. The reactions with adenine and thymine, and with the inorganic anions thiocyanate and thiosulfate, are also described.

Introduction

In the preceding paper[1] we described the use of negative-ion electrospray mass spectrometry (ESMS) for analysis of the rhenium carbonyl hydroxo(alkoxo) complexes $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ **1** and $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$ **2**, including the various fragmentation pathways observed for these species and their exchange reactions with other oxygen donor ligands. In this paper we describe the ligand exchange reactions of **1** with various sulfur-, selenium-, phosphorus- and nitrogen-based ligands. Complex **1** contains rhenium(I) and is therefore expected to have a strong affinity for soft donor ligands. Indeed, reactions of rhenium alkoxo complexes with second-row substrates such as thiols and secondary phosphines are considered to be irreversible, such as between the monorhenium complexes $[Re(OR)(CO)_3L_2]$ (R = Me or Et, L_2 = bidentate arsine or phosphine ligand) and H_2S, thiols and primary or secondary phosphines.[2] However, the $Re(CO)_3$ unit also forms stable complexes with hard ligands such as hydroxide,[3,4] indicating that it does not fit comfortably into the 'traditional' hard–soft acid–base scheme.



1, R = H
2, R = OMe

Results and discussion

General comments

The analysis of the dinuclear rhenium carbonyl hydroxo complex **1** by negative-ion electrospray mass spectrometry is described in the preceding paper.[1] Spectra at low cone voltages (5–20 V) are dominated by the parent ion $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ at *m*/*z* 591, so that exchange reactions with various ligands can easily be monitored by simply adding a small quantity of the ligand to a solution of **1**, and then recording the ESMS spectrum at different times.

The ligands investigated include a series of mono- and dithiols, benzeneselenol, thiocyanate, dithiocarbamates ($R_2NCS_2^-$), together with some difunctional thiol-based ligands such as thiosalicylic acid ($HSC_6H_4CO_2H$) and 3-sulfanylpropionic acid, $HSCH_2CH_2CO_2H$. The primary phosphine $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2PH_2)]$ was also studied for comparative purposes. The reactions of amines and amides have also been investigated.

Full details of the *m*/*z* values and relative intensities of the various major ions observed in this work are summarised in the electronic supplementary data. In all cases, the unchanged $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ and $[Re_3(OH)_4(CO)_9]^-$ ions were typically observed, particularly in the early stages of the reaction. At higher cone voltages (30–50 V) the dehydrated ion $[Re_2(O)$-

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† Probing the chemistry of the dinuclear rhenium carbonyl complexes $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ (R = H or Me) by electrospray mass spectrometry. Part 2.

Electronic supplementary information (ESI) available: full ES data for the reactions of complexes **1** and **2** with S- and Se-based ligands. See http://www.rsc.org/suppdata/dt/b0/b003897k/

Table 1 Major negative ions observed[a] in reactions of the complexes $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ **1** with *p*-toluenethiol, thiosalicylic acid and H_2S in MeCN

Mixture	Cone voltage/V (reaction time)	Ions (*m*/*z*)
1 + *p*-MeC_6H_4SH	5 (20 min)	**$[Re_2(OH)_3(CO)_6]^-$** (591), $[Re_2(OH)_2(SR)(CO)_6]^-$ (697), $[Re_3(OH)_4(CO)_9]^-$ (879, trace)
	5 (overnight)	**$[Re_2(OH)_2(SR)(CO)_6]^-$** (697), $[Re_2(OH)(SR)_2(CO)_6]^-$ (803), $[Re_3(OH)_4(CO)_9]^-$ (879, trace), $[Re_2(SR)_3(CO)_6]^-$ (909, trace)
	5 (1 week)	**$[Re_2(OH)(SR)_2(CO)_6]^-$** (803), $[Re_3(OH)_4(CO)_9]^-$ (879, trace), $[Re_2(SR)_3(CO)_6]^-$ (909)
1 + thiosalicylic acid (H_2tsal)	5 (1 min)	$[Re_2(OH)_3(CO)_6]^-$ (591, trace), **$[Re_2(OH)(tsal)(CO)_6]^-$** (709), **$[Re_2(OH)_2(Htsal)(CO)_6]^-$** (727), $[Re_2(OH)(tsal)(MeCN)(CO)_6]^-$ (750), $[Re_3(OH)_4(CO)_9]^-$ (879)
	5 (10 min)	$[Re_2(OH)_3(CO)_6]^-$ (591, trace), **$[Re_2(OH)(tsal)(CO)_6]^-$** (709), $[Re_2(OH)_2(Htsal)(CO)_6]^-$ (727), $[Re_2(OH)(tsal)(MeCN)(CO)_6]^-$ (750), $[Re_3(OH)_4(CO)_9]^-$ (879)
	5 (overnight)	**$[Re(tsal)(CO)_3]^-$** (423), $[Re(tsal)(CO)_3(NH_3)]^-$ (440)
1 + H_2S	5 (35 min)	**$[Re_2(OH)_3(CO)_6]^-$** (591), $[Re_2(OH)_2(SH)(CO)_6]^-$ (607), $[Re_2(OH)(SH)_2(CO)_6]^-$ (623), $[Re_2(SH)_3(CO)_6]^-$ (639)
	5 (overnight)	**$[Re_2(SH)_3(CO)_6]^-$ (639)** plus traces of $[Re_2(OH)_3(CO)_6]^-$ (591), $[Re_2(OH)_2(SH)(CO)_6]^-$ (607), $[Re_2(OH)(SH)_2(CO)_6]^-$ (623)
	50 (overnight)	$[Re_2(S)(SH)(CO)_4]^-$ (549), $[Re_2(S)(SH)(CO)_5]^-$ (577), **$[Re_2(S)(SH)(CO)_6]^-$** (605), $[Re_2(SH)_3(CO)_6]^-$ (639)

[a] The *m*/*z* value refers to the peak of greatest intensity in the isotope distribution pattern, calculated using the ISOTOPE program.[32] The major ions observed are indicated in **bold** type.

$(OH)(CO)_6]^-$ was also seen. These ions will not further be commented upon in the discussion.

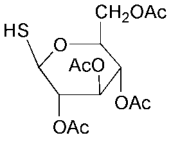
Reactions of complexes 1 and 2 with monofunctional thiols and PhSeH

Addition of *p*-toluenethiol (RSH) in excess to complex **1** results initially in a mixture of the species $[Re_2(OH)_n(SR)_{3-n}(CO)_6]^-$ ($n = 0$–3) which on standing overnight gives mainly the mono- and bis-thiolate anions $[Re_2(OH)_2(SR)(CO)_6]^-$ (*m*/*z* 697) and $[Re_2(OH)(SR)_2(CO)_6]^-$ (*m*/*z* 803), and after 1 week mainly the bis-thiolate species, even in the presence of an excess of thiol, Table 1. It is also worth noting that in some experiments there was some of the mono-exchanged Re_3 species present *viz.* $[Re_3(OH)_3(SR)(CO)_9]^-$ at *m*/*z* 985. This is in contrast to the lack of a methoxy analogue observed when complex **1** is treated with methanol, giving $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$ and unchanged $[Re_3(OH)_4(CO)_9]^-$. One possibility is that the SR for OH exchange has occurred on $[Re_3(OH)_4(CO)_9]^-$ directly, reflecting the greater ability for (more acidic) thiols to protonate the less basic {compared to $[Re_2(OH)_3(CO)_6]^-$} OH groups of $[Re_3(OH)_4(CO)_9]^-$.

When *p*-toluenethiol is added to the methoxy complex $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$ **2**, exchange of OMe for SR groups occurs, but slower than for the reaction of **1**. This is presumably due to the steric protection afforded by the methoxy groups. After 20 min little reaction had occurred, while after standing overnight there is fairly clean formation of the monosubstituted derivative $[Re_2(OMe)_2(SR)(CO)_6]^-$, and after 1 week fairly clean formation of the bis-substituted compound, together with some mono- and some tris-substituted species.

With benzeneselenol (PhSeH) and complex **1** similar results were also obtained, with formation of the mono- and di-substituted species $[Re_2(OH)_{3-n}(SePh)_n(CO)_6]^-$ ($n = 1$ or 2) occurring rapidly, but with no evidence of formation of the tris(selenolate) complex.

Similar results were obtained with mixtures of complex **1** and *n*-dodecanethiol, *n*-$C_{12}H_{25}SH$, β-D-thioglucose tetraacetate **3**,



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or 2-sulfanylethanol ($HSCH_2CH_2OH$) except that the rate of reaction appeared somewhat slower with the bulky thiols, possibly due to their greater steric bulk. These studies demonstrate the power of ESMS in monitoring reactions of such thiols, which would be expected to give complex NMR spectra. With 2-sulfanylethanol a (low intensity) intermediate ion at *m*/*z* 633 was observed, which may be $[Re_2(OH)(SCH_2CH_2O)(CO)_6]^-$ (containing a chelate ring Re–S–CH_2CH_2–O) or less likely, $[Re_2(O)(SCH_2CH_2OH)(CO)_6]^-$.

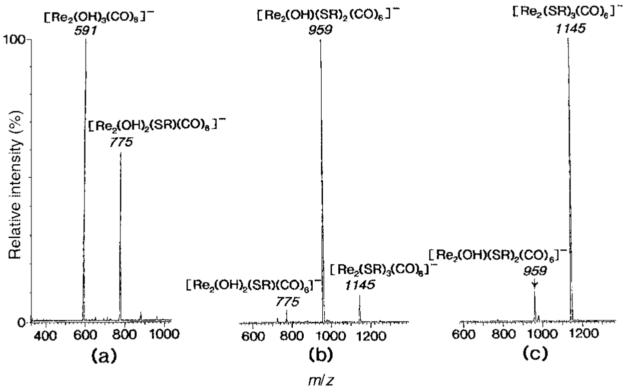


Fig. 1 Negative ion ES spectra (cone voltage 5 V) of a mixture of $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ **1** and *n*-dodecanethiol (RSH) in MeCN: (a) 25 min after addition, (b) after standing overnight, (c) after 1 week.

On standing the solutions of complex **1** and the above thiols overnight the tris(thiolate) anions $[Re_2(SR)_3(CO)_6]^-$ were formed in all cases (exclusively for 2-sulfanylethanol) but with the bis-substituted species $[Re_2(OH)(SC_{12}H_{25})_2(CO)_6]^-$ (*m*/*z* 959) the major species for 1-dodecanethiol. After 1 week, almost exclusively $[Re_2(SC_{12}H_{25})_3(CO)_6]^-$ (*m*/*z* 1144) and $[Re_2(SR)_3(CO)_6]^-$ (*m*/*z* 1631) (R = thioglucose tetraacetate) were formed, indicating relatively slow reactions. ES spectra at a cone voltage of 5 V showing the course of the reaction with dodecanethiol are given in Fig. 1. Addition of an excess of water to the solutions of $[Re_2(SC_{12}H_{25})_3(CO)_6]^-$ or $[Re_2(SCH_2CH_2OH)_3(CO)_6]^-$ caused no reversal to hydroxy species even after standing for 1 week, demonstrating the stability of the Re–thiolate combination. This could be due to stronger Re–S than Re–O bonds, and the fact that water is a weaker acid (pK_a *ca.* 16) compared to thiols (pK_a *ca.* 10).

Thiolate-bridged species of the type $[Re_2(\mu\text{-}SR)_3(CO)_6]^-$ have been described previously, for example the tris(thiobenzoate) complex $[Re_2\{SC(O)Ph\}_3(CO)_6]^-$, which was prepared from $[ReBr(CO)_5]$ and PhC(O)SM (M = K or Cs), has been shown by an X-ray crystallographic study to contain three bridging SR groups.[5] The complexes $[Et_4N]_2[M_2(\mu\text{-}SCH_2CH_2OH)_3(CO)_6]$ (M = Tc or Re) were prepared by reaction of $[Et_4N]_2[MCl_3(CO)_3]$ with 2-sulfanylethanol, and the technetium complex was structurally characterised.[6] A series of complexes $[Et_4N][Re_2(\mu\text{-SR})_3(CO)_6]$ (R = Me, Bu^t, Ph or C_6F_5) were prepared by reaction of $[Et_4N][Re_2(\mu\text{-Br})_3(CO)_6]$ with $[SnBu^n{}_3(SR)]$ in refluxing methanol.[7] Other methods, employing the sodium salt of the thiolate and a variety of other rhenium precursors $[Re_2Br_3(CO)_6]^-$, $[ReBr_2(CO)_4]^-$, $[ReBr_3(CO)_3]^{2-}$, have also been described for the synthesis of this type of complex.[7,8] Finally, reactions of $[MCp_2(SPh)_2]$ (M = Mo or W) with $[Re_2(CO)_{10}]$ give complexes containing the fulvalene (μ-η^5:η^5-$C_{10}H_8$; Fv) ligand, $[M_2FvCp_2(\mu\text{-SPh})][Re_2(\mu\text{-SPh})_3(CO)_6]$.[9] These complexes form part of a general class of the type $[Re_2(\mu\text{-X})_3(CO)_6]^-$, *e.g.* where X = anionic ligand.[10] Thiolate ligands are well known for their ability to bridge metal centres, but relatively few thiolate-containing dinuclear complexes containing three thiolate bridges have been synthesized,[11] though there are a number of examples of complexes $[(OC)_4M(\mu\text{-SR})_2M(CO)_4]$ (M = Mn or Re)[12] and of other rhenium carbonyl complexes containing bridging thiolate ligands.[13] Relatively few examples appear to exist regarding the synthesis of thiolate complexes from alkoxide complexes,[14,15] however, the ESMS studies described in this paper strongly suggest that it could be a very successful and convenient approach.

When the cone voltage is increased to 50 V the mono-*p*-toluenethiolato species (in a solution containing mainly this species) undergoes dehydration to give $[Re_2(O)(SR)(CO)_6]^-$ at *m*/*z* 679 and $[Re_2(O)(SR)(CO)_5]^-$ at *m*/*z* 651. In contrast, the bis-thiolate species is stable at 50 V, with no fragmentation occurring. The monosubstituted species $[Re_2(OH)_2(SePh)(CO)_6]^-$ also undergoes dehydration giving $[Re_2(O)(SePh)(CO)_6]^-$ at *m*/*z* 712. The dehydration of the mono-thiolate derivatives is the same behaviour as that observed for monosubstituted alkoxy and phenoxy derivatives, discussed in the preceding paper. On applying a cone voltage of 30 V to the monosubstituted ion $[Re_2(OH)_2(SCH_2CH_2OH)(CO)_6]^-$ the species $[Re_2(O)(SCH_2CH_2OH)(CO)_6]^-$ (*m*/*z* 633) was formed. At elevated cone voltages (50–70 V) the bis- and tris-substituted ions $[Re_2(OH)(SC_{12}H_{25})_2(CO)_6]^-$ and $[Re_2(SC_{12}H_{25})_3(CO)_6]^-$ are stable towards fragmentation by dehydration, as is also found for the bis(*p*-toluenethiolate) species above. This is consistent with two or more OH groups being required for intramolecular facile dehydration reaction to proceed, as would of course be expected. No evidence of fragmentation by β-hydride elimination was observed for $[Re_2(SC_{12}H_{25})_3(CO)_6]^-$ at 70 V. Similarly, $[Re_2(SCH_2CH_2OH)_3(CO)_6]^-$ showed appreciable stability at 50 V, with a base peak of the parent ion, and low intensity ions at *m*/*z* 665 and 693 ascribed to $[Re_2(SCH_2CH_2O)(SCH_2CH_2OH)(CO)_n]^-$ (n = 5 and 6), formed by elimination of 2-sulfanylethanol. In contrast, the methoxy and ethoxy derivatives $[Re_2(OR)_3(CO)_6]^-$ undergo facile β-hydride elimination processes at cone voltages of 50 V and higher.[1] Presumably, the stability of the C=O bond (compared to a C=S bond) formed on β-hydride elimination is the major driving force for the reaction with alkoxides when compared to thiolates; the stability of a Re–S compared to a Re–O bond may also be a contributing factor.

Reactions of complex 1 with H_2S and Na_2S

No reaction was observed between complex **1** and Na_2S in MeCN–water solution, consistent with the requirement for ‘acidic’ protons to be present in the incoming ligand. Na_2S will act as a source of base ($S^{2-} + H_2O \longrightarrow SH^- + OH^-$), and consistent with this the intensity of the $[Re_3(OH)_4(CO)_9]^-$ ion (*m*/*z* 878) decreased markedly on addition of Na_2S, similar to the addition of OH^-, as described previously.[1]

In contrast, H_2S (a weak acid) reacted with complex **1** in MeCN quite quickly, giving initially a mixture of **1**, mono-, di- and tri-substituted species $[Re_2(\mu\text{-OH})_n(\mu\text{-SH})_{3-n}(CO)_6]^-$ at *m*/*z* 591, 607, 623 and 639 respectively, at a cone voltage of 5 V. Data are summarised in Table 1. After standing overnight, the solution had turned pale yellow, and $[Re_2(\mu\text{-SH})_3(CO)_6]^-$ was the dominant ion, with a small amount of **1**, and traces of mono- and di-substituted species. No ($OH \longrightarrow SH$) exchange was observed on the trinuclear species $[Re_3(OH)_4(CO)_9]^-$. On increasing the cone voltage to 50 V the analogous fragmentation pathway is observed for $[Re_2(\mu\text{-SH})_3(CO)_6]^-$ as for **1**,[1] *i.e.* facile elimination of H_2S, together with CO loss, resulting in the ions $[Re_2(S)(SH)(CO)_6]^-$ (*m*/*z* 605), $[Re_2(S)(SH)(CO)_5]^-$ (*m*/*z* 577), and $[Re_2(S)(SH)(CO)_4]^-$ (*m*/*z* 549). Spectra at cone voltages of 5 and 50 V are shown in Fig. 2. At 70 V the dominant ions observed are $[Re_2(S)(SH)(CO)_3]^-$ (*m*/*z* 521) and $[Re_2(S)(SH)(CO)_4]^-$. After standing for several days, the 5 V spectrum of $[Re_2(\mu\text{-SH})_3(CO)_6]^-$ also showed (unassigned) species at *m*/*z* 454 and 1276.

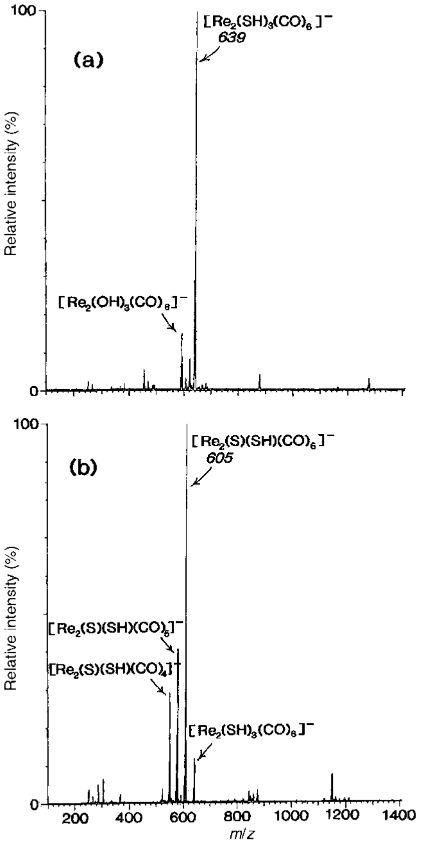


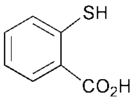
Fig. 2 Negative ion ES spectra of $[Re_2(\mu\text{-SH})_3(CO)_6]^-$ (generated from $[Re_2(\mu\text{-OH})_3(CO)_6]^-$ **1** and H_2S) in MeCN solution at cone voltages of (a) 5 and (b) 50 V, showing fragmentation by loss of H_2S and CO.

The species $[Re_2(\mu\text{-SH})_3(CO)_6]^-$ appears to be stable towards water, since a solution in MeCN still showed the ion as the base peak after addition of an excess of water and standing for 3 days. However, the addition of NaOH results in rapid reconversion into $[Re_2(\mu\text{-OH})_3(CO)_6]^-$, together with some ReO_4^- (*m*/*z* 251). When smaller quantities of NaOH are used the intermediate mixed OH/SH species $[Re_2(\mu\text{-OH})_n(\mu\text{-SH})_{3-n}(CO)_6]^-$ (n = 1 or 2) can be observed. It is noteworthy that the species $[Re_2(SH)_3(CO)_6]^-$ has not been reported, perhaps due to lack of a convenient synthetic route.

Reactions of complex 1 with difunctional thiolate ligands

Thiosalicylic acid. Selected data for the thiosalicylate system are summarised in Table 1. Thiosalicylic acid (H_2tsal, **4**) is able to co-ordinate to metal centres as either a monoanion or dianion, and can show a variety of bonding modes, from monodentate, to chelating, and bridging.[16,17] The 5 V ESMS spectrum of complex **1**, to which a small quantity of thiosalicylic acid had been added, showed complete and rapid (several minutes) consumption of **1** and formation of two new species, the mono(thiosalicylate)-substituted ion [Re$_2$(OH)-

(tsal)$(CO)_6]^-$ at m/z 709 and $[Re_2(OH)_2(Htsal)(CO)_6]^-$ (m/z 727). A possible structure for this ion is **5**, with a bridging thiolate ligand (if it is assumed that Re^I is soft in character), though an isomer with a bridging carboxylate is also possible. A likely structure for the m/z 709 species would contain one OH bridge, a bridging thiolate, together with a bridging oxygen from the carboxylate, *i.e.* **6**. This would maintain the expected six-co-ordination at both rhenium centres, while minimising steric strain; a structure involving bridging by both carboxylate oxygens, Re–O–C–O–Re, would probably be too strained. The acetonitrile solvated analogue of **6**, $[Re_2(OH)(tsal)(CO)_6(MeCN)]^-$ (m/z 750), was also observed at 5 V. This species is likely still to contain the thiolate bridge and a co-ordinated MeCN, perhaps with a monodentate (non-bridging) carboxylate group.



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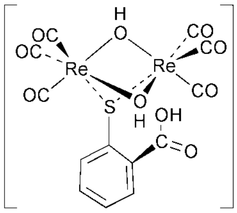

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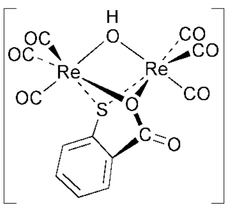

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Upon allowing the solution to stand for *ca.* 25 min new mononuclear ions identified as $[Re(tsal)(CO)_3]^-$ (m/z 423) and $[Re(tsal)(CO)_3(NH_3)]^-$ (m/z 440) are observed, while $[Re_2(OH)_2(Htsal)(CO)_6]^-$ (m/z 727) had almost disappeared, with $[Re_2(OH)(tsal)(CO)_6]^-$ (m/z 709) the base peak. The source of the ammonia is adventitious ammonia present in the acetonitrile solvent used. No di- or tri-thiosalicylate substituted species were observed, consistent with thiosalicylate being a good chelating and bridging ligand, able to take up two co-ordination sites on the Re.

On standing overnight only 2 ions are observed in the 5 V spectrum, $[Re(tsal)(CO)_3]^-$ (m/z 423, the base peak) and some $[Re(tsal)(CO)_3(NH_3)]^-$ (m/z 440). At the higher cone voltage of 20 V the $[Re(tsal)(CO)_3]^-$ ion becomes the base peak, indicating facile loss of the weakly co-ordinated NH_3 ligand. Additionally at 20 V decarboxylation of the thiosalicylate ligand begins to occur, giving the ion $[Re(SC_6H_4)(CO)_3]^-$ at m/z 379. Decarboxylation of thiosalicylate ligands in ESMS spectra of platinum(II),[17] mercury(II) and gold(I)[18] complexes has been observed previously. A new species at m/z 1115 also appears in the 30 V spectrum (and in spectra at higher cone voltages up to 70 V), tentatively assigned as $[Re_3(tsal)_2(CO)_9]^-$. By 50 V the ion $[Re(SC_6H_4)(CO)_2]^-$ (m/z 351) dominates the spectrum, together with $[Re(SC_6H_4)(CO)_3]^-$ (m/z 379) and $[Re(SC_6H_4)(CO)]^-$ (m/z 323). At 70 V the ions $[Re(SC_6H_4)]^-$ (m/z 295) and $[Re(SC_6H_4)(CO)]^-$ (m/z 323) dominate. After standing the rhenium–thiosalicylate solution for 2 weeks the $[Re(tsal)(CO)_3]^-$ ion at m/z 423 was essentially the only species observed at 5 V. It is worth noting that the dimeric manganese analogue of this ion, $[Mn_2(tsal)_2(CO)_6]^{2-}$, has been characterised by an X-ray diffraction study.[19] Rhenium thiosalicylate complexes have been synthesized by reaction of $[ReCl(CO)_5]$ with thiosalicylic acid, giving a neutral dimeric complex $[Re_2(HSC_6H_4CO_2)_2(CO)_6]$ with bridging carboxylates, and an equilibrium mixture of the tautomeric monomer species $[Re\{OC(O)C_6H_4SH\}(CO)_3L]$ and $[Re\{SC_6H_4C(OH)O\}(CO)_3L]$ (L = thf or Et_2O).[20] The anionic species $[Re(SC_6H_4CO_2)(CO)_3(thf)]^-$, closely related to one of the ions observed in this electrospray study, was also synthesized as its $AsPh_4^+$ salt.

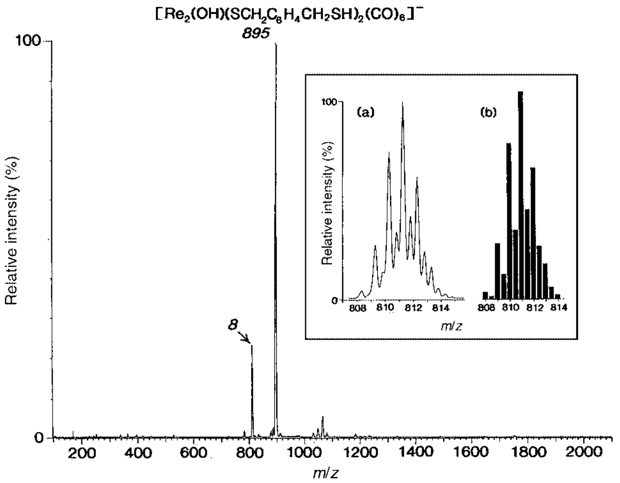
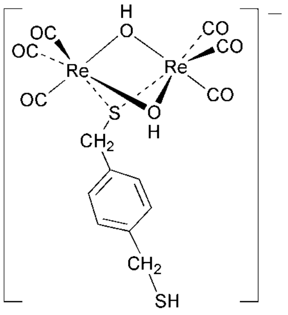


Fig. 3 Negative ion ES spectrum (cone voltage 5 V) of $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ **1** and benzene-1,4-dimethanethiol, $HSCH_2C_6H_4CH_2SH$, after 1 week reaction in MeCN. The inset shows a comparison of (a) experimental and (b) calculated isotope distribution patterns for the aggregate dianion **8** at m/z 811.

3-Sulfanylpropionic acid, $HSCH_2CH_2CO_2H$. When a small quantity of 3-sulfanylpropionic acid is added to complex **1** and the ES spectrum recorded at 5 V a new peak due to the monosubstituted species $[Re_2(OH)_2(SCH_2CH_2CO_2H)(CO)_6]^-$ (m/z 679) is seen. When an excess of the acid is added to **1** the latter was consumed and new intense ions at m/z 790 and 855 were observed, assigned as $[Re_2(SCH_2CH_2CO_2)(SCH_2CH_2CO_2H)(MeCN)(CO)_6]^-$ and $[Re_2(SCH_2CH_2CO_2H)_3(CO)_6]^-$ respectively. Increasing the cone voltage to 30 V results in loss of MeCN from the former ion, giving $[Re_2(SCH_2CH_2CO_2)(SCH_2CH_2CO_2H)(CO)_6]^-$ at m/z 749. The ion $[Re_2(SCH_2CH_2CO_2H)_3(CO)_6]^-$ was not observed for thiosalicylic acid, possibly because the backbone of the thiosalicylate ligand is rigid, with the SH and CO_2H groups *ortho* to each other, promoting chelation, and making the formation of a tris-substituted product unfavourable on steric grounds. On standing overnight (and after 1 week) the $[Re_2(SCH_2CH_2CO_2H)_3(CO)_6]^-$ ion was the dominant Re-containing ion, together with a minor ion at m/z 1231, assigned as $[Re_3(SCH_2CH_2CO_2H)_4(CO)_9]^-$. At the higher cone voltage of 50 V the Re_3 ion remained at low intensity, and $[Re_2(SCH_2CH_2CO_2H)_3(CO)_6]^-$ appeared to undergo fragmentation to give $[Re_2(SCH_2CH_2CO_2)(SCH_2CH_2CO_2H)(CO)_6]^-$ at m/z 749, by loss of $HSCH_2CH_2CO_2H$. $[Re_2(SCH_2CH_2CO_2H)_3(CO)_6]^-$ is analogous to $[Re_2(SCH_2CH_2OH)_3(CO)_6]^-$ reported previously.[6] These ESMS observations are consistent with the thiolate ligand derived from 3-sulfanylpropionic acid being more flexible than that derived from thiosalicylic acid, the latter preferring to form chelate complexes. It is also noteworthy that, compared to carboxylic acids (which cleave the Re_2 dimer forming monorhenium carboxylate species),[1] no such species were observed with 3-sulfanylpropionic acid, presumably because of the formation of three strong Re–S–Re bridges which stabilise the complex.

Benzene-1,2- and -1,4-dimethanethiol, $HSCH_2C_6H_4CH_2SH$. These dithiols were investigated to see if the $Re_2(CO)_6$ units could be linked together. Addition of benzene-1,4-dimethanethiol to complex **1** in MeCN gave the usual species in the ESMS spectrum at 5 V: $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ and $[Re_3(OH)_4(CO)_9]^-$, together with the mono-thiolate complex $[Re_2(OH)_2(SCH_2C_6H_4CH_2SH)(CO)_6]^-$ **7** at m/z 743, which increased in intensity with time. On standing overnight, the monosubstituted species was the base peak, with some disubstituted $[Re_2(OH)(SCH_2C_6H_4CH_2SH)_2(CO)_6]^-$ (m/z 895). On standing for 1 week the disubstituted species dominated the spectrum, together with a new species at m/z 811, Fig. 3. Examination of the isotope



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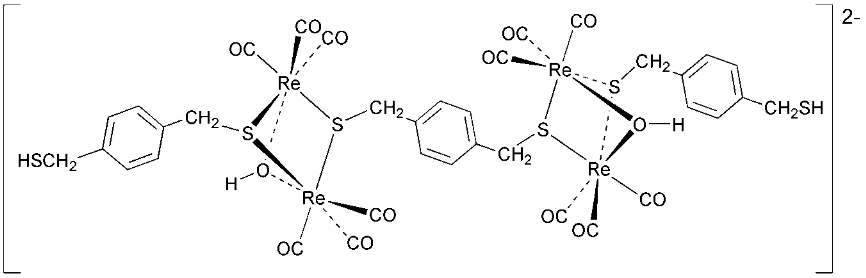

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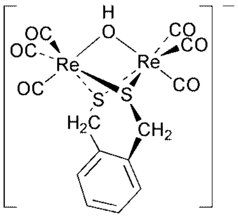
pattern indicated that this species was a dianion, with the characteristic 0.5 *m/z* separation of peaks. The species $[\{Re_2(OH)(SCH_2C_6H_4CH_2SH)(CO)_6\}_2(SCH_2C_6H_4CH_2S)]^{2-}$ gives a good match to the observed isotope pattern, Fig. 3 inset. A reasonable structure, based on the chemistry of this system, is **8**, with two $Re_2(\mu\text{-}OH)(CO)_6$ groups bridged by a $[SCH_2C_6H_4CH_2S]^{2-}$ ligand, and each S atom bridging a different Re_2 unit. The observation of this species again demonstrates the utility of the electrospray technique, and suggests that complex aggregates built from polyfunctional ligands and $Re_2(CO)_6$ units should be possible.

For benzene-1,2-dimethanethiol the mono-substituted ion $[Re_2(OH)_2(SCH_2C_6H_4CH_2SH)(CO)_6]^-$ (*m/z* 743) was formed quickly as the sole ion in the 5 V spectrum, in addition to unchanged complex **1**. On standing overnight all the *m/z* 743 ion disappeared, and was replaced by an ion at *m/z* 725 (plus an unidentified weak ion at *m/z* 895), formed by loss of water from the *m/z* 743 ion. At this low cone voltage no dehydration is expected to occur as a result of the ES process, and so this ion can tentatively be assigned to the species **9**, containing a bridging OH group, and a benzenedimethanethiolate ligand with thiolate bridges to both rhenium centres. The 1,4 isomer is unable to co-ordinate in this manner, accounting for the difference between the two thiols. After standing the solution for 1 week the 5 V ES spectrum still shows the *m/z* 725 ion as the base peak, together with an ion at *m/z* 877, assigned as the analogue in which the OH group has been replaced by a mono-deprotonated thiol, *i.e.* **10**. Thus, ESMS can conveniently be used to explore the co-ordination chemistry of related ligands.



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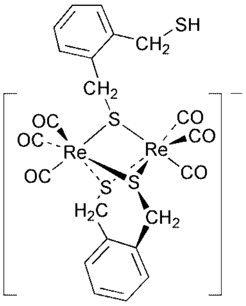

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Reactions of complex 1 with dithiocarbamates

Addition of a small quantity of $NH_4[S_2CN(CH_2)_4]$ to complex **1** before running the negative-ion ESMS spectrum gave {in addition to unchanged **1** and $[Re_3(OH)_4(CO)_9]^-$}, ions assigned as the mono- and di-substituted species $[Re_2(OH)_2\{S_2CN(CH_2)_4\}(CO)_6]^-$ and $[Re_2(OH)\{S_2CN(CH_2)_4\}_2(CO)_6]^-$ at *m/z* 720 and 849 respectively. The tris(dithiocarbamate) ion $[Re_2\{S_2CN(CH_2)_4\}_3(CO)_6]^-$ was not observed. On standing, the intensity of $[Re_2(OH)\{S_2CN(CH_2)_4\}_2(CO)_6]^-$ increased after several minutes. After standing overnight (there was no significant further change after 1 week) the major ion is a new species at *m/z* 563, assigned to the monorhenium species $[Re\{S_2CN(CH_2)_4\}_2(CO)_3]^-$. The dithiocarbamate ligand is capable of acting in either the chelating or (less commonly) bridging mode,[21] and the conversion of the dirhenium species into $[Re\{S_2CN(CH_2)_4\}_2(CO)_3]^-$ is not completely unexpected. Two weak ions, at *m/z* 1021 and 1049, were also observed; the former is assigned as $[Re_2\{S_2CN(CH_2)_4\}_3(MeCN)(CO_6)]^-$.

The reaction of complex **1** with $Na(S_2CNEt_2)$ in MeCN–water (to aid solubility) proceeded very slowly, but gave similar ions. After standing overnight, small ions at *m/z* 567 and 853 assigned as $[Re(S_2CNEt_2)_2(CO)_3]^-$ and $[Re_2(OH)(S_2CNEt_2)_2(CO)_6]^-$ respectively were observed, together with $S_2CNEt_2^-$ and $Na(S_2CNEt_2)_2^-$. No mono-substituted species was observed in this case. After 1 week, $[Re(S_2CNEt_2)_2(CO)_3]^-$ was the major species observed, with $[Re_2(OH)(S_2CNEt_2)_2(CO)_6]^-$ at *ca.* 30% relative intensity. Rhenium carbonyl dithiocarbamate species are known, for example from reaction of tetraethylthiuram disulfide, $(Et_2NCS_2)_2$, with $[ReCl(CO)_5]$, giving species such as $[Re(S_2CNEt_2)_3(CO)]$, $[Re(S_2CNEt_2)(CO)_3]_2$ and $[ReCl(S_2CNEt_2)(CO)_3]^-$.[22] The difference in reactivity of the two dithiocarbamates studied may be related to the fact that one was an ammonium salt (which contains relatively acidic protons, promoting the reaction of **1**), while the less reactive was a sodium salt.

Reactions of complex 1 with thiocyanate, selenocyanate, and thiosulfate ions

Addition of an excess of KSCN to complex **1** resulted in initial formation of some of the monosubstituted species $[Re_2(OH)_2(SCN)(CO)_6]^-$ (*m/z* 632) observed at a cone voltage of 5 V, and after *ca.* 20 min the di- and tri-substituted species

$[Re_2(OH)(SCN)_2(CO)_6]^-$ (*m*/*z* 673) and $[Re_2(SCN)_3(CO)_6]^-$ (*m*/*z* 714) were also seen, in addition to solvated species all containing three SCN^- ligands: $[Re_2(SCN)_3(MeCN)(CO)_6]^-$ (*m*/*z* 755), $[Re_2(SCN)_3(MeCN)_2(CO)_6]^-$ (*m*/*z* 796), and $[Re_2(SCN)_3(MeCN)_3(CO)_6]^-$ (*m*/*z* 837). The observation of the solvated ions possibly suggests non-bridging behaviour of some SCN^- ligands, leaving vacant co-ordination sites which are filled by MeCN solvent molecules, though the structures of these ions are unknown. In this regard it is noteworthy that solvated adducts of other tris-substituted species $[Re_2(\mu\text{-}X)_3(CO)_6]^-$ are not seen, with the exception of weak aqua adducts of $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$.[1] After standing for 2 days, monorhenium species were the dominant ions in the 5 V spectrum, namely $[Re(SCN)_2(CO)_3]^-$ (*m*/*z* 387) and its solvated analogues $[Re(SCN)_2(CO)_3(H_2O)]^-$ (*m*/*z* 405), $[Re(SCN)_2(MeCN)(CO)_3]^-$ (*m*/*z* 428) and $[Re(SCN)_2(MeCN)_2(CO)_3]^-$ (*m*/*z* 469), in addition to some unchanged **1**, $[Re_3(OH)_4(CO)_9]^-$, and $[Re_2(SCN)_3(MeCN)_n(CO)_6]^-$ ($n = 2$ or 3), again consistent with the relatively poor bridging ligand abilities of thiocyanate ions in the Re_2 system. Addition of KSeCN to **1** also gives the monosubstituted species $[Re_2(OH)_2(SeCN)(CO)_6]^-$ at *m*/*z* 680 in the 5 V ESMS spectrum. No disubstituted species was observed, even though an excess of selenocyanate was available for reaction, as shown by the presence of an intense $SeCN^-$ ion at *m*/*z* 106.

Addition of sodium thiosulfate to complex **1** in MeCN–water solution resulted in no immediate reaction, but after 2 days most of the original **1** had been consumed, the major species observed in the 5 V spectrum being $[Re(S_2O_3)(CO)_3]^-$ (*m*/*z* 383) and $[Re(S_2O_3)(CO)_3(H_2O)]^-$ (*m*/*z* 401), with a small amount of $[Re_2(OH)(S_2O_3)(CO)_6]^-$ at *m*/*z* 669.

Attempted reaction of complex 1 with a primary phosphine

One of us recently reported the synthesis of the completely air-stable primary phosphine RCH_2PH_2 (R = ferrocenyl);[23] preliminary studies suggest that the reactivity of this phosphine towards metal centres is not curtailed by its air-stability. Given the similarity in the chemistries of thiols and primary phosphines, we wished to investigate the synthesis of phosphido-bridged dirhenium complexes, monitoring reactions using ESMS. Rhenium carbonyl complexes with bridging phosphido ligands have been prepared previously, *e.g.* $[Re_3(\mu_3\text{-}H)_2(\mu\text{-}PPh_2)_3(CO)_6]$ and $[Re(\mu\text{-}PPh_2)(CO)_4]_2$,[24] though we are not aware of any analogues of the type $[Re_2(\mu\text{-}PR_2)_3(CO)_6]^-$.

The addition of an excess of RCH_2PH_2 to complex **1**, followed by recording the ESMS spectrum, surprisingly did not yield any such complexes after 1 hour, indicating a slower reaction than between **1** and thiols. After standing at room temperature for 1 week, **1** dominated the spectrum, together with some $[Re_3(OH)_4(CO)_9]^-$, a trace of ReO_4^-, and a small new ion at *m*/*z* 837, which could be $[Re_2(OH)_2\{PH(S)CH_2R\}(CO)_6]^-$ (from adventitious S_8 in the mass spectrometer) or $[Re_2(OH)_2\{PH(O)_2CH_2R\}(CO)_6]^-$, possibly formed by ReO_4^- catalysed oxidation (since RCH_2PH_2 is completely air-stable in solution on its own). Simpson and Bergman have commented upon the very slow reaction of the mononuclear complex $[Re(OEt)(CO)_3(Et_2PCH_2CH_2PEt_2)]$ with Ph_2PH,[2] observations which are paralleled here.

Reactions of complex 1 with nitrogen donor ligands (amines and amides)

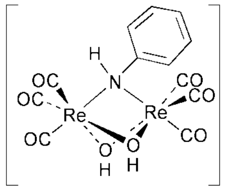
As a result of the facile exchange reactions which occur between complex **1** and alcohols or thiols we were interested in exploring the possibility of exchange reactions with amines and amides. The mononuclear alkoxide complexes $[Re(OR)(CO)_3L_2]$ (R = Me or Et; L_2 = bidentate phosphine or arsine) react reversibly with aniline to give the amido complex $[Re(NHPh)(CO)_3L_2]$.[2] Amido ligands are able to act as monodentate or bridging ligands towards transition metal centres[25] and exchange reactions of the platinum(II) hydroxo dimer $[(Ph_3P)_2Pt(\mu\text{-}OH)_2Pt(PPh_3)_2]^{2+}$ with amines and hydrazine have also recently been reported to give the species $[(Ph_3P)_2Pt(\mu\text{-}OH)(\mu\text{-}NHR)Pt(PPh_3)_2]^{2+}$ and $[(Ph_3P)_2Pt(\mu\text{-}NHR)_2Pt(PPh_3)_2]^{2+}$.[26] ESMS data for the various species observed in this study are summarised in Table 2.

Table 2 ESMS data for reactions of $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ **1** with nitrogen ligands, after reaction for 1 week in MeCN solution; cone voltage 5 V

Ligand	Major product ions[a] (*m*/*z*, %)
$PhNH_2$	$[Re_2(\mu\text{-}OH)_2(NHPh)(CO)_6]^-$ (666, 30%)
p-$O_2NC_6H_4NH_2$	$[Re_2(\mu\text{-}OH)_2(NHC_6H_4NO_2)(CO)_6]^-$ (711, 10%)
p-$MeOC_6H_4NH_2$	$[Re_2(\mu\text{-}OH)_2(NHC_6H_4OMe)(CO)_6]^-$ (696, 3%)
$MeC(O)NH_2$	$[Re_2(\mu\text{-}OH)_2\{NHC(O)Me\}(CO)_6]^-$ (632, 100%)
$PhC(O)NH_2$	$[Re_2(\mu\text{-}OH)_2\{NHC(O)Ph\}(CO)_6]^-$ (694, 100%)

[a] Identified by the most intense peak in the isotope distribution pattern, calculated using the ISOTOPE program.

The reaction of complex **1** with an excess of aniline in MeCN proceeded slowly, but after 1 week, about 30% of the starting **1** had converted into $[Re_2(\mu\text{-}OH)_2(NHPh)(CO)_6]^-$ (*m*/*z* 666), which presumably contains a bridging amido group, Re–NHPh–Re, **11**. Analogous weak ions were observed with *p*-nitroaniline and *p*-methoxyaniline. The reaction is much slower than that with most alcohols, phenol, and thiols, probably due to the much lower acidity of NH compared to that of OH and SH protons. It is also worth noting that the intensity of the *m*/*z* 878 ion, $[Re_3(OH)_4(CO)_9]^-$, typically observed in spectra of **1**, was of markedly lower intensity with added basic amines; the addition of hydroxide causes the same effect, as noted in the preceding paper.[1] In contrast, the reactions of **1** with a selection of primary alkylamines ($MeNH_2$, $EtNH_2$, Bu^nNH_2, $PhCH_2NH_2$) resulted in large numbers of unidentified ions together with residual complex **1** after standing for 1 week.



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We therefore turned our attention to amides, RC(O)NHR′, where the NH proton is much more acidic than in a free amine. Typical pK_a values for amine and amide protons are 40 and 15 respectively; the latter compares favourably with the value of alcohols (pK_a *ca.* 16). No reaction was observed between complex **1** and either acetanilide [$CH_3C(O)NHPh$] or *N*-phenylbenzamide [PhC(O)NHPh], presumably because of the steric bulk of the amide ligand. However, with the primary amide acetamide, $MeC(O)NH_2$, the monosubstituted species $[Re_2(\mu\text{-}OH)_2\{NHC(O)Me\}(CO)_6]^-$ (*m*/*z* 632) was formed slowly but cleanly. After standing overnight the monosubstituted ion was the base peak, and there was a trace amount of the bis-substituted species, but no tris-substituted species, as shown in Fig. 4. After 1 week only a small amount of **1** remained, and the dominant ion was $[Re_2(\mu\text{-}OH)_2\{NHC(O)Me\}(CO)_6]^-$, suggesting it is a good target for subsequent synthetic studies on a macroscopic scale. Benzamide, $PhC(O)NH_2$, behaved very similarly, giving the ion $[Re_2(\mu\text{-}OH)_2\{NHC(O)Ph\}(CO)_6]^-$ (*m*/*z* 694) except that there was no trace of the bis-substituted product. Clearly, the NH protons of primary amides are much more reactive than those of secondary amides. Mononuclear rhenium(I) amide derivatives of the type *trans*-$[Re\{\eta^2\text{-}NHC(O)Ph\}(CO)_2(PPh_3)_2]$ have been synthesized.[27] In contrast

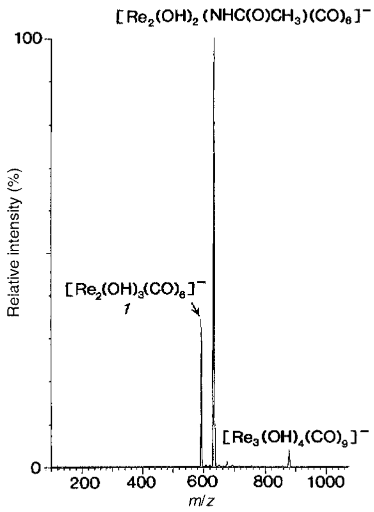


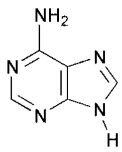
Fig. 4 Negative ion ES spectrum (cone voltage of 5 V) of [Re$_2$(μ-OH)$_3$(CO)$_6$]$^-$ **1** and acetamide, after standing overnight in MeCN, showing the formation of the amido species [Re$_2$(OH)$_2${NHC(O)Me}(CO)$_6$]$^-$ at *m*/*z* 632.

to the reactions with carboxamides, **1** did not react with an excess of urea [H$_2$NC(O)NH$_2$] in MeCN–water over a period of 1 week.

Reactions of complex 1 with the nucleosides adenine and thymine

Complexes **1** and **2**, and several other rhenium(I) alkoxo/hydroxo carbonyl complexes, were recently shown to have significant anti-tumour activity *in vitro*.[28] The complexes inhibit DNA synthesis and also cause DNA fragmentation. We were therefore interested in carrying out some preliminary studies with DNA bases. Understanding the interactions of metal centres with DNA components is of vital importance in the development of metallodrugs, such as the archetypal cisplatin, *cis*-[PtCl$_2$(NH$_3$)$_2$], a complex which interacts (after hydrolysis) with the nitrogen atoms of guanine groups present in DNA.[29]

A solution of complex **1** and adenine (HA, **12**) dissolved in MeCN (with some Me$_2$SO to aid solubility) resulted in formation of the monosubstituted species [Re$_2$(OH)$_2$(A)(CO)$_6$]$^-$ (*m*/*z* 708); this was the major ion after standing for 3 days, together with some [Re$_3$(OH)$_4$(CO)$_9$]$^-$ (*m*/*z* 878). A corresponding ion [Re$_2$(OH)$_2$(T)(CO)$_6$]$^-$ (*m*/*z* 699) was observed for thymine (HT; **13**). The imido proton of thymine is known to be quite acidic (pK_a 9.9);[30] adenine has a similar pK_a of 9.8,[31] probably for the primary amino group. Further studies are in progress regarding the interaction of **1** with important biomolecules.



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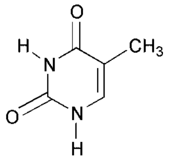

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Experimental

Materials

The compounds [Et$_4$N][Re$_2$(μ-OR)$_3$(CO)$_6$] (R = H or Me)[4] and the phosphine RCH$_2$PH$_2$[23] were synthesized by the literature procedures. H$_2$S was prepared by addition of dilute HCl to Na$_2$S·9H$_2$O (BDH). The following compounds were obtained from commercial sources and used as supplied: *p*-toluenethiol (Aldrich), *n*-dodecanethiol (Aldrich), 2-sulfanylethanol (Sigma), thiosalicylic acid (Sigma), 3-sulfanylpropionic acid (Aldrich), β-D-thioglucose tetraacetate (Aldrich), benzene-1,2-dimethanethiol (Aldrich), benzene-1,4-dimethanethiol (Aldrich), benzeneselenol (Aldrich), adenine (Aldrich), thymine (Aldrich), acetamide (BDH), aniline (BDH), *p*-nitroaniline (BDH), benzamide (BDH), acetanilide (BDH), sodium diethyldithiocarbamate (BDH), ammonium tetramethylenedithiocarbamate (BDH), potassium thiocyanate (BDH), potassium selenocyanate (BDH), and sodium thiosulfate (BDH).

Electrospray mass spectrometry

Details of the instrumentation and conditions used are given in the preceding paper.[1] All major ions were identified by comparison of their observed and calculated[32] isotope distribution patterns.

Acknowledgements

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