Ligand exchange reactions of [Re2(μ-OR)3(CO)6]$^-$ (R = H, Me) with sulfur, selenium, phosphorus and nitrogen donor ligands, investigated by electrospray mass spectrometry

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Probing the chemistry of the dinuclear rhenium carbonyl complexes $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ (R = H, Me) by electrospray mass spectrometry. 2. Ligand exchange reactions with sulfur, selenium, phosphorus and nitrogen donor ligands

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Received;

Graphical contents entry

Exchange reactions of the dinuclear rhenium complexes $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ (R = H, Me) with a wide range sulfur- and selenium-based ligands (thiols, PhSeH and dithiocarbamates), and amides lead to the identification of novel species such as $[Re_2(\mu\text{-}SH)_3(CO)_6]^-$ and the known thiolate analogues.

Abstract

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-dimethanethiols 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 the 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 mono-rhenium complexes $[Re(OR)(CO)_3L_2]$ (R = Me, 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.

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 preceeding 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 complex **1**, and then recording the ESMS spectrum at different times.

The ligands investigated include a series of mono- and di-thiols, benzeneselenol, thiocyanate, dithiocarbamates ($R_2NCS_2^-$), together with some difunctional thiol-based ligands such as thiosalicylic acid ($HSC_6H_4CO_2H$) and 3-mercaptopropionic acid, $HSCH_2CH_2CO_2H$. The primary phosphine $FcCH_2PH_2$ [Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$] 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 unreacted $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ 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 $[Re_2(O)(OH)(CO)_6]^-$ was also seen. These ions will not be further commented upon in the discussion.

Reactions of 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 excess 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 reacted with methanol, giving $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$ and unreacted $[Re_3(OH)_4(CO)_9]^-$. 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, together with some mono- and some tris-substituted species.

With benzeneselenol (PhSeH) and **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 **1** and *n*-dodecanethiol, *n*-$C_{12}H_{25}SH$, β-D-thioglucose tetra-acetate **3**, or 2-mercaptoethanol ($HSCH_2CH_2OH$) 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-mercaptoethanol, 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, $[Re_2(O)(SCH_2CH_2OH)(CO)_6]^-$.

On standing the solutions of **1** and the above thiols overnight the tris(thiolate) anions $[Re_2(SR)_3(CO)_6]^-$ were formed in all cases (exclusively for 2-mercaptoethanol) 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 tetra-acetate) were formed, indicating relatively slow reactions. ES spectra at a cone voltage of 5 V showing the course of the reaction with dodecanethiol are shown in Figure 1. Addition of excess 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 $Re(CO)_5Br$ 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, Re) were prepared by reaction of $[Et_4N]_2[MCl_3(CO)_3]$ with 2-mercaptoethanol, and the Tc 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 $Bu^n{}_3SnSR$ in refluxing methanol.[7] Other methods, employing the sodium salt of the thiolate and a variety of other rhenium precursors $[Re_2(CO)_6Br_3]^-$, $[Re(CO)_4Br_2]^-$, $[Re(CO)_3Br_3]^{2-}$ have also been described for the synthesis of this type of complex.[7,8] Finally, reactions of $[MCp_2(SPh)_2]$ (M = Mo, W) with $Re_2(CO)_{10}$ give the complexes containing the fulvalene (μ-η^5:η^5-$C_{10}H_8$; Fv) ligand, $[M_2Fv(\mu\text{-SPh})Cp_2][Re_2(\mu\text{-SPh})_3(CO)_6]$.[9] These complexes form part of a general class of complexes 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 synthesised,[11] though there are a number of examples of complexes $[(CO)_4M(\mu\text{-SR})_2M(CO)_4]$ (M = Mn, Re).[12] and of other Re 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 observed for the 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 $[Re_2(OH)(SC_{12}H_{25})(CO)_6]^-$ and $[Re_2(SC_{12}H_{25})_3(CO)_6]^-$ are stable towards fragmentation by dehydration, as also found for the bis(*p*-toluenethiolate) species above. This is consistent with two or more OH groups being required for the 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-mercaptoethanol. 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 bond compared to a Re-O bond may also be a contributing factor.

Reactions of 1 with H_2S and Na_2S

No reaction was observed between **1** and Na_2S in MeCN-H_2O solution, consistent with the requirement for 'acidic' protons to be present in the incoming ligand. Na_2S will act as a source of base ($S^{2-} + H_2O \rightarrow SH^- + OH^-$), 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 **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 → 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 Figure 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.

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 excess water and standing for 3 days. However, the addition of NaOH results in rapid reconversion to $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$, 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 1 with difunctional thiolate ligands

Thiosalicylic acid

Selected data for the thiosalicylate system are summarized in Table 1. Thiosalicylic acid (tsalH$_2$, **4**) is able to coordinate 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 **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 $[Re_2(OH)_2(tsalH)(CO)_6]^-$ (*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-coordination at both Re 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 to still contain the thiolate bridge and a coordinated MeCN ligand, perhaps with a monodentate (non-bridging) carboxylate group.

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 $[Re_2(OH)_2(tsalH)(CO)_6]^-$ (*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 coordination 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-coordinated 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 synthesised by reaction of $[ReCl(CO)_5]$ with thiosalicylic acid, giving a neutral dimeric complex $[Re_2(CO)_6(HSC_6H_4CO_2)_2]$ 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, 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 synthesised as its $AsPh_4^+$ salt.

3-Mercaptopropionic acid, $HSCH_2CH_2CO_2H$

When a small quantity of 3-mercaptopropionic acid is added to **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 unfavoured 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-mercaptopropionic 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 mono-rhenium carboxylate species),**[1]** no such species were observed with 3-mercaptopropionic acid, presumably because of the formation of three strong Re-S-Re bridges which stabilise the complex.

Benzene-1,2- dimethanethiol and benzene-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 **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, Figure 3. Examination of the isotope 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, Figure 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 unreacted **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 be tentatively assigned to the species **9**, containing a bridging OH group, and a benzenedimethanethiolate ligand with thiolate bridges to both Re centres. The 1,4-isomer is unable to coordinate 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 be conveniently used to explore the coordination chemistry of related ligands.

Reactions of 1 with dithiocarbamates

Addition of a small quantity of $NH_4[S_2CN(CH_2)_4]$ to **1** followed by running the negative-ion ESMS spectrum gave {in addition to unreacted **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 mono-rhenium 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 to $[Re\{S_2CN(CH_2)_4\}_2(CO)_3]^-$ is not completely unexpected. Two weak ions, at *m/z* 1021 and 1049 were also observed; the former is assigned as $[Re_2\{S_2CN(CH_2)_4\}_3(CO)_6(CH_3CN)]^-$.

The reaction of **1** with $Na(S_2CNEt_2)$ in MeCN-H_2O (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 in the literature, for example from reaction of diethylthiuram 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 as a sodium salt.

Reactions of 1 with thiocyanate, selenocyanate, and thiosulfate ions

Addition of excess KSCN to **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: $[Re_2(SCN)_3(CO)_6(MeCN)]^-$ (*m/z* 755), $[Re_2(SCN)_3(CO)_6(MeCN)_2]^-$ (*m/z* 796), and $[Re_2(SCN)_3(CO)_6(MeCN)_3]^-$ (*m/z* 837). The observation of the solvated ions possibly suggests non-bridging behaviour of some SCN^- ligands, leaving vacant coordination 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 aquo adducts of $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$.[1] After standing for 2 days, mono-rhenium 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), $[Re(SCN)_2(CO)_3(MeCN)]^-$ (*m/z* 428) and $[Re(SCN)_2(CO)_3(MeCN)_2]^-$ (*m/z* 469), in addition to some unreacted **1**, $[Re_3(OH)_4(CO)_9]^-$, and $[Re_2(SCN)_3(CO)_6(MeCN)_n]^-$ (n = 2,3), again consistent with 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 excess selenocyanate was available for reaction, as shown by the presence of an intense $SeCN^-$ ion at *m/z* 106.

Addition of sodium thiosulfate to **1** in MeCN-H_2O 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 1 with a primary phosphine

We recently reported the synthesis of the completely air-stable primary phosphine $FcCH_2PH_2$**[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 excess $FcCH_2PH_2$ to **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 $[Re_2(OH)_2\{PH(S)CH_2Fc\}(CO)_6]^-$ (from adventitious S_8 in the mass spectrometer) or $[Re_2(OH)_2\{PH(O)_2CH_2Fc\}(CO)_6]^-$, possibly formed by ReO_4^- catalysed oxidation (since $FcCH_2PH_2$ 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 1 with nitrogen donor ligands (amines and amides)

As a result of the facile exchange reactions which occur between **1** and alcohols or thiols we were interested in exploring the possibility of exchange reactions occurring with amines and amides. The mononuclear Re alkoxide complexes $[Re(OR)(CO)_3L_2]$ (R = Me, 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 has also been recently reported to give 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.

The reaction of **1** with excess aniline in MeCN proceeded slowly, but after 1 week, about 30% of the starting **1** had converted to $[Re_2(\mu\text{-}OH)_2(NHPh)(CO)_6]^-$ (*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 the reaction with most alcohols, phenol, and thiols, probably due to the much lower acidity of NH compared to 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.

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 **1** and either acetanilide $[CH_3C(O)NHPh]$ or benzamide [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 Figure 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 synthesised.**27** In contrast to the reactions with carboxamides, **1** did not react with an excess of urea $[H_2NC(O)NH_2]$ in $MeCN\text{-}H_2O$ over a period of 1 week.

Reactions of 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 **1** and adenine (AH, **12**) dissolved in MeCN (with some Me_2SO 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 (TH; **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.

Experimental

Materials

The compounds $[Et_4N][Re_2(\mu\text{-}OR)_3(CO)_6]$ (R = H, Me)[4] and the phosphine $FcCH_2PH_2$[23] were synthesised by the literature procedures. H_2S was prepared by addition of dilute HCl to $Na_2S.9H_2O$ (BDH). The following compounds were obtained from commercial sources and used as supplied: *p*-toluenethiol (Aldrich), 1-dodecanethiol (Aldrich), 2-mercaptoethanol (Sigma), thiosalicylic acid (Sigma), 3-mercaptopropionic acid (Aldrich), β-D-thioglucose tetra-acetate (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 pyrrolidinedithiocarbamate (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

We thank the National University of Singapore (RP 950695), the National Institute of Education, Singapore (RP 15/95 YYK), the University of Waikato, and the New Zealand

Lottery Grants Board for financial support. W. H. thanks the Asia 2000 Foundation of New Zealand for a travel grant, and Wendy Jackson for technical assistance.

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Electronic supplementary information available: Full table of ES data for reactions of **1** and **2** with sulfur- and selenium-based ligands.

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

Ligand	Cone voltage (V)	Major product ions‡ (*m/z*, %)
$PhNH_2$	5	$[Re_2(\mu\text{-}OH)_2(NHPh)(CO)_6]^-$ (666, 30%)
p-$O_2NC_6H_4NH_2$	5	$[Re_2(\mu\text{-}OH)_2(NHC_6H_4NO_2)(CO)_6]^-$ (711, 10%)
p-$MeOC_6H_4NH_2$	5	$[Re_2(\mu\text{-}OH)_2(NHC_6H_4OMe)(CO)_6]^-$ (696, 3%)
$CH_3C(O)NH_2$	5	$[Re_2(\mu\text{-}OH)_2\{NHC(O)Me\}(CO)_6]^-$ (632, 100%)
$PhC(O)NH_2$	5	$[Re_2(\mu\text{-}OH)_2\{NHC(O)Ph\}(CO)_6]^-$ (694, 100%)

‡ Ions are identified by the most intense peak in their isotope distribution pattern, calculated using the Isotope program.

Captions for Figures

Figure 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.

Figure 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 V and (b) 50 V, showing fragmentation by loss of H_2S and CO.

Figure 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.

Figure 4. Negative ion ES spectrum (cone voltage of 5 V) of $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ **1** and acetamide, after standing overnight in MeCN, showing the formation of the amido species $[Re_2(OH)_2\{NHC(O)CH_3\}(CO)_6]^-$ at *m/z* 632.