DALTON
FULL PAPER

Fragmentation pathways of $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ (R = H, Me) and ligand exchange reactions with oxygen donor ligands, investigated by electrospray mass spectrometry †

Chenghua Jiang,[a] T. S. Andy Hor,*[a] Yaw Kai Yan,*[b] William Henderson*[c] and Louise J. McCaffrey[c]

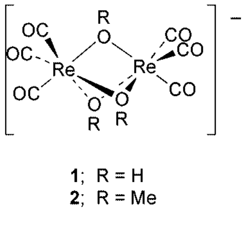
[a] *Department of Chemistry, Faculty of Science, 3 Science Drive 3, National University of Singapore, Kent Ridge 119260, Singapore*
[b] *Division of Chemistry, National Institute of Education, Nanyang Technological University, 469 Bukit Timah Road, Singapore 259756*
[c] *Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand*

Received 16th May 2000, Accepted 27th July 2000
Published on the Web 29th August 2000

The rhenium hydroxy and methoxy carbonyl complexes $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ (R = H or Me) have been studied by negative-ion electrospray mass spectrometry (ESMS). The complexes undergo facile exchange reactions with protic compounds, including alcohols and phenols. With dimethyl malonate, 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 conveniently, rapidly, and unambiguously be 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 $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ 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 $[Re_2(\mu\text{-}OR)_2(\mu\text{-dppf})(CO)_6]$ [R = H or Me; dppf = 1,1′-bis(diphenylphosphino)ferrocene] undergo substantial solvolysis and hydrolysis to give mainly mononuclear species; simple parent ions (*e.g.* $[M + H]^+$) 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 interest[1] since they are likely intermediates in reactions such as olefin carboalkoxylation[2] and in metal-catalysed hydrogenation of CO.[3] Water-soluble, low-valent carbonyl compounds of Re[4] and ^{99m}Tc[5] are also receiving much current attention due to their potential application in radioimmunotherapy and protein labelling. The formation of heterobimetallic aggregates from $[Re_3(\mu\text{-}OH)_4(CO)_9]^-$ has also recently been reported.[6]



1; R = H
2; R = Me

The dinuclear species $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ (R = H **1**; or OMe **2**) 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 carbonylhydroxo/aqua 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 $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$, which have, in principle, three exchangeable hydroxo or alkoxo ligands. Such exchange reactions have briefly been alluded to[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 has been compared to low temperature NMR spectroscopy.[15] In the case of the dinuclear rhenium 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

---

† 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 1.

Electronic supplementary (ESI) available: ESMS data for the complexes $[Re_2(\mu\text{-}OR)_2(\mu\text{-dppf})(CO)_6]$ (R = H or Me). See http://www.rsc.org/suppdata/dt/b0/b003893h/

DOI: 10.1039/b003893h

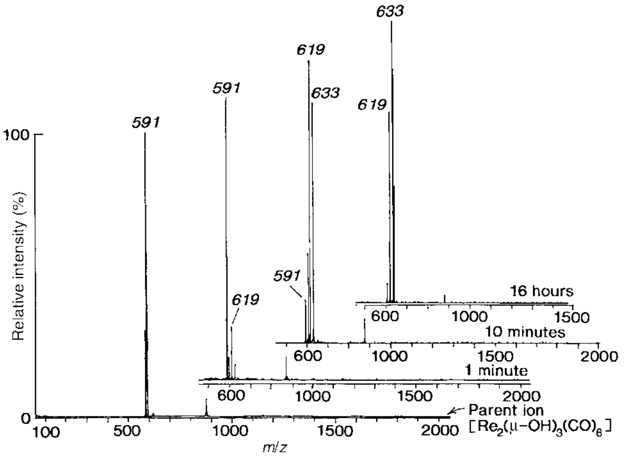


Fig. 1 Negative ion ES spectra (cone voltage 5 V) of $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ in MeCN at various times after addition of an excess of MeOH.

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 $[Re(CO)_3Br_3]^{2-}$ to the aqua complex $[Re(CO)_3(H_2O)_3]^+$ [10] and of base hydrolysis of $[Re(CH_3)O_3]$, which proceeds *via* Re–OH species;[16] other rhenium 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 complex **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 $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ is observed at *m/z* 591, together with a weak signal at *m/z* 879 corresponding to $[Re_3(OH)_4(CO)_9]^-$, Fig. 1 (bottom spectrum). The latter ion is most probably a side product formed during the synthesis of **1**.[9] This impurity can simply and quickly be converted into **1** by adding a drop of aqueous 2 M NaOH to the ESMS solution, consistent with eqn. (1).

$$2[Re_3(OH)_4(CO)_9]^- + OH^- \longrightarrow 3[Re_2(OH)_3(CO)_6]^- \quad (1)$$

The spectrum of **1** recorded in MeCN–water at a low cone voltage (5 V) was very similar to that in pure MeCN, except that a series of low intensity aquated ions $[Re_2(\mu\text{-}OH)_3(CO)_6 + nH_2O]^-$ 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 made with other strongly hydrogen-bonded systems.[19]

Exchange reactions of complexes 1 and 2 with alcohols

A summary of the extent of reaction of complexes **1** and **2** with different oxygen donor ligands is given in Table 1. During the course of our studies into complex **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.

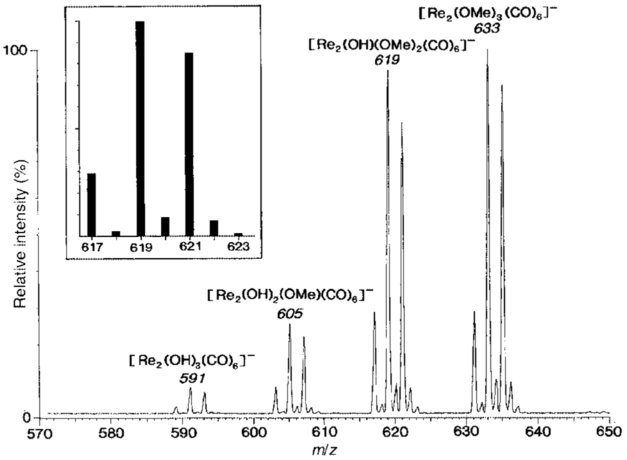
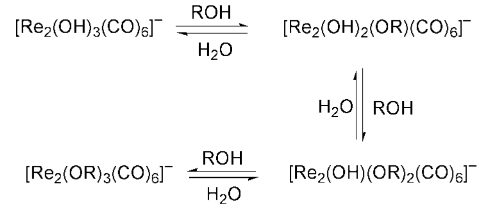


Fig. 2 High-resolution negative ion ES spectrum (cone voltage 5 V) of a solution of $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ **1** in MeCN, 10 min after addition of an excess of MeOH, showing the presence of the individual ions $[Re_2(OH)_n(OMe)_{3-n}(CO)_6]^-$ ($n = 0$–3). The inset shows the calculated isotope distribution pattern for the $n = 2$ ion.

About 1 min after addition of a few drops of methanol to the ESMS solution of complex **1** in MeCN the spectrum showed peaks at *m/z* 605, 619 and 633, corresponding respectively to the singly-, doubly- and triply-exchanged species $[Re_2(\mu\text{-}OH)_n(\mu\text{-}OMe)_{3-n}(CO)_6]^-$ ($n = 0$–2), Scheme 1. The intensity of the peaks due to the exchanged species rapidly grew with respect to the parent ion $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ over 10 min, although the exact relative intensities varied between experiments. On standing overnight (16 h) the main ion observed was $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$ **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 **2** was observed, together with a trace of the bis-methoxy species. Similar results were obtained using ethanol as the alcohol. The time-dependent exchange reaction of **1** with MeOH is illustrated in Fig. 1, and Fig. 2 shows the high resolution spectrum of the individual ions after 10 min. It is worth noting that even on prolonged standing the trirhenium species $[Re_3(\mu\text{-}OH)_4(CO)_9]^-$ was unaffected by methanol, in contrast to the facile replacement of OH groups on **1**. In the Re_3 species the OH groups are spread out between three rhenium centres, whereas in $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ all three OH groups bridge the same two Re atoms, so the negative charge in the Re_3 species will be better dissipated and the OH groups less nucleophilic.



Scheme 1

The ES spectrum of a pre-formed sample of complex **2** shows a strong parent ion peak (*m/z* 633) at low cone voltages. The ES spectra always contain traces of the ion $[Re_2(\mu\text{-}OH)(\mu\text{-}OMe)_2(CO)_6]^-$, 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 $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ **1**. Addition of 4 drops of methanol to this solution quickly (within 1 min) removed **1** and regenerated $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$, suggesting that OH ⟶ OMe exchange is more facile

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 (*m*/*z*, intensity)
1	—	$[Re_2(OH)_3(CO)_6]^-$ (591, s)
	Methanol	$[Re_2(OH)_n(OMe)_{3-n}(CO)_6]^-$ $n = 2(605, w), 1(619, m), 0(633, s)$
	Ethanol	$[Re_2(OH)_n(OEt)_{3-n}(CO)_6]^-$ $n = 2(619, w), 1(647, w), 0(675, s)$
	n-Octanol	$[Re_2(OH)_n(OOct)_{3-n}(CO)_6]^-$ $n = 2(703, m), 1(815, s), 0(927, m)$
	Phenol	$[Re_2(OH)_n(OPh)_{3-n}(CO)_6]^-$ $n = 2(667, m), 1(743, s), 0(819, w)$
	Bu^{t}OH	$[Re_2(OH)_2(OBu^t)(CO)_6]^-$ (647, s)
	Formic acid	$[Re_2(OH)_n(O_2CH)_{3-n}(CO)_6]^-$ $n = 2(619, w), 1(647, s)$
	RCO_2Me ($R = CH_2CO_2Me$)	$[Re_2(OH)_n(O_2CR)_{3-n}(CO)_6]^-$ $n = 2(691, s), 1(791, w)$ after 15 min $[Re(RCO_2)_2(CO)_3]^-$ (505, s) overnight
2	—	$[Re_2(OMe)_3(CO)_6]^-$ (633, s)
	Water	$[Re_2(OH)_{3-n}(OMe)_n(CO)_6]^-$ $n = 0(591, s), 1(605, w), 2(619, w)$
	Ethanol	$[Re_2(OMe)_n(OEt)_{3-n}(CO)_6]^-$ $n = 0(675, s), 1(661, w), 2(647, w)$
	Phenol	$[Re_2(OMe)_n(OPh)_{3-n}(CO)_6]^-$ $n = 0(819, w), 1(757, m), 2(695, s)$

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

The exchange reaction of complex **1** with *n*-octanol readily affords analogous species to those from methanol, and the final $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ product is formed completely after standing overnight. The reaction of **1** with Bu^{t}OH, however, only affords the singly exchanged species $[Re_2(\mu\text{-}OH)_2(\mu\text{-}OBu^t)(CO)_6]^-$ (*m*/*z* 647), even with an excess of Bu^{t}OH 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.

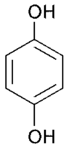
Proton transfer from ROH to the hydroxo ligands of complex **1** is probably the initial, and critical, step for the exchange reaction to proceed; a similar proton transfer mechanism has been proposed for the exchange of *fac*-$[Re(\eta^1\text{-}OR)(L)_2(CO)_3]$ with alcohols and phenols.[12,20] Consistent with this, the hydrogen-bonded proton of the complex $[Re\{(MeO)\cdots HOC_6H_4Me\}(CO)_3(Et_2PCH_2CH_2PEt_2)]$ was located in the 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 **1** is unreactive towards the weak carbon acid malononitrile $[CH_2(CN)_2]$ and **2** towards acetone and Me_2SO, even after standing overnight. Steric factors also clearly play a role in the exchange reactions, since the sterically bulky Bu^{t}OH can only exchange one OH group.

The results described in this section parallel the tendency for ligand exchange observed previously, for example the anion $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$ was found to convert into $[Re_2(\mu\text{-}OMe)_n(\mu\text{-}OEt)_{3-n}(CO)_6]^-$ during its crystallisation from ethanol.[14] The proposed mechanism of formation of the mixed-bridge trirhenium anion $[Re_3(\mu\text{-}OH)_2(\mu\text{-}OMe)(\mu_3\text{-}OMe)(CO)_9]^-$ also involves methoxo–hydroxo exchange on the reaction intermediates.[21]

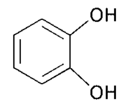
Exchange reactions of complexes 1 and 2 with phenols

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 an excess of phenol to **2**. The tris-phenoxy species $[Re_2(\mu\text{-}OPh)_3(CO)_6]^-$ has been prepared previously from the reaction of $[Re_2(CO)_{10}]$ and phenol in the presence of Me_3NO[21] or from $[Re_3(CO)_{10}(\mu\text{-}H)_4]^-$ and 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 $[Re_3(OH)_3(OPh)(CO)_9]^-$. However, with 2,4,6-tribromophenol (ROH), the monosubstituted species $[Re_2(OH)_2(OR)(CO)_6]^-$ (*m*/*z* 905) was formed rapidly, but even in the presence of an excess of 2,4,6-tribromophenol further substitution did not occur on standing.

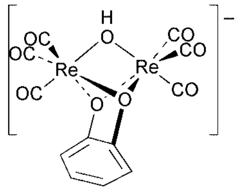
In a similar fashion, addition of an excess of hydroquinone (**3**) to complex **1** resulted in formation of the mono-substituted product $[Re_2(OH)_2(OC_6H_4OH)(CO)_6]^-$ (*m*/*z* 683), and over several days the parent **1** disappeared, the monosubstituted ion was the dominant species, with some bis-substituted $[Re_2(OH)(OC_6H_4OH)_2(CO)_6]^-$ (*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 $[Re_2(OH)(OC_6H_4O)(CO)_6]^-$ (*m*/*z* 665) and $[Re_2(OH)_2(OC_6H_4OH)(CO)_6]^-$ (*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: $[Re(OC_6H_4O)(CO)_3]^-$ (*m*/*z* 379), $[Re_2(OC_6H_4O)(OC_6H_4OH)(CO)_6]^-$ (*m*/*z* 757) together with $[Re_2(OH)(OC_6H_4OH)_2(CO)_6]^-$ (*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 $[Re_2(OC_6H_4O)(OC_6H_4OH)(CO)_6]^-$. For a mixture of phloroglucinol (**6**) and **1** the only major species observed after 3 d was the monosubstituted ion $[Re_2(OH)_2\{OC_6H_3(OH)_2\}(CO)_6]^-$ (*m*/*z* 699); as with hydroquinone, no chelation is possible. ESMS is thus very useful in exploring the different co-ordination possibilities of related ligands toward **1**.



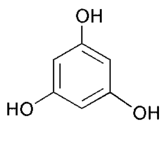
3



4



5



6

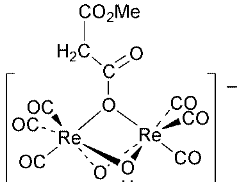
Reactions of complex 1 with carboxylic acids and phenylboronic acid

With a relatively strong acid (methanoic acid), the negative ion ES spectrum of complex **1** at 5 V shows an intense signal at *m*/*z* 647, assigned as $[Re_2(\mu\text{-}OH)(O_2CH)_2(CO)_6]^-$, together with a weak ion $[Re_2(\mu\text{-}OH)_2(O_2CH)(CO)_6]^-$ (*m*/*z* 619). Similarly, the addition of *ortho*-chlorobenzoic acid to **1** rapidly and almost quantitatively gave the mono-substituted species $[Re_2(OH)_2(O_2CC_6H_4Cl)(CO)_6]^-$ (*m*/*z* 729). The positive ion spectrum of **1** with added HCO_2H in MeCN at a cone voltage of 20 V showed monorhenium species, such as $[Re(MeCN)_3(CO)_3]^+$ (*m*/*z* 394), $[Re(MeCN)_2(CO)_4]^+$ (*m*/*z* 381) and $[Re(MeCN)_2(CO)_3]^+$ (*m*/*z* 353), which presumably result from acid cleavage of the bridging OH groups of **1**, followed by co-ordination of the solvent. In a related manner, the complex $[Re(O_2CMe)(CO)_3(dppf)]$ has also been synthesized from $[Re_2(\mu\text{-}OMe)_2(\mu\text{-}dppf)(CO)_6]^-$ 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.

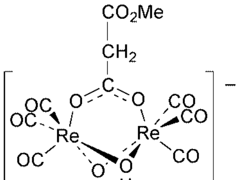
Compounds containing B–OH groups are known to react with hydroxylic compounds (ROH) forming B–OR linkages,[24] and so the reactivity of **1** towards phenylboronic acid $[PhB(OH)_2]$ was studied. After addition of an excess of $PhB(OH)_2$, the ES spectrum showed, in addition to considerable unchanged **1**, adduct ions formed by condensation, *viz.* $[Re_2(OH)_2\{OB(OH)Ph\}(CO)_6]^-$ (*m*/*z* 695) and $[Re_2(OH)\{OB(OH)Ph\}_2(CO)_6]^-$ (*m*/*z* 799), but on standing for 1 week these diminished in intensity, and an intense peak due to $[Re_3(OH)_4(CO)_9]^-$ was seen. The effect of acid on **1** has been documented previously,[9] and is the reverse of eqn. (1).

Reactions of complex 1 with esters

The reaction of complex **1** with dimethyl malonate ($MeO_2CCH_2CO_2Me$) rapidly gives the main species $[Re_2(OH)_2(O_2CCH_2CO_2Me)(CO)_6]^-$ at *m*/*z* 691. Only a small amount of the bis(carboxylate) species $[Re_2(OH)(O_2CCH_2CO_2Me)_2(CO)_6]^-$ (*m*/*z* 791) was observed. On standing overnight the main ion observed is the monorhenium complex $[Re(O_2CCH_2CO_2Me)_2(CO)_3]^-$ at *m*/*z* 505. These ions are formed by facile cleavage of an ester bond by a bridging OH group, possibly promoted by the basicity of the μ-OH groups of **1** which attack the ester carbonyl group. The dinuclear carboxylate species may have two possible structures which maintain six-co-ordination 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 co-ordination chemistry of carboxylates with rhenium has recently been summarised.[25]



7



8

Reaction of complex 1 with hydrogen peroxide and *tert*-butyl hydroperoxide (Bu^{t}OOH)

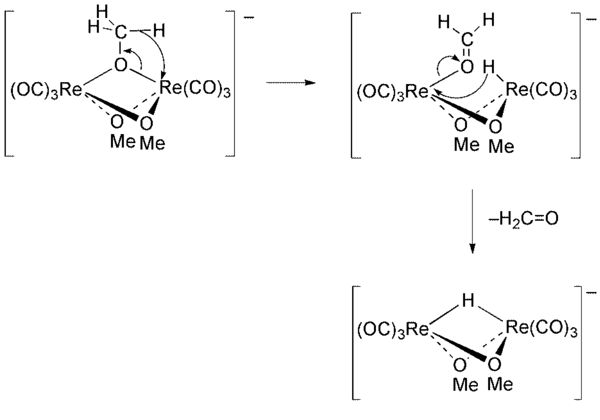
Addition of 2 drops of 27% H_2O_2 to a solution of complex **1** in MeCN resulted in immediate decomposition of **1** to the species ReO_4^- (*m*/*z* 251) and a minor unidentified species at *m*/*z* 285 containing 1 Re. This may be the peroxorhenate(v) species $[ReO_2(OOH)_2]^-$ and excellent agreement between observed and calculated isotope patterns was obtained. An alternative is the species $[ReO_4 + H_2O_2]^-$, but since no $[ReO_4 + H_2O]^-$ analogue is observed we favour the peroxorhenate assignment. This result is not completely unexpected, given that H_2O_2 is a powerful oxidising agent, able to oxidise Re to oxidation state 7. 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 H_2O_2 (1 drop of 6% solution). However, the peak due to **1** slowly decreased in intensity, and that due to ReO_4^- grew, and no hydroperoxy analogues of **1**, *viz.* $[Re_2(OH)_n(OOH)_{3-n}(CO)_6]^-$, could be observed. The reaction with a less reactive hydroperoxide, *tert*-butyl hydroperoxide (Bu^{t}OOH), was therefore investigated. Addition of an excess of Bu^{t}OOH to **1** in MeCN resulted in a much slower reaction than with H_2O_2, though the end product after *ca.* 20 min, ReO_4^-, was the same. The largest new species observed was at *m*/*z* 661, and this may be assigned as $[Re_2(O_2)(OO^tBu)(CO)_6]^-$ (the anticipated species $[Re_2(OH)_2(OO^tBu)(CO)_6]^-$ 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 complex **1** begins to occur at a cone voltage of 20 V, when a low abundance peak due to $[Re_2(O)(OH)(CO)_6]^-$ (*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 $[Re_2(O)(OH)(CO)_n]^-$ ($n = 3$–5). The dehydration of complex **1** is much more favourable than decarbonylation, since $[Re_2(\mu\text{-}OH)_3(CO)_n]^-$ ($n = 3$–5) ions 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 $[Re_4(O)(OH)_3(CO)_{12}]^-$ (*m*/*z* 1149) and $[Re_4(O)_2(OH)(CO)_{12}]^-$ (*m*/*z* 1131), while the ion $[Re_4(OH)_5(CO)_{12}]^-$ (*m*/*z* 1165) is much less abundant, consistent with higher degrees of dehydration at the higher cone voltage. Similarly, for the Re_3 species, $[Re_3(O)_2(CO)_9]^-$ (*m*/*z* 843) is more abundant than $[Re_3(O)(OH)_2(CO)_9]^-$ (*m*/*z* 861), which in turn is more abundant than the ion $[Re_3(OH)_4(CO)_9]^-$ (*m*/*z* 879). It is noteworthy that the Re_4 species are not observed at low cone voltages {unlike the Re_3 species $[Re_3(OH)_4(CO)_9]^-$}, 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 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, *e.g.* $[Re(O)(CO)_3]^-$ (*m*/*z* 287) and $[Re(O)(CO)_2]^-$ (*m*/*z* 259), besides the dehydrated and decarbonylated dirhenium species $[Re_2(O)(OH)(CO)_n]^-$.

Complex **2** fragments initially *via* β-hydride elimination, at cone voltages of 50 V and higher. The parent ion eliminates formaldehyde ($H_2C{=}O$) to form $[Re_2(H)(OMe)_2(CO)_6]^-$ (*m*/*z* 603), $[Re_2(H)_2(OMe)(CO)_6]^-$ (*m*/*z* 573) and finally the known species[7] $[Re_2(H)_3(CO)_6]^-$ (*m*/*z* 543). The proposed mechanism of β-hydride elimination of **2** is shown in Scheme 2. Decarb-



Scheme 2

onylation of the β-eliminated species also occurs at 50 V to give $[Re_2(H)(OMe)_2(CO)_5]^-$ (*m*/*z* 575) and $[Re_2(H)_2(OMe)(CO)_5]^-$ (*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, see Fig. 2.) At a higher cone voltage of 80 V more decarbonylated species are observed, such as $[Re_2(H)_3(CO)_5]^-$ and $[Re_2(H)(CO)_5]^-$ overlapping around *m*/*z* 515, $[Re_2(H)_3(CO)_4]^-$ (*m*/*z* 487), $[Re_2(H)_2(OMe)(CO)_2]^-$ (*m*/*z* 461) and some mononuclear species such as $[Re(H)_2(CO)_3]^-$ (*m*/*z* 271), and $[Re(H)_2(CO)_4]^-$ (*m*/*z* 299).

Support for the β-hydride mechanism comes from the elimination of ethanal (acetaldehyde) from the ion $[Re_2(\mu\text{-}OEt)_3(CO)_6]^-$, generated by addition of an excess of 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.* $[Re_2(H)(OEt)_2(CO)_6]^-$ (*m*/*z* 631), $[Re_2(H)_2(OEt)(CO)_6]^-$ (*m*/*z* 587), $[Re_2(H)_3(CO)_6]^-$ (*m*/*z* 543) and $[Re_2(H)_3(CO)_5]^-$ (*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 co-ordinated alkoxide has not been observed by ESMS, except from the stereoselective β-hydrogen elimination from nickel(II) glycoside complexes.[28] The monorhenium alkoxide complexes $[Re(OR)(CO)_3L_2]$ (R = Me, Et or Pr^i; 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 $[IrCp(PMe_3)Me]^+$ ($Cp = \eta^5\text{-}C_5H_5$) by R–H to form $[IrCp(PMe_3)(R)]^+$ *via* an elimination-addition or σ-bond metathesis mechanism.[30] ESMS studies of β-hydrogen elimination from metal alkoxo carbonyls may help in understanding 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 complex **1** and phenol which generates predominantly the monosubstituted $[Re_2(OH)_2(OPh)(CO)_6]^-$ (*m*/*z* 667) shows the ion $[Re_2(O)(OPh)(CO)_6]^-$ (*m*/*z* 649), which is formed by dehydration. On the other hand, the diphenoxo species $[Re_2(OH)(OPh)_2(CO)_6]^-$ (*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.* $[Re_2(O)(OPh)(CO)_n]^-$ (n = 3–5), together with mononuclear fragments, *e.g.* $[Re(O)(CO)_3]^-$ (*m*/*z* 287). For the monosubstituted species $[Re_2(OH)_2(OR)(CO)_6]^-$ (R = 2,4,6-tribromophenyl) at a cone voltage of 60 V the ion $[Re_2(O)(OR)(CO)_6]^-$ (*m*/*z* 887) was observed, together with $[Re_2(O)(OH)(CO)_6]^-$. Since $[Re_2(OH)_2(OR)(CO)_6]^-$ 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 $[Re_2(O)(OH)(CO)_6]^-$.

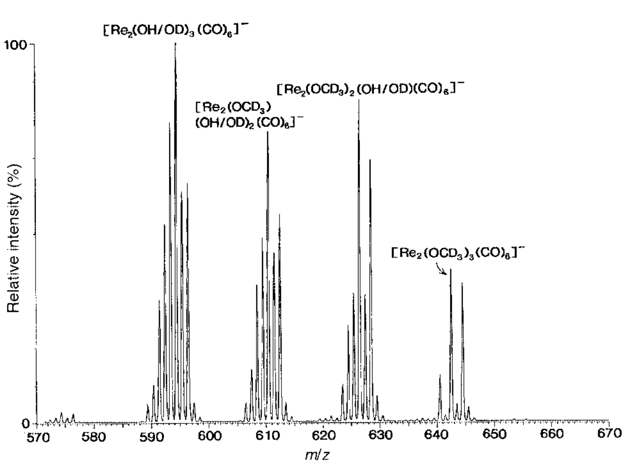


Fig. 3 Negative ion ES spectra (cone voltage 20 V) of $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ **1** in MeCN, 10 min after adding CD_3OD, showing the presence of OH/OD and OCD_3 exchanged species.

Deuterium labelling studies of complex 2

Confirmation of the β-hydride elimination mechanism discussed above was achieved by deuterium labelling of complex **2**. The species $[Re_2(\mu\text{-}OCD_3)_3(CO)_6]^-$ was conveniently generated by addition of an excess of CD_3OD to **1** (as described earlier for CH_3OH exchange) and investigated at high cone voltages. Several minutes after addition of three drops of CD_3OD 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 $[Re_2(OH/OD)_3(CO)_6]^-$ and its singly, doubly and triply (OH/OD ⟶ OCD_3) exchanged species respectively, Fig. 3. Overlap of species occurred in the spectrum, due to the exchange of H for D atoms (from the exchangeable D atoms of CD_3OD), which occurs more rapidly than the exchange of OH/OD by OCD_3 groups, and to a lesser extent due to the isotopic impurity of the CD_3OD (*i.e.* the presence of *e.g.* some CD_2HOD). The peaks of higher (OH/OD ⟶ OCD_3) exchanged species grew in intensity with time. On standing, the main species is $[Re_2(OCD_3)(CO)_6]^-$, with bis- and singly-exchanged species in successively lower abundance, and the parent ions $[Re_2(OH/OD)_3(CO)_6]^-$ had disappeared. Since the by-product of the (OH/OD ⟶ OCD_3) exchange reaction, water, can reverse the reaction, it is difficult to get pure $[Re_2(OCD_3)_3(CO)_6]^-$ at equilibrium. The equilibrated solution of **1** with an excess of CD_3OD was evaporated, the residue dissolved in fresh CD_3OD and monitored by ESMS. After 4 days the solution contained predominantly $[Re_2(OCD_3)_3(CO)_6]^-$. This species can also cleanly be obtained by the exchange reaction of $[Re_2(OMe)_3(CO)_6]^-$ **2** with an excess of CD_3OD for 4 days.

At a cone voltage of 50 V the ES spectrum of $[Re_2(OCD_3)_3(CO)_6]^-$ (Fig. 4) showed the ions $[Re_2(D)_n(OCD_3)_{3-n}(CO)_6]^-$ (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 $[Re_2(D)(OCD_3)_2(CO)_5]^-$ and $[Re_2(D)_2(OCD_3)(CO)_5]^-$ with the above species was observed around *m*/*z* 580 and 546. The ion $[Re_2(D)_3(CO)_5]^-$ was also detected in low intensity.

Fragmentation and ionisation of the neutral complexes $[Re_2(\mu\text{-}OR)_2(\mu\text{-}dppf)(CO)_6]$ (R = H or Me)

The complexes $[Re_2(\mu\text{-}OR)_2(\mu\text{-}dppf)(CO)_6]$ (R = H or Me) can be prepared by controlled acidolysis of $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ (R = H or 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 $[Re_2(\mu\text{-}OR)_2(\mu\text{-}dppf)(CO)_6]$ (R = H or Me) are largely common. In positive-ion mode at a cone voltage

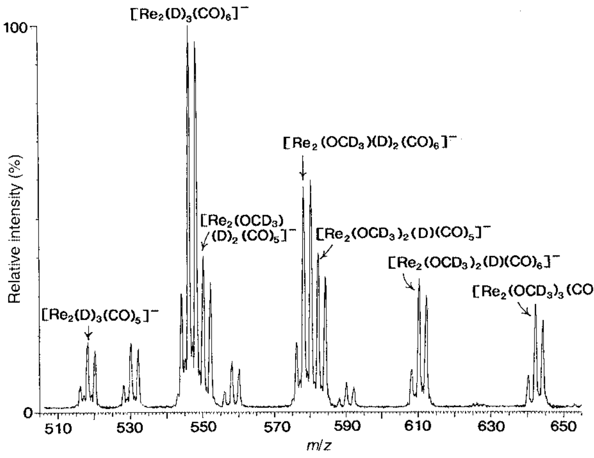


Fig. 4 Negative ion ES spectrum of $[Re_2(\mu\text{-}OCD_3)_3(CO)_6]^-$ in MeCN at a cone voltage of 50 V, showing the formation of Re–D species by β-deuteride elimination.

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) ReO_4^- is the common anion observed for both complexes, besides their correspondingly hydrolysed species.

For the hydroxy complex $[Re_2(\mu\text{-}OH)_2(\mu\text{-}dppf)(CO)_6]$, in addition to the common ions discussed above, minor ions $[Re_2(OH)(MeCN)_2(dppf)(CO)_6]^+$ (*m*/*z* 1194), $[M + H]^+$ (*m*/*z* 1129) and $[dppfO_2 + H]^+$ (*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 $[Re_2(OH)(dppf)(CO)_6]^+$ (*m*/*z* 1111). The latter ion can be formed from the parent compound $[Re_2(\mu\text{-}OH)_2(\mu\text{-}dppf)(CO)_6]$ 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 ReO_4^-) the trinuclear species $[Re_3(OH)_4(CO)_9]^-$ (*m*/*z* 878).

Conclusion

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 $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$. The strength of the technique lies with its convenience, and ability to provide information on exchanging sytems; 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 synthesize novel alkoxo-bridged rhenium complexes based on this simple exchange reaction, which is experimentally easy to carry out, and can rapidly and simply be monitored by ESMS. In the following paper we describe the use of ESMS in monitoring the chemistry of complexes $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ with S-, Se-, N- and P-based ligands.[32]

Experimental

The complexes $[Et_4N][Re_2(\mu\text{-}OH)_3(CO)_6]$, $[Et_4N][Re_2(\mu\text{-}OMe)_3(CO)_6]$ and $[Re_2(\mu\text{-}OR)_2(\mu\text{-}dppf)(CO)_6]$ (R = H or Me) were synthesized by the literature procedures.[9] Alcohols used were at least of LR grade, and used as supplied. Dimethyl malonate (BDH), phenylboronic acid (Aldrich), pyrocatechol (BDH), hydroquinone (Aldrich), phloroglucinol (Aldrich) and *tert*-butyl hydroperoxide (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 MeCN [or occasionally MeCN–water (1 : 1 v/v)] as the mobile phase. The MeCN was of HPLC grade, and the water doubly distilled prior to use. The sample solutions (2 mL), of approximate concentration (of complex **1** or **2**) 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 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.[33]

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 MeCN or MeCN–water mobile phase, which leads to *in situ* formation of the species $[Re_2(\mu\text{-}OH)_n(\mu\text{-}OR)_{3-n}(CO)_6]^-$ ($n = 1$–3).

Acknowledgements

We thank the National University of Singapore (RP 950695), the National Institute of Education, Singapore (RP 15/95 YYK) and the University of Waikato for financial support, including research scholarships to C. J. and L. J. McC. W. H. and L. J. McC. thank the Asia 2000 Foundation of New Zealand for a travel grant, and the New Zealand Lottery Grants Board for a grant-in-aid towards the purchase of the electrospray mass spectrometer. W. H. thanks Pat Gread and Wendy Jackson for technical assistance.

References

1 S. L. Randall, C. A. Miller, T. S. Janik, M. R. Churchill and J. D. Atwood, *Organometallics*, 1994, **13**, 141; E. W. Evans, M. B. H. Howlader and M. T. Atlay, *Transition Met. Chem.*, 1994, **19**, 183; E. Cariati, E. Lucenti, M. Pizzotti, D. Roberto and R. Ugo, *Organometallics*, 1996, **15**, 4122 and refs. therein.

2 H. E. Bryndza and W. Tam, *Chem. Rev.*, 1988, **88**, 1163; D. Milstein, *Acc. Chem. Res.*, 1988, **21**, 428.

3 D. Milstein, *J. Am. Chem. Soc.*, 1986, **108**, 3525.

4 W. A. Volkert and T. J. Hoffman, *Chem. Rev.*, 1999, **99**, 2269; S. Top, P. Morel and G. Jaouen, *Inorg. Chem. Commun.*, 1999, **2**, 7; M. B. Skaddan, F. R. Wüst and J. A. Katzenellenbogen, *J. Org. Chem.*, 1999, **64**, 8108; E. Campazzi, M. Cattabriga, L. Marvelli, A. Marchi, R. Rossi, M. R. Pieragnoli and M. Fogagnolo, *Inorg. Chim. Acta*, 1999, **286**, 46; R. Alberto, A. Egli, U. Abram, K. Hegetschweiler, V. Gramlich and P. A. Schubiger, *J. Chem. Soc., Dalton Trans.*, 1994, 2815; U. Abram, S. Abram, R. Alberto and R. Schibli, *Inorg. Chim. Acta*, 1996, **248**, 193 and refs. therein; D. J. Rose, K. P. Maresca, P. B. Kettler, Y. D. Chang, V. Soghomomian, Q. Chen, M. J. Abrams, S. K. Larsen and J. Zubieta, *Inorg. Chem.*, 1996, **35**, 3548; R. Alberto, R. Schibli, R. Waibel, U. Abram and A. P. Schubiger, *Coord. Chem. Rev.*, 1999, **190–192**, 901.

5 R. Alberto, R. Schibli, A. Egli, A. P. Schubiger, U. Abram and T. A. Kaden, *J. Am. Chem. Soc.*, 1998, **120**, 7987; R. Alberto, R. Schibli, A. P. Schubiger, U. Abram, H.-J. Pietzsch and B. Johannsen, *J. Am. Chem. Soc.*, 1999, **121**, 6076; R. Alberto, R. Schibli, A. Egli, U. Abram, S. Abram, T. A. Kaden and P. A. Schubiger, *Polyhedron*, 1998, **17**, 1133.
6 U. Brand, C. A. Wright and J. R. Shapley, *Inorg. Chem.*, 1999, **38**, 5910; W. A. Herrmann, A. Egli, E. Herdtweck, R. Alberto and F. Baumgärtner, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 432.
7 A. P. Ginsberg and M. J. Hawkes, *J. Am. Chem. Soc.*, 1968, **90**, 5930.
8 A. A. Ioganson, B. V. Lokshin, E. E. Kolobova and K. N. Anisimov, *J. Gen. Chem.*, 1974, **20**, 20 (translated from *Z. Obshch. Khim.*, 1974, **44**, 23); G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, *J. Organomet. Chem.*, 1978, **152**, 85; M. Freni and P. Romiti, *Atti Accad. Naz. Lincei, Mem. Cl. Sci. Fis., Mat. Nat. Rend.*, 1973, **55**, 515.
9 C. Jiang, Y.-S. Wen, L.-K. Liu, T. S. A. Hor and Y. K. Yan, *Organometallics*, 1998, **17**, 173.
10 A. Egli, K. Hegetschweiler, R. Alberto, U. Abram, R. Scibli, R. Hedinger, V. Gramlich, R. Kissner and P. A. Schubiger, *Organometallics*, 1997, **16**, 1833.
11 R. Alberto, A. Egli, U. Abram, K. Hegetschweiler, V. Gramlich and P. A. Schubiger, *J. Chem. Soc., Dalton Trans.*, 1994, 2815.
12 R. D. Simpson and R. G. Bergman, *Organometallics*, 1993, **12**, 781.
13 R. G. Bergman, *Polyhedron*, 1995, **14**, 3227; R. D. Simpson and R. G. Bergman, *Organometallics*, 1992, **11**, 4306.
14 G. Ciani, A. Sironi and A. Albinati, *Gazz. Chim. Ital.*, 1979, **109**, 615.
15 R. Colton, A. D'Agostino and J. C. Traeger, *Mass Spectrom. Rev.*, 1995, **14**, 79; W. Henderson, B. K. Nicholson and L. J. McCaffrey, *Polyhedron*, 1998, **17**, 4291.
16 J. H. Espenson, H. Tan, S. Mollah, R. S. Houk and M. D. Eager, *Inorg. Chem.*, 1998, **37**, 4621.
17 A. M. Bond, R. Colton, D. G. Humphrey, P. J. Mahon, G. A. Snook, V. Tedesco and J. N. Walter, *Organometallics*, 1998, **17**, 2977; H. Hori, J. Ishihara, M. Ishizuka, K. Koike, K. Takeuchi, T. Ibusuki and O. Ishitani, *Stud. Surf. Sci. Catal.*, 1998, **114**, 557; H. Hori, J. Ishihara, K. Koike, K. Takeuchi, T. Ibusuki and O. Ishitani, *Chem. Lett.*, 1997, **3**, 273; A. M. Bond, R. Colton, R. W. Gable, M. F. Mackay and J. N. Walter, *Inorg. Chem.*, 1997, **36**, 1181; C. E. C. A. Hop, J. T. Brady and R. Bakhtiar, *J. Am. Soc. Mass Spectrom.*, 1997, **8**, 191; H. Hori, O. Ishitani, K. Koike, K. Takeuchi and T. Ibusuki, *Anal. Sci.*, 1996, **12**, 587.
18 C. Jiang, W. Henderson, T. S. A. Hor, L. J. McCaffrey and Y. K. Yan, *Chem. Commun.*, 1998, 2029.
19 K. W. M. Siu, G. J. Gardner and S. S. Berman, *Org. Mass Spectrom.*, 1989, **24**, 931.
20 R. D. Simpson and R. G. Bergman, *Organometallics*, 1992, **11**, 3980.
21 C. Jiang, Y.-S. Wen, L.-K. Liu, T. S. A. Hor and Y. K. Yan, *J. Organomet. Chem.*, 1997, **543**, 179.
22 T. Beringhelli, G. Ciani, G. D'Alfonso, A. Sironi and M. Freni, *J. Chem. Soc., Dalton Trans.*, 1985, 1507.
23 Y. K. Yan, H. S. O. Chan, T. S. A. Hor, K. L. Tan, L. K. Liu and Y. S. Wen, *J. Chem. Soc., Dalton Trans.*, 1992, 423.
24 J. Emri and B. Györi, in *Comprehensive Co-ordination Chemistry*, ed. in chief G. Wilkinson, Pergamon, Oxford, 1987, vol. 3, ch. 24.
25 F. A. Cotton, E. V. Dikarev and M. A. Petrukhina, *Inorg. Chim. Acta*, 1999, **284**, 304.
26 H. E. Bryndza, J. C. Calabrese, M. Marsi, D. C. Roe, W. Tam and J. E. Bercaw, *J. Am. Chem. Soc.*, 1986, **108**, 4805; E. L. Muetterties, *Transition Metal Hydrides*, Marcel Dekker, New York, 1971, pp. 203–269.
27 I. Saura-Llamas and J. A. Gladysz, *J. Am. Chem. Soc.*, 1992, **114**, 2136; D. M. Hoffman, D. Lappas and D. A. Wierda, *J. Am. Chem. Soc.*, 1993, **115**, 2136.
28 G. Smith, S. F. Pedersen and J. A. Leary, *J. Org. Chem.*, 1997, **62**, 2152.
29 T. Yalcin, J. Wang, D. Wen and A. G. Harrison, *J. Am. Soc. Mass Spectrom.*, 1997, **8**, 749.
30 C. Hinderling, D. Feichtinger, D. A. Plattner and P. Chen, *J. Am. Chem. Soc.*, 1997, **119**, 10793; C. Hinderling, D. A. Plattner and P. Chen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 243.
31 W. Henderson and C. Evans, *Inorg. Chim. Acta*, 1999, **294**, 183; C. Decker, W. Henderson and B. K. Nicholson, *J. Chem. Soc., Dalton Trans.*, 1999, 3507.
32 C. Jiang, T. S. A. Hor, Y. K. Yan, W. Henderson and L. J. McCaffrey, *J. Chem. Soc., Dalton Trans.*, 2000, 3204.
33 L. J. Arnold, *J. Chem. Educ.*, 1992, **69**, 811.