Electrospray mass spectrometric studies of the rhenium hydroxy and methoxy carbonyl complexes $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ (R = H, Me)

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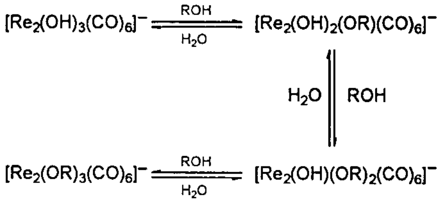
Exchange reactions of $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ (R = H, Me) with alcohols and phenol have been established by electrospray mass spectrometry (ESMS); dehydration of $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ and the β-hydride elimination reaction of $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$ have also been observed under ESMS conditions.

Transition-metal carbonyl hydroxides and alkoxides have been proposed as intermediates in a number of important reactions, such as metal-catalysed hydrogenation of CO,[1] the water–gas shift reaction,[2] and carboalkoxylation of alkenes.[3] Although the syntheses of the complexes $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ (R = H, Me, Et, Pr^i) were reported more than two decades ago,[4] the chemistry of these complexes have received relatively little attention.[5] This is perhaps due to the perceived limited scope of reactivity of these compounds. Simpson and Bergman recently reported the facile alkoxide-exchange reactions of the terminal-alkoxo complexes *fac*-$[Re(\eta^1\text{-}OR)(L)_2(CO)_3]$ (L = phosphine or arsine, R = Me, Et, Pr^i) with alcohols and phenols.[6] It is of interest to investigate the feasibility of analogous exchange reactions involving the bridging-alkoxo complexes $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$, which have in principle three exchangeable alkoxide or hydroxide ligands. Such exchange reactions have been briefly alluded to in the literature[4b,7] but no systematic study has been carried out on them.

The study of the alkoxide exchange reactions of the tris-alkoxo-bridged complexes is expected to be complicated by the formation of singly, doubly and triply-exchanged species which exist in equilibrium with each other (Scheme 1). Identification of these inter-converting species in solution by IR or NMR spectroscopy is expected to be very difficult, especially when the R group (*e.g. n*-octyl) gives a complex ^{1}H NMR spectrum.

We wish to report here that electrospray mass spectrometry (ESMS) is a very convenient yet informative technique that is appropriate for the study of the exchange reactions of the complexes $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ **1** and $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$ **2**.† Ionic species existing in equilibrium in solution are transferred intact into the gas phase in the spectrometer and can be directly identified by their *m/z* values, regardless of their rate of inter-conversion on the NMR timescale. Thus, the various exchanged species arising from the reactions of **1** and **2** with different alcohols can be unambiguously identified in the mass spectra and the relative abundance of these species at different times after addition of alcohol can be monitored.



Scheme 1

At a cone voltage of 5 V, solutions of complex **1** in MeCN (typically 0.1 mg ml^{-1}) give a clean strong signal of the parent ion at *m/z* 591/593, together with a weak ion signal at *m/z* 879 corresponding to $[Re_3(OH)_4(CO)_9]^-$.[8] The latter ion is most probably a side product during the synthesis of **1**.[5] This impurity can be converted to **1** simply by adding a drop of aqueous NaOH to the ESMS solution.[9]

About 1 min after addition of a few drops of methanol to the ESMS solution of **1**, the spectrum showed low intensity peaks at *m/z* 605/607, 619/621 and 633/635, corresponding respectively to the singly, doubly and triply (OH → OMe) exchanged species. The peaks of the exchanged species rapidly grew in intensity with respect to that of the parent ion $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ over 10 min. (Fig. 1), although the exact relative intensities of these peaks at 10 min showed some variability between experiments. On standing the solution overnight (16 h) the main ion observed was $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$, with the bis- and mono-methoxy ions still present in successively lower abundance, and no parent ion remaining. A clean intense peak of the permethoxylated ion was obtained on letting the solution stand for two weeks, with trace peaks of only the bis-methoxy species remaining. It is also noteworthy that throughout the experiment, the trirhenium ion $[Re_3(OH)_4(CO)_9]^-$ appeared to be unaffected by methanol. These results indicate that (OH → OMe) exchange is quite facile on complex **1**, with all three hydroxy ligands being replaceable.

The (OH → OMe) exchange is readily reversible, as indicated by the ESMS detection of small amounts of $[Re_2(\mu\text{-}$

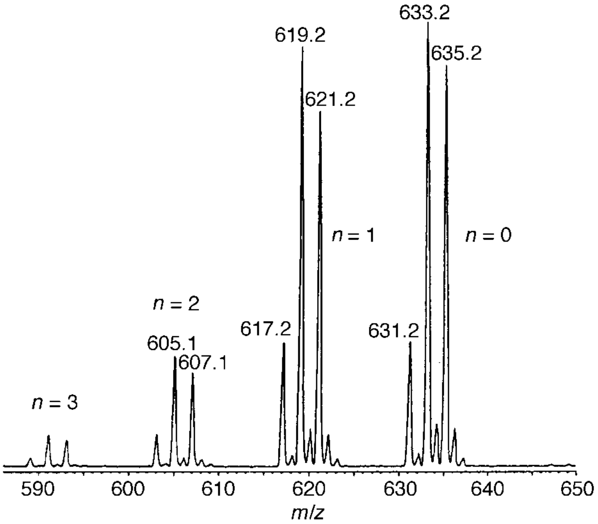


Fig. 1 High-resolution negative ion electrospray mass spectrum of a solution of complex **1** in MeCN, 10 min after addition of MeOH (cone voltage 5 V), showing the presence of the ions $[Re_2(OH)_n(OMe)_{3-n}(CO)_6]^-$ (n = 0–3)

Table 1 Exchange reactions of complexes **1** and **2** with various reagents

Complex	Reagent	Maximum number of OH/OMe groups exchanged
1	*tert*-Butanol	1
1	Methanol	3
1	Ethanol	3
1	*n*-Octanol	3
1	Phenol	3
1	*p*-Toluenethiol, MeC_6H_4SH	3
1	Benzeneselenol, PhSeH	2
1	$FcCH_2PH_2$ (Fc = ferrocenyl)	0
1	$H_2C(CN)_2$	0
2	Water	3
2	Ethanol	3
2	Phenol	3

$OMe)_2(\mu\text{-}OH)(CO)_6]^-$ even in a freshly made solution of complex **2** in MeCN (not rigorously dried). Other than this hydrolysis product, the spectrum contained only the strong signal of the intact **2** ion at *m/z* 633/635. On adding two drops of water to the ESMS solution, hydrolysis occured over a period of minutes to generate a mixture of mono-, bis- and tris-hydroxy complexes, and after 35 min the dominant ion was $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$. Addition of four drops of methanol to this solution quickly (within 1 min) removed $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ and regenerated $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$ as the most abundant ion. These results suggest that (OH → OMe) exchange is more facile than (OMe → OH) exchange, possibly due to the greater steric accessibility of the {Re(μ-OH)Re} unit compared to its methoxy analogue.

Exchange reactions of **1** and **2** with other protic compounds have also been investigated by ESMS, as summarised in Table 1. The results are consistent with an exchange mechanism that involves proton transfer to the hydroxy or methoxy ligands as the first step, since compounds with very weakly acidic protons such as malononitrile and ferrocenylmethylphosphine[10] do not displace the OH and OMe ligands. In this context, it is noteworthy that the electrospary mass spectrum of a solution of a 1 : 1 mixture of **1** and **2** in alcohol-free MeCN showed no OH/OMe scrambled species even after 24 h. Steric factors also play an important role in determining facility of reaction, as indicated by the ability of complex **1** to exchange for only one *tert*-butoxide group.

By themselves, complexes **1** and **2** also exhibit interesting fragmentation behaviour at higher cone voltages. Dehydration of **1** begins to occur at 20 V, when a low abundance peak due to $[Re_2(O)(OH)(CO)_6]^-$ (*m/z* 573/575) appears in the mass spectrum. At 40 V, this is the most abundant ion, with very little parent ion remaining. Decarbonylation of the dehydrated species begins to occur at a cone voltage of 60 V, as indicated by the presence of the ions $[Re_2(O)(OH)(CO)_n]^-$ (n = 3–5). Decarbonylation without dehydration apparently does not occur, since ions such as $[Re_2(\mu\text{-}OH)_3(CO)_n]^-$ (n = 3–5) are not detected throughout. This result clearly indicates that dehydration of complex **1** is energetically much more favourable than decarbonylation.

Dehydration does not occur with complex **2**, which fragments *via* β-hydride elimination instead, at a cone voltage of 50 V. The parent ion eliminates formaldehyde to form $[Re_2(H)(OMe)_2(CO)_6]^-$ (*m/z* 603/605), $[Re_2(H)_2(OMe)(CO)_6]^-$ (*m/z* 573/575), and finally the known species[4b] $[Re_2(H)_3(CO)_6]^-$ (*m/z* 543/545). Decarbonylation of the β-eliminated species also occur at 50 V to give $[Re_2(H)(OMe)_2(CO)_5]^-$ (*m/z* 575/577) and $[Re_2(H)_2(OMe)(CO)_5]^-$ (*m/z* 545/547). The peaks of these decarbonylated ions overlap with the peaks at *m/z* 573/575 and 543/545 respectively to give characteristic 'triplet' patterns. Confirmation of these ions was achieved by deuterium labelling, the species $[Re_2(OCD_3)_3(CO)_6]^-$ being generated by addition of excess CD_3OD to **1**. At high cone voltages, the expected mass shifts corresponding to the ions $[Re_2(D)_n(OCD_3)_{3-n}(CO)_6]^-$ (n = 0–3) were observed. Elimination of acetaldehyde also occurs in an analogous fashion from the ion $[Re_2(OEt)_3(CO)_6]^-$, which was generated by addition of ethanol to **1**. As far as we are aware, β-hydride elimination from coordinated alkoxide ligands has not been observed by ESMS previously.

In conclusion, this study has shown that the complex anions $[Re_2(\mu\text{-}OH)_3(CO)_6]^-$ **1** and $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$ **2** undergo facile exchange reactions with alcohols and phenol. The feasibility and extent of these reactions can be conveniently and unambiguously determined by electrospray mass spectrometry. The results also suggest that complex **1** can be used as a versatile starting material for the synthesis of a wide range of analogous $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$ and $[Re_2(\mu\text{-}SR)_3(CO)_6]^-$ complexes, by simple reaction of **1** with an excess of the appropriate alcohol or thiol. Other protic or electrophilic compounds can also be investigated for their reactivity with **1**, simply by adding the compound to a solution of **1** and recording the electrospray mass spectrum of the solution. Thus, ESMS can be used as a quick but accurate technique to screen for potentially useful reactions. The prospect of **1** showing interesting biological activity *via* interaction with the OH, SH and NH functional groups of biomolecules is also attractive and is currently being investigated in our laboratories.[11]

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Notes and References

† Electrospray mass spectra were obtained in the negative-ion mode with a VG Platform II quadrupole mass spectrometer using HPLC-grade MeCN as the mobile phase. The samples (in MeCN solution) were injected *via* a Rheodyne injector fitted with a 10 μl sample loop, and delivered to the spectrometer source (60 °C) at 0.01 ml min^{-1}. Nitrogen was used as the drying and nebulising gas, and the capillary voltage was 3.5 kV. Cone voltages were typically varied between 5 and 80 V in order to investigate the formation of fragment ions.

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

2 M. A. Bennett and T. W. Matheson, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1st edn., 1982, vol. 4.

3 H. E.Bryndza and W. Tam, *Chem. Rev.*, 1988, **88**, 1163.

4 (*a*) A. A. Ioganson, B. V. Lokshin, E. E. Kolobova and K. N. Anisimov, *J. General Chem.*, 1974, **20**, 20 (Translated from *Zh. Obshch. Khim.*, 1974, **44**, 23); (*b*) A. P. Ginsberg and M. J. Hawkes, *J. Am. Chem. Soc.*, 1968, **90**, 5930; (*c*) G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, *J. Organomet. Chem.*, 1978, **152**, 85; (*d*) M. Freni and P. Romiti, *Atti Accad. Naz. Lincei, Mem. Cl. Sci. Fis. Mat. Nat. Rend.*, 1973, **55**, 515.

5 C. Jiang, Y.-S. Wen, L.-K. Liu, T. S. A. Hor and Y. K. Yan, *Organometallics*, 1998, **17**, 173.

6 R. D. Simpson and R. G. Bergman, *Organometallics*, 1993, **12**, 781.

7 G. Ciani and A. Sironi, *Gazz. Chim. Ital.*, 1979, **109**, 615.

8 There is excellent agreement between observed and calculated isotope patterns (L. J. Arnold, *J. Chem. Ed.*, 1992, **69**, 811).

9 Consistent with the equation: 2 $[Re_3(OH)_4(CO)_9]^- + OH^- \rightarrow 3\ [Re_2(OH)_3(CO)_6]^-$. See also Ref. 11(*a*).

10 N. J. Goodwin, W. Henderson and B. K. Nicholson, *Chem. Commun.*, 1997, 31.

11 Water-soluble, low-valent rhenium compounds have received much attention recently due to their potential application in radioimmunotherapy and protein labelling. See: (*a*) R. Alberto, A. Egli, U. Abram, K. Hegetschweiler, V. Gramlich and P. A. Schubiger, *J. Chem. Soc., Dalton Trans.*, 1994, 2815 and references therein; (*b*) U. Abram, S. Abram, R. Alberto and R. Schibli, *Inorg. Chim. Acta*, 1996, **248**, 193 and references therein.

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