Easily Reversible Ionic Fragmentation of a Tetrahedral Unsaturated Rhenium Cluster, a Reappraisal of the Reaction of $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$ with Methanol

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The unsaturated tetrahedral cluster $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$ in the presence of weak donor molecules L, like methanol or acetone, reversibly fragments to unsaturated triangular cluster anions and to mononuclear cations, probably *via* spiked-triangular $[Re_4(\mu\text{-}H)_4(CO)_{12}L_4]$ intermediates.

It has been recently reported[1] that the unsaturated tetrahedral cluster $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]^2$ [compound **1**, 56 valence electrons (v.e.s)] easily forms $[Re_4H_4(CO)_{12}(MeOH)_4]$. The coordination of the four MeOH molecules was inferred from NMR data as well as from the presence of a $\{[MeOH]^4\}$ term in the rate law. No hypothesis on the structure of this species was presented. We have now found that this compound does not exist in the previously described conditions: compound **1** does add four MeOH molecules, but in solution ionic species are present, formed in a 'disproportionation' process.

When the red compound **1** was dissolved in MeOH at room temperature, bright yellow solutions were obtained, which showed conductivity typical of 1:1 electrolytes[3] (Λ_M = 95 Scm^{2}mol^{-1}, 1 2 × 10^{-3} mol dm^{-3}). In CD_3OD, three hydridic resonances were observed, whose intensity ratio and δ values are typical of unsaturated $[Re_3(\mu\text{-}H)_4(CO)_9L]^-$ species[4] (L = MeOH, compound **2**, δ −7.92, −8.56, −8.73, 1:2:1, 193 K). NMR† and reactivity data suggest the contemporary formation of $[Re(CO)_3(MeOH)_3]^+$ **3**, eqn. (1).

$$[Re_4(\mu_3\text{-}H)_4(CO)_{12}] + 4\,MeOH \rightarrow$$
$$[Re_3(\mu\text{-}H)_4(CO)_9(MeOH)]^- + [Re(CO)_3(MeOH)_3]^+ \qquad (1)$$

When the reaction of **1** with MeOH is performed in CH_2Cl_2 or $CHCl_3$, as in previous work,[1] the same ionic fragmentation occurs, as confirmed also by conductivity measurements. However, variable temperature ^{1}H NMR experiments (Fig. 1) revealed the occurrence of a fast dynamic equilibrium. The two hydridic resonances (3:1)[1] observed at 298 K, on lowering the temperature collapse and eventually give rise to signals attributable to two species **A** and **B**: **A**, δ −8.14, −8.58 and −9.02 (intensity 1:2:1, 183 K); **B**, δ −5.96 and −8.14 (3:1, 183 K) (two resonances accidentally overlap). The spectral changes are completely temperature reversible. We formulate the species **A** as the unsaturated anion **2**, whose relative amount strongly increases on lowering the temperature (Fig. 1), and on increasing the concentration of MeOH. At different temperatures, the intensities of the resonances of **3** remain constant, corresponding to the overall amount of **A** + **B**, in spite of the change of the **A/B** ratio, in line with both **A** and **B** being anionic species.

These results are consistent with the dissociative equilibrium [eqn. (2)] whose position and rate changes with temperature. At room temperature it is completely driven to the right and is fast on the NMR timescale.

$$A \rightleftharpoons B + MeOH \qquad (2)$$

It is therefore tempting to formulate **B** as a 'super-unsaturated' $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}H)(CO)_9]^-$ anion,‡ isoelectronic with the previously characterized[5] 44 v.e.s cluster $[Re_3(\mu_3\text{-}H)_2(CO)_6(\mu\text{-}PPh_2)_3]$, even if here stabilization by weak solvent coordination could be present. The same species **B** is formed when **1** is treated with acetone in $CDCl_3$ or CD_2Cl_2,§ but in this case it remains the unique species even at 183 K, indicating that acetone is a more labile ligand than methanol.

Compound **B** is probably the active species involved in the recently reported formation of the octahedral cluster anion $[Re_6H_7(CO)_{18}]^-$,[6] and of the BF_4^- derivative $[Re_3H_2(CO)_9(\mu_3\text{-}FBF_3)]^{2-}$,[7] both of which are promoted by the treatment of **1** with acetone.

The reactivity of the equilibrium mixture **A/B** is in agreement with these formulations. The addition of MeCN caused the instantaneous quantitative formation of $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^{-4}$ and $[Re(CO)_3(NCMe)_3]^+$.[8] By addition of CO at 213 K, the hydridic resonances of **A** and **B** were immediately replaced by those of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$,[9]‖ whilst the resonances of **3** disappeared much more slowly (as expected for the replacement of MeOH by the π-acidic CO in a cationic complex).

Complexes like $[Re_3(\mu\text{-}H)_4(CO)_9(MeOH)]^-$, containing hydridic H ligands and acidic hydroxy groups, are known to be

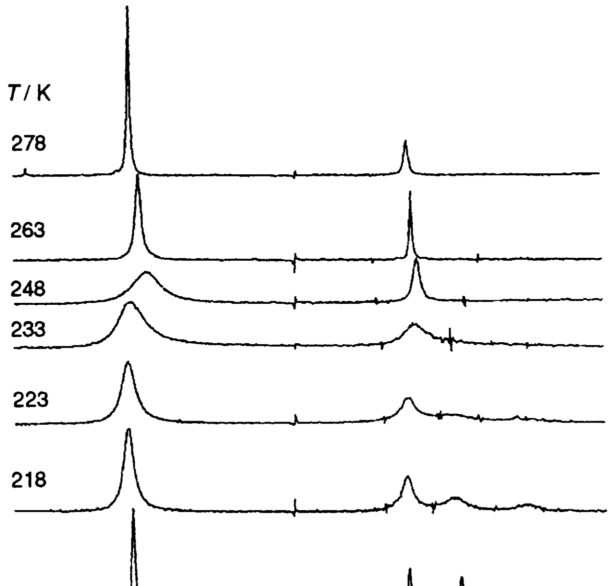
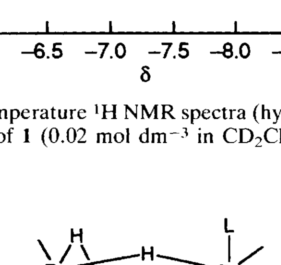


Fig. 1 Variable temperature ^{1}H NMR spectra (hydridic region) of the reaction mixture of **1** (0.02 mol dm^{-3} in CD_2Cl_2) with MeOH (0.5 mol dm^{-3})



2 L = MeOH

unstable towards H_2 elimination.[4,10] This accounts for the quite rapid formation, as a final stable product, of the already known[11] saturated anion $[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}OMe)]^-$ (48 v.e.s).¶

As already pointed out,[1] compound **1** is recovered in high yields from **A/B** mixtures upon removal of the solvent under vacuum or upon dilution of a $CDCl_3$ solution. In the case of acetone such reverse reaction is even easier than with methanol. This unusual electrophilic addition on an unsaturated cluster is probably driven by the interaction of $[Re(CO)_3S_n]^+$ fragments (S = MeOH, acetone or H_2O, $n < 3$) with a negatively polarized H ligand. The reaction could be of synthetic use for the formation of mixed-metal species, by using other 12-electron $ML_n{}^+$ fragments. Labile ligands such as methanol or acetone are required for this reaction to occur; with $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ and $[Re(CO)_3(NCMe)_3]^+$, for instance, compound **1** cannot be reobtained.

The reaction of **1** with MeOH was monitored at low temperature in order to obtain evidence of the possible presence of intermediates. In spite of the extremely low solubility of **1** in these conditions, we observed in CD_3OD at 210 K the intermediate formation of a species exhibiting a pattern of hydridic resonances consistent with an addition product $[Re_4(\mu\text{-}H)_4(CO)_{12}(MeOH)_4]$, with a spiked-triangle structure and C_s symmetry: δ −8.92 (s, 1), −10.56 (t, 1), −11.97 (d, 2, J_{HH} 3.5 Hz). In agreement with this, in the reaction of **1** with acetonitrile, two $[Re_4(\mu\text{-}H)_4(CO)_{12}(MeCN)_4]$ intermediates with a spiked-triangular structure, slowly decomposing mainly to $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ and $[Re(CO)_3(NCMe)_3]^+$, have been spectroscopically identified.[12] The propensity of **1** to add four two-electron donor species is also confirmed by the X-ray crystal structure of the spiked-triangle cluster formed in the reaction of **1** with tris(diphenylphosphino)methane, which coordinates unusually acting as an eight-electron donor.[13]

Even ligands as poor as methanol or acetone are therefore able to break the Re–H–Re interactions in **1**. The addition products are thermodynamically unstable and dissociate to triangular anionic unsaturated clusters. For particularly weak ligands, however, metal–ligand and metal–H–metal interactions are of comparable strength and the competition between these interactions can be driven to either side simply by changing the ligand concentration.

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Footnotes

† The resonances of the MeOH molecules coordinated in **2** and **3** are easily identified, because each molecule gives rise to a quartet and a doublet (J_{HH} 3.5 Hz), of relative intensity 1:3. CD_2Cl_2, 183 K, compound **2**: δ 6.2 (q) and 3.18 (d); compound **3**: δ 9.03 (q) and 3.60 (d).

‡ No resonance attributable to MeOH or H_2O coordinated in **B** could be detected.

§ Under these reaction conditions, a mixture of cations of formula $[Re(CO)_3(C_3H_6O)_n(H_2O)_{3-n}]^+$ is simultaneously formed: CD_2Cl_2, 213 K, $n = 3$, δ 2.49, $n = 2$, δ = 7.79 and 2.46 (1:6), $n = 1$, δ = 7.62 and 2.44 (2:3).

|| Only at longer times and at room temperature does this species transform into $[Re_3(\mu\text{-}H)_3(CO)_{12}]$, as reported in ref. 1. Moreover, the reaction of **1** with CO, reported in ref. 1 to give almost exclusively $[Re_3(\mu\text{-}H)_3(CO)_{12}]$, indeed also gives a substantial amount of $[HRe(CO)_5]$, as already reported in ref. 2.

¶ We have not been able to obtain evidences of the intermediate **A2** of ref. 1, formulated as a neutral cluster $[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}MeOH)]$, which should possess 46 v.e.s and an unlikely μ_3-MeOH ligand.

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