Formation of the highly unusual cyclic clusters $[MH(CO)_4]_n$ (M = Mn, n = 4–9; M = Re, n = 4–6) under laser desorption/ionisation conditions

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The positive and negative ion ultraviolet laser desorption mass spectra of the trinuclear clusters $[M_3H_3(CO)_{12}]$ (M = Mn **1** or Re **2**) have been recorded using laser desorption/ionisation time-of-flight mass spectrometry (LDI-TOF-MS). The spectra contain peaks corresponding to trinuclear clusters together with peaks at higher masses arising from the series of condensed products $[M_nH_{n-1}(CO)_{4n}]^-$ (where n = 4–9). These products are believed to have cyclic structures and to be formed by the stepwise insertion of $[MH(CO)_4]$ into a metal–metal bond.

Introduction

We have previously established that the laser irradiation of appropriate metal cluster precursors has in some cases led to the formation of supraclusters[1] and in others new series of simpler clusters[2] that although not unexpected have not previously been observed as the product of the usual synthetic methods. For example, irradiation of the homonuclear carbido-cluster $[Ru_6C(CO)_{17}]$ leads to the formation of a range of species $[Ru_6C(CO)_x]$, $[Ru_{12}C_2(CO)_x]$, $[Ru_{18}C_3(CO)_x]$, *etc.*[3] whereas irradiation of $[Ru_3(CO)_{12}]$ produces a series of anionic and cationic clusters derived from the series of parents $[Ru_4(CO)_{14}]$, $[Ru_5(CO)_{16}]$, $[Ru_6(CO)_{18}]$, *etc.*[4] similar to those established by more usual synthetic methods for osmium.[5] Clearly, laser synthesis potentially provides a route to a far wider range of cluster materials than has previously been envisaged. Although studies have been concerned previously with ultraviolet laser desorption/ionisation mass spectrometry, more recent studies have shown the possibility of direct synthetic routes involving laser irradiation of appropriate precursors to many related species.[6]

In this paper we wish to comment on our studies of the two trinuclear hydrido clusters $[Mn_3H_3(CO)_{12}]$ **1** and $[Re_3H_3(CO)_{12}]$ **2** and to report the formation of a series of clusters compounds with the basic formula $[M_nH_{n-1}(CO)_{4n}]^-$ (where n = 3–9 for Mn and 3–6 for Re), which we believe are based on cyclic metal arrangements. In these species, in which the $[MH(CO)_4]$ units may be taken to correspond to the isolobal CH_2 and iso-electronic units in carbon chemistry, rings with 3–9 units are thought to be present. In each case, we suggest these units are linked by direct M–M (two-centre/two-electron) bonds, supported by bridging (μ-H) ligands.

Results and discussion

The UV laser desorption/ionisation (LDI) mass spectra of the trinuclear trihydrido-clusters $[Mn_3H_3(CO)_{12}]$ **1** and $[Re_3H_3(CO)_{12}]$ **2** were recorded using two different time-of-flight instruments in both positive and negative mode. The essential features of the spectra are listed in Tables 1 and 2; the negative-ion mass spectra of **1** and **2** are shown in Figs. 1 and 2. Several aspects emerge. First, the parent $[M_3H_3(CO)_{12}]^-$ is not observed; instead $[M - H]^-$ is formed in both cases, and which must arise from the loss of a single proton in each case. This observation is in contrast to that normally observed in which $[M - CO]^-$ is usually favoured.[7] Secondly, a series of peaks based on tetranuclear, pentanuclear, hexanuclear, septa-nuclear, octanuclear and nonanuclear species and corresponding to the general formula $[M_nH_{n-1}(CO)_{4n}]^-$ are also observed (the series extends only to hexanuclear species for Re). Given that the parent compounds are observed as $[M - H]^-$ ions we are led to believe that this range of ions corresponds to the formation of the series of species $[MH(CO)_4]_n$. Members of this series have been characterised previously as the products of conventional synthetic methods and found to have molecular structures similar to those shown in Fig. 3. Examples, in addition to the parent clusters $[M_3H_{3-x}(CO)_{12}]^{x-}$ (M = Mn or Re; x = 0, 1 or 2),[8] include the higher members of the series: $[Re_4H_4(CO)_{16}]$, $[Re_4H_3(CO)_{16}]^-$,[9] $[Re_5H_5(CO)_{20}]$, and $[Re_5H_4(CO)_{20}]^-$.[10] The hydride ligands of the larger metallacycles appear on the inside of the ring, which is puckered. The related, isoelectronic indium-centered pentamanganese cluster $[Mn_5(\mu_5\text{-In})(CO)_{20}]$ is also known.[11]

In addition to the $[M - H]^-$ ion, ions are observed that correspond to the successive removal of CO ligands (see Table 1), which is a feature common to other systems studied both by LDI[1-4,7] and by other ionisation methods.[12] This loss of CO ligands is a function of laser power and as the intensity of the beam is increased CO stripping is increased. Open clusters such as those generated in these experiments often undergo post-source decay (PSD),[13] where the cluster loses additional CO ligands inside the flight tube. We believe that this process is prompted by the clusters shedding excess of energy *via* CO loss with subsequent polyhedral rearrangements of the metal core. An example of the process is shown for the pentanuclear cluster $[Mn_5H_4(CO)_{20}]^-$ in Scheme 1.

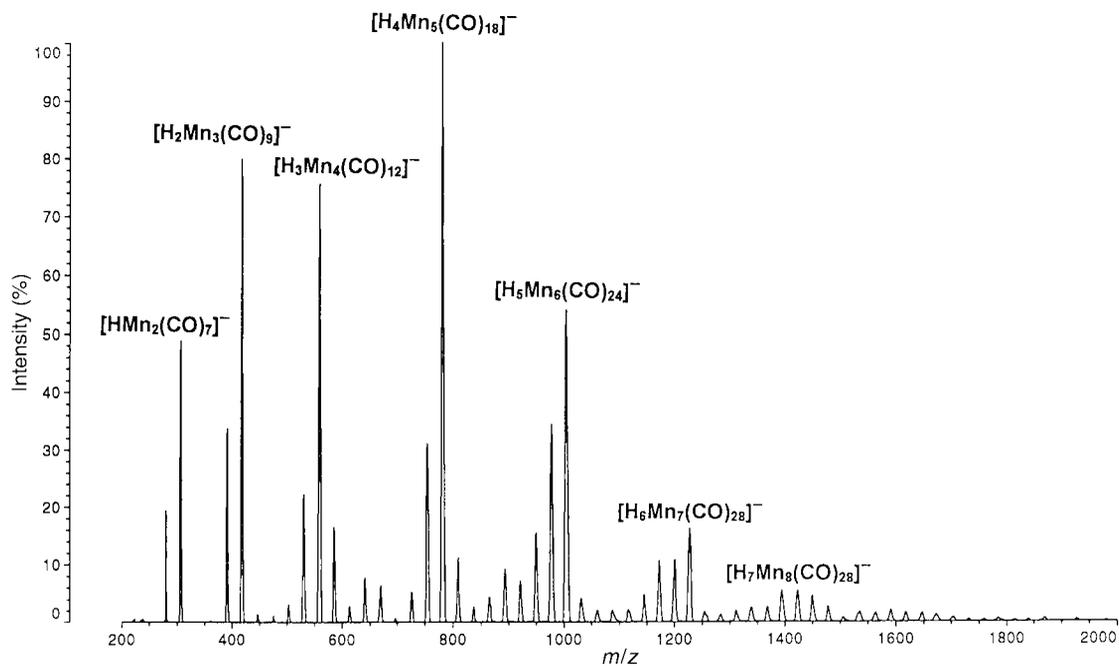**Fig. 1** Negative ion UV laser desorption/ionisation mass spectrum of $[Mn_3H_3(CO)_{12}]$ over the range m/z 200–2000.

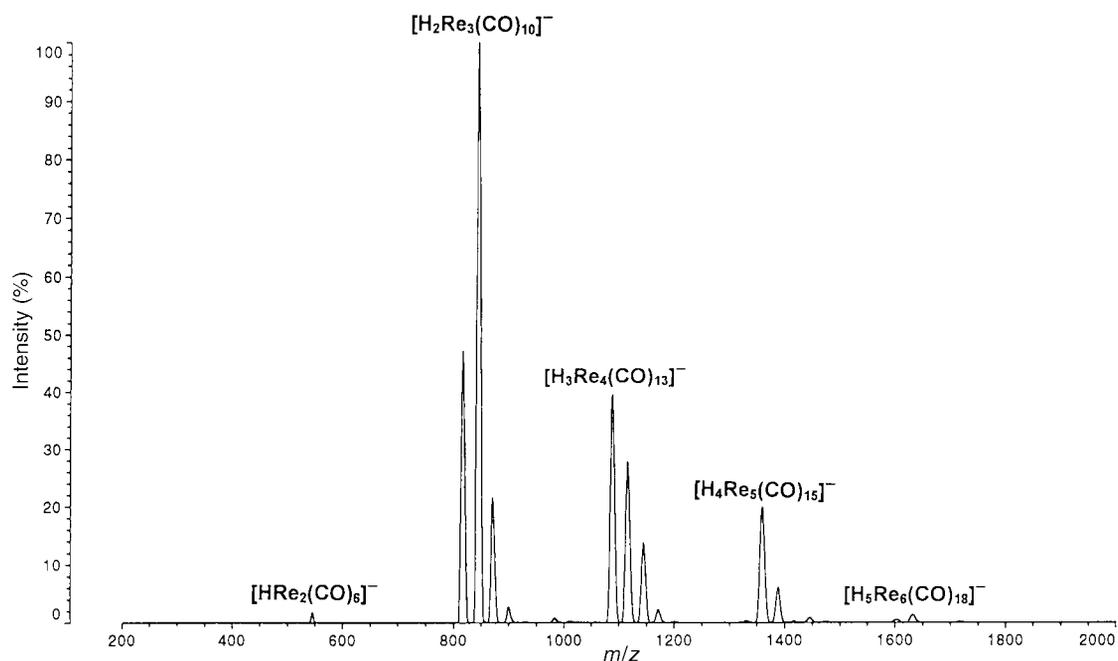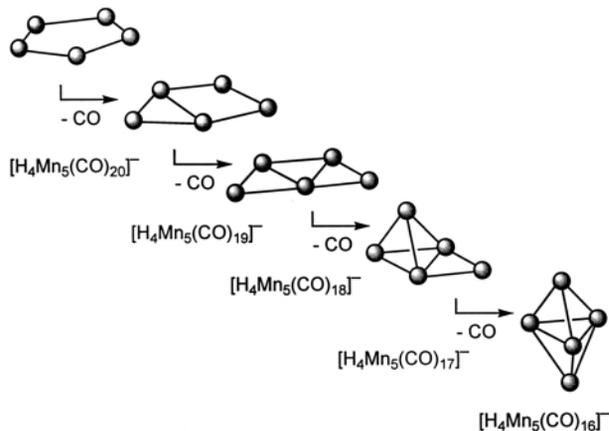**Fig. 2** Negative ion UV laser desorption/ionisation mass spectrum of $[Re_3H_3(CO)_{12}]$ over the range m/z 200–2000.

Scheme 1 Proposed core rearrangement of $[Mn_5H_4(CO)_{20}]^-$ with progressive CO stripping.

In the negative-ion spectrum of $[Mn_3H_3(CO)_{12}]$ peaks are also observed at m/z 306.7 and 279.0 which correspond to the binuclear species $[HMn_2(CO)_7]^-$ and $[HMn_2(CO)_6]^-$. These we believe correspond either to the binuclear parent $[Mn_2H_2(CO)_8]$ and its subsequent loss of H^+ or to the fragmentation of $[Mn_3H_2(CO)_{12}]^-$ to give $[Mn_2H(CO)_7]^-$ and $[MnH(CO)_5]$. The ejection of saturated fragments from parent ions is a feature of cluster decomposition and has been commented on previously.[1–4,7] In the positive-ion mode, peaks corresponding to the series of compounds $[Mn_nH_n(CO)_{4n}]^+$, $[Mn_nH_n(CO)_{4n+1}]^+$, and $[Mn_nH_n(CO)_{4n+2}]^+$ are also found (see Table 2). Opening of the ring by breaking a metal–metal bond, allowing co-ordination of an extra CO, is a phenomenon observed for $[Ru_3(CO)_{12}]$; that is, a peak appears in the positive-ion mode corresponding to $[Ru_3(CO)_{13}]^+$ and is assigned to a linear (or bent) structure.[4] Similarly, breaking the ring structure by the scission of one M–M bond forms a linear structure with an additional CO attached. What is novel about the $[Mn_nH_n$-

Table 1 Peak maxima (m/z) for principal envelopes observed in the negative ion UV laser desorption mass spectra of $[M_3H_3(CO)_{12}]$ where M = Mn or Re

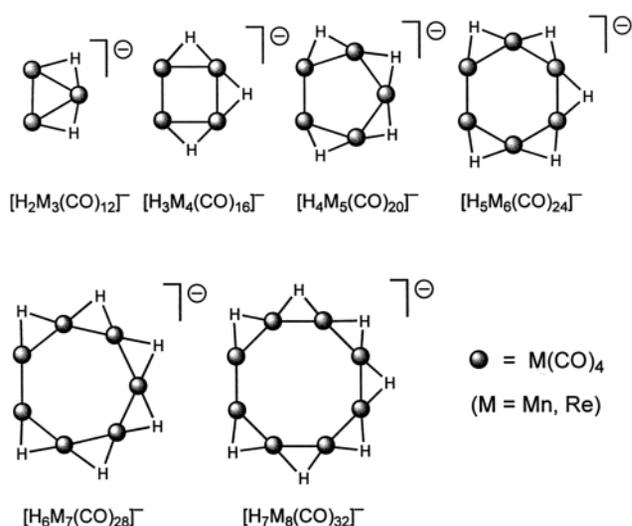|	Manganese			Rhenium		
Formula of ion	Obs.	Calc.	Intensity (%)	Obs.	Calc.	Intensity (%)
$[M_2H(CO)_6]^-$	279.0	278.9	20	541.9	541.5	2
$[M_2H(CO)_7]^-$	306.7	306.9	52	—	—	—
$[M_3H_2(CO)_8]^-$	391.1	390.8	32	—	—	—
$[M_3H_2(CO)_9]^-$	418.5	418.8	84	812.6	812.6	47
$[M_3H_2(CO)_{10}]^-$	446.9	446.8	3	840.7	840.6	100
$[M_3H_2(CO)_{11}]^-$	474.3	474.8	2	868.1	868.6	22
$[M_3H_2(CO)_{12}]^-$	502.8	502.8	4	896.1	896.6	3
$[M_4H_3(CO)_{11}]^-$	530.1	530.8	23	—	—	—
$[M_4H_3(CO)_{12}]^-$	558.8	558.8	80	1084.1	1085.8	4
$[M_4H_3(CO)_{13}]^-$	586.4	586.8	16	1111.8	1111.8	27
$[M_4H_3(CO)_{14}]^-$	614.0	614.8	4	1140.4	1139.8	14
$[M_4H_3(CO)_{15}]^-$	641.6	642.8	9	1167.4	1167.8	3
$[M_4H_3(CO)_{16}]^-$	670.7	670.8	7	1195.4	1195.8	1
$[M_5H_4(CO)_{14}]^-$	—	—	—	1327.4	1327.0	2
$[M_5H_4(CO)_{15}]^-$	698.2	698.7	1	1355.4	1355.0	20
$[M_5H_4(CO)_{16}]^-$	726.2	726.7	6	1384.0	1384.0	6
$[M_5H_4(CO)_{17}]^-$	754.2	754.7	33	1411.0	1411.0	2
$[M_5H_4(CO)_{18}]^-$	782.2	782.7	100	1439.0	1439.0	3
$[M_5H_4(CO)_{19}]^-$	810.2	810.7	11	1467.0	1467.0	1
$[M_5H_4(CO)_{20}]^-$	838.2	838.7	3	1495.0	1495.0	1
$[M_6H_5(CO)_{17}]^-$	—	—	—	1598.4	1598.2	2
$[M_6H_5(CO)_{18}]^-$	—	—	—	1626.2	1626.2	3
$[M_6H_5(CO)_{19}]^-$	866.2	866.6	5	—	—	—
$[M_6H_5(CO)_{20}]^-$	894.2	894.6	10	—	—	—
$[M_6H_5(CO)_{21}]^-$	922.2	922.6	8	—	—	—
$[M_6H_5(CO)_{22}]^-$	950.5	950.6	15	—	—	—
$[M_6H_5(CO)_{23}]^-$	978.4	978.6	36	1766.2	1766.2	1
$[M_6H_5(CO)_{24}]^-$	1006.2	1006.6	55	1794.6	1794.2	1
$[M_7H_6(CO)_{23}]^-$	1034.5	1034.6	5	—	—	—
$[M_7H_6(CO)_{24}]^-$	1062.5	1062.6	3	—	—	—
$[M_7H_6(CO)_{25}]^-$	1090.5	1090.6	3	—	—	—
$[M_7H_6(CO)_{26}]^-$	1118.5	1118.6	4	—	—	—
$[M_7H_6(CO)_{27}]^-$	1146.5	1146.6	7	—	—	—
$[M_7H_6(CO)_{28}]^-$	1174.5	1174.6	12	—	—	—
$[M_8H_7(CO)_{27}]^-$	1202.3	1202.5	12	—	—	—
$[M_8H_7(CO)_{28}]^-$	1230.3	1230.5	18	—	—	—
$[M_8H_7(CO)_{29}]^-$	1258.3	1258.5	3	—	—	—
$[M_8H_7(CO)_{30}]^-$	1286.3	1286.5	2	—	—	—
$[M_8H_7(CO)_{31}]^-$	1314.3	1314.5	3	—	—	—
$[M_8H_7(CO)_{32}]^-$	1342.3	1342.5	4	—	—	—
$[M_9H_8(CO)_{31}]^-$	1370.3	1370.4	3	—	—	—
$[M_9H_8(CO)_{32}]^-$	1398.3	1398.4	6	—	—	—
$[M_9H_8(CO)_{33}]^-$	1426.3	1426.4	6	—	—	—
$[M_9H_8(CO)_{34}]^-$	1454.3	1454.4	5	—	—	—
$[M_9H_8(CO)_{35}]^-$	1482.3	1482.4	3	—	—	—
$[M_9H_8(CO)_{36}]^-$	1510.3	1510.4	1	—	—	—

$(CO)_{4n}]$ system is that a further CO attaches and this can only be ascribed to the breaking of a further M–M bond without dissociation of a metal center. In the compound $[Re_2(\mu\text{-}H)_2(CO)_8]$, which from electron counting rules formally has a M=M double bond, MO calculations have found no direct M–M bond leading to the suggestion that it is bonded exclusively through hydrogen bridges.[14] In order to account for the addition of this CO the metal to which it attaches may be bonded through a pair of hydride bridges and not by M–M bonding. Alternatively, the interaction can be viewed as a dative donor–acceptor bond, such interactions having been characterised in related systems.[15] The situation for Re is essentially analogous though the maximum ring size extends only to six in both positive and negative ion modes.

In this work we believe that we have observed the formation of a range of species $[MH(CO)_4]_n$ ($n = 3$–10), which have cyclic structures related to their organic counterparts. These species are unusually stable, since ejection of CO ultimately to form *closo*-polyhedral species (*e.g.* tetrahedral, trigonal bipyramidal) does not appear to occur. The mechanism by which the new species are produced is unknown but we speculate that it might occur by the successive insertion of a $[MH(CO)_4]$ fragment into an existing M–M bond. One can only postulate the precise structures of these fascinating species, but given the molecular structure established for $[Re_5H_5(CO)_{20}]$ by single crystal X-ray analysis[10] we believe the cyclic structures shown in Fig. 3, in which the M–M bond(s) are supported by μ-H bridges, are not unreasonable. Significantly, in each structure each metal atom satisfies the 18 electron rule. Other structures (spiked rings, for example) may be proposed which fulfil the electronic requirements. However, spiked arrangements are generally less stable.

Table 2 Peak maxima (m/z) for principal envelopes observed in the positive ion UV laser desorption mass spectrum of $[M_3H_3(CO)_{12}]$ where M = Mn or Re

	Manganese			Rhenium		
Formula of ion	Obs.	Calc.	Intensity (%)	Obs.	Calc.	Intensity (%)
$[M_2H_2(CO)_7]^+$	307.5	307.9	2	—	—	—
$[M_2H_2(CO)_8]^+$	335.2	335.9	3	598.4	598.4	3
$[M_2H_2(CO)_9]^+$	363.8	363.9	84	626.4	626.4	100
$[M_2H_2(CO)_{10}]^+$	391.7	391.9	24	653.3	654.4	33
$[M_3H_3(CO)_{11}]^+$	475.9	475.9	4	869.5	869.6	2
$[M_3H_3(CO)_{12}]^+$	503.1	503.9	68	897.6	897.6	25
$[M_3H_3(CO)_{13}]^+$	532.3	531.9	100	925.8	925.6	82
$[M_3H_3(CO)_{14}]^+$	560.0	559.9	47	953.6	953.6	33
$[M_4H_4(CO)_{16}]^+$	672.3	671.9	2	1196.8	1196.8	2
$[M_4H_4(CO)_{17}]^+$	699.5	699.9	17	1224.8	1224.8	5
$[M_4H_4(CO)_{18}]^+$	727.6	727.9	26	1253.2	1252.8	24
$[M_5H_5(CO)_{20}]^+$	840.4	839.9	3	—	—	—
$[M_5H_5(CO)_{21}]^+$	867.2	867.9	6	—	—	—
$[M_5H_5(CO)_{22}]^+$	895.9	895.9	14	1556.2	1556.2	9
$[M_6H_6(CO)_{25}]^+$	1035.4	1035.9	2	—	—	—
$[M_6H_6(CO)_{26}]^+$	1064.1	1063.9	4	1851.1	1851.2	3
$[M_7H_7(CO)_{29}]^+$	1203.7	1203.9	2	—	—	—

$$[M_3H_2(CO)_{12}]^- + [MH(CO)_4] \longrightarrow [M_4H_3(CO)_{16}]^- \quad (3)$$

$$[M_4H_3(CO)_{16}]^- + [MH(CO)_4] \longrightarrow [M_5H_4(CO)_{20}]^- \quad (4)$$

$$[M_5H_4(CO)_{20}]^- + [MH(CO)_4] \longrightarrow [M_6H_5(CO)_{24}]^- \quad (5)$$

compounds for Fe, Ru and Os based on the molecular formula $[M(CO)_4]_n$ is known, and in this case two members have been recorded *viz.* the triangular clusters $[M_3(CO)_{12}]$ (M = Fe, Ru or Os) and the rectangular cluster $[Os_4(CO)_{16}]$.[16] The fundamental difference between these two proposed series, one based on $[M(CO)_4]_n$ and the other on $[MH(CO)_4]_n$, lies in the presence of the bridging hydride ligand.

Experimental

Acknowledgements
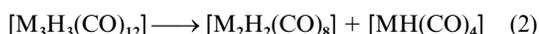
Fig. 3 Proposed structures for the species $[Mn_nH_{n-1}(CO)_{4n}]^-$ ($n = 3–8$).

Conclusion
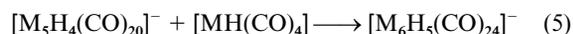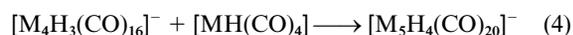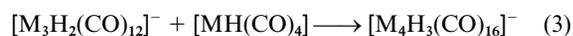
In these experiments we have been able to demonstrate that the compounds $[Mn_3H_3(CO)_{12}]$ **1** and $[Re_3H_3(CO)_{12}]$ **2** undergo extensive polymerisation reactions on irradiation to produce a range of species based on the formula $[MH(CO)_4]_n$. The nature of the reaction which leads to their formation has not been established but we believe that the 'key' step may be the formation of the highly active fragment $[MH(CO)_4]$ from the fragmentation of the parent. We tend to believe that the initial step involves the production of the neutral saturated monomer $[MH(CO)_5]$ according to eqn. (1) followed by CO loss, although

$$[M_3H_3(CO)_{12}] \longrightarrow [M_2H(CO)_7]^- + [MH(CO)_5] + H^+ \quad (1)$$

the alternative, eqn. (2) cannot be excluded. Successive addition

$$[M_3H_3(CO)_{12}] \longrightarrow [M_2H_2(CO)_8] + [MH(CO)_4] \quad (2)$$

of this fragment to the parent may then be considered to occur, eqns. (3)–(5), *etc.* It is interesting that a similar series of

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