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Edge-Bridging and Face-Bridging Hydrogen Atoms in Trinuclear Rhenium Carbonyl Hydrides

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The structures of the trinuclear rhenium carbonyl hydrides $H_3Re_3(CO)_n$ (n = 12, 11, 10, 9) have been investigated by density functional theory (DFT). The only structure found for $H_3Re_3(CO)_{12}$ is the experimentally known structure with each approximately 3.3 Å edge of a singly bonded Re_3 triangle bridged by a hydrogen atom and all terminal carbonyl groups. The two lowest energy $H_3Re_3(CO)_{11}$ structures lie within 0.5 kcal/mol in energy and are derived from this $H_3Re_3(CO)_{12}$ structure by loss of a carbonyl group with retention of the central $Re_3(\mu\text{-}H)_3$ core. A higher energy $H_3Re_3(CO)_{11}$ structure, closely related to the experimental structure for the isoelectronic dianion $H_3Re_3(CO)_{10}{}^{2-}$, is also found in which one of the Re=Re edges of double bond length (2.79 Å) is bridged by two hydrogen atoms. Loss of a carbonyl group from this $H_3Re_3(CO)_{11}$ structure with concurrent conversion of one of the edge-bridging hydrogen atoms to a face-bridging hydrogen atom gives the lowest energy $H_3Re_3(CO)_{10}$ structure. Further loss of a carbonyl group from this $(\mu_3\text{-}H)(\mu\text{-}H)_2Re_3(CO)_{10}$ structure with concurrent conversion of a second edge-bridging hydrogen atom to a face-bridging hydrogen atom leads to the lowest energy $H_3Re_3(CO)_9$ structure. This $(\mu_3\text{-}H)_2(\mu\text{-}H)Re_3(CO)_9$ structure with a central $Re_3(\mu_3\text{-}H)_2$ trigonal bipyramid appears to be a very favorable structure since it not only is the lowest energy $H_3Re_3(CO)_9$ structure but lies more than 22 kcal/mol below the next lowest energy $H_3Re_3(CO)_9$ structure.

Introduction

Metal carbonyl hydride chemistry dates back to the discovery of $H_2Fe(CO)_4$ and $HCo(CO)_4$ by Hieber and Blanchard in the 1930s.[1] These original metal carbonyl hydrides are only stable in the dilute gas phase, preferably in the presence of carbon monoxide. The much more stable metal carbonyl hydrides $HM(CO)_5$ (M = Mn, Re) were synthesized in the 1950s after the required homoleptic binuclear metal carbonyl starting materials $M_2(CO)_{10}$ became available. Thus, the reduction of $M_2(CO)_{10}$ with sodium amalgam to the corresponding anions $M(CO)_5{}^-$ followed by acidification with phosphoric acid provided a good route to the syntheses of the corresponding metal pentacarbonyl hydrides $HM(CO)_5$ (M = Mn,[2] Re[3]).

The chemistry of technetium has lagged behind that of its congeners manganese and rhenium since it is radioactive and not found in nature. In the 1960s, however, technetium as ammonium pertechnetate became readily available from nuclear fission products. Furthermore its radioactivity was modest ($t_{1/2} = 2.1 \times 10^5$ years) so that it could be handled in a conventional chemical laboratory with suitable precautions. This improved availability of technetium stimulated a study of its organometallic chemistry. This led to the discovery by Kaesz and co-workers of $Tc_2(CO)_{10}$, made by a high-pressure reaction of TcO_2 with carbon monoxide.[4]

Attempts to convert $Tc_2(CO)_{10}$ into $HTc(CO)_5$ using methods analogous to those outlined for manganese and rhenium above led to a surprise. Namely, the reaction of $Tc_2(CO)_{10}$ with sodium amalgam in THF followed by acidification with phosphoric acid gave only trace quantities of the volatile, rather unstable $HTc(CO)_5$, which was identified by its infrared spectrum.[5] This instability of $HTc(CO)_5$ contrasted with the much greater stability of $HMn(CO)_5$ and $HRe(CO)_5$. The major product from the attempted synthesis of $HTc(CO)_5$ was a less-volatile technetium carbonyl derivative, not identified in the original work. This observation stimulated a similar experiment with the rhenium carbonyl hydride system.[6] Because of the greater stability of the rhenium derivatives, it was necessary to heat the $HRe(CO)_5$ mixture to obtain this polynuclear rhenium carbonyl derivative, which turned out to be the trinuclear hydride $H_3Re_3(CO)_{12}$. The yields of $H_3Re_3(CO)_{12}$ from the pyrolysis of this $HRe(CO)_5$ mixture were, however, rather low. Better yields of $H_3Re_3(CO)_{12}$ were obtained by Kaesz and co-workers from the reaction of $Re_2(CO)_{10}$ with $NaBH_4$ in THF followed by acidification with phosphoric acid.[6] Later an improved synthesis of $H_3Re_3(CO)_{12}$ was discovered using the direct reaction of $Re_2(CO)_{10}$ with hydrogen gas at elevated temperatures.[7] Eventually the tech-

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netium derivative $H_3Tc_3(CO)_{12}$ was synthesized by an improved method and characterized structurally.[8] In addition, the manganese analogue $H_3Mn_3(CO)_{12}$ was synthesized by Johnson and Lewis by the reaction of $Mn_2(CO)_{10}$ with a base followed by acidification.[9,10]

The trinuclear metal carbonyl hydrides $H_3M_3(CO)_{12}$ (M = Mn, Tc, Re) form a series of stable compounds that are isoelectronic with the homoleptic trinuclear metal carbonyls $M'_3(CO)_{12}$ (M = Fe, Ru, Os), all of which are also stable compounds. The structures of the homoleptic trinuclear metal carbonyls are of interest since $Fe_3(CO)_{12}$ has a doubly bridged structure (Dahl[11]and Cotton[12]), whereas $M_3(CO)_{12}$ (M = Ru,[13] Os,[14,15]) have unbridged structures (Figure 1). All three trinuclear hydrides $H_3M_3(CO)_{12}$ (M = Mn, Tc, Re) have analogous structures in which each edge of the M_3 triangle is bridged by a hydrogen atom with all 12 carbonyl groups as terminal ligands (Figure 2).

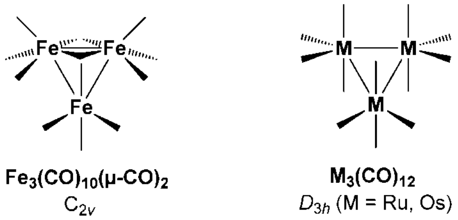


Figure 1. Structures of $M_3(CO)_{12}$ (M = Fe, Ru, Os). Carbonyl groups have been omitted for the sake of clarity.

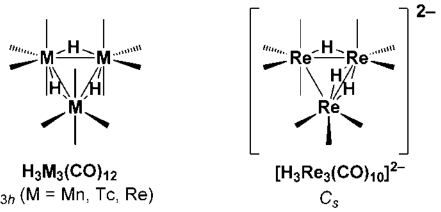


Figure 2. Structures of $H_3M_3(CO)_{12}$ (M = Mn, Tc, Re) and $[H_3Re_3(CO)_{10}]^{2-}$. Carbonyl groups have been omitted for clarity.

A potentially interesting area of chemistry that has not apparently been investigated is the decarbonylation of $H_3Re_3(CO)_{12}$ to give the unsaturated $H_3Re_3(CO)_n$ (n = 11, 10, 9). None of these unsaturated derivatives have been synthesized as a neutral compound, however, the trirhenium decacarbonyl trihydride dianion $H_3Re_3(CO)_{10}{}^{2-}$ has been synthesized as its tetraethylammonium salt by the degradation of the tetranuclear anion $H_4Re_4(CO)_{15}{}^{2-}$ according to the following reaction:[16]

$$H_4Re_4(CO)_{15}{}^{2-} \rightarrow H_3Re_3(CO)_{10}{}^{2-} + HRe(CO)_5$$

This dianion has an interesting unsymmetrical structure in which one of the edges of the Re_3 triangle is bridged by two hydrogen atoms, a second edge is bridged by a single hydrogen atom, and the third edge is unbridged (Figure 2). This dianion has been shown by temperature-dependent magnetization transfer ^{13}C NMR spectroscopic experiments to have interesting fluxional properties.[17]

We now report the systematic theoretical studies of $H_3Re_3(CO)_n$ (n = 12, 11, 10, 9). All of the lowest energy structures were found to have intact bonded Re_3 triangles. Structures were found with the Re–Re edges of these triangles bridged by either one or two hydrogen atoms as well as structures with hydrogen atoms bridging the entire Re_3 triangle. The lowest energy $H_3Re_3(CO)_9$ structure with a central $Re_3(\mu_3\text{-}H)_2$ trigonal bipyramid is of particular interest. Related structures exist for $H_3Mn_3(CO)_n$ (n = 12, 11, 10, 9),[18] however, the rhenium analogues are found experimentally to be significantly more stable.

The analogous technetium derivatives are not included in this theoretical study. Since the pioneering experimental work of Kaesz and co-workers on technetium carbonyls approximately 50 years ago,[4–7] regulations on handling the radioactive technetium in the laboratory in quantities suitable for synthetic work have become much more stringent in most countries. Therefore, the early work on technetium carbonyls is not likely to be repeated and extended to the technetium analogues of the rhenium compounds discussed in this paper.

Theoretical Methods

Density functional theoretical (DFT) methods have been employed as a practical and effective computational tool, especially for organometallic complexes.[19–23] In this study, all of the computations were carried out with two selected DFT methods implemented in the Gaussian 03 program suite.[24] The first method is the pure DFT method known as BP86, which combines Becke's 1988 exchange functional with Perdew's 1986 correlation functional.[25,26] The second method is the MPW1PW91 method,[27] a so-called second generation functional[28] based on the generalized gradient approximation (GGA) that combines the modified Perdew–Wang exchange functional with the Perdew–Wang 91 gradient-correlation functional.[29] The BP86 method has been shown to be reliable for first-row transition metal organometallic systems.[30,31] The MPW1PW91 method has been found to be more suitable for geometry optimization of the second- and third-row transition-metal systems.[32,33] Normally the BP86 method provides vibrational frequencies, particularly ν(CO) frequencies, that are closer to experimental values.

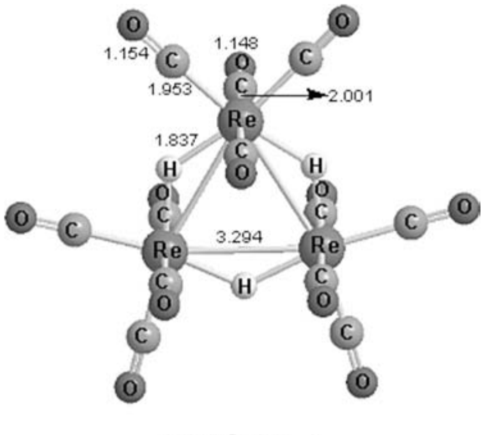
The two basis sets used here are the SDD basis set for the Re atom, and the double-ζ plus polarization (DZP) basis sets for the other (C, O, and H) atoms. The SDD basis sets combine DZ and Stuttgart–Dresden ECP (relativistic effective core potential) basis sets.[34] This can reduce the cost caused by the large numbers of electrons of the second-row transition metals. The DZP basis sets for C and O are Huzinaga–Dunning's contracted double-ζ contraction sets,[35,36] plus a set of spherical harmonic d polarization functions with orbital exponents $a_d(C) = 0.75$ and $a_d(O) = 0.85$ designated as (9s5p1d/4s2p1d). For hydrogen, a set of p polarization functions are used with $a_p(H) = 0.75$. For the trinuclear rhenium carbonyl hydride derivatives $H_3Re_3(CO)_{12}$, $H_3Re_3(CO)_{11}$, $H_3Re_3(CO)_{10}$, and $H_3Re_3(CO)_9$, there are 483, 453, 423, and 393 contracted Gaussian basis functions, respectively.

Structures are designated by **a-nS/T**, where **a** is the number of carbonyl groups, **n** orders the structures according to their relative energies for the same state by the MPW1PW91 method, and **S** or **T** designate singlet and triplet states, respectively. Thus the lowest lying singlet structure of $H_3Re_3(CO)_{10}$ is designated as **10-1S**. For comparison with the Re–Re distances found in the $H_3Re_3(CO)_n$ structures discussed in this paper, the typical lengths of formal Re–Re single bonds, Re=Re double bonds, Re≡Re triple bonds, and Re≣Re quadruple bonds are 3.04 Å in $Re_2(CO)_{10}$,[37] 2.72 Å in $(\eta^5\text{-}Me_5C_5)_2Re_2(CO)_4$,[38] 2.41 Å in $(\eta^5\text{-}Me_5C_5)_2Re_2(\mu\text{-}CO)_3$,[39] and 2.24 Å in $K_2Re_2Cl_8$,[40] respectively, all determined experimentally by X-ray crystallography.

Results

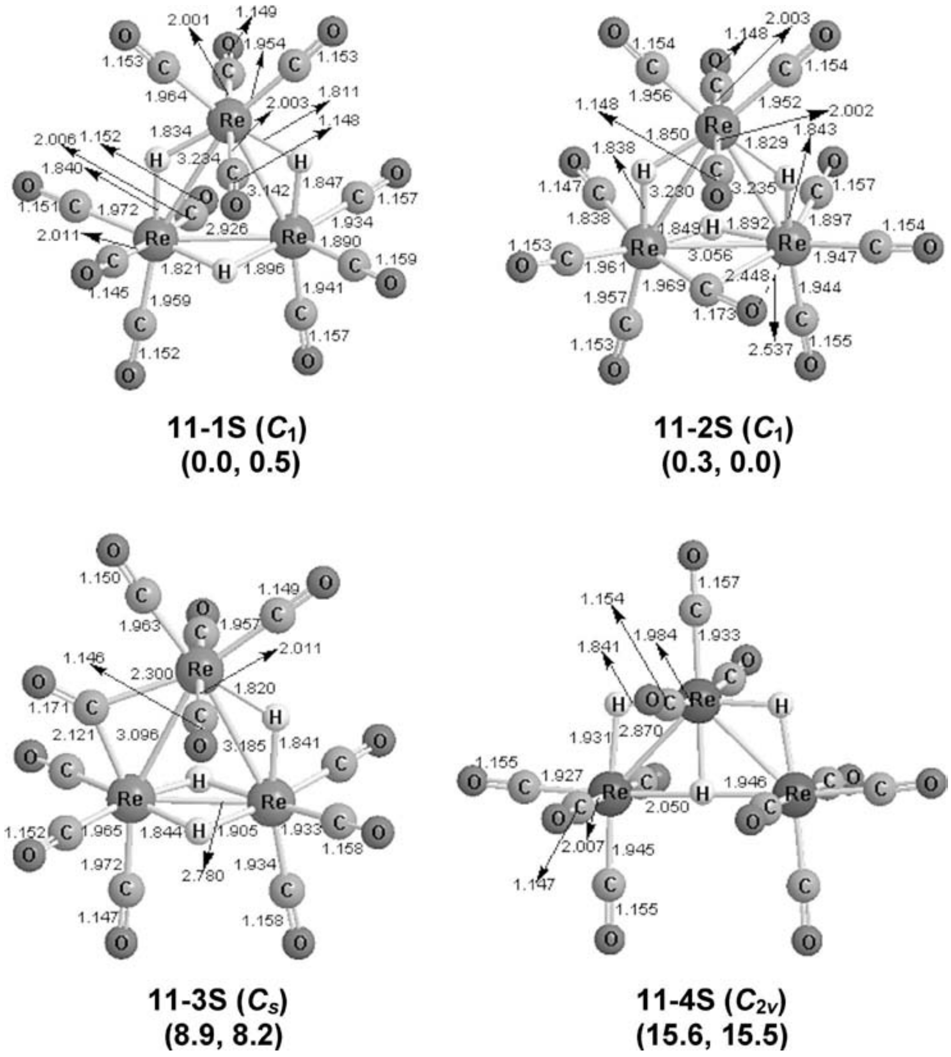
$H_3Re_3(CO)_{12}$

The only $H_3Re_3(CO)_{12}$ structure found in this work is the D_{3h} structure **12-1S** (Figure 3, Tables S19 and S23). This structure is a genuine minimum without any imaginary vibrational frequencies. In the D_{3h} structure, all twelve CO



12-1S (D_{3h})

Figure 3. Optimized structure of $H_3Re_3(CO)_{12}$. The bond lengths [Å] given are those determined by the MPW1PW91 method.



11-1S (C_1)
(0.0, 0.5)

11-2S (C_1)
(0.3, 0.0)

11-3S (C_s)
(8.9, 8.2)

11-4S (C_{2v})
(15.6, 15.5)

Figure 4. Optimized geometries of the four $H_3Re_3(CO)_{11}$ structures by MPW1PW91. The numbers in parentheses are the relative energies (ΔE in kcal/mol) predicted by the MPW1PW91 and BP86 methods. The bond lengths [Å] given are those determined by the MPW1PW91 method.

groups are terminal carbonyl groups just like the known[41] $H_3Mn_3(CO)_{12}$. The edge lengths of the central Re_3 triangle are 3.294 Å (MPW1PW91) or 3.335 Å (BP86) and each edge is bridged by a hydrogen atom. These predicted Re–Re distances in $H_3Re_3(CO)_{12}$ are close to the reported experimental Re–Re distances of 3.285 Å, determined by extended X-ray absorption fine structure spectroscopy (EXAFS),[42] as well as the Re–Re distances of 3.241(2) Å, determined by X-ray crystallography.[43] Each of the rhenium atoms in structure **12-1S** has the favored 18-electron configuration. The twelve predicted ν(CO) frequencies for the terminal CO groups in **12-1S** range from 1971 to 2100 cm^{-1} with predicted infrared active bands at 1984, 2003, 2013, and 2072 cm^{-1} by the BP86 method (Table S19). These predicted ν(CO) frequencies are close to the experimental medium-to-strong intensity ν(CO) frequencies of 1983, 2008, 2030, 2083, and 2093 cm^{-1} for $H_3Re_3(CO)_{12}$ in cyclohexane solution.[6] Three ν(ReH) frequencies are found around 1700 cm^{-1} in addition to three ν(ReH) frequencies ranging from 1102 to 995 cm^{-1}.

$H_3Re_3(CO)_{11}$

Four singlet structures were obtained for the unsaturated $H_3Re_3(CO)_{11}$ within 30 kcal/mol of the global minimum (Figure 4, Tables S20 and S24). The triplet $H_3Re_3(CO)_{11}$ structures were found to lie more than 30 kcal/mol higher and are of limited chemical significance; they are therefore not discussed here. The global minimum $H_3Re_3(CO)_{11}$ structure is either **11-1S** or **11-2S**, depending on the DFT method. Whereas structure **11-2S** is geometrically similar to the global minimum for $H_3Mn_3(CO)_{11}$ (**311-1** in ref.[18]), structure **11-1S** is similar to a high-energy structure for $H_3Mn_3(CO)_{11}$ (**311-4** in ref.[18]). Nevertheless, these two $H_3Re_3(CO)_{11}$ structures are degenerate in energy within 0.5 kcal/mol. Structure **11-1S** (C_1 symmetry) can be derived from the saturated **12-1S** by removing a carbonyl group. The three hydrogen atoms remain in the edge-bridging positions. The Re–Re bond lengths in **11-1S** are 3.234, 3.142, and 2.926 Å (MPW1PW91) or 3.267, 3.173, and 2.932 Å (BP86), respectively. The two longer Re–Re bonds (ca. 3.1 Å) correspond to formal single bonds, whereas the shorter Re=Re bond (ca. 2.9 Å) corresponds to a formal double bond. Thus all three Re atoms have the favorable 18 electron configurations. The predicted ν(CO) frequencies of the eleven terminal carbonyls in **11-1S** range from 1955 to 2090 cm^{-1} and the ν(ReH) frequencies range from 1677 to 1092 cm^{-1}.

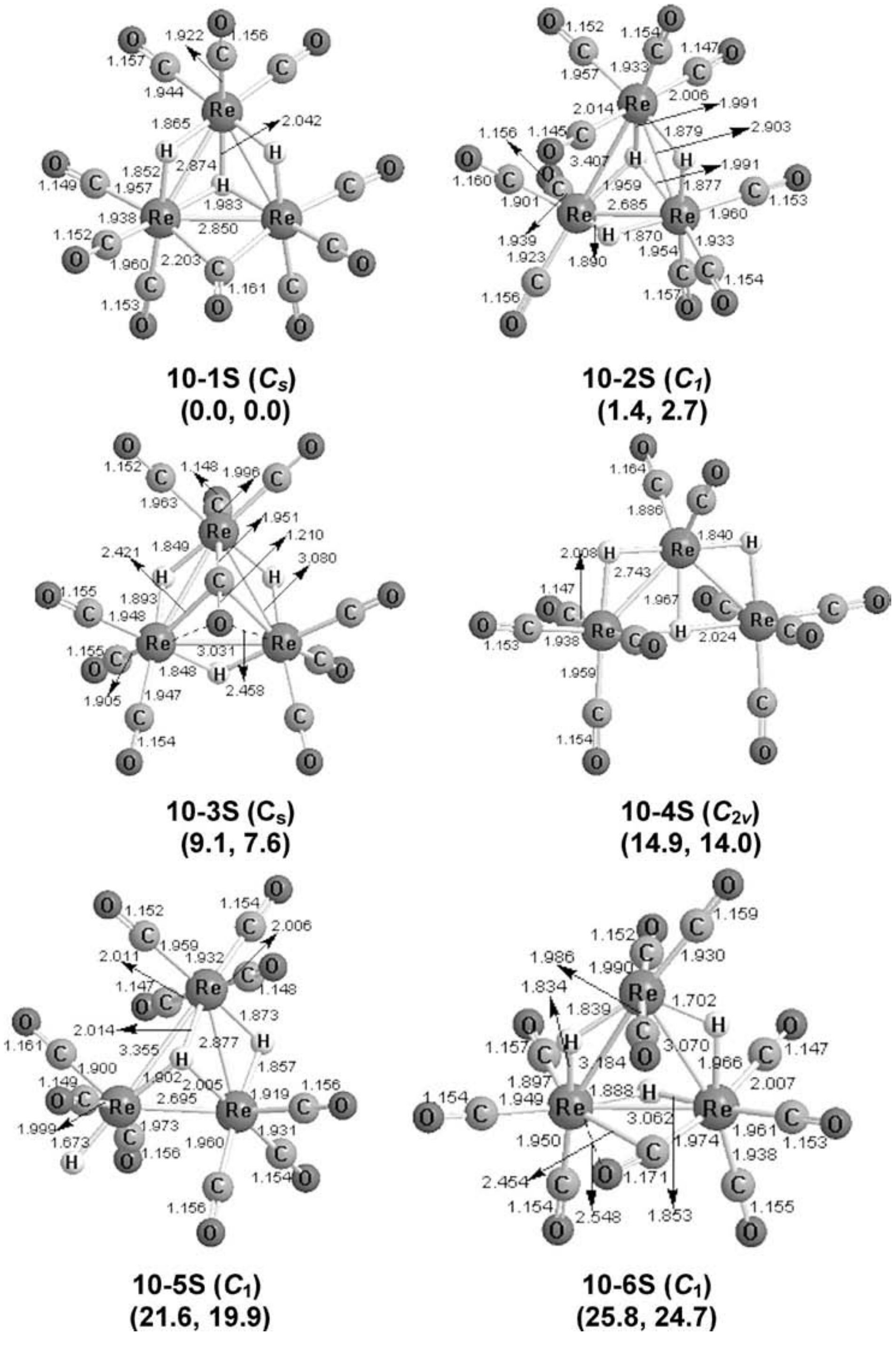
The $H_3Re_3(CO)_{11}$ structure **11-2S** with C_1 symmetry has a four-electron donating η^2-μ-CO bridging carbonyl group, as indicated by a short Re–O distance of 2.537 Å (MPW1PW91) or 2.535 Å (BP86) to the carbonyl group (Figure 4, Tables S20 and S24). The three Re–Re bond lengths are 3.235, 3.230, and 3.056 Å (MPW1PW91) or 3.275, 3.266, and 3.077 Å (BP86), which are all single bonds. The shortest of these single bonds is the one bridged by both the η^2-μ-CO group and the hydrogen atom. This gives all three Re atoms in **11-2S** the favored 18-electron configuration, after considering the four-electron donor bridging carbonyl group. One of the ν(CO) frequencies of **11-2S** is rather low, namely 1833 cm^{-1} (Table S20). This corresponds to the four-electron donating η^2-μ-CO bridging carbonyl group. The other ν(CO) frequencies, in the range 1966 to 2088 cm^{-1}, correspond to the 10 terminal carbonyl groups in **11-2S**. The ν(ReH) frequencies in **11-2S** range from 1108 to 1712 cm^{-1} (Table S20).

The $H_3Re_3(CO)_{11}$ structure **11-3S** (C_s symmetry) lies 8.9 kcal/mol (MPW1PW91) or 8.2 kcal/mol (BP86) in energy above **11-1S** (Figure 4, Tables S20 and S24). Structure **11-3S** has one bridging carbonyl group and three bridging hydrogen atoms, however, two of these hydrogen atoms bridge the same Re–Re bond. The edge lengths of the Re_3 triangle in **11-3S** are 3.185, 3.096, and 2.780 Å (MPW1PW91) or 3.225, 3.148, and 2.797 Å (BP86), with the shortest edge being the one bridged by the two hydrogen atoms. This predicted diprotonated Re=Re edge length of approximately 2.79 Å in the $H_3Re_3(CO)_{11}$ structure **11-3S** is essentially identical to the experimental diprotonated Re–Re edge length of 2.797(4) Å in the isoelectronic structure $H_3Re_3(CO)_{10}{}^{2-}$, determined by X-ray crystallography.[16] This short Re=Re edge length can be considered to correspond to a diprotonated double bond. The predicted bridging ν(CO) frequency in **11-3S** is 1844 cm^{-1}, whereas the other ν(CO) frequencies range from 1954 to 2096 cm^{-1}. The ν(ReH) frequencies range from 1654 to 1130 cm^{-1} (Table S20).

The fourth singlet $H_3Re_3(CO)_{11}$ structure **11-4S** is a C_{2v} structure lying 15.6 kcal/mol (MPW1PW91) or 15.5 kcal/mol (BP86) above **11-1S**. Structure **11-4S** has two edge-bridging hydrogen atoms as well as one hydrogen atom bridging all three rhenium atoms. A similar higher energy $H_3Mn_3(CO)_{11}$ structure was also found in the previous work.[18] One of the Re···Re distances in **11-4S** is very long at 4.099 Å (MPW1PW91) or 4.175 Å (BP86), indicating the absence of direct bonding between these two Re atoms. The other two Re–Re distances are 2.870 Å (MPW1PW91) or 2.892 Å (BP86), suggesting two formal Re=Re double bonds. The two Re=Re bonds in the Re_3 unit of **11-4S** combined with the presence of only two-electron donor CO groups give all three rhenium atoms the favored 18-electron configuration. The predicted ν(CO) frequencies for the eleven terminal CO groups in **11-4S** range from 1929 to 2095 cm^{-1}. The ν(ReH) frequencies range from 1497 to 990 cm^{-1}, among which the frequencies of 1195, 1171, and 990 cm^{-1} relate to the interaction of the rhenium atoms with the face-bridging hydrogen atom.

$H_3Re_3(CO)_{10}$

Six singlet $H_3Re_3(CO)_{10}$ structures (Figure 5, Tables S21 and S25) were found within 30 kcal/mol of the global minimum. Triplet $H_3Re_3(CO)_{10}$ structures were also studied but were all found to lie at least 30 kcal/mol above the global minimum and therefore are not discussed here. The



10-1S (C_s)
(0.0, 0.0)

10-2S (C_1)
(1.4, 2.7)

10-3S (C_s)
(9.1, 7.6)

10-4S (C_{2v})
(14.9, 14.0)

10-5S (C_1)
(21.6, 19.9)

10-6S (C_1)
(25.8, 24.7)

Figure 5. Six optimized singlet structures of $H_3Re_3(CO)_{10}$ by MPW1PW91. The numbers in parentheses are the relative energies (ΔE in kcal/mol) predicted by the MPW1PW91 and BP86 methods. The bond lengths [Å] given are those determined by the MPW1PW91 method.

$H_3Re_3(CO)_{10}$ global minimum **10-1S** is predicted to have C_s symmetry and to be geometrically similar to the global minimum for the analogous $H_3Mn_3(CO)_{10}$ (ref.[18]). Structure **10-1S** has one bridging carbonyl group and nine terminal CO groups. There are two edge-bridging hydrogen atoms as well as one hydrogen atom bridging the entire Re_3 triangle. In contrast to the low symmetry of the analogous $H_3Mn_3(CO)_{10}$ (an Mn_3 scalene triangle with predicted divergent edge lengths of 2.384, 2.704, and 3.304 Å), the Re–Re triangle in **10-1S** is nearly equilateral with Re–Re distances of 2.874, 2.874, and 2.850 Å (MPW1PW91) or 2.898, 2.898, and 2.883 Å (BP86). This suggests delocalized multiple Re–Re bonding in the Re_3 triangle of **10-1S** in contrast to localized bonding in the Mn_3 triangle of the otherwise analogous $H_3Mn_3(CO)_{10}$ structure. The predicted vibrational frequency for the bridging CO group in **10-1S** is

1886 cm^{-1}, whereas the remaining ν(CO) frequencies corresponding to the terminal CO groups range from 1958 to 2075 cm^{-1} (Table S21). The seven ν(ReH) frequencies of **10-1S** range from 1437 to 929 cm^{-1} (Table S21), among which the 1136, 1009, and 929 cm^{-1} frequencies correspond to Re–H interactions to the face-bridging hydrogen atom.

The next energetically low-lying singlet $H_3Re_3(CO)_{10}$ structure is the C_1 structure **10-2S**, lying only 1.4 kcal/mol (MPW1PW91) or 2.7 kcal/mol (BP86) above **10-1S** (Figure 5, Tables S21 and S25). Structure **10-2S**, like structure **10-1S**, has one hydrogen atom capping the Re_3 triangle. However, structure **10-2S**, unlike structure **10-1S**, has no bridging carbonyl group. The Re_3 triangle in **10-2S** is a scalene triangle similar to the Mn_3 triangle in the lowest energy $H_3Mn_3(CO)_{10}$ structure[18] with Re–Re distances of 2.685, 2.903, and 3.407 Å (MPW1PW91) or 2.706, 2.934, and 3.445 Å (BP86). Considering the two short Re=Re bonds (< 3.0 Å) as formal double bonds and the long Re–Re bond as a formal single bond leads to the favored 18-electron configuration for each Re atom. The predicted ν(CO) frequencies for CO groups in **10-2S**, all of which are terminal, fall in the range from 1948 to 2090 cm^{-1}. The predicted ν(ReH) frequencies for **10-2S** range from 858 to 1443 cm^{-1}, in which the 858, 1046, and 1443 cm^{-1} frequencies correspond to the Re–H interactions with the face-bridging hydrogen atom.

The $H_3Re_3(CO)_{10}$ structure **10-3S** (C_s symmetry) lies 9.1 kcal/mol (MPW1PW91) or 7.6 kcal/mol (BP86) above **10-1S** (Figure 5, Tables S21 and S25). Structure **10-3S** has one six-electron donating η^2-μ_3-CO carbonyl group bridging all three Re atoms, similar to structure **311-2** for $H_3Mn_3(CO)_{10}$ (ref.[18]). This unique carbonyl group in **10-3S** is similar to the six-electron donating η^2-μ_3-CO bridging carbonyl group found by X-ray crystallography in the trinuclear niobium derivative $(\eta^5\text{-}C_5H_5)_3Nb_3(CO)_6(\eta^2\text{-}\mu_3\text{-}CO)$.[44] This unusual six-electron donating η^2-μ_3-CO group in **10-3S** exhibits a very low ν(CO) frequency at 1617 cm^{-1}. The Re–Re distances in **10-3S** range from 3.03 to 3.08 Å (MPW1PW91) or 3.06 to 3.11 Å (BP86), corresponding to formal single bonds. All three rhenium atoms in **10-3S** have the favored 18-electron configuration since one of the CO groups is a six-electron donating η^2-μ_3-CO group.

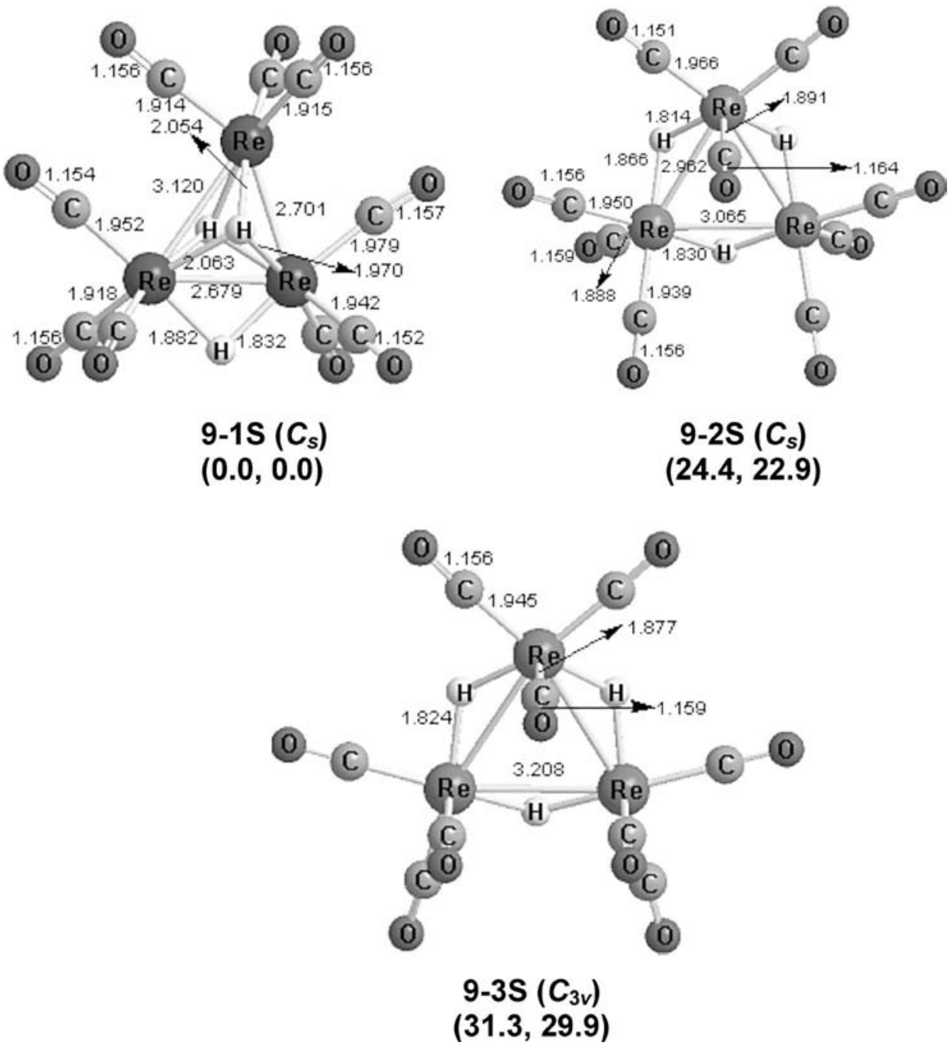
The $H_3Re_3(CO)_{10}$ structure **10-4S** (C_{2v} symmetry) lies 14.9 kcal/mol (MPW1PW91) or 14.0 kcal/mol (BP86) in energy above the global minimum **10-1S** (Figure 5, Tables S21 and S25). Structure **10-4S** has a very small imaginary vibrational frequency at 17*i* cm^{-1} predicted by the MPW1PW91 method, but all real frequencies predicted by the BP86 method. Structure **10-4S** has two edge-bridging hydrogen atoms as well as a hydrogen atom bridging all three rhenium atoms. Thus structure **10-4S** is similar to structure **310-3** for $H_3Mn_3(CO)_{10}$ in ref.[18]. One of the Re···Re distances in **10-4S** (that between the two bottom rhenium atoms in Figure 5) is very long at 4.043 Å (MPW1PW91) or 4.109 Å (BP86), implying no direct bonding interaction between these two Re atoms. The other two Re=Re distances of 2.743 Å (MPW1PW91) or 2.757 Å (BP86) correspond to formal double bonds. The predicted ν(ReH) frequencies for **10-4S** range from 1492 to 1024 cm^{-1}, among which the frequencies at 1024 and 1148 cm^{-1} correspond to the Re–H interactions involving the μ_3-H atom bridging all three rhenium atoms.

The fifth $H_3Re_3(CO)_{12}$ structure **10-5S**, lying 21.6 kcal/mol (MPW1PW91) or 19.9 kcal/mol (BP86) above **10-1S** in energy, has no symmetry and no imaginary vibrational frequencies. Structure **10-5S** has a terminal hydrogen atom, an edge-bridging μ-H hydrogen atom, and a face-bridging μ_3-H hydrogen atom. The Re_3 triangle in **10-5S** is a scalene triangle with Re–Re distances of 2.695, 2.877, and 3.355 Å (MPW1PW91) or 2.708, 2.902, and 3.403 Å (BP86). The long Re–Re distance can correspond to a formal single bond, whereas the two shorter Re=Re distances can correspond to formal double bonds leading to 18-electron configurations for the rhenium atoms. The ν(ReH) vibrational frequency of the special terminal hydrogen atom is relatively high at 2017 cm^{-1} compared with the ν(ReH) frequencies for the bridging hydrogen atoms.

The last singlet $H_3Re_3(CO)_{10}$ structure **10-6S** is a relatively high energy structure, lying 25.8 kcal/mol (MPW1PW91) or 24.7 kcal/mol (BP86) above the global minimum **10-1S** (Figure 5, Tables S21 and S25). Structure **10-6S** has a four-electron donor bridging η^2-μ-CO group characterized by a relatively low ν(CO) frequency of 1834 cm^{-1} (BP86). This $H_3Re_3(CO)_{10}$ structure **10-6S** is analogous to the $H_3Mn_3(CO)_{10}$ structure **310-5**.[18] The Re–Re distances in **10-6S** are 3.184, 3.070, and 3.062 Å (MPW1PW91) or 3.207, 3.086, and 3.077 Å (BP86), suggesting three formal single Re–Re bonds. This leads to a 16-electron configuration for one of the rhenium atoms, but the favored 18-electron configuration for the other two rhenium atoms.

$H_3Re_3(CO)_9$

Three low-lying singlet $H_3Re_3(CO)_9$ structures were found (Figure 6, Tables S22 and S26). Triplet $H_3Re_3(CO)_9$ structures were also investigated, but they all were all found to lie at least 30 kcal/mol above the global minimum, and therefore are not discussed in this paper. The $H_3Re_3(CO)_9$ global minimum **9-1S** (C_s symmetry) has one edge-bridging hydrogen atom and *two* hydrogen atoms bridging the entire Re_3 triangle. The latter form an $Re_3(\mu_3\text{-}H)_2$ trigonal bipyramid with the hydrogen atoms in the axial positions. The geometry of the $H_3Re_3(CO)_9$ structure **9-1S** is similar to that of the global minimum of $H_3Mn_3(CO)_9$ (structure **39-1** in ref.[18]). The $H_3Re_3(CO)_9$ structure **9-1S** is obviously a very favorable structure since it lies more than 22 kcal/mol below the next lowest energy $H_3Re_3(CO)_9$ structure **9-2S**. The Re–Re distances in **9-1S** are 3.120, 2.701, and 2.679 Å (MPW1PW91) or 3.141, 2.724, and 2.701 Å (BP86). The two shorter Re=Re distances of approximately 2.7 Å can correspond to formal double bonds, whereas the longer Re–Re distance of approximately 3.1 Å can correspond to a formal single bond. The predicted vibrational ν(CO) frequencies for the nine terminal CO groups range from 1953



9-1S (C_s)
(0.0, 0.0)

9-2S (C_s)
(24.4, 22.9)

9-3S (C_{3v})
(31.3, 29.9)

Figure 6. Six optimized singlet structures of $H_3Re_3(CO)_9$ by MPW1PW91. The numbers in parentheses are the relative energies (ΔE in kcal/mol) predicted by the MPW1PW91 and BP86 methods. The bond lengths [Å] given are those determined by the MPW1PW91 method.

to 2061 cm^{-1}. The ν(ReH) frequencies range from 828 to 1511 cm^{-1}, among which the 1269, 1191, 893, 883, 853, and 828 cm^{-1} correspond to the two triply bridging μ$_3$-H atoms.

The second $H_3Re_3(CO)_9$ structure **9-2S** (C_s symmetry) lies 24.4 kcal/mol (MPW1PW91) or 22.9 kcal/mol (BP86) above **9-1S** and has a very small imaginary vibrational frequency at 6*i* cm^{-1} (MPW1PW91) or 11*i* cm^{-1} (BP86). The 6*i* cm^{-1} (MPW1PW91) imaginary frequency can be removed by using a finer integration grid (120,974). Structure **9-2S** has three edge-bridging hydrogen atoms and all terminal carbonyl groups, and thus is geometrically similar to structure **39-4** of $H_3Mn_3(CO)_9$.[18] The Re_3 triangle in **9-2S** is an isosceles triangle with two Re–Re distances of 2.962 Å (MPW1PW91) or 2.981 Å (BP86) and a unique Re–Re distance of 3.065 Å (MPW1PW91) or 3.060 Å (BP86). These distances correspond to formal single bonds, giving each Re atom a 16-electron configuration. The predicted vibrational ν(CO) frequencies range from 1932 to 2052 cm^{-1}. The ν(ReH) frequencies range from 1640 to 1268 cm^{-1}.

The $H_3Re_3(CO)_9$ structure **9-3S** has a geometry very similar to **9-2S** except with the higher C_{3v} symmetry leading to an equilateral Re_3 triangle with 3.209 Å (MPW1PW91) or 3.208 Å (BP86) edge lengths corresponding to formal single bonds. Thus all three rhenium atoms in **9-3S** have 16-electron configurations. Structure **9-3S** lies 31.3 kcal/mol (MPW1PW91) or 29.9 kcal/mol (BP86) above **9-1S**, with a small imaginary vibrational frequency at 13*i* cm^{-1} (MPW1PW91) or 18*i* cm^{-1} (BP86). The small imaginary frequencies were not removed using the finer (120, 974) integration grid.

Thermochemistry

Table 1 lists the carbonyl dissociation energies (ΔE) for the trinuclear rhenium carbonyl hydrides based on the lowest energy structures. The carbonyl dissociation energies for all of the $H_3Re_3(CO)_n$ derivatives are larger than 33 kcal/

mol, indicating the stability of the trinuclear rhenium complexes towards CO dissociation. For comparison, the experimental carbonyl dissociation energies for $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$ are 27, 41, and 37 kcal/mol, respectively.[45]

Table 1. Energies [kcal/mol] for the successive removal of CO from $H_3Re_3(CO)_n$ (n = 12, 11, 10). All of the energies refer to the lowest energy structures of $H_3Re_3(CO)_n$ without zero-point energy corrections.

	MPW1PW91	BP86
$H_3Re_3(CO)_{12} \rightarrow H_3Re_3(CO)_{11} + CO$	38.1	38.4
$H_3Re_3(CO)_{11} \rightarrow H_3Re_3(CO)_{10} + CO$	34.9	34.5
$H_3Re_3(CO)_{10} \rightarrow H_3Re_3(CO)_9 + CO$	33.8	35.7

Table 2 lists the energies for the following disproportionation reactions (1) and (2).

$$2\ H_3Re_3(CO)_{11} \rightarrow H_3Re_3(CO)_{12} + H_3Re_3(CO)_{10} \quad (1)$$

$$2\ H_3Re_3(CO)_{10} \rightarrow H_3Re_3(CO)_{11} + H_3Re_3(CO)_9 \quad (2)$$

Table 2. Energies [kcal/mol] for the disproportionation reactions $2H_3Re_3(CO)_n \rightarrow H_3Re_3(CO)_{n+1} + H_3Re_3(CO)_{n-1}$. All of the energies refer to the lowest energy structures of $H_3Re_3(CO)_n$ without zero-point energy corrections.

	MPW1PW91	BP86
$2H_3Re_3(CO)_{11} \rightarrow H_3Re_3(CO)_{12} + H_3Re_3(CO)_{10}$	–3.2	–4.0
$2H_3Re_3(CO)_{10} \rightarrow H_3Re_3(CO)_{11} + H_3Re_3(CO)_9$	–1.1	1.2

The disproportionation energies for both $H_3Re_3(CO)_{11}$ and $H_3Re_3(CO)_{10}$ are small (within 5 kcal/mol, positive or negative), suggesting that both $H_3Re_3(CO)_{11}$ and $H_3Re_3(CO)_{10}$ have limited viability towards decomposition into $H_3Re_3(CO)_{12}$ and $H_3Re_3(CO)_9$.

Discussion

Only one $H_3Re_3(CO)_{12}$ structure, namely **12-1S**, was found, similar to the analogous manganese compound $H_3Mn_3(CO)_{12}$.[18] This structure **12-1S** has an equilateral Re_3 triangle with each edge bridged by a hydrogen atom. All twelve carbonyl groups are terminal carbonyl groups. Both $H_3Mn_3(CO)_{12}$ and $H_3Re_3(CO)_{12}$ have been synthesized.[6,46,47]

The two lowest energy $H_3Re_3(CO)_{11}$ structures, namely **11-1S** and **11-2S** (Figure 4), are found within 0.5 kcal/mol of each other. Both structures contain a central Re_3 triangle with each edge bridged by a hydrogen atom. These $H_3Re_3(CO)_{11}$ structures are derived from the $H_3Re_3(CO)_{12}$ structure **12-1S** by loss of a carbonyl group with subsequent reorganization of the eleven remaining carbonyl groups. In **11-1S** all eleven carbonyl groups remain as terminal carbonyl groups and one of the edges of the Re_3 triangle contracts from approximately 3.3 Å in $H_3Re_3(CO)_{12}$ to approximately 2.9 Å in **11-1S**. Thus one of the Re–Re single bonds in $H_3Re_3(CO)_{12}$ becomes an Re=Re double bond in the $H_3Re_3(CO)_{11}$ structure **11-1S** so that all three rhenium atoms in the latter structure retain the favored 18-electron configuration. In the other low energy $H_3Re_3(CO)_{11}$ structure **11-2S**, the three rhenium atoms retain the favored 18-electron configuration by one of the remaining eleven carbonyl groups becoming a four-electron donating η^2-μ-CO group bridging the shortest edge of the central Re_3 triangle. In **11-2S** all three Re–Re edges correspond to single bonds with lengths in the 3.0 to 3.3 Å range.

The third $H_3Re_3(CO)_{11}$ structure **11-3S**, lying approximately 9 kcal/mol above the global minimum, is of interest since one of the edges of its Re_3 triangle is bridged by two hydrogen atoms similar to that in the dianion $H_3Re_3(CO)_{10}^{2-}$, which has been isolated as its tetraethylammonium salt and structurally characterized by X-ray crystallography (Figure 7).[16] The predicted length of this doubly hydrogen-bridged Re–Re edge of approximately 2.78 Å in the $H_3Re_3(CO)_{11}$ structure **11-3S** (Figure 4) is essentially identical to the experimental length of approximately 2.80 Å for the corresponding doubly hydrogen-bridged Re–Re edge in $H_3Re_3(CO)_{10}^{2-}$. Note that $H_3Re_3(CO)_{10}^{2-}$ can be derived from $H_3Re_3(CO)_{11}$ by removal of a CO group and replacement of the two lost electrons from the CO group by reduction to a dianion. The known isoelectronic $H_2Os_3(CO)_{10}$ has a closely related structure and an experimentally shorter, doubly hydrogen-bridged Os–Os edge distance of 2.68 Å (Figure 7), also determined by X-ray crystallography.[48] The lengths of the doubly hydrogen-bridged edges in the M_3 triangles in these structures suggest their formulations as diprotonated M=M double bonds analogous to the view of the boron–boron bonding in diborane $B_2H_4(\mu\text{-}H)_2$ as a protonated B=B double bond. In this way, all three metal atoms in the three isoelectronic species $H_3Re_3(CO)_{11}$ (**11-3S**), $H_3Re_2(CO)_{10}^{2-}$, and $H_2Os_3(CO)_{10}$ can be considered as having the favored 18-electron configuration. An $H_3Mn_3(CO)_{11}$ structure analogous to the $H_3Re_3(CO)_{11}$ structure **11-3S** was previously found[8] at between 9 and 15 kcal/mol above the global minimum depending on the theoretical method used.

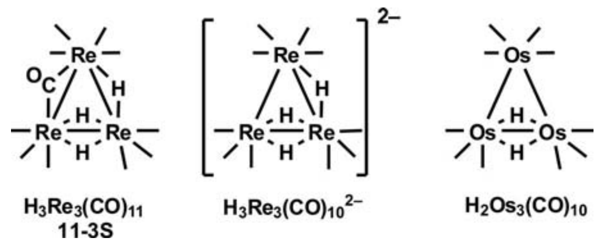


Figure 7. A comparison of the structures of the related species $H_3Re_3(CO)_{11}$, $H_3Re_3(CO)_{10}^{2-}$, and $H_2Os_3(CO)_{10}$. Terminal carbonyl groups have been omitted for clarity.

Another interesting structural feature found in two higher energy $H_3Re_3(CO)_n$ structures, namely the $H_3Re_3(CO)_{11}$ structure **11-4S** (Figure 4) and the $H_3Re_3(CO)_{10}$ structure **10-4S** (Figure 5), is a triply protonated Re=Re=Re unit (Figure 8). The central proton in such a unit is bonded to all three rhenium atoms of this Re=Re=Re unit whereas the outer two protons are each bonded only to one of the Re=Re edges (Figure 8). The distance between the "outer" rhenium atoms is a long non-bonding distance of approximately 4.0 Å. In counting the electrons in a triply protonated Re=Re=Re unit in $H_3Re_3(CO)_{11}$, each rhenium atom has a 17-electron configuration counting only the electrons from the carbonyl groups and the two Re=Re double bonds with lengths of 2.87 Å. Adding an electron from each of the three hydrogen atoms gives each of the three rhenium atoms in structure **11-4S** the favored 18-electron configuration.

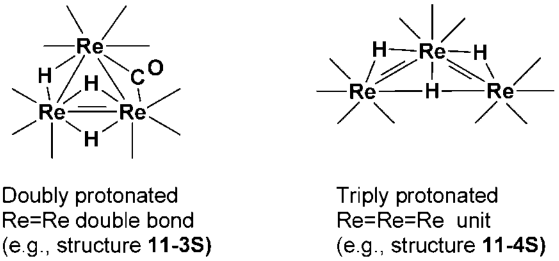


Figure 8. A comparison of the diprotonated Re=Re double bond in the $H_3Re_3(CO)_{11}$ structure **11-3S** and the triprotonated Re=Re=Re unit in the $H_3Re_3(CO)_{11}$ structure **11-4S**. Terminal carbonyl groups have been omitted for clarity.

The lowest energy structures of the more highly unsaturated $H_3Re_3(CO)_n$ (n = 10, 9) derivatives contain at least one hydrogen atom bridging the entire Re_3 triangle by forming a four-center Re_3H bond. Such a four-center bond is found on each of the four faces of the Re_4 tetrahedra of the cluster $(\mu_3\text{-}H)_4Re_4(CO)_{12}$, which has been synthesized and structurally characterized by a combination of X-ray crystallography and neutron powder diffraction techniques.[49] Loss of a carbonyl group from a trinuclear rhenium carbonyl hydride with an edge-bridging μ-H hydrogen atom leaves an empty orbital on the rhenium atom originally bearing this carbonyl group. This process can be accompanied by the originally edge-bridging hydrogen atom forming a three-center Re_2H bond becoming a face-bridging hydrogen atom forming a four-center Re_3H bond as illustrated in Figure 9. The extra orbital for this four-center bond is the rhenium orbital vacated by the loss of a carbonyl group. Thus the loss of a carbonyl group from a trinuclear rhenium carbonyl hydride with an edge-bridging hydrogen atom to give a product in which the edge-bridging hydrogen atom concurrently becomes a face-bridging hydrogen atom (Figure 9) does not involve a change in the effective electron count. In this way, the lowest energy structures found for $H_3Re_3(CO)_{10}$ and $H_3Re_3(CO)_9$ can be understood.

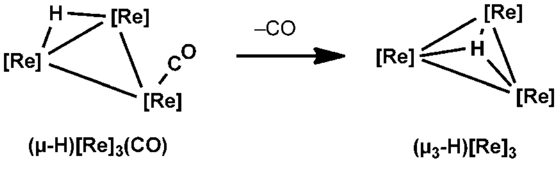


Figure 9. Conversion of an edge-bridging hydrogen atom to a face-bridging hydrogen atom upon loss of a carbonyl group from a trinuclear rhenium carbonyl hydride. The designation [Re] refers to the rhenium atoms and all other ligands not directly involved in this process.

The lowest energy $H_3Re_3(CO)_{10}$ structure **10-1S** (Figure 5) can be generated from the $H_3Re_3(CO)_{11}$ structure **11-3S** by loss of a carbonyl group from the $Re(CO)_4$ vertex with concurrent conversion of one of the two edge-bridging hydrogen atoms on the doubly bridged Re–Re edge to a face-bridging hydrogen atom (Figure 10). Repetition of this process by removing the unique bridging carbonyl group converts **10-1S** to the lowest energy $H_3Re_3(CO)_9$ structure **9-1S**. Even though an edge-bridging hydrogen atom remains on **9-1S**, this process cannot be continued one step further to give an $H_3Re_3(CO)_8$ structure, since in **9-1S** the two possible face-bridging hydrogen positions of the central Re_3 triangle are fully occupied in forming the $Re_3(\mu_3\text{-}H)_2$ trigonal bipyramid of **9-1S**. The lowest energy $H_3Re_3(CO)_n$ (n = 10, 9) structures **10-1S** and **9-1S** are similar to the lowest energy structures predicted[18] for the manganese analogues $H_3Mn_3(CO)_n$.

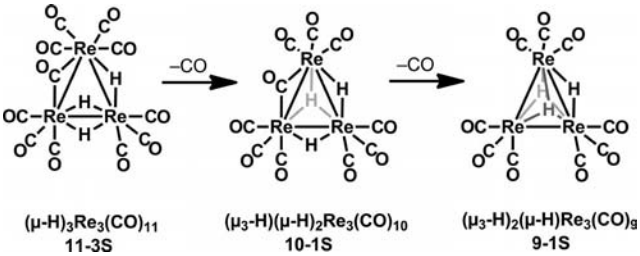
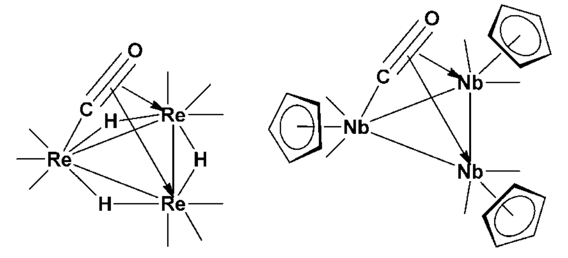


Figure 10. Successive decarbonylation of $H_3Re_3(CO)_{11}$ (**11-3S**) to give $H_3Re_3(CO)_{10}$ (**10-1S**) and $H_3Re_3(CO)_9$ (**9-1S**) with the concurrent formation of face-bridging hydrogen atoms by the process depicted in Figure 9.

The $H_3Re_3(CO)_9$ structure **9-1S** appears to be a particularly favored structure in $H_3Re_3(CO)_n$ chemistry since it lies more than 20 kcal/mol below the next lowest energy $H_3Re_3(CO)_9$ structure. Furthermore, neither $H_3Re_3(CO)_{11}$ nor $H_3Re_3(CO)_{10}$ are viable with respect to disproportionation reactions of the type $2H_3Re_3(CO)_n \rightarrow H_3Re_3(CO)_{n+1} + H_3Re_3(CO)_{n-1}$ since these reactions are essentially thermoneutral (Table 2). Therefore decarbonylation of $H_3Re_3(CO)_{12}$ is predicted to result in the loss of three carbonyl groups to directly give $H_3Re_3(CO)_9$ having structure **9-1S** without the observation of stable $H_3Re_3(CO)_{11}$ and $H_3Re_3(CO)_{10}$ intermediates (Table 1).

For $H_3Mn_3(CO)_{10}$, there is a second low-energy structure of the type $H_3Mn_3(CO)_9(\eta^2\text{-}\mu_3\text{-}CO)$.[18] This structure contains a six-electron donating $\eta^2\text{-}\mu_3$-CO group bonded to one manganese atom through an Mn–C bond and to the other two manganese atoms through the orthogonal π-bonds of this unique carbonyl group (Figure 11). This $H_3Mn_3(CO)_9(\eta^2\text{-}\mu_3\text{-}CO)$ structure is predicted[18] to have essentially the same energy as the $(\mu_3\text{-}H)(\mu\text{-}H)_2Mn_3(CO)_{10}$ structure. The corresponding $H_3Re_3(CO)_9(\eta^2\text{-}\mu_3\text{-}CO)$ structure **10-3S** (Figure 5), however, is predicted to lie somewhat higher in energy than the two lowest energy $H_3Re_3(CO)_{10}$ structures **10-1S** and **10-2S**, that is, approximately 8 kcal/mol above the global minimum **10-1S**. An example of a stable metal carbonyl derivative with a six-electron donating η^2-μ_3-CO group is the trinuclear niobium derivative $(\eta^5\text{-}C_5H_5)_3Nb_3(CO)_6(\eta^2\text{-}\mu_3\text{-}CO)$, synthesized and structurally characterized by Herrmann and co-workers.[44]



$(\mu\text{-}H)_3Re_3(CO)_9(\eta^2\text{-}\mu\text{-}CO)$
10-3S

$(\eta^5\text{-}C_5H_5)_3Nb_3(CO)_6(\eta^2\text{-}\mu\text{-}CO)$

Figure 11. Comparison between the predicted structure **10-3S** for $H_3Re_3(CO)_{10}$ and the experimentally known structure[40] of $(\eta^5\text{-}C_5H_5)_3Nb_3(CO)_6(\eta^2\text{-}\mu_3\text{-}CO)$.

Triplet $H_3Re_3(CO)_n$ (n = 11, 10, 9) structures were also investigated. They were, however, found to lie more than 30 kcal/mol in energy above the lowest energy singlet structures and thus are unlikely to be of much chemical significance. They are therefore not discussed in this paper.

Conclusion

The only structure found for $H_3Re_3(CO)_{12}$ is the experimentally known structure with each approximately 3.3 Å edge of a singly bonded Re_3 triangle bridged by a hydrogen atom and all carbonyl groups in a terminal arrangement (Figure 3). The two lowest energy $H_3Re_3(CO)_{11}$ structures lie within 0.5 kcal/mol in energy and are derived from this $H_3Re_3(CO)_{12}$ structure by loss of a carbonyl group with retention of the central $Re_3(\mu\text{-}H)_3$ core. In one of these low energy $H_3Re_3(CO)_{11}$ structures (**11-1S** in Figure 4), all eleven carbonyl groups remain in terminal positions but one of the Re=Re edges of the central $Re_3(\mu\text{-}H)_3$ triangle shortens to approximately 2.9 Å, corresponding to a formal double bond. In the other low energy $H_3Re_3(CO)_{11}$ structure (**11-2S** in Figure 4), one of the eleven carbonyl groups becomes a four-electron donating η^2-μ-CO bridging group with retention of the approximately 3.1 to 3.2 Å Re–Re single bond lengths in the central $Re_3(\mu\text{-}H)_3$ core. In both structures **11-1S** and **11-2S**, all three rhenium atoms have the favored 18-electron configuration.

A higher energy $H_3Re_3(CO)_{11}$ structure is found at approximately 8 kcal/mol above the global minimum in which one of the Re=Re edges of double bond length (2.79 Å) is bridged by two hydrogen atoms (**11-3S** in Figure 4). This $H_3Re_3(CO)_{11}$ structure is closely related to the structure of the known isoelectronic dianion $H_3Re_3(CO)_{10}{}^{2-}$, in which the doubly bridged Re=Re edge of the central Re_3 triangle was shown by X-ray crystallography to have essentially the same length (2.80 Å).[16] Loss of a carbonyl group from this $H_3Re_3(CO)_{11}$ structure with concurrent conversion of one of the edge-bridging hydrogen atoms to a face-bridging hydrogen atom gives the lowest energy $H_3Re_3(CO)_{10}$ structure (**10-1S** in Figure 5). Further loss of a carbonyl group from this $(\mu_3\text{-}H)(\mu\text{-}H)_2Re_3(CO)_{10}$ structure with concurrent conversion of a second edge-bridging hydrogen atom to a face-bridging hydrogen atom leads to the lowest energy $H_3Re_3(CO)_9$ structure (**9-1S** in Figure 6). This structure has a central $Re_3(\mu_3\text{-}H)_2$ trigonal bipyramid with the rhenium atoms in the equatorial positions and the hydrogen atoms in the axial positions. This $(\mu_3\text{-}H)_2(\mu\text{-}H)Re_3(CO)_9$ structure appears to be a very favorable structure since it not only is the lowest energy $H_3Re_3(CO)_9$ structure but lies more than 22 kcal/mol below the next lowest energy $H_3Re_3(CO)_9$ structure.

Supporting Information (see footnote on the first page of this article): Tables S1–S4: The theoretical harmonic vibrational frequencies for the 16 structures of $H_3Re_3(CO)_n$ (n = 12 to 9) using the BP86 method; Tables S6–S18: The theoretical harmonic vibrational frequencies for the 14 structures of $H_3Re_3(CO)_n$ (n = 12 to 9) using the MPW1PW91/SDD method; Tables S19–S22: The theoretical ν(CO) and ν(ReH) vibrational frequencies (cm^{-1}) and their infrared intensities (in parentheses, in km/mol) for $H_3Re_3(CO)_n$ (n = 12 to 9) using the BP86 method; Figures S1–S5: The optimized structure of $H_3Re_3(CO)_n$ (n = 12 to 9); complete Gaussian reference[24].

Acknowledgments

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