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RHENIUM CARBONYL CLUSTERS: SYNTHESIS, STRUCTURE, REACTIVITY

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CONTENTS

A. INTRODUCTION

Inorganic compounds containing the triangular trirhenium framework have been known for many years. In fact, the structure determination of $[Re_3Cl_{12}]^{3-}$ (which had long been thought to be monomeric $[ReCl_4]^-$) by X-ray diffraction in 1963 [1] constituted one of the first examples of a crystallographically characterized transition metal cluster. Since that time, a very large number of similar compounds containing the Re_3X_9 unit (where X is an anionic ligand) have been prepared and structurally characterized (for X = halide, see ref. 2(a); for X = halide, hydrocarbyl, see ref. 2(b)). In contrast, the number of rhenium clusters with low valent metal centers, i.e. primarily with neutral ligands such as carbonyls, has only recently begun to expand. The first rhenium carbonyl cluster, $H_3Re_3(CO)_{12}$, was reported by Kaesz and coworkers in 1964 [3(a)], but a 1980 review of the rhenium cluster literature [4] contained references to only about a dozen carbonyl clusters.

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Since then the field has grown rapidly. In addition to the much larger number of rhenium carbonyl clusters now known, several high nuclearity clusters (containing more than four metal atoms) have been discovered. This paper will survey the rhenium carbonyl cluster literature through mid-1988, describing the synthesis, spectroscopic and crystallographic characterization, and reactivity of these compounds. The term "cluster" is defined here as any complex containing three or more metal atoms connected by metal–metal bonds. By this definition, the compounds $[Re(CO)_3(\mu_3\text{-}X)]_4$ (X = halide or OR, for example), which contain 72 valence electrons and therefore have no metal–metal bonds, do not qualify as metal clusters.

As will be demonstrated in the following pages, a number of generalizations can be made about rhenium clusters. Rhenium, as a third-row transition metal, forms strong metal–metal bonds. Therefore the preparation of high nuclearity clusters is possible, in contrast to the chemistry of manganese. (The organometallic chemistry of technetium remains little explored.) As a group 7 element, however, rhenium is electron poor compared with the later transition metals, which form a wide variety of cluster compounds. Consequently, a number of features reflecting this property are often observed in rhenium clusters. In many complexes, ligands adopt bonding geometries which maximize the number of electrons they contribute to the cluster so that the cluster can achieve coordinative saturation. Common examples are three-electron halides and phosphides and four-electron interstitial carbides. Many clusters, especially those containing four or more rhenium atoms, have overall negative charge, again to achieve coordinative saturation. Hydrides are common in rhenium clusters, in many cases to stabilize this negative charge density. In many cases, however, coordinative saturation is not achieved. Such compounds are considered to contain formal Re–Re double bonds which are drawn as such, but often the observed reactivity does not agree with this assignment (i.e. the cluster is not particularly electrophilic).

B. SYNTHESIS

Virtually all rhenium carbonyl clusters have been synthesized, directly or indirectly, from $Re_2(CO)_{10}$. Synthetic methods used in cluster formation for other transition metals have been successfully employed: reduction by H_2 or H^-, reaction with OH^- and pyrolysis. The first two methods yield trinuclear and tetranuclear species; the third has resulted in clusters containing up to eight rhenium atoms.

Kaesz and coworkers employed the first technique, the reduction of a metal carbonyl with a hydrogen source, in preparing the earliest rhenium carbonyl clusters. Reaction of $Re_2(CO)_{10}$ either with H_2 in hydrocarbons at

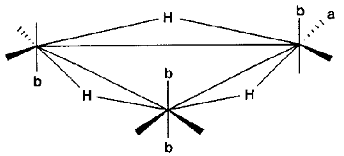


Fig. 1. Structure and ligand arrangements of $H_3Re_3(CO)_{12}$ and its derivatives.

170 °C or with $NaBH_4$ in refluxing tetrahydrofuran, (THF) followed by acid work-up, gives colorless $H_3Re_3(CO)_{12}$ as the major product [3]. Because of disorder problems the crystal structure of this compound has never been determined [5], but neutron diffraction studies of two derivatives, $H_3Re_3(CO)_{11}(PPh_3)$ and $H_3Re_3(CO)_8[(EtO)_2POP(OEt)_2]_2$, have been carried out [5,6]. Each of these complexes consists of a triangle of rhenium atoms, four two-electron ligands coordinated to each atom, with a hydride bridging each edge in the plane of the metal triangle (Fig. 1). In $H_3Re_3(CO)_{11}(PPh_3)$ the triphenylphosphine ligand occupies a radial position (Fig. 1, position a), whereas in $H_3Re_3(CO)_8[(EtO)_2POP(OEt)_2]_2$ the "POP" ligands occupy two axial sites on each side of the metal triangle (positions b). The structures of the conjugate bases of $H_3Re_3(CO)_{12}$, $[H_2Re_3(CO)_{12}]^-$ and $[HRe_3(CO)_{12}]^{2-}$, have also been determined [7,8]. As expected, the Re–Re bonds bridged by hydrides are significantly longer than the unbridged bonds (see Table 1).

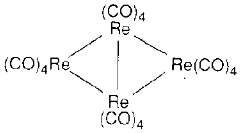
The reaction of $Re_2(CO)_{10}$ with $NaBH_4$ in refluxing THF affords an intense red solution from which a number of products, in addition to $H_3Re_3(CO)_{12}$, can be isolated. $[HRe_3(CO)_{12}]^{2-}$ can be precipitated from

TABLE 1

Re–Re bond distances (Å) for selected trirhenium complexes

Complex	Re–Re	Re(μ-H)Re	Ref.
$H_3Re_3(CO)_{11}(PPh_3)$		3.279 3.239 3.268	5
$H_3Re_3(CO)_{10}(NCMe)_2$		3.266 [a]	62
$H_3Re_3(CO)_{10}(py)_2$		3.292 [a]	73
$[H_2Re_3(CO)_{12}]^-$	3.035	3.173 3.181	7
$[H_2Re_3(CO)_{10}(PPh_3)_2]^-$	3.009	3.190 3.203	69
$[HRe_3(CO)_{12}]^{2-}$	3.014 (3.004) 3.018 (3.004)	3.125 (3.144)	8(a) (8(b))

[a] Average.



1

Fig. 2. Structure of $[Re_4(CO)_{16}]^{2-}$.

THF–ethanol as the tetraphenylarsonium salt [9], while $[Re_4(CO)_{16}]^{2-}$ (**1**) is crystallized from acetone–ethanol as the tetra-*n*-butylammonium salt [10]. The latter compound consists of two approximately equilateral edge-fused triangles of rhenium atoms (Fig. 2). A crystallographic twofold axis passing through the shared edge requires the metal framework to be planar. Treatment of this cluster with H_3PO_4 yields a compound which was originally formulated as either $[HRe_4(CO)_{16}]^-$ or $H_2Re_4(CO)_{16}$ [10(a)]. A complex with a similar carbonyl-region IR spectrum was synthesized by Gard and Brown [11] via the photolysis of $Re_2(CO)_9$(pyridine) and was formulated as $[HRe_4(CO)_{16}]^-$. A mixed salt, $[Et_4N]_2[Re_4(CO)_{16}] \cdot 1/2[Et_4N][H_2Re(CO)_4]$, has been reported from the pyrolysis of $[Et_4N][H_2Re(CO)_4]$ [8(b)]. The hydride ligands in the $[Et_4N][H_2Re(CO)_4]$ starting material are mutually *cis* [12], whereas in the mixed salt the hydrides are *trans*.

Refluxing the $Re_2(CO)_{10}$–$NaBH_4$ mixture overnight and then stirring at room temperature for days results in the formation of the tetrahedral anion $[H_6Re_4(CO)_{12}]^{2-}$ [13]. This complex has been the subject of two X-ray diffraction experiments: the first time as the tetraphenylarsonium salt (which was disordered) [13] and the second as the trimethylbenzylammonium salt [14]. The structural parameters from the second experiment were compared with those of the isoelectronic cluster $Ir_4(CO)_{12}$. The long Re–Re bond lengths (3.157 Å average) as well as the large M–M–C angles and small C–M–C angles indicate that the hydride ligands bridge the six metal–metal bonds.

Treatment of the red $Re_2(CO)_{10}$–$NaBH_4$ reaction solution with $NaRe(CO)_5$, followed by acidification with H_3PO_4, yields a compound formulated as $HRe_3(CO)_{14}$ [15]. On the basis of its carbonyl-region IR spectrum, this compound was originally postulated to adopt a linear structure with the hydride ligand bridging one of the metal–metal bonds. This hypothesis was later modified in view of the bent metal framework observed in the mixed-metal analogue $HRe_2Mn(CO)_{14}$ [16]. Only recently has a full X-ray structural analysis of the trirhenium complex appeared [17]. The metal skeleton is open, as required by the presence of 50 valence electrons, and bent to an angle of 107°. The hydrogen atom was not located but is believed to bridge an Re–Re bond, as inferred from the length of that bond (3.34 Å).

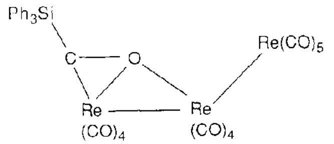


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Fig. 3. Structure of $Re_3(CO)_{13}(OCSiPh_3)$.

In essence, the Re–H bond of $HRe(CO)_5$ is acting as a two-electron ligand towards $Re_2(CO)_9$ or $ReMn(CO)_9$ in these compounds. As a two-electron ligand $HRe(CO)_5$ can be displaced from $HRe_3(CO)_{14}$ by CO to give $Re_2(CO)_{10}$. By using ^{13}CO, Harrill and Kaesz have found that the displacement is stereospecific: the added CO is found in a radial position in the product $Re_2(CO)_{10}$ [18].

A compound of similar geometry, $Re_3(CO)_{13}(OCSiPh_3)$ (**2**), has been isolated as a minor product from a mixture resulting from the sequential treatment of $Re_2(CO)_{10}$ with $LiSiPh_3$ in THF and CH_3SO_3F in CH_2Cl_2 [19]. The cluster has the structure shown in Fig. 3. The bridging acyl group must contribute three electrons if the complex is to be electron precise. The Re–Re–Re bond angle is 129°, much larger than the 107° found for $HRe_3(CO)_{14}$ [17]; this is to be expected because of the much greater bulk of the Ph_3SiCO group. The unbridged Re–Re bond lengths (3.10 Å in $HRe_3(CO)_{14}$ [17] and 3.085 Å in $Re_3(CO)_{13}(OCSiPh_3)$ [19]) are almost identical.

A large number of rhenium carbonyl clusters have been synthesized via the reaction of dirheniumdecacarbonyl with hydroxide ion. Refluxing $Re_2(CO)_{10}$ with KOH in methanol for 8–15 min affords the mononuclear complex $[H_2Re(CO)_4]^-$ [12], originally incorrectly identified as $[H_4Re_4(OMe)(CO)_{16}]^{3-}$ [20(a)]. On standing, ethanolic solutions of this compound deposit orange-yellow crystals of $[H_4Re_4(CO)_{15}]^{2-}$ (**3**), which adopt a "spiked triangle" configuration of rhenium atoms [20]. On the basis of X-ray and variable-temperature ^1H NMR data [21], the hydride ligands were assigned as shown in Fig. 4. Longer reflux times in methanol (6 h) give the previously described tetranuclear cluster $[H_6Re_4(CO)_{12}]^{2-}$ [24]. Boiling $[H_4Re_4(CO)_{15}]^{2-}$ in ethanol results in the formation of $[H_3Re_3(CO)_{10}]^{2-}$, $[H_3Re_3(\mu_3\text{-}O)(CO)_9]^{2-}$ or $[H_4Re_4(CO)_{13}]^{2-}$, depending on the reaction conditions [22–24]. In the absence of air, $[H_3Re_3(CO)_{10}]^{2-}$ (**4**) is the major product. This complex is an unsaturated 46-electron cluster, isoelectronic with the well-studied $H_2Os_3(CO)_{10}$. Treatment of $[H_3Re_3(CO)_{10}]^{2-}$ with $HClO_4$ yields $[H_4Re_3(CO)_{10}]^-$ (**5**) [25], which is also formally unsaturated. (The protonation can be reversed by treating $[H_4Re_3(CO)_{10}]^-$ with Bu_4NOH

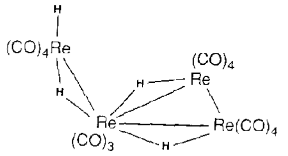

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Fig. 4. Structure of $[H_4Re_4(CO)_{15}]^{2-}$.

[26]). The monoanion can also be made by hydrogenation of $[H_2Re_3(CO)_{12}]^-$ [26]:

$$[H_2Re_3(CO)_{12}] \underset{CO(50\ atm)}{\overset{H_2(100\ atm)}{\rightleftharpoons}} [H_4Re_3(CO)_{10}]^-$$

In both the monoanion and the dianion, one Re–Re bond length (2.797 Å in $[H_3Re_3(CO)_{10}]^{2-}$ and 2.789 Å in $[H_4Re_3(CO)_{10}]^-$) [22,26] is significantly shorter than the other two. This bond is believed to be doubly protonated in both compounds (as implied by the observed disposition of the carbonyl ligands), so that the cluster geometries are as shown in Fig. 5 Both these compounds exhibit an extensive reaction chemistry which will be described in a later section.

$[H_3Re_3(\mu_3\text{-}O)(CO)_9]^{2-}$ is obtained when the $[H_4Re_4(CO)_{15}]^{2-}$ pyrolysis is run, or the reaction solution is allowed to cool, in air [23,24]. Boiling $[H_3Re_3(CO)_{10}]^{2-}$ or $[H_4Re_4(CO)_{13}]^{2-}$ in acetone under an oxygen atmosphere also yields the oxo compound [24]. The crystal structure [27] shows that the triply bridging oxygen atom closes up the trirhenium framework: in spite of hydride ligands bridging all three Re–Re bonds, the average metal–metal bond distance is 2.97 Å, equivalent to an unbridged bond distance. $[H_4Re_4(CO)_{13}]^{2-}$ is interesting because of the large number of carbonyl ligands around the tetrahedral metal core. An X-ray diffraction study [23] shows no tendency for the carbonyl ligands to adopt a bridged geometry to relieve the steric congestion.

High temperature pyrolysis is also a route to high nuclearity carbonyl clusters of rhenium. When $H_3Re_3(CO)_{12}$ is heated to 190 °C in hydrocarbon

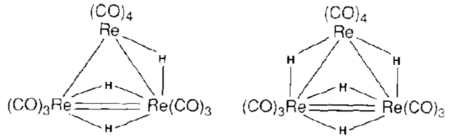

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Fig. 5. Structures of the unsaturated complexes $[H_3Re_3(CO)_{10}]^{2-}$ and $[H_4Re_3(CO)_{10}]^-$.

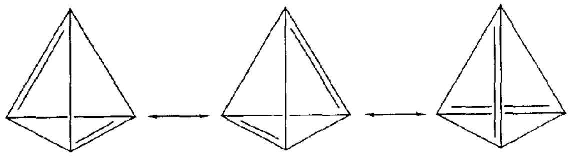

Fig. 6. Proposed hybridization scheme for $H_4Re_4(CO)_{12}$.

solution, the complex $H_4Re_4(CO)_{12}$ (**6**) is produced [28]. (This cluster can also be made directly from $Re_2(CO)_{10}$ under H_2 at 150–160 °C [29].) $H_4Re_4(CO)_{12}$ is a doubly unsaturated tetrahedron of metal atoms and contains only 56 valence electrons. The IR spectrum of this compound [28] and a subsequent X-ray diffraction study [30] indicate a highly symmetrical structure (the Re–Re bond lengths span a relatively narrow range: 2.896–2.945 Å). To account for these observations, a resonance hybrid structure was proposed (Fig. 6). A close examination of difference Fourier maps, in addition to the observed disposition of the carbonyl ligands vis-a-vis those in $[H_6Re_4(CO)_{12}]^{2-}$ (**7**) indicate that the hydride ligands bridge the faces of the tetrahedron rather than the edges [30] (see Fig. 7).

Pyrolysis of the anion $[H_2Re(CO)_4]^-$ gives a host of high nuclearity products. In refluxing alkanes (95–150 °C), $[Re_4(CO)_{16}]^{2-}$, $[H_2Re_3(CO)_{12}]^-$, $[H_3Re_3(CO)_{10}]^{2-}$, $[H_3Re_3(\mu_3\text{-}O)(CO)_9]^{2-}$, $[H_6Re_4(CO)_{12}]^{2-}$ and $[HRe_3(CO)_{12}]^{2-}$ are produced [8(b)]. At 235 °C in *n*-tetradecane–decalin, the hexanuclear cluster $[H_2Re_6C(CO)_{18}]^{2-}$ (**8**) is formed [31]. At 250 °C in *n*-tetradecane a mixture of $[Re_7C(CO)_{21}]^{3-}$ (**9**) [32] and $[Re_8C(CO)_{24}]^{2-}$ (**10**) [33] is observed. The crystal structures of these high nuclearity clusters have been determined: the metal framework of $[H_2Re_6C(CO)_{18}]^{2-}$ consists of an octahedron of rhenium atoms encapsulating a carbon atom, while $[Re_7C(CO)_{21}]^{3-}$ and $[Re_8C(CO)_{24}]^{2-}$ are monocapped and *trans*-bicapped octahedra respectively [31–33] (Fig. 8). The hydride ligands in $[H_2Re_6C(CO)_{18}]^{2-}$ were not directly located, but are assumed to bridge adjacent

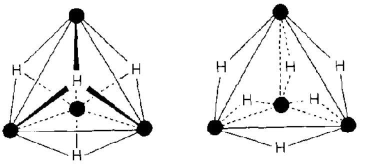

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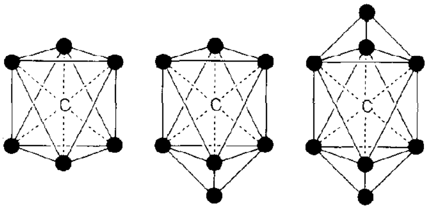
Fig. 7. Structures of $H_4Re_4(CO)_{12}$ and $[H_6Re_4(CO)_{12}]^{2-}$.



8 9 10

● = Re(CO)3

Fig. 8. Metal frameworks of $[H_2Re_6C(CO)_{18}]^{2-}$, $[Re_7C(CO)_{21}]^{3-}$ and $[Re_8C(CO)_{24}]^{2-}$.

faces of the metal octahedron on the basis of variable-temperature ^{13}C NMR spectroscopy [31]. This assignment has been called into question in the light of recent X-ray crystallographic work on $[HRe_7C(CO)_{21}]^{2-}$ [34].

Large carbonyl clusters of rhenium can also be prepared directly from $Re_2(CO)_{10}$ by pyrolytic reduction with sodium, in analogy to synthetic procedures developed for high nuclearity clusters of ruthenium and osmium [35]. Depending on the molar ratio of $Re_2(CO)_{10}$ to sodium the following clusters can be prepared: $[Re_4(CO)_{16}]^{2-}$, $[H_2Re_6C(CO)_{18}]^{2-}$, $[Re_7C(CO)_{21}]^{3-}$, $[Re_8C(CO)_{24}]^{2-}$, or a mixture of $[HRe_6C(CO)_{18}]^{3-}$ and $[HRe_5C(CO)_{16}]^{2-}$ [36,37]. (The interconversions of the first four of these clusters have been studied in detail [36].) $[HRe_6C(CO)_{18}]^{3-}$ is best viewed as the conjugate base of $[H_2Re_6C(CO)_{18}]^{2-}$ and as such is believed to adopt the same octahedral configuration of $Re(CO)_3$ units. $[HRe_5C(CO)_{16}]^{2-}$ (**11**) consists of a square-based pyramid of rhenium atoms, with one semibridging carbonyl and an exposed carbon atom lying 0.10 Å below the basal plane [37] (Fig. 9). The encapsulated carbide atoms are derived from carbonyls which have been cleaved during pyrolysis; the byproduct of this cleavage, CO_2, has been detected experimentally [36]. Detailed experimental studies of the $M-C_{carbide}$ vibrational modes have been carried out for several rhenium carbonyl carbido clusters [38].

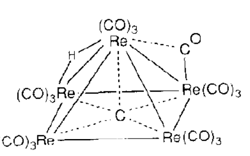


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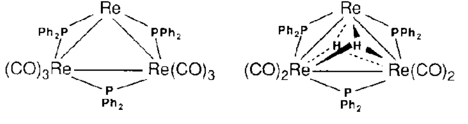
Fig. 9. Structure of $[HRe_5C(CO)_{16}]^{2-}$.

Haupt and coworkers have studied the high temperature reactivity of $Re_2(CO)_{10}$ with group 13 elements. Reaction of $Re_2(CO)_{10}$ with metallic indium in xylene at 220–230 °C gives $Re_4(CO)_{12}(\mu_3\text{-InRe(CO)}_5)_4$ [39]. This complex consists of a tetrahedron of $Re(CO)_3$ units, with each face capped by an $InRe(CO)_5$ group. The structure is analogous to that of $H_4Re_4(CO)_{12}$ (**6**), but since each $InRe(CO)_5$ group contributes two electrons to the cluster, the complex as a whole is saturated. The average Re–Re bond distance is 3.028 Å. The gallium analogue is prepared by the reaction of $Re_2(CO)_{10}$ with gallium halides in xylene at temperatures between 190 and 260 °C [40]. (This compound is reported to react with $HBEt_3^-$ to yield the tetraformyl complex $[Re_4(CO)_{12}(\mu_3\text{-GaRe(CO)}_4\text{(CHO)})_4]^-$ as indicated by an ^1H NMR signal at δ 16.2.) At lower temperatures (140 °C), GaI_3 reacts with $Re_2(CO)_{10}$ in the presence of elemental gallium to give the complex $Re_2(CO)_8(\mu\text{-GaRe(CO)}_5)_2$ [40,41]; this cluster condenses to the previously described $Re_4(CO)_{12}(\mu_3\text{-GaRe(CO)}_5)_4$ at 300 °C in a sealed tube. When GaI_3 is refluxed in xylene with *trans*-$Re_2(CO)_8(PPh_3)_2$, however, the compound $[Re(CO)_2(PPh_3)(\mu\text{-I})]_2(\mu\text{-GaRe(CO)}_4(PPh_3))$ is formed [42].

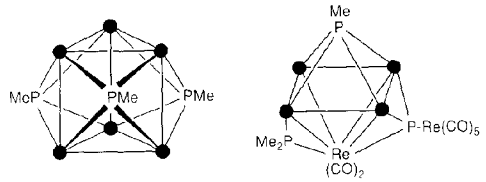
The pyrolysis of phosphine- and phosphido-substituted derivatives of $Re_2(CO)_{10}$ has been a subject of recent study. $Re_2(CO)_8(PPh_3)_2$ is converted to $Re_2(CO)_7(PPh_3)(\mu\text{-H})(\mu\text{-PPh}_2)$ at 160–180 °C; if this compound is heated to 240 °C, the trinuclear cluster $Re_3(CO)_9(\mu\text{-PPh}_2)_3$ (**12**) is obtained [43]. Similarly, $Re_2(CO)_9(PPh_3)$ is pyrolyzed to $Re_2(CO)_8(\mu\text{-H})(\mu\text{-PPh}_2)$ at 160–180 °C. Heating this product to 230 °C, however, affords $Re_3(CO)_6(\mu_3\text{-H})_2(\mu\text{-PPh}_2)_3$ (**13**), a 44-electron cluster which has been found to catalyze the hydrogenation of cyclohexene [44(a)]. Treatment of $Re_2(CO)_8(PPh_3)_2$ with H_2 gives $Re_3(CO)_9(\mu\text{-PPh}_2)_3$ directly, further reaction with H_2 yields $Re_3(CO)_6(\mu_3\text{-H})_2(\mu\text{-PPh}_2)_3$. A crystal structure of the latter complex [44(b)] shows no localization of unsaturation among the Re–Re bonds, as indicated by the bond lengths of 2.731, 2.726 and 2.734 Å. The structures of **12** and **13** are shown in Fig. 10.

The pyrolysis of the tetranuclear complex $Re_4Cl_2(CO)_{15}(MePPMePMe)$, a cyclic metallophosphine with no metal–metal bonds in hydrocarbon solution (230–250 °C) in the presence of $Re_2(CO)_{10}$ affords a mixture of the novel compounds $Re_6(CO)_{18}(\mu_4\text{-PMe})_3$ (**14**) and $Re_5(CO)_{14}(\mu_4\text{-PMe})(\mu\text{-}$



12 13

Fig. 10. Structures of $Re_3(CO)_9(\mu\text{-PPh}_2)_3$ and $H_2Re_3(CO)_6(\mu\text{-PPh}_2)_3$.



14 15

Fig. 11. Structures of $Re_6(CO)_{18}(\mu_4\text{-}PMe)_3$ and $Re_5(CO)_{14}(\mu_4\text{-}PMe)(\mu\text{-}PMe_2)(\mu_3\text{-}P[Re(CO)_5])$.

$PMe_2)(\mu_3\text{-}P[Re(CO)_5])$ (**15**) [45]. The former compared consists of a trigonal prism of metal atoms with methylphosphinidine ligands bridging the rectangular faces. The latter is a highly unusual unsymmetrical phosphine fragmentation product containing a square-based pyramid of metal atoms (Fig. 11).

Sulfur atoms have also been found to support unusual rhenium carbonyl cluster frameworks. Depending on the reaction conditions [46], the reaction of $Re(CO)_5Cl$ with $(Me_3Sn)_2S$ in dimethoxyethane (DME) yields a number of sulfur-containing clusters. Under mild conditions (temperatures up to 60 °C), $Re_2(CO)_8(\mu\text{-}SSnMe_3)_2$ and $Re_2(CO)_8(\mu\text{-}SSnMe_3)(\mu\text{-}SRe(CO)_5)$ are produced; in refluxing DME, the complexes $[Re(CO)_3(\mu_3\text{-}SSnMe_3)]_4$, $[Re(CO)_3(\mu_3\text{-}SRe(CO)_5)]_4$ and $Re_6S_3(CO)_{22}$ (**16**) are formed. Of these compounds, only the last contains metal–metal bonds; the structure, as determined in an X-ray diffraction experiment, is shown in Fig. 12.

Photolysis has been employed as a route to trinuclear rhenium clusters. The complex $HRe_3(CO)_{14}$ has been synthesized by the UV irradiation of $Re_2(CO)_{10}$ in the presence of H_2 [47,48]. Small amounts of $H_3Re_3(CO)_{12}$ have also been observed in this reaction. In similar studies, $HRe_3(CO)_{14}$ was isolated in fair yields from the irradiation of $Re_2(CO)_{10}$ and R_2ClSiH or R_3SiH ($R = C_6H_5$, CH_3) [49]. (The trirhenium product probably arises from

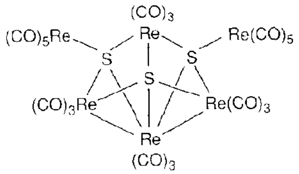


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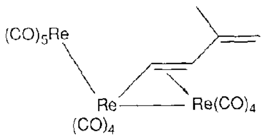
Fig. 12. Structure of $Re_6S_3(CO)_{22}$.



17

Fig. 13. Structure of $Re_3(CO)_{13}(\mu\text{-}\eta^{1,2}\text{-}C_5H_7)$.

the decomposition of unstable Re–Si complexes.) In fact, $HRe_3(CO)_{14}$ is very often observed when $Re_2(CO)_{10}$ is irradiated in the presence of a hydrogen source [17,50–52].

Photolysis of $Re_2(CO)_{10}$ in the presence of olefins results in ligand substitution and cluster building [53]. The initial substitution product, $Re_2(CO)_9(\eta^2\text{-olefin})$, reacts with additional $Re_2(CO)_{10}$ (or its photodecomposition product) to give the trinuclear clusters $Re_3(CO)_{13}(\mu\text{-}\eta^{1,2}\text{-vinyl})$ and $HRe_3(CO)_{11}(\mu\text{-}\eta^{1,2}\text{-vinyl})_2$. (Three isomers of the latter formulation are produced in the reaction with ethylene). $HRe_3(CO)_{14}$ is also formed. The crystal structure of $Re_3(CO)_{13}(\mu\text{-}\eta^{1,2}\text{-}C_5H_7)$ (**17**) has been solved (Fig. 13).

C. REACTIVITY

(i) Stoichiometric

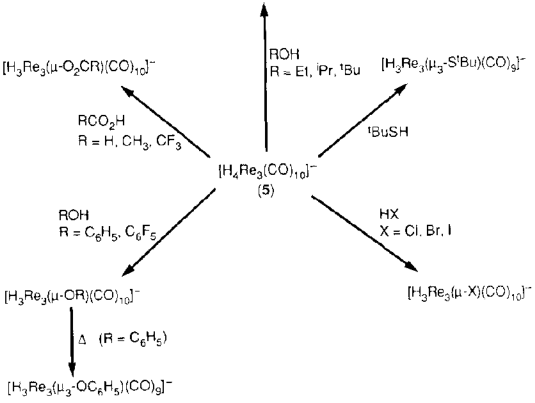
The reaction chemistry of $H_3Re_3(CO)_{12}$ does not appear extensive. In addition to the aforementioned pyrolysis to give $H_4Re_4(CO)_{12}$, the only reported reactions of $H_3Re_3(CO)_{12}$ are deprotonation with KOH to give $[H_2Re_3(CO)_{12}]^-$ [17] and phosphine substitution. To the latter category belong the syntheses of $H_3Re_3(CO)_{11}(PPh_3)$, $H_3Re_3(CO)_{10}(PPh_3)_2$, $H_3Re_3(CO)_9L_3$ ($L = PPh_3$, $P(OPh)_3$), $H_3Re_3(CO)_{10}(LL)$ and $H_3Re_3(CO)_8(LL)_2$ ($LL = Ph_2PCH_2PPh_2$, $(EtO)_2POP(OEt)_2$) [5,54]. The bidentate phosphine ligands LL are all (axial, axial)-bonded to the metal triangle, with the exception of one isomer of $H_3Re_3(CO)_{10}(EtO)_2POP(OEt)_2$; in this molecule the phosphine is an (axial, radial)-bonded chelate, as implied by ^1H NMR [54]. The triangular rhenium framework sometimes fragments under the conditions necessary for phosphine substitution. $Re_2(CO)_9(PPh_3)$ and $HRe(CO)_4(PPh_3)$ are observed in addition to the trirhenium products when $H_3Re_3(CO)_{12}$ is refluxed with PPh_3 in *n*-octane [5]. Similarly, the binuclear complexes $H_2Re_2(CO)_6(LL)$ appear as side-products when bidentate phosphines are allowed to react with $H_3Re_3(CO)_{12}$ [54(a)].

While thermal pyrolysis of $H_3Re_3(CO)_{12}$ results in cluster building to $H_4Re_4(CO)_{12}$, photolysis leads to fragmentation [55]. In the absence of free CO, $H_3Re_3(CO)_{12}$ is photolyzed quantitatively to the unsaturated dimer

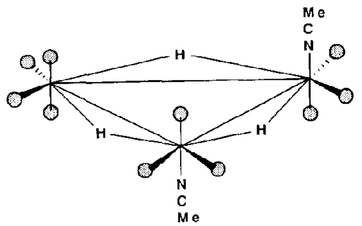
$H_2Re_2(CO)_8$. If CO is present, the primary photoproducts are $HRe(CO)_5$ and $Re_2(CO)_{10}$. A possible step at some point in these reactions is the homolytic cleavage of a hydride-bridged Re–Re bond to give an open structure with at least one terminal hydride, although no direct evidence for such an intermediate has been observed.

The dianion $[HRe_3(CO)_{12}]^{2-}$, first described by Kaesz [8(a)], possesses nucleophilic character. Reaction of this cluster with Me_3SnCl or Me_2SnCl_2 followed by acidification or hydrolysis respectively yields $HRe_3(\mu\text{-}SnMe_2)(CO)_{12}$ [9]. The $SnMe_2$ moiety asymetrically bridges an Re–Re bond of length 3.15 Å; the hydride is assumed to bridge the longest Re–Re bond (3.23 Å). Hoffmann has pointed out how the isolobal analogy between $Re(CO)_4^-$ and SnR_2 relates the molecules $[Re_3(\mu\text{-}SnMe_2)(CO)_{12}]^-$ and $[Re_4(CO)_{16}]^{2-}$ [56].

As mentioned previously, the unsaturated clusters $[H_3Re_3(CO)_{10}]^{2-}$ (4) and $[H_4Re_3(CO)_{10}]^-$ (5) have been prepared in good yields by Ciani, D'Alfonso and coworkers [25,26]. These workers have also extensively studied the reactivity of 5 which is isoelectronic with $H_2Os_3(CO)_{10}$. In contrast to the osmium compound, however, the rhenium cluster reacts with electrophiles. For example, species of the type HA (where A is a coordinating anion) react with 5 by abstracting H^- (from the doubly bridged Re–Re bond) with H^+ to liberate H_2 and adding A^- across an Re–Re bond (Scheme 1) [57–61]. The crystal structures of these products show that, as observed for $[H_3Re_3(\mu_3\text{-}O)(CO)_9]^{2-}$, an Re–Re bond bridged by both A and a hydride is significantly shorter than a bond bridged by a hydride alone. Weaker acids (e.g. alcohols) require higher reaction temperatures, which probably labilize an axial carbonyl on the $Re(CO)_4$ moiety and



Scheme 1.



18

● = CO

Fig. 14. Structure of $H_3Re_3(CO)_{10}(NCMe)_2$.

therefore lead to triply bridged products. Phenol, an acid of intermediate strength, gives doubly bridged $[H_3Re_3(\mu\text{-OPh})(CO)_{10}]^-$ which loses CO upon pyrolysis to give $[H_3Re_3(\mu_3\text{-OPh})(CO)_9]^-$ [60]. The reaction is reversed under CO at room temperature. Reaction of **5** with CF_3SO_3H, a strong non-coordinating acid, in acetonitrile affords $H_3Re_3(CO)_{10}(NCMe)_2$ (**18**) [62]. This compound is a disubstituted derivative of $H_3Re_3(CO)_{12}$, with the acetonitrile ligands in a *trans*-diaxial configuration (Fig. 14); its reactivity will be discussed below.

The complexes $[H_3Re_3(\mu_3\text{-O}^i\text{Pr})(CO)_9]^-$ and $[H_3Re_3(\mu\text{-O}^i\text{Pr})(CO)_{10}]$ have also been synthesized via the reaction of **5** with acetone [63]; the latter compound has been characterized crystallographically. The isopropoxide ligand is probably formed by cluster hydride attack on coordinated acetone.

The double-bond bridging hydrogen ligands of **5**, which exhibit hydridic character towards externally supplied electrophiles, can also reduce ligands in **5** itself. Treatment of **5** with $HB(s\text{-Bu})_3^-$ affords the crystallographically characterized complex $[H_3Re_3(\mu_3\text{-}\eta^2\text{-CH}_2O)(CO)_9]^{2-}$ **19** [64], the structure of which is shown in Fig. 15. An NMR study of the reaction solution at −40 °C revealed a proton resonance at δ 15.3, suggesting a formyl complex formed by H^- attack on one of the axial carbonyls of the $Re(CO)_4$ group; a double-bond bridging hydride is then transferred to the formyl carbon (whether this step is intramolecular or intermolecular is not known). The

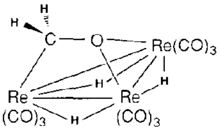


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Fig. 15. Structure of $[H_3Re_3(\mu_3\text{-}\eta^2\text{-CH}_2O)(CO)_9]^{2-}$.

oxygen atom of the resulting oxymethyl ligand coordinates to the unsaturated metal centers to complete the reaction. The bond lengths and angles of the oxymethyl ligand indicate an sp^3 hybridization of the carbon atom. One can consider this complex as a model for a surface-bound intermediate in the reductive hydrogenation of CO; indeed, acidification of **19** under CO at room temperature generates methanol and $[H_2Re_3(CO)_{12}]^-$. Since $[H_2Re_3(CO)_{12}]^-$ can then be rehydrogenated to $[H_4Re_3(CO)_{10}]^-$ [26], a cycle for the hydrogenation of CO to CH_3OH is complete.

In summary, then, the hydrogen ligands of **5**, which bridge the Re–Re double bond, are hydridic in character, i.e. one can be removed as H^- by acids, whereas those bridging the Re–Re single bonds are acidic, i.e. one can be removed with OH^- to give $[H_3Re_3(CO)_{10}]^{2-}$. In other words, **5** is amphoteric [26].

Other unusual reactions have been observed for **5**. For example, reaction of the cluster with a nitrosyl cation gives $[\{H_3Re_3(CO)_{10}\}_2(\mu_4\text{-}\eta^2\text{-}NO)]^-$, in which the NO^- anion functions as an eight-electron donor to two $H_3Re_3(CO)_{10}$ moieties [65]. Treatment of **5** with another oxidant, $C_7H_7^+$, gives neutral $H_2Re_3(CO)_{10}(\eta^5\text{-}C_7H_9)$ (**20**) [66]. The tropylium ion is believed to abstract H^- from $[H_4Re_3(CO)_{10}]^-$ to give "$H_3Re_3(CO)_{10} + C_7H_8$", the cycloheptatriene probably lightly stabilizes the 44-electron $H_3Re_3(CO)_{10}$ by functioning as a four-electron diolefin donor. If a donor species such as CO or RCN is present, $H_3Re_3(CO)_{10}L_2$ is produced; if not, C_7H_8 abstracts another hydride from the metal framework and completes the η^5 coordination. In this compound, one hydride ligand is believed to bridge the Re–Re edge opposite the vertex bearing the C_7H_9 ligand; the other triply bridges the Re_3 triangle (Fig. 16). This assignment is based on residual peaks in Fourier difference maps and is supported by a potential energy calculation.

Complex **5** exhibits enhanced CO lability at the axial positions of the $Re(CO)_4$ group, as shown by selective ^{13}CO enrichment at those positions [26]. This lability has been exploited in the synthesis of the monosubstituted clusters $[H_4Re_3(CO)_9L]^-$ (L = MeCN, PPh_3 and pyridine) [67]. Addition of one equivalent of Me_3NO to **5** in the presenc of the two-electron donor

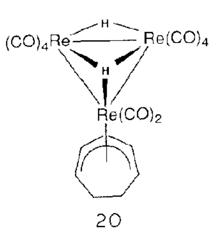

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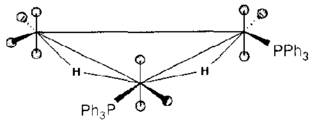
Fig. 16. Structure of $H_2Re_3(CO)_{10}(\eta^5\text{-}C_7H_9)$.



21

○ = CO

Fig. 17. Structure of $[H_2Re_3(CO)_{10}(PPh_3)_2]^-$.

yields the product, with L in an axial position on the rhenium atom opposite the double bond. These derivatives can also be prepared thermally. The acetonitrile complex has two potential reactive sites: the Re–Re double bond and the labile nitrile.

Treatment of **5** with a large excess of phosphine does not give the simple 48-electron addition product, in contrast to the behavior observed for $H_2Os_3(CO)_{10}$ [68]. Instead, loss of H_2 is observed, accompanied by the addition of two phosphine molecules to the $H_2Re_3(CO)_{10}$ core [69]. The crystal structure of $[H_2Re_3(CO)_{10}(PPh_3)_2]^-$ (**21**) shows the phosphines to be radially bound to the rhenium triangle (Fig. 17), in contrast to the *trans*-diaxial arrangement observed in $H_3Re_3(CO)_{10}(NCMe)_2$ (**18**) [62]. (Triphenylphosphine is also bound in a radial position in the crystallographically characterized sample of $H_3Re_3(CO)_{11}(PPh_3)$ [5], implying that the site of substitution may be sterically controlled, although an axially substituted isomer has reportedly been observed in solution [70].) No evidence has been observed for the possible intermediate $(\mu\text{-H})_3Re_3(H)(CO)_{10}(PPh_3)]^-$, the isoelectronic analogue to the known species $(\mu\text{-H})Os_3(H)(CO)_{10}L$ [68]. Reductive elimination of H_2 from this species would open the coordination site needed for the second molecule of phosphine.

If **5** is oxidized with Me_3NO in the absence of good donors, three new compounds are obtained [71]. The first two, characterized spectroscopically, are the 46-electron complexes $[H_4Re_3(CO)_9(NMe_3)]^-$ and $[H_4Re_3(CO)_9(ONMe_3)]^-$. The third compound, characterized by X-ray crystallography, is $[H_3Re_3(CO)_9(\mu_3\text{-O} \cdots H \cdots NMe_3)]^-$. This complex, which has an O–N bond distance of 2.502 Å, can be viewed either as a μ_3-OH compound hydrogen bonded to NMe_3, or as a μ_3-O compound incompletely protonated by Me_3NH^+. In fact, the complex can be prepared directly either by treatment of $[H_3Re_3(\mu_3\text{-OH})(CO)_9]^-$ (prepared by protonation of $[H_3Re_3(\mu_3\text{-O})(CO)_9]^{2-}$) with NMe_3 or by reaction of $[H_3Re_3(\mu_3\text{-O})(CO)_9]^{2-}$ with $[Me_3NH][Cl]$.

In contrast to **5**, the doubly-unsaturated cluster $H_4Re_4(CO)_{12}$ exhibits reactivity which is of little interest. Reaction of this complex with two-electron donors leads to cluster fragmentation rather than to addition or substitution [28]. For example, treatment of the cluster with CO at room temperature affords $H_3Re_3(CO)_{12}$ and $HRe(CO)_5$. The tetrahedral framework is maintained, however, when $H_4Re_4(CO)_{12}$ reacts with BH_4^- to yield $[H_6Re_4(CO)_{12}]^{2-}$ [28].

Following the isolobal analogy between H^+ and $Au(PPh_3)^+$, Ciani, D'Alfonso and coworkers have allowed $[H_3Re_3(CO)_{10}]^{2-}$ to react with $Au(PPh_3)Cl$ [72]. At −60 °C, the expected product $[H_3Re_3(CO)_{10}(\mu\text{-}AuPPh_3)]^-$ is observed spectroscopically. As the solution is warmed, CO is released and $[H_3Re_3(CO)_9(\mu_3\text{-}AuPPh_3)]^-$ is formed. This molecule is a 56-electron tetrahedral cluster, analogous to $H_4Re_4(CO)_{12}$. Indeed, the average Re–Re bond lengths in the two clusters are very similar (2.894 Å for Re_3Au [72] and 2.913 Å for Re_4 [30]). In $[H_3Re_3(CO)_9(\mu_3\text{-}AuPPh_3)]^-$, however, the hydride ligands, which were directly located, are all edge bridging rather than face bridging.

Iodine reacts with $[H_3Re_3(CO)_{10}]^{2-}$ in ethanol, formally adding I^+ to give $[H_3Re_3(\mu\text{-}I)(CO)_{10}]^-$ [73]. (A side-product, originally tentatively formulated as $[H_2Re_3(\mu\text{-}I)(CO)_{10}]^{2-}$, was subsequently identified as $[H_2Re_3(\mu\text{-}I)_2(CO)_{10}]^-$ [74].) Under these conditions, $[H_4Re_3(CO)_{10}]^-$ gives only $[H_3Re_3(\mu\text{-}I)(CO)_{10}]^-$, if pyridine is present, the complex $H_3Re_3(CO)_{10}(py)_2$ is produced. A crystal structure of the bis(pyridine) compound shows that the pyridine molecules coordinate to the metal framework in a *trans*-diaxial configuration, so that the compound is isostructural with $H_3Re_3(CO)_{10}(NCMe)_2$. In dichloromethane, the iodination reaction goes further [74]. The initially formed $[H_3Re_3(\mu\text{-}I)(CO)_{10}]^-$ reacts with excess I_2 to afford $[H_2Re_3(\mu\text{-}I)_2(CO)_{10}]^-$ (**22**). This anion has only two metal–metal bonds, as required by the number of valence electrons and as confirmed by an X-ray diffraction study (Fig. 18). Further reaction of this complex with I_2 results in degradation to dimeric species such as $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_{10}]^-$ (which was also structurally characterized) [74], leading ultimately to non-hydridic species such as $Re_2(\mu\text{-}I)_2(CO)_8$ and $[Re_2(\mu\text{-}I)_3(CO)_6]^-$. Curiously, however, no CO is released at any stage of the reaction.

As in $[H_4Re_3(CO)_{10}]^-$, the hydrogen ligands in $[H_6Re_4(CO)_{12}]^{2-}$ are hydridic in character. Reaction of $[H_6Re_4(CO)_{12}]^{2-}$ with CF_3SO_3H in acetone

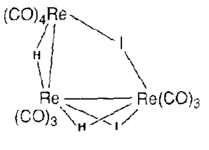


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Fig. 18. Structure of $[H_2Re_3(\mu\text{-}I)_2(CO)_{10}]^-$.

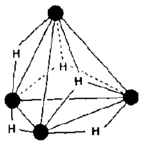

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Fig. 19. Structure of $[H_5Re_4(CO)_{12}]^-$.

results in loss of H_2 to afford the unsaturated 58-electron tetrahedral anion $[H_5Re_4(CO)_{12}]^-$ (**23**) [75]. (The reaction can be reversed with BH_4^-.) A crystal structure of this complex indicates that the unsaturation is partially delocalized over two opposite edges of the tetrahedron. The unsaturated metal–metal bond length, 2.857 Å, is intermediate between the length of the localized double bond of $[H_4Re_3(CO)_{10}]^-$ (2.789 Å) [26] and that of the completely delocalized double bonds of $H_4Re_4(CO)_{12}$ (2.913 Å) [30]. Another curious feature of this complex is the arrangement of the hydride ligands, all of which were located directly: three bridge the edges of one metal triangle; the other two are face bridging, so that each rhenium atom is bonded to three carbonyls and three hydrides (Fig. 19).

The 58-electron complex $[H_5Re_4(CO)_{12}]^-$ is in many structural details intermediate between the 56-electron $H_4Re_4(CO)_{12}$ and the 60-electron $[H_6Re_4(CO)_{12}]^{2-}$. As previously noted, $H_4Re_4(CO)_{12}$ contains all face-bridging hydrides, while $[H_6Re_4(CO)_{12}]^{2-}$ contains all edge-bridging hydrides; $[H_5Re_4(CO)_{12}]^-$ has both types. Owing to steric interactions with these hydrides, the carbonyl ligands in $H_4Re_4(CO)_{12}$ are eclipsed with respect to the metal–metal bonds, whereas in $[H_6Re_4(CO)_{12}]^{2-}$ they are staggered; the CO arrangement in $[H_5Re_4(CO)_{12}]^-$ is intermediate between these two extremes.

Like $[H_4Re_3(CO)_{10}]^-$, $H_3Re_3(CO)_{10}(NCMe)_2$ (**18**) has an analogue in osmium chemistry: $Os_3(CO)_{10}(NCMe)_2$. The acetonitrile ligands on **18**, as expected, show considerable lability. They can be displaced by nucleophiles such as CO, phosphines, pyridine, carboxylates and alkoxides [62]. (No structural information on the triphenylphosphine-substituted product was provided; it would be interesting to know whether the bulky phosphines end up in axial or radial sites.) An analogous compound, $H_3Re_3(CO)_{10}(NCPh)_2$, displays some interesting chemistry. It reacts with OH^- to yield $[H_3Re_3(\mu\text{-}OH)(CO)_{10}]^-$ and $[H_3Re_3(CO)_{10}(\mu\text{-}\eta^2\text{-}OC(Ph)NH)]^-$; the structure of the latter complex has been solved [76]. Addition of H^+ to this compound in benzonitrile regenerates the bis(nitrile) cluster complex and produces benzamide. This set of reactions represents a cycle for the hydrolysis of nitriles to amides under mild conditions.

Complex **18** can also be used as a building block to higher nuclearity clusters. If **18** is treated with $[H_2Re(CO)_4]^-$ in THF at 45 °C, the $[H_2Re(CO)_4]^-$ bridges an edge of the triangle, with concommitant loss of the acetonitrile ligands from the triangle, to give the butterfly cluster $[H_5Re_4(CO)_{14}]^-$ [77]. The hydrides were located in an X-ray diffraction experiment: they bridge the five metal–metal bonds of the butterfly.

The reactions of other rhenium carbonyl clusters with I_2 have been studied. The complex $[H_4Re_4(CO)_{15}]^{2-}$ (**3**) reacts with I_2 to give $[H_4Re_4(CO)_{15}I]^-$ in which the iodine atom is terminally bound to the "spike" on the metal triangle [78]. The hydride ligands now bridge the four metal–metal bonds, in contrast to the parent cluster [21], as indicated by the Re–Re bond lengths and the disposition of the carbonyl ligands. Further reaction of this cluster with I_2, results in loss of the spike to give $[H_3Re_3(CO)_{11}I]^-$. Again, the iodine atom is terminally bound, as required by the electron count (if the metal triangle is to be maintained) and as confirmed by a crystal structure determination [79]. Similarly, the reaction of I_2 with $[Re_7C(CO)_{21}]^{3-}$ under CO is reported to cleave the capping $Re(CO)_3$ group from the cluster to yield $[Re_6C(CO)_{19}]^{2-}$, although no structural details on this compound have appeared [80]. Further degradation gives the novel cluster $[Re_4C(CO)_{15}I]^-$ [80]. The metal framework of this anion consists of a tetrahedrally distorted square with a highly exposed carbide atom at the center of the square. (Alternatively, the complex can be viewed as a flattened butterfly without a hinge bond.) Three rhenium atoms are bonded to four carbonyl ligands each; the fourth is bonded to three carbonyls and a terminal iodine.

The reactivity of $[Re_7C(CO)_{21}]^{3-}$ with electrophiles has been the subject of a number of studies. While I_2 fragments the molecule, transition-metal-based electrophiles add to the cluster to give the mixed-metal products $[Re_7C(CO)_{21}ML_n]^{2-}$ [81–85]. When M = Ag, and bromide ion is present, the 16-metal complex $[\{Re_7C(CO)_{21}Ag\}_2(\mu\text{-}Br)]^{5-}$ is formed [81]. The crystal structures of $[Re_7C(CO)_{21}Au(PPh_3)]^{2-}$ [82], $[Re_7C(CO)_{21}Pt(C_4H_7)]^{2-}$ [83] and $[Re_7C(CO)_{21}Pd(C_9H_9)]^{2-}$ [84] have also been reported. These complexes and the Re_7Ag compound all adopt a *trans*-bicapped octahedral configuration of metal atoms. Some of the compounds $[Re_7C(CO)_{21}HgY]^{2-}$ (Y = halide, pseudohalide or hydrocarbyl) [85] undergo ligand-exchange reactions of the type

$$[Re_7C(CO)_{21}HgY]^{2-} + YHgZ \rightleftarrows [Re_7C(CO)_{21}HgZ]^{2-} + HgY_2$$

Non-metallic electrophiles also react with $[Re_7C(CO)_{21}]^3$. Treatment of the trianion with H^+ gives the hydrido species $[HRe_7C(CO)_{21}]^{2-}$ [81,82]. ^{13}C

and ^1H NMR studies show that this compound is a mixture of two isomers, differing only in the position of the hydride on the metal framework. The hydride ligand in both isomers was assigned a μ_3 (face bridging) mode on the basis of the solution ^{13}C NMR data and by analogy with the solid state structure of the "isolobal" $Au(PPh_3)^+$ adduct, $[Re_7C(CO)_{21}Au(PPh_3)]^{2-}$ [82]. X-ray crystallographic studies, however, appear to indicate that the hydrides of the two isomers of $[HRe_7C(CO)_{21}]^{2-}$ are edge bridging in the solid state [34]. NO^+ coordinates to the cluster as a three-electron ligand, displacing one CO molecule to yield $[Re_7C(CO)_{20}NO]^{2-}$ [86]. The NO ligand is believed to coordinate to one of the rhenium atoms on the face *trans* to the $Re(CO)_3$ cap. However, $C_7H_7^+$ does not coordinate to the cluster but rather oxidizes it, yielding the radical dianion $[Re_7C(CO)_{21}]^{2-}$ [87]. Carrying out the oxidation under CO results in the loss of another electron, followed by CO addition, to give $[Re_7C(CO)_{22}]^-$. An X-ray diffraction study of this compound reveals a unique feature among rhenium clusters: a fully bridging CO (on a crystallographic mirror plane) which bridges two metal atoms on the face *trans* to the capping $Re(CO)_3$ group. Bridging carbonyls have previously been observed in dirhenium complexes [88].

(ii) Catalytic

The catalytic behavior of low valent rhenium complexes has only recently come under study. Gates and coworkers have explored the catalytic activity of trinuclear and tetranuclear carbonyl clusters of rhenium on a variety of supports. On a hydrated silica surface at elevated temperatures, $H_4Re_4(CO)_{12}$ decomposes to $[Re(CO)_3OH]_4$, a cubane-type molecule with no metal–metal bonds; this system actively catalyzes propene metathesis under relatively mild conditions [89]. It was also discovered that the trinuclear clusters $H_3Re_3(CO)_{12}$ and $HRe_3(CO)_{14}$ display enhanced resistance to fragmentation by CO while adsorbed on silica. On MgO, $H_3Re_3(CO)_{12}$ catalyzes the hydrogenolysis of cyclopropene, a process which cannot be effected by the use of mononuclear rhenium catalyst precursors [90]. In related work, a Russian group has found that $H_4Re_4(CO)_{12}$ and $H_3Re_3(CO)_{12}$ catalyze the hydrogenolysis of a number of alkanes and cycloalkanes in the presence of organoaluminum compounds in hydrocarbon solution [91].

D. NMR STUDIES

Most of the NMR work done on rhenium carbonyl clusters has been undertaken as an aid to structural characterization, although some quantitative studies have been done (vide infra). ^1H NMR chemical shift data have

TABLE 2

^1H NMR data for selected rhenium carbonyl clusters

Complex	δ_H	Comment [a]	Ref.
$H_3Re_3(CO)_{12}$	−17.1		3(c)
$H_3Re_3(CO)_{10}(NCMe)_2$	−12.0		62
	−14.52		
$[H_4Re_4(CO)_{15}]^{2-}$	−16.93		21
	−15.95		
	−5.04	Terminal	
$[H_3Re_3(\mu_3\text{-}O)(CO)_9]^{2-}$	−12.8		24
$[H_4Re_3(CO)_{10}]^-$	−8.5	Bridges double bond	25
	−13.4		
$[H_4Re_3(CO)_9(PPh_3)]^-$	$\left.\begin{matrix}-7.55\\-8.71\end{matrix}\right\}$	Bridge double bond	67
	−12.18		
$H_4Re_4(CO)_{12}$	−5.08	Unsaturated; face-bridging	28
$[H_3Re_3(CO)_9(\mu_3\text{-}AuPPh_3)]^-$	−4.56	Unsaturated	72
$[H_5Re_4(CO)_{12}]^-$	−10.35	Unsaturated; three edge bridging, two face bridging; fluxional to −90 °C	75
$[H_2Re_6C(CO)_{18}]^{2-}$	−19.5	Face bridging	31
$H_2Re_3(CO)_{10}(\eta^5\text{-}C_7H_9)$	−14.20	One edge bridging;	66
	−15.60	Other face bridging	
$H_2Re_3(CO)_6(\mu\text{-}PPh_2)_3$	−18.20	Unsaturated; face bridging	44(a)

[a] All hydrides are edge bridging unless otherwise noted.

limited value in the determination of the atom coordination mode, but some generalizations can be made (see Table 2). Only one rhenium carbonyl cluster, $[H_4Re_4(CO)_{15}]^{2-}$, is thought to contain a terminally bound hydride ligand; this assignment was made partially on the basis of a relatively low field hydride resonance at δ −5.04 [21] (cf. for mononuclear rhenium hydrides: δ −5.88 for $HRe(CO)_5$ [47(b)]; δ −7.2 for $[H_2Re(CO)_4]^-$ [12]). As in osmium cluster chemistry [92,93], the presence of a terminal hydride ligand appears to depend on the presence of a "spiked" configuration of metal atoms. Another general trend is the shift of proton resonances in unsaturated compounds to lower field, with the hydrides which bridge the metal–metal multiple bond appearing furthest downfield. Otherwise the chemical shift of a given hydride appears to depend on a range of factors including metal–metal bond distance (and therefore M–H–M bond angles), the identity of other ligands bridging that bond, if any, and the charge on the cluster. It appears that chemical shift data are particularly useless in distinguishing between doubly and triply bridging hydrides (see, for example, the data for $H_2Re_3(CO)_{10}(\eta^5C_7H_9)$ in Table 2).

^{13}C NMR spectroscopy has also found use in structure characterization. While the presence of bridging hydrides on all three edges of a rhenium triangle appears to shut down all carbonyl fluxionality [26] *, the presence of an unbridged edge allows intramolecular ligand exchange to occur. For example, while $[H_4Re_3(CO)_{10}]^-$ is rigid up to 50 °C [26], $[H_3Re_3(CO)_{10}]^{2-}$ undergoes a number of fluxional processes which scramble the carbonyls [96]. ^1H and ^{13}C magnetization transfer experiments demonstrate that the hydride ligands do not move from the double-bonded edge to the single-bonded edge or vice versa; the scrambling arises from local carbonyl exchanges on rhenium atoms on the unbridged edge, together with the rotation of the acetylenic $[(CO)_3Re(\mu\text{-}H)_2Re(CO)_3]^{2-}$ moiety around the bond axis with $HRe(CO)_4$ [96(b)]. Hydride-hindered carbonyl exchange has also been invoked in rationalizing the ^{13}C NMR behavior of $[H_2Re_6C(CO)_{18}]^{2-}$ and $[HRe_7C(CO)_{21}]^{2-}$ [31,82].

Variable-temperature and variable-field ^{13}C NMR studies of several hydrido rhenium carbonyl clusters by Beringhelli et al. [96(a),97–99] have yielded some interesting results. The carbon nuclei of the carbonyls in $[H_3Re_3(CO)_{10}]^{2-}$ [96(a)] and $[H_4Re_3(CO)_{10}]^-$ [97,99] display relatively short spin-lattice relaxation times, T_1, of the order of 0.1–3 s. Quantitative determinations of T_1 as a function of temperature and magnetic field for $[H_4Re_3(CO)_{10}]^-$ indicate that the primary relaxation mechanism at 303 K is scalar coupling between the carbonyls and the quadrupolar rhenium nuclei. (Both naturally occurring isotopes of rhenium, ^{185}Re and ^{187}Re, have $I = 5/2$). At lower temperatures and higher fields, the chemical shift anisotropy mechanism becomes the dominant relaxation pathway, although scalar coupling is still significant. At 183 K, for the compound $[H_3Re_3(CO)_{10}]^{2-}$, the two mechanisms appear to contribute equally to carbon nuclei relaxation.

The T_1 data have also allowed the determination of $^{187}Re\text{–}C$ coupling constants. For $[H_4Re_3(CO)_{10}]^-$, the values for $J(^{187}Re\text{–}C)$ are 906 and 998 Hz for the carbonyls bonded to the unsaturated rhenium centers and 550 and 423 Hz for the radial and axial carbonyls on the $Re(CO)_4$ unit respectively [99]. For the acetonitrile-substituted compound $[H_4Re_3(CO)_9(NCCH_3)]^-$, the values for $J(^{187}Re\text{–}C)$ are about 1000 Hz for all of the

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* The ^{13}C NMR spectrum of $H_3Re_3(CO)_{12}$ does not seem to have been reported in the literature. This compound exhibits two singlets of equal intensity at δ 179.6 and 182.1 (toluene-d_8, 85 °C) [94]. There is no axial–radial exchange or even significant line broadening at temperatures up to 110 °C. Similarly, Kaesz has observed very high energy barriers between the axial and radial isomers of $H_3Re_3(CO)_{11}L$ ($L = PPh_3$, PEt_3 and $P(OMe)_3$) [70]. These results contrast sharply with the low energy axial–radial exchange observed for the isoelectronic complexes $M_3(CO)_{12}$ (M = Fe, Ru, Os) [95].

TABLE 3

Structural geometries of crystallographically characterized rhenium carbonyl clusters. (Unsaturated compounds have number of valence electrons in boldface.)

No. of metal atoms	Geometry	No. of valence electrons	Complex	Ref.
3	Triangle	**44**	$H_2Re_3(CO)_6(\mu\text{-}PPh_2)_3$	44
		46	$[H_3Re_3(CO)_{10}]^{2-}$	22
			$[H_4Re_3(CO)_{10}]^-$	25, 26
			$[H_4Re_3(CO)_9L]^-$ ($L = PPh_3$, pyridine)	67
		48	$H_3Re_3(CO)_{11}(PPh_3)$	5
			$H_3Re_3(CO)_8\{(EtO)_2POP(OEt)_2\}_2$	6, 54(a)
			$[H_2Re_3(CO)_{12}]^-$	7
			$[HRe_3(CO)_{12}]^{2-}$	8
			$Re_3(CO)_9(\mu\text{-}PPh_2)_3$	43
			$H_3Re_3(CO)_{10}(NCMe)_2$	62
			$H_3Re_3(CO)_{10}(\text{pyridine})_2$	73
			$[H_3Re_3(\mu_3\text{-}\eta^2\text{-}CH_2O)(CO)_9]^{2-}$	64
			$[H_3Re_3(\mu_3\text{-}O)(CO)_9]^{2-}$	22, 27
			$[\{H_3Re_3(CO)_{10}\}_2(\mu_4\text{-}\eta^2\text{-}NO)]^-$	65
			$H_2Re_3(CO)_{10}(\eta^5\text{-}C_7H_9)$	66
			$[H_2Re_3(CO)_{10}(PPh_3)_2]^-$	69
			$[H_3Re_3(CO)_9(\mu_3\text{-}O \cdots H \cdots NMe_3)]^-$	71
			$[H_3Re_3(CO)_{10}(\mu\text{-}\eta^2\text{-}OC(Ph)NH)]^-$	76
			$H_3Re_3(CO)_9(PPh_3)_3$	101
3	Triangle	48	$[H_3Re_3(CO)_{11}I]^-$	79
			$[H_3Re_3(\mu_3\text{-}S^tBu)(CO)_9]^-$	58
			$[H_3Re_3(\mu_3\text{-}OEt)(CO)_9]^-$	57
			$[H_3Re_3(\mu\text{-}OR)(CO)_{10}]^-$ ($R = C_6F_5$, ${}^iPr$)	60, 63
			$[H_3Re_3(\mu\text{-}Cl)(CO)_{10}]^-$	59
			$[H_3Re_3(\mu\text{-}O_2CR)(CO)_{10}]^-$ ($R = H, CF_3$)	61
	Bent open	50	$HRe_3(CO)_{14}$	17
			$Re_3(CO)_{13}(OCSiPh_3)$	19
			$Re_6S_3(CO)_{22}$	46
			$Re_3(CO)_{13}(\mu\text{-}\eta^{1,2}\text{-}C_5H_7)$	53
			$[H_2Re_3(\mu\text{-}I)_2(CO)_{10}]^-$	74
4	Tetrahedron	**56**	$H_4Re_4(CO)_{12}$	30
			$[H_3Re_3(CO)_9(\mu_3\text{-}AuPPh_3)]^-$	72
		58	$[H_5Re_4(CO)_{12}]^-$	75
		60	$[H_6Re_4(CO)_{12}]^{2-}$	13, 14
			$[H_4Re_4(CO)_{13}]^{2-}$	23
			$Re_4(CO)_{12}(\mu_3\text{-}InRe(CO)_5)_4$	39
	Fused triangles	62	$[Re_4(CO)_{16}]^{2-}$	8(b), 10
			$HRe_3(\mu\text{-}SnMe_2)(CO)_{12}$	9

TABLE 3 (continued)

No. of metal atoms	Geometry	No. of valence electrons	Complex	Ref.
	(Butterfly)		$[H_5Re_4(CO)_{14}]^-$	77
	Spiked triangle	64	$[H_4Re_4(CO)_{15}]^{2-}$	20
			$[H_4Re_4(CO)_{15}I]^-$	78
	Square	64	$[Re_4C(CO)_{15}I]^-$	80
5	Square-based pyramid	74	$[HRe_5C(CO)_{16}]^{2-}$	37
			$Re_5(CO)_{14}(\mu_4\text{-PMe})(\mu\text{-PMe}_2)(\mu_3\text{-P}[Re(CO)_5])$	45
6	Octahedron	86	$[H_2Re_6C(CO)_{18}]^{2-}$	31
	Trigonal prism	90	$Re_6(CO)_{18}(\mu_4\text{-PMe})_3$	45
7	Capped octahedron	98	$[Re_7C(CO)_{21}]^3$	32
			$[HRe_7C(CO)_{21}]^{2-}$ (two isomers)	34
			$[Re_7C(CO)_{22}]^-$	86
8	Bicapped octahedron	110	$[Re_8C(CO)_{24}]^{2-}$	33
			$[Re_7C(CO)_{21}Au(PPh_3)]^{2-}$	82
	Bicapped octahedron	110	$[Re_7C(CO)_{21}Pt(C_4H_7)]^{2-}$	83
			$[Re_7C(CO)_{21}Pd(C_9H_9)]^{2-}$	84
16	Two bicapped octahedra	220	$[\{Re_7C(CO)_{21}Ag\}_2(\mu\text{-Br})]^{5-}$	81

carbonyl ligands [99], indicating the effect of the poorer π-acceptor on the metal–C bonds of the $Re(CO)_3L$ moiety.

E. COMPILATION OF STRUCTURAL TYPES

A very recent review [100] has gathered structural data for rhenium clusters and includes space groups, bond distances and bond angles. In Table 3 the structurally characterized rhenium carbonyl clusters described in this paper, including mixed-metal clusters, are compiled by nuclearity, geometry and valence electron number.

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