the molecule involving Au–P bond breaking and formation is not very probable in view of the energies involved in such a process. A fluxional behavior without bond breaking is more appropriate, since the structure of the molecule in the crystalline state needs only slight displacements in the gold–ligand system for the equilibration of the P atoms. A more detailed report describing the fluxionality of gold phosphine clusters in solution as studied by variable-temperature and solid-state $^{31}P[^1H]$ NMR will be submitted shortly.

Acknowledgment. We thank Prof. Dr. Ir. J. J. Steggerda and Prof. Dr. P. T. Beurskens for their continuous interest and useful discussions. The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Pure Research (ZWO).

Registry No. $Au_4(dppmH)_3I_2$, 86885-93-0; $Au_4(PPh_3)_4(\mu\text{-}I)_2$, 78519-63-8.

Supplementary Material Available: Listings of structure factors, anisotropic thermal parameters, and positional and thermal parameters for the phenyl C atoms (77 pages). Ordering information is given on any current masthead page.

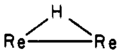
Contribution from the Centro di Studio del CNR sulla Sintesi e Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, 20133 Milano, Italy

Stepwise Degradation of the Unsaturated Cluster Tetrakis(μ-hydrido)decacarbonyltrirhenate(1–) by Reaction with Iodine. Crystal and Molecular Structures of the Tetraethylammonium Salts of the New Anions Bis(μ-hydrido)bis(μ-iodo)decacarbonyltrirhenate(1–) and (μ-Hydrido)bis(μ-iodo)hexacarbonyldirhenate(1–)

G. CIANI,* G. D'ALFONSO,* P. ROMITI, A. SIRONI, and M. FRENI

Received January 19, 1983

The reactions of the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with iodine have been investigated in various solvents. While in donor solvents, such as ethanol, the only product obtained is the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}I)(CO)_{10}]^-$, in dichloromethane and similar solvents the reaction proceeds with evolution of H_2, giving mixtures of products of variable composition, depending on the amounts of iodine. The process implies stepwise degradation, with progressive substitution of



bonds by Re–I–Re ones, leading, as a final result, to the dimeric species $[Re_2(\mu\text{-}I)_3(CO)_6]^-$ and $Re_2(\mu\text{-}I)_2(CO)_8$. The intermediate products have been isolated and characterized as $[Re_3(\mu\text{-}H)_3(\mu\text{-}I)(CO)_{10}]^-$ (first step), $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}]^-$ (second step), and $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6]^-$ *plus* $Re_2(\mu\text{-}H)(\mu\text{-}I)(CO)_8$ (third step). All the compounds have been spectroscopically characterized, and the crystal structures of the novel anions $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}]^-$ and $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6]^-$, as their tetraethylammonium salts, have been investigated by single-crystal X-ray analysis. The former species gives monoclinic crystals, space group $P2_1/n$, with $a = 9.685$ (2) Å, $b = 12.679$ (3) Å, $c = 24.439$ (5) Å, $\beta = 98.18$ (1)°, and $Z = 4$. The structure solution and refinements were based on 2646 significant counter data, the final R value being 0.025. The second species is monoclinic, space group $C2/c$, with $a = 14.601$ (1) Å, $b = 11.794$ (1) Å, $c = 14.548$ (1) Å, $\beta = 110.88$ (1)°, and $Z = 4$. Refinements, performed with 1353 significant counter intensities, led to a final R value of 0.030. The anion $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}]^-$ contains an open trimetal array, derived from a triangle with one broken edge bridged by an iodine atom. It shows one long hydrogen-bridged Re–Re interaction with 3.321 (1) Å, while the other Re–Re bond, double-bridged by one hydride and one iodide ligand, is shorter, 3.107 (1) Å. The values of the Re–I interactions are in the range 2.797 (1)–2.841 (1) Å. In the dinuclear anion $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6]^-$, of idealized C_{2v} symmetry, the rhenium atoms display an almost octahedral coordination with three CO groups and the bridging I and H atoms. Differently from other known $Re(\mu\text{-}X)_3Re$ systems, where X is a three-electron donor group, in this anion a formal direct metal–metal bond is required and this is reflected in the value of the Re–Re distance of 2.954 (1) Å. Also in the dinuclear compound $Re_2(\mu\text{-}H)(\mu\text{-}I)(CO)_8$, mainly characterized by mass spectroscopy, a Re–Re bond is considered to be present, representing a situation intermediate between those of $Re_2(\mu\text{-}H)_2(CO)_8$ and of $Re_2(\mu\text{-}I)_2(CO)_8$.

Introduction

The current interest in carbonyl cluster chemistry, after a fruitful period during which the principal aims were the synthesis and the characterization of new species, is now focused on the study of their reactivity. In the field of low-nuclearity clusters a particular interest is devoted to unsaturated compounds, such as $Os_3(\mu\text{-}H)_2(CO)_{10}$,[1a] whose chemistry has been widely studied:[1b] it contains a formally double metal–metal bond on the basis of the 18-electron rule, and the $Os(\mu\text{-}H)_2Os$ system has been described as a four-center four-electron bond[1c] or as a partially protonated double bond.[1d] Another member of this class of compounds is the anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (**1**)[2] (represented hereafter with a formal Re–Re double bond), and we are presently investigating its reactivity.

Unlike the isoelectronic $Os_3(\mu\text{-}H)_2(CO)_{10}$, it does not readily add nucleophilic ligands such as CO, PR_3, and unsaturated hydrocarbons, but it reacts rather easily with molecules that

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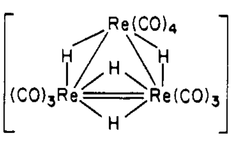
(1) (a) Johnson, B. F. G.; Lewis, J.; Kilty, P. A. *J. Chem. Soc. A* **1968**, 2859. (b) See for instance: Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1978**, *25*, 145. Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304 and references therein. (c) Broach, R. W.; Williams, J. W. *Ibid.* **1979**, *18*, 314. (d) Churchill, M. R.; De Boer, B. G.; Rotella, F. J. *Ibid.* **1976**, *15*, 1843.

(2) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1977**, *136*, C49.



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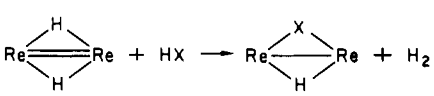
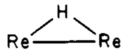
provide electrophilic groups able to subtract H^-, such as halogen acids[3] and carboxylic acids:[4]



The same type of reaction was observed to occur with I_2 in ethanol:[5]

$$[Re_3(\mu\text{-}H)_4(CO)_{10}]^- + I_2 \rightarrow [Re_3(\mu\text{-}H)_3(\mu\text{-}I)(CO)_{10}]^- + HI \quad (1)$$

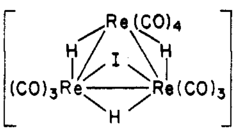
Since on repeating this reaction in dichloromethane solution we have observed H_2 evolution, we have undertaken a systematic analysis of the process and we report here on the step by step degradation of **1**, with progressive substitution of all the



interactions by Re–I–Re ones and final fragmentation to dimeric non-hydridic compounds. The characterization of the intermediate products is described, and the complete results of the X-ray analysis of two of them, namely the anions, $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}]^-$ and $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6]^-$, as their tetraethylammonium salts, are reported and discussed.

Results and Discussion

A previous investigation[5] showed that the reaction of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (**1**) with I_2 in ethanol, at room temperature, affords as the unique product the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}I)(CO)_{10}]^-$ (**2**) even in the presence of I_2 in excess and over

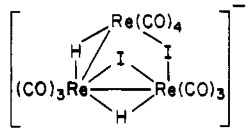


2

long reaction times. The hydride ligand is recovered as HI, according to eq 1.

When compound **1** is treated with I_2 in dichloromethane solution, at room temperature, a quite different and more complex process takes place. Mixtures of products, of different composition depending on the amount of I_2, are obtained, and the reaction proceeds until about 2 mol of iodine/mol of **1** has been added. In further contrast with the reaction in ethanol, gas evolution is observed. The gas was identified as H_2 by GLC analysis (CO being present only in traces) and several measurements, at different I_2/**1** ratios, indicated always ca. 1 mol of H_2 evolved/mol of I_2. When all the hydrogen atoms originally present in the parent compound **1** have been eliminated, gas evolution stops and further I_2 addition does not cause any reaction progress, the final products being non-hydridic dinuclear compounds, in which no metal–metal bond is present (see below).

In dichloromethane solution iodine, therefore, causes cluster demolition, while all the rhenium–carbonyl bonds remain unaffected. The successive steps through which the process occurs cannot be directly investigated because the reactions are too fast. However, ^1H NMR analyses of samples obtained with use of different I_2 amounts (I_2/**1** ratios from 0.25 to 2) show the presence of various hydride-containing compounds, which have been isolated and characterized as the new trinuclear anion $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}]^-$ (**3**), the monohydridic anion $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6]^-$ (**4**), and the neutral species $Re_2(\mu\text{-}H)(\mu\text{-}I)(CO)_8$ (**5**) besides the previously described compound **2**.[3,5]



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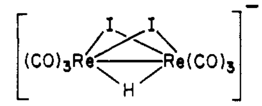

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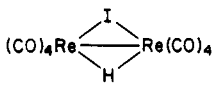

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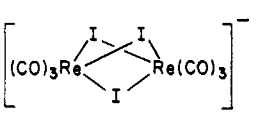
Compounds **3** and **4** have been characterized by X-ray analysis, while compound **5** has been identified mainly by mass spectroscopy.

The final products of cluster degradation are two already known dinuclear species, namely the monoanion $[Re_2(\mu\text{-}I)_3(CO)_6]^-$ (**6**) and the neutral $Re_2(\mu\text{-}I)_2(CO)_8$ (**7**). They have



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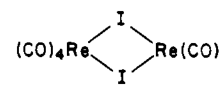

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been isolated in a molar ratio of ca. 2/1 and identified by elemental analysis, IR spectra, and mass spectroscopy for **7**. Both compounds were previously obtained from the monomer $ReI(CO)_5$, by pyrolysis reactions,[6,7] performed in the presence of $(NEt_4)I$ in the case of compound **6**. Their formation from compound **1** requires much milder conditions, in accord with the easier cleavage of M–H or M–M bonds relative to M–CO ones.

The overall degradation reaction follows the stoichiometry

$$2[Re_3(\mu\text{-}H)_4(CO)_{10}]^- + 4I_2 \rightarrow 2[Re_2(\mu\text{-}I)_3(CO)_6]^- + Re_2(\mu\text{-}I)_2(CO)_8 + 4H_2 \quad (2)$$

The isolation of intermediate species corresponding to the progressive substitution of H by I suggests a four-step process, such as that illustrated in Scheme I. In each step the overall valence electron number increases by two, since an iodide ligand acts as a three-electron donor, causing the cleavage of one Re–Re bond. The first attack of iodine occurs on the short, formally double, Re–Re bond of **1**, confirming that the hydrides bridging on this edge are the preferred sites of electrophilic attack in this species.[3-5] Compound **2** is also obtained by reaction of **1** with HI in acetone, and its structure was established by an X-ray structural determination of the analogous chloro derivative.[3] The succeeding step implies the substitution of a hydride bridging a lateral edge of the triangular cluster **2**, leading to compound **3**, in which another Re–Re bond is broken. The more symmetrical isomer (A in Scheme I), in which the two iodide ligands are bridging the same Re atoms (resembling the analogous osmium compounds

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(3) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1982**, *226*, C31.

(4) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Sironi, A.; Freni, M. *J Organomet. Chem.* **1982**, *223*, C46.

(5) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1980**, *186*, 353.

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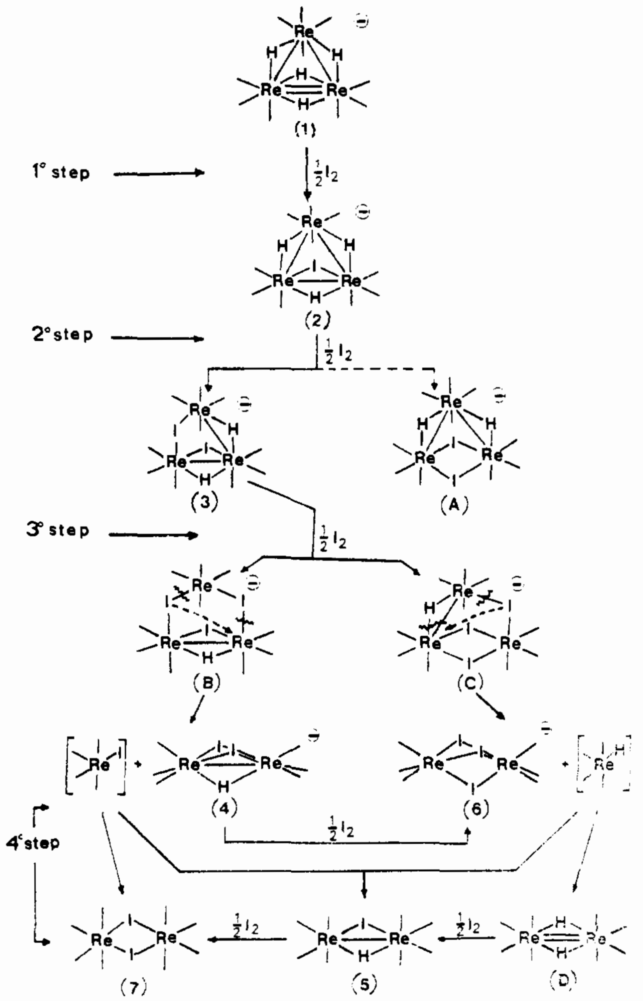
(7) Abel, E. W.; Hargreaves, G. B.; Wilkinson, G. *J. Chem. Soc. A* **1958**, 3149.

Scheme I



$Os_3(\mu\text{-}OCH_3)_2(CO)_{10}$[1a,8] or $Os_3(\mu\text{-}Cl)_2(CO)_{10}$[9]) is not observed, possibly because the inductive effect of the iodide ligand in **2** is sufficient to address selectively the electrophilic attack only on one of the two types of hydrides.

Compound **3** is the highest substitution derivative maintaining the trimetallic skeleton that has been isolated. In fact in the third step fragmentation of the cluster occurs, reasonably via intermediates, as B and C in Scheme I, unstable toward entropically favored rearrangements, which lead to dinuclear species, in the way suggested in Scheme I: anions **4** and **6** are obtained, together with the hypothetical monomeric [ReI(CO)$_4$] and [ReH(CO)$_4$] units, whose dimers are the neutral species **7**, **5**, and D. The last, the already known $Re_2(\mu\text{-}H)_2(CO)_8$ compound,[10] if formed, is not observed, probably because its unsaturation would make it the most reactive species in the reaction mixture.

The last step completes the substitution of H by I ligands in the two hydridic species still present at this point (**4** and **5**), leaving as final products only compounds **6** and **7**.

It must be noted that each step in Scheme I corresponds only in a formal way to the addition of one iodine atom with loss of one hydrogen atom, evolved as H_2. This will be discussed in more detail in connection with the effects of solvents on the whole reaction (see below).

The role of intermediates of compounds **2**, **3**, **4**, and **5** has been further confirmed by the fact that when each was treated, after isolation, with iodine, the same subsequent products were obtained. However, the derivatives corresponding to each particular step cannot be selectively isolated simply on stopping the addition of iodine at the correct stoichiometric ratio, mixtures being obtained in each case, whose approximate compositions are represented in Figure 1. Although the composition of these mixtures is rather dependent on the rate of addition of I_2, because the reactions are very fast and can proceed significantly while the reagents are mixed, the features represented in Figure 1 are of general validity; that is, compounds **2**, **4**, and **5** are always present in low yield.

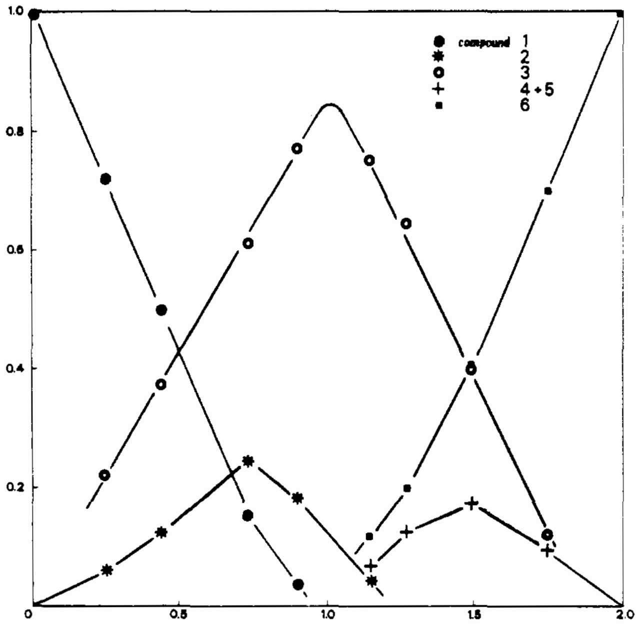


Figure 1. Composition of the reaction mixtures at various $I_2/\mathbf{1}$ ratios (values on the abscissa). The values on the ordinate represent the moles of each species per starting mole of **1** and were estimated by ^1H NMR analyses of nine samples obtained by treating 15-mg portions of **1**, dissolved in CH_2Cl_2, with different volumes of a 0.03 M solution of I_2 in CH_2Cl_2, by means of an adjustable micropipet. The amount of the non-hydridic compound **6** was estimated by difference. For clarity, only the sum of compounds **4** and **5** is reported, **5** being always in somewhat smaller amount than **4**.

The ^1H NMR spectra of samples corresponding to $I_2/\mathbf{1}$ ratios from 1 to 2 show an additional weak signal at τ 22.7, which might be tentatively assigned to the intermediate species C suggested in Scheme I, on the basis of the trend of the hydride chemical shifts for the isolated species (see Table III).

Description of the X-ray Structures of Compounds 3 and 4. Both crystal structures consist of packing of discrete anions and cations separated by normal van der Waals distances. In compound **4** the cations, which lie on twofold crystallographic axes, are disordered.

The structure of the anion $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}]^-$ (**3**) is shown in Figure 2. Bond distances and angles are reported in Table I. The anion contains an open trimetal array, of the type present in the isoelectronic (50 valence electrons) species $Re_3(\mu\text{-}H)(CO)_{14}$[11] and $Re_2Mn(\mu\text{-}H)(CO)_{14}$.[12] It is derived from the Re_3 triangle of the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}I)(CO)_{10}]^-$ (**2**) by substitution of a bridging one-electron-donor hydride on the Re1–Re3 bond with a three-electron donor iodide ligand and consequent cleavage of the subtended edge (Re1···Re3 = 4.314 (1) Å). The Re_3I1 moiety is a distorted square, with internal angles ranging from 84.23 (2)° (Re1–Re2–Re3) to 99.82 (3)° (Re1–I1–Re3). Each rhenium atom, if the direct

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(11) White, R. P.; Block, T. E.; Dahl, L. F., unpublished work (some details are given in ref 13).

(12) Kaesz, H. D.; Bau, R.; Churchill, M. R. *J. Am. Chem. Soc.* **1967**, *89*, 2775.

Table I. Selected Bond Parameters within the Anion $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}]^-$ (3)

Distances (Å)							
Re1–Re2	3.321 (1)	Re2–Hy1	1.91 (8)	Re2–C23	1.921 (17)	C14–O14	1.133 (14)
Re2–Re3	3.107 (1)	Re1–C11	1.937 (15)	Re3–C31	1.911 (15)	C21–O21	1.139 (16)
Re1–I1	2.797 (1)	Re1–C12	1.917 (14)	Re3–C32	1.857 (16)	C22–O22	1.158 (17)
Re3–I1	2.841 (1)	Re1–C13	2.009 (17)	Re3–C33	1.942 (17)	C23–O23	1.163 (17)
Re2–I2	2.819 (1)	Re1–C14	1.972 (14)	C11–O11	1.135 (15)	C31–O31	1.129 (15)
Re3–I2	2.806 (1)	Re2–C21	1.908 (16)	C12–O12	1.153 (14)	C32–O32	1.148 (17)
Re1–Hy1	1.70 (8)	Re2–C22	1.871 (17)	C13–O13	1.128 (17)	C33–O33	1.135 (16)

Angles (deg)					
Re1–Re2–Re3	84.23 (2)	Re1–Re2–C21	169.8 (5)	I1–Re3–I2	87.88 (3)
Re2–Re1–I1	84.94 (2)	Re1–Re2–C22	81.4 (4)	I1–Re3–C31	178.1 (4)
Re2–Re1–C11	169.2 (4)	Re1–Re2–C23	97.2 (4)	I1–Re3–C32	90.4 (5)
Re2–Re1–C12	90.9 (4)	Re1–Re2–Hy1	22 (2)	I1–Re3–C33	90.3 (5)
Re2–Re1–C13	80.1 (4)	Re3–Re2–I2	56.27 (2)	I2–Re3–C31	93.5 (4)
Re2–Re1–C14	97.0 (4)	Re3–Re2–C21	92.7 (4)	I2–Re3–C32	175.0 (5)
Re2–Re1–Hy1	24 (3)	Re3–Re2–C22	120.4 (4)	I2–Re3–C33	94.4 (5)
I1–Re1–C11	91.7 (4)	Re3–Re2–C23	150.2 (5)	C31–Re3–C32	88.1 (6)
I1–Re1–C12	175.9 (4)	I2–Re2–C21	91.4 (5)	C31–Re3–C33	90.9 (6)
I1–Re1–C13	85.8 (4)	I2–Re2–C22	175.5 (5)	C32–Re3–C33	90.9 (6)
I1–Re1–C14	90.5 (3)	I2–Re2–C23	94.0 (5)	Re1–I1–Re3	99.82 (3)
I1–Re1–Hy1	80 (3)	I2–Re2–Hy1	77 (2)	Re2–I2–Re3	67.05 (2)
C11–Re1–C12	92.3 (6)	C21–Re2–C22	91.8 (6)	Re1–Hy1–Re2	134 (5)
C11–Re1–C13	89.5 (6)	C21–Re2–C23	90.4 (6)	Re1–C11–O11	177.5 (13)
C11–Re1–C14	93.3 (6)	C21–Re2–Hy1	168 (2)	Re1–C12–O12	179.1 (14)
C11–Re1–Hy1	164 (3)	C22–Re2–C23	89.1 (6)	Re1–C13–O13	179.2 (13)
C12–Re1–C13	93.2 (6)	C22–Re2–Hy1	100 (2)	Re1–C14–O14	177.3 (13)
C12–Re1–C14	90.4 (5)	C23–Re2–Hy1	86 (2)	Re2–C21–O21	177.6 (15)
C12–Re1–Hy1	96 (3)	Re2–Re3–I1	88.36 (2)	Re2–C22–O22	177.6 (13)
C13–Re1–C14	175.4 (6)	Re2–Re3–I2	56.68 (2)	Re2–C23–O23	177.9 (15)
C13–Re1–Hy1	104 (3)	Re2–Re3–C31	91.3 (4)	Re3–C31–O31	179.5 (12)
C14–Re1–Hy1	73 (3)	Re2–Re3–C32	118.6 (4)	Re3–C32–O32	176.3 (13)
Re1–Re2–I2	94.95 (2)	Re2–Re3–C33	151.1 (5)	Re3–C33–O33	177.5 (14)

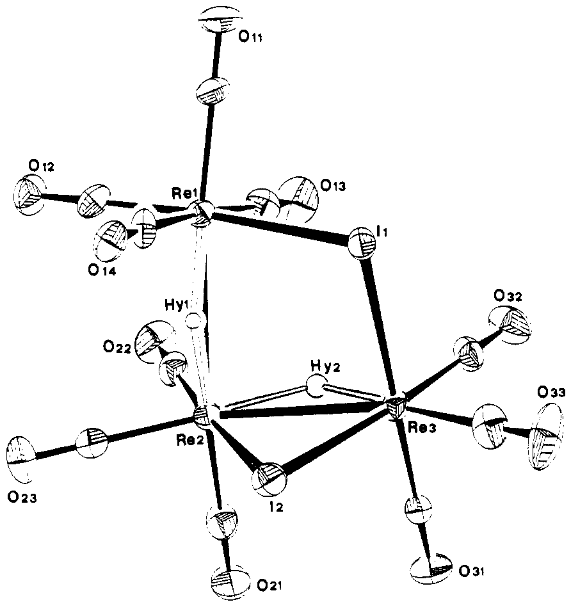

Figure 2. View of the anion $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}]^-$ (3). Numbering for the carbonyl groups is indicated on their oxygen atoms.

metal–metal interactions are ignored, exhibits a slightly distorted octahedral coordination: Re1 with one iodide, one hydride, and four CO ligands, Re2 with one iodide, two hydride, and three CO ligands, and Re3 with two iodide, one hydride, and three CO ligands. The three octahedral units are connected through the bridging atoms.

The Re1–Re2 hydrogen-bridged bond, 3.321 (1) Å, is rather long when compared with hydrogen-bridged Re–Re edges in triangular clusters. For instance in $[Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]^-$ the two edges that are bridged only by hydrides are ca. 0.11 Å shorter.[3] The observed lengthening is probably due to increased nonbonding interactions among the ligands on Re1 and Re2 in the open species, associated with the enlargement of the Re1–Re2–Re3 angle with respect to the values in the triangular species. Steric repulsions involving the CO groups were previously considered responsible for the difference observed in the Re–H–Re bonds of $Re_3(\mu\text{-}H)(CO)_{14}$ and $Re_2Mn(\mu\text{-}H)(CO)_{14}$, 3.295 (2) vs. 3.39 Å.[13]

The $Re(\mu\text{-}H)(\mu\text{-}I)Re$ interaction (Re2–Re3 3.107 (1) Å) belongs to a class of $M(\mu\text{-}H)(\mu\text{-}X)M$ systems, which has been widely studied.[14,15] It is markedly longer than the $Re(\mu\text{-}H)(\mu\text{-}Cl)Re$ bond in $[Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]^-$ (2.995 (2) Å),[3] the lengthening being in line with the suggestion[15] that the length of this type of bond increases with increasing size of X, but its extent appears to be excessive (see also below for the value of the $Re(\mu\text{-}H)(\mu\text{-}I)_2Re$ bond distance in compound **4**). Steric effects, like those invoked for the lengthening of the Re1–Re2 edge, may play the same role in this case.

The I1 ligand forms a slightly asymmetric bridge. The values of the Re–I bond distances in compound **3** (as well as in **4**) are very similar to the corresponding interactions in $Re_2(\mu\text{-}I)_2(CO)_8$ (mean value 2.820 Å).[16] They are also comparable with the Re–I (terminal) bonds in $[Re_4(\mu\text{-}H)_4I(CO)_{15}]^-$ (2.813 (2) Å)[17] and in $[Re_3(\mu\text{-}H)_3I(CO)_{11}]^-$ (2.839 (4) Å).[18] The Re1–I1–Re3 angle is somewhat larger than the Re–I–Re angles in $Re_2(\mu\text{-}I)_2(CO)_8$ (96.82 (4)°).[16] On the other hand, the Re2–I2–Re3 angle is very acute, 67.05 (2)°, smaller than the Re–Cl–Re angle in $[Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]^-$ (73.7 (2)°),[3] due to the elongation of the rhenium–halogen bonds.

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Table II. Interatomic Distances and Angles within the Anion $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6]^-$ (4)

Distances (Å)

Re–Re′	2.954 (1)	Re–C1	1.866 (12)	Re–Hy	1.76 (10)	C3–O3	1.137 (14)
Re–I	2.813 (1)	Re–C2	1.913 (11)	C1–O1	1.155 (13)	I···I′	3.785 (1)
Re–I′	2.827 (1)	Re–C3	1.873 (13)	C2–O2	1.133 (12)	I···Hy	3.09 (14)

Angles (deg)

Re′–Re–I′	58.18 (2)	I–Re–C1	172.2 (4)	C1–Re–C2	89.6 (5)
Re′–Re–I	58.64 (2)	I–Re–C2	97.6 (4)	C1–Re–C3	90.1 (6)
Re′–Re–Hy	33 (5)	I–Re–C3	92.7 (4)	C2–Re–C3	91.1 (5)
Re′–Re–C1	113.6 (4)	I′–Re–C1	91.8 (4)	Re–I–Re′	63.19 (2)
Re′–Re–C2	145.6 (3)	I′–Re–C2	98.0 (4)	Re–Hy–Re′	114 (9)
Re′–Re–C3	112.9 (4)	I′–Re–C3	170.8 (4)	Re–C1–O1	179.0 (11)
I–Re–I′	84.33 (3)	Hy–Re–C1	91 (3)	Re–C2–O2	179.4 (12)
I–Re–Hy	81 (3)	Hy–Re–C2	179 (5)	Re–C3–O3	178.7 (10)
I′–Re–Hy	81 (3)	Hy–Re–C3	90 (3)		

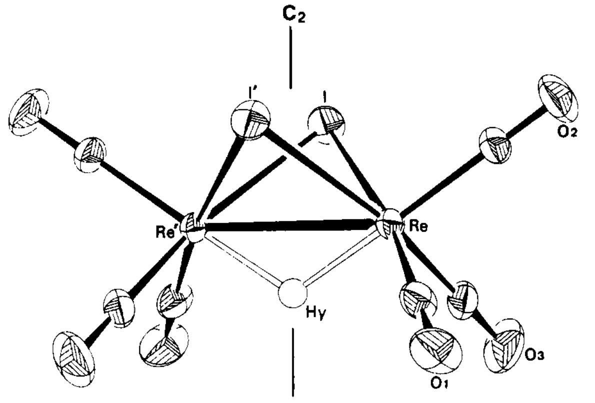

Figure 3. View of the anion $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6]^-$ (**4**). The direction of the twofold axis is shown. Numbering of the carbonyl groups is indicated on their oxygen atoms.

The carbonyls can be assigned to three classes, i.e. CO groups trans to iodides (four), to hydrides (four), or to CO (two), with mean Re–C bond lengths of 1.889, 1.927, and 1.990 Å, respectively. This trend is as expected, on passing from the π-donor iodide to the π-acceptor CO ligand.

Of the two hydride ligands, Hy1 has been refined while Hy2 has been located in its idealized position (see Experimental Section). The bond parameters involving Hy1 are affected by uncertainties too high for them to be discussed in detail. However, their values are in agreement with corresponding data reported in the literature.[14] In particular the asymmetry of the Re1–Hy1–Re2 bridge, though excessive, resembles that found for one of the hydrides of $Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}$ by a neutron diffraction study.[19] It must be noted that Hy1, with respect to the ideal calculated position exactly trans to the CO(11) and CO(21) groups with Re–H distances of 1.69 Å and a Re–H–Re angle of 159.0°, exhibits a significant outward displacement from the center of the Re1–Re2 edge.

The $(CO)_2Re(\mu\text{-}H)(\mu\text{-}I)Re(CO)_2$ moiety is almost planar, the largest displacement from the "best plane" being 0.11 Å, for the calculated Hy2. The acute dihedral angle between this plane and the plane defined by the three rhenium atoms is 80.0°.

The structure of the dinuclear anion $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6]^-$ (**4**) is illustrated in Figure 3. Bond distances and angles are given in Table II. The anion possesses a rigorous crystallographic C_2 symmetry, the twofold axis passing through the bridging hydride and the middle point of the Re–Re contact. However, its overall idealized symmetry is C_{2v}. If the intermetallic interaction is neglected, the rhenium atoms display slightly distorted octahedral coordinations, with the two octahedral units sharing a face, defined by the hydride and the two iodide ligands. The nature of the Re–Re interaction in this anion is quite different from that in the related species $[Re_2(\mu\text{-}I)_3(CO)_6]^-$ (**6**). The presence of a bridging hydride requires, from an electron count, a direct metal–metal bond or, better, a three-center Re–H–Re bond. This is reflected in the value of the Re–Re distance of 2.954 (1) Å, which is comparable with the intermetallic bonds in $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}O)(CO)_9]^{2-}$ (mean 2.968 Å)[20] and with the $Re(\mu\text{-}H)(\mu\text{-}Cl)Re$ bond in $[Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]^-$ (2.995 (2) Å).[3] On the other hand, it is significantly shorter than the $Re(\mu\text{-}X)_3Re$ contacts in the $[Re_2(\mu\text{-}X)_3(CO)_6]^-$ anions (X = OMe, 3.086 (3) Å;[21] X = Cl, 3.375 (1) Å;[22] X = Br, 3.46 Å[23]), the Re···Re interactions in these species being definitely nonbonding and strongly dependent on the nature of the bridging groups.

The Re–I bond lengths, mean 2.820 Å, are strictly comparable with those in compound **3** and with the other similar interactions cited above. The Re–I–Re′ angle is ca. 4° smaller than the Re2–I2–Re3 angle in **3**, in accord with the different values of the subtended Re–Re bond lengths.

The Re–C and C–O interactions are normal; the Re–C2 bond length, in almost exactly trans location with respect to the hydride (Hy–Re–C2 = 179 (5)°), is slightly longer (1.913 (11) Å) than the other ones (mean 1.870 Å), in accord with the trend found in **3**. The small shortening of corresponding Re–C interactions on passing from **3** to **4** is clearly related to the increase of the ratio of the anionic charge vs. metal atoms. The bridging hydride exhibits bond parameters that, although affected by high standard deviations, fall into the range of values found in analogous hydrogen-bridged systems.[14]

Spectroscopic Data. IR spectra in the ν(CO) region and ^1H NMR spectra of all the hydridic species are reported in Table III. The data for compounds **1** and **2**, determined with higher accuracy than those previously reported,[2,3] are given for comparison.

The ^1H NMR spectrum of the new compound **3** shows two hydridic resonances,[24] the lower field signal being attributable to the hydride bridging the Re2–Re3 edge (Hy2 in Figure 2), which is also bridged by an iodide ligand, because of the similar value of the chemical shift for the corresponding hydride in compound **2**. In this case, different from that observed for both compounds **1** and **2**, coupling occurs between the two hydrides, with a low coupling constant. This effect was previously observed only in another hydrido–carbonyl rhenium cluster compound, namely $[Re_4(\mu\text{-}H)_4I(CO)_{15}]^-$.[17]

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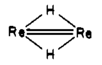
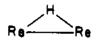
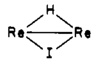
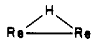
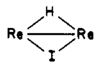
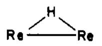
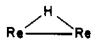
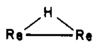
(24) Similar resonances were previously observed in the mixture obtained by reaction of the unsaturated dianion $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$ with I_2 in ethanol and were tentatively attributed to a species formulated as $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)(CO)_{10}]^{2-}$.[5]

Table III. Infrared and ^{1}H Nuclear Magnetic Resonance Data

no.	compd[a]	$\nu_{C=O}$, cm^{-1}	^{1}H resonance, τ[d]	assignment
1	$[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$	2094 w, 2026 m, 2001 vs, 1986 sh, 1945 m, 1930 sh, 1922 s[b]	18.53 (2)	
			23.38 (2)	
2	$[Re_3(\mu\text{-}H)_3(\mu\text{-}I)(CO)_{10}]^-$	2096 w, 2031 m, 2011 vs, 2000 vs, 1989 sh, 1946 m, 1930 ms, 1920 sh, 1906 s[b]	22.19 (1)	
			25.77 (2)	
3	$[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}]^-$	2105 w, 2036 m, 2013 vs, 1998 sh, 1947 sh, 1937 m, 1925 sh, 1922 m, 1913 s[b]	22.05 (1) doublet ($J_{H\text{-}H}$ = 1.2 Hz)	
			23.45 (1) doublet	
4	$[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6]^-$	2040 mw, 2020 s, 1920 s, 1910 s[b]	20.47 (1)	
5	$Re_2(\mu\text{-}H)(\mu\text{-}I)(CO)_8$	2120 vw, 2098 m, 2025 vs, 2003 s, 1967 s[c]	24.45	

[a] All the anions were obtained as tetraethylammonium salts. [b] In acetone solution. [c] In dichloromethane solution. [d] In deuterioacetone solution at 35 °C, Me_4Si as internal standard. Numbers in parentheses represent numbers of protons assigned, as determined by integration.

The values of the chemical shifts in all the compounds are lower than those usually found for hydrides in bridging locations in saturated hydrido–carbonyl clusters of rhenium, e.g. $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ (τ 27.2).[25] This fact and also the trend of values observed can be rationalized simply in terms of inductive effects of the iodide ligands. Similar inductive effects account for the decrease of the chemical shifts of hydrides in the $[Re_3(\mu\text{-}H)_3(\mu\text{-}X)(CO)_{10}]^-$ anions,[3] according to the sequence I > Br > Cl.[26]

The formulation of compound **5** is mainly based on its mass spectrum, and it is in agreement with both elemental analysis and the other spectroscopic data (Table III). The ν(CO) bands in the IR spectrum are comparable with those of the analogous chloro derivative $Re_2(\mu\text{-}H)(\mu\text{-}Cl)(CO)_8$, obtained previously in an unexpected way in the reaction of $NaRe(CO)_5$ with Ph_3SiCl.[27] The small differences between the patterns of **5** (C_{2v} symmetry) and **7** (D_{2h}) are strictly comparable with those between the corresponding chloro compounds,[28] the two higher bands in the hydridic species being shifted to lower frequencies and the other two bands in the opposite sense. The mass spectrum of **5** shows the expected molecular ion peak at m/e = 724 and the ions corresponding to stepwise elimination of eight carbonyl groups. The isotopic pattern of these ions is fully consistent with the presence of two rhenium atoms. Neither hydrogen nor iodine loss from the molecular ion is observed, as occurs when such ligands are in a bridging position.[29] Ions of type $[Re_2I(CO)_n]^+$, corresponding to H loss, appear starting from n = 6 and their amount increases as n decreases. By contrast, ions of type $[Re_2H(CO)_n]^+$ are always almost negligible and elimination of the iodine radical occurs significantly only when all the carbonyl groups have been lost. These features are the same as observed in the spectrum of the analogous chloro derivative.[27] Also ions of the types $[Re_2HI(CO)_nC]^+$ or $[Re_2I(CO)_nC]^+$ are present, arising from the fission of C–O bonds. Doubly charged ions of the types $[Re_2HI(CO)_n]^{2+}$ (n = 0,6) or $[Re_2I(CO)_n]^{2+}$ are also observed in significant amount, as is often found for the carbonyl derivatives of third-row transition metals. No cleavage of the dimetallic unit occurs until all the ligands have been removed. The mass spectrum of compound **7** shows features similar to those described for **5** and compares well with that previously reported.[30]

Solvent Effects. In order to clarify the reasons for the different reactivity of compound **1** with iodine on passing from ethanol to dichloromethane, we have performed the same reaction in other solvents and we have observed the following: (i) In tetrahydrofuran and in acetonitrile the reaction proceeds as in ethanol. (ii) In trichloromethane H_2 evolution occurs and the same intermediate and final products as in dichloromethane were spectroscopically identified, showing higher yields of compound **2**. (iii) In n-hexane H_2 evolution is observed and the final products are the same as obtained in dichloromethane. ^{1}H NMR analysis of samples at different $I_2/\mathbf{1}$ ratios showed, however, only a small amount of the intermediates. This can be explained by considering that this reaction is heterogeneous and the rate of transfer from the solid phase to the solution is probably lower than the rates of the successive substitution reactions.

It is therefore apparent that, in solvents having donor properties, such as ethanol, tetrahydrofuran or acetonitrile, the iodine molecules lose some electrophilic character due to the interactions that they establish with the solvent molecules, giving the "charge transfer" complexes responsible for the brown color of those solutions. In contrast, in the other solvents (violet solutions) the only nucleophilic species available for interactions with iodine are the hydrido–carbonyl rhenate anions and so the reactions can proceed up to complete hydride elimination. The different donor properties of the solvents can also account for the fate of the substituted hydrides, which are recovered as HI in the former type of solvents (ethanol etc.) and as H_2 in the other one. We have not observed HI formation in dichloromethane and similar solvents, but we cannot exclude that, as soon as it is formed, it further reacts with the hydridic compounds, causing H_2 development. To test this possibility, we have prepared a solution of dichloromethane saturated with gaseous HI. On treating compound **1** with different volumes of this solution, we have observed H_2 evolution and obtained the same intermediate and final products as in the reaction with iodine.[31]

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(25) Churchill, M. R.; Bird, P. H.; Kaesz, H. D.; Bau, R.; Fontal, B. *J. Am. Chem. Soc.* **1968**, *90*, 7135.

(26) In ref 3 the values of the chemical shift for the hydrides of $[Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]^-$, due to a misprint, were incorrectly reported, the correct values being τ 20.6 (1) and 24.3 (2).

(27) Curtis, M. D. *Inorg. Chem.* **1972**, *11*, 802. The same compound was also obtained by reaction of $[Re_3(\mu\text{-}H)(CO)_{12}]^{2-}$ with $(CH_3)_2SnCl_2$: Huie, B. T.; Kirtley, S. W.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1981**, *213*, 45.

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(29) Lewis, J.; Johnson, B. F. G. *Acc. Chem. Res.* **1968**, *1*, 245.

(30) Edgar, K.; Johnson, B. F. G.; Lewis, J.; Williams, I. G.; Wilson, J. M. *J. Chem. Soc. A* **1967**, 379.

It is therefore likely that also in dichloromethane the reaction proceeds through HI elimination and insertion of an iodide ligand. Then the hydridic compounds can undergo parallel attacks by both I_2 and HI.

On the other hand, the contribution of mechanisms involving molecular I_2 addition, followed by H_2 elimination, seems to be improbable because of the steric crowding about each rhenium atom. The dominant amount of products corresponding to substitution of an even number of H atoms (compounds **3**, **6**, and **7**, in steps 2 and 4 of Scheme I) could derive simply from kinetic factors, related perhaps to the higher probability for HI to react with the same anion from which it originates.

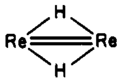
Concluding Remarks. The degradation process described in this paper is of a complex type, and to our knowledge, no example of similar studies of step by step cluster degradation up to elimination of all the metal–metal bonds has been previously reported.

A detailed mechanistic investigation is prevented by the difficulty of obtaining reliable kinetic parameters, since many fast parallel and series reactions occur.

Whatever the intimate mechanism involved, the following features can be outlined:

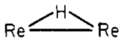
(i) No replacement of the carbonyl groups occurs in the reaction with I_2 at room temperature, as expected when the strength of the M–CO interactions is taken into account, and the original $Re(CO)_3$ and $Re(CO)_4$ units are preserved during the whole process.

(ii) The



system is the most reactive site, whichever the solvent used, and after substitution of one of these hydrides, with saturation of the cluster, the remaining one becomes much less reactive.

(iii) Substitution of the hydrides on the



bonds takes place only when the electrophilic properties of the iodine are not reduced by interaction with solvent.

(iv) The attack of iodine on a carbonyl cluster anion with all the edges bridged by hydrides occurs differently from that observed with other anionic cluster species, which undergo electrophilic I^+ addition, followed eventually by bridge formation and breaking of a M–M bond. Examples of these processes are

$[Rh_6(CO)_{15}]^{2-} + I_2 \rightarrow [Rh_6I(CO)_{15}]^- + I^-$[32]

$[Rh_7(CO)_{16}]^{3-} + I_2 \rightarrow [Rh_7(\mu\text{-}I)(CO)_{16}]^{2-} + I^-$[33]

$[Os_{10}C(CO)_{24}]^{2-} + I_2 \rightarrow [Os_{10}C(\mu\text{-}I)(CO)_{24}]^- + I^- \xrightarrow{I_2} Os_{10}C(\mu\text{-}I)_2(CO)_{24} + I^-$[34]

Few similar reactions with hydrido–carbonyl clusters have been studied which proceed in an analogous manner, the hydrides not being involved:

$[Re_4H(\mu\text{-}H)_3(CO)_{15}]^{2-} + I_2 \rightarrow [Re_4(\mu\text{-}H)_4I(CO)_{15}]^- + I^-$[17]

$[Os_4(\mu\text{-}H)_3(CO)_{12}]^- + I_2 \rightarrow Os_4(\mu\text{-}H)_3(\mu\text{-}I)(CO)_{12} + I^-$[35]

In the case of compound **1** substitution takes place, instead of addition, and the net anionic charge remains unchanged. The I_2 molecule plays a double role, acting as an electrophile in the subtraction of a hydride and as a nucleophile entering in the bridging location and removing a direct metal–metal bond.

Further studies on this type of system, using as starting materials species with both bridged and unbridged edges, such as $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ or $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$, are in progress in order to clarify the preferred site of attack of halogens.

Experimental Section

The parent compound $[Re_3(\mu\text{-}H)_4(CO)_{10}][N(C_2H_5)_4]$ was prepared as already described.[2,5] The reactions were performed under an N_2 atmosphere, in reagent grade solvents deoxygenated and purified by standard methods. The manipulations were initially performed under N_2, but when the stability of all the compounds in air had been established, unnecessary precautions were avoided.

Infrared spectra were recorded on a Perkin-Elmer 783 grating spectrophotometer, in 0.1 mm CaF_2 cells, and were calibrated with polystyrene film absorptions. NMR spectra were recorded by M. Bonfã on a Bruker 80 and on a Varian XL 200 FT spectrometer. Mass spectra were obtained by P. Russo on a Varian MAT 112 instrument with a direct inlet probe, at room temperature for compound **5** and at 100 °C for **7**, at 70 eV. Gas chromatographic analyses of the gas evolved in the reactions were performed on a Carlo Erba Fractovap M instrument, fitted with HWD and two 1-m columns in series (molecular sieves and silica gel), using as carrier Ar for H_2 and He for CO detection. Elemental analyses were performed by the Microanalytical Laboratory of the Milan University for C, H, and N, and by the Mikroanalytisches Labor Pascher in Bonn, West Germany, for I detection. Iodine solutions were prepared by dissolving weighed amounts of iodine in the proper solvent, in calibrated vessels; just before their use, the solutions were titrated, under N_2, in acetic acid–water medium and starch as indicator, with a freshly prepared 0.1 N $Na_2S_2O_3$ solution.

In a typical experiment the weighed amount of **1** was dissolved in the proper solvent, in a 25-mL reaction vessel fitted with a calibrated dropping funnel (5 mL, 0.01 mL graduated) and closed by a rubber septum. The iodine solution was let into the funnel, under N_2, and then the required amount of solution was dropped into the reaction vessel, at room temperature. Through the septum, gas and solution samples were taken for the GLC and spectroscopic analyses.

Reactions of Compound 1 with I_2 in Dichloromethane. (a) Isolation of $[Re_2(\mu\text{-}I)_3(CO)_6][N(C_2H_5)_4]$ (6) and $Re_2(\mu\text{-}I)_2(CO)_8$ (7). Compound **1** (50 mg) dissolved in 5 mL of CH_2Cl_2 was treated with 3.7 mL of a 0.029 M solution of I_2 in CH_2Cl_2 (2.1 mol of I_2/mol of **1**). The solution turned immediately from yellow to green to violet and did not change upon stirring for 15 min. The solution was concentrated under reduced pressure to a small volume (ca. 1 mL) and then treated with 20 mL of CCl_4, affording a violet precipitate of **6**, which was filtered, washed with CCl_4, and dried in vacuo (45 mg, yield 84% according to reaction 2). The filtrate was evaporated, giving a residue of **7**, which was dried in vacuo (19 mg, yield 87% according to reaction 2), and crystallized from hot $CHCl_3$, giving pale yellow crystals.

Compound **6** was reported[6] as a colorless species and as such was obtained by reaction of **1** with HI (see below). In this case crystallization by slow diffusion of $(C_2H_5)_2O$ in CH_2Cl_2 afforded translucent crystals with violet shades. The IR spectrum (ν(CO) 2016 s, 1916 s cm^{-1} in CH_2Cl_2 solution) and several elemental analyses, nevertheless, fully support the formulation of this material as compound **6**, the color being probably attributable to some unidentified iodine compound present at trace level. The color did not disappear upon treating with $Na_2S_2O_3$, and therefore it did not seem to be due to unreacted iodine. Anal. Calcd for $C_{14}H_{20}I_3NO_6Re_2$: C, 15.98; H, 1.92; N, 1.33; I, 36.21. Found (mean values): C, 16.3; H, 1.9; N, 1.5; I, 35.8.

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(31) It is noteworthy that the reaction of **1** with aqueous HI in solvents like acetone or tetrahydrofuran afforded only compound **2**, also in the presence of HI in excess.[3] Thus, the solvent effect on the behavior of HI seems to parallel that observed in the case of I_2.

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(b) Isolation of $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6][N(C_2H_5)_4]$ (4) and $Re_2(\mu\text{-}H)(\mu\text{-}I)(CO)_8$ (5). The procedure was the same as described above, 2.6 mL of the I_2 solution being used (1.5 mol of I_2/mol of **1**). After separation of the anionic and neutral compounds by precipitation with CCl_4, the precipitate was crystallized from $CH_2Cl_2/(C_2H_5)_2O$, affording a mixture of species from which 2 mg of colorless crystals of **4** (yield ca. 4%, based on the $Re_2(CO)_6$ moiety of **1**) was isolated by hand under the microscope; mp 250 °C. Anal. Calcd for $C_{14}H_{21}I_2NO_6Re_2$: C, 18.15; H, 2.29; N, 1.51. Found: C, 18.6; H, 2.3; N, 1.5. The compound dissolves well in CH_2Cl_2, C_4H_8O, $(CH_3)_2CO$, or CH_3CN, is less soluble in C_2H_5OH, CH_3OH, or $CHCl_3$ and even less in $(C_2H_5)_2O$, and can be considered insoluble in CCl_4, water, or saturated hydrocarbons.

The filtrate, evaporated to dryness, was treated once with 3 mL of *n*-hexane, giving a residue, composed mainly of **7**, and a solution, from which, after solvent elimination and drying in vacuo, 1.5 mg of the white compound **5** was obtained (yield ca. 8%, based on the $Re(CO)_4$ moiety of **1**). The compound was further purified by sublimination (60 °C, 0.1 mmHg); mp 107 °C. Anal. Calcd for $C_8HIO_8Re_2$: C, 13.26; I, 17.52. Found: C, 13.5; I, 17.5. The compound dissolves reasonably in all organic solvents, including the less polar ones such as hydrocarbons.

(c) Isolation of $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}][N(C_2H_5)_4]$ (3). The procedure was the same as described above, 1.75 mL of the I_2 solution being used (corresponding to an equimolar ratio of the reagents). The reaction mixture, nearly colorless, was evaporated to dryness, dissolved in 3.5 mL of CH_3OH, and treated with 2 mL of H_2O, causing the precipitation of the white compound **3** (21 mg after drying in vacuo, yield ca. 34%). The compound was purified by crystallization from $CH_2Cl_2/(C_2H_5)_2O$, giving colorless crystals. Anal. Calcd for $C_{18}H_{22}I_2NO_{10}Re_3$: C, 17.64; H, 1.81; N, 1.14. Found: C, 17.9; H, 1.7; N, 1.3. It melts with decomposition at 210 °C. The solubility of this compound is very similar to that of compound **4**, and the same occurs for compounds **2** and **6**: this fact accounts for the difficulty of separation of the anionic components of the mixtures and for the values of the isolated yields, significantly lower than the reaction yields estimated from the NMR analyses (Figure 1).

Reactions of 1 with I_2 in Trichloromethane. In five different experiments, 15-mg samples of **1**, dissolved in 5 mL of $CHCl_3$, were treated respectively with 0.26, 0.53, 0.77, 1.06, and 1.30 mL of a 0.024 M solution of I_2 in $CHCl_3$ (corresponding to I_2/**1** ratios of 0.4, 0.82, 1.20, 1.65, and 2, respectively). GLC analyses revealed in all cases H_2 evolution, while NMR analyses of the first four samples showed the hydridic signals of compounds from **1** to **5**. From the fifth sample only compounds **6** and **7** were isolated.

Reactions of 1 with I_2 in *n*-Hexane. In three different experiments 20-mg samples of **1**, suspended in 3 mL of *n*-hexane, were treated respectively with 0.69, 1.40, and 2.80 mL of a 0.0148 M solution of I_2 in C_6H_{14} (corresponding to I_2/**1** ratios of 0.5, 1, and 2, respectively). The suspensions were stirred for 30 min, and then gas samples were analyzed, showing H_2 development. The liquid and the solid phases were separated and spectroscopically analyzed. In the solution compounds **5** and/or **7** were present, while the solid material was composed mainly of unreacted **1** and/or **6**, with different ratios in the various samples, with only small amounts of compounds **2** and **3**.

Determinations of the Volume of Evolved H_2. Measurements were performed with standard gas microburets, on treating 30 mg of **1** with an exact volume of a solution of I_2 in the proper solvent. The results were as follows. Reactions in CH_2Cl_2: (a) I_2/**1** = 1, three determinations gave H_2/I_2 ratios of 1.3, 1.0, and 1.1, respectively; (b) I_2/**1** = 2 gave H_2/I_2 = 1.2; (c) I_2/**1** = 0.5 gave H_2/I_2 = 1.1. Reaction in $CHCl_3$: I_2/**1** = 1 gave H_2/I_2 = 1.1.

Reactions of 1 with I_2 in Donor Solvents (Ethanol, Tetrahydrofuran, and Acetonitrile). A 30-mg quantity of **1**, dissolved in 3 mL of the proper solvent, was treated with 1.03 mL of a 0.03 M I_2 solution in the same solvent. The IR and NMR spectra of a sample of the final solution showed the quantitative formation of compound **2**. Neither H_2 nor CO development was revealed by GLC. Further addition of 1 mL of the same I_2 solution did not cause any spectral change after up to 15 h. In order to detect HI presence, 20 mL of H_2O was added to the reaction mixtures obtained by treating 30 mg of **1**, in 1 mL of the proper solvent, with 1 mL of the I_2 solution. After filtration of the precipitate of the $N(C_2H_5)_4^+$ salt of **2**, the solutions were potentiometrically titrated with 0.01 N NaOH. The results, with blank titrations taken into account, gave H^+/**1** ratios from 0.80 to 0.95. The water used was previously boiled and cooled under N_2. Analogous measurements on the solutions obtained by treating the reaction mixtures in CH_2Cl_2 or $CHCl_3$ with *n*-hexane and then, after filtration, with a double volume of water did not show significant differences with respect to blank titrations.

Table IV. Crystallographic Data

compd	3	4
formula	$C_{18}H_{22}I_2NO_{10}Re_3$	$C_{14}H_{21}I_2NO_6Re_2$
fw	1224.8	925.5
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (nonstd setting of No. 14)	$C2/c$ (No. 15)
a, Å	9.685 (2)	14.601 (1)
b, Å	12.679 (3)	11.794 (1)
c, Å	24.439 (5)	14.548 (1)
β, deg	98.18 (1)	110.88 (1)
V, Å^3	2970.5 (20)	2340.7 (7)
D_{calcd}, g cm^{-3}	2.74	2.63
Z	4	4
F(000)	2192	1664
cryst dimens, mm	0.07 × 0.15 × 0.25	0.06 × 0.07 × 0.20
μ(Mo Kα), cm^{-1}	144.7	131.1
θ range, deg	3–23	3–25
reflcns measd	±*h*,*k*,*l*	±*h*,*k*,*l* (*h* + *k* = 2*n*)
no. of reflcns measd	4115	2147
no. of indep reflcns used in structural analysis	2646 [$I > 3\sigma(I)$]	1353 [$I > 3\sigma(I)$]
no. of variable parameters	266	109
weighting fudge factor *p*	0.03	0.03
R	0.025	0.030
R_w	0.030	0.037
GOF	1.071	1.227

Reactions of 1 with HI in Dichloromethane. Gaseous anhydrous hydrogen iodide was prepared from the reaction of I_2 with boiling tetralin, according to the method described by Hoffmann,[36] slightly modified by putting after the trap immersed in an ice bath a trap cooled by acetone/dry ice and containing anhydrous CH_2Cl_2. The saturated solution of HI so obtained, free from I_2, was allowed to equilibrate at room temperature and then titrated with 0.01 N NaOH (titer ca. 0.015 N) and immediately used. In five different experiments, 15-mg samples of **1**, dissolved in 2 mL of CH_2Cl_2, were treated respectively with 1, 1.5, 2, 3, and 4 mL of the HI solution. GLC analysis showed H_2 evolution, while IR and NMR analyses revealed the formation of all the intermediates and final products obtained in the reactions with I_2.

X-ray Analysis of Compounds 3 and 4. Data Collections. Colorless crystals of both compounds were investigated beforehand by precession photographs and were found to be monoclinic primitive (**3**) and monoclinic *C* centered (**4**), respectively. A flat parallelepiped of **3** of dimensions 0.07 × 0.15 × 0.25 mm and an elongated prism of **4** of dimensions 0.06 × 0.07 × 0.20 mm were mounted on glass fibers in the air and transferred to an automated Enraf-Nonius CAD4 diffractometer. The radiation used was graphite-monochromatized Mo Kα (λ = 0.71073 Å). In both cases the setting angles of 25 random reflections (16° < 2θ < 25°) were used to determine by least-squares fit accurate cell constants and orientation matrices. The crystallographic data are reported in Table IV. The two data collections were performed by the ω-scan method, within the limits 3° < θ < 23° (**3**) and 3° < θ < 25° (**4**), using variable scan speed (from 2 to 20°/min) and a variable scan range of $(\alpha + 0.35 \tan \theta)°$ (α = 0.9 (**3**) and 0.8 (**4**)), with a 25% extension at each end for background determination. The total number of collected data was 4115 for compound **3** and 2147 for **4**. The intensities of three standard reflections were measured every 2 h of X-ray exposure, and no significant decay was observed for either crystal.

The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied in both cases based on ψ scans (ψ 0–360° every 10°) of suitable reflections with χ values close to 90°; the maximum, minimum, and average relative trans-

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Table V. Final Positional Parameters within $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}][N(C_2H_5)_4]$ (3)

atom	*x*	*y*	*z*
Re1	0.13098 (5)	0.39095 (4)	0.39450 (2)
Re2	0.29869 (5)	0.21226 (4)	0.32948 (2)
Re3	0.55089 (5)	0.26867 (4)	0.41797 (2)
I1	0.36418 (8)	0.38124 (7)	0.47628 (3)
I2	0.38355 (9)	0.08977 (6)	0.42460 (4)
O11	0.0169 (10)	0.5829 (6)	0.4503 (4)
O12	−0.1142 (10)	0.3892 (9)	0.2998 (3)
O13	0.3136 (11)	0.5403 (9)	0.3317 (4)
O14	−0.0235 (8)	0.2306 (6)	0.4602 (3)
O21	0.4785 (10)	0.0848 (9)	0.2609 (4)
O22	0.2155 (11)	0.3591 (11)	0.2326 (3)
O23	0.0448 (10)	0.0705 (9)	0.2909 (5)
O31	0.7508 (10)	0.1550 (8)	0.3528 (4)
O32	0.7091 (11)	0.4669 (7)	0.4008 (4)
O33	0.7373 (10)	0.2241 (9)	0.5283 (4)
C11	0.059 (1)	0.5134 (10)	0.4287 (5)
C12	−0.022 (1)	0.3908 (10)	0.3354 (4)
C13	0.247 (1)	0.4863 (11)	0.3539 (5)
C14	0.031 (1)	0.2910 (9)	0.4365 (4)
C21	0.411 (1)	0.1307 (12)	0.2874 (5)
C22	0.244 (1)	0.3029 (12)	0.2699 (5)
C23	0.140 (1)	0.1247 (11)	0.3044 (6)
C31	0.677 (1)	0.1968 (9)	0.3771 (5)
C32	0.649 (1)	0.3919 (9)	0.4092 (5)
C33	0.671 (1)	0.2398 (9)	0.4869 (5)
N	0.233 (1)	0.1850 (8)	0.6352 (4)
Ct11	0.175 (2)	0.167 (1)	0.5762 (5)
Ct12	0.380 (1)	0.140 (1)	0.6473 (5)
Ct13	0.237 (2)	0.301 (1)	0.6444 (6)
Ct14	0.153 (2)	0.132 (1)	0.6748 (7)
Ct15	0.165 (2)	0.052 (1)	0.5573 (7)
Ct16	0.482 (2)	0.191 (1)	0.6138 (6)
Ct17	0.302 (2)	0.339 (2)	0.7000 (7)
Ct18	−0.001 (2)	0.168 (2)	0.6656 (7)
Hy1	0.190 (7)	0.268 (5)	0.382 (3)
Hy2	0.446	0.302	0.351

mission values were 1.00, 0.50, and 0.80 for **3** and 1.00, 0.82, and 0.92 for **4**, respectively.

Two sets of 2646 (**3**) and 1353 (**4**) independent significant reflections, with $I > 3\sigma(I)$, were used in the structure solutions and refinements.

Structure Solutions and Refinements. All computations were performed on a PDP 11/34 computer, using the Enraf-Nonius structure determination package (SDP) and the physical constants tabulated therein.

Both structures were solved by Patterson methods, which showed the locations of the heavy Re and I atoms. After preliminary refinements of the parameters of these atoms successive Fourier maps gave the positional parameters of all the non-hydrogen atoms.

In the structure of compound **4** both the anion and the cation were found to lie in special positions, about twofold crystallographic axes of the space group *C*2/*c*; the $N(C_2H_5)_4^+$ cation is disordered, with the nitrogen atoms positioned on the axis and the four ethyl groups doubled by the same axis, resulting in eight independent carbon atoms of half-weight.

Table VI. Final Positional Parameters within $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6][N(C_2H_5)_4]$ (4)

atom	*x*	*y*	*z*
Re	−0.09030 (3)	0.14463 (3)	0.16167 (3)
I	0.07575 (6)	0.01928 (7)	0.16810 (6)
O1	−0.2508 (7)	0.2926 (9)	0.1824 (9)
O2	−0.2435 (7)	−0.0016 (9)	0.0111 (8)
O3	−0.0753 (9)	0.2985 (10)	0.0026 (7)
C1	−0.1900 (8)	0.235 (1)	0.1742 (10)
C2	−0.1869 (9)	0.053 (1)	0.0674 (9)
C3	−0.0819 (10)	0.240 (1)	0.0619 (9)
N	0.0000	0.390 (1)	−0.2500
Ct1	0.075 (2)	0.383 (3)	−0.144 (2)
Ct2	0.076 (3)	0.499 (3)	−0.256 (3)
Ct3	−0.076 (3)	0.278 (3)	−0.255 (3)
Ct4	−0.041 (3)	0.399 (3)	−0.183 (3)
Ct5	−0.116 (2)	0.276 (3)	−0.402 (2)
Ct6	−0.157 (2)	0.280 (2)	−0.360 (2)
Ct7	0.085 (2)	0.513 (2)	−0.343 (2)
Ct8	−0.122 (2)	0.489 (2)	−0.183 (2)
Hy	0.0000	0.23 (2)	0.2500

The refinements were carried out by full-matrix least-squares methods. Anisotropic thermal factors were assigned to the anionic atoms, while the cations were refined isotropically, in both structures. In compound **3** the hydrogen atoms of the cation were located in their idealized positions (C–H = 0.95 Å, B = 5.0 Å^2), after each cycle of refinement, but not refined. Attempts were made to remove the disorder of the cation in the case of compound **4**, with the noncentrosymmetric *Cc* (No. 9) as space group, but refinements gave high correlations and unacceptable scattering in the bond parameters. Weights were assigned according to the formula $w = 1/\sigma_{F_o}{}^2$, where the σ values of the reflections were modified by a p fudge factor of 0.03 in both structures. The values of the conventional R and R_w factors were, at this point, 0.026 and 0.033 for **3** and 0.031 and 0.038 for **4**, respectively.

Difference-Fourier maps were subsequently performed in an attempt to locate the hydridic hydrogen atoms. In the case of compound **4** a suitable residual peak of ca. 0.8 e Å^{-3} was found, in addition to other comparable residues very close to the heavy Re and I atoms, lying on the twofold axis in the expected position for a bridging hydride. It was successfully refined, with convergence to reasonable bond parameters, although affected by high uncertainties. In the case of compound **3** the difference-Fourier synthesis showed as the highest residue a 0.82 e Å^{-3} peak close to the position expected for a bridging hydride on the Re1–Re2 edge, while only a minor suitable residue of 0.38 e Å^{-3} was found in a bridging location on the Re2–Re3 edge close to a higher peak of 0.62 e Å^{-3} (the second residual peak) at a distance of 1.3 Å from Re3. Almost the same situation was obtained on performing successive difference-Fourier maps at decreasing values of (sin θ)/λ down to 0.36. Refinements led to convergence for the locatable hydride, labeled Hy1, while the second one (Hy2) oscillated in position and moved unacceptably close to Re3. The idealized position of Hy2 was therefore calculated, determining the intersection point of the C23→Re2 and C33→Re3 vectors. This gave Re–H distances of 1.78 Å and a Re–H–Re angle of 121.4°. We then moved the hydride along the direction defined by the calculated point and the center of the Re2–Re3 edge slightly outward, in order to obtain Re–Hy2 bond lengths of 1.84 Å and a Re–H–Re angle of 114.7°. This atom was included in our model with fixed positional parameters and a fixed thermal factor of 5.0 Å^2. The final values of the agreement indices R and R_w were 0.025 and 0.030 for compound **3** and 0.030 and 0.037 for compound **4**, respectively. The final positional parameters are listed in Tables V and VI.

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Registry No. **1**, 64478-51-9; **2**, 81646-65-3; **3**, 86822-08-4; **4**, 86822-10-8; **5**, 60165-53-9; **6**, 68851-39-8; **7**, 15189-53-4.

Supplementary Material Available: Tables of thermal parameters for compounds **3** (Table A) and **4** (Table B), calculated cationic hydrogen positions for compound **3** (Table C), and observed and calculated structure factors for compounds **3** and **4** (32 pages). Ordering information is given on any current masthead page.