Synthesis, Solid-State Structure, Solution Dynamics, and Reactivity of the Trinuclear Open Cluster Anion $[Re_2(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]^-$

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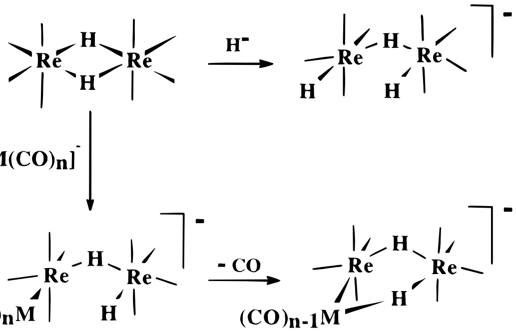
The addition of $[M(CO)_5]^-$ anions (M = Re, Mn) to the electronically unsaturated $[Re_2(\mu\text{-}H)_2(CO)_8]$ complex rapidly and selectively gives the trinuclear anions $[ReM(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]^-$ (M = Re, **2**; M = Mn, **3**). The single-crystal X-ray analysis of $[NEt_4]$**2** has revealed a fully staggered L-shaped structure. The anion **2** has been obtained with good selectivity also by reacting (i) $[Re_2(CO)_9(THF)]$ with $[H_2Re(CO)_4]^-$ and (ii) $[HRe_2(CO)_9]^-$ with $[HRe(CO)_5]$. The last reaction can be reversed upon treatment with CO. The reaction of the trinuclear open cluster $[Re_2(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$ with $[H_2Re(CO)_4]^-$ affords **2** as well, even if not quantitatively. ^1H and ^{13}C NMR spectra of **2** show conformational freedom around both the Re−Re interactions and a dynamic process exchanging the two hydrides and the carbonyls *trans* to them ($E_a = 67(2)$ kJ/mol). This last is attributable to a windshield-wiper motion of the $H_2Re(CO)_4$ fragment around the two *trans* diaxial carbonyls. The exchange of the hydrides with comparable $\Delta G^\ddagger$ has been observed also for **3**, suggesting that the same type of motion is occurring. ^{13}C-NMR studies of the related $[Re_2(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$ complex have shown the facile mobility of the bridging hydride between the two metal−metal interactions (at variance with the anion **2**), resulting in a "dynamic" C_{2v} symmetry of the molecule in solution. Upon heating, the anion **2** looses CO and gives irreversibly the previously known triangular cluster anion $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$. The addition of a strong acid (CF_3SO_3H) results in fragmentation of the trinuclear skeleton of **2**, affording $[HRe(CO)_5]$ and $[Re_2(\mu\text{-}H)_2(CO)_8]$.

Introduction

Rational and systematic syntheses of transition metal carbonyl clusters have been developed.[1] Among these, the reaction of ethylene-like $L_nM{=}ML_n$ complexes with carbenoid $:M'L_m$ organometallic fragments provides a well-established route to trimetallacyclopropane molecules.[2] This approach allowed in the last years the obtainment of several Re−Pt mixed-metal clusters, by reaction of the unsaturated complex $[Re_2(\mu\text{-}H)_2(CO)_8]$[3] (**1**) with PtL_2 species originated from $[Pt(PPh_3)_2(C_2H_4)]$ or $[Pt(C_8H_{12})_2]$.[4]

The ability of **1** to undergo the nucleophilic addition of hydride ligands,[5] as shown in Scheme 1, prompted us to investigate a different approach to the synthesis of trinuclear clusters from dinuclear unsaturated complexes, involving as the first step the addition to **1** of transition metal carbonylates, isolobal with halide anions (Scheme 1). This has been successfully performed with the $[Ir(CO)_4]^-$ anion.[6] In this case the addition product $[Re_2H(\mu\text{-}H)(CO)_8\{Ir(CO)_4\}]^-$ was exceedingly unstable and could be characterized only spectroscopically below −20 °C, because of easy CO evolution and cyclization. We report here on the reaction of **1** with the pentacarbonylmetalates of Re and Mn, which allowed the obtainment of the trinuclear anions $[ReM(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]^-$ (M = Re, **2**; M = Mn, **3**), in which the open cluster structure is significantly more stable. Alternative rationale routes to the trirhenium species **2** are also presented.

Scheme 1



⊗ Abstract published in *Advance ACS Abstracts,* August 1, 1996.

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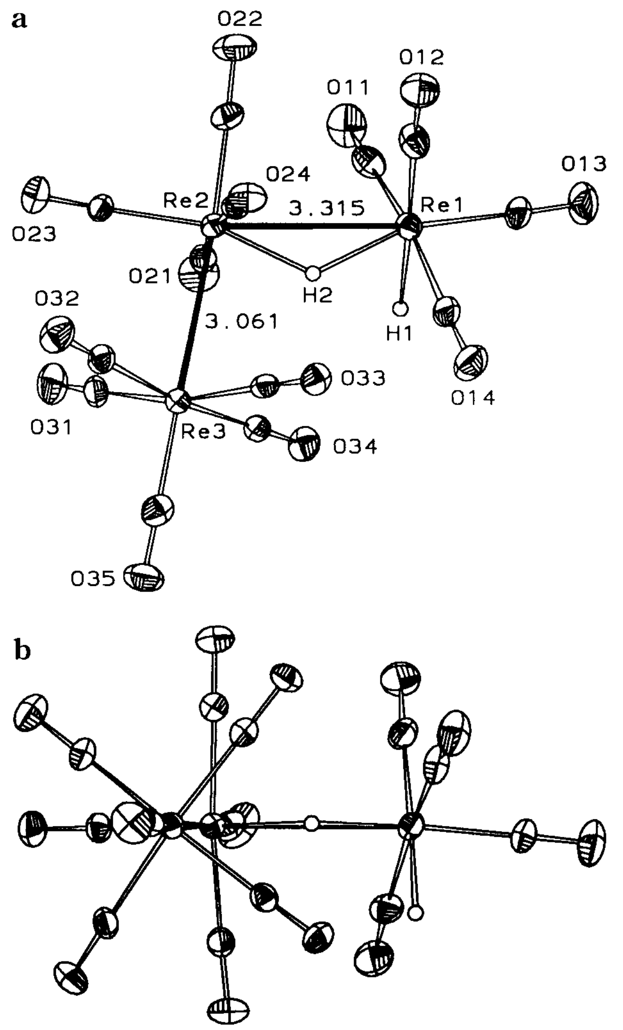

Figure 1. ORTEP views of the $[Re_2(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]^-$ anion (**2**): (a) along the normal to the metal atoms plane; (b) after 90° rotation around the Re(1)−Re(2) bond. Thermal ellipsoids are drawn at the 30% probability level. Hydride ligands are in calculated positions and are drawn with an arbitrary small radius.

Results and Discussion

The treatment of a THF solution of $[Re(CO)_5]^-$ [either Na^+, NEt_4^+, or $N(PPh_3)_2^+$ (PPN^+) as counterions] with equimolar $[Re_2(\mu\text{-}H)_2(CO)_8]$ (**1**) at 250 K causes the instantaneous formation of the addition derivative $[Re_2(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]^-$ (**2**). IR and NMR monitoring assessed the high selectivity of reaction 1.

$$[Re_2(\mu\text{-}H)_2(CO)_8] + [Re(CO)_5]^- \rightarrow [Re_2(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]^- \quad (1)$$

Solid-State Structure. The X-ray diffraction experiment has been performed on a single crystal of the $(NEt_4)^+$ salt of $[Re_2(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]^-$ (**2**). The crystal structure consists of the packing of discrete ions separated by normal van der Waals contacts. The overall stereochemistry of the anion **2** and the numbering scheme for the atoms are shown in Figure 1. Relevant bond distances and angles are reported in Table 1, while atomic coordinates and equivalent isotropic displacement parameters are available in the Supporting Information.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[Re_2(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]^-$ (2)

Re(1)−Re(2)	3.3150(8)	Re(2)−Re(3)	3.0610(8)
Re(1)−C(11)	1.96(2)	C(11)−O(11)	1.15(2)
Re(1)−C(12)	1.95(2)	C(12)−O(12)	1.15(2)
Re(1)−C(13)	1.91(1)	C(13)−O(13)	1.14(2)
Re(1)−C(14)	1.97(2)	C(14)−O(14)	1.13(2)
Re(2)−C(21)	1.97(2)	C(21)−O(21)	1.16(2)
Re(2)−C(22)	1.89(2)	C(22)−O(22)	1.17(2)
Re(2)−C(23)	1.92(1)	C(23)−O(23)	1.13(2)
Re(2)−C(24)	1.98(1)	C(24)−O(24)	1.13(2)
Re(3)−C(31)	2.01(2)	C(31)−O(31)	1.12(2)
Re(3)−C(32)	1.97(1)	C(32)−O(32)	1.14(2)
Re(3)−C(33)	1.98(2)	C(33)−O(33)	1.16(2)
Re(3)−C(34)	1.98(2)	C(34)−O(34)	1.14(2)
Re(3)−C(35)	1.91(2)	C(35)−O(35)	1.16(2)

Re(1)−Re(2)−Re(3)	103.01(2)	C(21)−Re(2)−Re(3)	85.0(4)
C(11)−Re(1)−Re(2)	78.1(5)	C(22)−Re(2)−Re(3)	175.6(5)
C(12)−Re(1)−Re(2)	85.7(5)	C(23)−Re(2)−Re(3)	86.1(4)
C(13)−Re(1)−Re(2)	170.8(5)	C(24)−Re(2)−Re(3)	89.3(4)
C(14)−Re(1)−Re(2)	102.2(4)	C(31)−Re(3)−Re(2)	84.6(5)
C(21)−Re(2)−Re(1)	85.6(4)	C(32)−Re(3)−Re(2)	85.6(4)
C(22)−Re(2)−Re(1)	81.4(5)	C(33)−Re(3)−Re(2)	82.7(4)
C(23)−Re(2)−Re(1)	170.8(4)	C(34)−Re(3)−Re(2)	86.9(4)
C(24)−Re(2)−Re(1)	89.5(4)	C(35)−Re(3)−Re(2)	178.2(4)

The L-shaped metal skeleton of **2** is similar to that found in $[Re_2(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$ (**4**),[7] $[MnRe(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$ (**5**),[8] $[ReMn(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$,[9] $[Mn_2(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$,[10] and $[Mn_2(CO)_9\{(\mu\text{-}H)Ta(CO)(C_5H_5)_2\}]$.[11] The presence of a bridging hydride apparently is the key factor in determining the L-shape of these 50 valence electron trinuclear clusters. In fact $[Mn_3(CO)_{14}]^-$,[12] $[MnFeMn(CO)_{14}]$,[13] $[ReIrReH(CO)_{13}]$,[14] and many others, which lack a bridging hydride, have a linear metal skeleton. However, when a pseudotetrahedral metal atom is forced in the middle position, like in $[(CO)_2CpRuZr(Cp)_2RuCp(CO)_2]$,[15] an L-shaped skeleton is also observed.

It is well-known that facing ML_5 units connected by a M−H−M bond can be mutually staggered or eclipsed, while, when joined by a (single) M−M bond, they are invariably staggered. In the title compound both the M−M-bonded $(CO)_5Re{-}ReM(CO)_4$ and the hydride-bridged $(CO)_4MRe{-}H{-}ReH(CO)_4$ moieties are staggered, like in $[Re_2(CO)_9(\mu\text{-}H)Re(CO)_5]$. However, all the related Mn−Re mixed-metal systems $[MnRe(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$, $[ReMn(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$, and $[Mn_2(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$ have a staggered/eclipsed conformation. Given that packing interactions are large enough to drive the staggered/eclipsed conformational choice of the $L_5M{-}H{-}ML_5$ system, as evidenced by the different stereochemistries of the $[W(CO)_5(\mu\text{-}H)W(CO)_5]^-$

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anion with different counterions (PPN^+ *vs* NEt_4^+),[16] we do not dare to offer any explanation for the different behavior of the Re−Re and the Mn−Re systems. As usual, staggered $L_5M{-}H{-}ML_5$ systems have shorter M−H−M bond distances than the eclipsed ones because of the more favorable interlocking of two nearby staggered unit (*i.e.* 3.315(1) Å in **2** *vs* 3.392(2) Å in **5**). On the contrary, staggered/staggered conformers have larger M−M−M bond angles (i.e. longer 1,3 M···M interactions) than the staggered/eclipsed ones because two staggering 1,2 relationships eventually afford a 1,3 eclipsed relationship between the ligands of the two (cis) terminal metal atoms (*i.e.* 103.01(2)° in **2** *vs* 98.09(7)° in **5**).

Even if lacking of clear-cut indications from the difference Fourier map, the locations of the hydrido ligands has been straightforward since the apparent hole in the coordination geometry of Re(1) clearly implies the presence of a terminal hydride while the lengthening of the Re(1)−Re(2) bond distance implies a bridging hydrido ligand. A detailed analysis of the Re−Re−C bond angles about Re(1) and Re(2), further surrogated by potential energy computations,[17] eventually allowed us to locate the bridging hydrido ligand substantially in the plane of the three metal atoms. The neutron diffraction study on $[Mn_2(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$[10] has clearly shown, for a staggered/eclipsed conformer, that the hydride also substantially lies in the plane of the three metal atoms. Thus, in spite of the large stereochemical differences between the staggered/staggered and the staggered/eclipsed conformers they share the "in-plane" location of the bridging hydrido ligand.

NMR Studies and Dynamic Behavior in Solution. The low-temperature ^1H NMR spectrum shows two hydridic resonances, at δ values typical of terminal (−5.7 ppm) and bridging (−16.6 ppm) hydrido ligands (J_{HH} = 4.0 Hz) in Re carbonyl complexes. On an increase of the temperature, these resonances broaden and collapse, indicating the occurrence of a dynamic process that exchanges the two types of hydrides. The rate constants at different temperatures, determined through the band shape analysis (see Experimental Section), led to an activation energy, E_a, of 63(1) kJ/mol.

To get a better insight into the mechanism of the dynamic process, a ^{13}C-enriched sample was prepared. The low-temperature spectrum (Figure 2a) showed eight signals in the carbonyl region, whose assignment (see Table 2 and Scheme 2) has been made on the basis of selective decouplings, of the behavior on raising the temperature, and of the ^{13}C relaxation times.

Selective decoupling experiments (see Figure 2) allowed the identification of the resonances of carbonyls C, E, F, G, and I of Scheme 2, as reported in Table 2.

The lowest field signal (intensity 4), not affected by selective decoupling, is attributable to the four mutually trans carbonyls A on Re(3). This resonance is broad at 193 K and broadens further on raising the temperature, being hardly detectable at room temperature. The same behavior is observed for the highest field signal (δ 187.7, intensity 1), thus suggesting the attribution to the carbonyl B of the same $Re(CO)_5$ moiety. This has been confirmed by the preparation of a sample of **2** selectively enriched in this site (see below). The broadening is not due to chemical exchange, since the line widths appear insensitive to the change of magnetic field ($\Delta\nu_{1/2}$ = 17 Hz at 4.7 T and 238 K *vs* $\Delta\nu_{1/2}$ = 20 Hz at 1.8 T and 235 K for the signal at 198.3 ppm), but is rather due to the coupling with the quadrupolar isotopes of rhenium (^{185}Re natural abundance 37.07%, $I = {}^5/_2$; ^{187}Re natural abundance 62.93%, $I = {}^5/_2$). It is likely that the

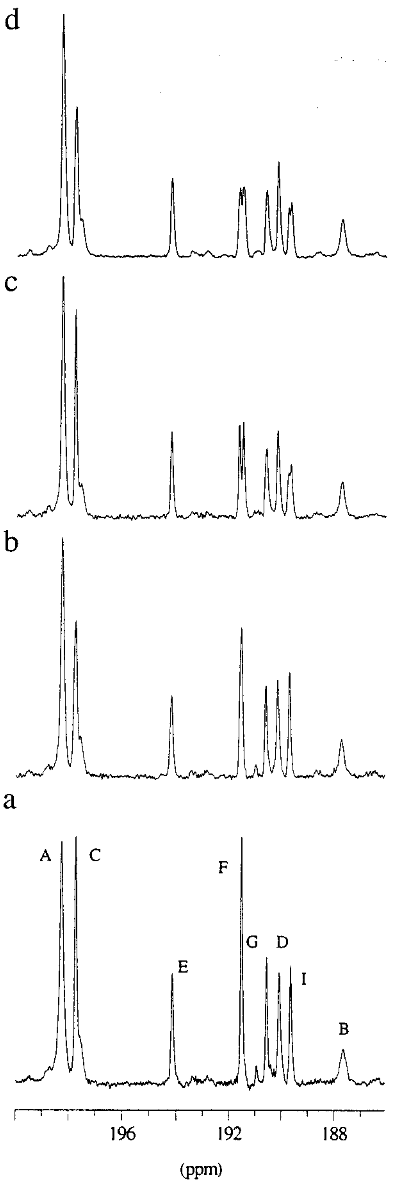

Figure 2. Carbonyl region of the ^{13}C NMR spectrum of the anion **2** (198 K, 50.3 MHz, THF-d_8): (a) ^1H decoupled; (b) selectively decoupled at −5.8 ppm; (c) selectively decoupled at −16.6 ppm; (d) ^1H coupled. The irradiation at −5.8 ppm (b) sharpens the resonances at 191.5(*2*) and 189.6(*1*) ppm in comparison with the coupled spectrum (d), while a minor effect is observed on the one at 190.6(*1*) ppm. After the irradiation of the bridging hydride (c) enhancement is observed for the signals at 197.7(*2*), 194.1(*1*), and 191.5(*2*) ppm, with minor effects on the other signals at 191.5−189.5 ppm. The signals at 191.5(*2*) and at 189.6(*1*) ppm show clearly a residual coupling (J_{CH} = 8 and 5 Hz, respectively). These carbonyls therefore can be identified as those bound to Re(1) (F and I in Scheme 2), *cis* to the terminal hydride, while the one at 190.6(*1*) ppm is G, *trans* to the terminal hydride.[47] The other resonance of intensity 2 is assigned to carbonyls C, and that at 194.1 ppm, to carbonyl E, both *cis* to the bridging hydride on Re(2).

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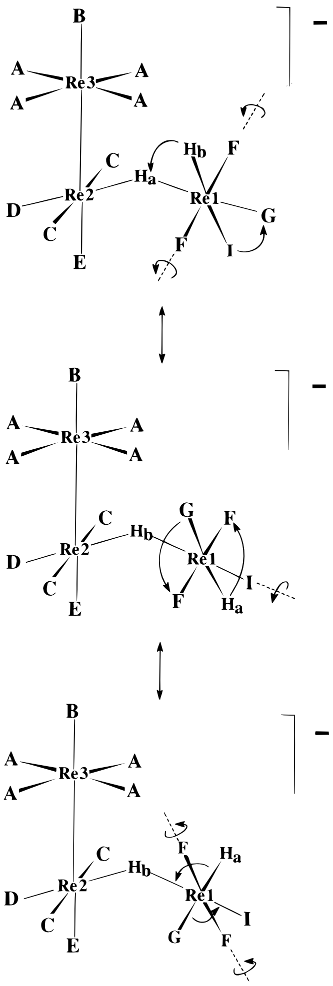
Table 2. Chemical Shifts, Relaxation Times (with the Uncertainties of the Last Digits in Parentheses), and Assignments of the ^{13}CO Resonances of Compound 2

δ (ppm)	rel intensity	T_1 (s)	assgnt
198.3	4	0.83(2)	A
197.8	2	0.51(1)	C
194.1	1	0.34(1)	E
191.5	2	1.12(2)	F
190.6	1	1.11(3)	G
190.1	1	0.29(2)	D
189.6	1	0.78(2)	I
187.7	1	0.53(5)	B

Scheme 2



relaxation time of Re(3) only at low temperatures is short enough to “decouple” these carbonyls.

^{13}C longitudinal relaxation times have been measured at 193 K at 4.7 T (Table 2). It has been previously shown[18] that the longitudinal relaxation of ^{13}C bound to rhenium is due to the scalar coupling interaction with the quadrupolar isotopes of rhenium. This mechanism makes the ^{13}C relaxation times sensitive to the T_2 of the metal to which they are bound and to the coupling constant with the metal that, in turn, is dependent on the nature of the ligand *trans* to the carbonyl. The comparison of the relaxation times of the carbonyls bound to the same metal can therefore be helpful for their assignments. The data in Table 2 confirm the results of the selective decoupling. As far as Re(1) is concerned, the mutually *trans* carbonyls F are expected to exhibit a small coupling constant with the metal due to their high *trans* influence and a long T_1 was indeed measured. The relaxation times of the carbonyls G and I (1.11 s *vs* 0.78 s) are in line with the greater *trans* influence of a terminal hydride with respect to a bridging one. The relaxation times of the carbonyls A and B bound to Re(3) (0.83 s *vs* 0.53 s) show the trend of *trans* influence CO > M−M. For the resonances of intensity 1 on Re(2) the known order of *trans* influence ($M-M > \mu\text{-}H$)[19] further supports the previous assignment (Table 2).

The overall results indicate therefore the following series of relative *trans* influence: $H(\text{terminal}) \approx CO > M-M > \mu\text{-}H$.

On the basis of the solid-state structure, thirteen carbonyl resonances were expected instead of the eight observed: the equivalence, already at low temperature, of the four equatorial carbonyls A on Re(3) and of the two mutually *trans* carbonyls C on Re(2) and F on Re(1) shows that there is conformational freedom of the external metal moieties around the M−M and M(μ-H)M bonds.

On an increase of the temperature, the resonances of carbonyls G and I broaden, collapse, and eventually give rise to an averaged signal ($\Delta\nu_{1/2} = 4$ Hz at 228 K and 9.5 Hz at 248 K). The simulation of the spectra recorded at different temperatures gave rate constants very close to the ones obtained by the proton spectra (see Experimental Section), indicating that the same process is responsible for the exchange of the carbonyls and of the hydrides. The activation energy obtained by the overall data is 67(2) kJ/mol. The most likely mechanism that could explain the observed exchange is a windshield-wiper motion of the Re(1) moiety around the two diaxial carbonyls F (Scheme 2). This motion, coupled with a rotation around the $H_b-Re(1)-I$ axis, leads to the simultaneous interchange of the bridging and the terminal hydride as well as of the two carbonyls I and G. A similar process was observed in the related $[Re_2H_2(\mu\text{-}H)(CO)_8]^-$ anion of Scheme 1,[5] but in the present case the motion is significantly more hindered ($\Delta G^\ddagger = 54(1)$ kJ mol^{-1} at 260 K for **2** *vs* $\Delta G^\ddagger = 42$ kJ mol^{-1} at 225 K for the trihydridic anion).

It is noteworthy that in compound **2** the exchange is strictly localized on the moiety bearing the two hydrides. Indeed ^{13}C NMR analysis of a sample of **2** prepared from ^{13}CO enriched $[Re(CO)_5]^-$ and natural abundance $[Re_2(\mu\text{-}H)_2(CO)_8]$ showed that *only* the resonances at 198.3 and 187.7 ppm had increased intensities, indicating that no intramolecular CO exchange had occurred, even in times much longer than the NMR time scale. Upon further addition of $[Re(CO)_5]^-$, in natural abundance, no broadening of the signals nor enhancement of the CO resonance of free $[Re(CO)_5]^-$ was observed, even at longer times, ruling out also intermolecular CO or fragment exchange.

In order to compare the dynamic behavior of compound **2** with that of the other L-shaped trirhenium cluster, we have prepared a ^{13}C-enriched sample of $[Re_2$-

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$(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$ (**4**), where the terminal hydride of **2** is formally substituted by a carbonyl. Even at low temperature, the ^{13}CO region of its NMR spectrum shows only four signals (δ 197.4(*1*), 192.5(*1*), 187.8(*4*), and 180.6(*1*) ppm, 50.32 MHz, 191 K, THF-d_8). The two high-field resonances are broader than the other ones and attributable to the two terminal $Re(CO)_5$ moieties, made equivalent by the easy exchange of the hydride between the two metal–metal interactions, that creates a "dynamic" C_{2v} symmetry. Therefore, at variance with **2**, the bridging hydride is highly mobile and interacts with all the three metals. A similar process is expected to be kinetically easy also in compound **2**. In this case, however, it would not be a mutual exchange but an isomerization leading to a species probably unfavored thermodynamically. A motion of a bridging hydride from a Mn–Re to a Mn–Mn interaction has been previously suggested to account for the Re–Mn exchange in $[Mn_2(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$.[9]

Decarbonylation of 2. In the previously reported[6] reaction of **1** with $[Ir(CO)_4]^-$, the Re_2Ir open cluster derivative was highly unstable and very rapidly eliminated a carbonyl ligand to give a triangular cluster species (Scheme 1). In the present case, CO loss from the $Re(CO)_5$ spike of **2** gives the previously known[20] triangular cluster anion $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$, according to eq 2. This reaction, however, is extremely slow, some

$$[Re_3H(\mu\text{-}H)(CO)_{13}]^- \rightarrow [Re_3(\mu\text{-}H)_2(CO)_{12}]^- + CO \quad (2)$$

unreacted **2** being still present after 45 h at reflux in tetrahydrofuran. Reaction 2 was not reversed upon treatment with CO, even on using a high CO pressure (100 atm, 20 h at room temperature).

The much higher cyclization rate for the Re_2Ir anion is likely related to the pentacoordination in the Ir spike, which allows the nucleophilic attack of the Re–H bond. In other words, the substitution of a carbonyl by the Re–H bond can proceed *via* an associative mechanism, while in the case of the anion **2** the rate-determining CO dissociation requires thermal activation. It is also noteworthy that while a number of clusters containing $Re(CO)_5$ spikes are known, no compound of this type has been reported with $Ir(CO)_4$.

Alternative Syntheses of 2. The view of **2** as a substitution derivative of $[Re_2(CO)_{10}]$ suggested to prepare it by reaction of the mononuclear anion $[H_2Re(CO)_4]^-$ [21] with a $[Re_2(CO)_9L]$ complex, containing a labile L ligand in radial position. The synthesis of H-bridged polynuclear complexes by interaction of an H "donor" with a coordinatively unsaturated "acceptor" is a well-established method[22] and in particular it has been previously used[10] for the synthesis of the L-shaped complex $[Mn_2(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$, by reaction of $[HRe(CO)_5]$ with $[Mn_2(CO)_9(\eta^1\text{-tolualdehyde})]$. The $[H_2Re(CO)_4]^-$ anion here used had been previously[23] found able to substitute two acetonitrile ligands in $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$, giving the tetranuclear butterfly cluster anion $[Re_4(\mu\text{-}H)_5(CO)_{14}]^-$. In the present case, however, no reaction was observed with $[Re_2(CO)_9(NCMe)]$, in agreement with the failure[10] of the attempted synthesis of the above Mn_2Re cluster by reaction of $[HRe(CO)_5]$ with $[Mn_2(CO)_9(NCMe)]$. The more reactive $[Re_2(CO)_9(THF)]$ starting material was then prepared, by treating $[Re_2(CO)_{10}]$ with anhydrous Me_3NO, in THF solution. The addition of equimolar $[H_2Re(CO)_4]^-$, at room temperature, in THF solution, caused the quick formation of **2** (eq 3), with very good selectivity, as judged by NMR monitoring.

$$[Re_2(CO)_9(OC_4H_8)] + [H_2Re(CO)_4]^- \rightarrow [Re_3H(\mu\text{-}H)(CO)_{13}]^- + C_4H_8O \quad (3)$$

The substitution of the neutral equatorial "ligand" $HRe(CO)_5$ in the open cluster $[Re_2(CO)_9\{(\mu\text{-}H)Re(CO)_5\}]$ (**4**) by the anionic and, therefore, stronger "ligand" $H_2Re(CO)_4^-$ was also attempted, according to eq 4. The

$$[Re_2(CO)_9\{(\mu\text{-}H)Re(CO)_5\}] + [H_2Re(CO)_4]^- \rightarrow [Re_2(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]^- + [HRe(CO)_5] \quad (4)$$

slow formation of **2** and $[HRe(CO)_5]$ was indeed observed but accompanied by several other bi- and trinuclear species, as detailed in the Experimental Section. Therefore, we cannot state with certainty that the observed **2** arose from reaction 4 rather than from some other rearrangement or condensation of the various hydrido–carbonyl species present in solution. The $[H_2Re(CO)_4]^-$ anion in solution at room temperature easily undergoes a number of condensation reactions to polynuclear species.[21] In particular, we have now shown that it is able to react with $[HRe(CO)_5]$, formed in reaction 4, giving mainly the dinuclear anion $[Re_2H_2(\mu\text{-}H)(CO)_8]^-$ [5] (eq 5), which is one of the observed byproducts.

$$[H_2Re(CO)_4]^- + [HRe(CO)_5] \rightarrow [Re_2H_2(\mu\text{-}H)(CO)_8]^- + CO \quad (5)$$

The analogous condensation between $[HRe(CO)_5]$ and the pentacarbonylrhenate (eq 6) has been recently

$$[Re(CO)_5]^- + [HRe(CO)_5] \rightarrow [HRe_2(CO)_9]^- + CO \quad (6)$$

$$[HRe_2(CO)_9]^- + [HRe(CO)_5] \rightarrow [Re_3H(\mu\text{-}H)(CO)_{13}]^- + CO \quad (7)$$

reported.[4] This suggested a further synthetic route to the anion **2**, using $[HRe_2(CO)_9]^-$,[5,24] according to eq 7. The reaction proceeds quite easily at room temperature and affords **2** with good selectivity.

Reactivity of 2. All the previously known L-shaped $[Re_{3-n}Mn_nH(CO)_{14}]$ molecules (n = 0, 1, 2) contain a $HRe(CO)_5$ molecule coordinated in radial position to a $[M_2(CO)_9]$ skeleton (M_2 = Re_2, MnRe, ReMn, or Mn_2). The few reactivity data available for these compounds indicate that the organometallic ligand can be displaced by classical ligands L, such as CO (or MeCN for the Re_2

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case), with formation of free $[HRe(CO)_5]$ and $[M_2(CO)_9L]$ derivatives.[7−10,25]

We investigated therefore the reactivity of the anion **2** with two-electron donors. If the above reported failure of substituting MeCN by $[H_2Re(CO)_4]^-$ in $[Re_2(CO)_9(NCMe)]$ was due to thermodynamic reasons, acetonitrile could be a ligand able to displace $[H_2Re(CO)_4]^-$. No reaction, however, was observed, even on using acetonitrile as solvent. In the presence of CO, on the contrary, a slow reaction took place, leading however not to $[Re_2(CO)_{10}]$ and $[H_2Re(CO)_4]^-$ but to $[HRe_2(CO)_9]^-$ and $[HRe(CO)_5]$, in equimolar ratio, according to the reverse of eq 7. In order to clarify the origin of the $[HRe(CO)_5]$ fragment, the reaction was monitored using natural abundance CO and the isotopomer of **2** selectively ^{13}CO enriched in the $Re(CO)_5$ spike. The ^{13}C NMR spectra showed that both the products $[HRe_2(CO)_9]^-$ and $[HRe(CO)_5]$ contained ^{13}CO.[26] The formation of a symmetrical intermediate containing two $[(\mu\text{-}H)Re(CO)_5]$ groups *cis* bound to a central $Re(CO)_4$ unit could account for this.

The reactivity with $[Re(CO)_5]^-$ was also investigated, to verify if this strong nucleophile[27] was able to substitute the $[H_2Re(CO)_4]^-$ "ligand" and/or to give mutual exchange with the $Re(CO)_5$ spike (a process detectable on using ^{13}CO-enriched isotopomers; see above). However, ^1H and ^{13}C NMR monitoring showed that no reaction occurs between **2** and the pentacarbonylrhenate. This allows also to rule out any significant protonic polarization of the hydrido ligands, since $[Re(CO)_5]^-$ is a strong Brönsted base.[28]

Further experiments were performed to verify if the H ligands have some hydridic (H^-) character, as is often the case for anionic transition metals hydrido complexes.[29] A relationship has been previously found between the ability of hydrido−carbonylates to serve as hydride donors and their tendency to interact with Lewis acids, such as alkali cations, at the metal hydride site.[30] This type of interaction can be revealed by observing the effect of the counterion on the δ value of the hydridic resonances: high-field shifts up to more than 1 ppm have been observed, in THF solution, for the alkali cations salts, with respect to the salts with larger cations, such as Et_4N^+ or PPN^+.[30] In the present case, the changes of chemical shifts of the hydridic resonances are small (δ −5.82 and −16.65 for Na^+, δ −5.77 and −16.62 for PPN^+, THF, 193 K), indicating that the interactions of the H ligands with the alkali cation (and therefore their hydridic character) are not particularly strong.

In line with this, strong acids did not cause significant H_2 evolution but rather clean fragmentation of the trinuclear unit, according to eq 8. The protonation

$$[Re_3H(\mu\text{-}H)(CO)_{13}]^- + H^+ \rightarrow [Re_2(\mu\text{-}H)_2(CO)_8] + [HRe(CO)_5] \quad (8)$$

likely occurs on the unbridged Re−Re interaction and weakens the metal−metal interaction. Reaction 1 is then reversed, $[HRe(CO)_5]$ being a worse donor than $[Re(CO)_5]^-$.

Mixed-Metal $[MnRe(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]^-$. The addition of $[Mn(CO)_5]^-$ to $[Re_2(\mu\text{-}H)_2(CO)_8]$ caused the instantaneous formation of a species that at 203 K exhibits two hydridic resonances, of the same integrated intensities, at δ values typical of a terminal (−5.79) and a bridging (−16.24) H ligand ($J_{HH} = 6.5$ Hz). The reaction product can therefore be formulated as the addition derivative $[ReMn(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]^-$ (**3**) with a structure analogous to that of **2**. The dynamic behavior in solution is also quite similar to that of **2**, because, on increasing the temperature, the hydridic resonances broaden and coalesce at room temperature, giving an averaged signal at δ −11.0 ppm (333 K), with $\Delta G^\ddagger = 55(1)$ kJ mol^{-1} at 263 K.

Conclusions. Three clean synthetic routes to the novel open cluster $[Re_2(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]^-$ anion have been found (Scheme 3). All involve condensation between a neutral and an anionic reagent and belong to three general types of cluster growth reactions:[1] (i) addition of organometallic fragments to an unsaturated complex;[2] (ii) substitution of a labile ligand by a H−M σ-donor anionic ligand;[22] (iii) substitution of a CO ligand by an anionic ligand (redox condensation).[31] Particularly interesting, within this latter class, are the clean reactions of $[HRe(CO)_5]$ with H−M anionic σ-donors (eqs 5 and 7).

It is also worth noting that method (i) has so far allowed the addition to $[Re_2(\mu\text{-}H)_2(CO)_8]$ only of carbenoid or anionic organometallic fragments, but we failed to add neutral H−M σ-donors, such as $[HRe(CO)_5]$. The fragmentation of **2** upon protonation indicates that this could be due not to a failure of the method (kinetic barrier) but to the thermodynamic instability of the hypothetical "$Re_3H(\mu\text{-}H)_2(CO)_{13}$" product with respect to $[Re_2(\mu\text{-}H)_2(CO)_8]$ and $[HRe(CO)_5]$.

The anion **2** exhibits the L-shape of the previously known 50 valence electron trinuclear clusters containing a bridging hydrido ligand. The substitution of a carbonyl in the complex **4** by an H^- ligand in **2** has only minor structural effects. The staggered−staggered conformation of **4** is maintained also in the solid-state structure of **2**. In solution, conformational freedom around the metal−metal interactions, even if H-bridged, has been indicated by the low-temperature ^{13}C NMR spectra of both the species, the number of ^{13}C signals being dictated only by the local symmetry.

On the contrary, the exchange of the bridging hydride between the two Re−Re interactions, which on a struc-

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(26) Further investigation on this point is on schedule. All the carbonyl sites of $[HRe_2(CO)_9]^-$ resulted homogeneously enriched in ^{13}CO. This could be due to some fluxional process exchanging the carbonyls between the two metallic sites: the ^{13}C-NMR analysis showed indeed that, above 273 K, in THF-d_8, all the resonances broaden,[24] but the reasons have still to be clarified (quadrupolar broadening[24] or/and localized or/and nonlocalized CO exchange). On the other hand, when reaction 7 was performed with ^{13}CO-enriched $[HRe_2(CO)_9]^-$ and natural abundance $[HRe(CO)_5]$, an equilibrium mixture was obtained in which the anion **2** and the unreacted reagents showed the same ^{13}CO abundance. This could be explained by the reversibility of the reaction and an intermetallic fluxionality of the carbonyls in $[HRe_2(CO)_9]^-$, but alternative explanations are possible.

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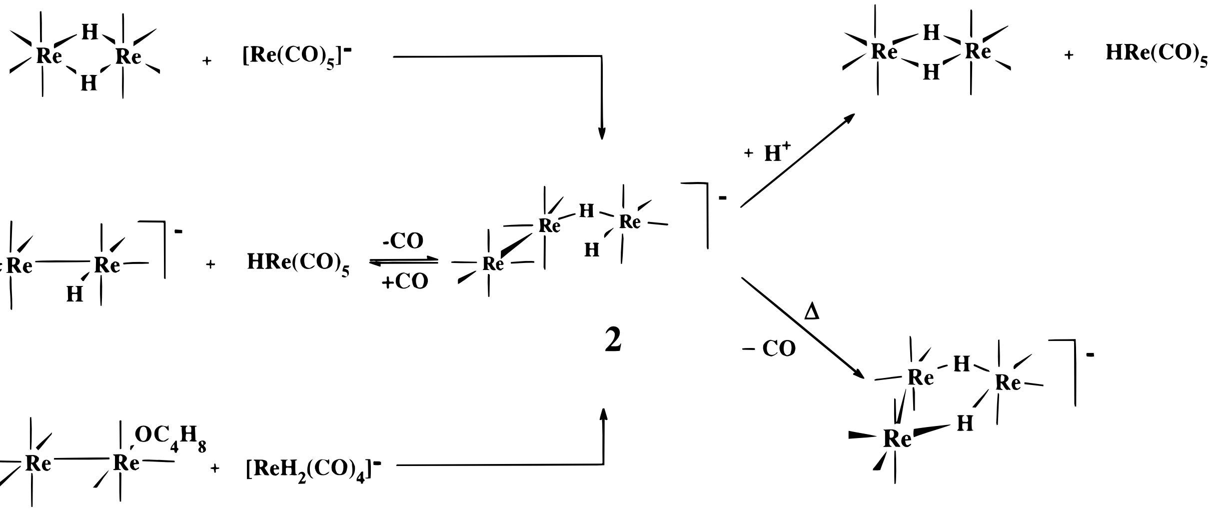
Scheme 3



tural ground is expected to be easy in both the species, has been observed only in **4**, where it is an adiabatic process. In the anion **2** the same process would give rise to an isomer, likely less stable.

Experimental Section

The reactions were performed under nitrogen, using the Schlenk technique, and solvents were deoxygenated and dried by standard methods. Literature methods were used for the preparation of [$Re_2(\mu\text{-}H)_2(CO)_8$],32 Na[$Re(CO)_5$],33 (PPN)[$Re(CO)_5$],4 ($PPh_4$)[$H_2Re(CO)_4$],34 ($NEt_4$)[$HRe_2(CO)_9$],5 [$Re_3(\mu\text{-}H)(CO)_{14}$],35 (PPN)[$Mn(CO)_5$],36 and ^{13}CO-enriched (about 25%) [$Re_2(CO)_{10}$].37 Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer in a 0.1-mm CaF_2 cell.

NMR spectra were recorded on Bruker AC200 and WP80 and Varian Gemini 200 spectrometers. The calibration of the temperature has been checked using the standard CD_3OD/CH_3OH solution and controlled by BVT-1000 (Bruker) or Stelar VTC90 (Varian) units. The NMR monitoring of the reactions involving **2** had to be performed always at low temperature, because of the coalescence of the hydridic resonances at room temperature. ^{13}C NMR spectra have been simulated allowing for the changes of the chemical shifts with the temperature and using an author's modified version of the QCPE program Multi Site EXchange.38 The ^{1}H spectra, for the coupling between the two hydrides, have been simulated using a modified version of DNMR3.39 In both cases, the goodness of the fit has been estimated visually through the superposition on the PC monitor of the simulated and experimental spectra (Supporting Information). The rate constants estimated accordingly from the ^{13}C spectra are $k = 3.5$, 15, 68, 115, 630, and 2700 s^{-1} at 238, 248, 258, 268, 278, and 288 K, respectively, and from the ^{1}H spectra, 2.2, 5.0, 14, 50, 140, 430, and 1000 s^{-1} at 233, 240, 248, 258, 268, 278, and 288 K, respectively.

The ^{13}C relaxation times have been measured using the standard inversion recovery pulse sequence, and the intensities of the signals were fitted to the proper equation by the routine provided by the spectrometer software. A total of 64 fid's have been averaged for 9 or 14 variable delays in two experiments optimized for the long and the short relaxation times.

Synthesis of [NEt_4][$Re_3H(\mu\text{-}H)(CO)_{13}$], [$NEt_4$]2. A sample of [$Re_2(\mu\text{-}H)_2(CO)_8$] (75 mg, 0.125 mmol) was added to a solution of Na[$Re(CO)_5$] (3 mL, 0.042 M) in THF, at −78 °C. The solution was allowed to warm up to room temperature and then evaporated to dryness. The residue was treated with about 6 mL of diethyl ether and filtered, and the solution was dried in vacuum. The residue was dissolved in 3 mL of deoxygenated water and treated with NEt_4BF_4 (54 mg, 0.24 mmol). A yellow precipitate formed immediately. It was washed with water, dried by repeated dissolution/evaporation cycles in anhydrous THF, and recrystallized from CH_2Cl_2/*n*-hexane to give [NEt_4]**2**, yield = 68%. Spectroscopic data for the anion **2**: IR (THF) ν(CO) 2099 vw, 2067 mw, 2032 m, 1991 vs, 1946 ms, 1924 m, 1907 mw; ^{1}H NMR (THF-d_8, 203 K) δ −5.70 (1), −16.56 (1) (J_{HH} = 4 Hz).

Synthesis of [PPN][$Re_3H(\mu\text{-}H)(CO)_{13}$], [PPN]2. The reaction was performed as above, using solid [PPN][$Re(CO)_5$]. The residue after evaporation to dryness was treated with diethyl ether (6 mL). The yellow solution was filtered, concentrated, and treated with *n*-hexane, to give a yellow precipitate of spectroscopically pure [PPN]**2**, yield = 80%.

Synthesis of ^{13}CO-Enriched Na[$Re_3H(\mu\text{-}H)(CO)_{13}$], Na2. The reaction was performed as above, using ^{13}CO-enriched [$Re_2(\mu\text{-}H)_2(CO)_8$] and Na[$Re(CO)_5$], prepared by the same sample of ^{13}CO-enriched [$Re_2(CO)_{10}$] (ca. 25%). The residue after evaporation to dryness was extracted with diethyl ether, filtered, dried in vacuum, and then dissolved in THF-d_8 for the ^{13}C NMR analysis (see Figure 2 and Table 2).

Decarbonylation of [$Re_3H(\mu\text{-}H)(CO)_{13}$]$^-$ (2). A sample of [NEt_4]**2** (14 mg, 0.013 mmol) was refluxed in THF for 45 h. The solution was evaporated to dryness and spectroscopically analyzed. IR and ^{1}H-NMR (acetone-d_6, 213 K) showed the almost quantitative formation of [$Re_3(\mu\text{-}H)_2(CO)_{12}$]$^-$ (unreacted **2** being ca. 6% of the triangular cluster anion). Very minor unidentified hydridic signals were also observed.

Treatment of [$Re_3(\mu\text{-}H)_2(CO)_{12}$]$^-$ with CO. Crystals of [PPh_4][$Re_3(\mu\text{-}H)_2(CO)_{12}$] (about 15 mg, 0.012 mmol, obtained from a solution of [PPh_4][$H_2Re(CO)_4$] in ethanol maintained under CO at room temperature for several days) were dissolved in acetone-d_6 and kept under 100 atm of CO for 21 h. The ^{1}H-NMR spectra (213 K) did not show any reaction.

Reaction of [$Re_2(CO)_9$(THF)] with [$H_2Re(CO)_4$]$^-$. [$Re_2(CO)_9$(THF)] was prepared following the method described by Koelle40 for [$Re_2(CO)_9(NCCH_3)$]: A sample of [$Re_2(CO)_{10}$] (20 mg, 0.031 mmol) was dissolved in THF at room temperature

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and treated with anhydrous Me_3NO (about 3 mg, 0.04 mmol). The solution became immediately bright yellow, and IR monitoring (1 h) showed the formation of a species with a ν(CO) pattern analogous to that reported[40] for $[Re_2(CO)_9(NCMe)]$: ν(CO) 2103 vw, 2041 m, 1990 vs, 1956 m, 1915 m cm^{-1}.[41] The solution was evaporated to dryness to remove completely the evolved Me_3N, and the residue, dissolved in THF, was treated with 1 equiv of $[PPh_4][H_2Re(CO)_4]$ (18 mg, 0.028 mmol). IR and ^{1}H-NNR monitoring showed the complete disappearance of the reagents in about 10 min at room temperature, to give mainly **2**, together with some $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ (ratio about 5:1). Minor unidentified hydridic resonances were observed at δ −5.22, −16.23, and −17.71 ppm.

Reaction of $[Re_3(\mu\text{-}H)(CO)_{14}]$ (4) with $[H_2Re(CO)_4]^-$. A sample of **4** (13.5 mg, 0.014 mmol) was dissolved in THF and treated with $[PPh_4][H_2Re(CO)_4]$ (9 mg, 0.014 mmol) at 203 K. No reaction was observed at this temperature. After 5 h at room temperature, the solution was evaporated to dryness. The solvent was trapped at low temperature, and the IR spectrum showed the presence of $[HRe(CO)_5]$. The residue was washed with *n*-hexane (that extracted some $[Re_2(CO)_{10}]$) and then was analyzed by NMR, which showed the presence of the anion **2** (ca. 50% of the hydridic species), $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ (ca. 20%), and $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ (ca. 30%). The reaction was repeated more times directly into NMR tubes, by dissolving **4** in THF-d_8 and adding equimolar $[PPh_4][H_2Re(CO)_4]$. Spectra acquired at low temperature, after different reaction times at room temperature, showed the slow formation of the anion **2** together with several other hydridic species: besides $[HRe(CO)_5]$ and the two triangular clusters cited above, the dinuclear anions $[HRe_2(CO)_9]^-$ and $[Re_2H_2(\mu\text{-}H)(CO)_8]^-$ were recognized, in varying amounts in the different experiments.

Reaction of $[H_2Re(CO)_4]^-$ with $[HRe(CO)_5]$. A sample of $[HRe(CO)_5]$ (2 μL, 0.014 mmol) was treated in THF-d_8 with $[PPh_4][H_2Re(CO)_4]$ (10 mg, 0.015 mmol). A spectrum acquired at 193 K, after 2.5 h at room temperature, showed the almost complete disappearance of the reagents, to give mainly $[Re_2H_2(\mu\text{-}H)(CO)_8]^-$ (ca. 82%), together with a minor amount of $[HRe_2(CO)_9]^-$ (10%) and of **2** itself (ca. 8%).

Reaction of $[HRe_2(CO)_9]^-$ with $[HRe(CO)_5]$. A sample of $[NEt_4][HRe_2(CO)_9]$ (22 mg, 0.029 mmol), dissolved in 3 mL of THF, was treated with $[HRe(CO)_5]$ (4 μL, 0.028 mmol). The solution was stirred at room temperature overnight and then evaporated to dryness. IR monitoring and ^{1}H NMR of the residue showed the presence only of **2**, besides some unreacted $[HRe_2(CO)_9]^-$. The same reaction was repeated for the NMR monitoring. A sample of $[NEt_4][HRe_2(CO)_9]$ ^{13}CO-enriched (32 mg, 0.042 mmol), dissolved in THF-d_8 in a Schlenk tube, was treated with $[HRe(CO)_5]$ (6 μL, 0.042 mmol). The solution was stirred for 1 h at room temperature. ^{1}H-NMR spectra, recorded at 203 K, showed only the reagents *plus* **2** (ca. 40%). The solution was transferred again into the Schlenk tube and stirred for 20 h, at room temperature. The NMR analysis showed **2** as the main species (77%), but the reagents were still present (in equimolar amount, ca. 17%), besides some $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ (ca. 6%).

Reaction of $[Re_3H(\mu\text{-}H)(CO)_{13}]^-$ (2) with CO. A sample of [PPN]**2** (25 mg, 0.017 mmol) was dissolved in 3 mL of THF under CO, and the solution was stirred at room temperature. IR monitoring showed the growth of the ν(CO) bands of $[HRe_2(CO)_9]^-$ (2084 vw, 2012 m, 1970 vs, 1925 m, 1888 m cm^{-1}) and $[HRe(CO)_5]$ (2015 cm^{-1}). After 6 h, the solution was evaporated to dryness and the solvent, trapped at −80 °C, showed the ν(CO) band of $[HRe(CO)_5]$. The ^{1}H NMR spectrum of the residue showed only the resonances of $[HRe_2(CO)_9]^-$ and of unreacted **2**. The reaction was also monitored by NMR. A sample of Na**2** (0.031 mmol, prepared by ^{13}CO-enriched $Na[Re(CO)_5]$ and natural abundance $[Re_2(\mu\text{-}H)_2(CO)_8]$), was dissolved in THF-$d_8$ under CO and stirred at room temperature. ^{13}C and ^{1}H NMR spectra acquired at 193 K at different times showed the progressive transformation of **2** into $[HRe(CO)_5]$ (δ −5.88) and $[HRe_2(CO)_9]^-$ (δ −7.15) (ratio ca. 1:1, $t_{1/2}$ ca. 6 h). The ^{13}C NMR spectra showed the appearance of the ^{13}CO resonances of $[HRe(CO)_5]$ (δ 184.67, 184.28, 4:1) and of $[HRe_2(CO)_9]^-$ [δ 202.2(*2*), 201.6(*4*), 199.2(*1*), 195.5(*1*), 190.7(*1*)].[42]

Table 3. Crystal Data and Structure Refinement Parameters for $[Re_2(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]^-$ (2)

formula	$C_{21}H_{22}NO_{13}Re_3$
fw	1055.02
cryst system	triclinic
space group	$P\bar{1}$
a, Å	8.975(1)
b, Å	9.685(1)
c, Å	17.449(2)
α, deg	79.57(1)
β, deg	82.40(1)
γ, deg	85.21(1)
V, Å3	1475.8(3)
Z	2
F(000)	968
D_{calc}, g cm^{-3}	2.374
temp, K	293 (2)
diffractometer	CAD4
radiation (graph monochr), Å	0.710 73
abs coeff, mm^{-1}	12.332
cryst size, mm	0.25 × 0.15 × 0.10
scan method	ω
scan interval, deg	$1.1 + 0.35 \tan \theta$
max time per reflcn, s	60
θ range, deg	3−25
index ranges	$-10 \leq h \leq 10, -11 \leq k \leq 11, 0 \leq l$ 20
reflcns collcd, indepdt	5159, 5159
cryst decay %	53
abs corr	ψ-scan
no. azimut reflcns	3
max and min transm	1.00 and 0.54
obs reflcn criterion	$T > 3\sigma(I)$
data/restraints/params	3745/0/312
goodness-of-fit on F_o^2	1.049
R indices[a]	R1 .0396, wR2, .0984
largest diff and hole, e Å^{-3}	1.626 and −1.571

[a] Weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 11.6816P]$, where $P = (F_o^2 + 2F_c^2)/3$. GOOF $= [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Reaction of $[Re_3H(\mu\text{-}H)(CO)_{13}]^-$ (2) with H^+. A sample of crystals of $[NEt_4]$**2** (10 mg, 0.009 mmol) was dissolved in CD_2Cl_2 and treated with CF_3SO_3H (0.8 μL, 0.009 mmol) at 193 K. ^{1}H NMR spectra at 203 K showed the quantitative formation of $[Re_2(\mu\text{-}H)_2(CO)_8]$ and $[HRe(CO)_5]$, in the ratio 1:1.

Reaction of $[Re_2(\mu\text{-}H)_2(CO)_8]$ with $[Mn(CO)_5]^-$. A sample of $[Re_2(\mu\text{-}H)_2(CO)_8]$ (20 mg, 0.033 mmol) was added to a THF solution of $[NEt_4][Mn(CO)_5]$ (0.4 mL, 0.08 M), at −78 °C. IR monitoring showed the complete disappearance of the reagents. No gas evolution (CO or H_2) was revealed by gas chromatographic analysis. The solution was allowed to warm to room temperature and evaporated to dryness, and the residue was crystallized from CH_2Cl_2/*n*-hexane, to give yellow crystals of $[NEt_4][ReMn(CO)_9\{(\mu\text{-}H)ReH(CO)_4\}]$. Spectroscopic data of the anion: IR (THF) ν(CO) 2096 vw, 2066 mw, 2031 m, 1995 s, 1981 s, 1955 sh, 1928 m, 1914 sh; ^{1}H NMR (THF-d_8, 223 K) δ −5.75 (*1*), −16.24 (*1*) (J_{HH} = 3.5 Hz). The reaction was repeated in a NMR tube: a sample of $[Re_2(\mu\text{-}H)_2(CO)_8]$ (11.0 mg, 0.018 mmol), dissolved in THF-d_8 at 193 K, was

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[41] Literature data (previous reference) for the analogous MeCN derivative: ν(CO) 2099(1), 2042(5), 2012(5.5), 1960 (br) (10) (this value is clearly a misprint: we have measured a value of 1990), 1963(4.6), 1942(5.5) cm^{-1}.

[42] It is interesting to note that the literature data[24] for the same $(NEt_4)[HRe_2(CO)_9]$ salt (at the same temperature and in the same solvent) differ slightly but significantly from ours only for the resonances attributable to the $Re(CO)_5$ moiety: 201.1 (vs 201.6) and 189.9 (vs 190.7) ppm. The only difference was the use of $Cr(acac)_3$ in the acquisition of the literature data.

treated with [PPN][Mn(CO)$_5$] (13.5 mg, 0.018 mmol): the ^{1}H NMR spectrum at 193 K showed the instantaneous and quantitative formation of [ReMn(CO)$_9${(μ-H)ReH(CO)$_4$}]$^-$.

X-ray Analysis of the [NEt$_4$][Re$_3$H(μ-H)(CO)$_{13}$] Salt. (a) Collection and Reduction of X-ray Data. A suitable crystal was chosen and mounted on a glass fiber tip onto a goniometer head. Single-crystal X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with the use of graphite-monochromatized Mo Kα radiation. The unit cell parameters and an orientation matrix relating the crystal axes to the diffractometer axes were determined by least-squares fit of the setting angles of 25 randomly distributed intense reflections with $10° < \theta < 14°$. The data collection was performed by the ω-scan method, at room temperature with variable scan speed (maximum scan time 60 s) and variable scan range. The crystal stability under diffraction condition was checked by monitoring three standard reflections every 180 min. The measured intensities were corrected for Lorentz, polarization, background, and decay effects and reduced to F_o^2. An empirical absorption correction based on ψ-scans, of three suitable reflections having χ values close to 90°,[43] followed by a "statistical" absorption correction (DIFABS[44]) was applied. Selected crystal data are summarized in Table 3.

(b) Solution and Structure Refinement. The structure was solved by direct methods (SIR92[45]) and difference Fourier methods. The structure was refined by full-matrix least squares against F_o^2 using reflections with $F_o^2 \geq 3\sigma(F_o^2)$ and the program SHELXL93[46] on a Silicon Graphics Indigo computer. Anisotropic displacement parameters were assigned to all the anion atoms (but the hydrides). The two independent tetraethylammonium cations were found to be disordered about two inversion centers and were refined isotropically. The hydride ligands positions were calculated by means of the program HYDEX[17] with $d_{\mathrm{M-H}} = 1.85$ Å for both terminal and bridging hydrides. The hydrides were introduced in the final stages of F_o calculations but not refined.

Note Added in Proof. Some recent investigations carried on in our lab suggest that the product of the reaction of [Re$_2$(CO)$_{10}$] with Me$_3$NO in THF, formulated above as [Re$_2$(CO)$_9$(THF)], could indeed be a mixture of species containing different labile ligands (the most likely candidates being THF itself or NMe$_3$).

Supporting Information Available: Tables of atomic coordinates and *U* values, anisotropic displacement parameters, and complete bond distances and angles and simulated and experimental ^{13}C and ^{1}H variable-temperature spectra (14 pages). Ordering information is given on any current masthead page.

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[47] In rhenium hydrido−carbonyl clusters *trans* J_{CH} are generally very small or not observed, at variance with what reported for related compounds of other transition metals.