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1,2-*eq,eq*-[$Re_2(CO)_8(THF)_2$]: A Reactive $Re_2(CO)_8$ Fragment That Easily Activates H−H and C−H Bonds

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The reaction of [$Re_2(\mu\text{-}H)_2(CO)_8$] (**1**) with diazomethane at 193 K in THF-d_8 gives the unstable [$Re_2(\mu\text{-}H)(\mu\text{-}CH_3)(CO)_8$] derivative (**2**) containing a methyl group arising from the insertion of CH_2 into a Re−H−Re bond. Isotopic perturbation of the equilibria by partial deuteration demonstrated that the methyl bridges the Re−Re bond in an unsymmetrical way, with a fast exchange between one agostic and two terminal C−H bonds. At temperatures higher than 253 K, **2** decomposes, in THF solution, with CH_4 elimination to give the novel red complex 1,2-*eq,eq*-[$Re_2(CO)_8(THF)_2$] (**3**), which was characterized by NMR spectroscopy and X-ray analysis. In the solid form a staggered conformer of C_2 symmetry was found. ^{13}C NMR analysis revealed the presence, in wet THF, of the aquo complexes [$Re_2(CO)_8(THF)(H_2O)$] (**4**) and [$Re_2(CO)_8(H_2O)_2$] (**5**), whose formation is favored at low temperature ($\Delta H°$ for the formation of **5** from **4**: $-14.4(2)$ kJ mol^{-1}). In solution, due to the lability of the THF ligands, **3** behaves as a "lightly stabilized" $Re_2(CO)_8$ fragment, capable of activating different E−H bonds. Reaction with HCl in THF leads to [$Re_2(\mu\text{-}H)(\mu\text{-}Cl)(CO)_8$], while with H_2 the unsaturated starting material [$Re_2(\mu\text{-}H)_2(CO)_8$] is obtained. In THF solution, at room temperature, reactions with phenylacetylene, styrene, and acetaldehyde give the derivatives of C−H activation [$Re_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)(CO)_8$], [$Re_2(\mu\text{-}H)(\mu\text{-}CH{=}C(H)Ph)(CO)_8$], and [$Re_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}C(Me)O)(CO)_8$]. Moreover, the activation of an sp^3 C−H bond in ethyl acetate occurs slowly when **3** is dissolved in the reactant itself, the resultant product being [$Re_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH_2C(O)OEt)(CO)_8$].

Introduction

Transition-metal complexes containing weakly coordinated ligands are of current interest.[1] In many reactions such complexes appear only as a transient species, as can be seen by the temporary coordination of the polar cosolvent in the classical Wilkinson mechanism of olefin hydrogenation.[2] In other cases these complexes are generated in solution as long-lived species or even isolated in the solid state. The facile dissociation of the labile ligands allows easy substitution and often provides the vacant site necessary for binding and activating several substrates. In organometallic chemistry this is well-illustrated by the rich chemistry displayed by the [$Os_3(CO)_{10}L_2$] (L = cyclooctene, MeCN) derivatives[3] or by the [$Cp_2Zr(CH_3)(THF)$]$^+$ cation.[4] Also significant are the [$IrH_2(solv)_2(PPh_3)_2$]$^+$ (solv = solvent)[5,6] and [$Cp^*Ir(CH_3)(ClCH_2Cl)(PMe_3)$]$^+$ cations,[7] both capable of alkane activation.

As far as the tetrahydrofuran ligand is concerned, the affinity of the hard donor oxygen atom for hard metallic centers accounts for the high number of THF adducts exhibited by transition-metal cations.[8,9] However, tet-

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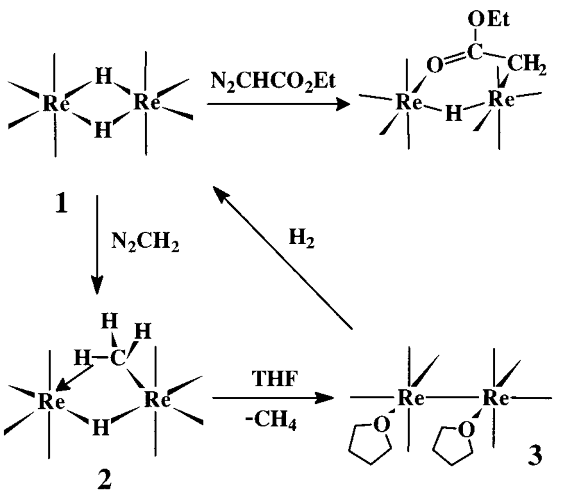
rahydrofuran is also able to bind metals in low oxidation states, as attested by the number of THF adducts displayed by Re(I) carbonyl complexes.[10] The only example of a THF molecule bonded to a Re(0) center is provided by the $[Re_2(CO)_9(THF)]$ species; this is formed, mixed with the corresponding $[Re_2(CO)_9(H_2O)]$ aquo species, by protonation of $[HRe_2(CO)_9]^-$ or by Me_3NO-induced decarbonylation of $[Re_2(CO)_{10}]$, in THF solution.[11,12] The THF lability in this complex is much higher than that of MeCN in the related $[Re_2(CO)_9(MeCN)]$ derivative,[13] allowing the synthesis of open-chain tri-[12] and tetranuclear[11] clusters by replacement of THF with hydridic complexes able to act as "ligands" through their M−H σ-bond electron density.[14]

We report here on the synthesis and characterization of a novel Re(0) complex containing two THF molecules, namely 1,2-*eq,eq*-$[Re_2(CO)_8(THF)_2]$. A related 1,2-*eq,eq*-$[Re_2(CO)_8(NCMe)_2]$ derivative was previously obtained by decarbonylation of $[Re_2(CO)_{10}]$ in MeCN solution with Me_3NO.[15−17] We and others[15] have tried Me_3NO oxidation in THF solution, but no product of disubstitution was obtained by this method. We now present a completely different approach, based on the dehydrogenation of the unsaturated dinuclear species $[Re_2(\mu\text{-}H)_2(CO)_8]$[18] with diazomethane. A thermally unstable μ-hydrido μ-methyl agostic derivative was detected as an intermediate in this reaction.

Results and Discussion

We have currently been investigating the reactivity of the "ethylene-like" complex $[Re_2(\mu\text{-}H)_2(CO)_8]$[19] (**1**; 32 valence electrons) with diazoalkanes. Earlier studies with diphenyldiazomethane and ethyl diazoacetate[25] showed a strict parallelism between the reactivity of **1** and that of the related unsaturated triosmium cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$.[26] In both cases the reaction with ethyl diazoacetate led to the insertion of the carbene fragment into a M−H bond of the $M(\mu\text{-}H)_2M$ moiety (Scheme 1). We have now found that **1** reacts rapidly also with diazomethane at 193 K, giving $[Re_2(\mu\text{-}H)(\mu\text{-}CH_3)(CO)_8]$ (**2**; Scheme 1), containing a methyl group arising from the insertion of CH_2 into a Re−H−Re bond.

Scheme 1



Reaction 1 was performed directly in an NMR tube, in THF-d_8, at 193 K, and the spectra revealed two resonances, in a 3:1 ratio, at δ −2.85 and −12.28 ppm, attributable to the methyl group and the bridging hydride, respectively. The unusual chemical shift of CH_3 is analogous to that reported by Calvert and Shapley[27] for $[Os_3(\mu\text{-}H)(\mu\text{-}CH_3)(CO)_{10}]$ (δ −3.6 ppm), obtained by reacting $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with diazomethane. In that case NMR experiments of isotopic perturbation of the equilibrium by partial deuteration were elegantly used to demonstrate that the methyl group bridged an Os−Os bond in an unsymmetrical way, with one of the three C−H bonds involved in an agostic interaction with an Os center.[27c] The fast exchange between the hydrogen in the agostic site and the two terminal hydrogens accounted for the unique resonance of the CH_3 group. Following the same approach, we prepared a partially deuterated sample of **2**, by reacting **1** with deuterium-enriched diazomethane.[28] The ^1H NMR spectra showed

$$[Re_2(\mu\text{-}H)_2(CO)_8] + CH_2N_2 \rightarrow [Re_2(\mu\text{-}H)(\mu\text{-}CH_3)(CO)_8] + N_2 \quad (1)$$

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[19] With the term "ethylene-like" we refer not only to the *formal* Re−Re double bond required by the electron counting rules but also, and chiefly, to some interesting analogies of reactivity (see for instance refs 20 and 21; see also ref 22), that find support in the isolobal analogy[23,24] between CH_2 and suitable organometallic fragments.

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the expected three signals for the three CH_3, CH_2D, and CHD_2 isotopomers of the methyl group, with $\Delta\delta$ on the order of tenths of ppm ($\delta(CH_3) - \delta(CH_2D) = 0.270$, $\delta(CH_2D) - \delta(CHD_2) = 0.330$ ppm, at 243 K), much higher than the $\Delta\delta$ value typical of secondary isotopic effects on the nuclear shielding.[29] The separation of the signals increased on lowering the temperature ($\Delta\delta = 0.295$ and 0.366 ppm, respectively, at 223 K and 0.325 and 0.414 ppm at 203 K), in accordance with the increasing shift of the equilibria toward the most stable forms, i.e., those with the ^1H isotope in the agostic site. Using the approach described by Calvert and Shapley,[27c] we estimated the energy difference between the D-bridged and the H-bridged forms as 645 ± 10 J/mol (544 ± 42 J/mol for the osmium analogue)[27c] and the chemical shifts of the resonances of the agostic and the terminally bound C−H protons as δ −8.31 and −0.16 ppm, respectively.

Low-temperature IR monitoring provided the ν(CO) absorptions of **2** (see Experimental Section): the pattern as well as the frequencies of these absorptions are very similar to those previously reported for a series of (μ-hydrido)(μ-alkenyl)$Re_2(CO)_8$ derivatives,[30] in line with the analogous idealized C_s symmetry.

Reaction 1 transforms the electronically unsaturated reactant **1** into the saturated (34 valence electrons) derivative **2**, owing to the replacement of one hydride by the three-electron-donor (agostic) methyl ligand. From a different point of view,[24] the same reaction can be described as the formation of a *di*metallacyclopropane, by addition of a carbene to the ethylene-like molecule [$Re_2(\mu\text{-}H)_2(CO)_8$]. The formation of *tri*metallacyclopropanes, by adding carbene isolobal analogues to [$Re_2(\mu\text{-}H)_2(CO)_8$], has already been reported.[20,24]

Complex **2** is stable in solution up to ca. 253 K. Above this temperature its resonances disappear and the solution becomes red (λ_{max} 485 nm). A small signal at δ 0.15 ppm and gas chromatographic analysis of the gas present in the NMR tube revealed methane evolution. The pattern of the ν(CO) bands of the final product (2066 w, 2005 m, 1959 s, 1946 sh, and 1898 m cm^{-1}, in THF) is comparable with that of previously known 1,2-*eq,eq*-[$Re_2(CO)_8L_2$] derivatives (L = MeCN,[15−17] pyridine,[31] P donor ligands[31,30]),[32] thus suggesting the formation of a diequatorial substitution derivative of [$Re_2(CO)_{10}$], as shown in Scheme 1 (where the eclipsed conformer is depicted):

$$[Re_2(\mu\text{-}H)(\mu\text{-}CH_3)(CO)_8] + 2THF \rightarrow [Re_2(CO)_8(THF)_2] + CH_4 \quad (2)$$

It has already been shown that reactants similar to **2**, such as the (μ-hydrido)(μ-alkenyl)dirhenium octacarbonyls prepared by the photochemical reactions of [$Re_2(CO)_{10}$] with 1-alkenes, are excellent precursors for 1,2-diequatorial substitution derivatives.[30] The 1,2-*eq,eq*-[$Re_2(CO)_8(THF)_2$] complex **3** can be obtained directly from **1**, according to eq 3, by performing the reaction with diazomethane at 273 K.

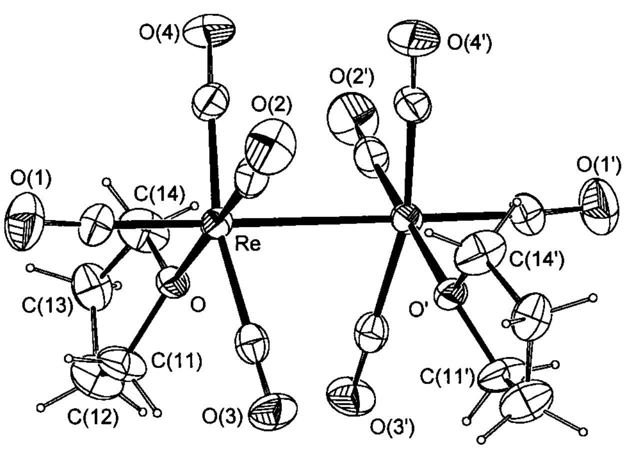

Figure 1. ORTEP views of the [$Re_2(CO)_8(THF)_2$] complex **3** with partial labeling scheme. Thermal ellipsoids are drawn at the 35% probability level.

$$[Re_2(\mu\text{-}H)_2(CO)_8] + CH_2N_2 + 2THF \rightarrow [Re_2(CO)_8(THF)_2] + N_2 + CH_4 \quad (3)$$

The ^1H NMR resonances of coordinated THF were detected in a low-temperature spectrum acquired immediately after dissolving an isolated sample of **3** in THF-d_8. They shifted downfield (by 0.23 and 0.10 ppm, for H_α and H_β, respectively) with respect to free THF, and in a few minutes disappeared, due to the fast substitution by the deuterated solvent.

The 1,2-*diequatorial* coordination of THF was further supported by the ^{13}C NMR data (three carbonyl resonances, in the ratio 2:1:1) and was eventually confirmed by single-crystal X-ray analysis.

Solid-State Structure of 3. The structure of **3** (Figure 1) is similar to that of [$Re_2(CO)_{10}$], having two square-pyramidal ReL_5 groups joined by a Re−Re single bond. The Re−Re bond distance, 3.0224(4) Å (see Table 1), is slightly shorter than that found for [$Re_2(CO)_{10}$], 3.041(1) Å.[33] The equatorial ligands adopt a staggered rotational conformation between the symmetry-related halves of the molecule (of C_2 point symmetry), with the THF ligands on the two Re centers staggered with a torsion angle between the oxygens of 125.8(2)°. The Re−O distance, 2.238(3) Å, is slightly longer than the values observed in rhenium(I) compounds (range 2.13−2.21 Å).[10c−f] No Re(0)−THF compounds are reported in the database. The THF-oxygen coordination is pyramidal, with the oxygen atom 0.294 Å from the Re,C(11),C(14) plane, suggesting that sp^3 hybridization is retained upon binding. The five-membered ring displays an envelope conformation with C(11) 0.43(1) Å out of the mean plane of the other atoms (maximum deviation from planarity 0.022 Å), probably to relieve the steric interaction with carbonyl 3′; the dihedral angle between the O,C(11),C(12) plane and the mean plane defined by C(12),C(13),C(14),O is 28.5(5)°. The mean plane of the THF ligand is tilted by 23.4° with respect to the equatorial plane defined by Re,C(2),C(3),C(4). The trans equatorial carbonyls C(3) and C(4) are bent toward the

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[Re_2(CO)_8(THF)_2]$ (3)

Re−Re	3.0224(4)	Re−C(1)	1.911(5)	Re−C(2)	1.883(6)
Re−C(3)	1.996(6)	Re−C(4)	1.982(6)	Re−O	2.238(3)
Re−Re−C(2)	90.66(2)	Re−Re−O	90.42(8)	O−Re−Re′−O′	125.8(2)
Re−Re−C(3)	82.46(1)	Re−Re−C(4)	84.51(2)	O−Re−Re′−C(2′)	52.9(2)
Re−O−C(14)	123.4(3)	Re−O−C(11)	120.6(3)	C(14)−O−C(11)	106.6(4)

opposite rhenium (average 83.5°), while the THF−Re−CO fragment is unaffected (average 90.5°). The order of the Re−C bond distances reflects the trans influence of the opposite ligand,[34] ranging from 1.883(6) Å for C(2) (trans to THF) to 1.911(5) Å for the axial C(1) up to 1.99 Å (average) for the two mutually trans atoms C(3) and C(4).

The NMR data in solution indicate the equivalence of the two $Re(CO)_4(THF)$ moieties. Most likely, this does not arise from a true C_2 symmetry of the whole molecule, as in the solid state, but from a fast rotation around the Re−Re bond, that averages different conformers and also generates equivalence in the two mutually trans carbonyls.

Reactivity of $[Re_2(CO)_8(THF)_2]$ (3). Complex **3** can be isolated as an orange-red solid, by precipitation from very concentrated THF solutions at low temperature. The solid can be manipulated in the air for short periods.

At room temperature, in anhydrous THF and in the absence of oxygen, the red color of **3** persists for some hours. A $t_{1/2}$ value of ca. 3 h was estimated by monitoring the disappearance of the absorption band at 485 nm. The main decomposition products, identified on the basis of the IR and ^{13}C NMR data, are the tetranuclear "cubane" complex $[Re_4(\mu_3\text{-}OH)_4(CO)_{12}]$[35] and the dinuclear species $[Re_2(CO)_9(solv)]$ (solv = THF, H_2O).[11,12]

^{13}C and ^1H NMR spectra have shown that, even in THF solution, the presence of water produces significant amounts of the two aquo derivatives $[Re_2(CO)_8(THF)(H_2O)]$ (**4**) and $[Re_2(CO)_8(H_2O)_2]$ (**5**), which arise from the partial or complete substitution of coordinated THF. The diaquo derivative **5** shows only three carbonylic resonances, in the ratio 2:1:1, in agreement with the presence of two equivalent *cis*-$Re(CO)_4$ moieties. The mixed derivative **4** gives six resonances (relative ratio 2:2:1:1:1:1), as expected for two nonequivalent *cis*-$Re(CO)_4$ groups. When water is added, the relative amount of the aquo complexes immediately increases. An experiment at 256 K showed that the [**4**]/[**3**] and [**5**]/[**4**] ratios increase linearly with the amount of added water. The values of the slopes provide an estimation of the equilibrium constants for the two substitution steps (17(1) and 13(1), respectively, at 256 K).

This facile substitution had previously been observed in the related $[Re_2(CO)_9(THF)]$ complex,[11,12] but the factors favoring water coordination are not immediately apparent. The low-frequency shift undergone by some of the ν(CO) bands of $[Re_2(CO)_8(solv)_2]$ upon substitution of water for THF (see below) suggests that water is able to provide a higher electron density to the Re centers. This is not attributable to an intrinsic higher σ-donor capability of water (gas-phase proton affinity: H_2O, 697 kJ mol^{-1}; C_4H_8O, 831 kJ mol^{-1})[36] but, rather, to steric factors that would allow the water molecule to approach more closely to Re. In the mixed aquo−THF derivative $[IrH_2(H_2O)(THF)(PPh_3)_2]^+$ the Ir−O distance for water was about 0.05 Å shorter than that of THF.[9]

Some insight into the factors favoring water coordination has been obtained by investigating the effects of temperature on the above equilibria. At room temperature, the ^1H NMR monitoring of the stepwise addition of water to a THF-d_8 solution of **3** showed that the [**5**]/[**4**] ratio increases linearly with the amount of water, but the slope is much less than at 256 K (5.0(2) vs 13). Moreover, it was clearly shown, in a variable-temperature experiment, that the overall amount of **4** + **5** as well as the [**5**]/[**4**] ratio decreased progressively when the temperature was increased from 253 to 298 K. A logarithmic plot of the [**5**]/[**4**] ratio vs $1/T$ provided an estimate of the $\Delta H°$ value for the reaction $\mathbf{4} + H_2O \rightleftarrows \mathbf{5}$ (−14.4(2) kJ mol^{-1}). The negative $\Delta S°$ value (−34(1) J mol^{-1} K^{-1}) shows that the formation of the aquo derivative **5** is enthalpically driven. It is reasonable to assume that also the formation of **4** is exothermic, due to the observed increase of the overall amount of **4** + **5** on decreasing the temperature.

When **3** was dissolved in THF-d_8 distilled from Na−benzoketyl directly into the NMR tube, the ^1H NMR spectra, at 298 K, showed the absence of **5** and only a minor amount of **4** (about 5%). The ν(CO) IR data reported above were acquired on dissolving some crystals of **3** in freshly distilled THF; therefore, they can be confidently attributed to true **3**. The addition of water produces little change in this region of the spectra, the main effect being observed for the band at 1898 cm^{-1}, which shifts down to 1886 cm^{-1} (minor shifts of about −3 cm^{-1} are observed for the bands at 2066 and 2005 cm^{-1}).

The resonances of water coordinated in **4** and **5** shift downfield on increasing water concentration, most likely due to increased hydrogen-bond interactions. For both complexes the variation of δ versus the concentration of water (M) is quite linear, the slope being higher at low temperature (0.94(2) and 0.66(1) ppm/M at 256 K, for **4** and **5**, respectively) than at room temperature (0.56(2) and 0.44(2) ppm/M), in agreement with the shift of the equilibria toward H-bonded species on lowering the temperature. This is also confirmed by the linear downfield shift, observed on lowering the temperature (at constant water concentration, ca. 0.1 M), of the signals for **4** and **5** and free water (slopes −5.92(1), −5.29(1), and −6.72(1) ppb/K, respectively).

Gard and Brown previously postulated[15] the aquo complex **5** to be an intermediate in the photochemical transformation of $[Re_2(CO)_{10}]$ into $[Re_4(\mu_3\text{-}OH)_4(CO)_{12}]$, in wet THF, but the complex was never identified. They also suggested that **5** under their reaction conditions

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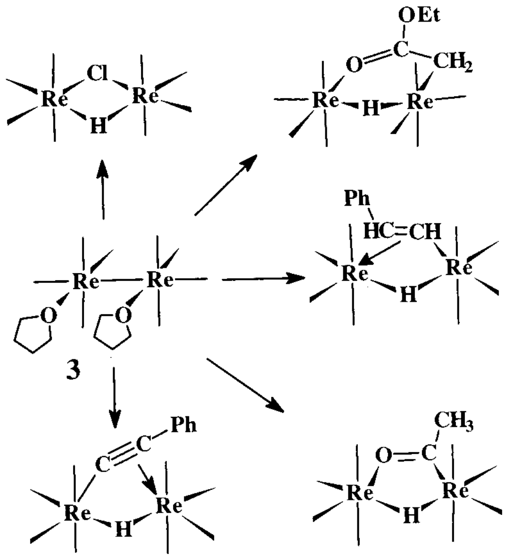
Scheme 2



rapidly decomposed to a μ-hydrido μ-hydroxo intermediate, never directly observed. In the early stages of the room-temperature decomposition of **3** in wet THF-d_8 we observed two ^{1}H NMR resonances, of the same intensity (δ 3.51 and -11.04 ppm), that could be attributed to this species. Until now our attempts to isolate it have failed, but, in the light of the reactivity patterns described below, the formation of a such a derivative is not unreasonable.

At room temperature, in dichloromethane solution **3** decomposes in a few minutes, giving an orange solution, whose ^{1}H NMR displays several hydridic resonances.[37] This indicates that **3** is able to cleave E−H bonds. Therefore, we investigated the reactivity of **3** with different types of E−H bonds more deeply (Scheme 2).

At room temperature, gaseous HCl reacted with a THF solution of **3** in less than 30 min, to give selectively [$Re_2(\mu\text{-}H)(\mu\text{-}Cl)(CO)_8$].[38]

With H_2, **3** reacted under atmospheric pressure, even in THF, leading to the dihydridic parent compound **1** (Scheme 1): after about 30 min, weak ν(CO) bands attributable to **1** were clearly recognizable in the IR spectrum. The transformation in **1** became instantaneous and quantitative when THF was replaced by dichloromethane.

To test the reactivity of **3** with C−H bonds (eq 4), we chose four organic molecules (namely phenylacetylene, styrene, acetaldehyde, and ethyl acetate) that (i) provide the full hybridization range of the carbon atom (from sp to sp^3) and (ii) afford products already known in the literature, allowing immediate recognition of the C−H oxidative addition, if it occurred. All the reactions were

$$[Re_2(CO)_8(THF)_2] + R{-}H \rightarrow [Re_2(\mu\text{-}H)(\mu\text{-}R)(CO)_8] + 2THF \quad (4)$$

performed at room temperature, by treating a THF-d_8 solution of **3** with a 5-fold excess of the R−H organic substrate in an NMR tube.

In the case of phenylacetylene the reaction was very fast, affording, almost quantitatively, the hydridic derivative [$Re_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)(CO)_8$][39,40] in the short time needed to acquire the NMR spectrum. Also in the presence of a strong excess of water the reaction proceeded rapidly, even at 243 K (ca. 30 min). The formation of [$Re_2(\mu\text{-}H)(\mu\text{-}CH{=}C(H)Ph)(CO)_8$][30,41] from the reaction with styrene was slightly slower, reaching completion in about 20 min at 298 K. In the case of acetaldehyde, the reaction was still highly selective, but much slower, requiring about 2.5 h for the complete transformation of **3** into [$Re_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}C(Me)O)(CO)_8$].[42] In contrast to this, no reaction of **3** with ethyl acetate was observed under the above conditions. The reaction proceeded only when ethyl acetate itself was used as solvent: after one night at room temperature, the NMR analysis revealed the formation of the expected [$Re_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH_2C(O)OEt)(CO)_8$] (previously obtained by reaction of ethyl diazoacetate with **1**).[25] The selectivity, however, was not as high as that of the above reactions involving sp or sp^2 carbon atoms (see Experimental Section).

Conclusions

The [$Re_2(\mu\text{-}H)(\mu\text{-}X)(CO)_8$] products (X = H, CR_n) obtained from [$Re_2(CO)_8(THF)_2$] (**3**) had previously been obtained by the addition of molecular hydrogen[43] or unsaturated organic molecules[30,39−42] to reactive fragments photochemically generated from [$Re_2(CO)_{10}$]. The easy occurrence of the reactions of **3** with H_2 and R−H (room temperature or lower, in THF itself) indicates that this novel complex does behave as a “lightly stabilized” $Re_2(CO)_8$ fragment, capable of activating H−H or C−H bonds under mild conditions. The reaction with ethyl acetate has demonstrated the possibility of room-temperature activation even of an sp^3 C−H bond. Therefore, the elimination of *two* carbonyls from the two metal atoms of [$Re_2(CO)_{10}$] substantially lowers the kinetic barrier for H−H or C−H bond activation. In connection with this, it is interesting to recall that laser flash photolysis studies[44] of the reaction of [$Re_2(CO)_{10}$] with olefins have recently provided kinetic evidence that the C−H oxidative addition occurs in an intermediate formed by displacement of a second carbonyl from the Re center adjacent to that bearing the olefin (coordinated to the *eq*-$Re_2(CO)_9$ fragment arising from the primary photoprocess).

The lack of reactivity between H_2 and the monosubstituted derivative [$Re_2(CO)_9(solv)$] (solv = THF, H_2O, no reaction in THF at 25 °C over 2 days)[15] could be explained by similar arguments. However, the clean addition of H_2 on a *single* vacant site, generated by dissociation of a ligand, has been observed for several polynuclear carbonyls.[45] The different behavior, on

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(37) The main signals are at δ −10.72, −10.97, −14.37, and −12.69 ppm. Only the last resonance is reasonably attributable to a previously known species, namely [$Re_2(\mu\text{-}H)(\mu\text{-}Cl)(CO)_8$] (lit.[38] δ −12.72 in $CDCl_3$). Attempts to identify the other species have been so far unsuccessful.

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varying *n* from 1 to 2, of the two $[Re_2(CO)_{10-n}(THF)_n]$ species is in contrast to what is observed for the analogous $[Os_3(CO)_{12-n}(NCCH_3)_n]$ derivatives ($n = 1, 2$), both species activating H_2 under mild conditions (1 atm, room temperature).[46,47] However, the $[Os_3H(\mu\text{-}H)(CO)_{10}L]$ products (L = CO, MeCN) are unstable toward the elimination of a ligand (CO or MeCN) from the adjacent Os center, and they both eventually afford $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, the electronically unsaturated analogue of $[Re_2(\mu\text{-}H)_2(CO)_8]$.[48] Therefore, though not a necessary prerequisite for H_2 oxidative addition, the presence of a labile ligand on a metal atom adjacent to that undergoing oxidative addition can be helpful in stabilizing the dihydridic product. The thermal instability of the expected $[Re_2H(\mu\text{-}H)(CO)_9]$ product, precluding stabilization by CO loss, could be responsible for the lack of H_2 activation by $[Re_2(CO)_9(solv)]$.[50]

It is noteworthy that much more drastic conditions are required for the related complex $[Re_2(CO)_8(NCMe)_2]$ to activate H_2 and C−H bonds. At 80 °C the reaction with H_2 occurs over several hours,[17] affording $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCCH_3)]$ (the unsaturated complex **1** being known to rearrange to triangular cluster species under these conditions).[18b] With phenylacetylene the reaction requires 5 h in refluxing CH_2Cl_2 and moreover gives $[Re_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)(CO)_7(NCMe)]$, which still contains one coordinated MeCN ligand[16] (a CO ligand is labilized rather than the second MeCN molecule, thus confirming the strength of the MeCN−Re(I) interaction).

Finally, it is to be noted that $[Re_2(CO)_8(THF)_2]$ is the key reagent in the method recently developed[22] for the synthesis of ring clusters, by condensation of complexes containing two very labile ligands with complexes containing two terminal hydrides and therefore able to act as “bidentate ligands”. The reaction of **3** with $[Re_3H_2(\mu\text{-}H)_2(CO)_{12}]^-$ has already allowed the synthesis of the first examples of five-membered rings, namely $[Re_5(\mu\text{-}H)_4(CO)_{20}]^-$ and $[Re_5(\mu\text{-}H)_5(CO)_{20}]$.[22] Studies aimed at exploring further applications of this method are in progress.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from Na/Ph_2CO (THF, diethyl ether) or P_2O_5 (CH_2Cl_2). $[Re_2(\mu\text{-}H)_2(CO)_8]$,[51] diazomethane[52] (a solution in diethyl ether), and deuterium-enriched diazomethane[28] were prepared according to literature methods. The titer of the diazomethane solution was checked by back-titration with NaOH after addition of a weighted excess of benzoic acid. All the other reagents were used as purchased from Aldrich. ^1H and ^{13}C NMR spectra were collected on Bruker AC200, Bruker DRX300, and Gemini 200 spectrometers. IR spectra were recorded on a Bruker Vector 22 instrument. Low-temperature monitoring was performed with a Graseby Specac P/N 21525 variable-temperature cell, with CaF_2 windows, equipped with a P/N 20120 temperature controller. The UV spectrum was acquired on a Kontron Uvikon 943 spectrophotometer. Microanalyses were performed at the microanalytical laboratory of the University of Milan.

Reaction of $[Re_2(\mu\text{-}H)_2(CO)_8]$ (1) with CH_2N_2 at 193 K. (a) NMR Monitoring. A sample of **1** (10.2 mg, 17.0 μmol) dissolved in THF-d_8 (0.7 mL) in an NMR tube at 193 K was treated with 100 μL of a diethyl ether solution of CH_2N_2 (ca. 0.138 M). The ^1H NMR spectrum at 193 K showed, besides the resonance of unreacted **1**, two novel signals (δ −2.85 and −12.28 ppm, ratio 3:1) attributable to $[Re_2(\mu\text{-}H)(\mu\text{-}CH_3)(CO)_8]$ (**2**). The temperature was progressively increased, and the disappearance of the signals of **2** occurred at 263 K. In the meantime, the growth of a signal at δ 0.15 ppm indicated CH_4 evolution. When the experiment was repeated using partially deuterated diazomethane, the ^1H NMR spectra, acquired at 203 K, showed three well-separated signals for the three CH_3, CH_2D, and CHD_2 isotopomers (δ −2.86, −3.18, and −3.59 ppm, respectively, at 203 K) and only one resonance for the bridging hydride (δ −12.30) of **2**. At 223 and 243 K the methyl signals shifted to δ −2.88, −3.17, −3.54 and δ −2.90, −3.17, −3.50 ppm, respectively.

(b) IR Monitoring. A sample of **1** (20 mg, 33.4 μmol) was dissolved in freshly distilled THF (5 mL) in a Schlenk tube and was treated, at 193 K, with 200 μL of a diethyl ether solution of CH_2N_2 (ca. 0.26 M). The solution was briefly shaken at room temperature, until a slight darkening was apparent, and then an aliquot was transferred, under N_2 pressure, into the variable-temperature IR cell, cooled to 213 K, through a previously N_2-purged and -cooled stainless steel capillary tube sealed to the cell. The IR spectra showed, besides **2**, some unreacted **1** and also some **3** (due to partial thermal decomposition during the transfer to the cell). Spectral subtractions gave the neat IR absorptions of **2** at 2121 (vw), 2086 (m), 2023 (vs), 2007 (m), 1983 (m), 1964 (s), and 1942 (m) cm^{-1}.

Preparation of $[Re_2(CO)_8(THF)_2]$ (3). A sample of **1** (98 mg, 0.164 mmol) was treated with freshly distilled THF (ca. 8 mL), cooled in an ice bath and decanted to eliminate a white insoluble residue. The clear solution was transferred via cannula to another Schlenk and treated, at 273 K, with 1.5 mL of a solution of diazomethane in diethyl ether (ca. 0.12 M). The reaction mixture immediately acquired a bright red color, and IR monitoring showed the formation of **3**. The solution was concentrated by evaporation under vacuum, at 273 K, until precipitate formation became evident (ca. 0.5 mL of volume). After the mixture stood overnight at 248 K, an orange-red precipitate of **3** was isolated by decantation from the cold solution (yield ca. 30%). Anal. Calcd for $C_{16}H_{16}O_{10}Re_2$: C, 25.94; H, 2.18. Found: C, 25.0; H, 2.1. The slightly lower content of carbon, with respect to the theoretical amount for **3**, might indicate the presence of a small amount of $[Re_2(CO)_8(THF)(H_2O)]$ (**4**). However, NMR analysis showed that the samples were contaminated by $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ (ca. 10%),[53] which is usually present in **1**. The calculated analysis for a mixture containing 90% of **3** and 10% of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ gave 25.0% C and 2.0% H, in excellent agreement with the experimental results. Crystals suitable for X-ray analysis were obtained from a very concentrated solution of **3** in THF at 243 K.^1H NMR (THF-d_8, 243 K): δ 1.90 (m, 4H), 3.87 (m, 4H).^{13}C NMR (THF-d_8, 256 K, relative ratios in parentheses): δ 216.76 (2), 197.75 (1), 193.96 (1). IR (THF, cm^{-1}) ν(CO) 2066 w, 2005 m, 1959 s, 1946 sh, 1898 m.

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(48) The expected $[Os_3H(\mu\text{-}H)(CO)_{10}(NCCH_3)]$ was not even seen as a product of the reaction of the disubstituted species $[Os_3(CO)_{10}(NCCH_3)_2]$ with H_2, which gave $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ directly.[47] Also the product $[Os_3H(\mu\text{-}H)(CO)_{11}]$, obtained from the monosubstituted species $[Os_3(CO)_{11}(NCCH_3)]$,[46] loses a carbonyl (at room temperature, in the absence of CO)[49] to give $[Os_3(\mu\text{-}H)_2(CO)_{10}]$.

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(53) The amount of this impurity has been estimated after converting **3** into $[Re_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)(CO)_8]$ by reaction with an excess of phenylacetylene, directly into an NMR tube.

Reaction of 3 with Water. (a) ^{13}C NMR Analysis at 256 K. A ^{13}CO-enriched sample of **1** (20.7 mg, 33.4 μmol) was dissolved in freshly distilled THF (10 mL) and treated at 273 K with 0.5 mL of a solution of CH_2N_2 in diethyl ether (ca. 0.1 M). After 1 h, the solution was evaporated to dryness and the residue dissolved in THF-d_8 at 193 K. The ^{13}C NMR spectra, at 256 K, showed three sets of signals, attributed to **3**−**5**, respectively, on the basis of change in intensity upon addition of water: **3**, see above; **4**, δ 218.2 (2), 215.7 (2), 197.7 (1), 197.5 (1), 195.2 (1), 193.3 (1) ppm; **5**, δ 217.1 (2), 197.6 (1), 194.3 (1). The resonances of coordinated water in the ^{1}H NMR spectrum were identified at δ −5.60 for **4** and −5.41 ppm for **5**. The integrated intensities of these resonances and the carbonylic ones allowed the estimation of the composition of the mixture: **3**, 0.46; **4**, 0.34; **5**, 0.20. Water was then added stepwise to the NMR tube, causing a fast increase in the relative amount of aquo complexes. The molar fractions of **3**−**5** became at first 0.10, 0.28, and 0.62 and then 0.05, 0.22, and 0.73 after the addition of 1.3 and 2.3 μL of water (corresponding to 2.2 and 3.8 equiv, respectively). The plots of the ratios [**4**]/[**3**] and [**5**]/[**4**] as a function of the concentrations of added water were satisfactorily linear, with slopes of 17(1) and 13(1), respectively. Upon addition of water, the protonic resonances of water coordinated in **4** and **5** shifted to lower field (δ 5.71 and 5.49 and δ 5.80 and 5.55 for **4** and **5**, after addition of 1.3 and 2.3 μL of H_2O, respectively), linearly with respect to the molar concentration of added water, with a slope of 0.94(2) and 0.66(1) ppm/*M*, for **4** and **5**, respectively.

(b) ^{1}H NMR Analysis at 298 K. An isolated sample of **3** (12 mg, 20 μmol) was dissolved in 0.6 mL of THF-d_8 distilled directly into the reaction vessel from Na−benzoketyl. A ^{1}H NMR spectrum (298 K) showed a weak resonance at δ 5.38 (attributable to the water molecule coordinated in **4**) and the absence of the corresponding signal of **5** (expected at δ 5.20). The amount of **4** was estimated as ca. 5%, on using as internal standard the resonance of [$Re_3(\mu\text{-H})_3(CO)_{12}$] (present as an impurity, ca. 10%). Different aliquots of water were then added and ^{1}H NMR spectra acquired after each addition (using a relaxation delay of 10 s to ensure reliable integration ratios). The [**5**]/[**4**] ratio, estimated from the integrated intensities of the respective water resonances, varied linearly vs water concentration, with a slope of 5.0(2). The chemical shift values of the resonances of water coordinated in **4** and **5** varied linearly with respect to [H_2O] (*M*), according to the equations $\delta = 5.374(4) + (0.56(2))[H_2O]$ and $\delta = 5.207(4) + (0.44(2))[H_2O]$, for **4** and **5**, respectively (for [H_2O] up to 0.4 *M*). In the meanwhile, also the resonance of free water underwent a similar linear downfield shift, with a slope of 0.53(2).

(c) Variable-Temperature Experiment. An isolated sample of **3** (7.7 mg, 10.4 μmol) was dissolved in 0.6 mL of THF-d_8 distilled directly into the reaction vessel from Na−benzoketyl. A ^{1}H NMR spectrum at 273 K showed the presence only of the resonance of **4**, at δ 5.50. Water (1 μL, 0.056 mmol) was then added, resulting in an increase in the intensity of the signal of **4** and in the appearance of the resonance of water coordinated in **5** (δ 5.39, [**5**]/[**4**] = 0.95). The temperature was lowered to 263 K and then to 253 K and subsequently raised, again to 273 K and then to 298 K. Several spectra were acquired at each temperature to ensure that equilibrium had been attained. The overall amount of **4** + **5** decreased from 73% at 253 K to 40% at 298 K (evaluated on attributing a concentration of 10% to the "internal standard" [$Re_3(\mu\text{-H})_3(CO)_{12}$], present as an impurity of **1**). A logarithmic plot of the [**5**]/[**4**] ratios at each temperature (1.55, 1.20, 0.95, and 0.55 at 253, 263, 273, and 298 K, respectively) vs 1/*T* was satisfactorily linear, according to the equation $\ln [\mathbf{5}]/[\mathbf{4}] = \ln [H_2O] + \ln K = \ln [H_2O] + \Delta S°/R - \Delta H°/RT$. The values of the slope and of the intercept ($(1.73(2) \times 10^3$ and −6.42(6), respectively) allowed the estimation of the thermodynamic parameters of the **4** $\rightleftarrows$ **5** equilibrium.

Reaction of 3 with HCl. Gaseous HCl was bubbled slowly through a THF (6 mL) solution of **3** (prepared in situ from **1** and diazomethane. After 30 min the solution was evaporated to dryness. IR (CH_2Cl_2) and NMR spectra ($CDCl_3$) showed the transformation of **3** into the already known complex [$Re_2(\mu\text{-H})(\mu\text{-Cl})(CO)_8$].[38] No other significant hydridic signal was detected in the ^{1}H NMR spectrum.

Reaction of 3 with H_2. A sample of **3** was prepared by treating **1** (14.4 mg, 24.1 μmol) with 0.2 mL of a solution of diazomethane (ca. 0.178 M) in THF (3 mL) at 273 K. H_2 was then bubbled through this solution at room temperature. The IR spectra of the solution showed the slow increase of the ν(CO) band at 2022 cm^{-1}, diagnostic of [$Re_2(\mu\text{-H})_2(CO)_8$]. The H_2 bubbling was continued until the THF solvent was removed; then CH_2Cl_2 was added, under an H_2 atmosphere. The color of the solution changed immediately from red-orange to yellow, and the IR spectra showed the quantitative formation of [$Re_2(\mu\text{-H})_2(CO)_8$].

Reaction of 3 with Phenylacetylene. A sample of isolated **3 (**13.0 mg, 17.6 μmol) was dissolved, at 273 K, in THF-d_8 distilled from Na−benzoketyl directly into the NMR tube and was treated with 9.8 μL (89 μmol, 5 equiv) of phenylacetylene. ^{1}H NMR monitoring, at room temperature, showed the nearly quantitative formation of [$Re_2(\mu\text{-H})(\mu\text{-C}{\equiv}CPh)(CO)_8$], complete within the few minutes necessary to acquire the spectrum. A minor unattributed resonance appeared at δ −9.80, with an integrated intensity ratio of 0.05 with respect to the signal at δ −12.95, attributed to [$Re_2(\mu\text{-H})(\mu\text{-C}{\equiv}CPh)(CO)_8$] (lit.[39] data ($CH_2Cl_2$): −13.01). The formulation of the reaction product was confirmed by its IR spectrum, recorded after evaporation of the solvent under vacuum: ν(CO) (*n*-hexane) 2119 vw, 2094 w, 2023 s, 2002 m, 1982 ms cm^{-1}.[39] No significant difference (but a decrease of the minor byproduct at δ −9.80) was observed when the same reaction was performed using as solvent THF-d_8 (Glaser AG Basel) as received (i.e. without anhydrification and therefore containing **3** and some **4**), or THF-d_8 treated with 5 μL of H_2O (and therefore containing mainly **4** and **5**).

Reaction of 3 with Styrene. This reaction was performed as described above (**3**, 7.4 mg, 10 μmol; styrene, 5.7 μL, 50 μmol). ^{1}H NMR monitoring showed the quantitative formation of [$Re_2(\mu\text{-H})(\mu\text{-C(H)}{=}C(H)Ph)(CO)_8$], complete within 20 min. The nature of the product was ascertained by comparison of the NMR and IR data with literature values.[40] No other hydridic derivative was formed in significant amount.

Reaction of 3 with Acetaldehyde. A sample of **3 (**7.2 mg, 9.7 μmol) was dissolved in THF-d_8, at 273 K, in a NMR tube and treated with 2.5 μL (44 μmol) of acetaldehyde. The progress of the reaction was followed by ^{1}H NMR spectroscopy, at room temperature, showing the progressive growth of the resonances of [$Re_2(\mu\text{-H})(\mu\text{-C(Me)O})(CO)_8$] at δ −14.0 (1) and 2.57 (3) (lit.[42] data: −14.01, 2.61). No other signal of significant intensity was observed in the hydridic region. The reaction went to completeness after about 2.5 h. The IR spectrum, recorded in *n*-hexane after evaporation of the solvent, was found to be very similar to the literature data (apart from an unattributed band at 2003 cm^{-1}).

Reaction of 3 with Ethyl Acetate. An isolated sample of **3** (5.1 mg, 6.9 μmol) was dissolved in ethyl acetate, giving a red solution. When the solution stood overnight at room temperature, the red color turned to yellow. The ethyl acetate was removed under vacuum and the residue dissolved in CD_2Cl_2. The ^{1}H NMR spectrum showed the resonances of [$Re_2(\mu\text{-H})(\mu\text{-}\eta^2\text{-}CH_2C(O)OEt)(CO)_8$].[25] An unattributed resonance at δ −15.35 (with integrated intensity of ca. 0.66 with respect to that at δ −14.60 of the main product) was also present, together with other very minor signals.

Crystallography. The crystal data for **3** are listed in Table 2; the selected bond distances and angles are given in Table 1. A columnlike crystal (0.38 × 0.08 × 0.08 mm) was mounted on a Siemens SMART CCD area-detector diffractometer, and

Table 2. Crystallographic Data for $[Re_2(CO)_8(THF)_2]$ (3)

chem formula	$C_{16}H_{16}O_{10}Re_2$	fw	740.69
cryst syst	orthorhombic	space group	*Fdd*2 (No. 43)
a	19.792(1) Å	*T*	20 °C
b	25.910(2) Å	*Z*	8
c	8.153(1) Å	ρ_{calcd}	2.353 g cm^{-3}
V	4180.9(6) Å^3	μ	11.618 mm^{-1}

R indices[a,b] ($F_o > 4\sigma(F_o)$; 2026 data)	R1 = 0.0164, wR2 = 0.0291
R indices[a,b] (all data)	R1 = 0.0220, wR2 = 0.0294

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0109P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

the data collection was performed at 293 K (graphite-monochromatized Mo Kα $\lambda = 0.710\,73$ Å) by the ω-scan method, within the limits $2 < \theta < 28°$ ($-25 < h < 25$, $-34 < k < 33$, $-10 < l < 10$). An empirical absorption correction was applied (SADABS),[54] maximum−minimum transmission being 0.505−0.233. The structure was solved by direct methods (SIR97)[55] and refined by full-matrix least squares on F_o^2 using all 2385 independent reflections and 128 parameters (for 11 562 data collected). Anisotropic thermal parameters were assigned to all the non-hydrogen atoms. The final difference electron density map showed no significant features. All calculations were performed using SHELX-97.[56] The assignment of the absolute structure was confirmed by the statistics and the refinement of the absolute structure parameter as implemented in SHELX-97, to a value of 0.036(9).[57]

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Supporting Information Available: Complete listings of atomic coordinates, thermal parameters and bond distances and angles for compound **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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