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NMR and DFT Analysis of $[Re_2H_2(CO)_9]$: Evidence of an η^2-H_2 Intermediate in a New Type of Fast Mutual Exchange between Terminal and Bridging Hydrides

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Abstract: Protonation of the anion $[Re_2H(CO)_9]^-$ (**1**) with a strong acid at 193 K affords the neutral complex $[Re_2H_2(CO)_9]$ (**2**), that in THF above 253 K irreversibly loses H_2 to give $[Re_2(CO)_9(THF)]$, previously obtained by room-temperature protonation of **1**. Treatment of **2** with NEt_4OH restores the starting anion **1**. Variable temperature ^1H and ^{13}C NMR spectra as well as T_1 measurements agree with the formulation of **2** as a classical $[Re_2H(\mu\text{-}H)(CO)_9]$ complex, in which two dynamic processes takes place. The "windshield-wiper motion" observed in several related complexes equalizes the two carbonyls trans to the hydrides (E_a = 44(1) kJ mol^{-1}), while another much faster process equalizes bridging and terminal hydrides already at 172 K. The variable temperature behavior of the ^1H transverse relaxation times revealed also proton exchange between **2**, water, and the parent anion **1** (due to the acidity of **2**), but such a process is too slow to account for the fast hydrides exchange in **2**. The nature of the latter process has been investigated both experimentally and theoretically. Kinetic data, obtained by the analysis of the variable temperature ^1H spectra (E_a = 24.5(5) kJ mol^{-1}), revealed a small normal kinetic isotope effect (ca. 1.5). The ^2H chemical shift of the fully deuterated isotopomer **2**-d_2 was found isochronous with **2**, thus ruling out the presence of a significant concentration of a nonclassical $[Re_2(\eta^2\text{-}H_2)(CO)_9]$ tautomer, in fast exchange with the classical dihydride. Density functional theory (DFT) calculations, carried out at the B3LYP level, confirmed the formulation of $[Re_2H_2(CO)_9]$ as a classical complex. However, when DFT was used to obtain a detailed description of the dynamic behavior of **2** in solution, a new type of hydride fast exchange emerged, involving the nonclassical tautomer as a relatively high energy (12.7 kJ mol^{-1}) intermediate. Isotopic perturbation of the equilibrium by partial deuteration of **2** indicated the preference of deuterium for the bridging sites, with $\Delta H^\circ = -475(4)$ J mol^{-1} and $\Delta S^\circ = -0.80(2)$ J K^{-1} mol^{-1}. The same preference was observed in the anion $[Re_2H(\mu\text{-}H)Cl(CO)_8]^-$.

Introduction

The reaction of transition-metal hydrido complexes with acids[1,2] can result either in H^+ addition[3] or in H_2 evolution, possibly via an unstable addition derivative.[4] Indeed, the protonation of metal hydrides has been widely used either to synthesize polyhydrides or to generate vacant coordination sites, allowing the binding of labile ligands or unusual reactivity patterns.[5] In past years, the protonation of the M−H bond has become a common method for generating dihydrogen complexes.[6−8] It has been argued that the hydride ligands are the kinetic site of protonation[3b,5b,9] and that the molecular hydrogen complexes might eventually lose H_2[10] or isomerize to classical hydridic tautomers[11] (or to equilibrium mixtures of hydrides and dihydrogen complexes).[12] In some cases, both direct protonation at the metal and attack at a hydrido ligand have been observed.[13]

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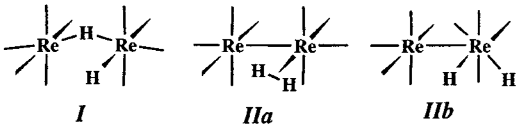
Also, the competition with the attack to ligands different from hydrides has been investigated.[2b,8g,14,15] More recently, attention has been drawn toward the steps preceding the proton transfer from the acid to the metal-hydride. Intermolecular MH···HA attractive interactions between the hydride and the acid (resulting in "dihydrogen bonds") have been evidenced,[16] and it has been suggested that they play an important role as intermediates (or transition states) in the protonation pathway to form dihydrogen complexes.[7b,10,17]

Chart 1



For anionic hydrido complexes, the protonation is an important step in the production of H_2 in the water-gas shift reaction.[18] We have recently reported the preparation of $[Re_2(CO)_9L]$ derivatives (L = THF or H_2O) by protonation of $[Re_2H(CO)_9]^-$ (**1**) with CF_3SO_3H, in THF solution, at room temperature.[19] Taking into account that the anion **1** is prepared from $[Re_2(CO)_{10}]$ through the classical attack of OH^- on a carbonyl ligand (reaction 1a), reaction 1b closes a water-gas shift cycle.

$$[Re_2(CO)_{10}] + OH^- \rightarrow [Re_2H(CO)_9]^- + CO_2 \qquad (1a)$$

$$[Re_2H(CO)_9]^- + H^+ + L \rightarrow [Re_2(CO)_9L] + H_2 \qquad (1b)$$

We have now investigated by NMR spectroscopy the same reaction at low temperature and obtained evidence of the formation of an unstable addition derivative $[Re_2H_2(CO)_9]$ (**2**). Reasonably, the kinetic product of the protonation is the nonclassical dihydrogen complex $[Re(CO)_4(H_2)Re(CO)_5]$ (**IIa** in Chart 1), which could eventually transform into one of the two possible classical dihydrides: $[Re(CO)_4H(\mu\text{-}H)Re(CO)_5]$ (**I**) or $[Re(CO)_4(H)_2Re(CO)_5]$ (**IIb**). Several examples of fast dihydride−dihydrogen equilibria have been reported,[8,12,20] and the possibility that fluxional processes equalizing hydrides involve a dihydrogen complex as an intermediate has been previously proposed, even in cases where no direct evidence for this dihydrogen complex was obtained.[6,21−23] Because NMR

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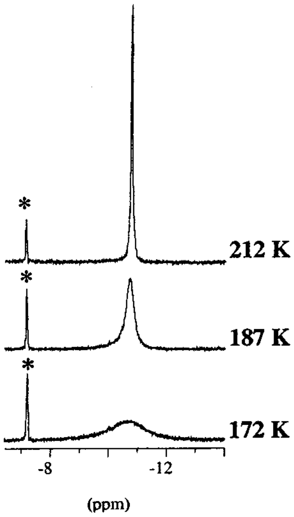

Figure 1. Selected variable temperature ^{1}H NMR spectra of $[Re_2H_2(CO)_9]$ (**2**, THF-d_8, 4.7 T). The asterisk marks the resonance of the reactant $[Re_2H(CO)_9]^-$ (**1**).

often fails in addressing the detailed reaction path and sometimes a full process can be silent to NMR, we have theoretically studied (part of) the potential energy surface of $[Re_2H_2(CO)_9]$ employing a density functional theory (DFT) method.

We report here the experiments that have led to the formulation of the protonation derivative **2** as a classical dihydridic species $[Re(CO)_4H(\mu\text{-}H)Re(CO)_5]$. A nonclassical tautomer (**IIa**) is however suggested, on the base of first principle DFT computations, to be an intermediate in a new type of hydride fast exchange. The preferential location of the deuterium atom in the bridging rather than in the terminal position, in the $[Re_2HD(CO)_9]$ isotopomer, is also discussed.

Results and Discussion

Synthesis of $[Re_2H_2(CO)_9]$. The addition of CF_3SO_3H to a solution of **1** in THF-d_8 at 193 K caused the instantaneous disappearance of the pale yellow color of the reactant and the formation of a novel species **2**, responsible for a broad hydridic resonance in the ^{1}H NMR spectrum (δ −10.75 ppm), that sharpened on raising the temperature (Figure 1). At temperatures higher than 253 K, the intensity of this signal rapidly decreased, due to the transformation of **2** into the $[Re_2(CO)_9L]$ species (L = THF or H_2O), previously obtained by the room-temperature protonation of **1**.

Compound **2** appears, therefore, as an intermediate in the proton-induced hydride abstraction from the anion **1**, and can be formulated as the neutral species $[Re_2H_2(CO)_9]$.

$$[Re_2H(CO)_9]^- + H^+ \rightarrow [Re_2H_2(CO)_9] \qquad (2a)$$

$$[Re_2H_2(CO)_9] + L \rightarrow [Re_2(CO)_9L] + H_2 \qquad (2b)$$

Reaction 2a is reversible; addition of 1 equiv of NEt_4OH, at 193 K, immediately and quantitatively restored the anion **1**. The investigation of the chemistry of **2** is strongly hampered by its thermal instability, also in a noncoordinating solvent, such as CD_2Cl_2. The reactivity data which have been obtained are provided in the Supporting Information.

NMR Solution Structure of $[Re_2H_2(CO)_9]$. The presence of a unique broad hydridic signal in the ^{1}H NMR spectrum of **2** down to 172 K could be consistent with all of the formulations depicted in Chart 1. The chemical shift value and the sharpening of the resonance on raising the temperature are in full agreement with the hypothesis of structure **I**, with a fast exchange of bridging and terminal hydrides.[24] Indeed, on supercooling to ca. 150 K a solution containing **2** and its monodeuterated isotopomer **2**-d_1 (see below), it has been possible to observe, at high magnetic field (11.7 T), the deconvolution of this signal into two separate broad resonances at δ −6.0 and −15.3 ppm. The ground-state formulation of compound **2** as the classical hydrido compound **I** is therefore fully supported.

Structure **I** agrees also with the observed longitudinal relaxation time (T_1) of the hydridic resonance. It is well known[6,25] that molecular hydrogen complexes exhibit very short T_1 values, due to the strong dipolar H···H interaction. The relaxation time, measured at 172 K (150 ms, 4.7 T) for the single broad resonance of **2**, is indeed short, but definitely much longer than what it is found for bona fide H_2 complexes. This short value, likely mainly due to the dipolar contribution of the rhenium isotopes,[26,27] is slightly shorter than what is found for other hydridic rhenium complexes[28] and could be a clue of the presence of a small amount of tautomer **IIa**.

In fact, in the presence of mixtures of classical and nonclassical tautomers, the T_1 value, measured at the minimum conditions, is a valuable tool for the estimate of the amount of a nonclassical tautomer, since the observed relaxation rate can be considered a weighted average between those of the classical and nonclassical tautomers.[6e,8e,30] In the present case, despite variable temperature measurements performed at different fields, we could not observe a minimum T_1, due to two opposing factors: (i) the temperature at which T_1 attains the minimum decreases with the field; (ii) the band width of a signal in the near fast exchange region increases with the field. Therefore, at 11.7 T at temperatures lower than 206 K, the signal was too broadened to allow reliable T_1 measurement, while at 4.7 T (where the signal is less broad), we did not observe the attainment of the minimum down to 172 K. Therefore, we could not pursue this approach.[31]

The ^{13}C NMR spectrum of **2** exhibits, at 172 K, the pattern typical of $[Re_2(CO)_9L]$ species,[32] that is, five carbonylic

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(24) Typical chemical shift values for rhenium hydrido-carbonyl complexes are in the range δ −5/−7 ppm for terminal hydrides and δ −15/−18 ppm for bridging ones.

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(31) Moreover, other considerations hamper the use of this approach in the present case: (i) a calculation of the expected T_1 for the classical tautomer at the minimum conditions will require the knowledge of the correlation time, and, since both the H−Re and H−H dipolar interactions contribute to the relaxation, this value is not univocally determined; (ii) the contribution of the H−H dipolar interaction within the classical tautomer depends highly on the conformation of this species; (iii) reliable representative relaxation times for a dihydrogen molecule bound on a cluster are not available, and the range of the relaxation times reported in the literature for mononuclear species is so large that the error in the estimated fraction could be as large as 1 order of magnitude.

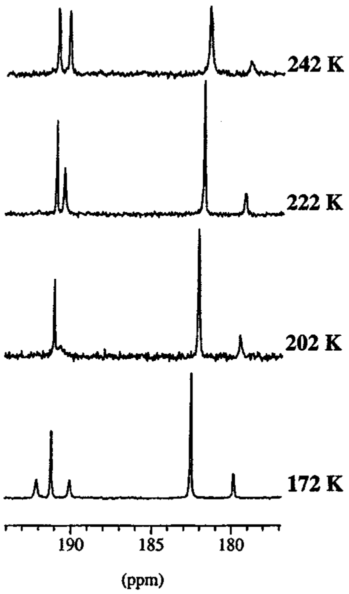

Figure 2. Selected variable temperature ^{13}C NMR spectra of a ^{13}CO-enriched sample of $[Re_2H_2(CO)_9]$ (**2**, THF-d_8, 4.7 T).

resonances, of relative intensity 1:2:1:4:1 (Figure 2). The two resonances of intensity one at lower fields are attributed to the singular carbonyls on the $Re(CO)_4L$ moiety (see Supporting Information); at 182 K, these signals broaden and, above 208 K, coalesce giving rise to an averaged signal (Figure 2). Band shape analysis of the variable temperature spectra allowed the evaluation of the rate constants for this dynamic process (see Table S1), from which $E_a = 44(1)$ kJ mol^{-1} was estimated.

The Different Time Scale of the Fluxionality of the Hydrides and of the Carbonyls. The variable temperature features of the ^1H and ^{13}C NMR spectra of **2** raise some matter. We have already observed several examples of exchange between terminal and bridging hydrides in $H_2Re(CO)_4$ moieties bound to other Re centers through a Re(μ-H)Re interaction (as it occurs in structure **I**).[19,29,33] In all these cases also a *synchronous* exchange process involving the two CO ligands trans to the hydrides has been observed in the ^{13}C NMR spectra. The two dynamic processes have been attributed to an alternating rotation of the $H_2Re(CO)_4$ fragment around the two mutually trans carbonyls (a "windshield-wiper motion"). In the present case, on the contrary, the scrambling of the hydrides and that of the carbonyls occur with very different time scales. Indeed, the presence of a broad but still averaged signal at a temperature as low as 172 K for two hydridic resonances (which are separated by almost 2000 Hz at 4.7 T) implies a process with a rate constant several thousands times higher than the constant (19 s^{-1}, see Table S1) measured for carbonyl exchange at the same temperature.

Therefore, even if the windshield-wiper motion of the terminal $H_2Re(CO)_4$ moiety is likely responsible for the equalization of the carbonyls, another, faster, process must occur, concerning only the hydrides.

This exchange could occur through an intramolecular process, or, alternatively, it could be the result of fast proton-transfer equilibria, involving either an excess of triflic acid[34] or bases, such as the solvent itself or adventitious water.[8e] The latter hypothesis is supported by the acidity of **2**, which is able to protonate a basic phosphine like PMe_2Ph (see Supporting Information).

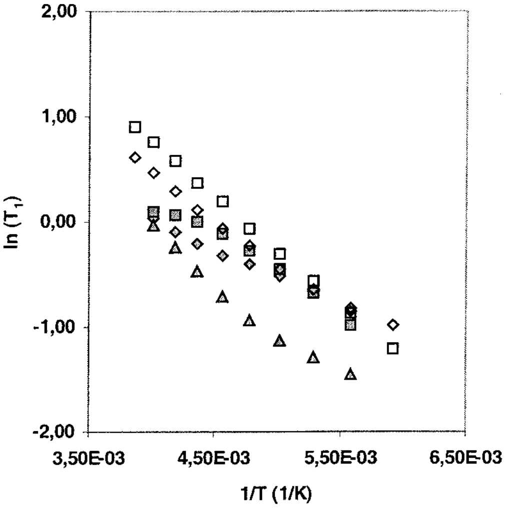

Figure 3. Temperature dependence of the ^1H longitudinal relaxation times: **2** (▲), **1** (◆), H_2O (■) present in the same solution. The white symbols indicate the values for **1** (◇) and H_2O (□) measured in the absence of **2** (THF-d_8, 7.05 T).

In fact, the variable temperature behavior of the ^1H relaxation times (measured at 7.05 T on a solution containing both **2** and the parent anion **1**) revealed the occurrence of exchange processes involving **2**, **1**, and water. Figure 3 shows that at the lowest temperatures the relaxation times of the anion **1** and of water were the same as measured in the absence of **2** (and were longer than those of **2**). On raising the temperature, the longitudinal relaxation times of **1** and of water increased less than observed in the absence of **2** and eventually at 250 K became similar to the one of **2** at the same temperature. Above this temperature, a slight, but sizable, increase of the line width of all the three species was also observed. These effects are emphasized on increasing the amount of water in the sample. The equalization of the relaxation times indicates that proton exchange is occurring between the three species.[30] Because no exchange was observed between **1** and water, in the absence of **2**, this implies that **2** is acidic enough to protonate water, that in turn mediates the exchange with the conjugated base **1**. The time scale of this process, however, is much slower than that of the exchange of the hydrides in **2**; indeed separate signals were observed for **2** and for the parent anion **1** (see Figure 1), and the line width of the latter resonance remained sharp on raising the temperature up to 250 K. This definitely rules out any hypothesis that hydride exchange in **2** is mediated by fast deprotonation of **2** by some basic species, since this would necessarily involve a fast exchange between **1** and **2**.[35]

The fast exchange of the two hydrides, therefore, most likely occurs through an *intra*molecular pathway, and this requires a transition structure, or an intermediate, where the two H atoms are equivalently bound to the $Re(CO)_4$ moiety (as **IIa** or **IIb**).

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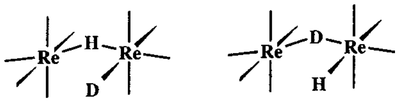
(32) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544−2545.

(33) Beringhelli, T.; D'Alfonso, G.; Ghidorsi, L.; Ciani, G.; Sironi, A.; Molinari, H. *Organometallics* **1987**, *6*, 1365−1367.

(34) This hypothesis, however, was ruled out by the observation that the line width of the signal of **2** was independent of the amount of acid used: 144 and 141 Hz, in the presence and in the absence of an excess of triflic acid, respectively, at 11.4 T, 194 K.

(35) In agreement with this, an averaged hydridic signal was observed for **2** at 178 K also in CD_2Cl_2, that is, in a solvent less amenable than THF to act as a proton shuttle.

Chart 2



I_{Hb} I_{Ht}

^1H and ^2H NMR analysis of the [$Re_2HD(CO)_9$] (**2**-d_1) and [$Re_2D_2(CO)_9$] (**2**-d_2) isotopomers was undertaken to discriminate between a two-site exchange (through a transition state) and a three-site exchange (through an intermediate). This analysis, however, could not discriminate between **IIa** and **IIb** as the possible structures of the transition state (or intermediate); this point was therefore investigated through the DFT computations described in the following.

NMR Analysis of the Mono- and Dideuterated Isotopomers of 2. In the presence of a fast mutual exchange equalizing different hydrogen sites, the partial substitution of ^1H by ^2H removes the degeneracy of the exchanging species, resulting in different averaged chemical shifts for the different isotopomers. This is the principle of the isotopic perturbation of the equilibria,[36] suggested by Saunders and co-workers,[39] and elegantly applied by Shapley[40] to demonstrate the occurrence of an Os−H−C agostic interaction.[41−43] In the present case, whatever the occurring dynamic process (two- or three-site exchange), the signal of **2**-d_1 should be significantly shifted with respect to that of **2**, because the populations of $\mathbf{I}_{Hb}$ and $\mathbf{I}_{Ht}$ (see Chart 2) would be different.

However, in the hypothesis of a three-site exchange, deuteration would modify the equilibrium ratio of the two tautomers **I** and **II**.[44] Therefore, the averaged resonances for the isotopomers **2** and **2**-d_2 should be somewhat different, *provided that **II** had a not negligible concentration and its chemical shift was significantly different from the averaged signal of **I***. A diagnostic of the existence of a significant concentration of **II** in solution would therefore be only the comparison of the chemical shift of the ^2H signal of **2**-d_2 with that of the ^1H signal of **2**.

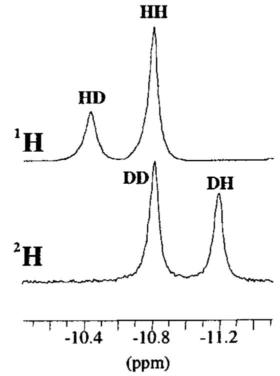


Figure 4. ^1H (upper trace, 218 K) and ^2H (lower trace, 215 K) NMR spectra of the hydridic region of solutions containing **2** + **2**-d_1 and **2**-d_1 + **2**-d_2, respectively (THF-d_8 or THF, 11.7 T).

Table 1. NMR Data for the Different Isotopomers of [$Re_2H_2(CO)_9$] (H = ^1H or ^2H) and Corresponding Fractional Populations of the **2**-d_1 Isotopomer Containing H in the Terminal Site (x_t) (11.7 T, THF-d_8)

^1H NMR

T (K)	δ **2**-d_1	δ **2**	$\Delta\delta$	x_t
231	−10.473	−10.812	0.339	0.537
218	−10.431	−10.800	0.369	0.540
206	−10.378	−10.785	0.407	0.544
194	ca. −10.33	−10.78	0.45	0.549

^2H NMR

T (K)	δ **2**-d_1	δ **2**-d_2	$\Delta\delta$	x_t
215	−11.183	−10.806	−0.377	0.541
203	−11.212	−10.788	−0.424	0.546
191	−11.24	−10.78	−0.46	0.550

The results of the ^1H and ^2H NMR measurements, performed at high magnetic field (11.7 T), are shown in Figure 4 and reported in Table 1. The chemical shift difference (^1H) among the two isotopomers **2** and **2**-d_1 is of the magnitude usually found when H/D substitution modifies the population of exchanging sites, and, as expected, this difference increases on lowering the temperature. At temperatures lower than 206 K, the broadening of the signals hampered an accurate estimate of their $\Delta\delta$. As above-mentioned, on supercooling this sample, due to the high field it has been possible to observe separate broad resonances in the region of the terminal and bridging hydrides (δ ca −6.0 and −15.3 ppm, respectively), but the quality of the spectrum prevented both the evaluation of any equilibrium isotope effect and the observation of the possible secondary isotopic shift for the signals of **2**-d_1.

As shown in Figure 4, ^2H NMR exhibited a resonance at the same δ value of **2**, and another one shifted to higher field. The resonance isochronous with that of **2** can be attributed only to the fully deuterated isotopomer **2**-d_2. The lack of isotopic perturbation is consistent with a two-site mutual exchange but does not rule out the possibility of a three-site process involving a "high" energy intermediate with negligible concentration. For

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(36) While the intrinsic secondary isotope shift is usually of the order of hundredths of ppm,[37,38] the isotopic perturbation of the equilibria leads to changes of the chemical shifts that amount to some tenths of ppm.[39−42]

(37) (a) Mantsch, H. H.; Saito, H.; Smith, I. C. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 211. (b) Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 105−234. (c) Jameson, C. J.; Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 3.

(38) For extensive references to isotope effects on chemical shifts of polyhydride complexes upon partial deuteration, see ref 8e.

(39) Saunders, M.; Jaffe, M. H.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2558−2559.

(40) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726−7727.

(41) For other applications of the principle of isotopic perturbation to agostic species, see for instance: (a) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1981**, 506−507. (b) Brookhart, M.; Lamanna, W.; Humprey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117−2126. (c) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134−1136. (d) Dawkins, G. M.; Green, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 41−43. (e) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem*. **1983**, *250*, 395−408 and references therein. (f) Jordan, R. F.; Bradley, P. K.; Baezinger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289−1291. (g) Green, M. L. H.; Hughes, A. K.; Popham, N. A.; Stephens, A. H. H.; Wong, L.-L. *J. Chem. Soc., Dalton Trans.* **1992**, 3077−3082. (h) Hamilton, D. H.; Shapley, J. R. *Organometallics* **2000**, *19*, 761−769.

(42) For the effect of partial deuteration on the chemical shift of complexes containing different hydrides or both hydrides and dihydrogen, see for instance: (a) Bianchini, C.; Laschi, F.; Peruzzini, M.; Ottaviani, F. M.; Vacca, A.; Zanello, P. *Inorg. Chem.* **1990**, *29*, 3394−2402. (b) Heinekey, D. M.; Oldham, W. J., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 3137−3138. (c) Heinekey, D. M.; Liegeois, A.; van Roon, M. *J. Am. Chem. Soc.* **1994**, *116*, 8388−8369. (d) Heinekey, D. M.; van roon, M. *J. Am. Chem. Soc.* **1996**, *118*, 12134−12140.

(43) For discussions concerning the precautions in the use of the method of the isotopic perturbation of the equilibrium, see ref 8c and Wang, Q.; Gillis, D. J.; Quyoum, R.; Jeremic, D.; Tudoret, M.-J.; Baird, M. C. *J. Organomet. Chem.* **1997**, *527*, 7−14.

(44) It has been previously observed[8c] that in the cases of equilibrium mixtures of classical and nonclassical tautomers, the isotopic perturbation of the chemical shift is expected to arise not only from the isotope fractionation between different sites in the classical tautomer, but also from the isotope effect on the equilibrium between the two tautomers; indeed dihydride ↔ dihydrogen equilibria are shifted to the right upon isotopic substitution.[6e,8c,45]

(45) Haward, M. T.; George, M. W.; Hamley, P.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1101−1103.

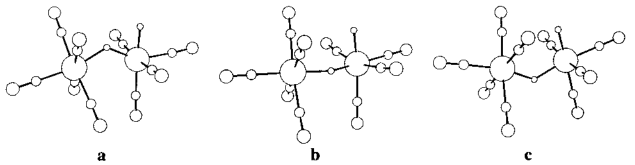

Figure 5. Cis/trans interconversion: optimized geometries of the two stable cis-**I** (a) and trans-**I** (c) conformers and of the asymmetric transition structure (b).

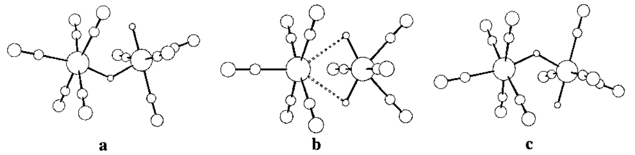

Figure 6. Windshield-wiper motion: the C_{2v} transition structure (b) interconnects two permutational isomers (a, c) of trans-**I**.

this reason, NMR cannot be used to ascertain the mechanism of this dynamic process.

Theoretical Characterization of the Potential Energy Surface (PES) of [$Re_2H_2(CO)_9$]. To shed some light on the nature of the fast hydrogen scrambling and to obtain a parametric description of two elemental dynamic processes of hydrido rhenium carbonyl clusters (to be used in the future in the modeling of larger members of this class), we have performed extensive DFT computations (B3LYP/TZ2P//B3LYP/DZP, see the Experimental Section) on this system, and we have obtained a detailed description of its dynamics in vacuo.

The Ground-State Structure and the Fast Cis/Trans Interconversion. Extensive searching of the PES has led to the recognition of the presence of two minima, very close in energy, interconnected by a transition structure as outlined in Figure 5.

The absolute minimum (cis-**I**, Figure 5a) has C_s symmetry, one terminal and one bridging hydrido ligand, a staggered arrangement of the two ReL_5 moieties, and a $H_t-Re-Re-H_b$ torsion angle of 0° (i.e., the two hydrides are on the same side of the molecule, hence cis, with respect to the Re−Re bond). The relative minimum (trans-**I**, Figure 5c, 1.8 kJ mol^{-1} higher in energy) has C_s symmetry, one terminal and one bridging hydrido ligand, a staggered arrangement of the two ReL_5 moieties, and a $H_t-Re-Re-H_b$ torsion angle of 180°. The interconnecting transition structure (Figure 5b) has no symmetry and lies 5.5 kJ mol^{-1} above the absolute minimum. The interconnecting reaction coordinate consists of a rotation of the bridging hydride around the Re−Re interaction with only minor changes of the surrounding atoms. Obviously this process is fast with respect to the NMR time scale and leaves no trace on NMR spectra.

The Windshield-Wiper Motion. From the consideration given in the NMR section, the most reasonable transition structure has C_{2v} symmetry. Accordingly, we started optimizing the postulated C_{2v} structure with two bridging hydrides reported in Figure 6b, and, upon reaching a stationary point, we confirmed by frequencies calculation that it was a first-order saddle point and that the imaginary normal coordinate was really interconnecting trans-**I** (Figure 6a), which is in fast exchange with cis-**I** (see Figure 5), to its permutational isomer (Figure 6c). The computed energy barrier for the process is 39.6 kJ mol^{-1}, a value in good agreement with the experimental value of 44(1) kJ mol^{-1}.

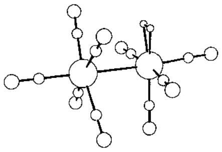

Figure 7. The optimized geometry of the transition structure of the fast hydrogen exchange.

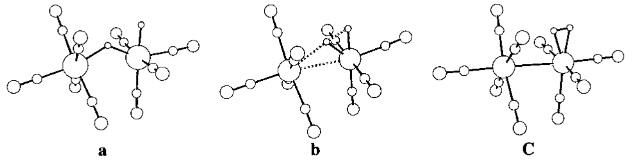

Figure 8. Cis-**I**/**IIa** interconversion: optimized geometries of the two stable cis-**I** (a) and **IIa** (c) isomer and of the transition structure (b).

The Fast Hydrogen Scrambling. The only experimental evidences to start with were the requirement of a reaction coordinate passing through a conformation with two “equivalently bound” hydrogen atoms and the stereochemical rigidity of the $Re(CO)_4$ moiety (i.e., no interchange between the two CO ligands trans to the hydrido ligands). To fulfill these requirements, we decided to assume the former by selecting a guess transition structure (or intermediate) with two equivalent (mirror related) hydrido ligands and (overall) C_s symmetry. In the C_s subspace, the optimized structure (Figure 7) corresponds to a minimum with a nonclassical structure. However, a frequencies computation showed that this structure is a first-order saddle point.

The imaginary eigenvector, corresponding to the H_2 rotation about the $Re-H_2$ axis, was followed downhill by minimizing a slightly perturbed structure (with no symmetry), and we reached the absolute minimum cis-**I**. However, this was not a real intrinsic reaction coordinate (IRC) computation, and, to check the possible presence of a stable nonclassical intermediate, we attempted also a minimization (in the C_s subspace) starting 90° ahead along the H_2 rotation about the $Re-H_2$ axis. Upon frequency checking, the optimized structure (Figure 8c) resulted to be a true minimum (of relative energy 12.7 kJ mol^{-1}). This minimum has a nonclassical structure, thus corresponding to **IIa** in Chart 1. Noteworthy, its relatively high energy agrees with the NMR evidence excluding the presence of significant amounts of **IIa** in solution. The effective occurrence of the interconversion between the two tautomers cis-**I** and **IIa** was checked by means of a quadratic synchronous transit computation, which afforded the expected transition structure (18.5 kJ mol^{-1}) with an incipient H···H bond (Figure 8b). In addition, extensive search of the PES of [$(CO)_5Re-ReH_2(CO)_4$] excluded the presence of a classical isomer **IIb**.

The computed energy barrier for the whole process is 27.2 kJ mol^{-1}, which reasonably matches the experimental value (23 kJ mol^{-1}, see below), and agrees with the observation that hydrogen scrambling is faster than the windshield-wiper motion.

A cut of the potential energy surface of [$Re_2H_2(CO)_9$] showing the windshield-wiper motion and the fast hydrogen scrambling is reported in Figure 9.

Kinetic Parameters and Isotope Effect for Hydride Exchange by NMR Measurements. The variable temperature ^1H spectra measured in a temperature range corresponding to near fast exchange regime provided kinetic data for this process. Three independent sets of data (Table 2, two sets from mixtures

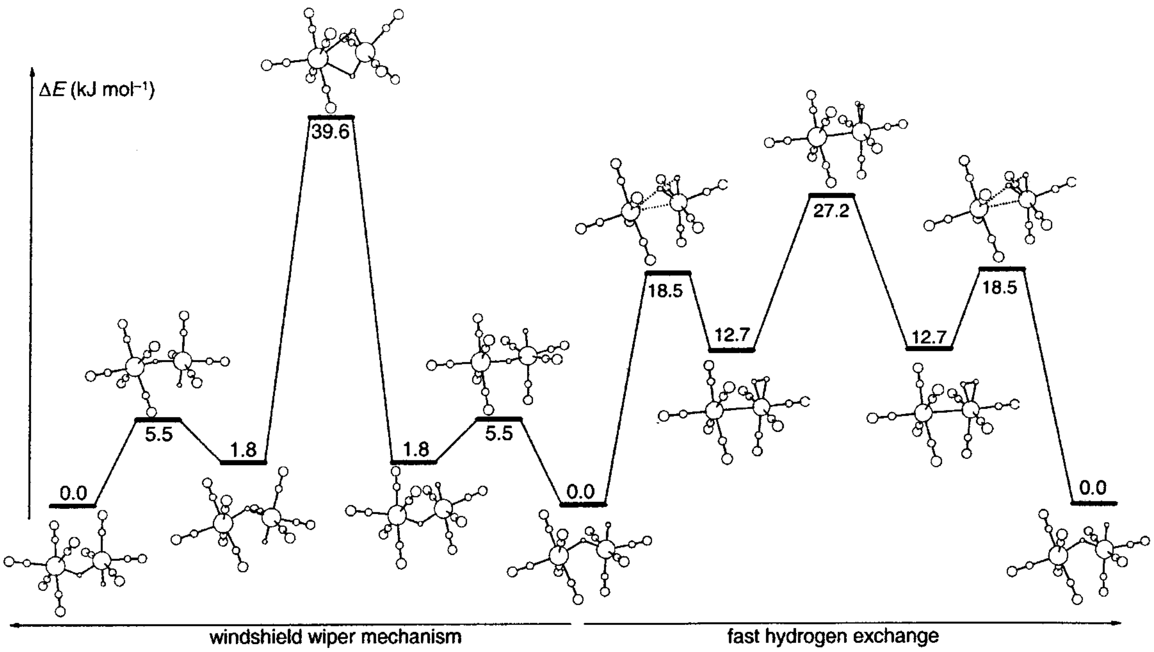

Figure 9. A cut of the potential energy surface of [$Re_2H_2(CO)_9$] showing the two proposed fluxional processes.

Table 2. Rate Constants for the Hydride Exchange in Compound **2** Evaluated from Line Width Analysis at Different Temperatures and Field Strengths

4.7 T		7.05 T		11.7 T	
T (K)	$k \times 10^{-5}$ (s^{-1})	*T* (K)	$k \times 10^{-5}$ (s^{-1})	*T* (K)	$k \times 10^{-5}$ (s^{-1})
		168	0.50		
		178	1.1		
		188	3.0	182	1.9
197	5.4	198	6.2	194	5.0
207	11	208	12	206	12
217	21	218	24	218	27
227	42	228	50	231	63
238	76				

Table 3. Activation Parameters for the Hydride Exchange in **2** and **2**-d_1, Estimated from the Kinetic Data of Tables 2 and 4, Respectively

field (T)	E_a (kJ mol^{-1})	ln *A*	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
		2		
4.7	25.4(4)	28.7(2)	23.6(4)	−12(2)
7.05	24.5(5)	28.2(3)	22.8(5)	−15(2)
11.7	25.0(4)	28.6(2)	23.2(4)	−12(2)
		2-d_1		
4.7	29.1(3)	30.4(2)	27.3(3)	2(2)
11.7	27.9(6)	29.8(3)	26.1(5)	−3(3)

Table 4. Rate Constants and Kinetic Isotope Effect for Hydride Exchange in **2**-d_1 at Different Temperatures and Field Strengths

4.7 T			11.7 T		
T (K)	$k \times 10^{-5}$ (s^{-1})	k_{HH}/k_{HD}	*T* (K)	$k \times 10^{-5}$ (s^{-1})	k_{HH}/k_{HD}
197	3.1	1.7	194	2.7	1.8
207	7.0	1.6	206	7.0	1.7
217	16	1.3	218	17	1.6
227	32	1.3	231	43	1.5

Table 5. Observed Δδ between the Resonances of **2**-d_1 and **2**, Corresponding Fractional Populations of the **2**-d_1 Isotopomer Containing H in the Terminal Site (x_t), and Equilibrium Ratio *K* between the Two Isomers $\mathbf{I}_{Ht}$ and $\mathbf{I}_{Hb}$ of **2**-d_1 (4.7 T)

T (K)	Δδ	x_t	*K*
197	0.4430	0.5483	1.214
207	0.4162	0.5451	1.198
217	0.3849	0.5417	1.182
227	0.3573	0.5387	1.168
238	0.3311	0.5359	1.155
249	0.3086	0.5334	1.143
254	0.2980	0.5323	1.138
259	0.2871	0.5311	1.133

containing both **2** and **2**-d_1 and one from a sample containing only **2**) were analyzed at different fields; the results are remarkably consistent, and the respective activation parameters, obtained according to Arrhenius and Eyring analysis, are reported in Table 3.

From the samples containing both the isotopomers, the rate constants for the $H_t \leftrightarrow H_b$ exchange in the mixed isotopomer **2**-d_1 were as well estimated, on using the fractional populations reported in Table 5. The kinetic constants (Table 4) revealed a small, but not negligible, normal kinetic isotope effect (1.3/1.8, in the temperature range 194/231 K). The corresponding activation parameters are shown in Table 3. The values of the kinetic isotope effect are in the range usually found in reactions of reductive-elimination or oxidative-addition of H_2 on electron-rich metal centers.[46,47] In particular, they compare well with the value of 1.40 previously found for reductive-elimination of H_2 from a trirutenium cluster containing a bridging and a terminal hydrido ligand, for which a three-center transition state (analogous to what is now called an η^2-H_2 complex) was proposed.[47a]

The same type of analysis was attempted for the ^{2}H data recorded at 11.7 T. Above 191 K, however, at the deuterium

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[46] See: Rosenberg, E. *Polyhedron* **1989**, *8*, 383−405 and references therein. See also: Bullock, R. M. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; pp 263−307.

[47] Values of kinetic isotope effect in the range 1.2−2 have been found in reaction involving oxidative-addition or reductive-elimination in carbonyl clusters. See for instance: (a) Bavaro, L. M.; Montangero, P.; Keister, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 4977−4981. (b) Hudson, R. H. E.; Poë, A. J.; Sampson, C. N.; Siegel, A. *J. Chem. Soc., Dalton Trans.* **1989**, 2235−2240. (c) Safarowic, F. J.; Bierdeman, D. J.; Keister, J. B. *J. Am. Chem. Soc.* **1996**, *118*, 11805−11812.

frequency, the time scale of the process gives rise to line widths insensitive to the rate constants, so only the values at 191 K could be reliably estimated: $k_{DH} = 2.9 \times 10^5$ s^{-1} and $k_{DD} = 1.9 \times 10^5$ s^{-1}, corresponding to a kinetic isotope effect of 1.5.

The Preference of Deuterium for the Bridging Site. Figure 4 shows that, as expected, the resonance of the mixed H/D isotopomer **2**-d_1 in the ^{2}H NMR spectra was shifted in the opposite way than that in the ^{1}H NMR spectrum, with respect to the δ value of the isotopomers **2**-d_2 and **2**, respectively. However, the direction of these shifts was at first sight rather surprising, since it is known that deuterium atoms tend to accumulate in the stiffer bonds and terminal hydridic sites exhibit higher stretching frequencies than do the bridging ones.[48] To the best of our knowledge, in the only other experiment where H/D exchange was used to perturb the resonance of bridging-terminal hydrides in fast exchange, concerning the $[Pt_2H_3(dppe)_2]^+$ cation (dppe = bis(diphenylphosphino)ethane), the deuterium atoms preferred the terminal location.[49]

However, since the isotopic enrichment at one site depends on the overall zero-point energy, we must take into account (at least) the contribution of all the stretching modes, which are *two* for a bridging and only *one* for a terminal H-ligand. On estimating the zero-point energies from the known force constants in the proper (available) reference compounds,[50] we foresee that in the case of rhenium hydrides the D atom should prefer the bridging site. On this simple ground, one should therefore expect a dominance of $\mathbf{I}_{Ht}$, causing the averaged signals of **2**-d_1 to be shifted to lower field in the ^{1}H NMR spectrum, and in the opposite way in the ^{2}H spectrum, as observed.

To check theoretically this hypothesis, we have computed the zero-point energies for both cis-$\mathbf{I}_{Hb}$ and cis-$\mathbf{I}_{Ht}$, and we have found that the latter is indeed more stable than the former by 65 J mol^{-1}. A closer analysis of the contributing vibrations shows that the bendings favor the cis-$\mathbf{I}_{Hb}$ isotopomer, but their contribution is overwhelmed by those of the stretchings, and, eventually, the cis-$\mathbf{I}_{Ht}$ isotopomer is favored.[51]

The NMR data allow the experimental estimate of this thermodynamic isotope effect. The $\Delta\delta$ between the ^{1}H resonances of isotopomers **2** and **2**-d_1 (Table 5) can be expressed as in eq 3, where x_t is the fractional population of the isomer of **2**-d_1 containing ^{1}H in the terminal site. This fractional population can, therefore, be calculated at each temperature, assuming that (i) the values of δ_t and δ_b observed in the supercooled spectrum can be considered the chemical shifts corresponding to stopped exchange; (ii) the $\delta_t - \delta_b$ does not change with temperature; and (iii) the isotopic effect on the chemical shift is negligible.

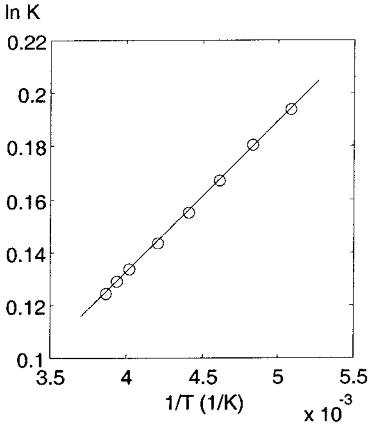
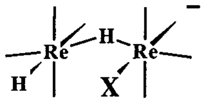


Figure 10. Thermodynamic isotope effect as a function of the temperature for the two isomers $\mathbf{I}_{Ht}$ and $\mathbf{I}_{Hb}$ of **2**-d_1 (the values of *K* are reported in Table 5).

Chart 3



$$\delta_{HD} - \delta_{HH} = x_t(\delta_t - \delta_b) - (\delta_t - \delta_b)/2 \qquad (3)$$

In this way, the following thermodynamic parameters for the interconversion $\mathbf{I}_{Hb} \rightleftarrows \mathbf{I}_{Ht}$ have been estimated: $\Delta H° = -475(4)$ J mol^{-1} and $\Delta S° = -0.80(2)$ J K^{-1} mol^{-1} (Figure 10). Very similar results can be evaluated also from the smaller set of higher field data reported in Table 1: $\Delta H° = -485(18)$ J mol^{-1} and $\Delta S° = -0.9(1)$ J K^{-1} mol^{-1} from the ^{1}H data, and $\Delta H° = -515(50)$ J mol^{-1} and $\Delta S° = -1.0(3)$ J K^{-1} mol^{-1} from the ^{2}H data.

To establish whether the preference of deuterium for the bridging sites was a general feature of rhenium complexes containing terminal and bridging hydrides, we prepared deuterated isotopomers of the anion $[Re_2H(\mu\text{-}H)Cl(CO)_8]^-$ (**3**).[52] This species (Chart 3, with X = Cl) exhibits a sharp averaged signal (δ −9.55 ppm) at temperatures higher than 273 K, which at ca. 215 K collapses, giving rise to two separate resonances at lower temperatures (δ −5.59 and −12.95 ppm, 168 K, THF-d_8), due to the terminal and the bridging hydrides.[53]

The ^{1}H and ^{2}H NMR spectra of the mixed H/D isotopomers **3**, **3**-d_1, and **3**-d_2 showed the same pattern as that observed for the corresponding isotopomers of **2**, that is, ^{1}H NMR (298 K, THF-d_8), −9.27 (**3**-d_1) versus −9.59 (**3**) ($\Delta\delta$ 0.32); ^{2}H NMR, −9.91 (**3**-d_1) versus −9.59 (**3**-d_2) ($\Delta\delta$ −0.32). Also in **3**, therefore, in the mixed H/D isotopomer, the deuterium atoms concentrate in the bridging position. From the averaged δ value,

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(48) Usually ν(Re−H) occurs at about 2000 cm^{-1} for terminal hydrides, while for bridging hydrides the ν asymmetric vibrations have been identified in the range 1700−1300 cm^{-1} (and the symmetric stretching modes at still lower frequencies, 1300−800 cm^{-1}), see for instance: (a) Anson, C. E.; Jayasooriya, U. A.; D'Alfonso, G.; Stanghellini, P. L. *J. Organomet. Chem.* **1989**, *372*, 85−97. (b) Jayasooriya, U. A.; Stotesbury, S. J.; Grinter, R.; Powell, D. B.; Sheppard, N. *Inorg. Chem.* **1986**, *25*, 2853−2857 and references therein.

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(50) $[HRe(CO)_5]$ $\nu_{Re-H} = 1882$ cm^{-1} (1313 cm^{-1} for the deuterated complex): Braterman, P. S.; Harrill, R. W.; Kaesz, H. D. *J. Am. Chem. Soc.* **1967**, *89*, 2851−2855. $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ $\nu_{as\ Re-H-Re} = 1692$ cm^{-1} $\nu_{s\ Re-H-Re} = 1111$ cm^{-1} (1220 and 806 cm^{-1} for the perdeuterated complex): Jayasooriya, U. A.; Stotesbury, S. J.; Grinter, R.; Powell, D. B.; Sheppard, N. *Inorg. Chem.* **1986**, *25*, 2853−2857.

(51) Note that, in principle, bendings can overwhelm stretchings. For instance, in a theoretical study concerning the equilibrium isotope effect for the addition of H_2 to the Vaska's complex *trans*-$[Ir(PR_3)_2(CO)X]$, it has been found that the four Ir−H bending modes have a crucial role in determining the observed *inverse* isotope effect (i.e., in making D_2 addition more favored than H_2 addition, despite the much higher strength of the H_2/D_2 bonds with respect to the Ir−H/D bonds): Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **1993**, *115*, 8019−8023.

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(53) The ^{13}C NMR spectrum of **3** at 173 K shows the six resonances (1:2:1:2:1:1) expected for the structure of Chart 3 and, on rising the temperature, the exchange of the two lower field resonances of intensity 1 (see Experimental Section). The kinetic constants evaluated for this exchange (Table S2) provided an activation energy [37(1) kJ mol^{-1}] quite similar to the one obtained for the exchange of the hydrides [38(1) kJ mol^{-1}, from band shape analysis of the variable temperature ^{1}H spectra; see the kinetic constants in Table S2]. In the anion **3**, the two processes (exchange of the hydrides and exchange of the carbonyls trans to them) can therefore be considered synchronous, occurring through the so-called windshield-wiper motion of the $H_2Re(CO)_4$ moiety.

the ratio between the concentrations of the two isotopomers can be calculated straightaway as 0.54/0.46 ($K_{Hb \rightleftarrows Ht} = 1.17$), corresponding to $\Delta G° = -400$ J mol^{-1} at 298 K.

The preference of deuterium for bridging sites seems, therefore, a general feature of compounds containing a terminal $H_2Re(CO)_4$ fragment.

Conclusions

The NMR analysis of [$Re_2H_2(CO)_9$] has demonstrated that the protonation of the anion [$Re_2H(CO)_9$]$^-$ affords a classical species containing a terminal and a bridging hydrido ligands (structure **I** of Chart 1). Several pieces of evidence ruled out the presence of a sizable amount of a nonclassical dihydrogen tautomer in fast exchange with the dihydride. However, DFT computations indicated that such a nonclassical tautomer is the intermediate of the fast dynamic process equalizing bridging and terminal hydrides in **2**. It is the relatively high energy of this tautomer with respect to the classical [$Re_2H(\mu\text{-}H)(CO)_9$] isomer (12.7 kJ mol^{-1}) that makes its concentration too low to allow its spectroscopic detection.

The novel fluxional process interchanging the hydrides via the η^2-hydrogen coordination is much faster than the so-called windshield-wiper motion and was never observed in the previously know dihydridic dinuclear rhenium(I) complexes with a structure analogous to that of **2**. Such complexes are mainly represented[54] by the anions of general formula [$Re_2H(\mu\text{-}H)X(CO)_8$]$^-$, that share the structure of Chart 3, with X = H,[33] Cl,[52] $Re(CO)_5$,[29] $HRe_2(CO)_9$);[19] in all these species the windshield-wiper motion was the only observed dynamic process. We can explain this difference on the basis of very qualitative "charge equalization" arguments. Indeed, assuming that an isomer with a good smearing of local charges is intrinsically favored over that with an odd charge distribution, we observe that for **2**, where unequal charge distribution affects the ground state, the energy gap between the ground state and the nonclassical intermediate should be lower than that in the [$Re_2H(\mu\text{-}H)X(CO)_8$]$^-$ anions, where the unequal charge distribution destabilizes the possible nonclassical tautomer.

Also, the instability of molecular hydrogen complexes on increasing the electron richness of the metal centers should be taken into account. This might explain the absence of very fast exchange processes in the neutral complex [$Re_2H(\mu\text{-}H)(CO)_8(PPh_3)$].[55]

Bona fide examples of coordination of intact molecular hydrogen on a polynuclear complex are still lacking, even if such a coordination mode has often been postulated as the transition state in reactions of oxidative-addition/reductive-elimination of H_2 on/from carbonyl clusters.[15c,47,56] Our findings support this view. Indeed, since we know that **IIa** is continuously formed (and destroyed) along the isomerization pathway of **2**, **IIa** has to be the intermediate also of the irreversible H_2 loss that we observe at temperatures higher than 250 K, when, most likely, the entropic contribution prevails over the enthalpic contribution.

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 [NEt_4][$Re_2H(CO)_9$],[33] [$Re_2(\mu\text{-}H)_2(CO)_8$],[57] [$Re_2(\mu\text{-}H)(\mu\text{-}D)(CO)_8$],[57] [$Re_2(\mu\text{-}D)_2(CO)_8$],[57] [$ReH(CO)_5$],[58] [PPN][$Re(CO)_5$],[59] and ^{13}CO-enriched (about 25%) [$Re_2(CO)_{10}$].[60] [$ReD(CO)_5$] was obtained by protonation with CF_3SO_3D of Na[$Re(CO)_5$] (obtained by the usual Na/Hg reduction of [$Re_2(CO)_{10}$]).

Infrared spectra were recorded on a Bruker Vector 22 FT spectrophotometer in 0.1 mm CaF_2 cells. Low-temperature IR spectra were recorded using the variable temperature cell Specac P/N 21425. NMR spectra were recorded on Bruker AC200, Bruker DRX300, and Bruker AMX500 spectrometers. Temperatures were measured using the standard CD_3OD/CH_3OH solution and controlled by BVT-1000 or BVT-2000 units. ^{1}H and ^{13}C NMR spectra have been simulated, allowing for the changes of the chemical shifts with the temperature, using an authors' modified version of the QCPE program Multi Site Exchange[61] or the Bruker's WINDYNAMICS software. A routine written for MATLAB was used to calculate the rate constants from the line widths of the resonances obtained through the deconvolution routine in WIN NMR.

The 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 routines running either on the spectrometers or on PCs (WIN NMR). From 10 to 14 variable delays were employed, and the recycle delay was always at least 5 times the longest expected T_1.

Preparation of [$Re_2H_2(CO)_9$]. Typically, a sample of [NEt_4]**1** (26 mg, 0.034 mmol) was dissolved in THF-d_8 in a NMR tube at 193 K and treated with CF_3SO_3H (3.0 μL, 0.034 mmol). A ^{1}H NMR spectrum at 193 K showed the instantaneous and selective formation of **2** (δ −10.78). A ^{13}CO-enriched sample of **2** was prepared as above, from ^{13}CO-enriched [NEt_4]**1** (40 mg, 0.053 mmol) and CF_3SO_3H (4.5 μL, 0.051 mmol). ^{13}C NMR (THF-d_8): 172 K, δ 192.13 (1), 191.23 (2), 190.08 (1), 182.56 (4), 179.86 (1); 238 K, δ 190.96 (2), 190.40 (2), 181.72 (4), 179.1 (1). The reaction was performed, as above, also in a Schlenk tube to acquire the IR data of **2** at low temperature; a sample of [NEt_4]**1** (12 mg, 0.016 mmol) was dissolved in THF and treated at 193 K with CF_3SO_3H (1.5 μL, 0.017 mmol). The IR spectrum recorded at ca. 233 K (Figure S1) showed the complete disappearance of the carbonyl bands of [NEt_4]**1** and the formation of new bands attributed to **2** at 2148vw, 2076w, 2035vs, 1980ms, 1966m, 1943m cm^{-1}, together with some very minor absorptions, attributed to [$Re_2(CO)_9THF$], originated from the thermal decomposition of **2**. Indeed, when the solution was allowed to warm to room temperature, the IR spectrum showed the quantitative transformation of **2** into [$Re_2(CO)_9THF$].[19]

To isolate **2** in the solid state, the reaction was repeated in diethyl ether. A sample of [NEt_4]**1** (40 mg, 0.053 mmol) was suspended in diethyl ether and treated at 193 K with CF_3SO_3H (4.5 μL, 0.051 mmol). The suspension was stirred at 193 K until all [NEt_4]**1** was dissolved. The fine white precipitate of [NEt_4][CF_3SO_3] was removed by filtration, at low temperature, and then cold *n*-hexane was added to the ethereal solution, under stirring. A white precipitate formed, that was isolated by decantation at 193 K and dried under vacuum. The color of the solid turned immediately from white to yellow when it reached room

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(54) Also, a neutral species analogous to **2**, [$Re_2H(\mu\text{-}H)(CO)_8(PPh_3)$], has been previously reported;[55] for this complex, the coalescence of the two hydridic resonances occurred only at temperatures higher than 243 K, but no detailed study of the nature of the exchange process was reported.

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temperature. The IR spectrum acquired at room temperature in THF showed ν(CO) bands at 2149vw, 2103w, 2081w, 2042s, 2013m, 1988vs, 1973s, 1959m, 1919m, 1888mw cm^{-1}. In a different preparation, the diethyl ether solution, after filtration, was gently layered with *n*-hexane. Diffusive mixing resulted in colorless crystals after 10 days at 193 K. Also the isolated crystals decomposed at room temperature, becoming pale yellow. Dissolution of some crystals in a minimal amount of CD_2Cl_2 at 193 K yielded a faintly yellow solution, and ^{1}H NMR spectrum acquired at 223 K exhibited resonances at δ −6.02, −12.77, −15.58 with integral ratio 1:0.4:4.3. The IR spectrum acquired at room temperature in THF on a single crystal showed ν(CO) bands at 2102w, 2096w, 2041m, 2015s, 1992vs, 1951m, 1916mw cm^{-1}.

Preparation of Deuterated Isotopomers of 2. (a) A sample of $[NEt_4][Re_2H(CO)_9]$ (40 mg, 0.053 mmol) was treated in an NMR tube with CF_3SO_3D (4.6 μL, 0.053 mmol) in THF-d_8 at 193 K. ^{1}H NMR data (THF-d_8, 218 K) for $[Re_2HD(CO)_9]$: δ −10.43, for $[Re_2H_2(CO)_9]$ δ −10.80. (b) A sample of $[NEt_4][Re_2D(CO)_9]$ was prepared by treating $[PPN][Re(CO)_5]$ (70 mg, 0.081 mmol) dissolved in THF (about 8 mL) with stoichiometric $[ReD(CO)_5]$ (11 μL).[59] The solution was stirred at room temperature for 10 min, concentrated, transferred in a NMR tube, and treated, at 193 K, with CF_3SO_3D (7 μL, 0.081 mmol). ^{2}H NMR data (THF, 215 K) $[Re_2HD(CO)_9]$: δ −11.18, $[Re_2D_2(CO)_9]$ δ −10.81.

Preparation of $[Re_2H(\mu\text{-}H)Cl(CO)_8]^-$ (3). A sample of $[Re_2(\mu\text{-}H)_2(CO)_8]$ (20 mg. 0.035 mmol) was dissolved in 4 mL of THF and treated, at room temperature, with PPNCl (18 mg, 0.031 mmol, PPN = bis(triphenylphosphine)iminium chloride). IR monitoring showed the instantaneous formation of **3**: ν(CO) (THF): 2098vw, 2068w, 1999vs, 1975s, 1937m, 1919sh. The same reaction was repeated in a NMR tube using ^{13}CO-enriched $[Re_2(\mu\text{-}H)_2(CO)_8]$ (23 mg, 0.053 mmol) and PPNCl (35 mg, 0.061 mmol) in THF-d_8. ^{1}H NMR data: 168 K, δ −5.59(1), −12.95(1); 298 K, δ −9.59. ^{13}C NMR data: 168 K, δ 191.94(1), 191.42(2), 191.10(1), 188.83(2), 186.96(1), 185.85(1). The two lower field resonances of intensity 1 (δ 191.94 and 191.10) were broad and collapsed on slightly raising the temperature, and at 213 K gave rise to an averaged signal. At 193 K, where these signals were at the coalescence, the low field signal of intensity 2 broadened significantly in the proton coupled spectrum, while the three high field resonances appeared unmodified. This latter set of resonances can therefore be attributed to the carbonyls of the $Re(CO)_4Cl$ moiety and the exchanging signals to the carbonyls trans to the hydrides on the other metal center.

Preparation of 3-d_1 and 3-d_2. A sample of partially deuterated **1** (20 mg, 0.035 mmol), prepared following the method described by Kaesz et al.,[57] was dissolved in a NMR tube in 0.5 mL of THF and treated, at room temperature, with PPNCl (18 mg, 0.031 mmol). ^{2}H NMR data: 298 K δ −9.59, −9.91 ppm. The same reaction was repeated in THF-d_8, and the ^{1}H NMR spectrum (room temperature) showed the signals of **3**-d_1 and **3** at δ −9.27 and −9.59, respectively.

Computational Details. All the calculations were done using an empirically parametrized density functional theory (DFT) method incorporating Becke's three-parameter hybrid functional[62] along with the Lee−Yang−Parr correlation functional[63] (B3LYP). A basis set incorporating the "small core" relativistic effective core potentials (ECP) of Hay and Wadt[64] was used for the rhenium atoms along with valence double-ζ functions[64] augmented with an energy-optimized set of 5p functions[65] and a polarization f function (α = 0.869),[66] yielding a final contraction of (441/441/21/1), similar but different from the basis set Lanl2DZ included in Gaussian 98.[67] The Dunning−Huzinaga valence double-ζ basis set[68] (D95V) with a single polarization (d,p) function was used for all remaining atoms. The total size of the system was 320 basis functions. Geometries were optimized in redundant internal coordinates,[69] employing the GDIIS algorithm,[70] until the maximum (root-mean-square) force was less than 0.00045 (0.00030) au. Explorative calculations were done without the imposition of any symmetry; however, final geometries have been optimized within the point groups specified in the text. The nature of the stationary points (true minima or transition structures) was assigned by analytical frequencies calculations, by which we obtain the zero-point vibrational energy correction. Single-point energies have been recomputed for all the species using an extended basis set of valence triple-ζ plus double polarization quality. For the rhenium atoms, the Hay and Wadt functions were augmented with a diffuse d function (α = 0.032) and two polarization f functions (α = 0.1738 and 0.4345) yielding a final contraction of (3311/3311/1111/11), while the 6-311G(2d,2p) basis set[71] was used for all remaining atoms. All the computations were performed with Gaussian 98.

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Supporting Information Available: Details concerning the ^{13}C NMR data and the reactivity of **2**, tables of the kinetic constants for carbonyl exchange in **2** and for hydride and carbonyl exchange in **3** (Tables S1, S2), low-temperature IR spectrum of **2** (Figure S1) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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