Rhenium-Platinum Mixed Metal Clusters. Characterization in Solution and Dynamic Behavior of the Isomers of $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$. An Example of a Labile Metal Fragment That Undergoes Intermolecular Exchange

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The cluster $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$ (1), which contains a $[ReH(CO)_5]$ molecule bound to the Pt atom of a Re_2Pt triangular cluster, exists in solution at low temperature as two isomers, with a ratio of *ca.* 19:1. The values of the $^1H-^{195}Pt$ coupling constants and the dynamic behavior suggest that in both the species $[ReH(CO)_5]$ is bound to Pt, but with different locations with respect to the H-bridged Re-Pt triangular edge: *cis* in the major one (**1a**), as found in the solid state structure, and *trans* in the minor isomer (**1b**). ^1H 2D EXSY experiments at 180 K showed the occurrence of two dynamic processes: one interconverts the two isomers, while the other one leads to intermolecular exchange of the $[ReH(CO)_5]$ fragment. The addition of $[ReH(CO)_5]$ caused a dramatic increase of the rate of this exchange even at 180 K and showed that this latter process is operative only in the major species **1a**. The isomerization rate, on the contrary, is insensitive to the addition of $[ReH(CO)_5]$, indicating its intramolecular nature. The rate constants of the two processes obtained at 180 K allowed the calculation of the activation parameters $\Delta G^{\ddagger}_{180} = 43.0$ kJ/mol and $\Delta G^{\ddagger}_{180} = 41.9$ kJ/mol for the isomerization and for $[ReH(CO)_5]$ exchange, respectively. Several indirect thermodynamic and kinetic evidences indicate that above 210 K one or more species, in fast exchange with the two isomers, are present in solution. At 264 K, a ^1H 2D EXSY experiment showed the onset of a new exchange process, implying the cleavage of the H-Re bond of the $[ReH(CO)_5]$ fragment, likely *via* oxidative addition of $[ReH(CO)_5]$ on Pt.

We have recently reported the synthesis of Re-Pt mixed metal clusters[1] containing from three to five metal atoms. The interest in the properties of these compounds as precursors or models of catalytic species prompted us to analyze in greater detail the dynamic behavior that some of them exhibit in solution.[2] We report here on the solution structural characterization and on the dynamic properties of the isomers of $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$ (compound 1), a cluster recently synthesized[1d] and shown by X-ray analysis to contain a $[ReH(CO)_5]$ molecule, bound to the Pt atom of a Re_2Pt triangular cluster through a $Re(\mu\text{-}H)Pt$ interaction (structure I of Chart 1). It is well-known that $[ReH(CO)_5]$, as other metal hydrides, can behave as a two-electron donor ligand toward coordinatively unsaturated complexes or compounds containing weakly coordinated ligands.[3,4] Indeed, $[ReH(CO)_5]$ has been shown to be at the top in a scale of relative nucleophilicity of a series of transition-metal hydrides toward $[EtC(O)(CH_3CN)Re(CO)_4]$.[4a] In compound 1, $[ReH(CO)_5]$ and CO, both bound to the Pt atom, are in a strict balance of their electronic properties toward the fragment $[Re_2Pt(\mu\text{-}H)_2(CO)_8]$ and no *bis* substitution of either ligand could be achieved.[1d] This is expected to give peculiar reactivity and/or dynamic properties to compound 1. We report here the ^1H NMR investigation of the solution properties of compound 1, which revealed *inter alia* an example of intermolecular exchange of a metal fragment.

Results and Discussion

The ^1H NMR spectrum of $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$ (compound 1), purified by flash chromatography, shows, at 180 K, two sets of three resonances in the hydride region (relative ratio *ca.* 19:1).[1d] The chemical shifts and couplings of both sets are compatible with a structure in which two hydrides bridge Pt-Re edges and one bridges a Re-Re interaction: **1a** (major species) $\delta = -5.44$ ($J_{H\text{-}Pt} = 633$ Hz), -8.57 ($J_{H\text{-}Pt} = 488$ Hz), -15.70 ($J_{H\text{-}Pt} = 38$ Hz); **1b** $\delta = -6.16$ ($J_{H\text{-}Pt} = 732$ Hz), -9.47 ($J_{H\text{-}Pt} = 673$ Hz), -16.32 ($J_{H\text{-}Pt} < 20$ Hz).

The variable temperature ^1H spectra (Figure 1) suggest that the two species are interconverting isomers. On raising the temperature from 180 K, in fact, the resonances of the minor isomer **1b** broaden and collapse at *ca.* 200 K, while, in the range 180-270 K, the resonances of the major isomer **1a** show broadening and coalescence and eventually give rise to fast exchange averaged signals, with significant changes with the temperature of the chemical shifts of the two low field multiplets. Above 270 K these multiplets broaden again, indicating the onset of a new dynamic process. A 2D EXSY experiment performed at 180 K

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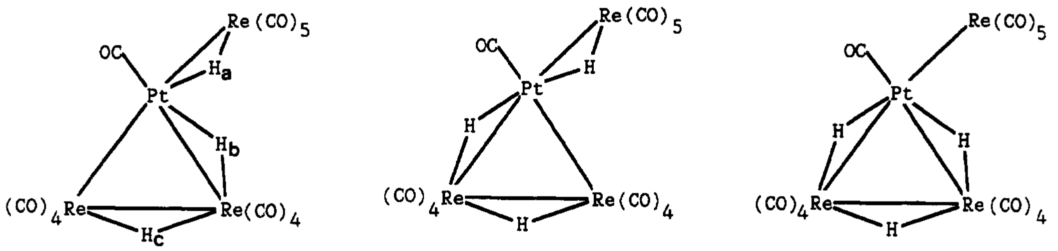
Chart 1



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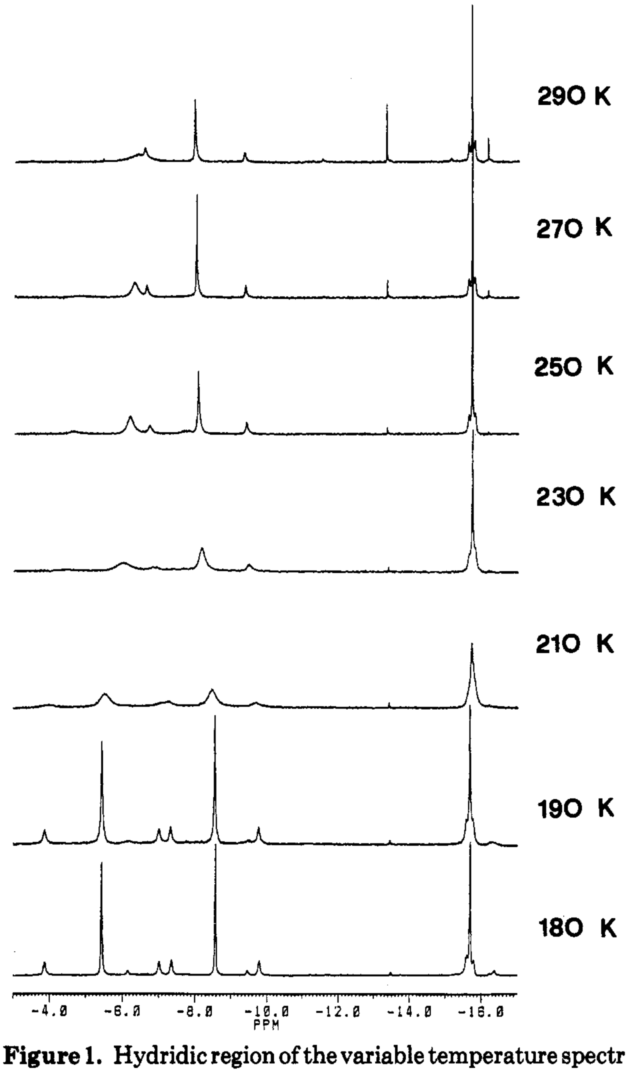

Figure 1. Hydridic region of the variable temperature spectra of compound 1 (200 MHz, CD_2Cl_2).

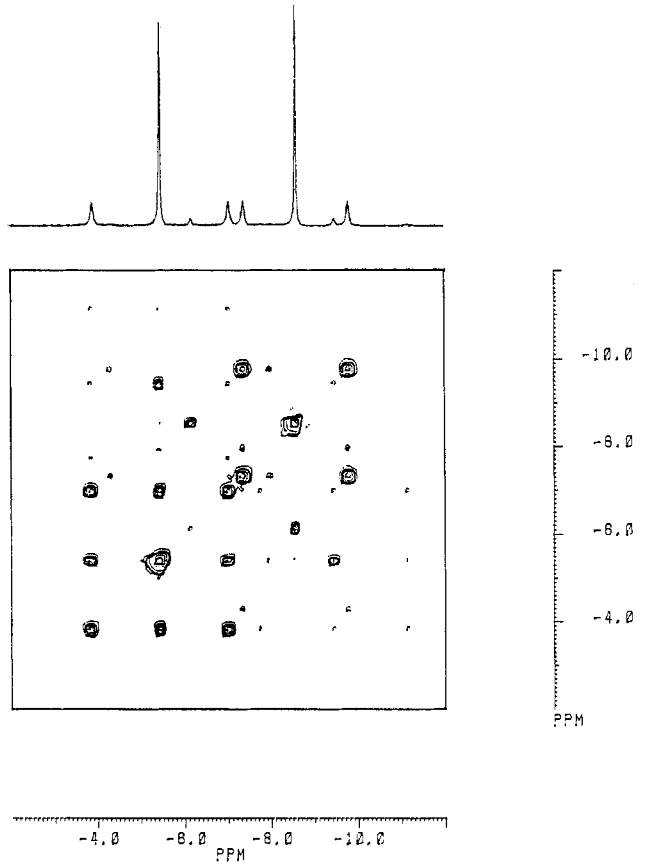

Figure 2. Contour plot of a ^1H 2D EXSY experiment (200 MHz, CD_2Cl_2, 180 K, τ_m = 0.2 s).

(Figure 2, see below) confirmed that the interconversion between the two isomers **1a** and **1b** is already operative at this temperature.

The most likely solution structures for the isomers of compound 1 are shown in Chart 1. Two of these structures (I and II) differ for the geometrical arrangement of the $[ReH(CO)_5]$ fragment around the Pt atom: *cis* (I) or *trans* (II) with respect to the bridged Pt–Re interaction. The *cis* isomer is the one isolated in the solid state and its structure has been characterized by X-ray single crystal analysis.[1d] A third isomer could arise from the oxidative addition of $[ReH(CO)_5]$ on the Pt atom. The nature of the isomers and the attributions of the resonances can be better discussed by taking into account the dynamic behavior observed at variable temperature.

Structural Characterization and Dynamic Behavior at 180 K. Two features of the 2D map shown in Figure 2 should be stressed. (i) The hydride at −8.57 ppm of **1a** exchanges with the hydride at −6.16 ppm of **1b**, and no cross-peaks are observed among the central signal at δ −8.57 and all the satellites. (ii) The hydride at −5.44 ppm of **1a** exchanges with the hydride at −9.47 ppm of **1b**, but in this case, cross-peaks are observed within all the components of the multiplet centered at −5.44 ppm as well as among these components and those of the multiplet at −9.47 ppm. The small amount of the minor isomer prevents the observation of any exchange within the multiplet of the hydride at δ −9.47.

The 2D results indicate that (i) the resonances at −8.57 (**1a**) and −6.16 (**1b**) ppm and those at −5.44 (**1a**) and −9.47 (**1b**) ppm are related in the two isomers, (ii) the hydrides at −8.57 and −6.16 ppm do not change the Pt atom to

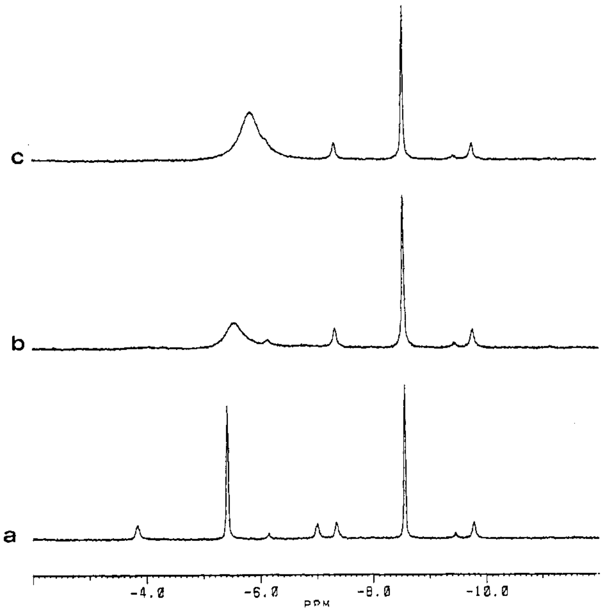

Figure 3. Hydridic region of the ^{1}H NMR spectrum of compound 1 (200 MHz, CD_2Cl_2, 180 K): (a) without [ReH(CO)$_5$]; (b) with *ca.* 0.3 equiv (1 μL) of [ReH(CO)$_5$]; (c) with *ca.* 1 equiv of [ReH(CO)$_5$].

which are bound, (iii) the hydride at −5.44 ppm, and possibly also the one at −9.47 ppm, undergo a process that requires the dissociation of the hydride, alone or bound to some other fragment, causing the randomization of the spins of the Pt atoms.[5]

The hydrides at −8.57 and −6.16 ppm can be identified as the hydrides that in all the species bridge a Pt–Re interaction in the triangular metal moiety (named hereafter as H_b) since the isomerization process maintains the integrity of the molecular framework to which they are bound.

The nature of the other process has been clarified by treating a solution of 1 with [ReH(CO)$_5$] (Figure 3). On increasing the amount of [ReH(CO)$_5$], the pseudotriplet at −5.44 ppm broadens and collapses into a single broad signal, indicating a fast exchange process between the cluster and the free ligand (free [ReH(CO)$_5$] δ = −6.11 ppm in CD_2Cl_2 at 180 K). This chemical behavior suggests for the major isomer one of the structures I or II: the exchange of the whole [ReH(CO)$_5$] moiety explains the randomization of the Pt spin, observed in the 2D map. Figure 3 shows also that the resonances of the minor isomer are not affected by the addition of [ReH(CO)$_5$], indicating that **1b** is not in fast exchange with [ReH(CO)$_5$] and also that the isomerization rate is unchanged. This means that the isomerization pathway is not related to the [ReH(CO)$_5$] exchange and that there are substantial differences in the structural and/or kinetic properties of the two isomers.

The exchange process observed only in the major isomer requires that in solution, besides equilibrium 1 between the two isomers, there is also equilibrium 2 that can be regarded as a substitution on a square planar complex, which usually follows solvolytic or associative pathways.[6]

$$\mathbf{1a} \rightleftharpoons \mathbf{1b} \qquad (1)$$

$$[Re_2PtH_2(CO)_9\{HRe(CO)_5\}] + [ReH(CO)_5]^* \rightleftharpoons [ReH(CO)_5] + [Re_2PtH_2(CO)_9\{HRe(CO)_5\}^*] \qquad (2)$$

This latter mechanism accounts for the strong increase of the rate of exchange on addition of [ReH(CO)$_5$]. The experiment reported in Figure 3 allowed a very rough estimate of the associative rate constant as 3×10^4 L/(mol s). The solvolytic pathway could be the source of free [ReH(CO)$_5$] that is required for the establishment of equilibrium 2, and the low nucleophilicity of dichloromethane could account for the undetectable amount of free [ReH(CO)$_5$]. However, as pointed out by one of the referees, the presence of [ReH(CO)$_5$] could arise also from contamination or slight decomposition of the sample. The labile nature of the [ReH(CO)$_5$] moiety has been chemically confirmed by its facile substitution with other bielectron donor ligands, different from CO.[7]

The coupling constants with ^{195}Pt of both the hydrides increase on going from isomer **1a** to **1b**, indicating that, in the minor isomer, both are located *trans* to ligands with a lower *trans* influence. Such an increase is particularly significant for H_b (488 Hz in **1a** and 732 Hz in **1b**, while for H_a 633 Hz in **1a** and 673 Hz in **1b**). The comparison of these values with the coupling constants of related compounds (see, for instance J_{H-Pt} = 720 Hz in the bow-tie cluster [Re$_4$Pt(μ-H)$_6$(CO)$_{16}$],[1c] where four bridging hydrides are bound to the Pt atom) supports the assignment of structure I to the major isomer and structure II to isomer **1b**, in accord with the small *trans* influence of a Re(μ-H)Pt bond, as recently observed in the mixed metal adduct [Re(CO)$_4$(μ-H)(μ-CO)Pt(PPh$_3$)$_2$][8] and in other triangular clusters, as isomer A of [Re$_2$Pt(μ-H)$_2$(PPh$_3$)$_2$(CO)$_8$][1a] or [Re$_2$Pt(μ-H)$_2$(CO)$_8$(1,5-C$_8$H$_{12}$)].[1d] Structure III for the minor isomer is very appealing for explaining the lack of exchange with [ReH(CO)$_5$], but both the hydrides remain *trans* to the same groups as in I (a carbonyl and a Re–Pt bond, respectively). Therefore it would be difficult to explain the observed increase of J_{H-Pt}, also taking into account that the formal increase in the oxidation state of Pt in III would lead to a decrease of the coupling constants.[9] If the above structure assignments are correct, the experiment reported in Figure 3 should indicate that the M–M moiety has a kinetic *trans* labilizing effect much stronger than the M(μ-H)M moiety. This finding parallels the already reported greater *trans* influence of the M–M interaction with respect to the M(μ-H)M one, observed on the basis of structural and

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[5] In a 2D EXSY map, when a nucleus *I* is scalar coupled to a heteronucleus *S*, cross-peaks within the multiplet of I can be observed when *S* has a short relaxation time and, during the mixing time, magnetization transfer occurs between the spin states of the unobserved nucleus S (Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon Press: Oxford, U.K., 1985; Chapter 9 (see also references therein)). When two nuclei *I*, both coupled with *S*, exchange, the occurrence of these cross-peaks can result in ambiguous information on the nature of the process, that is whether it is dissociative, with the loss of the spin correlation for the multiplets of I or intramolecular with a fast relaxation of *S* (or both). In the case of the coupling with ^{195}Pt, however, with this isotope being 33.7% of the natural abundance, the additional cross-peaks due to relaxation can appear only between the so-called "satellite" signals, leaving unaffected the central resonance due to Pt atoms with $I = 0$. This allows us to discriminate whether the exchange requires the loss of spin correlation between the observed nucleus and Pt, or not.

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spectroscopic data,[1a,d,10] and therefore could be related to a ground state destabilization.

Evaluation of the Rate Constants at 180 K. Due to the unfavorable ratio between the exchanging sites, both 1D and 2D magnetization transfer experiments have been performed to get independent evaluations of the rate constants of the dynamic processes observed in **1**.

Two types of 2D EXSY experiments were performed on samples of compound **1**: (i) one with ^{195}Pt decoupling (179 K) using a mixing time (τ_m) of 0.08 s; (ii) two without ^{195}Pt decoupling (181 K) with mixing times 0.2 and 0.08 s, respectively.

The first experiment allowed the detection of the isomerization process alone. When procedures already reported are followed,[2,11] two independent estimates of the rate constant can be obtained from the exchange pattern between H_a hydrides ($k_{i(1a\rightarrow1b)} = 1.16 \pm 0.22$ s^{-1}) and between H_b hydrides ($k_{i(1a\rightarrow1b)} = 0.97 \pm 0.18$ s^{-1}) (exchange between two sites with different populations).

The exchange between the hydrides bridging the Re–Re edges (H_c) is useless for quantitative purposes, since the diagonal signal of **1b** is so broadened to be undetectable.

In the coupled experiments, the intramolecular exchange of the hydrides H_b can be studied quantitatively as a two site exchange using only the volumes of the peaks generated by the atoms bound to Pt with $I = 0$.[2,5] The isomerization rate constants thus obtained [$k_{i(1a\rightarrow1b)} = 0.97 \pm 0.11$ s^{-1} (τ_m = 0.2 s) and 1.30 ± 0.15 s^{-1} (τ_m = 0.08 s)] are in fair agreement with those calculated through the decoupled experiment.

On the contrary, the exchange system of the hydrides H_a has, in principle, six sites with unequal populations. However, the dimensions of the problem can be reduced to four, neglecting the satellites of H_a in **1b** (see Experimental Section). The results of both the ^{195}Pt-coupled experiments indicate that the rate constants between the central resonance of the minor isomer and the satellites of the major one are zero; that is, there is no direct exchange between these sites and equilibrium 2 is not a step for the isomerization, as already proved by the experiment with added [ReH(CO)$_5$]. The small cross-peaks present in the 2D map with the longer mixing time (Figure 2) are therefore due to indirect transfer (higher order peaks),[11b,12] and the simple qualitative observation of a single 2D experiment would lead to a misleading conclusion.

The rates of the exchange between the central resonance at −5.44 ppm and its satellites and *vice versa* are 0.57 ± 0.14 and 2.27 ± 0.52 s^{-1} (τ_m = 0.2 s) and 0.59 ± 0.20 and 2.33 ± 0.88 s^{-1} (τ_m = 0.08 s), respectively. The rate constant of the [ReH(CO)$_5$] intermolecular exchange therefore results as $k_{ex} = 3.5 \pm 1.2$ s^{-1} (τ_m = 0.2 s) and 3.3 ± 1.1 s^{-1} (τ_m = 0.08 s), allowing for the difference in the natural abundance of the isotopomers.[13]

The rate constant for the exchange between the central resonances provides a further estimate of the rate of isomerization (1.5 ± 0.3 s^{-1} (τ_m = 0.2 s) and 1.8 ± 0.4 s^{-1} (τ_m = 0.08 s), respectively).

Selective population transfer (SPT) experiments have also been performed at 180 K in order to check independently the paths of magnetization, following the inversion of the resonances at −5.44 ppm (H_a) and −8.57 ppm (H_b) and of the low field satellite of H_a of the major isomer. For this last experiment the signal to noise ratio was so poor that only a qualitative analysis has been possible, while the results concerning the inversion of the two resonances at −5.44 and −8.57 ppm allowed an estimation of the rates of the transfer among the sites. Using T_1 data measured from separate experiments (*vide infra*), we obtained for the isomerization $k_i = 0.98 \pm 0.05$ s^{-1} (H_b inverted) and 0.97 ± 0.09 s^{-1} (H_a inverted), while for the intermolecular exchange $k_{ex} = 3.96 \pm 0.13$ s^{-1}. These values were obtained with a kinetic model that regards equilibria 1 and 2 as two independent processes (see supplementary material). However, by assuming equilibrium 2 as a step in the isomerization, no significant difference in the quality of the fittings was attained. The SPT experiments on H_a therefore cannot alone discriminate between the two kinetic models, while from the quantitative evaluation of the 2D EXSY experiments the independence of the two processes appears clearly.

Another SPT experiment was performd on the sample containing [ReH(CO)$_5$], following only the magnetization transfer after the inversion of H_b at 180 K. The rate constant obtained proved definitely that the isomerization is insensitive to the exchange of the [ReH(CO)$_5$] fragment ($k_i = 1.03 \pm 0.03$ s^{-1}).

Assuming for the two isomers the structures I and II, the hopping of the H_b hydride on the two edges would account easily for the isomerization. A similar process has already been observed in related triangular Re$_2$Pt clusters such as [Re$_2$Pt(μ-H)$_2$(CO)$_8$(PPh$_3$)$_2$] (isomer **1a**)[2] and [Re$_2$Pt(μ-H)$_2$(CO)$_8$(1,5-C$_8$H$_{12}$)][1d] and appears to require a relatively small amount of energy.

Behavior at Variable Temperature. The values of the chemical shifts and of the coupling constants of the resonances of H_a and H_b in the fast exchange regime (above 230 K) exceed those expected on the basis of the isomer ratio at 180 K and vary with the temperature, suggesting an increase of the molar fraction of **1b** with respect to **1a** on increasing the temperature. In this hypothesis, the ratios (R = **1a**/**1b**) between the two isomers have been calculated from the chemical shifts of the averaged resonances of H_b and H_c and the ^{195}Pt–^{1}H coupling constants of H_b. The temperature dependence of the chemical shifts, that can be observed only for **1a** and at the lower temperatures, is small and at the limits of the experimental uncertainties. Both allowing for the observed variations and assuming no temperature dependence, these values, plotted as ln R *vs* $(T)^{-1}$, together with the experimental ratio at 180 K, are fairly linear up to 250 K (the estimated reaction enthalpy and entropy for reaction 1 range from 8.8 to 7.2 kJ/mol and 25 to 16 J/(mol K), respectively) but at higher temperatures all the observed NMR parameters are not in agreement with those predicted by equ ilibrium 1, suggesting that one (or more) new species is (are) present and fast exchanging with both the isomers. Also, the results of the band shape analysis attempted in the range of temperatures 180–250 K shows an anomalous behavior. In fact, no satisfactory fitting could be achieved above 210 K by using either of the isomer

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[13] A [ReH(CO)$_5$] fragment that leaves a Pt isotope with $I = 0$ has the 66.3%, the 16.85%, and the 16.85% probability of reaching fragments with Pt isotopes with $I = 0$, $I = +^1/_2$, and $I = -^1/_2$, respectively. Therefore, the rate constant for the transfer of magnetization from the central signal to a satellite reflects only 1/0.1685 of the total events affecting a single molecule of **1a**.

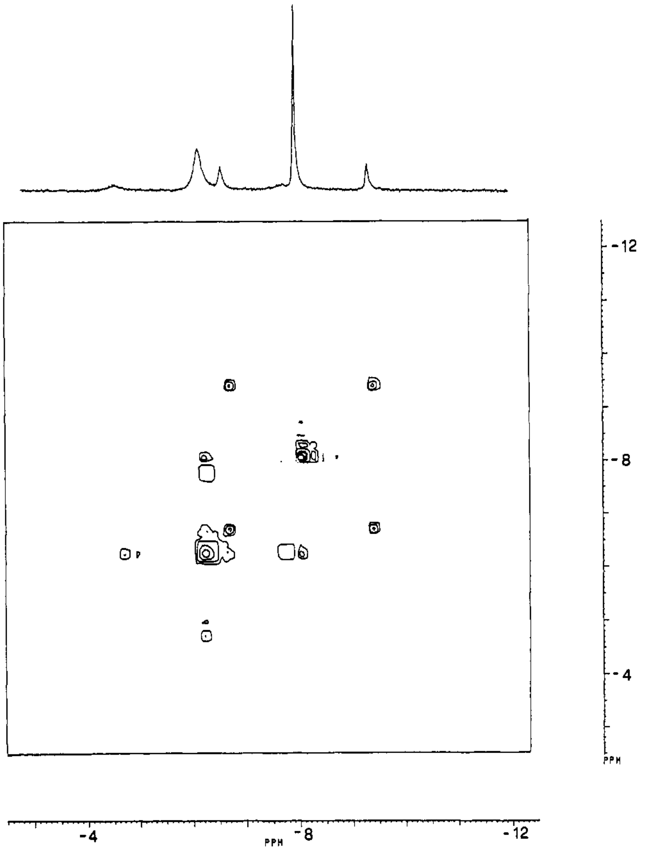

Figure 4. Contour plot of a ^1H 2D EXSY experiment (200 MHz, CD_2Cl_2, 264 K, $\tau_m = 0.2$ s). 1024 data points were collected over a spectral width of 5000 Hz for 96 increments of t_1. Gaussian weighting functions were applied in both dimensions after zero filling in F_1. On the top is reported the ^1H NMR spectrum at the same temperature.

ratios obtained from the thermodynamic data mentioned above or by assuming the molar fractions as parameters for the simulation procedure.

We have no definite evidence on the nature of the new species, which appear reversibly on changing the temperature in this system. It could arise from the solvolytic exchange of **1a**, which is expected to increase with the temperature, since this reaction is endothermic and disordering. Another hypothesis is suggested by the previously mentioned broadening of the low field multiplets observed above 270 K. Indeed, a 2D EXSY experiment at 264 K (Figure 4) reveals the occurrence of exchange between the averaged resonances of H_b and H_a. This implies the breaking of the H–Re bond of the external fragment and it is in line with the occurrence of an oxidative addition on Pt, leading to the formation of isomer III.

Measurements of Pt Relaxation Times. The fast relaxation of Pt affects both 2D EXSY and SPT experiments. In the quantitative analysis of these latter experiments an estimate of Pt T_1 is needed, together with those of the hydridic signals. At 179 K, the relaxation time of Pt was determined indirectly by observing the decay of the satellites of H_a and H_b of **1a**. The employed pulse[14a] sequence transfers Pt polarization onto protons using a single reverse DEPT scheme, and the mean of the values obtained is 0.02 s. This value is affected from high uncertainty but the order of magnitude is correct since 0.05 s is an upper estimate of $T_1(^{195}Pt)$ that can be obtained through the 2D EXSY experiment[5] with the shorter mixing time, from the cross-peaks between the satellites of H_b, by following the same procedures used for the calculations of the rate constant.

Conclusions

Two features of the behavior displayed by the two isomers of $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$ deserve some comments. The first point concerns the exchange of the $[ReH(CO)_5]$ moiety, that is observed only in the major isomer **1a**. Previously reported examples of similar processes in equilibrium systems involve the exchange of a metal fragment between different molecular species. For instance, Pt_3 fragments are exchanged between $[Pt_9(CO)_{18}]^{2-}$ and $[Pt_{12}(CO)_{24}]^{2-}$, and this "degenerate" process could be detected through the broadening of the ^{195}Pt resonances of the Pt_9 species,[15] the exchange rate (with traces of Pt_{12}) being comparable to the NMR time scale. An example of a nondegenerate exchange has been recently reported (eq 3) and in that case the process is slower, the equilibrium

$$HMn_2Re(CO)_{14} + HRe(CO)_5 \rightleftarrows HMnRe_2(CO)_{14} + HMn(CO)_5 \quad (3)$$

being attained within *ca.* 1 h.[16] The present case provides an example of a fast intermolecular "degenerate" exchange of the $[ReH(CO)_5]$ fragment between molecules of the same species (**1a**), and it can be perhaps better considered as an example of ligand lability. Studies aimed to prove the possibility of observing equilibria like (3), through the competition of other species toward "$Re_2Pt(\mu\text{-}H)_2(CO)_9$", are in progress.

The second point concerns isomer III. The exchange between the averaged resonances of H_a and of H_b, observed at 264 K, requires the cleavage of the H–Re bond in the $ReH(CO)_5$ fragment and suggests that one of the new species could be the product of the "oxidative addition" of $ReH(CO)_5$ on the "$Re_2Pt(\mu\text{-}H)_2(CO)_9$" fragment (or at least that III should be present as an intermediate species). In a polynuclear system this "oxidative addition" can be described simply as the migration of a bridging hydride between two adjacent metal–metal interactions. So, the attack of a rhenium hydride toward an osmium cluster containing labile ligands, as $[Os_3(CO)_{10}(C_8H_{14})_2]$, was found to occur with H migration, affording a structure of type III, Re-Os(μ-H)Os, in the case of $[ReH(CO)_5]$,[17] while a Re(μ-H)Os bond (structure type I or II, no migration) was found in the case of $[ReH(CO)_3(PMe_3)_2]$.[18] This was rationalized in terms of the preference of a bridging hydride for the more electron-rich metal–metal interaction.[18] In the present case, this argument would support structure III, while the solid state and the low temperature data clearly indicate a preference for the other structures, whatever the structure of **1b**. On the other hand, it has been already observed that a M–H bond acting as a ligand toward a second metal can be compared to a C–H agostic

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interaction.[19] Such interactions are usually considered as models of intermediates in the oxidative addition of a C–H bond on a metal center, but sometimes the agostic "intermediate" becomes the ground state species. The above results suggest that this is the case also for the Re–H bond toward Pt in compound 1.

Experimental Section

Compound 1 has been prepared as previously reported.[1d]

NMR experiments were performed on a Bruker AC-200 operating at 200.13 MHz for ^{1}H, equipped with a B-VT1000 temperature control unit, that ensures a precision of ±1 K. An external B-SV3 with a second synthesizer and an amplifier allowing up to a power of 80 W was used for decoupling and pulsing at the ^{195}Pt frequency while observing ^{1}H with a 5-mm "reverse probe". Before and after each experiment the temperature was calibrated with a CH_3OH/CD_3OD solution.[20] The used solutions were typically 0.04 M in CD_2Cl_2.

^{1}H and ^{1}H{^{195}Pt} 2D EXSY experiments were performed in phase-sensitive mode; at 180 K, 32 transients were collected over a sweep width of 4700 Hz for 232 or 256 t_1 increments, using as mixing times 0.2, 0.08 (coupled experiments), and 0.08 s (decoupled experiment), respectively; 1024 data points were used in the F_2 dimension. Before Fourier transformation, a Gaussian function was applied in F_1 after zero filling twice and then the 2D map was symmetrized. For the ^{195}Pt-decoupled experiment, the decoupler frequency was chosen after the measurement of the Pt chemical shift of **1a** by a ^{1}H–^{195}Pt reverse correlation experiment[1d] and of the measurement of only an approximate $\delta(^{195}\mathrm{Pt})$ for **1b** using ^{1}H{^{195}Pt} spectra. The values of the population for each site were determined by the integrals of the 1D spectrum.

In the bidimensional maps the volumes of the diagonal and of the cross-peaks were measured by means of the spectrometer's software routine and used to calculate the rate constants following literature procedures.[11] The exchange data set concerning the H_a resonances comprises, in principle, 36 peaks. Some of these were not observed, and among them, in neither of the coupled experiments, the diagonal peaks of the satellites of H_a in the minor isomer were not observed. This was a critical point in the analysis of the exchange of the H_a multiplets as a "six sites" problem, since, using zero for the volumes of the undetectable peaks, one or more of the eigenvalues resulted negative, leading to imaginary rate constants. The same occurred using for the volumes the sum of the noise level or $1/10^6$ of the smallest detectable peak. Assuming for the undetectable *diagonal* satellites only volumes that were "reasonable" (that is with a ratio with respect to their central resonance similar to that found for **1a**) but always under the detection limit, the rate constants became real and the figures did not change dramatically using either of the assumptions on the other undetectable peaks. Moreover, similar results were obtained in the calculations performed as a "four sites" problem, neglecting the satellites of H_a in **1b**. This last approach was therefore preferred, since at least the diagonal peaks were always measurable. The variances of the rate constants were determined according to the method suggested by Kuchel et al.[21] The uncertainty in the values of volumes ranged from 1% (for the central resonances in **1a**) to 100% (for the unobserved cross-peaks), while the uncertainty in the populations was 2%–5%.

Before SPT experiments, the T_1's of the hydrides and of the ^{195}Pt nucleus were measured at 179 K for **1a**. The values of $T_1(^1\mathrm{H})$ were determined by using the standard inversion recovery pulse sequence ($T_1 = 0.25 \pm 0.02$ s for all the signals), while $T_1(^{195}\mathrm{Pt})$ was determined by means of the detection of the ^{195}Pt satellites in the protonic spectrum, using a pulse sequence reported in literature.[14a] No presaturation of the ^{1}H resonances was performed. Nine spectra were acquired with variable delays between 0.1 ms and 0.12 s, 90° (^{195}Pt) = 24 μs, DEPT pulse (45°) = 2.2 μs, and DEPT delay ($1/2J$) = 0.8 ms. The $T_1(^{195}\mathrm{Pt})$ value was determined by fitting the intensities of the satellite resonances on a two-parameter monoexponential decaying function by means of ASYSTANT PLUS.

In the SPT experiments the 180 soft pulse was calibrated before every experiment; seventeen variable delays were used in the range from 0.0001 to 1.0 s, while the repetition time was 1.0 s. The equations used in the fitting the time course of the intensities of the signals are available as supplementary material.

The resonances of H_b have $\delta = -8.566$ and -6.155 ppm and $J_{H-Pt} = 488$ and 732 Hz in **1a** and **1b** at 180 K. After the coalescence a single resonance is observed whose parameters are $\delta = -8.185$ ppm and $J_{H-Pt} = 525$ Hz; $\delta = -8.131$ ppm and $J_{H-Pt} = 532$ Hz; $\delta = -8.085$ ppm and $J_{H-Pt} = 535$ Hz; $\delta = -8.053$ ppm and $J_{H-Pt} = 542$ Hz at 230, 240, 250, and 260 K, respectively. The resonances of H_c have $\delta = -15.695$ and -16.318 ppm in **1a** and **1b** at 180 K, while after the coalescence the single resonance has $\delta = -15.733, -15.730, -15.726, -15.719$, and -15.712 ppm at 220, 230, 240, 250, and 260 K, respectively.

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Supplementary Material Available: Textual presentation of the detailed procedure used for the fitting of the SPT experiments according to the two kinetic models (2 pages). Ordering information is given on any current masthead page.

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