Rhenium−Platinum Mixed-Metal Spiked-Triangle Clusters. Synthesis and X-ray Characterization of the Cluster Anions $[Re_2Pt(\mu\text{-}H)_2(CO)_9\{Re(CO)_5\}]^-$ and $[Re_2Pt(\mu\text{-}H)_2(CO)_9\{HRe_2(CO)_9\}]^-$

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The spiked-triangle cluster $[Re_2Pt(\mu\text{-}H)_2(CO)_9\{HRe(CO)_5\}]$ (**1**), which contains a $HRe(CO)_5$ molecule bound to the Pt vertex of a Re_2Pt triangle, reacts with methanolic NEt_4OH to give the red anion $[Re_2Pt(\mu\text{-}H)_2(CO)_9\{Re(CO)_5\}]^-$ (**2**), whose structure has been determined by single-crystal X-ray analysis of its NEt_4^+ salt. NMR monitoring showed the intermediate formation of a carbomethoxy derivative **3**, arising from the attack of OMe^- on a carbonyl of the $HRe(CO)_5$ group. The deprotonation of **1** can be performed also by a base as weak as pyridine. The anion **2** in solution is thermally unstable, and at room temperature it gives rise to complex mixtures. The main component has been identified, by X-ray analysis of its NEt_4^+ salt, as the anion $[Re_2Pt(\mu\text{-}H)_2(CO)_9\{HRe_2(CO)_9\}]^-$ (**4**), containing a $HRe_2(CO)_9^-$ complex bound to the Pt vertex of a Re_2Pt triangle, through a $Re(\mu\text{-}H)Pt$ bond. The anions **2** and **4** are better obtained by treating $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ (COD = 1,5-cyclooctadiene) with $[Re(CO)_5]^-$ or $[HRe_2(CO)_9]^-$, respectively, in the presence of CO. Experiments have been performed to clarify the origin of the $[HRe_2(CO)_9]^-$ fragment bound to Pt in **4**. The reaction between free $[HRe(CO)_5]$ and $[Re(CO)_5]^-$ produces in high yields the anion $[HRe_2(CO)_9]^-$, but this one does not displace $Re(CO)_5^-$ from **2**. The reaction between $[Re(CO)_5]^-$ and the complex **1** gives instantaneously the anion **2**. No reaction occurs upon treatment of the anion **2** with $[HRe(CO)_5]$. Variable-temperature NMR has revealed the occurrence in both the anions **3** and **4** of an intramolecular dynamic process equalizing the two hydrides bound to the Pt atom, with E_a = 70(1) and 74(7) kJ/mol, respectively.

Introduction

The importance of bimetallic platinum−rhenium catalysts in re-forming of petroleum prompted us[1] and other groups[2] to synthesize Re−Pt mixed-metal cluster complexes and to study their chemistry. In the course of the investigations on the reactivity of the triangular cluster complex $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ (COD = 1,5-cyclooctadiene), it was shown[1d] that the reaction with CO and $[HRe(CO)_5]$ gives the spiked-triangle derivative $[Re_2Pt(\mu\text{-}H)_2(CO)_9\{HRe(CO)_5\}]$ (compound **1** of Scheme 1), in which $[HRe(CO)_5]$ acts as a "ligand" on the Pt vertex of the cluster. The capability of M−H bonds to behave as two-electron donors toward metal centers has been widely exploited, first by the Venanzi's group,[3] and has been recently inserted into the more general concept of σ-bond complexes.[4]

We are currently investigating the chemical properties of the $HRe(CO)_5$ "ligand", and some of us have recently reported its peculiar lability, clearly evidenced by NMR studies.[5] Other aspects of its reactivity are presented in this work, concerning in particular the acidic character acquired, upon coordination, by the Re−H bond. Novel Re−Pt cluster anions containing the

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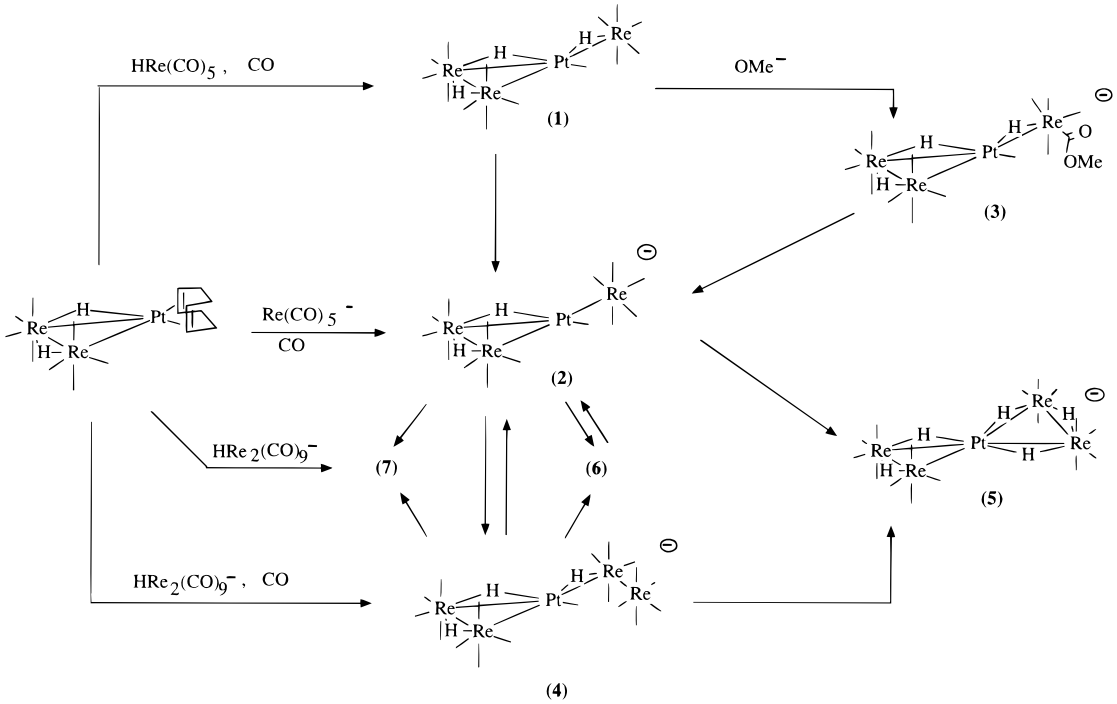
Scheme 1



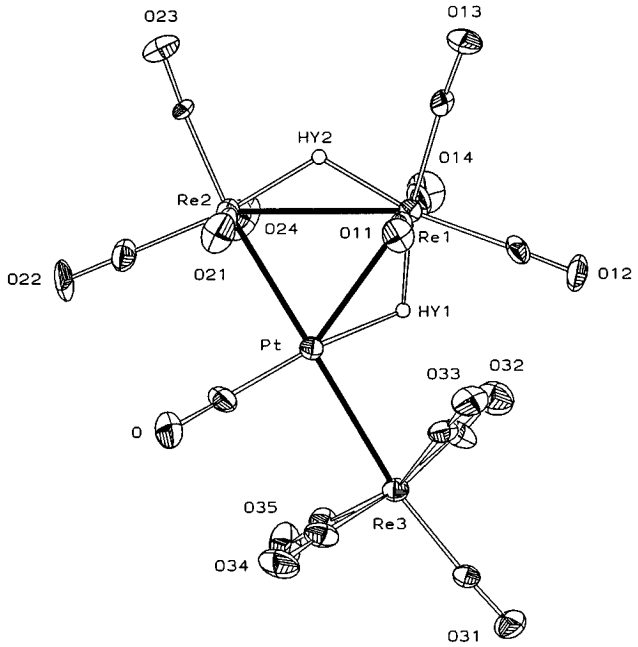


Figure 1. ORTEP view of the $[Re_2Pt(\mu\text{-}H)_2(CO)_9\{Re(CO)_5\}]^-$ anion (**2**). Thermal ellipsoids are drawn at the 30% probability level. Hydride ligands were given an arbitrary small radius.

same spiked-triangle structure of **1** have been obtained, and it will be shown that their behavior in solution exhibits some similarity, but also several significant differences, with respect to that of the parent neutral complex **1**.

Results and Discussion

The reaction of the light brown complex $[Re_2Pt(\mu\text{-}H)_2(CO)_9\{HRe(CO)_5\}]$ (**1**) with a stoichiometric amount of methanolic NEt_4OH, at 273 K, instantaneously gives dark red solutions, whose IR and NMR data are consistent with the formation of the novel anion $[Re_2Pt(\mu\text{-}H)_2(CO)_9\{Re(CO)_5\}]^-$ (**2**), as the main product. The treatment of **2** with stoichiometric CF_3SO_3H readily gives back the neutral complex **1**. The X-ray analysis of a crystal of the NEt_4^+ salt of **2** showed that the anion has the structure reported in Figure 1.

The anion **2** differs from the starting neutral complex **1** mainly by the removal of the proton belonging to the labile $HRe(CO)_5$ fragment. In other words, the $HRe(CO)_5$ ligand which is bound to the Pt atom in **1** has been replaced in **2** by a $Re(CO)_5^-$ anion. In keeping with this, we have obtained the anion **2** in high spectroscopic yields by addition of $[Re(CO)_5]^-$ to $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$, in the presence of CO (see Scheme 1). This reaction provides the best synthetic route to the anion **2**.

Table 1. NMR Data for the Complexes Described in This Paper (δ, ppm; in Parentheses J_{HPt}, Hz)[a]

compd	H_a	H_b	H_c
1[b]	−5.44(633)	−8.57(488)	−15.70(38)
2[c]		−6.40(460)	−15.70(31)
3[c]	−2.64[d](744)	−8.38[d](445)	−15.86(38)
4[c]	−4.61[d](750)	−8.53[d](456)	−15.74(36)
5[c,e]		−8.24(770)	−16.40
6[c]		−5.95(735)	
7[f]		−3.49(520)	−13.28(18)

[a] For the spiked-triangle complexes, H_a refers to the Pt(μ-H)Re moiety of the spike, H_b to that of the triangle, and H_c to the Re(μ-H)Re moiety. [b] CD_2Cl_2, 203 K. [c] C_4D_8O, 233 K. [d] Doublets, J_{HH} = 2 Hz. [e] Intensity ratio 3:2. [f] Intensity ratio 1:2.

Methoxo Derivative 3. Low-temperature (193 K) ^1H NMR monitoring of the reaction of **1** with methanolic NEt_4OH, in THF-d_8, showed the formation of a red species **3**, exhibiting three resonances in the hydridic region (see Table 1 and Figure 2a) and a further resonance, of triple integrated intensity, at δ 3.28. A resonance at δ 48.4 was also observed in the ^{13}C NMR spectrum (near the resonance of free methanol, at δ 49.8

(5) Beringhelli, T.; D'Alfonso, G.; Minoja, A. *Organometallics* **1994**, *13*, 663.

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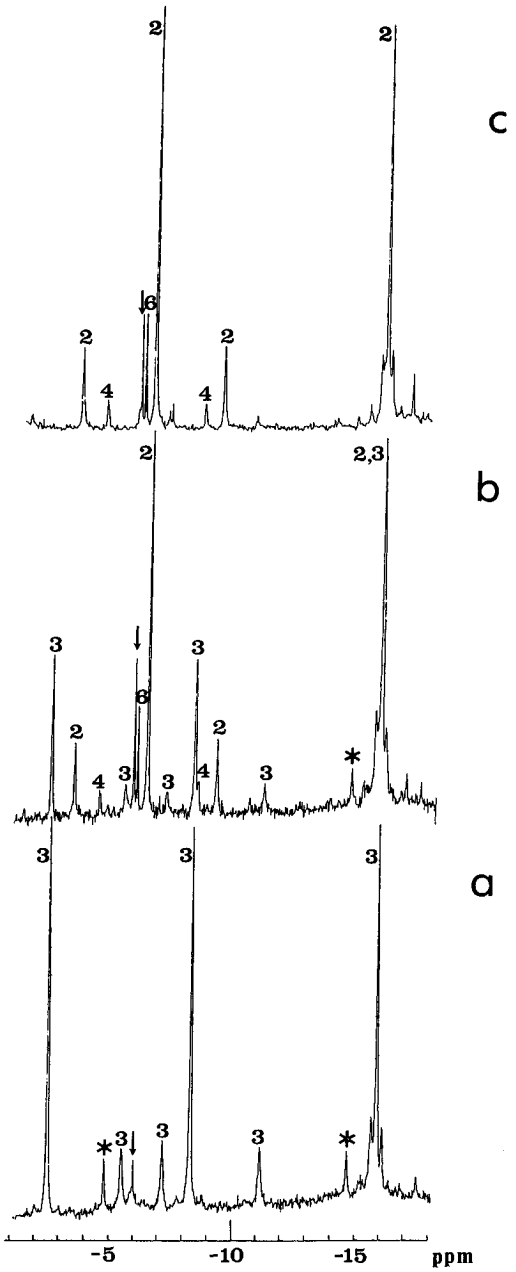

Figure 2. Hydridic region of selected NMR spectra (THF-d_8, 80 MHz, 203 K) of the mixture obtained by adding, in a screw cap NMR tube, 1 equiv of NaOMe in anhydrous methanol to $[Re_2Pt(\mu\text{-}H)_2(CO)_9\{HRe(CO)_5\}]$ (**1**), as described in the Experimental Section. (a) Spectrum acquired immediately after mixing the reagents at 193 K; the asterisks indicate minor unidentified by products. (b) Spectrum acquired after the sample was kept at 273 K for 50 min. (c) Spectrum acquired after 120 min at 273 K. The arrow indicates some free $[HRe(CO)_5]$. The spectra have been plotted with an arbitrary vertical scale. Only the high-field Pt satellite of the resonance of **3** at −2.6 ppm is shown.

in the same conditions). The formation of **3** was not observed on treating **1** with an *aqueous* solution of NEt_4OH,[6] whereas **3** was obtained upon treatment of **1** with a methanolic solution of NaOMe, or with solid NaOMe, in tetrahydrofuran. Chemical and spectroscopic evidence therefore clearly suggests that **3** contains a methoxo group. The formation of a methoxo derivative by reaction with methanolic NEt_4OH is not unexpected, since methanolic solution of hydroxides always contain the methoxide ion, methanol being a stronger acid than water.[7] The most likely site of attack of MeO^- is on a carbonyl ligand, to give a carbomethoxo group: this is supported by a weak absorption in the IR spectrum at 1595 cm^{-1}, which is typical of M−C(O)OR groups.[8]

The anion **3** at higher temperatures decomposes, affording **2** as the main product (see Figure 2). It seems therefore that the reaction with methoxide ions gives $[Re_3Pt(\mu\text{-}H)_3(CO)_{13}(COOMe)]^-$ (**3**) as the kinetic product, which then transforms into the thermodynamic product **2**. The rate of this transformation was markedly different in different experiments, indicating that it is not an intramolecular process. In particular, it resulted much faster in the reactions performed with methanolic NEt_4OH ($t_{1/2}$ < 5 min at 263 K) than in those performed with NaOMe in anhydrous methanol ($t_{1/2}$ ca. 25 min at 273 K), suggesting that water or OH^- ions could be involved in the conversion of **3** to **2**.

We could not unambiguously establish the site of attack of the methoxide anion, even if the two pairs of mutually *trans* carbonyls of the $Re(CO)_5$ moiety are the most likely candidates. The NMR data (Table 1) agree with this hypothesis. In fact, the hydride ligands bridging the triangular edges do not significantly change either their chemical shift or their J_{HPt}, with respect to the values observed in **1**: in particular, the J_{HPt} of the hydride bound to Pt maintains a value typical of H *trans* to a carbonyl in related systems (see Table 1 and ref 9). On the contrary, a significant change occurs for the chemical shift of the low-field resonance, which is attributed to the hydride belonging to the Pt(μ-H)Re moiety of the spike. It was not possible to recognize the signal due to the carbomethoxo group among the many resonances in the carbonyl region of the ^{13}C-NMR spectrum. However, the ^{13}C-NMR analysis provided evidence that the CO bound to Pt (clearly identified by its Pt satellites) is not involved in the OMe^- attack: in **3** this carbonyl has chemical shift and J_{CPt} (185.2 ppm and 1750 Hz, respectively, at 213 K, in THF-d_8) very similar to the values found for the analogous carbonyl in **1** (183.0 ppm and 1770 Hz, respectively, in the same conditions).

Acidity of 1. The deprotonation of **1** could also be performed by replacing the strong bases NEt_4OH or NaOMe with a much weaker base, such as pyridine, in tetrahydrofuran solution. The reaction was rather slow ($t_{1/2}$ ca. 40 min, at 233 K, using 1.8 equiv of pyridine), but showed a good selectivity, the anion **2** being by far the main reaction product (>90%, by NMR monitoring).

This reaction implies that compound **1** has a thermodynamic acidity higher than that of the pyridinium ion, which in turn suggests that the coordination of $[HRe(CO)_5]$ on the Pt atom significantly increases its acidity. In fact, the acidity of free $[HRe(CO)_5]$ was defined as very weak by the authors of its original synthesis,[10] and

(6) The reaction with aqueous NEt_4OH caused indeed extensive decomposition, and NMR monitoring revealed, besides the anions **2** and **6** (see below), also the formation of major amounts of free $[HRe(CO)_5]$.

(7) See for instance: March, J. *Advanced Organic Chemistry*, 3rd ed.; J. Wiley and Sons: New York, 1985; p 221 and references therein.

(8) See for instance: (a) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335. (b) Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 585. (c) Trautman, R. J.; Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 2355 and references therein.

(9) Beringhelli, T.; D'Alfonso, G.; Minoja, A. *Organometallics* **1991**, *10*, 394.

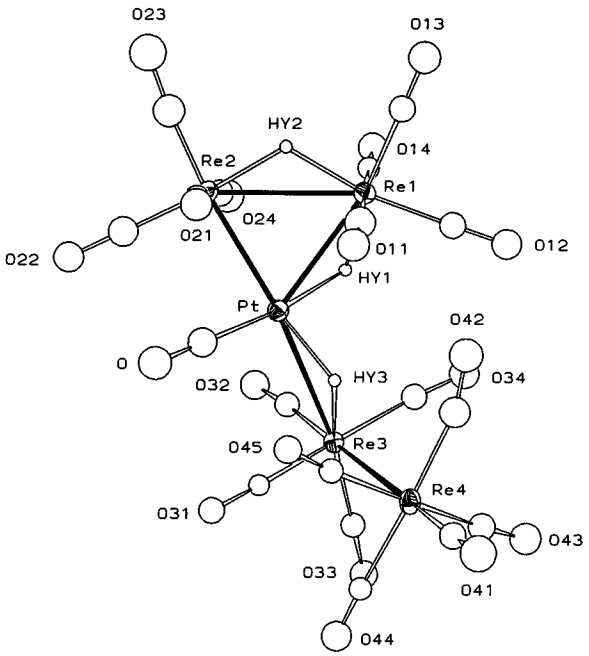

Figure 3. ORTEP view of the $[Re_2Pt(\mu\text{-}H)_2(CO)_9\{HRe_2(CO)_9\}]^-$ anion (**4**). Thermal ellipsoids are drawn at the 30% probability level. Hydride ligands were given an arbitrary small radius.

a pK_a of 13.6 in aqueous solution has been estimated[11] from the value measured in acetonitrile solution (pK_a = 21.1).[12] It has already been observed that hydrides in bridging locations are more acidic than terminals ones,[11] and these results are in line with this expectation. As for the effective mechanism of deprotonation, several pathways, different from the simple direct attack of pyridine on the hydride, could be envisaged, also taking into account the complex inter- and intramolecular equilibria[5] involving the $HRe(CO)_5$ ligand in **1**. The instability of **2** in these reaction mixtures (see below) prevented any further mechanistic investigation.

Novel Anion 4. The ^{1}H NMR spectra of the reaction mixtures containing **2**, whichever method used to synthesize it, always showed the presence of minor byproducts, whose amounts increased with time and on increasing the temperature up to room temperature. Most of them, as will be discussed below, are Re−Pt clusters, but resonances near δ −17 ppm suggest the formation also of homonuclear clusters of Re.[13]

An X-ray structure analysis of the NEt_4^+ salt of the main byproduct **4**, which is responsible for three hydridic resonances (Table 1), permitted its formulation as the anion $[Re_4Pt(\mu\text{-}H)_3(CO)_{18}]^-$. The structure (Figure 3) shows that in **4** the $Re(CO)_5^-$ group of **2** has been replaced by a $HRe_2(CO)_9^-$ ligand, bound to Pt through a Re(μ-H)Pt interaction.

A rational route to this species is provided by the direct reaction of $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ with 1 equiv of $[HRe_2(CO)_9]^-$ and CO. This reaction, as judged by NMR monitoring, is almost quantitative, at 193 K (see Figure 4). At higher temperatures, however, several other species are formed, including **2** itself, resulting in mixtures quite similar to those arising from the decomposition of **2**.

Several experiments have been performed in the attempt to clarify the origin of the dinuclear $HRe_2(CO)_9^-$ ligand in the reaction mixtures.

First, we have shown that the free anion $[HRe_2(CO)_9]^-$ can be easily obtained in high yields by the direct reaction between $[HRe(CO)_5]$ and $[PPN][Re(CO)_5]$ (eq 1), at room temperature. This reaction, even if clean, is not a convenient alternative to the previously reported[14] synthesis of $[HRe_2(CO)_9]^-$, by treatment of $[Re_2(CO)_{10}]$ with NEt_4OH.

$$[HRe(CO)_5] + [Re(CO)_5]^- \rightarrow [HRe_2(CO)_9]^- + CO \quad (1)$$

The easy formation of $[HRe_2(CO)_9]^-$ when $[HRe(CO)_5]$ is treated with $[Re(CO)_5]^-$ could explain the strong absorption at 1970 cm^{-1} observed by Norton et al. when $[HRe(CO)_5]$ was treated with bases to evaluate the pK_a of $[HRe(CO)_5]$.[12] Indeed the main IR absorption of $[HRe_2(CO)_9]^-$ lies at 1970 cm^{-1}. The analogous IR band at ca. 1970 cm^{-1}, usually observed in the preparation of $Na[Re(CO)_5]$ from $[Re_2(CO)_{10}]$ on Na/Hg, could also be attributed to the formation of some $[HRe_2(CO)_9]^-$, from the reaction of $[Re(CO)_5]^-$ with small amounts of $[HRe(CO)_5]$, originating from traces of water (possibly during the same IR monitoring).

However, the hypothesis that our byproduct **4** was originated from the substitution of $Re(CO)_5^-$ in **2** by free $[HRe_2(CO)_9]^-$, formed as in eq 1, has been ruled out, because no reaction was observed by treating **2** with 1 equiv of $[HRe_2(CO)_9]^-$, at room temperature.

Further experiments have also shown that the ligand $HRe_2(CO)_9^-$ cannot be formed by reactions analogous to reaction 1, involving $HRe(CO)_5$ or $Re(CO)_5^-$ moieties bound to Pt, in compounds **1** or **2**, respectively. In fact, the treatment of **2** with $[HRe(CO)_5]$ produced only a negligible amount of **4**, even at room temperature. Moreover, the addition of $[Re(CO)_5]^-$ to **1** at 203 K caused the instantaneous formation of **2** and free $[HRe(CO)_5]$. This could be the result either of the deprotonation of **1** by the strong base $[Re(CO)_5]^-$ or of the substitution of the labile ligand $HRe(CO)_5$ by the strong nucleophile $[Re(CO)_5]^-$. We favor the second hypothesis on the basis of the following experiment. Natural abundance **1** was treated with ^{13}CO-enriched $[Re(CO)_5]^-$ (δ 220.0 ppm, 213 K), to give **2** and $[HRe(CO)_5]$ as shown by the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum, acquired with a number of scans sufficient to reveal the resonances of the ^{13}C-enriched sites only, the signals of free $[HRe(CO)_5]$ (δ 183.8 and 184.2, 1:4) have not been recognized (the most intense signal being at 200.1 ppm, the chemical shift of one of the main resonances of **2**).

The formation of **4** must therefore involve more complex rearrangements of the Re_2Pt−Re skeleton of **2**, as demonstrated also by the formation, as minor byproduct, of the anion $[Re_4Pt(\mu\text{-}H)_5(CO)_{16}]^-$ (**5**), which

(10) Beck, W.; Hieber, W.; Braun, G. *Z. Anorg. Allg. Chem.* **1961**, *308*, 23.

(11) Kristjansdottir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH Publishers: New York, 1990; Chapter 9, p 309.

(12) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

(13) Hydrido ligands bridging Re−Re bonds usually give resonances near δ −17 ppm, in homo- or heteronuclear hydrido−carbonyl clusters, if the complexes are electronically saturated and the Re atoms do not bear ligands different from H and CO (see for instance: Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145. Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Moret, M.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1989**, 1143).

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

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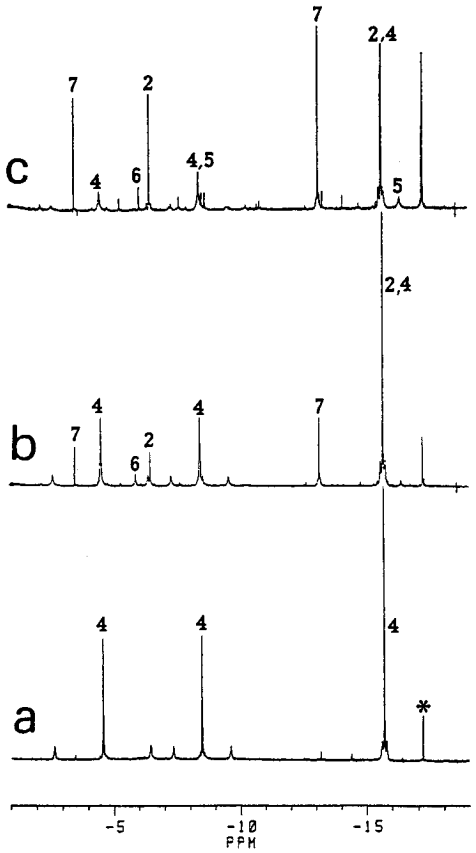

Figure 4. Hydridic region of selected NMR spectra of the mixture obtained by adding, in a screw cap NMR tube, 1 equiv of $[HRe_2(CO)_9]^-$ to $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$, in the presence of CO (CD_2Cl_2, 200 MHz). (a) Spectrum acquired at 263 K, immediately after mixing the reagents at 193 K; the asterisk indicates an impurity present in the reagents, likely $[Re_3(\mu\text{-}H)_3(CO)_{12}]$. (b) Spectrum acquired, at 283 K, 20 min after raising the temperature to this value. (c) Spectrum acquired at 293 K, after 1 night at ca. 4 °C and 1 hour at room temperature. The spectra have been plotted with an arbitrary vertical scale. The broadening of the two low-field resonances of **4** on increasing the temperature is due to the exchange process discussed in the text.

contains a distorted bow-tie cluster and was previously obtained by deprotonation of $[Re_4Pt(\mu\text{-}H)_6(CO)_{16}]$.[15]

Unidentified Byproducts 6 and 7. Two other, still unidentified, byproducts are usually present in these reaction mixtures, in variable amount. The first one (**6**) is observed when **2** is produced from strong bases or by using $[Re(CO)_5]^-$, and its concentration usually increases on increasing the temperature up to room temperature. It exhibits only one hydridic resonance, even at low temperature, with a strong coupling with Pt (see Table 1). The rate of its formation increases with the concentration of the strong base, and by contrast, upon addition of a strong acid, the species **6** disappeared preferentially with respect to **2**, seemingly giving **2** itself or **1**. Upon addition of 1 equiv of $[Re(CO)_5]^-$ to **2** (203 K), the quantitative conversion to **6** and $[HRe(CO)_5]$ was observed, with resonances of the same integrated intensities. These data suggest that **6** could be the dianion arising from deprotonation of **2**, even if this formulation can hardly justify the high value of the J_{HPt} observed for its single hydridic resonance.

Interestingly, the existence of an interconversion between **2** and **6** has been confirmed by a 2D EXSY experiment, performed at room temperature on a solution containing a typical mixture of species. The spectrum clearly showed the exchange between the hydride of **6** and the hydride of **2** bridging the Re–Re bond. In the previous hypothesis this would indicate a regiospecific proton exchange between the acid **2** and its conjugated base **6**.

The second unidentified byproduct (**7**) exhibits two ^1H resonances, in the ratio 1:2, and must therefore contain at least three hydridic ligands, two of which are not bound to Pt. It becomes the main reaction product when $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ is treated with $[HRe_2(CO)_9]^-$ *in the absence* of CO. The lack of solid-state X-ray crystal structure prevents any sound identification of this byproduct and of the previous one.

Behavior in Solution of the Novel Anions. The easy interconversion of all these species could arise from a lability of the organometallic fragments bound to the Pt atom, analogous to that previously observed in the starting compound **1**.[5] However, the lability of the anionic fragments in the species **2** and **4**, if existing, should be less pronounced than that of $HRe(CO)_5$ in **1**. In fact the addition of even small amount of free $[HRe(CO)_5]$ to compound **1** (at 180 K) caused a marked broadening of the involved resonances,[5] while the resonance of free $[HRe_2(CO)_9]^-$ remained sharp in the presence of **4**, even at room temperature. The exchange between free and coordinated $[HRe_2(CO)_9]^-$, which probably occurs, is therefore slow on the NMR time scale. It is reasonable to assume that the lability of $Re(CO)_5^-$ in **2** is at least as slow as that of $HRe_2(CO)_9^-$ in **4**, even if in **2** the hydridic "probe" of the lability of the organometallic fragment is lacking.

The impossibility to obtain clean samples of the novel anions hampered the identification of possible minor isomers (in the case of **1** the ratio between the isomers was ca. 20:1 at 180 K).[5] However the variable-temperature NMR spectra did not show any evidence of exchange processes, even with hidden exchange partners. Therefore other isomers, if existing, should be in very low amount and not rapidly interconverting with the main species.

The NMR spectra revealed, however, the occurrence, both in **4** and in the transient species **3**, of an intramolecular dynamic process equalizing the two hydrides bound to the Pt atom. The broadening of the resonances can be observed above 273 and 243 K for **4** and **3**, respectively, and the activation energies estimated by the line width measured in the limited range of the available temperatures are very similar: 74(7) and 70(1) kJ/mol, respectively. The exchange of the hydrides bridging the Re–Pt edges was observable also for compound **1** above 264 K[5] and should therefore be considered a common feature of this class of spiked-triangle clusters containing hydridic complexes acting as ligands. As already observed,[5] this exchange implies the breaking of the "donor" Re–H bond, in a sort of reversible oxidative addition on the Pt vertex. A reasonable intermediate for this process is in fact a species in which both the exchanging hydrides are bridging the Re–Pt interactions of the triangular cluster.

Description of the Structures of Compounds 2 and 4. Both crystal structures consist of the packing

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2 and 4

	2	4
Pt−Re(1)	2.924(2)	2.913(2)
Pt−Re(2)	2.7778(14)	2.761(2)
Pt−Re(3)	2.849(2)	3.025(2)
Re(1)−Re(2)	3.149(2)	3.145(2)
Re(3)−Re(4)		3.041(2)
Pt−C	1.81(3)	1.81(5)
Re(1)−C(11)	1.98(3)	1.88(5)
Re(1)−C(12)	1.97(3)	1.88(4)
Re(1)−C(13)	1.95(3)	1.96(5)
Re(1)−C(14)	1.99(4)	1.96(3)
Re(2)−C(21)	2.01(3)	1.95(4)
Re(2)−C(22)	1.95(3)	1.86(5)
Re(2)−C(23)	1.92(2)	1.79(6)
Re(2)−C(24)	2.01(3)	1.90(4)
Re(3)−C(31)	1.93(3)	1.91(3)
Re(3)−C(32)	1.98(4)	1.89(3)
Re(3)−C(33)	2.01(3)	1.92(4)
Re(3)−C(34)	1.99(3)	1.94(4)
Re(3)−C(35)	2.00(3)	
Re(4)−C(41)		1.84(4)
Re(4)−C(42)		1.96(6)
Re(4)−C(43)		1.96(4)
Re(4)−C(44)		2.05(4)
Re(4)−C(45)		1.99(3)
Re(1)−Pt−Re(2)	66.98(5)	67.26(6)
Re(1)−Pt−Re(3)	113.60(6)	118.92(6)
Re(2)−Pt−Re(3)	177.14(5)	159.11(6)
Pt−Re(1)−Re(2)	54.28(4)	54.06(5)
Pt−Re(2)−Re(1)	58.73(4)	58.68(6)
Pt−Re(3)−Re(4)		105.62(6)
C−Pt−Re(1)	153.2(8)	140.4(14)
C−Pt−Re(2)	88.6(9)	82.2(14)
C−Pt−Re(3)	91.3(9)	98.7(14)
C(11)−Re(1)−Pt	80.8(8)	74(2)
C(12)−Re(1)−Pt	105.4(7)	106.2(12)
C(13)−Re(1)−Pt	159.4(8)	157.6(10)
C(14)−Re(1)−Pt	96.9(9)	103.4(10)
C(11)−Re(1)−Re(2)	85.2(8)	87.5(14)
C(12)−Re(1)−Re(2)	159.7(7)	159.3(13)
C(13)−Re(1)−Re(2)	106.4(8)	112.3(11)
C(14)−Re(1)−Re(2)	94.3(9)	92.0(9)
C(21)−Re(2)−Pt	85.0(8)	90.0(11)
C(22)−Re(2)−Pt	98.2(8)	96.5(14)
C(23)−Re(2)−Pt	172.6(7)	173(2)
C(24)−Re(2)−Pt	85.8(7)	85.8(12)
C(21)−Re(2)−Re(1)	91.3(8)	95.8(11)
C(22)−Re(2)−Re(1)	156.7(8)	154.8(14)
C(23)−Re(2)−Re(1)	113.9(7)	115(2)
C(24)−Re(2)−Re(1)	85.4(9)	82.2(11)
C(31)−Re(3)−Pt	170.4(7)	87.9(9)
C(32)−Re(3)−Pt	83.8(11)	73.3(11)
C(33)−Re(3)−Pt	75.2(7)	167.2(10)
C(34)−Re(3)−Pt	88.5(8)	90.0(11)
C(35)−Re(3)−Pt	88.1(9)	
C(31)−Re(3)−Re(4)		83.4(8)
C(32)−Re(3)−Re(4)		178.9(11)
C(33)−Re(3)−Re(4)		86.1(10)
C(34)−Re(3)−Re(4)		89.9(10)
C(41)−Re(4)−Re(3)		176.3(12)
C(42)−Re(4)−Re(3)		86.0(13)
C(43)−Re(4)−Re(3)		89.0(10)
C(44)−Re(4)−Re(3)		85.0(8)
C(45)−Re(4)−Re(3)		83.4(9)

of discrete ions separated by normal van der Waals contacts. The molecular structures of $[Re_2Pt(\mu\text{-}H)_2(CO)_9\{Re(CO)_5\}]^-$ (**2**) and $[Re_2Pt(\mu\text{-}H)_2(CO)_9\{HRe_2(CO)_9\}]^-$ (**4**) are illustrated in Figures 1 and 3, while relevant bond distances and angles are reported in Table 1.

The tetranuclear anion **2** has a spiked triangular cluster shape with an irregular Re_2Pt moiety with two significantly different Pt−Re edges. Its structure can be formally obtained from that of **1** by removing the hydride ligand bridging the spike. Within the triangle two M−M edges support a hydride bridge and the Re atoms bear four terminal CO ligands, while the Pt atom bears one CO ligand and the $Re(CO)_5$ "spike". Considering the M−H−M bonds as occupying one coordination site, all the Re atoms have an essentially octahedral local geometry while the Pt atom is square planar. Coherently, given that the valence electron bookkeeping in clusters is influenced either by the shape of the cluster or by the local geometry of metal centers, **2** has two cluster valence electrons less than other spiked-triangles based only on "octahedral" metal atoms, like $[Re_3Ir(\mu\text{-}H)(CO)_{16}]^-$.[16]

Table 3. Summary of Crystal Data and Structure Refinement Parameters for 2 and 4

	2	4
formula	$C_{22}H_{22}NO_{14}PtRe_3$	$C_{26}H_{23}NO_{18}PtRe_4$
fw	1278.10	1577.34
cryst system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	13.236(4)	9.210(5)
b, Å	13.184(8)	12.436(5)
c, Å	19.139(3)	16.914(8)
α, deg		88.63(3)
β, deg	105.86(2)	88.50(4)
γ, deg		86.04(4)
V, Å^3	3213(2)	1932(2)
Z	4	2
F(000)	2304	1416
D(calc), g cm^{-3}	2.642	2.712
abs coeff, mm^{-1}	15.668	16.166
min rel transm fact	0.17	0.12
cryst size, mm	0.22 × 0.18 × 0.10	0.21 × 0.15 × 0.09
scan method	ω	ω
scan interval, deg	0.9 + 0.35 tan θ	0.9 + 0.35 tan θ
θ range, deg	3−25	3−23
index ranges, hkl	−15/15, 0/15, 0/22	−10/10, −13/13, 0/17
reflcns collcd	5866	5314
cryst decay, %	40	57
data/params	2414/325	2612/226
goodness-of-fit on F_o^2	1.046	1.076
R indices, $R1$, w$R2$	0.0418, 0.1031	0.0531, 0.1311
max peak and hole, e Å^{-3}	1.93, −1.22	1.36, −1.58
weighting scheme, a, b[a]	0.0594, 43.3790	0.0882, 20.9276

[a] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. GOOF $= [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

The structure of the pentanuclear anion **4** is related to that of **2**, but the spike is now a $[HRe_2(CO)_9]^-$ fragment which is connected to the Pt atom through a Re−H−Pt bond. Alternatively, **4** can be related to **1** by the formal replacement of a CO ligand with a $[Re(CO)_5]^-$ fragment.

As usual, the M−H−M bonds have been located, both in **2** and **4**, from the lengthening of the pertinent M−M distances and the widening of the M−M−L angles of the neighboring ligands. Subsequently, the "ideal" positions of the hydride ligands were calculated by use of the program HYDEX.[17]

In order to understand the major stereochemical features of **2** and **4** it is useful to compare their structures with that of **1**, which is the "structural" parent of the spike triangular kernel common to **2** and

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4. The Re_2Pt triangles have a similar ligand stereochemistry in the three derivatives and share a similar pattern of M–M interactions (which is mainly dictated by the presence/absence of the bridging hydrides). The Pt–Re(3) edge, the spike bond, which is hydrogen bridged in **1** and **4** but not in **2**, is "short" and substantially collinear with the Pt–Re(2) edge in **2** (2.849(2) Å), while is "long" and bends away from the Re_2Pt triangle in **1** and **4** (3.058(1) and 3.025(2) Å, respectively), the Re(3) atoms being significantly (more than 1 Å) displaced out of the triangular plane. Further, the equatorial ligands of the "spike" are eclipsed with respect to the ligands on the Pt atom in **1** and **4** but staggered in **2**. However, in all the three derivatives there is a similar long-range C···Pt interaction, "stabilizing" the square planar coordination of the Pt center, which is due to the bending toward the Pt atom of one of the Re(3) equatorial carbonyl ligands (Pt–Re(3)–C(31) 67.6(4)° in **1**, Pt–Re(3)–C33 75.2(7)° in **2**, and Pt–Re(3)–C(32) 73.3(11)° in **4**).

The Re(3)–Re(4) interaction (3.041 Å), the Re–C bond distances, and the overall conformation of the bonded $HRe_2(CO)_9$ fragment, in **4**, are similar to that found for the $Re_2(CO)_{10}$ molecule.[18]

At last we note that the Pt–Re interactions, *in the three derivatives*, clearly fall into four different classes, depending on the presence/absence of a bridging hydride and on being, or not, within the triangle. In fact, the Pt–Re bond distances are shorter than the Pt–H–Re one, but on top of that, those within the triangle (averages for the Pt–Re and Pt–H–Re, respectively, 2.771 and 2.927 Å) are markedly shorter that those within the spike (Pt–Re and Pt–H–Re (average), respectively, 2.849(2) and 3.047 Å).

Conclusions. Several anionic derivatives containing a spiked-triangle structure analogous to that of complex **1** have been obtained. It has been demonstrated that the dinuclear hydridocarbonylrhenate $[HRe_2(CO)_9]^-$ and the strong nucleophile $[Re(CO)_5]^-$ react with $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ exactly in the same way as $[HRe(CO)_5]$ does. Moreover, it has been shown that the Re(μ-H)Pt bond connecting the $HRe(CO)_5$ spike to the Pt vertex of the Re_2Pt triangle in **1** can be deprotonated without destroying the Re_2Pt–Re skeleton of the cluster. A base as weak as pyridine is able to do this, due to the enhanced acidity of the proton of $HRe(CO)_5$, when bound to Pt atom in **1**.

In line with the weakening of the "donor" Re–H bond, the hydride of the spike has been shown to exchange with the one bridging the *cis*-Pt–Re bond in the triangle, in all the derivatives in which the spike is connected to the Pt vertex through a Re(μ-H)Pt bond, namely the neutral complex **1** and the anions **3** and **4**. This suggests that in all these cases the hydride of the spike undergoes a fast reversible oxidative addition on the Pt center.

Complex **1**, however, remains unique as far as its dynamic behavior in solution is concerned, due both to the lability of the $HRe(CO)_5$ ligand and to the fast exchange among different isomers.[5] In the case of the anions here described, no evidence of the presence of isomers has been obtained. Moreover, the NMR spectra have unambiguously indicated that the $HRe_2(CO)_9^-$ spike in **4** does not show any lability, on the NMR time scale.

In spite of the lability of its spike, complex **1** is reasonably stable up to room temperature. On the contrary, the anions **2** and **4** are much more thermally unstable, easily giving rise to a variety of byproducts, only partially characterized. The most interesting features of these processes are the easy rearrangements of the $Re(CO)_5^-$ and $HRe_2(CO)_9^-$ spikes in the anions **2** and **4**. The complex $[HRe_2(CO)_9]^-$ is quite stable when it is free in solution, but it rapidly undergoes fragmentation when it is bound to Pt in the anion **4**, leading to the formation of a significant amount of **2** and **4**. On the contrary, the fragment $Re(CO)_5^-$ bound in **2** undergoes some kind of condensation, resulting in the formation of **4** from **2** *via* a process different from the condensation with $[HRe(CO)_5]$ that occurs when it is free in solution. These data indicate an active role of the Pt atom in modifying the reactivity of the rhenium complexes bound to it.

Experimental Section

The reactions were performed under nitrogen, using the Schlenk technique, and solvents deoxygenated and dried by standard methods. Literature methods were used for the preparation of $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$,[1d] $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$[1d] (**1**), $[HRe(CO)_5]$,[19] and $(NEt_4)[HRe_2(CO)_9]$.[14] (PPN)$[Re(CO)_5]$ was prepared by metathesis from $Na[Re(CO)_5]$ (obtained by the usual Na/Hg reduction of $Re_2(CO)_{10}$), following the method described by Gladysz et al. for the isolation of (PPN)$[Mn(CO)_5]$.[20] NMR spectra were recorded on Bruker AC200 and WP80 spectrometers.

Reactions of $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$ (1) with Strong Bases. Reaction with Methanolic NEt_4OH at 273 K. A sample of compound **1** (11 mg, 0.010 mmol), dissolved in C_4D_8O in a NMR tube, was treated at 273 K with methanolic 1.5 M NEt_4OH (8 μL, 0.012 mmol). The color of the solution turned immediately from yellow to red, and a ^{1}H-NMR spectrum, acquired at 273 K within 5 min, showed the formation of **2** (ca. 80%) and **3** (ca. 20%) (the resonances of the last species disappeared in a spectrum acquired after 20 min, at the same temperature). The addition of CF_3SO_3H (1.5 μL, 0.017 mmol) gave back compound **1** quantitatively.

Reaction with Methanolic NEt_4OH at 193 K. A sample of compound **1** (13 mg, 0.011 mmol), dissolved in C_4D_8O in a NMR tube, was treated at 198 K with methanolic 1.5 M NEt_4OH (10 μL, 0.015 mmol). The color of the solution turned immediately from yellow to red, and ^{1}H-NMR spectra showed the quantitative formation of **3**. Spectra acquired at 273 K showed the conversion of this species into **2** and **6** (ratio of the integrated intensities of the resonances of these two species about 4:1). The solution was transferred in a Schlenk tube, and the slow diffusion of *n*-hexane, at 253 K, produced red crystals of $[NEt_4]$**2**, together with a smaller amount of yellow crystals of $[NEt_4]$**4**. NMR (see Table 1) and IR spectra were acquired on isolated crystals of the two species. IR data (ν_{CO}, C_4H_8O solution): **2**, 2097 vw, 2068 m, 2034 ms, 2003 s, 1976 m, 1956 m, 1934 ms, 1909 mw cm^{-1}; **4**, 2088 vw, 2061 w, 2023 s, 1994 sh, 1960 s, 1941 sh, 1921 w, 1906 w cm^{-1}.

Reactions with NaOMe. The same reaction was repeated in anhydrous condition, by using a methanolic solution of NaOMe, prepared by addition of Na to MeOH distilled over Mg. Compound **1** was prepared *in situ* in a NMR tube at 253 K by treating $[Pt(COD)_2]$ (11 mg, 0.027 mmol) with $[Re_2(\mu\text{-}$

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$H)_2(CO)_8]$ (16 mg, 0.027 mmol) and then with $[HRe(CO)_5]$ (3 μL, 0.021 mmol) and CO (0.5 mL, ca. 0.02 mmol), in C_4D_8O. It was then treated, at 193 K, with 4.8 μL of the methanolic solution of NaOMe (5 M, 0.024 mmol). The NMR spectrum at 203 K showed the clean formation of **3** (Figure 2). The tube was then maintained at 273 K for different times, and spectra acquired at 203 K showed the disappearance of **3** ($t_{1/2}$ ca. 25 min), to give mainly **2** and a minor amount of **6**. At longer times also some **4** and **5** was observed: after 3 h, **2** (77%), **6** (17%), **4** (4%), and **5** (2%).

The reaction was repeated in a Schlenk tube, as above, to acquire the IR data of **3**: $\nu_{CO}(C_4H_8O)$ 2081 mw, 2063 ms, 2031 sh, 2008 vs, 1974 s, 1935 ms, 1910 vw, 1595 w, br cm^{-1}. When the solution in the IR cell was allowed to warm to room temperature, these bands were substituted by those of **2**.

The reaction was also performed by using solid NaOMe, prepared by evaporating to dryness a solution of Na in anhydrous MeOH. The addition of ca. 1 equiv of NaOMe to a sample of **1**, in an NMR tube, in C_4D_8O, at 211 K, caused the formation of **3**. A further addition of solid NaOMe caused the formation of a novel species characterized by three hydridic resonances at δ −3.53 (J_{HPt} = 675 Hz), −7.30 (J_{HPt} = 609 Hz), −14.05 (J_{HPt} ca. 40 Hz) (211 K), which can be tentatively formulated as a derivative of further attack of OMe^- on **3**.

Reaction of $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$ (1) with Pyridine. A sample of compound **1** (13 mg, 0.011 mmol), dissolved in C_4D_8O in a NMR tube, was treated at 203 K with pyridine (1.6 μL, 0.020 mmol). The tube was briefly shaken, and the color of the solution turned immediately from yellow to red. ^{1}H-NMR spectra, recorded at 233 K, showed the progressive transformation of **1** into **2**, with a $t_{1/2}$ of ca. 40 min. When the temperature was raised to 283 K, **2** slowly decomposed giving mainly **4** *plus* minor unidentified derivatives. The formation of **6** was not observed.

Reaction of $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ with $[Re(CO)_5]^-$. $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ was prepared *in situ* in a NMR tube at 253 K, by treating $[Pt(COD)_2]$ (12 mg, 0.029 mmol) with $[Re_2(\mu\text{-}H)_2(CO)_8]$ (18 mg, 0.030 mmol), in C_4D_8O. It was then treated with $(PPN)[Re(CO)_5]$ (25 mg, 0.029 mmol) and CO (0.5 mL, ca. 0.02 mmol), at 203 K. The tube was briefly shaken, and the color of the solution turned immediately to red. The NMR spectrum at 203 K showed the formation of **2**, but a significant amount of **6** was already present (ca. 10%) and increased rapidly to ca. 20% on raising the temperature to 223 K. At this temperature also the signals of **4** appeared, and at 283 K also those of **7** were observed (ca. 10% and 5%, respectively, at 293 K).

Reaction of $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ with $[HRe_2(CO)_9]^-$. $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ was prepared *in situ* in a NMR tube at 253 K, by treating $[Pt(COD)_2]$ (9 mg, 0.022 mmol) with $[Re_2(\mu\text{-}H)_2(CO)_8]$ (14 mg, 0.023 mmol), in CD_2Cl_2. It was then treated with $(NEt_4)[HRe_2(CO)_9]$ (16 mg, 0.020 mmol) and CO (0.5 mL, ca. 0.02 mmol) at 203 K. The NMR spectrum at 203 K showed the quantitative formation of **4**. At higher temperatures, slow decomposition was observed, as revealed by the appearance of the resonances of the anions **2**, **6**, **7**, and **5**. After 35 min at 283 K: **4** (70%), **2** (10%), **6** (10%), and **7** (10%). After about 2 h at room temperature, **4** (30%), **2** (30%), **6** (10%), **7** (15%), and **5** (15%) formed. A 2D EXSY experiment in the phase-sensitive mode was performed on this mixture, at 295 K. A total of 80 FIDs of 2K data points were collected for 421 increments of t_1 (τ_m = 200 ms, spectral width 4600 Hz, relaxation delay 1 s, zero filling to 2K in F_1, gaussian weighting function applied only in F_1).

Reaction of $[HRe(CO)_5]$ with $[Re(CO)_5]^-$. A sample of $(PPN)[Re(CO)_5]$ (12 mg, 0.014 mmol) dissolved in C_4H_8O, was treated with $[HRe(CO)_5]$ (2 μL, 0.014 mmol) at room temperature: the IR and ^{1}H-NMR spectra showed the almost quantitative formation of $[HRe_2(CO)_9]^-$.

X-ray Analysis of 2 and 4. (a) Collection and Reduction of X-ray Data. A suitable crystal of each compound was chosen and each separately mounted on a glass fiber tip onto a goniometer head. Single-crystal X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with the use of graphite-monochromatized Mo Kα radiation. The unit cell parameters and an orientation matrix relating the crystal axes to the diffractometer axes were determined by least-squares fit of the setting angles of 25 randomly distributed intense reflections with 10° < θ < 14°. The data collections were performed by the ω-scan method, at room temperature with variable scan speed (maximum scan time 60 s) and variable scan range. The crystal stability under diffraction conditions was checked by monitoring three standard reflections every 180 min. The measured intensities were corrected for Lorentz, polarization, background, and decay effects and reduced to F_o^2. An empirical absorption correction was applied using ψ-scans of three suitable reflections having χ values close to 90°.[21] For compound **4** a statistical absorption correction was also applied (DIFABS[22]) after the empirical one as described in ref 23. Selected crystal data are summarized in Table 3.

(b) Solution and Structure Refinement. The structures were solved by direct methods (SIR92[24]) and difference Fourier methods. The structures were refined by full-matrix least-squares against F_o^2 using reflections with $F_o^2 \geq 3\sigma(F_o^2)$ and the program SHELXL93[25] on a Silicon Graphics Indigo computer. Anisotropic displacement parameters were assigned to all the anion atoms in **2**, while for **4** only the metal atoms were given anisotropic displacement parameters. All tetraethylammonium cations were refined isotropically with hydrogen atoms riding on their parent carbon atoms and individual isotropic displacement parameters 1.5 times that of the pertinent carbon atom. The hydride ligands positions were calculated by means of the program HYDEX[17] with d_{M-H} = 1.83 Å. The hydrides were introduced in the final stages of F_o calculations but not refined. Selected bond parameters are reported in Table 2, while final atomic coordinates are provided in the Supporting Information material.

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Supporting Information Available: Tables of final atomic coordinates, anisotropic displacement parameters, and complete bond distances and angles and figures showing a ^{1}H 2D EXSY spectrum at 295 K of the reaction mixture described in the text and ^{1}H and ^{13}C NMR spectra of **1**−**3** (15 pages). Ordering information is given on any current masthead page.

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