Reactivity Patterns of the Unsaturated Tetrahedral Cluster $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$. Easy Addition of Four MeCN Molecules and 'Ionic' or 'Neutral' Fragmentation Pathways of the Spiked-triangle Intermediate $[Re_4(\mu\text{-}H)_4(CO)_{12}(NCMe)_4]$

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The unsaturated (56 valence electrons, v.e.s) tetrahedral cluster $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$ **1** readily added four acetonitrile molecules, affording two isomers **2a** and **2b** of the 64 v.e.s $[Re_4(\mu\text{-}H)_4(CO)_{12}(NCMe)_4]$ derivative, containing a spiked-triangle metallic skeleton. These isomers at room temperature rapidly underwent an ionic fragmentation to the known unsaturated triangular cluster anion $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ and to the cation $[Re(CO)_3(NCMe)_3]^+$. The rate of decomposition significantly increased at low [MeCN] concentration. Treatment of compounds **2a** and **2b** with the π-acidic ligand CO, in the absence of free acetonitrile, gave only neutral products. Monitoring by NMR spectroscopy has revealed the rapid stepwise substitution of the nitrile ligands, accompanied by fragmentation to the known saturated triangular clusters $[Re_3(\mu\text{-}H)_3(CO)_{12-n}(NCMe)_n]$ ($n = 1$–3) and to the mononuclear complexes $[ReH(CO)_{5-n}(NCMe)_n]$ ($n = 0$ or 1). The novel, unstable, mononuclear hydride $[ReH(CO)_4(NCMe)]$ has been obtained by treatment of $[ReH(CO)_5]$ with Me_3NO in acetonitrile and by reaction of $[ReH_2(CO)_4]^-$ with CF_3SO_3H, in acetonitrile. In the presence of free acetonitrile, compounds **2a** and **2b** reacted with CO more slowly and gave both anionic and neutral triangular clusters.

The unsaturated hydridocarbonyl complex $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$[1] **1** is a rare example of a tetrahedral cluster with only 56 valence electrons (v.e.s), *i.e.* four less than required by the noble-gas rule. This results in a peculiar reactivity, as shown by the remarkable features of most of the products that are currently being obtained.[2–6] The high reactivity was recognized by the authors of the original synthesis,[1a] who stated that the complex reacts quite easily with 'any substance of well-developed donor power, including solvents such as ether and acetonitrile'. They also realized that many of these reactions lead to degradation of the cluster, but the reaction products could be identified only in the case of CO {as the triangular cluster $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ and the mononuclear hydride $[ReH(CO)_5]$}.

We have recently identified[6] a fragmentation pathway of complex **1** different from that reported with CO: in the presence of donor solvents (solv), such as methanol and acetone, **1** readily gives the unsaturated triangular cluster anions $[Re_3(\mu\text{-}H)_4(CO)_9(solv)]^-$ and the $[Re(CO)_3(solv)_3]^+$ cations.

Here we present a spectroscopic study of the reaction of complex **1** with acetonitrile and of the different modes of fragmentation of the thermally unstable addition derivatives $[Re_4(\mu\text{-}H)_4(CO)_{12}(NCMe)_4]$. The results of this study allow a rationalization of the previously known reactivity data concerning $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$.

Results and Discussion

The reactions of complex **1** with acetonitrile were performed in non-donor solvents (usually CH_2Cl_2 or $CHCl_3$) or in acetonitrile itself, because donor solvents (such as acetone, tetrahydrofuran, methanol) react with **1**, as previously observed.[1,3,6] Treatment of compound **1** with an excess of acetonitrile (>4 equivalents) caused the instantaneous disappearance of the red colour of the reagent. Proton NMR spectra (Fig. 1) showed the formation of two species, each containing four hydrides and four co-ordinated MeCN molecules, which were therefore formulated as two isomers of an addition derivative $[Re_4(\mu\text{-}H)_4(CO)_{12}(NCMe)_4]$ **2**. Isomer **2a**, of higher symmetry, exhibits two nitrile and three hydride resonances (relative ratio 6:6:1:1:2), while in **2b** each nitrile and each hydride give separate signals.

Compounds **2a** and **2b** contain 64 v.e.s and therefore could possess either a spiked-triangle or a square arrangement of metal atoms. Spectroscopic and reactivity data clearly favour the first hypothesis. The two compounds can therefore be viewed as $[Re_3(\mu\text{-}H)_3(CO)_9L_2L']$ derivatives, L being the classical *n*-donor MeCN ligand and L′ the σ-donor 'ligand'[7,8] $HRe(CO)_3(NCMe)_2$. The most likely structures of **2a** and **2b** (Scheme 1) can therefore be derived from those of the related triangular cluster $[Re_3(\mu\text{-}H)_3(CO)_9L_3]$ (L = MeCN, Scheme 2),[9] where all the MeCN ligands are in the electronically favoured axial sites, one *trans* to the other two, with respect to the plane of the triangle. We attribute to **2b** a C_1 structure with the triangle-bound nitriles *trans* to each other and to **2a** a structure having C_s symmetry, with the nitriles *cis* to each other, but *trans* to the spike. The alternative, all-*cis* structure (of C_s symmetry and spectroscopically indistinguishable from the previous one) is considered less probable, because no example of all-*cis*-$[Re_3(\mu\text{-}H)_3(CO)_9L_3]$ species is known.

The resonances of the hydrides have been attributed as in Table 1, on the basis of their mutual couplings and of their low-field shift on increasing the substitution of carbonyls by acetonitrile molecules, previously shown[9] for triangular clusters of rhenium (see Table 1). For both isomers the lowest-field resonance (due to H_a) appears as a sharp singlet, while that of the hydride bound to the spike (H_d) is a triplet, due to coupling with the two adjacent hydrides (H_b and H_c). The doublet due to H_c in **2b** partially overlaps with the doublet due to the two equivalent hydrides of **2a**, in line with the close

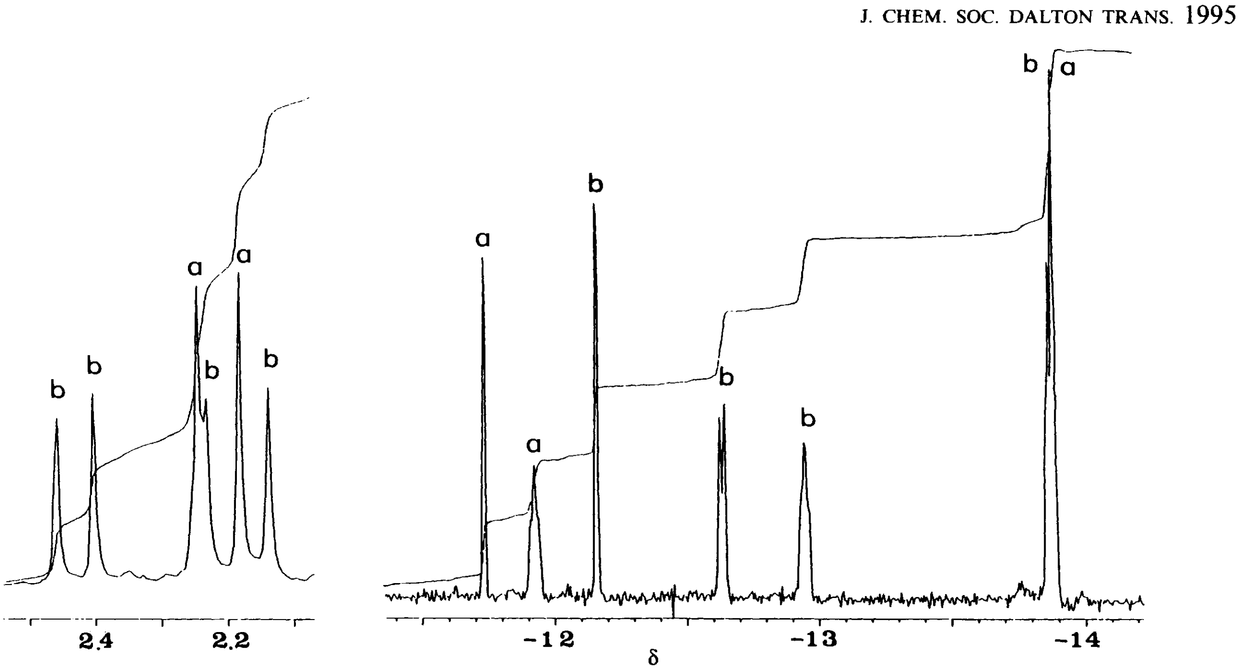
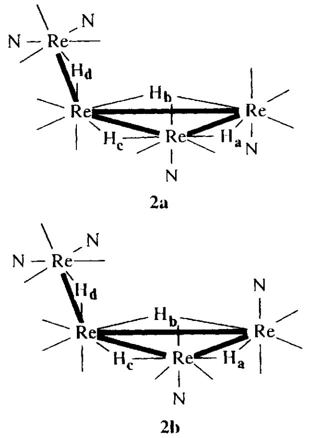


Fig. 1 Proton NMR spectrum of the two isomers **2a** and **2b** (200 MHz, CD_2Cl_2, 253 K), obtained by treating complex **1** with MeCN at low temperature. The vertical scale of the hydridic region is four times that of the methyl region



2a

2b

Scheme 1

analogy of the chemical environments of H_c in the two isomers. A similar pattern of coupling between the hydrides has been observed in the spiked-triangle cluster anion $[Re_4(\mu\text{-}H)_4(CO)_{15}I]^-$.[10] The difference of *ca.* 0.4 ppm between the resonances of H_a for the two isomers is in accord with the previous finding[9] that hydrides bridging between $Re(CO)_3$-(NCMe) moieties give lowest-field resonances when the two nitriles are mutually *cis* (see compound **5** in Table 1). The significant difference in δ for the two isomers for both H_b and H_d is possibly related to distortions induced by the presence of the nitrile *cis* to the spike 'ligand'.

It was impossible to obtain evidence of the formation of addition derivatives containing less than four nitrile molecules, even by stepwise addition of acetonitrile, at various temperatures, including 193 K. It must be remarked, however, that at low temperature compound **1** is highly insoluble and therefore the added nitrile is always in excess with respect to the amount of **1** in solution.

The relative amounts of the two isomers varies with MeCN concentration: **2b** is the dominant species in CD_2Cl_2 at low [MeCN], but the **2b**:**2a** ratio decreases on increasing [MeCN], from about 3.5:1 for [MeCN] < 0.5 mol dm^{-3} to about 1:1 in neat MeCN, at room temperature. This change is probably due to the variation of the polarity of the medium, because the relative amount of **2a** also increased upon addition of a polar solvent, such as acetone, not involved in the co-ordination.

The acquisition of accurate thermodynamic and kinetic data for the isomerization reaction is hampered by several factors, such as the insolubility of complex **1** at low temperature and the instability of **2** at temperatures higher than 273 K (see below). However, the following qualitative trends could be established. Isomer **2a** is kinetically slightly more favoured than **2b**. A **2b**:**2a** ratio lower than 1:1 was observed in low-temperature experiments, in which **1** was treated with variable amounts of MeCN (< 1 mol dm^{-3}) at 193 K and spectra were acquired at 243 K. This was a kinetic ratio: at higher temperatures, **2b** became the dominant isomer and remained as such, even on lowering the temperature to 243 K, for a time as long as 110 h. On raising the temperature in the range 253–300 K we always observed, in different experiments, a very small, reversible increase of the relative amount of **2b**, which therefore is the endothermic isomer. The variation of temperature, however, does not cause a perturbation away from equilibrium large enough to permit a reliable estimation of the rate of isomer interconversion. On the contrary, more relevant effects were observed upon addition of MeCN (see above): at 273 K the isomer ratio changed significantly reaching a new equilibrium in the time necessary to acquire an NMR spectrum. Moreover, the ratio between the isomers did not change in the course of their thermal decomposition at room temperature (see below), suggesting that isomerization is faster than fragmentation. On the contrary, the rate of isomerization is small at 243 K, because the kinetic **2b**:**2a** ratio increased quite slowly at this temperature.

Ionic Fragmentation of Compounds **2a** *and* **2b**.—In solution, at room temperature, the two isomers of $[Re_4(\mu\text{-}H)_4(CO)_{12}$-$(NCMe)_4]$ **2** decompose completely in a time ranging from a few hours to a few minutes according to the concentration of acetonitrile: the lower this concentration the higher is the rate of decomposition (see Fig. 2).

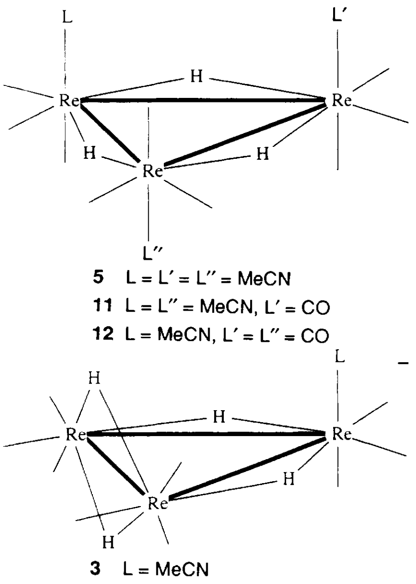
The main products of the decomposition (*ca.* 80%) are the already known unsaturated triangular cluster anion $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ **3** (see Scheme 2),[11] easily identified by its hydridic resonances, and the cation *fac*-$[Re(CO)_3(NCMe)_3]^+$ **4**,[12] unambiguously identified by its ν(CO) bands (2055 and

Table 1 Chemical shift values (CD_2Cl_2, 243 K) of the hydridic resonances of the spiked-triangle cluster compounds identified in this work. For comparison, the resonances of the triangular clusters $[Re_3(\mu\text{-}H)_3(CO)_{12-n}(NCMe)_n]$ (n = 1-3) are also shown.[b] In parentheses are given the relative intensities when different from 1

Compound	H_a[a]	H_b[a]	H_c[a]	H_d[a]
2a	−11.73	−13.9(2)		−11.92
2b	−12.16	−12.63	−13.9	−12.94
7a	−14.64	−15.74	−14.05	−12.41
8a	−17.49	−16.03(2)		−13.01
8b	−14.55	−16.06	−14.12	−13.94
9a	−17.38	−16.34(2)		−14.38

	Number of moieties bridged[b]		
	2	1	0
5	−11.6, −11.9(2)		
11	−11.9	−14.4(2)	
12		−14.4(2)	−17.0

[a] H_a, singlet; H_b and H_c, doublets; H_d, unresolved triplet (the labels refer to Scheme 1). Selective-decoupling experiments confirmed the coupling between each triplet and the corresponding doublets. [b] The labels indicate the number of $Re(CO)_3(NCMe)$ bridged by the hydride.



5 L = L′ = L″ = MeCN
11 L = L″ = MeCN, L′ = CO
12 L = MeCN, L′ = L″ = CO

3 L = MeCN
14 L = CO

Scheme 2

1955 cm^{-1}) and by the strong resonance of the nitriles (δ 2.47). Compounds **2a** and **2b** therefore undergo an ionic fragmentation, according to equation (1).

$$[Re_4(\mu\text{-}H)_4(CO)_{12}(NCMe)_4] \longrightarrow [Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^- + [Re(CO)_3(NCMe)_3]^+ \quad (1)$$

As mentioned in the introduction, analogous products had been previously obtained from the ionic fragmentation of the parent cluster **1** in donor solvents, such as methanol or acetone, according to equation (2).[6] In these cases, the formation of

$$[Re_4(\mu\text{-}H)_4(CO)_{12}] + 4\text{solv} \longrightarrow [Re_3(\mu\text{-}H)_4(CO)_9(\text{solv})]^- + [Re(CO)_3(\text{solv})_3]^+ \quad (2)$$

intermediate addition derivatives such as **2** could not be unambiguously established, but it is in agreement with the $[MeOH]^4$ term found in the rate law when solv = MeOH.[3] Reaction (2) is reminiscent of the disproportionation undergone by several carbonyl compounds, such as $[Co_2(CO)_8]$, in the presence of donor species,[13] even if in the present case no change of the formal oxidation number occurs. Similar room-temperature 'dismutations' to cationic and dianionic fragments, induced by MeCN, have also been observed for monoanionic rhenium carbido clusters.[14]

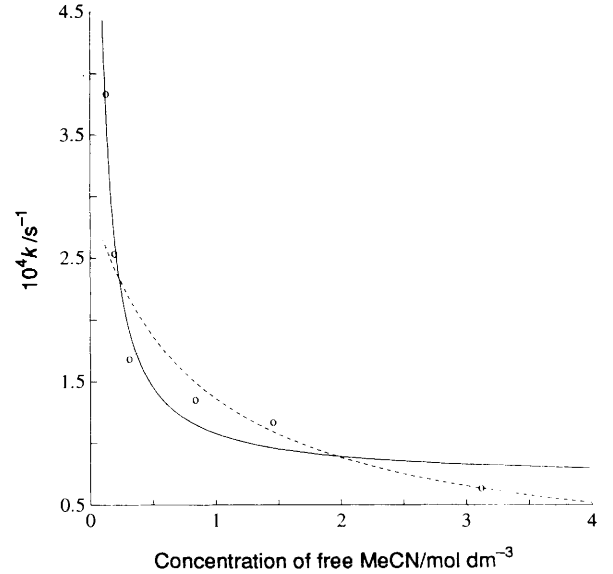


Fig. 2 First-order rate constants for the decomposition of isomers **2a** and **2b** at 300 K, in the presence of different concentrations of acetonitrile; (——) theoretical fit assuming a linear relationship between k and 1/[MeCN], (- - - -) theoretical fit assuming a linear relationship between $1/k$ and [MeCN]

As mentioned above, the ratio **2b**:**2a** did not change during the reaction. The disappearance of the overall amount of the two isomers **2a** and **2b** could be fitted by first-order plots. The values of k_1 evaluated in the presence of different concentrations of MeCN are reported in Fig. 2. The decrease of the reaction rate at high nitrile concentration indicates that the reaction goes through an initial *reversible* dissociation of a MeCN molecule bound to the triangle moiety.

The available kinetic data are not accurate enough to allow a deeper insight into the reaction mechanism. However, a linear relationship between k and 1/[MeCN] (continuous line, pre-equilibrium approximation) fits the sharp increase of the rate at low [MeCN] much better than a linear relationship between $1/k$ and [MeCN] (broken line, steady-state approximation). The fragmentation steps after nitrile dissociation can reasonably be pictured as follows. The vacant site left by the dissociation permits hydride (H^-) transfer from the rhenium 'spike', thus forming the unsaturated $Re(\mu\text{-}H)_2Re$ moiety. Co-ordination of a third nitrile on the $Re(CO)_3(NCMe)_2$ spike would then stabilize it as a cationic fragment. This step could become rate determining at very low [MeCN].

One reason for the uncertainty of the kinetic data is that reaction (1) is not the only decomposition pathway: three main by-products were usually formed, the overall amount of which was in the range 10–20%. Two of them have been identified as the neutral triangular cluster $[Re_3(\mu\text{-}H)_3(CO)_9(NCMe)_3]$ **5**, (Scheme 2)[9] and the dianion $[Re_4(\mu\text{-}H)_6(CO)_{12}]^{2-}$ **6**.[15] The third by-product, responsible for a resonance at δ −4.7, has not yet been identified. The presence of compound **5** in the reaction mixture could suggest the contemporary formation of the fragment $HRe(CO)_3(NCMe)_2$ (a species not reported in the literature), according to a 'neutral' decomposition pathway analogous to that observed in the presence of CO (see below). However, the time evolution of the appropriate resonances does not support the attribution of the unknown signal to this species. In fact the signal at δ −4.7 appears at the beginning of the reaction, while the resonances of **5** (as well that of **6**) usually occur later,* just when the unknown signal decreases. It is likely that **5** and **6** are formed at the expense of the unknown species, but further investigation on this point is necessary.

Reactions of Compounds **2a** *and* **2b** *with* CO.—The reactions were monitored by NMR spectroscopy. Solutions of complex **2** in an NMR tube were saturated with CO at 193 K and maintained at room temperature for different lengths of time (of the order of minutes, due to the high reaction rate). The spectra were then recorded at 243 K, the reaction being quenched at this temperature. The hydridic region of the spectra, although very crowded, was used to characterize the reaction products. The extensively overlapped resonances of the methyls, on the contrary, were not of diagnostic utility. Analysis of the relative intensities of the hydridic resonances in different spectra, as well as selective-decoupling experiments, allowed the attribution of these resonances to three already known triangular clusters and to four novel tetranuclear species, arising from the stepwise substitution of MeCN by CO in the isomers **2a** and **2b**.

Initially, we observed mainly the formation of one monosubstituted derivative $[Re_4(\mu\text{-}H)_4(CO)_{13}(NCMe)_3]$, to which the structure **7a** of Scheme 3 can be confidently attributed, on the basis of the chemical shift values in Table 1. The high-field shift of the resonances of H_a and H_b is particularly diagnostic of the substitution of MeCN by CO on the rhenium atom to which these hydrides are both bound.[9] The formation of only one monosubstituted derivative suggests that the nitrile *cis* to the spike in **2b** is more substitution labile than is the *trans* one.

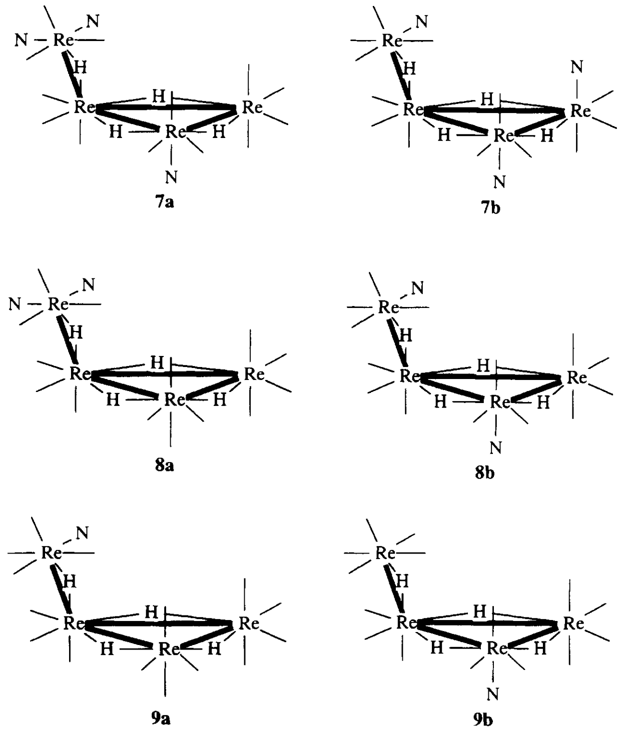
Before completion of the transformation of complex **2** into **7a**, other species were formed (see Table 2). One has been identified as the triangular cluster $[Re_3(\mu\text{-}H)_3(CO)_9(NCMe)_3]$ **5**, while the other two have been formulated as two isomers of the disubstituted tetranuclear derivative $[Re_4(\mu\text{-}H)_4(CO)_{14}(NCMe)_2]$ **8a** and **8b** (Scheme 3). Both can be formed from **7a**, by substitution of a nitrile bound either to the triangle or to the spike, respectively. These assignments are supported by the number and the δ values of the resonances of the two species (see in particular the high-field shift of H_a and H_c in **8a** and of H_d in **8b**, with respect to the signals of **7a**) and by selective-decoupling experiments.

The spectra of samples maintained at room temperature for longer times indicated the formation of another tetranuclear species, formulated as the trisubstituted derivative $[Re_4(\mu\text{-}H)_4(CO)_{15}(NCMe)]$, **9a** (Scheme 3) (see the high-field shift of H_d with respect to **8a**). This species is particularly stable, as it survives much longer than do the other tetranuclear derivatives (see Table 2, last line). The other dominant products at longer reaction times were the triangular clusters $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$ **11** and $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$ **12** (Scheme 2). These products, as well as compound **5** present at the beginning of the reaction, clearly arose from fragmentation of the tetranuclear derivatives as described above.

Table 2 Composition (%) of the mixtures of tri- and tetra-nuclear species formed during the reaction of complex **2** with CO, as evaluated by NMR monitoring

	Tetranuclear species					Trinuclear species				
						neutral			anionic	
t^a/min	**2**	**7a**	**8a**	**8b**	**9a**	**5**	**11**	**12**	**3**	**14**
0	94	—	—	—	—	—	—	—	6	—
0^b	89	5	—	—	—	—	—	—	3	3
1	16	61	6	6	—	6	—	—	—	5
3	—	50	12	15	—	12	3	—	—	7
4	—	47	15	17	—	9	5	—	—	7
5	—	42	15	16	3	11	6	—	—	6
8^c	—	21	22	23	9	7	9	—	—	9
12	—	12	21	24	18	4	17	—	—	9
17	—	8	19	13	22	—	25	5	—	8
17^d	—	—	—	—	42	—	34	16	—	8
77^e	—	—	—	—	38	—	30	25	—	7

[a] Overall time during which the sample was maintained at room temperature before acquiring the spectrum at 243 K. [b] Spectrum recorded immediately after the sample was saturated with CO at 193 K. [c] Spectrum recorded after another saturation with CO, at 193 K. [d] Spectrum recorded after the sample was maintained at 243 K for 3 d. [e] Spectrum recorded after the sample was treated again with CO at 193 K and maintained for 1 h at room temperature.



Scheme 3

In agreement with this, the presence of two mononuclear species was also detected. The first was $[ReH(CO)_5]$,[16] identified by its resonance at δ −5.97 (in CD_2Cl_2 at 243 K). The second (δ −3.10, CD_2Cl_2, 243 K) has been formulated as the novel hydridocarbonyl complex $[ReH(CO)_4(NCMe)]$ **13**, on the following grounds. At longer reaction times, under CO, its resonance is replaced by that of $[ReH(CO)_5]$. The δ value agrees well with the above-mentioned low-field shift caused by substitution of a carbonyl by a nitrile molecule. Moreover, we have prepared in two different ways, a species having the same δ value: from the reaction between $[ReH(CO)_5]$ and Me_3NO, in acetonitrile solution [equation (3)], and from the reaction of $[ReH_2(CO)_4]^-$ with CF_3SO_3H, in the same solvent [equation (4)]. The complex is highly unstable in the absence of acetonitrile and attempts to isolate it always resulted in extensive decomposition. For this reason the attribution of the resonance of the co-ordinated acetonitrile is subject to some

$$[ReH(CO)_5] + Me_3NO + MeCN \longrightarrow [ReH(CO)_4(NCMe)] + CO_2 + Me_3N \quad (3)$$

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* In some experiments, the signals of complex **5** appeared at the beginning, but with lower intensity than that at δ −4.7.

$$[ReH_2(CO)_4]^- + CF_3SO_3H + MeCN \longrightarrow [ReH(CO)_4(NCMe)] + H_2 + CF_3SO_3^- \quad (4)$$

uncertainty (see Experimental section). This instability is the most likely reason for the low intensity of the hydridic resonance of **13** (with respect to those of the triangular species **5**) in the initial reaction times, when the concentration of free MeCN is quite low. On the contrary, at longer reaction times, the sum of the integrated intensities of the two mononuclear compounds corresponded well with that of the trinuclear species, in agreement with their formation in equimolar ratios from fragmentation of tetranuclear species.

In the reaction of complex **2** with CO the extent of formation of ionic products was very low. Indeed, samples of **2** were always contaminated by various amounts of **3** (up to 10%), due to our inability completely to avoid reaction (1) during the isolation of **2**. Since compound **3** reacts rapidly with CO to give the anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ **14** (Scheme 2),[17] the reaction mixtures contained some **14** immediately after saturation with CO, but the amount of this species increased very little during the reaction (see Table 2).

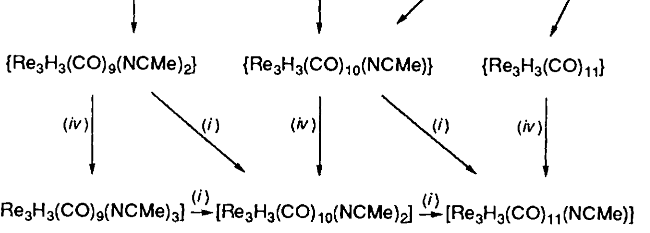
Therefore, mainly neutral species are formed in the reaction processes arising from the treatment of complex **2** with CO, in the absence of free acetonitrile. Such processes can be summarized as shown in Scheme 4: (*i*) stepwise substitution of MeCN by CO in tetranuclear species maintaining the spiked-triangle structure of **2** (upper horizontal pathway); (*ii*) fragmentation of the tetranuclear species to neutral mononuclear hydrides and neutral triangular clusters (vertical pathways); (*iii*) stepwise substitution of MeCN by CO in the products of the fragmentation (lower horizontal pathway). The fragmentation process can be viewed as the substitution of non-classical $HRe(CO)_{3+m}(NCMe)_{2-m}$ ($m = 0$–2) ligands by classical ligands, such as CO or MeCN. This could occur *via* the formation of $[Re_3H_3(CO)_{9+n}(NCMe)_{2-n}]$ ($n = 0$–2) unsaturated intermediates (Scheme 4), followed by competition between CO and MeCN for co-ordination at the vacant site.

The increase of the number of π-acidic carbonyls replacing MeCN molecules co-ordinated to the 'HRe spike' would not only reduce the Lewis basicity of the mononuclear hydride which constitutes the spike,[18] but also decrease its donor ability, as a non-classical 'ligand'. It has recently been observed by some of us that while $[ReH(CO)_5]$ behaves as a substitution-labile ligand when bound to the platinum vertex of a Re_2Pt triangular cluster,[19a] $[ReH(CO)_4(PPh_3)]$ does not.[19b] On the other hand, the increase of the number of carbonyls co-ordinated to the triangular cluster moiety is expected to decrease the lability of the other non-π-acidic ligands (including the non-classical ones). This has been clearly shown by the strong decrease in the rate of substitution of MeCN by CO in $[Re_3(\mu\text{-}H)_3(CO)_{9+n}(NCMe)_{3-n}]$, on increasing n from 0 to 2.[9]

The 'hydride-donor'[7] $ReH(CO)_4(NCMe)$ is therefore expected to be less labile when bound to $Re_3(\mu\text{-}H)_3(CO)_{11}$ or $Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)$ 'acceptor' moieties (**9a** and **8b**) than to $Re_3(\mu\text{-}H)_3(CO)_9(NCMe)_2$ (**7b**; only one of the possible isomers is shown in Scheme 3). Accordingly complex **9a** was the most stable substitution derivative, while **7b** was not observed in the reaction mixtures, probably because of a fragmentation rate higher than its formation rate. Also **9b** was not recognized, the $ReH(CO)_5$ ligand being too labile effectively to compete with CO or MeCN. However, **7b** and **9b** are shown in Scheme 4, because they are supposed to be the most active intermediates in the fragmentation process. In fact the fragmentation products are formed mainly in the initial reaction stages (from **7b** in our hypothesis) and at the end, whilst during the formation of the disubstituted species **8a** and **8b** their amounts remained almost constant. For the same reasons, Scheme 4 also includes the hypothetical fully substituted $[Re_3(\mu\text{-}H)_3(CO)_{11}\{HRe(CO)_5\}]$ derivative **10**, which would constitute a highly unstable spiked-triangle isomer of the recently characterized planar cluster $[Re_4(\mu\text{-}H)_4(CO)_{16}]$.[20] The formation of **10** is likely to be the rate-determining step of the slow disappearance of **9a**.

Several reasons can explain the different fragmentation modes in the presence of acetonitrile or of carbon monoxide. The substitution of a nitrile by a π-acidic ligand in the spikes of complexes **2a** and **2b** (or of their tetranuclear substitution derivatives) would labilize the spike itself, as discussed above. By contrast, π-acidic ligands are less prone than donor solvents to stabilize a cationic species. Moreover, the co-ordination of CO on the unsaturated intermediate formed by dissociation of a nitrile molecule from **2** will irreversibly remove the key intermediate in the formation of the unsaturated $Re(\mu\text{-}H)_2Re$ moiety.

When the reaction with CO was performed in the presence of free acetonitrile (*ca.* 0.8 mol dm^{-3}) significant differences were observed, as shown in Table 3 and Fig. 3. The most striking feature is that the reaction was much slower, since the complete disappearance of the reagents **2a** and **2b** required about 30 min, at room temperature. Moreover, significant amounts of ionic products, *i.e.* the $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ anion **14** and the $[Re(CO)_3(NCMe)_3]^+$ cation, were formed, even if the neutral triangular clusters $[Re_3(\mu\text{-}H)_3(CO)_{12-n}(NCMe)_n]$ ($n = 1$–3) remained the main fragmentation products. Finally, the ratio between neutral triangular fragmentation derivatives (Re_3) and



Scheme 4 (*i*) CO; (*ii*) $-[ReH(CO)_4(NCMe)_2]$; (*iii*) $-[ReH(CO)_5]$; (*iv*) MeCN

Table 3 Composition (%) of the mixtures of tri- and tetra-nuclear species formed during the reaction of complex **2** with CO, in the presence of 0.8 mol dm^{-3} MeCN, as evaluated by NMR monitoring

	Tetranuclear species					Trinuclear species			
						neutral			anionic
t^a/min	**2**	**7a**	**8a**	**8b**	**9a**	**5**	**11**	**12**	**14**
2.5	82	11	—	—	—	5	—	—	2[b]
6	60	25	1	—	—	12	—	—	2
11	34	39	2	—	—	21	—	—	4
21	9	46	3	1	—	29	4	—	8
41	—	42	7	3	—	30	7	—	11
96	—	31	8	2	—	30	14	—	15
256	—	16	11	1	2	25	26	—	20
486	—	7	12	—	3	21	34	—	23
840	—	2	12	—	4	17	36	5	24
1320	—	—	9	—	2	13	43	7	26

[a] Overall time during which the sample was maintained at room temperature. [b] The original sample was contaminated by a small amount (1–2%) of the anion **3**, which can be considered the source of this amount of **14**.

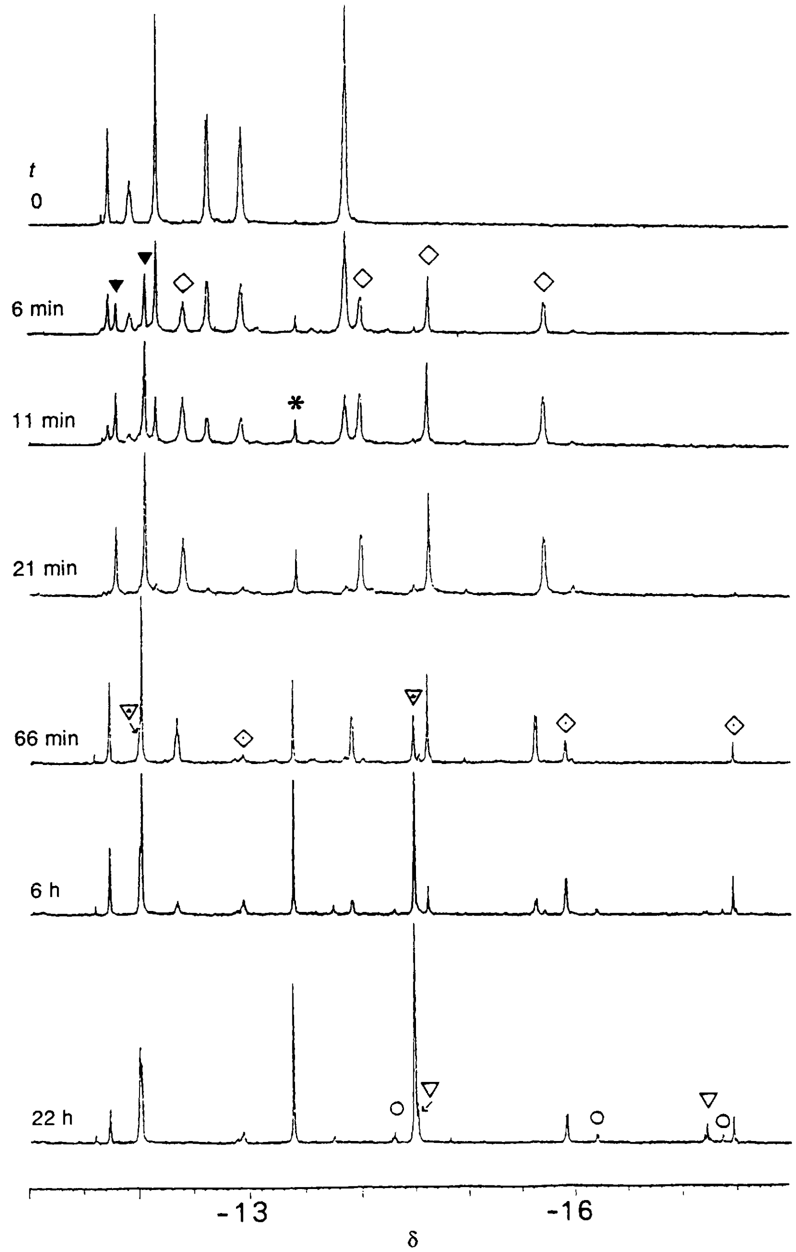


Fig. 3 Time evolution of the high-field part of the hydridic region during the reaction of complexes **2a** and **2b** with CO in the presence of acetonitrile (0.77 mol dm^{-3}). Assignments to compounds: ▼, **5**; ◇, **7a**; ✱, **14**; ▽, **11**; ◇, **8a**; ▽, **12**; ○, **9a**. The resonances of the reagents (upper spectrum) are not labelled. Compound **14** also exhibits a low-field resonance (δ −8.65, relative intensity 2 : 2) not shown. For details, see the Experimental section and Table 3

tetranuclear intermediates (Re_4) was much higher in this case than in the absence of free MeCN.

The presence of free MeCN is expected to slow down the reaction, by reducing the concentration of the unsaturated intermediate formed by dissociation of a nitrile co-ordinated on the triangular moiety of complexes **2a** and **2b**, as described above. This reduces the rate of formation of **7a** (and thus of its substitution derivatives **8** and **9**). The higher Re_3:Re_4 ratio observed in this case, compared to the experiment in the absence of MeCN, suggests that MeCN is less effective in quenching the substitution by CO of an acetonitrile bound to the rhenium spike. This favours the formation of **7b** over **7a** and therefore the formation of the fragmentation derivative $[Re_3(\mu\text{-}H)_3(CO)_9(NCMe)_3]$ **5**.

The anion **14** could arise by two pathways: ionic fragmentation of the intermediate $[Re_4(\mu\text{-}H)_4(CO)_{13}(NCMe)_3]$ **7a** and rapid carbonylation of the anion $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$, produced by the ionic fragmentation of **2a** and **2b** in the initial reaction stages. The course of the concentration of **14** with time shows that both pathways are operative, but the first one accounts for most of **14** formed. Then more than 90% of compounds **2a** and **2b** reacted according to pathways different from the ionic fragmentation (see Table 3), in spite of the presence of a relevant amount of MeCN.

Conclusion

This work has clearly demonstrated that the tetrahedral unsaturated cluster $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$ (56 v.e.s) easily adds double the number of ligands required to attain saturation. Instead of 60 v.e.s saturated tetrahedral metal clusters, 64 v.e.s derivatives are readily formed, having a spiked-triangle structure. An analogous behaviour is shown by the 58 v.e.s tetrahedral cluster anion $[Re_4(\mu_3\text{-}H)_2(\mu\text{-}H)_3(CO)_{12}]^-$, which preferentially adds two two-electron donor ligands L (L = CO, MeCN[21a] or PR_3[21b]), giving 62 v.e.s derivatives $[Re_4(\mu\text{-}H)_5(CO)_{12}L_2]^-$, containing a butterfly metal skeleton. It is interesting that the number of Re–Re [indeed Re(μ-H)Re] interactions present in the final products (four in the spiked triangle, five in the butterfly skeleton) coincides with the number of hydrides present in the respective starting compounds, suggesting that this number could dictate the preferred structure of the addition products, and therefore the number of added ligands.

The strong propensity of complex **1** to give 64 v.e.s derivatives accounts for the previous isolation of an addition derivative of **1** in which a typical tridentate ligand such as the 'tripod' behaves as an eight-electron donor.[2] These spiked-triangle addition derivatives, however, are unstable and at room temperature rapidly lose the 'spike', following different decomposition pathways, according to the nature of the ligands present (see Scheme 5).

In the presence of acetonitrile only, an 'ionic' pathway, leading to an unsaturated triangular cluster anion and a mononuclear cation, is the dominant fragmentation process of complexes **2a** and **2b**. The room-temperature reaction of the tetranuclear *unsaturated* cluster **1** with acetonitrile leads therefore to a trinuclear *unsaturated* cluster, through *saturated* intermediates. A similar transformation was previously observed[21a] in the reaction of the unsaturated anion $[Re_4(\mu_3\text{-}H)_2(\mu\text{-}H)_3(CO)_{12}]^-$ with acetonitrile, which affords the same unsaturated triangular cluster $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$, *via* the saturated butterfly intermediate $[Re_4(\mu\text{-}H)_5(CO)_{12}(NCMe)_2]^-$

We have previously reported that the dissolution of complex **1** in donor solvents, such as methanol, acetone, or tetrahydrofuran, directly affords triangular unsaturated $[Re_3(\mu\text{-}H)_4(CO)_9(solv)]^-$ anions and $[Re(CO)_3(solv)_3]^+$ cations.[6] The higher substitution lability of these ligands with respect to acetonitrile probably accounts for the difficulty in observing the $[Re_4(\mu\text{-}H)_4(CO)_{12}(solv)_4]$ addition intermediates. This is in agreement with the evidence presented here supporting the dissociation of a nitrile as the first step of the fragmentation of the spike-triangle intermediates.

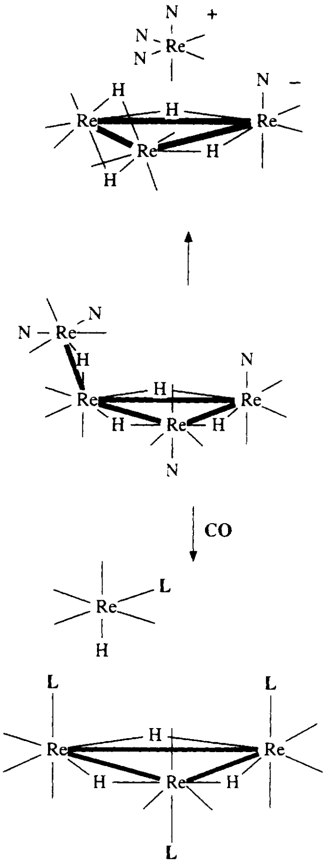
In the presence of the π-acid ligand CO, compounds **2a** and **2b** give derivatives of stepwise substitution of MeCN by CO, the stability of which is a function not only of the extent but also of the site of substitution (the 'hydride-donor' spike or the 'acceptor' triangular moiety). These intermediates decompose according to a different, 'neutral' pathway, leading to saturated triangular clusters and mononuclear hydrides. This fully agrees with the formation of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ and $[ReH(CO)_5]$ in the direct reaction of compound **1** with CO, as previously reported.[1]

However, the reaction with CO in the presence of MeCN, in which both ionic and neutral derivatives are formed, has shown that the preferred decomposition route of these compounds results from a subtle balance of kinetic factors. It has also demonstrated that the alternative between ionic and neutral cleavage is not restricted to $[Re_3(\mu\text{-}H)_3(CO)_9(NCMe)_2\{HRe(CO)_3(NCMe)_2\}]$ **2a** and **2b** only, but can concern other spiked-triangle clusters such as $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)\{HRe(CO)_3(NCMe)_2\}]$ **7a**.

The investigation of the reactions of complexes **2a**, **2b** and of **1** itself with P-donor ligands having different steric and electronic properties will probably throw further light on these reactivity patterns.

Experimental

Reactions were performed under N_2, using solvents deoxygenated and dried by standard methods. Deuteriated solvents were used as received. Proton NMR spectra were obtained on Bruker WP80 or AC200 spectrometers, IR spectra on a Perkin-Elmer 781 grating spectrophotometer, in CaF_2 cells. Literature methods have been used to prepare $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$[22] (in this way compound **1** is solvated by 2 molecules of benzene), $[ReH(CO)_5]$[16] and $[PPh_4][ReH_2(CO)_4]$.[23]



Scheme 5 L = CO or MeCN

Reaction of Complex 1 *with* MeCN.—Complex **1** (13 mg, 10^{-2} mmol) was dissolved at room temperature in freshly distilled MeCN (2.5 cm^3). The deep red solution instantaneously become colourless. The IR spectrum showed ν_{CO} bands at 2045mw, 2033m, 2018s, 2006m and 1932vs cm^{-1}. The same products were obtained on performing the reaction in CH_2Cl_2, at low temperature (253 K), to avoid the rapid decomposition of complex **2**. The NMR spectrum (CD_2Cl_2, 253 K) was consistent with the formation of the addition derivatives $[Re_4(\mu\text{-}H)_4(CO)_{12}(NCMe)_4]$ **2a** and **2b**: **2a**, δ 2.24 (s, 6), 2.18 (s, 6), −11.73 (s, 1), − 11.92 (t, 1, J_{HH} = 2.5) and −13.9 (d, 2, partially overlapping with a signal of **2b**); **2b**, δ 2.46 (s, 3), 2.40 (s, 3), 2.23 (s, 3), 2.14 (s, 3), −12.16 (s, 1), −12.63 (d, 1, J_{HH} = 3.5), −12.94 (t, 1, J_{HH} = 3.5 Hz) and −13.9 (d, 1, partially overlapping with a signal of **2a**). Selective-decoupling experiments and the analysis of reaction mixtures with different isomer ratios made unambiguous the assignments of the resonances to the two species. In particular, on irradiation at δ −13.9 the resonances at δ −12.63 and −12.94 of **2b** gave rise to an AB spin system, while the triplet of **2a** became a singlet. Upon irradiation at δ −12.94, the doublet of **2b** became a singlet and also the resonance at δ −13.9 sharpened. Upon addition of increasing amounts of MeCN (150, 200, 500 μl) two of the hydridic resonances of **2b** (δ −12.63 and −12.94) shifted progressively closer. In neat CD_3CN the two resonances overlapped at δ −12.61 (243 K).

Isomer Ratio and Isomer Interconversion.—In a first experiment, complex **1** (10 mg, 8.3 × 10^{-3} mmol) was dissolved in CD_2Cl_2 in an NMR tube, then the tube was almost completely dipped in a bath at 193 K. After addition of cold MeCN (10 μl, 0.19 mmol), the tube was briefly shaken, then transferred to the NMR probe at 243 K (Bruker WP80). A significant amount of a red residue due to unreacted **1** was present. The first spectrum showed a **2b**:**2a** ratio of 0.75:1, which slowly increased on maintaining the sample at 253 K (1.3:1 after 3.5 h). In the meantime the amount of sample in solution increased, due to the slow dissolution of **1**. On raising the temperature the ratio increased (2.9:1 at 295 K), but at the same time the thermal decomposition of compounds **2** began (see below).

In a second experiment, complex **1** (10 mg, 8.3×10^{-3} mmol) dissolved in CD_2Cl_2 in an NMR tube was treated with MeCN, (1 μl, 1.9×10^{-2} mmol, about one half of the stoichiometric amount required to give **2**) at 193 K, taking care to maintain the temperature as low as possible. The only hydridic signals observed in a spectrum at 193 K (Bruker WP80) were those of **2a** and **2b** (**2b**:**2a** ratio *ca.* 0.85:1), of very low intensity, due to the small amount of reacted (dissolved) **1**. The addition of more MeCN (1 μl) did not cause significant changes in the spectrum. The temperature of the probe was then raised to 243 K (**2b**:**2a** ratio *ca.* 0.9:1) and maintained for 1 h, after which the ratio was about 1.0:1. At 273 K the ratio rapidly increased to 2.5–2.9:1 (rather scattered values in different spectra, due to high noise). The sample was then kept at 243 K for 4 d after which a ratio of *ca.* 2.5:1 was observed. The ratio increased again on raising the temperature (2.8:1 at 273 K, 2.9:1 at 283 K, *ca.* 3.5:1 at 300 K), when rapid decomposition occurred.

In a third conclusive experiment complex **1** (15 mg, 1.2×10^{-2} mmol), in CD_2Cl_2, was treated, at low temperature, as described above, with MeCN (20 μl, 0.38 mmol) and transferred to the NMR probe at 243 K (Bruker AC200). A spectrum at this temperature showed a **2b**:**2a** ratio of 0.73:1. The temperature was raised to 260 K, and successive spectra showed the **2b**:**2a** ratio to increase to 2.3:1 within *ca.* 40 min. During this time, however, the amount of sample in solution increased, due to the increased solubility of **1**. At 278 K the dissolution of **1** was complete, and the **2b**:**2a** ratio was 2.5(1):1, decreasing to 2.3:1 after 1 h at 260 K. After 110 h at 243 K a spectrum acquired at this temperature showed a **2b**:**2a** ratio of 2.2:1. The temperature of this *homogeneous* sample was then varied as previously performed for the *heterogeneous* sample, affording the same changes in **2b**:**2a** ratio. The increase in temperature to 288 K did not significantly change the ratio. At this temperature, however, the fragmentation of **2a** and **2b** to compound **3** started, reaching a level of *ca.* 10% after 40 min. The equilibrium was then perturbed by addition of MeCN (50 μl) at 288 K: the **2b**:**2a** ratio decreased to 2.0(1):1 according to the spectrum acquired immediately after MeCN addition and did not change significantly in successive spectra. The temperature was decreased to 270 K (ratio **2b**:**2a** 1.8:1) and CD_3CN (100 μl) was added, causing a rapid decrease in the ratio to 1.4:1. The addition of $(CD_3)_2CO$ (200 μl) led to a ratio of 1.2(1):1.

To evaluate the effect of the concentration of MeCN on the ratio between the isomers, complex **1** (11 mg, 9.1×10^{-3} mmol) was dissolved in an NMR tube in $CDCl_3$ (500 μl), then treated at low temperature with increasing amounts of CD_3CN. After each addition the sample was maintained for 2 min at room temperature to allow equilibration, then spectra were acquired at 243 K. The following **2b**:**2a** ratios were observed (in brackets the overall amount of added acetonitrile, in μl): 3.6:1 (20), 3.0:1 (40), 1.9:1 (80), 1.2:1 (160). In neat CD_3CN a ratio of *ca.* 1.0:1 was measured (room temperature).

Thermal Decomposition of Complex **2**.—The reactions were monitored by NMR spectroscopy at 300 K, in CD_2Cl_2 solution, in the presence of different concentrations of MeCN. In a typical experiment, complex **1** (*ca.* 10^{-2} mmol), dissolved in an NMR tube in CD_2Cl_2 (0.5 cm^3), was treated at 193 K with the appropriate amount (5–100 μl) of MeCN. The tube was introduced into the NMR probe at 300 K and spectra were acquired at different times. The concentrations of the components of the reaction mixtures were evaluated from the integrated intensities of the hydridic resonances. First-order plots of the overall concentration of the isomers **2a** and **2b** *vs.* time were reasonably linear up to high conversion, allowing the estimate of the following kinetic constants (s^{-1}, with uncertainties of the least-squares slope in parentheses and the concentration of free MeCN in square brackets): $3.8(3) \times 10^{-4}$ [0.135], $2.5(1) \times 10^{-4}$ [0.19], $1.68(2) \times 10^{-4}$ [0.31], $1.35(3) \times 10^{-4}$ [0.84], $1.17(3) \times 10^{-4}$ [1.46], $6.3(2) \times 10^{-5}$ [3.12 mol dm^{-3}].

Reactions of $[Re_4(\mu\text{-}H)_4(CO)_{12}(NCMe)_4]$ *with* CO.—(*a*) *In the absence of free* MeCN. The reaction was monitored by NMR spectroscopy at 253 K, using a sample obtained by evaporating to dryness a CH_2Cl_2 solution of complex **2** prepared as above. The sample was dissolved in cold CD_2Cl_2, transferred to an NMR tube at 193 K, saturated with CO at the same temperature, and maintained at room temperature for different times before acquiring the spectra. Table 2 gives the time spent by the tube out of the probe (during which the sample temperature would not be constant). The concentrations of the tri- and tetra-nuclear components of the reaction mixtures have been calculated by normalization from the integrated intensities of the hydridic resonances. Besides the resonances of the species reported in Tables 1 and 2, a few unattributed signals of very low intensity were present in the spectra.

(*b*) *In the presence of free* MeCN. The reaction was repeated in the same way, by saturating with CO an NMR tube containing a sample of complex **2** generated *in situ* by addition of MeCN (20 μl, 0.38 mmol) to a solution of **1** (15 mg) in CD_2Cl_2 (0.5 cm^3) (see Table 3). After the first five spectra, the temperature of the probe was raised to 294 K and the spectra were acquired at programmed times (selected times are given in Table 3). The integrated intensity ratios of the mononuclear neutral products *vs.* the corresponding triangular neutral products were always smaller than 1:1, ranging from 0.9:1 at the beginning to 0.4:1 at the end, suggesting that the mononuclear hydridic species undergo some side reactions at longer times.

Reaction of $[ReH(CO)_5]$ *with* Me_3NO *in the Presence of* MeCN.—A sample of $[ReH(CO)_5]$ (13 mg, 0.040 mmol), in MeCN solution, was treated with freshly sublimed Me_3NO (4.5 mg, 0.060 mmol). After 30 min at room temperature the ν(CO) bands of the reagents were completely replaced by new bands at 2093w, 1985s and 1942ms cm^{-1}. When the reaction was repeated in a NMR tube in CD_3CN, the formation of a species having an hydridic resonance at δ −2.83 was observed. Attempts to isolate the product by evaporating the colourless solution to dryness resulted in complete decomposition to a bright yellow oily residue: NMR (δ, $CDCl_3$) −9.05 (minor signals at −14.38, −15.88 and −17.15); IR ν(CO) (CH_2Cl_2) 2113vw, 2096w, 2027vs, 2000s, 1984s, 1945 (sh) and 1912m cm^{-1}.

In order to identify the resonance of the nitrile molecule which is supposed to be bound in complex **13**, the reaction was repeated in CD_2Cl_2 solution, directly in a NMR tube: $[ReH(CO)_5]$ (5 μl, 0.034 mmol) was dissolved in CD_2Cl_2 (0.5 cm^3), then treated with MeCN (30 μl) and freshly sublimed Me_3NO (4 mg, 0.053 mmol). The NMR spectrum showed that only *ca.* 50% of the starting material had reacted, giving mainly **13** (δ −2.95 at 295 K and −3.10 at 243 K). A resonance at δ 2.26, of intensity *ca.* 3 with respect to the hydridic signal at δ −2.95, can be reasonably attributed to the co-ordinated MeCN molecule. However the noise due to the high concentration of free acetonitrile (δ 1.91) and the presence of other resonances in the range δ 2–3(including the very intense one due to NMe_3, at δ 2.12) make rather uncertain this attribution. The resonance disappeared upon addition of PPh_3

(2 equivalents), which resulted in the formation of [ReH(CO)$_4$(PPh$_3$)].

Reaction of [ReH$_2$(CO)$_4$]$^-$ *with* CF$_3$SO$_3$H *in the Presence of* MeCN.—A sample of [PPh$_4$][ReH$_2$(CO)$_4$] (13 mg, 0.020 mmol) was treated in MeCN with CF$_3$SO$_3$H (1.8 μl, 0.020 mmol), at room temperature. Gas evolution (H$_2$ by gas-chromatographic analysis on a molecular sieves column) was observed, and the IR spectrum showed mainly the ν(CO) bands of compound **13**. The reaction was repeated in an NMR tube, using CD$_3$CN as solvent: the only hydridic resonance observed was at δ −2.81 (spectroscopic yield 70%). Attempts to obtain compound **13** by protonation of [ReH$_2$(CO)$_4$]$^-$ in CD$_2$Cl$_2$, in the presence of 1.5 mol dm^{-3} MeCN gave **13**, but in low yields, the main hydridic resonances being at δ −11.3 and −15.0.

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References

1 (*a*) R. Saillant, G. Barcelo and H. Kaesz, *J. Am. Chem. Soc.*, 1970, **92**, 5739; (*b*) R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, 1976, **98**, 4687.
2 S. R. Wang, S.-L. Wang, C. P. Cheng and C. S. Yang, *J. Organomet. Chem.*, 1992, **431**, 215.
3 S. R. Wang and C. P. Cheng, *J. Chem. Soc., Chem. Commun.*, 1993, 470.
4 C. S. Yang and C. P. Cheng, *J. Chem. Soc., Dalton Trans.*, 1994, 2011.
5 C. S. Yang, H. C. Horng, F. L. Liao and C. P. Cheng, *J. Chem. Soc., Chem. Commun.*, 1994, 1637.
6 T. Beringhelli and G. D'Alfonso, *J. Chem. Soc., Chem. Commun.*, 1994, 2631.
7 L. M. Venanzi, *Coord. Chem. Rev.*, 1982, **43**, 251.
8 R. H. Crabtree, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 789.
9 T. Beringhelli, G. D'Alfonso, M. Freni, G. Ciani, M. Moret and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1989, 1143.
10 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, *J. Organomet. Chem.*, 1979, **170**, C15.
11 T. Beringhelli, G. D'Alfonso, M. Freni, G. Ciani, A. Sironi and H. Molinari, *J. Chem. Soc., Dalton Trans.*, 1986, 2691.
12 R. H. Reimann and E. Singleton, *J. Organomet. Chem.*, 1973, **59**, C24; R. E. Cristopher and L. M. Venanzi, *Inorg. Chim. Acta*, 1973, **7**, 489.
13 F. Calderazzo, R. Ercoli and G. Natta, in *Organic Synthesis via Metal Carbonyls*, eds. I. Wender and P. Pino, Wiley, New York, 1968, vol. 1 and refs. therein.
14 See, for instance, T. Beringhelli, G. D'Alfonso, H. Molinari and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1992, 689 and refs. therein.
15 H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley and M. R. Churchill, *J. Am. Chem. Soc.*, 1969, **91**, 1021.
16 W. Beck, W. Hieber and G. Braun, *Z. Anorg. Allg. Chem.*, 1961, **308**, 23.
17 T. Beringhelli, G. Ciani, G. D'Alfonso, H. Molinari and A. Sironi, *Inorg. Chem.*, 1985, **24**, 2666.
18 See, for instance, T. G. Richmond, F. Basolo and D. F. Shriver, *Organometallics*, 1982, **1**, 1624.
19 (*a*) T. Beringhelli, G. D'Alfonso and A. P. Minoja, *Organometallics*, 1994, **13**, 663; (*b*) T. Beringhelli, G. D'Alfonso and M. Bergamo, unpublished work.
20 N. Masciocchi, A. Sironi and G. D'Alfonso, *J. Am. Chem. Soc.*, 1990, **112**, 9395.
21 (*a*) T. Beringhelli, G. D'Alfonso, A. P. Minoja, G. Ciani and D. M. Proserpio, *Inorg. Chem.*, 1993, **32**, 803; (*b*) T. Beringhelli, G. D'Alfonso and M. Bergamo, unpublished work.
22 J. R. Johnson and H. D. Kaesz, *Inorg. Synth.*, 1978, **18**, 60.
23 G. F. P. Warnock, L. C. Moodie and J. E. Ellis, *J. Am. Chem. Soc.*, 1989, **111**, 2131.

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