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Multinuclear N.M.R. Studies of Transition Metal Carbonyl Clusters

SILVIO AIME

Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Turin, Italy

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In the past decade the availability of commercial n.m.r. instruments operating in FT mode has put a new and powerful tool in the hands of the organometallic chemists [1]. The extensive application of n.m.r. spectroscopy to transition metalcarbonyl clusters has allowed us to gain additional knowledge on the chemical bonding and solution structures, while the recently reported solid state n.m.r. spectrum of $Fe_3(CO)_{12}$ outlines the remarkable potential of this technique towards this class of molecules [2].

Generally, great attention has been devoted to the study of the intramolecular rearrangement of ligands since it has been suggested that ligand migration may play an important role in catalytic and stoichiometric reactions of transition metal clusters, and it can be of some utility to understand mobility phenomena of chemisorbed species on metal surfaces [3].

Since the first paper (in 1972) dealing with the dynamic behaviour of $[CpFe(CO)_2]_2$ studied by C-13 n.m.r. spectroscopy at variable temperature [4], a number of investigations have been reported showing the general occurrence of this phenomenon in metal carbonyl derivatives.

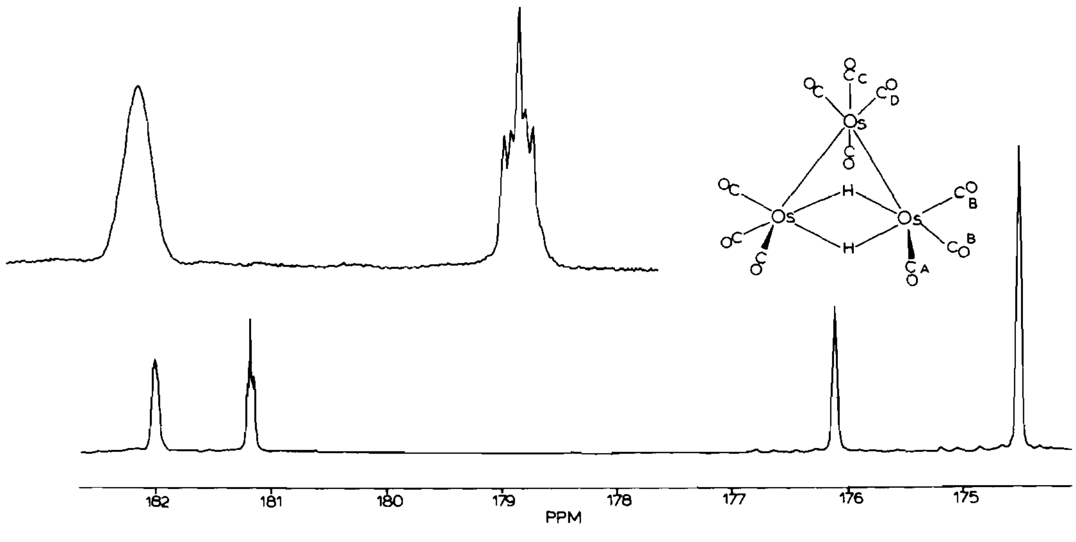
Much of the work has been done by C-13 n.m.r. spectroscopy, but it has been recently shown that the observation of other nuclei (*i.e.* O-17, metal nuclei...) can also provide valuable information.

The dynamic properties of several ligands (*i.e.* CO, H, CNR, unsaturated hydrocarbons...) are now well established; furthermore it is believed that the dynamic processes involving the ligands on the cluster surface are often coupled with a skeleton rearrangement within the metallic framework [5].

C-13 N.m.r. Studies

In order to overcome experimental difficulties (the natural abundance of ^{13}C nuclei is 1.1%), ^{13}CO enrichment of the samples is a common technique: the enrichment is usually in the range 10–20% to avoid unwanted broadening of the absorptions due to unresolved J_{CC} coupling. When highly ^{13}CO-enriched samples are investigated, $^2J_{CC}$ are easily detected [6]: a steric dependence seems to hold for $^2J_{CC}$ (as has already been established for $^2J_{CH}$ and $^2J_{CP}$) since $^2J_{CC}$ *cis* values are smaller than $^2J_{CC}$ *trans*. The observation of $^2J_{CC}$ can also assist in the assignment of CO resonances as has been shown in the case of $H_2Os_3(CO)_{10}$ [7].

At room temperature the $\{^1H\}$ C-13 n.m.r. spectrum of this compound showed four resonances in the relative intensity ratio of 2:2:2:4 from low to high field respectively. The assignment of CO_A and



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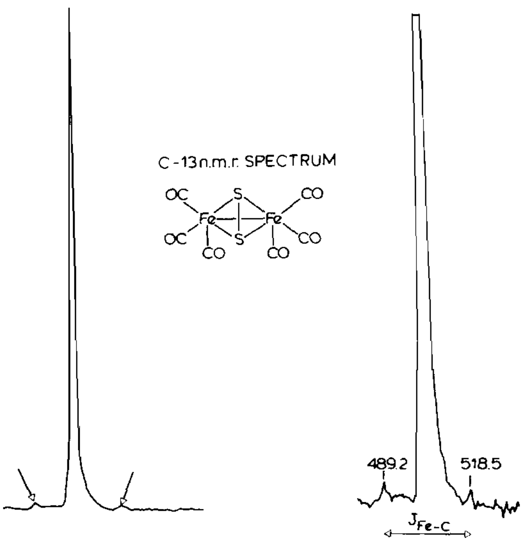
CO_B is straightforward on the base of the proton coupled spectrum and on behaviour at higher temperatures. CO_C and CO_D can be assigned to their respective signals only on the base of the observation of J_{CC} coupling constants. As is shown in the figure in the case of a ~80% ^{13}CO enriched sample, only one of the two low field absorptions shows a fine structure which corresponds to the presence of different isotopomers according to the number of ^{13}CO groups incorporated. Thus the quintuplet assigned to CO_C arises by overlap of a singlet (no C-13 in the equatorial position) with a doublet (one C-13 in the equatorial position) and with a triplet (two C-13 in the equatorial position). On the other hand CO_D appears as a broad envelope, because a further coupling with CO_A is operating.

On the same compound, the availability of highly ^{13}CO enriched samples (65–80%) has allowed the accurate determination of the CO exchange rate between A and B sites at +21 °C by Spin Magnetization Transfer when the rate of this process (0.349 sec^{-1}) is too slow for line shape analysis [8].

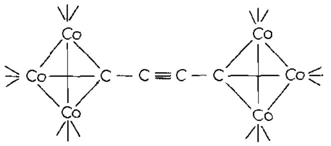
Furthermore, the use of ^{13}CO-enriched samples can facilitate the observation of satellite subspectra when the COs are bonded to metals with $I \neq 0$, as in the iron carbonyl derivatives (^{57}Fe, 2.2% nat. ab., $I = 1/2$) [9]. It has been possible to detect $^1J_{Fe-C}$ coupling constants in several $Fe(CO)_n$ fragments: since all the values fall in the range of 23–32 Hz, it seems reasonable to assume that the coupling constants for Fe–CO bonds exhibit only a small dependence on the nature of the other ligand bonded to iron. The detection of ^{57}Fe-satellites can also assist in elucidation of the dynamic processes occurring in molecules containing more than one iron atoms in cases in which the ^{13}C n.m.r. spectra are consistent with a fast intramolecular CO exchange. An example is given by molecules of formula $Fe_2(CO)_6X_2$ (X = S, SMe, SC_6H_5) whose VT C-13 n.m.r. spectra do not allow us to distinguish between the occurrence of a localized or delocalized carbonyl exchange. The observation of a doublet in the satellite sub-spectrum with an inner separation of 26.9–29.3 Hz (*i.e.* in the range corresponding to $^1J_{Fe-C}$) supports the view that only a polytopal rearrangement is occurring within each $Fe(CO)_3$ moiety.

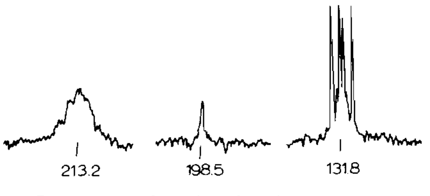
Since $^2J_{Fe-C}$ is expected to be very small (as found for $^2J_{Rh-C}$), the other doublet is hidden under the main resonance of the Fe-56 isotopomer.

An inspection of the Fe-57 satellite sub-spectrum of $Fe_3(CO)_{12}$ allows us to ascertain a 'hidden' rearrangement process into the metallic framework. In fact if the solid state structure of the Fe_3-triangle were maintained in solution, we would be expected to observe in the fast CO-exchange limit two sets of Fe-57 satellites, in 2:1 relative intensity ratio corresponding respectively to 4.4% of molecules containing the active iron in a basal position of the isoscele triangle and to 2.2% of molecules containing the active iron in the apical position. Since only a doublet (inner separation 8.3 Hz) is detected [8, 10] in the temperature range from −80 °C to +30 °C we conclude that the fast CO rearrangement is coupled with a dynamic process which makes the three iron atoms equivalent on the NMR time scale.



The use of C-13 labelled compounds can also contribute to establish the reaction path which leads to the formation of certain products not easily related to the starting reagents. For instance, the synthesis of $Co_6(CO)_{18}C_4$ [11] from $Co_2(CO)_8$ and $^{13}CCl_4$ has allowed us to establish unambiguously that all four carbons of the chain have originated from carbon tetrachloride [12].





Interestingly, the C_4-chain gives rise to an AA′XX′ system but unfortunately the low field portion is drastically broadened by the interaction with the quadrupolar cobalt nuclei. However, this observation suggests that the use of C-13 pluri-labelled reagents can be an important source of additional information; we are actually expanding this area of research by studying acetylene complexes obtained from $H-^{13}C\equiv{}^{13}C-H$.

An interesting debate has developed in recent years concerning the nature of the dynamic processes occurring in transition metal carbonyl clusters. The case of $Fe_3(CO)_{12}$ represents a good example to discuss the two approaches. According to the mechanism proposed by Cotton and Tromp [13], the pairwise opening of the two CO bridges generates an intermediate of *quasi* $[Os_3(CO)_{12}]$ structure of D_{3h} symmetry and this stage is followed by the formation of bridge pair around the successive Fe–Fe edges. The equivalence of all twelve COs is then obtained via numerous interconversions $C_{2v} \rightleftharpoons D_{3h}$.

Johnson's approach [14] is based on the consideration that the C_{2v} structure of $Fe_3(CO)_{12}$ results as a simple consequence of placing the Fe_3-triangle within the icosahedron defined by the twelve carbonyl ligands. The equivalence of the carbonyl groups is then obtained by simple re-orientation of the Fe_3-triangle within the icosahedron: this motion produces two new isomeric forms, one with all the COs in terminal position (but not equivalent to $Os_3(CO)_{12}$), and one with two COs bridging the opposite faces of the Fe_3-triangle.

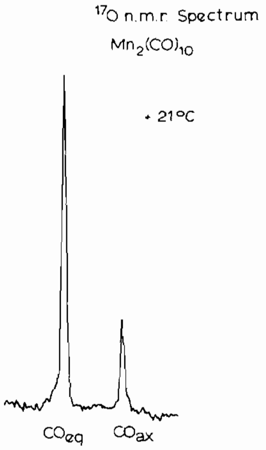
However, none of these mechanisms can explain the observed behaviour in the VT C-13 n.m.r. spectra of $Fe_3(CO)_{11}L$ ($L = PR_3$, $P(OR)_3$) [15]. For instance when $L = PMe_2Ph$, at −90 °C three absorptions are observed respectively at 224.0 (d, $J_{PC} = 8$ Hz), 212.3-(s) and 204.1 ppm (s) in the relative intensity ratio of 4:6:1. As the temperature is increased the two low fields broaden, collapse and merge into a new peak ($J_{PC} = 2$ Hz), but the signal of intensity 1 remains virtually unaffected. The observed behaviour certainly rules out the possibility that the low temperature spectrum corresponds to the 'frozen' structure.

In order to explain these findings, it was firstly recognized that the interconversion processes proposed by Johnson for $M_4(CO)_{12}$ molecules [16] can be extended to the $Fe_3(CO)_{12}$ case. Secondly, if it is assumed that in solution only the frontally substituted isomer $Fe_3(CO)_{11}L$ is present, it is possible to assign the observed patterns of resonances to the occurrence of the icosahedron–cubooctahedron interconversion by a single mode at low temperature and by all five possible modes at higher temperature to give the 10:1 observed pattern.

^{17}O N.m.r. Studies

In principle ^{17}O n.m.r. could have the same impact on the study of metal carbonyl clusters as found for ^{13}C n.m.r. spectroscopy. In practice there are, howeve, two major problems for ^{17}O studies: a) the low sensitivity (0.037% natural abundance, low magnetogyric ratio), and b) broad resonances are frequently obtained since the ^{17}O nucleus possesses a sizeable electric quadrupole moment.

NMR spectra of ^{17}O in natural abundance for a range of transition metal carbonyls have however shown that narrower linewidths (10–50 Hz) are observed in these compounds in respect to organic compounds [18]. A particularly useful case is the detection of the ^{17}O n.m.r. spectra of compounds containing metals with $I > 1/2$ (*i.e.* Mn, $I = 5/2$; Co, $I = 7/2$), whose ^{13}C spectra are usually broadened by a moderately rapid quadrupolar relaxation induced by these metals.

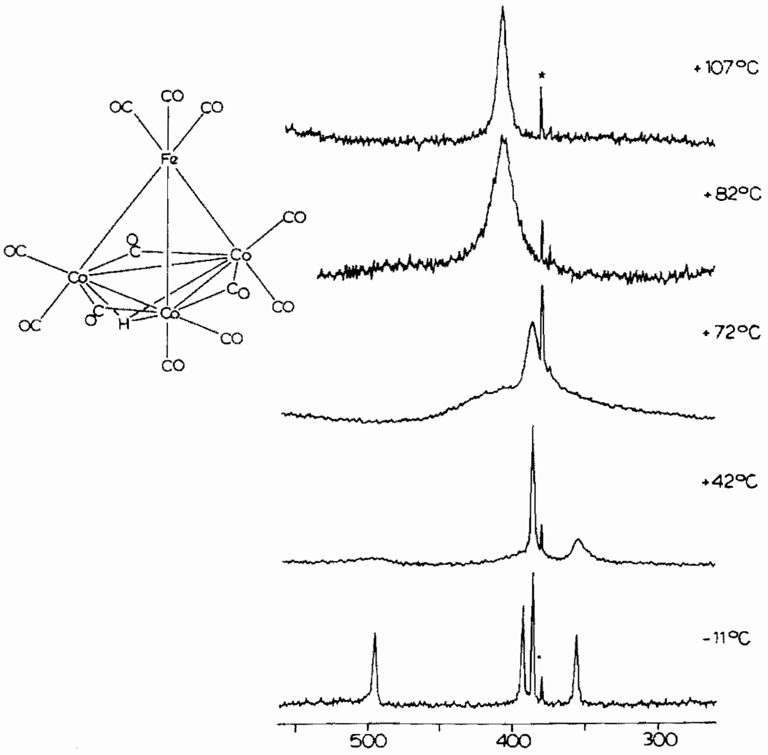


The advantages of large ^{17}O shifts at high magnetic fields (9.4 T) and lack of broadening of ^{17}O resonances by coupling to the quadrupolar ^{59}Co nuclei have enabled us to resolve the long standing problem of the solution structure and dynamics of $Co_4(CO)_{12}$ [19].

In fact, although a detailed analysis of the IR spectrum [20] and the Co-59 n.m.r. spectrum [21] were consistent with the C_{3v} structure found in the solid state, the C-13 n.m.r. spectrum showed three equally intense peaks supporting the presence in solution of a D_{2d} structure [22].

The low temperature O-17 n.m.r. spectrum shows four resonances (one in the bridging region and three in the terminal CO region) in the relative intensity ratio of 1:1:1:1, so that the C_{3v} structure is confirmed. Variable temperature work revealed a non selective exchange of CO ligands, supporting the view that an intermediate of T_d structure is involved in the process, as early suggested by Cotton [23]. The anomalies found in the C-13 n.m.r. spectrum may then be related to perturbations induced on the C-13 resonances by the quadrupolar Co-59 nuclei.

In the case of the related isoelectronic derivative $HFeCo_3(CO)_{12}$ the low temperature O-17 n.m.r. spectrum is in agreement with the C_{3v} structure, but a three stage process is observed as the temperature is increased. The first process is the in-plane exchange (or merry-go-round process) which involves the bridging carbonyls and one set of the terminal COs bonded to the cobalt atoms; a slight increase in the



temperature causes the involvement in the rearrangement process of the remaining set of terminal COs on the cobalt atoms. Finally, the last stage corresponds to the totally scrambled spectrum.

A further point of interest in O-17 n.m.r. spectroscopy of transition metal carbonyl clusters is based on the possibility to determine O-17 spin-lattice relaxation times [24]. This measurement is practically feasible, since O-17 T_1s are very short and the accumulation of a high number of transients is then possible in a short period of time.

Another advantage (in respect to C-13 T_1s) depends on the fact that the O-17 T_1s are dominated by the quadrupolar relaxation mechanism: it follows that it is then relatively easy to extract the molecular correlation times and to get further insight into the dynamic process of these molecules. We are currently investigating this point.

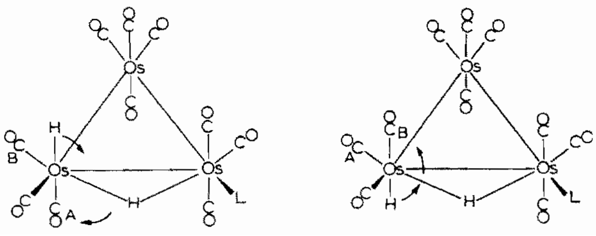
Relationship between Structure and Ligand Dynamics

Although the ligand mobility in metal cluster derivatives has been the subject of a number of studies, few investigations have been devoted to the relationship between the dynamic behaviour of different types of ligands on the same metal cluster.

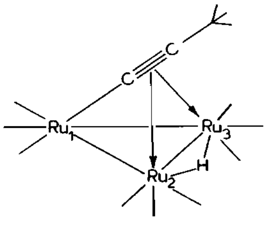
By simple addition of Lewis bases (L) to the coordinatively unsaturated hydrido-cluster $H_2Os_3(CO)_{10}$, the 1:1 adducts are easily formed [25]:

$$H_2Os_3(CO)_{10} + L \rightarrow H_2Os_3(CO)_{10}L$$
$$(L = PR_3, P(OR)_3)$$

The solid state structure of these adducts, as established by X-ray analysis when $L = PPh_3$, shows that the two hydrides occupy a bridging and terminal positions [26]. Two hydride absorptions are observed in the low temperature ^1H n.m.r. limiting spectrum, but as the temperature is increased a rearrangement takes place and a single broad resonance is observed at room temperature. The low temperature C-13 n.m.r. spectra are consistent with the solid state structure, and their behaviour at variable temperature shows that only two carbonyl groups (bonded to the osmium bearing the terminal hydride) undergo a rearrangement process. By considering that similar free energies of activation are evaluated for the two processes, it is suggested that CO_A-CO_B exchange and bridge-terminal hydride exchange are interdependent processes [27]:



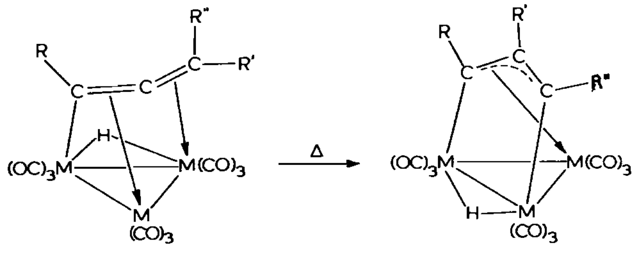
In this context we have investigated another hydride derivative, $HRu_3(CO)_9(-C{\equiv}C-Bu^t)$, obtained by oxidative addition of $HC{\equiv}CBu^t$ to $Ru_3(CO)_{12}$ [28]. Its V.T. C-13 n.m.r. spectra were reported a few years ago and it was shown that a three stage process is occurring in the CO scrambling; *i.e.* from low to high temperature: a) a localized exchange at Ru_1, b) a localized exchange at each Ru_2 and Ru_3 and c) a delocalized exchange over all the cluster.



The single resonance in the hydride region of the ^1H n.m.r. spectrum is of course unaffected over all the temperature range and no information can be extracted on the occurrence of an eventual mobility of this ligand and consequently on the relative effect of hydride motion on the CO rearrangement.

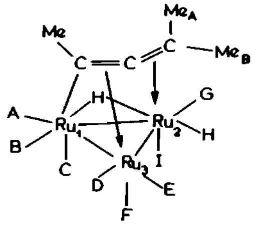
We then synthesized $DRu_3(CO)_9(-C{\equiv}C-Bu^t)$ [30] to determine if the axial–radial carbonyl exchange on Ru_2 and Ru_3 is effected on going from the hydride to the deuteride compound.

A careful comparison of the C-13 n.m.r. spectra from +26 °C to +60 °C shows that the CO exchange is distinctly slower in the deuteride compound and line-shape analysis gives an estimated value of $K_H/K_D = 2$. This observation clearly suggests that opening or at least stretching of the hydride bridge is connected with axial–radial CO exchange at Ru_2 and Ru_3. The thermal reactions of $M_3(CO)_{12}$ (M = Ru, Os) with internal alkynes or dienes occur through an oxidative addition pathway to form two isomeric compounds [31]:

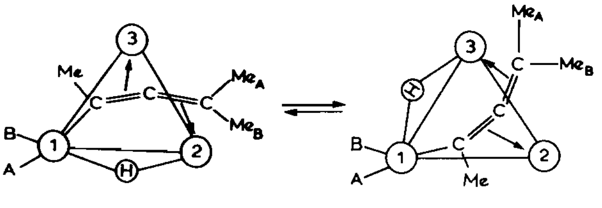


(A) (B)

The kinetically favoured isomer A contains a 1-η^1–1,2-η^2 allenyl ligand which isomerizes by heating to the more stable di-η^1–η^3 allyl isomer B, provided that R′ is a hydrogen atom. In spite of the complexity normally found in the reactions of metal carbonyl clusters with organic ligands, this tautomerization process can be envisaged as a single mechanistic step. It then seemed interesting to undertake a detailed study of the dynamic behaviour of isomer A to see if there exists a relationship between the intramolecular mobility of the ligands and the observed tautomerization process. A good candidate for this study is the allene derivative obtained in the reaction between $Ru_3(CO)_{12}$ and 4-methyl-2-pentyne [32]:

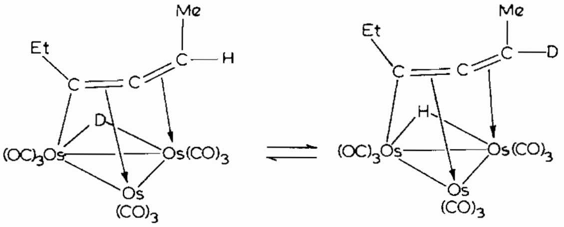


which cannot isomerize to the allyl form B. The V.T. ^1H n.m.r. spectra show that Me_A and Me_B are involved in a rearrangement process between −30 °C to +40 °C ($E_a = 56.0 + 1$ KJ/mol). On the other hand, three processes are observed in the C-13 n.m.r. spectra at variable temperature: a) below −50 °C a localized CO exchange at Ru_3 takes place; b) between +10 °C and +60 °C, a dynamic process is occurring to give a 1:6:2 absorption pattern, and c) at higher temperature the broadening of the resonances of relative intensity 1 and 2 indicates that a localized CO scrambling is occurring on Ru_1. These observations in the ^1H and ^{13}C n.m.r. spectra can be interpreted in terms of an 'edge-hopping' of the hydride from the Ru_1–Ru_2 to Ru_1–Ru_3 edge coupled with a 'wagging' motion of the allene ligand pivoting an C(2) [33]:



The analogous osmium derivative behaves similarly but the energy barriers involved with the various processes are higher as expected on going from Ru to Os compounds.

Further information on the high temperature behaviour of the allene isomer A arises from the ^1H n.m.r. spectra of $DOs_3(CO)_9[H_5C_2-C{=}C{=}C(H)-CH_3]$ [34]. We chose the osmium derivative since it is known that the thermal isomerization to the ally complex occurs only above 130 °C, allowing a sufficiently wide range of temperature before isomerization takes place. A toluene-d_8 solution of this compound was then heated at 110 °C in a sealed n.m.r. tube and the ^1H n.m.r. spectrum was recorded at 15 minutes intervals for a total period of 1.5 hours. By this ^1H n.m.r. monitoring a gradual increase of a signal in the hydride region was observed, accompanied by a decrease of the allenic hydrogen absorption. In addition a new singlet resonance appeared at the center of the methyl doublet. These results can be readily interpreted in terms of a selective hydrogen exchange between the cluster and the allenic C–H bond of the organic ligand as depicted in the following scheme:



This observation definitely rules out the possibility that the allene–allyl tautomerization occurs by simple hydrogen transfer from the terminal carbon to the central one of the unsaturated C_3 chain.

The body of these experimental results eventually supports the view of a direct relationship between intramolecular ligand mobility and the isomerization process, but this feature still needs further investigations.

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