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Fluxional behaviour of $[Ir_4(CO)_{11}H]^-$ in solution

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Abstract

The fluxional behaviour of $[Ir_4(CO)_{11}H]^-$ has been investigated by ^{13}C NMR. The fluxional mechanisms were deduced from a quantitative evaluation of the 2D-EXSY spectra, revealing two mechanisms of similar rates at 175 K. Unlike all other Ir_4 carbonyl clusters studied to date, whose fluxionalities are due only to CO site exchanges, the non-CO ligand participates in the lowest energy intramolecular process.

Introduction

Like many metal cluster compounds, $[Ir_4(CO)_{12}]$ and its substituted derivatives generally show some form of intramolecular exchange. Since, unlike the parent compound, many of these derivatives are soluble, their fluxionality can be studied using NMR techniques. Most of these clusters have a structure similar to the C_{3v} structure of $[Rh_4(CO)_{12}]$ [1], consisting of three edge-bridging ligands defining a basal plane of three iridium atoms, each having in addition two terminal ligands, and an apical iridium atom carrying three terminal ligands. The positions of the substituted ligands depend on their nature and the other ligands in the cluster. A few derivatives [2] show a structure similar to the T_d structure of $[Ir_4(CO)_{12}]$ [3] itself.

The fluxional behaviours of several monosubstituted tetranuclear iridium clusters, $[Ir_4(CO)_{11}L]$, have been studied to date ($L=PMePh_2$ [4], t-BuNC [5], SO_2 [6], Br^- [7], PEt_3 [8]) and the mechanisms involved appear to depend largely on the nature and position of the substituted ligand. One of these clusters, $[Ir_4(CO)_{11}(SO_2)]$ [6], contains a bridging ligand, SO_2, and studies of its dynamic behaviour indicated that the SO_2 ligand does not participate in the fluxionality. Since SO_2 is always found in a bridging position in metal clusters [9], it seems probable that this is because of the unavailability of the terminal bonding mode for this ligand, through which it would have to pass in order to migrate to a different position.

The metal cluster hydride $[Ir_4(CO)_{11}H]^-$ [10] has a ground state structure analogous to that of $[Ir_4(CO)_{11}(SO_2)]$ with the hydride replacing the SO_2 as the μ_2-bridging ligand [11]. However, the hydride ligand may have a terminal bonding mode accessible at moderate energy; indeed in $[Ir_4(CO)_{10}H_2]^{2-}$ the hydride ligands appear to occupy terminal positions even in the ground state [12]. Therefore, a study of $[Ir_4(CO)_{11}H]^-$ was undertaken to investigate whether the hydrogen atom is involved in any of its fluxional processes.

Experimental

$[Ir_4(CO)_{11}H]^-[P(CH_2C_6H_5)(C_6H_5)_3]^+$ was prepared according to the literature method [11] and its identity and purity checked by elemental analyses and IR and NMR spectroscopies. A sample was enriched to *c.* 40% ^{13}CO by equilibrating with ^{13}CO in CD_2Cl_2 at room temperature, then filtering. The ^{13}C NMR spectra were recorded on a Bruker WH-360 (90.55 MHz) in CD_2Cl_2 in a sealed 10 mm tube. The EXSY spectra were recorded at 175 K using TPPI [13]. No decoupling was used since the small $J(C–H)$ coupling observed for peak 1 is not a nuisance. No random variation of t_m was used since no ^{13}C scalar couplings are observed. For the quantitative analysis, two spectra were recorded. For the first (S_1), covering all the carbonyl peaks, 600 t_1 increments of 2-K transients were recorded with a spectral width of 9091 Hz and an offset of −29 634 Hz in both domains. For the second (S_2), covering carbonyl peaks 4 to 7, 512 t_1 increments of 2-K transients were recorded with a spectral width of 1701 Hz and an offset of −30 700 Hz in both domains. Before Fourier transformation, for both spectra, a squared cosine bell was applied in both domains and the FIDs were zero filled to 2-K in the F_1 domain.

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Peak integrals were obtained using the Bruker routine in DISNMR. Errors in the peak integrals were estimated by measuring integrals using the same area as for the peak but offset in the F_1 and F_2 directions, as close to the peak as was possible without overlapping any other peaks, giving values ϵ_1 and ϵ_2, respectively. The standard error (σ) in the peak integral was then taken as: $\sigma=\sqrt{(\epsilon_1^2+\epsilon_2^2)}$. The integral ($T$) of the total (square) region occupied by peaks 4 to 7 in S_1, and the integral (T') of the equivalent region in S_2, were measured. The peak integrals (I_1) measured in S_1 were then normalised to those of S_2 according to: $I_1'=I_1T'/T$. The values entered into the program D2DNMR were the averages of symmetrically equivalent cross peaks, the integrals of the diagonal peaks, and the corresponding σs. Where no peak was observed the integral was taken as zero and the σ as the smallest σ value found for the observed peaks.

NMR study

The structure of $[Ir_4(CO)_{11}H]^-$ is known from X-ray and neutron diffraction studies [11]. The arrangement of ligands is shown in Fig. 1. The carbonyl bridges are asymmetric with the longer bonds to iridium δ. There is a plane of symmetry passing through the hydrogen atom and the iridium atoms α and δ.

The ^{13}C NMR spectrum of $[Ir_4(CO)_{11}H]^-$ in CD_2Cl_2 shows a single peak at room temperature, but at 175 K the fluxional processes are sufficiently slow to distinguish all seven peaks expected from the structure. The observed δ values (relative to TMS) of these resonances are (1) 211.2, (2) 174.7, (3) 170.7, (4) 159.5, (5) 158.7, (6) 158.0 and (7) 156.9 ppm with relative intensities 2:2:1:2:2:1:1. The assignment of the signals was made using observed relations between chemical shift and carbonyl position types [14] (in ^{13}C NMR spectra of Ir_4 compounds, the δs are in the order: bridging > radial > axial ≈ apical) and the relative intensities. Peaks 1, 2 and 3 can be unambiguously assigned to carbonyls b, f and d, respectively, but 4 and 5 are either g or h and 6 and 7 are either c or e. As the temperature is raised all the peaks merge more or less simultaneously to give a single peak by about 220 K and it is not possible to distinguish any limited exchange process.

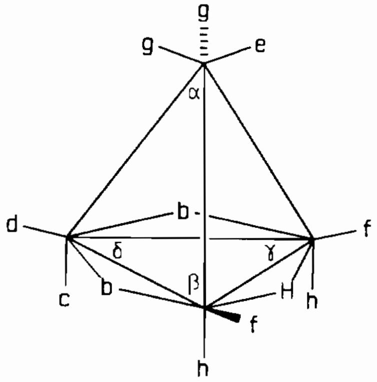

Fig. 1. Geometry of $[Ir_4(CO)_{11}H]^-$. The CO ligands are represented by the letters b to h and the iridium atoms are labelled with Greek letters (following the carbonyl labelling scheme used in earlier papers, carbonyl a is replaced by the hydrogen atom).

A 2D-EXSY spectrum at 175 K and with a mixing time of 14 ms (Fig. 2) showed the following exchanges: b with 5 and 6; f with 4 and 7; d with 5; 4 with 5 and f; 5 with 4, d and b; 6 with b and 7; 7 with f and 6. It is clear from the fact that peak 6 shows exchanges with more than one other carbonyl that, either there are at least two mechanisms operating, or second order peaks are observed. The number of exchanges observed for this peak remains two even when a mixing time as short as 2 ms is used and it is therefore impossible to separate the mechanisms by qualitative examination of the exchange spectrum. A quantitative analysis of the EXSY spectrum was undertaken in order to find the values in the exchange matrix, in the hope that these values could then be interpreted as a combination of individual mechanisms. The analysis was performed on data from EXSY spectra recorded with mixing times of 20 ms, using the program D2DNMR of Orell and co-workers [15]. The rate constants found for the observed exchanges are shown in Table 1.

Initially, it will be assumed that there are only two processes operating, on the grounds that if the exchange matrix can be adequately explained by just two processes, there will be no need to consider more. The fastest process will be termed A with rate constant k_A and the slower process B with rate constant k_B. Since some sites have a population of 1 and others a population of 2, the off-diagonal terms which may be present in the matrix will be k_A, $k_A/2$, k_B, $k_B/2$ and any sum of these. Of the two exchanges observed for peak 6 one, by definition the largest, must correspond to k_A and the other to k_B, since the population corresponding to peak 6 is one. From these values it is therefore possible to assign all the terms k_A, $k_A/2$, k_B and $k_B/2$. Of the exchanges for peak 5, two have already been assigned to $k_B/2$ and $k_A/2$, the third, since it has a value higher than either of these terms alone, must be the sum of the two. From a similar argument the exchange between peaks 4 and 2 can be assigned, and the matrix is completed by diagonal symmetrisation.

The next step is to deduce the mechanisms which are represented by this exchange matrix. In other substituted Ir_4 carbonyl clusters, two processes are generally observed; the 'merry-go-round' of the bridged and terminal COs, and the change of basal face. The intermediate of the 'merry-go-round' has now been

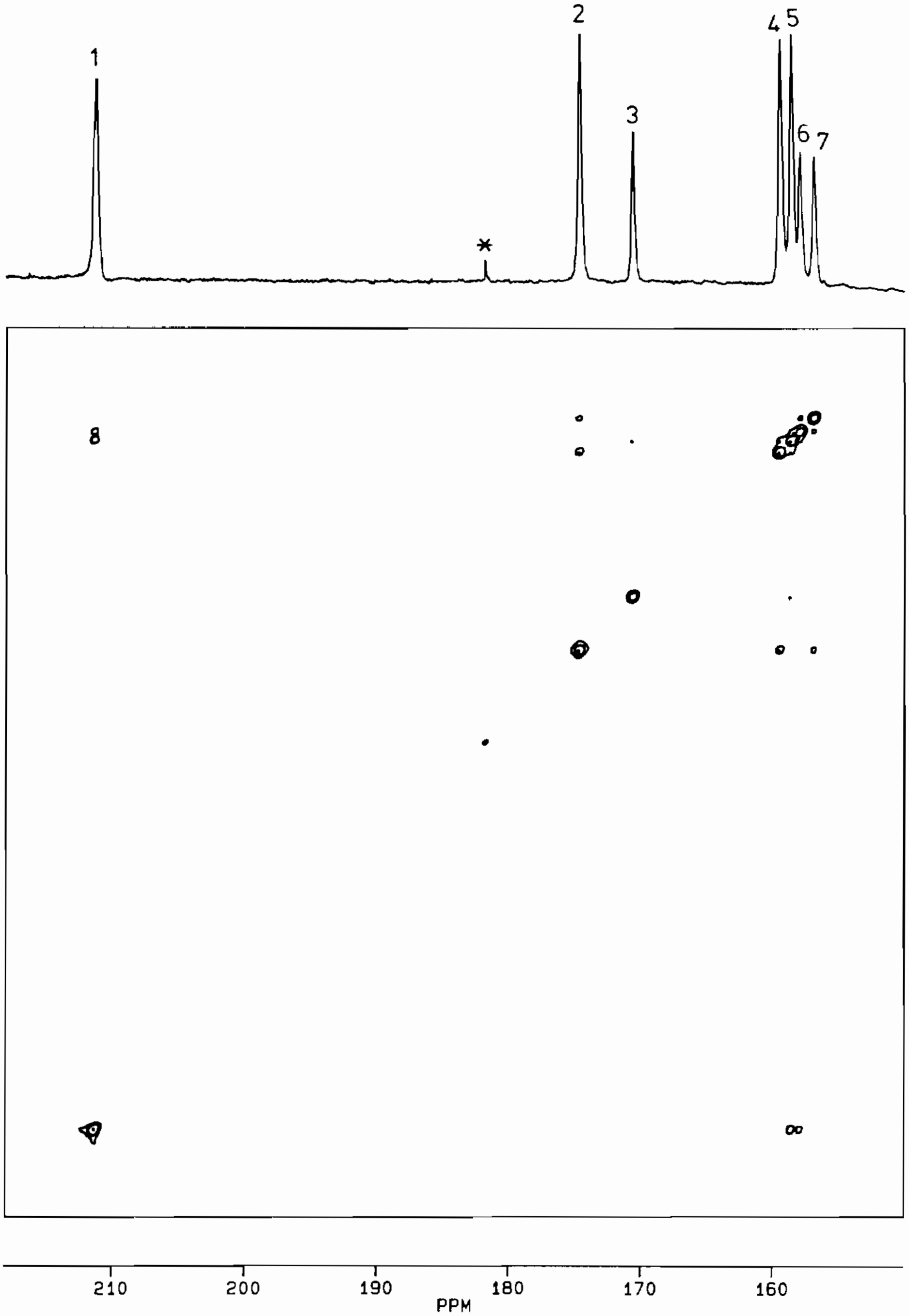

Fig. 2. 2D-^{13}C-EXSY spectrum of $[Ir_4(CO)_{11}H]^-$ in CD_2Cl_2 at 175 K with $t_m = 14$ ms (* = impurity).

experimentally determined for $[Ir_4(CO)_6(\mu\text{-}CO)_3(1,3,5\text{-trithiane})]$ [16] as being the unbridged isomer. In all cases the mechanisms are accounted for only by exchanges between bridging and terminal or between bridging and bridging carbonyls. Exchanges between terminal and terminal carbonyls have never been observed in a single step. Therefore the assumption will be made that exchange of a carbonyl from a terminal position on one iridium atom to a terminal position on another iridium atom in a single step is a high energy process which will not be observed here. The deduction of the mechanisms is complicated by the uncertain assignments of peaks 4 to 7 and it will be necessary to consider all possible combinations of assignments. It will be most convenient to consider process B first, since here peaks 6 and 7 show exchange only between each other and thus their assignments are not important.

First consider the assignment of peak 4 to carbonyl g and of peak 5 to carbonyl h. The exchange between

TABLE 1. Exchange matrix. The first line of each entry shows the value obtained from the analysis of the 2D-EXSY spectra with $t_m = 20$ ms, with the σ value in parentheses. Only those values for which statistically significant (2σ), positive values were obtained in both diagonally equivalent positions are shown. The second and third lines of each entry show, respectively, the algebraic form in terms of the rate constants k_A and k_B and the expected value, deduced from the values found for k_A and k_B

	1	2	3	4	5	6	7
1	$-k_A-k_B/2$				9.2(5) $k_A/2+k_B/2$ 8.1	6.1(4) $k_A/2$ 6.1	
2		$-k_A-k_B$		11.1(7) $k_A/2+k_B$ 10.0			5.7(6) $k_A/2$ 6.1
3			$-k_B$		3.9(5) k_B 3.9		
4		11.1(7) $k_A/2+k_B$ 10.0		$-k_A-k_B$	5.6(9) $k_A/2$ 6.1		
5	9.2(5) $k_A/2+k_B/2$ 8.1		1.9(5) $k_B/2$ 2.0	5.6(9) $k_A/2$ 6.1	$-k_A-k_B$		
6	12.2(4) k_A 12.2					$-k_A-k_B$	3.9(12) k_B 3.9
7		11.4(6) k_A 12.2				3.9(12) k_B 3.9	$-k_A-k_B$

peaks 2 and 4 would thus represent exchange of both f with both g carbonyls. However, the f carbonyls are terminal on different iridium atoms whereas the g carbonyls are terminal on the same iridium atom, implying a high energy terminal to terminal exchange. Therefore, the correct assignment is peak 4 to carbonyl h and peak 5 to carbonyl g. With this assignment there are four possible final arrangements of the ligands, but only two need be considered since the other two are simply mirror images of these. One of these arrangements is shown in Fig. 3 together with the carbonyl movements required to obtain it. The other arrangement which needs to be considered is that in which the positions of the d and apical b carbonyls are swapped. All the carbonyl movements would need to be the same as before except that of the b carbonyl bridging iridium atoms β and δ which would have to move to a position pseudo-*trans* to iridium β, with carbonyl d ending up pseudo-*trans* to iridium γ, which seems unlikely (while b is moving in a clockwise direction in the basal plane, d would need to be moving in an anticlockwise direction). Thus mechanism B is uniquely that process shown in Fig. 3 and corresponds to a mechanism previously observed in other compounds, notably $[Ir_4(CO)_{11}(SO_2)]$, and termed a synchronous face change [6].

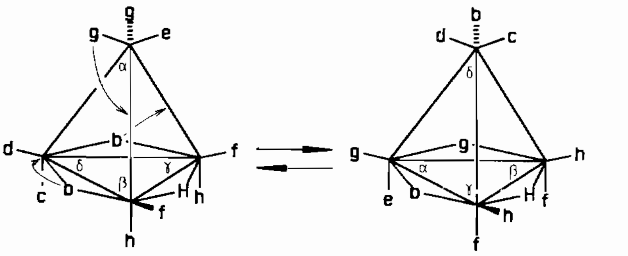

Fig. 3. Mechanism of the second lowest energy fluxional process (B) for $[Ir_4(CO)_{11}H]^-$.

The first thing to note about mechanism A is that carbonyl d does not exchange, and thus it must remain bonded to the same iridium atom. If the assignment of peak 6 to carbonyl e and peak 7 to carbonyl c is chosen then the exchange between peaks 2 and 6 represents movement of one f carbonyl to the c position. Since the c position is bonded to the same iridium as that of carbonyl d, this would require a terminal to terminal exchange and is thus excluded. Therefore, the correct assignment is peak 6 to carbonyl c and peak 7 to carbonyl e.

There are 16 possible arrangements of the final state of the cluster. Figure 4 represents 8 of these arrangements, the other 8 being simply mirror images of these. Fortunately, it is possible to show that some of these arrangements are unattainable. Firstly, consider that carbonyl position 1 in Fig. 4 is occupied by an f carbonyl.

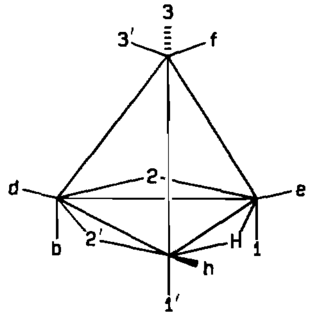

Fig. 4. Final geometry for process A with numbers in the positions of uncertain carbonyl assignments (1, 1′ = f or g; 2, 2′ = g or c; 3, 3′ = b or h).

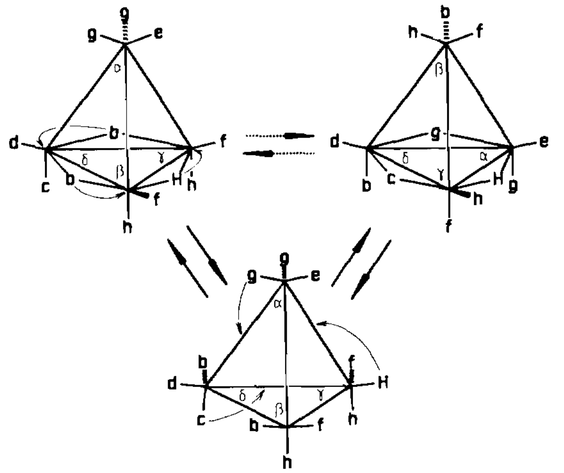

Fig. 5. Mechanism of the lowest energy fluxional process (A) for $[Ir_4(CO)_{11}H]^-$.

This is impossible since it requires the f and e carbonyls to be terminal on the same iridium atom and thus a terminal to terminal exchange to have occurred. Therefore position 1 must be occupied by a g carbonyl and 1′ by an f carbonyl. Now it can be seen that position 2 must be occupied by the other g carbonyl since the g carbonyls start terminal on the same iridium atom so must remain bonded to a common iridium atom in the final state. This leaves position 2′ occupied by the carbonyl c. It is not possible at this stage to determine the precise assignment for the 3 and 3′ positions.

The arrangement with carbonyl b assigned to position 3 and carbonyl h to position 3′ is shown in Fig. 5 together with the carbonyl movements required to obtain it. The exchange between bridged and axial positions represented by the exchange between carbonyls b and c seems improbable in a single step process, but can be achieved by passing through an unbridged intermediate as shown. This process has been observed in other tetrahedral metal clusters where it has also been presumed to pass through an unbridged intermediate [4, 17]. If the positions of b and h in the final state are now swapped, the b carbonyl bridging iridium atoms β and δ would have to move into a position pseudo-*trans* to iridium α, with the h carbonyl on iridium β ending up in a position pseudo-*trans* to iridium γ, which seems unlikely (as before, this would require movement of neighbouring COs in opposing directions). Thus mechanism A is uniquely that process shown in Fig. 5.

Discussion

The lowest energy fluxional process (mechanism A) for $[Ir_4(CO)_{11}H]^-$ is an opening of all bridging ligands to give an unbridged intermediate, followed by reformation of the bridges about the face defined by the iridium atoms α, γ and δ. The intermediate in this process has the same structure as that which is assumed to be the intermediate in the 'merry-go-round' process [18], and the final configuration is reached by continuing the movement of the carbonyls in the same direction as the bridge opening and reforming bridges about the same face. In $[Ir_4(CO)_{11}H]^-$ a 'merry-go-round' process would lead to a structure with three bridging carbonyls and a terminal hydride, which is not that of the ground state. The process would need to be repeated to reform the ground state structure and exchanges between carbonyls g and e and also between carbonyls h and c would be expected in the EXSY spectrum. Such exchanges are not observed in this compound. Rebridging of the unbridged intermediate about the face defined by the iridium atoms α, β and γ would also lead to a structure with a terminal hydride and is not observed. Mechanism A is notable since it is the first time that the substituted ligand has been seen to participate in the fluxional process of an Ir_4 cluster, presumably because the hydrogen atom has, like CO, several possible bonding modes.

The next lowest energy process is a synchronous face change (mechanism B), which is the same as the lowest energy process in $[Ir_4(CO)_{11}(SO_2)]$. That this process is no longer that of lowest energy is probably a simple consequence of the interposition of the new process, A, at a slightly lower energy.

Although both the processes found for $[Ir_4(CO)_{11}H]^-$ have previously been observed separately in other clusters as CO site exchanges, this is the first time that both processes have been observed together in the same cluster. For $[Ir_4(CO)_{10}(COD)]$, where all the bridging carbonyls are symmetric, only process A has been identified [17]. For certain other clusters, a ligand attached to one iridium atom shortens the bridging bonds to that atom. In these clusters only process B has been identified, and it has been suggested that process A is blocked because the necessity of breaking a short Ir–CO bridging bond would prevent the formation of the unbridged intermediate [7, 8, 17]. Process B does not require a short Ir–CO bridging bond to be broken. It is interesting to note that process A occurs in $[Ir_4(CO)_{11}H]^-$ despite the presence of asymmetric bridges. However, here, the structure is slightly different from those of the previously mentioned clusters since the two short bridging bonds are to different iridium atoms rather than to the same iridium atom [19]. In this case both processes require a short Ir–CO bridging bond to be broken.

Quantitative analysis of 2D-EXSY spectra has previously been used to find rate constants for mechanisms already determined [20] or to distinguish between proposed mechanisms [15, 21]. In this work, however, the mechanisms have been deduced from the spectral data, where such a determination was not possible by simple qualitative analysis of the spectrum. It is probable that this technique could be applied to other compounds where the presence of two or more mechanisms of similar energy complicates the analysis of their dynamic behaviour.

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