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Solution Structures and Dynamics of $Co_4(CO)_{12}$ and $HFeCo_3(CO)_{12-x}L_x$ (x = 0–3; L = group V Ligand)

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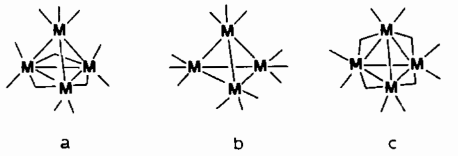
Variable temperature ^{13}C-n.m.r. spectra of $Co_4(CO)_{12}$ in viscous solution show that its solid state structure is maintained in solution and that total scrambling of the COs occurs. Variable temperature ^{13}C-n.m.r. spectra of $HFeCo_3(CO)_{12}$, isostructural with $Co_4(CO)_{12}$, show that this molecule is stereochemically non rigid only in the Co_3 unit. In the derivatives in which one or more COs are substituted with a group V ligand the cobalt bonded carbonyls are rigid. The substitution occurs by stepwise replacement of one carbonyl group on each of the cobalt atoms.

Introduction

The solution structure and the dynamics of metal carbonyls have been widely investigated [1], since Cotton first suggested that intramolecular carbonyl exchange can be a facile process [2], and applied this idea to rationalize the apparent discrepancy between the solid state structure of $Co_4(CO)_{12}$ (a; M = Co) [3] and the solution structure proposed at that time for it on the ir. evidence (c) [4]. The sequence a → b → c was proposed as a facile path for the structural change [2]. Variable temperature ^{13}C-n.m.r. spectra have shown that $Rh_4(CO)_{12}$ (a; M = Rh) is stereochemically non rigid and a repeated sequence a → b has been proposed to account for its dynamic behaviour [5]. Similarly carbonyl scrambling, occurring in two or more steps, has been observed for other tetranuclear carbonyl clusters of the cobalt group, *i.e.*, $RhCo_3(CO)_{12}$ [6] and $Ir_4(CO)_{11}PPh_2Me$ [7]. The ^{13}C-n.m.r. data obtained for $Co_4(CO)_{12}$ [8, 9] are contradictory with the complete analysis of the infrared spectrum [10] and ^{59}Co-n.m.r. results [9, 11, 12].

We have reinvestigated the ^{13}C-n.m.r. spectra of $Co_4(CO)_{12}$ and obtained variable temperature ^{13}C-n.m.r. spectra for $HFeCo_3(CO)_{12}$, isoelectronic with $Co_4(CO)_{12}$, and for some derivatives of it in which a group V ligand substitutes several carbonyls.



Results and Discussion

$Co_4(CO)_{12}$

The disagreement in the elucidation of the solution structure of $Co_4(CO)_{12}$ between the i.r. and ^{59}Co-n.m.r. results, and the ^{13}C-n.m.r. data has been recently discussed [1]. The i.r. [10] and ^{59}Co-n.m.r. [9, 11, 12] data are in favour of the maintainment in solution of the solid state structure (a) [3, 13, 14], whereas the ^{13}C-n.m.r. results so far reported [1, 8, 9] are consistent with structure (c). Three resonances of equal intensity, one in the region of the bridging carbonyls and two in the region of the terminal ones, have been observed in the low temperature limiting spectrum (–95 °C [9]) and it was suggested that the quadrupole moments of the cobalt atoms could be responsible for the anomalous intensity ratio [8]. These resonances have been observed to broaden upon raising the temperature, but the moderately rapid quadrupole induced relaxation of the Co prevented the observation of any signal above 10 °C. The comparison with variable temperature ^{13}C-n.m.r. spectra of other cobalt carbonyls allowed the authors to state that a non negligible contribution to the broadening of the CO resonances was given by fast carbonyl exchange [8]. We have tried to get more insight in the problem both by recording ^{13}C-n.m.r. spectra of $Co_4(CO)_{12}$ at higher magnetic field and at lower temperature than previously reported, and by obtaining spectra of a sample of $Co_4(CO)_{12}$ dissolved in a viscous medium. If $Co_4(CO)_{12}$ maintains structure (a) in solution, four resonances of equal intensity are expected at low temperature as found for $Rh_4(CO)_{12}$ [5]. Reasons accounting for one missing resonance in the 25.15 MHz spectrum can be either casual superposition of two resonances or insufficient signal to noise ratio to observe a broad resonance. Additionally localysed carbonyl exchange

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TABLE. ^{13}C Chemical Shifts of the Carbonyls in $HFeCo_3(CO)_{12}$ and Its Derivatives.[a]

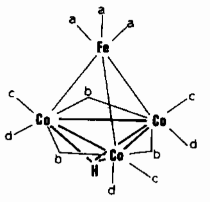
$HFeCo_3(CO)_{12}$(I)	CO_a 210.2(1), $CO_{b,c,d}$ 203.1(2)
$HFeCo_3(CO)_{11}P(C_6H_5)_3$(II)	CO_a 208.2(1)^b, CO_b 210.8(2), CO_c 238.4(2), CO_d 234.8(1), $CO_{f,g}$ 203.5(3), Co_e 191.0(2)
$HFeCo_3(CO)_{10}[P(C_6H_5)_3]_2$(III)	CO_a 210.9(2)^c, CO_b 211.8(1), CO_c 245.2(1), CO_d 243.1(2), $CO_{f,g}$ 207.8(3), CO_e 195.0(1)
$HFeCo_3(CO)_{10}[P(OC_6H_5)_3]_2$(IIIa)	CO_a 209.9(2)^d, CO_b 211.1(1), $CO_{c,d}$ 237.0(3), $CO_{f,g}$ 202.8(3) CO_e 190.9(1)
$HFeCo_3(CO)_9[P(OC_6H_5)_3]_3$(IV)	CO_a 211.0(3)^e, CO_b 240.0(3), CO_c 203.9(3)

[a] Relative intensity in parenthesis. [b] $^3J_{C-P}$ 9.5. [c] $^3J_{C-P}$ 9.8. [d] $^3J_{C-P}$ 17.0. [e] $^3J_{C-P}$ 14.3.

still fast on the n.m.r. time scale of the terminal carbonyls bonded to the basal Co_3 unit, can account for the observation of three resonances only in the 30°–−95 °C interval. It was then hoping to get some clues for one of these reasons that we have obtained spectra of a ^{13}CO enriched sample of $Co_4(CO)_{12}$ at 90.54 MHz in the −70°– −130 °C interval. However the spectra showed the same features as those obtained at lower magnetic field and at higher temperature. We have previously shown that the broadening of the resonances of carbon nuclei bonded to metals with $I > 1/2$ can be limited by using viscous solutions [15]. Actually one broad peak ($\nu_{1/2}$ ca. 70 Hz) has been observed at +61 °C for a ^{13}CO enriched sample of $Co_4(CO)_{12}$ in a 1:4 v/v mixture of $CDCl_3$ and Nujol at 206.1 ppm downfield from TMS. The position of this peak is in good accord with the weighted average of the peaks observed in the −32 °C spectrum of $Co_4(CO)_{12}$ in a 1:3 v/v mixture of $CDCl_3$ and Nujol (242.6, 195.6 and 192.5 ppm) if the actual populations are assumed to be from low to high field in the ratio 1:1:2 (205.8 ppm), or 1:2:1 (206.6). If the populations are assumed equal to the observed intensities the weighted average peak should be at 210.2 ppm. Thus these results confirm that fast carbonyl exchange takes place in $Co_4(CO)_{12}$ and prove that the complete dynamic ^{13}C-n.m.r. results are in agreement with other spectroscopic results in the determination of the solution structure of $Co_4(CO)_{12}$. However, the reasons for which the intensity ratio does not correspond to the population ratio is still undetermined.

$HFeCo_3(CO)_{12-x}L_x$ (x = 0–3; L = group V ligand)

The ^{13}C chemical shifts of the carbonyls for the lowest temperature spectrum obtained for each complex are reported in the Table. The labelling of the CO is referred to the drawings which represent $HFeCo_3(CO)_{12}$ and its monodentate mono-, bi-, and trisubstituted derivatives.



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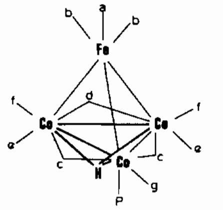

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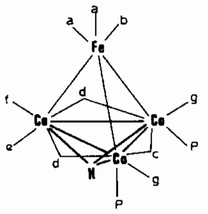

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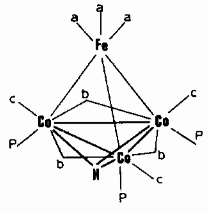

IV

Spectroscopic data [10, 16] have suggested that the mixed metal cluster $HFeCo_3(CO)_{12}$, isoelectronic with $Co_4(CO)_{12}$, has a structure similar to that of $Co_4(CO)_{12}$. The solid state structure has been determined for the trisubstituted derivative $HFeCo_3(CO)_9[P(OCH_3)_3]_3$: the $Fe(CO)_3$ unit is triply bridging the basal Co_3 plane in which three ligands (CO) are in a bridging position and six ligands (3 CO, 3 phosphite) are in a terminal one [17]. The hydride is capping the Co_3 face outside of the tetrahedral cluster as confirmed by a recent neutron diffraction study [18]. According to the above features four resonances are expected in the ^{13}C spectrum of $HFeCo_3(CO)_{12}$ (I) corresponding to the frozen structure. However in the lowest temperature spectrum obtained (−89 °C) for a ^{13}CO enriched sample only two resonances have been observed in the approximate ratio 1:2, the upfield one being broader ($\nu_{1/2}$ 3 and 8 Hz respectively). Upon raising the temperature up to 26 °C the upfield signal broadens markedly whereas the lowfield one remains sharp. The upfield signal is assigned to the COs bound to the cobalt atoms on the basis of the upfield shifts observed for the cobalt bonded carbonyls compared with the shifts of the

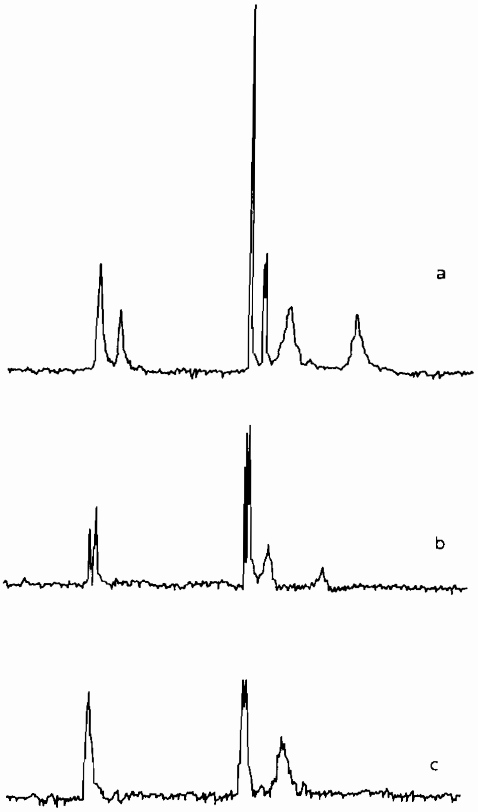

Figure 1. ^{13}C-n.m.r. spectra in the carbonyl region of $HFeCo_3(CO)_{11}P(C_6H_5)_3$ (II) at −85 °C (a), of $HFeCo_3(CO)_{10}[P(C_6H_5)_3]_2$ (III) at −87 °C (b), and of $HFeCo_3(CO)_9[P(OC_6H_5)_3]_3$ (IV) at −82 °C (c).

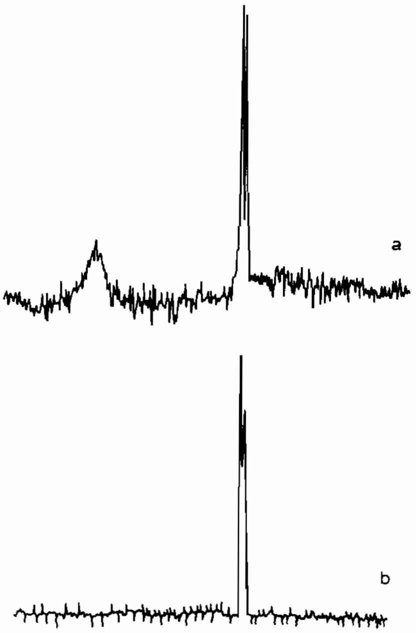

Figure 2. ^{13}C-n.m.r. spectra of the carbonyl region of $HFeCo_3(CO)_9[P(OC_6H_5)_3]_3$ (IV) at room temperature: 1:3 v/v $CDCl_3$: Nujol (a), $CDCl_3$ (b).

iron bonded carbonyls in $FeCo_2(CO)_9S$ [19], of the intensity ratio and of the expected broadening of the resonances of carbon nuclei bonded to nuclei having a quadrupolar moment [15, 19]. Thus the dynamic behaviour of I differs from that of $Co_4(CO)_{12}$ in that the carbonyls bonded to the triply bridging $Fe(CO)_3$ unit are not engaged in delocalised scrambling and in that the delocalised exchange of the bridging and terminal carbonyls in the basal Co_3 moiety is a lower energy process. A comparison of the anomalies in the intensity ratio of the CO resonances in I and in $Co_4(CO)_{12}$ suggests that these are to be associated in both cases with one of the two sets of terminal carbonyls in the basal Co_3 unit.

The resonances of the carbonyls observed in the ^{13}C-n.m.r. spectra at low temperature of the ^{13}CO enriched derivatives of I in which one or more carbonyls are substituted by a group V ligand indicate that upon substitution the structure of I is maintained. The limiting spectra for the monosubstituted case L = $P(C_6H_5)_3$, the disubstituted case L = $P(C_6H_5)_3$ and the trisubstituted one L = $P(OC_6H_5)_3$ are shown in Fig. 1. Contrary to the findings for $Co_4(CO)_{12}$ and the parent cluster, in each case the integrated intensities are in good accord with the total number of the carbonyls. The thermal decoupling of the resonances of the cobalt bonded carbonyls is not complete: this favours in II, III and IIIa superposition of two of the signals of the terminal COs and in IIIa superposition of the signals of the bridging carbonyls as well. Additionally this hinders the observation of the coupling constants of these carbonyls with the hydride and the phosphorus atoms. On the other hand, three bonds carbon phosphorus coupling constants are observed in each case for the iron bonded carbonyls but only when the ligands are *trans* to each other; $^3J_{C-P}$ is greater when the ligand is phosphite.

The data show that the successive substitution of the COs by phosphine or phosphite takes place by stepwise replacement of one carbonyl group on each of the cobalt atoms confirming earlier suggestions based on Mössbauer data [20], and that the substituents occupy in each derivative the same stereochemical environment. The assignment of this position as the axial one is based on the ^{13}C and ^{31}P observations reported for the complexes $Ir_4(CO)_{12-x}(PPh_2Me)_x$ (x = 1–4) [7] and on the X-ray analysis of $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ [17]. Both the chemical shifts of the set of COs bonded to the cobalt atoms and, to a lesser extent, of those of the set of COs bonded to the iron atom are at progressively low field on increasing the basicity and the number of substituents, in agreement with previous observations [7, 19]. Upon raising the temperature all the resonances of the cobalt bound carbonyls broaden severely and in the room temperature spectra they disappear in the base line, whereas the other resonances remain sharp. To remove the ambiguity between the broadening of the resonances due to chemical exchange and that due to progressively inefficient cobalt relaxation, the ^{13}C spectra of each sample have been also recorded at room temperature in a 1:3 v/v $CDCl_3$: Nujol solution. In Fig. 2 are reported, as an example, the room temperature spectra of IV in $CDCl_3$ and in viscous solution. In IV as in the other cases the resonances of the terminal carbonyls are not observable whereas a broad peak is observed in the region of the bridging COs. We cannot exclude that a non negligible contribution to the broadening of this peak comes from an exchange process, incipient at this temperature, in which the bridging carbonyls are involved but, even if it is so, this process takes place at a temperature well above that at which broadening of the resonances is observed in the non viscous solution. Thus the effect of the substituents is to increase largerly the energy barrier of the delocalised scrambling of the COs observed in the unsubstituted complex I. We feel that the disappearance in the base line of the resonances of the terminal COs, even in the viscous solution, is more likely to be explained on the basis of the larger values expected for the J of Co with the terminal carbonyls than those with the bridging carbonyls, rather than on the basis of localized carbonyl scrambling, which could occur for CO_e and CO_f in II, III and IIIa. Following the original proposal of Cotton [2, 21] and the evidence obtained in the study of the stereochemical non rigidity of metal carbonyls [1], it is commonly accepted that carbonyl delocalised scrambling in metal clusters is accomplished by successive fast interconversion between bridged and unbridged forms. The nature of these intermediates depends on the ground state of the molecule examined, *i.e.*, if the ground state is represented by the bridged form, the transition state, whose energy determines the energy of activation of the process, is unbridged and *viceversa* (Fig. 3). The substitution of a CO with a group V ligand is known to facilitate the formation of bridging carbonyls as a consequence of the increased charge on the cluster [7, 22, 23]. When the substitution takes place in a system with bridging carbonyls we can then expect that these are stabilized. The effect is proportional to the number of substituted COs. Thus the stereochemical rigidity of the COs of the Co_3 unit in the derivatives II–IV compared with the mobility of those of I can be explained on the basis of the increase of activation energy for the carbonyl exchange performed by the bridged–unbridged sequence as a consequence of the decrease of energy of the ground state. The lower energy barrier observed for the delocalised scrambling of COs in $Os_3(CO)_{10}(PEt_3)_2$ than in $Os_3(CO)_{11}(PEt_3)$ [24] is consistent with this scheme, being an example of the effect of the substitution of COs with phosphines when the ground state is an unbridged form.

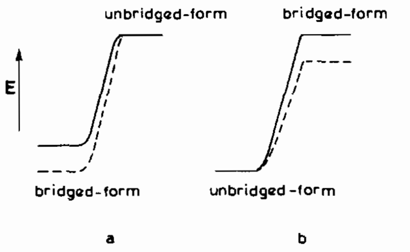

Figure 3. Qualitative potential energy diagram for the interconversion of bridged and unbridged forms of metal clusters. The dotted line shows the effect of the substitution of CO with group V ligand on the energy of the ground state (a) and on the energy of the transition state (b).

Experimental

$Co_4(CO)_{12}$ [25], $HFeCo_3(CO)_{12}$ [26] and $HFeCo_3(CO)_{12-x}L_x$ (x = 1 – 3; L = group V ligand) [20] have been prepared by the methods described in the literature. $Co_4(CO)_{12}$ and $HFeCo_3(CO)_{12}$ have been enriched by stirring for some days in a sealed ampoule at room temperature in the presence of <1 atmosphere of 90% enriched ^{13}CO (Stohler Isotope Chemicals).

^{13}C-n.m.r. spectra were recorded on a Jeol–PFT-100 and on a Bruker-HW-360 spectrometer operating respectively at 25.1 MHz and at 90.5 MHz in the Fourier transform mode. The chemical shifts are downfield positive with respect to internal tetramethylsilane. Accumulations of 500–5,000 transients were made at a spectral width of 1,000 or 5,000 Hz. Solutions were sealed *in vacuo* in 10 mm tubes together with $SiMe_4$ as an internal standard. The solvents were $CDCl_3$, $CDCl_3/CD_2Cl_2$ and CF_2Cl_2/CD_2Cl_2. Deuterated solvents were purchased from NMR Ltd, and used immediately after drying over molecular sieves.

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