97. Intramolecular Dynamics of Tetranuclear Iridium Carbonyl Cluster Compounds

Part 1

Bromotri-μ-carbonyloctacarbonyltetrairidate(1−)

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A 2D and variable-temperature ^{13}C-NMR study indicates that a CO-site exchange occurs in the title complex *via* several consecutive processes, the first being a 'merry-go-round' of the basal CO's, the second a switch of basal face not involving unbridged intermediates.

Introduction. – There is considerable interest in the chemistry of metal-carbonyl cluster compounds [1]. Due to their relative inertness, the tetranuclear carbonyl-cluster complexes of Ir are good candidates for studying the stereochemical arrangement of ligands around the metal core [2], the kinetics of CO-substitution reactions [3], and the fluxional processes in solution [4–8]. Unlike the inert insoluble $Ir_4(CO)_{12}$, its substituted derivatives bear CO ligands on different positions of the metal core. The recent synthesis of the reactive anion $[Ir_4(CO)_{11}Br]^-$ [9] has led to the preparation of many substituted tetranuclear carbonyl complexes [10][11] under mild conditions and in better yields than in the original studies [12]. We have, therefore, undertaken a systematic study of CO site exchange in mono- to tetrasubstituted carbonyl-cluster complexes of Ir by 2D and variable-temperature ^{13}C- and ^{31}P-NMR.

Several monosubstituted $Ir_4(CO)_{11}L$ complexes have previously been examined (L = PEt_3 [7], $PMePh_2$ [5], *t*-BuNC [4], and μ_2-SO_2 [8]), although 2D-NMR studies have not yet been reported. The CO ligands either bridge two Ir-atoms or are terminal. The three bridging CO's define the basal plane containing three Ir-atoms of the tetrahedral metal core. Terminal CO's are either apical if located on the fourth Ir-atom, radial when located more or less in the basal plane, or axial if approximately perpendicular to this basal plane.

Two isomers are known for $Ir_4(CO)_{11}(PR_3)$ with the phosphine ligand either in a radial or an axial positon. *Mann et al.* [7] have shown by DANTE experiments that for the axial isomer of $Ir_4(CO)_{11}(PEt_3)$, the site exchange process with the lowest activation energy is the 'merry-go-round' [13] of the basal CO's [7]. A higher-activation-energy process is the exchange of apical with basal CO's. The mechanism of the latter process is not clear, nor is the effect of the nature, number, and location of the non-CO ligand(s) on the feasibility of various site-exchange processes in these cluster compounds.

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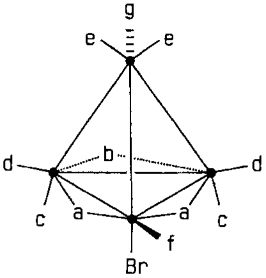
We present here a study of the fluxional behaviour of the anionic cluster compound $[Ir_4(CO)_{11}Br]^-$.

NMR Study of $NEt_4[Ir_4(CO)_{11}Br]$. – The structure of $[Ir_4(CO)_{11}Br]^-$ is known from an X-ray analysis [14]: the Br-atom is located on a basal Ir-atom and is axial. There are three bridging CO ligands; two bridges are asymmetric, since the CO ligands form shorter bonds with the Ir-atom bearing the bromide. Three CO's are radial, two axial and three apical.



In the ^{13}C-NMR spectrum of a ^{13}C enriched sample of $[Ir_4(CO)_{11}Br]^-$ in $(D_8)THF/CHFCl_2$ 4:1, all exchange processes are stopped at *ca.* −113°. At this temperature, 7 CO resonances are observed at δ (relative to TMS) 214.0 (a), 201.8 (b), 178.0 (f), 176.5 (d), 158.9, 156.9 (c,e), and 156.4 (g) ppm with relative intensities 2:1:1:2:2:2:1. The assignment of the signals follows the general observation that, in ^1H-, ^{13}C-, and ^{31}P-NMR of Ir_4 cluster compounds, the δ's of the ligands decrease in the positional sequence bridging > radial > axial ≈ apical [10], and by comparison with the ^{13}C-NMR spectrum of the axial isomer of $Ir_4(CO)_{11}(PEt_3)$ [7]. The signals at 158.9 and 156.9 ppm are due to the 4 CO's c and e, but fortunately a more precise assignment is of no importance for the discussion of the fluxionality of the complex.

As the temperature is raised from 160 K to 230 K, all the signals broaden, except g which remains sharp *(Fig. 1)*. We can distinguish the following two processes: *1)* a, b, d,

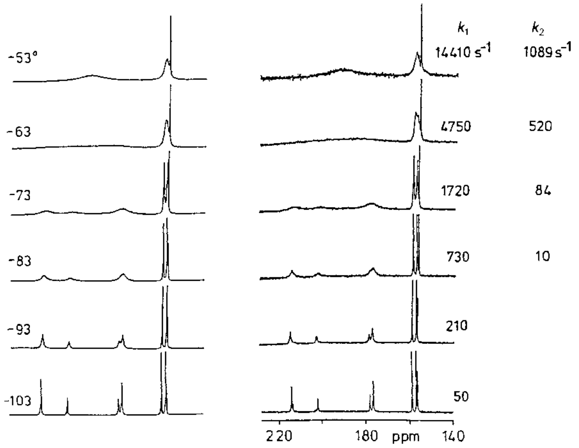


Fig. 1. *Variable-temperature ^{13}C-NMR spectra of $[Ir_4(CO)_{11}Br]^{-1}$ in $THF/CHFCl_2$ 4:1*

and f begin to exchange above 170 K; *2)* c and e begin to exchange above 190 K. The a–d–b–f site exchange is consistent with the 'merry-go-round' process of the basal CO's. This process has the lowest activation energy. We have undertaken a 2D-^{13}C-NMR study to determine the exact exchange mechanism of c and e.

The 2D-^{13}C-NMR spectra of $[Ir_4(CO)_{11}Br]^-$ were recorded at 175 K in (D_6)acetone *(Fig. 2)*. The a–d–b–f site exchange is clearly visible. The second fluxional process is also apparent, when a mixing time of 50 ms is used. This process corresponds to a site exchange d–c–e, while a, b, and f do *not* exchange with c or e. Since two apical CO's (e) now participate in the exchange, this second process must involve CO ligands bridging to alternative faces of the Ir_4 tetrahedron. Above *ca.* 230 K, further averaging of the CO's occur, but the highest energy mechanism(s) cannot be elucidated, since NOESY experiments are not conclusive at such temperatures or at lower temperatures using mixing times larger than 50 ms.

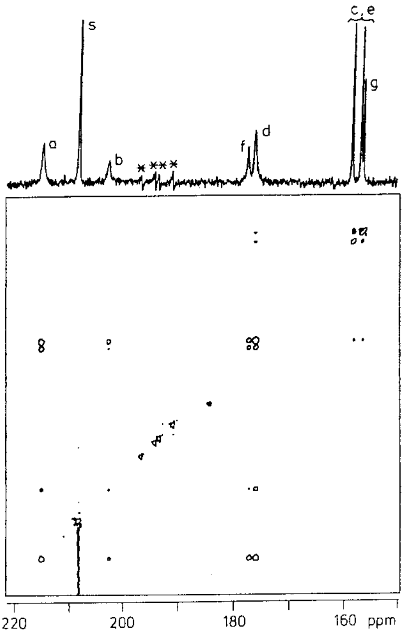
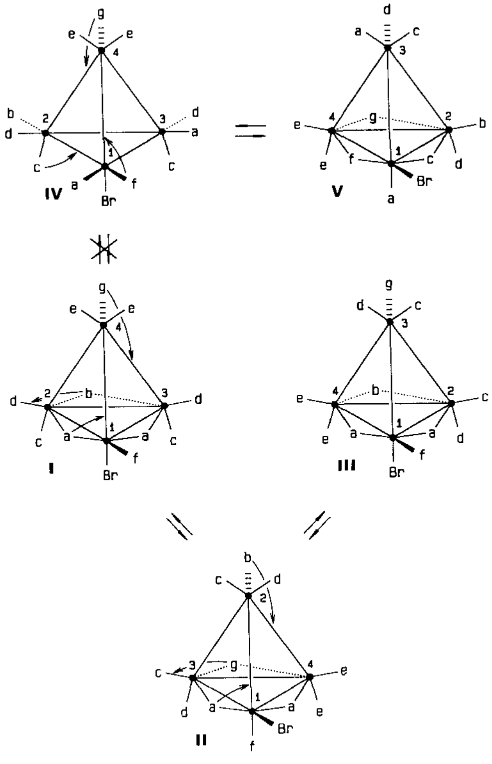


Fig. 2. *2D-^{13}C-NMR spectrum of $[Ir_4(CO)_{11}Br]^-$ in (D_6)acetone at 175 K* (mixing time: 50 ms; s = solvent; * = reflected signals)

The rate constants k_1 and k_2 of the first two processes were evaluated from line-shape analysis [15] of the variable temperature ^{13}C-NMR spectra using the following *Kubo-Sack* matrix elements: (a,a) = (b,b) = (f,f) = $-k_1$; (a,d) = (a,f) = (d,a) = (d,b) = $k_1/2$; (b,d) = (f,a) = k_1; (c,c) = (e,e) = $-k_2$; (c,d) = (c,e) = (d,c) = (d,e) = (e,c) = (e,d) = $k_2/2$; (d,d) = $-k_1 - k_2$. The general element is (i,j) = k/p where i = initial site, j = accessible site by single step exchange, k = rate constant, and $1/p$ = probability for i to reach site j [16].

The 'merry-go-round' has a $\Delta G^{\neq}_{298}$ of 37.0 ± 0.6 kJ · mol^{-1}. The second process has the same $\Delta G^{\neq}_{298}$ within an experimental error of 4 kJ · mol^{-1}. For the latter process, the simplest mechanism, consistent with the site-exchange sequence observed in 2D-NMR and *with*

Scheme



the 18-electrons rule, starts with synchronous edge-bridging of 2 CO's on one of the two triangular faces of configuration **I** which share the Ir_1–Ir_4 edge *(Scheme)*. This lead to the radial isomer **II** from which a second synchronous bridging of 2 CO's brings about the observed d–c–e exchange (configuration **III**) and leaves the unique apical CO (g) in its pseudo-*trans*-position relative to the Br ligand. This mechanism is quite similar to that of the first dynamic process observed in $Ir_4(CO)_{11}(\mu_2\text{-}SO_2)$ [8], but is at variance with that proposed by *Mann et al.* for the axial isomer of $Ir_4(CO)_{11}(PEt_3)$ [7]. The latter was proposed to go through two unbridged isomers, although 2D experiments were not performed to support this hypothesis. However, if an unbridged intermediate (configuration **IV**) is considered, a site exchange of a and f (configuration **V**) becomes inevitable, and is, therefore, not consistent with our observations in the present case.

In conclusion, the monosubstituted complex $[Ir_4(CO)_{11}Br]^-$ is fluxional on the NMR time scale, and the site exchange process with lowest activation energy are: *1)* a 'merry-go-round' of the basal CO's. Since the solid state structure shows that two CO's form asymmetrical bridges with shorter bonds to the same Ir-atom, this site exchange may not pass through an unbridged intermediate, as generally assumed [7][13]. This point will be discussed in a subsequent article; *2)* an edge-bridging of CO's on an alternative face of the tetrahedron containing the apical Ir-atom and the basal Ir-atom bearing the non-CO ligand. This process does not pass through unbridged intermediates.

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Experimental. – $NEt_4[Ir_4(CO)_{11}Br]$ was prepared from $Ir_4(CO)_{12}$ according to the procedure in [9]. The compound gave satisfactory elemental analyses. IR (THF; 298 K): ν(CO) 2079*w*, 2047 *vs*, 2039 *vs*, 2006 *vs*, 1889*w*, 1841*s*, 1829 (sh) [17]. It was enriched to *ca.* 30% ^{13}C by equilibrating the bromide with ^{13}CO (*I.C.N.*, Innerberg) in THF, filtering the dodecacarbonyl, and repeating the cycle. The ^{13}C-NMR spectra were recorded on a *Bruker WH-360* (90.55 MHz) in $(D_8)THF/CHFCl_2$ under normal atmosphere. The 2D-^{13}C-NMR spectra were obtained in (D_6)acetone at 175 K from NOESY experiments using TPPI [18]. 256 t_1 increments with 2-K transients were acquiered. The spectral width was 6493.5 Hz in the F_2 domain and 3246.8 Hz in the F_1 domain. The spectra were zero-filled to 2 K × 2 K and a shifted, squared sinus bell was applied in both domains prior to *Fourier* transformation.

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