The Mechanisms of Fluxionality of $[Ir_4(CO)_{11}(PEt_3)]$; A Reappraisal of the Mechanism of Carbonyl Fluxionality on Clusters

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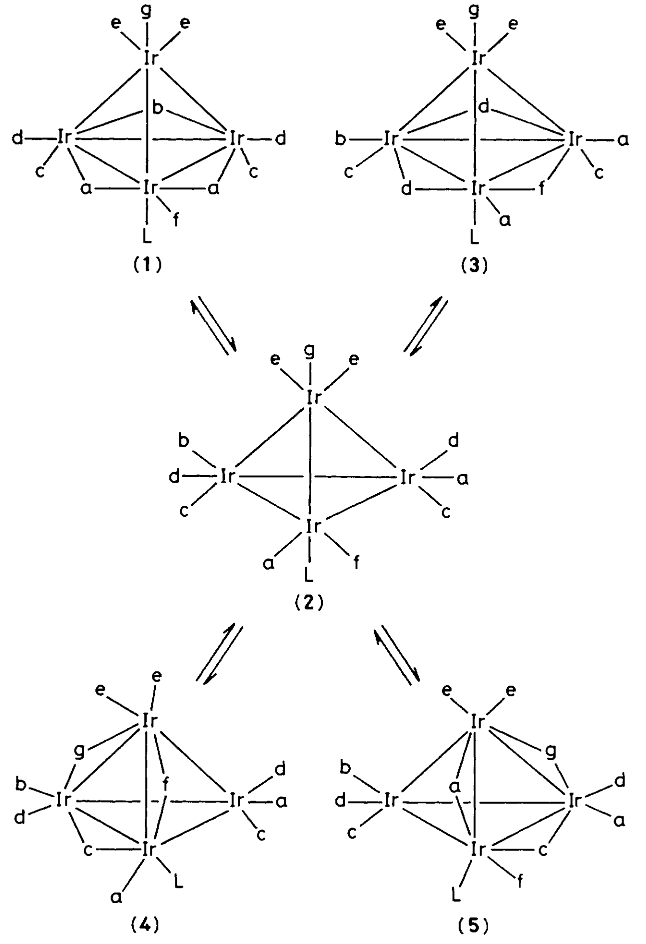
Contrary to previous reports, it is shown that the mechanism of fluxionality of $[Ir_4(CO)_{11}(PEt_3)]$ involves intermediates retaining bridging carbonyls, rather than a species containing only terminal carbonyl groups or an icosahedral–cubo-octahedral rearrangement. Two dynamic processes were identified.

There are two major theories of the mechanism of carbonyl scrambling on clusters. The first proposal was made by Cotton in 1966,[1] and involves concerted bridge opening and closing of the carbonyl ligands to move them around the cluster. Subsequently, this treatment was applied to $[Ir_4(CO)_{11}(PMePh_2)]$, (**1**; L = $PMePh_2$), by Stuntz and Shapley.[2] The mechanism, when applied to compound (**1**) involves bridge opening to give (**2**; L = $PMePh_2$), followed by bridge closing to give (**3**), (**4**), or (**5**), L = $PMePh_2$, see Scheme 1. Even when this work[2] was being published, it was inconsistent with observations on $[RhCo_3(CO)_{12}]$, (**6**), where exchange occurs between the bridging carbonyl groups and the terminal carbonyl groups bonded to cobalt and the two terminal carbonyls bonded to rhodium become equivalent, giving two sets of signals in the ratio of 10:2.[3] These observations were interpreted on the basis of a concerted bridge-breaking and -making mechanism. Subsequently, Johnson and Benfield revised their treatment of $[RhCo_3(CO)_{12}]$ to produce the second major theory. They proposed that the different types of carbonyl scrambling observed in $[M_4(CO)_{12}]$, M = Co, Rh, or Ir, type compounds could be explained in terms of 'the initial icosahedral arrangement of ligands rearranging along a well defined reaction coordinate *via* a cubo-octahedral transition state'.[4] In the case of compound (**1**), specific predictions were made in a reaction scheme.[5] These predictions are summarised in Scheme 2.

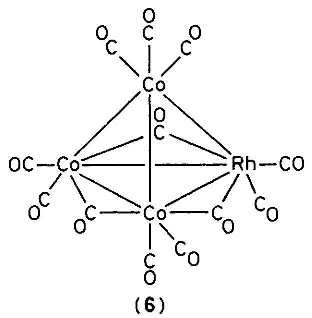
Most studies of carbonyl scrambling on clusters have relied on line-shape analysis. Such studies provide evidence for the rate of carbonyl groups leaving a specific site, but yield little information on the detailed mechanism. The Forsén–Hoffmann method of magnetisation transfer permits the labelling of one carbonyl with a non-equilibrium magnetisation, and then this magnetisation can be followed as it moves throughout the molecule.[6] This method has already been applied qualitatively to $[Ir_4(CO)_{11}(PEt_3)]$.[7] It was shown that the non-equilibrium magnetisation is transferred from C_bO to C_dO to C_aO to C_fO as expected, but that it was also transferred to C_cO and C_eO. The data could not be analysed quantitatively at the time due to the lack of any suitable analysis of the problem. Subsequently, Hawkes *et al.*,[8] Orrell and co-workers,[9] Muhandiram and McClung,[10] and ourselves[11] have produced quantitative methods of analysing such data. The power of the method was demonstrated by applying it to demonstrate the presence of four separate fluxional processes in $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$.[12] This was a relatively easy example to analyse quantitatively, consisting of a four-site and a three-site problem. The compound studied in this paper is far more complex, consisting of a 12- and two-site exchange problem.



Scheme 1. The Cotton mechanism for carbonyl scrambling in $[Ir_4(CO)_{11}(PEt_3)]$. The letters refer to carbonyl ligands

Results and Discussion

Magnetisation-transfer measurements have now been applied quantitatively to $[Ir_4(CO)_{11}(PEt_3)]$ at −84 °C. This compound consists of two interconverting isomers, (**1**) and (**7**), L = PEt_3, in the ratio of 6:1. Each isomer has seven different carbonyl sites, giving a 14-site exchange problem. The assignment of the signals is crucial to the mechanism. The assignment of the



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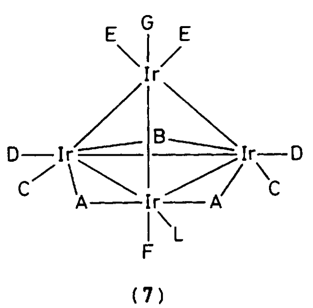

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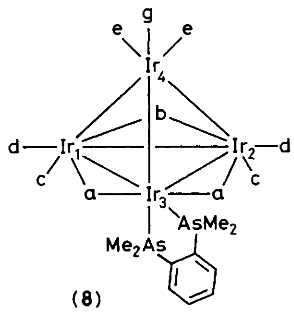

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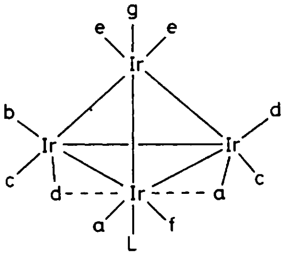

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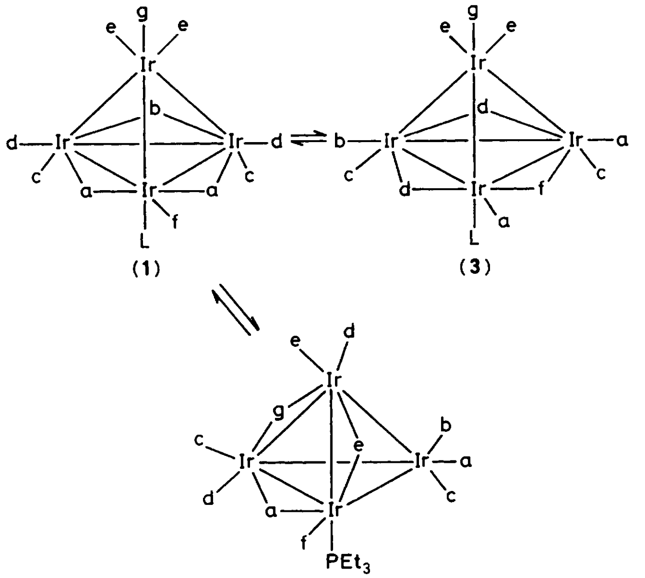

Scheme 2. The Johnson–Benfield mechanism for carbonyl scrambling in $[Ir_4(CO)_{11}(PEt_3)]$. The letters refer to carbonyl ligands

Table. Assignments and ^{13}C chemical shifts for $[Ir_4(CO)_{11}(PEt_3)]$, isomers (**1**) and (**7**)

Isomer (1)		Isomer (7)	
CO	$\delta(^{13}C)$	CO	$\delta(^{13}C)$
a	204.3	A	206.2
b	194.7	B	196.8
c	157.3	C	153.8
d	169.9	D	172.0 (J_{PC} = 12 Hz)
e	158.0	E	159.3
f	172.3	F	154.0 (J_{PC} = *ca.* 30 Hz)
g	155.1 (J_{PC} = 23 Hz)	G	153.1

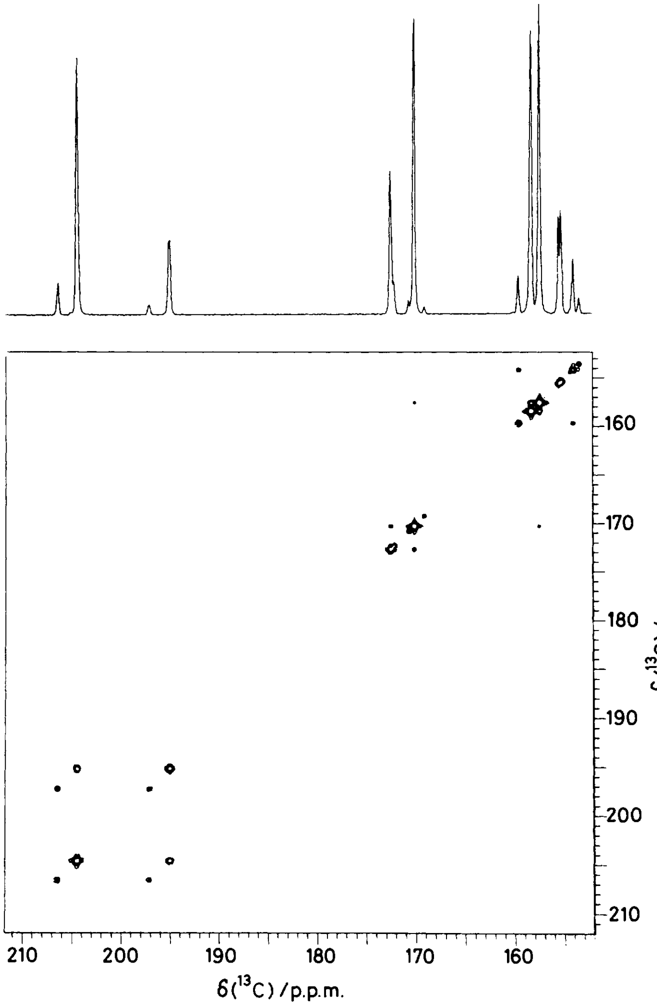

Figure 1. The 100.62-MHz COSY 90 ^{13}C n.m.r. spectrum of the carbonyl groups of $[Ir_4(CO)_{11}(PEt_3)]$ (*ca.* 50% ^{13}CO) in CD_2Cl_2 at −95 °C

bridging carbonyls is unambiguous, being based on chemical shift and intensity, at δ 204.3 and 194.7 p.p.m. for carbonyl C$_a$O and C$_b$O respectively, and δ 206.2 and 196.8 p.p.m. for carbonyls C$_A$O and C$_B$O respectively.* Previous work[2] has unambiguously shown that the equatorial carbonyls occur around δ 170 p.p.m. On the basis of intensity, the assignments C$_f$O at δ 172.3, C$_d$O at δ 169.9, and C$_D$O at δ 172.0 p.p.m. may be unambiguously made. The remaining carbonyls are clustered around δ 160 p.p.m. and are much more difficult to assign. On the basis of intensity, carbonyl C$_g$O may be unambiguously assigned at δ 155.1 p.p.m., $J(^{31}P-^{13}C)$ = 23 Hz. The remaining assignments are ambiguous with C$_c$O and C$_e$O at δ 158.0 and 157.3, C$_C$O and C$_E$O at δ 159.3 and 153.8, and C$_F$O and C$_G$O at δ 154.0 and 153.1 p.p.m. In an attempt to make further assignments, a $^{13}C-^{13}C$ correlation spectroscopy (COSY)-90 n.m.r. spectrum was measured on a 50% ^{13}CO-enriched sample at −95 °C, see Figure 1; $J(^{13}C-^{13}C)$ connectivities are observed between carbonyls C$_a$O and C$_b$O, C$_c$O and C$_e$O, C$_A$O and C$_B$O, C$_C$O and C$_E$O, and C$_d$O and the signal at δ 157.3 p.p.m. There is connectivity between carbonyls which are linear along a C–Ir–Ir–C bond. In addition there is a significant coupling between C$_d$O and either C$_c$O or C$_e$O. It is unreasonable that there should be a significant coupling between C$_d$O and C$_e$O,

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* Lower case subscripts refer to isomer (**1**), upper case to isomer (**7**).

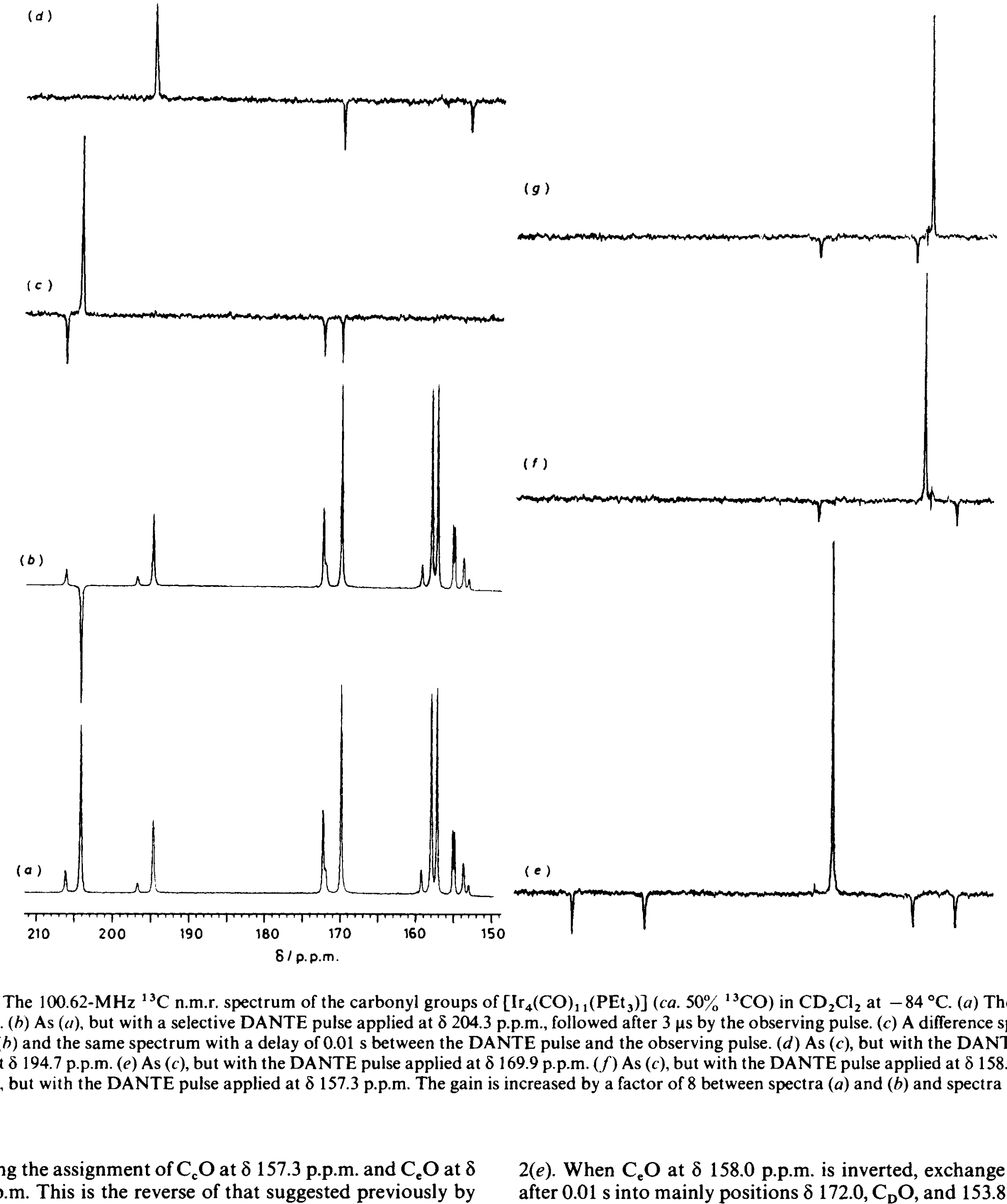


Figure 2. The 100.62-MHz ^{13}C n.m.r. spectrum of the carbonyl groups of $[Ir_4(CO)_{11}(PEt_3)]$ (*ca.* 50% ^{13}CO) in CD_2Cl_2 at −84 °C. (*a*) The simple spectrum. (*b*) As (*a*), but with a selective DANTE pulse applied at δ 204.3 p.p.m., followed after 3 μs by the observing pulse. (*c*) A difference spectrum between (*b*) and the same spectrum with a delay of 0.01 s between the DANTE pulse and the observing pulse. (*d*) As (*c*), but with the DANTE pulse applied at δ 194.7 p.p.m. (*e*) As (*c*), but with the DANTE pulse applied at δ 169.9 p.p.m. (*f*) As (*c*), but with the DANTE pulse applied at δ 158.0 p.p.m. (*g*) As (*c*), but with the DANTE pulse applied at δ 157.3 p.p.m. The gain is increased by a factor of 8 between spectra (*a*) and (*b*) and spectra (*b*)—(*g*)

permitting the assignment of C_cO at δ 157.3 p.p.m. and C_eO at δ 158.0 p.p.m. This is the reverse of that suggested previously by Stuntz and Shapley[2] for $[Ir_4(CO)_{11}(PMePh_2)]$, but there was no supporting evidence given for this assignment.

At −84 °C, the magnetisation-transfer measurements show that the exchange is very specific. As there could be some doubt about the assignment of some of the signals, the exchanging signals are identified by their chemical shifts. The simple ^{13}C n.m.r. spectrum is shown in Figure 2(*a*) for the carbonyl groups. When C_aO at δ 204.3 p.p.m. is inverted, see Figure 2(*b*), the exchange occurs after 0.01 s into mainly positions δ 206.2, C_AO, 172.3, C_fO, and 169.9, C_dO, see Figure 2(*c*). When C_bO at δ 194.7 p.p.m. is inverted, the exchange occurs after 0.01 s into mainly positions δ 169.9, C_dO, and 153.1 p.p.m., C_FO or C_GO, see Figure 2(*d*). When C_dO at δ 169.9 p.p.m. is inverted, the exchange occurs after 0.01 s into mainly positions δ 204.3, C_aO, 194.7, C_bO, 159.3 and 153.8 p.p.m., C_CO and C_EO, see Figure 2(*e*). When C_eO at δ 158.0 p.p.m. is inverted, exchange occurs after 0.01 s into mainly positions δ 172.0, C_DO, and 153.8 p.p.m., C_CO or C_EO, see Figure 2(*f*). When C_cO at δ 157.3 p.p.m. is inverted, exchange occurs after 0.01 s into mainly positions δ 172.0, C_DO, and 159.3 p.p.m., C_CO or C_EO, see Figure 2(*g*). Carbonyl groups C_gO and C_BO only exchange with each other. As a consequence, the problem is reduced to a 12-site and a two-site problem, and at room temperature two broad signals are observed in the intensity ratio 10:1, see Figure 3.

These observations are consistent with the presence of two mechanisms. The first one is a Cotton merry-go-round involving the exchange $C_bO \longleftrightarrow C_dO \longleftrightarrow C_aO \longleftrightarrow C_fO$. This mechanism explains the basic facts, but fails to explain the interconversion of the isomers (**1**) and (**7**). If the mechanism goes *via* the fully bridge-opened intermediate/transition state, (**2**), then reforming the bridges to give isomer (**7**) will cause the exchange $C_aO \longleftrightarrow C_AO$, C_CO, C_EO, C_FO; $C_b \longleftrightarrow C_DO$, C_GO;

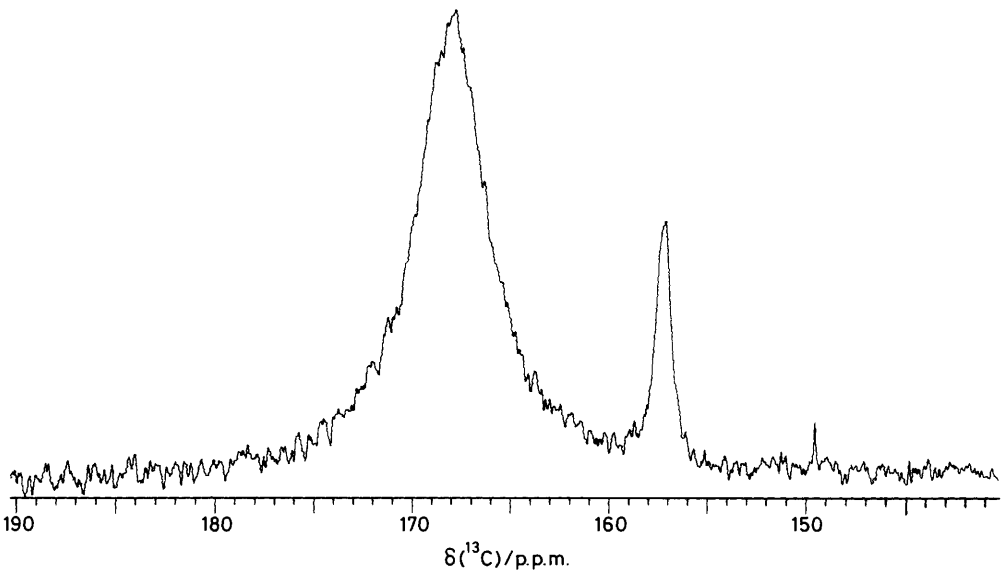
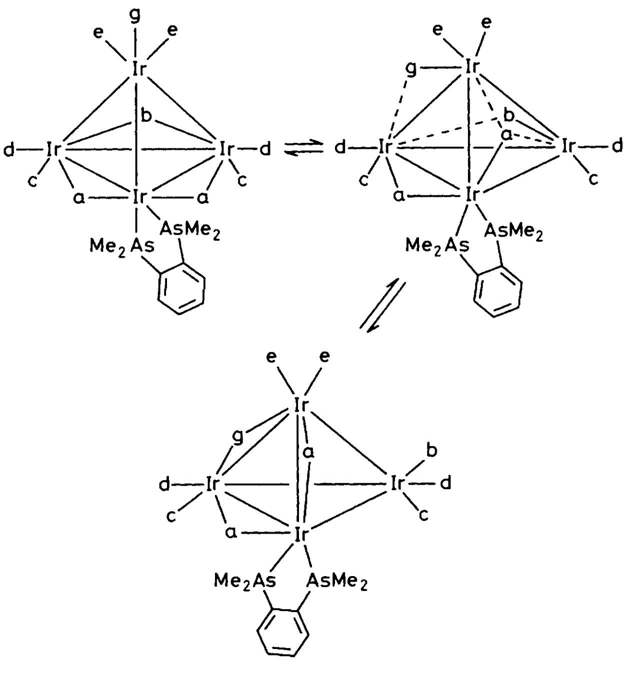


Figure 3. The room-temperature 100.62-MHz ^{13}C n.m.r. spectrum of the carbonyl groups of $[Ir_4(CO)_{11}(PEt_3)]$ in CD_2Cl_2

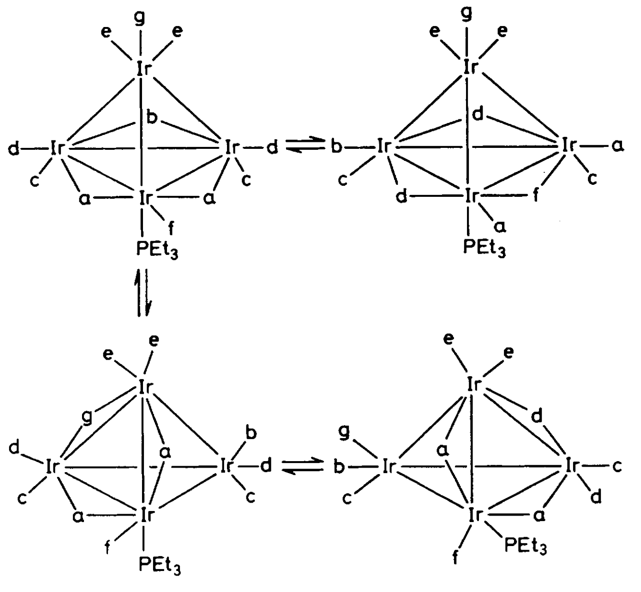


Scheme 3. The published mechanism for fluxionality of $[Ir_4(CO)_{10}\{1,2\text{-}(Me_2As)_2C_6H_4\}]$. The letters refer to carbonyl ligands

$C_cO \longleftrightarrow C_AO$, C_EO; $C_dO \longleftrightarrow C_CO$, C_DO, C_EO, C_GO; $C_fO \longleftrightarrow C_AO$, C_FO; and $C_g \longleftrightarrow C_BO$, see Scheme 1. This is inconsistent with the experimental observations. It is therefore concluded that the fully bridge-opened species, (**2**), is not involved in the dynamic process. The *X*-ray structure of $[Ir_4(CO)_{10}\{1,2\text{-}(Me_2As)_2C_6H_4\}]$, (**8**), shows that there is considerable asymmetry in the bridging carbonyl bonding, with the Ir(1)–C_aO bond being 2.257 Å, while the Ir(3)–C_aO bond is 2.012 Å.[13] This difference is attributed to the $1,2\text{-}(Me_2As)_2C_6H_4$ being a good σ donor and a poor π acceptor. Consequently Ir(3) is electron rich and forms a strong bond to the bridging carbonyl C_aO. The same effect should be present in $[Ir_4(CO)_{11}(PEt_3)]$, but to a lesser extent. It is therefore postulated that in the intermediate there are two semi-bridging carbonyl groups, as in (**9**; L = PEt_3). The presence of these semi-bridging carbonyl groups prevents the formation of compound (**7**) directly from (**9**), and the only fluxionality by this pathway is the observed Cotton merry-go-round $C_bO \longleftrightarrow C_dO \longleftrightarrow C_aO \longleftrightarrow C_fO$.

The second dynamic process is consistent with the mechanism proposed previously for $[Ir_4(CO)_{10}\{1,2\text{-}(Me_2As)_2C_6H_4\}]$. This mechanism (Scheme 3) predicts the interconversions $C_aO \longleftrightarrow C_AO$; $C_bO \longleftrightarrow C_GO$; $C_cO \longleftrightarrow C_DO$, C_EO; $C_dO \longleftrightarrow C_CO$, C_EO; $C_eO \longleftrightarrow C_CO$, C_DO; $C_fO \longleftrightarrow C_FO$; and $C_gO \longleftrightarrow C_BO$ exactly as is observed experimentally. On the basis of this mechanism the unassigned carbonyl signals in isomer (**3**) may be assigned as C_CO at δ 153.8, C_EO at 159.3, and C_FO at 153.1 p.p.m. This mechanism also provides a route for magnetisation transfer from C_dO to C_cO and C_eO *via* C_CO or C_EO, see Scheme 3.

Before the data could be fitted quantitatively,[11] due to the potentially large number of rates and relaxation times, assumptions had to be made. The first assumption concerned the relaxation times. The relaxation times of the carbonyl were measured at −95 °C. The terminal carbonyls were found to have T_1 of 0.20 s and bridging carbonyls have T_1 of 0.40 s. This variation in ^{13}CO T_1 values for bridging and terminal carbonyl groups has been noted previously in $[Rh_6(\mu_3\text{-}CO)_4(CO)_{12}]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ and attributed to differential chemical shift anisotropy.[14] It was therefore assumed that at −84 °C all the T_1 values for the terminal carbonyls are equal and the T_1 values of the bridging carbonyls are equal, and the two sets of T_1 values were related by a factor of 2. This yielded T_1 values of 0.50 and 0.25 s for the bridging and terminal carbonyls respectively at −84 °C. Fortunately, assumptions made about T_1 values make virtually no changes to the calculated rates. It was also necessary to make substantial assumptions in determining the rates. There are 66 rates required fully to describe a 12-site exchange problem. It was assumed that if no exchange was detected from one site into a second site in the first 0.02 s, then that exchange rate is zero. This only left the rates required for the mechanisms summarised in Scheme 4. All the rates for the single process in Scheme 4 were set equal, after due allowance had been made for the population in each site. This process only left two independent rate constants due to these



Scheme 4. The proposed mechanisms for the fluxionality of $[Ir_4(CO)_{11}(PEt_3)]$. The letters refer to carbonyl ligands

two mechanisms. A problem was also encountered with the signals at δ 153.8 p.p.m. which arises from the overlap of two signals, those due to C_CO and C_FO. The intensity was shared between these two groups according to the predictions of the fitting program.

The data were fitted quantitatively[10] to yield rates for $C_bO \longleftrightarrow C_dO \longleftrightarrow C_aO \longleftrightarrow C_fO$ of 2.2 ± 0.3 s^{-1}, and for $C_aO \longleftrightarrow C_AO = C_bO \longleftrightarrow C_GO = C_cO \longleftrightarrow C_DO$, $C_EO = C_dO \longleftrightarrow C_CO$, $C_EO = C_eO \longleftrightarrow C_CO$, $C_DO = C_fO \longleftrightarrow C_FO = C_gO \longleftrightarrow C_BO$ of 2.1 ± 0.3 s^{-1}. These rates correspond to $\Delta G^{\ddagger}$ of 10.6 kcal mol^{-1} (44.35 kJ mol^{-1}). These two mechanisms quantitatively explain the magnetisation transfer from C_dO to C_cO and C_eO *via* C_CO and C_EO. It is possible that as the rates of the two mechanisms are the same, then there is one common transition state, but we have failed to unify these two mechanisms. Further work is in hand to investigate whether these two rates are equal by chance or are equal in a variety of compounds.

The alternative mechanistic approach based on a rearrangement of the whole structure of the molecule does not fit the data, but is much closer in fitting the data than is a mechanism involving compound (**2**). Carbonyl scrambling in $[M_4(CO)_{12}]$ has been described as an icosahedral⟷cubo-octahedral⟷icosahedral rearrangement.[4] A detailed description of how this mechanism predicts movement of carbonyl ligands in $[Ir_4(CO)_{11}(PEt_3)]$ has appeared and the conclusions are summarised in Scheme 2. This treatment correctly predicts the exchange $C_bO \longleftrightarrow C_dO \longleftrightarrow C_aO \longleftrightarrow C_fO$, but is incorrect in predicting that C_aO exchanges to C_AO *and* C_EO and that C_eO exchanges to C_AO and C_CO.

In conclusion, the two observed mechanisms involve concerted bridge formation during the bridge opening, rather than the Cotton mechanism of concerted bridge opening followed by bridge closing. Recently, it has been shown that a similar concerted bridge formation during bridge opening provides the lowest-energy dynamic process in the $[Fe_3(CO)_{12}]$ system.[15]

Experimental

The ^{13}C n.m.r. measurements were carried out using a Bruker WH400 n.m.r. spectrometer. A 5-mm dedicated ^{13}C probe was used to carry out the measurements at 100.62 MHz. The temperature measurements were performed by replacing the sample tube by a tube containing dichloromethane and a thermocouple, attached to a Comark electronic thermometer.

The following experimental procedure was employed to carry out the DANTE[16] measurements. A suitable temperature was chosen so that there was a little line broadening due to exchange. After the spectrometer had stabilised at that temperature, the T_1 values of the carbonyls were estimated using the $10D_1–\pi–D_1–\frac{\pi}{2}$ pulse sequence, adjusting the delay, D_1, for the null signal. Subsequently, the relaxation delay was taken as $10D_1$. The DANTE pulse length was optimised for maximum signal inversion. The measurements were carried out using the pulse sequence: $\{$[read f.i.d.–$\{10D_1–(D_2–P_1)_{30}–D_3–\frac{\pi}{2}$–acquire$)_8$–write f.i.d.–change $D_3\}_m$–reset exchange delay, D_3, and DANTE pulse frequency$]_n$–reset exchange delay, D_3, and DANTE pulse frequency$\}_p$, with m typically 10, n typically 3, and p chosen to give adequate signal : noise ratio. Typical values are $D_1 = 3$ s, $D_2 = 0.2$ ms, $P_1 = 1.2$ μs, $D_3 = m$ values with the minimum being 3 μs and the largest being $10D_1$, and $\frac{\pi}{2}$ pulse = 12.5 μs. The remaining times are chosen to give a spread over the exchange and relaxation times, typically 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, and 0.4 s. This sequence has the advantage that any temperature drift during the experiment will be spread over all the measurements. With a value of $n = 3$, there are three separate irradiation points, producing three sets of data. For a series of experiments, one irradiation point is kept constant, while the other two are changed. This permits the comparison of different sets of experiments.

The compound $[Ir_4(CO)_{11}(PEt_3)]$ was synthesised using literature methods,[17] and enriched with ^{13}CO by stirring a dichloromethane solution under an atmosphere of 90% ^{13}CO for 24 h at 60 °C in a sealed tube.

Acknowledgements

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