

## Dynamics and fluxionality in metal carbonyl clusters: some old and new problems

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The cluster chemistry of the transition-metal carbonyls began soon after the discovery of the metal carbonyls themselves, with molecules such as  $[\text{Co}_2(\text{CO})_8]$ ,<sup>1</sup>  $[\text{Fe}_2(\text{CO})_9]$ <sup>2</sup> and  $[\text{Fe}_3(\text{CO})_{12}]$ <sup>3</sup> being prepared, although incompletely characterised at the time. The development of this field was greatly stimulated by the work of Hieber and co-workers from the 1930s onwards; these developments have been summarised by Hieber himself.<sup>4</sup> The first indication<sup>5</sup> in 1939 of the presence of a carbonyl bridged metal–metal bond in  $[\text{Fe}_2(\text{CO})_9]$  was one of the defining moments in the birth of cluster chemistry. With the advent of nuclear magnetic resonance spectroscopy, especially  $^{13}\text{C}$  NMR, it became clear that, in addition to their novel structures, these unusual molecules also possessed special dynamic or fluxional properties.<sup>6</sup> One of the earliest, classic, examples of this behaviour was provided by  $[\text{Fe}_3(\text{CO})_{12}]$ , which despite having five chemically distinct sets of carbonyl groups in the solid-state structure,<sup>7,8</sup> shows only a singlet in the solution  $^{13}\text{C}$  NMR spectrum down to  $-150\text{ }^\circ\text{C}$ .<sup>9</sup> We shall return to this molecule, and related molecules, later in this perspective.

The central reason why carbonyl clusters exhibit dynamic behaviour is that ancillary ligands such as carbon monoxide and hydrides may bind to ensembles of metal atoms in energetically similar, but geometrically distinct modes. Less commonly, the metal skeleton may also show a variability in geometry. An example of metal skeletal fluxionality is provided by the anion  $[\text{Rh}_9(\mu_9\text{-P})(\text{CO})_{21}]^{2-}$  which has a capped square-antiprismatic metal skeleton in the solid state.<sup>10</sup> In accordance with the  $^{31}\text{P}$  NMR spectrum, which indicated a fluxional metal skeleton in solution,<sup>10</sup> direct  $^{103}\text{Rh}$  NMR observation showed three  $^{103}\text{Rh}$  signals at  $-80\text{ }^\circ\text{C}$  but only one signal at the weighted mean shift at ambient temperatures,<sup>11</sup> due to the rearrangement of the capped square-antiprismatic metal framework, presumably *via* a tricapped trigonal prism or similar geometry.

For fluxional molecules in general, one or more structures lie so close in energy to the ground-state structure, that they are easily accessible thermally. These excited-state structures provide the pathway for the atomic site permutations which are manifest in the NMR spectra. The identification and exact characterisation of the excited-state geometries remains a formidable problem in the study of fluxional molecules. In the opinion of the author, the most likely method for solving this problem will come from high-level quantum-chemical calculations. Given the soft potential-energy hypersurface between these structures, this will not be an easy task.

Experimentally, a variety of techniques in dynamic NMR spectroscopy (DNMR<sup>12</sup>) are widely used to examine the fluxional behaviour of metal carbonyl clusters. The underlying reason why NMR spectroscopy is the technique *par excellence* for the study of fluxional molecules is that the exchange processes occur at roughly similar rates as the differences in resonance frequencies of the NMR signals of the exchanging nuclei. This is, of course, the well known time-scale effect,<sup>13</sup> and it is of interest to note recent work which suggests that extremely fast exchange processes in metal carbonyls may even cause coales-

cence on the much shorter IR time-scale.<sup>14</sup> In this perspective, we show that variable-temperature X-ray crystallography may also provide useful and complementary information about dynamic processes in the solid state.

The vast majority of DNMR studies on clusters have been carried out in solution phase, where the rapid tumbling of these (relatively) small molecules gives rise to correlation times  $\tau_c$  typically of the order of 10–100 ps. This results in an averaging of the anisotropic chemical shift tensor to the observed isotropic shift, and the averaging of the often large dipolar couplings to zero. This simplification does not usually occur in the solid phase, and in this case it is possible to extract more information than from the solution phase.

The most widely used DNMR technique is still variable-temperature lineshape analysis, using computer programs such as DNMR3<sup>15</sup> to simulate the bandshape. It is a relatively simple experiment, and provided that accurate static parameters can be measured (not always easy or possible), then accurate exchange rate constants may be obtained. When trying to elucidate the mechanisms of fluxional exchange, it is generally more useful to consider the exchange rate constants, rather than the more easily obtainable free energies of activation  $\Delta G^\ddagger$ , particularly when several simultaneous dynamic processes are occurring. This latter parameter is rather insensitive, and is notoriously difficult to reproduce accurately between different laboratories investigating the same exchange process.

One major drawback of the lineshape technique is that a *model* for the exchange process or processes is required for the analysis. In simple cases this may not be a problem, but for metal carbonyl clusters with several simultaneous exchange processes, it is often a far from trivial exercise to elucidate mechanisms from the total bandshape. It is also quite likely that the overall bandshape will not be sensitive to all the required parameters.

A second general method of investigating fluxional exchange involves the concept of magnetisation transfer,<sup>16</sup> whereby a non-equilibrium magnetisation is induced in one site, and is then carried through to other chemical sites by the exchange process(es). This may be accomplished in a one-dimensional experiment by direct selective excitation of a single resonance, followed by an analysis of the time-dependent intensities of other signals. For heteronuclei, multi-pulse techniques such as DANTE<sup>17</sup> are often used to effect this excitation. Alternatively, excitation of all relevant nuclei may be performed in a single two-dimensional experiment, *i.e.* nuclear Overhauser effect spectroscopy (NOESY) or more accurately termed exchange spectroscopy (EXSY) experiment.<sup>18</sup> These magnetisation transfer experiments are the methods of choice in complex exchanging systems, since the individual site-to-site exchange rate constants may be obtained *a priori* without recourse to any preconceived mechanism. Using such techniques, we have demonstrated<sup>19a</sup> that the fluxional behaviour of  $[\text{Ru}_3(\mu\text{-H})(\text{CCBu}^t)(\text{CO})_9]$  is more complex than previously realised.<sup>19b</sup>

It is important to be aware of the limitations of these NMR experiments. The site-to-site exchange rate constants tell us

about the rates at which the nuclear *permutations* occur during the dynamic process. They do not provide any *direct* information about the mechanistic pathway, nor on the nature of the transition state or intermediates. For instance, one commonly observed exchange process in metal carbonyl clusters is the so-called tripodal rotation of  $M(\text{CO})_3$  groups. A well studied example is provided by the allyl cluster  $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-}\eta^3\text{-CMeCHCMe})(\text{CO})_9]$ .<sup>20</sup> It was shown that the three chemically distinct CO ligands in the two chemically equivalent  $\text{Ru}(\text{CO})_3$  groups undergo mutual exchange with each other, with experimentally identical exchange rate constants.<sup>20</sup> The intuitively most likely mechanism is a concerted rotation about the fragment  $C_3$  axis, but this is not directly proven by this experiment; other more complex exchange pathways involving consecutive pairwise exchange cannot be ruled out. However, in view of further recent studies on tripodal rotation in other systems, the concerted mechanism seems now proven beyond reasonable doubt.<sup>19a,21</sup>

One experiment which *can* provide some direct information about the transition state comes from measurements of the activation volumes,  $\Delta V^\ddagger$ , of fluxional processes. Roulet and co-workers<sup>22</sup> have shown, for instance, that the cluster  $[\text{Ir}_4(\text{CO})_9(\mu_3\text{-L})]$  ( $L = 1,3,5\text{-trithiane}$ ) consists of two isomers in solution, one with three bridging CO ligands around the basal plane, the other with an all-terminal CO arrangement. The magnitude of the activation volume for isomer interconversion strongly implies a symmetric transition state with three semi-bridging carbonyl groups. In another study, Keister *et al.*<sup>23</sup> have measured activation volumes for hydride exchange in  $[\text{Os}_3(\text{H})(\mu\text{-H})(\text{CO})_{10}(\text{PPh}_3)]$  and  $[\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-CHCO}_2\text{Me})(\text{CO})_6]$ , and conclude that transition states with terminal hydrides are the most likely. It should be emphasised however that this method depends critically on an estimate of the partial molar volumes of both reactant and transition state. Given the well known variability in metal–metal bond lengths,<sup>24</sup> and by implication in the volume of the metal cluster itself, it is clear that some caution needs to be exercised in the interpretation of these results.

## Mechanisms of Carbonyl Exchange

Despite the problems mentioned above in identifying the excited-state geometries of fluxional clusters, a number of general empirical models for the fluxional interchange between structures have been proposed. In certain cases, the fluxional processes lead only to localised exchanges. The so-called tripodal rotation, where *fac*- $M(\text{CO})_3$  groups undergo an apparent rotation about their three-fold axis, is a well known example of this behaviour. An interesting case is provided by  $[\text{Os}_6(\text{CO})_{18}]^{25}$  in which it was possible to observe three independent tripodal exchanges, for the three chemically distinct  $\text{Os}(\text{CO})_3$  moieties. A similar three-fold exchange may also occur in  $M(\text{CO})_4$  groups, as was shown in  $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-CX})(\text{CO})_{10}]$  ( $X = \text{Ph}^{26a}$  or  $\text{OMe}^{26b}$ ). In this case one of the axial carbonyls is not involved in the exchange.

In many instances however the exchange is of a less localised nature, and often leads to complete scrambling of carbonyl ligands. There have been two *general* mechanisms proposed to explain this phenomenon. An early suggestion by Cotton<sup>27</sup> was the so-called ‘merry-go-round’ mechanism, whereby there is a concerted migration of carbonyls between terminal and bridging sites about a metal–metal bond. This was originally proposed to explain the fluxional behaviour of  $[\text{Co}_4(\text{CO})_{12}]$ , but this ‘merry-go-round’ model may also be extended to explain similar motions around a metal–metal edge, *e.g.* in  $[\text{Fe}_3(\text{CO})_{12}]$ ,<sup>8</sup> about square metal planes, *e.g.* in  $[\text{Rh}_6(\mu_6\text{-C})(\text{CO})_{13}]^{2-}$ ,<sup>28</sup> or even hexagonal planes as in  $[\text{Rh}_{13}(\mu\text{-H})_n(\text{CO})_{24}]^{n-5}$ .<sup>29</sup> Analysis of the anisotropic thermal parameters from an accurate X-ray diffraction study<sup>30</sup> on  $[\text{Rh}_6(\mu_6\text{-C})(\text{CO})_{13}]^{2-}$  has led to the suggestion that these may provide further direct information regarding the fluxional pathway. One set of carbonyls situated in an equatorial

plane show much greater thermal motion within this plane, and this is consistent with the solution <sup>13</sup>C NMR data.<sup>28</sup> Unfortunately this type of study has not, as yet, been extended to many other carbonyl clusters. In some instances, *e.g.* with phosphine-substituted derivatives of  $[\text{Os}_3(\text{CO})_{12}]$ , it has been shown that the presence of the phosphine ligand blocks certain pathways, and prevents complete scrambling over all metal sites.<sup>31</sup>

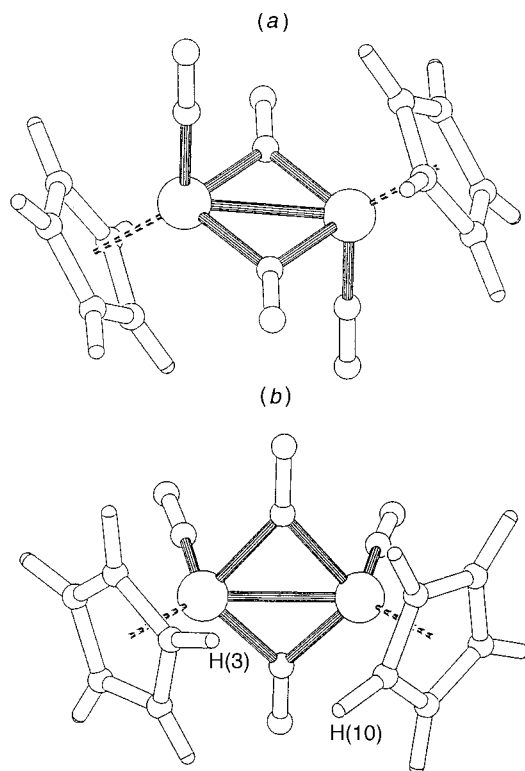
The second general fluxional mechanism proposed is the Ligand Polyhedral Model of Johnson, which has been reviewed recently.<sup>32</sup> This model, originally proposed in 1976,<sup>33</sup> involves consideration of the symmetry of the ligand polytope, and the generalised motions which occur between a relatively rigid metal skeleton and this ligand polytope. Cases have been considered where the ligand polytope remains relatively rigid, and also cases where there is a change in the symmetry of the ligand polytope, such as icosahedral  $\longleftrightarrow$  cubeoctahedral or icosahedral  $\longleftrightarrow$  anticubeoctahedral. The Ligand Polyhedral Model (LPM) approach to fluxionality has not only been applied to homoleptic carbonyl clusters, but also to simple ligand-substituted derivatives.<sup>34</sup> For such substituted derivatives, it is important to bear in mind that the steric and electronic requirements of individual ligands may introduce restrictions to the generalities of the LPM.

Finally it is worth emphasising here that, in the *solution* phase where molecules are tumbling rapidly, it is never possible to determine absolute atomic motion within molecules, only *relative* atomic motion. The question of whether a metal core rotates within a fixed ligand polytope, or *vice versa*, cannot be answered, and the distinction is essentially meaningless. In the solid state, however, this is no longer the case, as will be shown below. In the remaining part of this perspective, I will present a few specific cases of dynamics in small transition-metal clusters. These examples demonstrate that, even in systems which at first sight seem already well understood, some new insights may be on offer.

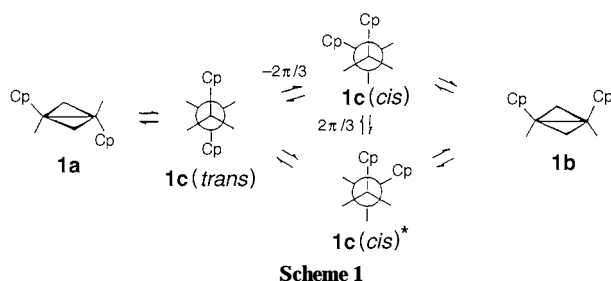
## Fluxionality in $[\text{Fe}_2(\text{CO})_4\text{Cp}_2]$

The dinuclear iron complex  $[\text{Fe}_2(\text{CO})_4\text{Cp}_2]$  **1** ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) and related molecules were some of the earliest studied fluxional compounds possessing metal–metal bonds.<sup>35</sup> Indeed molecule **1** is now a text-book<sup>36</sup> example of metal carbonyl fluxionality. It has long been established that **1** exists as several isomers in solution, a *trans*-bridged form **1a**, a *cis*-bridged form **1b**, and a non-bridged form **1c**. Crystal structures of both **1a**<sup>37</sup> and **1b**<sup>38</sup> have been obtained, and their structures are shown in Fig. 1. Since the non-bridged form (**1c**) is present in only minor quantities, no definitive structural information has been obtained on this isomer.

A fluxional mechanism operating in **1** was proposed by Adams and Cotton<sup>39</sup> on the basis of <sup>1</sup>H and <sup>13</sup>C NMR studies.<sup>35</sup> The central feature of their mechanism is the idea that the non-bridged form (**1c**) exists as several conformers in solution [**1c**(*trans*), **1c**(*cis*) and **1c**(*cis*)\*, see Scheme 1], related by a rotation about the Fe–Fe bond. The NMR studies indicated that the *cis*- and *trans*-bridged forms **1a** and **1b** undergo rapid intermolecular exchange at ambient temperatures, but this exchange can be slowed sufficiently at low temperatures to observe separate signals. The minor isomer **1c** has not been directly detected by NMR spectroscopy, as far as the author is aware, although IR bands attributed to this isomer have been reported. This may be explained by the observation of another exchange process, which manifests itself in the <sup>13</sup>C NMR spectra, *i.e.* that of apparent intramolecular carbonyl exchange between terminal and bridging sites. For the *trans* isomer **1a**, this intramolecular exchange is rapid on the NMR time-scale, even at the lowest temperatures studied, and this results in an *averaged* CO signal at *ca.*  $\delta$  240, while for the *cis* isomer **1b** separate signals for the bridged ( $\delta \approx 270$ ) and terminal ( $\delta \approx 210$ ) carbonyls are observed below 260 K. The



**Fig. 1** Structures of (a) the *trans* isomer **1a** and (b) the *cis* isomer **1b** of [Fe<sub>2</sub>(CO)<sub>4</sub>Cp<sub>2</sub>]

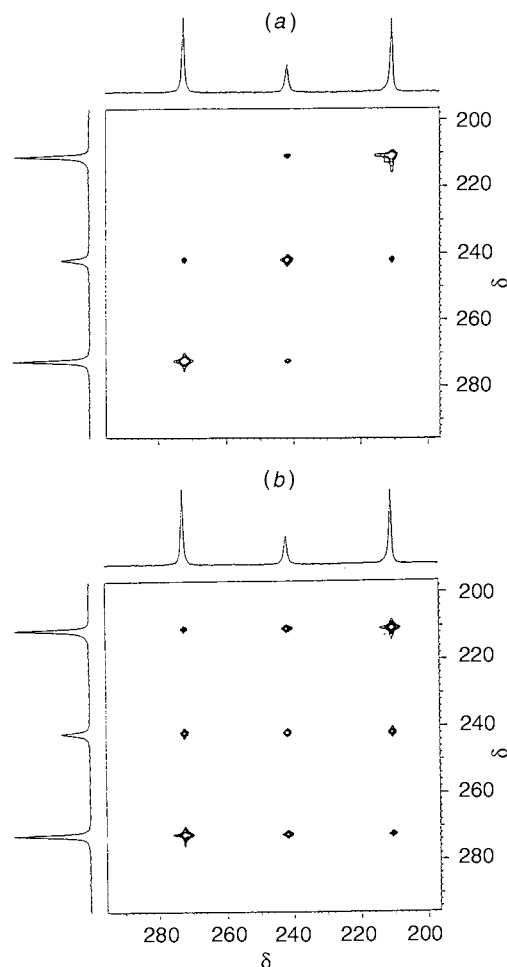


**Scheme 1**

Adams–Cotton mechanism<sup>39</sup> clearly explains why the *trans* isomer **1a** has a much lower activation barrier to bridge-terminal exchange than the *cis* isomer. If the bridge-opening bridge-closing process is fast compared with other dynamic processes, then passage of **1a** through **1c**(*trans*) back to **1a** will result in complete equilibration of the carbonyls, since all four COs are homotopic in the bridge-opened intermediate **1c**(*trans*).

This is not the case for the *cis* isomer **1b**, since if the opening is stereospecific, the rapid passage of **1b** through **1c**(*cis*) back to **1b** will not result in CO scrambling. The same pair of carbonyls in **1c**(*cis*) which were the bridging carbonyls in **1b** must collapse back to bridging carbonyls in **1b**. The only process which can lead to apparent exchange between bridging and terminal COs in **1b** is a rotation about the Fe–Fe bond in the opened form, **1c**, *i.e.* an interchange between **1c**(*cis*) and its enantiomer **1c**(*cis*)\*. This can be achieved either by a 2π/3 rotation, or by a 4π/3 rotation *via* **1c**(*trans*). Since we know that the exchange barrier between **1a** and **1c**(*trans*) is much smaller than the barrier to isomerisation, this latter route cannot be responsible for a *direct* exchange between **1c**(*cis*) and its enantiomer **1c**(*cis*)\*. The early <sup>13</sup>C NMR studies<sup>35d</sup> appeared to show that there was a direct exchange between the bridging and terminal carbonyls in **1b**, and Adams and Cotton<sup>39</sup> concluded that the activation barriers to rotation about the Fe–Fe bond in **1c** in the non-equivalent directions **1c**(*cis*) → **1c**(*trans*) and **1c**(*cis*) → **1c**(*cis*)\* were approximately the same.

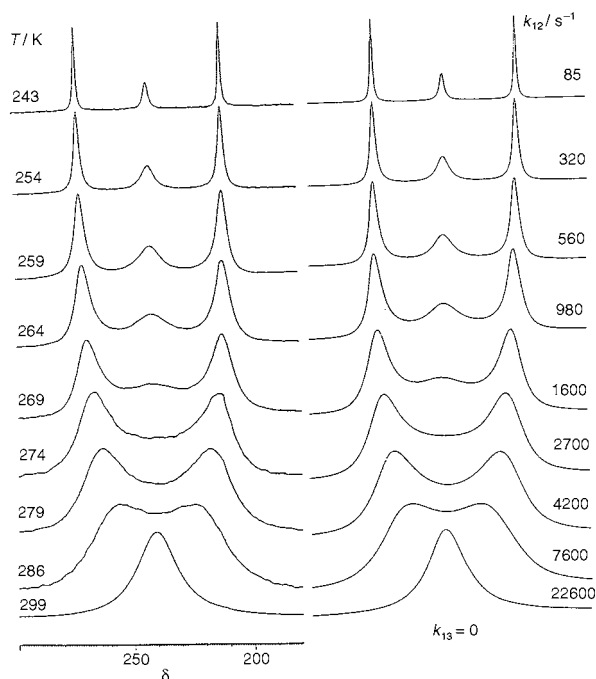
We have subsequently shown<sup>40</sup> that this apparent exchange



**Fig. 2** The <sup>13</sup>C EXSY spectra of compound **1** at 224 K in the carbonyl region with mixing time (a) 0.02 and (b) 0.1 s

between the bridging and terminal carbonyls in **1b** does not occur, or more precisely, that the exchange behaviour in **1** can be satisfactorily modelled on the assumption that the direct exchange rate constant is zero at all measured temperatures. The <sup>13</sup>C EXSY spectra for compound **1** are shown in Fig. 2. At the shortest mixing time there is no visible cross-peak between the signals at δ ≈ 270 (signal 1, due to the bridging COs of **1b**) and δ ≈ 210 (signal 3, due to the terminal COs of **1b**), indicating no significant exchange between these signals. At the longer mixing time a cross-peak is observed, but a quantitative analysis of the volume integrals of these spectra by the method of Sales and co-workers<sup>41</sup> shows that the *direct* exchange rate constant between these two signals (*k*<sub>13</sub>) is negligible. We therefore find no experimental evidence for a *direct* exchange between the terminal and bridging carbonyls in the *cis* isomer **1b**. All exchange occurs *via* the *trans* species **1a**, and this relayed exchange is responsible for the appearance of a cross-peak between the signals at δ 270 and 210 at the longer mixing time. Moreover a full bandshape analysis, shown in Fig. 3, is also entirely consistent with a zero exchange rate constant *k*<sub>13</sub> over the whole temperature range.

There are two conclusions which may be drawn. (i) The direct intramolecular exchange rate constant in **1b** is perhaps one or two orders of magnitude smaller than the intermolecular exchange between **1a** and **1b**. It is very difficult to detect slow exchange processes in the presence of much faster ones, and if the slow process was, say 100 times slower, the difference in activation barriers would be only *ca.* 10–15 kJ mol<sup>-1</sup>. This is essentially the Adams–Cotton proposal.<sup>39</sup> (ii) On the other hand, the direct intramolecular exchange rate may be very much slower still, with a substantially higher activation barrier, in excess of say 50–100 kJ mol<sup>-1</sup>.

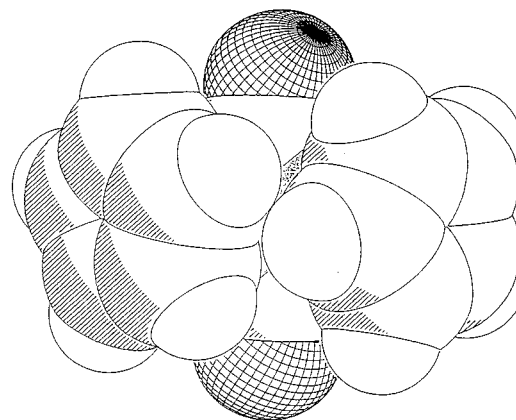


**Fig. 3** Experimental (left) and simulated variable-temperature  $^{13}\text{C}$  NMR spectra of compound **1** in the carbonyl region. These spectra were simulated with the bridge-terminal CO exchange rate constant for compound **1b** ( $k_{13}$ ) set to zero at all temperatures

There is no clear-cut experimental evidence for compound **1** to distinguish these two conclusions,<sup>†</sup> although by the principle of Occam's razor, the second conclusion may be preferred, in that fewer assumptions are required. In accordance with the spirit of a Dalton Perspective, I ask the readers indulgence to explore the second possibility.

First of all, it is worth pointing out that the analogous exchange rate constant in  $[\text{Fe}(\text{CO})_3(\text{CNMe})\text{Cp}_2]$  has been shown by Mann and co-workers<sup>44</sup> to be close to zero as well, so our observations may be more general. Several authors<sup>35,43</sup> have suggested that the apparently high barrier for the rotation between **1c(cis)** and **1c(cis)\*** has steric origins, *i.e.* there is a difficulty for the large cyclopentadienyl groups to pass each other. This view seems reasonable until one considers the reported crystal structure of **1b**. As can be seen from Fig. 1, or more clearly from the space-filling view shown in Fig. 4, the cyclopentadienyl groups are very close; indeed looking along the Fe-Fe bond, they are effectively eclipsed. The shortest H-H contact distance  $[\text{H}(3) \cdots \text{H}(10)]$  is *ca.* 2.4 Å which is twice the van der Waals radius for hydrogen. Despite these apparently unfavourable steric interactions, it is worth remembering that isomer **1b** is the *most stable* isomer in solution, regardless of the solvent system, and it may therefore be of some interest to examine theoretically why this is the case.

<sup>†</sup> Cotton and co-workers have carried out a number of studies of systems related to compound **1**, and as far as we are aware none of these is at variance with our proposal of a single unbridged intermediate. The only case which gave us some concern is the study<sup>42</sup> on  $[\text{Fe}_2(\text{CO})_4(\text{C}_5\text{H}_4\text{CMe}_2\text{CMe}_2\text{C}_5\text{H}_4)]$ . Here the two Cp units are tied together with a  $\text{C}_2$  chain, hence the *trans* isomer is not accessible. The carbonyls are reported to undergo exchange with an activation barrier similar to that of **1**. Since it was believed at the time that the measured exchange observed in **1** was due to bridge-terminal exchange in the *cis* isomer, they concluded that this evidence provided definitive proof of their mechanism. However, as we have subsequently shown, this exchange observed in **1** is in fact due to interisomer exchange {not possible in  $[\text{Fe}_2(\text{CO})_4(\text{C}_5\text{H}_4\text{CMe}_2\text{CMe}_2\text{C}_5\text{H}_4)]$ }, and the evidence regarding this compound is less clear-cut. It may be that the tying together of the two Cp rings either considerably raises the energy of a *cis*-bridged form, or considerably lowers the energy of a *cis*-unbridged form. See for example the structure of  $[\text{Ru}_2(\text{CO})_4(\text{C}_5\text{H}_4\text{C}_5\text{H}_4)]$ , which has an all-terminal CO arrangement.<sup>43</sup>



**Fig. 4** Space-filling view of the structure of compound **1b**. The view is the same as that given in Fig. 1(b)

It is tempting to suggest that the proposed all-terminal rotamers **1c(cis)** and **1c(cis)\*** cannot interconvert directly by a rotation about the Fe-Fe bond, because, as they approach the eclipsed position, the molecule collapses into the much more stable *cis*-bridged form **1b**. In fact, considering the NMR data as a whole, it is unnecessary to invoke the existence of the rotamers **1c(cis)** and **1c(cis)\*** as *stable intermediates* at all. The experimental observations for compound **1** can all be explained on the basis of only three isomers being present in appreciable concentrations in solution, *i.e.* **1a**, **1b** and **1c(trans)**. Within this scenario, the bridged isomers **1a** and **1b** open to give **1c(trans)** directly as the sole intermediate, with structures such as **1c(cis)** and **1c(cis)\*** perhaps being transition states. Some evidence for this proposal comes from matrix isolation studies on **1** at 12 K by Rest and co-workers.<sup>45</sup> They found that the *trans* isomer **1a** undergoes photolytic bridge opening to give a species with the same IR bands as the previously observed unbridged species, while the *cis* isomer **1b** does not undergo photolytic bridge opening to give an all-terminal species. Since rotation about the Fe-Fe bond is unlikely at 12 K, Rest and co-workers<sup>45</sup> conclude that the IR observed unbridged minor isomer is **1c(trans)**.

### Fluxionality in $[\text{M}_3(\text{CO})_{12}]$ (M = Fe, Ru or Os)

The simple metal clusters of the iron triad  $[\text{M}_3(\text{CO})_{12}]$  (M = Fe **2**, Ru **3** or Os **4**) pose special and exemplary problems regarding metal carbonyl fluxionality. The latter two molecules are simpler cases as regards their structures and fluxional behaviour. In the solid state they are isostructural, and possess very similar distorted anticubeoctahedral arrangements of CO ligands surrounding an ordered  $\text{M}_3$  triangle.<sup>46</sup> The molecular structure approximates to  $D_{3h}$ , although cluster **3** shows a small distortion towards a  $D_3$  structure. Cluster **3** is highly fluxional in solution, and in a recent elegant study, Aime *et al.*<sup>47</sup> have obtained a barrier for axial-equatorial exchange of around 20  $\text{kJ mol}^{-1}$ . As is usual, the barrier to axial-equatorial exchange in the heavier congener **4** is considerably higher  $\approx 70 \text{ kJ mol}^{-1}$ .<sup>48</sup> By using a sample of **4** enriched in  $^{187}\text{Os}$ , Koridze *et al.*<sup>49</sup> have demonstrated unequivocally that this exchange occurs by intermetallic CO migration. Solid-state  $^{13}\text{C}$  CPMAS (cross polarisation magic angle spinning) studies of both **3** and **4** show no evidence for fluxional motion in the solid phase.<sup>50</sup>

For cluster **2** the situation is considerably more complex and interesting. The saga of the various and numerous structural studies on **2**, both in solution and in the solid phase, by a variety of experimental and theoretical techniques, has been repeated many times, and space does not permit a detailed recapitulation here: the interested reader is directed to ref. 51 for a recent resumé. In a nut-shell, cluster **2** in the solid phase<sup>7,8</sup> at room temperature has a disordered structure. The carbonyl ligand polytope corresponds to a distorted icosahedron, in contrast to

the anticubeoctahedron found for **3** and **4**, and the metal triangle is statistically disordered over two sites, as required by the crystallographic inversion centre in the space group  $P2_1/n$ . This is the well known 'Star of David' disorder, which has been observed in a number of other related clusters.<sup>52</sup> It arises because the distorted icosahedral CO cage is, to a first approximation, invariant to inversion, so that there is little energy difference between either orientation of the  $\text{Fe}_3$  triangle. The room-temperature molecular structure of **2** shows two asymmetric carbonyl bridges,<sup>8</sup> although as will be discussed below, this asymmetry is more apparent than real. The molecular symmetry is thus  $C_2$  but is close to  $C_{2v}$ .

In solution phase, despite many studies, the situation still remains less than certain. What is clear beyond reasonable doubt however is that several isomers are present in solution. The IR spectrum<sup>53</sup> is very simple, and not consistent with any one structure (though the possibility of exchange on the IR time-scale<sup>54</sup> has been mooted), and EXAFS studies<sup>55</sup> also lead to the same conclusion. Favoured structures are the  $C_2$  bridged form (as in the solid) and the unbridged  $D_3$  or  $D_{3h}$  forms, although less symmetrical structures may also be present. Molecular mechanical calculations<sup>56,57</sup> indicate that the  $D_3$  form is of the lowest energy. In terms of a fluxional mechanism little can be directly ascertained from the  $^{13}\text{C}$  NMR spectrum of **2**, since it is a sharp singlet down to  $-150^\circ\text{C}$ .<sup>9</sup>

In the solid phase however the experimental NMR evidence is much more interesting. Hanson *et al.*<sup>58</sup> have reported that at low temperature the  $^{13}\text{C}$  CPMAS NMR spectrum of **2** is consistent with the room-temperature crystal structure, in that bridging and terminal environments may be distinguished. On warming to room temperature, there is a pair-wise coalescence to give six signals, one of which may be assigned to the average of bridging and terminal CO resonances. They proposed<sup>58</sup> a mechanism whereby the  $\text{Fe}_3$  triangle rotates about the pseudo- $C_3$  axis by  $60^\circ$  jumps, a proposal consistent with the observed crystallographic disorder. In a later broad-line  $^{13}\text{C}$  NMR study Aime and Gobetto<sup>59</sup> concluded that, at elevated temperatures, the COs experienced 'an averaging process with partial loss of the axial pattern'. They suggested large amplitude motions of the CO ligands, though the process described by Hanson *et al.*<sup>58</sup> would also lead to axial-bridging exchange.

However on the basis of solution NMR studies on a number of phosphine, phosphite and isocyanide derivatives of **2**, three other general mechanisms for fluxionality in these species have been proposed. Following early suggestions of Johnson,<sup>33,60</sup> the Ligand Polyhedral Model has been developed in a number of papers<sup>61</sup> to give a detailed account of the exchange process in **2**, both in the solution phase and the solid state. In essence, the first stage of the process is proposed to involve a libration of the  $\text{Fe}_3$  triangle about the molecular  $C_2$  axis. This involves a change in molecular structure from  $C_2$  to  $D_3$ . The  $D_3$  form can then collapse back to the  $C_2$  form but with the bridging carbonyls situated about a different Fe-Fe edge, leading to total CO scrambling. Consideration of the anisotropic displacement parameters of the two Fe atoms associated with the bridging CO ligands has been cited<sup>61a,b</sup> as confirmatory evidence for this proposal. In solution, an additional possibility is that the ligand polyhedron can interconvert from an icosahedron to the anticubeoctahedral complementary geometry.<sup>61c</sup>

Mann and co-workers<sup>62</sup> proposed a second mechanism, the 'concerted bridge-opening-bridge-closing mechanism'. This has been applied specifically to cluster **2**, both in solution and solid phase, and appears to lead to the same predicted exchanges (in solution) as the Johnson proposal. Lentz and Marschall<sup>63</sup> have offered yet a third proposal for the solution fluxionality of  $[\text{Fe}_3(\text{CO})_{11}(\text{CNCf}_3)]$  and derivatives  $[\text{Fe}_3(\text{CO})_{10}(\text{CNCf}_3)(\text{PR}_3)]$  involving rotation of the  $\text{Fe}_3$  triangle within the icosahedral ligand polytope, about one of the five-fold axes. All three approaches share some common features, and it is not the

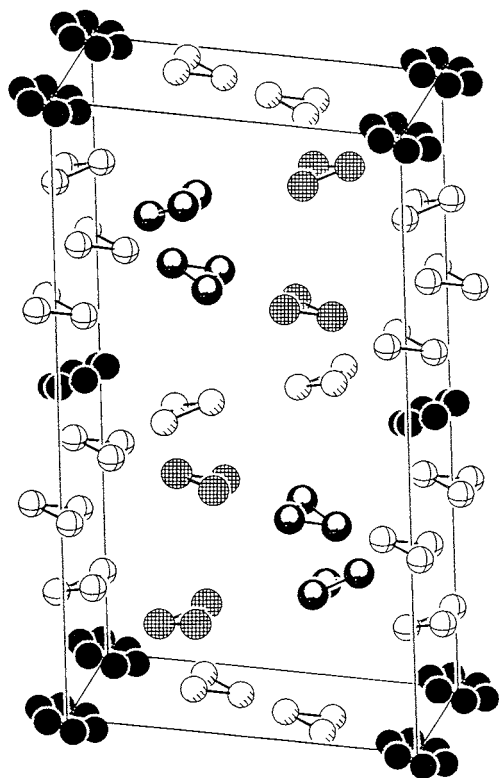
intention of the author to enter this (sometimes personal) fray: both Johnson *et al.*<sup>61d</sup> and Mann<sup>64</sup> consider that the Lentz and Marschall mechanism<sup>63</sup> is consistent with their own proposals. We merely present here our own results, which have a bearing on these matters.

In 1994, in an effort to gain some more understanding of the solid-state dynamics of cluster **2**, we reported<sup>51</sup> our investigations into the effect of temperature on the crystal structure of  $[\text{Fe}_3(\text{CO})_{12}]$ . In this study we found that there was a small but significant change in the molecular structure, leading to more symmetric carbonyl bridges at low temperature, such that at 100 K (the lowest temperature studied) the molecular structure was very close to idealised  $C_{2v}$ . In this paper we stated that 'in our experiments there was no trace, down to 100 K, of phase transitions to other crystal systems or to the non-centrosymmetric space group  $P2_1$ '. Unfortunately, further very recent and unpublished crystallographic studies using a diffractometer equipped with an area-detector have shown this statement to be incorrect, or rather misleading.

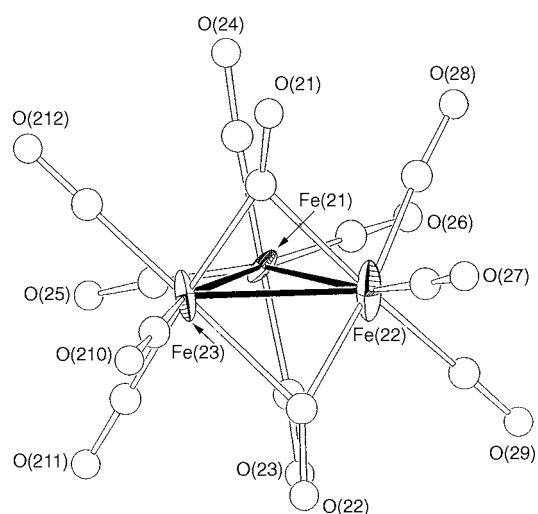
There is indeed a reversible phase change at  $\approx 210 (\pm 10)$  K to a second monoclinic phase with the same space group, but with a unit cell nine times the size of the room temperature unit cell. While this article is not a proper forum to present new and unpublished results in any great detail, we will present here a resumé of the most important aspects of this study because of its relevance to the topic under discussion.

The new unit cell is a super-cell of the room temperature unit cell, with a longer range order arising because of partial ordering in the orientation of the  $\text{Fe}_3$  triangles within the carbonyl cage. There are only small differences between the packing of the carbonyl ligands in the high- and low-temperature phases. In the low-temperature phase, the asymmetric unit consists of five independent molecules of  $[\text{Fe}_3(\text{CO})_{12}]$ , four complete molecules and one half-molecule. The four complete molecules reside in general positions, and the fifth half-molecule is situated about an inversion centre at the origin, as in the room-temperature phase. The arrangement of the metal triangles within the unit cell is shown in Fig. 5. Although not required by crystallographic symmetry, all of the four independent molecules in general positions show a 'Star of David' disorder in the metal atoms. This is not 50:50 as observed at room temperature, but varies from 95:5 to 65:35 for the four independent molecules. These results immediately provide categorical proof that the disorder observed at room temperature is *dynamic* in nature, as has long been suspected. The dynamic process involves the *effective* rotation of the  $\text{Fe}_3$  triangle about the pseudo-three-fold axis, which is of course entirely consistent with the  $^{13}\text{C}$  NMR data of Hanson *et al.*<sup>58</sup> mentioned above. The reader should be aware that we did not induce any mechanistic implications about the *pathway* of the metal triangle migration from our statement of *effective* rotation, merely that the only populated minima observed from the crystallographic results are those where the triangle is rotated by  $60^\circ$  (or  $120$  or  $180^\circ$ ).

Perhaps of more interest to the general reader is the light this new structural determination throws on the *molecular* structure of  $[\text{Fe}_3(\text{CO})_{12}]$ . Three of the four complete molecules in general positions have structures which are very similar to that described in our earlier low temperature study,<sup>51</sup> *i.e.* they approximate to idealised  $C_{2v}$  symmetry with essentially symmetric bridging carbonyls. The fourth complete molecule, shown in Fig. 6, has a less regular  $C_2$  structure with distinctly asymmetric carbonyl bridges. Moreover the  $\text{Fe}(\text{CO})_4$  unit is tilted relative to the  $\text{Fe}_3$  plane, which is typical of the orientation of the  $\text{M}(\text{CO})_4$  units found in the clusters with  $D_3$  symmetry, *e.g.*  $[\text{FeRu}_2(\text{CO})_{12}]$  (see below). This molecule may therefore be viewed as a 'snap-shot' of the Johnson  $C_2$  libration mode<sup>61</sup> mentioned above. In short, the structural flexibility of  $[\text{Fe}_3(\text{CO})_{12}]$ , long suspected in solution, has now been directly demonstrated in the solid phase.



**Fig. 5** The distribution of  $\text{Fe}_3$  triangles within the unit cell of  $[\text{Fe}_3(\text{CO})_{12}]$  from a structure determination at 174 K. The long axis is the monoclinic  $b$  axis, and each independent  $\text{Fe}_3$  triangle is drawn with a different graphic. Only the *major* components of each disordered triangle are shown, except for the molecule which resides on the inversion centre at the origin (drawn in solid black), where both components of the 50:50 disorder are shown



**Fig. 6** One of the five independent molecules of  $[\text{Fe}_3(\text{CO})_{12}]$  showing the distorted  $C_2$  symmetry (see text)

The bridge asymmetry found in the earlier room-temperature study of Cotton and Troup<sup>8</sup> is, we believe, more apparent than real, and partially an artefact of the refinement method. A comparison between refinement of a room-temperature X-ray diffraction data set ( $\theta_{\text{max}} = 30^\circ$ ) of  $[\text{Fe}_3(\text{CO})_{12}]$  using either isotropic or anisotropic thermal parameters for the light atoms, shows a considerable, and *statistically significant* variation in the Fe–C (bridging) distances for the two refinement methods. This is very likely to be due to the close proximity ( $\approx 0.25\text{--}0.35$  Å) of the half-carbon atoms for the two centrosymmetrically related images, a distance closer than the nominal resolution ( $\approx 0.7$  Å) of the experiment. The standard deviations obtained

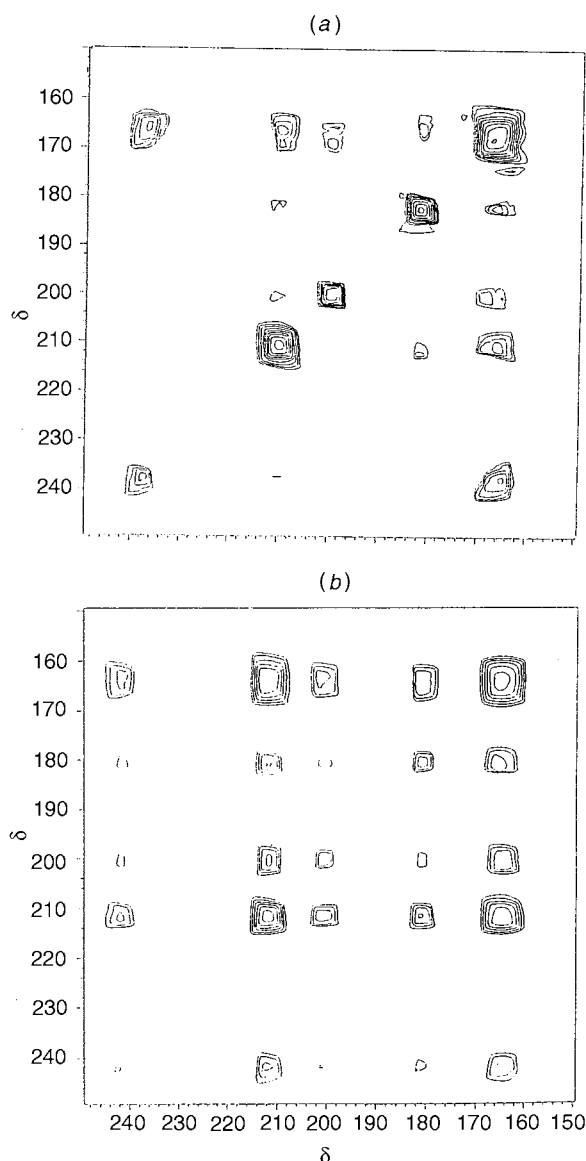
from the least-squares refinement of this disordered structure are almost certainly an underestimate, and as recently pointed out by Martin and Orpen<sup>24a</sup> the true e.s.d. (or standard uncertainty) is likely to be even higher. At best, we can say that the bridges show only a slight ( $\approx 0.1$  Å) asymmetry at room temperature.

We have also shown that similar temperature-induced phase changes occur for the related molecules  $[\text{Fe}_2\text{M}(\text{CO})_{12}]$  ( $M = \text{Ru}$ <sup>65</sup> **5** or  $\text{Os}$ <sup>66</sup> **6**) and for  $[\text{FeRu}_2(\text{CO})_{12}]$  **7**.<sup>65</sup> The structure of **6** at room temperature was first reported by Churchill and Fettinger.<sup>67</sup> There are two independent molecules in the asymmetric unit, which are similar but not identical, and which have the  $[\text{Fe}_3(\text{CO})_{12}]$  structure with a pair of slightly asymmetric bridging carbonyls spanning the Fe–Fe bond. Both molecules show a ‘Star of David’ disorder of the metal atoms, but in a ratio of 88:12 rather than 50:50 as seen for  $[\text{Fe}_3(\text{CO})_{12}]$ . The three-fold symmetry of the triangle is now broken by the presence of the Os atom. The second position is related to the primary image by a pseudo-inversion centre or two-fold axis, so that the Os atom is effectively rotated by  $180^\circ$ . On cooling to 223 K this secondary image disappears for both molecules, and the structure becomes perfectly ordered. The change is reversible, thus clearly showing the disorder to be dynamic in nature. On warming to 373 K a phase change occurred, giving a unit cell very similar in dimensions to  $[\text{Fe}_3(\text{CO})_{12}]$  at room temperature. This indicates the onset of a further dynamic process, but unfortunately the crystal proved unstable at this temperature, and no data could be collected to confirm this.

We were also able to obtain  $^{13}\text{C}$  CPMAS NMR data on crystalline solid **6**, which provided further information on this dynamic process.<sup>66</sup> The spectrum at 210 K was consistent with the solid-state structure, even to the extent that three of the four independent bridging carbonyl positions were resolved. On warming to 323 K the resonances become broader, indicating a possible chemical exchange in the solid. Solid-state  $^{13}\text{C}$  EXSY experiments (see Fig. 7) confirmed this, and several mechanisms were considered. The qualitative EXSY data precluded a direct  $180^\circ$  triangular jump, and it was concluded that the most likely mechanism was a staged process involving  $60^\circ$  jumps. We originally proposed<sup>66</sup> an activation barrier of  $\approx 42$  kJ mol<sup>-1</sup> for this process, but further recent quantitative EXSY data suggest that this is likely to be an underestimate.

The ruthenium analogue, cluster **5** is isomorphous and isostructural with cluster **6**, showing virtually identical behaviour.<sup>65</sup> Luckily, the high-temperature phase change now occurs at a slightly lower temperature, between 313 and 323 K, and the compound was sufficiently stable at this temperature to obtain a complete data set. Analysis of this data set showed that, in this phase, cluster **6** is isomorphous and isostructural with  $[\text{Fe}_3(\text{CO})_{12}]$  at room temperature, with a 50:50 disorder of the  $\text{Fe}_2\text{Ru}$  triangle sited at a crystallographic inversion centre. Conversely, lowering the temperature of the non-centrosymmetric phase to 223 K results in a perfectly ordered structure, as observed for the osmium analogue. The excellent quality of the crystal sample of **5** has yielded perhaps the most accurate determination to date of the  $[\text{Fe}_3(\text{CO})_{12}]$  structural archetype. As shown in Fig. 8, the two independent molecules are similar but not identical. In one of the independent molecules, the bridging carbonyls are only marginally asymmetric, with bridge asymmetries of 0.073 and 0.085 Å (e.s.d. 0.006 Å), while in the other molecule the bridge asymmetry is more marked (bridge asymmetries of 0.207 and 0.180 Å). In other aspects, the two molecules are essentially identical, even to the extent of their anisotropic displacement parameters, which are remarkably consistent.

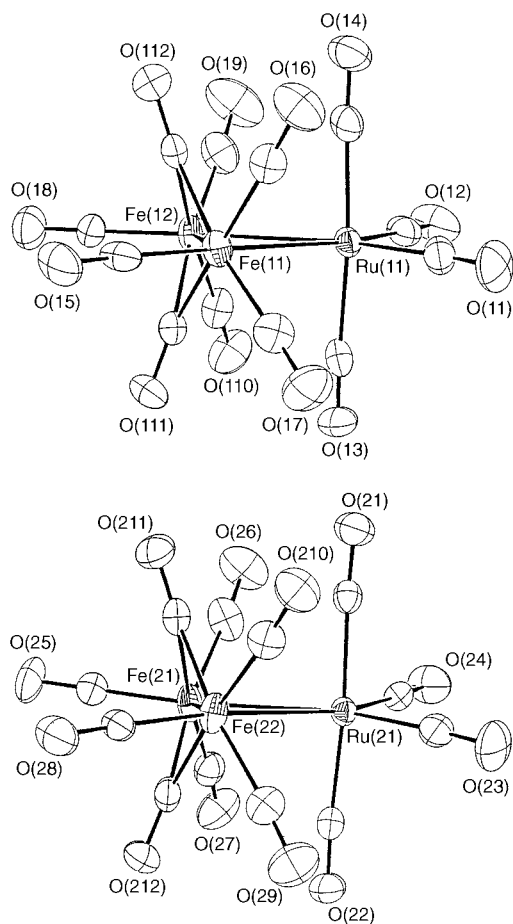
The structure of  $[\text{FeRu}_2(\text{CO})_{12}]$  **7** proved surprisingly interesting.<sup>65</sup> Earlier IR<sup>53,68</sup> and Mössbauer<sup>69</sup> studies had indicated an all-terminal structure, possibly with a  $D_3$  distortion. Venäläinen and Pakkanen<sup>70</sup> reported a room-temperature unit cell, but could not resolve the disorder. Again, we have shown that this



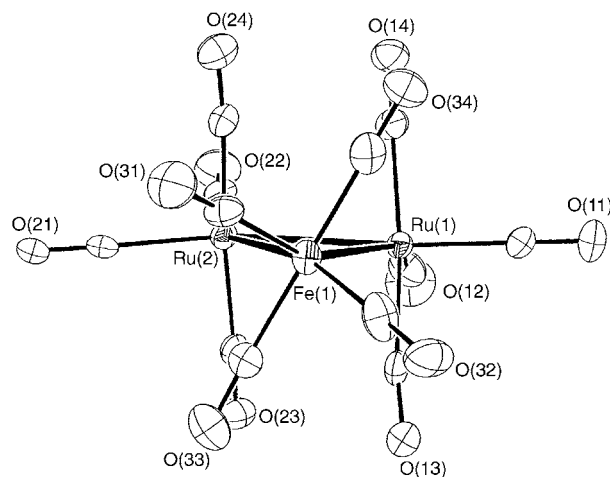
**Fig. 7** The  $^{13}\text{C}$  EXSY spectrum of  $[\text{Fe}_2\text{Os}(\text{CO})_{12}]$  taken at  $33^\circ\text{C}$  with mixing time (a) 0.02 and (b) 0.2 s

cluster undergoes a phase transition, from a centrosymmetric disordered phase at temperatures above 228 K, to a non-centrosymmetric phase below this temperature. The non-centrosymmetric phase is disordered in the metal atom positions immediately below the phase transition temperature, but is perfectly ordered at 173 K. The molecular structure of **7** is shown in Fig. 9. The cluster possesses approximate  $C_2$  symmetry, but the overall geometry is that of the  $D_3$  type structure. This structural type has been proposed as a key intermediate in the Ligand Polyhedral approach<sup>32</sup> to cluster fluxionality in  $[\text{M}_3(\text{CO})_{12}]$  clusters, and molecular mechanical calculations by Lauher<sup>56</sup> and Sironi<sup>57</sup> indicate that this geometry is very favourable. Until now however this geometry has only been observed in substitution derivatives, being particularly marked in bis- and tris-phosphine and -phosphite complexes, e.g.  $[\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2]$ .<sup>71</sup>

The structure at room temperature has also been resolved. The molecular structure of **7** is the same as at 173 K, but less accurately determined. More interesting is the nature of the disorder in the metal triangles, which is shown in Fig. 10. The  $\text{FeRu}_2$  triangle resides on a site of  $2/m$  crystallographic symmetry, so the disorder is more complex than found for the other systems we have investigated. There are two major 'Star of David' components at  $\approx 82\%$  populations, and a second set of four positions containing the remaining metal atom density.



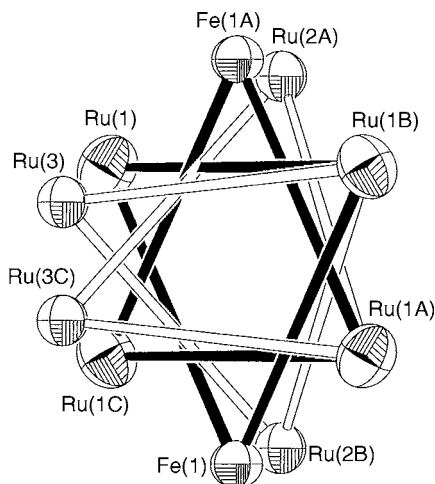
**Fig. 8** Structures of the two independent molecules  $[\text{Fe}_2\text{Ru}(\text{CO})_{12}]$  **5** at 223 K, showing their great similarity



**Fig. 9** Molecular structure of  $[\text{FeRu}_2(\text{CO})_{12}]$  **7** at 173 K

The two Ru atoms in these secondary images lie considerably out of the plane of the main 'Star of David' component, though the Fe atoms are coincident with the sites labelled Ru(1). We propose that these secondary images represent a pathway for the migration of the metal triangle from one of the 'Star of David' components to the other (i.e. an overall effective rotation of  $180^\circ$ ). Such a motion is necessary to convert the low-temperature ordered non-centrosymmetric phase to the disordered centrosymmetric room-temperature phase.

In all these phase transformations, the most significant atomic motions are suffered by the metal atoms. There is a small complementary motion of the carbonyl ligand polytope which is also required, but the atomic displacements involved are generally around 0.5 Å or less. The crystal lattice provides an



**Fig. 10** The extended 'Star of David' disorder in the metal atom positions of  $[\text{FeRu}_2(\text{CO})_{12}]$  **7** at ambient temperature

absolute frame of reference, making it possible to state categorically that the metal atoms *must* move. From the crystallographic evidence alone, it is impossible to determine whether the light atoms also move significantly, *i.e.* whether the whole molecule rotates *intact* within the lattice. The close intermolecular packing indicates this is unlikely {from our study at 173 K the average atomic volume for  $[\text{Fe}_3(\text{CO})_{12}]$  is only  $14.3 \text{ \AA}^3$ }, and our solid-state NMR results on  $[\text{Fe}_2\text{Os}(\text{CO})_{12}]$  also strongly suggest that the intact rotation does not occur.

Our recent investigations on the isocyanide-substituted cluster  $[\text{Ru}_3(\text{CO})_{11}(\text{CNBu}^t)]$  **8** are of great relevance to this question. The room-temperature crystal structure of complex **8** was first reported in 1981 by Bruce *et al.*<sup>52a</sup> in which they noted that there was a 'Star of David' disorder (86:14%) in the ruthenium atoms. The structure has an axial isocyanide ligand, with a marked overall  $D_3$  distortion of the cluster geometry. We have recently<sup>72</sup> conducted a re-examination of the crystal structure of this cluster, and we find that at 100 K the disorder in the metal positions effectively disappears, but it re-appears at room temperature. This result of course indicates that the disorder is dynamic in origin, but much more importantly it also demonstrates beyond doubt, that (at least in this case) the ligand polytope does *not rotate* in the lattice, but remains relatively fixed. The isocyanide ligand, which is electronically similar to a carbonyl group, provides a 'marker' for one of the ligand sites, and a close examination of the disorder in the light atom positions indicates that the ligating C and the N atom move by only  $\approx 0.5\text{--}0.9 \text{ \AA}$ . The barrier to this dynamic process is evidently quite low, and it must be accomplished by an *effective* rotation of the  $\text{Ru}_3$  triangle by  $\approx 60^\circ$  about its pseudo-three-fold axis. In this case however no 'out-of-plane' metal atom positions were observed.

In conclusion, we have convincingly demonstrated that the metal triangle disorder observed in  $[\text{Fe}_3(\text{CO})_{12}]$ ,  $[\text{Fe}_2\text{M}(\text{CO})_{12}]$  ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ),  $[\text{FeRu}_2(\text{CO})_{12}]$  and  $[\text{Ru}_3(\text{CO})_{11}(\text{CNBu}^t)]$  arise from dynamic phenomena. There is a complex phase change on cooling  $[\text{Fe}_3(\text{CO})_{12}]$  below 210 K, and clearly our earlier conclusions<sup>51</sup> regarding the low-temperature structure are of limited value, since this previous description must represent an *average* of several structures. Likewise, other conclusions based on this earlier report,<sup>51</sup> *e.g.* a recent interpretation<sup>73</sup> of the variable-temperature Mössbauer spectra of  $[\text{Fe}_3(\text{CO})_{12}]$  may also need to be re-assessed in the light of the new results presented here.

### Structural Flexibility in Heteroplatinum Clusters

Another area of dynamic clusters we have explored is that of small heteroplatinum clusters.<sup>74</sup> Although these species show the normal ligand migration processes common to other

transition-metal clusters they also display a certain flexibility in the metal skeleton. Thus we find that the normal electron counting rules<sup>75</sup> are not always applicable, and moreover for the same formal electron count, a number of different metal skeletal geometries are possible.

For instance for 60 cluster valence electron (CVE) tetranuclear transition-metal species, a *tetrahedral* metal skeleton is predicted, and this is observed in a multitude of examples. However with an  $\text{M}_3\text{Pt}$  ( $\text{M} = \text{Fe}$ ,  $\text{Ru}$  or  $\text{Os}$ ) metal skeleton, we have found that as well as the tetrahedral geometry, others are found with almost equal frequency. Thus the cluster  $[\text{Ru}_3\text{Pt}(\mu\text{-H})(\mu_3\text{-COMe})(\text{CO})_{10}(\text{PPr}^i_3)]$  **9** has an almost regular tetrahedral geometry (allowing for the differing bridging ligands) in the solid state, and in solution the rapid migration of the hydride ligand results in an equilibration of all the Pt–Ru bonds on the NMR time-scale. However, on the much shorter EXAFS time-scale, the irregularity of the Pt–Ru bonds in **9** is still evident in solution.<sup>76</sup>

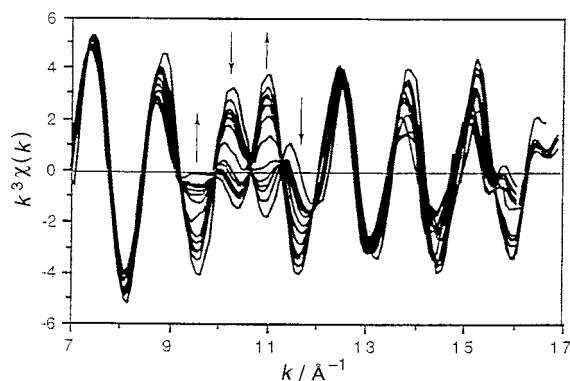
The related allyl species  $[\text{Ru}_3\text{Pt}(\mu\text{-H})(\mu_3\text{-CMeCHCMe})(\text{CO})_9(\text{PPr}^i_3)]$  **10** also has a somewhat distorted tetrahedral metal skeleton.<sup>77</sup> Surprisingly, although **10** possesses a pseudo-mirror plane in the solid state, as determined by the X-ray diffraction study, and also an effective mirror plane on the NMR time-scale, the two Pt–Ru bonds related by the pseudo-mirror plane are not equivalent [ $2.746(1)$  and  $2.959(1) \text{ \AA}$ ], and there seems no obvious reason for this. This discrepancy in the instantaneous structure of **10** is also present in solution according to the EXAFS data, and indeed also shows up in the solid-state structure<sup>78</sup> of the derivative  $[\text{Ru}_3\text{Pt}(\mu\text{-H})(\mu_3\text{-CMeCHCMe})(\text{CO})_8(\text{PPr}^i_3)_2]$  where a phosphine ligand replaces an axial carbonyl on one of the pairs of 'equivalent' ruthenium atoms. Solid-state packing effects cannot therefore account for this observation, and we view this geometry as a step on the way to the other commonly observed metal skeletal geometry, namely the butterfly  $\text{M}_3\text{Pt}$  geometry.

This latter geometry is conceptually derived from the tetrahedron by the elongation and breaking of one of the M–Pt bonds. The non-bonding M–Pt distance is of the order of  $\approx 3.5 \text{ \AA}$  or longer. It is for this reason that the structure of **10** is interesting. Examples of the butterfly geometry include  $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)_2]$  **11**<sup>79</sup> and the alkyne cluster  $[\text{Ru}_3\text{Pt}(\mu_3\text{-PhCCPh})(\text{CO})_{10}(\text{PPr}^i_3)]$ .<sup>77</sup> The latter species has a long non-bonding Pt–Ru distance of  $4.037(1) \text{ \AA}$ . A further point along this structural coordinate is provided by the species  $[\text{Ru}_3\text{Pt}(\mu\text{-CO})_2(\text{CO})_{10}(\text{PPr}^i_3)_2]$  **12**<sup>78</sup> and the related species  $[\text{Os}_3\text{Pd}(\mu\text{-CO})_2(\text{CO})_{10}\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$  **13**.<sup>78</sup> These both have a *planar* butterfly skeleton. All the examples quoted above are formally 60 CVE clusters.

Cluster **12** can be made in high yield, and some reactions have been studied.<sup>78</sup> Treatment with dihydrogen affords as the principal product the 60 CVE cluster  $[\text{Ru}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)_2]$  **14**. Cluster **14** is an analogue of the osmium–platinum species **11**, but interestingly **14** has a slightly distorted tetrahedral metal skeleton, in contrast to the butterfly geometry of **11**. Thus even for apparently very similar clusters, the dominating structures in the solid state may be substantially different. In solution however it has been shown that both **11** and **14** exist as isomers in rapid exchange on the NMR time-scale. The process of isomer exchange almost certainly corresponds to a flexing of the metal skeletal geometry, *i.e.* we can say that this butterfly is *flapping its wings* rapidly in solution on the NMR time-scale. Such a process of butterfly  $\rightleftharpoons$  tetrahedral interconversion was also proposed to account for the carbonyl fluxionality of  $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{11}(\text{PR}_3)]$  some nine years ago,<sup>80</sup> before much of the structural evidence presented here was available.

Perhaps the most well characterised metal-skeletal rearrangement of  $\text{M}_3\text{Pt}$  clusters is that which occurs in the reversible tautomerisation of the hydrido-alkynyl cluster  $[\text{Ru}_3\text{Pt}(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-CCBu}^t)(\text{CO})_9(\text{dppe})]$  **15** to the vinylidene species  $[\text{Ru}_3\text{Pt}\{\mu_4\text{-}\eta^2\text{-CCBu}^t(\text{H})\}(\text{CO})_9(\text{dppe})]$  **16** ( $\text{dppe} = \text{Ph}_2\text{-}$





**Fig. 11** The time-dependent Pt L<sub>III</sub>-edge EXAFS spectra of [Ru<sub>3</sub>Pt(μ-H)(μ<sub>4</sub>-η<sup>2</sup>-CCBu)(CO)<sub>9</sub>(dppe)] **15** in thf solution over a 12 h period

PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>). This involves a hydride transfer to the β-carbon of the alkynyl ligand, and this migration is accompanied by a change in the metal geometry from a spiked-triangle in **15** to a non-planar butterfly in **16**, as was shown by the crystal structures of these complexes.<sup>81</sup> Mechanistic studies indicate that this process involves an intramolecular hydrogen shift, not a reversible deprotonation-protonation mechanism. Studies using the deuterio derivative of **15** show<sup>82</sup> an inverse kinetic deuterium isotope effect. This is quite common in reactions where there is a reversible hydrogen transfer from a heavy metal atom to a light atom, and in the present context it implies that there is substantial C–H (vinylidene) bonding in the transition state. The rate constants for the fluxional rotation of the Pt(diphosphine) unit in several derivatives of **15** follows the same general order as the rate constants for tautomerisation. This is consistent with the view that the rotation process provides an important contribution to the activation barrier for tautomerisation.<sup>82</sup>

We have followed the change in metal geometry which accompanies this tautomerisation process directly in solution by means of Pt (L<sub>III</sub>) EXAFS spectroscopy.<sup>83</sup> The Pt atom is a very suitable probe, since there is one Pt–Ru bond present in **15** (with two rather long non-bonded contacts), while there are two essentially equivalent Pt–Ru bonds in **16**. The time-dependent EXAFS spectra of a solution of **15** in tetrahydrofuran (thf) are shown in Fig. 11. These display clear isosbestic points, demonstrating that cluster **15** converts directly to cluster **16** without any detectable intermediates.

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