Evidence for the Pathway of Metal Triangle Rotation in Solid $M_3(CO)_{12}$: Variable-Temperature X-ray Structures of $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$

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Summary: $Fe_2Ru(CO)_{12}$ has the $Fe_3(CO)_{12}$ structure, while $FeRu_2(CO)_{12}$ has an all-terminal D_3 structure: the metal disorder in $FeRu_2(CO)_{12}$ at high temperatures provides direct evidence for the pathway of metal triangle rotation in the solid state.

The solid-state and solution structures and dynamic behavior of the simple metal carbonyls $M_3(CO)_{12}$ of the iron triad remain a subject of ongoing interest,[1,2] even though these molecules are some of the earliest characterized examples of carbonyl cluster compounds. We have recently demonstrated[2] that the metal disorder in $Fe_2Os(CO)_{12}$, initially reported by Churchill and Fettinger,[3] arises from a dynamic process involving the rotation of the metal triangle in the solid state. Variable-temperature solid-state ^{13}C MAS NMR spectra strongly indicated a mechanism whereby the metal triangle rotates within a relatively rigid carbonyl manifold. However, the exact pathway of the 180° rotational motion of the Fe_2Os triangle was not established.

Although mixed-metal clusters $M_3(CO)_{12}$ (M = Fe, Ru, Os) having all possible metal permutations except $FeRuOs(CO)_{12}$ are known,[4] the only structural determination to date has been for $Fe_2Os(CO)_{12}$.[2,3] The structures of a number of phosphine derivatives of the Fe−Ru species $Fe_2Ru(CO)_{12}$ (**1**) and $FeRu_2(CO)_{12}$ (**2**) have been determined,[4,5] and a combination of IR[6] and Mössbauer[7] spectroscopic studies suggested that **1** has the $Fe_3(CO)_{12}$ structure, while **2** has an all-terminal CO arrangement with a possible D_3 distortion. Venäläinen and Pakkanen[5] have reported a unit cell for **2** but indicated that the structure was disordered, and no satisfactory resolution of the molecular structure was possible.

Herein we report that the disorder problems in both **1** and **2** have been resolved. Moreover, at sufficiently low temperatures both structures become perfectly ordered.[13] At and below 313 K, cluster **1** is isomorphous and isostructural with $Fe_2Os(CO)_{12}$,[2,3] with two independent molecules in the monoclinic space group *Pn*. At 223 K the metal atoms are ordered, and raising the temperature causes a partial "Star of David" disorder to appear. Above 313 K, cluster **1** undergoes a phase transition to $P2_1/n$ with a halving of the *b* axis and becomes isomorphous and isostructural with $Fe_3(CO)_{12}$. The disorder of the metal atoms is now 50:50, as required by the inversion center. This observation confirms earlier suspicions[2,3] of the very close structural and crystallographic relationship between these species and provides yet further evidence that the observed disorder[1a−c] in $Fe_3(CO)_{12}$ itself is dynamic in nature.[1k−m]

Perhaps of greater potential interest is the behavior of **2**. At 173 K, the molecule packs in the noncentrosymmetric orthorhombic space group *C*2*cb*, with a *c* axial length of 22.639(4) Å. The asymmetric unit, shown in Figure 1, comprises an ordered single molecule of $FeRu_2(CO)_{12}$ residing in a general position. Cluster **2** 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[8] to fluxional motion of $M_3(CO)_{12}$, and molecular mechanical calculations by Lauher[9] and more recently by Sironi[10] indicate that this geometry is very favorable. Indeed, on the basis of steric arguments alone, it is predicted[9,10] to be the ground-state structure for M = Fe, Ru, Os. To date, however, the distortion toward D_3 geometry has only been ob-

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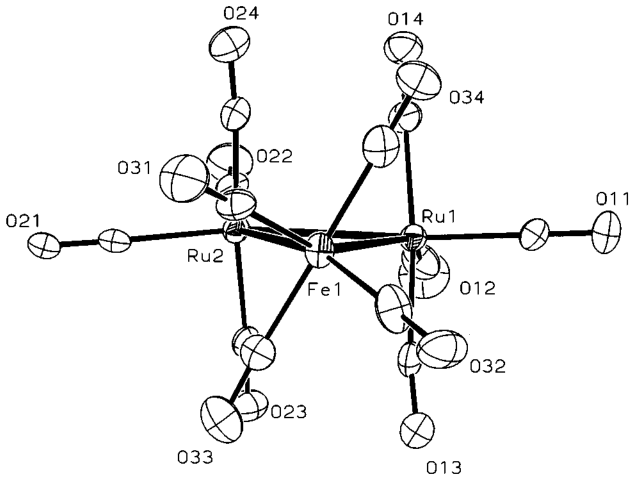

Figure 1. Molecular structure and atomic labeling scheme for $FeRu_2(CO)_{12}$ (**2**) at 173 K. Relevant metrical parameters are as follows: bond distances (Å): Fe(1)−Ru(1) = 2.775(2), Fe(1)−Ru(2) = 2.763(2), Ru(1)−Ru(2) = 2.8059(9), Fe−C 1.764(11)−1.833(11), Ru−C = 1.923(9)−1.968(10). Torsion angles (deg): C(12)−Ru(1)−Ru(2)−C(22) = −32.7(4), C(13)−Ru(1)−Ru(2)−C(23) = −36.3(4), C(14)−Ru(1)−Ru(2)−C(24) = −35.4(4), C(13)−Ru(1)−Fe(1)−C(33) = −38.8(4), C(14)−Ru(1)−Fe(1)−C(34) = −36.4(4), C(11)−Ru(1)−Fe(1)−C(33) = −29.0(5), C(21)−Ru(2)−Fe(1)−C(31) = −31.2(5), C(23)−Ru(2)−Fe(1)−C(33) = −36.1(4), C(24)−Ru(2)−Fe(1)−C(34) = −37.8(5).

served in substitution derivatives,[11] being particularly marked in bis- and tris(phosphite) and bis- and tris(phosphine) complexes, e.g. $Ru_3(CO)_{10}(PPh_3)_2$.[11b] Cluster **2** thus provides the first example of the D_3 structure for a homoleptic $M_3(CO)_{12}$ carbonyl.

As the temperature is raised up to ~228 K, secondary images of the metal triangle appear, with no apparent change in the space group. These secondary images are shown in Figure 2 for the structural determination at 223 K. The major component triangle A and triangle B are coplanar and are rotated by 180° relative to each other. The remaining triangle C lies distinctly out of the plane of the other two.

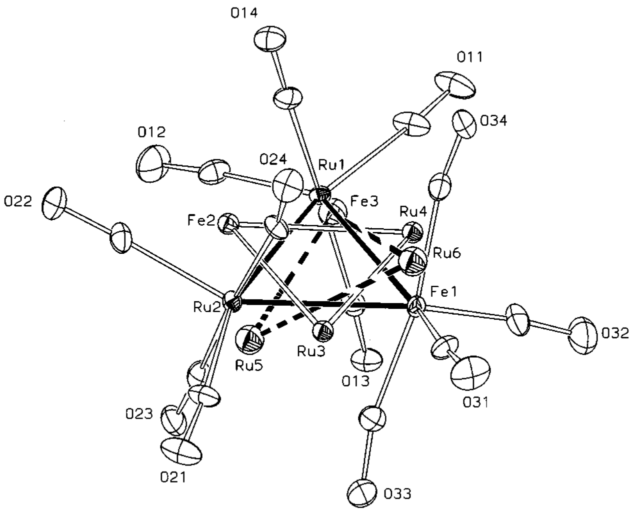

Figure 2. Molecular structure of $FeRu_2(CO)_{12}$ (**2**) at 223 K, showing the disordered metal triangles: triangle A (solid line), population 86%; triangle B (open line), population 9%; triangle C (dashed line), population 5%.

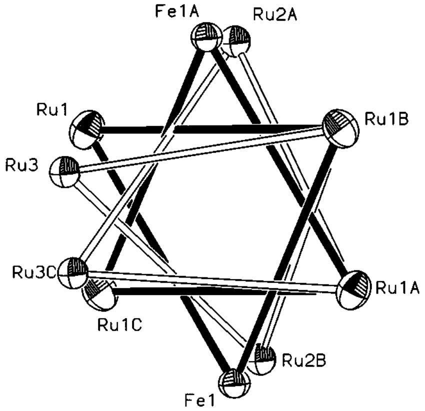

Figure 3. View of the extended "Star of David" disorder in the metal atom positions of $FeRu_2(CO)_{12}$ (**2**) at 291 K, illustrating the proposed pathway for metal triangle rotation. The sites marked as Ru(1), Ru(1A), Ru(1B), and Ru(1C) coincide with the sites of the Fe atoms for the minor component. For clarity, only two of the four minor component triangles are shown: the other four Ru(2) and Ru(3) positions are related centrosymmetrically to those illustrated.

Above 228 K a phase transition occurs, with the *c* axial length being halved.[13] The new space group is the centrosymmetric *Ccmb*, and the molecule of **2** now lies on a site of 2/*m* crystallographic symmetry. Due to the higher site symmetry, the disorder is more complex. Nevertheless, it has proved possible to deconvolute the *molecular* structure of **2**. It closely resembles that determined for **2** at the lower temperatures, albeit with a lesser accuracy. The most interesting facet of the crystal structure, however, concerns the extended "Star of David" disorder in the metal sites. This is illustrated in Figure 3, where the major component triangles (Fe(1)−Ru(1)−Ru(1B) and Fe(1A)−Ru(1A)−Ru(1C)) are shown together with two of the four (centrosymmetrically related) minor component triangles. The refined population of the major component is 81.4(7)% at 291 K.

We believe that the disorder shown in Figure 3 represents a pathway for the migration of the metal triangles in $M_3(CO)_{12}$ clusters in general and for $Fe_2M(CO)_{12}$ (M = Ru, Os) in particular. The observed disorder in the latter (ref 2 and above) implies an overall 180° rotation about the triangular 3-fold axis. Figure 3 indicates that this may occur in steps of 60°, the Fe(1) atom migrating via the sites labeled Fe(1) → Ru(1A) → Ru(1B) → Fe(1A). This process involves substantial out-of-plane displacements for the corresponding Ru atoms. There is strong evidence from the metal atom anisotropic thermal parameters of both $Fe_3(CO)_{12}$[1c,e,f] and $Fe_2Os(CO)_{12}$[2,3] that a low-energy librational motion about the molecular C_2 axis is possible. Furthermore, molecular mechanics calculations by Sironi[10] indicate this to be a very soft mode. Since the packing in $M_3(CO)_{12}$ clusters is based on a tight

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intermolecular CO···CO interlocking,[1d,g] it is reasonable to assume that for low-energy dynamic processes only a small relative motion of the CO groups is permissible in the solid state. On this basis, the *molecular* structure of the 60 and 120° intermediate forms of **2** may be deduced as being of C_2 geometry, with a pair of bridging (or semibridging) carbonyls across the Ru−Ru bond. We note that an earlier variable-temperature NMR study by Hanson *et al.*[1k] on $Fe_3(CO)_{12}$ has been interpreted in terms of a 60° rotation of the metal triangle about the 3-fold axis. Due to the degeneracy of the Fe_3 triangle, a 180° rotation involving 60° steps with out-of-plane intermediates is also consistent with Hanson's results.

In conclusion, we have demonstrated that a phase change from a noncentrosymmetric and ordered structure at low temperature to a disordered centrosymmetric phase at higher temperatures occurs for both $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$, albeit involving different space groups. This has also been previously suggested for $Fe_2Os(CO)_{12}$[2] and thus appears to be general for molecules of this type. The phase change involves a halving of one of the axes at the higher temperature and can easily be rationalized in terms of the packing of the metal triangles.[3] In **2**, for instance, the triangles are packed in layers along the *c* axis in a zigzag AA′BB′ arrangement, which becomes an ABAB arrangement at high temperatures because of the 50:50 disorder. A reexamination of the structure of $Fe_3(CO)_{12}$ at temperatures much lower than those in our earlier study[1c] may reveal a similar behavior.

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Supporting Information Available: Listings of crystal data and refinement details, positional and thermal parameters, and bond distances and angles for **1** and **2** at various temperatures (44 pages). Ordering information is given on any current masthead page.

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(13) Single crystal data were collected on CAD4 (Glasgow, Bologna) and Siemens P4 (Glasgow) diffractometers, equipped with low-temperature devices. For $Fe_2Ru(CO)_{12}$ data were collected at 223 K (Glasgow), 298 K (Glasgow), 313 K (Bologna), and 323 K (Bologna). For $FeRu_2(CO)_{12}$ data were collected in Glasgow (Siemens P4 unless otherwise indicated) at 173, 223, 228, 233, 243, 291 (CAD4), and 293 K. The phase-transition temperature for $FeRu_2(CO)_{12}$ was established from axial photographs taken at 3 K temperature intervals in the range 223−238 K. The data sets at 228 and 233 K were too close to the transition temperature to be considered reliable, in view of the temperature instability (±5 K) of the Siemens P4. Two samples of both $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ were used. Details of all data sets are given in the Supporting Information. Data were corrected for absorption either by semiempirical ψ-scans[12a] or by the method of Stuart and Walker.[12b] All atoms were allowed anisotropic thermal motion except for the low-occupancy disordered metal positions and the C atoms in **1** at 323 K . Refinement on F^2 was by full-matrix methods using SHELXL93.[12c] The electron density associated with the disordered metal positions was examined carefully using Fourier contour maps to ensure that spurious features were not included in the analyses. In all cases the disordered site positions corresponded to spherical or near-spherical maxima in the electron-density function, and all could be successfully refined as partially occupied metal atoms. All analyses were of similar quality; representative details are given below. $\mathbf{Fe_2Ru(CO)_{12}}$: 223 K, $a = 8.3068(8)$ Å, $b = 22.468(3)$ Å, $c = 8.8830(13)$ Å, $\beta = 96.531(9)°$, monoclinic, space group Pn, 3505 independent data, 489 parameters, $R_w(F^2) = 0.0633$, $R_F = 0.0239$ for 3425 data with $I > 2\sigma(I)$; 323 K, $a = 8.400(5)$ Å, $b = 11.420(5)$ Å, $c = 8.943(5)$ Å, $\beta = 96.84(5)°$, monoclinic, space group $P2_1/n$, 1454 independent data, 185 parameters, $R_w(F^2) = 0.1874$, $R_F = 0.0648$ for 1293 data with $I > 2\sigma(I)$. $\mathbf{FeRu_2(CO)_{12}}$: 173 K, $a = 11.6326(12)$ Å, $b = 12.8789(13)$ Å, $c = 22.639(4)$ Å, orthorhombic, space group $C2cb$, 2698 independent data, 246 parameters, $R_w(F^2) = 0.0844$, $R_F = 0.0357$ for 2394 data with $I > 2\sigma(I)$; 223 K, $a = 11.6381(11)$ Å, $b = 12.9718(12)$ Å, $c = 22.816(5)$ Å, orthorhombic, space group $C2cb$, 2848 independent data, 259 parameters, $R_w(F^2) = 0.1004$, $R_F = 0.0420$ for 2270 data with $I > 2\sigma(I)$; 291 K, $a = 11.6581(3)$ Å, $b = 13.1117(14)$ Å, $c = 11.5085(8)$ Å, orthorhombic, space group $Ccmb$, 813 independent data, 105 parameters, $R_w(F^2) = 0.1134$, $R_F = 0.0387$ for 689 data with $I > 2\sigma(I)$.