Relationship between CO Fluxionality of Carbonyl Clusters in Solution and Thermal Motion in the Solid State

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Using difference vibrational parameters obtained from solid state X-ray data for $[Ph_4P]_2[Rh_6C(CO)_{13}]$ and evaluated along different internuclear directions, it has been possible to show for $[Rh_6C(CO)_{13}]^{2-}$ that there is extensive vibrational motion of the carbonyl ligands around the Rh_4-equatorial plane (Rh 1, 3, 5, 6); this behaviour in the solid state is exactly in accord with the lowest energy CO migrational pathway found by previous n.m.r. studies in solution.

Extensive use has already been made of anisotropic vibrational ('thermal') parameters as obtained from X-ray single crystal studies of organic molecules for predicting and rationalizing reaction pathways.[1] Recently similar approaches were used to investigate low-spin–high-spin dynamic Jahn–Teller distortions in solid Cu^{II} and Fe^{III} complexes[2,3] as well as magnetic and phase transitions in niobium clusters.[4] However, because of the complexity and lack of accurate X-ray measurements, such an approach has not been so far applied to transition metal carbonyl clusters, although Muetterties[5] previously suggested that X-ray crystallography could provide information about low energy intramolecular rearrangement processes.

We now provide the first evidence from solid state X-ray data of $[Rh_6C(CO)_{13}]^{2-}$ (a structure previously reported[6]), which shows that there is a strongly correlated vibrational motion of seven carbonyl ligands in the Rh_4-equatorial plane [Rh 1, 3, 5, 6, see Figures 1 and 2(a)], while the other carbonyls in the other two equatorial planes (Figure 2b,c) are much less mobile and their motion is uncorrelated. This is

exactly in accord with previous fluxional n.m.r. studies in solution on the same species.[7]

In order to make a reliable interpretation of the vibrational motion it was necessary to undertake a new data collection on

Table 1. Mean values of $|\Delta_{A,B}|$ ($\times 10^4$ Å^2) computed along interatomic directions for the three octahedral equators.

	Eq(1)[a]	Eq(2)[b]	Eq(3)[c]
C_{CO}–C carbide	182	98	108
C_{CO}–outer Rh-atoms[d]	207—205	50—61	66—64
C_{CO}–C_{CO}[e]	46	159	154[f]

[a] See Figure 2(a). [b] See Figure 2(b). [c] See Figure 2(c). [d] $\bar{\Delta}$ Values refer to the two Rh-atoms above and below each equatorial plane. [e] $\bar{\Delta}$ values refer to interatomic directions between consecutive C-atoms in each equatorial plane ('CO-belt'). [f] C(1) and C(2) bonded to Rh(1) but not coplanar with Eq(3) were included [without C(1) and C(2) $\bar{\Delta}$ = 95].
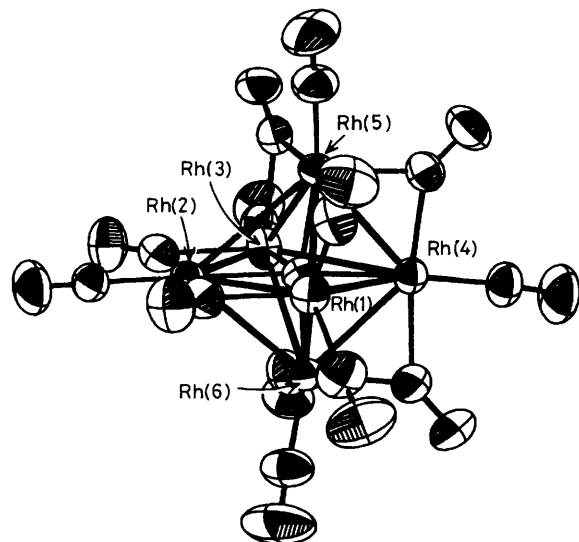
Figure 1. ORTEP drawing of $[Rh_6C(CO)_{13}]^{2-}$ showing 50% thermal ellipsoids.

crystals of $[Rh_6C(CO)_{13}]^{2-}$. The quality of the crystals permitted collection at room temperature of a much larger and accurate data set than the one previously used.†

The method used for the evaluation of correlated vibrational motions between bonded or non-bonded atom pairs is based on the 'rigid body' test,[8] which is a generalization of the Hirshfeld 'rigid bond' postulate.[9] The basic assumption is that the difference between mean square displacements of pairs of atoms, as derived from anisotropic vibrational parameters, evaluated along internuclear directions $[\Delta_{A,B} = z^2_{a,b} - z^2_{b,a}]$ within the same molecule should approach zero if the atom pair(s) behaves as a rigid body in its motion. When this condition is not satisfied information about the relative motion of one atom (or of groups of atoms) with respect to other parts of the molecule can be obtained.[8] Using this approach[10] it was possible to calculate mean values of $\Delta_{A,B}$, ($\bar{\Delta}$ for several different reference points within the molecule. The results are shown in Table 1 with respect to the three octahedral equators shown in Figure 2(a,b,c).

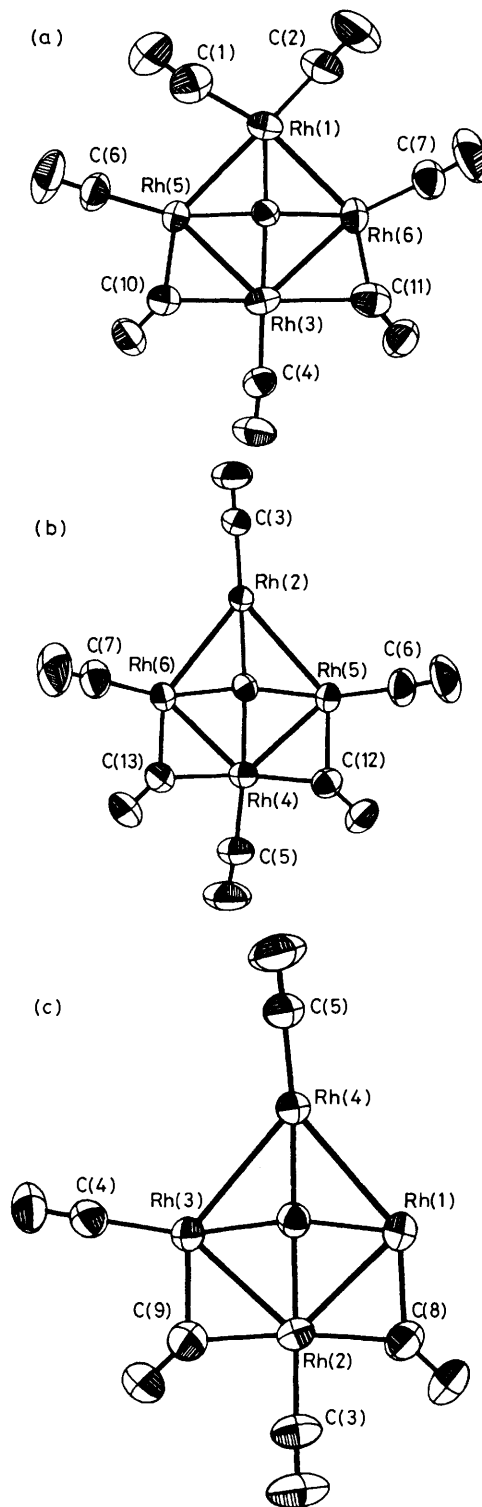The most useful reference points are the metal atoms above and below each equatorial plane and the central carbide atom.

Figure 2. ORTEP drawings of the three equatorial planes of $[Rh_6C(CO)_{13}]^{2-}$ showing 50% thermal ellipsoids.

It can be seen that the carbonyls in one equatorial plane, Eq(1), undergo more extensive motion than those in the other two equatorial planes. Furthermore $\bar{\Delta}$ values computed along interatomic directions joining consecutive C-atoms within each equatorial plane ('CO-belt') show that the vibrational

motion of the CO-groups is strongly correlated only in one equatorial plane, Figure 2(a).

These solid state results are in exact accord with the lowest energy carbonyl migration previously found using n.m.r. methods in solution.[7] However it should be emphasized that our vibrational motion analysis does not implicate actual occurrence of fluxionality processes in the solid state of the kind postulated from solid state n.m.r. data on some metal carbonyl clusters by Hanson *et al.*[11] Nonetheless these *X*-ray data support a preferred movement of the CO ligands around a fixed metal octahedron rather than movement of the metal framework within the carbonyl envelope.

Such an approach offers a powerful link between thermal motion in the solid state and preferred migrational pathways in solution.

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