On the Relationship Between Crystallographic and Spectroscopic Evidence of Dynamic Processes in the Solid State. The Case of the Osmium Cluster 'Helicopters'†

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The reorientational motion of the C_6H_6 and CH_2CH_2 ligands in $[Os_3(CO)_8(\eta^2\text{-}CH_2CH_2)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$, evidenced in the solid by ^{13}C cross-polarization magic angle spinning n.m.r. spectroscopy, has been examined by means of the atom–atom potential energy method. The results show that the motion of the ethene fragment is correlated to that of the benzene fragment and controlled primarily by intramolecular energy terms, while the crystal packing does not create relevant intermolecular barriers. The possibility of similar reorientational processes in solid $[Os_3(CO)_7(\mu_3\text{-}\sigma:\eta^2:\sigma\text{-}C_2Me_2)(\eta^6\text{-}C_6H_6)]$ has also been explored and the results compared with the *X*-ray crystallographic indication of extensive in-plane librational motion of the C_6H_6 ligand. In neither case does reorientation of the $Os(CO)_3$ groups appear to be a possibility.

In previous papers we have shown that information on the occurrence of reorientational processes of molecular fragments bound to metal centres in solid organometallic compounds is contained in the results of 'conventional' *X*-ray diffraction studies.[1–3] In the cases of the *cis* and *trans* isomers of $[Fe_2(CO)_4(C_5H_5)_2]$[1] and of the species $[Cr(C_6H_6)_2]$, $[Cr(CO)_3(C_6H_6)]$, and $[Cr(CO)_3(C_6H_5Me)]$[2] a correlation between the available spectroscopic data [^1H wide-line n.m.r., ^{13}C cross-polarization magic angle spinning (c.p.m.a.s.) n.m.r., Raman, quasi-elastic neutron scattering, *etc.*] and the diffraction experiments could be made. It was shown that information of dynamic nature can be extracted from the anisotropic displacement parameters (atomic 'thermal' parameters, hereafter a.d.p.) by means of thermal motion analysis based on the translation, libration, and correlation tensors approach (TLS approach),[4] when diffraction data of reasonable accuracy and possibly collected at different temperatures are available.

Furthermore, the control exerted by the crystal packing on the reorientational motions can be studied by semiempirical calculations based on the atom–atom potential-energy method.[5–7] It is worth recalling that neither method requires special treatment of the diffraction data, rather use is made of the entire information yielded by *X*-ray or neutron diffraction experiments.

In this paper we apply such methods to the trinuclear osmium 'helicopters' $[Os_3(CO)_8(C_2H_4)(C_6H_6)]$ (**1**)[8] and $[Os_3(CO)_7(C_2Me_2)(C_6H_6)]$ (**2**)[9] which have been shown by n.m.r. techniques to be remarkably non-rigid both in solution and in the solid state.[8,10] The aim of this study is two-fold: first, a critical examination of the rearrangement mechanism proposed for (**1**) on the basis of the n.m.r. experiments, and secondly, a test of the 'prediction' capability of the methods based on thermal motion analysis and potential-energy barrier calculations on the occurrence of dynamic processes for (**2**) in the absence of solid-state spectroscopic information.

Methodology

As previously shown[1,2] the potential-energy barriers associated with molecular-fragment reorientational processes can be evaluated by means of the atom–atom potential-energy method.[5] The method is well documented and will not be described in detail. The crystal is supposed to be made up of discrete molecular units, held together by van der Waals interactions without any contribution of an ionic nature.

The potential energy (p.e. hereafter) is thus obtained as a simple function of the interatomic separations in the crystal by summing repulsive and attractive terms in the function (1)

$$\text{p.e.} = \Sigma_i \Sigma_j A e^{-Br_{ij}} - C r_{ij}^{-6} \qquad (1)$$

where r_{ij} is the distance between each atom of the reference molecule and the atoms of the surrounding molecules distributed according to crystal symmetry. A cut-off distance of 10 Å was chosen to ensure convergence of the summation. The values of the coefficients *A*, *B*, and *C* for O, C, and H atoms were taken from the current literature.[11] The metal-atom contribution was not taken into account. We have previously[1,7] demonstrated that neglect of this contribution in metal-atom clusters or complexes affects only the values of the p.e. minima and has no effect on the height of the p.e. barriers which are dominated by the outer O, C, and H atoms, given that the metal core is totally encapsulated within the ligand envelope. It should be clear, however, that while atom–atom p.e. calculations can provide reliable estimates of the p.e. of a molecule in crystals of organic substances,[6,12] this can never be the case for multimetal co-ordination compounds. In these latter systems the usefulness of the method is confined to the evaluation of *how* the p.e. function varies during the reorientational process. Reorientations were performed by ±180° rigid-body rotation of the molecular fragments around appropriately defined axes and by calculating the p.e. values at 10° steps unless otherwise specified.

The molecular packing was considered to be static during the motion, thus retaining the space-group symmetry without involving co-operation of the molecules surrounding the reference molecule. Atomic co-ordinates and space groups for compounds (**1**) and (**2**) were taken from the original structural reports.[8,9]

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† *Non-S.I. unit employed:* cal = 4.184 J.

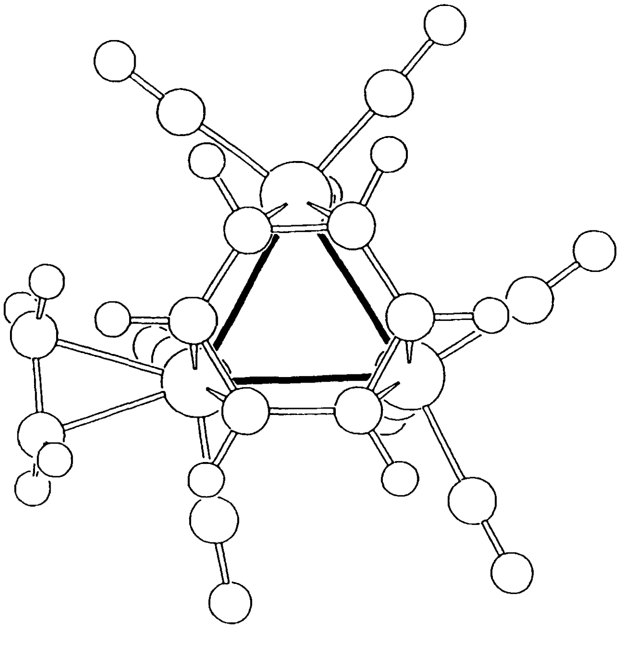

Figure 1. The molecular structure of $[Os_3(CO)_8(\eta^2\text{-}CH_2CH_2)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$[8]

An important difference between the species discussed herein and the mononuclear and dinuclear examples previously studied arises from the molecular complexity of the former species. While intramolecular non-bonding interactions have little (if any) influence on the arene-fragment reorientational motions in the chromium-derivatives or in $[Fe_2(CO)_4(C_5H_5)_2]$ and, as such, can be neglected, this is not the case for the organometallic 'helicopters.' On the contrary, it will be shown that intramolecular energy terms are even more effective than those due to the packing arrangement in controlling the dynamic behaviour of (**1**) and (**2**). Therefore both inter- and intra-molecular potential functions have to be considered in order to establish the extent of reorientational freedom of the organic fragments, and special care has to be adopted in considering the combined effect of the two terms. For this purpose the intramolecular contributions to the p.e. barriers to motion were evaluated by means of the same Buckingham potentials used for the intermolecular case. This choice may seem rather arbitrary because the coefficients used in the potentials are essentially derived from thermodynamic properties (sublimation energies, *etc.*)[5a] related to the forces holding the molecules together in the crystal, thus bearing no direct relationship with non-bonding interactions at work within a molecule. However, it should be emphasized that we are interested in *barriers* not in *minima*, *i.e.* we are actually looking at the steeply rising part (the exponential term) of the interatomic potential, which is mainly determined by the interatomic separation.[5b] Incidentally, this also applies to the intermolecular potential: during reorientation very little contribution is derived from the far-away surrounding molecules (which yield a more or less constant attractive background), the barriers being almost completely determined by the close neighbours (actually a very few molecules, and sometimes atoms, contribute most of the repulsions). In this respect, provided that a coherent choice is adopted and that no absolute values of the p.e. minima are sought, a meaningful comparison of the intra- and inter-molecular potential barriers can be carried out on a relative basis.

Relative p.e. profiles were thus obtained for both intermolecular [ΔE(inter.)] and intramolecular [ΔE(intra.)] contributions as ΔE = p.e. − p.e.(min.) where p.e. is a function of the rotation angle and p.e. (min) is its minimum value [which for p.e.(inter.) invariably corresponds to the observed structure].

It is worth stressing that a relevant contribution to ΔE(inter.) and ΔE(intra.) is given by the H atoms of the arene and alkene fragments. Unfortunately, H-atom positions are not easily determined by *X*-ray diffraction in species of this complexity and are usually geometrically defined conforming to the symmetry of the free fragments. This appears to be a critical point for the C_6H_6 and CH_2CH_2 fragments in (**1**) because the ligand-to-metal interactions do certainly cause appreciable deviation from the model geometry. In order to cope with this problem different modellings of the H-atom positions were tested and the results compared (see next section).

The mean-square librational amplitude of the C_6H_6 fragment in compound (**2**) around its idealized six-fold axis was evaluated from the atomic a.d.p. by carrying out a rigid-body motion analysis[13] based on the T L S approach. In such a calculation the contribution of the Os atom co-ordinated to the benzene ligand had to be included to avoid the singularity problem associated with the motion of a flat hexagonal moiety.[2,14]

Potential-energy calculations were performed by using a slightly modified version of the program OPEC.[15] Thermal-motion analysis was performed by using the THMA10[16] program.

Results and Discussion

Reorientational Processes in Solid Compound (**1**).—The molecular structure of compound (**1**) is shown in Figure 1. The ^{13}C c.p.m.a.s. n.m.r. spectrum of polycrystalline (**1**) indicates the occurrence of chemical exchange processes involving both the CH_2CH_2 and C_6H_6 fragments.[10] It has been shown that the ethene ligand undergoes reorientation about the Os–(C_2H_4) axis while the face-capping benzene executes ring 'jumps' between discrete nuclear sites in the temperature range 250—330 K. The activation energy for these processes (*ca.* 13 kcal mol^{-1}) in the solid has been found to be little more than in solution, suggesting that the barriers are mainly due to intramolecular interactions. It has not been possible to establish, however, whether the similarity of the activation energies for the C_6H_6 and CH_2CH_2 reorientational processes implies that the motions of the two fragments are correlated in the solid. Exchange between the CO groups of the two $Os(CO)_3$ units in (**1**) has also been inferred on the basis of resonance broadening, while the two CO groups co-ordinated to the Os atom bearing the ethene fragment are supposed to be static.[10]

All these reorientational processes were examined by means of atom–atom p.e. calculations and the results are now discussed. Two models for H-atom positions were tested (C–H distances set at 1.08 Å): (*a*) benzene H atoms coplanar with the C_6 ring, ethene H atoms in the plane perpendicular to the co-ordination axis; and (*b*) benzene and ethene H atoms bent out-of-plane (15°) as observed in $[Ru_3(CO)_9(C_6H_6)]$ which contains a similarly bound C_6H_6 group.[17] These two models can be seen as two extremes and have nearly opposite effects on the intra- and inter-molecular barriers to motion. Model (*a*) causes a certain underestimation of ΔE(inter.) and overestimation of ΔE(intra.) because the 'clashing' H atoms of the two moieties within the reference molecule are closer together, while they are further away from the surrounding molecules in the crystal. Model (*b*) works the other way round, leading to increase of ΔE(inter.) (because the outer atoms of the neighbouring molecules are closer together) and to decrease of ΔE(intra.) (because the clashing atoms are further away). However, the two effects compensate each other so that the final results do not differ appreciably. For this reason only the results

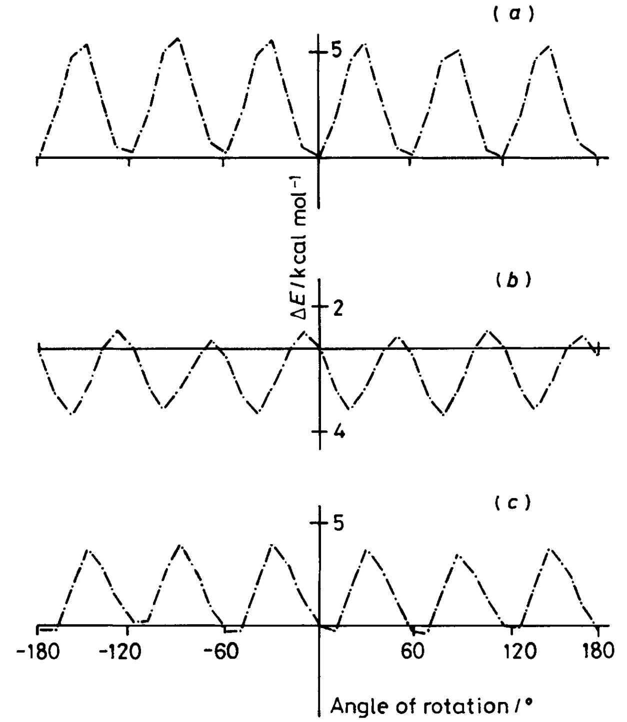

Figure 2. Relative potential energies ΔE(inter.) (*a*), ΔE(intra.) (*b*), and ΔE(tot.) (*c*) *vs.* angle of rotation of benzene in compound (**1**). The CH_2CH_2 group is kept 'static' in its original position during reorientation

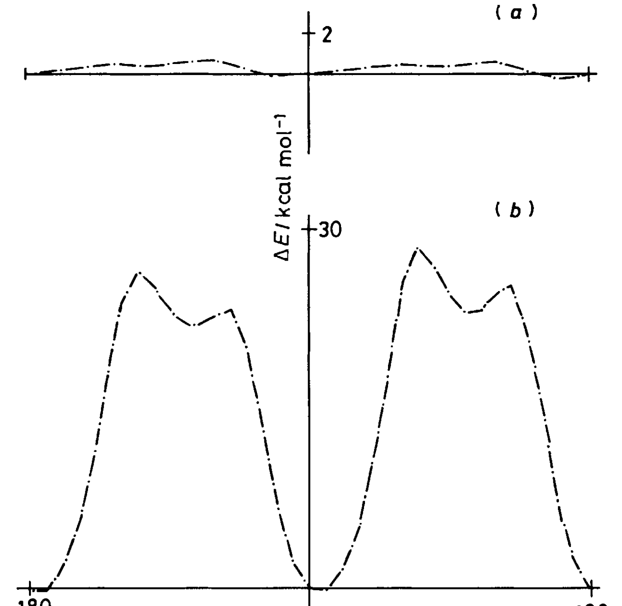

Figure 3. Relative potential energies ΔE(inter.) (*a*) and ΔE(intra.) (*b*) for CH_2CH_2 reorientation in compound (**1**). The C_6H_6 group is kept 'static', in its original position during reorientation

obtained with model (*b*), which is based on some sort of experimental evidence, will be described in detail.

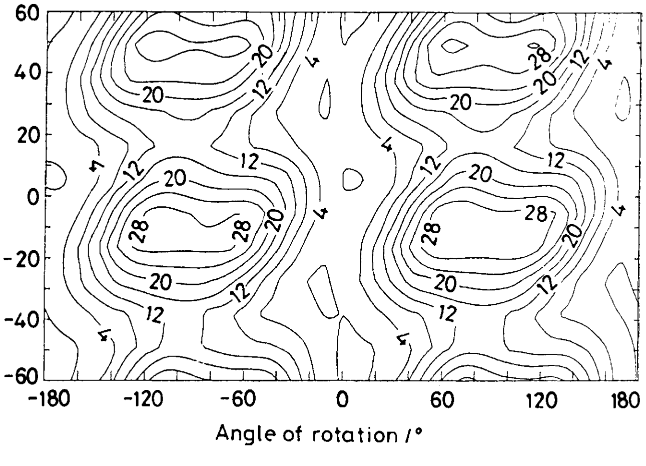

Figure 4. Topographic map of the combined reorientations of the C_6H_6 (abscissa) and CH_2CH_2 groups (ordinate) in compound (**1**). Relative ΔE(intra.) in kcal mol^{-1} is drawn at 4 kcal mol^{-1} steps, the minimum being set to 0 kcal mol^{-1} for the original orientations of the two groups

Let us examine the benzene reorientational motion first. Values of ΔE(inter.), ΔE(intra.), and ΔE(tot.) (the sum of the two previous functions), calculated as discussed above, for a complete reorientation of the benzene fragment around an axis passing through the centre of the C_6 ring and the centre of the Os_3 triangle at 10° steps are reported in Figure 2. The CH_2CH_2 ligand is kept static during the benzene motion (see also below). From examination of Figure 2 the following conclusions can be drawn: (1) the molecular packing creates a small barrier (*ca.* 5 kcal mol^{-1}, see top of Figure 2) to the process; minima of equivalent energy are seen for each 60° 'hop' of the C atoms from one position to the next; (2) ΔE(intra.) also shows a sinusoidal behaviour, though almost out-of-phase with ΔE(inter.); and (3) ΔE(tot.) retains the $\pi/6$ aspect of ΔE(inter.) and ΔE(intra.) though the minima do not correspond exactly to 60° rotations from the original orientation.

It can be said that neither inter- or intra-molecular interactions prevent the benzene ring from undergoing reorientation in the solid, in good agreement with the spectroscopic observations.

The ethene reorientation is more complicated to study. Values of ΔE(inter.) and ΔE(intra.) for a complete rotation of the ligand around an axis passing through the midpoint of the C=C bond and the co-ordinated Os atom, in the presence of a static benzene, are shown in Figure 3 (note that the energy scales are different in the two graphs). It can be seen that intermolecular interactions are almost negligible, while the upsurge of high intramolecular repulsions would appear to prevent reorientation of the fragment.

We have then explored the effect of a concerted benzene and ethene motion by allowing full reorientation of this latter fragment (between −180 and +180°) every 10° rotational step of the benzene ligand (between −60 and +60° from the original position). In such a way a three-dimensional plot of ΔE(intra.) can be obtained and the result is shown in Figure 4. As seen before, if the benzene ligand is kept static (0° rotation in the ordinates), unsurmountable energy 'mountains' are encountered by the CH_2CH_2 fragment during the motion; at the most, librations between *ca.* −20 and +20° around the equilibrium position are allowed (see vertical channel in Figure 4). If the benzene ligand is otherwise allowed to displace during the CH_2CH_2 motion and if the activation energy of *ca.* 13 kcal mol^{-1} yielded by the m.a.s. n.m.r. experiment is taken as reference,[10] then around +20° rotation from the starting position (and therefore at +80 and +140°) and −40° (hence at −100 and −160°) sufficient 'space' is left for the ethene to pass through (horizontal channels in Figure 4).

More difficult to understand is the apparent equilibration of the tricarbonyl groups. As shown in Figure 5 (and as invariably observed when dealing with tricarbonyl group reorientation[2])

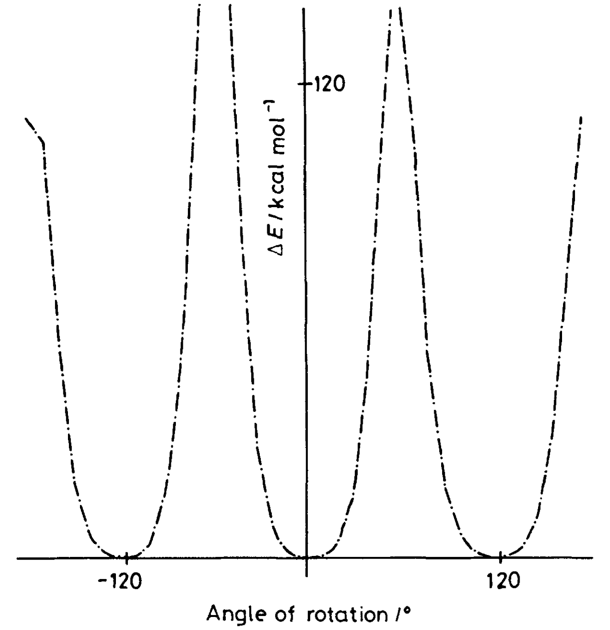

Figure 5. Relative potential energy ΔE(inter.) for tricarbonyl group reorientation in compound (**1**)

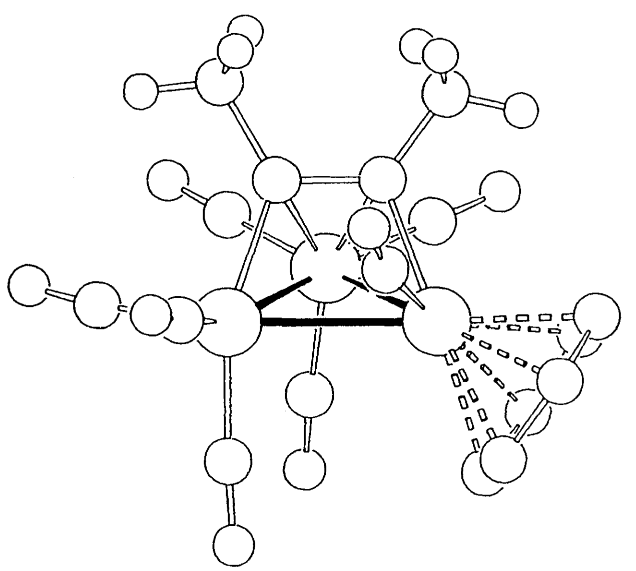

Figure 6. The molecular structure of $[Os_3(CO)_8(\mu_3\text{-}\sigma{:}\eta^2{:}\sigma\text{-}C_2Me_2)(\eta^6\text{-}C_6H_6)]$[9]

minima of equivalent energy are seen at −120 and +120° rotation around the symmetry axis of the $(CO)_3$ unit, corresponding to 'site swapping' between the CO groups, although the intermolecular barrier in between is extremely high, so that full reorientation cannot occur. It may well be that large amplitude torsions of the $Os(CO)_3$ groups are the cause of the resonance broadening observed on the n.m.r. time-scale.[10] As previously discussed for $[Cr(CO)_3(C_6H_6)]$ and $[Cr(CO)_3(C_6H_5Me)]$,[2] oscillation of the tricarbonyl groups around their three-fold axes can yield *apparent* site exchange with no need for true full-scale reorientations.

In conclusion: (*a*) the molecular packing does not severely oppose reorientation of the benzene and ethene fragments; (*b*) the p.e. energy barrier to motion is essentially of intramolecular nature; (*c*) the ethene fragment can reorient only when (and if) benzene 'gives way,' that is to say the motion of the CH_2CH_2 fragment is correlated to that of the C_6H_6 one and the energy barrier obtained by m.a.s. n.m.r. reflects both inter- and intramolecular interactions; and (*d*) on the contrary, tricarbonyl-group reorientation appears to be totally prevented by the molecular packing.

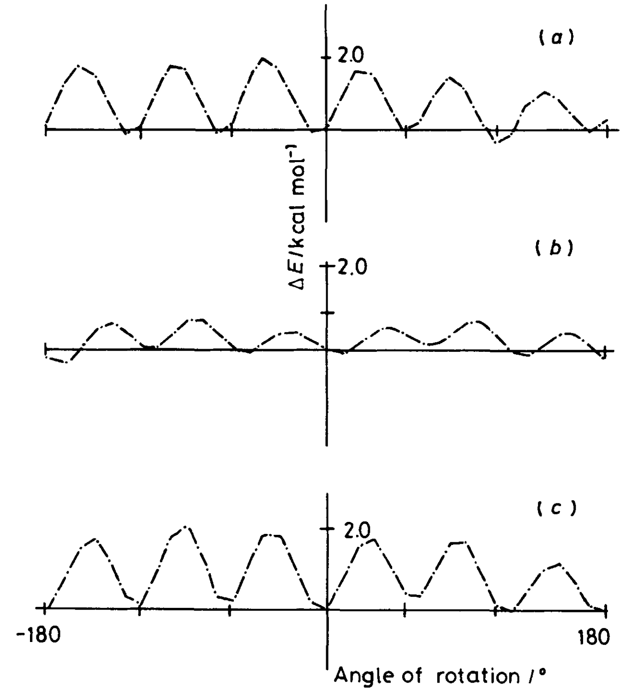

Figure 7. Relative potential energies ΔE(inter.) (*a*), ΔE(intra.) (*b*), and ΔE(tot.) (*c*) for C_6H_6 reorientation in compound (**2**) (the C_2Me_2 group is 'static')

Reorientational Processes in Solid Compound (**2**).—The molecular structure of compound (**2**) is shown in Figure 6. Since we have no spectroscopic information on the dynamic behaviour in the solid state for (**2**), this is a case in which p.e. calculations will be used to attempt 'predictions' on the occurrence of reorientational motions (if any) in the solid state.

Figure 7 collects ΔE(inter.), ΔE(intra.), and ΔE(tot.) for benzene reorientation in (**2**), the benzene ligand being now η^6 co-ordinated to one Os atom of the metal framework. The H atoms were put in calculated positions (1.08 Å) coplanar with the C_6 ring. It can easily be seen that the crystal packing [ΔE(inter.)] offers a limited hindrance to rotation of the fragment around its co-ordination axis. Intramolecular terms are almost negligible. Facile benzene reorientation is therefore easily predicted for compound(**2**).

On the contrary, the MeCCMe ligand cannot reorient around the axis passing through the midpoint of the C–C bond and the centre of the osmium triangle, as shown in Figures 8 and 9 for ΔE(inter.) and ΔE(intra.), respectively: extremely high barriers to rotation are opposed by the crystal packing (certainly because of the bulky Me groups sticking out of the molecule) and by intramolecular repulsions due to the surrounding CO groups. A correct modelling of the MeCCMe reorientation is, however, prevented by the bent geometry adopted by the ligand over the osmium triangle.[9] The reorientational motion (if any) should imply 'straightening' of the ligand, which is also expected to be opposed by the surrounding molecules in the crystal. Behaviour similar to that observed for (**1**) is shown by the tricarbonyl groups.

Let us examine the benzene reorientation in further detail. A projection in the benzene plane of the C-atom a.d.p. derived from the *X*-ray structural determination[9] is shown in Figure 10. The a.d.p. orientation clearly indicates a preferential

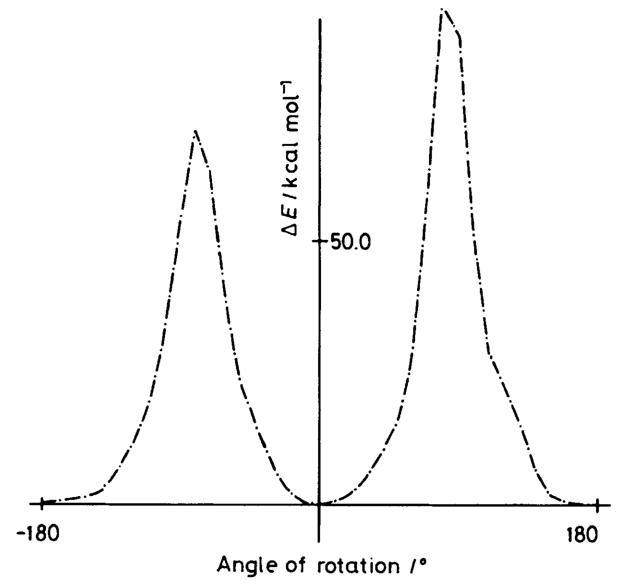

Figure 8. Relative potential energy ΔE(inter.) for reorientation of the C_2Me_2 group in compound (**2**) (the C_6H_6 group is 'static')

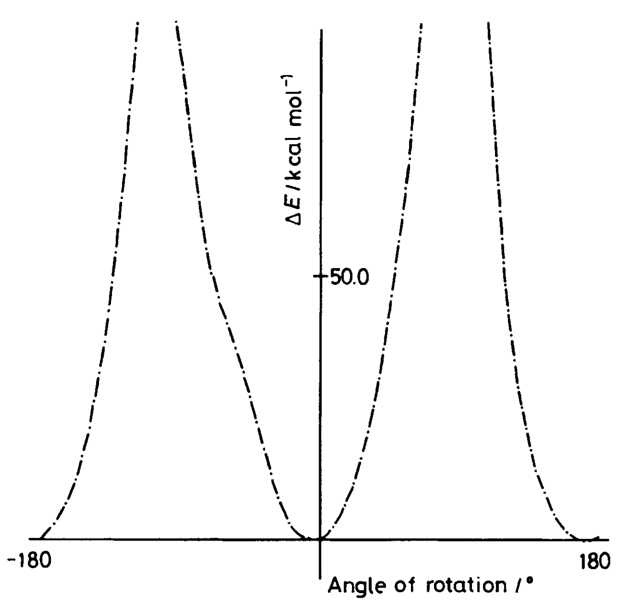

Figure 9. Relative potential energy ΔE(intra.) for reorientation of the C_2Me_2 group in compound (**2**) (the C_6H_6 group is 'static')

libration of the group around the axis passing through its centre and the co-ordinated Os atom. Thermal motion analysis confirms this observation: root-mean-square librational amplitudes (L tensors)[4,13] evidence a considerably anisotropic motion ($L_1 \gg L_2 \approx L_3$: 11.0, 2.7, 2.0°).

Thus, we have a rather consistent picture of this motion: not only the a.d.p. of the atoms involved in the reorientational process and the L-tensor values obtained from thermal motion analysis indicate clearly a preferential in-plane oscillation of the benzene fragment, but also the p.e. barrier obtained by the atom–atom potential method is quite low. This behaviour is strictly comparable with that of the C_5H_5 and C_6H_6 groups in the systems previously studied and whose dynamic behaviour in the solid state has been ascertained by spectroscopic techniques.[1,2]

Finally it is interesting that the packing coefficients of

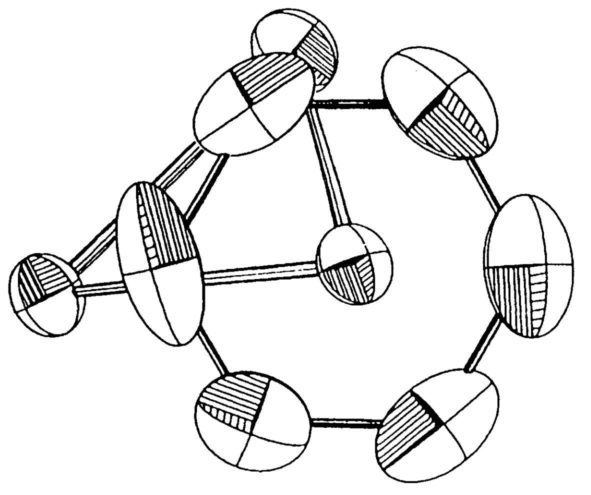

Figure 10. ORTEP projection of the C_6H_6 group a.d.p. in compound (**2**) showing the extensive in-plane librational motion of the ligand

been ascertained to be 'static' in the solid.[19] This observation confirms that dynamic behaviour in the solid state is somewhat related to a 'loose' crystal packing, which may well derive from the presence of fragments whose 'shapes' make difficult an optimization of the intermolecular interactions.

Conclusion

We have shown that the reorientational motion in the solid state of small organic fragments bound to transition-metal clusters can be studied by the atom–atom approach. Application of the method to species of such complexity requires rather drastic assumptions and yields only qualitative (or, at the most, semiquantitative) information on the intra- and inter-molecular potential barrier to motion. Nonetheless, we have found that calculations of this kind provide the right order of magnitude[1,2] of the potential barriers, and can be used for a critical examination of the averaging mechanisms proposed on the basis of spectroscopic experiments. When diffraction data of sufficient quality are available, the study of the anisotropic displacement parameters can also yield important complementary indications on the reorientational motions.

In conclusion, we believe that the *combined* use of the two methods can afford useful information in our understanding of the dynamic processes occurring in the solid state, and represents a powerful tool for the interpretation of spectroscopic results.

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