Dynamics and Molecular Aggregation in Crystalline $[\{M(C_5H_5)\}_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5R)]$ [M = Co, R = CH(Ph)Me, CH_2CH_2Ph or CHCHMe; M = Rh, R = H] Clusters†

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The intermolecular aggregation in crystalline arene clusters of the type $[\{M(C_5H_5)\}_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5R)]$ [M = Co, R = CH(Ph)Me, CH_2CH_2Ph or CHCHMe; M = Rh, R = H] has been investigated by atom–atom packing potential-energy calculations and computer graphics. The ease of reorientation of the arene fragments and of the cyclopentadienyl ligands in the solid state has been investigated by calculating intramolecular and intermolecular potential-energy barriers. It has been shown that, except for the benzene ligand in $[\{Rh(C_5H_5)\}_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$, the facial arenes cannot undergo reorientation in the solid state, whereas the reorientational motion of the cyclopentadienyl ligands is under intramolecular control.

Neutral transition-metal clusters have been shown to form typical van der Waals crystals.[1] The structures of these crystals are controlled primarily by molecular size and shape.[2] It has also been shown that the molecular structure of flexible molecules in the solid state is not necessarily identical to that in solution or in the gas phase, since crystal forces can affect the molecular structure observed in the solid state[3] to a significant extent. In these cases, the relationship between the structure of the individual molecular entity and that of the crystal can be very elusive because the two structures undergo a simultaneous optimization of intramolecular and intermolecular bondings. Although much progress has been made in recent years in the understanding of the crystal packing of molecules, the nature of the intermolecular forces is far from being fully understood. This aspect in crystal-structure studies becomes intriguing when dealing with arene clusters.[4] These molecules are, in general, highly fluxional because of the delocalized nature of the interaction of the arene ligands with the metal atoms. In arene–carbonyl clusters the reorientational motion of the arene(s) combines with carbonyl scrambling over the cluster framework to yield extremely flexible structural systems both in solution and in the solid state.[5]

In this paper we focus on the interplay between molecule and crystal structures for some arene clusters of the type $[\{M(cp)\}_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5R)]$ (cp = $\eta^5\text{-}C_5H_5$; M = Co, C_6H_5R = ring and/or side-chain substituted styrenes;[6] M = Rh, R = H[7]) which have been recently synthesized and characterized in the solid state.

Both the tricobalt and trirhodium clusters are assembled from a mononuclear precursor on the arene. In the case of cobalt, the olefinic side chain of an alkenylarene is used as a landing strip for the first Co(cp) fragment {generated thermally from $[Co(cp)(C_2H_4)_2]$ or $[Co(cp)(C_6Me_6)]$}. The final products of such one-pot reactions are $\{Co(cp)\}_3$ cluster complexes with face-capping alkenylbenzene ligands. Derivatives with saturated side chains are obtainable from the alkenylbenzene clusters by catalytic hydrogenations.[5] In the case of rhodium, the Rh(cp) fragments {generated by irradiation of $[Rh(cp)(C_2H_4)_2]$} are added stepwise directly to the benzene, thereby giving isolable mono- and di-nuclear intermediates.[7]

We shall concentrate on the relationship between the type of arene fragment and the molecular organization in the solid state. In particular we are seeking answers to the following questions. (*i*) Do arene clusters of the $[\{M(cp)\}_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5R)]$ type establish different packing patterns from those observed in crystals of arene–carbonyl clusters? (*ii*) Is it possible to relate the behaviour observed in solution with key structural features, such as arene–cp or cp–cp intramolecular interactions? (*iii*) Is it possible to predict the occurrence of reorientational phenomena in the solid state?

It is worth mentioning the method of analysis. The crystal structure of a given compound can be decoded by studying the distribution and interaction of the first-neighbouring molecules among the molecules surrounding the one arbitrarily chosen as reference.[3,4] Methods based on empirical packing potential-energy calculations within the pairwise atom–atom approach[8] or packing analysis based on graphical methods[9] are used to identify the first neighbouring molecules and to study number, distribution and interactions between these molecules. This approach has been shown to yield an accurate knowledge of the intermolecular interlocking as well as an estimate of the reorientational barriers opposing motion in the solid state.[4]

Results and Discussion

The trinuclear cobalt clusters of the type $[\{M(cp)\}_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5R)]$ [M = Co or Rh] are isoelectronic with the cluster species $[M_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ (M = Ru[10a] or Os[10b]) and their derivatives, which constitute the only other examples of trinuclear metal clusters possessing facially bound arenes.

The cluster $[\{Co(cp)\}_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5CHCHMe)]$ is composed of an equilateral triangle of cobalt atoms with the arene ligand lying almost parallel to the metal triangle and the side chain extended in a *trans* configuration with the benzene fragment. The structure of $[\{Co(cp)\}_3\{\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5\text{-}C(Ph)CH_2\}]$ is closely related to that of the methylstyrene derivative. The structures of the derivatives containing 1,1-diphenylethane, 1,2-diphenylethane or 2-phenylbut-2-ene

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

have also been reported to be similar to those of the above complexes.[10]

More recently the structure of the rhodium derivative $[\{Rh(cp)\}_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ has been determined showing that the facial benzene is bound to the cluster in a manner similar to that observed in $[M_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (M = Ru[11a] or Os[11b]). The structure of the rhodium cluster can be ideally derived from that of the carbonyl species by substitution of three Rh(cp) units for the three $M(CO)_3$ units in these latter clusters. The rhodium triangle is almost equilateral. In all face-capping arene ligands some alternation of the carbon–carbon bond lengths resulting in a Kekule-type distortion is observed. Several accurate crystallographic studies show that the C–H bond vectors bend away from the arene plane.[5,6]

In solution both the arene and cyclopentadienyl ligands undergo rotation. The dynamic behaviour of the species $[\{Co(cp)\}_3(\mu_3\text{-}C_6H_5R)]$ and its stereochemical consequences has been studied in some detail.[5a,10b] The elementary step of the rotation of the arene relative to the tricobalt cluster was shown by two-dimensional exchange NMR spectroscopy to be a series of 1,2-shifts of the cobalt atoms with respect to the C_6 ring. Depending on the symmetry of the arene ligand, enantiomers and/or diastereomers are interconverted by the dynamic process. Rotation of the substituted arenes but not of the cyclopentadienyl rings could be slowed down on the NMR timescale in solution at low temperature. Free enthalpies of activation range from 11.5 to 13.6 kcal mol^{-1}.[5a,10b]

We have attempted to relate the dynamic behaviour observed in solution with the knowledge of the solid-state structures. As mentioned above, the intramolecular and intermolecular reorientational barrier for both the arene fragments and the cyclopentadienyl ligands can be estimated by means of atom–atom potential-energy barrier calculations.[4] Use is made of the Buckingham-type expression for the packing potential energy, p.p.e. = $\Sigma_i\Sigma_j[A\exp(-Br_{ij}) - Cr_{ij}^{-6}]$, where r_{ij} represents an interatomic non-bonding distance, and the indexes i and j in the summation run, respectively, over all atoms of the reference molecule and of the surrounding molecules distributed in the lattice according to crystal symmetry. Mirsky's set of parameters was used as coefficients in the potential-energy function.[12] The cobalt and rhodium atoms were treated as the corresponding noble gas atoms. The energy profiles were calculated by allowing the cyclopentadienyl ligands and arene fragments to reorientate around the ligand–metal co-ordination axis (or around the axis perpendicular to the M_3 triangle in the case of facial arenes) and by calculating the potential energy for a complete rotation of the fragment between ± 180° at 10° rotational steps. Potential-energy barriers (p.b.) were obtained as p.b. = p.p.e. − p.p.e.(min), where p.p.e.(min) is the value corresponding to the observed structure (0° rotation).

In order to evaluate the efficiency of volume occupation in the crystal structures the packing coefficients (p.c.) were calculated by means of the expression p.c. = $(V_{mol}\cdot Z)/V_{cell}$ where the van der Waals molecular volumes (V_{mol}) were obtained from the available sets of coordinates by the integration method put forward by Gavezzotti.[8d] This method is preferable to the Kitaigorodsky's 'intersecting-cups' model[8c] when the atomic connectivity, as in the cases discussed herein, is very high for some atoms.

The molecular organization is the solid state has also been examined by studying the number and distribution of the first neighbouring molecules around the one chosen for reference. The presence of preferential packing motifs can be easily ascertained. All basic information on the species under investigation, $[\{Co(cp)\}_3\{\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5CH(Ph)Me\}]$ **1**, $[\{Co(cp)\}_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5CH_2CH_2Ph)]$ **2**, $[\{Co(cp)\}_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5CHCHMe)]$ **3** and $[\{Rh(cp)\}_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **4**, as well as the values of some crystal parameters, such as p.c., p.p.e. and the values of the potential energy barriers to reorientation, are reported in Table 1.

With respect to these data the following general considerations can be made. The packing coefficients range between 0.72 and 0.76. The average of 0.74 is appreciably larger than the packing coefficients observed in crystalline arene–carbonyl clusters (0.65–0.70).[13] The tighter packing attained by arene–cyclopentadienyl clusters in their crystals reflects the more efficient interlocking attained by the cyclopentadienyl, as distinct from the carbonyl, ligands. The intermolecular interlocking in the carbonyl species is based on the interpenetration of trigonal $(CO)_3$ units formed by three carbonyl ligands linked to the same metal atom and/or tetragonal $(CO)_4$ units, formed by two pairs of ligands bound to two neighbouring metals of the cluster framework, whereas the arene fragments tend to form graphitic-type interactions.[5b]

Packing potential energy (p.p.e.) values are smaller for cluster **3** (−67.8 kcal mol^{-1}) than for **1** or **2** (−76.2 and −73.9 kcal mol^{-1} respectively). The difference can be attributed to the smaller number of atoms in molecule **3**. The p.p.e. value calculated for cluster **4** is rather low (−72.9 kcal mol^{-1}) for a species containing the heavier rhodium atoms which contribute *ca.* 21% of the total cohesive energy, whereas in **1**–**3** the contribution of the cobalt atoms is *ca.* 10%.

The crystal structure of species **4** deserves some comment. The molecular unit (see Fig. 1) presents a rather unusual distribution of ligands around the triangular metal frame. The cluster can be viewed as enclosed by a set of four discs (the three cyclopentadienyl ligands and the facial benzene) whose centres occupy roughly the vertices of a tetrahedron. Molecular

Table 1 Relevant crystal qualifiers and potential-energy barriers to reorientation

Compound	Space group	p.p.e./ kcal mol^{-1}	p.c.	p.b. (intra)/ kcal mol^{-1}	p.b. (inter)/ kcal mol^{-1}	p.b. (total)/ kcal mol^{-1}
1 $[\{Co(cp)\}_3\{\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5CH(Ph)Me\}]$	*Cc*	−76.17	0.73	14.3	2.2	16.1
				2.8	5.0	6.1
				6.1	1.3	7.2
2 $[\{Co(cp)\}_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5CH_2CH_2Ph)]$	$P2_1$	−73.89	0.72	6.7	1.0	7.3
				3.5	0.6	4.0
				4.9	1.1	5.8
3 $[\{Co(cp)\}_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5CHCHMe)]$	$P2_1$	−67.83	0.74	8.0	1.8	9.7
				3.6	4.9	8.2
				4.2	1.5	3.5
4 $[\{Rh(cp)\}_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$	$P2_1nm$	−72.86	0.76	3.9[a]	3.5[a]	6.8[a]
				2.5[a]	0.9[a]	3.3[a]
				0.3[b]	4.0[b]	4.1[b]

[a] Two crystallographically independent cp rings. [b] The $\mu_3\text{-}\eta^2:\eta^2:\eta^2$-benzene ring.

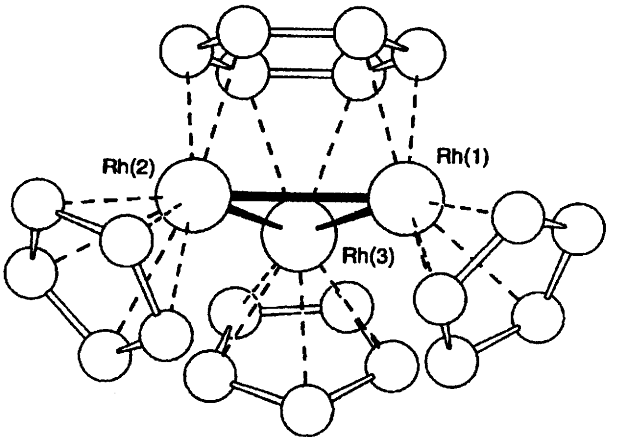

Fig. 1 The molecular structure of species **4**, H atoms have been omitted for clarity

interlocking for this species is very efficient as reflected in the very high packing coefficient (0.76). Although the packing coefficients are based on a rather approximate estimate of the molecular volumes it is interesting to compare the values obtained for the compounds described here with those of typical organic crystals. The average packing coefficient for hydrocarbons, for example, is 0.715, while the packing coefficient of benzene is 0.714, and for cyclohexane 0.707.[13]

In the case of cluster **4** the overall packing arrangement is cubooctahedral. Fig. 2 shows a simplified view of the molecular distribution around the one chosen for reference, the twelve first-neighbouring molecules describing a 3:6:3 layer structure common to most close-packed structures of organic and organometallic molecules. It appears that the shape of the molecule allows an efficient interlocking between neighbouring molecules without large voids in the crystal structure. An alternative projection of the same molecules constituting the cubooctahedral arrangement shown in Fig. 2 is given in Fig. 3. It is easy to appreciate how all the benzene ligands are nearly parallel to the layers defined by the rhodium triangles.

The atom–atom pairwise potential-energy method also allows the estimate of the potential-energy barriers opposing the reorientational motion of unsaturated fragments bound in a delocalized manner to one or more metal centres.[4] The separate contribution of the intramolecular [p.b.(intra)] and intermolecular [p.b.(inter)] energy terms to the total reorientational barrier can also be obtained (Table 1). While p.b.(inter) depends strictly on the molecular arrangement in the crystal structure, p.b.(intra) reflects the steric hindrance to motion and is therefore related to the hypothetical behaviour of an 'isolated molecule' with no interaction with the environment. The internal contribution arising from the bonding interaction between the ligand and the metal is not accounted for. In general, the internal barrier to rotation of the C_5H_5 rings is small if not negligible, in keeping with the behaviour observed in solution where one resonance is invariably observed for the cyclopentadienyl hydrogen atoms in ^1H NMR spectra.

The arene fragments in the clusters **1**–**3** all possess bulky side chains which are easily locked within the crystal structure. Thus it is not surprising that the p.b.(inter) values obtained for reorientation of the arene parallel to the cluster surface are extremely high (> 50 kcal mol^{-1}) for all three species. This is not so for the rhodium species **4** where the barrier to 60° reorientational jumps is quite low. This barrier appears to be essentially determined by the packing since the intramolecular contribution (0.226 kcal mol^{-1}) is sufficiently small to be negligible. This is not so for the cyclopentadienyl ligands which present a large intramolecular contribution to reorientation. Since benzene is not affected, the cyclopentadienyl rings obstruct each other's motion. It will be shown below that the cobalt clusters show a similar behaviour. The two crystallographically independent cyclopentadienyl rings in cluster **4** show, on the other hand, a marked difference at the intermolecular level with a barrier for cp(1) almost three times that of cp(2) (3.52 *versus* 0.88 kcal mol^{-1}).

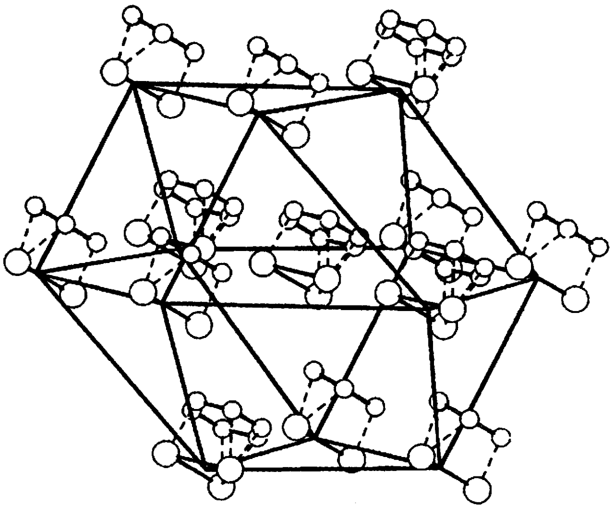

Fig. 2 The molecular distribution in crystalline **4** with the twelve first-neighbouring molecules describing a cubooctahedral 3:6:3 layer structure

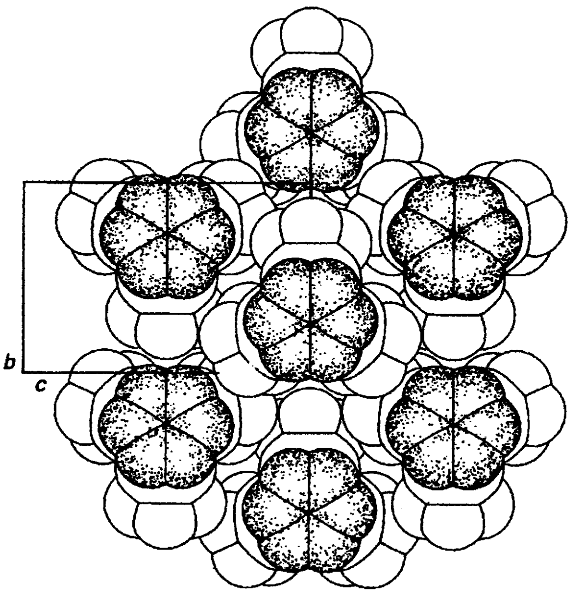

Fig. 3 Projection down the *a* axis in the crystal structure of cluster **4** showing a space-filling representation of the molecular distribution

It is worth recalling here that the value of the barrier for benzene reorientation in crystalline **4** is strictly comparable to that calculated for $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ at room temperature (4.5 kcal mol^{-1}) and also to that found in many other cluster compounds carrying facial arenes.[4] By analogy with these systems and given the highly fluxional behaviour in solution, it is possible to conclude with a certain degree of confidence that both benzene and cyclopentadienyl ligands are capable of reorientational motion in the solid state at room temperature. The disorder observed for cp(2) in the crystal structure (the ring occupies two alternative orientations of equal population [7]) is in agreement with the observation for this ligand of the lowest intermolecular and total barrier to motion.

We will now examine the reorientational motion of the cyclopentadienyl ligands in more detail. The molecular structure of cluster **1**, as obtained from a single-crystal

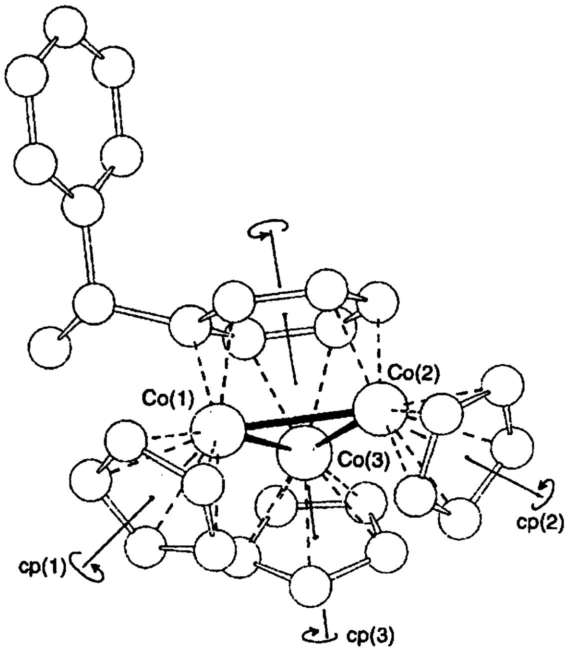

Fig. 4 The molecular structure of cluster **1**

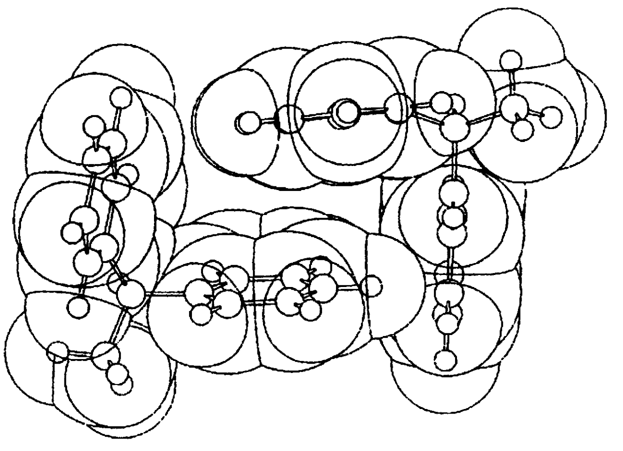

Fig. 5 Direct interaction between two molecules of cluster **1**

diffraction study,[5a] is shown in Fig. 4. The molecular interlocking is particularly interesting, for as shown in Fig. 5 there is a direct interaction between two molecules where the facially bound phenyl ring of one molecule is nearly parallel to the neighbouring phenyl ring (separated by *ca.* 4 Å).

The reorientation of the cyclopentadienyl rings about the axes joining the midpoint of each ring to the metal atoms to which they are bound deserves a closer look. In the 'static' approximation (*viz.* with only one cp reorientation at a time and the surrounding cp rings kept static) the behaviour of three rings is apparently very different. The cp(1) ring has a large p.b.(intra) barrier (14.3 kcal mol^{-1}) whereas p.b.(inter) is small (2.2 kcal mol^{-1}); the cp(2) ring, on the contrary, can rotate freely in the 'isolated' molecule but would have to use a total of 6.1 kcal mol^{-1} to reorientate in the crystal structure. In order to understand the origin of these differences we have explored the effect of a simultaneous motion of the cp(1) and cp(2) rings. If the two rings are allowed to reorientate together the p.b.(intra) barrier for the former ring decreases to *ca.* 8 kcal mol^{-1}. It is important to stress that the minima and maxima of p.b.(inter) and p.b.(intra) do not necessarily coincide. This is the reason why the total potential-energy barrier is not always the exact sum of the other two terms.[14]

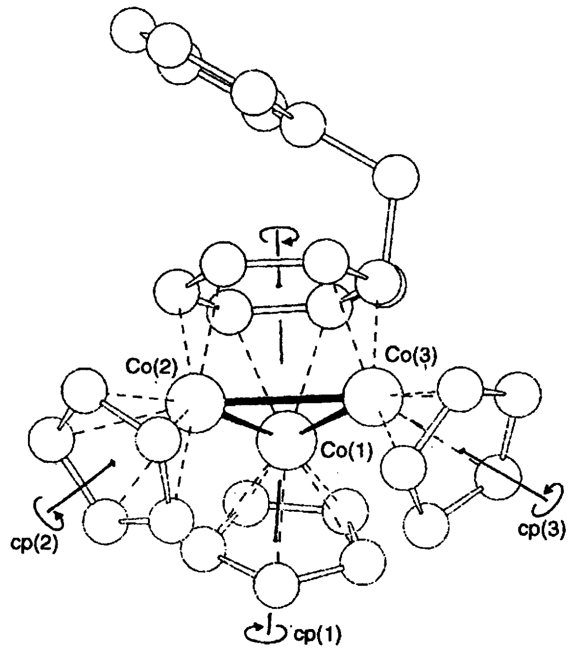

Fig. 6 The molecular structure of cluster **2**

In cluster **2** the location of the phenyl group of the diphenylethane system allows a different type of intermolecular interlocking. The molecular structure of **2** is shown in Fig. 6. No preferential interactions between the C_6 systems is observed. As in the case of cluster **1** the highest contributions to the total potential-energy barrier (4.0–7.3 kcal mol^{-1}) come from the intramolecular terms (3.5–6.7 kcal mol^{-1}), whereas the crystal structure offers almost negligible hindrance to reorientational motion. This is particularly relevant for these species because it has been demonstrated in several instances that the 'static environment' approximation leads to overestimation of the intermolecular barriers.

As before, the presence of the facial ligand forces the cyclopentadienyl ligands into close contact below the cluster plane. Thus it is very likely that the p.b.(intra) values will decrease substantially if simultaneous motion occurs. Similarly the motion of the cyclopentadienyl rings in **3** is mainly under intramolecular control. As for clusters **1** and **2** it is always the cp(1) ring which is close to the 'side arm' of the facial arene, which encounters the highest p.b.(intra).

Conclusion

In this paper we have examined the steric aspects of the reorientational processes that may occur in solution or in the solid state in cluster species of the type $[\{M(cp)\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_5R)]$ which, contrary to all previously examined arene clusters, do not possess carbonyl ligands.

It has been possible to show that, while the facial-substituted arenes cannot undergo reorientation in the solid state, the cyclopentadienyl ligand can reorientate. For this latter motion, however, the potential-energy barriers mainly originate in intramolecular steric interactions between the cyclopentadienyl ligands rather than by intermolecular interlocking in spite of the fact that the packing efficiency of these species is high. In particular, in crystalline $[\{Rh(cp)\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$ both the benzene fragment and the cyclopentadienyl ligands can undergo reorientational jumps.

Our findings are in keeping with our previous observation that unsaturated organic fragments co-ordinated to metal centres with substantial bonding delocalization can undergo a rotational jumping motion in the solid state as a function of the shape of the fragment. This means that the more regular the shape the lower is the reorientational barrier, *viz.* disc-like benzene and cyclopentadienyl ligands are always able to reorientate in the crystal lattice, whereas less regular fragments which present side arms, such as the substituted arenes present in clusters **1**–**3**, are locked in place by the surrounding molecules.

This conclusion is supported by the very few spectroscopic experiments carried out on solid samples of arene clusters. The ^{13}C cross-polarization magic angle spinning NMR experimental results are available only for solid $[Os_3(CO)_8(\eta^2\text{-}C_2H_4)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$[15] and those spectra recorded in the range 220–335 K indicate the occurrence of exchange processes involving both the face-capping C_6H_6 ligand and the η^2-bound C_2H_4 fragment. Benzene and ethene reorientational motions have the same activation energy (*ca.* 13 kcal mol^{-1}).[16] In the solid state, as well as in solution, these processes are mainly under *intramolecular* control and are correlated.

The dynamic behaviour of many other arene clusters has been similarly approached showing that benzene reorientation can occur irrespective of the cluster nuclearity and of the mode of bonding of the ring (whether μ_3-$\eta^2:\eta^2:\eta^2$ or η^6). The potential-energy barrier to reorientation of C_6H_6 fragments in low and high nuclearity arene–carbonyl clusters is invariably between 2 and 9 kcal mol^{-1}.[4] No systematic differences can be detected between face-capping and terminal bonding modes. This is in agreement with the highly fluxional behaviour of these species in solution. In crystalline $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$, for instance, the calculated potential barrier is 4.5 and 6.3 kcal mol^{-1} at room temperature and 193 K, respectively.[10a] In crystalline $[Os_3(CO)_7(\mu_3\text{-}\eta^2\text{-}C_2Me_2)(\eta^6\text{-}C_6H_6)]$ benzene reorientation occurs with a potential-energy barrier of 2.1 kcal mol^{-1}, while, not surprisingly, reorientation of the C_2Me_2 ligand is forbidden.

The fact that the value of the barrier for benzene reorientation in crystalline **4** is strictly comparable to that calculated for $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ and for many other cluster compounds carrying facial arenes strengthens the idea that, given the delocalized nature of the ligand–cluster bonding, arene reorientational processes in the solid state are controlled primarily by the shape of the reorienting fragment and not by the different molecular and crystal structures.[4]

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