

Ligand Stereochemistry of Metal Clusters Containing π -Bonded Ligands

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Abstract: The dummy atom formalism, originally proposed by Doman, Landis, and Bosnich for metallocenes, has been generalized in order to deal with any kind of π -bonding ligands and cluster faces (which can also be seen as polyhapto moieties). A modified VESCF approach has been used to derive a general force field for η^n -coordinated π -bonding ligands whose performances are comparable with those of the best current force fields for cyclopentadienyl derivatives but can be used also for μ_3 - η^2 : η^2 : η^2 and even complex coordination modes. This approach, which can be considered a further step in the building up of a general force field for metal (carbonyl) clusters, has been tested by rationalizing the dynamic stereochemistry in solution of two classes of triangular clusters: $M_3L_3(CO)_3$ ($M = Co, Rh, Ir$; $L = \eta^5$ -Cp, η^5 -Cp*, η^5 -Ind) and $Co_3(\eta^5$ -Cp) $_3(\mu_3$ - η^2 : η^2 : η^2 -RR'C₆H₄) ($R = R' = H, Me, Et$ and $R = Me, Et, iPr$; $R' = H$).

The chemistry of carbonyl clusters has long since passed the point where carbonyls are the only ligands and new metal geometries only are of primary importance. Over the years, plenty of new mixed-ligand “organometallic” clusters have been synthesized along with the systematic study of the reactivity of organic fragments toward clusters. An area within this field which has been extensively studied, both for the potential catalytic implications and for a number of theoretical features discovered, is that concerning the interaction of π -ligands with clusters.¹

The presence of a mixed-ligand envelope, in general, and the polyhapticity of π -ligands, in particular, drive to the edge the most common qualitative model of cluster ligand stereochemistry, the Ligand Polyhedral Model (LPM),² which hardly can be applied to such systems. However, Molecular Mechanics (MM) could in principle deal with such complex systems, provided that a suitable force field for π -ligands is developed.

MM has been brought into the cluster realm by the pioneering work of Lauher, who has translated the kernel of LPM (*i.e.* the freedom of carbonyls to float about the metal cage or, alternatively, the freedom of the metal cage to librate within the ligand envelope)² into the MM formalism.³ Lauher's idea of an equal potential surface (EPS) can be easily implemented into a standard MM program, as we have done for the Allinger suite of programs,^{4,5} by allowing a variable M–CO connectivity in the so-called local connectivity approach.⁶ However, the lack of a definite M–CO connectivity, which is intrinsic to the EPS approach, may result in sterically allowed but electronically unreasonable structures.⁷ In a conventional MM study the connectivity of the atoms is exactly defined (and is not allowed to change during the minimization) and, as a consequence, the number of valence electrons of each atom is also strictly controlled. On the contrary, within the EPS formalism, which

allows a variable connectivity of the metals, we lose control of the local number of valence electrons on each metal center. As a consequence, we have limited the freedom of the carbonyl ligands about the metal cage by introducing a new component of the force field which addresses the fulfillments of the local electron book-keeping and favors the conformations associated with the better spread of the total charge.⁷ Moreover, given that MM3 van der Waals (vdW) parameters can be used to correctly describe both *intra*- and *intermolecular* interactions,^{5c} we are actually able to minimize the conformation of a molecule within a fixed, or periodically updated, crystal lattice,⁸ as we have shown by rationalizing the solid state dynamics of Fe₃-(CO)₁₂.⁹ Here we report our attempts to develop a suitable force field for π -ligands bonded to vertices, edges, or faces of metal carbonyl clusters.

Force Field

All the computations have been done employing a local version of MM3 upgraded for dealing with (i) carbonyl ligands in the local connectivity approach,⁶ (ii) formal local charge distributions,⁷ (iii) crystal lattices,⁸ and (iv) “dummy” atoms as described in the following.

Dummy Atoms. Organometallic complexes bearing π -bonding ligands present special challenges in defining the connectivity pattern and it is convenient to simplify the overall topology by using dummy atoms. In other words, we attribute the connectivity of a group of selected atoms (for instance, an allylic moiety, a cyclopentadienyl group, or a cluster face) as a whole to a “dummy” atom (hereafter D), located at the centroid of the group, which will carry all the valence forces acting on the original group. The dummy atom formalism, which has been originally proposed by Doman, Landis, and Bosnich for metallocenes,¹⁰ can be easily generalized in order to deal with (i) any kind of π -bonding ligands and, of higher importance in this context, (ii) cluster faces. This will allow molecular mechanics computations on clusters with face-capping arenes, or “helicopters”, by representing both C₆ and M₃ moieties with dummy atoms.

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1996.

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Since we are going to deal with unsymmetrical systems, where the M–D–C bond angles and/or M–C bond distances are not necessarily equivalent, we have slightly modified the original dummy atom scheme by allowing variable M–D–C bond angles in order to reproduce the observed bonding asymmetry, such as those observed in allylic and indenyl systems. In particular we allow for slightly longer distances for the hinge atoms of the indenyl moiety by removing the 90° setting in the natural values of the M–D–C bond angles.

π -Bonding Ligands. π -Bonding ligands are organic fragments containing a conjugated π -electronic system which can interact with one or more metal atoms. Conjugated (uncoordinated) π -electron systems are normally dealt with (in MM3) by computing pertinent C–C bond order within the VESCF approximation,¹¹ in order to determine (cycle after cycle) the actual values of natural bond lengths, stretching force constants, and twofold torsional constants. At variance, π -bonded cyclopentadienyl derivatives have been treated as conventional fragments, with no reference to their conjugated nature, extracting an *ad hoc* force field from the fitting of the observed geometries and vibrational frequencies of pertinent reference derivatives. This latter approach could be easily generalized to deal with $C_nH_n \eta^n$ bonded systems. However, when less symmetric coordination modes or more complex conjugated molecules are present, the more general VESCF approach, requiring only a few “new” parameters, becomes attractive.

In the following we will show that the *modified* VESCF approach, besides offering a straightforward breakthrough to the force field of complex π -bonded organometallics, is substantially equivalent to the existing force field of metal cyclopentadienyl derivatives.¹⁰

The modified VESCF approach substantially consists of the following steps: (i) the conjugated π -system is addressed by defining the π -atoms in the usual way making no difference between “free” and π -bonded atoms; (ii) the number of electrons within the conjugated π -system is incremented (or decremented) by considering the usual charge attributed to the coordinated π -molecules (*i.e.* one more for each cyclopentadienyl ligand or one less for each tropylium ligand); (iii) the derived bond orders (p_{ij}) are used to compute the twofold torsional constants (V2) about the C_i – C_j bond in the usual way; and (iv) the derived p_{ij} are downsized by a weakening factor ($w_{ij} = k_w(M-C)/\langle M-C \rangle_{ij}$),¹² inversely proportional to the average bond distance, before computing the natural bond length and stretching force constant for C_i – C_j bonds.

The electrons added according to step (ii) artificially increase p_{ij} values of cyclopentadienyl and indenyl ligands but this is necessary in order to deal with a close shell (and to reach aromaticity for each ligand). The downsizing of p_{ij} values described in (iv) is aimed to take into account the weakening of C–C bond orders due to metal coordination and to correct for the above mentioned p_{ij} artificial increase.¹³ Note that according to step (iii) we do not weaken the twofold torsional constants about the C_i – C_j bond; moreover, we have slightly

Table 1

term ^a	parameters ^b
$M_3L_3(CO)_3^c$	
stretch Co–Co	$r_o = 2.44 \text{ \AA}$ (fixed value)
stretch Ir–Ir	$r_o = 2.67 \text{ \AA}$ (fixed value)
stretch Co–D _{Cp}	$r_o = 1.70 \text{ \AA}$, $k = 2.85$
stretch Ir–D _{Cp}	$r_o = 1.90 \text{ \AA}$, $k = 2.85$
bend M–D _{Cp} –C _{Cp}	$k = 1.40$
torsion H–C _{sp²} –C _{sp²} –C _{sp²}	$V_1 = 0.25$, $V_2 = 9.00$, $V_3 = 0.40$
Cp bond order weakening constant	$k_w = 0.50$
$Co_3Cp_3(\text{arene})_3$	
stretch Co–Co	$r_o = 2.50 \text{ \AA}$ (fixed value)
stretch Co–D _{Cp}	as above
stretch D _{Co} –D _{Ar}	$r_o = 1.83 \text{ \AA}$, $k = 5.00$
bend M–D _{Cp} –C _{Cp}	as above
bend D _{Co} –D _{Ar} –C _{Ar}	$k = 5.00$
bend D _{Ar} –D _{Co} –C _O	$k = 5.00$
torsion Co–D _{Co} –D _{Ar} –C _{Ar}	$V_6 = 14.70$
torsion H–C _{sp²} –C _{sp²} –C _{sp²}	as above
Cp bond order weakening constant	as above
Ar bond order weakening constant	$k_w = 0.40$

^a D_{Cp}, D_{Ar}, and D_{Co} are dummy centroids of the cyclopentadienyl (or indenyl) ring, arene ring, and Co₃ face, respectively; C_{Cp} and C_{Ar} are cyclopentadienyl (or indenyl) and arene carbons. ^b Units for the force constants: stretch md \AA^{-1} , bend md \AA rad^{-2} , torsion kcal mol⁻¹. ^c Parameters for carbonyl ligands, within the local connectivity approach, are provided in refs 6 and 7.

modified the MM3 threefold torsional constant (V3) for the H–C_{sp²}–C_{sp²}–C_{sp²} torsional term (as reported in Table 1). This has been found to be necessary in order to obtain the best agreement between computed and observed ferrocene vibrational frequencies, Table S1 in Supporting Information, with particular reference to torsional modes.

Note that the comparison reported in Table S1 (Supporting Information) between our vibrational frequencies and those computed by Doman, Landis, and Bosnich for ferrocene¹⁰ clearly shows that the two force fields are substantially equivalent.

The same approach can be applied to systems containing π -ligands bridging two or more metal atoms. In order to account for the preferential relative orientation of the M_m and C_n moieties, we add to the force field an N -fold torsional term $E = (V_N/2mn)\sum_i\sum_j(1 + \cos(N\omega_{ij}))$, where ω_{ij} addresses the M_i – D_M – D_C – C_j angles. In particular, dealing with arene ligands capping triangular faces, the torsional potential will be sixfold. Arene molecules, when bonded in such a way, show a Kekulé-type bond length alternation.¹⁴ However, the extent of this distortion is so small and difficult to determine that we neglect it.

Van der Waals Interactions. In order to ensure the continuity of the energy functional in the presence of a variable connectivity (*i.e.* to allow a smooth interchange of the M/C bonding and non-bonding terms), we previously set to zero the metal atom vdW parameters, since we were dealing only with binary metal carbonyl clusters.⁶ However, when conventional ligands (*i.e.* those possessing a definite connectivity and not bound to lie on the EPS) are also present, in order to avoid their collapse on a metal atom, the contribution of the metals to the vdW interaction energy must be considered. Accordingly, all 1,3 vdW interactions about the metal atoms, except for $M\cdots CCO$ and $M\cdots OCO$, are considered in the present computations. In the presence of the dummy atom formalism, however, the concept of 1,3 vdW is not immediately clear and the reader is directed to Figure 1 for further insight. All the vdW

(14) This has been explained in terms of a diminution of conjugation due to the mixing of HOMO and LUMO. Wadepohl, H.; Zhu, L. *J. Organomet. Chem.* **1989**, 376, 115.

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(12) Where k_w is the weakening constant reported on Table 1, $\langle M-C \rangle$ is the M–C average value for the particular π group while, $\langle M-C \rangle_{ij}$ is the average for the particular bond. The value of k_w has been fixed in order to reproduce the observed C–C bond lengths.

(13) The proposed methodology works when donation and back-donation are cooperative (both weakening the C–C bonds) as in alkenes and η^n - C_nH_n derivatives. More generally one should consider a non-integer HOMO (and LUMO) occupation for each coordinated π -group. However, MM3-VESCF treats the whole set of conjugated π -atoms as a single system and it is not trivial, even if possible (given that cross matrix elements between different p-ligands are close to zero), to select the proper orbitals to populate or depopulate.

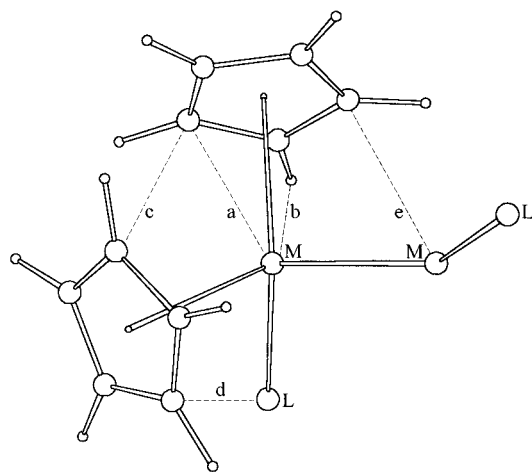


Figure 1. A sketch of the vdW interactions about a metal atom (M and L address metal and ligand atoms, respectively). Interactions **a** and **b** are not considered since they are a 1,2 M–C bond and 1,3 contact about a non metal center, respectively. On the contrary, interactions **c**, **d** and **e** are considered since they are 1,3 contacts about a metal centre.

parameters for the transition metals have been taken from ref 15.

Results and Discussion

The Stereochemistry of $M_3L_3(CO)_3$ ($M = Co, Rh, Ir$; $L = Cp, Cp^*, Ind$) Clusters. Several $M_3L_3(CO)_3$ clusters have been characterized in the past years and the molecular structures and the chemistry of these and related cluster complexes have recently been reviewed.¹⁶ Four different stereoisomers have been observed, depending on the different metals, ligands, and reaction conditions used (see Table 2, which also reports some information on their fluxional behavior in solution), namely: **A** (having three edge-bridging COs), **B** (having one terminal and two edge-bridging COs), **C** (having three terminal COs, two below and one above the metal triangle), and **D** (having one face- and two edge-bridging COs). Structural formulas for the above structural types are outlined in Scheme 1 together with that of **E** (a hypothetical isomer having three terminal COs on the same side of the metal triangle). We have computed the steric energies for the five different isomers in correspondence with two possible metals (Co and Ir, the latter being considered equivalent to Rh, at least from a steric point of view) and three different ligands Cp (cyclopentadienyl), Cp* (per-methylated cyclopentadienyl), and Ind (indenyl); our results are reported on Table 3.

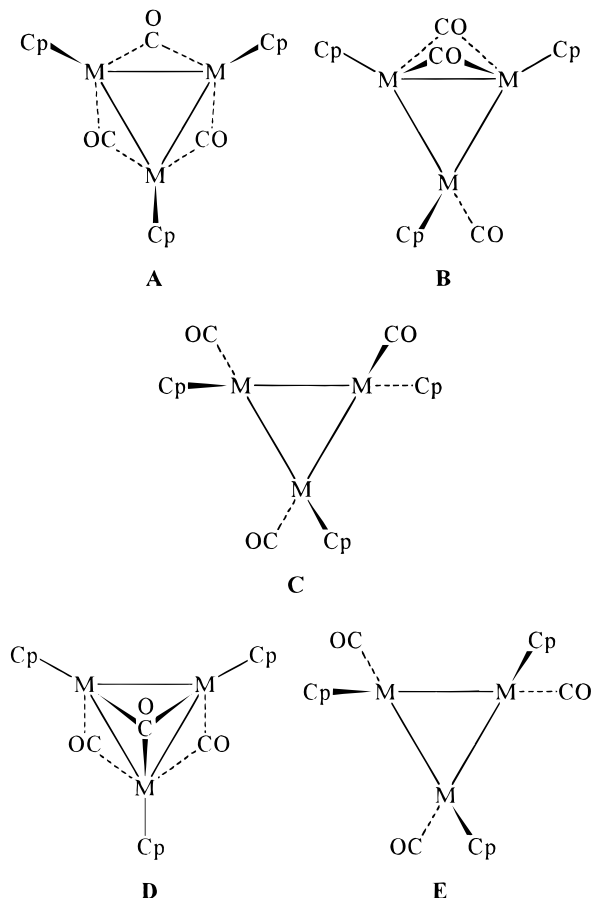
The above computations have all been performed with the parameters reported on Table 1 in order to obtain comparable steric energies. However, due to the large variability of metal–metal bond distances in metal cluster, the “molecular modeling” capabilities of our force field have to be checked only after the assumption of the actual metal cage dimensions. Accordingly, we have determined the “theoretical” structures for the **A** and **B** stereoisomers, which are the only true minima on the steric potential energy surface (PES) for the Cp derivatives (*vide infra*), starting from the experimental geometries, constraining the metal atoms to the experimental bond distances, and leaving the ligands to reach the closest minimum on the PES. The reached minima were substantially coincident with those obtained with the averaged M–M bond distances, reported in Table 1, used all through this paper. However, it is now possible to plot (in Figure 2) the “theoretical” vs the experimental

Table 2^a

	Cp	Cp*	Ind
Co ₃	A (A)^b D (B)^{b,c}	D (D)^d	
Rh ₃	A (A)^{e,f} B (B)^g	D (D)^h	(A) ⁱ
Ir ₃	C (C)^j		A (A)^k
M ₂ M'	A (A)^l (B)^m	(D)ⁿ	(A)^k

^a Structural data in bold and in parentheses refer to solid state and solution, respectively. ^b Robben, M. P.; Geiger, W. E.; Rheingold, A. L. *Inorg. Chem.* **1994**, *33*, 5615. ^c (CoCp)₃ and (CoCp*)₃: Bailey W. I., Jr.; Cotton, F. A.; Jamerson, J. D.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 3131. ^d (CoCp*)₂(CoCp'): Cirjak, L. M.; Huang, J.-S.; Zhu, Z.-H.; Dahl, L. F. *J. Am. Chem. Soc.* **1980**, *102*, 6623. ^e Mills, O. S.; Paulus, E. F. *J. Organomet. Chem.* **1967**, *10*, 331. Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 7433. ^f (RhCp)₃·acetone: Faraone, F.; Lo Schiavo, S.; Bruno, G.; Piraino, P.; Bombieri, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1813. ^g Paulus, E. F. *Acta Crystallogr.* **1969**, *B25*, 2206. ^h Brunner, H.; Janietz, N.; Wachter, J.; Neumann, H.-P.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1990**, *388*, 203. Aldridge, M. L.; Green, M.; Howard, J. A. K.; Pain, G. N.; Porter, S. J.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1333. ⁱ Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 648. ^j Shapley, J. R.; Adair, P. C.; Lawson, R. J. *Inorg. Chem.* **1982**, *21*, 1701. ^k (RhInd)₃(IrInd)_{3-x} ($x = 0-2$): Comstock, M. C.; Wilson, S. R.; Shapley, J. R. *Organometallics* **1994**, *13*, 3805. ^l (CoCp)₂(IrCp*): Hörlein, R.; Herrmann, W. A.; Barnes, C. E.; Weber, C.; Krüger, C.; Ziegler, M. L.; Zahn, T. J. *Organomet. Chem.* **1987**, *321*, 257. ^m (CoCp)₂(IrCp*): Herrmann, W. A.; Barnes, C. E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1985**, *4*, 172. ⁿ (CoCp)₂(RhCp*) and (CoCp)(RhCp*)₂: Barnes, C. E.; Dial, M. R. *Organometallics* **1988**, *7*, 782.

Scheme 1



structures and to quantify their similarity through the proper rmsd values, namely, 0.17 and 0.19 Å for **A** and **B**, respectively.

As for the Cp derivatives, our computations show that all the isomers have similar steric energies. However, while there

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Table 3^a

	Cp		Cp*		Ind	
	Co	Ir	Co	Ir	Co	Ir
A	0.0	0.0	6.3	3.3	2.2	0.0
B	0.2	0.9	1.9*	1.6*	1.2*	2.5*
C	2.2*	1.8*	7.3*	4.3*	4.7*	6.0*
D	2.5*	1.2*	0.0	0.0	0.0	0.8
E	5.5*	3.0*	24.0*	15.5*	10.6*	9.8*
reference E_s	-8.2	-18.1	-12.5	-33.4	2.1	-12.3

^a All steric energies (E_s) are in kcal mol⁻¹ and relative to the most stable isomer whose steric energy is reported in the last row as reference E_s . Values marked with an asterisk do not correspond to a minimum in the PES but, rather, have been obtained by imposing the metrical constraints necessary to fix the desired stereochemistry.

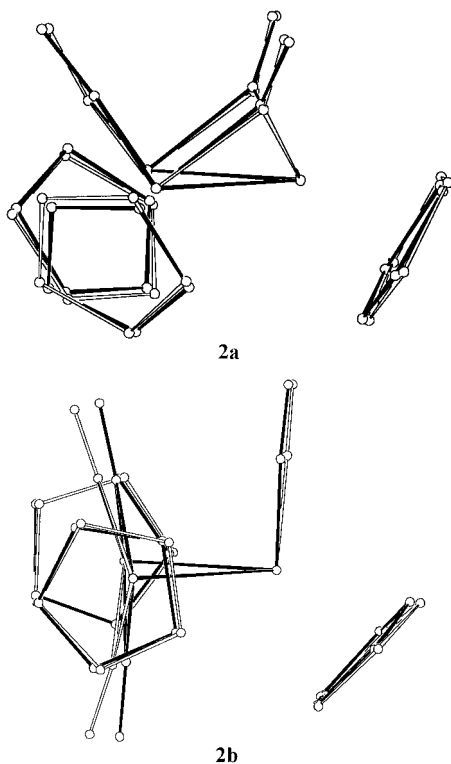


Figure 2. Comparative plot for the “theoretical” and experimental (solid bonds) stereochemistry of (a) **A** vs $\text{Co}_3\text{Cp}_3(\text{CO})_3$ (stereoisomer **A**) and (b) **B** vs $\text{Rh}_3\text{Cp}_3(\text{CO})_3$ (stereoisomer **B**).

is a soft reaction path relating **B**, **C**, and **D**, since **C** and **D** are two maxima along the $\text{C} \rightleftharpoons \text{B} \rightleftharpoons \text{D}$ reaction coordinate (see Scheme 2) and no further energy is required for the process to occur (see Table 3), isomer **A** lies in a region of the steric PES which cannot be easily reached. The barrier for the $\text{A} \rightleftharpoons \text{B}$ conversion, sketched in Scheme 2, has been computed for the Co derivative to be 16.5 kcal mol⁻¹, and it arises mainly from the energy required to move one CO ligand to the opposite side of the Co_3 triangle.¹⁷ Such a large barrier agrees with the fact that, once **A** is formed, it does not interconvert to a different stereoisomer (and vice versa).¹⁸

(17) The barrier has been evaluated driving one of the three equivalent carbonyls of isomer **A** from one side of the M_3 plane to the other one. This has been done, step by step, constraining its elevation above (or below) the M_3 plane. The conformation spontaneously evolves to that of isomer **B** which is, on steric grounds for the $\text{M}_3\text{Cp}_3(\text{CO})_3$ system, more stable than **C** and **D** (see main text and Table 3).

(18) Strictly speaking the barrier is not large enough to justify the lack of the $\text{A} \rightleftharpoons \text{B}$ interconversion at room temperature. However, we think that steric factors alone cannot properly handle conformations too far from equilibrium particularly when these are associated to heavily distorted local coordinations of the metal atoms. Hence, the steric value should be an underestimate of the real one.

The overall picture for the Cp* and Ind derivatives is substantially similar to that of the Cp derivatives. However, the minimum energy isomer (between **B**, **C**, and **D**) is now **D** and the low-energy fluxional process possibly involves the **D** and **B** isomers only, given the moderately higher energy of **C**.

According to the data in Table 3 and to the above consideration we manage to account for (i) the stability of isomer **A** (for the Cp and Ind derivatives) and for its reluctance to isomerize, (ii) the stability of isomer **D** for the Cp* derivatives and for its fluxional behavior in solution ($\text{B} \rightleftharpoons \text{D}$), and (iii) the easy fluxional behavior in solution of the Cp derivatives ($\text{C} \rightleftharpoons \text{B} \rightleftharpoons \text{D}$). However, with the present force field, **D** and **C** are not local minima for the Cp derivatives and we cannot account for their observation for $\text{Co}_3\text{Cp}_3(\text{CO})_3$ and $\text{Ir}_3\text{Cp}_3(\text{CO})_3$, respectively (see Table 2 for the pertinent references). We think that the failure to correctly describe such a simple system is the lack of parametrization of the stereochemical preference of light metals for bridged structures. In fact, as suggested by Evans,¹⁹ the formation of structures containing bridging carbonyls is favored, owing to the greater number of M–L σ -bonds, for the lighter elements because of the more contracted nature of nd orbital and the greater $(n+1)p$ – nd mixing for $n=3$. This view has been recently supported by extended Hückel (EH) computations on $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}$)²⁰ and $\text{M}_3\text{L}_3(\text{CO})_3$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$)²¹ clusters showing that bridge formation implies occupation of previously empty, high energy, orbitals with metal–metal antibonding character which are lowered via interaction with π^* orbitals of the bridging carbonyls. Such a repulsive M–M interaction is more relevant for diffuse d orbitals and eventually favors nonbridged structures for 4d and/or 5d metal clusters. In this respect the $(\text{Ind})_3\text{Ir}_3(\mu_2\text{-CO})_3$ derivative is exceptional because the cluster bears three edge-bridging (isomer **A**) rather than three terminal carbonyls (isomer **C** or **E**). This behavior has been related to the presence of an $\eta^5 \rightarrow \eta^3$ distortion of the three indenyl ligands and naively assigned to “electronic factors” on the base of EH computations on $(\text{allyl})_3\text{Ir}_3(\text{CO})_3$ [and $(\text{allyl})_2\text{Ir}_2(\text{CO})_3$].²¹ However, even in the presence of marked allylic distortions, to infer from $(\text{allyl})_3\text{Ir}_3(\text{CO})_3$ about $(\text{Ind})_3\text{Ir}_3(\text{CO})_3$ sounds somewhat doubtful since the two derivatives are not isoelectronic. At variance, given the relative steric energies of the two pertinent stereoisomers **A** and **E** (Table 3), our MM computations offer a good “steric” reason for the observed stereochemical choice which, substantially, depends on the preference of the $(\text{CO})_3$ moiety (on one side of the metal triangle) to be staggered (as in **A**) rather than eclipsed (as in **E**) with respect to the $(\text{Ind})_3$ moiety (on the other side of the metal triangle). Similar arguments are responsible for the higher energy of **C**, which also lacks of bridging COs, with respect to **A**; moreover, **A** and **C** belonging to different regions of the PES (see the above discussion on the Cp derivatives) cannot easily interconvert once formed and their (possible) existence depends on the reaction conditions.

The Fluxional Behavior of $\text{Co}_3\text{Cp}_3(\text{Arene})$ Clusters in Solution. Starting from $\text{Os}_3(\text{CO})_9(\text{benzene})$, the first molecule containing a $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -arene moiety to be structurally characterized,²² the study of arene cluster has become a fast growing area of research and much experimental and theoretical work has been devoted to this field²³ often in the light of the cluster/

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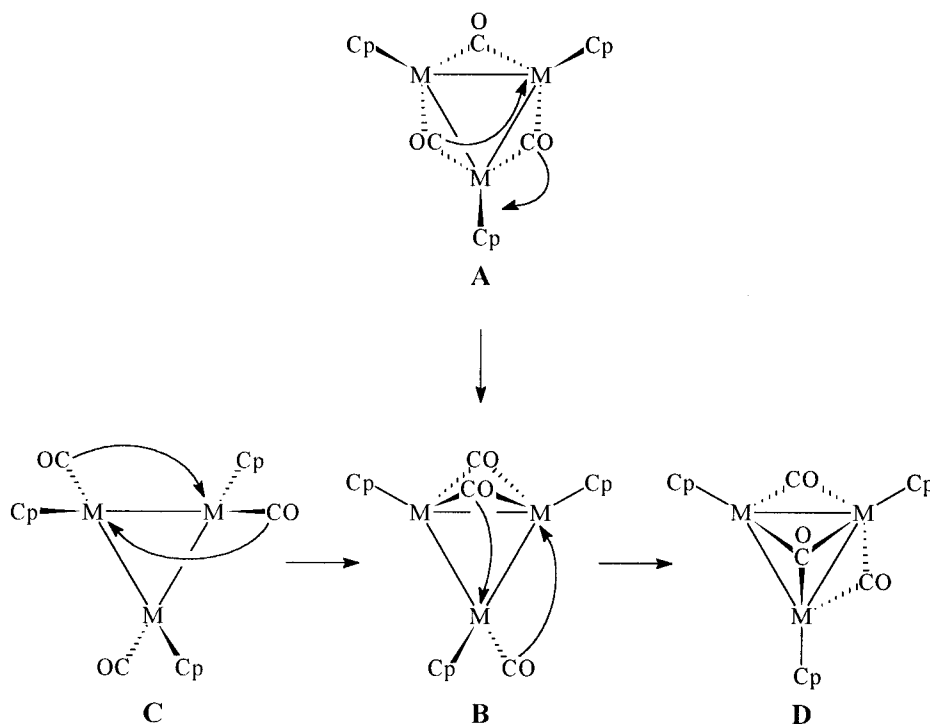
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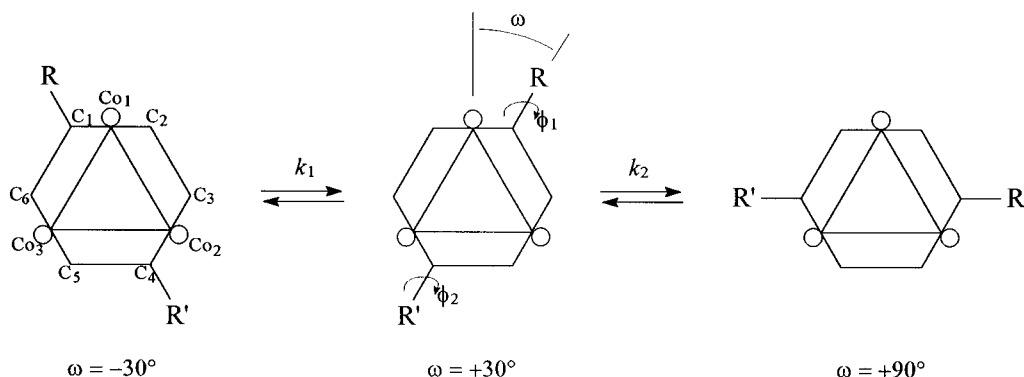
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Scheme 2



Scheme 3



surface analogy.²⁴ The related $\text{Co}_3\text{Cp}_3(\text{arene})$ molecules have received particular attention for their dynamical behavior in solution which has been studied by ^1H and ^{13}C NMR spectroscopy.²⁵ This latter family of molecules, given the contemporary presence of three η^5 -cyclopentadienyl ligands and of one μ_3 - η^2 : η^2 : η^2 -arene, is particularly suitable for demonstrating the performances of our approach since the cyclopentadienyl ligands, the metal triangle, and the μ_3 -arene will be represented by dummy atoms D_{Cp} , D_{Co} , and D_{Ar} , respectively.

We have computed the (steric) energy profiles for the rotation of different monosubstituted and para-disubstituted arenes $\text{RR}'\text{C}_6\text{H}_4$ above a Co_3Cp_3 moiety. This has been done sampling the conformational space defined by the torsional angles $\text{Co}(1)-\text{D}_{\text{Co}}-\text{D}_{\text{Ar}}-\text{C}(1)$ (ω , from -30° to 90° with step 10°), $\text{C}(2)-\text{C}(1)-\text{R}-\text{H}$ (ϕ_1 , from 0° to 360° with step 10°) and, when needed, $\text{C}(5)-\text{C}(4)-\text{R}'-\text{H}$ (ϕ_2 , from 0° to 360° with step 10°), by minimizing the steric energy of the whole molecule in all the points. The symmetry-independent part of the above dynamic process (for a general arene) and the labeling are sketched in Scheme 3.

Monosubstituted arenes ($\text{R}' = \text{H}$) are expected to have two different rotational barriers, ΔH_1 and ΔH_2 , depending on

(24) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

(25) Wade, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 247.

whether the substituent moves across a (CoCp) group (rate constant k_1) or between two groups (rate constant k_2). Obviously, unsymmetrical para-disubstituted arenes ($\text{R} \neq \text{R}'$) will behave like the monosubstituted ones; while, for symmetrically para-disubstituted arenes ($\text{R} = \text{R}'$), the two above dynamic processes become degenerate and only one rotational barrier ΔH_{12} (and rate constant k_{12}) will be observed.

First of all we have computed the energy profile for $\text{Co}_3\text{Cp}_3(\text{RR}'\text{C}_6\text{H}_4)$ ($\text{R} = \text{R}' = \text{Et}$, **1**) in order to determine the $\text{Co}-\text{D}_{\text{Co}}-\text{D}_{\text{Ar}}-\text{C}$ torsional constant by matching the experimental rotational barrier.²⁵ The actual value of such a torsional constant is reported in Table 1 and its contribution to the steric energy is fundamental since, otherwise, the eclipsed conformation results are slightly more stable than those of the staggered conformation (while μ_3 - η^2 : η^2 : η^2 -arenes are found to be invariably staggered with respect to the metal triangular face) and the energy profile results are rather flat (while the observed rotational barrier for **1** is ca. 14 kcal mol^{-1}).²⁵ In the following we will address such (overall) torsional contribution [$E = V_6(1 + \cos(6\omega))/2$], which favors the best orbital match between the cluster and the arene, as "electronic" factors (dashed line in Figure 3) while we will use the term steric factors to address all the other contributions to the steric energy.

Assuming the transferability of the above $\text{Co}-\text{D}_{\text{Co}}-\text{D}_{\text{Ar}}-$

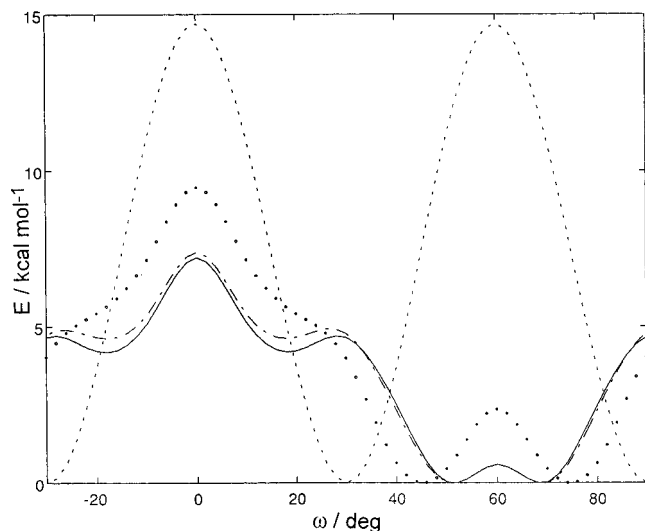


Figure 3. Steric (R = Me, continuous line; R = Et, dashed-dotted line; R = ⁱPr, dotted line) vs “electronic” (dashed line) contribution to the potential energy profiles for the rotation (ω) of different monosubstituted arenes about the $D_{Co}-D_{Ar}$ axis. Energies are relative to the minimum for each profile. We have sampled ω in the range $-30/+90^\circ$; however, for the actual arenes, the symmetry-independent part is only $0/60^\circ$. Accordingly, we have symmetrized the resulting energies (which were, anyway, very similar, apart from small effects due to the slow convergence speed).

C_{Ar} torsional constant, we then computed the energy profile for (R = R' = H) **2** and the resulting rotational barrier was found to be 16 kcal mol⁻¹. It is worth noting that the rotational barrier for **2** is higher than that for **1** which, nevertheless, has bulkier substituents. This is not surprising since the overall barrier is due to a combination of steric and “electronic” factors which promote different relative conformations of the substituted arene with respect to the underneath (CpCO)₃ moiety. In particular, “electronic” factors disfavor sp² arene carbons on top of metals and have periodicity of 60° and minima at $30 \pm 60^\circ$ (values refer to ω angle) and their weight, at most, depends on the ability of R to polarize the arene π electrons and not from bulkiness. At variance, for each substituent R, steric factors favor substantially staggered R/Cp conformations and have a periodicity of 120° and their weight depends on the bulkiness of R. However, as shown in Figure 3, the steric contribution to the rotational barrier is not easily predictable without detailed computations. The overall effect is straightforward in the case of monosubstituted arenes since the out-of-phase behavior of steric and electronic factors is not further complicated by the need of considering contributions from more substituents. Indeed, the results of our computations on monosubstituted arene derivatives (R = Me, Et, ⁱPr; R' = H; see Figures 3 and 4) confirm that (i) on moving from $+30^\circ$ to -30° both electronic and steric effects contribute to rise ΔH_1 (and to lower k_1) since for $\omega = 0^\circ$ there are three sp² arene carbons on top of a metal and an eclipsed R/Cp conformation and (ii) on moving from $+30^\circ$ to 90° electronic and steric effects are out of phase since for $\omega = 60^\circ$ there are still three sp² arene carbons on top of a metal but a staggered R/Cp conformation. This eventually results in a lowering of ΔH_2 with respect to ΔH_1 (i.e. to an increase of k_2 with respect to k_1).

The rotational barrier for para-disubstituted derivatives ΔH_{12} , given that R and R' are far enough apart to undergo uncoupled motions, will be substantially the average of ΔH_1 and ΔH_2 of the pertinent monosubstituted derivatives (i.e. $2\Delta H_{12} \approx \Delta H_1 + \Delta H_2$). Accordingly, if steric factors lower ΔH_2 [($E_{60} - E_{30}$) is negative] more than they rise ΔH_1 [($E_0 - E_{30}$) is positive] with respect to their pure “electronic” value, the overall steric

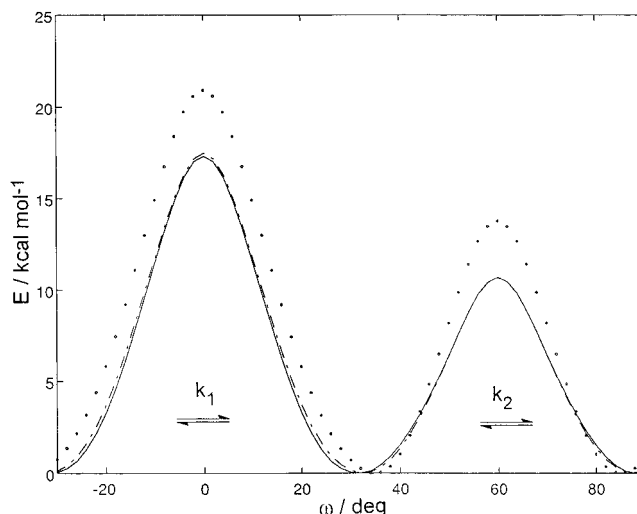


Figure 4. Potential energy profiles for the rotation (ω) of different monosubstituted arenes (R = Me, continuous line; R = Et, dashed-dotted line; R = ⁱPr, dotted line) about the $D_{Co}-D_{Ar}$ axis. Energies are relative to the minimum for each profile. The computed energy barriers are as follows: R = Me, $\Delta H_1 = 17.3$, $\Delta H_2 = 10.7$; R = Et, $\Delta H_1 = 17.5$, $\Delta H_2 = 10.7$; R = ⁱPr, $\Delta H_1 = 20.9$, $\Delta H_2 = 13.8$ (kcal mol⁻¹).

contribution to ΔH_{12} will be negative (this happens for R = Me and Et but not for R = ⁱPr; see Figure 3). This eventually explains why the rotational barrier for **1** is lower than that for **2** in spite of its bulkier substituents.

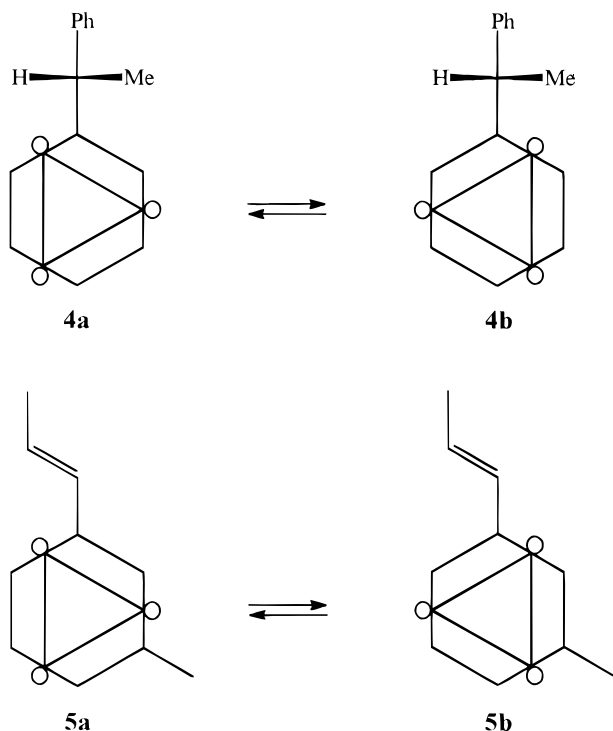
Our “theoretical” results on the rotational barrier for the monosubstituted arenes, reported in Figure 4, can only be compared with the experimental value determined for the R = ⁱPr; R' = H derivative (**3**). According to ¹H EXSY NMR experiments, Wadepohl has clearly shown that²⁵ for **3** there is a large difference between the two potential energy barriers associated with k_1 and k_2 .²⁶ Moreover, from a band shape analysis of the methyl resonances, he has also determined the effective time constant (k_{ef}) for the exchange of the diastereotopic methyl sites (the weighted mean of k_1 and k_2 , which should be close to k_2) and the pertinent ΔG_{ef}^\ddagger (14 kcal mol⁻¹, at 290 K). Our computations affording $\Delta H_1 > \Delta H_2$ (20.9 vs 13.8 kcal mol⁻¹) confirm that $k_1 \ll k_2$. However, the computed value for ΔH_2 is clearly different from the measured ΔH_{ef}^\ddagger (17 kcal mol⁻¹).²⁷ This discrepancy can be attributed either to a non-transferability of the $Co-D_{Co}-D_{Ar}-C_{Ar}$ torsional constant, i.e. to a different electronic influence of the different substituents on the charge distribution of the aromatic ring, or to the uncertainty of band shape analysis for this system which is complicated by the multistep nature of the overall process.²⁶

In spite of the failure to obtain a better estimate of ΔH_{ef}^\ddagger our computations account for the subtle energetic differences between rotational diastereoisomers. When the arenes are prochiral and have two heterotopic faces, upon coordination they afford two chiral diastereomers which interconvert by arene rotation and are not isoenergetic any longer. In the case of $Co_3-Cp_3[1,1-diphenylethane]$ (**4**) and $Co_3Cp_3[trans-1-(m-tolyl)-propene]$ (**5**) the rotameric diastereomers **4a/4b** (and **5a/5b**), reported in Scheme 4, have been studied by Wadepohl, who has shown that **4a** is more stable than **4b** for more than 2 kcal mol⁻¹, while **5a** and **5b** are very close in energy (less than 0.2 kcal mol⁻¹). Indeed, in good agreement with the above experimental results, we have computed that **4a** is the lower

(26) Wadepohl, H. In *The synergy between dynamics and reactivity at clusters and surfaces*; Farrugia, L. J., Ed.; Nato ASI Series C: Mathematical and Physical Sciences; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1995; No. 465, p 175.

(27) Wadepohl, H. Personal communication.

Scheme 4



energy isomer (**4b** is lying 2.3 kcal mol⁻¹ above in energy) and that **5a** and **5b** differ by only 0.2 kcal mol⁻¹.

Conclusions

In this paper we have focused our attention on the stereochemistry and the dynamics of metal cluster containing π -bonded ligands. We have dealt mainly with η^5 -cyclopentadienyls and μ_3 - η^2 : η^2 : η^2 -arenes but the dummy atom approach is general and can be straightforwardly applied to any π -bonded ligand, from η^3 -allyls to μ - η^3 : η^2 -C₇H₇.²⁸ With only slight modifications of the force field one could also deal with the fluxional behavior of selected metal carboranes, given the isolobal relationship between [C₂B₉H₁₁]²⁻ and [C₅H₅]⁻ and triple-decker compounds.

This has been a further step in the building up of a general force field for the metal (carbonyl) cluster. The modeling of the “soft” PES of metal carbonyl clusters has been possible because the local connectivity approach allows the fluxional ligands (like the carbonyls) to be dealt with, freeing the metal-to-ligand actual connectivity while tightening the cluster-to-ligand global one. From this point of view we can look at the double dummy atoms formalism, here used to model μ_3 - η^2 : η^2 : η^2 -arenes, as a further generalization of the local connectivity approach since now it is the face-arene connectivity to be conserved.

In the present approach the overall ligand stereochemistry about the metal cluster is controlled by three different factors: (i) valence forces, which are responsible for the cluster-to-ligand bonding (local or not) and for explicitly stated stereochemical preferences or avoidances (like that disfavoring sp² arene carbons on top of metals in μ_3 - η^2 : η^2 : η^2 -arenes); (ii) van der Waals (and Coulombic) interactions, which are largely responsible for the ligand stereochemistry; and (iii) local charge interactions, which address the fulfilments of the local electron book-keeping and favor a better spread of the total charge on the cluster.

(28) However, for isolated η^2 -bonded alkenes in order to keep the alkene “plane” almost perpendicular to the M–D vector, since the two carbon atoms are not enough to define the plane, we must also consider either M–D–C–H torsion or M–D–H bending terms.

On attempting to rationalize the fluxional behavior of Co₃Cp₃(arene) in solution we have shown (Figure 3) that steric and “electronic” factors favor different conformations along the reaction path reported in Scheme 3 and that the steric contribution to the rotational barrier cannot be foreseen without detailed MM computations.²⁹ This eventually implies that the benzene derivative (which, however, has never been synthesized) should have a larger rotational barrier than the “bulkier” para diethylbenzene derivative.

Our computational results for the M₃L₃(CO)₃ system clearly show that not all the stable isomers which have been observed in solution or in the solid state belong to a minimum of the steric PES. This is due to the lack (in the force field) of some specific valence force (“electronic”) term accounting for the different preference of different metals for bridging ligands and/or to the solvent/packing effects (i.e. to the difficulties of dealing with *intermolecular* interaction in a general way). The above “electronic” factors are particularly relevant for the iridium derivatives (since it is well known that third transition elements “avoid” bridging carbonyls) where they should promote stereoisomers **C** and **E**. Interestingly, **C** has been observed only for Ir₃Cp₃(CO)₃ (and not for the Co and Rh analogues) but **E** has never been detected; this has been easily accounted for by showing that **E** is strongly destabilized on steric grounds (with respect to **A**). “Electronic” factors dominate the Ir₃Cp₃(CO)₃ stereochemistry while they cannot outweigh steric factors in Ir₃Ind₃(CO)₃; hence, according to the data in Table 3, the energetic bias due to the aforementioned factors should be greater than 2.2 but lower than 9.8 kcal mol⁻¹ and, reasonably, much closer to the former than to the latter value.

Given the above pitfall, it is still difficult to use MM computations to foresee the correct stereochemistry of a given species if a few stereoisomers have similar energies (tentatively, within 3 kcal mol⁻¹) and a different carbonyl connectivity pattern.³⁰ However, if two stereoisomers share the same connectivity pattern, then the conventional MM rules apply and steric energies should be reliable within 0.5 kcal mol⁻¹ (or less). Accordingly, we believe that the agreement between experimental and “theoretical” energy differences for the two couples of rotameric stereoisomers **4a/4b** and **5a/5b** has not been reached by chance.

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Supporting Information Available: Table showing the comparison of the observed and computed vibrational frequencies for ferrocene (1 page). See any current masthead page for ordering and Internet access instructions.

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(29) *Inter alia*, it is worth to note that, given the different shape of the underneath moiety, the steric contributions to the rotational barrier in Os₃(CO)₉(Arene) are in phase with the “electronic” contributions, i.e. they favor the same conformation.

(30) Even in the presence of a different carbonyl connectivity pattern, steric energies can be safely used to justify small distortions around a given geometry or to exclude a particularly crowded stereoisomer.