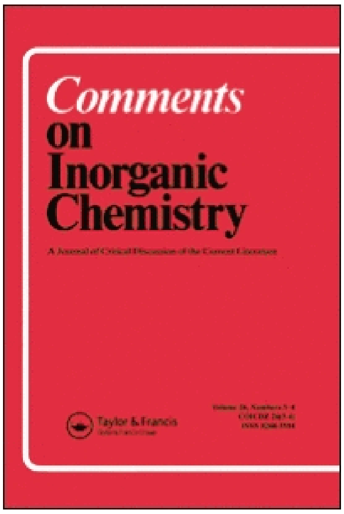

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Haptotropic Shifts of Indenyl and Other Related π Ligands

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The ring slippage reaction, induced by ligand addition or by reduction, is an important reaction in organometallic chemistry, and has been theoretically studied in recent years, using ab initio methods, in several systems such as $[(\eta^5\text{-X})Mn(CO)_3]$ (X can be one among a wide variety of rings), $[Mo(\eta^5\text{-Ind})(CO)_2(L)_2]^+$ (L=CO, phosphite), $[Mo(\eta^5\text{-Cp})(\eta^5\text{-Ind})L_2]^{2+}$. The slippage process is driven by a tendency to decrease the antibonding character of the HOMO after two electrons are added to the system and, usually, a structural rearrangement of the complex (or the ring) takes place, depending on the characteristics of the polyene in the ring. Larger rings are found to slip more easily, although they don't fold, in opposition to what happens to indenyl in all examples known.

Keywords: *Haptotropic shifts; Ring slippage; Indenyl effect; Molecular orbital calculations; DFT calculations*

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* Corresponding Author.

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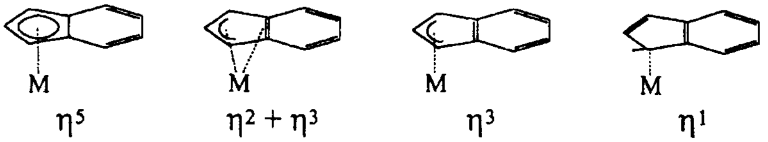
1. INTRODUCTION

Basolo[1] introduced the term "indenyl effect" to describe the acceleration observed in some reaction rates when a cyclopentadienyl (C_5H_5, Cp) ligand of a complex was replaced by an indenyl one (C_9H_7, Ind). It was ascribed to the easiest $\eta^5 \rightarrow \eta^3$ haptotropic shift experienced by the indenyl ring compared to the Cp, and its importance in catalysis has been widely invoked.[2] The likely existence of several coordination modes for the indenyl ligand (SCHEME 1), namely η^5, $\eta^2 + \eta^3$, η^3, and η^1, makes such haptotropic migrations possible.



SCHEME 1

Much experimental[3] and theoretical[3f,3ee,3ff,4] work has dealt with studying and understanding the factors which determine indenyl (and other rings) slippage reactions. Searching the Cambridge Crystallographic Data Base[5] has also been of major importance in acquiring a good structural knowledge of the coordination modes. Contrarily to what might be expected, the ideal η^5 coordination, with five equivalent M-C bonds, is not common among indenyl complexes, though it is the rule in similar Cp complexes. Most complexes distinctly show the $\eta^2 + \eta^3$ coordination, where two of the five M-C bonds are significantly longer than the other three, but still within bonding range.

Indenyl slippage may be induced by ligand addition, as has been observed in the reaction of $[Mo(\eta^5\text{-Ind})(CO)_2(L)_2]^+$ with acetonitrile when L = NCMe, but not when the coming ligand is different from acetonitrile. Also, the reaction only takes place for a specific choice of L ligands (mainly π-donors).[4j] The same reaction type has been thought to occur in other systems, such as the one initially studied by Basolo et al, $[(\eta^5\text{-X})Mn(CO)_3]$ (X = Cp; Ind; $C_{13}H_9$, Flu;[1,3a] C_5Me_5, Cp*[3b]) where the rate of substitution of CO by phosphine increased dramatically upon replacement of Cp by Ind, as could be explained by a first step where a phosphine induced $\eta^5 \rightarrow \eta^3$ haptrotopic shift would open a coordination position at the metal. Many other examples have followed.[3y,3z,4m,6]

An increase in electron count at the metal resulting from reduction (chemical or electrochemical) has also been found to lead to $\eta^5 \rightarrow \eta^3$ indenyl slippage in systems such as $[V(\eta^5\text{-Cp})_2(CO)_2]$[7], $[Mn(\eta^5\text{-Cp})(CO)_3]$[8], $[Rh(\eta^5\text{-Cp})(\eta^4\text{-cod})]$[9] and in the $[Mo(\eta^5\text{-Cp})(\eta^5\text{-Ind})L_2]^{2+}$family of compounds for a large variety of L (L = CO, $P(OR)_3$, PMe_3, CNR; L_2 = dppe, bipy, etc.).[4k,10] They were also theoretically studied for $[Mo(\eta^5\text{-Ind})(\eta^5\text{-X})L_2]^{2+}$ (L = CO; x = Flu, cpp, H_2cpp, where cpp=$C_{15}H_9$ and H_2cpp=$C_{15}H_{11}$).[11]

Many of these reactions have also been analysed in detail using several computational approaches and the more relevant results will be discussed in the next sections.

2. LIGAND INDUCED HAPTOTROPIC SHIFTS

The reaction between $[Mo(\eta^5\text{-Ind})(CO)_2(L)_2]^+$ and acetonitrile for several L coligands has been studied in detail experimentally and was also the object of a theoretical study.[4j]One puzzling aspect of such reaction was how dependent the reaction outcome was from the coligand L, in particular that it took place for L = NCMe, but not not for L = CNMe, these two species being of comparable size. An interesting aspect of this system, which extends to other indenyl derivatives, namely $[Mn(\eta^5\text{-Ring})(CO)_3]$ and ring slippage induced by phosphines, deals with the different structural preferences exhibited by the η^5 and the η^3 complexes. As the need to reorient the ring is a central issue to our discussion, we start by examining it in some relevant complexes.

2.1 Structures of η^5 and η^3 complexes

The calculated structures for some pairs of complexes showing the η^5 and the η^3 coordination modes are given in Figure 1.

For the Mo derivatives, the structures shown were optimized using DFT calculations[12] (ADF program[13]) and agree quite well with the experimental ones (the model for the calculations considered NCH instead of NCMe).[4j,14] The factors determining these preferences have been discussed elsewhere: the η^5-Ind ring lies opposite the carbonyl

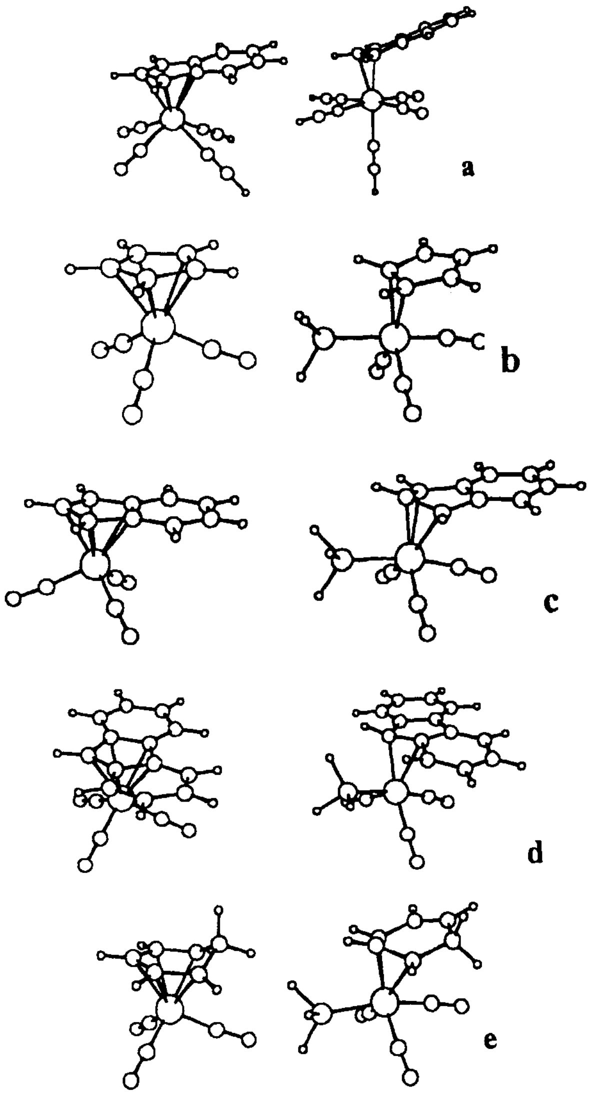
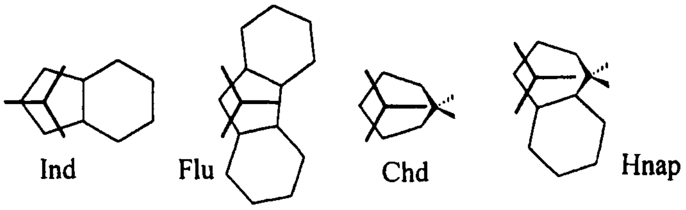


FIGURE 1 Molecular structures of a) $[Mo(\eta^5\text{-Ind})(CO)_2(NCH)_2]^+$ and $[Mo(\eta^3\text{-Ind})(CO)_2(NCH)_3]^+$; b) $[Mn(\eta^5\text{-Cp})(CO)_3]$ and $[Mn(\eta^2\text{-Cp})(CO)_3(PH_3)]$; c) $[Mn(\eta^5\text{-Ind})(CO)_3]$ and $[Mn(\eta^3\text{-Ind})(CO)_3(PH_3)]$; d) $[Mn(\eta^5\text{-Flu})(CO)_3]$ and $[Mn(\eta^3\text{-Flu})(CO)_3(PH_3)]$; e) $[Mn(\eta^5\text{-Chd})(CO)_3]$ and $[Mn(\eta^3\text{-Chd})(CO)_3(PH_3)]$ (Chd = C_6H_7)

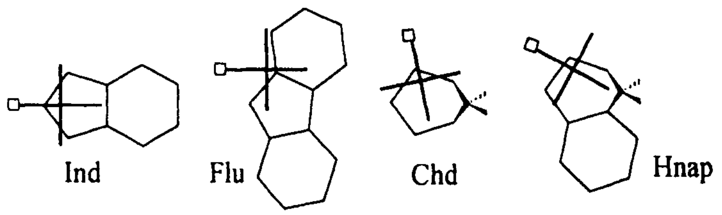
groups, while the folded η^3-Ind ring lies over them.[4j] Back donation to the carbonyls is maximized in these conformations. The theoretical studies (Gaussian 98,[15] B3LYP HF/DFT hybrid functional[16]) performed on the Mn derivatives included a wider range of rings, in order to consider more effects: Cp and Ind, which may slip and fold; fluorenyl, which may slip, but cannot fold; open pentadienyls (cyclohexadienyl and 1-hydronaphtalene), which may slip and fold. In the starting complexes [Mn(η^5-Ring)(CO)$_3$], the electronic preferences are not very strong, as the rotation barrier for the simplest ring (Cp) is small. Steric constraints will therefore be determining when the rings bears a substituent. For Ind, the benzene lies over two carbonyls, while the different topology of Flu forces the opposite conformation; Chd and Hnaph have a similar effect owing to the presence of the methylene group adjacent to the polyene in the ring (SCHEME 2).



SCHEME 2

The addition of a phosphine (PH$_3$ in the model) changes the pseudo-octahedral symmetry of the d^6 Mn complexes, in such a way that the η^5-Ring is replaced, from a geometrical point of view, by the η^3-Ring plus the phosphine. The adjustment can be envisaged as slippage (and sometimes folding) of the ring with a pivoting of the Mn(CO)$_3$ fragment, in order to open a coordination position for the incoming ligand. Again steric interactions between ring/carbonyls and ring/phosphine will determine the final geometry (SCHEME 3; square shows PH$_3$ position).

A common feature of these structures is that the incoming ligand, bulkier than CO, occupies a position below the allylic part of the ring, for steric reasons. Taking that into account, it can be seen that for Ind the arrangement of the Mn(CO)$_3$ group relative to the ring has changed: one



SCHEME 3

CO lies under the benzene part of Ind, and Flu prefers an exo-allylic coordination.[3ii,11] Therefore, the $Mn(CO)_3$ group must migrate along the ring. Chd and Hnaph are open polyenes, so that the allyl is created on one side and a double bond remains at the other extreme. Migration of $Mn(CO)_3$ is required again. For Hnaph, the benzene tail forces a rotation of $Mn(CO)_3(PH_3)$ relative to the ring to relieve steric constraints. Cp is different in that a planar η^2 coordination is found (FIGURE 1b). These geometric features show that a rearrangement of the ring is usually needed when a $\eta^5 \rightarrow \eta^3$ haptotropic shift takes place.

2.2 $\eta^5 \rightarrow \eta^3$ haptotropic shifts induced by ligand addition

Let us go back to the ring slippage reaction induced in $[Mo(\eta^5\text{-Ind})(CO)_2(NCMe)_2]^+$ by approach of acetonitrile.[4j] The extra electron pair donated by the incoming ligand would occupy the LUMO of the complex which is strongly Mo-Ind antibonding. The ring slippage contributes to a decrease of this antibonding character with the concomitant lowering of the energy. This effect is reflected in the LUMO of $[Mo(\eta^5\text{-Ind})(CO)_2(NCMe)_2]^+$ and the HOMO of $[Mo(\eta^3\text{-Ind})(CO)_2(NCH)_3]^+$, which are shown in FIGURE 2 in a tridimensional plot, and were calculated using the extended Hückel method[17] (CACAO program[18]). The Mo-CO bonding character of both orbitals can be noticed.

It is also important to remember that the ring slippage process starts to take place at a relatively long distance, such as 367 pm, between the incoming nitrile and the metal, emphasising the importance of stabilising the HOMO of the new species being formed. The other aspect of

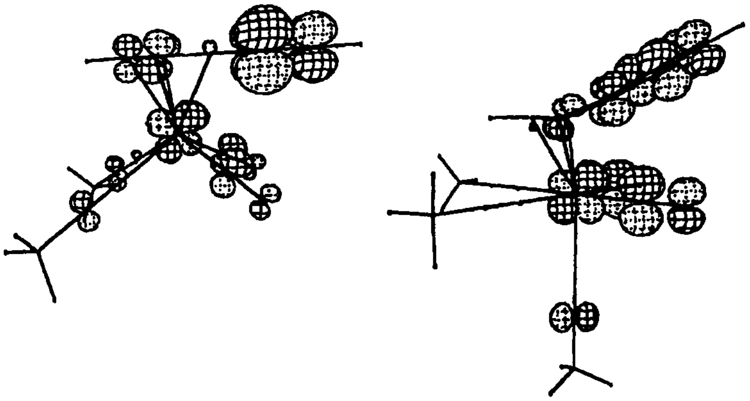


FIGURE 2 The LUMO of $[Mo(\eta^5\text{-Ind})(CO)_2(NCMe)_2]^+$(left) and the HOMO of $[Mo(\eta^3\text{-Ind})(CO)_2(NCH)_3]^+$ (right)

this reaction concerns its specificity, as it only occurs for a few coligands L, usually π-donors, and other reactions, such as substitution, take place for other ligands. The L = CNMe example was particularly puzzling, as at first sight this ligand does not seem too different from NCMe, namely in bulk. However, the energetics of the reactions differ, as shown below (DFT calculations).

$$[Mo(\eta^5\text{-Ind})(CO)_2(NCH)_2]^+ + NCH \rightarrow [Mo(\eta^3\text{-Ind})(CO)_2(NCH)_3]^+$$
$$\Delta H = -12.1 \text{ kJ/mol}$$

$$[Mo(\eta^5\text{-Ind})(CO)_2(CNH)_2]^+ + NCH \rightarrow$$
$$[Mo(\eta^3\text{-Ind})(CO)_2(CHN)_2(NCH)]^+$$
$$\Delta H = 40.1 \text{ kJ/mol}$$

Addition of NCH is exothermic for the nitrile complex, but endothermic for the isonitrile one. As the process is associative, it is disfavored by entropy changes, and unlikely to occur when $\Delta H > 0$, under normal conditions. Solvent effects should be very similar in both cases. The phosphine addition to $[Mn(\eta^5\text{-Ring})(CO)_3]$ was studied theoretically more recently and in more detail, namely the transition states were also determined.[4m] As an example, the stationay points along the reaction for Ring = Ind can be seen in FIGURE 3 and the results are qualitatively similar for other rings, if the different structural features discussed above are taken into account.

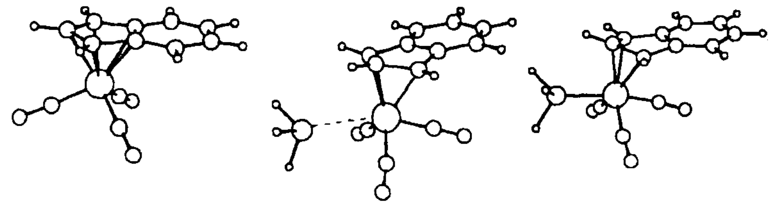


FIGURE 3 The calculated structures (DFT/B3LYP) of [Mn(η^5-Ind)(CO)$_3$](left), [Mn(η^3-Ind)(CO)$_3$(PH$_3$)] (right) and the transition state leading from one to the other (center)

The factors examined for the Mo system also hold in the reaction depicted in FIGURE 3: η^5 to η^3 migration helps relieve the Mn-Ind antibonding character of the new HOMO, and there is already a pronounced folding of the indenyl ring at the transition state. Typically, η^5-Ind is planar or very close to it, while η^3-Ind exhibits a larger fold angle, in the range 20 – 30°. On the other hand, the folding at the transition state is smaller (17° compared to 24° in the Mn system). For some other rings, there is no folding (not significant for Cp, and impossible for Flu). The energetics of this associative process can also be examined (TABLE I).

TABLE I Energy changes and activation energies (kJ/mol) for the reaction [Mn(η^5-Ring)(CO)$_3$] + PH$_3$ → [Mn(η^3-Ring)(CO)$_3$(PH$_3$)], for several rings

Ring	ΔE	$\Delta E^{\#}$
Cp	137.9	171.4
Ind	87.8	125.4
Flu	20.9	92.0
Chd	62.7	117.0
Hnaph	4.2	66.9

The activation energies approximately parallel the reaction energies, but all reactions are endothermic. It should be stated, however, that these reactions correspond to the first step of a pathway where CO is eliminated and final products [Mn(η^5-Ring)$(CO)_2(PH_3)$] are formed. Comparisons must be made with kinetic data and other effects must also be taken into account.[1] Besides, PH_3 is, as a model, farther from the phosphines used in the reactions than NCH is from NCMe (in this case the diference is negligible), if we want to compare with the previous example. In this context, the $\Delta E^{\ddagger}$ values give an order of reactivity Hnaph > Flu > Chd ~Ind ≫ Cp which reflects kinetic data from several experimental studies.[1,3z] A correlation was found[4m] between the (η^5-Ring)-M bond strength in the reactants and the ease of the haptotropic shift, and, thus, the reaction rate.

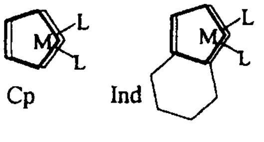
3. REDUCTIVELY INDUCED HAPTOTROPIC SHIFTS

Haptotropic shifts can be induced by the addition of two electrons in a reduction process, instead of the coordination of a new ligand. This seems to be an easier process to take place, as the number of ligands around the metal does not change, but, in spite of this, the ligands must adapt to the new electronic situation and geometrical changes also take place. Another challenging aspect is that it is possible to trap, either experimentally or computationally, the intermediate which is formed after a one electron reduction and compare it to the initial and final states.

3.1 Structures of η^x complexes

The geometries of [Mn(η^5-Ring)$(CO)_3$] complexes were discussed above, except for Ring = NC_4H_4 (pyrrolyl, pyr) and SC_4H_4 (thiophene, tp), where DFT/B3LYP calculations show that they adopt the same geometry as shown in SCHEME 2 for Flu and Chd.[41]The mixed [Mo(η^5-Cp)(η^5-Ring)$L_2]^{2+}$ compounds have also been studied for Ring = Cp, Ind. The bis(Cp) derivatives exhibit eclipsed, staggered or in-between conformations for the rings (SCHEME 4, left),[5] as the rotation barrier for the Cp is rather small and packing effects, besides interligand repulsion (Cp-L), may be dominant.[19] The preferred arrangement of the rings is the one shown. [M(η^5-Cp)$_2(CO)_2]^{3+}$ also follow this pattern for M = Mn, Re, according to DFT/B3LYP calculations.[4n] When

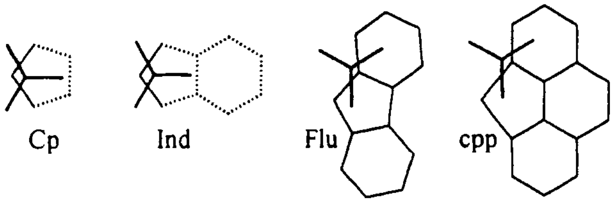
Ind replaces one Cp, there is no space for this larger ring to occupy a position trans to the L_2 ligands (L = $P(OMe)_3$, PMe_3, CNR; L_2 = dppe, bipy, etc.), and a rotation of the indenyl ring (close to 90°) takes place (SCHEME 4, right).[4i,k,10b]



SCHEME 4

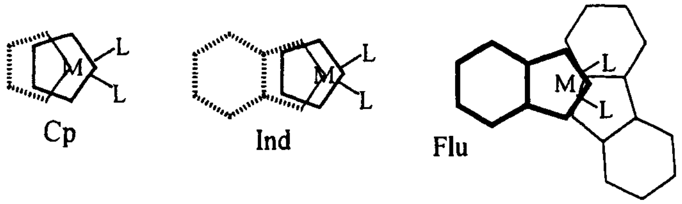
The structures of the same complexes after undergoing a 2-electron reduction were studied either by X-ray crystal diffraction or by theoretical methods (only these, when the compounds were not isolated).

The geometries of $[Mn(\eta^3\text{-Ring})(CO)_3]^{2-}$ complexes (rings defined as above) were optimized using DFT/B3LYP calculations, except for pyr and tp, where a preference for σ coordination of the heterocyclic ring was found, in order to take advantage of the electron lone pair in the heteroatom.[41] For the Cp derivative, the preferred conformation has the $Mn(CO)_3$fragment rotated 180° relative to the position observed in the η^5 compound (SCHEME 5). The ring is slipped but not folded. Two possibilities were examined for the Ind complex, namely the slipped and the exocyclic coordinations, the first being preferred by 40 kJ/mol and leading to folding of the ring (17°). In the larger rings which cannot bend (Flu, cpp, and H_2cpp), the exocyclic coordination of the allyl is always preferred (SCHEME 5).



SCHEME 5

Let us now examine the bismetallocene derivatives. [Mo(η^5-Cp)(η^3-Cp)L_2] compounds exhibit a folded and slipped Cp ring, the same arrangement being found for [Mo(η^5-Cp)(η^3-Ind)L_2], as shown in SCHEME 6. The ligand-ligand repulsion is less important with η^3- than with η^5- rings, allowing an eclipsed arrangement of the rings.[4i,k,10b] As the ring folds away from the metal, the carbon atoms also move away from the Cp ring (dashed lines in SCHEME 6). The calculated structure of [Mo(η^5-Cp)(η^3-Cp)$(CO)_2$] very much resembles the observed for the analogous W derivative.[3d] In this η^3 coordination mode, three M-C bonds of Cp or Ind are distinctly shorter than the remaining two (above 3 Å, outside bonding distance). Calculations were also performed for the analogous Mn and Re complexes, the only significant difference lying on the arrangement of the η^3-Ring. For Re, the most stable conformation is the same as for Mo and W, while for Mn the bent side of η^3-Cp lies over the CO groups, similarly to what was experimentally found for [Cr(η^5-Cp*)(η^3-Cp*)$(CO)_2$].[3e]



SCHEME 6

The geometries of the related complexes [Mo(η^5-Ind)(η^3-Ring)L_2] compounds (Ring = Flu, cpp, and H_2cpp) can also be examined in this section, although they were synthesized in a different way, with the purpose to find out which of the rings (Ind or Ring) would adopt the η^3 coordination mode, in order to keep the 18 electron count on the metal.[3ii] The preferred geometry is shown in SCHEME 6 for the Flu derivative and is the same when the Flu ring is substituted by cpp or H_2cpp, which also bind the metal in an exo-allylic mode. These preferences, namely the tendency of the larger ring to slip (Ind > Cp; Flu, cpp, H_2cpp > Ind), can be explained on the basis of the weaker M-C bonds these rings can make to the metal. In a Cp, three of the five π orbitals can donate electrons to the metal, namely the a_{1g} and the e_{1g} sets, which combine with s, z^2 and xz, yz, respectively. As the number of carbons atoms, and therefore the size of the ring, increases, the number of π orbitals also increases, but the appropriate orbitals are the same. The contribution of the carbons in the C_5 ring to the π orbitals is increasingly smaller, the larger the ring (100% in Cp, 56% in Ind, 38% in Flu, etc), and the metal-ring bond becomes weaker.

3.2 $\eta^5 \rightarrow \eta^3$ haptotropic shifts induced by reduction; intermediates and their structural features

Even in the absence of extra ligands, reduction induces geometrical changes in the coordination mode of the ring, besides the change in hapticity. Hence, slippage and folding must in some cases be accompanied by other rearrangements. The driving force for these changes is again the stabilization of the LUMO of the starting species, which becomes the HOMO of the reduced complex, owing to smaller overlap between metal and ring orbitals in a metal-ring antibonding orbital.

No transition states were calculated for these reactions, but an intermediate was predicted from DFT calculations (ADF), for the one electron reduction reaction of $[Mo(\eta^5\text{-}Cp)(\eta^5\text{-}Ind)L_2]^{2+}$ (L= $P(OMe)_3$, modelled by $P(OH)_3$), and later experimentally detected and characterized (cyclic voltammetry, ESR).[10b,20] The geometry of this intermediate is shown in FIGURE 4, between those of the parent compound $[Mo(\eta^5\text{-}Cp)(\eta^5\text{-}Ind)\{P(OH)_3\}_2]^{2+}$, and the reduced species $[Mo(\eta^5\text{-}Cp)(\eta^3\text{-}Ind)\{P(OH)_3\}_2]$.

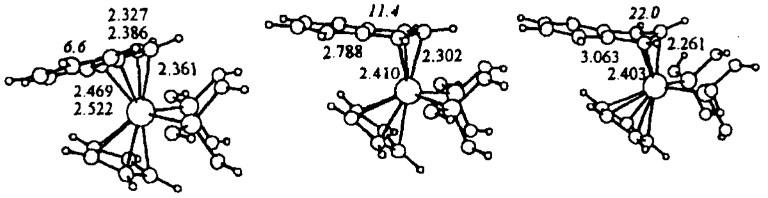


FIGURE 4 The calculated structures (ADF) of $[Mo(\eta^5\text{-}Cp)(\eta^5\text{-}Ind)\{P(OH)_3\}_2]^{2+}$ (left), $[Mo(\eta^5\text{-}Cp)(\eta\text{-}Ind)\{P(OH)_3\}_2]^+$ (center), and $[Mo(\eta^5\text{-}Cp)(\eta^3\text{-}Ind)\{P(OH)_3\}_2]$ (right)

$[Mo(\eta^3\text{-}Cp)(\eta\text{-}Ind)\{P(OH)_3\}_2]^+$ is a paramagnetic complex, which could be prepared by adding equivalent amounts of the η^5-Ind and the

η^3-Ind compounds, but was not stable for long enough to grow crystals for X-ray diffraction studies. The coordination of the indenyl group is in between those observed for the limiting species. The Mo-C distances, which make a very useful indicator,[4i] are 2.361, 2.386, 2.327, 2.522, and 2.469 Å, typical of a η^2+η^3 coordination, in the dication. The molecule is very asymmetric, as sketched in SCHEME 4, with an almost planar ring (fold 6.6°), and P-Mo-P angle 90.1°. The neutral complex is more symmetric (SCHEME 6), and although the calculations were performed without symmetry constraints, only three different Mo-C distances were found (2.261, 2.403, 3.063 Å), the larger one being outside bonding range, as expected. The fold angle of the ring became 22.0° and the P-Mo-P angle 83.2°. The paramagnetic intermediate shows some features of the neutral complex, as the fold angle is already 11.4°, while the Mo-C distances are 2.302, 2.410, and 2.788 Å. The molecule has become rather symmetric (only three different Mo-C bond lengths), and the distance between the metal and the hinge carbons is much longer than a normal Mo-C bond, but much shorter than what was found in the neutral complex. This type of geometry has been observed before in the complex $[(\eta\text{-Ind})_2\text{Ni}]$. While $[(\eta^5\text{-Ind})_2\text{Fe}]$ holds an 18 electron count, the related Ni species has two extra electrons and is formally a 20 electron complex. $[(\eta^5\text{-Ind})_2\text{Fe}]$ exhibits an almost perfect η^5 coordination, with two eclipsed indenyl rings. The Fe-C distances are 2.035, 2.042, 2.054, 2.092, 2.104 Å for one ring and similar for the other. The X-ray structure of the Ni derivative, on the other hand, shows a staggered arrangement of the rings, with Ni-C bonds of 1.973, 2.068, 2.057, 2.480, and 2.482 Å, suggesting a coordination between η^3 and η^5, as 2.480 Å is not decidedly outside bonding range, but is an extremely long bond length. The rings are folded by 13.7 and 14.1°. These characteristics may be interpreted, considering that, upon going from Fe to Ni, the two extra electrons would occupy a M-Ind antibonding orbital. Slippage would relieve the antibonding character of this orbital, making it more stable. As two electrons are added, each ring receives only one electron in average. Therefore, this situation is reminding of the paramagnetic intermediate in the Mo system. Another comparable geometry was shown in FIGURE 3. The transition state in the PH_3 induced indenyl slippage in $[\text{Mn}(\eta^5\text{-Ind})(\text{CO})_3]$ also shows this coordination mode on the indenyl ring, halfway between η^5 and η^3, with two much longer bonds (and very weak) and some folding.

4. WHAT MAKES RINGS BEHAVE DIFFERENTLY?

In most of the previous sections, the behavior of indenyl was discussed, though in some systems that of other rings (Cp, Flu, cpp, etc) was also analysed. The conclusion from kinetic studies in tricarbonylmanganese derivatives (TABLE I) indicate Hnaph > Flu > Chd ~Ind ≫ Cp as the order of decreasing reactivity of the complexes. In the Mo systems discussed in 3, mixed IndCp complexes were found to react much more easily than the analogous Cp_2 derivatives, as discussed in detail elsewhere.[4k] In this system, only in the biscarbonyl $[(\eta^5\text{-Cp})_2Mo(CO)_2]^{2+}$ was Cp observed to slip upon reduction, as back donation to CO helps stabilize the final η^3-Cp ligand. This issue was discussed in more detail in another publication,[4n] along with the aspect that often "slipped Cp" rings are not folded, contrary to what is found in indenyls.

A fundamental aspect lies in the weakening of the M-(η^5-Ring) bond, as the size of the ring increases (see 3.1), making the slippage process easier.[4k,11] The stabilization of the resulting η^3-Ring complex is also important, and the possibility of folding helps relieving steric interactions, as is observed in Ind, in contrast to other rings, such as Flu. The balance between these effects may be determining for a slippage process to take place.

4. CONCLUSIONS

Several general conclusions may be drawn from these detailed theoretical studies.

1. The larger the ring, and the larger its π system, the easier the slippage becomes. This behavior is explained by the fact that larger rings bind more weakly to the metal centers when they are η^5 coordinated.
2. η^3-Cp rings have not often been observed. The classic example, $[(\eta^5\text{-Cp})(\eta^3\text{-Cp})W(CO)_2]$, shows a pronounced folding.[3d] This structure is reproduced in theoretical calculations, but in other examples, namely mono-Cp derivatives, only a slippage without folding was predicted, and no examples could be found.
3. Heterocycles exhibit a marked tendency to coordinate η^1. Clear η^3 coordination has never been observed (and was predicted to be unfa-

vored relative to η^1), although η^5 coordination has been achieved when adequate substituents are present in the ring.

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