The Nature of the Indenyl Effect

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Abstract: The η^5-to-η^3 coordination shift of cyclopentadienyl ($Cp = C_5H_5^-$) and indenyl ($Ind = C_9H_7^-$) ligands in molybdenocene complexes, $[(\eta^5\text{-Cp}')(\eta^5\text{-Cp})Mo(CO)_2]^{2+}$ (Cp′ = Cp or Ind), driven by a two-electron reduction of those species, was studied and compared by means of molecular orbital calculations (B3LYP HF/DFT hybrid functional, DZP basis sets). The results obtained, in terms of optimized geometries, relative energies, and bond analysis parameters, compare well with the experimental data, and verify the well-known *indenyl effect*, that is, a significantly more facile η^5-to-η^3 rearrangement for the indenyl ligand when compared to cyclopentadienyl. However, the study of the folding of free Cp and Ind, combined with the ($\eta^{5/3}$-Cp′)–M bond analysis, shows that the observed difference is not the result of an intrinsic characteristic of the indenyl ligand, such as the traditionally accepted aromaticity gain in the benzene ring formed in η^3-Ind complexes. Instead, it is directly related to the Cp′–M bond strength. While the difference in the energy required to fold the two free ligands is negligible ($\leq 1\,kcal\,mol^{-1}$ for folding angles up to 20°), the (η^5-Cp)–M bond is stronger than that of (η^5-Ind)–M; however, the opposite situation is found for the η^3 coordination mode. The net result, for Cp′ = Ind, is a destabilization of the η^5 complexes and a stabilization of the η^3 intermediates or transition states yielding smaller activation energies and faster reaction rates for processes in which that is the rate-determining step.

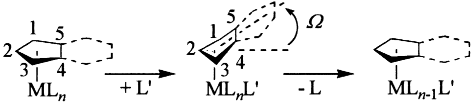
Keywords: ab initio calculations · coordination modes · cyclopentadienyl ligands · indenyl effect · molybdenum

Introduction

The coordination mode of a π ligand in an organometallic complex depends on the metal-electron count. The number of atoms directly bonded to the metal, that is, the hapticity of the hydrocarbon π ligands, often varies in order to compensate changes of the total electron number in the metal coordination sphere. The resulting rearrangements of the complex geometry and ligand coordination mode have been known for a long time for ligands such as cyclopentadienyl ($Cp = C_5H_5^-$) or indenyl ($Ind = C_9H_7^-$) and have been described as "ring slippage" or "ring folding" processes,[1] or by the more general designation of "haptotropic shifts".[2]

The most widely studied of those processes is certainly the η^5-to-η^3 shift observed in some complexes when a reduction, or the addition of a donor ligand, L′, increases the formal number of metal electrons by two. In this case, the excess electron density at the metal center is released by the cleavage of two out of the five M–C bonds to change the π ligand coordination from pentahapto (η^5) to trihapto (η^3). The importance of those processes was first noticed in studies of associative substitution reactions of electronically saturated complexes. A substantial increase in the reaction rates was observed for indenyl complexes, when compared to their cyclopentadienyl analogues.[3–9] This gave rise to the term *indenyl effect*[7] and its explanation, proposed then and still accepted today, is based in an enhanced stability of the η^3-Cp′ intermediates, for Cp′ = Ind, as a consequence of the aromaticity gain of the benzene ring formed by the six uncoordinated carbon atoms (Scheme 1).

Given the fundamental role played by haptotropic shifts in many important reactions in organometallic chemistry, such as catalytic processes,[10–16] a considerable effort has been



Scheme 1.

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undertaken in the study of low-hapticity π-ligand complexes, with slipped or folded coordination modes. These generally correspond to unstable intermediates that are very difficult to isolate and characterize. However, the understanding of their bonding and reactivity is crucial for a more complete knowledge of the reaction mechanisms. A large number of ligands has been tested, as a survey of the Cambridge Structural Database (CSD)[17] shows. There are structurally characterized complexes with η^3-coordinated Cp, in solution[18] and in the solid state,[19, 20] as well as ligands with larger π systems, such as fluorenyl ($C_{13}H_9^-$), cyclopentha[*def*]phenantrenyl ($C_{15}H_9^-$),[21–28] and 1-hydronaphthalene ($C_{10}H_9^-$);[29, 30] however, the most studied ligand is certainly indenyl.[21, 31–56]

Since the early papers by the Hoffmann group[2, 57, 58] a large amount of work has been devoted to the theoretical understanding of haptotropic shifts. Although most addressed the bonding and coordination geometries of cyclopentadienyl and indenyl,[59–67] or specifically the indenyl effect,[33–35, 38, 68, 69] the larger ligands, such as fluorenyl and cyclopentha[*def*]phenantrenyl, were also studied.[24, 25, 28, 70] The theoretical studies on haptotropic shifts have been recently reviewed for indenyl[71] and other ligands.[72]

In all the theoretical work, the nature of the indenyl effect was always assumed to be based on the increased stability of η^3-Ind complexes owing to the benzene aromaticity, as initially proposed by Mawby and Hart-Davies in 1969.[3] However, experimental data based on calorimetric studies of Mo and W complexes with Cp and Ind,[73] as well as theoretical studies focused on the indenyl effect,[33, 69] hinted that the more facile η^5-to-η^3 ring slippage showed by indenyl, when compared to cyclopentadienyl, might be related to the Cp′−M bond strength, specially in the η^5-coordination mode.

In this work, ab initio[74] and density functional theory (DFT)[75] calculations, complemented by an extended Hückel[76, 77] orbital analysis, are used to investigate the electronic factors behind the indenyl effect. The system chosen, the Group 6 bent metallocenes, such as $[(\eta^5\text{-Cp}')(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2]^{2+}$ (Cp′ = Cp or Ind), presents η^5-to-η^3 shifts of both Cp and Ind upon a two-electron reduction, and some X-ray structures of the corresponding η^3-Cp′ complexes have been determined.[19, 20, 32]

Results and Discussion

The comparative study of two related compounds, namely the bis(cyclopentadienyl) complex $[(\eta^5\text{-Cp})_2\text{Mo}(\text{CO})_2]^{2+}$ and the mixed-ring species $[(\eta^5\text{-Ind})(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2]^{2+}$, both of which are electronically saturated 18-electron complexes, has already been reported in an earlier attempt to understand the η^5-to-η^3 shift of cyclopentadienyl and indenyl, from an experimental and a theoretical point of view.[33, 34] A two-electron reduction of those complexes yields the corresponding neutral molecules with a slipped coordination of one ring (η^3-Cp′), therefore keeping the 18-electron count by the cleavage of two M−C(Cp′) bonds.

The DFT/B3LYP-optimized structures of the different (Ind)(Cp) and bis(Cp) complexes are represented in Figures 1 and 2, respectively, along with the more relevant structural parameters and the ν(CO) stretching frequencies. Of all the structural parameters defined to characterize the Cp′ hapticity,[49] the five M−C*x* ($x = 1-5$) bond lengths and the folding angle, Ω (defined as the angle between the plane of C1, C2, and C3, and mean plane of C1, C3, C4, and C5, see Scheme 1) will be used in the following discussion.

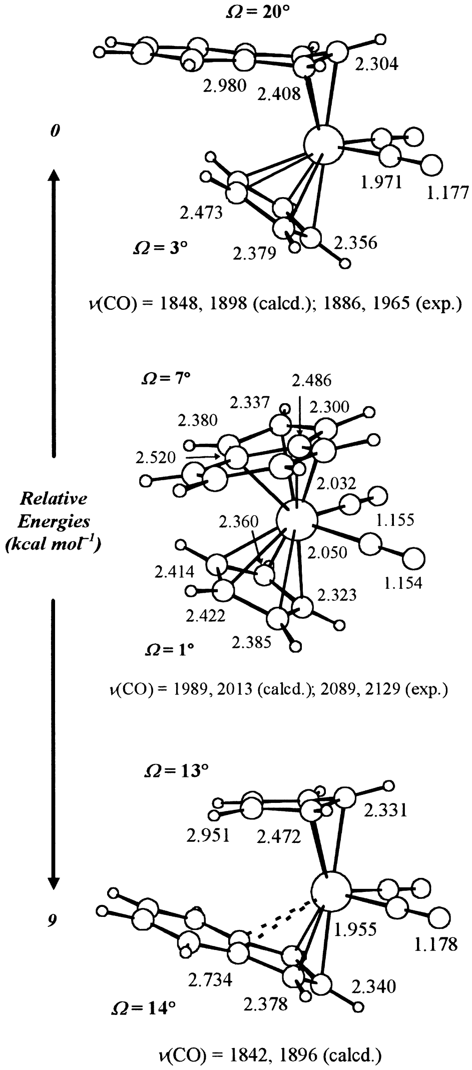
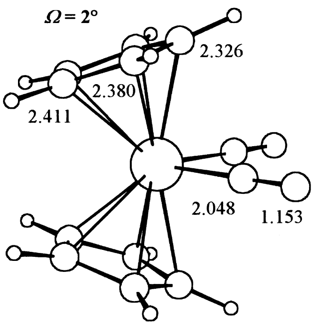
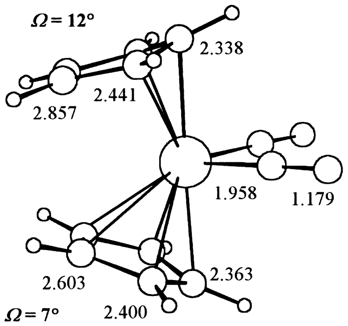


Figure 1. Optimized structures (B3LYP/DZP) of $[(\eta^3\text{-Ind})(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2]$ (top), $[(\eta^5\text{-Ind})(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2]^{2+}$ (centre), and $[(\eta^3\text{-Cp})(\eta\text{-Ind})\text{Mo}(\text{CO})_2]$ (bottom), with the more relevant structural parameters [distances in Å], the calculated and experimental ν(CO) stretching frequencies [cm^{-1}] and the relative energies between the two neutral complexes [$\text{kcal}\,\text{mol}^{-1}$].

The quality of the calculated structures can only be unequivocally tested for $[(\eta^3\text{-Ind})(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2]$, since this is the only complex with a full structural characterization obtained by X-ray diffraction.[32] This reduction product $[(\eta^3\text{-Ind})(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2]$ (Figure 1, top) exhibits a clear η^3 coordination of the indenyl ligand, with a significant folding angle ($\Omega = 20°$), two carbons atoms beyond bonding distances ($d_{\text{M-C4/5}} > 2.9$ Å) and the other three well within the normal range for M−C bonds (2.3–2.4 Å). A much smaller distortion is found in the coordination of the second π ligand, η^5-Cp, in $[(\eta^3\text{-Ind})(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2]$, when compared to its bis(Cp) analogue (Figure 2, bottom), as shown by the folding angle



ν(CO) = 2001, 2024 (calcd.); 2108, 2139 (exp.)



ν(CO) = 1834, 1895 (calcd.); 1838, 1952 (exp.)

Figure 2. Optimized structures (B3LYP/DZP) of $[(\eta^5\text{-Cp})_2\text{Mo(CO)}_2]^{2+}$ (top) and $[(\eta^3\text{-Cp})(\eta^5\text{-Cp})\text{Mo(CO)}_2]$ (bottom), with the more relevant structural parameters [distances in Å], and the calculated and experimental ν(CO) stretching frequencies [cm^{-1}].

($\Omega = 3°$) and the M–C4/5 distances (2.5 Å). The optimized structure is in very good agreement with the experimental one, with mean and maximum absolute deviations of 0.035 and 0.067 Å, respectively, for the bond lengths around the metal coordination sphere (M–C and C–O). The calculated bond angles are also very similar to the experimental values: CO-Mo-CO = 81° (calcd) and 82° (exptl), Ind-Mo-Cp = 127° (calcd and exptl), the same happening with the ligand folding angles (Ω), 20° (calcd) and 21° (exptl) for Ind, and 3° (calcd) and 2° (exptl) for Cp. The calculated ν(CO) stretching frequencies also agree with the experimental values,[32] with 2% and 4% deviations, as well as for the next complexes (the mean and maximum absolute deviations are 4% and 5% for the complexes in Figures 1 and 2). Therefore, the description provided by the theoretical approach used is adequate for the discussions intended here. The optimized geometry for $[(\eta^3\text{-Ind})(\eta^5\text{-Cp})\text{Mo(CO)}_2]$ has C_s symmetry, based on a plane defined by the metal and the two C_5 ring centroids. Indeed, this is a general feature of all the reduced complexes.

The mixed-ring dicationic complex $[(\eta^5\text{-Ind})(\eta^5\text{-Cp})\text{Mo(CO)}_2]^{2+}$ (Figure 1, center) presents a typical η^5-Cp ring, which is practically planar ($\Omega = 1°$), with five similar M–C(Cp) bond lengths (2.3–2.4 Å). The coordination geometry of the indenyl ligand is also the common one in "η^5-Ind" complexes, and should, perhaps, be more accurately called $\eta^3+\eta^2$, as recently suggested.[71, 72] In fact, a small distortion of this ligand is found ($\Omega = 7°$) and the two hinge carbon atoms (C4 and C5) have M–C(Cp) bond lengths slightly longer (≈2.5 Å) than those of the three allylic carbon atoms ($d_{\text{M–C1/2/3}} = 2.3–2.4$ Å). The relative conformation of the two π ligands minimizes the steric repulsion between the benzene portion of indenyl and the cyclopentadienyl opposite, this being a common feature of the (Cp)(Ind) mixed-ring metallocenes.[72]

An alternative product from the two-electron reduction of the mixed-ring dication was also optimized: $[(\eta^3\text{-Cp})(\eta\text{-Ind})\text{Mo(CO)}_2]$ (Figure 1, bottom). In this case, the geometrical rearrangement associated with the haptotropic shift was forced to occur in the Cp ligand (see Computational Methods), and the resulting coordination mode of this ligand is equivalent to what is found for the shifted η^3-Cp ligand in the corresponding bis(Cp) complex (Figure 2, bottom), with similar folding angle ($\Omega = 13°$) and M–C(η^3-Cp) distances (2.3–2.5 Å for C1, C2 and C3; and 3.0 Å for C4 and C5). However, the indenyl coordination deserves some attention. In fact, a quite distorted Ind is present in $[(\eta^3\text{-Cp})(\eta\text{-Ind})\text{Mo(CO)}_2]$, with a folding angle ($\Omega = 14°$) which lies between the values commonly found for the $\eta^3+\eta^2$ and the η^3 modes ($\Omega < 10°$ and $20 < \Omega < 30°$, respectively[71]) and two very long M–C distances (2.7 Å). This is an intermediate coordination geometry of indenyl and can be found in $[\text{Ind}_2\text{Ni}]$,[78] formally a 20-electron species, with an extra electron, on average, for each indenyl ligand. This indenyl coordination geometry, which lies between the fully coordinated $\eta^3+\eta^2$ and the slipped η^3, is also present in $[(\eta\text{-Ind})(\eta^5\text{-Cp})\text{Mo}\{\text{P(OMe)}_3\}_2]^+$, the "half-way" product of a two-electron reduction of the corresponding dication,[72, 79] a species closely related to the those studied here. In the case of $[(\eta^3\text{-Cp})(\eta\text{-Ind})\text{Mo(CO)}_2]$, a sharing of the geometrical rearrangements between the two π ligands (Cp and Ind), as a consequence of the reduction, is observed, in a way that has no parallel to what is found in the η^3-Ind complex (Figure 1, top; see above).

A C_{2v} symmetrical structure was obtained for $[(\eta^5\text{-Cp})(\eta^5\text{-Cp})\text{Mo(CO)}_2]^{2+}$ (Figure 2, top), despite the absence of any constraints in the calculations (see Computational Methods). Consequently, the optimized structure has equivalent coordination geometries for the two carbonyls, as well as for the two Cp ligands. An almost perfect η^5 coordination is found for these ligands, with negligible folding angles ($\Omega = 2°$), and a short range of the M–C(Cp) bonding lengths: 2.3–2.4 Å. The geometry of this dication (η^5 complex) is similar to those found[17] in the well-studied family of bent metallocenes. A two-electron reduction of that species results in the neutral $[(\eta^3\text{-Cp})(\eta^5\text{-Cp})\text{Mo(CO)}_2]$ complex (Figure 2, bottom). Here, one of the Cp rings coordinates in a η^3 mode, with three carbon atoms within bonding distances ($2.3 < d_{\text{M–C}} < 2.4$ Å), a significant folding angle $\Omega = 12°$, and two very long M–C(Cp) distances ($d_{\text{M–C}} > 2.8$ Å). The second Cp ligand presents also some distortion, although to a much lesser extent, with $\Omega = 7°$ and two M–C(Cp) distances slightly longer than the normal bond values (2.6 Å for C4 and C5, see Scheme 1 for the carbon numbering). The changes of the complex electronic structure upon the reduction are, thus, reflected in the coordination geometry of the two Cp rings.

The geometry calculated for $[(\eta^3\text{-Cp})(\eta^5\text{-Cp})\text{Mo(CO)}_2]$ compares well with the experimental structure determined for its tungsten analogue,[19] with equivalent overall geometrical features. The larger folding of the η^3-Cp ligand found for the W complex ($\Omega = 20°$), relative to that calculated for the Mo species ($\Omega = 12°$) is expected for a 5d metal[67] and compares well with the value optimized for the same complex by a different approach ($\Omega = 14°$).[33]

Some points emerge from the structural analysis of the optimized complexes, discussed above. The complexes are forced to undergo geometrical rearrangements to accommodate the increase of electronic density on the metal, resulting from the reduction. Although the η^5-to-η^3 shift of the Cp′ ligand is the most visible effect of the reduction, it is by no means the only one. Indeed, the increased metal-to-carbonyl backdonation leads to shorter M–C(CO) distances, going from $d_{M-C} > 2.03$ Å in the dications, to $d_{M-C} \leq 1.97$ Å in the reduced complexes, as well as to an increase in the C–O bond lengths, from 1.15 to 1.18 Å, in the same order. This is also reflected by the calculated ν(CO) frequencies that drop from 1989–2024 cm^{-1} in the η^5 reactants to 1834–1898 cm^{-1} in the reduced products. The experimental frequencies show the same trend.

Figure 3 shows the frontier orbitals of three model complexes (see Computational Methods), namely the LUMO of $[(\eta^5\text{-Ind})(\eta^5\text{-Cp})Mo(CO)_2]^{2+}$ (Figure 3, center), and the HOMO of the reduced species. Two products are compared, corresponding to haptotropic shifts on the two Cp′ ligands, the η^3-Ind complex (Figure 3, top) and the η^3-Cp species (Figure 3, bottom).

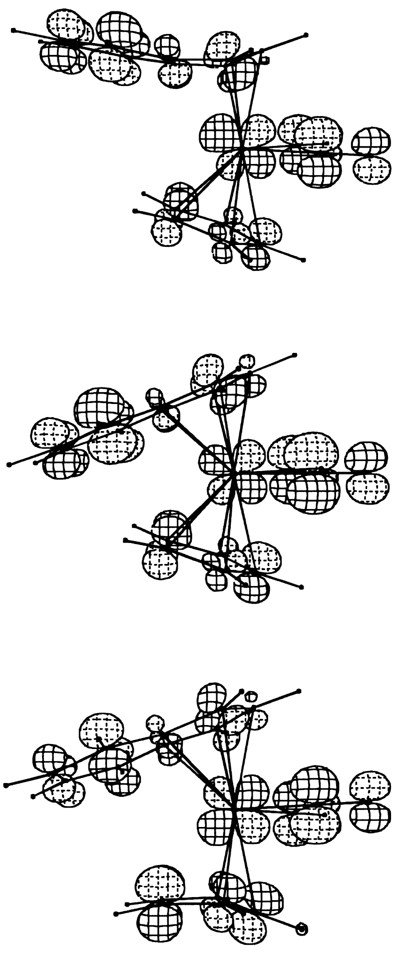


Figure 3. Three-dimensional representations (EHMO) of the π_s* orbital of model complexes $[(\eta\text{-Cp}')(\eta\text{-Cp})Mo(CO)_2]^{2+/0}$: the LUMO of $[(\eta^5\text{-Ind})(\eta^5\text{-Cp})Mo(CO)_2]^{2+}$ (center), and the HOMO of $[(\eta^3\text{-Ind})(\eta^5\text{-Cp})Mo(CO)_2]$ (top) and $[(\eta^5\text{-Ind})(\eta^3\text{-Cp})Mo(CO)_2]$ (bottom).

In fact, the LUMO of the reactant ($[(\eta^5\text{-Ind})(\eta^5\text{-Cp})Mo(CO)_2]^{2+}$, in Figure 3 example) is the orbital that receives the two electrons corresponding to the reduction process, giving rise to the HOMO of the reduced species. Therefore, the geometrical transformations discussed above are a direct consequence of the occupation of that orbital. There is a M–CO π-bonding interaction, between metal *xz* orbital and the carbonyl π orbital. On the other hand, the same orbital presents a π-antibonding character for the M–Cp′ interaction, it is a π_s* orbital, where "s" stands for symmetrical with respect to the C_s plane found in all the reduced species. The stabilization of the reduced species is achieved by three separate processes: 1) the shortening of the M–C(CO) distances, 2) the elongation of the C–O distances on the carbonyls, and 3) the elongation of the M–C4/5 bond lengths in the Cp′ ligand (that is, the haptotropic shift). The first corresponds to an enhanced bonding interaction, and the last two result in the release of antibonding character.

The increased tendency of indenyl to undergo η^5-to-η^3 shifts, when compared with the cyclopentadienyl ligand, namely, the indenyl effect, is also apparent in the optimized structures (Figures 1 and 2). On the one hand, the η^3-coordination mode is much more clearly achieved for Cp′ = Ind, with a significantly larger folding angle ($\Omega = 20°$) than those found the η^3-Cp species ($\Omega = 12°$ and 13°), which suggests that this geometry should be more favorable for Ind. On the other hand, the geometrical changes of the "unslipped" η^5-Cp′ ligand in the reduced complexes are clearly more important for the η^3-Cp products than for the η^3-Ind one, $[(\eta^3\text{-Ind})(\eta^5\text{-Cp})Mo(CO)_2]$ (see discussion above), which indicates that the costs associated with the geometrical rearrangements are taken essentially by Ind in the last molecule, and must be shared, to some extent, between the two Cp′ ligands in the η^3-Cp complexes. This is clearly seen in the relative energies of the two different reduced complexes with mixed rings (Figure 1, top and bottom); the η^3-Ind species is 9 kcal mol^{-1} more stable than the η^3-Cp complex.

The traditional explanation for the indenyl effect[3] (see Introduction) is based on an intrinsic characteristic of the indenyl ligand. If this is so, then the folding of a metal-free indenyl anion should be more favourable than the same process with a cyclopentadienyl anion. To check this hypothesis, calculations were performed on the free ligands, Cp and Ind. Thus, starting from the fully optimized planar ligands, each was progressively folded around the C1–C3 axis up to a 20° folding angle, and the energy required to achieve this distortion (the difference between the energies of the folded and the planar geometries) is represented in Figure 4, for both ligands.

These results show that a folded geometry is, in fact, more favorable for indenyl than for cyclopentadienyl, or more simply, it takes more energy to fold Cp than to fold Ind to the same extent. *However, the energy difference of this process between the two ligands is practically negligible (≤1 kcal mol^{-1}).* Thus, there is no *intrinsic* characteristic of a folded indenyl (such as the benzene aromaticity gain) clearly

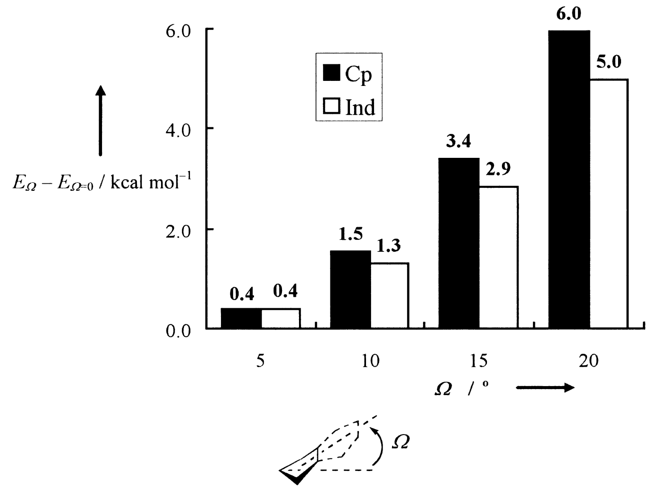


Figure 4. Energetic cost (B3LYP/DZP) for the folding of free Cp and Ind.

distinguishing this ligand from a cyclopentadienyl in the same situation, which might either be interpreted as the key factor for an enhanced stability of the η^3 complexes of the former ligand, or explain the indenyl effect, particularly taking into account that factors as large as 10^8 have been found for the reaction rates of analogous complexes of the two ligands.[7] In fact, the energy difference between a free planar Cp and the bent Cp ligand with the geometry shown in the $[(\eta^3\text{-Cp})(\eta^5\text{-Cp})Mo(CO)_2]$ complex is 4 kcal mol^{-1}, while for Ind the difference between a planar geometry and the bent indenyl ligand with the geometry observed in $[(\eta^3\text{-Ind})(\eta^5\text{-Cp})Mo(CO)_2]$ is 8 kcal mol^{-1}. This reflects the different degrees of distortion of those ligands in the reduced complexes ($\Omega = 12°$ and $20°$, respectively). Thus, although the small energy difference stated in Figure 4 points towards the right direction, the main factor behind the indenyl effect has to be sought elsewhere.

If the relatively more facile η^5-to-η^3 shift observed for Cp′ = Ind complexes, when compared with the Cp analogues, is not the result of an intrinsic characteristic of the indenyl ligand, then it should be related to differences in the M−Cp′ bond. The comparison between the M−Cp′ bonding for the two ligands may start with the analysis of M−C(Cp′) mean distances obtained from the optimized structures of the five complexes presented in Figures 1 and 2. For the η^5 complexes, the M−C(Cp′) mean distance is shorter for Cp (1.38 Å) than for Ind (1.40 Å). The opposite is found for the η^3 species, with the M−C(Cp′) mean distance to the three allylic carbons (C1, C2 and C3) being 2.37 Å for the η^3-Ind complex, and 2.41 and 2.43 Å for the η^3-Cp species. This seems to indicate that a (η^5-Cp′)−M bond is stronger for Cp than for Ind, the opposite being found for the η^3-coordination mode.

The electronic factors behind the differences found for the bonding of the Cp′ ligands were studied by means of a natural population analysis (NPA), a method that gives reliable charges,[80] and the evaluation of the M−Cp′ Wiberg indexes (WI) on the optimized complexes, as well as by the corresponding extended Hückel overlap population (OP) on model complexes (see Computational Methods), two sets of values which scale as bond strengths. The results are shown in Figure 5.

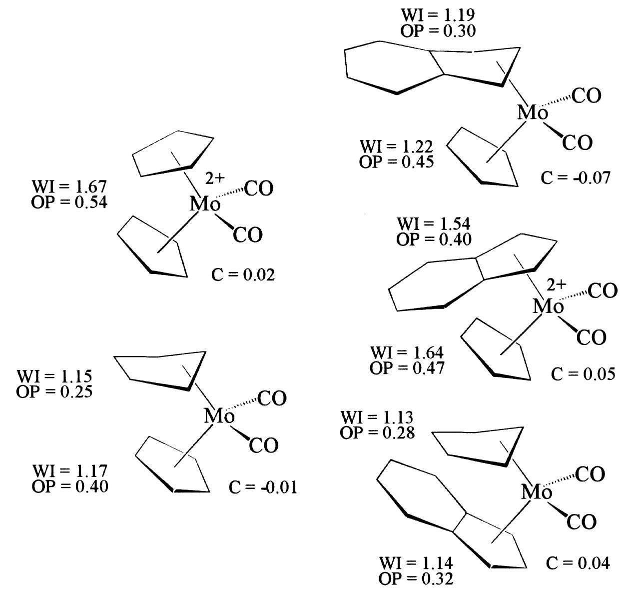


Figure 5. M−Cp′ bond parameters for $[(\eta\text{-Cp}')(\eta\text{-Cp})Mo(CO)_2]^{2+/0}$: molybdenum NPA charges (C) and Wiberg indexes, for the optimized molecules (WI), and extended Hückel overlap populations, for model complexes (OP).

The η^5 coordination of the Cp′ ligands can be compared in the two dicationic species. In the bis(Cp) complex, equal parameters are obtained for the two Cp ligands, given the C_{2v} symmetry of the molecule (WI = 1.67, OP = 0.54). Similar values are found for the (η^5-Cp)−M bond in $[(\eta^5\text{-Ind})(\eta^5\text{-Cp})Mo(CO)_2]^{2+}$ (WI = 1.64, OP = 0.47). However, the (η^5-Ind)−M bond is significantly weaker (WI = 1.54, OP = 0.40). On the other hand, in the reduced complexes, the (η^3-Ind)−M bond (WI = 1.19, OP = 0.30) is considerably stronger than (η^3-Cp)−M (WI = 1.15 and 1.13, OP = 0.25 and 0.28 for the bis(Cp) and the mixed-ring complexes, respectively). This reflects the trend shown by the M−C distances, confirming the electronic nature of the differences found. Thus, for a η^5 coordination, the cyclopentadienyl bond is stronger than the indenyl one, and η^3-Ind forms a stronger bond to the metal than η^3-Cp. This is further shown by the metal NPA charges. In fact, as the M−Cp′ bond is formally based on three two-electron donations from the ligand to the metal,[67] a stronger bond corresponds to an increased donation and, thus, to an electronically richer metal. In this way, a less positive Mo is found in the bis(Cp) dicationic complex ($C_{Mo} = 0.02$) than in the corresponding mixed-ring species ($C_{Mo} = 0.05$), showing that a more effective donation is achieved by means of a second Cp than by a Ind. The opposite is observed in the $[(\eta^3\text{-Cp}')(\eta^5\text{-Cp})Mo(CO)_2]$ reduced complexes, where the metal charges ($C_{Mo} = -0.01$ and -0.07 for Cp′ = Cp and Ind, respectively) reveal a stronger donation from Cp′ = Ind. The weakening of the "unslipped" cyclopentadienyl (η^5-Cp)−M coordination and its degree of distortion (see structural discussion above) are also reflected in the results of Figure 5. The decrease observed in the (η^5-Cp)−M bond parameters with the reduction is higher for the bis(Cp) complex (30 % for WI and 26 % for OP) than for the mixed-ring species (26 % for WI and 4 % for OP).

The nature of the M–Cp′ interaction and the nodal characteristics of the Cp′ π orbitals for Cp and Ind, explain the differences observed in the bonding of those ligands to a metal in the two coordination modes. In fact, Cp coordinates through five carbon atoms, the entire π system, while for Ind only a fraction of that system is used and, consequently, only a fraction of the electronic density of the π orbitals is actually involved in the interaction to the metal. This was shown to be the cause of a weakening of the (η^5-X)–M bond strength with the increase of the ligands X π-system.[69, 70] On the other hand, the symmetry breaking introduced by the Ind benzene ring produces changes on the nodal characteristics of the ligand's π orbitals with respect to those of a Cp ligand. While the D_{5h} symmetry of cyclopentadienyl forces equal contributions for the five carbon atoms, for Ind the two hinge carbons (C4 and C5) have small contributions to this ligand $4\pi_s$ orbital.[38] This is the orbital that interacts with metal xz orbital to give rise to the M–Cp′ π_s interaction and to the frontier molecular orbitals shown in Figure 3. The consequence is a smaller overlap between the indenyl and the metallic fragment orbitals, resulting in a weaker Ind–M interaction, as shown by the overlap population for that interaction in each case: OP(π_s) = 0.23 for (η^5-Ind)$^-$ – [(η^5-Cp)Mo(CO)$_2$]$^{3+}$, and OP(π_s) = 0.29 for (η^5-Cp)$^-$ – [(η^5-Cp)Mo(CO)$_2$]$^{3+}$. For a typical 18-electron complex, such as the dications [(η^5-Cp′)(η^5-Cp)Mo(CO)$_2$]$^{2+}$, in which all the Cp′–M antibonding orbitals are empty (π_s* is the LUMO of those species, see Figure 3), the result is a stronger Cp′–M bond for Cp′ = Cp, as shown by the bond parameters in Figure 5. However, in the reduced η^3-Cp′ complexes, π_s* becomes occupied (in fact, it becomes the HOMO of these complexes, see Figure 3) and, in this case, a weaker Cp′–M π_s interaction for indenyl means that for this ligand, a less antibonding orbital is occupied which thus yields a stronger Ind–M bond and a more stable molecule. This is entirely reflected in the HOMO of the reduced complexes represented in Figure 3. The π_s* orbital is more stable by 2.5 kcal mol^{-1} for the η^3-Ind species (Figure 3, top) than for the η^3-Cp complex (Figure 3, bottom), as a consequence of a reduced Cp′–M antibonding character for Ind: the (η^3-Cp′)$^-$ – [(η^5-Cp)Mo(CO)$_2$]$^+$ overlap population resulting from the occupation of that orbital is −0.18 for Cp′ = Ind and −0.21 for Cp′ = Cp. The reasons for these differences can be traced to a poorer participation of the Cp′ ligand in the π_s* orbital for Cp′ = Ind. In fact, the fraction of this electronic density of the orbital in the five coordinating carbons of Cp′ is 10% in the Ind species and 21% in the Cp complex.

Once the differences of the Cp′–M bonding for indenyl and cyclopentadienyl in the η^5- and the η^3-coordination modes are well established, we are able to rationalize the indenyl effect. Stronger (η^5-Cp′)–M bonds for Cp′ = Cp than for Cp′ = Ind should mean that η^5-coordinated cyclopentadienyl ligands form more stable complexes than their indenyl analogues. Besides, stronger M–C(Cp′) bonds will lead to a more difficult η^5-to-η^3 shift, since this rearrangement is based on the breaking of two of those bonds. On the other hand, the enhanced interaction with the metal achieved by indenyl in the η^3-coordination mode, should indicate that η^3-Ind complexes are more stable than the equivalent η^3-Cp species. If this is true, then the indenyl effect results directly from those differences in stability. A smaller energy difference between the η^5 reactants and the η^3 intermediates (or transition states) for Ind means smaller activation energies and faster reactions in those cases in which this is the limiting step (see Figure 6).

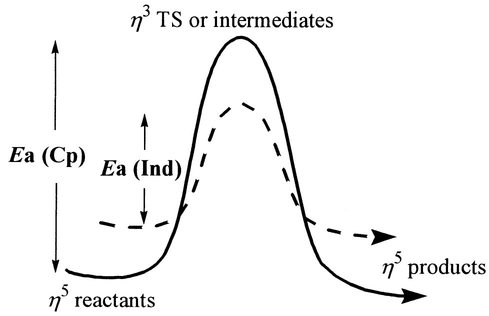


Figure 6. New interpretation of the indenyl effect.

However, the relationship between the Cp′–M bond strength and the stability of the corresponding molecule may not necessarily be straightforward, and some additional effort is needed to determine fully the relative stability of the Cp′ complexes in the two coordination geometries. For the reduced η^3 species this is simply done by comparing the two reduction products derived from the mixed-ring complex, [(η^5-Ind)(η^5-Cp)Mo(CO)$_2$]$^{2+}$. The increased stability of the η^3-Ind complex (9 kcal mol^{-1}), when compared to the η^3-Cp species, is directly given by their relative energies (Figure 1). For the η^5 reactants, a direct comparison is not possible, since different molecules are involved: [(η^5-Cp)(η^5-Cp)Mo(CO)$_2$]$^{2+}$ and [(η^5-Ind)(η^5-Cp)Mo(CO)$_2$]$^{2+}$. Nevertheless, a thermodynamic preference of the bis(Cp) species over the mixed-ring complex is clearly suggested by the calculated energy variation associated with the Cp′ substitution reaction [Eq. (1)].

$$[(\eta^5\text{-Cp})_2\text{Mo(CO)}_2]^{2+} + \text{Ind} \longrightarrow [(\eta^5\text{-Ind})(\eta^5\text{-Cp})\text{Mo(CO)}_2]^{2+} + \text{Cp}; \ \Delta E = 36\ \text{kcal mol}^{-1} \quad (1)$$

These results, although different in nature, essentially support the findings of Hoff and Kubas,[73] who proposed that the most significant contribution to the indenyl effect might be thermodynamic differences in the ground state. We add a second aspect, namely, that the intermediates derived from indenyl have lower energies, which suggests that kinetic effects also play a role.

Conclusion

A two-electron reduction of the electronically saturated complexes [(η^5-Cp′)(η^5-Cp)Mo(CO)$_2$]$^{2+}$ (Cp′ = Cp or Ind) yields the corresponding neutral species with a η^3-coordinated Cp′ ligand. Although the η^5-to-η^3 haptotropic shift of the π ligand, Cp′, is the more visible effect of the reduction, other structural changes also occur, namely weakening of the M–Cp bond to the second π ligand, strengthening of the M–C(CO) bond and weakening of the C–O bond. These changes can be traced to the HOMO of the reduced complexes, which is the orbital that becomes occupied on reduction. This orbital exhibits an antibonding (π_s*) character between the metal and the polyenic ligands (Cp and Cp′) and a bonding character between metal and carbonyl.

The detailed comparative analysis of the bonding of indenyl and cyclopentadienyl ligands in $[(\eta^5\text{-Cp}')(\eta^5\text{-Cp})\text{Mo(CO)}_2]^{2+}$ (Cp′ = Cp or Ind) and their reduction products led us to propose a new interpretation of the indenyl effect, that is, the increased ability of indenyl to undertake η^5-to-η^3 shifts, when compared to cyclopentadienyl. Indeed, the study of the electronic factors behind that effect showed that it does not rely on an intrinsic characteristic of the indenyl ligand, such as the traditionally assumed gain of aromaticity in the benzene ring formed by the six uncoordinated carbon atoms. On the contrary, it is a direct consequence of the different bonding of the π ligands to the metal in the two coordination modes (η^5 and η^3):

1) The (η^5-Cp)−M bond is stronger than the (η^5-Ind)−M bond.
2) The (η^3-Cp)−M bond is weaker than the (η^3-Ind)−M bond.

This is reflected in the relative stability of the corresponding complexes: η^5-Cp complexes are more stable than their Ind analogues, and η^3-Cp species are less stable than their Ind analogues. The energy difference between the η^5 reactants and the η^3 intermediates, or transition states, is, therefore, smaller for indenyl, yielding smaller activation energies and faster reactions for the complexes of this ligand, when the haptotropic shift occurs in the rate-determining step. Therefore, the indenyl effect is based on the stability of *both* the η^5 reactants and the η^3 intermediates, and displays both a thermodynamic and a kinetic origin.

Computational Details

The geometry optimizations were accomplished by means of ab initio and DFT calculations performed with the Gaussian 98 program.[81] The B3LYP hybrid functional was used in all optimizations. That functional includes a mixture of Hartree–Fock[74] exchange with DFT[75] exchange-correlation, given by Becke's three-parameter functional[82] with the Lee, Yang and Parr correlation functional, which includes both local and non-local terms.[83, 84] DZP quality basis sets were used in all the calculations: standard 3-21G* for C, H and O[85] and LanL2DZ[86, 87] with an added f-polarization function[88] for Mo. This B3LYP/DZP approach has produced reliable results for the study of haptotropic shifts on a variety of systems.[67, 69, 70] All the optimized geometries are the result of full optimizations without any symmetry constraints, with the exception of the $[(\eta^3\text{-Cp})(\eta\text{-Ind})\text{Mo(CO)}_2]$ complex. In this case, a model complex with η^5-Ind and η^3-Cp coordination (based on the $[(\eta^3\text{-Ind})(\eta^5\text{-Cp})\text{Mo(CO)}_2]$ crystal structure[32]) was optimized, keeping the five Mo–C(Ind) bond lengths fixed; the cyclopentadienyl coordination geometry thus obtained was then fixed, and the indenyl position allowed to relax, yielding the final geometry. All the stationary points were confirmed by frequency calculations and the energies were zero-point corrected. The frequencies presented were scaled by a factor of 0.9613.[89] A natural population analysis (NPA)[90] was performed in order to evaluate the charge distribution on the optimized complexes, and the Wiberg indexes[91] obtained were used as a measure of the Cp′−M bond strength. The Cp′−M Wiberg index in each species was taken as the sum of the five M−C(Cp′) indexes.

The extended Hückel calculations[76, 77] were performed with the CACAO program[92] and modified H_{ij} values were used.[93] The basis set for the metal atoms consisted of ns, np and $(n-1)$d orbitals. The s and p orbitals were described by single Slater-type wave functions, and the d orbitals were taken as contracted linear combinations of two Slater-type wave functions. The parameters used for Mo were the following (H_{ii} [eV], ζ): 5s −8.77, 1.960; 5p −5.60, 1.900; 4d −11.06, 4.542, 1.901 (ζ_2), 0.5899 (C1), 0.5899 (C2). Standard parameters were used for other atoms. Calculations were performed on models based on the optimized geometries with idealised maximum symmetry, and the following distances [Å]: M−(C_5 ring centroid) 2.00, M−C(CO) 2.00, C−O 1.15, C−C 1.40, C−H 1.08; and angles [°]: Cp-Mo-Cp′ (Cp′ = Cp, Ind) 140, CO-Mo-CO 80, Ω 30.

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