Haptotropic Shifts and Fluxionality of Cyclopentadienyl in Mixed-Hapticity Complexes: A DFT Mechanistic Study

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DFT calculations were used to study the mechanism of all fluxional processes of cyclopentadienyl ligands (Cp = C_5H_5) in a molybdenum bis(imido) complex, [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$]. Four dynamic processes could be identified: (1) rotation of η^5-Cp in its plane, (2) rotation of η^1-Cp around the Mo−C bond, (3) metallotropic migration along the ring carbons of η^1-Cp, and (4) interchange between the two Cp ligands, η^1-Cp and η^5-Cp. The mechanism obtained for process 3 corresponds to a [1,2]-migration, in agreement with experimental NMR studies. The mechanism of process 4 corresponds to a single-step path, and the calculated activation energy (15 kcal mol^{-1}) matches exactly the experimental value. No η^3-Cp intermediates could be found in any process.

Introduction

The existence of fluxional processes or dynamic behavior in molecules attracted much interest since the early 1960s,[1−3] when Cotton et al. proposed the term “stereochemically nonrigid” for those species.[4] The reason for this interest is understandable. In fact, well-established covalent bonds in stable compounds are broken and formed in intramolecular rearrangements that may occur easily at room temperature and, sometimes, cannot be frozen in the temperature range practicable for most analytical techniques. The development of variable-temperature NMR spectroscopy[5] transformed fluxionality in molecules into a familiar phenomenon, but by no means diminished its interest. Many dynamic processes can be viewed as “intramolecular reactions” and, thus, represent excellent models for computational studies on reaction mechanisms. Their simplicity arises from the fact that all changes occur within a single molecule, avoiding problems often found in more complex reactions, e.g., solvation.

Haptotropic shifts of π-ligands in general, and of cyclopentadienyl (Cp = C_5H_5) in particular, are widely known processes that correspond to the adjustment of the number of M−C bonds to the metal electron count.[6,7] For example, electrochemical reduction or ligand addition, increasing by two the number of metal electrons, may induce the breaking of two M−C(Cp) bonds, i.e., a shift from η^5-Cp to η^3-Cp. These processes take part in the mechanism of many important reactions such as in catalytic systems.[8−14] Indeed, cyclopentadienyl complexes are often fluxional, and of special interest are mixed-hapticity species with one η^1 and one η^5-Cp. In these cases, intramolecular haptotropic rearrangements leading to the interchange of the two Cp ligands may occur, as well documented for a number of molecules.[15−25] In a recent report on bis(imido) complexes, [M(η^5-Cp)(η^1-Cp)(NR)$_2$] (M = Mo, R = ^{t}Bu; or M = W, R = ^{t}Bu, Mes),[26] no less than three different fluxional processes could be detected by NMR spectroscopy: rotation around the M−C$_{ipso}$ bond of η^1-Cp, migration of the metal along the ring carbons of this ligand, and interconversion between η^1-Cp and η^5-Cp. Equivalent dynamic processes were observed previously in the isolobal Nb complex, [Nb(η^5-Cp)$_2$(η^1-Cp)(N^{t}Bu)],[27] but in both cases the experimental data did not allow the establishment of

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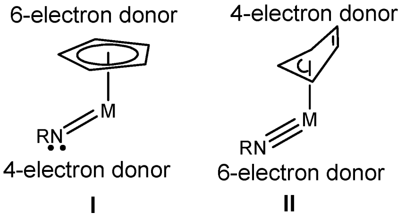
Chart 1



a complete mechanism for Cp fluxionality. The existence of η^3-Cp species as putative intermediates in the haptotropic shift has been postulated, and the possibility that such species could be common intermediates in the metallotropic migration has also been discussed.[26,27]

The Mo complex above, [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$], is formally an 18-electron Mo(VI) complex (d^0) with η^5-Cp donating six electrons, η^1-Cp donating two, and the remaining 10 being provided by the imido ligands (N^{t}Bu^{2-}). The 18-electron count is reached with, on average, one imido donating four and the other donating six electrons (**I** and **II** in Chart 1, respectively). These ligands are electronically versatile and can establish two or three bonds to the metal. Such flexibility has been repeatedly used to justify the existence of Cp dynamic behavior in imido complexes, such as [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$][26] and [Nb(η^5-Cp)$_2$(η^1-Cp)(N^{t}Bu)].[27] In these cases it has been argued that the stabilization of electron poorer metal centers in intermediates or transition states could be achieved through an increase of the M−imido bond order.

This work reports a comprehensive DFT[28] mechanistic investigation of all Cp fluxional processes mentioned above, plus rotation of η^5-Cp in its plane, in the Mo complex [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$]. Many other species could have been selected for a representative case study, e.g., [Nb(η^5-Cp)$_2$(η^1-Cp)(N^{t}Bu)]. However, the Mo molecule, besides representing a better choice in terms of computational cost, has also been the subject of a recent study[26] that provided a reliable experimental value of activation energy for the Cp interchange process.

Results and Discussion

The comparison between the structure calculated for [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$] (Figure 1) and the X-ray structure of the related W complex [W(η^5-Cp)(η^1-Cp)(NMes)$_2$][26] provides a test for the performance of the theoretical method (see Computational Details). Despite the differences between the two complexes, the geometries are equivalent, with mean and maximum absolute deviations for the M−X distances of 0.04 and 0.10 Å, respectively, showing that the method provides a good structural description of the system.

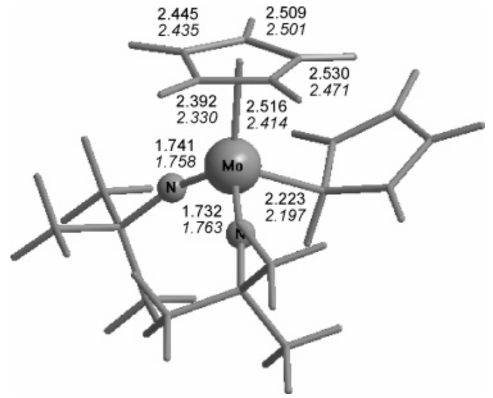


Figure 1. Optimized geometry (PBE1PBE/b1) for [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$]. The calculated M−X distances (Å) are presented, as well as the experimental values (italics) observed for the related [W(η^5-Cp)(η^1-Cp)(NMes)$_2$] complex.

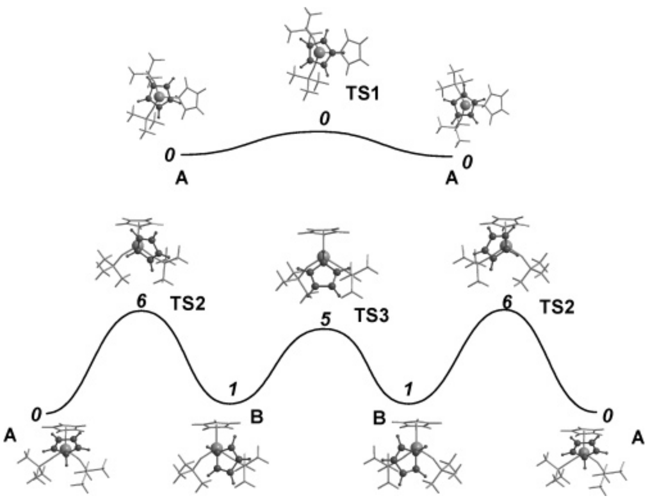


Figure 2. Energy profiles for the rotation of η^5-Cp (top) and η^1-Cp (bottom) in [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$]. The minima and the transition states were optimized (PBE1PBE/b1), and the obtained structures are presented with the moving Cp highlighted. The energy values (kcal mol^{-1}, italics) are referred to the most stable conformer, **A**.

The energy profiles calculated for the rotation of each Cp ligand in [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$] are represented in Figure 2. Rotation of η^5-Cp occurs very easily, with practically no activation energy ($E_a \approx 0$ kcal mol^{-1}),[29] explaining why this process could be neither frozen nor experimentally detected.[26] In the corresponding transition state (**TS1**) the rotating η^5-Cp ligand presents an intermediate conformation, and the overall geometry around the metal is similar to the one existing in the minimum, with differences in the M−X distances within 0.01 Å. The moving ligand is clearly η^5-coordinated, and the mean M−C(Cp) distance (2.48 Å) is maintained along the process.

A complete rotation of η^1-Cp follows a three-step mechanism (Figure 2, bottom). In the more stable conformer (**A**) η^1-Cp eclipses the η^5-Cp ligand in a geometry similar to the one determined in the X-ray structure of the W complex (Figure 1). Rotation of η^1-Cp around the Mo−C bond, going through **TS2**, generates a slightly less stable conformer (**B**) with that ligand in front of one of the imido ligands. A second step, through **TS3**, brings **B** into an equivalent structure, but now with η^1-Cp eclipsing the other N^{t}Bu ligand. The final step is equivalent to the first one and regenerates **A**. In each transition state, **TS2** and **TS3**, the conformation of the rotating ligand is intermediate between the corresponding minima, and the structural changes of the molecule during the entire process are minimal. The more relevant feature is a small elongation of the M−C$_{ipso}$ distance in the transition states (2.27 Å in **TS2** and 2.25 Å in **TS3**), when compared to the minima (2.22 Å). This corresponds to a slight weakening of the Mo−(η^1-Cp) bond, as shown by the Mo−C Wiberg indices (WI):[30] 0.59 in the minima, 0.57 in **TS2**, and 0.58 in **TS3**. The negligible structural

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(29) If free energy is considered, the barrier becomes 1 kcal mol^{-1}. Free energy was obtained at 298.15 K and 1 atm by conversion of the zero-point-corrected electronic energies with the thermal energy corrections based on the calculated structural and vibrational frequency data.

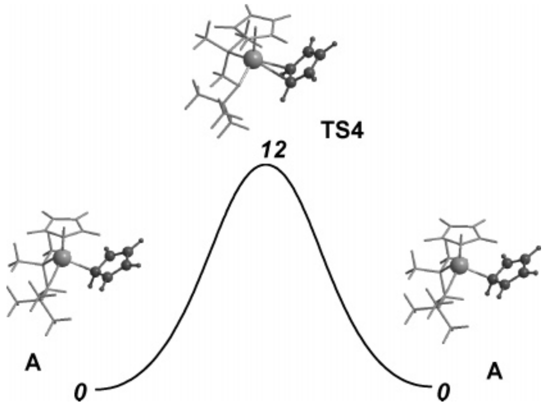

Figure 3. Energy profile for the metallotropic migration along η^1-Cp in [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$]. The minimum and the transition state were optimized (PBE1PBE/b1), and the obtained structures are presented with η^1-Cp highlighted. The energy values (kcal mol^{-1}, italics) are referred to **A**.

rearrangement suffered by the molecule along the process results in a very easy rotation, with overall activation energy of 6 kcal mol^{-1}, justifying why this rotation could be detected only for the W complex, with the bulkier mesityl substituents.[26]

The energy profile calculated for migration of the metallic fragment along the carbon atoms of the η^1-coordinated Cp ligand is represented in Figure 3.[31] The mechanism obtained corresponds to a one-step path in which the metal hops between two adjacent carbons, in a [1,2]-shift with simultaneous breaking of one M−C bond and formation of the other, as initially proposed by Cotton et al. based on NMR evidence[4] and confirmed later, on the same grounds, for systems such as [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$][26] and [Nb(η^5-Cp)$_2$(η^1-Cp)(N^{t}Bu)].[27] The process starts with a σ-bonded Cp in a clear η^1 mode, in **A**, evolving to a species with two weaker Mo−C bonds, in what may be viewed as a η^2-Cp, in the transition state (**TS4**). Here, the Cp ligand remains planar, with a folding angle[32] of $\Omega = 179°$, and the Mo−C(Cp) distances (2.50 and 2.52 Å) and Wiberg indices (0.26 and 0.28) are characteristic of a π-bonded ligand. The N−Mo−N angle is pratically equal in **A** (108°) and **TS4** (106°). The activation energy obtained (12 kcal mol^{-1}) is quite accessible, in accordance with a process occurring at room temperature. The possibility of a [1,3]-migration path occurring at higher temperatures and the existence of η^3-Cp intermediates could not be discarded on experimental grounds.[26] However, several attempts to optimize the corresponding transition state were unfruitful, suggesting that this mechanism is unlikely. When a [1,3]-mechanism is forced, the η^5-Cp ligand starts to shift and the transition state for (η^1-Cp)/(η^5-Cp) exchange, **TS5** (see below), is obtained. This is an indication of electronic saturation in **A**, since a η^1-Cp to η^3-Cp shift would represent an increase of the metal electron count resulting in a species with more than 18 electrons. The system avoids this by shifting the η^5-Cp ligand.

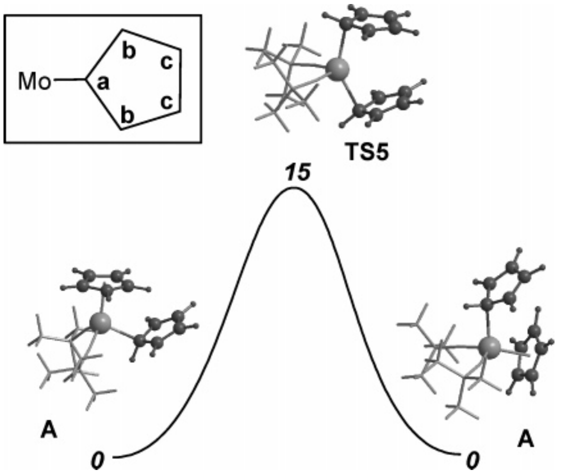

Figure 4. Energy profile for the interchange between Cp ligands in [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$] and C(Cp) labeling in **TS5**. The minimum and the transition state were optimized (PBE1PBE/b1), and the obtained structures are presented with the Cp ligands highlighted. The energy values (kcal mol^{-1}, italics) are referred to **A**.

The evolution of the electronic structure of the molecule along the metallotropic shift is worth considering. Although the shifting Cp remains formally a two-electron donor along the process, a π-bonded η^2-Cp, as in **TS4**, is expected to be a poorer donor than the σ-coordinated Cp (η^1) existing in **A**. This is confirmed by the charge of the Cp ligand, obtained by a natural population analysis (NPA):[33] −0.34 in **A** and −0.42 in **TS4**. The Cp is more negative in **TS4**, meaning that it donates less electron density to the metal. The increase in electron density of η^2-Cp in **TS4** could also derive from better back-donation from the metal. However, the NPA charge at the metal is practically the same in **A** (1.06) and **TS4** (1.07), showing that the metal remains Mo(VI) along the process and indicating electronic compensation from the other ligands. The electronically flexible imido ligands are the obvious candidates for such compensation since they can establish two or three formal bonds to the metal (Chart 1). Interestingly, and perhaps somewhat surprisingly, in the case of the metallotropic migration in [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$] the greater part of the electronic compensation of the metal does not come from the imido ligands, but from η^5-Cp. The NPA charge of the imido ligands in **TS4** is only 0.01 higher (less negative) than in **A**, while the η^5-Cp charge varies from −0.21 (**A**) to −0.17 (**TS4**). The net effect of the increased electron donation from η^5-Cp in **TS4** is a stronger Mo−(η^5-Cp) bond, as shown by the Mo−C Wiberg indices: 0.12−0.28 (**A**) and 0.14−0.35 (**TS4**).

The last fluxional process studied is the interconversion between the two cyclopentadienyl ligands, η^5-Cp and η^1-Cp, in [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$]. The corresponding energy profile is represented in Figure 4. The mechanism follows a one-step path in which the Cp ligand originally coordinated in a η^5 mode ends up σ-bonded (η^1), while the reverse happens with the other Cp, initially η^1-coordinated. In the transition state (**TS5**) the N−Mo−N angle remains unchanged with respect to **A**, and both Cp ligands present equivalent coordination modes that are intermediate between η^5 and η^1. In fact, **TS5** has pseudo-

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(30) (a) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083. (b) Wiberg indices are electronic parameters related to the electron density between atoms. They can be obtained from a natural population analysis and provide an indication of the bond strength.

(31) An equivalent mechanism ($E_a = 13$ kcal mol^{-1}) was obtained for the metallotropic shift in the less stable conformer, **B**. The corresponding profile is presented as Supporting Information (Figure S1).

(32) (a) Faller, J. W.; Crabtree, R. H.; Habib A. *Organometallics* **1985**, *4*, 929. (b) Ω can be defined as the angle between (1) the plane of C$_a$ and the two C$_b$ atoms and (2) the mean plane of the two C$_b$ and the two C$_c$ atoms (see Figure 4 for C$_{Cp}$ labeling).

(33) (a) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 41. (b) Carpenter, J. E. Ph.D. Thesis, University of Wisconsin, Madison WI, 1987. (c) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (d) Reed, A. E.;Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066. (e) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 1736. (f) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (g) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (h) Weinhold, F.; Carpenter, J. E. *The Structure of Small Molecules and Ions*; Plenum: NY, 1988; p 227.

C_{2v} symmetry with the ligands equivalent, two by two. The coordination geometry of Cp in **TS5** could be taken as η^3, with two very long Mo−C distances (>3.4 Å). However, a closer look reveals a very strong Mo−C_a bond (see Figure 4 for carbon labeling) with a distance (2.23 Å) and a Wiberg index (WI = 0.48) characteristic of a σ bond, while the next bonds, Mo−C_b, are rather long (2.78−2.84 Å) and weak (WI = 0.07). In other words, the coordination geometry of Cp in **TS5** is best described as η^1 rather than η^3. Accordingly, the coordinated Cp ligands show a high degree of localization of the $C_b{=}C_c$ double bonds (d = 1.37−1.38 Å, WI = 1.59−1.60), when compared with C_a−C_b (d = 1.45−1.46 Å, WI = 1.15) and C_c−C_c (d = 1.44 Å, WI = 1.24). In addition, the Cp ligands in **TS5** are practically planar (Ω = 176°), indicating that the interchange between Cp ligands in [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$] follows a ring slippage mechanism, rather than ring folding, in good agreement with what was found to be favored in [M(η^5-Cp)L_3] complexes.[34] Despite numerous attempts, no η^3-Cp complex could be optimized and, thus, the possibility of an alternative mechanism with such species as intermediate seems unlikely.

The variation of the charge distribution in the molecule, along the Cp interconversion path, is also of interest. Going from one η^5-Cp and one η^1-Cp, in **A**, to two η^1-Cp, in **TS5**, represents a significant loss of electron density in the metal that, in this case, has to be balanced by the imido ligands. This is confirmed by the reinforcement of the Mo−N bonds, which become shorter (1.72 Å) and stronger (WI = 1.87 and 1.88) in **TS5** than in **A** (d = 1.73 and 1.74 Å, WI = 1.79 and 1.84). However, this compensation is considerably less efficient than the one performed by η^5-Cp in the transition state for metallotropic migration (**TS4**). While in **TS4** the metal NPA charge is only 0.01 higher than in **A**, in the transition state for Cp interchange (**TS5**) the metal center is considerably more positive, with a charge (1.24) that is 0.18 higher than in the minima, **A**. These results suggest than the electronic flexibility of the imido ligands and its role on the stabilization of the molecule along the dynamic processes have been probably overestimated, at least in this system. The electronic changes around the metal justify why this interconvertion process is the most difficult of the four Cp fluxional processes. The corresponding activation energy (15 kcal mol^{-1}) indicates a process that may occur around room temperature and matches exactly the experimental value, determined by NMR spectroscopy.[26]

Conclusions

The fluxionality of cyclopentadienyl ligands in [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$] was investigated, and four different processes were studied: (1) rotation of η^5-Cp, (2) rotation of η^1-Cp, (3) metallotropic migration along the carbon atoms of η^1-Cp, and (4) Cp exchange between η^1-Cp and η^5-Cp, in increasing order of activation energy. The first two are very facile processes that interconvert conformers of the molecule, while 3 and 4 are more difficult, but still have associated energy barriers that are rather accessible and indicative of room-temperature fluxionality.

The presence of η^3-Cp intermediates in the metallotropic migration or in the Cp exchange processes is not confirmed, as such species could not be optimized. Instead, one-step mechanisms were obtained for these two dynamic processes. In addition, the results indicate that although some stabilization of the molecule is achieved through the reinforcement of Mo−NR bonds in order to balance the loss of Mo−C(Cp) bonds broken along the processes, the importance of this stabilization is small and, thus, the role of the imido ligands and their electronic flexibility seems to be less important than expected and often invoked.

Computational Details

All calculations reported in the text were performed using the Gaussian 03 software package[35] and the PBE1PBE functional, without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including a 25% mixture of Hartree−Fock[36] exchange with DFT[28] exchange−correlation, given by the Perdew, Burke, and Ernzerhof functional (PBE).[37] The optimized geometries were obtained with the LanL2DZ basis set[38] augmented with an f-polarization function[39] for Mo and a standard 6-31G(d,p)[40] for the remaining elements (basis b1). Transition state optimizations were performed with the synchronous transit-guided quasi-Newton method (STQN) developed by Schlegel et al.[41] Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides and obtaining the minima presented on the energy profiles. A natural population analysis (NPA)[33] and the resulting Wiberg indices[30] were used to study the electronic structure and bonding of the optimized species. Basis set convergence, in size, was tested through single-point energy calculations with a VTZP basis set (basis b2): Stuttgart/Dresden ECP with valence triple-ζ (SDD)[42] and an added f-polarization function[39] for Mo and standard 6-311G(d,p)[43] for the remaining elements. The activation energies obtained at the PBE1PBE/b2//PBE1PBE/b1 level are within 1.5 kcal mol^{-1} of the values obtained with the smaller basis set (PBE1PBE/b1), and thus, the latter are used in the text.

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The calculations were repeated with the B3PW91[44,45] and the B3LYP[44,46] functionals. The results obtained with B3PW91 are equivalent to the ones provided by PBE1PBE with maximum differences in activation energy of 1.3 kcal kcal mol^{-1}. However, B3LYP was found to underestimate the energy barrier for the exchange between η^1-Cp and η^5-Cp ($E_a = 11$ kcal mol^{-1}), resulting in an inversion on the order of the two less favored processes. With B3LYP, the haptotropic shift becomes slightly easier than metallotropic migration ($E_a = 12$ kcal mol^{-1}). Interestingly, the stereochemical influence of the ^{t}Bu groups as N-substituents seems to be minimal with respect to the fluxional processes of Cp. Calculations performed with B3LYP on a model with methyl substituents, [Mo(η^5-Cp)(η^1-Cp)(NMe)$_2$], yielded activation energies within 1 kcal mol^{-1} of the values obtained for [Mo(η^5-Cp)(η^1-Cp)(N^{t}Bu)$_2$]. The energy profiles for the various processes, obtained with B3PW91 and with B3LYP (with ^{t}Bu and Me as N-substituents), are presented as Supporting Information.

Supporting Information Available: Table S1, with relevant structural parameters for processes 3 and 4. Energy profiles for the metallotropic shift in **B** (Figure S1) and for all Cp fluxional processes in [Mo(η^5-Cp)(η^1-Cp)(NR)$_2$] calculated with B3PW91 (Figure S2 with R = ^{t}Bu) and calculated with B3LYP (Figure S3 with R = ^{t}Bu and Figure S4 with R = Me). Tables of atomic coordinates for all the optimized species. This material is available free of charge via the Internet at http://pubs.acs.org.

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