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C. R. Chimie 8 (2005) 1497–1505

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High and low barriers to haptotropic shifts across polycyclic surfaces: the relevance of aromatic character during the migration process

Stacey Brydges [a], Nada Reginato [a], Laurence P. Cuffe [b], Corey M. Seward [b], Michael J. McGlinchey [a,b,*]

[a] *Department of Chemistry, McMaster University, Hamilton, Ont., Canada L8S 4M1*
[b] *Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland*

Received 15 May 2004; accepted 15 September 2004

Abstract

Haptotropic shifts of ML_n fragments, such as $(C_5H_5)Fe$, $Mn(CO)_3$ or $Cr(CO)_3$, across polycyclic carbon frameworks generally follow a 'non least-motion' trajectory. In the absence of a definitive and unifying rationale for the preference of migratory pathways documented in previous experimental studies, a theoretical explanation has been sought. The potential energy surfaces (PES) for the migrations of organometallic fragments over the surfaces of *syn*- and *anti*-dibenzpentalene (**19** and **20**, respectively) were initially surveyed at the extended Hückel level; subsequently, the migration barriers were refined by DFT calculations. The results suggest that the development of aromatic character during the migration process can play an important role in determining the activation energy barrier. The capacity of the organic substrate to retain π-electron delocalization during the rearrangement adds a new dimension to the topological picture of metal–ligand interacting orbitals first established for bicyclic systems. ***To cite this article: S. Brydges et al. C.R. Chimie 8 (2005)***.

Résumé

Les déplacements haptotropiques de fragments ML_n, tels que $(C_5H_5)Fe$, $Mn(CO)_3$ ou $Cr(CO)_3$, au travers de *maillages en carbone polycyclique* ne suit généralement pas une trajectoire des moindres déplacements. En l'absence d'une rationalisation générale des déplacements préférentiels observés dans les études expérimentales précédentes, nous avons recherché une explication théorique. Les potentiels d'énergie de surface pour le déplacement de fragments organométalliques sur des surfaces de dibenzopentalène *syn*- et *anti*- (respectivement **19** et **20**) ont été tout d'abord examinés au moyen de calculs de Hückel étendus ; les barrières de migration ont été affinées ensuite par calculs DFT. Les résultats suggèrent que le développement du caractère aromatique durant le processus de déplacement joue un rôle important dans la détermination de la barrière d'activation de l'énergie. La capacité des substrats organiques à conserver la délocalisation d'électron π durant le réarrangement ajoute une

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* Corresponding author.
E-mail address: michael.mcglinchey@ucd.ie (M.J. McGlinchey).

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doi:10.1016/j.crci.2004.09.019

dimension nouvelle à la représentation topologique des orbitales entre le métal et le ligand, établie dans un premier temps pour les systèmes bicycliques. ***Pour citer cet article : S. Brydges et al. C.R.Chimie 8 (2005)***.

Keywords: Dibenzpentalenes; Organometallic migrations; EHMO and DFT calculations

Mots-clés : Dibenzopentalènes ; Migrations organométalliques ; Calculs EHMO et DFT

1. Introduction

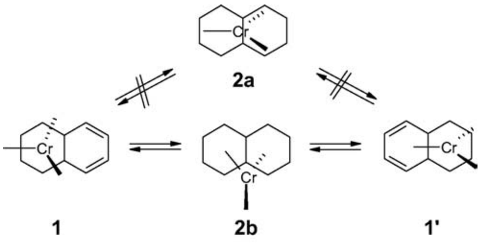
Advances in chemical bonding theory, catalytic activity and reactivity of organometallic compounds have been impacted substantially by the burgeoning data on dynamic molecular processes. Two types in particular – sigmatropic and haptotropic rearrangements of either σ-bonded elements or π-bonded metal moieties, respectively – are promoted by the rich variety of polycyclic platforms available today. Although the capacity of these transformations is dictated by the topological properties of the interacting orbitals, the same organic substrate does not necessarily support both sigmatropic and haptotropic migrations with equal facility. In this vein, we here discuss some fascinating experimental data on metal complexes of dibenzpentalenes that have thus far remained unexplained.

Since their disclosure in 1971 [1], the major regularities of inter-ring haptotropic shifts have been defined by Albright et al. [2] and most recently surveyed by Oprunenko [3]. Disregarding competing intermolecular dissociative pathways, it has been shown that as ML_n fragments traverse the faces of π systems, direct migration across the common bond between fused rings is typically a symmetry disallowed process (cf. sigmatropic shifts) and a circuitous minimum energy route is followed [2]. However, persistent ambiguities in the nature of transition states and intermediates make it difficult to distill kinetic and thermodynamic effects. Two bicyclic examples (vide infra) demonstrate these claims and provide the necessary design for other polycyclic models.

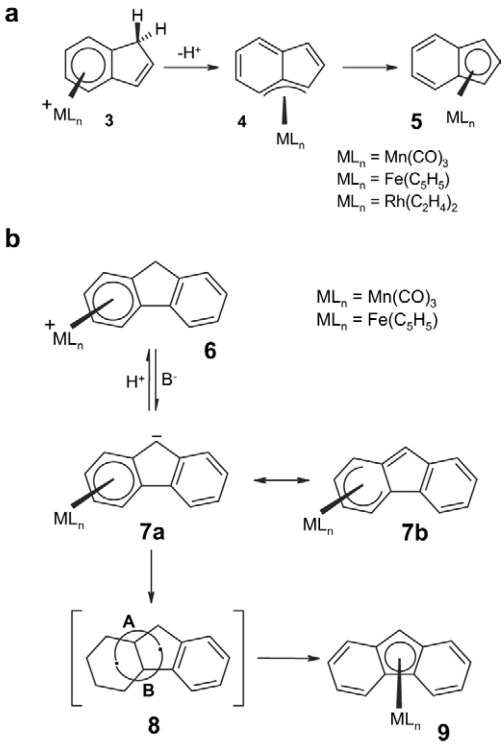
The migrations of a metal fragment over the two six-membered rings in appropriately substituted naphthalenes (as well as acenaphthenes or biphenylenes) have been the subject of a number of elegant experimental studies [4]. For the unlabeled $(\eta^6\text{-}C_{10}H_8)Cr(CO)_3$ **1**, the potential energy landscape (at the EHMO level of approximation) features both a transition state and an η^3-allylic-type local minimum (**2b**) lying 27 and 21 kcal mol^{-1}, respectively, above the ground state (Scheme 1) [2]. This contrasts with the DFT-predicted lowest energy η^6-to-η^6 degenerate rearrangement, which proceeds via a C_s-symmetric trimethylene-methane-type first order saddle point (ΔE = 30.4 kcal mol^{-1}) only [5].

An appreciable body of experimental information also exists for η^6-to-η^5 interconversions in indenyl-ML_n complexes [6] and fluorenyl analogs [7]. In the asymmetric ligand, the pH-dependent rearrangement between the pentahapto (favored) and hexahapto isomers involves a non-least motion path and coordinatively unsaturated η^3-allylic-type minimum, as demonstrated for the (indenyl)$Fe(C_5H_5)$ system **3**–**5** (Scheme 2a) [2]. Benzannulation of the indenyl scaffold destroys the five to six ring internal plane of symmetry and the non-degenerate η^6-to-η^5 exchange proceeds through one of two peripherally bound η^3 minima (pathways A or B, see Scheme 2b) [2]. Reversibility and isomer distribution aside, deprotonation of an $[(\eta^6\text{-fluorene})ML_n]$ species, **6**, where $ML_n = Mn(CO)_3^+$ or $Fe(C_5H_5)^+$, has yielded isolable zwitterionic intermediates, **7a**, which are perhaps better described as having an η^5-bonded metal, and an exocyclic double bond, **7b**, before undergoing migration to **9**.

A π-manifold for η^5-to-η^5 haptotropic rearrangements is provided by the third bicyclic example, pen-

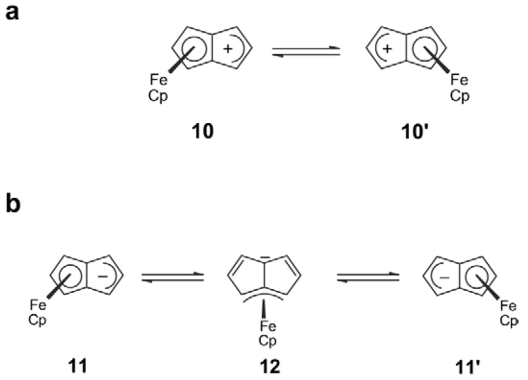


Scheme 1. η^6-to-η^6 migratory pathway of a $Cr(CO)_3$ unit in naphthalene.



Scheme 2. η^6-to-η^5 haptotropic shift in (**a**) indenyl and (**b**) fluorenyl systems, (**3**–**5**) and (**6**–**9**), respectively.

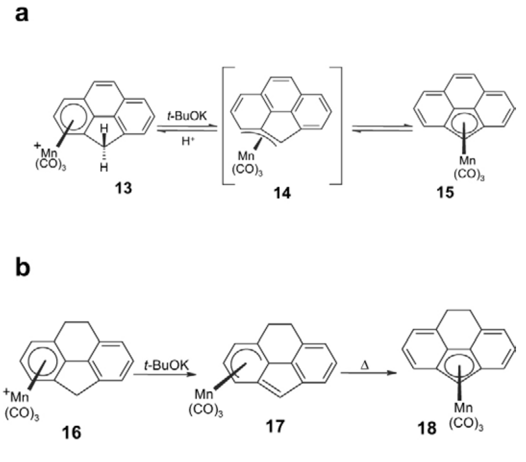
talene. Theoretical (EHMO level) considerations of the (pentalene)Fe(C_5H_5) system in both its cationic and anionic forms (**10** and **11**, respectively) identified two distinct bonding topologies [2]. In the former case, one of the primary frontier metal–ligand orbital overlaps is maintained during a least-motion transit; the calculated trajectory takes the FeCp moiety only 0.6 Å away from the midpoint of the central carbon-carbon bond (Scheme 3a). The addition of two electrons, as in **11**, results in the loss of both iron-pentalene bonding interactions and renders the least-motion pathway highly unfavorable. Instead, the migration route is extended to the carbocyclic periphery via an η^3-intermediate **12**, as depicted in Scheme 3b. To generalize, Albright, Hoffmann et al. advanced an electron-counting rule such that when the total number of electrons supplied by the polycyclic ligand and the metal equals $4q + 2$, where $q = 2, 3, ...$, then haptotropic shifts passing directly under the common bond are forbidden. On the other hand, when this sum equals $4q$, the process is partially allowed.



Scheme 3. η^5-to-η^5 haptotropic rearrangement of FeCp in (**a**) cationic and (**b**) anionic forms of pentalene.

2. An aromaticity argument advanced

Although early attempts to intercept an η^3-structure analogous to **4** were unsuccessful [8], indirect support for such an intermediate/transition state in fused polycyclic systems was claimed. Deprotonation of (η^6-cyclopenta[*def*]phenanthrene)$Mn(CO)_3^+$, **13**, yields the corresponding (η^5-cyclopenta[*def*]phenanthrenyl)-$Mn(CO)_3$, **15**, even at –40 °C (Scheme 4a) [9]. In contrast, deprotonation of the analogous (η^6-8,9-dihydrocyclopenta[*def*]phenanthrene)$Mn(CO)_3^+$, **16**, furnishes **17**, in which the manganese maintains its attachment to the external six-membered ring (comparable to the fluorenyl complexes, **7**). Complex **17** does not undergo a haptotropic shift to generate the centrally-bonded (η^5-

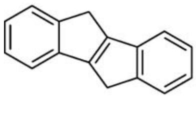


Scheme 4. The facility of haptotropic shifts in (**a**) (cyclopenta[*def*]-phenanthrenyl)ML_n complexes **13**–**15** is diminished in (**b**) its dihydro analog, **16**–**18**.

cyclopenta[*def*]phenanthrenyl)Mn$(CO)_3$, **18**, even when left at room temperature for 72 h; the rearrangement occurs only when the molecule is heated in hexane at 60 °C for an hour (Scheme 4b). This result was interpreted in terms of maintaining the 10π-naphthalene-type aromatic character in **14** (as shown in Scheme 4a) that is not available to the dihydro analog [9].

Gratifyingly, a recent X-ray crystallographic study [10] has unequivocally established the structure of *exo*-(η^3-cyclopenta[*def*]phenanthrenyl)Mo$(CO)_2$(η^5-indenyl), which provides strong support for the intermediacy of *exo*-(η^3-cyclopenta[*def*]phenanthrenyl)-Mn$(CO)_3$, **14**[1]. However, these data have been reinterpreted in terms of the enhanced strength of the η^3-bonding mode in indenyl systems relative to that found in cyclopentadienyl complexes, and the normally invoked model of increased aromaticity in the transition state is not considered to be the major factor [11].

It would be instructive, therefore, to examine other multicyclic systems containing the pentalene, indene and/or naphthalene substructures that present potentially competitive pathways for η^5-to-η^5, η^6-to-η^5/η^5-to-η^6 and η^6-to-η^6 inter-ring haptotropic rearrangements. Theoretical studies of these processes, even at the extended Hückel level, may help to clarify general regularities associated with the nature of the transition states and the magnitude of the activation energies that need to be surmounted. Organometallic derivatives of the two fused polycyclic ligands **19** and **20** exhibit very different dynamic behavior and thus have been selected as challenging candidates for a preliminary qualitative mechanistic survey using potential energy surfaces (PES) calculated by the EHMO approach [12][2]. Subsequently, the migration barriers indicated from the initial survey have been more extensively studied at the DFT level [13][3].



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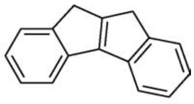

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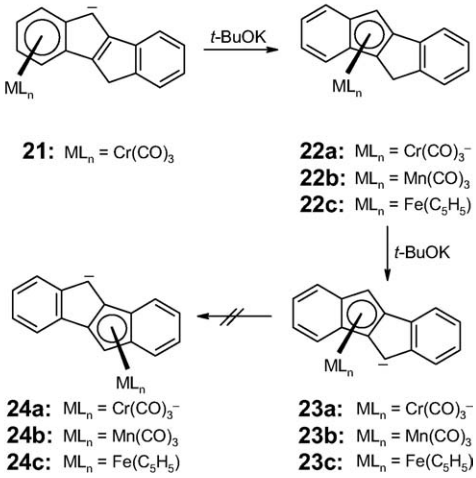
3. Results and discussion

3.1. Anti- and syn-dibenzpentalene complexes

Despite synthetic excursions into benzannulated versions of pentalene [14], the first and only experimental evidence for an η^5-to-η^5 haptotropic rearrangement was provided by Ustynuk's laboratory in 1990 [15]. The chromium and manganese tricarbonyl complexes of the isomeric ligands, 5,10-dihydroindeno[2,1-*a*]indene and 9,10-dihydroindeno[1,2-*a*]indene, **19** and **20**, which are more trivially named as derivatives of *anti*- and *syn*-dibenzpentalene, respectively, were prepared and their dynamic properties analyzed. The anionic complex [(η^6-*anti*-dibenzpentalenyl)Cr$(CO)_3$]$^{1-}$, **21**, rearranges readily and irreversibly into its η^5 isomer, **22a**, whereas the di-anionic complex [(η^5-*anti*-dibenzpentalenyl) Cr$(CO)_3$]$^{2-}$, **23a**, does not interconvert with its pentahapto derivative **24a** (Scheme 5). Likewise, the corresponding mono-anionic manganese tricarbonyl complex, [(η^5-*anti*-dibenzpentalene)Mn$(CO)_3$]$^{1-}$, **23b**, fails to undergo η^5-to-η^5 interconversion. This is in complete contrast to the fluxional behavior of the isomeric



Scheme 5. η^6-to-η^5 rearrangements in organometallic complexes (**21**–**24c**) of 5,10-dihydroindeno[2,1-*a*]indene, **19**.

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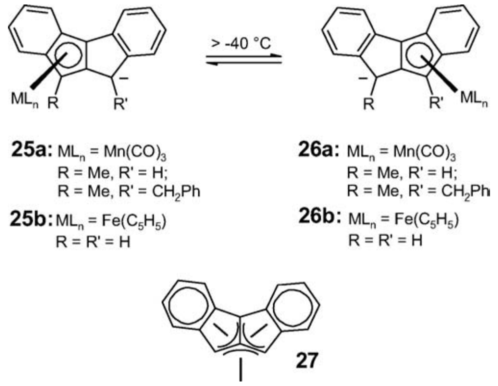
[1] However, analogous η^3-fluorenyl complexes are known. See, for example, [10].

[2] Extended Hückel calculations were carried out by using the program CACAO, Version 5.0, 1998.

[3] All calculations were corrected for zero point energy and were verified by appropriate frequency calculations. Calculations were carried out by using G03 Rev B 04 with the B3LYP functional and Pople's 6-31G* basis set for all atoms.



Scheme 6. η^5-to-η^5 rearrangements in organometallic complexes (**25**–**26**) of 9,10-dihydroindeno[1,2-*a*]indene, **20**.

species, $[(\eta^5$-*syn*-dibenzpentalenyl$)\mathrm{Mn(CO)_3}]^{1-}$, **25a**, which exhibits rapid η^5-to-η^5 interconversion with **26a**, even at –40 °C (Scheme 6); NMR lineshape analyses yielded an activation energy barrier of approximately 15 kcal mol^{-1}.

The very different dynamic behavior of the complexes derived from *anti*- and *syn*-dibenzpentalenes, **19** and **20**, has been tentatively rationalized in terms of the symmetries of the pentalene frontier orbitals [15], but no simple picture has emerged. In **19**, the ligand has a twofold axis, whereas in **20** there is a mirror plane bisecting the bond shared by the two five-membered rings. Clearly, it is not a question of the number of electrons supplied by the ligand and the metal totaling 4*q* + 2 in one instance, and 4*q* in the other, since these molecules are isomeric.

These fascinating results prompted us to calculate PES for the migration of an ML$_n$ unit across the anionic forms of **19** and **20**. Initially, the organometallic fragment selected was $(C_5H_5)Fe^+$, which is isolobal to $\mathrm{Mn(CO)_3}^+$ but does not require that one take account of the different orientation of the tripod at each point since rotation about the metal-Cp axis has a very low barrier [16]. Following the method used previously for (pentalene)FeCp$^+$, the iron was held at a constant distance of 1.59 Å from the plane of each dibenzpentalenyl ligand, and allowed to move across the polycyclic framework in steps of 0.1 Å to generate the PES shown as Figs. 1 and 2.

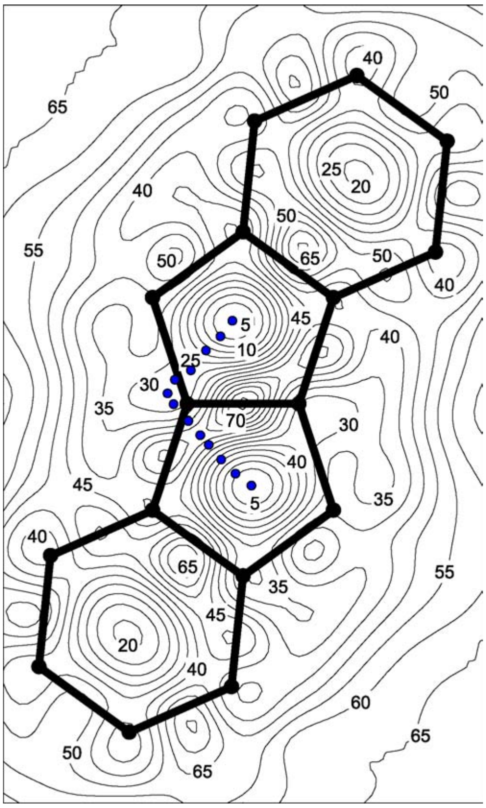


Fig. 1. Potential energy hypersurface (EHMO-calculated) for the migration of an $[Fe(C_5H_5)]^+$ fragment over the di-anion of the *anti*-dibenzpentalene framework, **19**. Solid contour lines are incremented in units of 5 kcal mol^{-1}, and the reaction path is superimposed as a dotted line.

In viewing the PES for the *anti* isomer **19** (Fig. 1), the most obvious result is the greatly disfavored (~72 kcal mol^{-1}) least-motion pathway directly across the common bond between the five-membered rings (see **23c** → **24c** in Scheme 5). Moreover, the alternative route that bypasses the center of this bond still requires that the migrating group surmount a barrier of ~45 kcal mol^{-1} and, as mentioned previously [15], this η^5-to-η^5 shift is not observed experimentally for the manganese and chromium complexes shown in Scheme 5. Interestingly, the η^6-to-η^5 haptotropic shift, **21** → **22a**, does proceed irreversibly, and the PES indicates why this should be so. When the CpFe moiety is initially bonded to the six-membered ring it must—and experimentally does in the case of **21**—traverse a barrier of ~33 kcal mol^{-1} before attaining the metallocenyl-type structure (cf. **22a**). However, the reverse process starts from the η^5-isomer that is approximately 18 kcal mol^{-1} more stable than the η^6-bonded structure, (cf. **21**), and so raises the barrier to more than 50 kcal mol^{-1}, and renders the η^5-to-η^6 haptotropic shift both thermodynamically and kinetically non-viable.

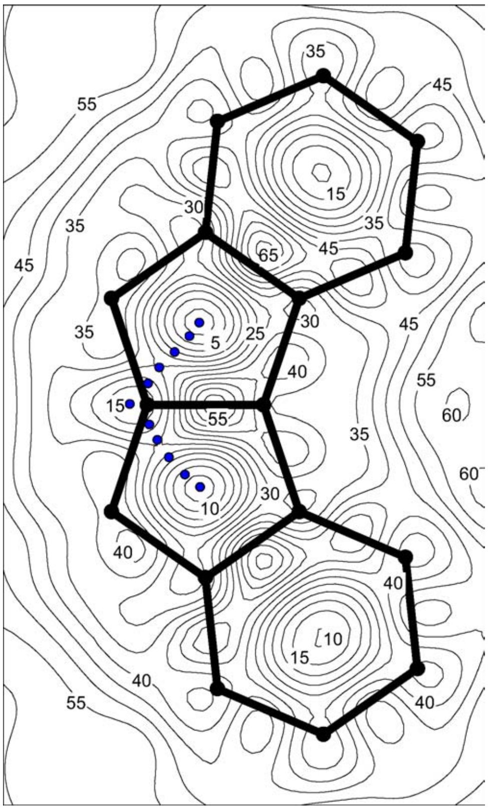


Fig. 2. Potential energy hypersurface (EHMO-calculated) for the migration of an $[Fe(C_5H_5)]^+$ fragment over the di-anion of the *syn*-dibenzpentalene framework, **20**. Solid contour lines are incremented in units of 5 kcal mol^{-1}, and the reaction path is superimposed as a dotted line.

These values should be compared with the corresponding results for the (indenyl)FeCp system for which the η^5 geometry was calculated to be favored over the η^6 structure by about 19 kcal mol^{-1}, and the η^6-to-η^5 barrier was estimated as 35 kcal mol^{-1} [2].

As illustrated in Fig. 2, the situation is radically different for the corresponding *syn* isomer **20**, for which the η^5-to-η^5 haptotropic shift process shown in Scheme 6 occurs readily with an experimental barrier for the manganese complex, **25a**, of approximately 15 kcal mol^{-1} [15]. The PES for [(*syn*-η^5-dibenzpentalenyl)FeCp]$^{1-}$ reveals a relatively low energy pathway by which the organometallic fragment can migrate between the five-membered rings. The favored trajectory takes the iron atom almost directly underneath a ring junction carbon to yield an intermediate structure only 10 kcal mol^{-1} less stable than the η^5 minimum; the highest point on this route is approximately 25 kcal mol^{-1} above the ground state, which is about half of that required in the *anti*-analog **23c**.

One can relate these calculations and the experimental observations on the dibenzpentalenyl complexes back to our previous discussion concerning (cyclopenta[*def*]phenanthrenyl)Mn(CO)$_3$, **15**, and its dihydro analogs, **17** and **18**. In the former system, one could invoke the aromatic character of the intermediate (and/or transition state), **14**, which lowers the activation energy for the migration process, somewhat analogs to Basolo's famous 'indenyl effect' for ligand displacements in (indenyl)Rh(CO)$_2$ versus (cyclopentadienyl)Rh(CO)$_2$ complexes [17]. In [(*syn*-dibenzpentalenyl)FeCp]$^{1-}$, **25b/26b**, the intermediate possesses two 6π aromatic rings while the metal is essentially in an (η^4-trimethylenemethane)ML$_n$ local environment, as in **27**.

For comparative purposes, Fig. 3 depicts the EHMO-calculated trajectory for the η^5-to-η^5 haptotropic shift

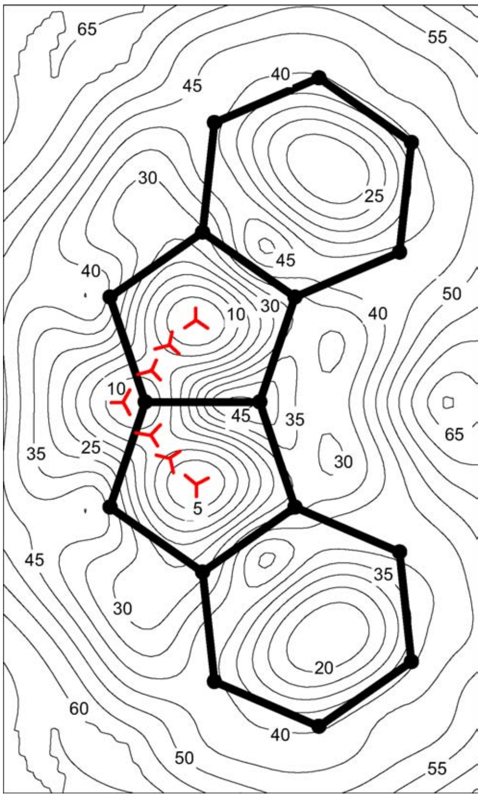
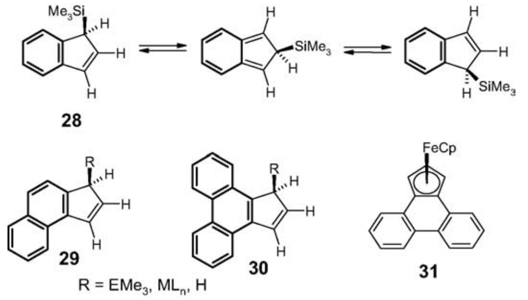


Fig. 3. Potential energy hypersurface (EHMO-calculated) for the migration of an $[Mn(CO)_3]^+$ moiety over the di-anion of the *syn*-dibenzpentalene framework, **20**. Solid contour lines are incremented in units of 5 kcal mol^{-1}, and the minimum energy trajectory with corresponding orientations of the tripod is depicted as a series of (⅄) symbols.

in [(*syn*-dibenzpentalene)Mn(CO)$_3$]$^{1-}$, **25a** (R = R′ = H), and yields an activation energy barrier of 14 kcal mol^{-1}. It is noticeable how the favored orientation of the tripod changes during the migration such that at the 'trimethylenemethane structure' the manganese is essentially in an octahedral environment as would be anticipated for a d^6 [Mn(CO)$_3$]$^+$ fragment[4]. As in the iron derivative, the η^6-to-η^5 and η^5-to-η^6 routes are more energetically demanding, with estimated barriers of 26 and 41 kcal mol^{-1}, respectively.

Having established the general behavioral patterns for the *anti*- and *syn*-dibenzpentalene complexes **23** and **25**, it was deemed appropriate to evaluate the migration barriers at a higher level of computation, namely DFT. For the (*syn*-dibenzpentalene)tricarbonylchromium dianion, **23a**, the geometry- and energy-minimized ground state was the expected η^5-structure, as found at the EHMO level; the barrier for migration of the chromium towards the trimethylenemethane-type structure was evaluated as 9.7 kcal mol^{-1}. In the analogous manganese mono-anionic species, **25a** (R = R′ = H), the calculated energies for the η^5-isomer and for the trimethylenemethane-type η^4-structure lie within 1.3 kcal mol^{-1} of each other, suggesting that both sites may be partially populated. A search was made for the transition state connecting these two minima and a point was located (and characterized with a single negative frequency of 157 cm^{-1}) lying 11.6 kcal mol^{-1} above the ground state. The manganese was calculated to be 1.86 Å below the ring center at the η^5-site, and 1.99 Å below the ring junction carbon at the η^4-position; however, at the transition state, the metal is now 1.95 Å from the plane of the polycyclic ligand. The NMR-derived barrier for the interconversion of **25a** and **26a** was reported as 14.9 kcal mol^{-1}, but is somewhat complicated by the existence of the temperature-dependent equilibrium [15].

In contrast, although the DFT calculations revealed an η^5-bonded energy minimum for the *anti* complex **25b**, we were unable to locate a transition state for migration of a metal between the two five-membered rings. Thus, the general features of the potential energy landscape indicated at the EHMO level of approximation are supported by higher level calculations.



Scheme 7. Sigmatropic shifts in a series of benzindenes (**28**–**30**).

4. Concluding remarks

These patterns of haptotropic shifts, which are controlled by the interactions of the ML$_n$ fragment with the π-manifold of the ligand, may be profitably compared with the sigmatropic migrations of R$_3$M groups (M = Si, Ge or Sn) or of (C$_5$H$_5$)(CO)$_2$Fe across similar polycyclic frameworks [19,20]. Beyond orbital considerations, the energy requirements of both types of rearrangements can be correlated with the aromatic character of the transition state and/or intermediates.

For example, the barriers to [1,5]-suprafacial silatropic shifts in the indenyl system **28** (Scheme 7) are dramatically reduced from 25 kcal mol^{-1} to 22 and 18 kcal mol^{-1}, respectively, upon mono- and dibenzannulation (cf. **29** and **30**), which allows the isoindene intermediates (and their accompanying transition states) to retain an increasing degree of aromaticity [21]. In fact, the isoindene derived from cyclopenta[*l*]phenanthrene (**30**, R = H) is sufficiently long-lived as to undergo a Diels–Alder dimerization with its progenitor [22].

Metal π-complexes of fused polycycles may present a variety of competing reaction pathways for (η^5-to-η^5, η^6-to-η^5/η^5-to-η^6 and η^6-to-η^6) haptotropic shifts, as demonstrated by the cases examined herein. For these processes, the transition state (or intermediate) is generally of the η^3 or η^4 type such that cyclic π-electron delocalization can be maintained as the ML$_n$ traverses a circuitous route on the molecular periphery. To this end, indene (**3**) and fluorene (**6**) skeletons are suitable substrates for η^6-to-η^5 migrations; however, depending on their sites of attachment, further fusion of benzene rings, such as in **31** [23], can actually diminish the aromatic stabilization of certain isomeric forms and thus limit the migratory possibilities. These kinetic and thermodynamic trends are not easily discerned from or

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[4] Although (trimethylenemethane)Mn(CO)$_3$$^+$ has not, to our knowledge, been reported, the analogous (TMM)Fe(CO)$_3$ system does indeed adopt the staggered orientation [18].

related to the constitution of the organic ligand, providing merit to the use of an initial EHMO approximation of the energy landscape. Subsequent application of more rigorous quantum-mechanical methods to the study of haptotropic transformations enhances both the accuracy of mechanistic details, particularly the nature of saddle points, and the predictive aspects of this electronic structure and bonding argument.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). S.B. gratefully acknowledges both the Government of Ontario and NSERC for graduate scholarships; C.M.S. thanks NSERC for a post-doctoral fellowship. We thank Dr. M. Tacke for his interest, and a reviewer for helpful comments.

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