Ring-whizzing in polyene-PtL₂ complexes revisited

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Abstract

Ring-whizzing was investigated by hybrid DFT methods in a number of polyene–Pt(diphosphinylethane) complexes. The polyenes included cyclopropenium⁺, cyclobutadiene, cyclopentadienyl⁺, hexafluorobenzene, cycloheptatrienyl⁺, cyclooctatetraene, octafluorocyclooctatetraene, 6-radialene, pentalene, phenalenium⁺, naphthalene and octafluoronaphthalene. The HOMO of a d¹⁰ ML₂ group (with b₂ symmetry) interacting with the LUMO of the polyene was used as a model to explain the occurrence of minima and maxima on the potential energy surface.

Introduction

Polyene–transition metal complexes were found to undergo fluxional rearrangements as early as 1956 with the preparation of Cp₂Fe(CO)₂ [1]. The migration of an ML₂ unit around the periphery of a cyclic polyene is commonly called ring-whizzing, purportedly ascribed to Rowland Pettit [2]. A more inclusive term is haptotropic rearrangement [3] wherein a metal atom changes its hapticity along the reaction path. Haptotropic rearrangements in ML₃ and MCp complexes are numerous [4-9] and have found use in synthetic strategies [10], switching devices [11-13] and energy storage [14,15]. Much less is known about the polyene–ML₂ analogs. There are two classes of compounds; one set consists of d⁸ ML₂ compounds [16-19] and the other, which we will be concerned with, are the d¹⁰ ML₂ class. There is ample precedent for four basic coordination geometries exhibited by these compounds. These are shown in Figure 1. Notice that in each case the orientation of the ML₂ unit is tied to the coordination number of the polyene and total electron count. One of us undertook a theoretical survey of these compounds at the extended Hückel level a number of years ago [20,21]. In the present contribution we shall revisit some of these rearrangements using DFT theory, as well as, investigate some new compounds.
A d\textsuperscript{10} ML\textsubscript{2} fragment possesses a high-lying HOMO, shown by 5 in Figure 2, which has a\textsubscript{2} symmetry and a low-lying LUMO, 6, of a\textsubscript{1} symmetry [22]. An energetically favorable reaction path will be one that maximizes the interactions of these orbitals with the orbitals of a coordinated polyene. The lowest occupied polyene \(\pi\) level is fully symmetric and, therefore, 6 can always interact with it. On the other hand, the LUMO in the \(\pi\) system may not always have the correct symmetry to interact with the b\textsubscript{2} orbital on ML\textsubscript{2} and it is the evolution of this overlap that has an important impact on the reaction path and activation energy. We will also have an occasion to consider a lower lying filled orbital of b\textsubscript{1} symmetry, 7.

![Figure 2: The important valence orbitals of a d\textsuperscript{10} ML\textsubscript{2} group, 5–7, along with the computed structures of Pt(PH\textsubscript{3})\textsubscript{2} and Pt(dpe).](image)

Polyene–ML\textsubscript{2} complexes are very fragile which in turn makes it somewhat difficult to compute the reaction path. The bond dissociation energy for ethylene–Pt(PH\textsubscript{3})\textsubscript{2} is only about 17 kcal/mol [23]. There are two ways in which the metal–polyene bond can be strengthened. The electron affinity of C\textsubscript{6}F\textsubscript{6} is much larger than that for benzene [24]. Consequently interaction of the filled b\textsubscript{2} fragment orbital with the LUMO of C\textsubscript{6}F\textsubscript{6} is expected to be larger and the binding energy larger than that for benzene. The M and L that we shall use in this work is Pt and a phosphine. The second method employs the use of a bidentate phosphine. In this regard we have chosen diphosphinylethane (dpe). This idea here is that the P–Pt–P angle is around 100° in polyene–ML\textsubscript{2} complexes. Upon dissociation the 14 electron PtL\textsubscript{2} complex strongly prefers to be linear [22]. So the computed ground state for Pt(PH\textsubscript{3})\textsubscript{2}, shown in 8, is calculated to be 29 kcal/mol more stable than one where the P–Pt–P bond angle was constrained to be 99°. This of course is not the case for Pt(dpe), 9. The P–Pt–P angle remains at 98°. Thus, the bond dissociation energy in polyene–Pt(dpe) complexes rises along with the attendant barriers for haptotropic rearrangements. This has been analyzed and quantified in detail by Massera and Frenking [23] for olefin–ML\textsubscript{2} compounds.

**Results and Discussion**

**A. Cyclic polyene–Pt(dpe) examples**

The most simple of the cyclic polyenes is the cyclopropenium cation. Its LUMO is a degenerate par of \(\pi\) orbitals, labeled e\textsuperscript{a} and e\textsuperscript{b} in Figure 3. It is easy to see that e\textsuperscript{a} interacts with the b\textsubscript{1} orbital of ML\textsubscript{2} at an \(\eta^2\) geometry. Indeed this is the computed ground state for C\textsubscript{3}H\textsubscript{3}–Pt(dpe)+ as shown from a side view, 10, in Figure 3. The transition state for shifting Pt(dpe) from one C–C bond to another passes through a geometry very close to \(\eta^1\), as shown by 11. Here b\textsubscript{2} interacts with e\textsuperscript{c} and along the reaction path a combination of the e\textsuperscript{d} degenerate set. The essential features can be found elsewhere [21]. The Gibbs free energy difference between the two structures is small: 4.1 kcal/mol.
Figure 3: The empty degenerate set of π orbitals in the cyclopropenium cation is shown on the left side. On the right are the two optimized structures of C₃H₃–Pt(dpe)⁺.

Figure 4: Two unoccupied MOs for Cp⁺ are shown on the left side. The two stationary points for Cp–Pt(dpe)⁺ are given by 13 and 14. To conserve space the groups around the phosphorus atoms have been removed.

(2.4 kcal/mol for L = PH₃). This is in accord with four structures of (Ph₃C₃)M(PPh₃)₂⁺ X⁻ where M = Ni, Pd, and Pt and X⁻ = ClO₄ and PF₆, which show a progressive movement of the ML₂ unit over the face of the cyclopropenium ring [36]. These structures serve to chart this reaction path and this is consistent with a small reaction barrier with the resultant structure being determined by crystal packing effects. The details have been reported previously [21,36]. The optimizations reveal that the coordinated C–C bond is much longer, 1.62 Å, than the other two, 1.38 Å. This compares favorably to the M = Pt, X⁻ = PF₆ structure [37] where the C–C distances are 1.58(2) and 1.39 Å, respectively.

The situation for Cp–Pt(dpe)⁺ is very similar to the cyclopropenium case. Counting this as Cp⁺ means that there are two unoccupied orbitals that the b₂ HOMO on ML₂ can interact with. Each is one member of a degenerate set and they are shown on the left side of Figure 4. The two stationary points on the potential energy surface are displayed from a top view on the right side of Figure 4. The e″₂ fragment orbital can interact with b₂ to form an η³ complex as shown in 13. An η⁵ geometry, 14, will be favored using the empty e″₁ orbital. The computed Gibbs free energy difference between the two is very small, namely 1.5 kcal/mol favoring η³. A recent search of the Cambridge crystallographic database [38] reveals 29 structures of the Cp and indenyl-M(PR₃)₂⁺ type where M = Ni, Pd, Pt. For the more general CpML₂ case where M = Fe through Pt there are 1074 hits. The majority of these structures are close to the η⁵ type although most have a significant range of M–C bond distances. For example, in cyclopentadienyl-platinum-bis(diphenylphosphinophenobiphenyl) [39] there are two Pt–C distances at 2.26(1) Å and one at 2.33(1) Å. The conformation of the PtL₂ unit with
respect to the Cp ring is approximately that given by 13. Accordingly, the remaining two Pt–C distances are 2.37(1) Å. For optimized 13 the corresponding set of distances is 2.29, 2.34 and 2.45 Å, respectively. The indenyl-M(PR$_3$)$_2$$^+$ examples are decidedly η$^3$ as a consequence of the perturbation generated by the benzo substituent. Normally one would do the electron counting in these molecules as Cp$^-$ and d$^8$ ML$_2$ yielding an 18-electron complex. The b$_2$ fragment orbital is now formally empty and the e$_1^+$ set is filled. A full discussion of the bonding in these compounds may be found elsewhere [22].

Another polyene with two coordination geometries is cyclobutadiene. The e$_g$ set shown on the left side of Figure 5 is half-filled. It is easy to see that one member has the correct symmetry to interact with b$_2$ ML$_2$ at both the η$^2$ and η$^4$ geometries. We found for cyclobutadiene–Pt(dpe) that the η$^2$ geometry, 15, is 6.5 kcal/mol more stable than the η$^4$ geometry, 16. For L = PH$_3$ the energy difference is even larger, 10.5 kcal/mol. These results are a little surprising in that the energy difference is larger than what we expected. We are aware of only one structure at this electron count, Ph$_4$C$_4$–Ni(PEt$_3$)$_2$ [40], and it is clearly η$^4$. As we shall see later, the difference between Ni and Pt can be significant but for the time being, experiment and theory are not in agreement with each other.

Benzene–Ni(PR$_3$)$_2$ compounds have been known for some time [41]. An η$^2$ geometry has been observed to be the precursor to C–F bond insertion for F$_6$C$_6$ complexes [42] and a number of theoretical studies have been carried out [43-46] which address this reaction. There are two arene–Pt(PR$_3$)$_2$ structures in the literature [47,48] and both have η$^2$ geometries. The barrier for ring whizzing in (CF$_3$)$_6$C$_6$–Pt(PEt$_3$)$_2$ has been measured to be ≈11 kcal/mol [41]. One member of the LUMO e$_{1g}$ set in benzene has a large overlap with the b$_2$ ML$_2$ MO. The computed ground state structure for η$^2$ F$_6$C$_6$–Pt(dpe), 17 in Figure 6 agrees well with the experiment. The issue is whether the transition state for ring whizzing favors the interaction between e$_{1g}$ and b$_2$ shown from a top view in 18 or 19. Extended Hückel

Figure 6: The ground and transition state for ring whizzing in F$_6$C$_6$–Pt(dpe), 17 and 20, respectively. The dominant bonding interaction for two possible transition states, 18 and 19 along with the HOMO, 21 and LUMO, 22, in the η$^1$ transition state.

Figure 5: The half-filled degenerate π orbitals in cyclobutadiene. The computed ground state (15) and transition state (16) for cyclobutadiene–Pt(dpe) on the right.
calculations favored the former [20,21]. Our present day calculations, however, favor 19. The structure is shown in 20. Special care was taken to search for a transition state where the Pt(dpe) group was rotated by 90° but none was found. The activation barrier was computed to be 7.4 kcal/mol. Reinhold, McGrady and Perutz [46] obtained a barrier of 6.4 kcal/mol for the same molecule using the B3LYP hybrid functional and a different basis set. The computed geometric parameters for the molecules are very close to each other. One Pt–C bond is short (2.10 Å) while the other two flanking bonds are 2.52 Å. Thus, 20 strongly resembles an η^1 14 electron complex with a “T” shaped geometry. An easy way to view these results is to take a linear combination of b^2 (5) and a_4 (6). This will generate two equivalent dsp hybrids. One will be filled and can interact with one component of the e_g LUMO, 21, in Figure 6 and the other will remain empty, 22.

Another highly fluxional molecule is cycloheptatrienyl–Pt(dpe)^+ which exhibits a situation similar to that described for Cp–Pt(dpe)^+. The ground state is again an η^3 structure. This is in agreement with several substituted cycloheptatrienyl–PdL_2 complexes [49]. We looked hard for an η^5 species but instead found an η^2 structure which serves as a transition state for ring whizzing. The activation barrier was computed to be 3.2 kcal/mol. Barriers from 10.5 to 7.6 kcal/mol were found for the Pd complexes [49]. Interestingly an η^1 transition structure with one imaginary frequency was also discovered. It was found to be 7.2 kcal/mol above the ground state.

We thought that radialenes would be an attractive candidate as a ligand and would exhibit a facile haptotropic rearrangement when coordinated to Pt(dpe). The LUMO is all-in phase combination of olefinic π^* as shown for 6-radialene by 23 in Figure 7. Therefore, the ML_2 b_2 fragment would retain a sizable portion of its overlap on going from an η^2 to η^4 geometry. For some time 6-radialene and many alkyl derivatives have been known [50]. It is extraordinarily reactive and a bis-Fe(CO)_3 derivative of 5-radialene has recently been prepared [51]. The structure of 6-radialene is strongly distorted into a chair form with a boat conformation slightly higher in energy [51]. The D_{sh} structure lies higher in energy by 17.1 kcal/mol [51]. Our optimization of the η^2 ground state shows a twisted boat conformation to be the most stable, 24, in Figure 7. The activation barrier was found to be 13.7 kcal/mol. We thought that by tying the ends of the olefins together via a CH_2 group would force the ligand to be flat. In fact there are compounds analogous to this having O, S and Se as the linker that are in fact flat [52]. Our calculations reveal that the η^2 ground state, 25, and the η^4 transition state, 26, are essentially flat, but the energy difference is only lowered to 13.0 kcal/mol. In 25 the two Pt–C bond distances are 2.17 Å, however, in 26 they are considerably lengthened. The inner Pt–C distances are 2.36 Å and the ones adjacent to the CH_2 group are 2.61 Å! The principal destabilization in 26 is due to the interaction between b_1 (7) and the HOMO on 6-radialene, which is the totally antibonding combination of π orbitals, 27.

![Figure 7: The LUMO, 23, and HOMO, 27, in 6-radialene. The optimized η^2 ground states are shown in 24 and 25 while 26 shows the geometry for one η^4 transition state.](image)

B. The strange case of cyclooctatetraene

Cyclooctatetraene (COT) has been a favorite ligand since the dawn of organometallic chemistry [2]. Figure 8 shows two representations for the half-filled e_{2g} set of π orbitals in the flat D_{sh} geometry. One can see from the representation in a) that an η^2 or η^3 conformation are possibilities. In b) one can envision η^1 or η^3 as potential structures. The optimized structures for C_8F_8–Pt(dpe) are illustrated in Figure 9. To conserve space the groups around the phosphorus atoms have been removed. COT and C_8F_8 have a tub shaped structure with D_{2ad} symmetry [53,54]. As expected an η^2 structure, 28, was found to be a minimum. A 1,4-diyl minimum was also found where there are two Pt–C σ bonds, 30. This structure has also been suggested by means of the low temperature ^31P and ^13C NMR of COT-Pt(R_2PCH_2CH_2PR_2), R = iPr [55]. The transition state that interconnects 28 to 30 is shown in 29. The coordination geometry around Pt is typical of that in η^2 olefin complexes. What is novel is that the COT (and C_8F_8) ring is essentially flat with the uncoordinated portion of the polyene having alternating C–C...
bond lengths of ≈1.45 and 1.35 Å. This is in fact the structure of an analogous Ni complex as determined by X-ray crystallography [56]. The haptotropic rearrangement of 28 to 30 does not permute all of the carbon atoms in the COT ring. There is a mirror plane in the plane of the paper for all of the structures in Figure 9. This equivalences the carbons on the front side of the paper with those on the back side. Compounds 28–30 do not have a mirror plane perpendicular to this and, therefore, C2 (see 28) does not become equivalent to C3, etc. As we shall see, a structure akin to 35 would accomplish this. In searching for another structure that accomplishes this we discovered tricyclic 32. The transition state that converts 28 into 32 is 31. For the C₈F₈ complex, 28, the Pt–C distances are 2.08 Å. In 31 the corresponding distances are 2.11 and 2.26 Å with the dashed green bond being formed measuring at 2.32 Å. In COT–Pt(dpe) the transition state 31 is akin to an η₃ complex with the three Pt–C bond lengths calculated to be 2.22–2.26 Å. Since 32 has Cₛ symmetry (discounting the dpe ligand), it serves as a way-point for ring-whizzing. It is easy to see the electronic basis for ring folding and construction of the tricyclic molecule. Consider that in 28 the filled ML₂ b₂ orbital coordinates to the two lower p AOs in the upper component of e₂u in Figure 8a. Then empty a₁ interacts with the filled b₂ ML₂ orbital and a₁ interacts with the filled e₂u. This is explicitly drawn in 33 and 34, respectively, of Figure 10. The important consequence of this motion is that the p AO on the opposite side of the ring in 34 has the correct phase to generate a C–C σ bond and this collapses to bicyclic 32.

Figure 8: Two representations for the half-filled e₂u set of π orbitals in cyclooctatetraene.

Figure 10: The two important bonding interactions for transition state 31 are drawn in 33 and 34.

Figure 9: The stationary points found on the potential energy surface of C₈F₈–Pt(dpe). For clarity the groups around the phosphines have been removed. The relative energies for this compound, as well as COT–Pt(dpe) are given below each structure.
Our calculations find that \( \text{C}_8\text{F}_8\text{–Pt(dpe)} \) will be caught in the deep potential energy well of the tricyclic isomer, 32. Hughes and co-workers have shown that experimentally this is indeed the case [57,58]. With PPh\(_3\) and AsPh\(_3\) ligands compounds analogous to 30 are initially formed from the reaction of \( \text{C}_8\text{F}_8\) and a Pt(0) precursor. 30 then irreversibly rearranges in solution to 32 overnight at room temperature. This is also in accord with our calculations. Notice that going from 30 to 32 requires the passage through transition state 29, which requires 29 kcal/mol. We think that the reason why 29 lies much higher in energy than the COT analog is due to the energy cost associated with flattening the ligand to a \( D_{4h} \) type of geometry. For COT itself this entails an energy cost of 10–13 kcal/mol [59]. We find that the conversion for \( \text{C}_8\text{F}_8\) is nearly triple this amount, namely 29.9 kcal/mol [60].

The picture for COT–Pt(dpe) is not so clear. Our calculations would have 28, 30 and 32 in rapid equilibrium with the overwhelming majority of the equilibrium shifted to the tricyclic compound. The low temperature \( ^{31}\text{P} \) and \( ^{13}\text{C} \) NMR of COT–Pt(R\(_2\)PCH\(_2\)CH\(_2\)PR\(_2\)), \( R = \text{iPr} \) [55], clearly shows that either 28 or 31 (the authors prefer 31) is in rapid equilibrium with 30. There is no spectroscopic evidence consistent with the existence of 32. It may well be the case that bulky iPr groups in place of hydrogens alter the relative energetics. Perhaps computations with a different functional and/or a larger basis set might bring theory and experiment into agreement. Furthermore, moving from Pt to the isoelectronic Ni also can have a significant impact. An X-ray of the COT–Ni complex [56] reveals the structure is analogous to that for 29. An X-ray of another Ni complex [60] produces a bis-\( \eta^2 \) isomer, 35. This is also true for \( \text{C}_8\text{F}_8\text{–Ni} \) complexes with certain ligand sets [57,58]. We carried out a number of potential energy minimizations as shown in Figure 11 starting from 35, as well as, \( \eta^1 \), 36, and \( \eta^3 \), 37. Unfortunately none of these produced new stationary points. We will return to this Ni versus Pt issue later.

C. Polycyclic examples

Pentalene metal complexes have been the subject of a number of investigations [61], as well as, theoretical explorations of haptotropic rearrangements with ML\(_3\) and MCP [62,63]. However, we are not aware of any complexes with a d\(^{10}\) ML\(_2\) group. Pentalene has an energetically low-lying LUMO and close to it another empty orbital. These are shown in 38 and 39, respectively, in Figure 12. It is easy to see that in 38 the \( b_2 \) ML\(_2\) fragment orbital can interact in an \( \eta^3 \) mode both within the five-membered ring, as well as, between the two. 39 has the correct topology to interact with \( b_2 \) in \( \eta^2 \) and \( \eta^3 \) modes. We were able to locate four stationary points on the potential energy surface of pentalene–Pt(dpe). These are shown from a top view along with their relative energies in Figure 12. Here again the hydrogens and ethano-bridge connected to the phosphorus atoms has

\[
\begin{align*}
\Delta G &= 7.7 \text{ kcal/mol} \\
&= 41\,^\ddagger \\
0.0 \text{ kcal/mol} \\
8.6 \text{ kcal/mol} \\
2.4 \text{ kcal/mol} \\
\end{align*}
\]

\( \Delta G \) for the energies shown in Figure 12. The LUMO and LUMO+1 shown in 38 and 39, respectively. The four stationary points found for pentalene–Pt(dpe) are displayed in 40–43 along with their relative energies. The groups connected to the phosphorus atoms are not shown.
been removed for clarity. We find that the \( \eta^2 \) structure, 40, to be the ground state. A low energy \( \eta^3 \) transition state, 41, at 7.7 kcal/mol serves to equivalence the top and bottom halves of the pentalene ligand. The Pt(dpe) group can migrate from one ring to the other via the \( \eta^3 \) structure, 42. Again the activation energy associated with the transition state 43 is predicted to be small at 8.6 kcal/mol. We anticipate that pentalene–Pt(PR\(_3\))\(_2\) will be a highly fluxional molecule.

The situation for phenalenium–Pt(dpe)\(^+\) is very similar. The LUMO for phenalenium\(^+\) is a rigorously non-bonding MO, 44 in Figure 13. One expects and finds \( \eta^3 \) structures both within and between rings as given by 45 and 46, respectively, with essentially identical relative energies. Experimentally, all known complexes [64-67] are akin to 45. Our calculated barrier of 14.7 kcal/mol via 47 seems a bit too low. The measured barrier in two Pd(tmeda) complexes was 21.4 and 21.6 kcal/mol [66]. No signs of fluxionality was found in a substituted phenalenium–Pt(PPh\(_3\))\(_2\) complex [67].

Naphthalene and anthracene–Ni(PR\(_3\))\(_2\) compounds have been known and studied for some time [45,46,68-75]. We are, however, unaware of any Pt(PR\(_3\))\(_2\) examples. The ground state structures of the Ni compounds possess an \( \eta^2 \) geometry where the Ni is coordinated to a carbon–carbon bond adjacent to the ring fusion. Our calculations on octafluoronaphthalene–Ni(dpe) and –Pt(dpe) (as well as naphthalene–Pt(dpe) itself) are in good agreement with experiment. A top view of the structure is shown by 48 in Figure 14. This offers a good overlap between the LUMO in C\(_{10}\)F\(_8\), 49, and the b\(_2\) HOMO, 5, in Pt(dpe). It was thought [20] that migration of an ML\(_2\) unit from one ring to another would involve an \( \eta^3 \) structure where Pt would bond to C(1), C(9) and C(8). For the carbon numbering system please see 48. Bonding between b\(_2\) ML\(_2\) and the b\(_{1g}\) MO would be retained. Unfortunately this is not quite the entire story. One of the stationary points is shown by 50. The a\(_u\) HOMO, 51, in C\(_{10}\)F\(_8\) also has a significant overlap with b\(_3\) at this geometry. Since these two fragment orbitals are both filled, there is also considerable destabilization. What we find is that this expanse of the potential energy surface is a twixtyl intermediate [76]. At the stationary point given by 50 there is one imaginary frequency of 17i cm\(^{-1}\); at another closer to \( \eta^3 \) the computed frequencies are all positive but one is tiny, 15 cm\(^{-1}\). So this region of the coordinate space is analogous to a plateau; the potential energy is essentially flat. The activation energy to attain 50 in C\(_{10}\)F\(_8\)–Pt(dpe) was computed to be 13.7 kcal/mol; in C\(_{10}\)F\(_8\)–Pt(dpe) the barrier was 14.8 kcal/mol. This is in line with an NMR derived barrier of about 15 kcal/mol for C\(_{10}\)H\(_8\)NiL\(_2\) [74] and 15–20 kcal/mol for anthracene–Ni(PR\(_3\))\(_2\) [69,70]. Oprunenko and Gloriozov [75] have calculated the \( \eta^3 \) transition state to lie at a relative energy of 12.2 kcal/mol for naphthalene–Ni(P(SiMe\(_3\)))\(_2\) using the PBE functional and a different basis set than that employed here. Jones and co-workers [45] have undertaken an exhaustive study of ring whizzing and oxidative addition in a series of cyano and methyl substituted naphthalene–Ni(dmpe) complexes at the B3LYP level. Structures analogous to 50 were reported at relative energies of 12–17.5 kcal/mol. We do find in C\(_{10}\)F\(_8\)–Pt(dpe) that there is a second path for the haptotropic rearrangement from one ring to the other. Here the Pt(dpe) group migrates further in towards the ring junction with a weakly bound transition state of 21.9 kcal/mol and ending at an \( \eta^2 \) minimum where the C(9) and C(10) atoms are coordinated to Pt at a relative energy of 17.9 kcal/mol. The latter structures were also computed to lie at high energies by Jones and co-workers [45]. So, at this point theory and experiment appear to be in agreement for the NiL\(_2\) and PtL\(_2\) cases.

But the story does not end here. Experimentally there is a low energy process that converts, 48, to the equivalent \( \eta^2 \) structure where the ML\(_2\) group is coordinated to C(3) and C(4). This is also the case for anthracene–NiL\(_2\). The experimental barriers range \( \approx \)5–6 kcal/mol [69,70,74]. The aforementioned calculations [45,75] yield barriers of 4.2–9.5 kcal/mol in reasonable agreement with the experiment. The structures of these
transition states resemble \( \eta^4 \) species with the geometry akin to 52 in Figure 15. This is not the case for \( \text{C}_{10}\text{F}_8-\text{Pt(dpe)} \) or \( \text{C}_{10}\text{H}_8-\text{Pt(dpe)} \). The barriers are calculated to be 17.1 and 17.4 kcal/mol, respectively. Furthermore, the barrier for \( \text{C}_{10}\text{H}_8-\text{Pt(dpe)} \) using the B3LYP function generates a barrier of 17.8 kcal/mol. Using the M06 functional for \( \text{C}_{10}\text{F}_8-\text{Ni(dpe)} \) yields a barrier of 6.1 kcal/mol which is in line with the calculations by others. Therefore, the discrepancy must lie in the difference between Pt and Ni. There is also a difference in the metrical details of these transition states. For the Ni examples the Ni–C(1) and Ni–C(4) distances are \( \approx \)0.3 Å longer than the Ni–C(2) and Ni–(3) ones (see 48 for the numbering scheme).

For the Pt complexes we find this difference to be about twice as large. In other words, the Pt cases are closer to \( \eta^2 \) complexes where the olefinic portion of the ligand is rotated by 90° from the minimum energy conformation given in 1. We will return to this point shortly. One might think that the overlap between \( \text{b}_2 \) ML_2 and the LUMO, 49, from the \( \eta^2 \) ground state to \( \eta^4 \) will be retained and, thus, the activation energy will be small. However, note that at \( \eta^4 \) the overlap between the filled \( \text{b}_1 \) fragment orbital, 7, and the \( \text{a}_u \) HOMO on \( \text{C}_{10}\text{F}_8 \) is turned on and this is repulsive. With this in mind it is tempting to put forward the hypothesis that the 3d AOs in Ni are very contracted and their overlap at \( \eta^4 \) is not so large. Hence the \( \text{a}_u - \text{b}_1 \) repulsion is not so large and it is the mixing of 4p character in the Ni \( \text{b}_1 \) orbital that retains reasonable overlap with \( \text{b}_1 \)). On the other hand, the Pt 5d AO is more diffuse and consequently more bonding is lost at \( \eta^4 \) than its Ni congener. But this cannot be the whole story. Massera and Frenking [23] have shown that there is essentially no energy difference between the bond dissociation energy (BDE) in ethylene–Ni(dpe) and the Pt analog. Furthermore, their calculated BDE for ethylene–Pt(\( \text{PH}_3 \)) is in very good agreement with that found [23] at the CCSD(T) level with a large basis set. On the other hand, Reinhold, McGrady and Perutz have reported [46] that \( \text{C}_6\text{H}_6 \) and \( \text{C}_6\text{F}_6-\text{Pt(dpe)} \) BDEs are about 8 kcal/mol less than that for the Ni(dpe) analogs.

A close examination of the potential energy surface in \( \text{C}_{10}\text{F}_8-\text{Pt(dpe)} \) revealed the existence of another \( \eta^2 \) minimum, 53, in Figure 15. It lies 13.7 kcal/mol above the ground state. This is in line with the corresponding minima found by Jones and co-workers [45] in the substituted naphthalene–Ni(dmpe) compounds (\( \approx \)13 kcal/mol). So our calculations put the \( \eta^2 \) minimum, 53, to be 3.4 kcal/mol more stable than the \( \eta^4 \) transition state, 52. However, the latter does not serve as the
waypoint for the former. An η1 structure, 54, was found to be the transition state for the haptotropic rearrangement of 48 to 53. Notice that passage through the η2 intermediate causes the phosphines to become equivalent. Benn and co-workers [74] in fact observe phosphine equivalence with a barrier of approximately 13 kcal/mol for the naphthalene–Ni(PR₃)₂ compounds. Our calculations put 54 to be 14.9 kcal/mol above the ground state, 48. This is in reasonable agreement with the NMR results [74]. The reaction path and associated electronic details for the 48 to 54 to 53 haptotropic shift is precisely analogous to that within one ring, whereas, in the Ni analog the former is much slower than the latter.

Conclusion
Our original thesis that the ML₂ b₂ interaction with the LUMO of the polyene dictated the reaction path was largely fulfilled. Often this guided our exploration of the potential energy surfaces. But molecules, like life, sometimes yield unexpected conclusions. We miss you, Peter Hofmann.

Supporting Information
Supporting Information File 1
The molecular geometry and total electronic energy for the molecules in this work are given in .xyz format. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modeling program such as Mercury (http://www.ccdc.cam.ac.uk/pages/Home.aspx). Molecular geometry and total electronic energy data.
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-12-135-S1.xyz]

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