

## Molecular Dials: Hindered Rotations in Mono- and Diferrocenyl Anthracenes and Triptycenes

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**Abstract:** The syntheses, X-ray crystal structures, and molecular dynamics of 9-ferrocenylanthracene, **3**, 9,10-diferrocenylanthracene, **4**, 9-ferrocenyltriptycene, **7**, and 9,10-diferrocenyltriptycene, **8**, are reported. At 193 K, **3** exhibits  $C_s$  symmetry via oscillation of the ferrocenyl only about the anthracene plane; at higher temperatures, complete rotation about the C(9)–ferrocenyl linkage becomes evident with a barrier of 10.6 kcal mol<sup>-1</sup>. At 193 K, the ferrocenyls in **4** give rise to syn ( $C_{2v}$ ) and anti ( $C_{2h}$ ) rotamers that also interconvert at room temperature. In the corresponding triptycyl systems, **7** and **8**, these rotational barriers increase to 17 kcal mol<sup>-1</sup>; 9,10-diferrocenyltriptycene exists as slowly interconverting meso and racemic rotamers, in which the ferrocenyl moieties are, respectively, eclipsed ( $C_{2v}$ ) or staggered ( $C_2$ ). 2D-EXSY NMR data recorded with different mixing times indicate clearly that these interconversions proceed in a stepwise manner, for example, *rac*→*meso*→*rac*, thus behaving as a set of molecular dials.

### Introduction

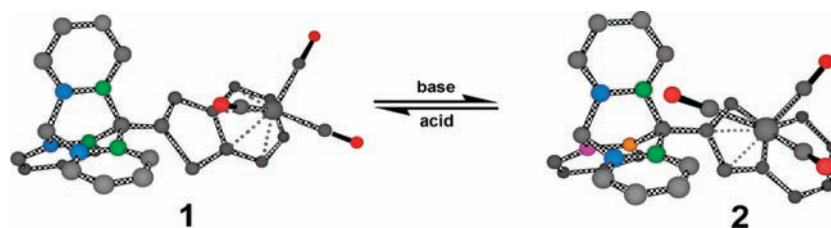
Internal rotation is a central phenomenon in chemistry whereby molecular systems access different conformations in a stepwise manner. While these interconversions often occur spontaneously, there are growing numbers of reports on chemically or photochemically mediated conformational transformations, such as unidirectional rotations<sup>1</sup> and controlled molecular brakes<sup>2</sup> or gyroscopes.<sup>3</sup> With the long-term goal of developing practical organic or organometallic molecular machines or switches,<sup>4</sup> it could be particularly useful to be able to predict the ease of the rotation of a specific molecular fragment in a given environment. Moreover, this could also enhance our understanding of, and ability to design, chiral catalysts or other reagents whose function critically depends on the stability and lability of intermediate conformations.<sup>5</sup>

Recent reports from this laboratory described the structure and dynamics of an organometallic molecular brake, whereby deprotonation of [{( $\eta^6$ -2-(9-triptycyl)indene}Cr(CO)<sub>3</sub>], **1**, re-

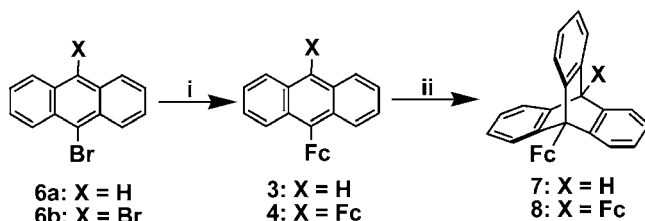
sulted in a haptotropic migration<sup>6</sup> of the bulky metal carbonyl fragment onto the adjacent five-membered ring, as in **2**, thus blocking rotation of the triptycene paddlewheel (Scheme 1).<sup>7</sup> Nevertheless, one can readily appreciate that, rather than using a deprotonation/reprotonation sequence to control haptotropic shifts, an electrochemically driven redox approach<sup>8</sup> could be more convenient. Moreover, the role played by ferrocenyl moieties in the design of catalysts for asymmetric synthesis,<sup>9</sup> in dendrimers,<sup>10</sup> and in a range of molecular machines<sup>11</sup> has been crucial. To this end, we chose to probe the ability of the

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Scheme 1. An Organometallic Molecular Brake<sup>a</sup>

<sup>a</sup> The triptycene paddlewheel in **1** is free to rotate, but, upon deprotonation, the organometallic tripod undergoes an  $\eta^6$  to  $\eta^5$  haptotropic shift and blocks the paddlewheel rotation in **2**.

Scheme 2. Syntheses of Mono- and Diferrocenyl Anthracenes and Triptycenes, **3**, **4**, **7**, and **8**<sup>a</sup>

<sup>a</sup> Reagents and conditions: (i) ferrocenylboronic acid (**5**),  $\text{Bu}_4\text{NOH}$ ,  $\text{PdCl}_2(\text{dppf})$ , dioxane, 90 °C, 24 h; (ii) *o*- $\text{BrC}_6\text{H}_4\text{F}$ ,  $\text{BuLi}$ , toluene, -5 °C.

ferrocenyl moiety to hinder intramolecular rotations,<sup>12</sup> and here we report the syntheses, structures, and dynamic behavior of mono- and diferrocenyl anthracenes and triptycenes.

## Results and Discussion

**Ferrocenyl-Anthracenes.** Initially, the efficient preparation of the mono- and diferrocenylanthracenes, **3** and **4**, respectively, from ferrocenylboronic acid, **5**, proved to be nontrivial as the Pd-catalyzed cross-coupling with 9-bromoanthracene or 9,10-dibromoanthracene, **6a** or **6b**, respectively, fails unless rigorous adjustment of conditions has been made (large excess of ferrocenylboronic acid, nearly stoichiometric amount of catalyst).<sup>11b</sup> However, when tetrabutylammonium hydroxide in 1,4-dioxane is used as the base, and  $(\text{dppf})\text{PdCl}_2$  is used as the catalyst, the respective salts of **5** are fully soluble, and **3** and **4** are obtained in high yields (Scheme 2).

As shown in Figure 1, the ferrocenyl unit in **3** adopts a dihedral angle of 45° relative to the anthracene, which itself folds 4° from planarity. This phenomenon is amplified in **4** such that the anthracene is “diagonally” distorted through 8° and the ferrocenyls are rotated 89° from each other, thus engendering  $C_2$  symmetry (Figure 2).

The room-temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3**, prepared by the palladium-catalyzed coupling of chlorozinciferrocene

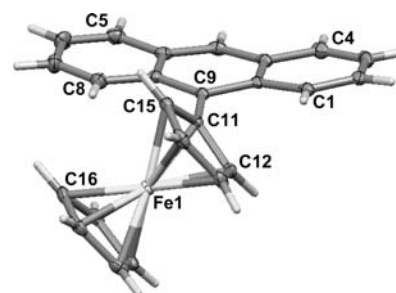


Figure 1. Molecular structure of 9-ferrocenylanthracene, **3**.

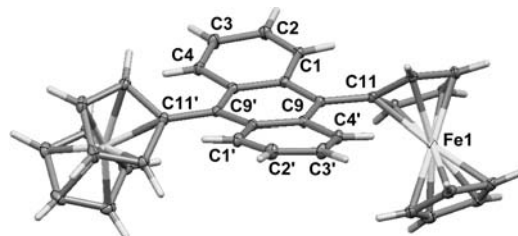


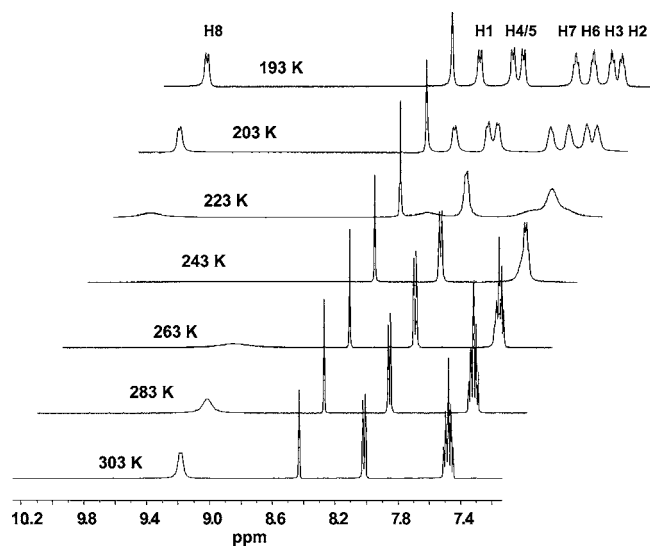
Figure 2. Molecular structure of 9,10-diferrocenylanthracene, **4**.

with 9-bromoanthracene, were originally reported by Butler,<sup>13</sup> and their simplicity indicated a low barrier to rotation on the NMR time-scale. However, the 500 MHz  $^1\text{H}$  NMR spectrum of **3** at 193 K (Figure 3) revealed the nonequivalence of the terminal benzo rings of the anthracene while maintaining the mirror symmetry of the iron-complexed  $\text{C}_5\text{H}_4$  ring. At this temperature, hindered rotation on the NMR time-scale together with the very large diamagnetic anisotropy of the ferrocenyl moiety<sup>14</sup> resulted in the H-1 and H-8 protons of the anthracene fragment being separated by 1.7 ppm. Evidently, the system racemizes, via a low energy process, by oscillation of the ferrocenyl group about the mirror plane containing the anthracene framework, and so exhibits time-averaged  $C_3$  symmetry, as depicted in Scheme 3. However, peak coalescence data indicate a rotational barrier of ca.  $10.6 \pm 0.5 \text{ kcal mol}^{-1}$ ; at this point, the ferrocenyl moiety can access both peripheral rings and both faces of the anthracene, and so the molecule exhibits effective  $C_{2v}$  symmetry on the NMR time-scale. This behavior is in good agreement with DFT B3LYP calculations that furnish a barrier of 10.9 kcal/mol for process (ii).

Turning now to 9,10-diferrocenylanthracene, **4**, we see that it can exist in syn or anti forms, and at 193 K these atropisomers are indeed detectable. In the syn rotamer (38%), the time-averaged  $C_{2v}$  symmetry gives rise to two pairs of proton

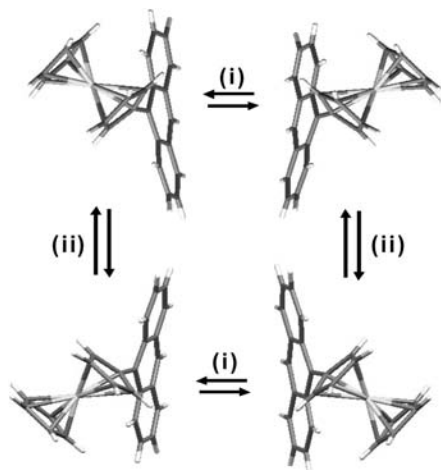
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**Figure 3.** Sections of the variable-temperature 500 MHz  $^1\text{H}$  NMR spectra of 9-ferrocenylanthracene, **3**, over the range 193–303 K.

**Scheme 3.** Exchange Behavior in 9-Ferrocenylanthracene, **3**<sup>a</sup>



<sup>a</sup> (i) Low energy ( $C_s$  symmetric) oscillation of the ferrocenyl group relative to the anthracene ring plane; (ii) higher energy ( $C_{2v}$  symmetric) process whereby rotation of the ferrocenyl moiety about the C(9)–C(11) bond equilibrates the terminal benzo rings.

environments for each of the external benzo rings; in contrast, in the anti isomer (62%), the time-averaged  $C_{2h}$  symmetry renders nonequivalent all four protons in each benzo ring.

In the X-ray crystal structure of **4**, shown in Figure 2, the two ferrocenyl fragments are located on the same face of the anthracene, but, because there is a substantial barrier ( $\sim 11$  kcal mol $^{-1}$  from peak coalescence measurements) to either of them becoming coplanar with the central ring system, this actually represents an anti rotamer. This latter molecule exhibits time-averaged  $C_{2h}$  symmetry in solution at low temperature via oscillation of both ferrocenyl moieties about the anthracene ring plane, analogous to the lower energy exchange process (i) in Scheme 3.

**Ferrocenyl-Triptycenes.** While the addition of benzyne to 1-ferrocenyl anthracene in 1% yield has previously been reported,<sup>15</sup> we found that generating benzyne via the lithiation of *o*-bromofluorobenzene in toluene furnished the sterically

hindered mono- and diferrocenyltriptycenes, **7** and **8**, respectively, in yields ranging from 47% to 57%, a significant improvement from previous reports of the addition of benzyne to 9,10-diarylanthracenes.<sup>16</sup>

In 9-ferrocenyltriptycene, **7**, the angles between the outer blades of the triptycene are 117.9°, 123.2°, and 118.9°, the latter one being the valley proximate to the ferrocenyl substituent, which is bent away from the 3-fold axis such that the angle C(10)–C(9)–C(17) is 172.5° (Figure 4). On a 500 MHz instrument, ferrocenyl rotation is slow on both the  $^1\text{H}$  and the  $^{13}\text{C}$  NMR time-scales, even at room temperature, and the resonances attributable to the paddlewheel blades are each split in a 2:1 ratio. 2D-EXSY data over the temperature range 253–323 K yielded a rotational barrier of  $16.5 \pm 0.5$  kcal mol $^{-1}$ .

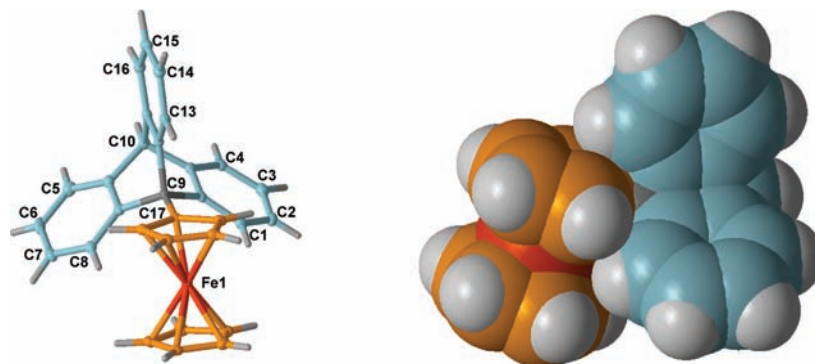
The NMR spectra of 9,10-diferrocenyltriptycene, **8**, at 298 K (Figure 5) reveal the existence of two atropisomers: (i) a  $C_{2v}$ -symmetric isomer, *meso*-**8**, in which the ferrocenyl moieties are aligned within the same valley between benzo blades; in this rotamer each blade possesses two pairs of equivalent nuclei, thus giving rise to a 4:4:2:2 set of  $^1\text{H}$  NMR resonances; and (ii) a  $C_2$ -symmetric isomer, *rac*-**8**, in which the ferrocenyls are positioned adjacent to different valleys; the unique blade again reveals a 2:2  $^1\text{H}$  NMR peak pattern, but the hydrogens for each of the two outer blades now appear as a doublet–triplet–triplet–doublet set of resonances. Interestingly, the *meso*:*rac* ratio remains at 1:2 over the range 253–323 K, indicating them to be energetically equivalent. The X-ray crystal structure of 9,10-diferrocenyltriptycene, **8** (Figure 6), is that of the  $C_2$ -symmetric atropisomer *rac*-**8** in which, once again, the ferrocenyl moieties are each bent away from the 3-fold axis of the triptycene such that C(9)–C(10)–C(17) is 172.3° and C(10)–C(9)–C(27) = 173.6°. The dihedral angles between the unique benzo ring and the  $C_2$ -related blades are 114.0° and 117.4°; the angle between the latter two has opened up to 128.5°. Surprisingly perhaps, the widest angle between the blades is that valley in which neither of the ferrocenyl moieties is located.

When virtual internal rotation of the ferrocenyl fragment about the C(9)–C(17) single bond was probed, it transpired that the triptycene hydrogens H-1, H-8, and H-13 come within 1.25, 1.25, and 0.74 Å, respectively, of the ferrocenyl hydrogens. Although taken individually each of these interactions would not be expected to evoke a substantial rotational barrier, in reality the possibility of a triple simultaneous interaction cannot be discounted. This scenario would be enhanced by the inevitable further bending of the ferrocenyl fragment away from  $C_3$  axis of the triptycene.

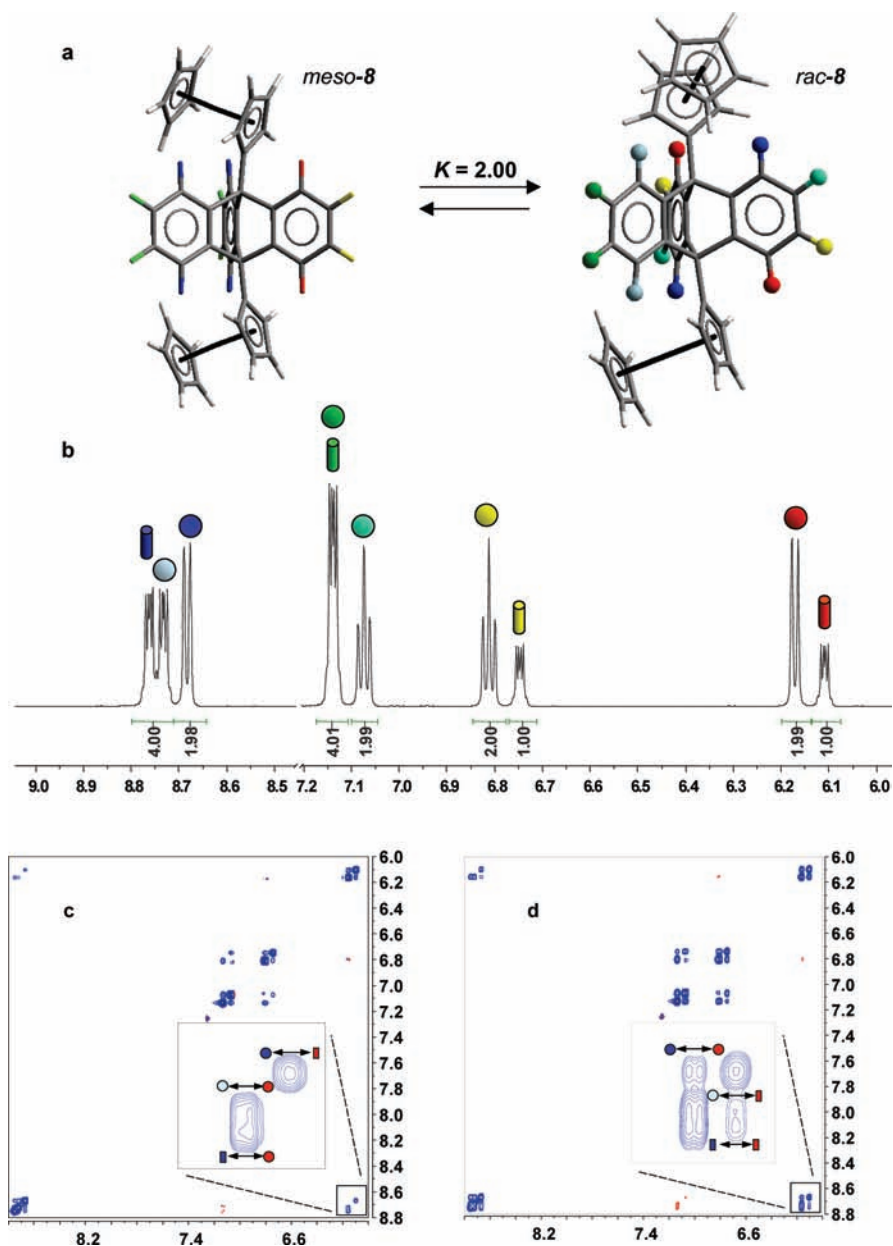
The fluxional behavior of the *meso* ( $C_{2v}$ ) and *rac* ( $C_2$ ) atropisomers of 9,10-diferrocenyltriptycene, **8**, is dramatically displayed in the 2D-EXSY spectra (Figure 5c and d), which reveal that exchange between the *rac* isomers must proceed in a stepwise manner via the mirror-symmetric *meso* structure. Rotation of a ferrocenyl group in *rac*-**8** relative to the  $C_3$  axis of the triptycene exchanges one of its doubly degenerate benzo rings with the unique blade that lies in the molecular mirror plane of *meso*-**8**. Concomitantly, one of the mirror-symmetric benzo rings of *meso*-**8** exchanges with the unique blade of *rac*-**8**. With a relatively short mixing time (50 ms), the only cross-peaks visible are those revealing single-step exchange between corresponding protons in the rotamers. However, after a longer mixing time (300 ms), second generation cross-peaks are evident revealing exchange between sites within the *meso* (or *rac*)

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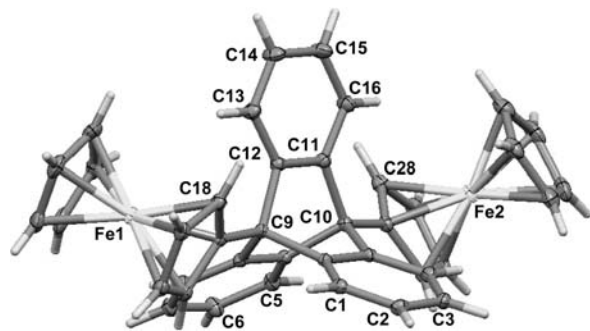
**Figure 4.** X-ray crystal structure of 9-ferrocenyltritycene, **7**, and also a space-fill representation (side view).



**Figure 5.** Dynamic behavior of 9,10-diferrocenyltritycene, **8**. (a) The  $C_2$ -symmetric eclipsed rotamer *meso-8* is in equilibrium with the doubly abundant  $C_2$ -symmetric staggered rotamer *rac-8*; (b) section of the 600 MHz  $^1\text{H}$  NMR spectra of **8**; (c) 600 MHz  $^1\text{H}$ - $^1\text{H}$  EXSY spectrum of **8** at  $T_m = 50$  ms showing cross-peaks arising only from the one-stage exchange processes *meso-8* ↔ *rac-8* and degenerate *rac-8* ↔ *rac-8*; and (d) at  $T_m = 300$  ms, additional second-generation peaks are observed attributable to two-step processes, for example, *meso* → *rac* → *meso*. The cross-peaks are enlarged in the inset.

isomers; this can only occur via the other rotamer, that is, *meso* → *rac* → *meso* or *rac* → *meso* → *rac*. The rotational barrier

was found to be  $16.8 \pm 0.5$  kcal mol $^{-1}$ , in good agreement with the observed value for 9-ferrocenyltritycene, **7**.



**Figure 6.** Molecular structure of 9,10-diferrocenyltritycene, *rac*-**8**, emphasizing its  $C_2$  symmetry.

Although the rotational freedom of closely situated bulky, rigid organic groups is often low,<sup>17</sup> systems containing such “sterically demanding” moieties as 9-triptycyls are known to undergo essentially unhindered rotation at low temperatures due to their tightly interlocked gear-like orientation.<sup>18</sup> In contrast, rotational barriers in binaphthyls<sup>19</sup> and their isostructural isoquinolines,<sup>20</sup> biaryls,<sup>21</sup> and biindenyls<sup>18b</sup> can reach 20–25 kcal mol<sup>-1</sup>. Sternhell has suggested that in 2,2',6,6'-tetrasubstituted biphenyls the experimental barriers can be deconvoluted into contributions from each substituent, and the magnitude of the barrier is a simple linear function of nominal steric overlap of the interacting groups;<sup>22</sup> however, this view has been challenged.<sup>23</sup> Recently, we have applied a similar formalism, which involves the virtual rotation of selected fragments of X-ray crystallographically determined molecular structures, and elucidation of the nominal closest approach distance (CAD) of these fragments.<sup>24</sup> The results for aryl- or indenyl-anthracenes, -tritycenes, and -barrelenes suggest that high barriers arise from multiple simultaneous close steric contacts.

Now, taking the X-ray crystal structure of **3**, and carrying out a virtual rotation of the ferrocenyl substituent so as to model the low energy  $C_s$  transition state, the nominal closest approach distance (CAD) of a hydrogen (H-16) in the  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> ring to H-8 of the anthracene is 1.5 Å. However, virtual rotation of the ferrocenyl moiety through 90° would position both H-12 and H-15 within 1.2 Å of their anthracenyl neighbors, H-1 and H-8. In practice, however, as reported recently for a series of sterically

crowded biaryls,<sup>25</sup> the system presumably distorts so as to avoid such an unfavorable transition state.

It has been demonstrated that the rotation barriers arising from double steric repulsions in 9-aryl-anthracenes (15–18 kcal mol<sup>-1</sup>) are higher than those in the corresponding triptycenes (8–12 kcal mol<sup>-1</sup>) in which potential steric interactions can be alleviated through a “duck-and-dodge” bending of the planar aryl moiety into the valley between the triptycene blades.<sup>24</sup> However, the present work reveals that this situation is reversed for  $\eta^5$ -(C<sub>5</sub>H<sub>4</sub>)ML<sub>*n*</sub> derivatives of anthracene (barrier 11–12 kcal mol<sup>-1</sup>) or triptycene (barrier 16–17 kcal mol<sup>-1</sup>). Three-dimensional organometallic moieties (such as ferrocene, which behaves as a rotating pentagonal prism of height 3.3 Å and diameter 4.5 Å<sup>26</sup>) cannot readily avoid multiple interactions engendered by the need to bend away from the 3-fold axis of the triptycene.

The temperature independence of the equilibrium constant (2:1) between the racemic and the meso forms of 9,10-diferrocenyl-triptycene, **8**, indicates that the two rotamers are energetically equivalent, and that there is only minimal interaction between the two metal sandwich fragments, which exhibit independent, rather than correlated,<sup>27</sup> hindered rotation behavior. The overall behavior is that of a set of molecular dials, each of which can rotate only one position at a time.

The findings reported here suggest that molecular mechanical systems can be engineered and assembled from rigid interlinked molecular fragments in a fashion such that the distortion of the fragments is minimal. However, the energy barriers for interconversion of the conformations (in this case, rotamers) are governed by the structure of the rigid molecular framework and can be very significant. This situation of kinetically slow interconversion of energetically degenerate diastereomeric rotamers is particularly attractive as it provides a new structural motif for functional molecular mechanical systems such as rotational switches and memory devices. For instance, the combination of a rigid triptycene core with two stereochemically mobile and electrochemically active ferrocenyl moieties could have the potential for use in novel molecular tunnel junction devices. Other applications might include molecular rotors, machines and motors, molecular recognition systems, and sensors.<sup>4,11d,e</sup>

## Experimental Section

All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Column chromatography separations were carried out on a Buchi Sepacor machine with UV absorbance detector using silica gel particle size 40–63 mm. Routine and variable-temperature NMR spectra were acquired on Varian VNMRs 500 and 600 MHz systems and a Varian Inova 500 MHz spectrometer. Assignments were based on standard <sup>1</sup>H–<sup>1</sup>H and <sup>1</sup>H–<sup>13</sup>C two-dimensional techniques, and <sup>1</sup>H–<sup>1</sup>H 2D NOESY measurements. Melting points were determined on a Gallenkamp instrument in air and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin.

**9-Ferrocenylantracene (3).** To a stirred solution containing **6a** (0.128 g, 0.5 mmol), the boronic acid **5** (0.138 g, 0.6 mmol), and dichloro-bis(diphenylphosphinoferrocene)palladium(II) (8 mg, 0.01 mmol) in 1,4-dioxane (6 mL) was added an aqueous tetrabu-

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tylammonium hydroxide solution (1 M, 0.6 mL). The reaction mixture was stirred for 24 h at 90 °C, after which time it was concentrated, extracted with dichloromethane (100 mL), washed with aqueous sodium bicarbonate, concentrated, and separated (eluent 5% dichloromethane in cyclohexane) to afford **3** (120 mg, 66%) as a dark red solid whose spectroscopic characteristics were consistent with the previously reported data.<sup>13</sup> <sup>1</sup>H NMR (500 MHz, 303 K, CD<sub>2</sub>Cl<sub>2</sub>, numbering as in Figure 1): δ = 9.20 (2H<sub>1/8</sub>, br, s), 8.43 (1H<sub>10</sub>, s), 8.01 (2H<sub>4/5</sub>, d, *J* = 8 Hz), 7.50 (2H<sub>2/7</sub>, t, *J* = 8 Hz), 7.46 (2H<sub>3/6</sub>, t, *J* = 9 Hz), 4.79 (2H<sub>12/15</sub>, d, *J* = 2 Hz), 4.61 (2H<sub>13/14</sub>, d, *J* = 2 Hz), 4.25 (5H<sub>16</sub>, s). <sup>13</sup>C NMR (125 MHz, 303 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = 132.0 (C<sub>9</sub>), 131.6 (C<sub>4a/8b</sub>), 130.5 (C<sub>4b,8a</sub>), 128.4 (C<sub>4/5</sub>), 127.7 (C<sub>1/8</sub>), 126.6 (C<sub>10</sub>), 124.8 (C<sub>3/6</sub>), 124.2 (C<sub>2/7</sub>), 84.2 (C<sub>11</sub>), 73.2 (C<sub>12,15</sub>), 69.8 (C<sub>16–20</sub>), 67.8 (C<sub>13/14</sub>).

**9,10-Diferrocenylanthracene (4).** This compound was prepared from **6b** and the acid **5** in 90% yield as a dark red solid whose characteristics were consistent with the previously reported data.<sup>13</sup> <sup>1</sup>H NMR (numbering as in Figure 2, 500 MHz, 303 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.13 (4H<sub>1/4/1/4'</sub>, m), 7.42 (4H<sub>2/3/2/3'</sub>, m), 4.75 (4H<sub>12/15/12/15'</sub>, t, *J* = 1.6 Hz), 4.61 (4H<sub>13/14/13/14'</sub>, t, *J* = 1.6 Hz), 4.26 (10H<sub>16–20/16'–20'</sub>, s). <sup>13</sup>C NMR (125 MHz, 303 K, CD<sub>2</sub>Cl<sub>2</sub>): δ = 131.7 (C<sub>9,9'</sub>), 130.7 (C<sub>4a/4a'</sub>), 128.2 (C<sub>1/1'</sub>), 123.6 (C<sub>2/2'</sub>), 84.8 (C<sub>11/11'</sub>), 73.5 (C<sub>12/15/12/15'</sub>), 69.8 (C<sub>16–20/16'–20'</sub>), 67.8 (C<sub>13/14/13/14'</sub>).

**9-Ferrocenyltritycene (7).** To a stirred solution containing **3** (0.090 g, 0.25 mmol) and *o*-bromofluorobenzene (0.228 g, 1.3 mmol) in toluene (6 mL) was added a solution of *n*-butyllithium (1.6 M, 0.8 mL) at –5 °C. The reaction mixture was stirred for 16 h at ambient temperature, washed with aqueous ammonium chloride, concentrated, and separated (5–25% dichloromethane in cyclohexane) to give **7** (63 mg, 57%) as an orange solid: mp >310 °C (dec). <sup>1</sup>H NMR (numbering as in Figure S1, 600 MHz, 303 K, CDCl<sub>3</sub>): δ = 8.58 (2H<sub>1/8</sub>, d, *J* = 7.6 Hz), 7.40 (2H<sub>4/5</sub>, d, *J* = 7.1 Hz), 7.35 (1H<sub>16</sub>, d, *J* = 7.4 Hz), 7.09 (2H<sub>2/7</sub>, t, *J* = 7.5 Hz), 7.01 (2H<sub>3/6</sub>, t, *J* = 7.4 Hz), 6.95 (1H<sub>15</sub>, t, *J* = 7.4 Hz), 6.78 (1H<sub>14</sub>, t, *J* = 7.5 Hz), 6.16 (H<sub>13</sub>, d, *J* = 7.6 Hz), 5.36 (H<sub>10</sub>, s), 4.61 (2H<sub>19/20</sub>, t, *J* = 2 Hz), 4.59 (2H<sub>18/21</sub>, d, *J* = 2 Hz), 4.38 (5H<sub>22–26</sub>, s). <sup>13</sup>C NMR (150 MHz, 303 K, CDCl<sub>3</sub>): δ = 149.6 (C<sub>12</sub>), 147.5 (C<sub>4a/8b</sub>),

145.8 (C<sub>4b,8a</sub>), 144.3 (C<sub>11</sub>), 125.3 (C<sub>15</sub>), 124.73 (C<sub>3/6</sub>), 124.70 (C<sub>14</sub>), 124.44 (C<sub>13</sub>), 124.38 (C<sub>2/7</sub>), 124.3 (C<sub>1/8</sub>), 123.7 (C<sub>4/5</sub>), 122.5 (C<sub>16</sub>), 84.0 (C<sub>17</sub>), 70.6 (C<sub>18/21</sub>), 69.6 (C<sub>22</sub>), 68.6 (C<sub>19/20</sub>), 54.9 (C<sub>9</sub>), 54.8 (C<sub>10</sub>). HRMS: calcd for C<sub>30</sub>H<sub>22</sub>Fe 438.1071; found 438.1085. Anal. Calcd for C<sub>30</sub>H<sub>22</sub>Fe: C, 82.20; H, 5.06. Found: C, 81.91; H, 5.03.

**9,10-Diferrocenyltritycene (8).** This compound was prepared from **4** in 44% yield; an orange solid: mp >315 °C (dec). <sup>1</sup>H NMR indicated the presence of two conformations *meso-8* and *rac-8* in a 1:2 ratio. *meso-8*, <sup>1</sup>H NMR (numbering as in Figure S2, 600 MHz, 303 K, CDCl<sub>3</sub>): δ = 8.75 (4H<sub>1/4/5/8</sub>, m), 7.12 (4H<sub>2/3/6/7</sub>, m), 6.73 (2H<sub>14/15</sub>, m), 6.11 (2H<sub>13/16</sub>, m), 4.64 (4H<sub>19/20/29/30</sub>, s), 4.61 (4H<sub>18/21/28/31</sub>, s), 4.40 (10H<sub>22–26/32–36</sub>, s). <sup>13</sup>C NMR (150 MHz, 303 K, CDCl<sub>3</sub>): δ = 148.4 (C<sub>11/12</sub>), 147.94 (C<sub>4a/4b/8a/8b</sub>), 124.87 (C<sub>14/15</sub>), 124.3 (C<sub>1/4/5/8</sub>), 123.88 (C<sub>2/3/6/7</sub>), 123.45 (C<sub>13/16</sub>), 84.27 (C<sub>17/27</sub>), 71.05 (C<sub>18/21/28/31</sub>), 69.75 (C<sub>22–26/32–36</sub>), 68.76 (C<sub>19/20/29/30</sub>), 54.20 (C<sub>9/10</sub>). *rac-8*, <sup>1</sup>H NMR: δ = 8.73 (2H<sub>13/16</sub>, m), 8.68 (2H<sub>4/8</sub>, d, *J* = 7.6 Hz), 7.12 (2H<sub>14/15</sub>, m), 7.06 (2H<sub>3/7</sub>, t, *J* = 7.6 Hz), 6.80 (2H<sub>2/6</sub>, t, *J* = 7.6 Hz), 6.16 (2H<sub>1/5</sub>, d, *J* = 7.6 Hz), 4.64 (4H<sub>19/20/29/30</sub>, s), 4.64 (2H<sub>21/31</sub>, s), 4.55 (2H<sub>18/28</sub>, s), 4.41 (10H<sub>22–26/32–36</sub>, s). <sup>13</sup>C NMR: δ = 151.9 (C<sub>4b/8b</sub>), 148.0 (C<sub>11/12</sub>), 144.66 (C<sub>4a/8a</sub>), 124.69 (C<sub>1/5</sub>), 124.51 (C<sub>3/7</sub>), 124.19 (C<sub>2/6/13/16</sub>), 123.76 (C<sub>14/15</sub>), 123.07 (C<sub>4/8</sub>), 84.26 (C<sub>17/27</sub>), 71.05 (C<sub>18/21/28/31</sub>), 69.73 (C<sub>22–26/32–35</sub>), 68.74 (C<sub>19/20</sub>), 54.24 (C<sub>9/10</sub>). HRMS: calcd for C<sub>30</sub>H<sub>30</sub>Fe<sub>2</sub> 622.1046; found 622.1070. Anal. Calcd for C<sub>40</sub>H<sub>30</sub>Fe<sub>2</sub>: C, 77.20; H, 4.86. Found: C, 77.54; H, 4.94.

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**Supporting Information Available:** Crystallographic details (CIF) for molecules **3**, **4**, **7**, and **8**, and details of (2D <sup>1</sup>H–<sup>1</sup>H EXSY) exchange spectra of **7** and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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