

# Octamethyloctahydrodibenzofluorenyl: Electronic Comparisons between a Sterically Expanded Ligand and Its Cyclopentadienyl Analogues

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Incorporating the octamethyloctahydrodibenzofluorenyl (Oct) ligand into metallocene and constrained geometry olefin polymerization catalysts has profound catalytic consequences. The steric influences are undoubtedly important, but it is shown herein that electronics likely also play a crucial role. The electron richness of the Oct<sup>−</sup> anion was directly measured by competitive deprotonation experiments, which reveal that the pK<sub>a</sub> of OctH is 3.9 units higher than that of fluorene. The HOMO–LUMO gap decreases by about 0.6 kcal/mol for each additional tertiary alkyl group appended to the metallocene R<sub>2</sub>C(C<sub>5</sub>H<sub>4</sub>)(C<sub>13</sub>H<sub>8</sub>)ZrCl<sub>2</sub> (R = Me or Ph) in the 2, 3, 6, and 7 positions of the fluorenyl moiety, indicating the ability of these groups to increase the HOMO energy by electron donation. The carbonyl stretching frequencies for η<sup>5</sup>-OctMn(CO)<sub>3</sub> (2009, 1924 cm<sup>−1</sup>) demonstrated that the Oct ligand is the most electron donating in the series of CpMn(CO)<sub>3</sub>, Cp<sup>\*</sup>Mn(CO)<sub>3</sub>, and (C<sub>13</sub>H<sub>9</sub>)Mn(CO)<sub>3</sub>. DFT calculations universally corroborate these experimental findings.

## Introduction

Since their discovery, metallocenes have received considerable attention as olefin polymerization catalysts.<sup>1</sup> In the early 1990s, a new class of single-site catalyst<sup>2</sup> was reported that contained a cyclopentadienyl-based bridged η<sup>1</sup>-amido ligand.<sup>3</sup> These catalysts, termed “constrained geometry catalysts” (CGCs), have been extensively studied because their ability to incorporate larger olefins in ethylene/α-olefin copolymerizations makes them

ideally suited for the industrial preparation of linear low-density polyethylene (LLDPE).

Recent work in the areas of *ansa*-metallocenes<sup>4,5</sup> and CGCs<sup>6,7</sup> has incorporated the sterically expanded fluorene derivative 2,2,5,5,8,8,11,11-octamethyl-2,3,4,5,8,9,10,11-octahydrodibenzo[*b,e*]fluorene (OctH) into highly active and stereoselective catalysts for olefin polymerization. OctH was first reported in 1980<sup>8</sup> and can easily be synthesized in >200 g batches (92% yield) based on a specific solvent modification (nitromethane) of the original procedure.<sup>6</sup> Recently, there have been numerous reports focusing on how ligand steric environments affect olefin polymerization catalysis.<sup>9</sup> In particular, the addition of steric bulk to the fluorene plane—in the form of the Oct moiety—greatly increases the syndiospecificity of both *ansa*-metallocene<sup>5</sup> and CGC<sup>10</sup> propylene polymerization catalysts, presumably for steric reasons. However, there are relatively few reports that directly address

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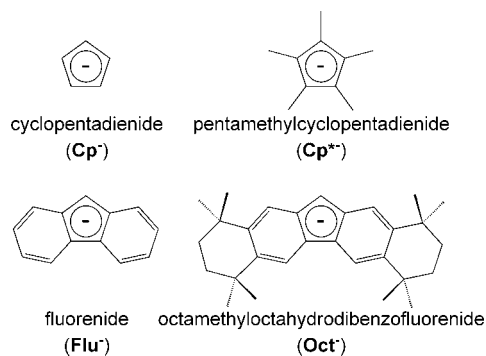
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**Figure 1.** The series of Cp-based ligands explored.

the *electronic* consequences of incorporating sterically expanded ligands into transition metal-based catalysts.<sup>11,12</sup>

In this paper we have explored the electronic differences of several cyclopentadienyl-based ligands (Figure 1) via density functional theory (DFT) calculations, as well as NMR, UV–visible, and infrared (IR) spectroscopies. We have synthesized both metallocene and nonmetallocene transition metal complexes of these ligands using early and mid transition metals in order to suggest that the revealed trends are general for the series of Cp-based ligands.

## Results and Discussion

**FluH vs OctH: NMR Studies and DFT Calculations.** One indication of the electronic nature of molecules is the NMR chemical shift of their respective nuclei.<sup>13</sup> As the electron density on an atom increases, the nucleus becomes more shielded. As a result, its NMR resonance shifts to lower ppm. Of particular interest is the doubly benzylic CH<sub>2</sub> group of both FluH and OctH. The <sup>13</sup>C NMR spectra (in CDCl<sub>3</sub>) show a difference of 0.66 ppm for this methylene carbon ( $\delta$  36.17 for OctH vs  $\delta$  36.83 for FluH). The methylene protons also follow the expected trend; the <sup>1</sup>H NMR spectra show a difference of 0.09 ppm ( $\delta$  3.85 for OctH vs  $\delta$  3.94 for FluH).

Additionally, the competitive deprotonation of OctH and FluH by increasing amounts of *tert*-butyllithium was followed by <sup>1</sup>H NMR in tetrahydrofuran-*d*<sub>8</sub>. An equilibrium constant, *K*<sub>eq</sub>, of 7500 was measured for the equilibrium shown in Figure 2. This suggests that the *pK*<sub>a</sub> of OctH is 3.9 units greater than that of FluH; given a literature value of 23.0 for the *pK*<sub>a</sub> of FluH,<sup>14</sup> the *pK*<sub>a</sub> of OctH is 26.9. Since OctH contains four tertiary alkyl groups on the fluorene ring, this result correlates well with the previous determination that a single *para tert*-butyl group increases the *pK*<sub>a</sub> of toluene by 0.87 units.<sup>15</sup>

In addition to the NMR studies above, DFT calculations (B3LYP/6-31G<sup>+</sup>) were carried out on the isodesmic reaction depicted in Figure 2. From these calculations, a  $\Delta H$  of  $-2.64$

kcal/mol and a  $\Delta G$  of  $-2.65$  kcal/mol (at 298.15 K,  $\Delta S = +0.015$  cal/mol K) were determined, indicating that the reaction favors the products. This value for  $\Delta G$  translates to a *K*<sub>eq</sub> of 87.5, compared to 7500 for the NMR experiment. The discrepancy is at least partially attributable to the fact that the DFT calculations represent the gas phase reaction and ignore solvent effects. In a vacuum the stability of the spacious Oct<sup>-</sup> anion will likely be overestimated, thereby placing too much emphasis on the starting materials. Indeed the NMR experiment, which includes solvent effects (tetrahydrofuran-*d*<sub>8</sub>), suggests a  $\Delta H$  of  $-5.3$  kcal/mol (when  $\Delta S$  is considered negligible).

**UV–Visible Spectroscopy.** To assess the electronic ramifications of the sterically expanded Oct-based ligands on transition metal complexes, a series of *ansa*-zirconocenes was synthesized that utilize the Flu and Oct moieties (Figure 3); these bear the Flu ligand (**1-Me**, **1-Ph**), the Tet ligand (tetramethyltetrahydrodibenzofluorenyl, **2-Ph**), or the Oct ligand (**3-Me**, **3-Ph**) and either an isopropylidene (R = Me) or diphenylmethylidene (R = Ph) bridge. UV–vis spectroscopy was employed to probe the energetics of ligand-to-metal charge transfer (LMCT) in these metallocene complexes. As the *ansa* ligand becomes more electron rich, the LMCT should become more facile, thereby shifting the LMCT bands to longer wavelengths (lower energy). Figure 4 shows the UV–vis absorption spectra for the five *ansa*-zirconocenes of Figure 3. The addition of four tertiary alkyl substituents to fluorene shifts the  $\lambda_{\max}$  of the metallocene by approximately 22 nm. For the isopropylidene bridge, the  $\lambda_{\max}$  shifts from 493 to 516 nm when Oct (**3-Me**) is substituted for Flu (**1-Me**), which corresponds to a 2.58 kcal/mol decrease in energy for the LMCT. For the diphenylmethylidene bridge, the  $\lambda_{\max}$  shifts from 500 to 521 nm when Oct (**3-Ph**) is substituted for Flu (**1-Ph**), which corresponds to a 2.30 kcal/mol decrease in energy for the LMCT. Note that  $\lambda_{\max}$  of the Tet complex (**2-Ph**, 510 nm) is directly between those of the Flu and Oct species.

**DFT Calculations.** In addition, density functional theory (DFT) calculations (B3LYP 6-31G<sup>\*\*</sup>/LanL2DZ) were performed on *ansa*-metallocenes **1-Me** and **3-Me**. From these calculations, molecular orbitals (HOMO, LUMO, Figure 5) as well as the HOMO–LUMO energy gaps were determined. The HOMO–LUMO gaps are relevant because they represent a ligand-to-metal charge transfer (LMCT) and are arguably a measure of the Flu or Oct ligand electronic stability via its HOMO contribution. As indicated in Figure 5 and Table 1, the HOMOs for **1-Me** and **3-Me** are largely Flu/Oct-based (63.4–64.8%), whereas the LUMOs are largely metal-based (33.5–33.6%). Flu-based **1-Me** and Oct-based **3-Me** were calculated to have HOMO–LUMO gaps of 35.77 and 33.89 kcal/mol, respectively. This indicates that the LMCT is a lower energy transition for the Oct-based metallocene by 1.88 kcal/mol. This correlates reasonably well with the 2.58 kcal/mol difference in  $\lambda_{\max}$  observed by UV–vis spectroscopy.

**Infrared Studies.** Manganese tricarbonyl compounds of Cp, Flu, and Oct were synthesized in order to further quantify the electronic differences among the ligands and to demonstrate that these differences are specific to the ligands (Figure 6). The synthesis of OctMn(CO)<sub>3</sub> (**7**)<sup>16</sup> followed that for the fluorenyl analogue (**6**),<sup>17</sup> and its X-ray crystal structure confirms the targeted tricarbonyl ligation and  $\eta^5$ -hapticity (Figure 7 and Table 2). The electronic environment imparted by the organic ligands

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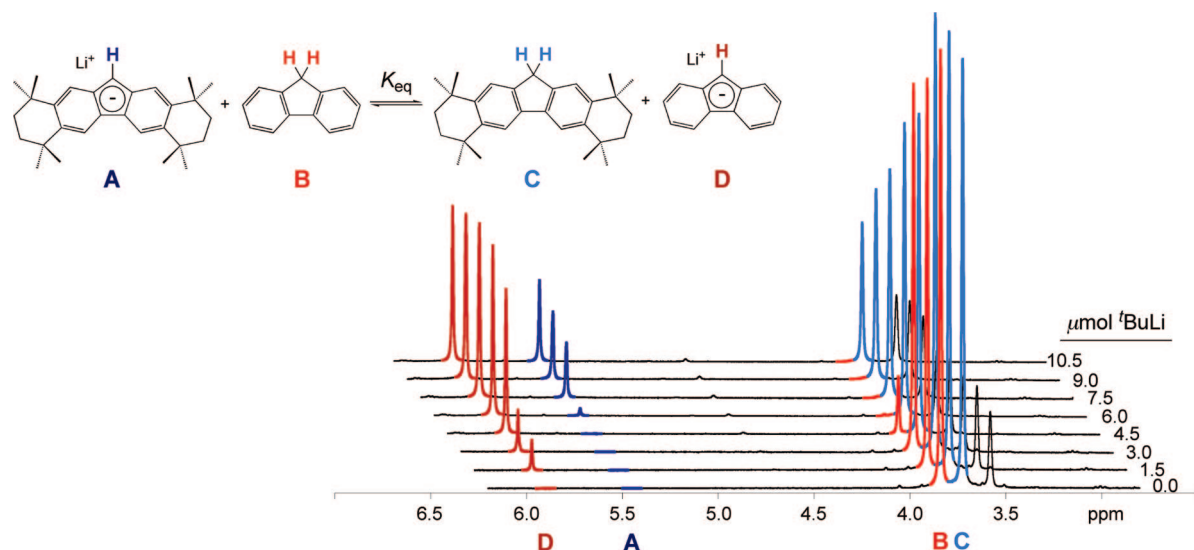
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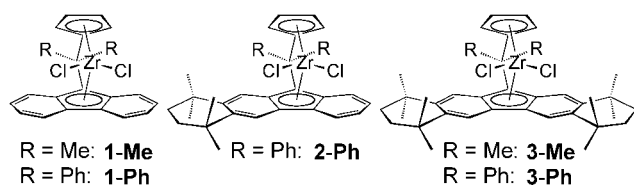
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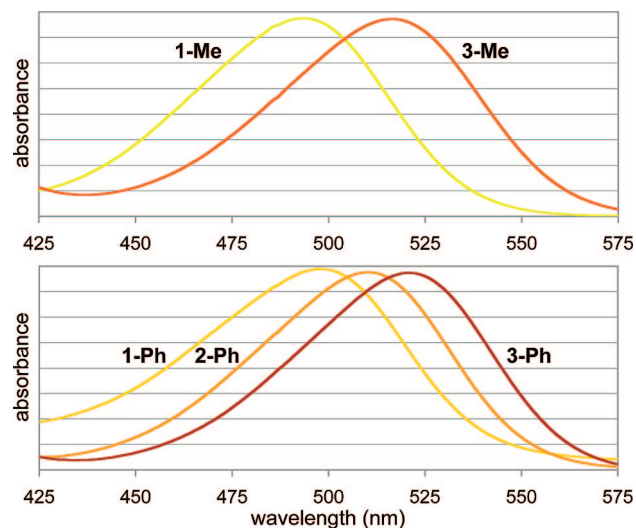
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**Figure 2.** Competitive deprotonation of FluH (red) and OctH (blue) by *tert*-butyl lithium in THF-*d*<sub>6</sub>.

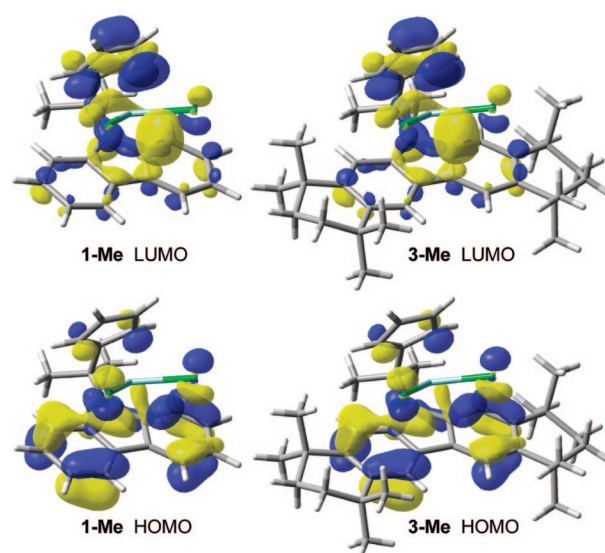


**Figure 3.** The *ansa*-metallocenes investigated.



**Figure 4.** UV-vis spectra of metallocenes **1-Me**, **3-Me**, **1-Ph**, **2-Ph**, and **3-Ph**.

was assessed according to the carbonyl stretching frequencies measured by infrared spectroscopy, a technique previously employed for a series of electronically variable indenyl ligands.<sup>12b,18</sup> Representative spectra are shown in Figure 8, and all relevant carbonyl stretching frequencies are cataloged in Table 3. Compared to the Cp analogue (**4**), the manganese centers in **5** and **6** are more electron rich, owing to electron donation of Cp\* methyl groups and the greater electron density of the 14-electron  $\pi$  system of Flu<sup>-</sup>. However, the Oct-based species (**7**) exhibits the lowest carbonyl stretching frequencies and is the most electron rich, due to the four electron-donating



**Figure 5.** Calculated HOMO and LUMO molecular orbitals for **1-Me** and **3-Me**.

tertiary alkyl groups. Note that the Oct ligand is even more donating than Cp\*. Although the steric consequences of Oct seem to prohibit the formation of a bis(Oct) zirconocene dichloride, Parkin and co-workers have recently shown that pentamethylcyclopentadienyl is one of the most electron-donating cyclopentadienyl ligands available in a large series of zirconocenes.<sup>19</sup>

## Conclusions

The octamethyloctahydrodibenzofluorenyl (Oct) ligand has been compared to several cyclopentadienyl-based ligands in both metallocene and non-metallocene complexes via DFT calculations, UV-vis, and IR. In addition, the free protonated ligand was compared to FluH by NMR and DFT calculations. In all cases, Oct is measurably more electron rich than the other ligands studied, as well as other cyclopentadienyl-based

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Table 1. Calculated Energies and Molecular Orbital Distributions

	energy (kcal/mol)	% Zr	% Cl	% Flu/Oct	% bridge	% Cp
1-Me HOMO	-160.64	16.63	7.28	64.84	0.36	10.90
1-Me LUMO	-124.87	33.62	4.27	15.61	6.70	39.80
LUMO-HOMO	35.77					
3-Me HOMO	-146.21	18.27	7.96	63.41	0.39	9.97
3-Me LUMO	-112.32	33.48	4.45	16.82	6.59	38.67
LUMO-HOMO	33.89					

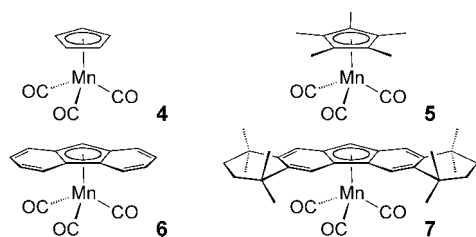


Figure 6. Cp-based ligand effects have been assessed via IR spectroscopy of these manganese tricarbonyl complexes.

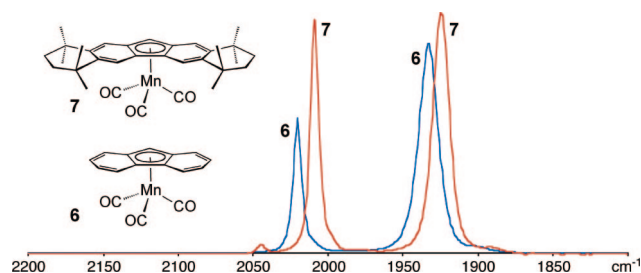


Figure 8. Representative IR spectra for 6 (blue) and 7 (red).

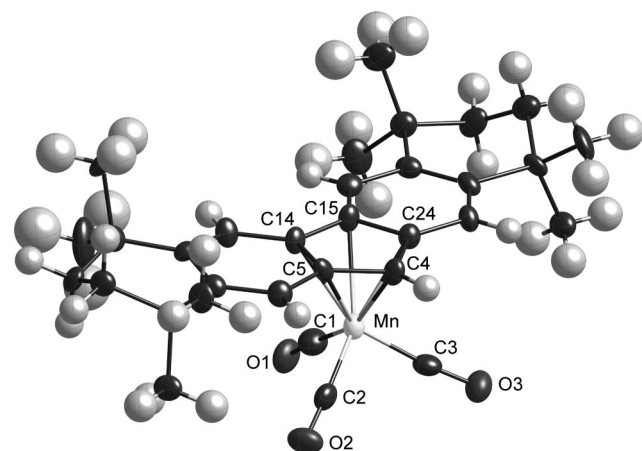
Table 3. Manganese Carbonyl Stretching Frequencies in Tetrahydrofuran

compound	substituent	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )	
		symmetric	asymmetric
4	Cp	2022	1933
5 <sup>a</sup>	Cp*	2017	1928
6	Flu	2016	1933
7	Oct	2009	1924

<sup>a</sup> Stretching frequencies as reported in ref 20, obtained in pentane or hexane.

Table 4. X-ray Data Collection and Processing Parameters for  $\eta^5$ -OctMn(CO)<sub>3</sub> (7)

empirical formula	C <sub>32</sub> H <sub>37</sub> O <sub>3</sub> Mn
fw	524.56
temperature (K)	110(2)
wavelength (Å)	0.71073
cryst syst	orthorhombic
space group	<i>Pna</i> 2 <sub>1</sub>
<i>a</i> (Å)	26.234(7)
<i>b</i> (Å)	16.479(5)
<i>c</i> (Å)	6.3671(18)
$\alpha$ (deg)	90
$\beta$ (deg)	90
$\gamma$ (deg)	90
volume (Å <sup>3</sup> )	2752.5(13)
<i>Z</i>	4
density (calc, gcm <sup>-3</sup> )	1.266
$\mu$ (mm <sup>-1</sup> )	0.510
cryst size (mm <sup>3</sup> )	0.20 × 0.10 × 0.05
2 $\theta$ , <i>R</i> (int)	50.88°, 0.0935
no. of reflns	19 867
no. of indep reflns	4728
no. of data/restraints/params	4728/525/471
GOF ( <i>F</i> <sup>2</sup> )	1.036
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0730
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1706
<i>R</i> <sub>1</sub> (all data)	0.0934
<i>wR</i> <sub>2</sub> (all data)	0.1845
largest diff peak, hole (e Å <sup>-3</sup> )	0.391, -0.483

Figure 7. X-ray crystal structure of  $\eta^5$ -OctMn(CO)<sub>3</sub> (7) shown with 50% probability ellipsoids.Table 2. Selected Bond Lengths (Å) and Angles (deg) for  $\eta^5$ -OctMn(CO)<sub>3</sub> (7)

Mn-C1	1.745(9)	O1-C1-Mn	176.4(10)
Mn-C2	1.768(11)	O2-C2-Mn	175.3(10)
Mn-C3	1.768(7)	O3-C3-Mn	174.8(7)
Mn-C4	2.098(6)	C1-Mn-C2	95.1(5)
Mn-C5	2.195(6)	C2-Mn-C3	92.6(4)
Mn-C14	2.215(6)	C3-Mn-C1	94.9(4)
Mn-C15	2.235(6)	C4-Mn-C1	158.5(4)
Mn-C24	2.196(6)	C4-Mn-C2	102.2(4)
C1-O1	1.202(9)	C4-Mn-C3	97.0(3)
C2-O2	1.165(11)		
C3-O3	1.182(8)		

ligands reported.<sup>19</sup> Although the steric features of this large (14 Å) ligand are somewhat obvious, the results of these investigations demonstrate that its four tertiary alkyl groups have significant electronic consequences as well. The electron richness of this ligand undoubtedly contributes to the unusual finding of  $\eta^1$ -hapticity in the corresponding constrained geometry catalyst, Me<sub>2</sub>Si( $\eta^1$ -C<sub>29</sub>H<sub>36</sub>)( $\eta^1$ -N-*t*-Bu)ZrCl<sub>2</sub>·OEt<sub>2</sub>.<sup>7</sup> The electron richness also reasonably explains the unusual proclivity of this catalytic system (upon activation with methylaluminumoxane) for  $\alpha$ -olefins relative to ethylene.<sup>6</sup> Because the ligand is electron rich, there may be a particularly shallow potential energy well for ring slippage from  $\eta^5$  to  $\eta^1$ . Upon ring slippage to  $\eta^1$ , it is plausible that there may

be less steric discrimination between monomers, and the electronic nature of the substrate may prevail. This appears to be the best explanation for the observation that this catalyst system is more reactive toward 1-octene than it is toward ethylene.<sup>6</sup> Indeed, the Oct ligand cannot be fully understood in terms of simple sterics; its electronic features may be equally, if not more, important.

## Experimental Section

**General Considerations.** All air-sensitive procedures were performed under a purified nitrogen atmosphere in a glovebox or by using standard Schlenk line and vacuum line techniques. Solvents were sparged with nitrogen, dried over molecular sieves using an MBraun solvent purification system, and dispensed into oven-dried Straus flasks. All other chemicals were used as received. Metalloenes **1–3** were synthesized according to literature procedures.<sup>5a,21</sup> CpMn(CO)<sub>3</sub> (**4**) was purchased from Strem. Compound **6** (FluMn(CO)<sub>3</sub>) was synthesized using a procedure analogous to that previously published.<sup>17</sup>

**Theoretical Calculations.** DFT calculations were carried out with the Gaussian 03 suite of programs<sup>22</sup> using the gradient-corrected Becke exchange functional<sup>23</sup> and the correlation functional of Lee, Yang, and Parr<sup>24</sup> (B3LYP). Full geometry optimization calculations were carried out on OctH, FluH, OctLi, and FluLi using a 6-31G<sup>+</sup> basis set.<sup>25</sup> The reaction enthalpy ( $\Delta H$ ) was derived from the energy of each molecule (from the single-point calculation) corrected to enthalpy by the “thermal correction to enthalpy term” obtained from the frequency calculation. Single-point calculations were carried out on **1-Me** and **3-Me** using the geometries obtained from the crystal structures using a LanL2DZ basis set<sup>26</sup> for the Zr atom and 6-31G\*\* for all other atoms.<sup>27</sup>

**FluLi.** In a nitrogen-filled glovebox, fluorene (45.05 g, 271.03 mmol) was added to a 500 mL round-bottom flask, and this was attached to a swivel frit. The frit was then evacuated on the vacuum line and diethyl ether (300 mL) condensed in at 77 K. As the solution was warming to room temperature, *n*-butyllithium (120 mL of a 2.5 M solution in hexanes, 300 mmol) was added via syringe. After 16 h the solvent was removed *in vacuo*. Heptane (250 mL) and diethyl ether (100 mL) were vacuum transferred in at 77 K. The mixture was warmed to room temperature and stirred for 1 h, at which time the solid product was collected by filtration. The ether was then removed *in vacuo*, and the product was washed with heptane (2 × 25 mL). Drying *in vacuo* afforded the yellow product in 95.3% yield (44.47 g).

**Synthesis of ( $\eta^5$ -C<sub>13</sub>H<sub>9</sub>)Mn(CO)<sub>3</sub> (**6**).** In a nitrogen-filled glovebox, FluLi (0.344 g, 2.00 mmol) and BrMn(CO)<sub>5</sub> (0.550 g, 2.00 mmol) were combined in a 100 mL receiving flask, which was then sealed with a 180° needle valve. The flask was then evacuated on the vacuum line, and THF (50 mL) was condensed in at 77 K. The reaction was slowly warmed to room temperature and stirred for 23 h, at which time the solvent was removed *in vacuo*. The resulting yellow solid was extracted into pentane (60 mL) and filtered through a pad of Celite inside a swivel frit. Concentration to 5 mL afforded the title compound as a yellow

powder. The precipitated solid was then collected by filtration, washed with pentane, and dried *in vacuo* to yield 0.258 g (42.4%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.57 (d, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, 2H, Ar-H), 7.04 (d, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, 2H, Ar-H), 6.81 (t, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 2H, Ar-H), 6.74 (t, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 2H, Ar-H), 4.93 (s, 1H, Ar-H-Ar). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  127.4, 125.3, 125.0, 124.8, 106.7, 95.7, 60.4, 22.62.

**2,5-Dichloro-2,5-dimethylhexane.** A 4 L Erlenmeyer flask was charged with 200.00 g of 2,5-dimethyl-2,5-hexanediol and 1.0 L of concentrated aqueous HCl. The resulting slurry, which was periodically shaken by hand, sat at room temperature for 48 h. Water was added (~800 mL) and the slurry was extracted with diethyl ether (3 × 250 mL). The combined ether layers were dried over MgSO<sub>4</sub> and concentrated to ~200 mL. The flask was heated to redissolve the formed precipitate, then slowly cooled to recrystallize the product. The white crystalline solid (237.6 g, 94.7%) was isolated via vacuum filtration using a water aspirator and dried overnight on the filter. (The product easily sublimes, so drying *in vacuo* is discouraged.) <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ , 1.98 (s, 4H, CH<sub>2</sub>) 1.58 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  70.4, 41.4, 32.9.

**OctH.** A nitrogen-purged 1 L round-bottom flask was charged with fluorene (22.65 g, 136.3 mmol) and 2,5-dichloro-2,5-dimethylhexane (50.00 g, 273.2 mmol), and the solids were dissolved in ~450 mL of nitromethane. A solution of AlCl<sub>3</sub> (22.30 g in 50 mL nitromethane) was added via syringe over 20 min. The resulting dark blue slurry was stirred at room temperature for 48 h. The reaction mixture was poured into 1 L of ice water, and the resulting light green precipitate was collected via vacuum filtration. The solid was triturated in dry ethanol for 24 h, isolated by filtration, and recrystallized from hot toluene to yield 48.3 g (92.1%) of octamethyloctahydrodibenzofluorene as a white crystalline solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.63 (s, 2H, CH<sub>1</sub>), 7.41 (s, 2H, CH<sub>1</sub>), 3.75 (s, 2H, Ar<sub>2</sub>CH<sub>2</sub>), 1.72 (apparent s, 8H, CH<sub>2</sub>), 1.38 (s, 12H, CH<sub>3</sub>), 1.32 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  143.6, 143.5, 141.2, 139.8, 123.2, 117.6, 36.6, 35.8, 35.7, 34.95, 34.93, 32.7, 32.6.

**OctLi.** In a nitrogen-filled glovebox, octamethyloctahydrodibenzofluorene (4.13 g, 10.69 mmol) was dissolved in toluene (50 mL) and *n*-butyllithium (5.13 mL of a 2.5 M solution in hexanes, 13 mmol) was added via syringe. The flask was attached to a swivel frit, and the apparatus was affixed to the vacuum line. After heating to 75 °C for 14 h, the precipitated solid was collected by filtration. Drying *in vacuo* afforded the pink product in 97.0% yield (4.070 g).

**( $\eta^5$ -C<sub>29</sub>H<sub>37</sub>)Mn(CO)<sub>3</sub> (**7**).**<sup>16</sup> In a nitrogen-filled glovebox, OctLi (0.786 g, 2.00 mmol) and BrMn(CO)<sub>5</sub> (0.550 g, 2.00 mmol) were combined in a 100 mL receiving flask, which was then sealed with a 180° needle valve. The flask was evacuated on the vacuum line, and THF (50 mL) was condensed in at 77 K. The reaction was slowly warmed to room temperature and stirred for 24 h, at which time the solvent was removed *in vacuo*. The resulting yellow solid was extracted into pentane (60 mL) and filtered through a pad of Celite inside a swivel frit. Concentration to 20 mL and stirring overnight afforded the title compound as a yellow powder. The precipitated solid was then collected by filtration, washed with pentane, and dried *in vacuo* to yield 0.180 g. A second crop was obtained from subsequent concentration of the filtrate to 6 mL to yield 0.319 g. The yield for two crops is 0.499 g (47.6%). Yellow, needle-like crystals were grown from a saturated solution in pentane that was slowly evaporated into a surrounding solution of toluene at -35 °C. Crystals can also be grown by cooling a saturated solution in pentane to -35 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.09 (s, 2H, Oct-CH<sub>1</sub>), 7.33 (s, 2H, Oct-CH<sub>1</sub>), 5.22 (s, 1H, Oct-C<sup>9</sup>H<sub>1</sub>), 1.52 (apparent s, 8H, Oct-CH<sub>2</sub>), 1.30 (s, 6H, Oct-CH<sub>3</sub>), 1.29 (s, 6H, Oct-CH<sub>3</sub>), 1.23 (s, 6H, Oct-CH<sub>3</sub>), 1.21 (s, 6H, Oct-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR

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(C<sub>6</sub>D<sub>6</sub>):  $\delta$  227.1, 147.5, 144.0, 122.4, 121.6, 106.3, 95.5, 58.2, 35.5, 35.40, 35.36, 35.36, 33.0, 32.94, 32.92, 32.7.

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**Supporting Information Available:** Theoretical and synthetic details, NMR and IR spectra, figures and coordinates of DFT-optimized structures, and X-ray structural data for **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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