Synthesis and Properties of Pyrrole-Substituted Cyclopentadienes

Markus Scherer, Jonathan L. Sessler,* Andreas Gebauer, and Vincent Lynch

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78705

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Recently, Berlin and Lash independently reported syntheses of so-called carbaporphyrins (**1**), an achievement that marks an important milestone in the development of new porphyrin analogues.[1] The synthetic route involved a "3 + 1" condensation between a tripyrrane fragment and a stabilized cyclopentadiene subunit (Scheme 1). The success of this strategy has led us to consider whether it might be possible to generate small, acyclic cyclopentadiene−pyrrole conjugates. Such fragments could serve as potential precursors to other "carba macrocycles" as well as possible platforms for the entry into the hitherto unexplored realm of pyrrole−metallocene chemistry. In this report, we describe the synthesis and properties of the mono- and dipyrrole-functionalized cyclopentadiene systems **4a**,**b** and **6a**−**c**. To the best of our knowledge, these constitute the first acyclic pyrrole−cyclopentadiene conjugates to be described in the literature.[2]

The key step leading to the monopyrrole-functionalized cyclopentadiene involves the reaction between sodium cyclopentadienide anion (NaCp) and an activated, benzyl-like pyrrole (i.e., either an α-acetoxymethylpyrrole[3] **2** or an α-chloromethylpyrrole[4] **3**) as shown in Scheme 2.[5] In all cases an inseparable regioisomeric mixture, consisting of species **4a** and **4b** in an approximately 1:1 ratio, was obtained. In both **4a** and **4b** the Cp moities are substituted in their vinylic positions (indeed, the presence of an allylic functionalized analog has never been observed). Although characterized in the form of a mixture, room temperature ^{1}H NMR spectra recorded in $CDCl_3$ revealed well-resolved signals arising from the methylene groups in the Cp units. On this basis, it is assumed that sigmatropic shifts, involving migrations of elements around the Cp perimeter, are not favored. Likewise, no evidence of a Diels−Alder type dimerization process has ever been observed, even when **4a** and **4b** were subject to prolonged heating in toluene at reflux.

The dipyrrole-substituted cyclopentadienes **6a**−**c** were prepared from the cyclopentadienes **4a**,**b** generated as described above. These latter systems, used in the form of a mixture, were activated by deprotonating with 2 equiv of NaH. This resulted in the formation of a single formal dianionic intermediate, **5**. This nucleophilic species, in turn, was reacted with **2** to give the disubstituted materials **6a**−**c**. Not surprisingly, as shown in Scheme 2, a mixture of isomers was also obtained in this case. Fortunately, in this instance, it proved possible to separate the individual isomers (*vide infra*). On the other hand, **6a**−**c** were obtained in lower yields than **4a**,**b**. This is the result, presumably, of undefined side-reactions arising, perhaps, from NH-deprotonation.[6]

Once the assignments were made (see below) it became clear that in the mixture formed by the reaction of **5** with **2** it was the 5,5-, 1,2-, and 2,3 isomers (**6a**, **6b**, and **6c**, respectively) that were obtained with the first of these being formed in highest yield over the 1,2- and 2,3-species. Interestingly, no other isomers appeared to have been produced. Specifically, no evidence for the formation of a 1,4-substituted species was obtained.[7]

As implied above, it proved easy to separate the individual species present in the mixture **6a**−**c**. This was done *via* a fractional crystallization procedure involving the use of Et_2O at −30 °C. In the case of the *tert*-butyl ester the 2,3-substituted cyclopentadiene **6b** was found to be obtained quantitatively after a first recrystallization. A second recrystallization under the same conditions then allowed the 1,2-isomer **6c** to be isolated from the more soluble 5,5-compound **6a**. Using a similar procedure, we also succeeded in obtaining the ethyl esters **6a**−**c** in pure form. In this case, interestingly, the 1,2-isomer **6c** was found to exhibit a lower solubility than the corresponding 2,3-substituted species **6c**.[8]

Providing structural assignments for isomers **6a**−**c** proved to be straightforward for **6a** but more difficult for isomers **6b** and **6c**. In the case of **6a**, the use of ^{1}H and ^{13}C NMR spectroscopic analyses allowed the structure to be determined unambiguously. This is because this isomer contains no methylene protons within the Cp core. Furthermore, an exact analogy for the substitution pattern of this isomer, and its Cp-derived ^{1}H NMR signals, was found in the known material 5,5-bis(trimethylgermyl)cyclopentadiene.[9]

* Author to whom correspondence should be addressed. Phone: +512-471-5009, e-mail: sessler@mail.utexas.edu.

(1) (a) Berlin, K. *Angew. Chem.* **1996**, *108*, 1955; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1820. (b) Lash, T. D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 839. (c) Lash, T. D., Hayes, M. J. *Ibid.* **1997**, *36*, 840.

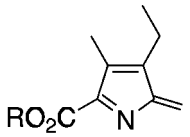
(2) Only a pyrrolylfulvene has been mentioned in the literature: Treibs, A.; Häberle, N. *Liebig's Ann. Chem.* **1970**, *739*, 220.

(3) Johnson, A. W.; Kay, I. T.; Markham, E.; Price, P.; Shaw, K. B. *J. Chem. Soc.* **1959**, 3416.

(4) Ballantine, J. A.; Jackson, A. H.; Kenner, G. W.; McGillivray, G. *Tetrahedron* **1966**, Supplement No. 7, 241.

(5) Such an organometallic-based approach to pyrrole functionalization appears to be without precedent in the context of pyrrole-related chemistry. It does, however, have ample antecedents in the more general literature. See, for example: Rees, W. S.; Dippel, K. A. *Org. Prep. Proceed. Int.* **1992**, *24*, 527; Jutzi, P.; Dahlhaus, J. *Synthesis* **1993**, 684.

(6) In an attempt to augment the yield of **6a**−**c**, an effort was made to N-protect the starting materials **4a**,**b**. However, we were unable to obtain such N-protected species using a variety of reagents. Separately, we found that an N-protected (H replaced by Me or *t*-Boc) form of the (acetoxymethyl)pyrrole **2** failed to react with cyclopentadienide anion. This latter result, in accord with literature suggestions (a) Evans, J. N. S.; Fagerness, P. E.; Mackenzie, N. E.; Scott, A. I. *J. Am. Chem. Soc.* **1984**, *106*, 5738. (b) Falk, H.; Schlederer, T. *Monatsh. Chem.* **1981**, *112*, 501), can be rationalized in terms of an inability to form a presumed-to-be-requisite azafulvene intermediate **7** as shown below.



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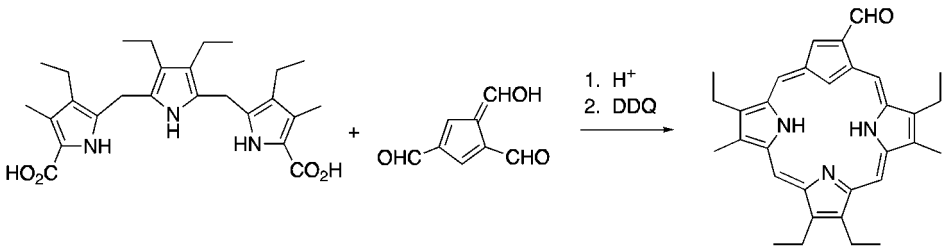
(7) Unfortunately, this fact has precluded the syntheses of carbaporphyrins using these precursors.

(8) Here, it is worth mentioning that a mixture consisting of **6a**−**c** was already isolated as a side-product during the synthesis of the cyclopentadienylpyrromethanes **4a**,**b**. It is likely that the NaCp, which had to be used in excess, causes the cyclopentadiene units present in **4a**,**b** to undergo deprotonation. The resulting anions then react with **2** to form **6a**−**c**.

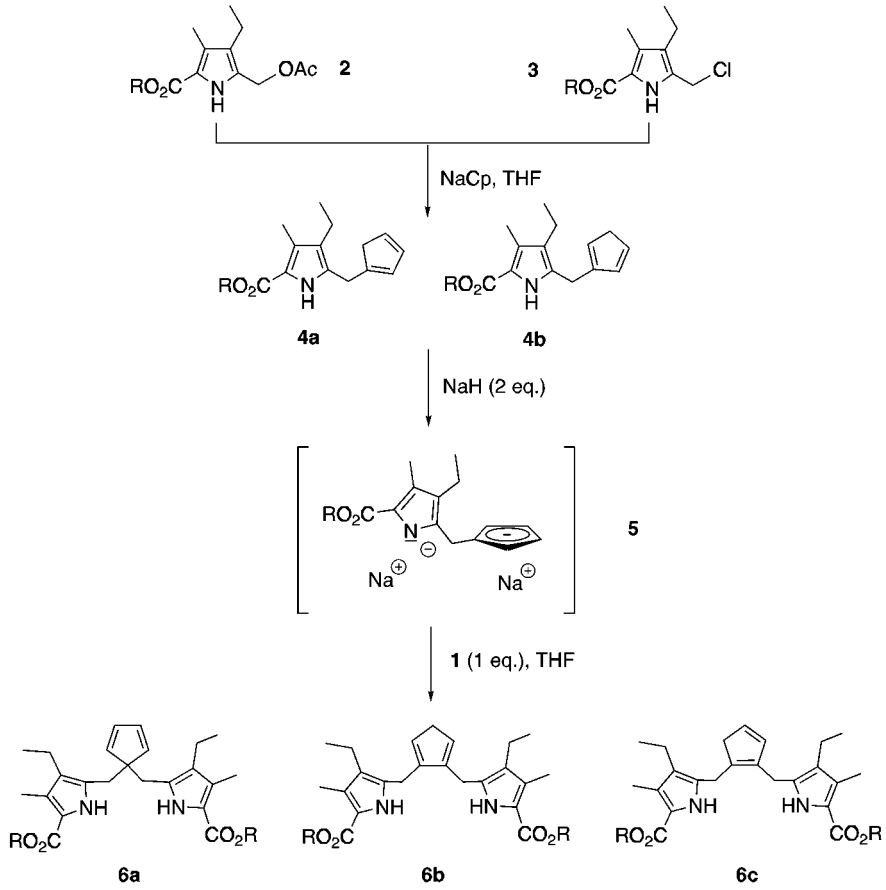
(9) A predilection toward geminal 5,5-substituted cyclopentadienes was also observed in the syntheses of bis(trimethylsilyl-, germyl-, and stannyl)cyclopentadienes, systems obtained *via* metathesis as well: Ustynyuk, Y. A.; Kisin, A. V.; Zenkin, A. A. *J. Organomet. Chem.* **1972**, *37*, 101.

S0022-3263(97)00818-9 CCC: $14.00

Scheme 1



Scheme 2. Synthesis of Mono- (4a,b) and Dipyrrole (6a−c)-Substituted Cyclopentadienes



2: R = Et, *t*-Bu, Bn; **3**: R = Et, Bn; **4a,b**: R = Et, *t*-Bu, Bn; **5**: R = Et, *t*-Bu; **6a-c**: R = Et, *t*-Bu

In the case of **6c** (R = Et) the assignment was made using X-ray diffraction methods. Here suitable single crystals were obtained from $CHCl_3$ under conditions of slow solvent evaporation. As seen in Figure 1, the structure clearly reveals the 1,2-substitution pattern in the Cp moiety.[10] Because of our interest in the location of the double bonds on the cyclopentadiene ring, the hydrogen atoms on this moiety were observed from a ΔF map and refined with isotropic displacement parameters. Furthermore, the relevant bond lengths in the Cp subunit are within the expected range typical for carbon−carbon double bonds (C_1-C_2: 1.350(7) Å; C_3-C_4: 1.358(8) Å) and single bonds (C_2-C_3: 1.470(9), C_4-C_5: 1.445(11), C_1-C_5: 1.501(8)). These values are consistent with those expected for the assigned configuration.

With the configuration of isomers **6a** and **6c** assigned, only the structure of **6b** remained undetermined. Proton and ^{13}C NMR spectral analyses were insufficient to allow an unambiguous assignment. The spectra in question, however, were only consistent with a highly symmetric structure. On the basis of this, isomer **6b** was considered to correspond to either a 2,3- or 1,4-substituted Cp derivative.

In order to characterize systems **6a−c** more fully and to assign more completely the structure of **6b**, investigations into the possible fluxional properties of these isomers were made. In the case of **6a** no indications of sigmatropic rearrangement processes were observed. This was true even under conditions of prolonged heating in toluene at reflux. Systems **6b** and **6c**, on the other

(10) X-ray experimental for $C_{27}H_{36}N_2O_4$: colorless needles by slow evaporation from $CHCl_3$, crystal size = 0.13 × 0.17 × 0.31 mm, triclinic, $P\bar{1}$, $Z = 2$, $a = 10.882(1)$ Å, $b = 11.218(1)$ Å, $c = 12.282(1)$ Å, $\beta = 111.44(1)$, $V = 1257.1(2)$ Å^3, $\rho_{calc} = 1.20$ g/cc, $F(000) = 488$. A total of 5657 reflections were measured, 4830 unique ($R_{int} = 0.062$) on a Siemens P4 diffractometer using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was refined on F^2 to a $R_w = 0.209$, with a conventional $R = 0.0784$, with a goodness of fit = 0.999 for 323 refined parameters. The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The data can be obtained, on request, from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK.

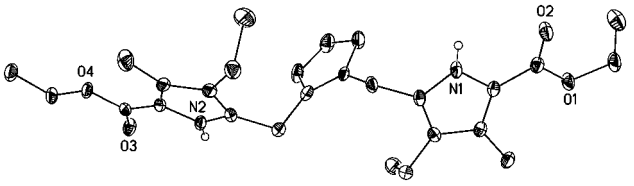


Figure 1. X-ray structure of **6c** (ethyl ester); thermal ellipsoids are scaled to the 30% probability level.

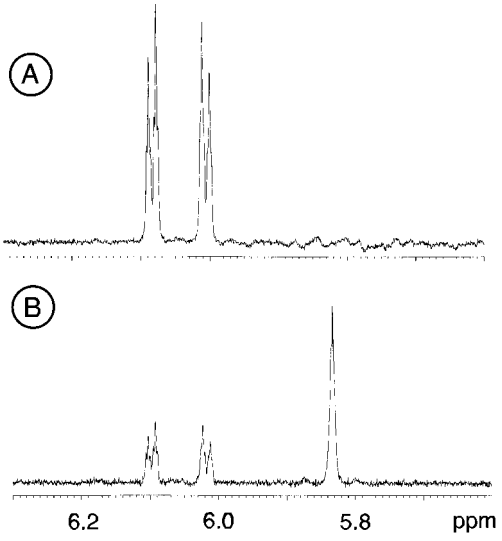


Figure 2. ^{1}H NMR spectroscopic study of the ethyl esters **6c** and **6b** carried out in in toluene-d_8; (500 MHz; room temperature). The region showing the vinylic cyclopentadiene protons is depicted (the multiplet at 6.05 ppm is ascribed to **6c** whereas the broad singlet at 5.8 ppm is assigned to **6b**). A: spectrum of untreated **6c**. B: spectrum obtained after heating a toluene-d_8 solution of **6c** at reflux for 40 min and then cooling back to room temperature.

hand, showed more interesting characteristics. Indeed, at high temperatures they were found to interconvert. This chemistry, which establishes the structure of **6b** as being the 2,3-isomer as shown in Scheme 2, is reflected in Figure 2. Specifically, although no rearrangement processes are observable at room temperature, when pure toluene solutions of **6c** are heated it can be seen that a second signal ascribable to the vinylic Cp protons grows in as a function of increased temperature. Further, at equilibrium, a ca. 1:1 ratio of these two signals is found to exist. The new signal that was found to grow in as solutions of **6c** are heated was found to correspond to the vinylic Cp protons of compound **6b**. This same signal, not surprisingly, was found to decrease in intensity (in favor of the signal for **6c**) when pure solutions of **6b** in toluene are heated. Thus, whether one starts from **6b** or **6c**, an identical final spectrum is obtained.

Since the rearrangement products obtained by heating toluene solutions of either **6b** or **6c** bear substituents exclusively in the Cp vinyl positions, the observed rearrangement process implicates a hydrogen shift rather than a carbon shift. Structure **6b** can thus be assigned unambiguously as being the 2,3-substituted Cp derivative. By contrast, were a carbon migration taking place, heating **6c** would lead to the formation of not only allylic 2,5- but also geminal 5,5-substituted materials (e.g., **6a**). However, such species are never observed. Using similar logic, the possibility of concurrent carbon and hydrogen fluxionality can be ruled out. Such processes would give rise to the coincident formation of more than two isomers, something that is not observed.[11]

In summary, a facile synthetic pathway leading to cyclopentadiene-substituted pyrrolic entities has been described. Such systems could constitute important organometallic precursors and might represent interesting products in their own right. For instance, using the Cp systems **6c** (R = Et) we recently succeeded in synthesizing a 1,1′,2,2′-tetrapyrrolic-substituted ferrocene derivative. This species undergoes a remarkable self-assembly process both in solution and in the solid state.[12a] We have also found out that species **4a**,**b** (R = Bn) may be used as a precursor for the generation of dipyrrolic bridged *ansa*-ferrocenes, materials that exhibit interesting anion-binding properties.[12b]

Experimental Section

General. Proton and ^{13}C NMR spectra, and low and high resolution CI mass spectra, were obtained using instrumentation described previously.[12a] Tetrahydrofuran (THF) was dried by distillation under nitrogen from sodium melt. Methanol was dried by distillation from calcium hydride under a nitrogen atmosphere. *tert*-Butyl hypochlorite[13] was synthesized according to a literature procedure. All other solvents, acids, bases, and reagents were obtained from commercial sources and used as received unless indicated otherwise. Pyrrolic starting compounds of general formula **2**[3] and **3**[4] as well as 2-(*tert*-butoxycarbonyl)-4-ethyl-3-methyl-5-methylpyrrole[14] are well known. Some of the specific derivatives used in this study have not, apparently, been described in the literature. Brief summaries of their syntheses as well as relevant characterization data are, therefore, included here.

2-(*tert*-Butoxycarbonyl)-4-ethyl-3-methyl-5-methylpyrrole. *tert*-Butyl acetoacetate (159 g, 0.99 mol) was dissolved in glacial acetic acid (250 mL) and cooled to 0 °C. To this, a solution of $NaNO_2$ (77.3 g, 1.12 mol) dissolved in water (100 mL) was added dropwise, so as to maintain the temperature below 40 °C. The resulting mixture was stirred for 1 h and subsequently added *via* an addition funnel to a mechanically stirred solution of 3-ethyl-2,4-pentadione (143.3 g, 1.12 mol) in acetic acid (250 mL). Zinc (granules, 230 g, 3.52 mol) was also added concurrently over the course of 2 h. The mixture was stirred overnight and then poured into 1 L of water. The precipitate that formed was filtered off, washed with water, and redissolved in 1 L of dichloromethane. The resulting aqueous phase was separated off and discarded. The organic phase was collected, dried over $NaSO_4$, and then taken to dryness *in vacuo* to afford the crude product. Recrystallization from EtOH (500 mL) then gave 117.50 g (53%) of the title compound. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (t, 3H), 1.52 (s, 9H), 2.16 (s, 3H), 2.22 (s, 3H), 2.33 (q, 2H), 8.52 (bs, 1H); LRMS (CI+) *m/e*: 223 (74), 168 (100); HRMS (CI+) *m/e* calcd for $C_{13}H_{21}NO_2$: 223.1572, found: 223.1563.

5-(Acetoxymethyl)-2-(*tert*-butoxycarbonyl)-4-ethyl-3-methylpyrrole (2). 2-(*tert*-Butoxycarbonyl)-4-ethyl-3-methyl-5-methylpyrrole (47.94 g, 215 mmol) was dissolved in 1 L of glacial acetic acid under an argon blanket. Lead tetraacetate (100 g, 225 mmol) was then added all at once while the solution was stirred vigorously. The reaction mixture was stirred at room temperature for an additional 2 h and then poured into 2 L of ice−water. The precipitate that formed was filtered off and washed thoroughly with water before it was taken up in 700 mL of dichloromethane, washed with water (2 × 300 mL),

(11) For a review discussing *inter alia* the rearrangement behavior of two-fold substituted Cp systems, see: Jutzi, P. *Chem. Rev.* **1986**, *86*, 983−996.

(12) (a) Scherer, M.; Sessler, J. L.; Moini, M.; Gebauer, A.; Lynch, V. *Chem. Eur. J.*, in press. (b) Scherer, M.; Sessler, J. L.; Gebauer , A.; Lynch, V. *Chem. Commun.*, submitted.

(13) Teeter, H. M.; Bell, E. W. *Org. Synth.* **1952**, *32*, 20−22.

(14) Bullock, E.; Johnson, A. W.; Markham, E.; Shaw, K. B. *J. Chem. Soc.* **1958**, 1438.

$NaCl_{sat.}$ (1 × 300 mL) and finally dried over $NaSO_4$. The solvent was removed using a rotary evaporator to give a crude product that, after recrystallization from EtOH (200 mL) produced **2** in 91% yield (54.98 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, 3H), 1.55 (s, 9H), 2.04 (s, 3H), 2.23 (s, 3H), 2.46 (q, 2H), 4.99 (s, 2H), 8.85 (bs, 1H); LRMS (CI+) *m*/**e**: 281 (82), 222 (100); HRMS (CI+) *m/e* calcd for $C_{15}H_{23}NO_4$: 281.1627, found: 281.1628.

2-(Chloromethyl)-5-(ethoxycarbonyl)-3-ethyl-4-methylpyrrole (3). Over the course of 10 min, a solution of *tert*-butyl hypochlorite (5.54 g, 51.3 mmol) in CCl_4 (40 mL) was added to a vigorously stirred solution of 2-(ethoxycarbonyl)-4-ethyl-3-methyl-5-methylpyrrole[13] (10.00 g, 51.3 mmol) in dry CCl_4 (500 mL) held at 3 °C. After 1 h, the reaction mixture was concentrated to 100 mL with the aid of a rotary evaporator. In order to precipitate the product, the solution was then stored for 1.5 h at a temperature of −10 °C. Subsequently, the crystallized compound was filtered off and washed with hexanes to afford **3** (8.34 g, 71%). The product, which was used without further purification, should be stored under nitrogen well protected from light. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (t, 3H), 1.33 (t, 3H), 2.28 (s, 3H), 2.41 (q, 2H), 4.28 (q, 2H), 4.65 (s, 2H), 8.98 (bs, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.1, 14.3, 15.3, 17.0, 36.5, 59.9, 125.7, 126.1, 127.4, 127.9, 161.4. LRMS (CI +) *m/e*: 230 (68), 196 (100); HRMS (CI+) *m/e* calcd for $C_{11}H_{17}ClNO_2$: 230.0948, found: 230.0950.

Syntheses of Monopyrrole-Substituted Cyclopentadienes 4a and 4b (Generalized Procedure). By using Schlenk-techniques, 59.3 mmol, respectively, of the ethyl-, *tert*-butyl, and benzyl ester forms of **2** was dissolved in dry THF (300 mL) under an argon blanket. This solution was then cooled to 0 °C. Subsequently, a 2.0 M solution of NaCp in THF (0.119 mmol, Aldrich) was added dropwise over the course of 30 min. The resulting mixture was stirred for 4 h while being allowed to warm to room temperature. At this juncture, the reaction was quenched by the addition of dry MeOH (150 mL) and, after 30 more min, by the addition of degassed water (200 mL). After stirring for an additional 45 min, Et_2O (350 mL) was added, and the phases were separated. The aqueous layer was extracted with Et_2O (2 × 100 mL), and the combined organic phases were washed with water (3 × 150 mL) and $NaCl_{sat.}$ (1 × 150 mL). After drying over $MgSO_4$, the solvent was removed from the organic phase and the resulting residue dried *in vacuo* for 4 h. The resulting crude product was taken up in a small amount of CH_2Cl_2 and purified using flash column chromatography (80 × 5 cm; silica gel; eluant: initially 30% hexanes in CH_2Cl_2 but then decreasing hexanes). The two monopyrrole-substituted cyclopentadiene isomers **4a** and **4b** were eluted together as the first main fraction.

5-(Cyclopentadien-1-ylmethyl)-2-(ethoxycarbonyl)-4-ethyl-3-methylpyrrole (4a, R = Et) and 5-(Cyclopentadien-2-ylmethyl)-2-(ethoxycarbonyl)-4-ethyl-3-methylpyrrole (4b, R = Et). Using the above procedure, these compounds were obtained in a combined yield of 75%. By using this same method starting with **3** instead of **2**, a 58% yield was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02, 1.03 (2 × t, 3H), 1.31 (t, 3H), 2.27 (s, 3H), 2.38, 2.39 (2 × q, 2H), 2.83 and 2.84 (2 × s, 2H), 3.62, 3.65 (2 × s), 4.25, 4.26 (q, 2H), 6.04−6.44 (m, 3H), 8.50 (bs, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.5, 14.6, 15.5, 17.2, 26.7, 27.5, 41.5, 43.3, 59.7, 117.6, 123.8, 123.9, 126.5, 128.4, 128.8, 130.8, 131.4, 131.9, 132.3, 134.0, 134.8, 143.1, 145.4, 161.9. LRMS (CI+) *m/e*: 260 (98), 196 (100); HRMS (CI+) *m/e* calcd for $C_{16}H_{22}NO_2$: 260.1650, found: 260.1646; CHN analysis calcd (found): C 74.10 (74.19), H 8.16 (8.16), N 5.40 (5.31).

5-(Cyclopentadien-1-ylmethyl)-2-(*tert*-butoxycarbonyl)-4-ethyl-3-methylpyrrole (4a, R = *t*-Bu) and 5-(Cyclopentadien-2-ylmethyl)-2-(*tert*-butoxycarbonyl)-4-ethyl-3-methylpyrrole (4b, R = *t*-Bu). Using the above procedure, these materials were obtained in a combined yield of 57%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02, 1.03 (2 × t, 3H), 1.52, 1.53 (2 × s, 9H), 2.24 (s, 3H), 2.39, 2.41 (2 × q, 2H), 2.84 and 2.97 (2 × bs, 2H), 3.61, 3.65 (2 × s), 6.06−6.40 (m, 3H), 8.36 (bs, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.5, 15.6, 17.2, 26.6, 27.5, 28.5, 41.5, 43.2, 80.1, 118.3, 124.0, 124.1, 125.9, 128.4, 128.8, 130.1, 130.9, 131.8, 132.3, 134.0, 134.7, 143.1, 145.3, 161.8. LRMS (CI+) *m/e*: 288 (100), 232 (99); HRMS (CI+) *m/e* calcd for $C_{18}H_{25}NO_2$: 287.1885, found: 287.1881; CHN analysis calcd (found): C 75.22 (75.12), H 8.77 (8.64), N 4.87 (4.71).

5-(Cyclopentadien-1-ylmethyl)-2-(benzyloxycarbonyl)-4-ethyl-3-methylpyrrole (4a, R = Bn) and 5-(Cyclopentadien-2-ylmethyl)-2-(benzyloxycarbonyl)-4-ethyl-3-methylpyrrole (4b, R = Bn). Using the generalized procedure noted above, these isomers were isolated in a combined yield of 71%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02, 1.03 (2 × t, 3H), 2.29 (s, 3H), 2.00, 2.17 (2 × q, 2H), 2.83 and 2.97 (2 × s, 2H), 3.62, 3.65 (2 × s), 5.26 (s, 2H), 6.05−6.44 (m, 3H), 7.29−7.41 (m, 5H), 8.50 (bs, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.6, 15.4, 15.5, 17.1, 17.2, 26.7, 27.5, 41.5, 43.2, 65.3, 65.4, 116.9, 123.9, 124.1, 127.2, 127.3, 127.9, 128.0, 128.1, 128.4, 128.5, 128.9, 131.3, 131.8, 132.2, 133.9, 134.8, 136.7, 143.0, 145.2, 161.4. LRMS (CI+) *m/e*: 321 (100), 256 (65); HRMS (CI+) *m/e* calcd for $C_{21}H_{23}NO_2$: 321.1729, found: 321.1724; CHN analysis calcd (found): C 78.47 (78.39), H 7.21 (7.22), N 4.36 (4.38).

Synthesis of Dipyrrole-Substituted Cyclopentadienes 6a−c (R = Et). Using Schlenk-techniques, fresh NaH (0.96 g, 40 mmol) was suspended in 120 mL of dry THF. While maintaining the temperature at 0 °C, a solution consisting of an isomeric mixture of **4a**,**b** (R = Et; 5.17 g, 20 mmol) in THF (180 mL) was added dropwise over the course of 45 min. The resulting mixture was then stirred for additional 2 h. At this juncture, while still maintaining a temperature of 0 °C, a solution of **2** (R = Et) (5.08, 20 mmol) in THF (50 mL) was added over the course of 30 min. The resulting dark-colored mixture was then stirred for 24 h under an argon atmosphere before the reaction was quenched by the addition of water (150 mL). The emulsion that resulted was stirred for 30 min before dichloromethane (200 mL) was added. The phases were separated with the aqueous layer being further extracted with dichloromethane (2 × 100 mL). The organic phases were combined and washed with water (2 × 100 mL) and $NaCl_{sat.}$ (1 × 100 mL) before being dried over $MgSO_4$. The solvent was then removed using a rotary evaporator. The resulting crude product was dried in high vacuum for 3 h, taken up in dichloromethane and then purified by flash column chromatography (50 × 5 cm; silica gel; eluant: CH_2Cl_2). Unreacted **4a**,**b** (1.87 g; 7.2 mmol) was isolated as the first main fraction. The last main fraction contained the desired products **6a−c** as an isomeric mixture. These isomers were separated by treating the dried residue, obtained after removing the solvent from the relevant chromatography fractions with 30 mL of diethyl ether. This caused the 1,2-substituted cyclopentadiene **6c** to begin precipitating even at room temperature. Storing the ether solution at −30 °C for 48 h then resulted in a more quantitative precipitation of this species (**6c**). Filtration afforded **6c** (0.524 g, 9.0%). The product obtained in this way was usually pure. However, as needed, this crystallization procedure could be repeated until pure **6c** was in fact obtained. Carrying out a second low temperature recrystallization from diethyl ether but employing the filtrate obtained after solid **6c** had been collected off, allowed the precipitation of material that was enriched in **6b** over **6a**. Fractional recrystallization of this mixture yielded 0.158 g (0.3 mmol, 2.7%) of pure **6b** (as the precipitate) and 0.926 g (1.1 mmol, 16.0%) of pure **6a** (from the filtrate).

5,5-Bis(2-(ethoxycarbonyl)-4-ethyl-3-methylpyrrol-5-ylmethyl)cyclopentadiene (6a): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, 6H), 1.31 (t, 6H), 2.22 (s, 6H), 2.34 (q, 4H), 2.89 (s, 4H), 4.22 (q, 4H), 6.35 (m, 4H), 8.41 (bs, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.5, 14.6, 15.4, 17.3, 31.1, 59.6, 60.4, 117.2, 124.5, 125.9, 129.2, 132.2, 142.8, 161.6. LRMS (CI+) *m/e*: 453 (100); HRMS (CI+) *m/e* calcd for $C_{27}H_{37}N_2O_4$: 453.2753, found: 453.2749, CHN analysis calcd (found): C 71.65 (71.53), H 8.02 (7.98), N 6.19 (6.21).

2,3-Bis(2-(ethoxycarbonyl)-4-ethyl-3-methylpyrrol-5-ylmethyl)cyclopentadiene (6b): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, 6H), 1.31 (t, 6H), 2.25 (s, 6H), 2.35 (q, 4H), 2.71 (s, 2H), 3.56 (s, 4H), 4.25 (q, 4H), 6.07 (bs, 2H) 8.41 (bs, 2H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 10.3, 14.5, 16.0,

17.8, 28.1, 45.1, 60.0, 117.8, 124.2, 127.1, 128.4, 130.8, 144.3, 161.9. LRMS (CI+) *m/e*: 453 (65), 407 (100); HRMS (CI+) *m/e* calcd for $C_{27}H_{36}N_2O_4$: 452.2675, found: 453.2668, CHN analysis calcd (found): C 71.65 (71.03), H 8.02 (8.06), N 6.19 (6.15).

1,2-Bis(2-(ethoxycarbonyl)-4-ethyl-3-methylpyrrol-5-ylmethyl)cyclopentadiene (6c): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (t, 6H), 1.31 (t, 6H), 2.26 (s, 6H), 2.38 (q, 4H), 2.90 (s, 2H), 3.61 (d, 4H), 4.25 (q, 4H), 6.24 (m, 2H), 8.29 (bs, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.4, 14.5, 15.3, 15.4, 17.2, 24.2, 24.9, 44.3, 59.7, 117.3, 117.4, 123.6, 123.8, 126.8, 130.5, 131.2, 132.0, 134.6, 137.0, 138.1, 161.8. LRMS (CI +) *m/e*: 452 (37), 407 (100); HRMS (CI+) *m/e* calcd for $C_{27}H_{36}N_2O_4$: 452.2675, found: 452.2666, CHN analysis calcd (found): C 71.65 (71.46), H 8.02 (8.01), N 6.19 (6.14).

Synthesis of Dipyrrole-Substituted Cyclopentadienes 6a-c (R = *t*-Bu). These materials were prepared using a procedure essentially identical to the one noted above. In this instance, the first fraction off the flash chromatography column (60 × 5 cm; silica gel; eluant: CH_2Cl_2) proved again to be unreacted **4a**,**b** (1.95 g; 6.8 mmol). Likewise, the last main fraction eluted from the column was found to contain products **6a**−**c** as an isomeric mixture. In this case, the separation of the isomers involved extracting the dried residue from the chromatography column with 40 mL of diethyl ether. This resulted in the formation of a slurry due to the insoluble nature of the 2,3-substituted isomer **6b**. A more quantitative precipitation of this isomer was achieved by storing the ether slurry at −30 °C overnight. This afforded 1.70 g (3.3 mmol; 15.7%) of **6b**. The filtrate, obtained after filtering off **6b**, was reduced to a volume of 30 mL and recrystallized from diethyl ether at −30 °C as above. This resulted in the precipitation of the 1,2-substituted Cp compound **6c** (0.96 g, 1.9 mmol, 8.9%). After the precipitation of **6c** was complete, 2.41 g (4.7 mmol, 21.9%) of **6a** could be isolated from the filtrate.

5,5-Bis(2-(*tert*-butoxycarbonyl)-4-ethyl-3-methylpyrrol-5-ylmethyl)cyclopentadiene (6a): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, 6H), 1.52 (s, 18H), 2.19 (s, 6H), 2.34 (q, 4H), 2.88 (s, 4H), 6.35 (m, 4H), 8.39 (bs, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.5, 15.4, 17.3, 28.6, 31.2, 60.5, 80.0, 118.4, 124.4, 124.9, 128.5, 132.1, 143.0, 161.2. LRMS (CI+) *m/e*: 509 (100); HRMS (CI+) *m/e* calcd for $C_{31}H_{44}N_2O_4$: 508.3301, found: 508.3294, CHN analysis calcd (found): C 73.19 (73.11), H 8.72 (8.73), N 5.51 (5.42).

2,3-Bis(2-(*tert*-butoxycarbonyl)-4-ethyl-3-methylpyrrol-5-ylmethyl)cyclopentadiene (6b): ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.96 (t, 6H), 1.52 (s, 18H), 2.22 (s, 6H), 2.33 (q, 4H), 2.95 (s, 2H), 3.48 (s, 4H), 6.07 (bs, 2H) 8.37 (bs, 2H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 10.6, 15.6, 17.5, 25.6, 28.7, 39.9, 80.3, 119.1, 124.1, 126.1, 129.8, 130.9, 143.9, 161.5; LRMS (CI+) *m/e*: 508 (24), 299 (100); HRMS (CI+) *m/e* calcd for $C_{31}H_{44}N_2O_4$: 508.3301, found: 508.3290, CHN analysis calcd (found): C 73.19 (72.64), H 8.72 (8.75), N 5.51 (5.47).

1,2-Bis(2-(*tert*-butoxycarbonyl)-4-ethyl-3-methylpyrrol-5-ylmethyl)cyclopentadiene (6c): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 (t, 6H), 1.53 (s, 18H), 2.20 (s, 6H), 2.35 (q, 4H), 2.91 (s, 2H), 3.63 (d, 4H), 6.24 (m, 2H), 8.30 (bs, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.3, 15.4, 15.5, 17.2, 24.1, 24.8, 28.6, 44.1, 80.1, 117.1, 117.5, 123.5, 124.0, 126.3, 130.4, 131.0, 131.8, 134.4, 137.0, 138.0, 161.6. LRMS (CI +) *m/e*: 509 (75), 435 (100); HRMS (CI+) *m/e* calcd for $C_{31}H_{44}N_2O_4$: 508.3301, found: 508.3302, CHN analysis calcd (found): C 73.19 (73.20), H 8.72 (8.79), N 5.51 (5.51).

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Supporting Information Available: X-ray experimental for **6c** and tables of crystallographic data, collection procedures, parameters, complete atomic coordinates, bond distances and angles, torsion angles, and least square planes (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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