H, Me$_3$Si); ^{13}C NMR (CDCl$_3$) δ 183.29 (s, C=O), 44.50 (t, CN), 37.83 (t), 30.37 (t), 29.82 (t), 23.48 (t), 0.06 (q); MS m/e EI 185 (M$^+$).

1-Aza-2-methyl-1-cycloheptene (1e): bp 65 °C (35 mmHg); IR (neat) 2920, 2840, 1645, 1425, 1360 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.55 (t, J = 5 Hz, 2 H, CH$_2$N), 2.37 (t, J = 5 Hz, CH$_2$C=), 2.04 (s, 3 H, Me), 1.78 (quintet, J = 7 Hz, 2 H, CH$_2$), 1.52 (m, 2 H), 1.45 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 176.19 (s, CN), 51.59 (t, CH$_2$N), 34.0 (t), 31.37 (t), 29.22 (t), 26.24 (q), 22.95 (t); MS m/e EI 111 (M$^+$).

2-(Trimethylsilyl)-2-azacyclooctanone (2f): bp 87 °C (2.5 mmHg); IR (neat) 2910, 2845, 1645, 1615, 1440, 1385, 1240, 1050, 840 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.24 (m, 2 H, CH$_2$N), 2.38 (m, 2 H, CH$_2$CO), 1.70 (m, 2 H), 1.47 (m, 6 H), 0.19 (s, 9 H, Me$_3$Si); ^{13}C NMR (CDCl$_3$) 182.33 (s, C=O), 43.57 (t, CN), 34.06 (t), 32.51 (t), 28.38 (t), 26.3 (t), 23.95 (t), 0.03 (q, Me$_3$Si); MS m/e EI 199 (M$^+$).

1-Aza-2-methyl-1-cyclooctene (1f): bp 45 °C (15 mmHg); IR (neat) 2900, 1630 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.44 (m, 2 H, CH$_2$N), 2.25 (m, 2 H, CH$_2$C=), 1.93 (s, 3 H, Me), 1.62 (m, 2 H), 1.49 (m, 2 H), 1.37 (m, 2 H), 1.28 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 172.15 (s, C=N), 48.80 (t, CN), 29.67 (2 C, t), 27.28 (t), 27.04 (q), 25.84 (t), 24.48 (t); MS m/e EI 125 (M$^+$).

2-(Trimethylsilyl)-2-azacyclononanone (2g): bp 70 °C (0.5 mmHg); IR (neat) 2950, 2880, 1630, 1430 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.28 (m, 2 H, CH$_2$N), 2.39 (m, 2 H, CH$_2$CO), 1.73 (m, 2 H), 1.50 (m, 4 H), 1.44 (m, 4 H), 0.19 (s, 9 H, Me$_3$Si); ^{13}C NMR (CDCl$_3$) δ 182.54 (s, CO), 45.39 (t, CN), 34.84 (t), 30.42 (t), 28.38 (t), 25.43 (t), 24.6 (t), 22.02 (t), 0.04 (q); MS m/e EI 213 (M$^+$).

1-Aza-2-methyl-1-cyclononene (1g): bp 70 °C (0.5 mmHg); IR (neat) 2910, 2840, 1640, 1450, 1350 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.67 (t, J = 7 Hz, 2 H, CH$_2$N), 2.42 (t, J = 7 Hz, 2 H, CH$_2$C=), 2.13 (s, 3 H, Me), 1.79 (m, 2 H), 1.58 (m, 2 H), 1.43 (m, 2 H), 1.31 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 174.59 (s, C=N), 43.64 (t, CN), 42.04 (t), 33.58 (t), 29.74 (t), 29.13 (t), 29.02 (t), 26.59 (q), 23.67 (t); MS m/e EI 139 (M$^+$).

3-Hydroxy-2-pyrrolidinone (4). To a cold (−20 °C) solution of 3.5 mL (0.025 mol) of diisopropylamine in 50 mL of THF under argon was added 15.6 mL (0.025 mol) of n-BuLi (1.6 M solution in THF). After being stirred at −20 °C for 30 min, the solution was cooled to −40 °C, and a solution of 3.228 g (0.021 mol) of **2a** in 10 mL of THF was added via cannula. The resulting green solution was warmed to −20 °C and stirred at this temperature for 1.5 h, after which 4.75 g (0.027 mol) of bis(trimethylsilyl)peroxide was added, and the yellow solution was warmed to 25 °C. After 12 h, the solution was diluted with 1.62 g (0.027 mol) of acetic acid and 2 mL of brine, and the solvent was removed on a rotary evaporator. The residue was diluted with 50 mL of CH$_2$Cl$_2$, filtered through Celite, and concentrated to give 2.973 g of an oil, to which was added 3.6 g (0.06 mol) of acetic acid, 5 mL of MeOH, and 30 mL of CHCl$_3$. After being stirred at 25 °C for 5 h, the solution was concentrated to dryness and flash chromatographed on silica gel column using a mixture of ethyl acetate and methanol as eluant to give 0.912 g (43% yield) of 3-hydroxy-2-pyrrolidinone: mp 95–96 °C (lit.[12] 102–103 °C); IR (Nujol) 3300 (broad s), 2920, 2850, 1650 (s), 1450, 1280, 1110 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.87 (broad s, 1 H, NH), 4.34 (t, J = 8 Hz, 1 H, CHO), 4.25 (broad s, 1 H, OH), 3.44 (m, 1 H, CHN), 3.32 (m, 1 H, CHN), 2.52 (m, 1 H), 2.09 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 179.11 (s, C=O), 69.05 (d, CO), 38.78 (t, CN), 29.91 (t); MS, m/e EI 101 (M$^+$).

3-[(*tert*-Butyldimethylsilyl)oxy]-2-pyrrolidinone (3h). A mixture of 1.34 g (0.0134 mol) of 3-hydroxy-2-pyrrolidinone (4), 4.44 g (0.0295 mol) of *tert*-butyldimethylsilyl chloride, 5.41 g (0.0536 mol) of triethylamine, and 0.164 g (0.0013 mol) of 4-(dimethylamino)pyridine in 30 mL of CH$_2$Cl$_2$ under argon was stirred at 25 °C for 3 h. The mixture was diluted with 250 mL of ether, washed with 50 mL of H$_2$O, 30 mL of 1 N HCl, 30 mL of aqueous NaHCO$_3$ solution, and 30 mL of brine, dried (MgSO$_4$), and concentrated to give 4.45 g of N-(*tert*-butyldimethylsilyl)-3-[(*tert*-butyldimethylsilyl)oxy]-2-pyrrolidinone. This product was dissolved in 80 mL of THF, the solution was cooled to 0 °C, and 6.7 mL (6.7 mmol) of n-Bu$_4$NF (1.0 M in THF) was added. After being stirred for 2 h at 0 °C, the solution was diluted with 300 mL of ether, washed with 50 mL of H$_2$O and 30 mL of brine, dried (MgSO$_4$), concentrated, and flash chromatographed on a silica gel column with a mixture of ether and methanol as eluant to give 2.62 g (91% yield) of **3h**: mp 77–78 °C; IR (neat) 3300, 2930, 2860, 1680 (s, C=O), 1275, 1070 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.33 (broad s, 1 H, NH), 4.26 (t, J = 8 Hz, 1 H, CHO), 3.38 (td, J = 9 Hz, 3 Hz, 1 H, CHN), 3.25 (td, J = 9, 8 Hz, 1 H, CHN), 2.37 (m, 1 H), 2.04 (m, 1 H), 0.92 (s, 9 H, t-Bu), 0.16 (s, 3 H, MeSi), 0.15 (s, 3 H, MeSi); ^{13}C NMR (CDCl$_3$) δ 177.08 (s, C=O), 70.68 (d, CHO), 38.46 (t, CN), 31.47 (t), 25.74 (q, 3 C, t-Bu), 18.24 (s, CSi), −4.58 (q, MeSi), −5.14 (q, MeSi); MS m/e EI 215 (M$^+$).

3-[(*tert*-Butyldimethylsilyl)oxy]-1-(trimethylsilyl)-2-pyrrolidinone (2h): an oil; IR (neat) 2950, 2845, 1680 (s, C=O), 1450, 1370, 1360, 1250, 1128, 1075 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.24 (t, J = 8 Hz, 1 H, CHO), 3.30 (td, J = 8, 3 Hz, 1 H, CHN), 3.17 (td, J = 8, 6 Hz, 1 H, CHN), 2.29 (m, 1 H), 1.94 (dq, J = 12, 8 Hz, 1 H), 0.91 (s, 9 H, t-Bu), 0.27 (s, 9 H, Me$_3$Si), 0.15 (s, 3 H, MeSi), 0.13 (s, 3 H, MeSi); ^{13}C NMR (CDCl$_3$) δ 181.0 (s, C=O), 72.09 (d, CO), 41.58 (d, CN), 31.87 (t, CH$_2$), 25.78 (q, 3 C, t-Bu), 18.29 (s, t-Bu), −1.38 (q, 3 C, Me$_3$Si), −4.55 (q, MeSi), −5.16 (q, MeSi); MS m/e CI 288 (M + 1).

4-[(*tert*-Butyldimethylsilyl)oxy]-3,4-dihydro-5-methyl-2*H*-pyrrole (1h): an oil; IR (neat) 2940, 2840, 1640, 1455, 1350, 1248, 1110 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.60 (t, J = 7.5 Hz, 1 H, CHO), 3.88 (m, 1 H, CH$_2$N), 3.57 (m, 1 H, CH$_2$N), 2.21 (m, 1 H), 2.02 (s, 3 H, Me), 1.7 (m, 1 H), 0.91 (s, 9 H, t-Bu), 0.15 (s, 3 H, MeSi), 0.12 (s, 3 H, MeSi); ^{13}C NMR (CDCl$_3$) δ 176.53 (s, C=N), 79.72 (d, CO), 57.38 (t, CN), 33.55 (t), 25.71 (q, 3 C, t-Bu), 18.03 (s, t-Bu), 16.59 (q, CH$_3$), −4.64 (q, MeSi), −5.04 (q, MeSi); MS m/e EI 213 (M$^+$).

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Registry No. **1a**, 872-32-2; **1b**, 64319-86-4; **1c**, 1192-29-6; **1d**, 1462-92-6; **1e**, 3338-03-2; **1f**, 126645-91-8; **1g**, 126645-92-9; **1h**, 126645-93-0; **2a**, 14468-90-7; **2d**, 3553-93-3; **2e**, 3553-94-4; **2f**, 57012-52-9; **2g**, 14468-91-8; **2h**, 126645-94-1; **3a**, 616-45-5; **3d**, 675-20-7; **3e**, 105-60-2; **3f**, 673-66-5; **3g**, 935-30-8; **3h**, 126645-95-2; 4, 15166-68-4; H$_2$N(CH$_2$)$_3$CH=CHCH$_3$, 60168-05-0; N-(*tert*-butyldimethylsilyl)-3-[(*tert*-butyldimethylsilyl)oxy]-2-pyrrolidinone, 126645-96-3; N-vinylvalerolactam, 4370-23-4.

Supplementary Material Available: Elemental analyses for compounds **1a–e**, **2f–h**, and **1h** and ^{13}C NMR spectra of compounds **1f** and **1g** (3 pages). Ordering information is given on any current masthead page.

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(12) Ringdahl, B.; Cymerman Craig, J. *Acta Chem. Scand.* **1980**, *B34*, 731.

Chiral Bismetallocenes with C_2 Symmetry

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The development of methods for positioning metal centers within defined chiral environments continues to be an objective of considerable interest, in large part because of the potential applications such metal centers have to asymmetric synthesis.[1] A recurring theme, attractive

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(1) Among recent leading references and reviews, see: Ojima, I.; Clos, N.; Bastos, C. *Tetrahedron* **1989**, *22*, 6901–6939. Brunner, H. *Top. Stereochem.* **1988**, *18*, 129–247. Bosnich, B. *Asymmetric Catalysis* (NATO ASI Series E 103); Martinus Nijhoff: Dordrecht, 1986. *Asymmetric Synthesis, Vol. 5, Chiral Catalysis*, Morrison, J. D., Ed.; Academic: Orlando, FL, 1985.

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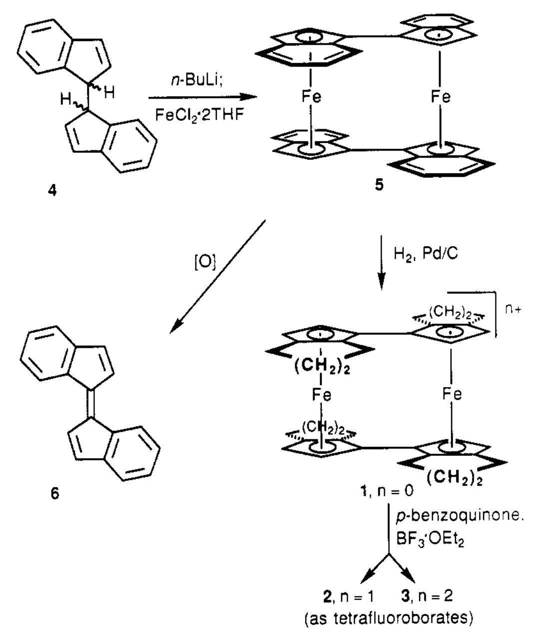
Scheme I



because of the simplifications in design it permits, is the incorporation of chirality in the form of a C_2-symmetric element.[2] To date, however, virtually all such chiral, C_2-symmetric systems have involved only a single metal center.

Bimetallic, C_2-symmetric assemblies, wherein the two metals are not only decidedly asymmetric but also proximate, offer additional possibilities, particularly if they are conformationally restricted. For example, (i) the chirality around one metal could reinforce the chirality around the other (e.g., as in chiral bidentate Lewis acids[3]) or (ii) the two metals could each serve as coordination sites for the simultaneous binding of two reactant molecules preliminary to an asymmetrically induced reaction between them.[4]

As the initial step toward the examination of such systems, we now report the first synthesis and resolution of C_2-symmetric[5] bismetallocenes, the bisferrocene derivative **1** and the corresponding mono- and dications **2** and **3**.[7] The synthesis is concise and it, and a chromatographic method of resolution, should be readily applicable to the preparation of other chiral bismetallocenes.

The preparation of (±)-**1**–**3** is outlined in Scheme I, with the first step being modeled on the known synthesis of bis(fulvalene)diiron.[8] Thus, reaction of the dilithium salt of 1,1′-bi-1*H*-indene **4**[9] with FeCl$_2$·2THF,[8] in THF, gave in 38% yield (±)-**5** as the major product. Subsequent resolution of derivatives of **5** (vide infra) established that **5** is the *d,l* and not the meso isomer. The ^{1}H NMR spectrum of crude **5** suggested that production of **5** may have been accompanied by formation of minor amounts of the meso isomer, but the latter was not isolated in pure form. Purification of (±)-**5** by Soxhlet extraction into hexane and then precipitation afforded analytically pure material.

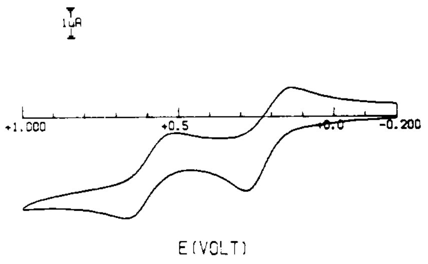


Figure 1. Cyclic voltammogram of **5**. See text and Experimental Section for details.

Compound **5** is extremely air-sensitive in solution; this sensitivity was also manifested in the many unsuccessful attempts at controlled chemical oxidations of the metal centers of **5**, using oxidants including benzoquinone/BF$_3$·OEt$_2$,[10,11] TCNQ,[8] benzoquinone/picric acid,[8] H_2O_2/AcOH,[12] H_2SO_4,[13] and I_2 in benzene or in CH_2Cl_2.[14] In all cases decomposition took place to yield 1,1′-biindenylidene (**6**) and iron oxides. In contrast to the attempts at chemical oxidation, analytical electrolysis of (±)-**5** (cyclic voltammetry) in dichloromethane solution containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte, under argon, clearly showed (see Figure 1) two reversible, one-electron oxidation steps, at $E_{1/2}$ = +0.21 and +0.60 V. As in the attempts at chemical oxidations, however, bulk electrolysis of (±)-**5**, under an inert atmosphere in a 0.1 M solution of TBAP in dichloromethane, also resulted in decomposition on passing either 1 or 2 equiv of charge through the solution.

Removal[15] of the unsaturation within the six-membered rings by hydrogenation of (±)-**5** to (±)-**1** provided the solution to the problem of instability, presumably because the driving force toward regaining aromaticity in the benzenoid rings of **5** is no longer present in **1**. Hydrogenation of (±)-**5** with 10% Pd/C as catalyst in THF went smoothly to give (±)-**1**, the air-stable, hexadecahydro derivative of (±)-**5**. Oxidation of (±)-**1** could then be effected[10,11] straightforwardly to generate, as desired, either the monocation (±)-**2** or the dication (±)-**3** as their tetrafluoroborates.

Two methods for the resolution of **1**–**3** were developed.[16]

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(2) For a recent review of C_2-symmetric compounds, see: Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581–1590.

(3) For leading references to examples of achiral bidentate Lewis acids, see, inter alia: Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *Organometallics* **1987**, *6*, 153–156. Katz, H. E. *J. Org. Chem.* **1985**, *50*, 5027–5032. Newcomb, M.; Blanda, M. T.; Azuma, Y.; Delord, T. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1159–1160. Karol, T. J.; Hutchinson, J. P.; Hyde, J. R.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* **1982**, *1*, 404–405. Shriver, D. F.; Biallas, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 1078–1081.

(4) For surveys of reactions of coordinated ligands, see, inter alia: Hay, R. W. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 6, pp 411–485. Black, D. St. C. *Ibid.* Vol. 6, pp 155–227. Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G. W., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, pp 463–498.

(5) Strictly speaking, since **1**, **3** (and perhaps[7b,8] **2**) have three C_2 axes of symmetry, they are classified[6] D_2-symmetric.

(6) Cf.: le Noble, W. J. *Highlights of Organic Chemistry*; Marcel Dekker: New York, 1974; p 162.

(7) For earlier reports of racemic, but potentially resolvable C_2-symmetric, neutral bisferrocenes, see: (a) Katz, T. J.; Balogh, V.; Schulman, J. *J. Am. Chem. Soc.* **1968**, *90*, 734–739. (b) Talham, D. R.; Cowan, D. O. *Organometallics* **1987**, *6*, 932–937 and references therein.

(8) LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhoff, U. T.; Eilbracht, P.; Candela, G. A.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181–3187.

(9) Escher, A.; Rutsch, W.; Neuenschwander, M. *Helv. Chim. Acta* **1986**, *69*, 1644–1654.

(10) Mueller-Westerhoff, U. T.; Eilbracht, D. *J. Am. Chem. Soc.* **1972**, *94*, 9272–9274.

(11) Mueller-Westerhoff, U. T.; Eilbracht, D. *Tetrahedron Lett.* **1973**, 1855–1858.

(12) Fischer, E. O.; Seus, D. *Z. Naturforsch.* **1954**, *9b*, 386.

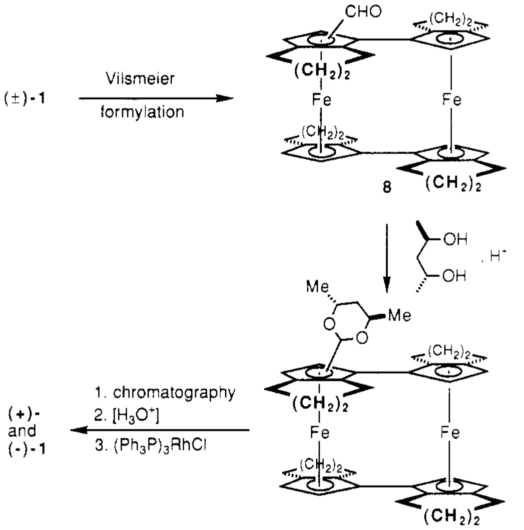
(13) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955–970.

(14) Morrison, W. H., Jr.; Hendrickson, D. N. *J. Chem. Phys.* **1973**, *59*, 380–386.

(15) That the six-membered rings in **5** might be selectively hydrogenated was suggested by the findings of Fischer and Seus (ref 12).

(16) For general references, see: Hawkins, S. C. J. *Configuration of Metal Complexes*; Wiley-Interscience: New York, 1971; pp 310–317. Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates and Resolutions*; Wiley-Interscience: New York, 1981; pp 268–273.

Scheme II



9a/9b
(diastereomeric mixture)

The first, and ultimately inferior, method was a classical resolution. This was achieved through the monocationic form (i.e., **2**) by making natural L-tartrate the counterion,[17] thus producing a diastereomeric pair (**7a**/**7b**) of the tartrates of (+)-**2**/(−)-**2**. Preparation of **7a**/**7b** was carried out in quantitative yield by benzoquinone oxidation of (±)-**1** in the presence of L-tartaric acid. Multiple recrystallizations, as described in the Experimental Section, led to the separation of the diastereomers **7a** and **7b**. Owing to their intense color, optical rotations of **7a**/**7b** (or the corresponding dicationic forms) could not be measured using either a Na or Hg lamp source, even at high dilution, and the paramagnetic nature of **7a**/**7b** rendered ^{1}H NMR data unreliable. Consequently, monitoring the progress of the resolution was done by reduction of small quantities (ca. 5 mg) of material enriched in **7a** or **7b**, obtained from the fractional recrystallizations, to the neutral compound [(+)-**1**/(−)-**1**] with zinc in acetic acid, and then taking the optical rotation. The maximum rotations of (+)- and (−)-**1** obtained by this method were $[\alpha]^{20}_{\mathrm{D}}$ +3000° (c = 0.050, CH_2Cl_2) and $[\alpha]^{20}_{\mathrm{D}}$ −2900° (c = 0.050, CH_2Cl_2).

Attempts at performing a resolution of (±)-**3** using L-tartrate as the counterion of the dicationic form by precipitation of (±)-**3** with L-tartaric acid, L-sodium tartrate, or L-disodium tartrate, in D_2O or CD_3OD, always resulted in a reduction of the dication **3** to its monocationic form **2** as indicated by a color change from brown to the green typical of the monocation, and a more complex ^{1}H NMR spectrum similar to that of (±)-**2**.

Because of the tediousness of the classical resolution via **7**, as well as uncertainty as to whether complete separation of the antipodes had been achieved, an operationally simpler and unequivocal method for resolution was sought. A satisfactory solution was realized by employing the sequence of reactions outlined in Scheme II, wherein resolution is accomplished by chromatographic separation of the diastereomeric ketals **9a**/**9b**.

Vilsmeier formylation[18] of (±)-**1**, using N-methylformanilide/$POCl_3$, gave only one of the two possible regioisomeric monoaldehydes **8** as the sole product.[19] Acetalization of (±)-**8** with (2R,4R)-(−)-pentane-2,4-diol provided the diastereomeric cyclic acetals **9a**/**9b**, which were efficiently separated by column chromatography on silica gel. Hydrolysis, using pyridinium p-toluenesulfonate in MeOH/THF, of the separated cyclic acetals **9a** and **9b** gave (−)-**8** and (+)-**8**. The aldehydes (−)-**8** and (+)-**8** were then decarbonylated using Wilkinson's catalyst to give back, fully resolved, (−)-**1** and (+)-**1**, respectively, $[\alpha]^{20}_{\mathrm{D}}$ −2940° (c = 0.100, CH_2Cl_2), and $[\alpha]^{20}_{\mathrm{D}}$ +2930° (c = 0.100, CH_2Cl_2). Conversion of (+)- and (−)-**1** to the individual[20] enantiomers of monocation **2** and dication **3** can be accomplished as in the racemic series.

Conclusion

The synthesis of **1**-**3** and their resolution demonstrate the convenient construction of optically active C_2-symmetric binuclear metallocenes and open doors to other derivatives by variation of the organic framework and/or the metal.[21]

Experimental Section

General. Melting points were determined in Pyrex capillaries in a Mel-Temp melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian XL-300 spectrometer; in all cases chemical shifts are reported in parts per million (ppm) downfield from internal tetramethylsilane. Routine mass spectra (EI) were obtained by direct insertion using a Hewlett-Packard 5985 GC/MS spectrometer. Exact mass measurements were conducted at the NIH-MSU Mass Spectrometry Facility, Michigan State University, East Lansing, MI. Infrared spectra were recorded on a Nicolet (5000) FT spectrometer. Whatman polyester-backed silica gel (250 μm) UV 254 flexible plates were used for analytical TLC. Column chromatography was conducted on silica gel 60 (average particle size ~40 μm, J. T. Baker). High-performance liquid chromatography (HPLC) was performed using a Beckman 126 liquid chromatograph equipped with a Beckman 163 variable-wavelength UV detector set at 254 nm. Electrochemical experiments[23] were performed with a BAS-100A electrochemical analyzer. A platinum button working electrode, approximate area 0.08 cm^2, a platinum wire counter electrode, and a reference saturated calomel electrode (SCE), separated from the solution with a bridge, comprised the three electrode system. All potentials were measured vs the SCE reference. The supporting electrolyte was 0.10 M tetra-n-butylammonium perchlorate (TBAP). Bulk electrolysis experiments were performed with a large platinum grid electrode (approximate area 1 cm^2). In this case the counter electrode was separated from the working electrode and reference electrode with a glass frit. The cells used for cyclic voltammetry and bulk electrolysis were designed for inert-atmosphere studies.[23]

Reactions sensitive to air or moisture were conducted in oven- or flame-dried glassware under an atmosphere of dry argon. With respect to solvents, the term "dry" means freshly distilled from sodium benzophenone ketyl (THF, diethyl ether, benzene, hexane, pentane) except that dichloromethane and acetonitrile were distilled from CaH_2. Petroleum ether refers to the fraction of petroleum ether that boils between 35 and 60 °C. The phrase

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[17] This technique[16] was also examined with the chiral counterions (1S)-10-camphorsulfonate, (R)-1,1′-binaphthyl phosphate, (S)-Mosher-carboxylate, and (R)-mandelate, but they yielded no separation of the diastereomers by crystallization or HPLC on a silica gel column.

[18] Pauson, P. L.; Watts, W. E. *J. Chem. Soc.* **1962**, 3880–3896.

[19] Which of the two possible regioisomers is actually formed has not been established.

[20] The absolute stereochemistries of the (+)- and (−)-antipodes of 1–3 have not been determined.

[21] We recently reported[22a] that ferrocenium ion (as its hexafluorophosphate) functions as a Lewis acid for the catalysis of Diels-Alder reactions. The possibility that the antipodes of **2** or **3** might serve as chiral (bidentate?) catalysts was briefly examined. From the standpoint of accelerating the rate of Diels-Alder reactions (the reaction of *trans*-cinnamaldehyde, methacrolein, acrylic acid, and N,N-dimethylacrylamide with cyclopentadiene in CH_2Cl_2 were examined[22]), **3** proved superior to ferrocenium hexafluorophosphate[22] (rate acceleration was not observed with **2**), but (+)- and (−)-**3** gave no significant asymmetric induction (<10% ee in all cases).

[22] (a) Kelly, T. R.; Maity, S. K.; Meghani, P.; Chandrakumar, N. *Tetrahedron Lett.* **1989**, *30*, 1357–1360. (b) Note footnote 7 therein.

[23] For general experimental considerations, see: Anderson, J. E.; Yao, L.-L.; Kadich, K. M. *J. Am. Chem. Soc.* **1987**, *109*, 1106–1111.

"evaporation of the solvent in vacuo" or equivalent phrases mean that solvents were removed on a rotary evaporator at aspirator vacuum and that remaining traces of volatiles were then removed on a vacuum pump. Filtrations under argon were performed using a pair of Schlenk flasks connected by a "U-tube" partitioned with a porosity 3 glass frit. Elemental analyses were performed by Robertson Laboratory, Inc., Madison, NJ.

(±)-Bis(1,1'-bi-1*H*-indenyl)diiron [(±)-5]. To 20.0 g (87.0 mmol) of 1,1'-bi-1*H*-indene[24] (4) dissolved in 500 mL of dry THF under argon at -10 °C (ice/MeOH bath) was added *n*-BuLi (2.5 M in hexane, 70 mL, 175 mmol) dropwise over 15 min, taking care that the internal temperature did not rise above +5 °C. The resulting yellow solution was stirred for 15 min at 0 °C before cooling to -40 °C (MeCN/dry ice bath), causing a slurry to form. $FeCl_2 \cdot 2THF$[8] (24.0 g, 88.6 mmol) slurried in 400 mL of dry THF under argon was added rapidly via a wide-bore cannula, producing immediately a deep green solution. After 15 min the cooling bath was removed, and the reaction mixture was further stirred for 4 h at room temperature. The solvents were removed under high vacuum (0.5–1 Torr), argon was then admitted, and the deep-green, air-sensitive, solid residue was transferred to the thimble of a large Soxhlet extraction apparatus flushed with argon. The residue was extracted continuously with dry hexane, *under an argon atmosphere* (using a positive pressure of Ar and a bubbler) for 4 days. At this stage, the hexane extract contained ca 6.0 g of (±)-5 as a dark green solid suspended in a black solution; (±)-5 was isolated by cooling the suspension to 0 °C, filtering under argon (Schlenk techniques: see General section), and drying under high vacuum. Further extraction of the residue in the thimble gave an additional ca. 0.5 g of (±)-5 per day over a further period of 7 days, for a total yield of (±)-5 of 9.3 g (38%). An analytically pure sample of (±)-5, mp 245 °C dec, was prepared by repeating the above extraction on the isolated solid. IR (Nujol mull): 1335, 1200, 1120, 1104, 1035, 990, 880, 830, 815, and 737 cm^{-1}. MS: *m/z* (relative intensity) 568 ($M^{\bullet+}$, 70), 341 (16), 284 (86), 226 (100), 202 (27), and 113 (79). ^1H NMR ($CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 4 H), 7.55 (d, *J* = 8.3 Hz, 4 H), 7.25 (t, *J* = 6.9 Hz, 4 H), 7.05 (t, *J* = 6.9 Hz, 4 H), 5.94 (d, *J* = 1.3 Hz, 4 H), 3.97 (d, *J* = 1.3 Hz, 4 H). Anal. Calcd for $C_{36}H_{24}Fe_2$: C, 76.06; H, 4.22. Found: C, 75.96; H, 4.02.

Compound (±)-5 is stable to air as a solid, but its dark green solutions rapidly decompose in air to give iron oxides and an orange solution of 1,1'-biindenylidene (6).[9]

Cyclic Voltammetry[23] of (±)-5 (Figure 1). A sample of (±)-5 (11 mg, 0.020 mmol) was dissolved in 15 mL of a 0.10 M solution of tetra-*n*-butylammonium perchlorate (TBAP) in dichloromethane, under a stream of argon gas in a "one" compartment type cell equipped with a saturated calomel electrode (SCE) for reference. Experimental conditions were: initial $E = -200$ mV; high $E = 1000$ mV; low $E = -200$ mV; $\Delta V = 100$ mV/s.

Bulk Electrolyses of (±)-5.[23] Fifty milligrams (0.090 mmol) of (±)-5 was dissolved in 20 mL of a 0.10 M solution of TBAP in dry dichloromethane under a stream of argon at 0 °C, in a "two" compartment type cell equipped with a SCE for reference. The solution was maintained at a potential difference of 1 V for 41 min. The solution turned from dark green to green/yellow during electrolysis and finally to orange/yellow; the only organic material isolated was characterized as 1,1'-biindenylidene (6),[9] which was obtained in virtually quantitative yield by chromatography using 1:1 petroleum ether/EtOAc on silica gel.

(±)-Bis(1,1'-bi-1*H*-tetrahydroindenyl)diiron [(±)-1]. In a 1-L, round-bottomed Schlenk flask, 3.00 g (5.28 mmol) of (±)-5 was dissolved in 500 mL of dry THF under argon. Activated 10% Pd/C (Aldrich, 1.5 g) was added, and the argon gas was replaced with a hydrogen gas atmosphere by evacuation and admittance of H_2 gas several times, and an atmosphere of H_2 was then maintained at balloon pressure. The reaction mixture was stirred rapidly, and the progress of the reaction was monitored by TLC (1:1 petroleum ether/CH_2Cl_2). Completion of the reaction (ca. 24 h) was indicated when a single orange component was evident on TLC (caution is advised as some products of incomplete hydrogenation appear as a single red component with the same R_f value as that of the desired, fully hydrogenated product). The reaction mixture was filtered through Celite; evaporation of the solvent in vacuo afforded crude (±)-1 as an orange solid. Purification by recrystallization from hexane/CH_2Cl_2 gave analytically pure (±)-1 (2.26 g, 73%) as orange prisms, mp 280 °C dec, stable in air both as a solid and dissolved in organic solvents. IR (Nujol mull): 3083, 1642, 1237, 1157, 1104, 1064, 1025, 905, 865, and 819 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.95 (d, *J* = 2.1 Hz, 4 H), 4.22 (d, *J* = 2.1 Hz, 4 H), 3.30 (m, 4 H), 2.6–1.2 (m, 28 H). MS: *m/z* (relative intensity) 584 ($M^{\bullet+}$, 100), 342 (36), 292 (100), 228 (25). Anal. Calcd for $C_{36}H_{40}Fe_2$: C, 73.96; H, 6.85. Found: C, 73.30; H, 6.84.

(±)-Bis(1,1'-bi-1*H*-tetrahydroindenyl)diiron(II,III) Tetrafluoroborate [(±)-2]. A mixture of (±)-1 (100 mg, 0.17 mmol) and benzoquinone (9.2 mg, 0.086 mmol) was slurried, at room temperature, in dry acetonitrile (8 mL) under argon. Boron trifluoride etherate (0.24 mL, 1.9 mmol) was added dropwise over 1 min via syringe, and the resulting dark green solution was further stirred for 10 h. Dry ether (200 mL) was then added, and the dark green precipitate produced was filtered off under argon. Recrystallization of the residue from CH_2Cl_2 gave pure (±)-2 (108 mg, 94%) as long, dark green needles, mp >360 °C. The ^1H NMR spectrum was very broad (paramagnetism). IR (Nujol mull): 1635, 1290, 1244, 1091, 1058, 832, 732, and 692 cm^{-1}. Anal. Calcd for $C_{36}H_{40}Fe_2BF_4 \cdot CH_2Cl_2$; C, 58.73; H, 5.55; Cl, 9.39. Found: C, 59.00; H, 5.61; Cl, 9.09.

(±)-Bis(1,1'-bi-1*H*-tetrahydroindenyl)diiron(III,III) Bistetrafluoroborate [(±)-3]. A mixture of (±)-1 (100 mg, 0.17 mmol) and benzoquinone (37 mg, 0.34 mmol) was slurried, at room temperature, in dry acetonitrile (8 mL) under argon. Boron trifluoride etherate (0.16 mL, 1.3 mmol) was added dropwise over 1 min via syringe, and the resulting dark brown solution was further stirred for 1 h. Dry ether (200 mL) was then added, and the dark brown precipitate of (±)-3 was filtered off under argon, further washed with dry ether (50 mL), and finally dried under high vacuum to give 129 mg (99%) of (±)-3, mp >360 °C. IR (Nujol mull): 3100, 1635, 1297, 1244, 1204, 1078, 1051, and 825 cm^{-1}. ^1H NMR (D_2O): δ 5.41 (d, *J* = 1 Hz, 4 H), 3.10 (d, *J* = 1 Hz, 4 H), 2.80 (m, 4 H), 2.50 (m, 4 H), 1.80–0.00 (3 m, 24 H). Anal. Calcd for $C_{36}H_{40}Fe_2B_2F_8$: C, 56.99; H, 5.28. Found: C, 56.81; H, 5.24.

(+)- and (−)-Bis(1,1'-bi-1*H*-tetrahydroindenyl)diiron(II,III) L-Tartrate (7a/7b). A solution of (±)-1 (400 mg, 0.68 mmol), benzoquinone (80 mg, 0.74 mmol), and L-(+)-tartaric acid (104 mg, 0.69 mmol) in 60 mL of dry dichloromethane was stirred, under argon, for 2 days. The solvent was removed in vacuo leaving a deep green solid residue which was washed with diethyl ether (100 mL) and filtered with further washing with diethyl ether (2 × 100 mL). The deep green solid was then taken up into a minimum volume of boiling dichloromethane and allowed to cool slowly to room temperature over 1 h and then maintained at +4 °C for 12 h and then at -15 °C for a further 12 h. Filtration of the precipitated solid and repetition of the above recrystallization procedure on the solid, twice, afforded pure the first of the two diastereomers, **7a** (30 mg, 15%), as an amorphous solid, mp >360 °C. Combination of the mother liquors enriched in the other diastereomer (**7b**) and subjecting them to the above recrystallization procedure three times gave diastereomer **7b** (20 mg, 10%) in pure form, mp >360 °C, as long, deep green needles. (Because of the intense color of **7a** and **7b**, optical rotations of these salts could not be measured, even at very high dilution.)

The enantiomeric purity of the individual fractions from recrystallization was monitored by taking a small quantity (ca. 5 mg) of **7a** or **7b** from the bulk material and subjecting it to reduction, using Zn/AcOH (as described below), to give (+)- or (−)-1 and then, after purification, measuring the optical rotation.

7a. IR (Nujol mull): 3630–2350 br, 1722, 1609, 1323, 1250, 1111, 839, 732, and 693 cm^{-1}. Anal. Calcd for $C_{40}H_{45}O_6Fe_2$: C, 65.40; H, 6.10. Found: C, 65.40; H, 5.88.

7b. IR (Nujol mull): 3600–2375 br, 1735, 1662, 1509, 1244, 1210, 1131, 1071, 837, 726, and 692 cm^{-1}. Anal. Calcd for $C_{40}H_{45}O_6Fe_2$: C, 65.40; H, 6.10. Found: C, 65.19; H, 5.91.

Preparation of (+)- and (−)-1 by Reduction of the Diastereomeric Salts 7a and 7b. Tartrate **7a** (30 mg, 0.041 mmol) was dissolved in dichloromethane (3 mL) and glacial acetic acid (0.5 mL). Activated zinc powder (50 mg) was added in one portion to the rapidly stirred mixture. After 3 min the excess zinc was

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(24) Heimer, N. E.; Hajjatie, M.; Panetta, C. A. *J. Org. Chem.* 1982, *47*, 2593–2598. See also: Nicolet, P.; Sanches, J.-Y.; Benaboura, A.; Abadie, M. J. M. *Synthesis* 1987, 202–203.

filtered off and washed with CH_2Cl_2; the filtrate and washings were evaporated in vacuo to afford the crude product as an orange solid, which was purified by passing it through a short column of silica gel, eluting with dichloromethane, to give (+)-**1** (22.7 mg, 95%), $[\alpha]^{20}_{\mathrm{D}}$ +3000° (c = 0.050, CH_2Cl_2).

Similarly, reduction of **7b** gave (−)-**1** in 92% yield; $[\alpha]^{20}_{\mathrm{D}}$ −2900° (c = 0.050, CH_2Cl_2). All spectral and TLC data for (+)- and (−)-**1** were identical with those obtained for (±)-**1** (except for the optical rotations).

Preparation of (±)-8 by Formylation of (±)-1. *N*-Methylformanilide (0.88 mL, 7.13 mmol) and freshly distilled phosphorus oxychloride (0.66 mL, 7.10 mmol) were mixed and left to stand at room temperature for 1 h under argon. Then (±)-**1** (208 mg, 0.36 mmol) dissolved in dry dichloromethane (30 mL) was added, via syringe, and the reaction mixture was stirred at room temperature for 2 days. Ice water (10 mL) was added, and the mixture was left to stir for 3 h to ensure complete destruction of the complex. The product was extracted with dichloromethane (2 × 20 mL), and the combined extracts were dried (Na_2SO_4) and evaporated in vacuo, affording the crude product as a red gum. Purification by silica gel chromatography, eluting with dichloromethane, gave pure monoaldehyde (±)-**8** (205 mg, 94%) as an orange solid. A sample of analytical purity, mp 280 °C dec, was prepared as orange-red prisms by recrystallization from hexane/CH_2Cl_2. IR (Nujol mull): 3076, 1655, 1330, 1244, 1078, 826, and 712 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 10.10 (s, 1 H), 5.53 (s, 1 H), 4.97 (d, J = 2.1 Hz, 1 H), 4.83 (d, J = 2.1 Hz, 1 H), 4.65 (d, J = 2.1 Hz, 1 H), 4.43 (d, J = 2.1 Hz, 1 H), 4.33 (d, J = 2.1 Hz, 1 H), 4.24 (d, J = 2.1 Hz, 1 H), 3.60–1.00 (m, 32 H). MS: m/z (relative intensity), 612 ($M^{\bullet +}$, 100), 342 (20), 306 (26), 228 (20). Anal. Calcd for $C_{37}H_{40}Fe_2O$: C, 72.55; H, 6.54. Found: C, 72.02; H, 6.50.

Cyclic Acetals 9a and 9b. Aldehyde (±)-**8** (235 mg, 0.38 mmol) was treated with (2*R*,4*R*)-(−)-2,4-pentanediol (80 mg, 0.77 mmol), pyridinium *p*-toluenesulfonate (193 mg, 0.77 mmol), and triethyl orthoformate (0.32 mL, 1.93 mmol) in dry dichloromethane (30 mL) under argon. After stirring at room temperature for 24 h, water (10 mL) was added, the organic phase was collected and dried ($MgSO_4$), and the solvent was removed in vacuo, affording a pale yellow gum. The diastereomeric mixture was then separated by silica gel chromatography on a 6 in. long, 1 in. diameter column [monitored visually and by TLC (silica gel/CH_2Cl_2)], eluting with freshly distilled dichloromethane, to give firstly **9a** (94 mg, 70% of theory) and secondly **9b** (91 mg, 68% of theory) as pale yellow gums. A third fraction containing the aldehyde (±)-**8** (70 mg), presumably arising from partial hydrolysis on the column, was also recovered.

9a. IR (neat): 2930, 2850, 1436, 1376, 1237, 1157, 1131, and 812 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.91 (s, 1 H), 5.10 (s, 1 H), 4.94 (d, J = 1 Hz, 1 H), 4.80 (d, J = 1 Hz, 1 H), 4.43 (m, 1 H), 4.20 (m, 3 H), 3.20 (m, 4 H), 2.50–1.00 (m, 38 H). MS: m/z (relative intensity), 698 ($M^{\bullet +}$, 100), 349 (100), 292 (81), 228 (64), 69 (100). Exact mass calcd for $C_{42}H_{50}O_2$ 698.2510, found 698.2553.

9b. IR (neat): 3096, 3070, 2924, 2851, 1436, 1376, 1237, 1157, 1131, and 819 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 5.75 (s, 1 H), 5.14 (s, 1 H), 4.94 (d, J = 1 Hz, 1 H), 4.88 (d, J = 1 Hz, 1 H), 4.85 (d, J = 1 Hz, 1 H), 4.23 (d, J = Hz, 1 H), 4.21 (d, J = 1 Hz, 1 H), 3.95 (d, J = 1 Hz, 1 H), 3.20 (m, 4 H), 2.60–1.00 (m, 38 H). MS: m/z (relative intensity), 698 ($M^{\bullet +}$, 100), 349 (100), 292 (80), 228 (60), 69 (100). Exact mass calcd for for $C_{42}H_{50}Fe_2O_2$ 698.2510, found 698.2560.

Preparation of (−)- and (+)-8 by Hydrolysis of Acetals 9a and 9b. Acetal **9a** (90 mg, 0.129 mmol) was dissolved in 3 mL of 1:1 MeOH/THF and treated with pyridinium *p*-toluenesulfonate (100 mg, 0.40 mmol), causing the solution to turn immediately from yellow to orange. Water (10 mL) was then added after 3 min, and the product was extracted into dichloromethane (2 × 10 mL). After combining and drying (Na_2SO_4) the extracts, evaporation of the solvent in vacuo gave the crude product as an orange solid. Purification by passing it through a short plug of silica gel eluting with dichloromethane gave (−)-**8** (75 mg, 95%) as an orange solid, $[\alpha]^{20}_{\mathrm{D}}$ −3410° (c = 0.100, CH_2Cl_2).

Similarly, hydrolysis of **9b** gave (+)-**8** (95% yield), $[\alpha]^{20}_{\mathrm{D}}$ +3400° (c = 0.100, CH_2Cl_2). All spectral data and TLC behavior for (+)- and (−)-**8** were identical with those obtained for (±)-**8** except the optical rotation.

Preparation of (−)- and (+)-1 by Decarbonylation of (−)- and (+)-(8). The optically pure aldehyde (−)-**8** (52 mg, 0.085 mmol) was heated with Wilkinson's catalyst (86 mg, 0.093 mmol, Aldrich) under argon in toluene (2 mL) contained in a sealed tube at 170–180 °C for 6 h. The toluene was evaporated in vacuo, and the crude product was purified by silica gel chromatography, eluting with dichloromethane to give (−)-**1** (36 mg, 73%), $[\alpha]^{20}_{\mathrm{D}}$ −2940° (c = 0.100, CH_2Cl_2).

Similarly, decarbonylation of (+)-**8** gave (+)-**1** (70% yield), $[\alpha]^{20}_{\mathrm{D}}$ +2930° (c = 0.100, CH_2Cl_2). All spectral data and TLC behavior for (+)- and (−)-**1** were identical with those obtained for (±)-**1** except for optical rotation.

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An Alternative Route to 2-Substituted Indoles via *N*-Aminal-Directed Lithiation

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The directing effect of (dialkylamino)methyl (aminal) groups in carbocyclic metalation chemistry is well known.[1] Recently, we have found that aminal groups can also be successfully employed as protecting groups for the NH of heterocyclic compounds and as directing groups for the subsequent lithiation of heterocyclic compounds. This methodology works well for a variety of NH-containing heterocycles, including carbazole, imidazole, benzimidazole, and pyrazole.[2] In all these cases, the aminal group is easily introduced and directs the lithiation to the appropriate site. The removal of the aminal group is then achieved by gentle warming with aqueous HCl during the workup. Overall, the methodology provides an efficient two-step route to the synthesis of a variety of substituted heterocycles.

Concurrent with our own research into the use of aminal derivatives as NH-protecting and lithiation-directing groups, several other groups have investigated similar *N*-aminal-directed lithiation using other heterocycles. Muchowski and Hess reported the lithiation of 6-(dimethylamino)-1-azofulvene dimer **1**.[3] After reaction with an electrophile and subsequent hydrolysis of the *N*-aminal, the corresponding 5-substituted pyrrole-2-aldehydes **2** were obtained in good yields. More recently, Hlasta and Bell reported the use of (dimethylamino)methyl as a directing group for the lithiation of indole and subsequent reactions with electrophiles, but they were unable to effect the re-

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