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Preparation of the 1,2-Di-*tert*-butylcyclopentadienyl Anion and a Transition Metal Derivative. Crystal Structure of 1,1′,2,2′-Tetra-*tert*-butylferrocene

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The titanium promoted cyclization of the diketone $Bu^tC(O)CH_2CH_2CH_2C(O)Bu^t$, **1**, affords 1,2-di-*tert*-butyl-1,2-cyclopentanediol, **2**. Further reaction of **2** with $POCl_3$ in hot pyridine results in dehydration to give the new vicinally di-*tert*-butyl-substituted cyclopentadiene, **3**, which exists mainly as the 1,5-di-*tert*-butylcyclopentadiene tautomer **3b**. As with other cyclopentadienes, **3** reacts cleanly with Bu^nLi to give the corresponding lithium cyclopentadienide, **4**, which in turn reacts with $FeCl_2\cdot 2THF$ to form 1,1′,2,2′-tetra-*tert*-butylferrocene, **5**. The structure of **5** has been confirmed by single crystal X-ray crystallography: Crystal data for **5** with Mo Kα ($\lambda = 0.7107$ Å) radiation at 246 K: $C_{26}H_{42}Fe$, $a = 16.135(3)$ Å, $b = 8.416(1)$ Å, $c = 16.800(3)$ Å, orthorhombic space group *Cmca* (No. 64), $Z = 4$, $R = 0.0543$, $R_w = 0.0734$.

Introduction

Despite the plethora of organometallic complexes containing η^5-cyclopentadienyl ($C_5H_{5-n}R_n$) ligands, remarkably few have the general formula 1,2-$C_5H_3R_2$, i.e. in which two substituents occupy a mutually vicinal arrangement on the ring. In fact, the only known 1,1′,2,2′-tetraalkylferrocene complexes are the tetramethyl[1a] and -ethyl[1b,c] complexes. Recently, there has been considerable interest in the structures, dynamic properties, and chemistry of main group, transition metal, and f-group metal complexes with cyclopentadienyl ligands containing bulky substituents, such as *tert*-butyl and trimethylsilyl.[2,3] In light of this general interest in sterically demanding cyclopentadienyl ligands, it was striking that the bulky cyclopentadienyl ligand (1,2-$C_5H_3Bu^t_2$) was unknown. Here we describe its synthesis, spectroscopic characterization, and the X-ray structural characterization of its ferrocene derivative.

Various strategies have been employed for the preparation of bulky cyclopentadienes. For example, mono-*tert*-butylcyclopentadiene has been prepared from cyclopentadienylmagnesium bromide and *tert*-butyl chloride.[4-6] Alternatively, the lithium salt of *tert*-butylcyclopentadiene can be prepared from dimethylfulvene and methyllithium.[7,8] The 1,3-di-*tert*-butylcyclopentadiene was first prepared from (mono-*tert*-butylcyclopentadienyl)magnesium bromide and *tert*-butyl chloride.[9] Venier and Casserly have recently reported an alternative preparation of di-*tert*-butylcyclopentadiene by alkylation of cyclopentadiene with *tert*-butyl bromide under phase-transfer conditions (aqueous KOH and Adogen 464, 90% yield).[10] Sitzmann reported the first preparation of 1,3,5-tri-*tert*-butylcyclopentadiene from the sodium salt of 1,3-di-*tert*-butylcyclopentadienyl anion and *tert*-butyl iodide.[11]

Another approach commonly used for the preparation of cyclopentadienes substituted with bulky groups is to build up the C_5 ring system from a combination of smaller carbon units, where the substituents are already present. This method is utilized in the preparation of compounds such as pentamethylcyclopentadiene[12] and tetra-*tert*-butylcyclopentadiene.[13]

As shown by Riemschneider[9] and Venier,[10] the preparation of the vicinity disubstituted isomer of di-*tert*-butylcyclopentadiene cannot be accomplished by replacement of the hydrogens of unsubstituted cyclopentadiene by *tert*-butyl groups due to ready formation of 1,3-di-*tert*-butylcyclopentadiene. Assembling the C_5 skeleton from smaller carbon units is the only viable alternative for its preparation. The successful approach described here is based upon the preparation of 3,4-di-*tert*-butylthiophene[14] and using a modified procedure of Corey.[15]

Results and Discussion

Preparation of diketone **1** (Scheme 1) was achieved via a Michael reaction of (*tert*-butylvinyl)oxy)trimethylsi-

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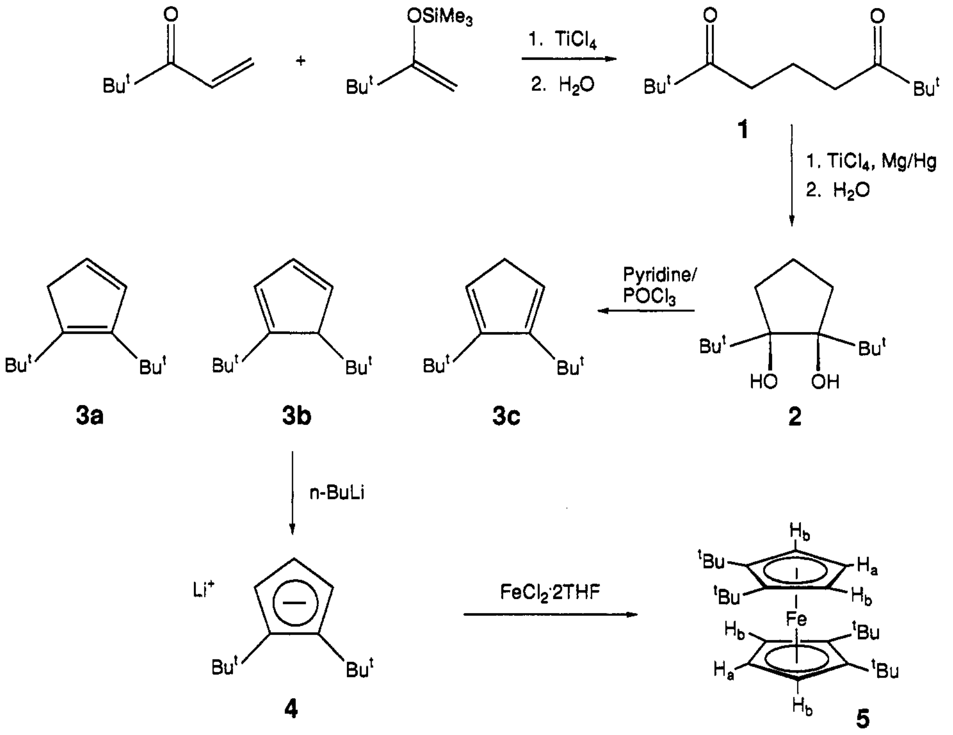
Scheme 1



lane,[16] with *tert*-butyl vinyl ketone[17] in the presence of titanium tetrachloride.[18] Treatment of 1 with the Ti(II) species generated by reaction of $TiCl_4$ and amalgamated magnesium affords *cis*-1,2-di-*tert*-butylcyclopentane-1,2-diol (**2**) in 41% yield. Compound 2 may be recrystallized from hexanes to give long, clear needles of the diol, which was characterized by its ^1H NMR, $^{13}C\{^1H\}$ NMR, and IR spectra. The ^1H NMR ($CDCl_3$) spectrum includes a singlet at δ 1.15 for the two equivalent *tert*-butyl groups and multiplets for the six ring protons. The hydroxyl protons appear as a sharp singlet at δ 2.70 in the ^1H NMR spectrum. Confirmation of the presence of hydroxyl protons was made when a $CDCl_3$ solution of the diol was shaken with deuterium oxide and disappearance of the signal at δ 2.70 was observed. Two-dimensional ^1H–^1H COSY NMR indicated the ring hydrogens were coupled to each other, although unambiguous shift assignments could not be made. As expected, five resonances are observed in the $^{13}C\{^1H\}$ NMR spectrum.

The infrared spectrum (CH_2Cl_2) of 2 includes a sharp absorbance at 3612 cm^{-1} and a broad absorbance at 3526 cm^{-1}, indicating two different types of O–H bonds are present in solution. The broad adsorbance may be due to intramolecular hydrogen bonding which weakens the O–H bond and shifts the absorbance to lower frequency. The sharp absorbance is presumably due to non-hydrogen bonded O–H. The inconsistency between the IR (two resonances) and ^1H NMR (one resonance) data is observed presumably because the time scales of the IR (10^{-13} s^{-1}) and NMR (10^{-1} to 10^{-9} s^{-1}) experiments are different. Interconversion between "free" O–H and hydrogen bonded O–H is slow enough that two distinct species are observed on the IR time scale, but is too fast to be observed on the NMR time scale. The singlet observed for the hydroxyl protons in the ^1H NMR spectrum of 2 must then represent an average of the two species.

Dehydration of 2 to give the vicinial di-*tert*-butylcyclopentadiene 3, was achieved by heating 2 in pyridine at 80 °C with phosphorus oxychloride. In the presence of phosphorus oxychloride the hydroxyl groups are converted into a dichlorophosphate complex, which is then eliminated upon abstraction of proton by a molecule of pyridine. The pyridine serves not only as the base in the elimination step of the reaction but also as the reaction solvent. Eliminations of tertiary alcohols to give alkenes, using phosphorus oxychloride, have been carried out at ambient temperature.[19–21] However, attempts to dehydrate 2 at ambient temperature were unsuccessful, leaving only unreacted starting material.

The vicinal di-*tert*-butylcyclopentadiene 3 is a viscous, orange oil, as is the 1,3-isomer.[10] Complicated ^1H and $^{13}C\{^1H\}$ NMR spectra are observed for 1,3-di-*tert*-butylcyclopentadiene, due to the presence of various tautomers.[10] While there are three possible tautomers of the vicinally substituted di-*tert*-butylcyclopentadiene, **3a**, **3b**, and **3c**, the ^1H NMR ($CDCl_3$) spectrum is relatively simple, containing two singlets (δ 1.09, 1.26) a doublet of doublets (δ 2.95), and a multiplet (δ 6.30) in a ratio of 9:9:1:3, respectively. Two different *tert*-butyl groups and three downfield protons make these data consistent with the 1,5-di-*tert*-butyl tautomer **3b**, as shown in Scheme 1. This tautomer may predominate because it is the only one that does not put two *tert*-butyl groups on adjacent sp^2 carbon atoms, and hence allows minimum steric repulsion between these groups. Molecular mechanics calculations (PC-MODEL) indicate that this tautomer is also lower in energy than the other tautomers **3a** and **3c**. The ^1H NMR ($CDCl_3$) spectrum also contains three singlets (δ 1.32, 1.34, 1.35)

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and other multiplets downfield. The ratio of the major product **3b** to these minor products is 8:1. These minor peaks are likely due to tautomers **3a** and **3c**. The $^{13}C\{^1H\}$ NMR spectrum exhibits five resonances for the ring carbon atoms; four of these resonances are shifted downfield. The diene carbon atom substituted with the *tert*-butyl group was readily identified by its chemical shift (δ 160.26). The sp^3 carbon atom substituted with the *tert*-butyl group was located upfield of the olefin carbon atoms at δ 64.22. Two resonances were observed for the *tert*-butyl groups (C_{sp^3}), but the shifts of the quaternary carbon atoms could not be unambiguously assigned due to the presence of other unidentified peaks in the spectrum. These peaks are again likely due to the tautomers of **3**. GC–MS analysis of the dehydration product shows only one compound is present. This product has a molecular ion peak (M^+, m/e 178) which is consistent with the diene product **3**.

Preparation of (1,2-di-*tert*-butylcyclopentadienyl)lithium, **4**, is accomplished at ambient temperature by deprotonation of the diene **3** in petroleum ether using Bu^{n}Li. Compound **4** is most conveniently prepared if crude **3** is not isolated but rather treated directly with Bu^{n}Li. In dimethyl sulfoxided_6, the ^{1}H NMR of **4** shows resonances at 1.26 (s, 36H, CH_3), 4.84 (t, $^3J_{HH} = 3.17$ Hz, $2H_1$), and 5.32 ppm (d, $^3J_{HH} = 3.17$ Hz, $4H_2$). As expected, the ^{13}C NMR is also simple with five singlets [δ_C 32.9 (CCH_3), 35.4 (CH_3), 96.8 (CH_b), 103.3 (CH_a), 122.8 ($CC(CH_3)_3$)] representing the five different carbon environments. Attempts to grow X-ray quality crystals of **4** failed, but derivatization to give a ferrocene was accomplished straightforwardly.

Compound **4** was allowed to react with $FeCl_2 \cdot 2THF$ in THF. An orange solid was obtained, and upon sublimation, 1,1′,2,2′-tetra-*tert*-butylferrocene, **5**, was collected in 90% yield. The ^{1}H NMR spectrum exhibits one sharp singlet (1.40 ppm) for all of the *tert*-butyl protons. A doublet (4.18 ppm. $^3J_{HH} = 3$ Hz, $4H_b$) and a triplet at (4.13 ppm, $^3J_{HH} = 3$ Hz, $2H_a$) are observed for the ring protons. The $^{13}C\{^1H\}$ NMR spectrum contains five singlets, two for the methyl and quaternary carbons of the equivalent *tert*-butyl groups and three for the ring carbon atoms.

A single crystal X-ray crystallographic analysis of **5** was carried out to determine the solid state conformation of the complex. Details of the structure determination, data collection, and refinement are provided in Table 1. The molecular structure and atom labeling scheme, and some selected bond lengths and angles, are shown in Figure 1a. An alternative view of the molecule is provided in Figure 1b. Fractional atomic coordinates are presented in Table 2.

In an isomeric complex, 1,1′,3,3′-tetra-*tert*-butylferrocene, relief of the steric strain between the two rings is achieved via bending of the molecule such that the dihedral angle between the ring planes is 7°, a phenomenon not previously seen in other ferrocene complexes.[22] However, its isomer **5** adopts a sandwich arrangement with the two rings exactly parallel and staggered. The orientation of the two cyclopentadienyl rings is dictated by the four bulky *tert*-butyl groups, with steric considerations forcing the *tert*-butyl groups of one ring as far apart as possible from those on the second ring, with the result that the substituents on one ring are related to those on the other by a center of inversion located at the iron atom. The bond length between the *tert*-butyl bearing carbons in **5** [C(1)–C(1c) [1.468(6) Å)] is significantly longer than the bond lengths for other sterically demanding ferrocene complexes similar to **5**, such as decamethylferrocene [$d_{C\text{–}C} = 1.419(2)$ Å],[23] decabenzylferrocene [$d_{C\text{–}C} = 1.435(3)$ Å],[24] and the C–C bond lengths in the phenyl-substituted ring of pentaphenylferrocene [$d_{C\text{–}C} = 1.438$ Å].[25] In ferrocene the distance of interest is 1.389 Å.[26] Iron to ring carbon bond lengths in **5** are similar to those in other comparable complexes.

Table 1. Structure Determination Summary for 5

	Crystal Data
empirical formula	$C_{26}H_{42}Fe$
color; habit	yellow block
cryst size (mm)	0.14 × 0.42 × 0.64
cryst syst	orthorhombic
space group	*Cmca*
unit cell dimens	
a, Å	16.135(3)
b, Å	8.416(1)
c, Å	16.800(3)
vol, Å^3	2281.4(7)
Z	4
fw	410.4
density (calc), Mg/m^3	1.195
abs coeff, mm^{-1}	0.669
$F(000)$	896
	Data Collection
diffractometer used	Siemens P4
radiation (λ, Å)	Mo Kα (0.710 73)
temp, K	246
monochromator	highly oriented graphite crystal
2θ range, deg	4.0–55.0
scan type	Wyckoff
scan speed, deg/min	variable; 7.32–19.53 in ω
scan range (ω), deg	1.00
background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
no. of standard reflns	3 measured every 197 reflns
index ranges	$0 \le h \le 20, -10 \le k \le 0, -21 \le l \le 1$
no. of reflns collcd	1447
no. of ind reflns (R_{int}, %)	1361 (1.80)
no. of obsd reflns	1023 ($F > 4.0\sigma(F)$)
abs corr	N/A
	Solution and Refinement
system used	Siemens SHELXTL PLUS (PC version)
solution	direct methods
refinement method	full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$
absolute structure	N/A
extinction correction	N/A
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0015F^2$
no. of param refined	65
final R indices (obsd data), %	$R = 5.43$, $R_w = 7.34$
R indices (all data), %	$R = 7.19$, $R_w = 7.84$
goodness-of-fit	1.41
largest and mean Δ/σ	0.008, 0.001
data-to-param ratio	15.7:1
largest diff peak, ϵ Å^{-3}	0.65
largest diff hole, ϵ Å^{-3}	–0.43

In addition to the elongated C(1)–C(1c) bond length, the steric stress associated with adjacent *tert*-butyl groups

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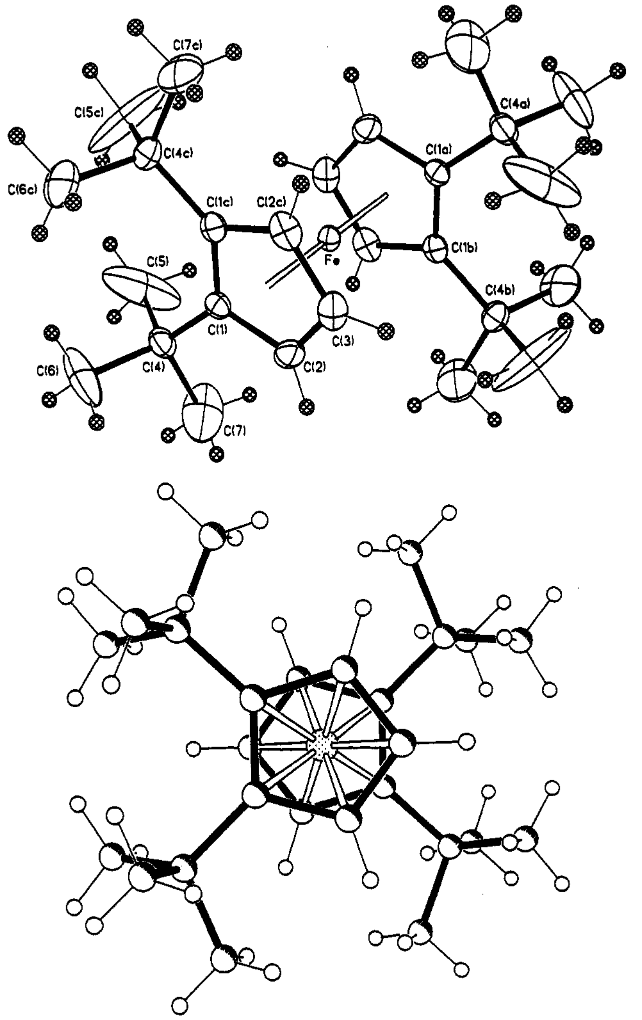

Figure 1. (a, top) Perspective drawing of **5** with ellipsoids drawn to 35% probability. Selected bond distances (Å) and angles (deg). Fe–C(1) 2.082(3), Fe–C(2) 2.043(3), Fe–C(3) 2.055(5), C(1)–C(2) 1.433(5), C(2)–C(3) 1.410(5), C(1)–C(4) 1.530(5); C(2c)–C(3)–C(2) 106.8(4), C(3)–C(2)–C(1) 110.5(3), C(2)–C(1)–C(1c) 106.1(2), C(2)–C(1)–C(4) 120.0(3), C(4)–C(1)–C(1c) 133.4(2). (b, bottom) View of **5** down the ring centroid–iron vector.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å $\times 10^3$) for 5

	x	*y*	*z*	*U*(eq)[a]
Fe	0	0	0	22.2(2)
C(1)	−455(2)	814(4)	1086(2)	27.4(9)
C(2)	−702(2)	−792(4)	931(2)	37(1)
C(3)	0	−1774(6)	841(3)	39(2)
C(4)	−1107(2)	2061(4)	1302(2)	36(1)
C(5)	−1016(4)	3622(6)	914(5)	154(4)
C(6)	−1112(3)	2302(7)	2191(3)	92(2)
C(7)	−1965(3)	1479(8)	1084(4)	117(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

on the five-membered ring could have been relieved by a torsional twist about the C1–C(1c) bond axis or bending of the *tert*-butyl groups to an *exo* position, but this is not observed. Instead, the steric strain of the *tert*-butyl groups is relieved by in-plane deformations manifested by the aforementioned elongated C1–C(1c) bond axis and by in-plane angle deviations. Ideally, the C(1c)–C(1)–C(4) and C(2)–C(1)–C(4) bond angles should be 126°, but they are experimentally found to be 133.4(2) and 120.0(3)°, respectively. The C(1c)–C(1)–C(2) bond angle should be 108° but is found to be 106.1(2)°. These deviations from ideality show that the *tert*-butyl groups are forced away from one another, giving a larger C(1c)–C(1)–C(4) angle and smaller C(2)–C(1)–C(4) and C(1c)–C(1)–C(2) bond angles. This type of in-plane deformation was previously observed in the structure of a rhodium complex containing the 1,2,3-tri-*tert*-butylcyclopentadienyl ligand.[27]

In summary, lithium 1,2-di-*tert*-butylcyclopentadienide can be readily prepared in 70% overall yield from 1,2-di-*tert*-butylcyclopentane-1,2-diol and phosphorus oxychloride in pyridine followed by lithiation of the crude diene product by *n*-butyllithium. The subsequent preparation of 1,1′,2,2′-di-*tert*-butylcyclopentadienyl ferrocene serves to confirm the identity of the cyclopentadienyl moiety. Further complexes of this new ligand will be reported in due course.

Experimental Section

Unless otherwise noted, all reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen which had been deoxygenated over BASF catalyst and dried using Aquasorb. Benzene, diethyl ether, and tetrahydrofuran (THF) were distilled under nitrogen from sodium or potassium benzophenone ketyl; chloroform and carbon tetrachloride, from molecular sieves (4 Å); and pyridine, acetonitrile, and hexanes, from CaH_2. ^1H NMR (300 MHz) and ^{13}C and $^{13}C\{^1H\}$ (75 MHz) NMR spectra were recorded on a Varian XL-300 spectrometer or a Varian UNITY plus 300 system in the solvent indicated. Chemical shifts are reported as ppm downfield of internal TMS and are referenced to the solvent peak. IR spectra were recorded on a Bio-Rad Digilab FTS-40 Fourier transform infrared spectrophotometer or a Perkin-Elmer Model 1600 FT-IR spectrophotometer. GC–MS spectra were obtained using a Hewlett Packard HP 5971A ion source. Melting points of samples in capillaries open to the air were obtained using a Thomas Hoover device and are uncorrected. Microanalysis was performed by Schwarzkopf Microanalytical Laboratory (Woodside, NY).

$FeCl_2$ was obtained from Johnson-Matthey Aesar/Alfa. *tert*-Butyl vinyl ketone,[17] ((*tert*-butylvinyl)oxy)trimethylsilane,[16] and $FeCl_2\cdot 2THF$[28] were prepared according to the literature procedure. Phosphorus oxychloride, titanium tetrachloride, magnesium powder (50 mesh), and *n*-butyllithium were purchased from Aldrich and used without further purification. Mercuric chloride was purchased from Fisher and used without further purification.

Preparation of 2,2,8,8-Tetramethylnonane-3,7-dione (1). Using a modified procedure of Narasaka,[18] a solution of *tert*-butyl vinyl ketone (15.00 g, 0.134 mol) in dichloromethane (25 mL) was added dropwise to a −78 °C solution of titanium tetrachloride (14.70 mL, 0.134 mol) in dichloromethane (250 mL). A solution of ((*tert*-butylvinyl)oxy)trimethylsilane (23.05 g, 0.134 mol) in dichloromethane (25 mL) was then added dropwise and the mixture quenched with aqueous K_2CO_3 (25 g in 200 mL of water). After warming to room temperature, the solution was filtered, the layers were separated, and the aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic fractions were washed with saturated brine, dried with anhydrous $MgSO_4$, filtered out, and concentrated by rotary evaporator to give a colorless oil which solidified on standing. Purification by vacuum distillation (73–78 °C, 10^{-3} Torr) yielded **1** (11.00 g, 39%). Spectral data were consistent with reported values.[29]

Preparation of *cis*-1,2-Di-*tert*-butylcyclopentane-1,2-diol (2). Using a modified procedure of Corey,[15] a magnesium

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amalgam was prepared by stirring mercuric chloride (1.69 g, 6.20 mmol) and magnesium powder (50 mesh, 5.50 g, 0.226 mol), in THF (40 mL) at ambient temperature for 30 min, under an argon atmosphere. The turbid supernatant liquid was withdrawn by syringe and the remaining amalgam washed with THF (3 × 30 mL). THF (150 mL) was added to the resulting gray amalgam. The slurry was cooled to −30 °C, by a limited dry ice in a 2-propanol bath, and treated dropwise with $TiCl_4$ (9.30 mL, 0.085 mol) to give a yellow-green mixture. The mixture was warmed to 0 °C, and then a solution of 1 (6.00 g, 0.028 mmol) in THF (10 mL) was added dropwise. When the mixture returned to 0 °C, the reaction was immediately quenched with a saturated K_2CO_3 solution (50 mL), warmed to room temperature, and stirred for 0.5 h. The resulting dark blue mixture was diluted with ether (300 mL) and filtered in air. The combined organic fractions were washed with saturated brine, dried over $MgSO_4$, filtered and concentrated to afford a cream-colored solid. Crude 2 was crystallized from hexanes to obtain a white, crystalline solid (2.50 g, 41%). Mp: 88–89 °C. ^1H NMR (300 MHz, C_6D_6): δ_H 1.15 (s, 18H, CH_3), 1.27 (m, 1H), 1.70 (m, 3H), 1.88 (m, 2H), 2.40 (s, 2H, OH). ^1H NMR (300 MHz, $CDCl_3$): δ_H 1.13 (s, 18H, CH_3), 1.44 (m, 1H), 1.80 (m, 3H), 2.03 (m, 2H), 2.70 (s, 2H, OH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ_C 18.8 (s, $\mathit{C}CC(CH_3)_3$), 26.4 (s, $\mathit{C}CH_2CC(CH_3)_3$), 34.2 (s, $C(\mathit{C}H_3)_3$), 37.9 (s, $\mathit{C}(CH_3)_3$), 91.1 (s, $\mathit{C}OH$). IR (CH_2Cl_2, cm^{-1}): 3612 (sh, OH), 3526 (br, OH). Anal. Calcd for $C_{13}H_{26}O_2$: C, 72.84; H, 12.23. Found: C, 73.26; H, 12.17.

D_2O (1 mL) was added to a $CDCl_3$ solution (50 mg in 2 mL) of the diol in an NMR tube. The sample was shaken, and a ^1H NMR spectrum was obtained. Disappearance of the resonance at 2.70 ppm was observed, indicating this peak represented the hydroxyl protons.

Preparation of Vicinial Di-*tert*-butylcyclopentadiene (3). The diol, 2, (1.55 g, 7.23 mmol) was combined with pyridine (25 mL) and the mixture cooled in an ice bath. Phosphorus oxychloride (5.0 mL, 53.64 mmol) was added to the stirred mixture in 1-mL charges over a period of 5 min. The resulting orange mixture was heated at 80 °C. The mixture darkened as the reaction proceeded. After 25.5 h, heating was discontinued, the mixture was cooled to ambient temperature and hexanes (25 mL) was added. The resulting mixture was cooled in an ice bath and distilled water (20 mL) was slowly added. The layers were separated and the aqueous layer was extracted with hexanes (3 × 50 mL). The combined organic fractions were extracted with 20% HCl (3 × 50 mL) and 20% aqueous ammonium chloride solution (3 × 50 mL) and then dried with $MgSO_4$ and filtered through a small plug of silica gel. The solvent was removed under aspirator vacuum. An orange viscous liquid (1.04 g, 81%) was obtained. The GC–MS of the product indicated a single component (M^+, *m/e* 178) was present. ^1H NMR (300 MHz, $CDCl_3$): δ_H 1.09 (s, 9H, CH_3), 1.26 (s, 9H, CH_3), 2.95 (dd, $^3J_{HH}$ = 3 Hz, $^5J_{HH}$ = 1 Hz, 1H, CH), 6.30 (m, 3H, CH); additional peaks included δ_H 1.32 (s), 1.34 (s), 1.35 (s), 1.47 (m), 1.65 (m), 2.24 (m), 2.52 (m), 2.69, 3.11, 6.16, 6.64. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ_C 30.56 (s, CH_3), 32.24 (s, CH_3), 64.22 (s, CH^tBu), 129.11, 130.00, 137.41, 160.26 ($C_{olefin}Bu^t$); additional peaks included δ_C 14.34, 22.88, 31.81, 32.75, 33.01, 34.13, 34.35, 37.06. Mass spectrum: *m/e* 178 (M^+, 20), 163 (13), 121 ($-C(CH_3)_3$, 16), 107 (73), 93 (9), 91 (98), 77 (49), 65 (28), 57 (100, base, $C(CH_3)_3$), 51 (17).

Preparation of the 1,2-Di-*tert*-butylcyclopentadienyl Anion (4). Diene 3 (1.04 g, 5.83 mmol) was dissolved in petroleum ether (20 mL), the solution was cooled to −78 °C, and *n*-BuLi (2.33 mL, 2.5 M in hexanes, 5.82 mmol) was added dropwise via syringe. Upon warming to room temperature, the solution became cloudy, and stirring was continued overnight. The white precipitate was collected on a Schlenk frit, washed with hexane (2 × 20 mL), and dried *in vacuo* to give 4 (0.691 g). A second crop of 4 (0.076 g) was collected from the filtrate after stirring an additional 48 h to give a total yield of 0.767 g 4 (72%). Alternatively, this complex may be prepared without isolation of 3. ^1H NMR (300 MHz, $OS(CD_3)_2$): δ_H 1.26 (s, 36H, CH_3), 4.84 (t, $^3J_{HH}$ = 3.17 Hz, $2H_a$), 5.32 (d, $^3J_{HH}$ = 3.17 Hz, $4H_b$). $^{13}C\{^1H\}$ NMR (75 MHz, $OS(CD_3)_2$): δ_C 32.9 (s, $\mathit{C}(CH_3)_3$), 35.4 (s, $C(\mathit{C}H_3)_3$), 96.8 (s, CH_a), 103.3 (s, CH_b), 122.8 (s, $\mathit{C}C(CH_3)_3$).

Preparation of 1,1′,2,2′-Tetra-*tert*-butylferrocene (5). A slurry of $FeCl_2 \cdot 2THF$ (0.078 g, 0.287 mmol) in THF (10 mL) was transferred via cannula into a 0 °C slurry of 4 (0.102 g, 0.554 mmol) in THF (10 mL). Immediate formation of an amber solution was observed. The solution was allowed to stir at ambient temperature for 1.5 h, and then the solvent was removed under reduced pressure. The residue was extracted with petroleum ether (3 × 10 mL), and the solvent was removed under reduced pressure. Isolation of the ferrocene derivative was accomplished by gradient sublimation (−30 to +130 °C, 10^{-4} Torr). Compound 5 (0.102 g, 90%) was obtained as an orange solid. A crystal suitable for diffraction was obtained by slow evaporation of a pentane solution of 5, at ambient temperature. Mp: 214 °C. ^1H NMR (300 MHz, C_6D_6): δ_H 1.40 (s, 36H, CH_3), 4.13 (t, $^3J_{HH}$ = 3 Hz, $2H_a$), 4.18 (d, $^3J_{HH}$ = 3 Hz, $4H_b$). ^{13}C NMR (75 MHz, C_6D_6): δ_C 32.92 (m, $\mathit{C}(CH_3)_3$), 34.46 (quartet of septets, $^1J_{CH}$ = 125 Hz, $^3J_{CH}$ = 5Hz, $C(\mathit{C}H_3)_3$), 66.50 (dt, $^1J_{CH}$ = 173 Hz, $^2J_{CH}$ = 5 Hz, $\mathit{C}H_a$), 71.22 (ddd, $^1J_{CH}$ = 171 Hz, $^2J_{CH}$ = 7 Hz, $^3J_{CH}$ = 7 Hz, $\mathit{C}H_b$), 96.52 (m, $\mathit{C}C(CH_3)_3$). Anal. Calcd for $C_{26}H_{42}Fe$: C, 76.08; H, 10.31. Found: C, 75.89; H, 10.38.

Crystal Structure Determination. A crystal of 5 suitable for X-ray structural determination was mounted on a glass fiber with epoxy cement. Crystal, data collection, and refinement parameters are collected in Table 1. The unit-cell parameters were obtained from the least squares fit of 25 reflections (4° ≤ 2Θ ≤ 55°). The systematic absences in the diffraction data uniquely established the space group as *Cmca* (No. 64). The semiempirical absorption correction program XABS was applied to the data set.[30]

The structure was solved by direct methods which located the Fe atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (d_{CH} = 0.960 Å, $U = 1.2U$ for attached C). All non-hydrogen atoms were refined with anisotropic thermal parameters. The asymmetric unit contains one independent half-molecule which resides on a crystallographic inversion center. All software and the sources of the scattering factors are contained in the SHELXTL-PLUS(4.2) program library.[31]

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Supplementary Material Available: Complete listings of bond distances and angles, anisotropic displacement coefficients, H-atom coordinates, and isotropic displacement coefficients for 5 (2 pages). Ordering information is given on any current masthead page.

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