

Synthesis and structural characterization of Hexa(cyclohexyl)ferrocene, $[1,2,4-(C_6H_{11})_3C_5H_2]_2Fe$

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Abstract

1,2,4-tricyclohexylcyclopentadiene can be formed from the phase-transfer catalyzed addition of cyclohexyl bromide to cyclopentadiene. Reaction of two equivalents of its lithium salt with $FeCl_2$ in THF produces the corresponding substituted ferrocene. Crystals of orange $[1,2,4-(C_6H_{11})_3C_5H_2]_2Fe$ grown from toluene are monoclinic, space group $C2/c$, with $a = 16.386$ (4) Å, $b = 12.142$ (3) Å, $c = 21.003$ (3) Å, $\beta = 107.38$ (1), and $D_{calcd} = 1.131$ g cm⁻³ for $Z = 4$. Least-squares refinement based on 1291 observed reflections led to a final R value of 0.049. The molecule possesses a classic sandwich geometry with staggered rings and a crystallographically imposed two-fold rotation axis passing through the metal center. Despite the presence of six cyclohexyl rings, the cyclopentadienyl ligands can orient themselves around the iron to avoid unfavorable inter-ring steric interactions. As a result, the average Fe–C ring distance of 2.06 (1) Å in hexa(cyclohexyl)ferrocene is not significantly longer than the corresponding distance in ferrocene itself.

Key words: Ferrocenes; Iron; Cyclopentadienes; Metallocenes

1. Introduction

An estimated 80% of all transition metal organometallic compounds contain one or more cyclopentadienyl rings [1], yet the versatility of the basic C_5R_5 framework seems far from exhausted. There has been increasing demand for sterically bulky cyclopentadienes because these rings often confer enhanced kinetic stability on complexes with large metal centers (e.g. *s*-block, lanthanide and actinide complexes) [2,3]. Many routes to these highly substituted rings are tedious, often requiring the sequential addition of sterically bulky groups. For example, the production of tetraisopropylcyclopentadiene by the stepwise addition of isopropyl bromide to C_5H_6 requires over ten steps, and produces the diene in low yield [4]. An exception to this generalization is the recent report by Venier and Casserly [5] of the facile phase-transfer catalyzed synthesis of di- and tri-*t*-Bu)cyclopentadienes in up to 90% yield. We have modified the procedure to produce tri- and tetraisopropylcyclopentadiene in single-

pot syntheses in good yields, and have incorporated the rings into a variety of main-group complexes [6–8]. We report here the use of the phase-transfer method in the synthesis of tricyclohexylcyclopentadiene, and the latter's use in the preparation of hexa(cyclohexyl)ferrocene. Although 1,1'-bis[(cyclohexyl)ferrocene] $[(C_6H_{11})C_5H_4]_2Fe$ has been described [9,10], the present compound represents the first metallocene with more than a single cyclohexyl group per Cp ring.

2. Experimental details

2.1. General considerations

Unless otherwise noted, chemicals were handled with high vacuum, Schlenk, or drybox techniques. Proton NMR spectra were obtained at 300 MHz with a Bruker NR-300 spectrometer and were referenced to the residual proton resonances of C_6D_6 (δ 7.15); carbon (¹³C) NMR spectra were recorded at 75.5 MHz on a Bruker NR-300 spectrometer and were referenced to the residual ¹³C resonances of C_6D_6 (δ 128.0). Infrared data were obtained on a Perkin-Elmer 1600 FT spectrometer.

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2.2. Materials

Anhydrous ferrous chloride, *n*-butyllithium, AdogenTM 464 and cyclohexyl bromide were purchased from Aldrich. Cyclopentadiene was obtained by thermal cracking of the commercial dimer (MCB). Solvents were dried and degassed using standard methods [11]. NMR solvents were vacuum distilled from Na/K (22/78) alloy. Other commercially available reagents were used without purification.

2.3. Synthesis of tricyclohexylcyclopentadiene

To a 3 L three-neck Morton flask fitted with a condenser, mechanical stirrer, heating mantle, thermometer and an inlet adapter was added aqueous KOH (50%, 790 mL, *ca.* 10 mol) and AdogenTM 464 (10 g). Freshly cracked cyclopentadiene (21.0 mL, 0.254 mol) and cyclohexyl bromide (150 mL, 1.22 mol) were added and stirring was started. The mixture turned brown and became warm (50°C). The vigorously stirred mixture was maintained at 60°C overnight, after which it was extracted with hexane (3 × 50 mL). The hexane was then removed by rotary evaporation to leave a brown oil.

The oil was transferred to a 25 cm × 7.5 cm silica gel chromatography column and eluted with hexane. A yellow band was collected from which most of the hexane was removed by rotary evaporation (6 h, 40°C at 15 torr). The remaining solvent was removed under higher vacuum (10⁻³ torr), leaving crude tricyclohexylcyclopentadiene (mixture of isomers) as a thick amber oil (64.7 g, 81%). It was not possible to distill the product, even at 200°C and 10⁻⁶ torr. ¹H NMR (C₆D₆): δ 5.68–6.26 (several peaks, vinyl ring-CH), 2.84 (s, ring-CH₂), 2.80 (s, ring-CH₂), 2.53–2.74 (m, cyclohexyl-CH), 2.36–2.53 (m, cyclohexyl-CH), 2.10–2.36 (m, cyclohexyl-CH), 1.42–2.10 (m, cyclohexyl-CH₂), 0.83–1.42 (m, cyclohexyl-CH₂). Confirmation of the 1,2,4-substitution pattern in the diene was obtained by the synthesis of its ferrocene derivative.

2.4. Preparation of [1,2,4-(C₆H₁₁)₃C₅H₂]₂Fe

A 2.08 g portion (6.53 mmol) of Li[(C₆H₁₁)₃C₅H₂] (made from the reaction of *n*-BuLi in hexane and the diene from the above preparation) was dissolved in THF (25 mL). Anhydrous FeCl₂ (0.435 g, 3.43 mol) was added to the solution and the mixture stirred overnight. At this point the air-stable mixture of products was taken from the glovebox, and the solvent was removed by rotary evaporation. Toluene (30 mL) was added to the black residue. The solution was heated to boiling and suction filtered while hot. The toluene was removed under vacuum and the resultant oil was placed on a 12 cm × 2 cm silica gel column and eluted with toluene. An orange-yellow band was collected and the

solvent removed, leaving crude hexa(cyclohexyl)ferrocene as an orange-red oil. Crystallization was accomplished from acetone or acetone/water mixtures, yielding spectroscopically clean amber crystals (0.514 g, 23% yield), 190–192°C (dec.). Anal. Calc. for C₄₆H₇₀Fe: C, 81.38; H, 10.39. Found: C, 81.09; H, 10.82. ¹H NMR: δ 3.96 (s, ring-CH), 1.0–2.7 (br m, C₆H₅). ¹³C NMR (assignments made by means of DEPT pulse sequences): δ 91.77 (ring-C), 91.15 (ring-C), 64.56 (ring-CH), 38.26 (cyclohexyl CH₂), 37.57 (cyclohexyl CH), 36.30 (cyclohexyl CH), 34.74 (cyclohexyl CH₂), 33.74 (cyclohexyl CH₂), 27.80 (cyclohexyl CH₂), 27.57 (cyclohexyl CH₂), 27.25 (cyclohexyl CH₂), 26.88 (cyclohexyl CH₂). Principal IR bands (KBr pellet, cm⁻¹): 2922 s, 2849 s, 1445 m, 1344 w, 1261 m, 1095 m, 1026 m. Mass spectrum (EI) *m/z*: 678 (M⁺), 595 (M⁺ - C₆H₁₁), 512 (M⁺ - 2C₆H₁₁), 429 (M⁺ - 3C₆H₁₁).

2.5. X-ray Crystallography of [1,2,4-(C₆H₁₁)₃C₅H₂]₂Fe

Attempts were made to grow crystals of [1,2,4-(C₆H₁₁)₃C₅H₂]₂Fe from a variety of solvents, but only those from toluene proved to be suitable for diffraction study. A total of five crystals were examined on the diffractometer. Initial examination of the diffraction vectors obtained during a random search indicated that the crystals were twinned. Most of them were also poorly diffracting, but the best one was retained for further examination. All measurements were performed at 20 ± 1°C on a Rigaku AFC6S diffractometer with graphite monochromated Cu-Kα (λ = 1.5418 Å) radiation. Relevant crystal and data collection parameters for the present study are given in Table 1.

In the most strongly diffracting sample, the INDEX TWIN routine of the TEXSAN crystallographic package identified a self-consistent set of vectors that fit a triclinic cell, and a Delauney reduction did not suggest the presence of higher symmetry. During preliminary data collection, a systematic absence was apparent for 00*l* reflections with *l* = odd, which is inconsistent with a triclinic lattice. Additional reflections were then collected, and the INDEX TWIN program now identified 25 vectors describing a monoclinic cell. A Delauney reduction indicated that this cell was C-centered; it was proven to be correct by the successful solution and refinement of the structure.

Data collection was performed using a continuous ω-2θ scan with stationary backgrounds. No decay was evident in the intensities of three representative reflections measured after every 150 reflections. Data were reduced to a unique set of intensities and associated sigma values in the usual manner. The structure was solved by a combination of Patterson, direct methods (DIRDIF) and Fourier techniques. An empirical absorp-

TABLE 1. Crystal data and summary of data collection for [1,2,4-(C₆H₁₁)₃C₅H₂]₂Fe

Formula	C ₄₆ H ₇₀ Fe
<i>f</i> _w	678.91
Color of crystal	amber
Crystal dimensions (mm)	0.18 × 0.45 × 0.50
Space group	C2/c
Cell dimension (at 20°C, 25 reflections)	
<i>a</i> (Å)	16.386(4)
<i>b</i> (Å)	12.142(3)
<i>c</i> (Å)	21.003(3)
<i>β</i> (deg)	107.38(1)
<i>V</i> (Å ³)	3988(3)
<i>Z</i>	4
<i>D</i> (calc.) (g cm ⁻³)	1.131
Wavelength (Å)	1.54178
Abs. coeff. (cm ⁻¹)	32.24
Type of scan	$\omega - 2\theta$
Scan speed, deg min ⁻¹ (in omega)	4.0
Scan width	1.73 + 0.30 tan θ
Background counting	Stationary counts;
peaks/background counting time	= 2:1
Limits of data collection	6° ≤ 2 θ ≤ 120°
Total no. of reflections collected	4165
No. of unique intensities	2110
No. with <i>F</i> > 3.00 σ (<i>F</i>)	1291
<i>R</i> (<i>F</i>)	0.049
<i>R</i> _w (<i>F</i>)	0.059
Goodness of fit	1.98
Max Δ/σ in final cycle	0.01
Max/min peak	
(Final diff. map) (e Å ⁻³)	0.34 / -0.23

TABLE 2. Fractional coordinates and isotropic thermal parameters (Å²) for the non-hydrogen atoms in [1,2,4-(C₆H₁₁)₃C₅H₂]₂Fe

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} ^a
Fe(1)	0 ^b	0.0902(1)	1/4 ^b	2.22(8)
C(1)	-0.0183(3)	0.1488(5)	0.1552(4)	2.3(3)
C(2)	-0.0166(3)	0.0304(5)	0.1549(4)	2.4(3)
C(3)	0.0644(3)	-0.0023(5)	0.1981(4)	2.3(3)
C(4)	0.1130(3)	0.0928(5)	0.2255(3)	2.3(3)
C(5)	0.0611(4)	0.1855(5)	0.1984(3)	2.7(3)
C(11)	-0.0846(4)	0.2225(5)	0.1095(4)	3.0(4)
C(12)	-0.1078(4)	0.3237(5)	0.1448(4)	3.9(4)
C(13)	-0.1723(4)	0.3985(6)	0.0944(5)	5.3(5)
C(14)	-0.1395(6)	0.4346(7)	0.0382(5)	6.2(5)
C(15)	-0.1167(5)	0.3359(7)	0.0029(4)	5.5(5)
C(16)	-0.0525(4)	0.2626(6)	0.0523(4)	4.3(4)
C(21)	-0.0820(3)	-0.0477(5)	0.1129(5)	2.5(4)
C(22)	-0.0738(4)	-0.0533(5)	0.0431(5)	3.5(4)
C(23)	-0.1365(4)	-0.1346(6)	-0.0036(4)	4.3(4)
C(24)	-0.1282(4)	-0.2474(6)	0.0276(5)	4.3(4)
C(25)	-0.1384(4)	-0.2434(5)	0.0973(5)	4.0(4)
C(26)	-0.0743(4)	-0.1637(5)	0.1418(4)	3.5(4)
C(41)	0.2048(3)	0.0944(5)	0.2701(3)	2.9(3)
C(42)	0.2429(4)	-0.0192(5)	0.2869(4)	3.8(4)
C(43)	0.3346(4)	-0.0144(6)	0.3344(4)	4.6(4)
C(44)	0.3900(4)	0.0539(7)	0.3031(4)	5.9(5)
C(45)	0.3539(4)	0.1653(7)	0.2844(5)	6.7(5)
C(46)	0.2612(4)	0.1597(6)	0.2379(4)	4.7(4)

^a Isotropic values for those atoms refined anisotropically are calculated using the formula given by W.C. Hamilton, *Acta Crystallogr.* 12 (1959) 609–610.

^b Not refined.

tion correction using the program DIFABS was applied to the data. All non-hydrogen atoms were refined anisotropically. As not all the hydrogen atoms were evident on a difference Fourier map, their positions were calculated using idealized geometries based on packing considerations and *d* (C–H) = 0.95 Å. The positions were fixed for the final cycles of refinement. A final difference map was featureless. Positional parameters are provided in Table 2; non-hydrogen bond distances and angles are summarized in Table 3.

3. Results and discussion

3.1. Synthesis of Tricyclohexylcyclopentadiene

The one-pot reaction of cyclopentadiene and five equivalents of cyclohexyl bromide under basic conditions produces tricyclohexylcyclopentadiene in high yield, with little evidence for lower or higher degrees of substitution. Purification of the crude product is difficult, as the diene is a highly viscous oil that is not easily manipulated; it does not distill under vacuum. The multiple, broad resonances observed in its ¹H NMR spectrum (especially in the vinyl region) indicate that

the oil is a mixture of isomers. The diene readily reacts with *n*-butyllithium to generate a solid lithium salt.

3.2. Synthesis and Properties of [1,2,4-(C₆H₁₁)₃C₅H₂]₂Fe

The ferrocene derivative of tricyclohexylcyclopentadiene was prepared from Li[(C₆H₁₁)₃C₅H₂]₂ and FeCl₂ in THF. Hexa(cyclohexyl)ferrocene was isolated as a red-orange, air-stable compound. The modest recrystallized yield partially reflects its high solubility in organic solvents, including aromatics and alkanes. Many combinations of solvents used in attempts at crystal-

TABLE 3. Summary of bond distances and angles for [1,2,4-(C₆H₁₁)₃C₅H₂]₂Fe

Fe–C (ring) (av.)	2.06(1) Å
Fe–ring centroid	1.66 Å
Planarity of Cp ring	within 0.002 Å
C–C (Cp ring) (av.)	1.42(2) Å
C(ring)–cyclohexyl (<i>ipso</i> C) (av.)	1.51(1) Å
C–C (cyclohexyl ring) (av.)	1.52(2) Å
Av. displacement of <i>ipso</i> carbons from ring plane	0.14 Å
displacement angle (α)	5.3°

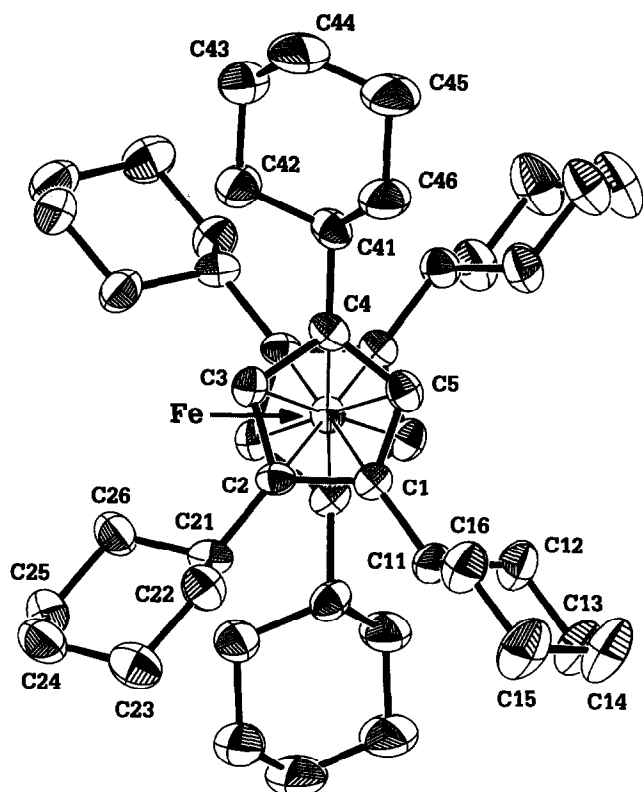


Fig. 1. ORTEP view of non-hydrogen atoms of $[1,2,4-(C_6H_{11})_3C_5H_2]_2Fe$, giving the numbering scheme used in Table 2. Thermal ellipsoids are shown at the 50% level.

lization yielded only oils; a solid was eventually obtained by precipitation from an acetone/water mixture; sometimes the use of acetone alone would induce crystallization.

In the proton NMR spectrum of hexa(cyclohexyl) ferrocene, the peaks corresponding to the cyclohexyl protons appear as broad, uninterpretable multiplets. Such broadening is indicative of hindered rotation of the cyclohexyl groups. In contrast, the ^{13}C NMR spectrum contains sharp, well-defined peaks for the cyclopentadienyl ligand. However, the observation of seven resonances for the cyclohexyl methylene carbon atoms when only six would be expected for a 1,2,4 ring-substitution pattern again points to a loss of symmetry caused by hindered cyclohexyl group rotation.

In its EI-mass spectrum, hexa(cyclohexyl) ferrocene displays the expected parent ion (M^+) peak at $m/z = 678$, along with peaks corresponding to the loss of one, two, and three cyclohexyl rings. The compound undergoes a reversible one-electron oxidation in CH_2Cl_2 at +0.16 V *vs.* SCE. For comparison, ferrocene undergoes oxidation at +0.44 V, and decamethylferrocene at -0.12 V in the same solvent [12]. Thus the metal center in $[1,2,4-(C_6H_{11})_3C_5H_2]_2Fe$ is somewhat more electron-rich than in ferrocene, as expected from the

electron-donating ability of the cyclohexyl groups. Alkyl groups have previously been shown to exert a roughly additive effect on the oxidation potentials of substituted ferrocenes [13]; the potential of the hexasubstituted $[1,2,4-(C_6H_{11})_3C_5H_2]_2Fe$, which lies nearly halfway between ferrocene and the decasubstituted Cp_2^*Fe , follows this trend.

3.3. Structure of $[1,2,4-(C_6H_{11})_3C_5H_2]_2Fe$

Crystals of $[1,2,4-(C_6H_{11})_3C_5H_2]_2Fe$ were grown by slow evaporation of a saturated toluene solution and studied by X-ray diffraction. The molecule displays a classic sandwich geometry, with a crystallographically imposed two-fold rotation axis passing through the iron atom (Fig. 1).

The rings adopt an almost perfectly staggered arrangement (twist angle of 34.1° , *vs.* 36° for a perfect stagger), which serves to minimize contacts between the cyclohexyl groups. If the orientation of a cyclohexyl ring is defined as the angle between the ring plane and the plane formed by the two methylene carbons next to an *ipso* carbon and the adjacent ring carbon, the orientations around the ring are 79.0° , 56.9° and 36.1° (involving C1, C2, and C4 respectively). A result of the cyclohexyl orientations is that the metallocene is less sterically crowded than might be expected; all inter-ring $C \cdots C'$ contacts involving the cyclohexyl groups are greater than 3.8 Å, and thus of little energetic significance (Fig. 2).

The efficient packing of the cyclohexyl groups generates little structural distortion in the iron-ring parameters. The cyclopentadienyl rings are tilted only 2.0° relative to each other, and the *ipso* carbons of

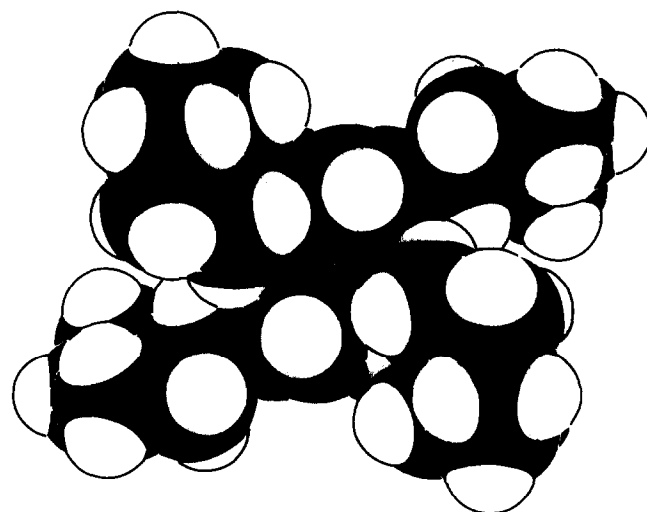


Fig. 2. Space-filling view of $[1,2,4-(C_6H_{11})_3C_5H_2]_2Fe$, illustrating the manner in which the cyclohexyl orientations minimize close inter-ring contacts.

each cyclohexyl group are displaced an average of 0.14 Å from the ring plane. The average Fe–C (ring) distance of 2.06 (1) Å is not significantly longer than that in ferrocene (2.03 Å) [14] or Cp₂*Fe (2.050 (2) Å) [15]. Perhaps the lack of greater steric impact may be more understandable if the cyclohexyl ligand is considered as a type of constrained isopropyl group; the extra bulk of the C₆H₁₁ unit extends away from the cyclopentadienyl ring, leaving the basic Cp'FeCp' framework undisturbed.

4. Conclusion

The synthesis of hexa(cyclohexyl)ferrocene enlarges the known range of metallocenes containing "supra-cyclopentadienyl" rings [1]. The ability of the cyclohexyl substituents to pack to minimize unfavorable contacts allows the metallocene core to remain relatively unaltered. Such packing makes cyclohexyl group rotation more difficult, however, as evidenced by the broad resonances observed in proton NMR spectra. Whether such efficient packing would be maintained in the more highly substituted tetra- and penta(cyclohexyl)cyclopentadienes remains unknown. We are currently investigating the synthesis of these hydrocarbons and their metal derivatives.

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