

Article

Syntheses and Crystal Structures of Ferrocenoindenes

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Abstract: Ferrocenoindenes display planar chirality and thus represent valuable ligands for asymmetric catalysis. Here, we report on the synthesis of novel 3-(1,1-dibromomethylene)ferroceno[1,2-a]indene, (Z)-3-(1-bromomethylene)-6-iodoferroceno[1,2-a]indene, and benzo[5,6-f]ferroceno[2,3,a]inden-1-one. Any application-oriented design of chiral catalysts requires fundamental knowledge about the ligands involved, not only in terms of atom-connectivity, but also in terms of their three-dimensional structure and steric demand. Therefore, the crystal structures of 2-ferrocenylbenzoic acid, ferroceno[1,2-a]indene, and (Z)-3-(1-bromomethylene)-6-iodoferroceno[1,2-a]indene have been determined. The bond-lengths that can be retrieved therefrom also allow for an estimation of the reactivity of the aryl-iodo, bromo-methylidene and dibromomethylidene moieties.

Keywords: ferrocene; ferrocenoindene; planar chiral; racemic crystal

1. Introduction

Metallocene-based ligands, and here particularly ferrocene-, ruthenocene- and cobaltocene-based systems are of interest due to their unique and intriguing properties such as reversibility of oxidation state, Lewis-base/Lewis-acid behavior, and steric design [1]. Their interactive and cooperative effects are uncovered by probing spectroscopic, photonic, magnetic, electronic and Moessbauer behavior of

these substances [2]. The resulting design as well as manufacture of new materials represent two key steps in the advancement of technology, as it depends almost completely on the rate at which useful new materials can be devised and synthesized [3]. Due to its stability and availability and the vast repertoire of elaborated derivation sequences, ferrocene is again favored over other metallocenes [4] or other organometallic fragments [5]. In particular, planar chiral ferrocenes are important ligands in the area of homogeneous asymmetric catalysis [6]. In order to enforce coplanarity, the pendant ferrocene has to be attached by anellation instead of simple substitution based on one single bond. Such systems can be provided by a straightforward, optimized route based on ferroceno[2,3-a]indenone and its derivatives [7]. While chiral diphosphoferrocenes such as Josiphos[®], Taniaphos[®], MandyPhos[®] and BoPhoz[®] have successfully been used in enantioselective reactions [8–11], planar chiral ferroceno[2,3-a]indenes have found application as ligands in stereoselective metallocene-catalyzed olefin polymerization [7] as well as redox active incorporates for macromolecular arrays [12]. In this contribution we describe the synthesis of ferroceno[2,3-a]indenes relevant to the above mentioned applications. The crystal structures of three selected compounds are presented.

2. Results and Discussion

Starting from 2-ferrocenylbenzoic acid (**1**), 2-ferrocenylbenzoyl chloride was prepared using PCl_5 and cyclized by intramolecular Friedel-Crafts acylation using AlCl_3 to give ferroceno[2,3-a]inden-1-one (**2**), a planar chiral compound, as a racemate (Scheme 1) [7,13]. Separation of the two enantiomers by HPLC on a β -cyclodextrin-derived chiral column has been reported [13]. Several synthetic routes to ferroceno[2,3-a]indene (**3**) have been disclosed: (1) reduction of **2** with LiAlH_4 to diastereomeric ferroceno[2,3-a]inden-1-ols, subsequent formation of a cationic complex, and reduction with Na/NH_3 [7]; or (2) direct hydrogenation of **2** [7]. Alternatively, intramolecular Friedel-Crafts alkylation of 2-ferrocenylbenzylic chloride using AlCl_3 [14] also gave the indene **3** in low yield. Single crystals of the starting material **1** were obtained from CH_2Cl_2 . The radical cation of indene **3** yielded an interesting dimer, the crystal structure of which has been determined [15].

The new dibromo-compound, 3-(1,1-dibromomethylene)ferroceno[1,2-a]indene (**4**), was obtained by Wittig-type reaction of **2** with $\text{CBr}_4/\text{PPh}_3$ in good yield and gave X-ray quality crystals from CH_2Cl_2 . Reaction of **3** with *n*-butyllithium followed by the addition of Cl_2SiMe_2 gave the dimethylsilylene-bridged compound *rac*-bis(4H-indeno[2,3-a]ferrocen-4-yl)dimethylsilane, the crystal structure of which has been reported [16]. This compound has been used for the manufacture of Zr-based metallocenes for 1-olefin polymerization and copolymerization with norborn-2-ene [7].

By analogy, 6-iodoferroceno[2,3-a]inden-1-one (**6**) was accessible from 5-iodo-2-ferrocenylbenzoic acid (**5**) [13]. This compound was used for a Sonogashira-Hagihara coupling [13]. A Wittig bromomethylenation gave the new 3-(bromomethylene)-6-iodoferroceno-[1,2-a]indene (**7**) in acceptable yield. The *E* and *Z* isomers were separated, and the *Z* isomer crystallized from CH_2Cl_2 . This ferrocene-annellate offers all the potential for Pd-mediated coupling reactions with two sites of different reactivity ($\text{Br} < \text{I}$). By analogy again, ferroceno[2,3-a]benzo[5,6]inden-1-one (**9**) was prepared from 3-ferrocenyl-2-naphthoic acid (**8**).

The asymmetric units of **1**, **3**, and **7** contain two nearly identical molecules. In all crystals the axes of the centroids of the five-membered rings through the iron atoms Fe1 and Fe2 are approximately

perpendicular to each other. The ferrocene moieties adopt eclipsed conformations. Between the molecules are no strong interactions, except for **1**, where two molecules form an eight-membered ring via hydrogen bonding of the two carboxylic acid groups (Figure 1) ($O_2-H\cdots O_3$: $H\cdots O_3$ 1.75(4) Å and $O_2\cdots O_3$ 2.620(3) Å, O_2-H-O_3 170(4)°; $O_4-H\cdots O_1$: $H\cdots O_4$ 1.86(5) Å and $O_4\cdots O_1$ 2.713(3) Å, O_4-H-O_1 169(4)°). However, the two independent molecules in the structures of **3** and **7** represent enantiomers due to their planar chirality, as can be seen from the overlays in Figures 2 and 3. These are therefore racemic crystals. Crystal data and structure refinement details are summarized in Table 1.

Scheme 1. Synthesis of ferrocenoindenes and ferrocenobenzoindenes.

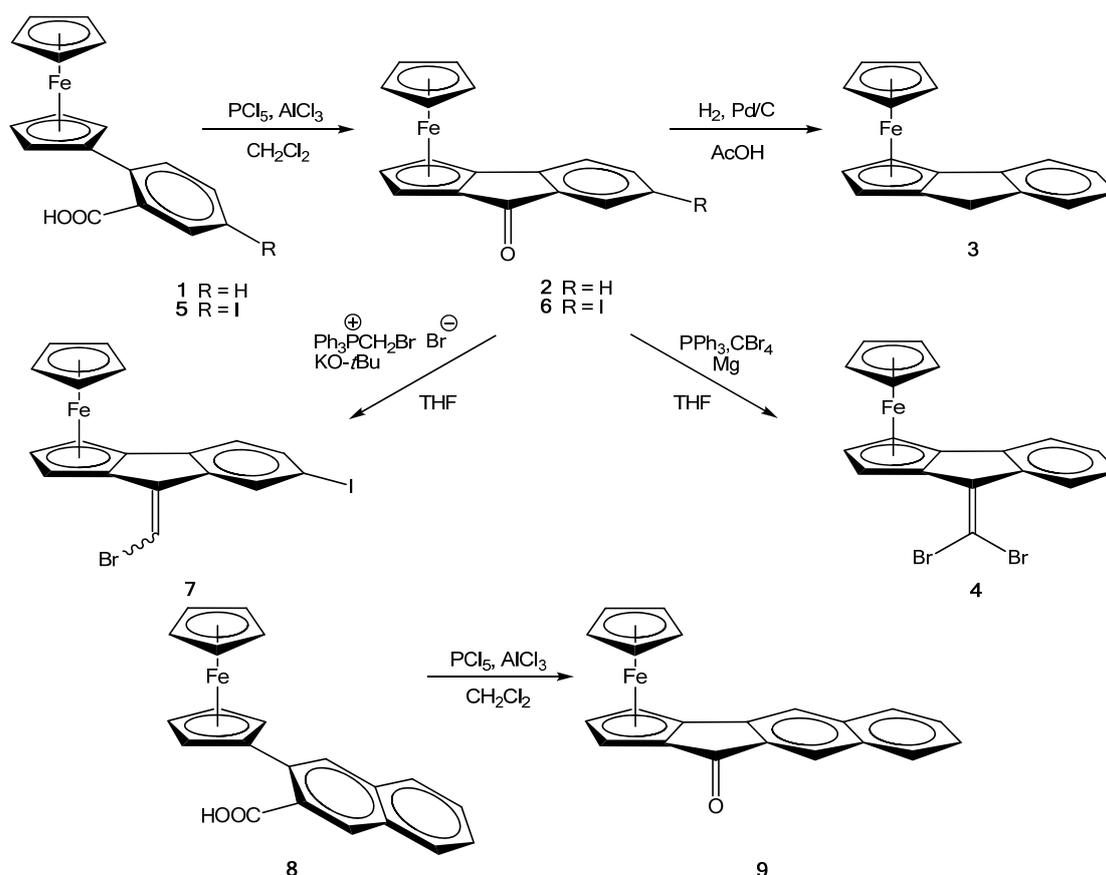


Figure 1. Hydrogen bonding between two independent molecules of **1**.

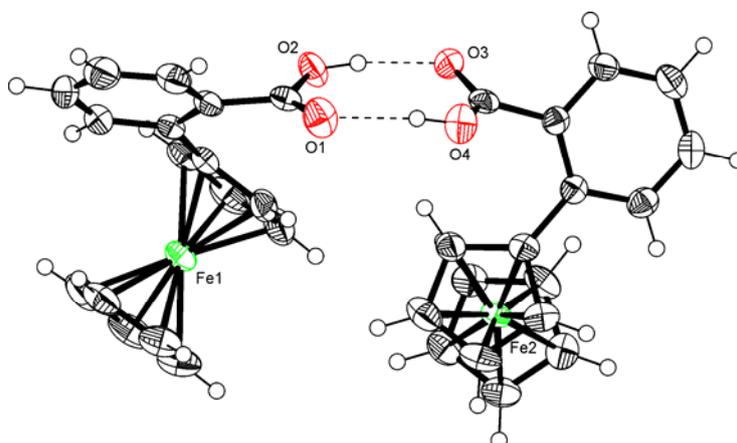


Figure 2. (a) Two independent molecules in the crystal structure of **3**; (b) Overlay of the two enantiomers.

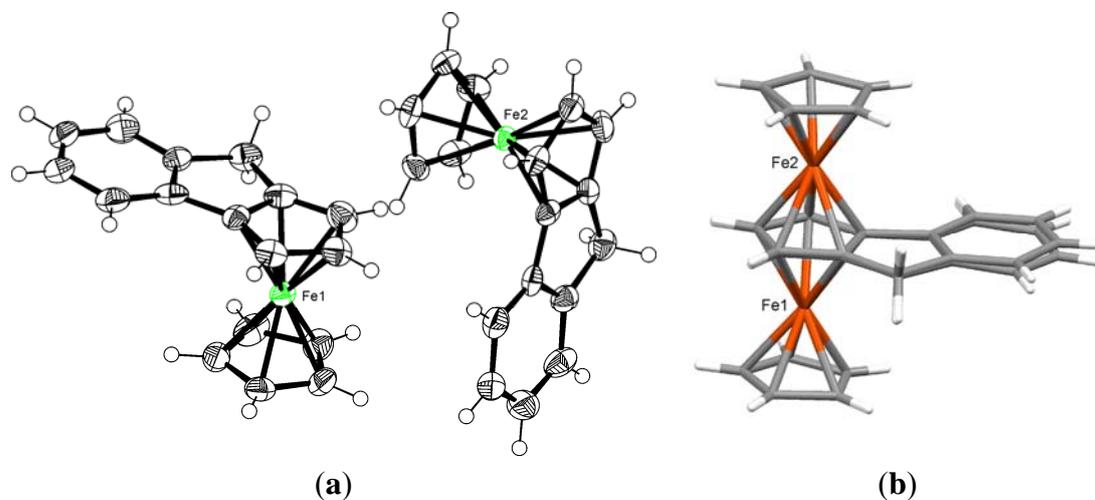


Figure 3. (a) Two independent molecules in the crystal structure of **7**; (b) Overlay of the two enantiomers.

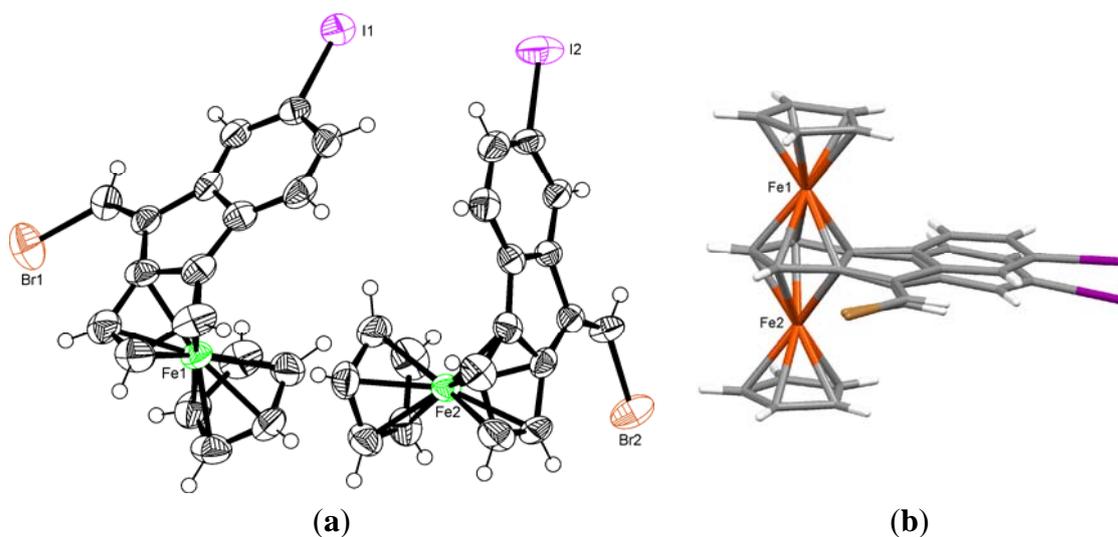


Table 1. Crystal data and structure refinement details.

Compound	1	3	7
CCDC no.	904160	904161	904162
Chemical formula	C ₁₇ H ₁₄ FeO ₂	C ₁₇ H ₁₄ Fe	C ₁₈ H ₁₂ BrFeI
<i>M_r</i>	306.13	274.13	490.94
Crystal size/mm ³	0.40 × 0.25 × 0.15	0.60 × 0.60 × 0.20	0.60 × 0.30 × 0.25
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	7.918(2)	12.12(2)	7.244(1)
<i>b</i> /Å	12.389(2)	19.85(3)	12.262(2)
<i>c</i> /Å	14.420(3)	10.18(2)	19.820(2)

Table 1. Cont.

Compound	1	3	7
$\alpha/^\circ$	99.27(2)	90	73.45(1)
$\beta/^\circ$	95.58(2)	90.05(9)	88.98(1)
$\gamma/^\circ$	101.29(2)	90	73.18(1)
$V/\text{\AA}^3$	1356.9(5)	2449(7)	1611.4(4)
Z	4	8	4
$D_x/\text{g cm}^{-3}$	1.50	1.49	2.02
μ/mm^{-1}	1.11	1.21	5.32
$F(000)/e$	632	1136	936
Temperature/K	218	213	293
$\theta_{\text{max}}/^\circ$	23.0	23.0	25.0
h, k, l range	$0 \leq h \leq 8$ $-13 \leq k \leq 13$ $-15 \leq l \leq 15$	$-13 \leq h \leq 13$ $-1 \leq k \leq 21$ $-1 \leq l \leq 11$	$-1 \leq h \leq 8$ $-14 \leq k \leq 14$ $-23 \leq l \leq 23$
Absorption correction	None	ψ scan	ψ scan
Measured reflections	3897	4407	6429
Independent reflections (R_{int})	3577 (0.020)	3368 (0.026)	5601 (0.034)
Observed reflections [$I \geq 2\sigma(I)$]	3026	2732	3672
Restraints/parameters	2/370	0/326	0/380
R_1/wR_2 [$I \geq 2\sigma(I)$]	0.030/0.069	0.034/0.072	0.045/0.090
R_1/wR_2 (all data)	0.039/0.072	0.051/0.077	0.089/0.101
Goodness of fit	1.02	1.02	0.97
$\Delta\rho_{\text{max/min}}/e \text{\AA}^{-3}$	0.33/−0.26	0.29/−0.21	0.98/−0.72

3. Experimental Section

All reactions were carried out in the absence of air using standard Schlenk techniques. Solvents were deoxygenated, purified and dried using standard procedures. Instrumentation: Bruker AC 200 and Varian Gemini 200 (^1H and ^{13}C NMR); Nicolet 510 FT-IR (IR); Varian CH-7 (MS); Siemens P4 (X-ray). Melting points were determined on a Kofler hot-plate microscope and are uncorrected. The synthesis and the spectroscopic data of 2-ferrocenylbenzoic acid (**1**) [7,17], ferroceno[2,3-*a*]inden-1-one (**2**) [7,17], ferroceno[1,2-*a*]indene (**3**) [7], 2-ferrocenyl-5-iodobenzoic acid (**5**) [13], 6-iodoferroceno[2,3-*a*]inden-1-one (**6**) [13], and 3-ferrocenyl-2-naphthoic acid (**8**) [18] have been reported elsewhere.

3.1. 3-(1,1-Dibromomethylene)ferroceno[1,2-*a*]indene (**4**)

Triphenylphosphine (1365 mg, 5.206 mmol) and CBr_4 (863 mg, 2.603 mmol) were dissolved in THF (10 mL), magnesium (63 mg, 2.603 mmol, activated with mercury (II) chloride) was added, and the mixture was stirred for 30 min. **2** (500 mg, 1.74 mmol) was added, the mixture was stirred at room temperature for 20 h and finally refluxed for another 48 h. The product was obtained by flash chromatography over silica gel (G60, hexane). Yield: 546 mg (71%); m.p. 116 °C. IR (KBr): 3054 w, 2925 w, 2238 w, 1777 w, 1729 w, 1605 m, 1574 m, 1495 m, 1465 m, 1430 m, 1410 m, 1362 m, 1316 w, 1301 m, 1258 m, 1216 w, 1167 w, 1148 m, 1125 m, 1106 s, 1082 w, 1055 w, 1044 m, 1023 m, 1000 s, 969 m, 940 w, 907 vs, 874 w, 857 w, 837 s, 824 m, 807 vs, 780 s, 755 vs, 726 m, 695 s,

677 w, 619 w, 596 m, 579 s, 563 w, 521 vs, 500 vs, 467 s, 442 s. ^1H NMR (CDCl_3): δ 3.90 (s, 5H), 4.37 (t, 1H, $J = 2.44$), 4.58 (d, 1H, $J = 2.44$), 5.07 (d, 1H, $J = 2.44$), 6.97–7.63 (m, 4H). ^{13}C NMR (CDCl_3): δ 62.2, 66.4, 67.4, 68.6, 72.2, 72.1, 82.2, 99.4, 120.8, 125.7, 129.7, 132.7, 134.2, 134.6. MS (EI, 70 eV): m/z (%) = 444 (100), 364 (81), 260 (16), 184 (20), 163 (23), 151 (13), 121 (9).

3.2. 3-(1-Bromomethylene)-6-iodoferroceno[1,2-*a*]indene (7)

A suspension of (1-bromomethyl)triphenylphosphonium bromide (12.1 g, 27.8 mmol) in THF (20 mL) was cooled to -90 °C and *t*-BuOK (3.1 g, 27.8 mmol) was added. After 10 min, indenone **6** (8.0 g, 18.5 mmol) was added, the mixture was warmed to room temperature and stirred overnight. The solvent was removed, H_2O was added, and the mixture was extracted with Et_2O (4×50 mL). Pure products were obtained by repeated chromatography (silica G60, hexane). Yield: 6.0 g (66%).

(*Z*)-Isomer: m.p. 89–91 °C. IR (KBr): 3080 s, 2923 w, 2360 w, 1625 s, 1590 w, 1555 m, 1493 s, 1438 s, 1409 s, 1385 w, 1360 m, 1310 m, 1273 w, 1254 w, 1233 m, 1196 m, 1165 w, 1135 w, 1104 s, 1081 m, 1054 s, 1038 w, 1013 m, 1000 s, 961 m, 903 w, 884 w, 872 w, 859 w, 820 vs, 808 vs, 783 m, 758 s, 733 s, 706 m, 695 s, 644 s, 614 s, 604 s, 577 m, 533 s, 502 m, 482 s, 459 vs, 434 w. ^1H NMR (CDCl_3): δ 3.95 (s, 5H), 4.50 (t, 1H, $J = 2.5$), 4.67 (d, 1H, $J = 2.5$), 5.16 (d, 1H, $J = 2.5$), 7.05 (s, 1H), 7.08 (d, 1H, $J = 7.9$), 7.52 (dd, 1H, $J = 1.8$, $J = 7.9$), 7.67 (d, 1H, $J = 1.5$). ^{13}C NMR (CDCl_3): δ 62.6, 66.6, 72.7, 86.0, 90.1, 72.2, 100.5, 122.5, 128.8, 130.3, 137.8, 140.3, 141.8, 144.0. MS (EI, 70 eV): m/z (%) = 491 (65), 490 (100), 411 (11), 243 (6), 163 (36).

(*E*)-Isomer: IR (KBr): 3064 w, 2921 s, 2852 m, 1713 w, 1625 m, 1549 m, 1490 m, 1438 m, 1409 m, 1385 w, 1360 w, 1310 w, 1258 m, 1196 w, 1146 w, 1106 s, 1079 m, 1057 m, 1038 w, 1015 w, 1001 m, 903 w, 895 s, 818 vs, 780 w, 758 w, 729 m, 718 w, 695 m, 685 m, 644 w, 614 m, 569 m, 558 w, 533 m, 500 m, 482 m, 459 vs. ^1H NMR (CDCl_3): δ 4.03 (s, 5H), 4.63 (s, 1H), 4.82 (s, 1H), 5.28 (s, 1H), 6.95 (s, 1H), 7.01–7.72 (m, 3H). ^{13}C NMR (CDCl_3): δ 62.6, 66.6, 72.7, 86.0, 90.1, 72.2, 100.5, 122.5, 130.2, 135.1, 137.8, 140.3, 141.7, 143.9.

3.3. Benzo[5,6,*f*]ferroceno[2,3-*a*]inden-1-one (9)

A solution of acid **8** (0.777 g, 2.18 mmol) in CH_2Cl_2 (20 mL) was cooled to 0 °C. PCl_5 (477 mg, 2.29 mmol) was added, and the solution was stirred for 4 h at room temperature, then cooled again to 0 °C, and AlCl_3 (0.305 g, 2.29 mmol) was added. The mixture was stirred overnight, poured on a solution of citric acid (1 M, 40 mL) and ice, and extracted with Et_2O . The product was purified by chromatography over silica (G60, hexane). Yield: 574 mg (78%); m.p. 152 °C. IR (KBr): 3054 s, 2927 s, 1684 vs, 1629 vs, 1590 w, 1511 w, 1486 m, 1453 m, 1430 s, 1414 m, 1393 w, 1331 m, 1254 s, 1218 s, 1191 w, 1140 m, 1113 s, 1036 m, 1009 m, 982 m, 955 m, 905 s, 864 w, 824 m, 793 m, 783 vs, 764 s, 749 vs, 710 w, 617 w, 525 w, 504 m, 484 vs, 475 s, 467 s. ^1H NMR (CDCl_3): δ 4.10 (s, 5H), 4.87–4.89 (t, 1H), 5.01–5.03 (t, 2H), 7.34–8.00 (m, 6H). ^{13}C NMR (CDCl_3): δ 66.6, 66.8, 73.5, 73.9, 76.8, 81.5, 118.6, 124.0, 127.0, 128.7, 128.9, 131.1, 137.2, 138.8, 196.2. UV-Vis (CH_3CN): λ_{max} (log ϵ) = 238 (4.60), 254 (4.54), 287 (4.62), 395 (3.31), 493 (3.20). MS (EI, 70 eV): m/z (%) = 339 (26), 338 (100).

3.4. Crystal Structure Determination of Compounds 1, 3, and 7

Intensity data were collected on a Bruker P4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The unit cell parameters were determined and refined from around 25 randomly selected reflections, obtained by P4 automatic routines. Data were measured via ω scans and corrected for Lorentz and polarization effects. For **3** and **7** an empirical absorption correction (ψ scan) was applied. The structures were solved by direct methods (SHELXS-86) [19] and refined by a full matrix least-squares procedure using F^2 (SHELXL-97) [20]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located by difference Fourier methods, but in the refinement they were included in calculated positions and refined with isotropic displacement parameters $U_{\text{iso}} = 1.2 U_{\text{eq}}$ of the attached carbon atoms. Only the hydrogen atoms at O(2) and O(4) of **1** were refined with isotropic displacement parameters. The structure of **3** was solved using a pseudo-merohedral twinning. This twinning can be described by a rotation around the a^* - or c^* -axis or by mirroring through the a^*b^* - or c^*b^* -planes, respectively. The twin ratio was around 2.7:1. By using the twin matrix the R_1 value changed from 0.141 to 0.034. CCDC reference numbers: 904160–904162. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

4. Conclusions

In summary, the synthetic routes to a series of substituted ferrocenoindenes and ferrocenobenzoindenes are presented. They are accessible via intramolecular Friedel-Crafts reactions. It should be stated that all indene-type compounds are produced as racemates; however, these can be separated via chiral HPLC. Therefore, the concept is valid for the synthesis of enantiomerically pure ferrocenoindenes and ferrocenobenzoindenes which may in due course be utilized as ligands in catalysis and asymmetric synthesis, respectively.

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