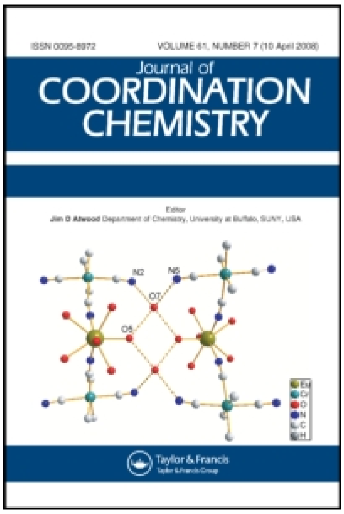


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

The synthesis and structure of a thiobenzyl-functionalized dibenzoferrocene complex

Owen J. Curnow[a]; Rong Shang[a]
[a] Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand

To cite this Article Curnow, Owen J. and Shang, Rong(2010) 'The synthesis and structure of a thiobenzyl-functionalized dibenzoferrocene complex', Journal of Coordination Chemistry, 63: 14, 2790 — 2799, First published on: 09 March 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958971003690447

URL: http://dx.doi.org/10.1080/00958971003690447

Journal of Coordination Chemistry
Vol. 63, Nos. 14–16, 20 July–20 August 2010, 2790–2799

The synthesis and structure of a thiobenzyl-functionalized dibenzoferrocene complex

OWEN J. CURNOW* and RONG SHANG

Department of Chemistry, University of Canterbury, Private Bag 4800,
Christchurch 8140, New Zealand

(*Received 10 December 2009; in final form 29 January 2010*)

3-(Thiobenzyl)indene (**2**) was prepared from lithium indenide and dibenzyl disulfide. Deprotonation with BuLi/TMEDA in THF and the addition of $FeCl_2$ gave the expected 1 : 1 mixture of *rac-* and *meso*-bis(1-thiobenzylindenyl)iron(II) (**3**). ^{13}C-NMR studies in THF suggest that **3** undergoes a ring-flipping process to interconvert *rac-* and *meso*-**3**. Complex **3** exhibits a reversible cyclic voltammogram with an oxidation potential of –177 mV *versus* the Fc/Fc^+ couple in dichloromethane. Indene (**2**) and ferrocene (**3**) were also characterised by X-ray crystallography.

Keywords: Ferrocene; Indenyl; Iron; Thioether

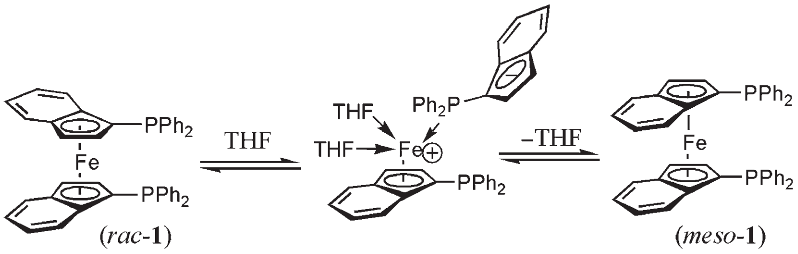
1. Introduction

Functionalized ferrocenes have been intensively investigated for a wide range of properties and applications [1]. The stability and stereochemical rigidity of the cyclopentadienyl–iron interaction is one of the reasons that ferrocenes are of such interest. Stereochemical rigidity is particularly important for planar chiral ferrocenyl phosphine complexes as any ring-flipping process would result in the racemization of the planar chiral center. In 2002, we first reported the remarkably facile ring-flipping process of bis(1-diphenylphosphinoindenyl)iron(II) (**1**) in which the *rac* and *meso* isomers interconvert in THF solution at ambient temperatures (scheme 1) [2]. A number of experiments indicated that the likely mechanism involves the reversible displacement of indenide by THF with the continued coordination of the ligand *via* the phosphine [3]. Subsequent studies have attempted to elucidate the steric and electronic factors involved in this process [4]. Although a number of thioether-functionalized ferrocenes are known [5], analogous indenyl compounds are unknown for iron, while, in the previously reported and well-characterized example, Rausch and coworkers [6] described the synthesis and styrene-polymerization ability of (1-thiomethylindenyl)-trichlorotitanium, although no structural study has been reported. Some 2-thioalkyl-substituted zirconocenes have been reported in the patent literature; however, no characterization data were included [7].

---

*Corresponding author. Email: owen.curnow@canterbury.ac.nz

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958971003690447



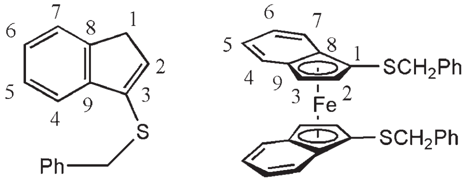
Scheme 1. Ring-flipping process for **1**.

2. Experimental

All experimental work was carried out under the argon or dinitrogen atmosphere using standard Schlenk techniques unless otherwise noted. THF and diethylether were distilled from Na/benzophenone under argon prior to use. Hexane and dichloromethane were distilled from calcium hydride under argon. Ethanol was distilled over magnesium turnings under argon. ^{1}H- and ^{13}C{^{1}H}-NMR data were collected on a Varian Unity-300 spectrometer operating at 300 and 75 MHz, respectively. Spectra were measured at ambient temperature with the residual solvent as internal standard. The numbering scheme for the NMR assignments is given in scheme 2. EI mass spectra were collected on a Kratos MS80RFA mass spectrometer. Elemental analyses were carried out by Campbell Microanalytical Services, University of Otago, Dunedin. UV-Vis spectra were obtained on a VARIAN Cary 50 Probe UV-Vis Spectrophotometer using 1 cm cuvettes. Electrochemical measurements were made in CH_2Cl_2 with 0.1 mol $[Bu_4N]BF_4$ electrolyte and using a three-electrode cell comprising of a platinum-disk working electrode (1 mm diameter), a platinum-wire auxiliary electrode, and a Ag/Ag^+ pseudo reference electrode. Sample concentration was 1.3 mmol. Voltammetry was performed using an Autolab Eco Chemie (The Netherlands) with the associated GPES software. All potentials are reported *versus* the ferrocene/ferrocenium (Fc/Fc^+) couple after referencing to *in situ* ferrocene. Electrochemical measurements were made at ambient temperature under an inert atmosphere. All reagents were used as supplied commercially.

2.1. *Synthesis of 3-(thiobenzyl)indene (2)*

Freshly distilled indene (9.3 mL, 0.080 mol) was added dropwise *via* a syringe to a stirred solution of *n*-BuLi (50 mL, 1.6 mol, 0.080 mol) in hexane (100 mL) on an ice-bath. A pale yellow solution was formed with a white precipitate. The solution was allowed to warm to the ambient temperature and then stirred overnight. Dibenzyldisulfide (19.7 g, 0.080 mol) was then added portion-wise and the reaction mixture was stirred vigorously for a further 12 h. A pink solution with a white precipitate was formed. This mixture was then filtered through a Celite column (10 × 3.5 cm). An orange solid was left after the evaporation of the solution. The crude product was flash chromatographed through alumina using diethylether : hexane (3 : 7). Recrystallization from hexane afforded 9.4 g (46%) of colorless needle-like crystals of **2**. ^{1}H-NMR ($CDCl_3$): δ 7.42–7.20 (m, 9H, H4/7



Scheme 2. Numbering scheme for NMR assignments.

and Ph), 6.21 (t, $^3J_{HH}$ 2.4, 1H, H2), 4.17 (s, 2H, CH_2Ph), 3.41 (d, $^3J_{HH}$ 2.4, 2H, indene CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 36.7 (C1), 38.5 (benzyl CH_2), 119.3 (C4), 123.7 (C7), 125.3 (C6), 126.3 (C5), 127.3 (C2), 127.3 (*p*-Ph), 128.5 (*m*-Ph), 128.8 (*o*-Ph), 137.1 (*ipso*-Ph), 137.5 (C9/3), 143.3 (C8), 143.6 (C3/9). Quaternary carbon atom peaks could not be assigned unambiguously. Mass spec. (EI, *m*/*z*(%)): 239.1 (100, M^+). Anal. Calcd for $C_{16}H_{14}S$ (%): C, 80.62; H, 5.92; S, 13.45. Found (%): C, 80.14; H, 5.96; S, 13.41.

2.2. *Synthesis of bis(1-benzylthioindenyl)iron(II) (3)*

n-BuLi (4.30 mL, 6.88 mmol) was added dropwise to a solution of **2** (1.64 g, 6.88 mmol) in freshly distilled THF (100 mL) and TMEDA (0.7 mL) at −78°C. The solution immediately turned yellow-brown. After 2.5 h at −78°C, anhydrous $FeCl_2 \cdot 1.5THF$ (0.81 g, 3.4 mmol) was added to the light brown solution, which then quickly darkened in color. Vigorous stirring at −78°C for 50 min was carried out before removing the cold bath and the solution was allowed to gradually warm to the ambient temperature. The solution was filtered through a Celite column using diethylether and a dark green solution was collected. The solvent was removed *in vacuo* and a black oily residue was obtained. ^1H- and $^{13}C\{^1H\}$-NMR spectra of the crude product indicated that indene **2** and both ferrocene isomers are present. The *rac*/*meso* ratio in the $^{13}C\{^1H\}$-NMR spectrum was approximately 1 : 1. The crude product was then redissolved in freshly distilled THF (20 mL) and stirred for 20 h. The solution was filtered through a Celite column using diethylether and the solvent was removed *in vacuo*. The $^{13}C\{^1H\}$-NMR spectrum of the dark red oil showed a *rac* : *meso* ratio of approximately 1 : 0.6. Further recrystallization from diethylether afforded 0.11 g (2.3%) of dark red *rac*-**3**. The ^{13}C-NMR chemical shifts reported here are the values corrected for paramagnetic impurities, as described in the "Supplementary material". Interestingly, the quaternary C atoms are more strongly affected by the paramagnetic impurities than the tertiary C atoms which are more strongly affected than the secondary C atoms, by averages of 1.96, 1.84, and 1.72 ppm, respectively, in the crude solution and by 4.53, 4.31, and 4.00 ppm, respectively, in the isomerized solution. *rac*-Isomer: ^1H-NMR ($CDCl_3$): δ 3.60 (4H, s, CH_2), 4.16 (2H, s, H2/3), 4.58 (2H, s, H2/3), 6.68–7.42 (18H, m). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 41.8 (CH_2), 64.6 (C3), 71.1 (C1), 77.2 (C2), 88.1 (C8/9), 89.0 (C9/8), 123.0 (C4), 123.4 (C7), 123.6 (C6), 125.1 (C5), 126.7 (*p*-Ph), 128.2 (*m*-Ph), 128.7 (*o*-Ph), 138.4 (*ipso*-Ph). *meso*-Isomer: $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 41.4 (CH_2), 62.9 (C3), 71.7 (C1), 77.4 (C2), 87.6 (C8/9), 89.0 (C9/8), 123.6 (C4), 124.2 (C7), 124.9 (C6), 125.4 (C2), 126.6 (*p*-Ph), 128.1 (*m*-Ph), 128.8 (*o*-Ph), 128.4 (i*pso*-Ph). Anal. Calcd for $C_{32}H_{22}FeS_2$ (%): C, 73.00; H, 4.21. Found (%): C, 70.17; H, 4.18. Values are low due to the unavoidable decomposition of the product.

2.3. *X-ray crystallography*

Crystal data and experimental details are given in table 1. For each compound, a crystal was mounted on a glass fiber. Data were collected using a Bruker–Nonius diffractometer equipped with an APEX-II CCD area detector and the associated software. Processing was carried out by the use of SAINT [8], which applied Lorentz and polarization corrections to 3-D integrated diffraction spots. The program SADABS [8] was utilized for the scaling of diffraction data, the application of decay corrections, and empirical absorption corrections based on redundant reflections. The structures were solved by direct methods [9]. Both structures were refined by least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogens were added as riding contributors at calculated positions with isotropic thermal parameters based on the attached carbon.

3. Results and discussion

3.1. *Synthesis of 3-(thiobenzyl)indene (2)*

3-(Thiobenzyl)indene was prepared by a route analogous to that used by Rausch and coworkers [6] for the preparation of 3-(thiomethyl)indene: dibenzyldisulfide was added

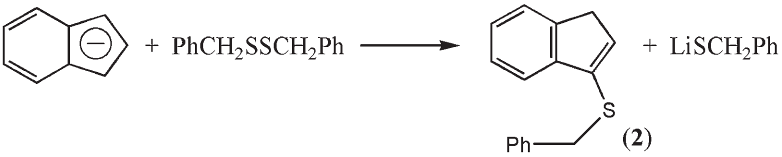
Table 1. Details of crystallographic collection and refinement data for **2** and *rac*-**3**.

	2	*rac*-**3**
Empirical formula	$C_{16}H_{14}S$	$C_{16}H_{13}Fe_{0.50}S$
Formula weight	238.33	265.25
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*P2(1)/c*	*C2/c*
Unit cell dimensions (Å, °)		
a	12.5484(4)	10.9413(4)
b	5.5266(2)	14.6122(6)
c	18.7392(6)	15.7579(7)
α	90	90
β	107.460(2)	90.9660(10)
γ	90	90
Volume (Å^3), Z	1239.69(7), 4	2518.96(18), 8
Calculated density (g cm^{-3})	1.277	1.399
Absorption coefficient (mm^{-1})	0.234	0.784
F(000)	504	1104
Crystal size (mm^3)	0.60 × 0.45 × 0.26	0.40 × 0.40 × 0.08
θ range for data collection (°)	1.70–34.70	2.59–31.59
Limiting indices	$-18 \le h \le 19$; $-8 \le k \le 8$; $-28 \le l \le 28$	$-15 \le h \le 11$; $-17 \le k \le 21$; $-17 \le l \le 19$
Reflections collected	22,355	6932
Independent reflections	4511 [R(int) = 0.0277]	3428 [R(int) = 0.0158]
Completeness to $\theta = 34.70$ (%)	84.7	94.1
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4511/0/155	3428/0/159
Goodness-of-fit on F^2	1.193	1.154
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0355$, $wR_2 = 0.1300$	$R_1 = 0.0307$, $wR_2 = 0.0838$
R indices (all data)	$R_1 = 0.0411$, $wR_2 = 0.1410$	$R_1 = 0.0383$, $wR_2 = 0.0979$
Largest difference peak and hole (e Å^{-3})	0.536 and −0.250	0.624 and −0.431

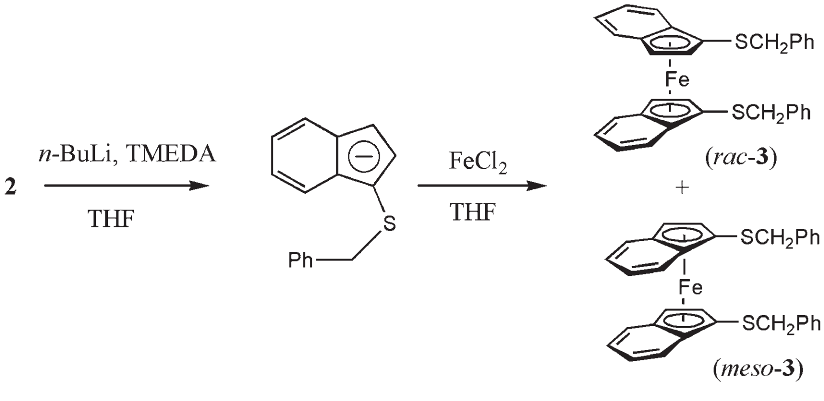
to a suspension of lithium indenide in hexane and the product was isolated *via* chromatography (scheme 3). NMR spectra indicated that the 3-isomer had been isolated; possibly as a result of the isomerization of the expected 1-isomer during the alumina filtration step, as has been observed for analogous indenylphosphines [10]. However, it is also possible that the lithium benzylthiolate coproduct could have acted as a catalyst for this isomerization *via* a deprotonation/protonation mechanism. The structure of **2** was further confirmed by an X-ray crystallographic study that was undertaken to compare the indene with the coordinated indenide.

3.2. *Synthesis and characterization of rac- and meso-bis(1-thiobenzylindenyl) iron(II) (3)*

Treatment of indene **2** with *n*-BuLi in THF gave a precipitate of the indenide that reacts poorly with $FeCl_2$. Addition of TMEDA dissolves the lithium indenide which then produces the expected ferrocene product **3** upon reaction with $FeCl_2$ (scheme 4). ^{13}C-NMR spectra indicated that both *rac* and *meso* isomers formed in approximately equal amounts (figure 1a). After stirring the mixture of isomers for 20 h in THF, the ratio changed to approximately 1 : 0.6 (figure 1b). Unfortunately, a significant amount of decomposition/hydrolysis was observed with the formation of free indene and paramagnetic materials. Thus, one cannot say unambiguously that the change in the ratio is due to an isomerization process rather than a difference in the rate of decomposition. Attempts to follow the reaction by NMR in THF-d_8 proved futile due to the extreme sensitivity of **3** to the traces of water. However, it should be noted that



Scheme 3. Synthesis of 3-(thiobenzyl)indene (**2**).



Scheme 4. Synthesis of **3**.

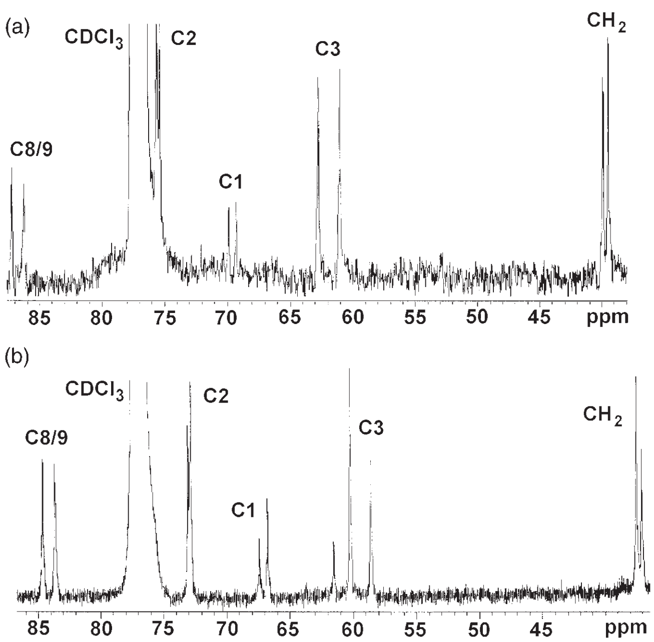


Figure 1. (a) ^{13}C-NMR spectrum of **3** in $CDCl_3$ before isomerization. (b) ^{13}C-NMR spectrum of **3** in $CDCl_3$ after stirring for 20 h in THF. The differences in the chemical shift relative to solvent $CDCl_3$ are due to the presence of different amounts of paramagnetic decomposition products.

the mechanistic studies on the rate of hydrolysis for **1** [3] showed that the hydrolysis mechanism involves the same intermediate as the isomerization process. Thus, the intermediate responsible for isomerization is likely to be present suggesting that ring-flipping is likely to be occurring.

Electrochemistry of **3** was investigated to compare the electronic effect of the thiobenzyl substituent with other substituents. Cyclic voltammetry in CH_2Cl_2 gave a single reversible ($\Delta E_p = 87$ mV compared to 92 mV for the internal ferrocene standard) redox process with E_0 at −177 mV *versus* the Fc/Fc^+ couple (figure 2). Any difference between the two isomers, therefore, is likely to be insignificant. This is a lower oxidation potential than the phosphino analogue **1** (−140 mV) [11], but is higher than the unsubstituted dibenzoferrocene (−278 mV) [12], 1,1′-dimethyl-substituted dibenzoferrocene (−375 mV) [12], and bis(1-trimethylsilyl)-substituted dibenzoferrocene (−275 mV) [13]. Similar trends have been observed in the analogous cyclopentadienyl systems [14]. Notably, **3** has a higher oxidation potential than methyl- and trimethylsilyl-substituted bis(phosphinoindenyl)iron(II) complexes (−220 to −350 mV) that have been reported to date and have not been observed to undergo ring-flipping. This is consistent with the electrophilicity of the metal center being an important factor in facilitating the attack by THF, the first step in the ring-flipping process.

As with other dibenzoferrocenes, **3** exhibits two absorption bands in the UV-Vis region (figure 3), a strong band at 415 nm ($\varepsilon = 855\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) and a weaker band at 545 nm ($\varepsilon = 203\ \mathrm{L\,mol^{-1}\,cm^{-1}}$). These are at slightly higher energy than the

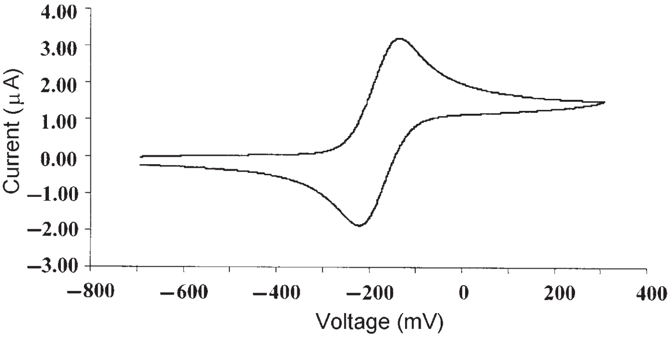


Figure 2. Cyclic voltammogram of **3** (1.3×10^{-3} mol) in CH_2Cl_2 relative to Fc/Fc^+.

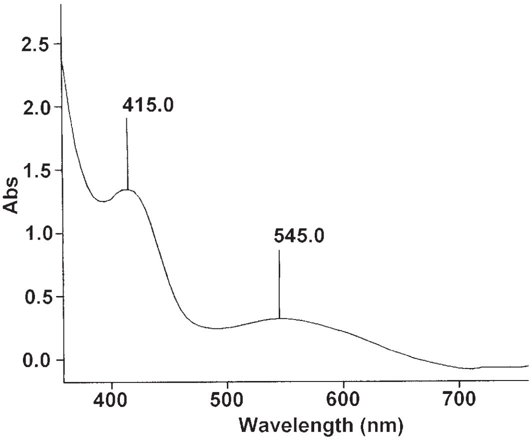


Figure 3. UV-Vis spectrum of **3** (1.6×10^{-3} mol) in CH_2Cl_2.

corresponding bands in **1**: 420 ($\varepsilon = 870\,\mathrm{L\,mol^{-1}\,cm^{-1}}$) and 565 nm ($\varepsilon = 265\,\mathrm{L\,mol^{-1}\,cm^{-1}}$), respectively. These bands have been attributed to d–d transitions [13].

3.3. *Crystallographic studies*

The solid state structures of **2** and *rac*-**3** were determined by X-ray crystallography. Collection and refinement data are given in table 1 and selected bond distances and angles are given in table 2. The structure of indene **2** (a thermal ellipsoid plot is shown in figure 4) is consistent with the 3-isomer: C3 has a trigonal planar geometry (sum of angles = 360.0°) and the C2–C3 distance is significantly shorter than the C1–C2 and C3–C9 distances (1.3531(12) Å *vs.* 1.5075(12) Å and 1.4698(12) Å). The thiobenzyl substituent lies in the plane of the indene with C2–C3–S–C10 = 0.4° and a *trans* configuration about S–C10 (C3–S–C10–C11 = 173.3°). The phenyl group, however, lies

Table 2. Selected bond distances (Å) and angles (°) for **2** and *rac*-**3**.

	2	*rac*-**3**
Fe–CNT		1.654
Fe–C1		2.0401(15)
Fe–C2		2.0185(13)
Fe–C3		2.0334(14)
Fe–C8		2.0928(14)
Fe–C9		2.0933(13)
S–C3	1.7440(9)	1.7547(17)
S–C10	1.8170(9)	1.8280(17)
C1–C2	1.5075(12)	1.425(2)
C1–C8	1.5061(13)	1.436(2)
C2–C3	1.3531(12)	1.436(2)
C3–C9	1.4698(12)	1.4394(19)
C4–C5	1.3934(13)	1.361(2)
C4–C9	1.3924(12)	1.423(2)
C5–C6	1.3951(14)	1.421(3)
C6–C7	1.3968(14)	1.361(2)
C7–C8	1.3895(13)	1.426(2)
C8–C9	1.4045(11)	1.440(2)
C10–C11	1.5062(12)	1.505(2)
CNT–Fe–CNT		179.11
CNT–C3–S		174.86
C3–S–C10	101.04(4)	102.53(9)
C2–C3–C9	109.61(8)	107.35(14)
C2–C3–S	130.70(7)	126.27(11)
C9–C3–S	119.67(6)	126.15(12)
C11–C10–S	108.63(6)	113.81(11)

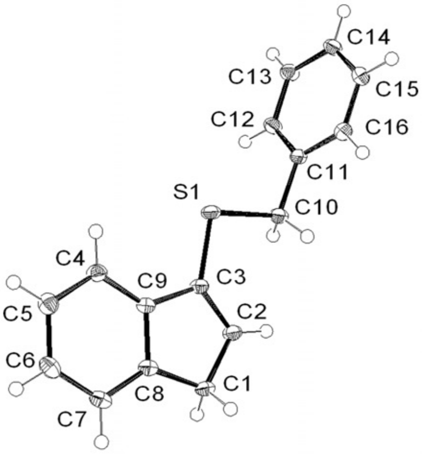


Figure 4. ORTEP of indene **2**.

approximately perpendicular to this plane (S–C10–C11–C12 = 75.7°). Some steric repulsion between the benzyl group and indene are apparent in the wide C2–C3–S angle (130.70(7)°) compared to the C9–C3–S angle (119.67(6)°). Similar effects are apparent in $Ph_2P(C_9H_7)$ (127.8(1)° and 123.2(1)°) [15] and **1** (130.3° and 123.8°) [4], whereas no significant effect is observed in $PhP(S)(C_9H_7)_2$ (124.2–126.8°) [10a].

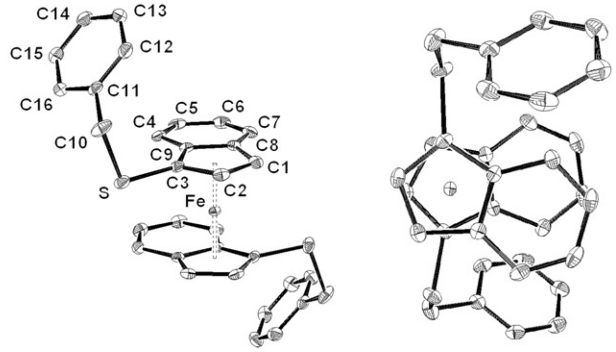


Figure 5. ORTEP of *rac*-**3** showing atomic labeling scheme and the view down the centroid–centroid axis of the five-membered rings. Hydrogen atoms have been omitted for clarity.

Thermal ellipsoid plots of *rac*-**3** are shown in figure 5. It was found to pack in the monoclinic $C2/c$ space group with the C_2-symmetric molecules lying on the crystallographic C_2 axes. In complete contrast to the indene, the thiobenzyl group in *rac*-**3** is oriented out of the indenyl plane (C2–C3–S–C10 = 94.1°) and adopts a twisted *cis* conformation about the S–C10 bond (C3–S–C10–C11 = 65.8°). Consequently, the C2–C3–S and C9–C3–S angles are very similar due to the lack of steric repulsion: 126.15(12)° and 126.27(11)°, respectively. The indenyl rings show a π-offset arrangement (figure 5) to maximize the π–π stacking interactions [16] with a rotation angle, RA (the angle formed by two lines determined by the centroids of the five- and six-membered rings), of 23.4°. This is similar to those exhibited by *rac*-**1** (20.8°) and *rac*-bis(1-diphenylphosphino-4,7-dimethylindenyl)iron(II) (*rac*-**4**) (12.1°) [4]; however, the offset in those complexes was in the opposite direction: consequently, the torsion angle C3–CNT–CNT″C3′ is greater for *rac*-**2** (167.5°) than for the phosphino analogues (123.1° and 131.9°, respectively). The direction of offset in the phosphino analogues was attributed to favorable CH–π-arene hydrogen bonding between the diphenylphosphino groups [4]. Curiously, the fold angle (FA) of *rac*-**3** (angle between the planes defined by the five- and six-membered rings) is 4.1° with the six-membered ring bent towards the Fe atom. In contrast, the 14 FA angles reported in [4, 12] are all less than 2.8° (or have the six-membered ring pointed away from the Fe atom). Similarly, the thiobenzyl S atom is bent towards the Fe atom by 5.1° (CNT–C3–S = 174.9°), whereas almost all other substituents on dibenzoferrocenes are bent away [4, 12], the notable exceptions being *rac*-**1** (bent in by 3.9°) and *rac*-**4** (one phosphino group is bent in by 3.6°) [4]. There appears to be a general trend of substituents bending towards the metal as the oxidation potential increases, and this may facilitate ring-flipping in **1** and **3**. These structural effects are also likely to be related to the short Fe–CNT distances in **3** of 1.654 Å: The fourteen Fe–CNT distances reported in [4, 12] range from 1.666 to 1.707 Å (average of 1.68 Å).

4. Conclusions

This article has described the synthesis of a thiobenzyl-functionalized dibenzoferrocene that appears to undergo ring-flipping in THF. Cyclic voltammetry and X-ray crystallographic studies are consistent with an electrophilic iron center that may enhance the attack of THF to initiate the ring-flipping process. Unfortunately, the system reported here does not allow us to discriminate between steric and electronic effects on the ring-flipping process, and further work will be required to separate these factors.

Supplementary material

Crystallographic data for structural analyses reported in this article have been deposited with the Cambridge Crystallographic Data Centre with the CCDC nos. 756465 (**2**) and 756466 (*rac*-**3**). Corrections required for ^{13}C-NMR chemical shifts of **2** by the comparison of the indene peaks in $CDCl_3$ and in ferrocene solutions before and after isomerization are given in table 1S. Observed and corrected ^{13}C-NMR chemical shifts for **3** are given in table 2S.

Acknowledgments

We are grateful to Prof. Ward T. Robinson for assistance with the X-ray crystallographic studies and to Dr Paula Brooksby for the cyclic voltammetry studies.

References

[1] (a) P. Štěpnička (Ed.). *Ferrocenes: Ligands, Materials and Biomolecules*, John Wiley and Sons, Ltd, Chichester (2008); (b) A. Togni, T. Hayashi (Eds.). *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*, VCH, Weinheim (1995).
[2] O.J. Curnow, G.M. Fern. *Organometallics*, **21**, 2827 (2002).
[3] O.J. Curnow, G.M. Fern, M.L. Hamilton, A. Zahl, R. van Eldik. *Organometallics*, **23**, 906 (2004).
[4] O.J. Curnow, G.M. Fern, M.L. Hamilton, E.M. Jenkins. *J. Organomet. Chem.*, **689**, 1897 (2004).
[5] U. Siemeling. In *Ferrocenes: Ligands, Materials and Biomolecules*, P. Štěpnička (Ed.), pp. 141–176, John Wiley and Sons, Ltd, Chichester (2008).
[6] T.E. Ready, J.C.W. Chien, M.D. Rausch. *J. Organomet. Chem.*, **519**, 21 (1996).
[7] J. van Beek, J.G. de Vries, J.H. Arts, R. Persad, G.H.J. van Doremaele, PCT International Application WO94/11406, 1994.
[8] *SAINT* and *SADABS*. *Siemens Analytical*, Vol. 6, , Madison, WI (1994).
[9] *SHELXTL*. Vol. 6, Bruker AXS Inc, Madison, WI, (2000).
[10] (a) C. Lensink, G.J. Gainsford. *Aust. J. Chem.*, **51**, 667 (1998); (b) J.J. Adams, D.E. Berry, O.J. Curnow, G.M. Fern, M.L. Hamilton, H.J. Kitto, J.R. Pipal. *Aust. J. Chem.*, **56**, 1153 (2003).
[11] O.J. Curnow, G.M. Fern, E.M. Jenkins. *J. Organomet. Chem.*, **691**, 643 (2006).
[12] O.J. Curnow, G.M. Fern. *J. Organomet. Chem.*, **690**, 3018 (2005).
[13] O.J. Curnow, G.M. Fern, S. Klaib, U. Bohme, H. Lang, R. Holze. *J. Electroanal. Chem.*, **585**, 167 (2005).
[14] (a) V.C. Gibson, N.J. Long, C.K. Williams, M. Fontani, P. Zanello. *Dalton Trans.*, 3599 (2003); (b) S. Zurcher, V. Gramlich, D. Von Arx, A. Togni. *Inorg. Chem.*, **37**, 4015 (1998).
[15] K.A. Fallis, G.K. Anderson, N.P. Rath. *Organometallics*, **11**, 885 (1992).
[16] C. Janiak. *J. Chem. Soc., Dalton Trans.*, 3885 (2000).