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Rearrangements and dimerizations of congested ferrocenyl allyl alcohols

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Abstract

Starting with the α,β-unsaturated ketones tigloylferrocene (**1**) and tetramethylcyclopent-2-enone, the corresponding ferrocenylallyl alcohols were prepared. Under acidic (aqueous) conditions, in order to eliminate water for the generation of olefinic derivatives, competitive allylic rearrangements are predominant. The in situ generated allyl cations undergo subsequent electrophilic additions. The parent tigloylferrocene-derived alcohols **2** and **4** preferentially form dimers of which one distinct stereoisomer, **6**, was separated and fully characterized. In the case of tetramethylferrocenylcyclopentenol, a stabilized divinyl cation is generated by allylic rearrangements involving hydride shifts and a C–C scission step, (retro-reaction of a Nazarov-type cyclization), followed by a protic H_2O readdition/elimination sequence, which affords 4-ferrocenyl-4-hydroxy-2,3,5,6-tetramethyloxane (**8**) as the major product. Based on isolated intermediate allylic alcohols, the respective mechanisms of formation of the final products are postulated. X-ray structure determinations of the dimer **6**, the isomorphic ferrocenyloxanes **8a**, **8b**, and 1,1′-ditigloylferrocene (**9**) are presented. The unique crystal packing of **9** (eclipsed conformation due to a lowered spatial extent of the molecule) is examined. A supplementary ^{57}Fe Mössbauer study revealed a comparatively low quadrupole splitting (QS) interaction and a very small temperature dependence of the QS in **9**.

Keywords: Ferrocene; Crystal structures

1. Introduction

The extraordinary power of ferrocene substituents in the stabilization of adjacent cationic domains is, as expected, also operative in allylic functionalities [1]. However, multiple cumulative stabilization or sterically demanding substitution is normally required in order to realize systems with no tendency for further electrophilic reactivity [2]. A supportive additional stabilization of allyl cations may therefore be induced by multiple methylation, which was the preparative goal of this investigation of novel ferrocenylcarbinol derivatives [3]. The present comparison [4] of these vinylated, respectively doubly vinylated (extended allylic) counterparts was stimulated by the potential of cooperative behavior, provided by competing carbocation stabilizing substitutents (ferrocenyl- and methylated vinyl moieties), which should result in a combination of steric and electronic stabilization modes [5]. Furthermore, the compounds investigated allow the construction of new closely linked metallocenes, which represent illustrative models of metal-metal interaction processes [6] as well as cooperative systems for catalysis research, i.e. ferrocenylated *ansa*-zirconocenes [7].

The required synthetic accessibility of the interesting subgroup of (electron rich) alkylated ferrocenylic allyl alcohols relies on carbanion additions to methylated indanones [8], 2,3,4,5-tetramethylcyclopent-2-enone and related progenitors [6]. The final formation of cyclopentadienyl (Cp) ligands is generally achieved by acid catalyzed H_2O elimination, despite the often low to

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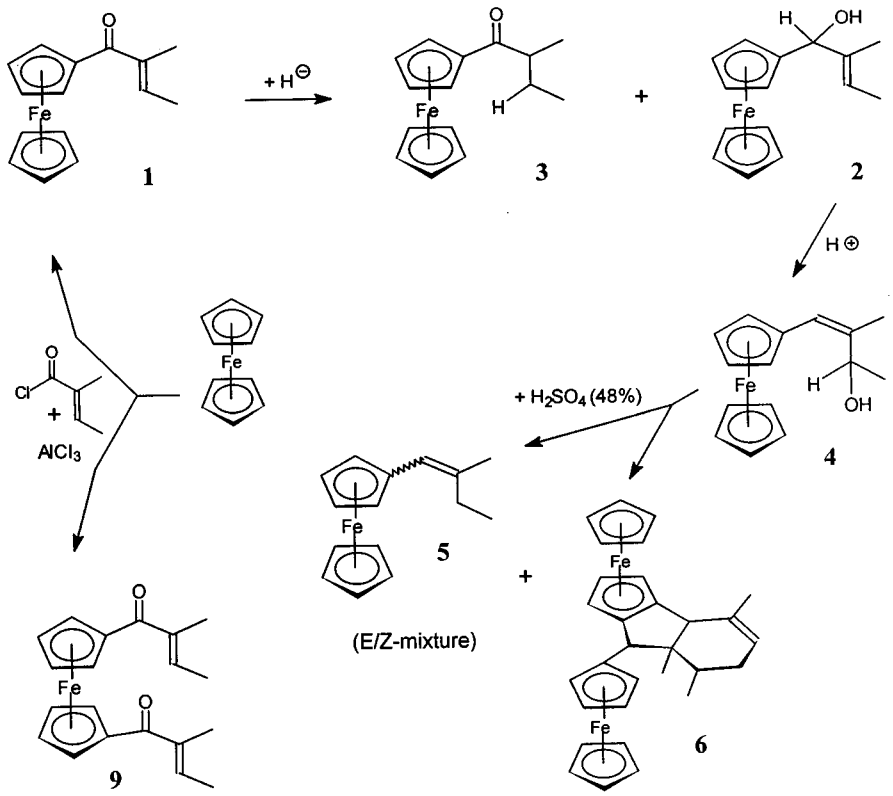


Scheme 1. Synthesis of tigloylferrocenes **1** and **9**. Formation of **5** and **6** via reduction and electrophilic dimerization.

moderate yields, caused by side reactions of the involved carbocations, especially in bifunctional derivatives [9]. Therefore, some expensive or tedious alternative routes, and strictly controlled reaction conditions are eventually necessary to avoid undesired reaction pathways [6b,10]. The results reported in the present contribution reveal some further understanding of these adverse synthetic aspects of the chemistry of metallocenylcyclopentadienyls.

2. Results and discussion

2.1. The open chain derived methallylic system

Tigloylferrocene (**1**) was simply prepared by a Friedel–Crafts acylation of ferrocene with tigloyl chloride, also affording ditigloylferrocene (**9**) as a byproduct (see Sections 4 and 4.16). Hydride reduction of the target compound **1** proceeds as expected by 1,2-addition to yield the ferrocenylallyl alcohol **2**, and additionally — by a Michael-type attack — the ketone **3**. For **2**, no cyclization to a methylated pentalene, respectively to a phane-cyclisized structure, which is possible for several related systems, e.g. tigloyl-tetramethylbenzene [8], 1,3 diferrocenylallyl alcohol [11] or acryloylferrocene [12], has been observed. Instead, allylic rearrangements of **2** to **4**, electrophilic dimerizations to **6** and even reductive conversions to **5** occur in the concentrated sulfuric acid medium applied (Scheme 1).

Compound **6**, of which formation is believed to proceed via a rearrangement of the alcohol **4**, incorporates one ferrocenediyl- and one simple ferrocenyl moiety (Fig. 1). The secondary product 4 represents a ferrocenylbutadiene equivalent, which is formally incorporated in **6**. The respective ferrocenylbutadiene may

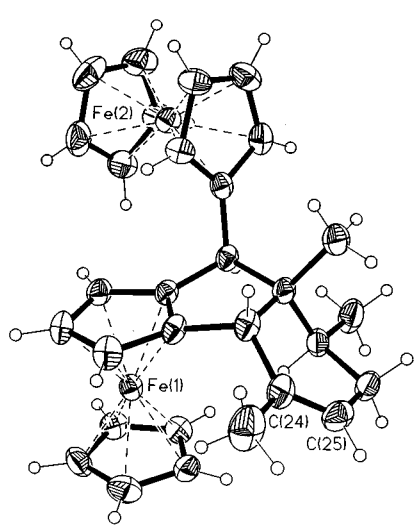
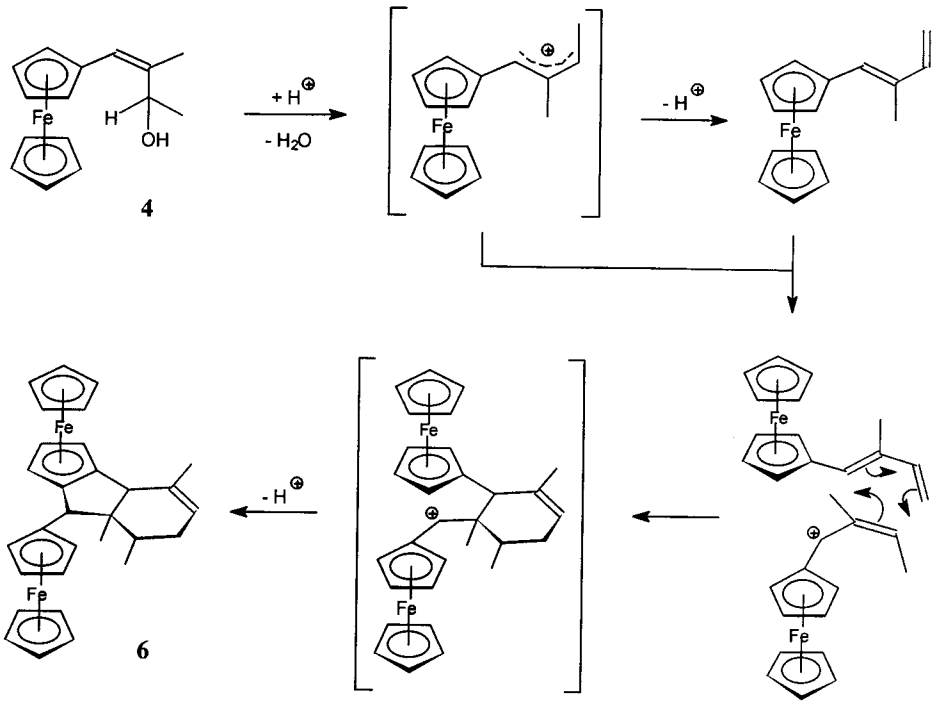


Fig. 1. X-ray structure of **6**.



Scheme 2. Reaction pathway for the formation of **6**.

be generated by water elimination of the 2/4 couple, via deprotonation of the parent allyl cation. The resulting ferrocenylbutadiene would be available for a further electrophilic addition of the abundant allylium mesomer, followed by the terminating substitution step onto the doubly linked ferrocene part (Scheme 2).

From a binary reaction medium, consisting of dichloromethane–aqueous sulfuric acid (see Section 4), continuous color changes of the reaction constituents in both the organic and the aqueous phase, are indicative of migratory reaction processes resembling phase transfer conditions. However, the proposed dimerization mechanism remains speculative, since no neutral butadiene was identified.

2.2. The ring-closed derived methallylic system

For the conversion of 2,3,4,5-tetramethylcyclopent-2-en-1-one with dilithiated [13] or monolithiated ferrocenes, again two primary products are possible: 3-ferrocenyl-2,3,4,5-tetramethylcyclopentan-1-one from a 1,4-addition, and 1-ferrocenyl-2,3,4,5-tetramethylcyclopent-2-en-1-ol from the 1,2-addition. In contrast to unsubstituted cyclopentenone [14] and tigloylferrocene (**1**), and in accordance with our own findings as well as with results already published by others [15], 1,2-addition represents the main reaction pathway (Scheme 3).

This addition proceeds cleanly and the selectivity of this step is remarkable, as lithioferrocene must be regarded as a medium 'soft' nucleophile, which should also result in 1,4-addition. Nevertheless, the methyl group seems to provide enough steric protection to favor 1,2-addition. However, any following intentional water elimination is inherently handicapped by adverse pathways of electrocyclizations, which, on the other hand, may serve as useful preparative concepts for substituted tetramethyl-cyclopentadienyl compounds via divinylcarbinols [16]. These intermediate cationic cyclopentadienyls are again capable of typical allylic side reactions (see Scheme 3).

The use of pyridinium 4-toluenesulfonate (PPTS) instead of toluenesulfonic acid shifts the product distribution in favor of the Cp-fraction, but in any case, additional **7** and **8** can be isolated, which gives clear evidence for the formation of their divinyl-ferrocenylmethylcation progenitor, an intermediate system which must have been formed by the involvement of respective hydride shifts (see Scheme 4). As expected, the direct formation of **8** from divinyl-ferrocenylcarbinol **7** is also possible by treatment with aqueous acid.

Ferrocenyloxane **8** is the most stable compound of the entire reaction system. It shows a remarkable tendency to crystallize and can therefore easily be isolated in 20–30% yield based on monolithioferrocene (Fig. 2 for the isomorphic crystalline form **8b**).

3. Conclusions

The exhaustive combination of methyl- and ferrocenyl groups in allylic systems may not sufficiently prevent electrophilic intra- and intermolecular self sub-

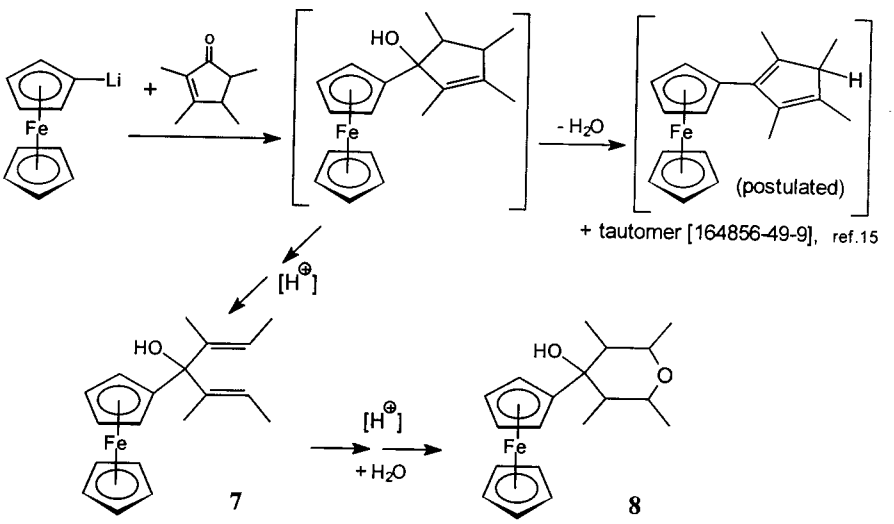
stitutions during the common allylic rearrangement cascades. On the other hand, this behavior can be exploited for the preparation of interesting and novel substituted ferrocene monomers and dimers, e.g. **6**.

Compound **8** is thus identified as the predominant byproduct of the classical cyclopentenone-carbanion addition route to prepare Fec-tetramethylcyclopentadienes and represents a very intriguing ferrocenyl carbinol in its own right.

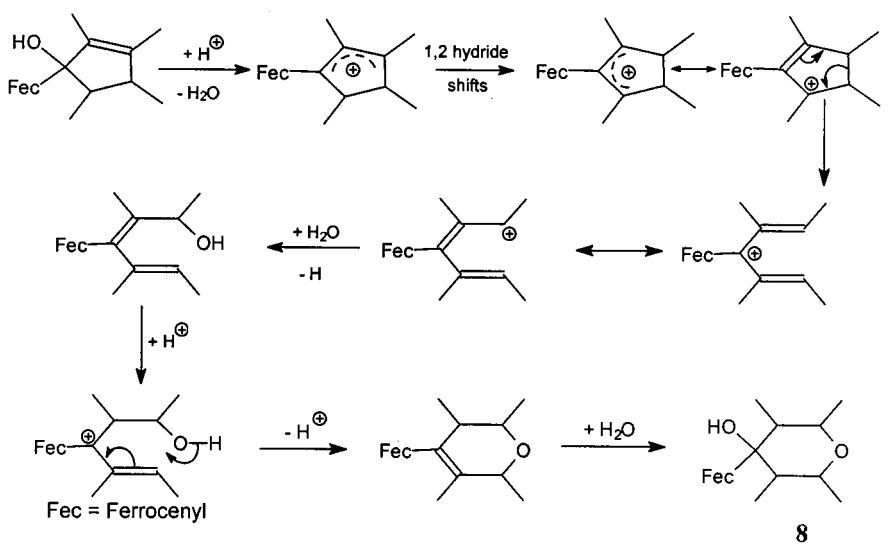
4. Experimental

All reactions were carried out in the absence of air using standard Schlenk techniques unless stated otherwise. Solvents were deoxygenated, purified and dried prior to use. Purchased starting materials were used without any further purification. Other reagents or educts such as lithioferrocene [17] were prepared according to literature procedures. Instrumentation: Bruker AC 200 and Varian Gemini 200 (^{1}H- 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 apparatus and are uncorrected. Microanalyses were obtained from the Analytical Department of Lenzing AG, Lenzing, Austria and from the Department of Physical Chemistry, University of Vienna, Austria, and were found to be consistent with the theoretical values.

The Mössbauer spectrometer, its method of calibration, the method of data reduction and thermal control have been described earlier [2].



Scheme 3. Reaction pathway for the formation of **8**.



Scheme 4. Postulated formation of **8** via a retro-Nazarov-type reaction.

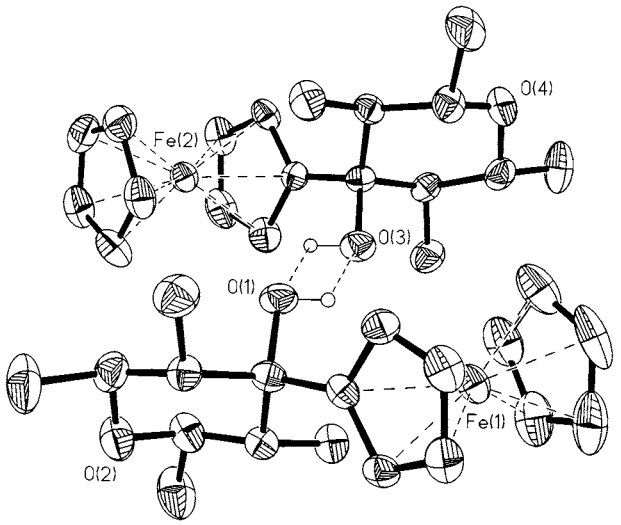


Fig. 2. X-ray structure of the isomorphic form **8b**.

All spectra acquired in the present study consist of two well-resolved components of a quadrupole split pattern, and these have been analyzed with the isomer shift (IS), quadrupole interaction (QS), line width and intensity allowed to vary as independent parameters. All IS are with respect to the centroid of an alpha-Fe spectrum at room temperature.

*4.1. (E)-1-Ferrocenyl-2-methylbut-2-enone (tigloylferrocene) (**1**)*

Aluminum chloride (0.950 g, 7.13 mmol) was suspended in 15 ml of dichloromethane in a Schlenk vessel under an atmosphere of argon. A solution of ferrocene (1.30 g, 6.99 mmol) and tigloyl chloride [8] (0.73 ml, 0.790 g, 6.64 mmol) in 15 ml of dichloromethane was added dropwise at room temperature (r.t.). After the addition was complete, the reaction mixture was stirred for a further 75 min. The resulting dark-violet mixture was poured on a solution of citric acid (2.10 g, 10.9 mmol) in 50 ml of water and 30 g of ice. The organic layer was separated and the remaining aqueous phase was washed twice with dichloromethane (20 ml portions each). The combined organic layers were washed with 30 ml of saturated aqueous NaCl solution and dried over Na_2SO_4. The solvent was removed and the residue (1.84 g) was purified by means of chromatography (Silica 60, 15:85 THF–*n*-hexane). Yields: 1.55 g (87.1%) tigloylferrocene (**1**), 0.139 g (11.9%) 1,1′-ditigloylferrocene (**9**).

*4.2. Tigloylferrocene (**1**)*

Red crystals, m.p. 38 – 40°C. Selected IR data (KBr): 1632 vs ($\nu_{C=O}$), 1611 versus ($\nu_{C=C}$) cm^{-1}. ^{1}H-NMR ($CDCl_3$, TMS; *cp* refers to cyclopentadienyl): δ 1.84 (dq, 3H, $^3J = 6.9$ Hz, $^5J = 1.2$ Hz, ω-CH_3), 1.94 (dq, 3H, CH_3), 4.17 (s, 5H, *unsubst. cp*), 4.47 ('t', 2H, *subst. cp*), 4.78 ('t', 2H, *subst. cp*), 6.55 (qq, 1H, $^3J = 6.9$ Hz, $^4J = 1.5$ Hz, C*H*). ^{13}C-NMR ($CDCl_3$, TMS): δ 12.88 (*C*H_3), 14.24 (ω-*C*H_3); 69.89, 71.10, 71.67 (*ferrocenyl*); 133.50 (*C*H). MS (EI, 70 eV): *m*/*z* 268 [M^+, 100%], 213 [$M^+ - C_4H_7$, 16%], 185 [$M^+ - C_5H_7O$, 23%). Anal. Calc. for $C_{15}H_{16}FeO$: C, 67.19; H, 6.01; O, 5.97. Found: C, 67.03; H, 5.99; O, 6.54.

*4.3. 1,1′-Ditigloylferrocene (**9**)*

Dark-red crystals, m.p. 97–98°C. Selected IR data (KBr): 1644 vs, 1629 vs, 1619 vs cm^{-1}. ^{1}H-NMR ($CDCl_3$, TMS): δ 1.76 (dq, 6H, $^3J = 6.9$ Hz, $^5J = 1.2$ Hz, ω-CH_3), 1.84 (dq, 6H, CH_3), 4.38 ('t', 4H, *subst. cp*), 4.66 ('t', 4H, *subst. cp*), 6.43 (qq, 2H, $^3J = 6.9$ Hz, $^4J = 1.5$ Hz, C*H*). ^{13}C-NMR ($CDCl_3$, TMS): δ 12.60 (*C*H_3), 14.33 (ω-*C*H_3); 72.64, 73.42 (*ferrocenyl*); 135.02 (*C*H), 138.26 (*quaternary C*), 199.38 (C=O). MS (EI, 70 eV): *m*/*z* 350 [M^+, 100%]. Anal. Calc. for $C_{20}H_{22}FeO_2$: C, 68.59; H, 6.33; O, 9.14. Found: C, 68.33; H, 6.29; O, 9.24. Single crystals, suitable for X-ray analysis, were obtained by crystallization from ether. For the X-ray data refer to Table 1 and Fig. 4, respectively.

*4.4. rac-(E)-1-Ferrocenyl-2-methylbut-2-en-1-ol (**2**)*

Tigloylferrocene (1.80 g, 6.71 mmol) was dissolved in 100 ml THF and the solution was cooled to − 90°C. A total of 7.38 ml of 1.0 a M solution of lithium triethylborohydride (7.38 mmol, 1.1 equiv.) was syringed slowly into the stirred solution. The reaction mixture was stirred for 30 min at − 90°C, warmed to r.t., reduced in volume to approximately 15 ml, hydrolyzed by addition of 100 ml ice–water, and extracted with diethyl ether (3 × 50 ml). The combined organic layers were dried over Na_2SO_4 and the solvents were removed in vacuo. According to TLC, only products **2** and **3** were formed during the reaction. These two compounds were separated by means of chromatography (Al_2O_3 basic, 50:50 diethyl ether–*n*-hexane). However, at this conditions a further allylic rearrangement of compound **2**–**4** occurs (Scheme 1). Therefore only traces of **2** and compounds **3** and **4** as main products could be isolated: *rac*-4-ferrocenyl-3-methylbut-3-en-2-ol (4), (1.558 g, 86.0%); *rac*-1-ferrocenyl-2-methylbutan-1-one (**3**), (0.250 g, 13.8%); *rac*-(*E*)-1-ferrocenyl-2-methylbut-2-en-1-ol (**2**), (traces).

*4.5. rac-(E)-1-Ferrocenyl-2-methylbut-2-en-1-ol (**2**)*

Yellow orange oil. Selected IR data (KBr): 3437 br s, (ν_{O-H}) cm^{-1}. ^{1}H-NMR ($CDCl_3$, TMS): δ 1.50 (s, 3H, CH_3), 1.51 (d, 3H, ω-CH_3), 2.13 (s, 1H, O*H*), 4.06 (s, 2H, *subst. cp*), 4.12 (s, 5H, *unsubst. cp*), 4.21 (s, 2H, *subst. cp*), 4.72 (s, 1H, C*H*OH), 5.45 (q, 1H, $^3J = 5.5$ Hz, =C*H*–). ^{13}C-NMR ($CDCl_3$, TMS): δ 11.46 (*C*H_3),

13.01 (ω-*C*H$_3$); 65.26, 67.41, 67.61, 68.25, 92.66 (*ferrocenyl*); 75.53 (*C*HOH), 120.58 (=*C*H–CH$_3$), 137.35 (–*C*=CH–). MS (EI, 70 eV): *m*/*z* 270 [M$^+$, 100%], 253 [M$^+$ − OH, 22%]. Anal. Calc. for $C_{15}H_{18}FeO$: C, 66.69; H, 6.72; O, 5.92. Found: C, 66.83; H, 6.82; O, 6.11.

4.6. rac-4-Ferrocenyl-3-methylbut-3-en-2-ol (4)

Orange red oil. Selected IR data (KBr): 3371 br s, (ν_{O-H}) cm^{-1}. ^{1}H-NMR ($CDCl_3$, TMS): δ 1.22 (d, 3H, $^3J = 6.4$ Hz, ω-C*H*$_3$), 1.74 (d, 3H, $J = 1.2$ Hz, C*H*$_3$), 1.99 (s, 1H, O*H*), 4.01 (s, 5H, *unsubst. cp*), 4.11 ('t', 2H, *subst. cp*), 4.18 (q, 1H, $^3J = 6.4$ Hz, C*H*OH), 4.24 ('t', 2H, *subst. cp*), 6.05 (s, 1H, =C*H*–). ^{13}C-NMR ($CDCl_3$, TMS): δ 13.37 (*C*H$_3$); 21.74 (*C*H$_3$); 68.18, 68.88, 68.99, 69.02, 82.24 (*ferrocenyl*); 73.58 (*C*HOH), 121.20 (=*C*H–), 138.20 (CH=*C*–). MS (EI, 70 eV): *m*/*z* 270 [M$^+$, 100%], 121 [M$^+$ − $C_{10}H_{13}O$, 21%], 85 [M$^+$ − $C_{10}H_9Fe$, 42%]. Anal. Calc. for $C_{15}H_{18}FeO$: C, 66.69; H, 6.72; O, 5.92. Found: C, 66.58; H, 6.76; O, 6.07.

4.7. rac-1-Ferrocenyl-2-methylbutan-1-one (3)

Red crystals, m.p. 41–44°C. Selected IR data (KBr): 1663 vs ($\nu_{C=O}$) cm^{-1}. ^{1}H-NMR ($CDCl_3$, TMS): δ 0.88 (t, 3H, $^3J = 7.3$ Hz, CH_2–C*H*$_3$), 1.12 (d, 3H, $^3J = 7.0$ Hz, C*H*$_3$), 1.31–1.45 (m, 1H, C*H*$_A$H$_B$), 1.66–1.80 (m, 1H, CH$_A$*H*$_B$), 2.83 (q, 1H, $^3J = 7.0$ Hz, C*H*–CH$_3$), 4.12 (s, 5H, *unsubst. cp*), 4.41 ('t', 2H, *subst. cp*), 4.68–4.73 (m, 2H, *subst. cp*). ^{13}C-NMR ($CDCl_3$, TMS): δ 11.96 (*C*H$_3$), 17.07 (*C*H$_3$), 26.77 (*C*H$_2$), 44.08 (*C*H); 69.15,

Table 1
Crystal data and structure refinement for **6**, **8a**, **8b** and **9**

	6	**8a**	**8b**	**9**
Molecular formula	$C_{30}H_{32}Fe_2$	$C_{19}H_{26}FeO_2$	$C_{19}H_{26}FeO_2$	$C_{20}H_{22}FeO_2$
Formula weight	504.26	342.25	342.25	350.24
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	*Cc* (no. 9)	*Pbca* (no. 61)
a (pm)	985.7(2)	746.8(1)	749.40(10)	1111.5(2)
b (pm)	1033.0(2)	1174.8(2)	2232.4(3)	1255.2(2)
c (pm)	1249.2(2)	2070.9(4)	2031.7(2)	2486.5(3)
α (°)	78.62(3)	97.13(3)	90	90
β (°)	74.68(3)	96.61(3)	93.91(1)	90
γ (°)	73.67(3)	107.88(3)	90	90
V (nm^3)	1.1668(4)	1.6930(5)	3.3910(7)	3.4691(9)
Z	2	4	8	8
Temperature (K)	293(2)	293(2)	293(2)	293(2)
D_{calc} (Mg m^{-3})	1.435	1.343	1.341	1.341
Absoption coefficient (mm^{-1})	1.259	0.895	0.894	0.876
F(000)	528	728	1456	1472
Color, habit	Orange, prism	Orange, prism	Orange, prism	Red, needle
Crystal size (mm)	0.2 × 0.1 × 0.1	0.3 × 0.2 × 0.2	0.6 × 0.3 × 0.2	0.3 × 0.2 × 0.2
θ Range for data collection (°)	1.71–22.50	1.00–23.00	3.10–23.00	1.64–20.50
Index ranges	$-1 \le h \le 13$; $-14 \le k \le 14$; $-17 \le l \le 17$	$-1 \le h \le 10$; $-13 \le k \le 13$; $-25 \le l \le 25$	$-1 \le h \le 8$; $-1 \le k \le 26$; $-24 \le l \le 24$	$-1 \le h \le 15$; $-1 \le k \le 17$; $-1 \le l \le 34$
Number of reflections collected	3689	5969	3168	2270
Number of independent reflections	3050 ($R_{int} = 0.0473$)	4695 ($R_{int} = 0.0232$)	2983 ($R_{int} = 0.0188$)	1742 ($R_{int} = 0.0403$)
Number of reflections with $I > 2\sigma(I)$	2286	3601	2560	1100
Absorption correction	None	ψ-Scan	ψ-Scan	None
Max and min transmission		0.964 and 0.859	0.931 and 0.837	
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2816/0/290	4327/2/406	2908/4/405	1541/0/212
Goodness-of-fit on F^2	1.029	1.034	1.053	1.048
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0357$; $wR_2 = 0.0736$	$R_1 = 0.0370$; $wR_2 = 0.0815$	$R_1 = 0.0363$; $wR_2 = 0.0748$	$R_1 = 0.0491$; $wR_2 = 0.1005$
R indices (all data)	$R_1 = 0.0636$; $wR_2 = 0.1046$	$R_1 = 0.0606$; $wR_2 = 0.1398$	$R_1 = 0.0485$; $wR_2 = 0.0837$	$R_1 = 0.1056$; $wR_2 = 0.1547$
Largest difference peak and hole (e nm^{-3})	240 and −269	236 and −255	203 and −226	298 and −289

69.39, 71.93, 72.00, 78.67 (*ferrocenyl*); 208.30 (*C*=O). MS (EI, 70 eV): *m*/*z* 270 [M^+, 100%], 213 [M^+–C_4H_9, 65%], 185 [$M^+ - C_5H_5O$, 44%]. Anal. Calc. for $C_{15}H_{18}FeO$: C, 66.69; H, 6.72; O, 5.92. Found: C, 66.89; H, 6.91; O, 6.25.

4.8. Reaction of rac-4-Ferrocenyl-3-methylbut-3-en-2-ol (4) with sulfuric acid (48%)

rac-4-Ferrocenyl-3-methylbut-3-en-2-ol (1.95 g, 7.23 mmol) was dissolved in 50 ml of diethyl ether. Sulfuric acid (5 ml, 48%) was added under vigorous stirring and the mixture was stirred for 16 h. Water (50 ml) was added, the organic layer was separated and the pH of the aqueous layer was changed to 12 using 2 N NaOH. The aqueous layer was extracted twice with 50 ml portions of diethyl ether, the organic layers were combined, washed with 40 ml of saturated aqueous $NaHCO_3$ solution and dried over Na_2SO_4. Prepurification by means of flash chromatography (Silica 60, 50/50 diethyl ether–*n*-hexane). Three compounds were separated from the crude mixture (1.3 g) by repeated chromatography (Silica 60, *n*-hexane): (*E*,*Z*)-1-ferrocenyl-2-methylbut-1-ene (**5**); *rac*-4-ferrocenyl-4a,5,6,8a-tetrahydro-4a,5,8-trimethyl-4*H*-indeno[2,3-*a*]ferrocene (**6**). It is worth noting, that the primarily formed main dimerization product is not stable and no conclusive characterization was possible. The compounds **5** and **6** were identified as byproducts.

4.9. (E/Z)-1-Ferrocenyl-2-methylbut-1-ene (5)

Analytical data given for mixture of *E*/*Z* isomers; orange yellow oil. Selected IR data (KBr): 3097 m, 2964 s, 2927 s, 1636 m cm^{-1}. ^{1}H-NMR ($CDCl_3$, TMS): δ 1.06 (t, 3H, $^3J = 7.3$ Hz, CH_2–CH_3), 1.08, (t, 3H, $^3J = 7.6$ Hz, CH_2–CH_3), 1.77 (d, 3H, $^4J = 1.5$ Hz, CH_3), 1.81 (d, 3H, $^4J = 1.2$ Hz, CH_3), 2.08 (q, 1H, $^3J = 7.3$ Hz, CH_2), 2.23 (q, 1H, $^3J = 7.6$ Hz, CH_2), 4.07 (s, 5H, *unsubst. cp*), 4.08 (s, 5H, *unsubst. cp*), 4.1–4.2 (m, 4H, *subst. cps*), 4.24 ('t', 2H, *subst. cp*), 4.27 ('t', 2H, *subst. cp*), 5.86 (d, 1H, –*H*C=C–), 5.88 (d, 1H, $^4J = 1.2$ Hz, –*H*C=C–). ^{13}C-NMR ($CDCl_3$, TMS): δ 12.58, 12.97 (CH_2–CH_3); 23.89, 26.13 (CH_3); 29.69, 33.52 (CH_2–CH_3); 67.79, 67.85, 68.47, 68.75, 68.90, 83.43, 83.86 (*ferrocenyl*); 119.84, 120.85 (–H*C*=C–); 125.50, 137.98 (–HC=*C*–). MS (EI, 70 eV): *m*/*z* 254 [M^+, 100%], 239 [$M^+ - CH_3$, 12%], 223 [$M^+ - C_2H_5$, 10%], 185 [$M^+ - C_5H_9$, 9%], 121 [$M^+ - C_{10}H_{13}$, 29%]. Anal. Calc. for $C_{15}H_{18}Fe$: C, 70.89; H, 7.14. Found: C, 70.67; H, 7.01.

4.10. rac-4-Ferrocenyl-4a,5,6,8a-tetrahydro-4a,5,8-trimethyl-4H-indeno[2,3-a]ferrocene (6)

Orange crystals, m.p. 144–145°C. Selected IR data (KBr): 3087 m, 2958 s, 492 vs, 480 vs cm^{-1}. ^{1}H-NMR ($CDCl_3$, TMS): δ 0.30 (s, 3H, CH_3), 0.93 (d, 3H, $^3J = 7.0$ Hz, CH–CH_3), 1.81 (s, 3H, =C–CH_3), 1.81 (1H, CH–CH_3), 2.1–2.4 (m, 2H, CH_2), 2.43 (s, 1H, C*H*), 3.51 (s, 1H, C*H*–ferrocene), 4.04 (s, 5H, *unsubst. cp*), 4.16 (s, 5H, *unsubst. cp*), 3.7–4.4 (m, 7H, *subst. cps*), 5.34–5.37 (m, 1H, –C=C*H*–). ^{13}C-NMR ($CDCl_3$, TMS): δ 16.87 (CH_3), 20.30 (CH_3), 22.84 (CH_3); 31.22, 33.22, 46.79, 49.52, 55.42, 60.94, 61.76, 66.49, 66.98, 67.70, 67.96, 68.14, 68.56, 69.30; 90.10 (*quaternary C of ferrocene*), 94.79 (*quaternary C of ferrocene*), 97.27 (*quaternary C of ferrocene*), 118.50 (–C=*C*H–), 135.19 (–*C*=CH–). MS (EI, 70 eV): *m*/*z* 504 [M^+, 100%], 439 [$M^+ - C_5H_5$, 8%], 383 [$M^+ - C_5H_5Fe$, 16%), 319 [$M^+ - C_{10}H_9Fe$, 11%]. Anal. Calc. for $C_{30}H_{32}Fe_2$: C, 71.45; H, 6.40. Found: C, 70.18; H, 6.47. Single crystals, suitable for X-ray analysis, were obtained by crystallization from diethyl ether.

4.11. Reaction of monolithioferrocene with 2,3,4,5-tetramethylcyclopent-2-en-1-one and chromatographic work-up

Monolithioferrocene (0.977 g, 5.09 mmol) was suspended in 30 ml THF, which was pre-chilled to −60°C, and tetramethylcyclopent-2-enone (0.8 ml, 5.3 mmol) was added dropwise. The reaction mixture was warmed to r.t., the solvent was removed in vacuo and the residue was dissolved in diethyl ether. Due to allylic rearrangement under the conditions of chromatography four different compounds were isolated (Silica 60, 220–440 mesh, 25:75 diethyl ether–petroleum ether). (a) Ferrocene; (b) (2,3,4,5-tetramethyl-1,3-cyclopentadien-1-yl)ferrocene [164856-49-9] [15]; (c) (2*E*,5*E*)-3,5-dimethyl-4-ferrocenyl-hepta-2,5-dien-4-ol (**7**); (d) 4-ferrocenyl-4-hydroxy-2,3,5,6-tetramethyloxane (**8**); yield: 20–30%.

4.12. (2E,5E)-3,5-Dimethyl-4-ferrocenyl-hepta-2,5-dien-4-ol (7)

Orange oil, selected IR data (KBr): 3550 m (ν_{O-H}), 1695 vs ($\nu_{C=C}$), 1650 s, 1560 s cm^{-1}. ^{1}H-NMR ($CDCl_3$, TMS): δ 1.35 (s, 6H, 2 × CH_3), 1.56 (d, 6H, $^3J = 6.7$ Hz, 2 × =CH–CH_3), 2.22 (s, 1H, O*H*), 4.10–4.19 (m, 9H, *ferrocenyl*), 5.72 (q, 2H, $^3J = 6.7$ Hz, 2 × =C*H*–CH_3). ^{13}C-NMR ($CDCl_3$, TMS): δ 12.86 (2 × CH_3), 13.01 (2 × CH_3); 65.62, 66.97, 67.37, 67.59, 68.10 (*ferrocenyl*); 117.12 (2 × –C=*C*H–). MS (EI, 70 eV): *m*/*z* 324 [M^+, 25%]. Anal. Calc. for $C_{19}H_{24}FeO$: C, 70.38; H, 7.46; O, 4.93. Found: C, 70.17; H, 7.45; O, 5.17.

4.13. 4-Ferrocenyl-4-hydroxy-2,3,5,6-tetramethyloxane (8)

Orange crystals, m.p. 110–111°C. Selected IR data (KBr): 3554 m (ν_{O-H}) cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ 0.91 (d, 6H, $^3J = 6.6$ Hz, 2 × CH_3), 1.07 (d, 6H, $^3J = 6.2$

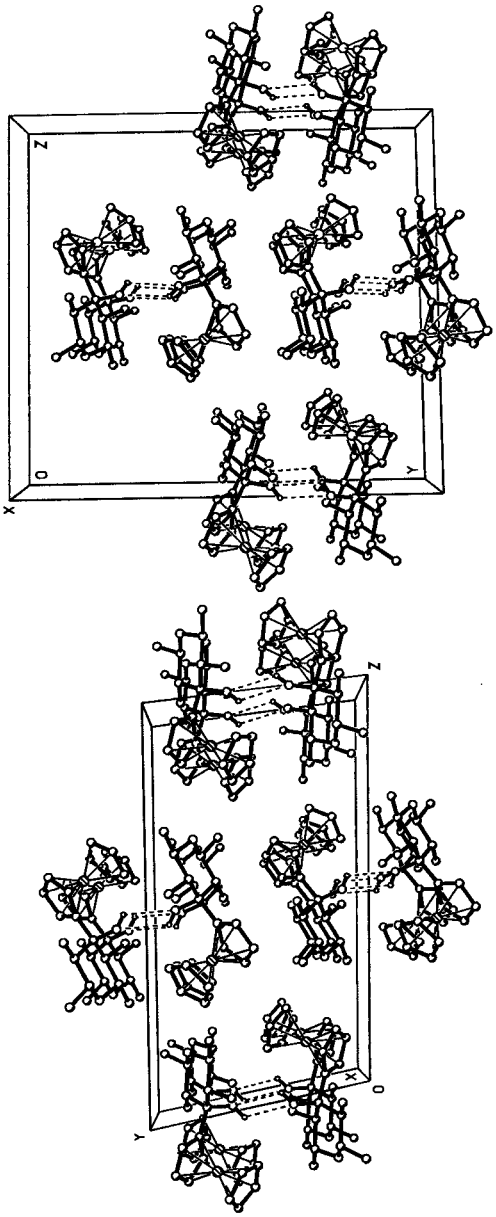


Fig. 3. Crystal lattices of the isomorphic forms **8a** and **8b**.

Hz, $2 \times CH_3$), 1.32–1.47 (m, 2H, $2 \times$ C–C*H*–CH_3), 3.37–3.52 (m, 2H, $2 \times$ O–C*H*–CH_3), 3.73 (s, 1H, O*H*), 4.10 ('t', 2H, *subst. cp*), 4.13 (s, 5H, *unsubst. cp*), 4.16 ('t', 2H, *subst. cp*). ^{13}C-NMR ($CDCl_3$, TMS): δ 11.72 ($2 \times$ C–CH–CH_3), 20.48 ($2 \times$ O–CH–CH_3), 46.72 ($2 \times$ C–*C*H–CH_3); 66.73, 67.24, 69.13, 72.97 (*ferrocenyl*); 73.63 ($2 \times$ O–*C*H–CH_3), 96.93 (*quaternary C*). MS (EI, 70 eV): *m*/*z* 342 [M^+, 100%]. Anal. Calc. for $C_{19}H_{26}FeO_2$: C, 66.36; H, 7.66; O, 9.35. Found C, 66.33; H, 7.38; O, 9.85. Single crystals of **8a**, suitable for X-ray analysis, were obtained by crystallization from 1:3 diethyl ether–petroleum ether. Single crystals of **8b** were obtained by sublimation.

*4.14. X-ray structure determinations of **6**, **8a**, **8b** and **9** (Figs. 1–4)*

X-ray structures of **6**, **8a**, **8b** and **9** were measured on a Siemens P4 diffractometer with graphite-monochromatized Mo–K_α radiation ($\lambda = 71.073$ pm). Crystal data, data collection, and refinement parameters of **6**, **8a**, **8b** and **9** are summarized in Table 1. The unit cells were determined by automatic indexing of 25 to 35 centered reflections, obtained by P4 automatic routines. Data were measured via ω-scan and corrected for Lorentz and polarization effects, and an empirical absorption correction was made for **8a** and **8b**. The structures were solved by direct methods, SHELXS-86 [18], and refined by a full-matrix least-squares procedure using SHELXS-93 [19]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of carbon atoms were placed in calculated positions. The hydrogen atoms of hydroxy groups in **8a** and **8b** were located and refined isotropically. For complete crystallographic data, tables of bond lengths, bond angles, anisotropic thermal parameters, calculated hydrogen atomic coordinates, and final atomic coordinates, see supporting information.

*4.15. Polymorphism of **8a** and **8b***

Compound **8** crystallizes in two polymorphic forms, **8a** in the centrosymmetric space group *P*1, **8b** in the non-symmetric space group *Cc*, both with two independent molecules in the asymmetric unit. In **8b** these two molecules are connected by weak hydrogen bonding and build up a dimeric unit (Fig. 2) with large O···H distances of 250 and 258 pm, and non-tetrahedral angels $C_{11} - O_1 \cdots H$ of 141.1° and $C_{31} - O_3 \cdots H$ of 142.3°. Therefore this kind of connection may be better described by dipole–dipole interactions of the hydroxyl groups. The analogous dimerization is observed in **8a**, but in contrast to **8b**, each of the two independent molecules is connected by its own symmetry equivalent part through an inversion center. The O···H distances are 253 and 258 pm, with an angle of 138.0° (for both). The comparison of all dimeric units **8a** with **8b** shows that they have nearly the same conformation. The difference of the two polymorphic forms can be seen in Fig. 4. The dimers are stacked by van der Waal's forces and build up nearly squared columns parallel to the *a*-axis. The alternate columns along the *c*-axis have different displacements in the direction of the *b*-axis in **8a** and **8b** (Fig. 3).

*4.16. X-ray structural results and conformational characteristics of **9***

In the solid state, the tigloyl substitutents are located at the same side of the ferrocenyl moiety. Due to the

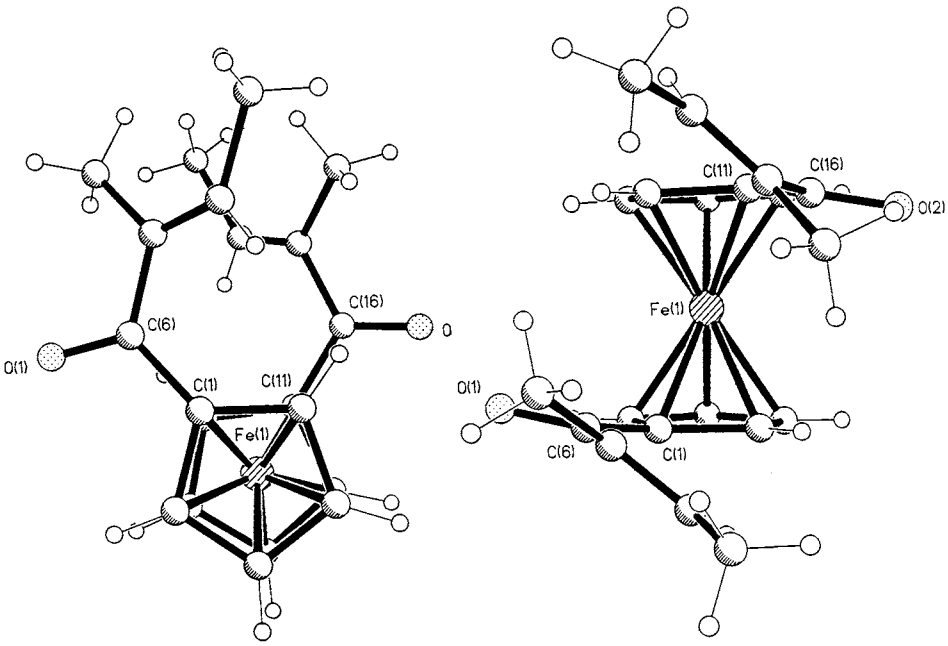


Fig. 4. X-ray structure of **9**.

sterical demands between the Cp-hydrogen at C2 and the olefinic hydrogen at C9 (220 pm), respectively the Cp-hydrogen at C15 and the olefinic hydrogen at C19 (228 pm), the two tigloyl ligands are twisted around the bonds C6–C7 and C16–C17. This results in a torsion angle of $-32°$ for C1–C6–C7–C9 and $-39°$ for C11–C16–C17–C19, respectively. This twisting is additionally favored by an increase in the distance between the two methyl groups. Thus, the distance between C10–C18 and C8–C20 is 387 and 407 pm, respectively. The interesting crystal architecture of **9** is attributable to packing requirements and electrostatic stabilization; this is also reflected by a striking deviation of coplanarity between the aromatic Cp-planes and the cross-conjugated substituents (Fig. 4).

Compound **9** represents another example of non covalently bent ferrocenes [10b]. Consequently, the plane distortion of 3.0(5)° corresponds to differing distances between the substituent bearing carbons C(1) and C(11) and their opposite Cp-carbons C15 and C2, as well as for all other opposite Cp-carbon pairs (C1–C15 = 330, C2–C11 = 335, C3–C12 = 332, C4–C13 = 324, and C5–C14 = 323 pm).

This preferential lattice architecture, which results in obviously very low motional freedom is also reflected in unusual Mössbauer parameters compared to commonly substituted ferrocenes [20]. In particular, the isomer shift (at 90 K) is smaller by ~ 0.02 mm/s than in the parent ferrocene, but comparable to that observed in ring-substituted polymethylferrocenes such as the nonamethyl and deca-methyl homologues.

More pronounced is the decrease in the QS parameter (2.165 ± 0.004 mm/s at 90 K compared to 2.419 ± 0.001 mms in ferrocene and 2.473 ± 0.002 mm/s in decamethylferrocene). It is clear that this decrease in the QS parameter does not arise primarily from the small (2.98°) tilt angle of the five-membered rings, since comparable ring-tilt compounds do not show this effect [21]. The temperature dependence of the quadrupole splitting, QS(T), in **9** is negligible over the range $90 < T < 230$ K.

As noted above, the well resolved components of the T-independent ^{57}Fe Mössbauer data have been fitted to two independent resonance lines, and the area ratio R ($= A(+)/A(-)$, where A is the area under the resonance line at more positive and more negative velocities than the spectrum centroid) is essentially T independent over the indicated range. This result reflects a negligible motion anisotrophy of the metal atom motion with respect to the symmetry axis perpendicular to the (almost co-planar) Cp rings.

Finally, it is worth noting that the T-dependence of the recoil-free fraction (as extracted from the T-dependent area under the resonance curve, as appropriate for an 'optically thin' absorber) shows no evidence for a phase transition of the type noted in ferrocene [22] and in Cp*FeP5 [23] and Cp*FeAs5 [24] in which there is a phase transition from staggered to eclipsed conformation of the Cp rings. In the bistigloyl compound **9**, the eclipsed ring conformation observed in the room temperature X-ray diffraction study appears to obtain over the entire temperature range of the Mössbauer measurements here reported.

5. Supplementary material

Tables of crystal data and structure refinement details, anisotropic thermal parameters, fractional atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms, all bond lengths and angles, and fractional atomic coordinates for the hydrogen atoms for **6**, **8a**, **8b** and **9**. Ordering information is given on any current masthead page. The authors have deposited atomic coordinates for structures **6**, **8a**, **8b** and **9** with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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