

Reactions of 2,3-diferrocenylcyclopropenone with methyllithium and phenyllithium

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Abstract

Reactions of 2,3-diferrocenylcyclopropenone with methyllithium and phenyllithium afford products of the nucleophilic opening of the three-membered ring, viz., α, β -unsaturated ketones (*cis*-3,4-diferrocenylbut-3-en-2-one and *cis*-2,3-diferrocenyl-1-phenylprop-2-enone) and allylic alcohols (*cis*-3,4-diferrocenyl-2-methylbut-3-en-2-ol and *cis*-1,1-diphenyl-2,3-diferrocenylprop-2-en-1-ol). The insertion product of a methyl(diferrocenyl)vinylcarbenoid into a σ -bond of the starting compound, viz., 2,3,4-triferrocenyl-4-(1-ferrocenyl-2-oxopropyl)cyclobutenone, along with intramolecular *ortho*-alkylation products, viz., 2,3-diferrocenylindanone and 2,3-diferrocenyl-2-hydroxyindanone, were also isolated. X-ray diffraction data for triferrocenylcyclobutenone and 2,3-diferrocenyl-2-hydroxyindanone are presented.

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1. Introduction

The interest in compounds of the cyclopropenone series stems from the inherent polar pseudoaromatic structures representing two mesomeric forms (1) \leftrightarrow (2) [1,2] (Scheme 1), high strain energies, planarity, chemical reactivity of the cyclopropane moiety [1–3], and possible practical applications.

Cyclopropenones are ambident compounds, which react with nucleophilic, electrophilic, and bipolar reagents and with compounds with high densities of π -electronic systems [4].

Current chemical literature contains numerous publications devoted to the synthesis and investigations into chemical properties of aryl- and alkyl-substituted cyclopropenones, their hetero-analogs incorporating Group 15 and Group 16 elements (S, Se, N, P), and

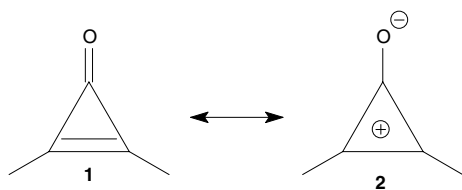
cyclopropenones bearing such substituents at the C=C— bond as HO–, F–, etc. [4].

Ferrocenyl-substituted cyclopropenones have not virtually been studied so far. 2,3-Diferrocenylcyclopropenone (3) was first isolated in low yield (~7%) in 1975 [5] by low-temperature alkylation of ferrocene with tetrachlorocyclopropane in the presence of $AlCl_3$. Later, this method has been improved, which allowed preparation of 2,3-diferrocenylcyclopropenone (3) in virtually quantitative yield [6,7]. The availability and stability of compound 3 allowed studies on its chemical transformations. It was found that 2,3-diferrocenylcyclopropenone (3) easily underwent three-membered ring opening to give *cis*-2,3-diferrocenylacrylic acid derivatives [6] (Scheme 2).

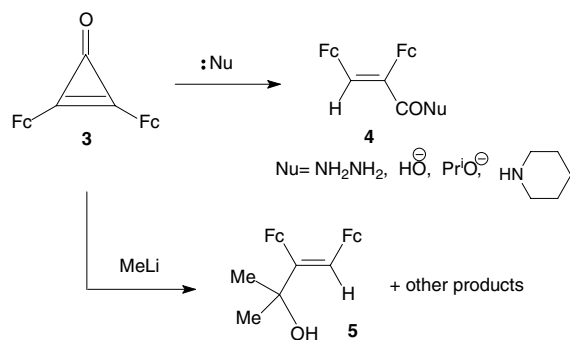
cis-3,4-Diferrocenyl-2-methylbut-3-en-2-ol (5) was isolated as the main reaction product with methyllithium [6]. It is noteworthy that compounds 4 and 5 comprising functional groups together with the ferrocenyl; residues at the double bond have gained prominence by virtue of their exciting structure, chemical reactivity, and potential use as molecular building

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Scheme 1.



Scheme 2.

blocks and in the realm of supramolecular chemistry as redox switching receptors [8].

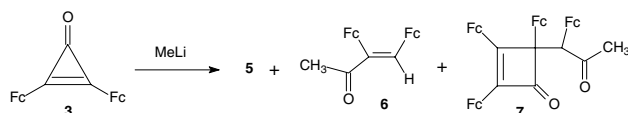
In the present paper, we report the results of a detailed study on the reactions of 2,3-diferrocenylcyclopropenone (**3**) with organolithium compounds, viz., methyllithium and phenyllithium.

2. Results and discussion

We have found that 2,3-diferrocenylcyclopropenone (**3**) reacts with an excess of methyllithium to give a mixture of several products, the main components being the alcohol **5** [6], 3,4-diferrocenylbut-3-en-2-one (**6**), and 2,3,4-triferrocenyl-4-(1-ferrocenyl-2-oxopropyl)cyclobutene (**7**) (Scheme 3).

The structures of compounds **6** and **7** were established based on the data from ^1H and ^{13}C NMR spectroscopy and elemental analysis (see Section 4).

Previously [6], we have demonstrated that compound **5** was formed as a single isomer with *cis* arrangement of the ferrocenyl groups. Diferrocenylbutenone **6** was also isolated as a single isomer. ^1H NMR data suggest analogous *cis* arrangement of the ferrocenyl groups.



Scheme 3.

Bright-violet compound **7** was obtained as an individual diastereomer in $\sim 8\%$ yield. Its structure followed from spectroscopic data. Thus its ^1H NMR spectrum contained signals for four unsubstituted cyclopentadienyl rings of the ferrocene units together with signals for substituted cyclopentadienyl fragments and singlets for the methyl and methine groups. The ^{13}C NMR spectrum contained signals for four *ipso* carbon atoms of the ferrocenyl fragments, two carbonyl carbon atoms, three carbon atoms bearing no hydrogen atoms, the methyl and methine groups, and CH groups of the ferrocenyl substituents. The mass spectrum of compound **7** manifested the presence of a molecular ion with m/z 860, which points to its dimeric nature and confirms its structure.

The spatial configuration of triferrocenylcyclobutene **7** was established by X-ray diffraction analysis of a single crystal prepared by crystallization from dichloromethane (Table 1). The general view of the molecule **7** is shown in Fig. 1. The four-membered ring is a planar scalene quadrangle. The C=C bond length is equal to 1.370 (7) Å and the sharp angle at C(42) is 81.0(4)°. The bond angles at C(41), C(43), and C(44) are close to 90° (91.0(5)°, 95.1(5)°, and 92.3(5)°, respectively). The lengths of the C=O, Fe–C, and carbon–carbon bonds of the ferrocenyl rings, as well as the geometrical parameters of the ferrocene sandwiches are close to standard values [9].

The reaction of 2,3-diferrocenylcyclopropenone (**3**) with phenyllithium results also in several products including α , β -unsaturated ketone (**8**), alcohol (**9**), 2,3-diferrocenylindan-1-one (**10**), and 2,3-diferrocenyl-2-hydroxyindan-1-one (**11**) (Scheme 4).

^1H and ^{13}C NMR data suggest that compounds **8** and **9** were formed as single geometrical isomers, presumably, with the *cis* orientation of the ferrocenyl substit-

Table 1
Selected bond lengths and bond angles for compounds **7** and **11**

Selected bond lengths, r (Å)		Selected bond angles, ω (°)	
<i>Compound 7</i>			
C(41)–C(42)	1.580(8)	C(41)–C(42)–C(43)	81.0(4)
C(42)–C(43)	1.571(8)	C(42)–C(43)–C(44)	95.1(5)
C(43)–C(44)	1.370(7)	C(43)–C(44)–C(41)	92.3(5)
C(44)–C(41)	1.466(8)	C(44)–C(41)–C(42)	91.0(5)
C(41)–O(1)	1.199(6)	C(21)–C(42)–C(45)	115.3(5)
C(42)–C(45)	1.565(8)	C(21)–C(42)–C(43)	109.0(5)
C(45)–C(46)	1.527(8)	C(45)–C(42)–C(41)	118.7(5)
C(46)–C(47)	1.479(9)	C(1)–C(43)–C(44)	138.4(6)
<i>Compound 11</i>			
C(46)–O(2)	1.211(7)	C(11)–C(44)–C(43)	137.6(6)
C(18)–C(19)	1.380(5)	C(18)–C(19)–C(13)	110.2(3)
C(18)–C(11)	1.519(4)	C(19)–C(13)–C(12)	105.2(3)
C(11)–C(12)	1.558(5)	C(13)–C(12)–C(11)	103.2(3)
C(12)–C(13)	1.551(5)	C(12)–C(11)–C(18)	101.7(3)
C(13)–C(19)	1.472(5)	C(11)–C(18)–C(19)	111.0(3)
C(13)–O(2)	1.197(4)	O(1)–C(12)–C(13)	109.0(3)
C(12)–O(1)	1.419(4)	O(2)–C(13)–C(19)	128.4(3)
C(12)–C(20)	1.506(5)	O(2)–C(13)–C(12)	126.3(3)

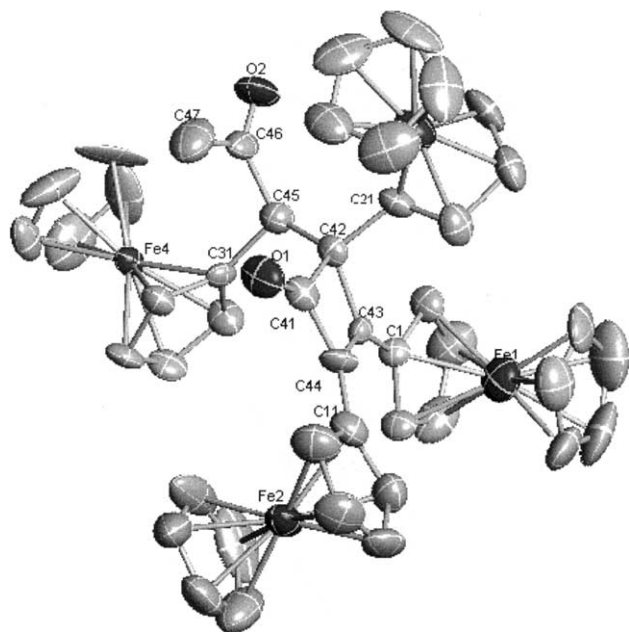
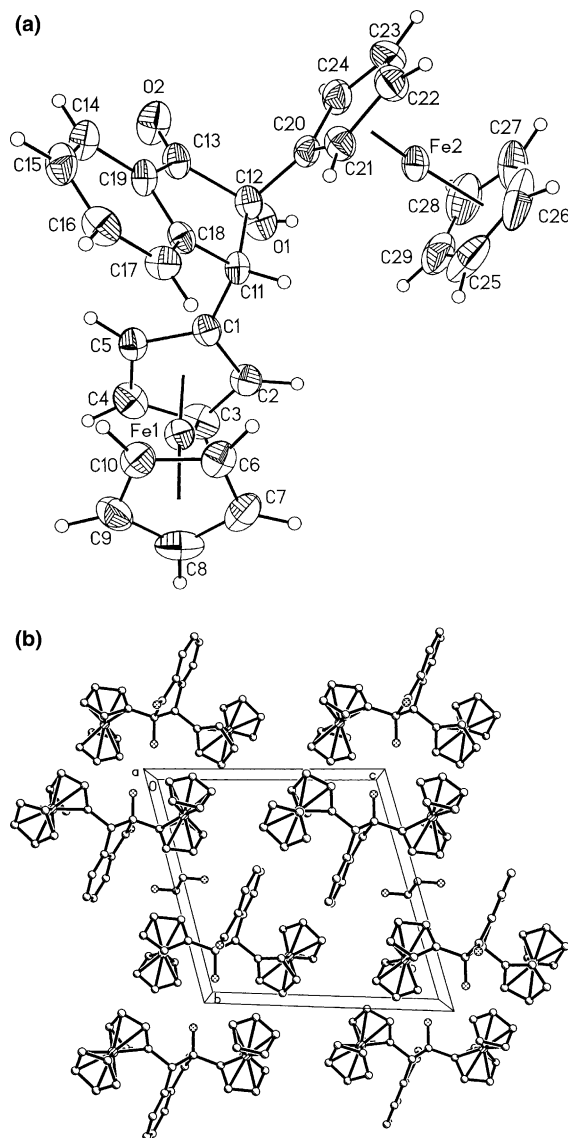


Fig. 1. Crystal structure of compound 7.

uents [6]. 2,3-Diferrocenylindan-1-ones (**10** and **11**) were obtained as single diastereomeric forms (see Section 4). The IR, ^1H and ^{13}C NMR spectroscopic data corroborate completely the structures of compounds **8–11**.

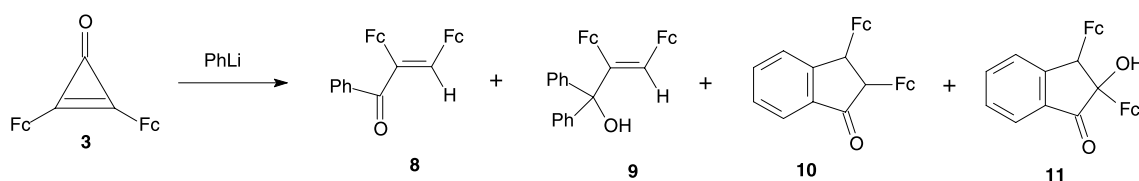
The spatial structure of 2-hydroxyindan-1-one (**11**) was determined by X-ray diffraction analysis of a single crystal prepared by crystallization from ethylene glycol (Table 1). The overall view of molecule **11** is shown in Fig. 2(a). The molecular packing in the crystal is presented in Fig. 2(b). According to X-ray diffraction data, the molecule **11** contains *ortho*-disubstituted benzene ring fused to a five-membered ring. The ferrocenyl substituents in positions 2 and 3 of the five-membered ring are *trans* oriented, the hydroxy and carbonyl groups occupy adjacent positions of the five-membered ring. The Fe–C and carbon–carbon bonds of the ferrocene sandwiches as well as their geometrical parameters are similar to those in related compounds [10,11].

All the reaction products **5–11** are apparently formed as a result of three-membered ring opening in the addition products (**12a,b**) of the organolithium compounds at the carbonyl group of the cyclopropenone **3** to produce diferrocenylvinyl carbenoid intermediates (**13a,b**). The latter abstract proton from the solvent to

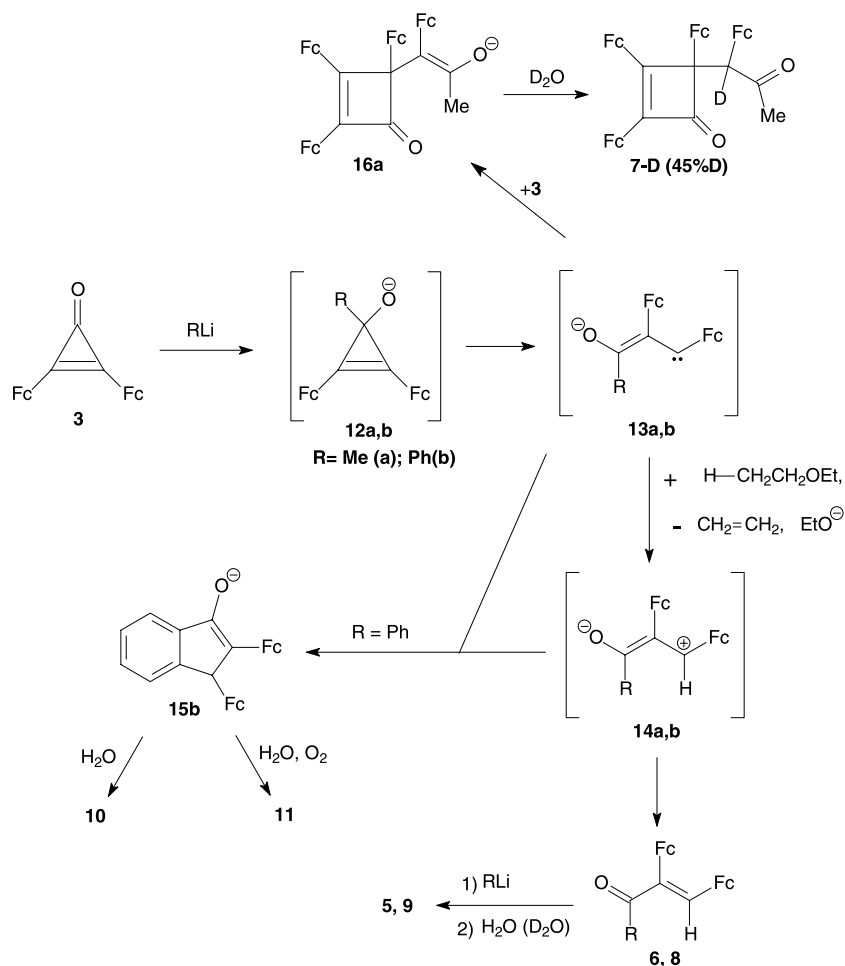
Fig. 2. (a) Crystal structure of compound **11**. (b) Crystal packing of **11**.

afford enones **6** and **8**. The addition of the second molecule of the organolithium reagent to the carbonyl groups of the enones **6** and **8** yields the alcohols **5** and **9**, respectively (Scheme 5).

The intramolecular alkylation of the phenyl fragment in intermediates **13b** or (**14b**) results in enolate (**15b**). The insertion of the carbenoid **13a** into a σ -bond of the original cyclopropenone **3** affords enolate (**16a**).



Scheme 4.



Quenching of the reaction mixtures with water converts all the intermediates (**15b**) (this can also be subjected to simultaneous oxidation by the atmospheric oxygen) and (**16a**) into the final products **7**, **10** and **11**.

The results obtained in quenching of the reaction of methyl lithium with 2,3-diferrocenylcyclopropanone **3** with deuterium oxide support the reaction scheme proposed. No deuterium was detected in compounds **5** and **6** obtained, which suggests the abstraction of proton by the carbenoid intermediate from the solvent. Deuterium (45%) was present only in the cyclobutenone **7** as a result of isomerization of the enol form **16a** into the keto form **7-D**.

3. Conclusion

Thus, based on the results obtained one may conclude that the reactions of 2,3-diferrocenylcyclopropanone (**3**) with organolithium compounds involve nucleophilic opening of the cyclopropanone ring into diferrocenylvinyl carbenoids leading to linear products (the main process) and several side processes such as

(i) cyclopropanone recyclization with ring expansion and formation of triferrocenylcyclobutenone and (ii) intramolecular alkylation of the phenyl fragment in small-ring opening intermediates leading to diferrocenylindanone derivatives, the former process prevailing.

4. Experimental

All the solvents were dried according to the standard procedures and were freshly distilled before use. Column chromatography was carried out on alumina (Brockmann activity III). The ^1H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in CDCl_3 with Me_4Si as the internal standard. The mass spectra were obtained on Varian MAT CH-6 instrument (EI-MS, 70 eV). An Elemental Analysis System GmbH was used for elemental analyses.

The following reagents were purchased from Aldrich: tetrachlorocyclopropane, 98%; ferrocene, 98%; aluminum chloride, 99.88%; methyl lithium (1.6 M solution in

diethyl ether); phenyllithium (1.9 M solution in cyclohexane–diethyl ether); deuterium oxide, 100.00 atom% D.

The X-ray diffraction patterns were recorded on a Siemens P4/PC/ ω diffractometer (compound **7**) and a Bruker Smart Apex CCD area detector/ ω diffractometer (compound **11**). The crystallographic data, the experimental conditions, and corrections are given in Tables 1 and 2.

2,3-Diferrocenylcyclopropenone (**3**) was prepared by alkylation of ferrocene with tetrachlorocyclopropene in the presence of AlCl₃ as described in [6], the yield was 86%, orange crystals, m.p. 182–183 °C (lit. [6]: m.p. 182–183 °C).

4.1. Reaction of 2,3-diferrocenylcyclopropenone (**3**) with methyllithium

A 1.6 M solution of methyllithium in diethyl ether (40.0 ml) was added with stirring in an inert atmosphere to a solution of the cyclopropenone **3** (4.2 g, 10 mmol) in dry benzene (200 ml). The mixture was stirred for 3 h at ambient temperature and then water (100 ml) was added. The organic layer was separated, washed with water (2 × 50 ml), the solvent was removed in vacuo, and the residue was chromatographed on alumina (hexane–diethyl ether, 3:1). The following products were isolated: enone **6**, red powder, yield 0.75 g (17%), m.p. 125–

126 °C; alcohol **5**, orange crystals, yield 2.7 g (60%), m.p. 132–133 °C (lit. [6]: m.p. 132–133 °C); cyclobutenone (**7**), violet crystals, yield 0.35 g (8%), m.p. 287–288 °C (decomp.).

cis-3,4-Diferrocenyl-2-methylbut-3-en-2-one (**6**): ¹H NMR: δ 2.55 (3H, s, CH₃), 4.04 (5H, s, C₅H₅), 4.06 (5H, s, C₅H₅), 4.22 (4H, m, C₅H₄), 4.28 (2H, m, C₅H₄), 4.40 (2H, m, C₅H₄), 7.20 (1H, s, CH=). ¹³C NMR: 27.48 (CH₃); 67.78, 69.90, 70.83, 70.86 (2C₅H₄); 69.23, 69.46 (2 C₅H₅); 79.44, 79.67 (2C_{ipso}Fc); 137.88 (CH=); 135.48 (C); 198.35 (C=O). Anal. Calc. for C₂₄H₂₂Fe₂O: C, 65.79 H, 5.06; Fe, 25.50. Found: C, 65.56; H, 5.23; Fe, 25.71%. MS: *m/z* 438 [M]⁺.

2,3,4-Triferrocenyl-4-(1-ferrocenyl-2-oxopropyl)cyclobutenone (**7**): ¹H NMR: δ 2.73 (3H, s, CH₃), 4.00 (5H, s, C₅H₅), 4.07 (5H, s, C₅H₅), 4.19 (5H, s, C₅H₅), 4.22 (5H, s, C₅H₅), 3.31 (1H, s, CH), 3.93 (1H, m, C₅H₄), 3.96 (1H, m, C₅H₄), 4.09 (2H, m, C₅H₄), 4.17 (1H, m, C₅H₄), 4.23 (2H, m, C₅H₄), 4.33 (1H, m, C₅H₄), 4.36 (2H, m, C₅H₄), 4.44 (1H, m, C₅H₄), 4.48 (1H, m, C₅H₄), 4.50 (1H, m, C₅H₄), 4.75 (1H, m, C₅H₄), 4.90 (1H, m, C₅H₄), 4.94 (1H, m, C₅H₄). ¹³C NMR: δ 31.52 (CH₃); 58.82 (CH); 67.32, 67.40 (2C), 67.63, 68.41, 68.57, 68.66 (2C), 68.84, 69.13, 69.23, 70.47, 70.54, 70.91 (2C), 71.45 (4C₅H₄) 68.90, 69.18, 69.48, 69.93 (4C₅H₅); 72.43 (C); 73.04, 74.82, 80.29, 89.70 (4C_{ipso}Fc); 140.01, 167.99 (2C); 187.86, 206.25 (2C=O). Anal. Calc. for

Table 2
Crystal data, data collection and refinement parameters for compounds **7** and **11**

Data	7	11
Molecular formula	C ₄₇ H ₄₀ Fe ₄ O ₂	C ₂₉ H ₂₄ Fe ₂ O ₂ · ½C ₂ H ₆ O ₂
Formula weight (g mol ⁻¹)	860.19	547.22
Temperature (K)	291(2)	291(2)
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	12.740(3)	7.8714(6)
<i>b</i> (Å)	11.478(3)	12.7243(10)
<i>c</i> (Å)	25.279(5)	12.7392(10)
α (°C)	90.0	72.491(2)
β (°C)	101.71(2)	78.003(2)
γ (°C)	90.0	81.526(2)
<i>V</i> (Å ³)	3619.8(15)	1185.31(16)
<i>Z</i>	4	2
<i>D</i> _{calc.} (Mg mm ⁻³)	1.578	1.533
Absorption coefficient (mm ⁻¹)	1.612	1.255
<i>F</i> (000)	1768	566
Radiation, λ (Å)	Mo K α , 0.71073	Mo K α , 0.71073
Monochromator	Graphite	Graphite
θ range (°)	1.96–25.01	1.70–25.00
Reflections collected	6682	9760
Reflections independent	6373	4179
<i>R</i> _{int}	0.0617	0.0522
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0527, <i>wR</i> ₂ = 0.0601	<i>R</i> ₁ = 0.0469, <i>wR</i> ₂ = 0.0984
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1515, <i>wR</i> ₂ = 0.0742	<i>R</i> ₁ = 0.0684, <i>wR</i> ₂ = 0.1044
Data/restraints/parameters	6373/0/479	4179/0/312
Refinement method	Full-matrix-least-squares on <i>F</i> ²	Full-matrix-least-squares on <i>F</i> ²
Goodness-of fit	0.743	0.913
Minimum/maximum residual electron density (e Å ⁻³)	–0.329/0.387	–0.513/0.707

$C_{47}H_{40}Fe_4O_2$: C, 65.62; H, 4.69; Fe, 25.97. Found: C, 65.79; H, 4.45; Fe, 26.11%. MS: m/z 860 $[M]^+$.

Compound **7-D**: 1H NMR: δ 2.72 (3H, s, CH_3), 4.01 (5H, s, C_5H_5), 4.07 (5H, s, C_5H_5), 4.18 (5H, s, C_5H_5), 4.23 (5H, s, C_5H_5), 3.30 (0.55H, bs, CH), 3.94 (1H, m, C_5H_4), 3.97 (1H, m, C_5H_4), 4.09 (2H, m, C_5H_4), 4.16 (1H, m, C_5H_4), 4.20 (2H, m, C_5H_4), 4.33 (1H, m, C_5H_4), 4.35 (2H, m, C_5H_4), 4.44 (1H, m, C_5H_4), 4.47 (1H, m, C_5H_4), 4.50 (1H, m, C_5H_4), 4.73 (1H, m, C_5H_4), 4.89 (1H, m, C_5H_4), 4.93 (1H, m, C_5H_4).

4.2. Reaction of 2,3-diferrocenylcyclopropenone (**3**) with phenyllithium

A 1.9 M solution of phenyllithium in a cyclohexane–diethyl ether mixture (35.0 ml) was added with stirring in an inert atmosphere to a solution of the cyclopropenone **3** (4.2 g, 10 mmol) in dry benzene (200 ml). The mixture was stirred for 3 h at ambient temperature and then water (100 ml) was added. The organic layer was separated, washed with water (2×50 ml), the solvent was removed in vacuo, and the residue was chromatographed on alumina (hexane–diethyl ether, 2:1). The following products were isolated: enone **8**, red powder, yield 0.8 g (16%), m.p. 147–148 °C; alcohol **9**, orange powder, yield 3.1 g (55%), m.p. 163–164 °C; indanone **10**, yellow crystals, yield 0.55 g (11%), m.p. 129–131 °C; 2-hydroxyindanone **11**, yellow crystals, yield 0.26 g (5%), m.p. 171–172 °C.

cis-2,3-Diferrocenyl-1-phenylprop-2-enone (**8**): 1H NMR: δ 4.22 (5H, s, C_5H_5), 4.26 (5H, s, C_5H_5), 4.09 (2H, m, C_5H_4), 4.12 (2H, m, C_5H_4), 4.18 (2H, m, C_5H_4), 4.36 (2H, m, C_5H_4), 7.08 (1H, s, $CH=$), 7.11–7.48 (5H, m, C_6H_5). Anal. Calc. for $C_{29}H_{24}Fe_2O$: C, 69.63; H, 4.83; Fe, 22.33. Found: C, 69.84; H, 4.76; Fe, 22.51%. MS: m/z 500 $[M]^+$.

cis-1,1-Diphenyl-2,3-diferrocenylprop-2-en-1-ol (**9**): 1H NMR: δ 3.89 (5H, s, C_5H_5), 3.93 (5H, s, C_5H_5), 3.69 (2H, m, C_5H_4), 4.01 (2H, m, C_5H_4), 4.08 (2H, m, C_5H_4), 4.34 (2H, m, C_5H_4), 5.67 (1H, bs, OH), 6.02 (1H, s, $CH=$), 7.30–7.53 (10H, m, $2C_6H_5$). ^{13}C NMR: δ 68.40, 68.56, 69.68, 71.25 ($2C_5H_4$); 68.87, 69.34 ($2C_5H_5$); 81.50, 83.71 ($2C_{ipso}Fc$); 83.42 (C); 127.18 ($CH=$); 127.74, 128.51, 133.19 ($2C_6H_5$); 136.27 (C); 147.01 ($2C_{ipso}$). Anal. Calc. for $C_{35}H_{30}Fe_2O$: C, 72.69; H, 5.92; Fe, 19.32. Found: C, 72.86; H, 5.73; Fe, 19.47%. MS: m/z 578 $[M]^+$.

2,3-Diferrocenylindanone (**10**): 1H NMR: δ 4.10 (5H, s, C_5H_5), 4.19 (5H, s, C_5H_5), 3.84 (1H, m, C_5H_4), 3.98 (1H, m, C_5H_4), 4.14 (2H, m, C_5H_4), 4.17 (2H, m, C_5H_4), 4.20 (1H, m, C_5H_4), 4.23 (1H, m, C_5H_4), 4.48 (1H, d, CH, $J = 3.3$ Hz), 4.60 (1H, d, CH, $J = 3.3$ Hz), 7.36–7.70 (4H, m, C_6H_4). Anal. Calc. for $C_{29}H_{24}Fe_2O$: C, 69.63; H, 4.84; Fe, 22.33. Found: C, 69.81; H, 4.63; Fe, 22.47%. MS: m/z 500 $[M]^+$.

2,3-Diferrocenyl-2-hydroxyindanone (**11**): 1H NMR: δ 3.12 (1H, bs, OH), 4.15 (5H, s, C_5H_5), 4.20 (5H, s, C_5H_5), 3.89 (1H, m, C_5H_4), 3.93 (1H, m, C_5H_4), 4.10 (1H, m, C_5H_4), 4.12 (2H, m, C_5H_4).

4.19 (1H, m, C_5H_4), 4.26 (1H, m, C_5H_4), 4.28 (1H, m, C_5H_4), 4.56 (1H, s, CH), 7.48 (1H, m, C_6H_4), 7.71–7.86 (3H, m, C_6H_4). ^{13}C NMR: δ 52.80 (CH); 66.14, 66.43, 67.82, 67.90, 68.09, 68.15, 68.48, 70.20 ($2C_5H_4$); 68.92, 68.94 ($2C_5H_5$); 81.06 (C); 88.11, 92.15 ($2C_{ipso}Fc$); 124.54, 127.27, 128.59, 135.01 (C_6H_4); 134.46, 137.10 ($2C_{ipso}$); 182.91 ($C=O$). Anal. Calc. for $C_{29}H_{24}Fe_2O_2$: C, 67.47; H, 4.69; Fe, 21.64. Found: C, 67.26; H, 4.77; Fe, 21.45%. MS: m/z 516 $[M]^+$.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 232039 for compound **7** and No. 232040 for compound **11**. 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](http://www.ccdc.cam.ac.uk)).

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References

- [1] A. Greenberg, R.P.T. Tomkins, M. Dobrovolny, J.F. Liebman, *J. Am. Chem. Soc.* 105 (1983) 6855.
- [2] P.H.M. Budzellar, E. Kraka, D. Cremer, P.V.R. Schleyer, *J. Am. Chem. Soc.* 108 (1986) 561.
- [3] H. Dahn, M.-N. Ung-Truong, *Helv. Chim. Acta* 70 (1987) 2130.
- [4] K. Komatsu, T. Kitagawa, *Chem. Rev.* 103 (2003) 1371.
- [5] I. Agranat, E. Aharon-Shalom, *J. Am. Chem. Soc.* 35 (1975) 3829.
- [6] E.I. Klimova, T. Klimova Berestneva, L. Ruiz Ramirez, A. Cinguantini, M. Corsini, P. Zanello, S. Hernandez Ortega, M. Martinez Garcia, *Eur. J. Org. Chem.* (2003) 4265.
- [7] E.I. Klimova, T. Klimova Berestneva, A. Cinguantini, M. Corsini, P. Zanello, R.A. Toscano, S. Hernandez Ortega, M. Martinez Garcia, *Org. Biomol. Chem.* 1 (2003) 1.
- [8] A. Togni, T. Hayashi (Eds.), *Ferrocenes*, VCH, Weinheim, 1995.
- [9] L.E. Sutton (Ed.), *Tables of Interatomic Distances and Configuration in Molecules and Ions*, The Chemical Society, London, 1965.
- [10] E.I. Klimova, T. Klimova Berestneva, L. Ruiz Ramirez, M. Martinez Garcia, C. Alvarez Toledano, P.G. Espinosa, R.A. Toscano, *J. Organomet. Chem.* 545–546 (1997) 191.
- [11] E.I. Klimova, M. Martinez Garcia, T. Klimova, C. Alvarez Toledano, R.A. Toscano, R. Moreno Esparza, L. Ruiz Ramirez, *J. Organomet. Chem.* 566 (1998) 175.