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The reactions of semicarbazide and thiosemicarbazide with ferrocenyl-substituted α,β-enones

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Abstract

Semicarbazide (hydrochloride) and thiosemicarbazide react with α,β-unsaturated ketones of the ferrocene series in excess of ^{t}BuOK to give 1-carbamoyl- and 1-thiocarbamoyl(ferrocenyl)-4,5-dihydropyrazoles. The condensation with thiosemicarbazide is accompanied by the fragmentation of the starting α,β-enones resulting in ferrocenecarbaldehyde or acetylferrocene thiosemicarbazones.

Keywords: Ferrocene; Semicarbazide; Thiosemicarbazide; 1-Carbamoyl-4,5-dihydropyrazole; 1-Thiocarbamoyl-4,5-dihydropyrazole

1. Introduction

The chemistry of hetero- and carbocycles with ferrocenyl substituents is based on sufficiently high accessibility of the starting α,β-unsaturated carbonyl compounds of the ferrocene series. Thus the latter react with hydrazine in aqueous ethanol to give unstable, 1-nonsubstituted 4,5-dihydropyrazoles, which are converted into stable 1-acetyl derivatives by acylation [1–3]. Arylhydrazines react with ferrocenyl enones in an acidic medium [4,5] to give 1-aryl-substituted 4,5-dihydropyrazoles. Under basic conditions, ferrocenylchalcones react with thiourea yielding ferrocenyltetrahydropyrimidinethiones [6]. The characteristic features of all these reactions are their selectivity, high yields of the final products, and ease of their isolation.

It is known that pyrazole, dyhydropyrazole, pyrimidine, dihydro- and tetrahydropyrimidine fragments are abundant components of the structures of diverse biologically active compounds [2,7,8], which stimulates further investigations into the synthesis and studies of pharmacological properties of ferrocenyl-substituted nitrogen-containing heterocycles.

The use of semicarbazides and thiosemicarbazides for the construction of heterocyclic systems has not been studied so far. As a rule, semicarbazides and thiosemicarbazides are employed for the identification of carbonyl compounds by converting them, in the presence of acids, into crystalline derivatives, semicarbazones and thiosemicarbazones, respectively [9,10]. On the other hand, semicarbazides represent hydrazine and urea derivatives simultaneously, and thus, these might react with α,β-unsaturated ketones yielding compounds of the dihydropyrazole or tetrahydropyrimidine series, the potentially biologically active structures, which is of substantial interest.

2. Results and discussion

Here we report the results of our studies on the reactions of semicarbazide and thiosemicarbazide with ferrocenyl-substituted α,β-unsaturated ketones. The starting compounds used were represented by linear (**1a**–**g**) and cyclic (**2**–**4**) chalcones (Scheme 1) prepared by the condensation of the respective carbaldehydes and ketones under standard conditions [3,11].

We found that semicarbazides do not react with the chalcones **1a**–**g** and **2**–**4** in acidic or neutral aqueous-

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ethanolic media. The conditions of choice were boiling of the reactants in anhydrous isopropyl alcohol in the presence of ^{t}BuOK leading to 1-carbamoyl- and 1-thiocarbamoyl(ferrocenyl)-4,5-dihydropyrazoles **5a**–**g**, **7a**,**b**, **8a**,**b**, **9a**,**b**, and **6a**–**g**, respectively (Schemes 2 and 3).

It is noteworthy that the reaction of the chalcones **1**–**4** with semicarbazide occurs without any complications, and 1-carbamoyl-4,5-dihydropyrazoles **5**, **7**–**9** were isolated in 58–71% yields. Bicyclic carbamoyldihydropyrazoles **7**–**9** are formed as ca. 1:1 mixtures of two diastereomers with *trans*- and *cis*-orientations of the H(4) and H(5) protons in dihydropyrazole rings. The *trans*- (**7a**–**9a**) and *cis*-isomers (**7b**–**9b**) are easily separated by column chromatography on alumina.

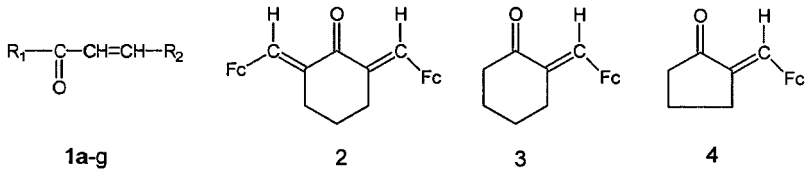
The condensation of the chalcones **1a**–**g** with thiosemicarbazide is accompanied by the fragmentation of the starting chalcones, so that the main reaction products, viz. 1-thiocarbamoyl derivatives **6a**–**g** (yields ca. 50–65%) were formed along with acetylferrocene thiosemicarbazone (**10**) [10] (yields ca. 10–15% from **1a**–**c**), ferrocenecarbaldehyde thiosemicarbazone (**11**) [9] (yields 10–20% from **1e**–**g**), or a mixture of **10** (ca. 7%) and **11** (ca. 8%) from **1d**.

Reactions of cyclic enones **2**–**4** with thiosemicarbazide do not result in the formation of 1-thiocarbamoyl-substituted dihydropyrazoles of the type **12**. In all cases, only fragmentation of the chalcones occurs to give the thiosemicarbazone **11** [9] (ca. 75% yield).

Compounds **5**–**9** were characterized by ^{1}H- and ^{13}C-NMR spectral data (Tables 1 and 2) and data from elemental analyses (Table 3) which corroborate completely their structures as 4,5-dihydropyrazole derivatives.

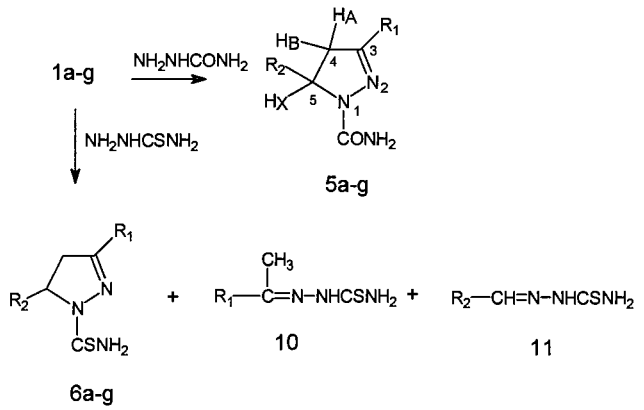
The ^{1}H-NMR spectra of compounds **5a**–**g** and **6a**–**g** contain the characteristic ABX proton spin systems and differ essentially from each other depending on the position of the ferrocenyl group in the heterocyclic ring. Thus the presence of the metallocene substituent at position 3 of the dihydropyrazole ring (**5a**–**c**, **6a**–**c**) is typical of the pronounced upfield shift of the H(A) protons (δ = ca. 3.0), the difference ($\delta_{H(B)}-\delta_{H(A)}$) being equal to ca. 0.5–0.6 ppm. In the spectra of dihydropyrazoles **5e**–**g** and **6e**–**g** with the ferrocenyl group at position 5, the H(A) protons were present at lower fields (δ = ca. 3.6–3.7). Regarding the signals for the H(B) and H(X) protons and those for the NH_2 group, these are little affected, being equal to ca. 0.02–0.09 ppm.

For dihydropyrazoles with two ferrocenyl substituents (**5d**, **6d**), the parameters of the ABX proton



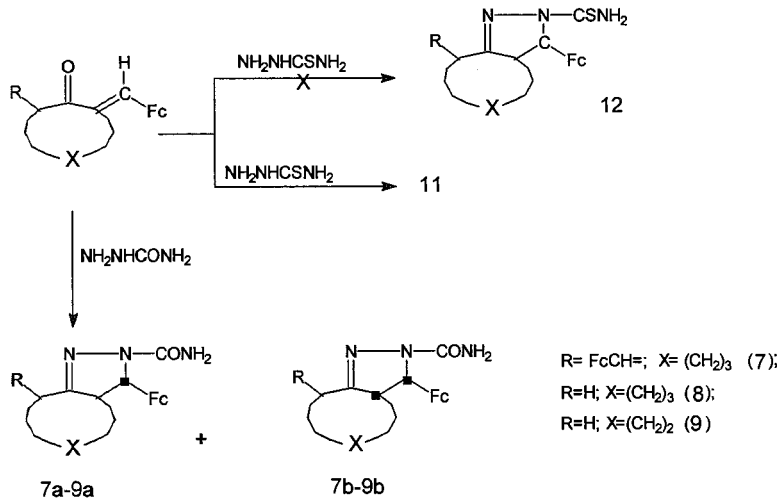
R_1 = Fc, R_2 = Ph (a); R_1 = Fc, R_2 = p-$C_6H_4OCH_3$ (b); R_1 = Fc, R_2 = p-C_6H_4Br (c);
R_1 = R_2 = Fc (d); R_1 = Ph, R_2 = Fc (e); R_1 = p-$C_6H_4OCH_3$, R_2 = Fc (f); R_1 = p-C_6H_4Br, R_2 = Fc (g)
Fc = $C_5H_5FeC_5H_4$

Scheme 1.



R_1 = Fc, R_2 = Ph (a); R_1 = Fc, R_2 = p-$C_6H_4OCH_3$ (b); R_1 = Fc, R_2 = p-C_6H_4Br (c);
R_1 = R_2 = Fc (d); R_1 = Ph, R_2 = Fc (e); R_1 = p-$C_6H_4OCH_3$, R_2 = Fc (f); R_1 = p-C_6H_4Br, R_2 = Fc (g)
Fc = $C_5H_5FeC_5H_4$

Scheme 2.



Scheme 3.

system are similar to those for the 5-ferrocenyl derivatives, which points toward the greater effect of the ferrocenyl substituent at position 5.

The isomeric position of the ferrocenyl group in 1-carbamoyl- (**5a**–**g**) and 1-thiocarbamoyldihydropyrazoles (**6a**–**g**) affects strongly the pattern of the signals for the protons of the ferrocenyl group itself. Thus, all the protons of the substituted cyclopentadienyl ring in 3-ferrocenyl-substituted dihydropyrazoles (**5a**–**c**, **6a**–**c**) resonate at lower fields than those of the nonsubstituted cyclopentadienyl ring, i.e. the effect of the dihydropyrazole ring in this case is analogous to that of a strong electron-withdrawing substituent [12]. In 5-ferrocenyldihydropyrazoles (**5d**–**g**, **6d**–**g**), the heterocycle acts as a weak electron acceptor, and some protons of the substituted cyclopentadienyl ring resonate at higher fields than the protons of the C_5H_5 group. The spectral differences observed between 3- and 5-ferrocenyl-1-carbamoyl- (and -1-thiocarbamoyl-) 4,5-dihydropyrazoles are typical of all the ferrocenyldihydropyrazoles of the analogous structures obtained so far [3–5], which can be employed for the NMR-based identification of isomeric ferrocenyldihydropyrazoles.

Compounds **7a**–**9a** were attributed to *trans*-isomers and **7b**–**9b**, to *cis*-isomers based on the known criteria. Identification of 1-acetyl-substituted bicyclic ferrocenyldihydropyrazoles by ^{1}H-NMR and X-ray diffraction methods has been described earlier [13,14]. It was shown that the chemical shift values and spin–spin coupling constants for the protons H(5) of the ferrocenyldihydropyrazole fragments are diagnostic regarding their *trans*- or *cis*-orientation with respect to H(4): the chemical shifts for H(5) of *trans*-isomers are found in lower fields, and the coupling constants are larger, than those for the *cis*-isomers. According to ^{1}H-NMR spectral data for compounds **7a**–**9a**, the H(5) protons resonate at 5.31, 5.30, and 5.41, and the vicinal coupling constants $^2J_{H(4),H(5)}$ are equal to 10.3, 10.4, and 10.0 Hz, respectively. Chemical shifts of analogous protons of compounds **7b**–**9b** are found at higher fields ($\delta = 4.77$, 4.70, and 4.87), while the vicinal coupling constants are smaller ($^2J_{H(4),H(5)} = 6.8$, 4.0, and 7.0 Hz, respectively). Thus, comparison of these spectral data with those for the previously identified compounds [13,14] allows one to ascribe the *trans*-structure to compounds **7a**–**9a** with pseudo-axial orientation of H(4) and H(5) and pseudo-equatorial position of the ferrocene residue. Apparently, protons H(4) and H(5) in compounds **7b**–**9b** occupy *cis*-positions.

Analysis of the ^{13}C-NMR spectra of compounds **5a**–**g** and **6a**–**g** (Table 2) also allows one to reveal characteristic differences for 3- and 5-ferrocenyl-substituted dihydropyrazoles. Thus signals for C_{ipso}Fc for **5a**–**c** and **6a**–**c** are located at higher fields (δ = ca. 74–76) than the signals of analogous carbon atoms of 5-ferrocenyl derivatives **5e**–**g** and **6e**–**g** (δ = ca. 87–89). The ^{13}C-NMR spectra of 3,5-diferrocenyldihydropyrazoles (**5d**, **6d**) contain two types of signals for C_{ipso}Fc, viz. $\delta = 75.65$, 88.61 and 74.24, 87.45, respectively.

We found that 1-carbamoyl- and 1-thiocarbamoyl-(ferrocenyl)dihydropyrazoles behave as ligands and form 2:1 complexes with transition metals (Cu^{II}, Ni^{II}, and Co^{II}). Analysis of the structures of these complexes is now in progress.

3. Experimental

The ^{1}H- 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.

Column chromatography was carried out on alumina (Brockmann activity III) using hexane–$CHCl_3$ (1:1, v/v) or hexane–benzene (2:1, v/v) as the eluent.

The chalcones **1a**–**d** were synthesized from acetylferrocene and the corresponding carbaldehydes, compounds **1e**–**g**, **2**–**4** were prepared from ferrocenecarb-

Table 1
^{1}H-NMR spectral data of compounds **5a**–**g**, **6a**–**g**, **7a**,**b**, **8a**,**b** and **9a**,**b** (δ, J (Hz)

Compound	C_5H_5 (s)	C_5H_4 (m)	ABX (dd), AX (d)	CH_2 (m), CH_3 (s), NH_2 (bs)	Ar
5a	4.09	4.37 (2H), 4.49 (1H), 4.63 (1H)	2.97 (H_A), 3.67 (H_B), 5.48 (H_X), (J_{AB} = 17.4, J_{AX} = 4.5, J_{BX} = 11.7)	5.40 (2H)	7.25–7.60 (m, 5H)
5b	4.12	4.38 (2H), 4.50 (1H), 4.63 (1H)	2.93 (H_A), 3.67 (H_B), 5.41 (H_X), (J_{AB} = 16.9, J_{AX} = 11.6, J_{BX} = 10.5)	3.77 (3H), 5.28 (2H)	6.87 (d, 2H), 7.19 (d, 2H) (J = 7.2)
5c	4.20	4.42 (2H), 4.61 (1H), 4.72 (1H)	2.99 (H_A), 3.80 (H_B), 6.01 (H_X), (J_{AB} = 16.9, J_{AX} = 9.0, J_{BX} = 10.5)	6.98 (2H)	7.15 (d, 2H), 7.52 (d, 2H) (J = 9.1)
5d	4.17, 4.22	4.07 (1H), 4.11 (2H), 4.41 (3H), 4.70 (2H)	3.34 (H_A), 3.62 (H_B), 5.29 (H_X), (J_{AB} = 17.2, J_{AX} = 4.0, J_{BX} = 11.3)	5.23 (2H)	–
5e	4.20	4.09 (1H), 4.30 (2H), 4.48 (1H)	3.57 (H_A), 3.72 (H_B), 5.30 (H_X), (J_{AB} = 17.5, J_{AX} = 4.0, J_{BX} = 11.0)	5.25 (2H)	7.48 (m, 3H), 7.78 (m,2H)
5f	4.14	4.10 (1H), 4.35 (1H), 4.46 (1H), 4.54 (1H)	3.50 (H_A), 3.67 (H_B), 5.36 (H_X), (J_{AB} = 17.2, J_{AX} = 4.0, J_{BX} = 10.8)	3.87 (3H), 5.30 (2H)	6.96 (d, 2H), 7.71 (d, 2H) (J = 8.7)
5g	4.19	4.12 (1H), 4.24 (1H), 4.35 (1H), 4.4.38 (1H)	3.63 (H_A), 3.82 (H_B), 5.85 (H_X), (J_{AB} = 17.0, J_{AX} = 3.0, J_{BX} = 10.1)	6.81 (2H)	7.66 (d, 2H), 7.77 (d, 2H) (J = 8.7)
6a	4.07	4.46 (2H), 4.53 (1H), 4.67 (1H)	3.01 (H_A), 3.73 (H_B), 6.00 (H_X), (J_{AB} = 17.4, J_{AX} = 3.0, J_{BX} = 11.1)	6.98 (2H)	7.20–7.30 (m, 3H), 7.35–7.43 (m, 2H)
6b	4.10	4.45 (2H), 4.54 (1H), 4.67 (1H)	3.0 (H_A), 3.71 (H_B), 5.96 (H_X), (J_{AB} = 17.3, J_{AX} = 3.1, J_{BX} = 11.0)	3.77 (3H), 6.99 (2H)	6.88 (d, 2H), 7.16 (d, 2H) (J = 8.8)
6c	4.20	4.48 (2H), 4.58 (1H), 4.69 (1H)	3.0 (H_A), 3.78 (H_B), 5.93 (H_X), (J_{AB} = 17.1, J_{AX} = 3.0, J_{BX} = 11.1)	6.84 (2H)	7.12 (d, 2H), 7.50 (d, 2H) (J = 8.5)
6d	4.17, 4.24	4.07 (1H), 4.13 (1H), 4.19(1H), 4.49 (2H), 4.65 (1H), 4.71 (1H), 4.71 (1H)	3.46 (H_A), 3.67 (H_B), 5.88 (H_X), (J_{AB} = 17.1, J_{AX} = 3.0, J_{BX} = 10.5)	6.77 (2H)	–
6e	4.18	4.05 (1H), 4.12 (1H), 4.20 (1H), 4.79 (1H)	3.68 (H_A), 3.80 (H_B), 5.95 (H_X), (J_{AB} = 17.3, J_{AX} = 4.2, J_{BX} = 9.04)	6.85 (2H)	7.47 (m, 3H), 7.85 (m,2H)
6f	4.14	4.05 (1H), 4.11 (1H), 4.20 (1H), 4.77 (1H)	3.65 (H_A), 3.74 (H_B), 5.93 (H_X), (J_{AB} = 16.8, J_{AX} = 3.3, J_{BX} = 10.2)	3.89 (3H), 6.80 (2H)	7.01 (d, 2H), 7.70 (d, 2H) (J = 9.0)
6g	4.19	4.0 (1H), 4.03 (1H), 4.06 (1H), 4.74 (1H)	3.62 (H_A), 3.81 (H_B), 5.91 (H_X), (J_{AB} = 17.2, J_{AX} = 3.3, J_{BX} = 10.2)	6.80 (2H)	7.64 (d, 2H), 7.73 (d, 2H) (J = 9.0)
7a	4.23, 4.30	3.92 (1H), 4.01 (1H), 4.15 (2H), 4.18 (2H), 4.41 (1H), 4.52 (1H)	3.25 (H_A), 5.31 (H_X), (J_{AX} = 10.3)	1.65 (2H), 2.05 (1H), 2.38 (2H), 3.08 (1H), 5.54 (2H), 7.05 (d, 1H, J = 1.5)	–
7b	4.15, 4.17	4.29 (5H), 4.32 (1H), 4.39 (1H), 4.42 (1H)	3.42 (H_A), 4.77 (H_X), (J_{AX} = 6.8)	1.70 (2H), 1.98 (1H), 2.20 (2H), 3.0 (1H), 5.29 (2H), 6.78 (d, 1H, J = 2.0)	–
8a	4.25	3.80 (1H), 3.98 (1H), 4.12(2H)	3.02 (H_A), 5.30 (H_X), (J_{AX} = 10.4)	1.54–2.67 (8H), 5.51 (2H)	–
8b	4.17	4.07 (1H), 4.16 (1H), 4.36(2H)	3.24 (H_A), 4.70 (H_X), (J_{AX} = 4.0)	1.48–2.07 (8H), 5.14 (2H)	–
9a	4.23	4.21 (2H), 4.42 (2H)	3.52 (H_A), 5.41 (H_X), (J_{AX} = 10.0)	2.2.0 (2H), 2.26 (2H), 2.52.52(2H), 5.30 (2H)	–
9b	4.14	3.91 (1H), 4.09 (1H), 4.16 (2H)	3.68 (H_A), 4.87 (H_X), (J_{AX} = 7.0)	1.89 (2H), 2.20 (2H), 2.48 (2H), 5.18 (2H)	–

Table 2
^{13}C-NMR spectral data of compounds **5a–g**, **6a**,**b**,**d–f** and **7b** (δ)

Compound	C_5H_5	C_5H_4	$C_{ipso}Fc$	CH_2	CH	CH_3, Ar	C=N, C=S, C=O	C
5a	69.3	66.9, 67.6, 70.1, 70.3	75.3	44.4	59.2	125.1, 127.5, 128.8	153.6, 155.2	142.6
5b	69.3	66.9, 67.5, 70.1, 70.3	75.4	44.4	58.8	55.2, 114.2, 126.4	153.7, 158.8	134.9, 155.7
5c	69.3	67.0, 67.8, 70.8, 70.9	74.5	44.6	63.3	127.8, 130.8	155.4, 157.9	123.2, 142.0
5d	68.1, 68.8	65.1, 66.6, 67.0, 67.1, 67.2, 69.4, 69.5, 69.5	75.6, 88.6	40.1	54.1	–	152.4, 154.7	–
5e	69.3	66.4, 68.8, 68.9, 70.4	89.1	40.6	55.9	126.7, 129.1, 130.5	153.2, 156.5	131.7
5f	69.3	68.3, 68.3, 69.2, 70.0	88.4	40.2	55.4	55.3, 114.2, 127.9	151.4, 161.1	124.2, 155.4
5g	68.3	65.6, 67.8, 68.0, 70.7	87.5	40.3	58.1	127.1, 132.0	154.6, 156.7	124.3, 128.8
6a	69.5	67.3, 68.1, 70.9, 71.0	74.0	44.4	62.9	125.1, 127.6, 128.9	159.0, 175.4	141.7
6b	69.6	67.4, 68.1, 71.0, 71.1	74.1	44.4	55.3	62.4, 114.2, 126.4	159.1, 175.3	133.9, 158.9
6d	68.7, 69.7	65.6, 67.5, 68.1, 68.1, 68.2, 70.8, 71.0, 71.4	74.2, 87.4	41.8	58.5	–	159.3, 175.0	–
6e	68.6	65.9, 68.2 (2C), 71.2	87.1	40.7	59.1	126.9, 128.9, 131.0	156.6, 175.8	130.7
6f	68.6	66.1, 68.2 (2C), 71.1	87.4	40.8	59.1	55.5, 114.4, 128.6	162.0, 175.9	123.3, 156.6
7b	68.3, 69.2	66.9, 67.9, 68.0, 68.3, 68.9, 69.4, 69.4, 70.6	80.4, 90.0	24.6, 29.2, 31.4	55.5, 61.7, 125.8	–	157.3, 158.0	127.2

aldehyde, and the corresponding ketones in aqueous-ethanolic alkali [3,11].

3.1. Synthesis of 1-carbamoyl- and 1-thiocarbamoyl(ferrocenyl)-4,5-dihydropyrazoles (general procedure)

A mixture of a ferrocenylchalcone (**1**–**4**) (3.3 mmol), semicarbazide hydrochloride or thiosemicarbazide (6 mmol), and ^{t}BuOK (7 and 4 mmol, respectively) in dry isopropyl alcohol (150 ml) was stirred and boiled under reflux until the bright coloration because of the chalcone disappeared (ca. 3–5 h). The reaction mixture was cooled and partitioned between benzene and water (150 ml each). The organic layer was separated, washed several times with water, and the solvent was evaporated in vacuo. The residue was chromatographed on a column with alumina. The following compounds were isolated:

1. Thiosemicarbazones **10**, m.p. (dec.): 188–189 °C (literature data [10]: m.p. (dec.): 190 °C) and **11**, m.p. (dec.): 177–178 °C (literature data [9]: m.p. (dec.): 176.5–177.5 °C).
2. Dihydropyrazoles **5a**–**g**, **6a**–**g**, *trans*-**7a**–**9a**.
3. *cis*-Dihydropyrazoles **7b**–**9b**.

*3.2. 2-Carbamoyl-3-ferrocenyl-7-ferrocenylmethylidene-2,3,3a,4,5,6,7-heptahydroindazole (**7a**,**b**)*

A mixture of 1.6 g (3.3 mmol) of 2,6-bis-(ferrocenylmethylidene)cyclohexanone (**2**), 0.7 g (6 mmol) of semicarbazide hydrochloride and 0.8 g (7 mmol) of ^{t}BuOK in 150 ml of dry isopropyl alcohol was stirred and boiled under reflux for 3 h. The reaction mixture was cooled and partitioned between benzene and water (150 ml each). The organic layer was separated and washed with water. The solvent was removed by heating in vacuum and the remaining oil was separated by chromatography on a column with alumina (hexane–$CHCl_3$, 1:1). The *trans*-isomer **7a** was obtained as orange crystals (yield: 0.72 g (40.5%); m.p. (dec.): 264–265 °C) and the *cis*-isomer **7b** was obtained as an

Table 3
Yields, melting point and elemental analysis data for the synthesized compounds

Compound	Yield (%)	M.p. (dec.) (°C)	Molecular formula	Found (%)					Calculated (%)				
				C	H	Br	Fe	N	C	H	Br	Fe	N
5a	65	207–208	$C_{20}H_{19}FeN_3O$	64.4	5.3	–	14.7	11.1	64.4	5.1	–	15.0	11.3
5b	67	231–232	$C_{21}H_{21}FeN_3O_2$	62.7	5.1	–	14.1	10.3	62.5	5.2	–	13.9	10.4
5c	64	217–218	$C_{20}H_{18}BrFeN_3O$	53.3	3.9	17.4	12.5	9.1	53.1	4.0	17.7	12.3	9.3
5d	56	258–259	$C_{24}H_{23}Fe_2N_3O$	60.1	4.7	–	23.4	8.9	59.9	4.8	–	23.2	8.7
5e	71	219–220	$C_{20}H_{19}FeN_3O$	64.2	5.0	–	15.1	11.7	64.4	5.1	–	15.0	11.3
5f	68	244–245	$C_{21}H_{21}FeN_3O_2$	62.3	5.4	–	13.7	10.6	62.6	5.2	–	13.9	10.4
5g	69	223–224	$C_{20}H_{18}BrFeN_3O$	52.9	4.2	17.9	12.3	9.4	53.1	4.0	17.7	12.3	9.3
6a	59	204–205	$C_{20}H_{19}FeN_3S$	61.6	5.1	–	14.2	10.9	61.7	4.9	–	14.4	10.8
6b	57	224–225	$C_{21}H_{21}FeN_3OS$	60.3	4.9	–	13.5	10.1	60.2	5.1	–	13.3	10.0
6c	59	255–256	$C_{20}H_{18}BrFeN_3S$	51.5	4.0	16.9	12.0	9.0	51.3	3.9	17.1	12.0	9.0
6d	62	258–259	$C_{24}H_{23}Fe_2N_3S$	57.8	4.9	–	22.3	8.3	58.0	4.6	–	22.5	8.4
6e	65	221–222	$C_{20}H_{19}FeN_3S$	61.6	4.8	–	14.4	11.0	61.7	4.9	–	14.4	10.8
6f	58	248–249	$C_{21}H_{21}FeN_3OS$	60.3	4.8	–	13.5	9.8	60.2	5.1	–	13.3	10.0
6g	57.5	231–232	$C_{20}H_{18}BrFeN_3S$	51.5	3.7	16.9	12.0	8.8	51.3	3.9	17.1	12.0	9.0
7a	40.5	264–265	$C_{29}H_{29}Fe_2N_3O$	63.8	5.2	–	20.3	7.7	63.7	5.3	–	20.4	7.7
7b	32	259–260	$C_{29}H_{29}Fe_2N_3O$	63.5	5.5	–	20.6	7.4	63.7	5.3	–	20.4	7.7
8a	30	256–258	$C_{18}H_{21}FeN_3O$	61.7	5.9	–	16.2	12.1	61.6	6.0	–	15.9	12.0
8b	28	223–224	$C_{18}H_{21}FeN_3O$	61.4	6.2	–	15.7	12.1	61.6	6.0	–	15.9	12.0
9a	29	215–216	$C_{17}H_{19}FeN_3O$	60.3	5.9	–	16.7	12.6	60.5	5.7	–	16.6	12.5
9b	30	199–201	$C_{17}H_{19}FeN_3O$	60.7	5.4	–	16.4	12.4	60.5	5.7	–	16.6	12.5

orange powder (yield: 0.57 g (32%); m.p. (dec.): 259–260 °C).

*3.3. 3,5-Diferrocenyl-1-thiocarbamoyl-4,5-dihydropyrazole (**6d**)*

Similarly, a mixture of 1.4 g (3.3 mmol) of 1,3-diferrocenyl-2-propenone (**1d**), 0.55 g (3.3 mmol) of thiosemicarbazide and 0.45 g (4 mmol) of ^{t}BuOK in 150 ml of dry isopropyl alcohol was stirred and boiled for 4 h. After the corresponding workup and chromatography (a 2:1 hexane–$CHCl_3$ mixture as the eluent) thiosemicarbazone of acetylferrocene **10** (yield: 0.07 g (7%)), thiosemicarbazone of ferrocenylcarbaldehyde **11** (yield: 0.075 g (8%)) and dihydropyrazole **6d** (yield: 1.02 g (62%); m.p. (dec.): 258–259 °C) were obtained.

Compounds **5a**–**g**, **6a**–**c**, **e**–**g**, **8a**,**b** and **9a**,**b** were synthesized analogously. The yields of compounds **5**–**9**, their melting points and elemental analysis data are listed in Table 3.

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