Organometallic Chemistry

1-Thiocarbamoyl(ferrocenyl)-4,5-dihydropyrazoles

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Thiosemicarbazide reacts with aryl β-ferrocenylvinyl ketones and β-arylvinyl ferrocenyl ketones in the presence of Bu^tOK to give 1-thiocarbamoyl-5- and -3-ferrocenyl-4,5-dihydropyrazoles, respectively. The complexes of 3-ferrocenyl-5-phenyl-, 3,5-diferrocenyl-, and 3-ferrocenyl-5-*p*-methoxyphenyl-1-thiocarbamoyl-4,5-dihydropyrazoles with Cu^{II} are described.

Key words: ferrocene, thiosemicarbazide, 1-thiocarbamoyl(ferrocenyl)-4,5-dihydropyrazoles, Cu^{II} complexes with 4,5-dihydropyrazoles.

Studies into the chemistry of hetero- and carbocycles containing the ferrocene fragment are facilitated by the fact that the starting compounds of the ferrocene series are rather readily accessible, which allows the preparation of various products containing heterocyclic substituents.[1,2] These products find wide practical use.[2] The addition of hydrazines[3,4] and thiourea[5] to ferrocenyl-substituted chalcones is characterized by good selectivity, the reactions afford the final products in high yields, and these products can be easily isolated. The synthesis and pharmacological properties of ferrocenyl-containing nitrogen heterocycles attract interest because many ferrocenyl-4,5-dihydropyrazoles[3,4] and tetrahydropyrimidinethiones[5] exhibit biological activities.[6]

Data on the use of thiosemicarbazide for the preparation of ferrocenyl-containing heterocyclic systems are lacking in the literature. The Cu^{II} complexes with thiosemicarbazones of ferrocenecarbaldehyde,[7] acetylferrocene, and 1,1′-diacetylferrocene[8] were synthesized.

Biological activities of transition metal complexes are also well known.[9] In this connection, it is of interest to examine the potentialities of the synthesis of heterocycles

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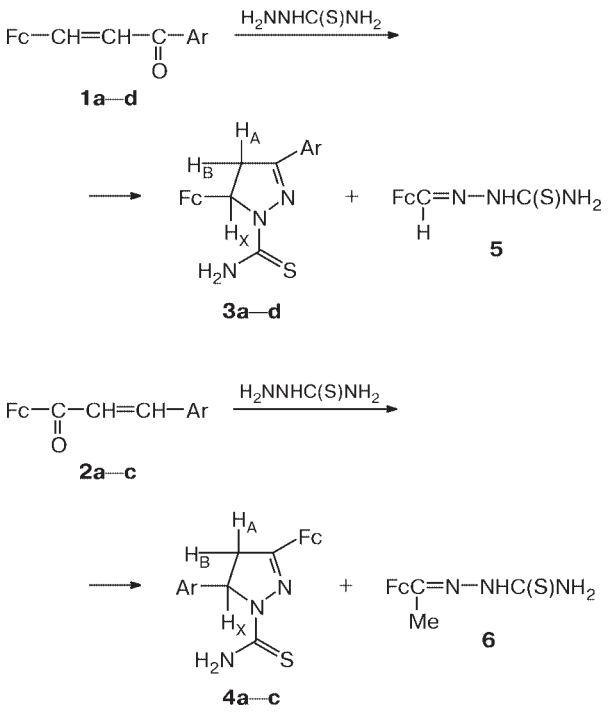
based on ferrocene and thiosemicarbazide derivatives and to explore the possibilities of the use of these compounds as ligands for the preparation of transition metal complexes.

Results and Discussion

In the present study, we examined the reactions of thiosemicarbazide with ferrocenyl-substituted α,β-unsaturated ketones **1a—d** and **2a—c**, which have been prepared by condensation of the corresponding carbaldehydes with methyl ketones in aqueous-ethanolic alkali.[4] We found that thiosemicarbazide reacted with chalcones **1a—d** and **2a—c** on refluxing in anhydrous Pr^iOH in the presence of Bu^tOK to give 1-thiocarbamoyl(ferrocenyl)-4,5-dihydropyrazoles **3a—d** and **4a—c**, respectively, in 60—70% yields (Scheme 1). In all cases, the reactions were accompanied by fragmentation of the starting compounds **1a—d** and **2a—c** to form thiosemicarbazones of ferrocenecarbaldehyde (**5**)[7] and acetylferrocene (**6**),[8] respectively (the yields were 10—20%; from chalcone **1d**, thiosemicarbazones **5** and **6** were obtained in approximately equal amounts, the yields were 8—9%).

Scheme 1



Ar = Ph (**a**); *p*-$MeOC_6H_4$ (**b**); *p*-BrC_6H_4 (**c**); Fc (**d**)

The resulting compounds were characterized by IR, UV, ^{1}H NMR, and ^{13}C NMR spectroscopy and by elemental analysis (see the Experimental section), which unambiguously confirmed their structures.

The ^{1}H NMR spectra of products **3a—d** and **4a—c** contain ABX-spin systems of protons characteristic of 4,5-dihydropyrazoles and vary substantially depending on the position of the ferrocenyl substituent in the heterocycle. In the spectra of dihydropyrazoles **3a—c** containing the ferrocenyl group at position 5, the signals for the geminal H_A and H_B protons are observed at δ 3.6—3.8 and differ little in chemical shifts (Δδ ~0.09—0.19). To the contrary, the presence of the ferrocenyl substituent at position 3 of dihydropyrazoles **4a—c** leads to a noticeable upfield shift of one of the signals of the methylene group (δ ~3.0); Δδ is ~0.7—0.8. In the presence of two ferrocenyl substituents (at positions 3 and 5; compound **3d**), the chemical shifts of the protons of the heterocycle are close to those for 5-ferrocenyl derivatives **3a—c**.

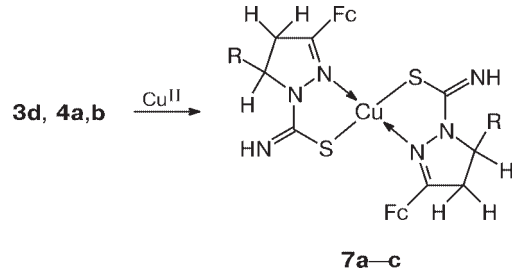
The isomeric position of the ferrocenyl group in thiocarbamoyldihydropyrazoles also affects the chemical shifts of its protons. Thus in the spectra of 3-ferrocenyl derivatives **4a—c**, all signals for the protons of the substituted cyclopentadienyl ring of ferrocene are shifted downfield with respect to the signal of the unsubstituted cyclopentadienyl ring, *i.e.*, in this case, the influence of the dihydropyrazole fragment is analogous to the effect of a strong electron-withdrawing substituent[10] due apparently to the interaction between the π-electron system of ferrocene and the π-electrons of the C=N bond of dihydropyrazole. In the spectra of 5-ferrocenyldihydropyrazoles **3a—d** containing the Fc-substituent at the sp^3-hybridized C atom, some signals for the protons of the substituted ferrocene ring are shifted upfield with respect to the signal for the protons of the C_5H_5 group. The above-mentioned distinctions between 1-thiocarbamoyl-3- and -5-ferrocenyl-4,5-dihydropyrazoles are typical of all structurally similar ferrocenyldihydropyrazoles[4] and can be used for spectral identification of isomeric ferrocenyldihydropyrazoles.

Chirality of the dihydropyrazole ring serving as a substituent in ferrocene is manifested in splitting of the signals for the α-protons of the substituted cyclopentadienyl ring of ferrocene. This splitting is more substantial in the case of the 5-ferrocenyl derivatives than in the case of the 3-ferrocenyl derivatives.

According to the data from mass spectrometry and elemental analysis, compounds **3d** and **4a**,**b** form stable complexes **7a—c** with Cu^{II} with the composition 2 : 1 (Scheme 2). The structures assigned to these compounds are confirmed by the IR, UV, ^{1}H NMR, and ^{13}C NMR spectroscopic data and by analysis of the analogous structures available in the literature.[7,8]

In the ^{1}H NMR spectra of compounds **7a—c**, the signals for the H_X protons and the NH group are substantially shifted upfield (Δδ ~0.5—0.8 and 0.58—0.77, respectively) compared to those of the initial ligands, and the spin-spin coupling constants J_{AX} are increased (4.65, 7.35, and 4.2 Hz, respectively). The presence of two sig-

Scheme 2



7a—c

7: R = Fc (**a**), Ph (**b**), *p*-$MeOC_6H_4$ (**c**)

nals for C_{ipso}Fc in the ^{13}C NMR spectra of complexes **7b**,**c** is additional supporting evidence for the proposed structures.

Experimental

The IR spectra were recorded on a Specord 75-IR spectrometer in KBr pellets. The UV spectra were measured on a Specord UV-VIS spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Unity Nova Varian instrument (300 and 75 MHz, respectively) with Me_4Si as the internal standard. The mass spectra were obtained on a Varian MAT CH-6 spectrometer (70 eV). Chromatography was carried out using Al_2O_3 (Brockmann activity III).

Synthesis of 1-thiocarbamoyl(ferrocenyl)-4,5-dihydropyrazoles (general procedure). A mixture of chalcone **1a—d** or **2a—c** (10 mmol), thiosemicarbazide (20 mmol), Bu^tOK (15 mmol), and anhydrous Pr^iOH (150 mL) was refluxed with stirring for ~3—5 h until the bright-red color of the chalcone disappeared and a yellow (in the case of compounds **1a—c**) or orange (in the cases of compounds **1d** and **2a—c**) solution was obtained. Then the solution was rapidly poured into water (200 mL). The precipitate that formed was filtered off, washed several times with water on a filter, dried, and recrystallized from benzene. The crystals obtained were virtually pure 1-thiocarbamoyldihydropyrazoles **3a—d** and **4a—c** (the yields were 50—60%). The benzene filtrate was concentrated *in vacuo* and the residue was chromatographed on Al_2O_3 (a 1 : 1 hexane—chloroform mixture as the eluent). Thiosemicarbazones **5** or **6** (the yields were 8—20%) and pyrazoles **3a—d** and **4a—c** (the yields were 5—15%) were additionally obtained.

5-Ferrocenyl-3-phenyl-1-thiocarbamoyl-4,5-dihydropyrazole (3a). Yellow crystals, m.p. 221—222 °C. Found (%): C, 61.61; H, 4.86; Fe, 14.46; N, 10.87. $C_{20}H_{19}FeN_3S$. Calculated (%): C, 61.72; H, 4.92; Fe, 14.35; N, 10.79. ^{1}H NMR ($CDCl_3$), δ: 3.68 (dd, 1 H, CH_A, J = 4.2 Hz, J = 17.3 Hz); 3.80 (dd, 1 H, CH_B, J = 9.1 Hz, J = 17.3 Hz); 4.18 (s, 5 H, C_5H_5); 4.05, 4.12, 4.20, and 4.79 (all m, 1 H each, C_5H_4); 5.95 (dd, 1 H, CH_X, J = 4.2 Hz, J = 9.0 Hz); 6.85 (br.s, 2 H, NH_2); 7.46—7.51 and 7.70—7.85 (both m, 3 + 2 H, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 40.66 (CH_2); 59.13 (CH); 68.58 (C_5H_5); 65.92, 68.18, 68.19, 71.20 (C_5H_4); 87.12 (C_{ipso}Fc); 126.87, 128.95, 131.04 (C_6H_5); 130.68 (C_{ipso}); 158.62 (C=N); 175.80 (C=S).

5-Ferrocenyl-3-(4-methoxyphenyl)-1-thiocarbamoyl-4,5-dihydropyrazole (3b). Yellow crystals, m.p. 248—249 °C. Found (%): C, 60.27; H, 4.89; Fe, 13.50; N, 9.93. $C_{21}H_{21}FeN_3OS$. Calculated (%): C, 60.16; H, 5.05; Fe, 13.32; N, 10.02. ^{1}H NMR ($CDCl_3$), δ: 3.65 (dd, 1 H, CH_A, J = 3.3 Hz, J = 16.8 Hz); 3.74 (dd, 1 H, CH_B, J = 10.0 Hz, J = 16.8 Hz); 3.89 (s, 3 H, Me); 4.14 (s, 5 H, C_5H_5); 4.05. 4.11, 4.20, and 4.77 (all m, 1 H each, C_5H_4); 5.93 (dd, 1 H, CH, J = 3.3 Hz, J = 10.0 Hz); 6.80 (br.s, 2 H, NH_2); 7.01 and 7.70 (both d, 2 H each, C_6H_4, J = 9.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 40.77 (CH_2); 55.52 (CH); 59.06 (Me); 68.63 (C_5H_5); 66.07, 68.19, 68.21, 71.06 (C_5H_4); 87.37 (C_{ipso}Fc); 114.45, 128.64 (C_6H_4); 123.32 (C_{ipso}); 156.59 (C—O); 162.01 (C=N); 175.89 (C=S).

3-(4-Bromophenyl)-5-ferrocenyl-1-thiocarbamoyl-4,5-dihydropyrazole (3c). Yellow crystals, m.p. 231—232 °C. Found (%): C, 51.48; H, 3.72; Br, 16.86; Fe, 12.05; N, 8.78. $C_{20}H_{18}BrFeN_3S$. Calculated (%): C, 51.31; H, 3.87; Br, 17.08; Fe, 11.94; N, 8.97. ^{1}H NMR (DMSO-d_6), δ: 3.62 (dd, 1 H, CH_A, J = 3.3 Hz, J = 17.2 Hz); 3.81 (dd, 1 H, CH_B, J = 10.2 Hz, J = 17.2 Hz); 4.19 (s, 5 H, C_5H_5); 4.02, 4.04, 4.08, and 4.74 (all m, 1 H each, C_5H_4); 5.91 (dd, 1 H, CH_X, J = 3.3 Hz, J = 10.2 Hz); 6.80 and 7.05 (both br.s, 1 H each, NH_2); 7.64 and 7.73 (both d, 2 H each, C_6H_4, J = 9.0 Hz). ^{13}C NMR (DMSO-d_6), δ: 40.41 (CH_2); 59.09 (CH); 68.43 (C_5H_5); 65.68, 67.94, 68.01, 70.85 (C_5H_4); 86.92 (C_{ipso}Fc); 128.13, 132.02 (C_6H_4); 125.29, 129.43 (2 C); 155.75 (C=N); 175.61 (C=S).

3,5-Diferrocenyl-1-thiocarbamoyl-4,5-dihydropyrazole (3d). Orange crystals, m.p. 258—259 °C. Found (%): C, 57.79; H, 4.88; Fe, 22.31; N, 8.30. $C_{24}H_{23}Fe_2N_3S$. Calculated (%): C, 58.00; H, 4.65; Fe, 22.47; N, 8.45. ^{1}H NMR (DMSO-d_6), δ: 3.46 (dd, 1 H, CH_A, J = 3.0 Hz, J = 17.1 Hz); 3.67 (dd, 1 H, CH_B, J = 10.5 Hz, J = 17.1 Hz); 4.17 and 4.24 (both s, 5 H each, 2 C_5H_5); 4.07, 4.13, 4.19, 4.49, 4.65, 4.73, and 4.83 (all m, 8 H, 2 C_5H_4); 5.88 (dd, 1 H, CH_X, J = 3.0 Hz, J = 10.5 Hz); 6.77 (br.s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 41.83 (CH_2); 58.51 (CH); 68.66, 69.67 (2 C_5H_5); 65.61, 67.55, 68.10, 68.11, 68.22, 70.77, 71.03, 71.42 (2 C_5H_4); 74.24, 87.45 (2 C_{ipso}Fc); 159.28 (C=N); 174.98 (C=S). IR, ν/cm^{-1}: 3422, 3270, 3146, 3086, 1584, 1500, 1446, 1355, 1205, 1107, 1064. UV ($CHCl_3$), λ_{max}/nm: 224, 310, 451.

3-Ferrocenyl-5-phenyl-1-thiocarbamoyl-4,5-dihydropyrazole (4a). Orange crystals, m.p. 204—205 °C. Found (%): C, 61.59; H, 5.07; Fe, 14.22; N, 10.93. $C_{20}H_{19}FeN_3S$. Calculated (%): C, 61.72; H, 4.92; Fe, 14.35; N, 10.79. ^{1}H NMR ($CDCl_3$), δ: 3.01 (dd, 1 H, CH_A, J = 3.0 Hz, J = 17.4 Hz); 3.73 (dd, 1 H, CH_B, J = 11.1 Hz, J = 17.4 Hz); 4.07 (s, 5 H, C_5H_5); 4.46, 4.53, and 4.67 (all m, 2 + 1 + 1 H, C_5H_4); 6.00 (dd, 1 H, CH_X, J = 3.0 Hz, J = 11.1 Hz); 6.98 (br.s, 2 H, NH_2); 7.20—7.31 and 7.34—7.40 (both m, 3 + 2 H, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 44.37 (CH_2); 62.86 (CH); 69.51 (C_5H_5); 67.30, 68.13, 70.93, 71.04 (C_5H_4); 73.98 (C_{ipso}Fc); 125.08, 127.60, 128.89 (C_6H_5); 141.69 (C_{ipso}); 158.99 (C=N); 175.36 (C=S). IR (KBr), ν/cm^{-1}: 3428, 3283, 3149, 3089, 1585, 1502, 1457, 1363, 1213, 1112, 1009. UV ($CHCl_3$), λ_{max}/nm: 244, 322, 459.

3-Ferrocenyl-5-(4-methoxyphenyl)-1-thiocarbamoyl-4,5-dihydropyrazole (4b). Orange crystals, m.p. 224—225 °C. Found (%): C, 60.29; H, 4.39; Fe, 13.51; N, 10.11. $C_{21}H_{21}FeN_3OS$. Calculated (%): C, 60.16; H, 5.05; Fe, 13.32; N, 10.02. ^{1}H NMR ($CDCl_3$), δ: 3.00 (dd, 1 H, CH_A, J = 3.1 Hz, J = 17.3 Hz); 3.71 (dd, 1 H, CH_B, J = 11.0 Hz, J = 17.3 Hz); 3.77 (s, 3 H, Me); 4.10 (s, 5 H, C_5H_5); 4.45, 4.54, and 4.67 (all m, 2 + 1 + 1 H, C_5H_4); 5.96 (dd, 1 H, CH_X, J = 3.1 Hz, J = 11.0 Hz); 6.99 (br.s, 2 H, NH_2); 7.88 and 7.16 (both d,

2 H each, C_6H_4, $J = 8.8$ Hz). ^{13}C NMR ($CDCl_3$), δ: 44.42 (CH_2); 55.26 (Me); 62.43 (CH); 69.58 (C_5H_5); 67.39, 68.14, 70.97, 71.06 (C_5H_4); 74.14 (C_{ipso}Fc); 114.25, 126.43 (C_6H_4); 133.95 (C_{ipso}); 158.94 (C—O); 159.05 (C=N); 175.34 (C=S). IR, ν/cm^{-1}: 3436, 3347, 3285, 3137, 3083, 1590, 1491, 1467, 1361, 1256, 1119, 1023. UV ($CHCl_3$), λ/nm: 237, 318, 460.

5-(4-Bromophenyl)-3-ferrocenyl-1-thiocarbamoyl-4,5-dihydropyrazole (4c). Yellow crystals, m.p. 255—256 °C. Found (%): C, 51.18; H, 4.03; Br, 16.88; Fe, 12.09; N, 9.02. $C_{20}H_{18}BrFeN_3S$. Calculated (%): C, 51.31; H, 3.87; Br, 17.08; Fe, 11.94; N, 8.97. ^1H NMR (DMSO-d_6), δ: 3.00 (dd, 1 H, CH_A, $J = 3.0$ Hz, $J = 17.1$ Hz); 3.78 (dd, 1 H, CH_B, $J = 11.1$ Hz, $J = 17.1$ Hz); 4.20 (s, 5 H, C_5H_5); 4.48, 4.58, and 4.69 (all m, 2 + 1 + 1 H, C_5H_4); 5.93 (dd, 1 H, CH_X, $J = 3.0$ Hz, $J = 11.1$ Hz); 6.84 (br.s, 2 H, NH_2); 7.12 and 7.50 (both d, 2 H each, C_6H_4, $J = 8.5$ Hz). ^{13}C NMR (DMSO-d_6), δ: 43.96 (CH_2); 62.13 (CH); 69.36 (C_5H_5); 67.25, 67.96, 70.94, 71.02 (C_5H_4); 73.43 (C_{ipso}Fc); 126.78, 131.80 (C_6H_4); 121.17, 140.71 (2 C); 159.26 (C=N); 174.76 (C=S).

Ferrocenecarbaldehyde thiosemicarbazone (5). M.p. 188—189 °C (*cf.* lit. data[7,11]: m.p. 190 °C). ^1H NMR (DMSO-d_6), δ: 4.12 (s, 5 H, C_5H_5); 4.42 and 4.58 (both m, 2 H each, C_5H_4); 6.50 and 7.15 (both br.s, 1 H each); 7.83 and 10.15 (both s, 1 H each). MS, *m/z*: 287 $[M]^+$.

Acetylferrocene thiosemicarbazone (6). M.p. 177—178 °C. (*cf.* lit. data[8]: m.p. 176.5—177.5 °C). MS, *m/z*: 299 $[M]^+$.

Synthesis of Cu^{II} complexes with 1-thiocarbamoyl(ferrocenyl)-4,5-dihydropyrazoles (general procedure). A solution of $Cu(OAc)_2$ (1 mmol) in acetone was added to a solution of dihydropyrazole **3d**, **4a**,**b** (2 mmol) in a mixture of EtOH (50 mL) and benzene (50 mL). The resulting mixture was refluxed for 8 h after which the solvent was distilled off *in vacuo* and the residue was chromatographed on Al_2O_3 (a 1 : 4 hexane—$CHCl_3$ mixture as the eluent) to obtain the starting dihydropyrazole (50—60%) and its complex with metal (~30%).

Bis(3,5-diferrocenyl-4,5-dihydropyrazole-1-carbothioimidato-*N*^{2},*S*)copper(II) (complex 7a). An orange powder, decomposes at 327—329 °C. Found (%): C, 54.71; H, 4.03; N, 8.12. $C_{48}H_{44}CuFe_4N_6S_2$. Calculated (%): C, 54.63; H, 4.20; N, 7.96. ^1H NMR (DMSO-d_6), δ: 3.16 (dd, 2 H, 2 CH, $J = 7.4$ Hz, $J = 16.7$ Hz); 3.52 (dd, 2 H, 2 CH_B, $J = 10.7$ Hz, $J = 16.7$ Hz); 4.19 and 4.26 (both s, 10 H each, 4 C_5H_5); 4.17, 4.21, 4.30, 4.32, 4.43, 4.61, and 4.63 (all m, 2 + 2 + 2 + 4 + 2 + 2 + 2 H, 4 C_5H_4); 5.08 (dd, 2 H, 2 CH_X, $J = 7.4$ Hz, $J = 10.7$ Hz); 6.00 (br.s, 2 H, 2 NH). IR, ν/cm^{-1}: 3426, 3091, 2926, 2212, 1582, 1513, 1414, 1305. UV ($CHCl_3$), λ/nm: 258, 342, 470. MS, *m/z*: 1056 $[M]^+$.

Bis(3-ferrocenyl-5-phenyl-4,5-dihydropyrazole-1-carbothioimidato-*N*^{2},*S*)copper(II) (complex 7b). A finely crystalline orange powder, decomposes at >300 °C. Found (%): C, 57.10; H, 4.45; N, 9.86. $C_{40}H_{36}CuFe_2N_6S_2$. Calculated (%): C, 57.23; H, 4.33; N, 10.01. ^1H NMR ($CDCl_3$), δ: 2.96 (dd, 2 H, 2 CH_A, $J = 4.7$ Hz, $J = 17.4$ Hz); 3.67 (dd, 2 H, 2 CH_B, $J = 11.7$ Hz, $J = 17.4$ Hz); 4.09 (s, 10 H, 2 C_5H_5); 4.38 (m, 4 H, C_5H_4); 4.49 and 4.63 (both m, 2 H each, C_5H_4); 5.40 (br.s, 2 H, 2 NH); 5.48 (dd, 2 H, 2 CH_X, $J = 4.7$ Hz, $J = 11.7$ Hz); 7.20—7.41 (m, 10 H, 2 C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 44.45 (2 CH_2); 59.36 (2 CH); 69.35 (2 C_5H_5); 66.96, 67.55, 70.17, 70.30 (2 C_5H_4); 69.57, 75.44 (2 C_{ipso}Fc); 125.22, 127.52, 128.93 (2 C_6H_5); 142.69 (2 C_{ipso}); 153.65 (2 C=N); 155.08 (HN=C—S). IR, ν/cm^{-1}: 3483, 3260, 3190, 2960, 2200, 1672, 1583, 1498, 1431, 1314. UV, λ/nm ($CHCl_3$): 258, 330, 453. MS, *m/z*: 841 $[M]^+$.

Bis[3-ferrocenyl-5-(4-methoxyphenyl)-4,5-dihydropyrazole-1-carbothioimidato-*N*^{2},*S*)]copper(II) (complex 7c). A finely crystalline orange powder, decomposes at >320 °C. Found (%): C, 56.27; H, 4.59; N, 9.15. $C_{42}H_{40}CuFe_2N_6O_2S_2$. Calculated (%): C, 56.05; H, 4.48; N, 9.33. ^1H NMR ($CDCl_3$), δ: 2.96 (dd, 2 H, 2 CH_A, $J = 4.5$ Hz, $J = 17.2$ Hz); 3.65 (dd, 2 H, 2 CH_B, $J = 12.0$ Hz, $J = 17.2$ Hz); 3.77 (s, 6 H, 2 Me); 4.12 (s, 10 H, 2 C_5H_5); 4.38, 4.50, and 4.63 (all m, 4 + 2 + 2 H, 2 C_5H_4); 5.27 (br.s, 2 H, 2 NH); 5.42 (dd, 2 H, 2 CH_X, $J = 4.5$ Hz, $J = 12.0$ Hz); 6.88 (d, 4 H, C_6H_4, $J = 8.7$ Hz); 7.20 (d, 4 H, C_6H_4, $J = 8.7$ Hz). ^{13}C NMR ($CDCl_3$), δ: 44.46 (2 CH_2); 57.26 (2 Me); 58.92 (2 CH); 69.33 (2 C_5H_5); 66.72, 67.64, 70.35, 70.76 (2 C_5H_4); 70.56, 76.47 (2 C_{ipso}Fc); 123.45, 128.34 (2 C_6H_4); 136.12 (2 C_{ipso}); 157.11 (2 C—O); 154.02 (2 C=N); 156.28 (2 HN=C—S). IR, ν/cm^{-1}: 3476, 3255, 3180, 2913, 2224, 1683, 1586, 1484, 1433, 1334. UV ($CHCl_3$), λ_{max}/nm: 252, 334, 464. MS, *m/z*: 901 $[M]^+$.

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