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New 1,2,3-Selenadiazole and 1,2,3-Thiadiazole Derivatives

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Abstract: New 1,2,3-thiadiazole and 1,2,3-selenadiazole derivatives, **14-23**, were prepared from the ketones **1-5** via the corresponding semicarbazones or hydrazones **6-12**. The Hurd-Mori and Lalezari methods were used, respectively, for the preparation of these 1,2,3-thiadiazole and 1,2,3-selenadiazole derivatives. The intermediate **13** was also trapped, separated and fully characterized. These derivatives are important for photocrosslinking processes and due to their potential biological activity.

Keywords: Semicarbazone, hydrazone, ferrocene, 1,2,3-selenadiazole, 1,2,3-thiadiazole.

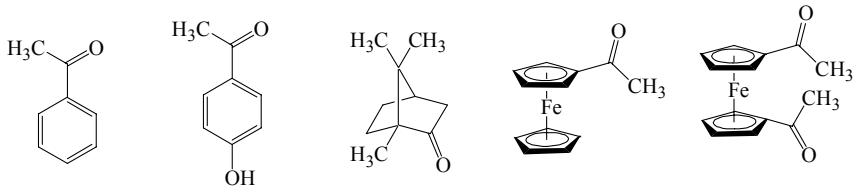
Introduction:

Interest in the synthesis of selenium and sulfur containing compounds and the further utilization of these compounds in organic synthesis has been steadily increasing recently [1]. Particular interest in 1,2,3-selenadiazole and 1,2,3-thiadiazole derivatives stems from the fact that they can undergo a wide variety of reactions where they act as 1,3-dipoles or as a source of selenium or sulfur and hence they have attracted much attention for the synthesis of different organoselenium and organosulfur compounds [2] in both the acyclic and cyclic series [3]. In spite of the obvious attraction of Se and S-heterocycles, only a few preparative routes have been described. Lalezari *et al.* [4-6] were the first to report the synthesis of a 1,2,3-selenadiazole ring by analogy with the 1,2,3-thiadiazole system, which had been prepared previously by Hurd and Mori [7]. We report herein the synthesis of new compounds containing 1,2,3-selenadiazole and 1,2,3-thiadiazole rings using the Lalezari *et al*. and Hurd and Mori methods.

Results and Discussion

Our synthetic procedure for new 1,2,3-selenadiazole and 1,2,3-thiadiazole derivatives started from a variety of ketones **1-5** containing α-methylene groups (Scheme 1) that were first converted into their corresponding tosyl or acyl hydrazones or semicarbazones and then further converted into 1,2,3-selenadiazole ring derivatives by the selenium dioxide oxidative ring closure of these semicarbazone or hydrazone derivatives [8-11] and into 1,2,3-thiadiazoles by reaction of the hydrazones or semicarbazones with thionyl chloride [12-16].

Scheme 1. Ketones used in the preparation of new 1,2,3-thiadiazole and 1,2,3-selenadiazole compounds.



(1) **(2)** **(3)** **(4)** **(5)**

The general equations for the preparation of 1,2,3-selenadiazole and 1,2,3-thiadiazole derivatives are shown in Scheme 2.

Scheme 2

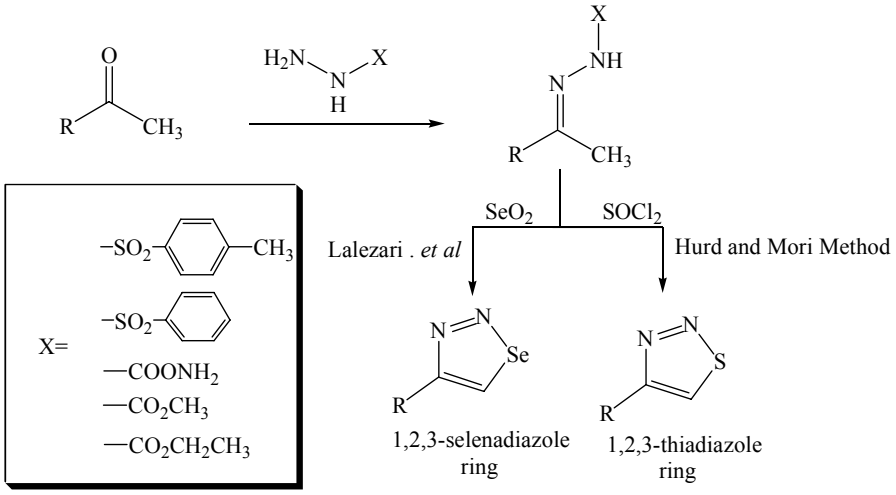


Table 1 shows the structures of the newly prepared compounds, melting point ranges and the percentage yields of these compounds.

Table 1.

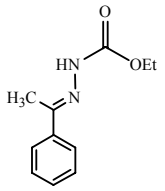
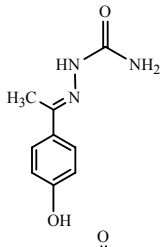
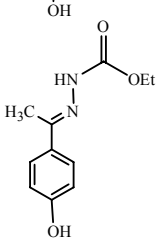
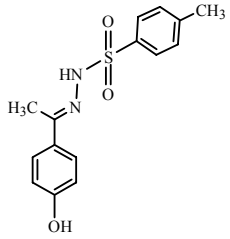
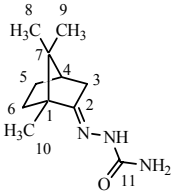
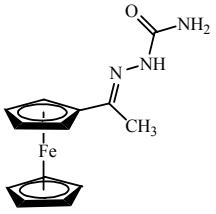
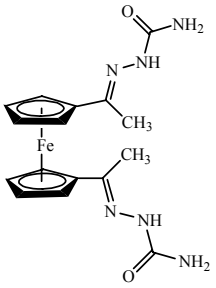
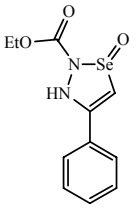
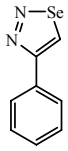
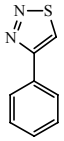
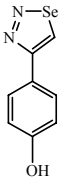
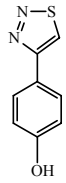
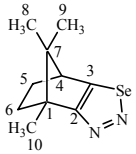
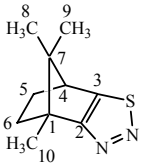
Number	Structure	Melting Point (°C)	%Yield
6		112-114	83
7		124-125	Quantitative
8		181-182	Quantitative
9		146-148	86
10		220-222	74
11		215-216	70

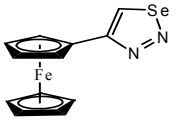
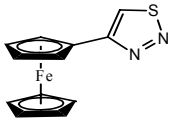
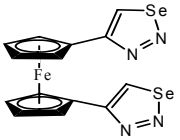
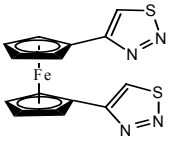
Table 1. Cont.

Number	Structure	Melting Point (°C)	%Yield
12		236-238	66
13		91-92	69
14		107-109	74
15		126-128	83
16		132-133	79* / 84**
17		149-151	76
18		144-146	50
19		161-163	58

* When using semicarbazone **7**

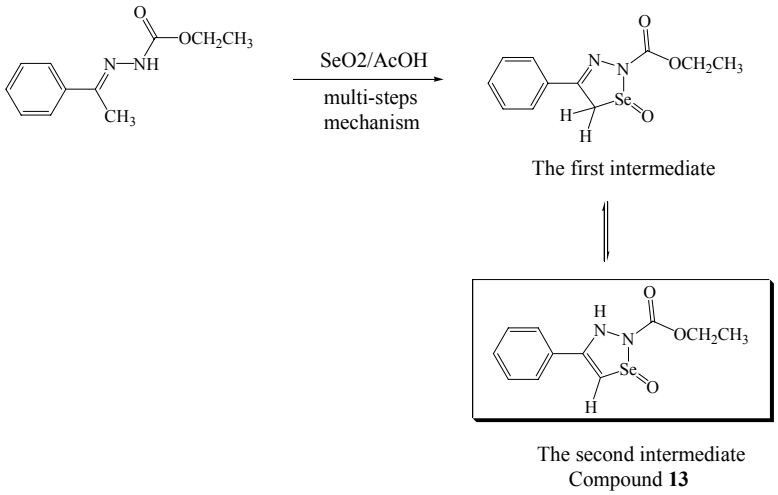
** When using hydrazone **8**

Table 1. Cont.

Number	Structure	Melting Point (°C)	% Yield
20		119-120	60
21		132-134	66
22		141-143	53
23		158-160	61

Compound **13** was of particular interest as it represents the first isolable and stable intermediate in the mechanism for 1,2,3-selenadiazole ring cyclization. Scheme 3 shows the proposed mechanism for the formation of compound **13**. Its structure was confirmed by IR, ^{1}H-NMR, ^{13}C-NMR, mass spectrometry and elemental analysis.

Scheme 3. Mechanism for the formation of compound **13**



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Experimental

General

The solvents used were purified by standard procedures. The melting points (m.p) were determined on an Electrothermal digital melting point apparatus and uncorrected. Infrared (IR) spectra of pure substances were recorded for KBr pellets using a NICOLET 410 FT-IR spectrometer (ν in cm^{-1}). The ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker AM 400 and AC200 spectrometers in $CDCl_3$ or DMSO-d_6. The spectral data are reported in delta (δ) units relative to the TMS reference peak. The mass spectra were registered using MAT CH7A (Varian, EI: 70eV Ionizing energy, electron ionization) and MAT95 (Finnigan, FD: 5kV Ionizing energy, field desorption) instruments. The signals are given as m/z with the relative intensity between brackets. Elemental analyses were performed in the analytical laboratory of the Institute of Organic Chemistry of University of Mainz, Germany. D-(+)-camphor, acetyl ferrocene, diacetyl ferrocene, *p*-hydroxyacetophenone, acetophenone, ethyl hydrazine carboxylate, semicarbazide hydrochloride and sodium acetate were obtained from Aldrich.

General procedure for the preparation of semicarbazones **7**, **10**, **11** *and* **12**.

A mixture of semicarbazide hydrochloride (1.00 equivalent) and sodium acetate (1.00 equivalent) was dissolved in absolute ethanol (45 mL). The mixture was heated for 15 min under reflux, then filtered while hot to remove precipitated sodium chloride. The filtrate was then mixed with *p*-hydroxyacetophenone (**2,** 0.95 equivalents), D-(+)-camphor (**3,** 0.95 equivalents), acetyl ferrocene (**4**, 0.95 equivalents) or diacetyl ferrocene (**5**, 0.45 equivalents), respectively, and the resulting mixtures were heated to reflux, a few drops of concentrated hydrochloric acid were added and heating under reflux with continuous removal of the generated water was continued overnight. The solvent was removed under vacuum and the residue was washed with diethyl ether or chloroform.

N′-[1-(4-Hydroxyphenyl)-ethylidene] semicarbazone (**7**). White solid powder, yield = quantitative; IR: ν 3448, 3220, 1667, 1572, 1411, 1351 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 2.16 (s, 3H, CH_3), 6.98/7.65 (AA′BB′, 4H, aromatic H), 9.97 (s, 1H, N-H); ^{13}C-NMR (DMSO-d_6): δ 14.2 (CH_3), 114.8/127.6 (CH, phenylene), 131.3/158.7 (C_q, phenylene), 148.9 (CN), 154.3 (CO); MS (m/z, %): 193 (M^+, 100%); Anal. Calcd. for $C_9H_{11}N_3O_2$: C, 55.95; H, 5.74; N, 21.75. Found: C, 55.91; H, 5.68; N, 21.81.

N′-(1,7,7-Trimethylbicyclo[2.2.1]hept-2-ylidene) semicarbazone (**10**). Pale white-green solid, yield = 74%; IR: ν 3462, 3199, 2949, 1688, 1585, 1489 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 0.65 (s, 3H, C_{10}), 0.85 (s, 3H at C_9), 0.91 (s, 3H at C_8),1.23/1.72 (2m, 4H at C_5, C_6), 1.89 (d, 2H, C_3), 2.28 (m, 1H at C_4), 5.14 (s, 2H, NH_2), 8.76 (s, 1H, N-H); ^{13}C-NMR (DMSO-d_6): δ 54.84 (C_1), 157.48 (C_2), 34.18 (C_3), 43.47 (C_4), 26.99 (C_5), 32.56 (C_6), 47.53 (C_7), 19.32 (C_8), 18.62 (C_9), 11.34 (C_{10}) and 161.74 (C_{11}); MS (m/z, %): 209 (M^+, 100%); Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15; N, 20.08. Found: C, 63.05; H, 9.10; N, 19.90.

Acetyl ferrocene semicarbazone (**11**). Reddish orange solid, yield = 70% yield; IR: ν 3468, 3192, 3096, 1700, 1572, 1431 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.11 (s, 3H, CH_3-C=N), 4.13 (s, 5H, unsubstituted cyclopentadienyl ring), 4.52 and 4.30 (2d, 4H, monosubstituted cyclopentadienyl ring), 8.38 (s, 1H, N-H); ^{13}C-NMR ($CDCl_3$): δ 14.14 ($\underline{C}H_3$-C=N), 147.20 ($\underline{C}$=N), 157.54 (N-$\underline{C}$(O)-N), 69.15, 69.80, 66.65, 83.44 (10C, cyclopentadienyl rings); MS (m/z, %) : 285 (M^+, 100%); Anal. Calcd. for $C_{13}H_{15}N_3OFe$: C, 54.57; H, 5.64; N, 14.69. Found: C, 54.39; H, 5.54; N, 14.52.

Diacetylferrocene semicarbazone (**12**). Dark reddish solid, yield = 68% yield; IR: ν 3456, 3191, 1712, 1568, 1436 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.14 (s, 6H, CH_3-C=N), 4.59 and 4.37 (2d, 8H, monosubstituted cyclopentadienyl rings), 8.32 (s, 2H, N-H); ^{13}C-NMR ($CDCl_3$): δ 14.28 (2C, $\underline{C}H_3$-C=N), 147.39 (2C, $\underline{C}$=N), 156.97 (2C, N-$\underline{C}$(O)-N), 69.16, 69.83, 83.24 (10C, cyclopentadienyl rings); MS (m/z, %) : 384 (M^+, 100%); Anal. Calcd. for $C_{16}H_{20}N_6O_2Fe$: C, 50.02; H, 5.25; N, 21.87. Found: C, 50.08; H, 5.21; N, 21.79.

General procedure for the preparation of hydrazones **6** *and* **8**

A mixture of acetophenone (**1,** 1.00 equivalent) or 4-hydroxyacetophenone (**2,** 1.00 equivalent) and ethyl hydrazine carboxylate (1.20 equivalents) was dissolved in dry, hot chloroform (80 mL). When the reaction mixture started refluxing, two drops of concentrated hydrochloric acid were added and the mixture was then refluxed overnight with continuous removal of the water generated. The solvent was removed under vacuum and the residue was washed several times with diethyl ether or chloroform to remove excess reactants.

N'-[1-phenylethylidene]hydrazine carboxylic acid ethyl ester (**6**). White solid powder, yield = 83%; IR: ν 3192, 3051, 2975, 1732, 1540, 1035 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 1.24 (t, 3H, CH_2CH_3), 2.19 (s, 3H, CH_3-C=N), 4.14 (q, 2H, CH_2CH_3), 7.27-7.33 (m, 3H, aromatic), 7.69-7.71 (m, 2H, aromatic), 10.09 (s, 1H, N-H); ^{13}C-NMR (DMSO-d_6): δ 13.93 ($OCH_2\underline{C}H_3$), 14.71 ($\underline{C}H_3$-C=N), 60.61 ($O\underline{C}H_2CH_3$), 148.93 ($\underline{C}$=N), 154.34 (O-$\underline{C}$(O)-N), 126.11, 128.32, 128.89 and 138.47 (aromatic carbons); MS (m/z, %): 206 (M^+, 100%); Anal. Calcd. for $C_{11}H_{14}N_2O_2$: C, 64.06; H, 6.84; N, 13.58. Found: C, 63.70; H, 6.79; N, 13.60.

N'-[1-(hydroxyphenyl)ethylidene]hydrazine carboxylic acid ethyl ester (**8**). White solid powder, yield = quantitative; IR: ν 3385, 3263, 1726, 1610, 1501, 1406 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 1.28 (t, 3H, CH_2CH_3), 2.21 (s, 3H, CH_3-C=N), 4.16 (q, 2H, CH_2CH_3), 7.28/7.70 (AA′BB′, 4H, aromatic), 9.97 (s, 1H, N-H); ^{13}C-NMR (DMSO-d_6): δ 13.97 ($OCH_2\underline{C}H_3$), 14.77 ($\underline{C}H_3$-C=N), 60.58 ($O\underline{C}H_2CH_3$), 148.94 ($\underline{C}$=N), 154.47 (O-$\underline{C}$(O)-N), 114.3/127.9 (CH, phenylene), 131.2/158.9 (Cq, phenylene); MS (m/z, %): 222 (M^+, 100%); Anal. Calcd. for $C_{11}H_{14}N_2O_3$: C, 59.44; H, 6.34; N, 12.60. Found: C, 59.49; H, 6.40; N, 12.66.

N'-[1-(hydroxyphenyl)ethylidene]hydrazine tosylate (**9**).

Acetophenone (2.50 mmol) was added to a warm solution of *p*-toluenesulfonic acid hydrazide (2.70 mmol) in dry ethanol (30 mL). The solution was refluxed for 1.0 hr and then concentrated to one-half of its original volume. After cooling the reaction mixture to room temperature, the product precipitated as a colorless powder which was washed with a small amount of cooled ethanol and dried

to afford the title compound in 86% yield; IR: ν 3385, 3263, 1726, 1610, 1501, 1406 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 2.21/2.38 (2s, 6H, CH_3), 6.84/7.73 (AA′BB′, 4H, aromatic), 7.37/7.54 (AA′BB′, 8H, toluene), 10.31 (s, 1H, N-H); ^{13}C-NMR (DMSO-d_6): δ 14.19 (CH_3), 20.72 (CH_3, toluene), 114.17/127.63 (CH, phenylene), 130.51/159.80 (Cq, phenylene), 127.71/129.83 (CH, toluene), 136.58/143.29 (Cq, toluene), 152.64 (C=N); MS (m/z, %): 304 (M^+, 100%); Anal. Calcd. for $C_{15}H_{16}N_2O_3S$: C, 59.19; H, 5.30; N, 9.24; S, 10.53. Found: C, 59.22; H, 5.26; N, 9.31; S, 10.59.

General procedure for the preparation of 1,2,3-selenadiazole derivatives **13**, **15**, **17**, **19**, **21**

Each of the semicarbazones **7** (1.98 mmol), **10** (1.68 mmol), **11** (0.29 mmol) or **12** (1.00 mmol) or the hydrazones **6** or **8** (2.50 mmol), respectively, was dissolved in glacial acetic acid (40 mL) with vigorous stirring and gentle heating to 40-45 ºC (in case of the hydrazone **6**, the solution was stirred at room temperature). The solution was treated with selenium dioxide powder (2.70 mmol, 3.60 mmol, 0.57 mmol, 4.00 mmol or 2.72 mmol, respectively) and the mixture was kept under vigorous stirring. After ca. 2 min the color of the mixture becomes red. Monitoring of the reaction by TLC (eluent: 1:4 ethyl acetate-hexane) showed that the reaction was complete in 24 hr. Thes mixture were filtered and the filtrates poured into ice water and extracted with $CDCl_3$ (3×50 mL). The combined organic layers were washed with saturated sodium hydrogen carbonate solution. dried over magnesium sulphate and the solvent was removed under vacuum to afford the crude title compounds, which were further purifed as indicated under each heading.

Ethyl-3,5-dihydro-4-phenyl-1-oxo-1,2,3-selenadiazole-2-carboxylate (**13**). The residue was washed with hexane and the insoluble solid was chromatographed using 1:3 ethyl acetate-hexane as eluent to give compound **13** as a pale yellow solid in 69% yield; IR: ν 3206, 2982, 1739, 1694, 1598, 1515, 1226, 726 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.29 (t, 3H, CH_2CH_3), 4.30 (q, 2H, CH_2CH_3), 7.20-7.22 (m, 3H, aromatic), 7.49-7.51 (m, 2H, aromatic), 8.62 (s, 1H, N-H), 9.71 (s, 1H, proton at C_5 of selenadiazole ring); ^{13}C-NMR ($CDCl_3$): δ 14.45 ($OCH_2\underline{C}H_3$), 63.19 ($O\underline{C}H_2CH_3$), 126.29, 126.85, 128.35 and 129.78 for benzene carbons, 130.77 and 149.50 for C_4 and C_5 carbons of the 1,2,3-selenadiazole ring, 152.48 for O-$\underline{C}$(O)-N; MS (m/z, %): 283 (M^+, 100%); Anal. Calcd. For $C_{11}H_{12}O_3N_2Se$: C, 46.64; H, 4.24; N, 9.89. Found: C, 46.53; H, 4.12; N, 9.79.

4-Phenyl-[1,2,3]-selenadiazole (**14**). The residue was chromatographed using 1:4 ethyl acetate-hexane as mobile phase to give a yellow solid of compound **14** in 74% yield; IR: ν 3061, 1687, 1591, 1483, 1235 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.29-7.33 (m, 3H, aromatic), 7.54-7.56 (m, 2H, aromatic), 8.93 (s, 1H, selenadiazole ring); ^{13}C-NMR ($CDCl_3$): δ 126.41, 127.62, 127.90 and 130.73 for benzene carbons, 162.53 and 133.41 for C4 and C5 carbons of the selenadiazole ring); MS (m/z, %): 209 (M^+, 100%); Anal. Calcd. For $C_8H_6N_2Se$: C, 45.95; H, 2.89; N, 13.40. Found: C, 45.78; H, 2.93; N, 13.49.

4-[1,2,3]-Selenadiazole-4-yl-phenol (**16**). The residue was recrystalized from acetone/hexane to give a faint gray solid of compound **16** in 79% yield (when semicarbazone **7** is used) and 84% yield (when hydrazone **8** is used); IR: ν 3429, 3077, 1604, 1527, 1468, 1245, 803 cm^{-1} ; ^{1}H-NMR ($CDCl_3$): δ 2.10 (s, 1H, OH group), 6.90/7.90 (AA′BB′, 4H, phenylene), 9.20 (s, 1H, selenadiazole ring); ^{13}C-NMR

($CDCl_3$): δ 114.81/126.40 (CH, phenylene), 129.82/158.70 (Cq, phenylene), 162.41/133.29 (C4/C5, selenadiazole ring carbons); MS (m/z, %): 225 (M^+, 100%); Anal. Calcd. For $C_8H_6N_2OSe$: C, 42.69; H, 2.69; N, 12.44. Found: C, 42.74; H, 2.63; N, 12.48.

7,10,10-Trimethyl-3-selena-4,5-diaza-tricyclo[5.2.1.$0^{2,6}$]deca-2(6),4-diene (**18**). The crude product was chromatograhed using 1:4 ethyl acetate-hexane as mobile phase to give a pale yellow-brown solid of compound **18** in 50% yield; IR: ν 2949, 1540, 1420, 1232 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 0.72 (s, 3H at C_9), 0.89 (s, 3H at C_{10}), 1.05 (s, 3H at C_8), 1.44/1.82 (2m, 4H at C_5, C_6), 2.29 (m, 1H at C_4); ^{13}C-NMR ($CDCl_3$): δ (61.57, C_1), (166.52, C_2), (153.80, C_3), (43.92, C_4), (27.28, C_5), (32.41, C_6), (48.05, C_7), (19.52, C_8), (18.59, C_9), (11.09, C_{10}); MS (m/z, %): 238 (M^+, 100%); Anal. Calcd. For $C_{10}H_{14}N_2Se$: C, 49.80; H, 5.85; N, 11.61. Found C, 49.71; H, 5.84; N, 11.60.

[1,2,3]-Selenadiazole-4-yl-ferrocene (**20**). The crude product was purified as indicated for compound **18** to give an orange solid of compound **20** in 60% yield; IR: ν 3083, 1700, 1528, 1400, 1258, 816 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 8.89 (s, 1H, proton at C_5 selenadiazole ring), 4.17 (s, 5H, unsubstituted cyclopentadienyl ring), 4.47/5.00 (2d, 4H, monosubstituted cyclopentadienyl ring); ^{13}C-NMR ($CDCl_3$): δ 162.52 and 133.28 for C_4 and C_5 selenadiazole ring, 68.04, 69.45, 69.71 and 85.00 for the carbons of the mono and unsubstituted cyclopentadienyl rings; MS (m/z, %): 318 (M^+, 100%); Anal. Calcd. For $C_{12}H_{10}N_2SeFe$: C, 45.31; H, 3.49; N, 8.81. Found: C, 45.22; H, 3.47; N, 8.75.

Di-[1,2,3]-selenadiazole-4-yl-ferrocene (**22**). The crude product was chromatographed like compound **18** to give an orange solid of compound **22** in 64% yield; IR: ν 3075, 1693, 1528, 1403, 1248, 821 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 8.91 (s, 2H, selenadiazole rings), 4.45/5.13 (2d, 8H, monosubstituted cyclopentadienyl rings); ^{13}C-NMR ($CDCl_3$): δ 162.68/133.32 (C_4/C_5, selenadiazole rings), 69.37, 69.82 and 85.26 for the carbons of the monosubstituted cyclopentadienyl rings; MS (m/z, %): 448 (M^+, 100%); Anal. Calcd. For $C_{14}H_{10}N_4Se_2Fe$: C, 37.53; H, 2.25; N, 12.50. Found: C, 37.51; H, 2.29; N, 12.41.

General procedure for the preparation of 1,2,3-thiadiazole derivatives **15**, **17**, **19**, **21** *and* **23** [13].

An excess amount of thionyl chloride was stirred at 0 ºC and the hydrazones or semicarbazones **6**, **7**, **8**, **10**, **11** or **12** were added in several portions. The mixtures were stirred at room temperature overnight until no more hydrogen chloride was produced. The remaining thionyl chloride was evaporated under vacuum and the residue was washed with diethyl ether to give good yields of the corresponding 1,2,3-thiadiazoles as fine powders. A recrystallization from chloroform or dimethyl-sulfoxide was carried out when necessary.

4-Phenyl-[1,2,3]-thiadiazole (**15**). Beige powder, yield = 83%; IR: ν 3094, 1605, 1456, 1408, 1281, 1068, 921 cm^{-1} ; ^{1}H-NMR (DMSO-d_6): δ 7.28-7.31 (m, 3H, aromatic), 7.53-7.55 (m, 2H, aromatic), 8.89 (s, 1H, selenadiazole ring); ^{13}C-NMR (DMSO-d_6): δ 126.81, 127.42, 127.90 and 130.81 for benzene carbons, 161.31 and 134.60 for C4 and C5 carbons of the thiadiazole ring; MS (m/z, %): 162

(M^+, 100%); Anal. Calcd. For $C_8H_6N_2S$: C, 59.24; H, 3.73; N, 17.27, S, 19.77. Found: C, 45.78; H, 2.93; N, 13.49, S, 19.59.

4-[1,2,3]-Thiadiazole-4-yl-phenol (**17**). Pale brown powder, yield = 76%; IR: ν 3413, 3109, 1597, 1501, 1450, 1411, 1278, 1073, 927 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 2.16 (s, 1H, OH group), 7.21/7.56 (AA′BB′, 4H, phenylene), 8.83 (s, 1H, thiadiazole ring); ^{13}C-NMR (DMSO-d_6): δ 116.21/127.80 (CH, phenylene), 130.61/159.11 (Cq, phenylene), 161.70/133.80 (C4/C5, thiadiazole ring carbons); MS (m/z, %): 178 (M^+, 100%); Anal. Calcd. For $C_8H_6N_2OS$: C, 53.92; H, 3.39; N, 15.72, S, 17.99. Found: C, 53.71; H, 3.28; N, 15.61, S, 17.93.

7,10,10-Trimethyl-3-thia-4,5-diaza-tricyclo[5.2.1.0^{2,6}]deca-2(6),4-diene (**19**). Pale yellow powder, yield = 58%; IR: ν 2963, 1609, 1459, 1406, 1283, 925 cm^{-1} ; ^{1}H-NMR ($CDCl_3$): δ 0.76 (s, 3H at C_9), 0.93 (s, 3H at C_{10}), 1.08 (s, 3H at C_8), the peaks for the other protons were observed between (1.43-2.38); ^{13}C-NMR ($CDCl_3$): δ 61.64 (C_1), 166.81 (C_2), 154.04 (C_3), 44.11 (C_4), 27.26 (C_5), 32.40 (C_6), 48.08 (C_7), 19.73 (C_8), 18.91 (C_9), 11.04 (C_{10}); MS (m/z, %): 194 (M^+, 100%); Anal. Calcd. For $C_{10}H_{14}N_2S$: C, 61.82; H, 7.26; N, 14.42. Found C, 61.85; H, 7.28; N, 14.46.

[1,2,3]-Thiadiazole-4-yl-ferrocene (**21**). Yellow powder, yield = 66%; IR: ν 3068, 1608, 1458, 1413, 1274, 927 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 8.67 (s, 1H, proton at C_5 thiadiazole ring), 4.15 (s, 5H, unsubstituted cyclopentadienyl ring), 4.43/5.10 (2d, 4H, monosubstituted cyclopentadienyl ring); ^{13}C-NMR ($CDCl_3$): δ 162.36 and 133.49 for C_4 and C_5 thiadiazole ring, 68.12, 69.53, 69.68 and 84.89 for the carbons of the mono- and unsubstituted cyclopentadienyl rings; MS (m/z, %): 270 (M^+, 100%); Anal. Calcd. For $C_{12}H_{10}N_2SFe$: C, 53.36; H, 3.73; N, 10.37. Found: C, 53.61; H, 3.70; N, 10.42.

Di-[1,2,3]-thiadiazole-4-yl-ferrocene (**23**). Yellow powder, yield = 61%; IR: ν 3081, 1613, 1457, 1420, 1268, 926 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 8.72 (s, 2H, thiadiazole rings), 4.47/5.11 (2d, 8H, monosubstituted cyclopentadienyl rings); ^{13}C-NMR ($CDCl_3$): δ 161.97/133.14 (C_4/C_5, selenadiazole rings), 69.48, 69.71 and 84.99 for the carbons of the monosubstituted cyclopentadienyl rings; MS (m/z, %): 354 (M^+, 100%); Anal. Calcd. For $C_{14}H_{10}N_4S_2Fe$: C, 47.47; H, 2.84; N, 15.82. Found: C, 47.56; H, 2.90; N, 15.84.

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Sample availability: Available from the authors