DOI: 10.1002/ejoc.200900505

A Novel Synthesis of Ferrocenylpyridazines

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Keywords: Metallocenes / Cations / Nitrogen heterocycles / Structure elucidation

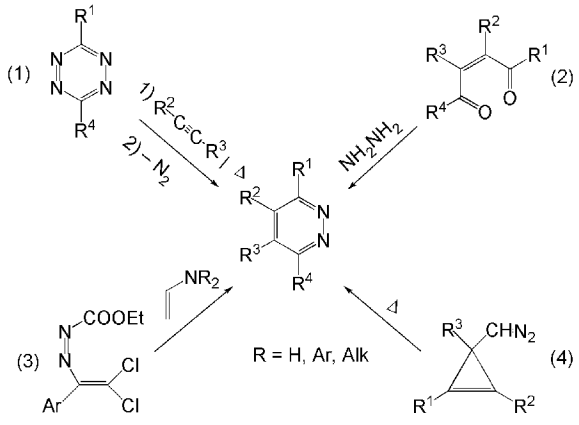
The reaction of 3-[acyl(ethoxycarbonyl)]methylidene-, 3-diethoxycarbonylmethylidene-, and 3-diacylmethylidene-1,2-diferrocenylcyclopropenes with hydrazine at 80–85 °C afforded 3,4,5,6-tetrasubstituted 5-acyl(-ethoxycarbonyl)pyridazines (**3a**–**f**) in 65–70 % yield. The structures of the obtained ferrocenylpyridazines were determined by IR and ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The structures of 5-ethoxycarbonyl- and 5-acetyl-3-ferrocenyl-4-ferrocenylmethyl-6-methylpyridazines (**3a**, **3d**) were confirmed by the data from X-ray diffraction analysis.

Introduction

The interest in compounds of the pyridazine series is associated with their unique biological activities.[1–5] Some pyridazine derivatives are applied as herbicides, anthelmintics, and cardiotonics in the treatment of heart failure, and so on. This stimulates the search for newer methods for the direct access to functionalized aromatic pyridazine systems with substituents at the 3–6-positions of the ring.[5]

The currently known approaches to the synthesis of aromatic pyridazines include: (1) [4+2] Cycloaddition of alkynes to 1,2,4,5-tetrazines followed by elimination of an N_2 molecule from the Diels–Alder type cycloadduct.[6] (2) [4+2] Cycloaddition of dichlorodiazadienes to alicyclic azomethines.[7] (3) Coupling of α,β-unsaturated 1,4-diketones with hydrazine.[8] (4) Intramolecular transformation of cyclopropenyldiazomethanes[9] (Scheme 1).

Aromatic ferrocenyl-substituted pyridazines have not hitherto been studied and their synthesis has not been documented. However, the interest in heterocyclic compounds bearing ferrocenyl substituents in the molecules can be traced from the very discovery of ferrocene. This is determined by a peculiar chemical behavior of such compounds due to the mutual influence of the metallocene and heterocyclic moieties. Information on the synthesis of ferocenyl heterocycles, their physicochemical properties, and practical applications can be found in review papers.[10–13] In particular, the biological activity of many nitrogen heterocycles, such as quinuclidines, pyrazolines, pyrazoles, pyrimidines,



Scheme 1.

and tetrahydropyridazines, bearing ferrocenyl substituents has been highlighted. It may be expected that aromatic ferrocenylpyridazines will also prove valuable; for example, they possess diverse biological activities and they may find use as potential bioreceptor ligands, and so on.

Here we report a novel method for the synthesis of aromatic pyridazines with ferrocenyl and functional substituents in the aromatic nucleus. This evolved from our investigations into the chemical properties of diferrocenylcyclopropene derivatives.

Results and Discussion

1,3-Dicarbonyl compounds (**1a**–**f**) react with 1-morpholino- (or 1-piperidino-)-2,3-diferrocenylcyclopropenilyum terafluoroborates as described earlier[14,15] to afford 3-[acyl(ethoxycarbonyl)]methylidene-1,2-diferrocenylcyclopropenes and 3-diacylmethylidene-1,2-diferrocenylcyclopropenes (**2a**–**f**) in 55–65% yield; these compounds are used as starting compounds (Scheme 2).

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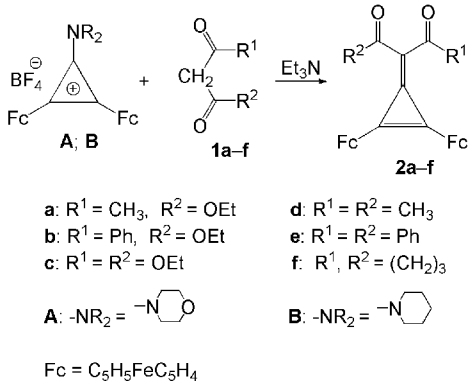
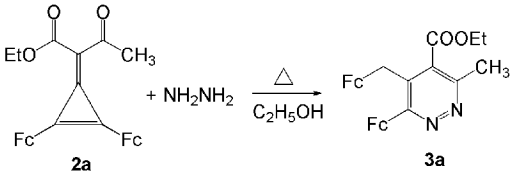


Scheme 2.

We found that diferrocenylcyclopropene **2a** reacts with hydrazine in boiling ethanol to afford regioselectively only one reaction product, methylpyridazine **3a** (Scheme 3).



Scheme 3.

Compound **3a** is an orange crystalline substance; its structure was established on the basis of the data from IR and ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. Thus, its ^{1}H NMR spectrum contains signals for two methyl groups [δ = 1.33 (t), 2.60 (s) ppm], two methylene groups [δ = 4.01 (s), 4.33 (q) ppm, for the $FcCH_2$ and $MeCH_2$ fragments], as well as signals for the protons of two ferrocenyl fragments. Data from the ^{13}C NMR spectrum corroborate the presence of two methyl and two methylene groups, two ferrocenyl fragments, as well as signals for two C_{ipso}Fc carbon atoms, four quaternary carbon atoms, and one C=O group.

The structure of compound **3a** was determined by X-ray diffraction analysis of a single crystal prepared by crystallization from chloroform. The general view of molecule **3a** is shown in Figure 1, and the main geometrical parameters are given in Table 1.

The six-membered ring with two adjacent nitrogen atoms is the central fragment of molecule **3a**. A characteristic feature of the crystal structure of **3a** is the presence of two molecules in the unit cell with ferrocenyl substituents pulled together. Data from the X-ray analysis show that the N1–N2, C24–C23, and C23–C22 bonds in compound **3a** are somewhat longer [d = 1.342(3) Å, d = 1.404(5) Å, d = 1.386(4) Å, respectively] than the standard values of 1.330, 1.393, and 1.375 Å.[16] The N1–C24, N2–C21, and C21–C22 bond lengths are equal to 1.310(5), 1.340(4), and 1.417(4) Å, respectively. The lengths of the C–Fe and C–C bonds in the ferrocenyl substituents, as well as the geometric parameters of the ferrocene sandwiches, are close to standard values.[17]

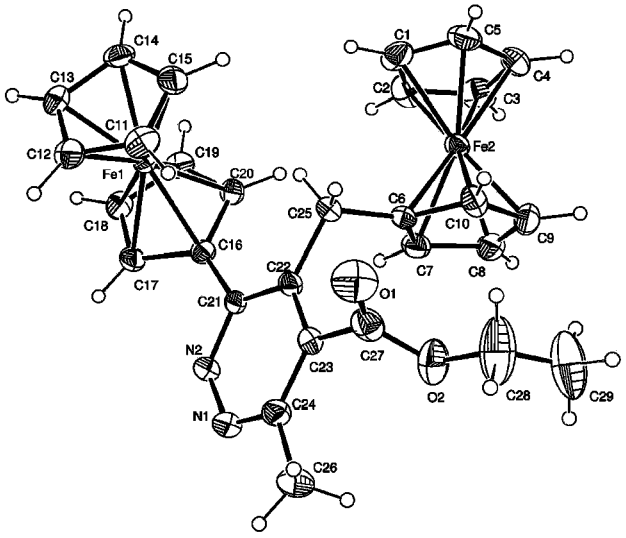
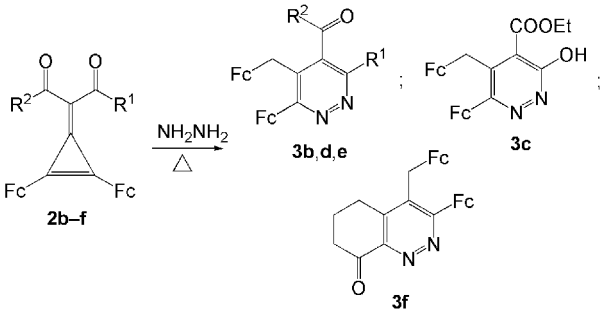


Figure 1. Crystal structure of **3a**.

Table 1. Selected bond lengths and angles for compounds **3a** and **3d**.

Bond lengths [Å]		Bond angles [°]	
3a			
N1–N2	1.342(4)	N1–N2–C21	120.9(3)
C24–N1	1.310(5)	N2–N1–C24	120.5(3)
C21–N2	1.340(4)	N2–C21–C22	121.6(3)
C21–C22	1.417(4)	C21–C22–C23	115.9(3)
C22–C23	1.386(4)	C22–C23–C24	119.4(3)
C23–C24	1.404(5)	C23–C24–N1	121.6(3)
C22–C25	1.508(4)	N1–C24–C26	116.1(3)
C24–C26	1.510(5)	C24–C23–C27	120.6(3)
3d			
N1–N2	1.335(3)	C21–N1–N2	121.6(2)
N1–C21	1.342(3)	C24–N2–N1	120.1(2)
C21–C22	1.411(4)	N1–C21–C22	121.4(2)
C22–C23	1.390(4)	C21–C22–C23	116.1(2)
C23–C24	1.407(4)	C22–C23–C24	119.4(3)
C24–N2	1.325(4)	C23–C24–N2	121.3(3)
C24–C25	1.505(4)	N2–C24–C25	114.8(3)
C23–C26	1.517(4)	C24–C23–C26	120.3(3)
C22–C28	1.514(4)	C23–C22–C28	121.0(2)

Analogously, hydrazine reacts with cyclopropenes **2b–f** (Scheme 4).



Scheme 4.

The structures of compounds **3b–f** were established on the basis of the data from IR and ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. Their ^{1}H NMR spectra all contain characteristic singlets for the methylene groups of the $FcCH_2$ fragments and the necessary amount of signals for the protons of other substituents. Data from the ^{13}C NMR spectra corroborate the structures of compounds **3b–f**.

The structure of pyridazine **3d** was also determined by X-ray diffraction analysis of single crystals prepared by crystallization from chloroform. The general view of molecule **3d** is shown in Figure 2; selected bond lengths and bond angles are listed in Table 1.

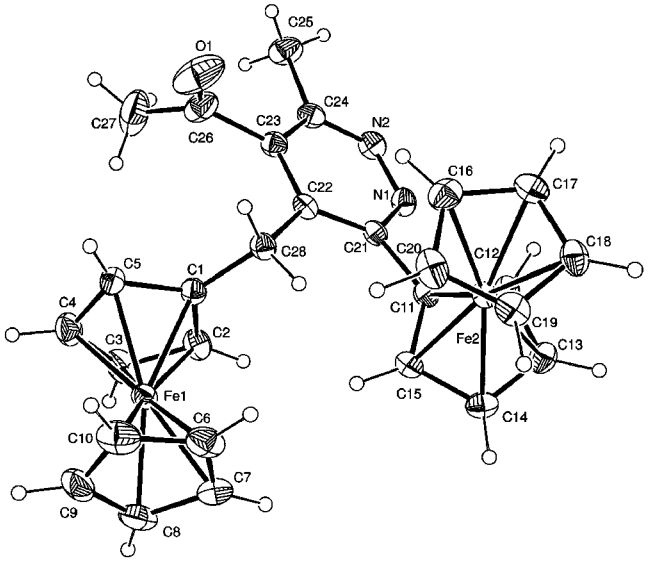
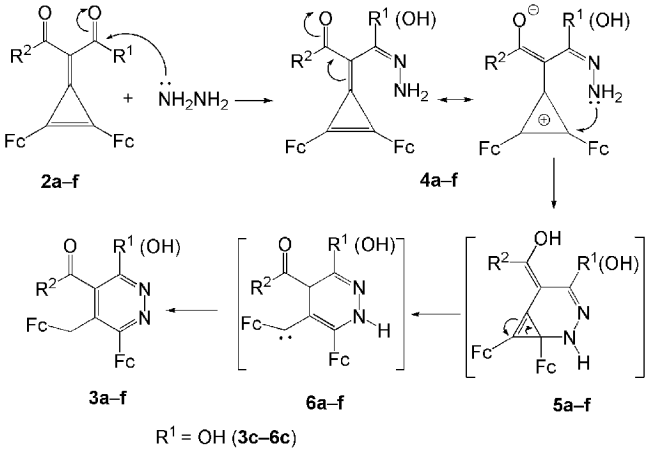


Figure 2. Crystal structure of **3d**.

A possible reaction pathway is illustrated in Scheme 5. Hydrazine reacts with diferrocenylcyclopropenes **2a–f** with formation of hydrazones **4a**,**b**,**d–f** and hydrazide **4c** as the primary products. They possess pseudoaromatic character.[18,19] The cationic part of these structures is a cyclopropenylium with Hückel aromaticity,[18] which plays an important role in the reactions with nucleophiles.[19] The NH_2 group of the hydrazone or of the hydrazide fragment attacks the carbon atom of the cyclopropenylium cation. Opening of the three-membered ring[20] of bicyclic intermediates **5a–f** involves the C-3 bridgehead carbon atom bearing the ferrocenyl substituent and follows the conventional pathway to afford ferrocenyl(vinyl)carbenes.[21–24] Aromatization of vinylcarbenes with migration of the hydrogen atoms to the carbene site ultimately results in pyridazines.

Hydrazones **4d** and **4e**[21] have previously been identified by us as the primary reaction products of **2d** and **2e** with hydrazine at 15–20 °C, and they were isolated from the reaction mixtures and characterized by using physicochemical methods. To confirm the postulated mechanism of pyridazine formation, we have examined the behavior of hydrazones **4d** and **4e** on prolonged storage of their solutions in benzene and acetonitrile at ambient temperature and on brief heating at reflux. It was found that hydrazones **4d** and **4e** completely transform into pyridazines **3d** and **3e** in 25–30 h at low temperature and in 3–5 h at reflux temperature. The yields of isolated pyridazines **3d** and **3e** were 65–70%.



Scheme 5.

Conclusions

Thus, the reactions of 3-diacylmethylidene-, 3-[acyl(ethoxycarbonyl)]methylidene-, and 3-diethoxycarbonylmethylidene-1,2-diferrocenylcyclopropenes with hydrazine give rise to aromatic pyridazines with different substituents in the heterocycle. This method of synthesis of pyridazines, obviously, requires more detailed studies aimed at extension of its potential for the application in organic synthesis.

Experimental Section

General: All the solvents were dried according to the standard procedures and were freshly distilled before use.[25] Column chromatography was carried out on alumina (Brockmann activity III). The ^{1}H and ^{13}C NMR spectra were recorded with a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$, with Me_4Si as the internal standard. The IR spectra were measured with an FTIR spectrophotometer (Spectrum RXI Perkin–Elmer instruments) using KBr pellets. Mass spectra were obtained with a Varian MAT CH-6 instrument (EI MS, 70 eV). Elementar Analysensysteme LECO CHNS-900 was used for elemental analyses. The following reagents were purchased from Aldrich: tetrachlorocyclopropene, 98%; ferrocene, 98%; aluminum chloride, 99.99%; triethyloxonium tetrafluoroborate, 1.0 M solution in dichloromethane; morpholine, 99+%; piperidine, 99%; triethylamine, 99+%; ethyl acetoacetate, 99+%; ethyl bebzoylacetate, 90%; diethyl malonate, 99%; 2,4-pentanedione, 99+%; dibenzoylmethane, 98%;1,3-cyclohexanedione, 97%; hydrazine monohydrate, 98%. 2,3-Diferrocenylcyclopropenone was obtained from ferrocene and tetrachlorocyclopropene in the presence of $AlCl_3$ according to the standard procedure.[19] Ethoxy(diferrocenyl)cyclopropenylium tetrafluoroborate was obtained from 2,3-diferrocenylcyclopropenone in the presence of triethyloxonium tetrafluoroborate (1.0 M in dichloromethane).[14] Morpholino- and piperidino(differocenyl)-cyclopropenylium tetrafluoroborates were obtained from ethoxy(diferrocenyl)cyclopropenylium tetrafluoroborate and morpholine or piperidine in dichloromethane.[14,23] Freshly prepared and

thoroughly dried dialkylamino(differocenyl)cyclopropenylium tetrafluoroborates were employed in the synthesis of 1,2-diferrocenylcyclopropenes **2a**–**f**.[23,24] Reactions were carried out in freshly distilled dry solvents. Hydrazones **4d** and **4e** were obtained by treating ethanolic **2d** and **2e** with hydrazine monohydrate (3 h at 20 °C; yields 60–62%).[21]

Reaction of Dialkylamino(diferrocenyl)cyclopropenylium Tetrafluoroborates with 1,3-Cyclohexanedione 1f: β-Diketone **1f** (6 mmol) and Et_3N (10 mL) were added with stirring to a mixture of diferrocenyl(morpholino)- or (piperidino)cyclopropenylium tetrafluoroborates (3 mmol) in dry benzene (50 mL). After stirring for 6 h at 80 °C, the volatiles were removed in vacuo; chromatography of the residue on Al_2O_3 (hexane/dichloromethane, 10:1) gave **2f**. Yield: 1.12–1.20 g (72–77%), orange crystals, m.p. 234–235 °C. IR (KBr): $\tilde{\nu}$ = 698, 783, 805, 879, 954, 1020, 1049, 1077, 1145, 1234, 1289, 1368, 1397, 1416, 1448, 1487, 1611, 1678, 1851, 2979, 3095 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.09 (m, 2 H, CH_2), 2.59 (m, 4 H, 2 CH_2), 4.24 (s, 10 H, 2 C_5H_5), 4.75 (m, 4 H, C_5H_4), 5.43 (m, 4 H, C_5H_4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.7 (CH_2), 37.9 (2 CH_2), 63.9 (C), 70.3 (2 C_5H_5), 73.0, 73.3 (2 C_5H_4), 102.3 (2 C_{ipso}Fc), 137.1, 141.7 (2 C), 196.1 (2 C=O) ppm. $C_{29}H_{24}Fe_2O_2$ (516): calcd. C 67.47, H 4.69, Fe 21.64; found C 67.62, H 4.53, Fe 21.71. MS: *m*/*z* = 516 $[M]^+$.

Reaction of Dialkylamino(diferrocenyl)cyclopropenylium Tetrafluoroborates with Diethyl Malonate: The reaction of diferrocenyl(morpholino)- or (piperidino)cyclopropenylium tetrafluoroborates (3 mmol) with diethyl malonate **1c** (0.96 g, 6 mmol) and Et_3N (10 mL) in dry benzene (50 mL) was carried out under conditions described above; subsequent chromatography afforded **2c** (1.20 g, 71%) as orange crystals. M.p. 187–188 °C (ref.[15] 187–188 °C).

Reaction of 1,2-Diferrocenylcyclopropene 2a–f with Hydrazine: A solution of compounds **2a**–**f** (0.5 mmol) and hydrazine hydrate (2.0 mL) in ethanol (20 mL) was stirred for 6 h at 78 °C. The reaction mixture was evaporated in vacuo, and the residue was purified by chromatography (Al_2O_3; hexane/ether, 4:1) to give pyridazines **3a**–**f**.

5-(Ethoxycarbonyl)-3-ferrocenyl-4-ferrocenylmethyl-6-methylpyridazine (3a): Yield: 0.16 g (62%), orange powder, m.p. 204–205 °C. IR (KBr): $\tilde{\nu}$ = 506, 594, 699, 824, 896, 941, 1008, 1035, 1101, 1112, 1168, 1239, 1293, 1358, 1399, 1405, 1428, 1441, 1567, 1593, 1670, 1695, 1720, 2893, 2948, 3099 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 6.9 Hz, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 4.01 (s, 2 H, CH_2), 4.09 (s, 5 H, C_5H_5), 4.21 (s, 5 H, C_5H_5), 3.94 (m, 2 H, C_5H_4), 3.99 (m, 2 H, C_5H_4), 4.47 (m, 2 H, C_5H_4), 4.94 (m, 2 H, C_5H_4), 4.33 (q, *J* = 6.9 Hz,2 H, CH_2) ppm. ^{13}C NMR (75 MHz $CDCl_3$): δ = 14.1, 28.8 (2 CH_3), 56.2, 61.9 (2 CH_2), 68.9, 70.0 (2 C_5H_5), 67.4, 69.4, 69.4, 70.8 (2 C_5H_4), 82.4, 85.0 (2 C_{ipso}Fc), 143.2, 144.9, 145.04, 147.8 (4 C), 206.7 (C=O) ppm. $C_{29}H_{28}Fe_2N_2O_2$ (548): calcd. C 63.53, H 5.15, Fe 20.37, N 5.11; found C 63.62, H 5.28, Fe 20.11, N 5.04. MS: *m*/*z* = 548 $[M]^+$.

5-(Ethoxycarbonyl)-3-ferrocenyl-4-ferrocenylmethyl-6-phenylpyridazine (3b): Yield: 0.21 g (67%), orange powder, m.p. 221–223 °C. IR (KBr): $\tilde{\nu}$ = 499, 592, 701, 820, 884, 933, 1004, 1024, 1081, 1125, 1184, 1243, 1298, 1343, 1405, 1422, 1443, 1562, 1597, 1669, 1702, 1722, 2896, 2974, 3090 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.17 (t, *J* = 7.2 Hz, 3 H, CH_3), 4.08 (q, *J* = 7.2 Hz, 2 H, CH_2) 4.19 (s, 2 H, CH_2), 4.21 (s, 5 H, C_5H_5), 4.26 (s, 5 H, C_5H_5), 4.47 (m, 1 H, C_5H_4), 4.53 (m, 1 H, C_5H_4), 4.56 (m, 1 H, C_5H_4), 4.59 (m, 1 H, C_5H_4), 4.84 (m, 1 H, C_5H_4), 4.95 (m, 2 H, C_5H_4), 5.08 (m, 1 H, C_5H_4), 7.39–8.10 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1 (CH_3), 59.1, 61.7 (2 CH_2), 69.8, 70.2 (2 C_5H_5), 69.3, 69.6, 70.0, 71.4 (2 C_5H_4), 81.7, 82.4 (2 C_{ipso}Fc), 127.6, 127.6, 130.0 (C_6H_5), 132.2, 133.5, 135.1, 142.3, 147.1 (5 C), 204.9 (C=O) ppm. $C_{34}H_{30}Fe_2N_2O_2$ (610): calcd. C 66.91, H 4.96, Fe 18.30, N 4.59; found C 66.79, H 5.01, Fe 18.42, N 4.47. MS: *m*/*z* = 610 $[M]^+$.

5-(Ethoxycarbonyl)-3-ferrocenyl-4-ferrocenylmethyl-6-hydroxypyridazine (3c): Yield: 0.17 g (60%), orange powder, m.p. 193–194 °C. IR (KBr): $\tilde{\nu}$ = 496, 592, 702, 812, 901, 934, 1002, 1025, 1100, 1120, 1146, 1242, 1291, 1345, 1391, 1403, 1422, 1444, 1571, 1597, 1668, 1693, 1721, 2890, 2967, 3091, 3439 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.41 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.84 (br. s, 1 H, OH), 3.81 (s, 2 H, CH_2), 4.00 (s, 5 H, C_5H_5), 4.23 (s, 5 H, C_5H_5), 3.89 (m, 2 H, C_5H_4), 3.98 (m, 2 H, C_5H_4), 4.37 (m, 2 H, C_5H_4), 4.51 (m, 2 H, C_5H_4), 4.42 (q, *J* = 7.2 Hz, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 58.0, 62.2 (2 CH_2), 68.9, 70.0 (2 C_5H_5), 67.5, 68.2, 68.7, 70.6 (2 C_5H_4), 81.9, 84.0 (2 C_{ipso}Fc), 126.1, 128.8, 130.8, 132.5 (4 C), 201.1 (C=O) ppm. $C_{28}H_{26}Fe_2N_2O_3$ (550): calcd. C 61.12, H 4.76, Fe 20.30, N 5.09; found C 61.25, H 4.61, Fe 20.41, N 4.98. MS: *m*/*z* = 550 $[M]^+$.

5-Acetyl-3-ferrocenyl-4-ferrocenylmethyl-6-methylpyridazine (3d): Yield: 0.184 g (71%), orange powder, m.p. 208–209 °C. IR (KBr): $\tilde{\nu}$ = 499, 792, 811, 886, 966, 1007, 1063, 1104, 1162, 1231, 1284, 1367, 1395, 1426, 1458, 1572, 1603, 1676, 1712, 1726, 2903, 2970, 3087 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.23 (s, 3 H, CH_3), 2.61 (s, 3 H, CH_3), 4.02 (s, 2 H, CH_2), 4.21 (s, 5 H, C_5H_5), 4.29 (s, 5 H, C_5H_5), 4.09 (m, 2 H, C_5H_4), 4.15 (m, 2 H, C_5H_4), 4.43 (m, 2 H, C_5H_4), 5.13 (m, 2 H, C_5H_4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.5, 28.5 (CH_3), 58.0 (CH_2), 69.1, 70.2 (2 C_5H_5), 67.8, 69.5, 70.3, 71.1 (2 C_5H_4), 82.4, 84.9 (2 C_{ipso}Fc), 148.4, 149.9, 151.1, 155.2 (4 C), 203.1 (C=O) ppm. $C_{28}H_{26}Fe_2N_2O$ (518): calcd. C 64.89, H 5.06, Fe 21.55, N 5.40; found C 64.77, H 4.98, Fe 21.64, N 5.31. MS: *m*/*z* = 518 $[M]^+$.

5-Benzoyl-3-ferrocenyl-4-ferrocenylmethyl-6-phenylpyridazine (3e): Yield: 0.21 g (65%), orange powder, m.p. 264–266 °C. IR (KBr): $\tilde{\nu}$ = 589, 704, 823, 911, 993, 1001, 1054, 1098, 1103, 1178, 1245, 1349, 1394, 1410, 1467, 1529, 1606, 1678, 1693, 1704, 2899, 2993, 3089 cm^{-1}. ^1H NMR (300 MHz $CDCl_3$): δ = 3.98 (s, 5 H, C_5H_5), 4.24 (s, 5 H, C_5H_5), 4.54 (s, 2 H, CH_2), 3.62 (m, 2 H, C_5H_4), 4.18 (m, 2 H, C_5H_4), 4.98 (m, 2 H, C_5H_4), 5.18 (m, 2 H, C_5H_4), 7.12–7.47 (m, 10 H, 2C_6H_5) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.0 (CH_2), 68.8, 70.1 (2 C_5H_5), 67.7, 67.8, 68.7, 69.8 (2 C_5H_4), 83.9, 84.7 (2 C_{ipso}Fc), 128.3, 129.0, 129.2, 129.3, 133.8, 135.7 (2 C_6H_5), 136.4, 139.3, 145.3, 146.3, 147.3, 148.1 (6 C), 206.2 (C=O) ppm. $C_{38}H_{30}Fe_2N_2O$ (642): calcd. C 71.05, H 4.71, Fe 17.39, N 4.36; found C 69.96, H 4.88, Fe 17.45, N 4.29. MS: *m*/*z* = 642 $[M]^+$.

3-Ferrocenyl-4-ferrocenylmethyl-5-oxo-5,6,7,8-tetrahydrocinnoline (3f): Yield: 0.17 g (64%), orange powder, m.p. 212–213 °C. IR (KBr): $\tilde{\nu}$ = 503, 790, 820, 900, 959, 1002, 1061, 1101, 1149, 1234, 1278, 1360, 1405, 1427, 1460, 1571, 1600, 1681, 1711, 1720, 2912, 2979, 3088 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.16 (m, 2 H, CH_2), 2.68 (m, 2 H, CH_2), 3.28 (m, 2 H, CH_2), 4.48 (s, 2 H, CH_2), 4.04 (s, 5 H, C_5H_5), 4.21 (s, 5 H, C_5H_5), 3.89 (m, 2 H, C_5H_4), 3.95 (m, 2 H, C_5H_4), 4.44 (m, 2 H, C_5H_4), 4.88 (m, 2 H, C_5H_4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 34.5, 41.4, 52.2, 58.1 (4 CH_2), 69.3, 70.0 (2 C_5H_5), 68.2, 69.3, 70.2, 71.3 (2 C_5H_4), 82.3, 84.0 (2 C_{ipso}Fc), 147.8, 148.6, 150.0, 153.1 (4 C), 202.7 (C=O) ppm. $C_{29}H_{26}Fe_2N_2O$ (530): calcd. C 65.69, H 4.94, Fe 21.07, N 5.28; found C 65.83, H 4.87, Fe 21.19, N 5.17. MS: *m*/*z* = 530 $[M]^+$.

Transformation of the Hydrazones of 4d and 4e into Pyridazines 3d and 3e: A solution of hydrazones **4d** or **4e** (1 mmol) in ethanol (50 mL) was heated at reflux for 6 h and concentrated. The residue was purified by chromatography on Al_2O_3 (hexane/dichlorometh-

ane, 4:1) to give 0.36–0.38 g (70–74%) (from **4d**) or 0.46–0.48 g (72–75%) (from **4e**) of compounds **3d** or **3e**, respectively.

Crystal Structure Determination: The unit cell parameters and the X-ray diffraction intensities were recorded with a Siemens P4 diffractometer. The structures of compounds **3a** and **3d** were solved by direct method (SHELXS-97[26]) and refined using full-matrix least-squares on F^2. CCDC-729326 (for **3a**) and -729327 (for **3d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

$C_{29}H_{28}Fe_2N_2O_2$ (3a): M = 48.23.18 g mol^{-1}, triclinic $P\bar{1}$, a = 7.5510(8) Å, b = 8.8040(10) Å, c = 18.706(2) Å, α = 95.709(10)°, β = 96.534(10)°, γ = 101.983(9)°, V = 1198.8(2) Å^3, T = 298(2) K, Z = 2, ρ = 1.519 M m^{-3}, λ (Mo-K_α) = 0.71073 Å, F(000) = 568, absorption coefficient 1.240 mm^{-1}, index ranges: $1 \le h \le 10$, $-11 \le k \le 11$, $-25 \le l \le 25$, scan range $2.21 \le \theta \le 29.00°$, 6239 independent reflections, R_{int} = 0.0341, 7598 total reflections, 318 refineable parameters, final R indices [$I > 2\sigma(I)$] R_1 = 0.0547, wR_2 = 0.1353, R indices (all data) R_1 = 0.0847, wR_2 = 0.1477, goodness-of-fit on F^2 1.024, largest difference peak and hole 0.706/–0.505 e Å^{-3}.

$C_{28}H_{26}Fe_2N_2O$ (3d): M = 518.21 g mol^{-1}, triclinic $P\bar{1}$, a = 7.6071(7) Å, b = 8.9171(8) Å, c = 17.3061(19) Å, α = 98.069(9)°, β = 91.673(8)°, γ = 103.625(8)°, V = 1127.2(2) Å^3, T = 293(2) K, Z = 2, ρ = 1.527 Mg m^{-3}, λ (Mo-K_α) = 0.71073 Å, F(000) = 536, absorption coefficient 1.311 mm^{-1}, index ranges $-1 \le h \le 10$, $-12 \le k \le 12$, $-24 \le l \le 24$, scan range $1.19 \le \theta \le 30.00°$, 6589 independent reflections, R_{int} = 0.0257, 7964 total reflections, 247 refineable parameters, final R indices [$I > 2\sigma(I)$] R_1 = 0.0485, wR_2 = 0.1099, R indices (all data) R_1 = 0.0837, wR_2 = 0.1280, goodness-of-fit on F^2 1.011, largest difference peak and hole 0.423/–0.424 e Å^{-3}.

Acknowledgments

This work was supported by the Direccion General de Asuntos de Personal Academico – Universidad Nacional Autonoma de Mexico (DGAPA–UNAM), Mexico (grant IN 214209).

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Received: May 7, 2009
Published Online: July 17, 2009

