Synthesis and properties of ferrocenylalkyl derivatives of indazole

V. V. Gumenyuk, Z. A. Starikova, Yu. S. Nekrasov, and V. N. Babin*

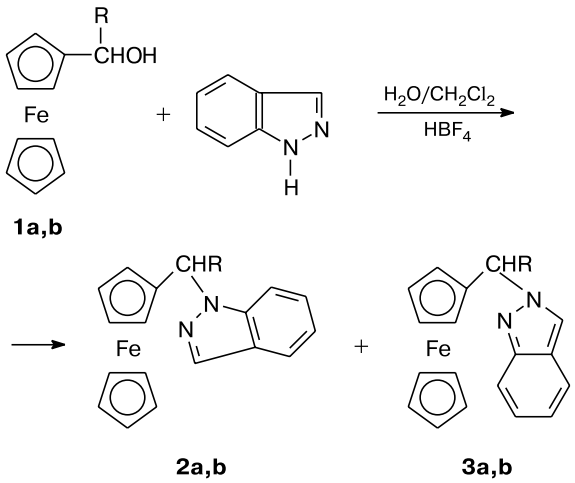
A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: gumen@ineos.ac.ru

Ferrocenylmethylation and α-ferrocenylethylation of indazole were carried out for the first time. Both reactions afforded two isomers, which were characterized by physical and physicochemical methods, among them by X-ray diffraction analysis. 1-(α-Ferrocenylethyl)indazole is thermally more stable than the 2-substituted isomer. Both isomers serve as ferrocenylalkylating agents with respect to *s*-triazole.

Key words: ferrocenylalkylation, indazole, isomers, X-ray diffraction analysis.

Acid-catalyzed ferrocenylalkylation performed in two-phase media with the use of (α-hydroxyalkyl)ferrocenes **1** is one of the most convenient procedures for the synthesis of α-ferrocenylalkylazoles,[1—4] including those possessing antitumor activity and low toxicity.[5—7] In the present study, with the aim of preparing new compounds of this series and as part of continuing studies of the properties of polydentate ligands in ferrocenylalkylation reactions, we synthesized 1- and 2-ferrocenylalkylindazoles **2a,b** and **3a,b** (Scheme 1) and examined some of their properties. Under analogous conditions, the reactions involving the sodium salt of indazole instead of indazole by itself afforded the same reaction products.

Scheme 1



R = Me (**a**); H (**b**)

Results and Discussion

Compounds **2a** and **3a** were generated in a ratio of 2 : 1, whereas compounds **2b** and **3b** were obtained in virtually equal amounts. All reaction products are yellow or orange crystalline compounds, which are soluble in many organic solvents and insoluble in water. The melting points of the 1-isomers are lower than those of the 2-isomers, and the melting points of ferrocenylethylindazoles are lower than those of the corresponding ferrocenylmethyl derivatives (m.p. 93—95 °C and 141—143 °C for **2a** and **2b**, respectively; 119—120 °C and 162—163 °C for **3a** and **3b**, respectively). The mass spectra of these compounds have rather intense molecular ion peaks $[M]^+$ at m/z = 330 (for **2a** and **3a**) and m/z = 316 (for **2b** and **3b**). The main directions of $[M]^+$ fragmentation (I = 100%) of the ferrocenylmethyl derivatives of indazoles involve the following processes. First, this is the simple cleavage of the metal—ligand bonds to form the $[CpFe]^+$ ions with m/z = 121 and the $[M - Cp]^+$ ions with m/z = 265 or the cleavage of the heterocycle—alkyl bonds to form the $[FcCH_2]^+$ ions with m/z = 199 and the $[Ind]^+$ ions with m/z = 117. Second, this is the rearrangement accompanied by migration of the hydrogen atom from the heterocycle to the ferrocenyl fragment ($[FcCH_3]^+$ ion with m/z = 200) and migration of the heterocycle to the iron atom ($[CpFeInd]^+$ and $[FeInd]^+$ ions with m/z = 238 and 173, respectively). For the ferrocenylethyl-containing compounds, the predominant direction of $[M]^+$ fragmentation involves elimination of indazole to give vinylferrocene with m/z = 212 (I = 100%), which is characteristic of ferrocenylethylazoles.[8]

A comparison of the ^{1}H NMR spectra of the resulting compounds with each other and with the spectra of the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1744—1748, October, 2002.

1066-5285/02/5110-1894 $27.00

Table 1. ^{1}H NMR spectra of substituted indazoles ($CDCl_3$, δ, *J*/Hz)

Compound	H(3)	H(4)	H(5)	H(6)	H(7)	Other signals
2a	7.95 s	7.66 (d, *J* = 8.85)	7.03 m	7.22—7.45		5.68 (q, 1 H, CH); 4.28 s; 4.15—4.03 (m, 4 H, substituted Cp); 4.08 (s, 5 H, unsubstituted Cp); 1.91 (d, 3 H, CH_3, *J* = 7.9)
3a	7.66 s	7.51 (d, *J* = 7.7)	6.97 m	7.19 m	7.65 (d, *J* = 8.4)	5.65 (q, 1 H, CH); 4.36 m; 4.20—4.11 (m, 4 H, substitutedCp); 4.14 (s, 5 H, unsubstituted Cp); 1.95 (d, 3 H, CH_3, *J* = 7.0)
2b	7.97 s	7.71 (d, *J* = 8.0)	7.11 m	7.25—7.50		5.31 (s, 2 H, CH_2); 4.27, 4.10 (both s, 2 H each, substituted Cp); 4.15 (s, 5 H, unsubstituted Cp)
3b	7.69 s	7.48 (d, *J* = 8.4)	6.94 m	7.15 m	7.62 (d, *J* = 8.7)	5.22 (s, 2 H, CH_2); 4.28—4.03 (group of signals, 9 H, Cp)
1-Methylindazole[9]	7.94	7.71	7.10	7.34	7.59	3.95 *N*-Me
2-Methylindazole[9]	7.67	7.56	7.02	7.26	7.68	3.80 *N*-Me

corresponding methylindazoles provided evidence for their close similarity (Table 1). There are no substantial differences in the IR spectra of these isomers as well (see the Experimental section).

Because of this, the structures of compounds **3a** and **3b** were established by X-ray diffraction study. The crystals of compounds **3a** and **3b** were grown from a solution in hexane at *ca.* −8 °C and from a solution in $CDCl_3$ at room temperature, respectively.

The molecular structures of compounds **3a** and **3b** are shown in Figs. 1 and 2, respectively. In both compounds, the ferrocenylalkyl group is bound to the N(2) atom. Therefore, these compounds are 2*H*-indazole derivatives and would be expected to have *ortho*-quinoid structures, which are also typical of the corresponding alkyl derivatives of indazole.[9—11]

The indazole systems in molecules **3a** and **3b** are substantially distorted. The ideal *ortho*-quinoid structures do not occur because the bonds in the five-membered ring are essentially delocalized although the quinoid form in the benzene ring is more pronounced. The C(5)—C(6) and C(7)—C(8) bonds in **3a** and the C(10)—C(11) bond in **3b** are substantially shorter than the remaining bonds (Table 2). Hence, the superposition of the quinoid and 1*H*-indazole forms should be ignored and only the *ortho*-quinoid structure with the bond delocalization in the five-membered heterocycle should be considered.

The crystal structure of compound **3b** contains two independent molecules located on the crystallographic plane *m* resulting in disordering of the heterocycle, the N(1) and C(8) atoms occupying close positions. One of the independent molecules is shown in Fig. 2. Selected bond lengths (Å) in two independent molecules are as follows: N(1)—N(2), 1.404(14) and 1.405(9); N(2)—C(8), 1.234(17) and 1.260(14); N(1)—C(9), 1.404(14) and 1.434(10); C(8)—C(9), 1.35(2) and 1.29(2) (average values are 1.40(1), 1.26(2), 1.42(1), and 1.32(2), respectively); C(6)—C(7), 1.499(3) and 1.498(3); C(7)—N(2), 1.474(3) and 1.474(2); C(9)—C(9A), 1.416(4) and 1.412(4); Fe—C(Cp), 2.036—2.054(2).

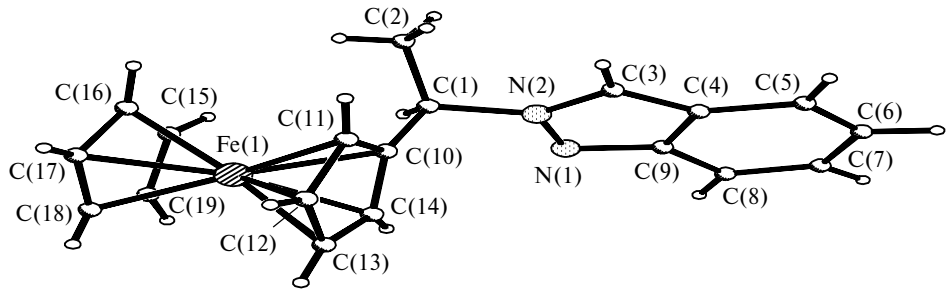


Fig. 1. Molecular structure of compound **3a**.

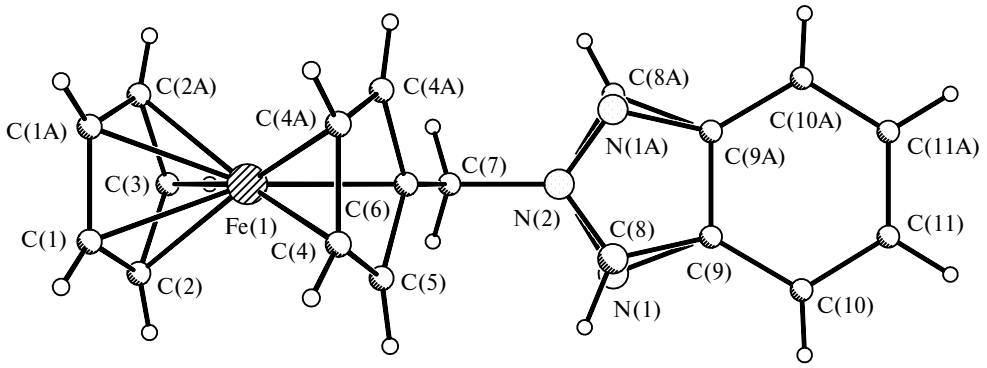


Fig. 2. Molecular structure of compound **3b**.

In the *ortho*-quinoid structures containing the methyl substituent at the N(2) atom of indazole,[10,11] the $C(CH_3)$—N(2) and N(1)—N(2) bonds are equalized (1.344—1.355 Å), whereas the N(1)—C(9) bonds (see Fig. 1) are shorter than the C(3)—C(4) bonds (1.355, 1.360 and 1.389, 1.392 Å, respectively) and are identical with those observed in **3a**. It is difficult to adequately analyze the geometric parameters of compound **3b** because its diazacycle in the crystal structure is disordered. However, the N(2)—C(8) bond in compound **3b** is also shorter than the C(8)—C(9) bond. It should be noted that the bond delocalization in the five-membered diazacycle is observed in all molecules with the *ortho*-quinoid form of 2-substituted indazoles, which are available in the Cambridge Structural Database (CSD).[12]

In both molecules, the indazole fragment is planar and the exocyclic carbon atom (C(1) in **3a** and C(7) in **3b**) lies in the plane of the fragment. The dihedral angles between the planes of the indazole and Cp fragments are 109.2 in **3a** and 112.7 and 109.4° in **3b**. The geometry of the Cp ring in compound **3a** is characterized by an elongation of the C(11)—C(10) and C(10)—C(14) bonds (average, 1.423 Å) compared to the remaining bonds in the ring (1.399—1.414 Å) and also by a decrease in the C(11)—C(10)—C(14) bond angle to 107.1(2)° (the remaining angles are 108.3°). In molecule **3b**, an analogous elongation of the bonds is much less pronounced. The exocyclic C(Cp)—C(1 or 7) bond length (1.505(3) Å in **3a** and 1.498(3) Å in **3b**) is close to the standard $C(Cp)—C_{sp^3}$ bond length.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in compound **3a**

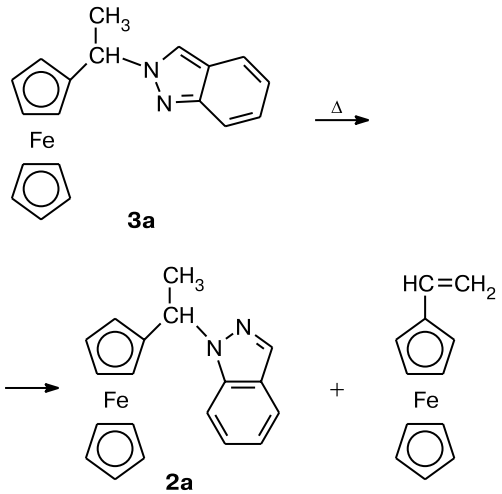
Bond	*d*/Å	Angle	ω/deg
Fe(1)—C(Cp)	2.025—2.050(3)	C(3)—N(2)—N(1)	113.7(2)
		C(3)—N(2)—C(1)	128.4(2)
N(2)—C(3)	1.337(3)	N(1)—N(2)—C(1)	117.9(2)
C(3)—C(4)	1.383(3)	N(2)—N(1)—C(9)	103.5(2)
C(4)—C(9)	1.412(4)	N(2)—C(3)—C(4)	107.0(2)
C(4)—C(5)	1.427(4)	C(3)—C(4)—C(9)	104.2(2)
C(5)—C(6)	1.362(5)	C(3)—C(4)—C(5)	135.9(3)
C(6)—C(7)	1.396(5)	C(9)—C(4)—C(5)	119.9(2)
C(7)—C(8)	1.363(5)	C(6)—C(5)—C(4)	117.7(3)
C(8)—C(9)	1.417(4)	C(5)—C(6)—C(7)	122.0(3)
C(9)—N(1)	1.352(3)	C(8)—C(7)—C(6)	122.3(3)
N(1)—N(2)	1.351(2)	C(7)—C(8)—C(9)	117.4(3)
N(2)—C(1)	1.483(3)	N(1)—C(9)—C(4)	111.6(2)
C(1)—C(10)	1.505(3)	N(1)—C(9)—C(8)	127.7(3)
C(10)—C(14)	1.420(3)	C(4)—C(9)—C(8)	120.7(2)
C(10)—C(11)	1.426(3)	C(14)—C(10)—C(11)	107.1(2)

The N(2)—C(1) bond in compound **3a** (1.483(3) Å) is somewhat longer than the average value (1.469 Å)[13] typical of the C_{sp^3}—N bonds with the participation of the three-coordinate nitrogen atom. In compound **3b**, this bond length is close to the standard value (1.474 Å). Analysis of the C—C and C—N bond lengths in the $Fc—C(R^1,R^2)—N(R^3R^4)$ fragments of compounds available in the CSD demonstrated that the C—N bond length depends primarily on the nature of the R^3R^4 substituents, whereas the R^1,R^2 substituents have virtually no effect on this bond. Thus, the bond lengths between the C atom and the NHPh, NMe_2 (or $N(Alk)_2$), and N=CHPh groups are 1.451—1.454 Å, 1.459—1.472 Å, and 1.472 Å, respectively. In the ferrocenylalkyl derivatives of nucleic bases, the C—N bond lengths are in the range of 1.470—1.485 Å [14—16] and are larger than the value averaged over 52 different N(9)-substituted adenines devoid of the Fc substituent (1.459 Å).

An elongation of the C—N bond in ferrocenylalkyl derivatives of nucleic bases is indicative of its lability, which made it possible to use these compounds as ferrocenylalkylating agents.[3,14,16] It is also known that 2-acylindazoles are good acylating agents[9] and can undergo isomerization to give 1-acylindazoles. In this connection, we studied thermal stability of compounds **2a**,**b** and **3a**,**b** and examined the possibility of the transfer of the ferrocenylalkyl group from these compounds to another substrate. It was found that refluxing of 2-isomers **3a**,**b** in a tetrahydrofuran solution in air for 15 h (inter-

ruption for 12 h) led to the partial transformation of these isomers into the 1-isomers. 2-Ferrocenylmethylindazole appeared to be more stable than its α-ethyl analog and its conversion was only 5—10%, whereas 2-(α-ferrocenylethyl)indazole was converted by almost 50%. In addition, the latter reaction afforded a small amount of vinylferrocene and its dimer (Scheme 2). It should be noted that under the same conditions, solutions of 1-isomers **2a**,**b** did not undergo noticeable changes during the same period of time.

Scheme 2

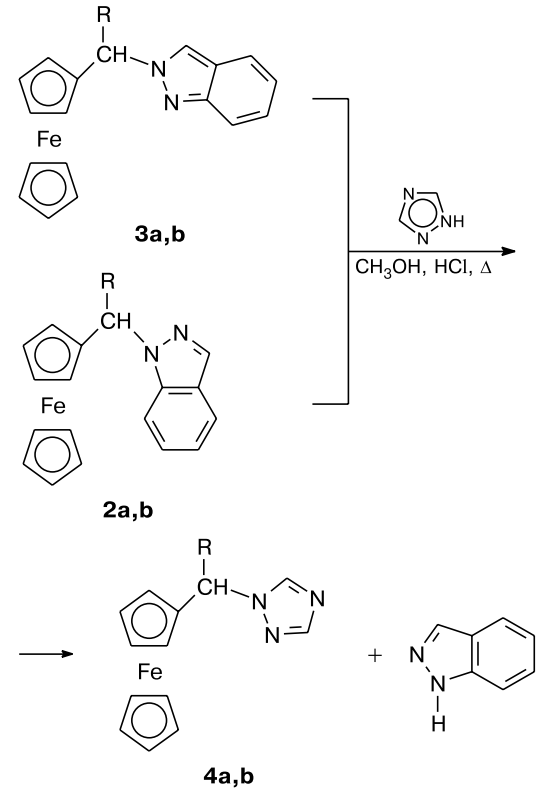


Refluxing of methanolic solutions of each of the four compounds, which were acidified with concentrated HCl, in the presence of 1,2,4-triazole for 2.5 h gave rise to the corresponding *N*-ferrocenylalkyl-1,2,4-triazoles **4a,b** with the molecular masses $[M]^+$ with m/z = 281 and 267, respectively (Scheme 3). In these four reactions, the yields of compounds **4a,b** differed only slightly (25—35% for **2a** and **3a**; 20—25% for **2b** and **3b**). Ferrocenylalkylation of triazole was accompanied by the transformation of 2-substituted indazole derivatives **3a**,**b** into 1-ferrocenylalkylindazoles **2a**,**b**.

α-Ferrocenylethylation of *s*-triazole also gave rise to vinylferrocene, its dimer, and trimer, whereas ferrocenylmethylation afforded a small amount of unidentified decomposition products. It can be suggested that α-ferrocenylalkylation of *s*-triazole is the reversible reaction. This conclusion is evidenced by the fact that 1-*N*-(α-ferrocenylethyl)-1,2,4-triazole (**4a**) prepared independently (according to the reaction analogous to that presented in Scheme 1) readily performed ferrocenylethylation of indazole under the above-mentioned conditions. In this reaction, 1-(α-ferrocenylethyl)indazole (**2a**) was selectively generated.

Therefore, an elongation of the C—N bond between the indazole fragment and the alkyl group in compound **3a** compared to that in **3b** correlates with a decrease in its thermal stability, but has a lesser effect on the ferrocenylalkylating ability.

Scheme 3



R = Me (**a**); H (**b**)

Experimental

The IR spectra were recorded on a UR-20 spectrometer (Carl Zeiss) in KBr pellets. The mass spectra (EI) were measured on an MS-890 instrument (Kratos) with direct inlet of the sample; the temperature of the ionization chamber was 200—220 °C; the energy of ionizing electrons was 70 eV. The ^{1}H NMR spectra were measured at ~20 °C on a Bruker WP-200-SY instrument operating at 200.13 MHz. Chromatography was carried out with the use of aluminum oxide (Brockmann activity II); pH of a 10% aqueous solution was 9—10. Indazole was prepared according to a known procedure.[17]

1- and 2-(α-Ferrocenylethyl)indazoles (2a and 3a). A 38% aqueous solution of fluoroboric acid (2.13 mL) was added with vigorous stirring to a mixture of indazole (1.18 g, 10 mmol) and α-hydroxyethylferrocene (2.30 g, 10 mmol) in chloroform (10 mL). The reaction mixture was stirred for 5 min. Then distilled water (100 mL) was added and the acid was neutralized with aqueous ammonia. The reaction mixture was treated with ether (100 mL), the organic layer was separated, and the solvent was evaporated in air. The solid residue was dissolved in chloroform and chromatographed on Al_2O_3. The dark-yellow band

was eluted with benzene. After removal of the solvent, 1-(α-ferrocenylethyl)indazole (**2a**) was obtained in a yield of 2.05 g (62%), m.p. 93—95 °C. IR, ν/cm^{-1}: ferrocene: 492, 518, 820, 842, 1005 (shoulder), 1024, 1110, 1420, 3070, and 3110; heterocycle: 912, 1185, 1478, 1508, 1627. Found (%): C, 68.96; H, 5.40; N, 8.19. $C_{19}H_{18}N_2Fe$. Calculated (%): C, 69.09; H, 5.45; N, 8.49. The pale-yellow band was eluted with chloroform. After removal of the solvent, 2-(α-ferrocenylethyl)indazole (**3a**) was obtained in a yield of 0.96 g (29%), m.p. 119—120 °C. Compound **3a** was recrystallized from hexane. IR, ν/cm^{-1}: ferrocene: 480, 508, 826, 1005, 1110, 1391, 3110, and 3135 (br); heterocycle: 911, 1141, 1152, 1458, 1478, and 1638.

1- and 2-Ferrocenylmethylindazoles (2b and 3b) were prepared from indazole (3 mmol) and ferrocenylmethanol (3 mmol) according to the above-described procedure. The yield of 1-ferrocenylmethylindazole (**2b**) was 0.44 g (46%), m.p. 141—143 °C. The yield of 2-ferrocenylmethylindazole (**3b**) was 0.39 g (41%), m.p. 162—163 °C. IR of **2b**, ν/cm^{-1}: ferrocene: 488, 507, 830, 843, 1012, 1110, 1425, 2937, and 2957; heterocycle: 915, 1172, 1476, 1510, and 1627. IR of **3b**, ν/cm^{-1}: ferrocene: 480—505 (br), 830, 1010, 1114, 1393, 3070, and 3085; heterocycle: 915, 1180, 1476, 1525, and 1638. Found (%): C, 68.27; H, 5.30; N, 8.86. $C_{18}H_{16}N_2Fe$. Calculated: C, 68.35; H, 5.06; N, 8.86.

Reactions of ferrocenylethylindazoles 2a and 3a with 1,2,4-triazole. Indazole **2a** or **3a** (0.07 g, 0.2 mmol) was dissolved in ethanol on heating. Then a solution of 1,2,4-triazole (0.01 g, 0.2 mmol) in H_2O (1.5 mL) and concentrated HCl (0.09 mL) was added. The reaction mixture was refluxed for 2.5 h, cooled, neutralized with aqueous ammonia, and extracted with dimethyl ether. The organic layer was separated. Thin-layer chromatography on silica gel afforded vinylferrocene along with its dimer and trimer ([M$^+$] m/z = 212, 424, and 636) using hexane as the eluent; compound **2a** or the mixture **2a**+**3a** ([M$^+$] m/z = 330) using benzene as the eluent; and 1-(α-ferrocenylethyl)-1,2,4-triazole[14] (**4a**) ([M$^+$] m/z = 281) using methanol as the eluent. ^{1}H NMR of **4a** (d_6-acetone), δ: 8.28 and 7.75 (both s, 1 H each, C(3)H and C(5)H); 5.45 (m, 1 H, CH); 4.18 (s, 5 H, unsubstituted Cp ring); 3.80—4.40 (group of signals, 4 H, substituted Cp ring); 1.70 (d, 3 H, CH_3, J = 5.8 Hz).

Reaction of ferrocenylethyltriazole 4a with indazole. 1-(α-Ferrocenylethyl)-1,2,4-triazole (**4a**) (0.06 g, 0.2 mmol), which was prepared from *s*-triazole and α-hydroxyethylferrocene analogously to ferrocenylethylindazoles, was dissolved in methanol on heating. Then a solution of indazole (0.02 g, 0.2 mmol) in H_2O (1.5 mL) and concentrated HCl (0.09 mL) was added. The reaction mixture was refluxed for 2.5 h, cooled, neutralized with aqueous ammonia, and extracted with dimethyl ether. The organic layer was separated. According to the mass-spectrometric data, the mixture contained vinylferrocene along with its dimer ([M$^+$] m/z = 212 and 424), ferrocenylethylindazole ([M$^+$] m/z = 330) as the major compound, and a small amount of 1-*N*-(α-ferrocenylethyl)-1,2,4-triazole[14] **4a** ([M$^+$] m/z = 281). A comparative chromatogram on a Silufol plate showed the presence of only 1-(α-ferrocenylethylindazole) (**2a**). Isomer **3a** was absent.

Study of thermal stability of compounds 2a and 3a. Compounds **2a** and **3a** (0.033 g, 0.1 mmol) each were placed in 5-mL one-neck flasks. Then THF (1 mL), which was freshly distilled over $LiAlH_4$, was added. The reaction mixtures were refluxed for 15 h. Comparative chromatograms on Silufol plates were obtained each hour (and compared with those of the starting compounds). After cooling, thin-layer chromatography of the reactions mixiture on Al_2O_3 was carried out to isolate vinylferrocene[18] ([M]$^+$ m/z = 212, m.p. 49—51 °C) along with its dimer ([M]$^+$ m/z = 424) for compound **3a** using hexane as the eluent, compound **2a** (40—45%) using dimethyl ether as the eluent, and compound **3a** (50%) using chloroform as the eluent. In the case of indazole **2a**, no changes were observed.

X-ray diffraction study of compound 3a was performed on an automated Enraf-Nonius CAD4 diffractometer (Mo-Kα radiation, graphite monochromator, θ_{max} = 25°) at ~20 °C. Pale-yellow transparent crystals of $C_{19}H_{18}FeN_2$ (M = 330.20) are monoclinic, a = 12.742(3) Å, b = 9.895(2) Å, c = 12.764(3) Å, β = 106.78(3)°, V = 1540.8(5) Å^3, space group $P2_1/n$, Z = 4, d_{calc} = 1.423 g cm^{-3}. A total of 2704 independent reflections were measured (R_{int} = 0.0440). The structure was solved by direct methods and refined by the least-squares method based on F^2_{hkl} with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms, whose positions were revealed from difference electron density syntheses. The final reliability factors were as follows: R_1 = 0.0461 (calculated based on F_{hkl} for 2202 reflections with $I > 2\sigma(I)$), wR_2 = 0.0990 (calculated based on F^2_{hkl} for all independent reflections), 271 refinable parameters.

X-ray diffraction study of compound 3b. Pale-yellow needle-like crystals of **3b** ($C_{18}H_{16}FeN_2$ M = 316.18) are monoclinic, at 110 K a = 23.260(5) Å, b = 10.313(2) Å, c = 13.023(3) Å, β = 117.302(4)°, V = 2776(1) Å^3, space group $C2/m$, Z = 8, d_{calc} = 1.513 g cm^{-3}. A total of 11705 reflections were collected on a Bruker SMART 1000 CCD area detector diffractometer (λMo-K$_\alpha$ radiation, $2\theta_{max}$ = 60.08°) at 110 K from a single crystal of dimensions 0.1×0.2×0.5 mm. The data were processed with the use of the SAINT[19] and SADABS[20] programs (T_{max} = 0.928, T_{min} = 0.164) to obtain 4199 independent reflections (R_{int} = 0.0454), which were used for the solution and refinement of the structure. The structure was solved by direct methods. The nonhydrogen atoms were located from difference electron density syntheses and refined anisotropically based on F^2_{hkl}. The positions of all hydrogen atoms were revealed and refined isotropically, except for the H atoms at the disordered nitrogen atoms in the indazole rings, which were refined with fixed B_{iso} = 0.5. The final reliability factors were as follows: R_1 = 0.0429 (calculated based on F_{hkl} for 3556 reflections with $I > 2\sigma(I)$), wR_2 = 0.1213 (calculated based on F^2_{hkl} for all 4199 reflections), GOOF = 1.032; 291 refinable parameters.

All calculations were carried out with the use of the SHELXTL PLUS 5 program package.[21] The complete X-ray diffraction data were deposited with the Cambridge Structural Database.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos. 00-03-32807 and 99-07-90133).

References

1. N. S. Kochetkova, V. I. Boev, L. V. Popova, and V. N. Babin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1397 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **6** (Engl. Transl.)].
2. V. I. Boev, L. V. Snegur, V. N. Babin, and Yu. S. Nekrasov, *Usp. Khim.*, 1997, **66**, 874 [*Russ. Chem. Rev.*, 1997, **66**, 613 (Engl. Transl.)].

3. Yu. S. Nekrasov, Zh. V. Zhilina, V. V. Gumenyuk, L. V. Snegur, N. S. Sergeeva, and V. N. Babin, *Zh. Vsesoyuz. Khim. Obshch. im. D. I. Mendeleeva*, 1997, **41**, 117 [*Mendeleev Chem. J.*, 1997, **41**, 172 (Engl. Transl.)].
4. L. V. Snegur, V. I. Boev, Yu. S. Nekrasov, M. M. Ilyin, V. A. Davankov, Z. A. Starikova, A. I. Yanovsky, A. F. Kolomiets, and V. N. Babin, *J. Organomet. Chem.*, 1999, **580**, 26.
5. L. V. Popova, V. N. Babin, R. B. Materikova, V. I. Boev, A. E. Snegireva, N. P. Borodina, G. M. Shaposhnikova, and O. B. Bychenko, *Vth IUPAC Symp. Organomet. Chem. (Italy, Florence, 1989)*, p. 28.
6. L. V. Popova, V. N. Babin, Yu. A. Belousov, Yu. S. Nekrasov, A. E. Snegireva, N. P. Borodina, G. M. Shaposhnikova, O. B. Bychenko, P. M. Raevskii, N. B. Morozova, A. I. Ilyina, and K. G. Shcitkov, *Appl. Organomet. Chem.*, 1993, **7**, 85.
7. V. N. Babin, P. M. Raevskii, K. G. Shchitkov, L. V. Snegur, and Yu. S. Nekrasov, *Zh. Vseross. Khim. Obshch. im. D. I. Mendeleeva*, 1995, **39**, 19 [*Mendeleev Chem. J.*, 1995, **39**, 17 (Engl. Transl.)].
8. Zh. V. Zhilina, V. V. Gumenyuk, Z. A. Starikova, A. I. Yanovsky, A. P. Pleshkova, D. V. Zverev, V. N. Babin, and Yu. S. Nekrasov, *School-Conference for Young Scientists "Organometallic Chemistry towards the 21st Century," 100 Anniversary of Academician A. N. Nesmeyanov (Moscow, 6—11 September, 1999)*, Moscow, 1999, p. 9.
9. *Comprehensive Heterocyclic Chemistry*, Eds. A. R. Katritzky and Ch. W. Rees, Pergamon Press, New York, 1984, **5**, 169—303.
10. A. H´Naifi, J.-M. Leger, and A. Carpy, *Acta Crystallogr., Sect. C (Cryst. Struct. Commun.)*, 1986, **42**, 339.
11. P. Fludzinski, D. A. Evrard, W. E. Bloomquist, W. B. Lacefield, W. Pfeifer, D. Jones, J. B. Deeter, and M. L. Cohen, *J. Med. Chem.*, 1987, **30**, 1535.
12. *Cambrige Structural Database*, April 2001.
13. *Structure Correlation*, Eds. H.-B. Burgi and J. D. Dunitz, VCH, Weinheim-New York, 1994, **2**, pp. 767—784.
14. Zh. V. Zhilina, Ph. D. (Chem.) Thesis, A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, Moscow, 1999, 130 pp. (in Russian).
15. A. Houlton, Ch. J. Isaak, A. E. Gibson, B. R. Horrocks, W. Clegg, and M. R. J. Elsegood, *J. Chem. Soc., Dalton Trans.*, 1999, 3229.
16. Zh. V. Zhilina, V. V. Gumenyuk, Yu. S. Nekrasov, V. N. Babin, L. V. Snegur, Z. A. Starikova, and A. I. Yanovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1828 [*Russ. Chem. Bull.*, 1998, **47**, 1781 (Engl. Transl.)].
17. R. Huisgen and K. Bast, *Organic Syntheses*, 1962, **42**, 62.
18. F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, 1955, **77**, 6295.
19. *SMART V5.051 and SAINT V5.00, Area Detector Control and Integration Software*, 1998, Bruker AXS Inc., Madison, WI-53719, USA.
20. G. M. Sheldrick, *SADABS*, 1997, Bruker AXS Inc., Madison, WI-53719,USA.
21. G. M. Sheldrick, *SHELXTL Ver. 5.0. Software Reference Manual, Siemens Industrial Automation*, Inc., Madison, 1995.

Received May 5, 2002;
in revised form July 9, 2002