ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 12, pp. 1788–1796. © Pleiades Publishing, Ltd., 2007.
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Condensation of Fluoroalkyl-Containing 1,2,3-Trione 2-Arylhydrazones with Methylamine

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Received December 1, 2006

Abstract—Fluoroalkyl-containing 1,2,3-trione 2-arylhydrazones react with methylamine in different ways, depending on the substrate structure. Arylhydrazones having a short fluoroalkyl substituent (R_F = CF_3, HCF_2CF_2) react at the carbonyl group adjacent to the nonfluorinated substituent to give 3-alkyl(aryl)-2-aryldiazenyl-3-methylamino-1-polyfluoroalkylprop-2-en-1-ones. Arylhydrazones with a long-chain fluoroalkyl group (R_F = C_3F_7 and longer) and a bulky nonfluorinated group take up methylamine molecule at the carbonyl group linked to the fluorinated substituent, and the subsequent haloform reaction yields *N*-methyl-2-arylhydrazono-3-oxobutanamides. Both types of products are formed in reactions of methylamine with 1,2,3-triketone 2-arylhydrazones having a long fluoroalkyl group and methyl group at the other carbonyl group. Template condensation of fluoroalkyl-containing 1,2,3-trione 2-arylhydrazones with methylamine over Ni(II) template gives bis[3-alkyl(aryl)-1-polyfluoroalkyl-3-methylamino-2-aryldiazenylprop-2-en-1-onato-*N*,*N*′]-nickel(II), regardless of the size of the fluoroalkyl substituent. The same complexes and their copper analogs can be obtained by treatment of 3-alkyl(aryl)-2-aryldiazenyl-3-methylamino-1-polyfluoroalkylprop-2-en-1-ones with the corresponding metal salts.

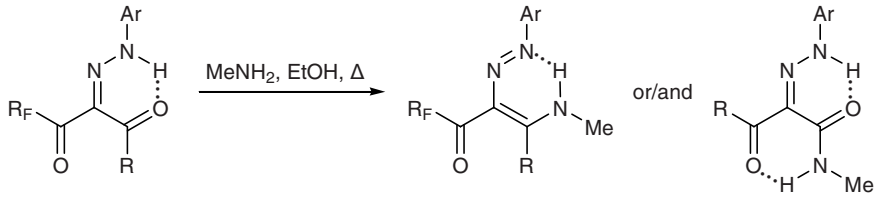
DOI: 10.1134/S1070428007120081

Fluoroalkyl-containing 1,3-diketones react with amines to give regioisomeric N-substituted 1,3-enamino ketones which are used as reagents for determination of transition metals by extraction in combination with gas chromatography, and their complexes with metals exhibit catalytic activity in various processes [1, 2]. The structure of the resulting 1,3-enamino ketone depends primarily on the nature of substituents in the initial fluorinated 1,3-diketone. Condensation of 3-alkyl-1-fluoroalkyl-1,3-diketones, regardless of the length of the fluoroalkyl group, occurs at the carbonyl group linked to the nonfluorinated substituent and yields 1,3-enamino ketones in which the amino group is located in the β-position with respect to the fluoroalkyl moiety. 3-Aryl-1-fluoroalkyl-1,3-diketones give rise to mixtures of regioisomeric 1,3-enamino ketones [3]. The major products in the condensations of trifluoromethyl- and difluoromethyl-containing 1,3-diketones are 1,3-enamino ketones in which the fluorinated group and the amino group are attached to the same carbon atom (80–90%), and the fraction of this isomer decreases in going to substrates having longer polyfluoroalkyl substituents [3–5]. The above condensations are accompanied by acid decomposition as a side process. In addition, unlike nonfluorinated analogs, fluoroalkyl-containing 1,3-diketones exhibit acidic properties [6], and they react with strongly basic amines in nonpolar medium to form stable salts [7].

In the present work we examined reactions of methylamine with polyfluoroalkyl-containing 1,3-diketones having a bulky electron-donating substituent in the 2-position, namely 1,2,3-trione 2-arylhydrazones **I**, with a view to obtain new 1,3-enamino ketones as promising ligands. We also planned to compare the reactivity of compounds **I** toward amines with the reactivity of the corresponding fluorinated 1,3-diketones having no substituent in the 2-position.

Molecules of 3-alkyl(aryl)-1-fluoroalkylpropane-1,2,3-trione 2-arylhydrazones **I** possess two nonequiv-

Scheme 1.



Ia–Ii **IIa–IIg** **IIIf–IIIi**

$R_F = CF_3$, R = Me, Ar = Ph (**a**), R = Ph, Ar = 4-MeC_6H_4 (**b**); $R_F = H(CF_2)_2$, Ar = 4-$MeOC_6H_4$, R = Me (**c**), Ph (**d**), Ar = 4-MeC_6H_4, R = Bu (**e**); $R_F = C_3F_7$, Ar = 4-$MeOC_6H_4$, R = Me (**f**), Ar = 4-MeC_6H_4, R = Ph (**i**); $R_F = C_4F_9$, Ar = 4-MeC_6H_4, R = Me (**g**); $R_F = H(CF_2)_4$, Ar = 4-$MeOC_6H_4$, R = *t*-Bu (**h**).

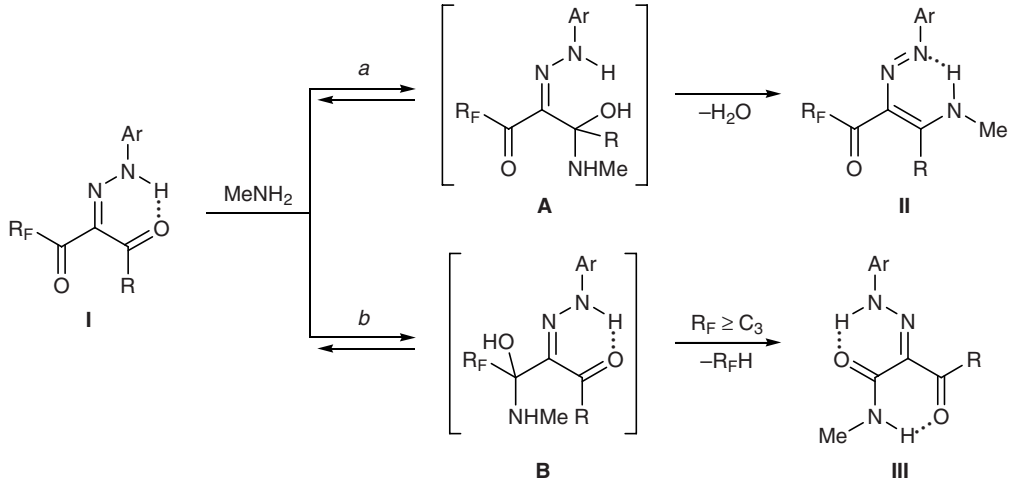
alent electrophilic carbonyl groups, one of which is linked to polyfluoroalkyl substituent, and the other, to nonfluorinated moiety. Therefore, the condensation of compounds **I** may be expected to give two regioisomeric products as a result of reaction at one or another carbonyl group and/or condensation product at both carbonyl groups.

We found that 1,2,3-trione 2-arylhydrazones **Ia–Ie** having a short fluoroalkyl group ($R_F = CF_3$, CHF_2CF_2) react with methylamine in ethanol on heating to give 2-aryldiazenyl-3-aminoprop-2-en-1-ones **IIa–IIe** (Scheme 1). Here, the result of the reaction does not depend to an appreciable extent on the nature of the nonfluorinated moiety, in contrast to analogous transformations of fluorinated 1,3-diketones having no substituent in the 2-position [3–5]. The reactions were carried out with excess methylamine until complete conversion of initial arylhydrazone **I** according to the TLC data (reaction time 20 min). No condensation occurred when chloroform was used as solvent.

The structure of compounds **II** was determined by analysis of their NMR spectra. The ^{13}C NMR spectra of **IIa**, **IIb**, and **IIe** in $CDCl_3$ (see Experimental) contained a downfield multiplet at δ_C 176–180 ppm, corresponding to the carbonyl carbon atom linked to the polyfluoroalkyl group. This means that compounds were formed via condensation at the nonfluorinated acyl group. Comparison of the ^1H and ^{19}F NMR spectra of **IIc** and **IId** indicated their similar structures.

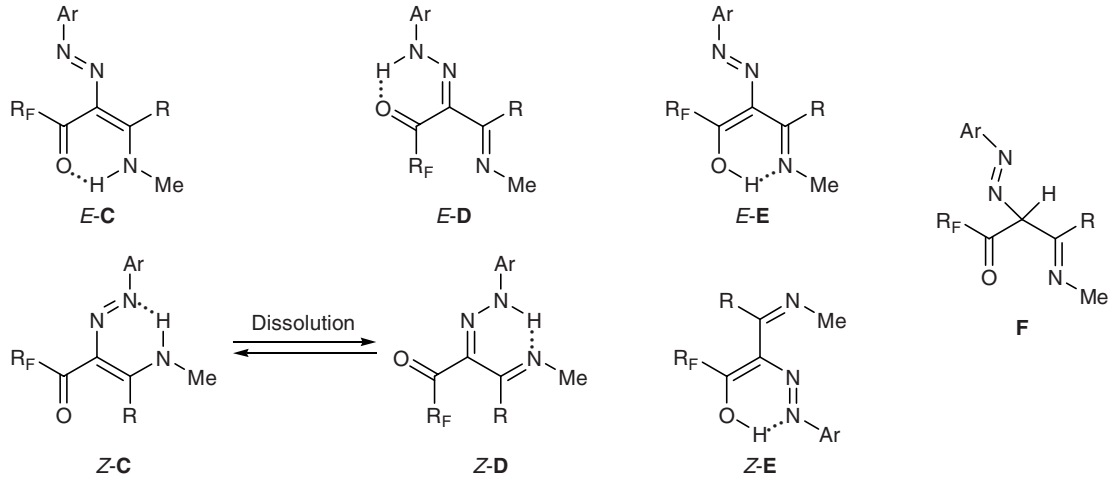
The reactions of methylamine with 1,2,3-trione 2-arylhydrazones **If** ($R_F = C_3F_7$) and **Ig** ($R_F = C_4F_9$) having a longer fluorinated alkyl group and methyl group at the other carbonyl carbon atom were not selective. Apart from expected products **IIf** and **IIg**, we isolated from the reaction mixtures *N*-methyl-2-arylhydrazono-3-oxobutanamides **IIIf** and **IIIg** (Scheme 1). The latter were likely to result from nucleophilic addition of methylamine at the fluorinated acyl moiety, followed by haloform reaction of intermediate adduct with elimination of fluoroalkane. Analogous reactions of arylhydrazones **Ih** and **Ii** ($R_F = C_4F_9$, C_3F_7) having a bulky *tert*-butyl or phenyl substituents gave only amides **IIIh** and **IIIi**. All reactions were carried out under analogous conditions, but

Scheme 2.



I **A** **II** **B** **III**

Scheme 3.



a longer time (~1 h) was necessary to achieve the complete conversion of compounds **If–Ii**.

Scheme 2 shows a probable reaction mechanism. Arylhydrazones **I** possess two nonequivalent electrophilic centers and are capable of taking up methylamine at both carbonyl carbon atoms with formation of intermediates **A** (path *a*) and **B** (path *b*). Obviously, intermediate **A** is quickly stabilized via elimination of water molecule with formation of enamino ketone **II**. Intermediate **B** should be more stable than **A** due to effect of the electron-withdrawing polyfluoroalkyl group. Therefore, in the reactions with arylhydrazones **Ia–Ie** having short-chain fluoroalkyl groups, the equilibrium is displaced toward formation of amines **II**. Stabilization of intermediates **B** with long-chain polyfluoroalkyl groups can also involve elimination of the corresponding fluorinated alkane with formation of amides **III**. Haloform reaction of compounds having long polyfluorinated substituents becomes possible due to formation of more stable carbanions [8]. The predominant formation of amides **IIIh** and **IIIi** in the reactions with arylhydrazones **Ih** and **Ii** may be rationalized in terms of steric hindrances created by the bulky phenyl or *tert*-butyl group to nucleophilic attack on the neighboring carbonyl carbon atom.

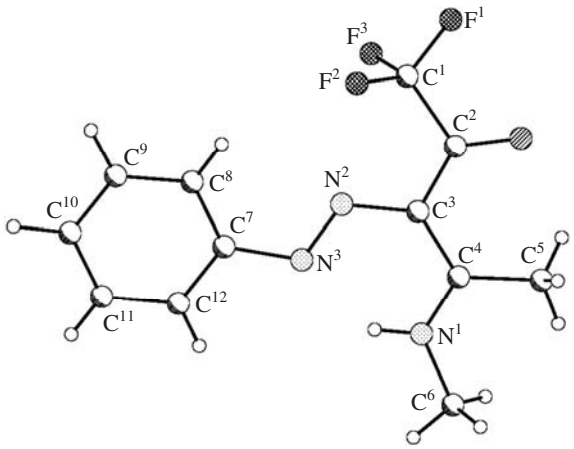


Fig. 1. Structure of the molecule of (3*Z*)-1,1,1-trifluoro-4-methylamino-3-(phenyldiazenyl)pent-3-en-2-one (**IIa**) according to the X-ray diffraction data.

Compounds **IIa–IIg** are complex tautomeric systems: they could give rise to azo–hydrazone, keto–enol, and imine–enamine tautomerism, i.e., tautomeric structures **C–F** are possible (Scheme 3). In addition, tautomers **C–E** can exist as *Z* and *E* isomers differing in orientation of substituents with respect to the C=C or C=N double bond; *Z* and *E* isomers can be stabilized by intramolecular hydrogen bond.

The ^{1}H and ^{19}F NMR spectra of compounds **IIa–IIg** in $CDCl_3$, and of **IIa** additionally in DMF-d_7 and acetone-d_6, contained only one set of signals, indicating that only one isomer is present in solution. Taking into account that the ^{13}C NMR spectra of **IIa**, **IIb**, and **IIe** contain a signal from carbonyl carbon atom of the polyfluoroacyl group, azoiminoenol tautomers **E** can be ruled out. The ^{1}H NMR spectra lacked doublet signals assignable to protons of the NHC**H**$_3$ group in azoenaminoketone tautomer **C** and singlet typical of CH proton in azoiminoketone tautomer **F**. On the other hand, the chemical shift of the NH proton (δ 14.67–14.49 ppm) conforms better to arylhydrazone fragment in hydrazonoiminoketone tautomer **D**, involved in intramolecular hydrogen bond [9], than to the N**H**CH$_3$ proton of azoenaminoketone **C** [3–5]. These findings led us to conclude that compounds **II** in chloroform solution exist as *E* or *Z* isomers of hydrazonoiminoketone tautomer **D**.

On the basis of the NMR and X-ray diffraction data, initial arylhydrazones **I** were previously assigned the hydrazodiketone structure with intramolecular hydrogen bond involving the carbonyl oxygen atom in the nonfluorinated fragment [10]. The steric structure of compounds **II** was determined by comparing parameters of their NMR spectra with the corresponding data for initial arylhydrazones **I**. In the ^{19}F NMR spectra of trifluoroacetyl derivatives **Ia**, **Ib** and **IIa**, **IIb** in $CDCl_3$, the fluorine nuclei resonated in the same region, at δ_F 92–93 ppm. Compounds **IIa** and **IIb** displayed in the ^{13}C NMR spectra quartets at δ_C 176–177 ppm with a coupling constant $^2J_{CF}$ of 30.5–31 Hz, which are typical of free trifluoroacetyl group [10, 11]. Likewise, no appreciable differences were observed in the spectral parameters of condensation products **IIc–IIg** and initial arylhydrazones **Ic–Ig** having other fluoroalkyl substituents. Therefore, we presumed that compounds **IIa–IIg** in chloroform solution exist as *Z* isomers of tautomer **D** in which intramolecular hydrogen bond involves the arylhydrazone and methylimine fragments, while the polyfluoroacyl group remains unbound.

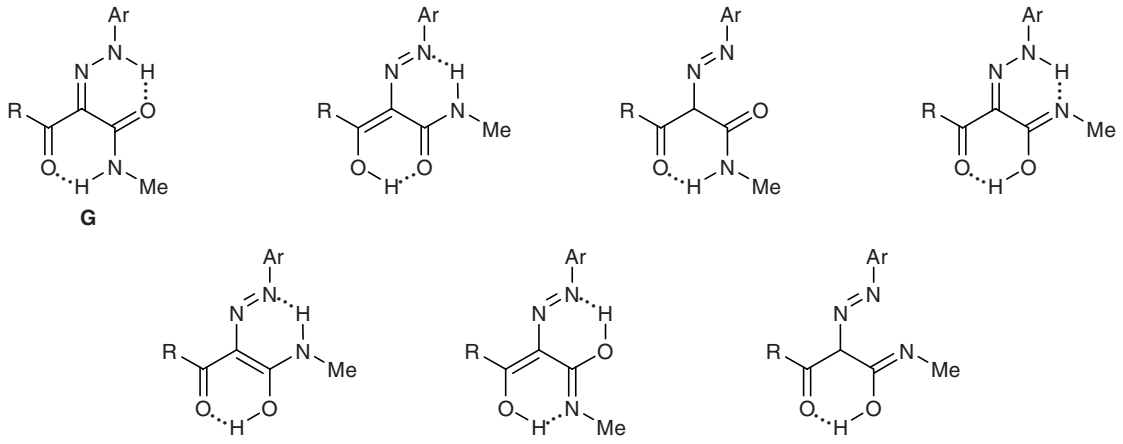
The structure of compounds **II** in crystal was determined by X-ray analysis using enamino ketone **IIa** as an example. We found that in the crystalline state it exists as *Z*-azoenaminoketone isomer **C** in which the N^3 and H^1 atoms form intramolecular hydrogen bond. The distance $N^3 \cdots H^1$ is 1.89(3) Å, and the angles $N^1H^1N^3$ and $N^2N^3H^1$ are 137.90 and 101.84°, respectively (Fig. 1, see table). Comparison of the IR spectra of crystalline samples of compounds **IIa–IIg** indicated that they have similar structures. Presumably, dissolution of **IIa–IIg** is accompanied by transformation of tautomer **C** into **D** as a result of enamine–imine and azo–hydrazone isomerizations (Scheme 3).

Amides **IIIf–IIIi** are also capable of undergoing various tautomeric transformations. Theoretically, seven tautomers are possible (Scheme 4). However, compounds **IIIf–IIIi** showed only one set of signals in the ^1H NMR spectra. The spectra contained a doublet signal at δ 2.88–2.97 ppm (J = 4.9–5.0 Hz) from protons of the methyl group on the nitrogen atom, a very broad singlet from the N**H**Me proton at δ 9.32–9.49 ppm, and a downfield singlet from the arylhydrazone NH proton at δ 14.78–15.00 ppm. In the ^{13}C NMR spectrum of **IIIf** in $CDCl_3$ we observed two downfield signals at δ_C 166.06 and 198.77 ppm, corresponding to carbonyl carbon atoms in the amide and acetyl groups. These data led us to prefer hydrazonoketoamide structure **G** for amides **IIIf–IIIi**.

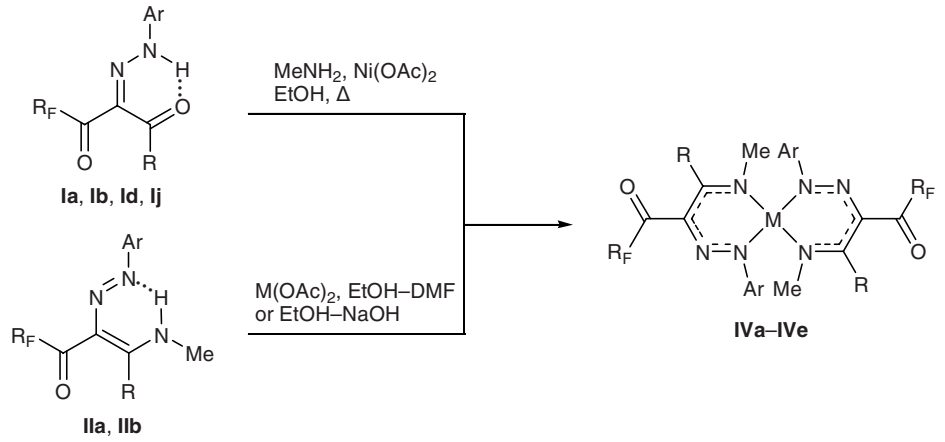
We also found that fluoroalkyl-containing 1,2,3-trione 2-arylhydrazones **Ia**, **Ib**, **Id**, and **Ij** react with methylamine over Ni(II) template to give chelates **IVa** and **IVc–IVe** (Scheme 5). The template procedure is advantageous, for it provides the possibility for synthesizing metal complexes with ligands having a long fluoroalkyl group ($R_F = C_3F_7$) and a bulky nonfluorinated substituent. An alternative method for the synthesis of **IV** involves treatment of methyl- and phenyl-substituted 3-alkyl(aryl)-2-aryldiazenyl-3-methylamino-1-polyfluoroalkylprop-2-en-1-ones **IIa** and **IIb** with metal salts (Scheme 5). Complexes with other metals, e.g., copper, can be obtained in such a way.

Three different modes of coordination are possible in complexes **IV** (structures **H**, **J**, and **K**). Structure **H** implies metal coordination at the nitrogen atoms in the arylhydrazone and methylimine fragments, coordination with participation of the arylhydrazone and carbonyl groups gives rise to structure **J**, and structure **K** corresponds to coordination at the carbonyl oxygen atom and nitrogen atom of the methylimino group.

Scheme 4.

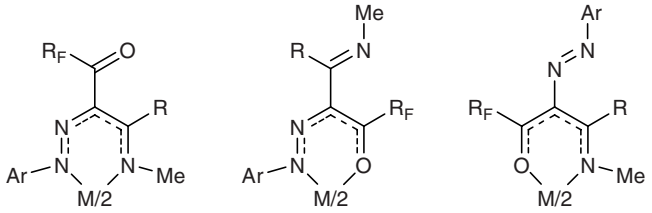


Scheme 5.



Ij, $R_F = C_3F_7$, R = Ph, Ar = 4-$MeOC_6H_4$; **IV**, $R_F = CF_3$, R = Me, Ar = Ph, M = Ni (**a**), Cu (**b**); $R_F = H(CF_2)_2$, R = Ph, Ar = 4-$MeOC_6H_4$, M = Ni (**c**); $R_F = C_3F_7$, R = Ph, Ar = 4-$MeOC_6H_4$, M = Ni (**d**); $R_F = CF_3$, R = Ph, Ar = 4-MeC_6H_4, M = Ni (**e**).

According to published data, nickel chelate derived from 2-phenyliminopentane-3,4-dione 3-phenylhydrazone has the structure of bis[4-methylamino-3-(phenyldiazenyl)pent-3-en-2-onato-N^3,N^4]nickel(II) where the coordination entity includes four nitrogen atoms [12]. In the IR spectra of complexes **IVa**–**IVc** and **IVe** absorption bands corresponding to the polyfluoroacyl group are located in the same region as in the spectra of initial enamino ketones **IIa** and **IIb** (1675–1665 cm^{-1}). Nickel chelate **IVa** is characterized by diamagnetic shift of the N-methyl and phenyl proton signals in the ^1H NMR spectrum relative to the corresponding signals of free ligand **IIa**. This may be due to effect of the central nickel ion on the nearby protons. On the other hand, the fluorine nuclei in compounds **IIa** and **VIa** resonate in the same region of the ^{19}F NMR spectrum (see Experimental). Taking into account the IR and NMR spectra of compounds **IVa**–**IVe** and published data, we believe that coordination to the central metal ion in these complexes involves four electron-donating nitrogen atoms in the arylhydrazone and methylimine fragments (structure **H**) and that the carbonyl group is not involved. This assumption was confirmed by the X-ray diffraction data for complex **IVb** (see table).



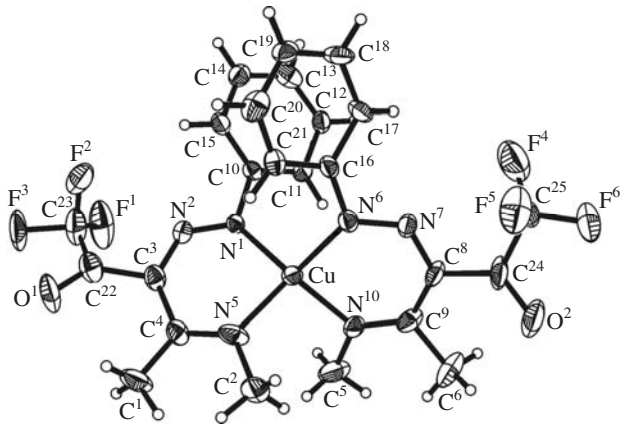


Fig. 2. Structure of the molecule of bis[1,1,1-trifluoro-4-methylamino-3-(phenyldiazenyl)pent-3-en-2-onato-N^3,N^4]-copper(II) (**IVb**) according to the X-ray diffraction data.

The crystalline structure of **IVb** is formed by crystallographically independent molecules (Fig. 2) located in the general position. The coordination entity is a distorted tetrahedron whose center is occupied by copper(II) ion, and the N^1, N^5, N^6, and N^{10} atoms are located at the apices. The distances between the copper ion and nitrogen atoms are Cu–N^1 1.943(6), Cu–N^6 1.909(6), Cu–N^5 1.936(7), and Cu–N^{10} 1.954(6) Å; the angles N^1CuN^5, N^5CuN^{10}, $N^{10}CuN^6$, and N^6CuN^1 are 93.7(3), 99.8(2), 91.8(3), and 101.8(1)°, respectively; the diagonal angles N^1CuN^{10} and N^5CuN^6 are 139.1(3) and 140.5(3)°, respectively. The distance between the mean-square planes of the phenyl substituents is 3.60 Å, and the dihedral angle between them is equal to 22.4°. The dihedral angle between the CuN^1N^5 and CuN^6N^{10} planes is 56.6°. The chelate rings adopt

a stepped conformation. The dihedral angle between the CuN^1N^5 and $N^1N^2C^3C^4N^5$ planes is 178.5°, and the angle between the CuN^6N^{10} and $N^6N^7C^8C^9N^{10}$ planes is slightly smaller (177.6°).

Molecules **IVb** in crystal are arranged in such a way that the trifluoromethyl groups are oriented toward each other, giving rise to insignificantly shortened intermolecular F–H contacts (d = 2.38 Å; cf. the corresponding sum of the van der Waals radii, 2.54 Å [13]).

Thus the results of the present study showed that introduction of a bulky arylhydrazono substituent into molecules of fluorinated 1,3-diketones changes their reactivity toward primary amines. First, arylhydrazones **I** do not form salts with amines since their acidity is reduced due to effect of electron-donating arylhydrazono group. Second, the reaction direction is determined primarily by the length of the polyfluoroalkyl substituent. Third, the reaction with methylamine involves haloform cleavage mainly typical of ketones rather than acid cleavage typical of 1,3-dicarbonyl compounds. The difference in the behaviors of 1,3-diketones and 1,2,3-trione 2-arylhydrazones **I** may be rationalized by the absence of conjugation between the electrophilic centers (carbonyl groups) in the latter. As a result, arylhydrazones **I** behave as compounds having isolated carbonyl groups. 3-Alkyl(aryl)-2-aryldiazenyl-3-methylamino-1-polyfluoroalkylprop-2-en-1-ones **II** are promising as ligands for binding transition metal ions.

EXPERIMENTAL

The melting points were measured in open capillaries and were not corrected. The IR spectra were recorded in the frequency range from 400 to 4000 cm^{-1} on a Perkin–Elmer Spectrum One spectrometer with Fourier transform from samples dispersed in mineral oil. The NMR spectra were measured from solutions in $CDCl_3$ or DMF-d_7 (compounds **IIa** and **IVa**) on a Bruker DRX-400 spectrometer (400.13 MHz for ^1H, 100.6 MHz for ^{13}C, and 376 MHz for ^{19}F) relative to tetramethylsilane (^1H and ^{13}C) or hexafluorobenzene (^{19}F). The elemental compositions were determined on a Perkin–Elmer PE 2400 Series II analyzer. The mass spectra were obtained on a Varian MAT-311A instrument. Silica gel Merck 60 (0.063–0.200 mm) was used for column chromatography (eluent chloroform).

Single crystals of enamino ketone **IIa** were obtained by crystallization from methylene chloride–hexane (4:1). The X-ray diffraction data were acquired on an Xcalibur-3 diffractometer with a CCD detector [graphite monochromator, CuK_α irradiation, λ = 1.54180 Å, temperature 295(2) K, ω-scanning]. Absorption by the crystal was taken into account analytically according to the multifaceted crystal model with the use of CrysAlis RED 1.171.28c4 program. The structure was solved by the direct method on the basis of the Fourier difference syntheses. The positions and temperature parameters of non-hydrogen atoms were refined by the least-squares procedure in full-matrix anisotropic approximation.

Single crystals of complex **IVb** were obtained by crystallization from methylene chloride–hexane (3:1). The X-ray diffraction data were acquired at room temperature on a KM-4 diffractometer [graphite monochromator, MoK_α irradiation, λ = 0.7107 Å, temperature 295(2) K, ω/2θ scanning]. The structure was solved by the direct methods, followed by Fourier syntheses, using SHELXS-97 program [14] and was refined by the least-squares procedure in full-matrix anisotropic approximation for all non-hydrogen atoms

Crystallographic data and parameters of X-ray diffraction experiments for compounds **IIa** and **IVb**[a]

Parameter	**IIa**	**IVb**
Formula	$C_{12}H_{12}F_3N_3O$	$C_{24}H_{22}CuF_6N_6O_2$
Molecular weight	271.25	604.02
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	Cc
a, Å	7.425(4)	12.777(3)
b, Å	19.656(4)	10.578(2)
c, Å	9.062(2)	19.093(4)
β, deg	107.01 (2)	92.63(3)
V, $Å^3$	1264.7(5)	2577.8(9)
Z	4	4
d_{calc}, g/cm^3	1.425	1.56
μ, mm^{-1}	0.107	0.925
Total number of reflections	2377	3776
Number of independent reflections	1881	3776
Divergence factor R	0.058	0.049
Number of refined parameters	189	353

[a] The complete sets of crystallographic data for compounds **IIa** and **IVb** were deposited to the Cambridge Crystallographic Data Center (entry nos. CCDC 612411 and CCDC 296474, respectively; *www.ccdc.cam.ac.uk/conts/retrieving.html*).

using SHELXL-97 program [14]. The reflection intensities were corrected for absorption semiempirically [15]. The coordinates of hydrogen atoms were calculated from the geometry considerations. The principal crystallographic parameters of compounds **IIa** and **IVb** and some parameters of X-ray diffraction experiments are given in table.

Initial fluoroalkyl-containing 1,2,3-trione 2-arylhydrazones (**I**) were synthesized according to the procedure described in [9].

Reaction of 1,2,3-trione 2-arylhydrazones I with methylamine (*general procedure*). Excess gaseous methylamine was bubbled through a solution of 3 mmol of arylhydrazone **Ia–Ii** in 30 ml of ethanol on heating. The substrate conversion was monitored by TLC. When the reaction was complete, the precipitate was filtered off, recrystallized from ethanol, and dried under reduced pressure. In the reactions with hydrazones **If** and **Ig** the products were separated by column chromatography.

(3*Z*)-1,1,1-Trifluoro-4-methylamino-3-phenyldiazenylpent-3-en-2-one (IIa). Yield 200 mg (74%), yellow crystals, mp 150–152°C. IR spectrum, ν, cm^{-1}: 3420, 1610 (NH); 1665 (C=O); 1590, 1570, 1495 (N=N, C=C); 1190–1150 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.62 s (3H, Me), 3.19 s (3H, NMe), 7.27–7.65 m (5H, Ph), 14.67 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.18 (C^6), 30.15 (C^5), 118.62 q (C^1, $^1J_{CF}$ = 292.0 Hz), 121.02 (C^8, C^{12}), 123.75 (C^{10}), 125.15 (C^9, C^{11}), 128.12 (C^7), 151.38 (C^3), 165.70 (C^4), 177.65 q (C^2, $^2J_{CF}$ = 30.5 Hz). ^{19}F NMR spectrum: δ_F 92.70 ppm, s. ^{1}H NMR spectrum (DMF-d_7), δ, ppm: 2.69 s (3H, Me), 3.37 s (3H, NMe), 7.32–7.77 m (5H, Ph), 14.15 br.s (1H, NH). ^{19}F NMR spectrum: δ_F 95.73 ppm, s. Found, %: C 53.05; H 4.55; F 20.75; N 15.82. $C_{12}H_{12}F_3N_3O$. Calculated, %: C 53.14; H 4.46; F 21.01; N 15.49.

(3*Z*)-1,1,1-Trifluoro-4-methylamino-3-(4-methylphenyl)diazenyl-4-phenylbut-3-en-2-one (IIb). Yield 247 mg (71%), orange powder, mp 123–125°C. IR spectrum, ν, cm^{-1}: 3350, 1595 (NH); 1680 (C=O); 1590, 1575, 1500 (N=N, C=C); 1185–1130 (C–F). ^{1}H NMR spectrum, δ, ppm: 2.40 s (3H, Me), 2.92 s (3H, NMe), 7.27–7.59 m (9H, H_{arom}), 14.60 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 21.24 (C^6), 31.74 (Me), 118.25 q (C^1, $^1J_{CF}$ = 292.3 Hz), 120.80 (C^8, C^{12}), 123.13 (C^{10}), 129.04 (C^9, C^{11}), 129.54 (C^7), 126.36 (C^o), 129.83 (C^p), 131.66 (C^m), 138.44 (C^i), 148.95 (C^3), 163.80 (C^4), 176.60 q (C^2, $^2J_{CF}$ = 31.0 Hz). ^{19}F NMR spectrum: δ_F 92.70 ppm, s. Found, %: C 62.05; H 4.73; F 16.54; N 12.12. $C_{18}H_{16}F_3N_3O$. Calculated, %: C 62.24; H 4.64; F 16.41; N 12.10.

(4*Z*)-1,1,2,2-Tetrafluoro-4-(4-methoxyphenyl)diazenyl-5-methylaminohex-4-en-3-one (IIc). Yield 223 mg (67%), yellow crystals, mp 145–147°C. IR spectrum, ν, cm^{-1}: 3450, 1610 (NH); 1655 (C=O); 1605, 1585, 1500 (N=N, C=C); 1200–1100 (C–F). ^{1}H NMR spectrum, δ, ppm: 2.62 s (3H, Me), 3.18 s (3H, NMe), 3.86 s (3H, OMe), 6.45 t.t (1H, HCF_2, $^2J_{HF}$ = 54.2, $^3J_{HF}$ = 5.7 Hz), 7.23–7.42 m (4H, C_6H_4), 14.49 br.s (1H, NH). ^{19}F NMR spectrum, δ_F, ppm: 25.56 d.t (2F, HCF_2, $^2J_{FH}$ = 54.2, $^3J_{FF}$ = 8.5 Hz), 41.83 m (2F, CF_2). Found, %: C 50.20; H 4.57; F 22.68; N 12.78. $C_{14}H_{15}F_4N_3O_2$. Calculated, %: C 50.45; H 4.54; F 22.80; N 12.61.

(1*Z*)-4,4,5,5-Tetrafluoro-2-(4-methoxyphenyl)diazenyl-1-methylamino-1-phenylpent-1-en-3-one (IId). Yield 273 mg (69%), yellow crystals, mp 108–110°C. IR spectrum, ν, cm^{-1}: 3400, 1610 (NH); 1665 (C=O); 1590, 1575, 1495 (N=N, C=C); 1190–1150 (C–F). ^{1}H NMR spectrum, δ, ppm: 2.91 s (3H, NMe), 3.87 s (3H, OMe), 6.42 t.t (1H, HCF_2, $^2J_{HF}$ = 54.0, $^3J_{HF}$ = 5.5 Hz), 6.98–7.57 m (9H, H_{arom}), 14.29 s (1H, NH). ^{19}F NMR spectrum, δ_F, ppm: 25.12 d.t (2F, HCF_2, $^2J_{FH}$ = 54.0, $^3J_{FF}$ = 8.3 Hz), 41.45 m (2F, CF_2). Found, %: C 57.61; H 4.41; F 19.03; N 10.66. $C_{19}H_{17}F_4N_3O_2$. Calculated, %: C 57.72; H 4.33; F 19.22; N 10.63.

(4*Z*)-1,1,2,2-Tetrafluoro-5-methylamino-4-(4-methylphenyl)diazenylnon-4-en-3-one (IIe). Yield 280 mg (78%), yellow crystals, mp 90–92°C. IR spectrum, ν, cm^{-1}: 3400, 1610 (NH); 1670 (C=O); 1605, 1580, 1490 (N=N, C=C); 1200–1100 (C–F). ^{1}H NMR spectrum, δ, ppm: 1.00 t (3H, Me, $^3J_{HH}$ = 7.3 Hz), 1.55 m (2H, CH_2, $^3J_{HH}$ = 7.3 Hz), 1.60 m (2H, CH_2, $^3J_{HH}$ = 7.3 Hz), 2.39 s (3H, Me), 3.00 m (2H, CH_2, $^3J_{HH}$ = 7.3 Hz), 3.21 s (3H, NMe), 6.45 t.t (1H, HCF_2, $^2J_{HF}$ = 54.2, $^3J_{HF}$ = 5.7 Hz), 7.23–7.42 m (4H, C_6H_4), 14.49 s (1H, NH). ^{19}F NMR spectrum, δ_F, ppm: 25.78 d.t (2F, HCF_2, $^2J_{FH}$ = 54.2, $^3J_{FF}$ = 8.2 Hz), 41.99 m (2F, CF_2). ^{13}C NMR spectrum, δ_C, ppm: 13.69 (CH_3); 21.21 ($\mathbf{C}H_3C_6H_4$); 23.13 (C^9); 28.52, 28.97, 29.42 (C^6, C^7, C^8); 110.87 t.t (C^1, $^1J_{CF}$ = 255.0, $^2J_{CF}$ = 28.0 Hz); 112.34 t.t (C^2, $^1J_{CF}$ = 255.0, $^2J_{CF}$ = 28.0 Hz); 120.70 (C^o); 124.32 (C^p); 130.02 (C^m); 138.31 (C^i); 149.67 (C^4); 169.00 (C^5); 180.32 t (C^3, $^2J_{CF}$ = 22.5 Hz). Found, %: C 56.73; H 5.88; F 21.17; N 11.86. $C_{17}H_{21}F_4N_3O$. Calculated, %: C 56.82; H 5.89; F 21.15; N 11.69.

(2*Z*)-5,5,6,6,7,7,7-Heptafluoro-3-(4-methoxyphenyl)diazenyl-2-methylaminohept-2-en-4-one

(IIf). Yield 160 mg (40%), yellow powder, mp 112–114°C. IR spectrum, ν, cm^{-1}: 3450, 1605 (NH); 1655 (C=O); 1590, 1505, 1495 (N=N, C=C); 1250–1190 (C–F). ^1H NMR spectrum, δ, ppm: 2.61 s (3H, Me), 3.19 s (3H, NMe), 3.85 s (3H, OMe), 6.94–7.60 m (4H, C_6H_4), 14.56 br.s (1H, NH). ^{19}F NMR spectrum, δ_F, ppm: 38.15 m (2F, CF_2), 51.45 m (2F, CF_2), 81.47 m (3F, CF_3). Found, %: C 44.87; H 3.24; F 32.94; N 10.60. $C_{15}H_{14}F_7N_3O_2$. Calculated, %: C 44.90; H 3.52; F 33.14; N 10.47.

(2*Z*)-5,5,6,6,7,7,8,8,8-Nonafluoro-3-(4-methylphenyl)diazenyl-2-methylaminooct-2-en-4-one (IIg). Yield 165 mg (38%), yellow powder, mp 100–102°C. IR spectrum, ν, cm^{-1}: 3470, 1610 (NH); 1660 (C=O); 1600, 1500, 1490 (N=N, C=C); 1245–1130 (C–F). ^1H NMR spectrum, δ, ppm: 2.38 s (3H, Me), 2.60 s (3H, Me), 3.21 s (3H, NMe), 7.21–7.53 m (4H, C_6H_4), 14.52 s (1H, NH). ^{19}F NMR spectrum, δ_F, ppm: 36.65 m (2F, CF_2), 41.48 m (2F, CF_2), 51.89 m (2F, CF_2), 80.84 m (3F, CF_3). Found, %: C 44.20; H 3.21; F 39.40; N 9.61. $C_{16}H_{14}F_9N_3O$. Calculated, %: C 44.15; H 3.24; F 39.28; N 9.65.

(2*Z*)-2-(4-Methoxyphenylhydrazono)-*N*-methyl-3-oxobutanamide (IIIf). Yield 87 mg (35%), light yellow crystals, mp 116–118°C. IR spectrum, ν, cm^{-1}: 3295, 1625 (NH); 1660 (C=O); 1620, 1590, 1540 (C=C, C=N). ^1H NMR spectrum, δ, ppm: 2.50 s (3H, Me), 2.90 d (3H, NMe, $^3J_{HH}$ = 5.0 Hz), 3.83 s (3H, OMe), 6.92–7.33 m (4H, C_6H_4), 9.35 br.s (1H, N**H**Me), 14.87 s (1H, NNH). ^{13}C NMR spectrum, δ_C, ppm: 25.01, 25.85 (C**C**H_3, NCH_3), 55.58 (OCH_3), 114.84 (C^o), 116.94 (C^m), 125.57 (C^p), 135.62 (C^i), 157.31 (C^2), 166.06 (C^1), 198.77 (C^3). Found, %: C 57.67; H 6.15; N 16.83. $C_{12}H_{15}N_3O_3$. Calculated, %: C 57.82; H 6.07; N 16.86.

(2*Z*)-*N*-Methyl-2-(4-methylphenylhydrazono)-3-oxobutanamide (IIIg). Yield 86 mg (37%), light yellow crystals, mp 123–125°C. IR spectrum, ν, cm^{-1}: 3300, 1620 (NH); 1655 (C=O); 1615, 1590, 1520 (C=C, C=N). ^1H NMR spectrum, δ, ppm: 2.35 s (3H, C_6H_4**C**H_3), 2.51 s (3H, Me), 2.90 d (3H, NMe, $^3J_{HH}$ = 5.0 Hz), 7.17–7.27 m (4H, C_6H_4), 9.32 br.s (1H, N**H**Me), 14.78 s (1H, NNH). Found, %: C 61.84; H 6.52; N 18.27. $C_{12}H_{15}N_3O_2$. Calculated, %: C 61.79; H 6.48; N 18.01.

(2*Z*)-2-(4-Methoxyphenylhydrazono)-*N*-methyl-4,4-dimethyl-3-oxopentanamide (IIIh). Yield 160 mg (55%), light yellow powder, mp 144–146°C. IR spectrum, ν, cm^{-1}: 3280, 1615 (NH); 1645 (C=O); 1590, 1545, 1510 (C=C, C=N). ^1H NMR spectrum, δ, ppm: 1.41 s (9H, *t*-Bu), 2.88 d (3H, NMe, $^3J_{HH}$ = 4.9 Hz), 3.82 s (3H, OMe), 6.92–7.31 m (4H, C_6H_4), 9.49 br.s (1H, N**H**Me), 15.00 s (1H, NNH). Found, %: C 62.10; H 7.58; N 14.56. $C_{15}H_{21}N_3O_3$. Calculated, %: C 61.84; H 7.27; N 14.42.

(2*Z*)-*N*-Methyl-2-(4-methylphenylhydrazono)-3-oxo-3-phenylpropanamide (IIIi). Yield 175 mg (62%), light yellow powder, mp 124–126°C. IR spectrum, ν, cm^{-1}: 3325, 1610 (NH); 1640 (C=O); 1585, 1535, 1510 (C=C, C=N). ^1H NMR spectrum, δ, ppm: 2.31 s (3H, Me), 2.97 d (3H, NMe, $^3J_{HH}$ = 5.0 Hz), 7.04–7.12 m (4H, C_6H_4), 7.26–7.75 m (5H, Ph), 9.45 br.s (1H, N**H**Me), 14.88 s (1H, NNH). Found, %: C 56.91; H 4.79; N 11.67. $C_{17}H_{18}N_3O_2$. Calculated, %: C 56.89; H 4.77; N 11.71.

3-Alkyl(aryl)-2-aryldiazenyl-3-methylamino-1-polyfluoroalkylprop-2-en-1-one metal complexes IV (*general procedure*). *a*. Gaseous methylamine was bubbled through a solution of 3 mmol of arylhydrazone **Ia**, **Ib**, **Id**, or **Ij** and 0.34 g (1.5 mmol) of Ni(II) acetate in 40 ml of ethanol, heated to 40°C. The precipitate was filtered off and purified by column chromatography to isolate complex **IVa**, **IVc**, **IVd**, or **IVe**.

b. Nickel(II) acetate, 1.35 g (6 mmol), was added to a solution of 3 mmol of amine **IIa** in a mixture of 2 ml of DMF and 6 ml of ethanol. The mixture was stirred for 1 h at 20°C, and the precipitate was filtered off, washed with aqueous ethanol (1:1), and dried.

c. Amine **IIa**, 3 mmol, was dissolved in 30 ml of ethanol, a 1% solution of sodium hydroxide was added to adjust the mixture to pH 9, and a solution of 0.22 g (1.5 mmol) of copper(II) acetate in 10 ml of water was added dropwise. The mixture was stirred for 2 h at 20°C, and the precipitate was filtered off and recrystallized from ethanol to obtain complex **IVb**.

Bis[1,1,1-trifluoro-4-methylamino-3-(phenyldiazenyl)pent-3-en-2-onato-N^3,N^4]nickel(II) (IVa). Yield 245 mg (82%) (*a*), 218 mg (73%) (*b*), dark red powder, mp >250°C. IR spectrum, ν, cm^{-1}: 1670 (C=O); 1595, 1560, 1500 (C=C, C=N); 1170–1150 (C–F). ^1H NMR spectrum, δ, ppm: 2.58 s (3H, Me), 3.09 s (3H, NCH_3), 7.03–7.52 m (5H, Ph). ^{19}F NMR spectrum: δ_F 95.37 ppm, s. Found, %: C 48.11; H 3.52; F 18.80; N 14.07. $C_{24}H_{22}F_6N_6NiO_2$. Calculated, %: C 48.11; H 3.70; F 19.02; N 14.03.

Bis[1,1,1-trifluoro-4-methylamino-3-(phenyldiazenyl)pent-3-en-2-onato-N^3,N^4]copper(II) (IVb). Yield 214 mg (71%) (*c*), dark green powder, mp 227–229°C. IR spectrum, ν, cm^{-1}: 1675 (C=O); 1600, 1580, 1550 (C=C, C=N); 1200–1100 (C–F). Mass spectrum

(electron impact, 70 eV): *m*/*z* 603 (I_{rel} 4.46%) $[M]^+$. Found, %: C 47.12; H 3.60; F 18.98; N 14.12. $C_{24}H_{22}CuF_6N_6O_2$. Calculated, %: C 47.42; H 3.67; F 18.87; N 13.91.

Bis[4,4,5,5-tetrafluoro-2-(4-methoxyphenyl)diazenyl-1-methylamino-1-phenylpent-1-en-3-onato-N^1,N^2]nickel(II) (IVc). Yield 316 mg (78%) (*a*), dark red powder, mp >250°C. IR spectrum, ν, cm^{-1}: 1665 (C=O); 1560, 1540, 1500 (C=C, C=N); 1175–1140 (C–F). Found, %: C 53.83; H 3.59; F 17.77; N 9.81. $C_{38}H_{32}F_8N_6NiO_4$. Calculated, %: C 53.86; H 3.81; F 17.94; N 9.92.

Bis[4,4,5,5,6,6,6-heptafluoro-2-(4-methoxyphenyl)diazenyl-1-methylamino-1-phenylhex-1-en-3-onato-N^1,N^2]nickel(II) (IVd). Yield 326 mg (68%) (*a*), dark red powder, mp >250°C. IR spectrum, ν, cm^{-1}: 1660 (C=O); 1605, 1590, 1505 (C=C, C=N); 1250–1160 (C–F). Found, %: C 48.78; H 3.30; F 27.17; N 8.35. $C_{40}H_{30}F_{14}N_6NiO_4$. Calculated, %: C 48.86; H 3.08; F 27.05; N 8.55.

Bis[1,1,1-trifluoro-4-methylamino-3-(4-methylphenyl)diazenyl)-4-phenylbut-3-en-2-onato-N^3,N^4]-nickel(II) (IVe). Yield 282 mg (75%) (*a*), dark red powder, mp >250°C. IR spectrum, ν, cm^{-1}: 1665 (C=O); 1560, 1540, 1500 (C=C, C=N); 1175–1140 (C–F). ^{1}H NMR spectrum, δ, ppm: 2.30 s (3H, Me), 2.50 s (3H, NMe), 7.34–8.06 m (4H, C_6H_4). Found, %: C 57.23; H 4.04; F 15.02; N 11.30. $C_{36}H_{30}F_6N_6O_2Ni$. Calculated, %: C 57.55; H 4.02; F 15.17; N 11.18.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 05-03-32384), by the President of the Russian Federation (project no. MK-1707.2005.3), and by the Russian Foundation for Support of Russian Science.

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