ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2024, Vol. 50, No. 7, pp. 458–468. © Pleiades Publishing, Ltd., 2024.

Synthesis of (η^6-Arene)tricarbonylchromium Complexes of 1,3-Benzodioxanes

N. Yu. Grishina[a], *, E. V. Sazonova[a], P. S. Ushakova[a], N. V. Somov[a], E. A. Medvedeva[a], A. Yu. Shishkin[a], and A. N. Artemov[a]

[a] *Lobachevskii National Research State University, Nizhny Novgorod, Russia*

**e-mail: zarovkinan@mail.ru*

Received January 25, 2024; revised April 3, 2024; accepted April 4, 2024

Abstract—The reactions of triammino(tricarbonyl)chromium (**I**) with 1,3-benzodioxane (L^1), 2-methyl-1,3-benzodioxane (L^2), and 2-phenyl-1,3-benzodioxane (L^3) afford new complexes: (η^6-$C_8H_8O_2$)$Cr(CO)_3$ (**II**), *exo*- and *endo*-[2-Me-(η^6-$C_8H_7O_2$)]$Cr(CO)_3$ (**III**, **IV**), *exo*- and *endo*-[2-Ph-(η^6-$C_8H_7O_2$)]$Cr(CO)_3$ (**V**, **VI**), [2-(η^6-Ph)-$C_8H_7O_2$]$Cr(CO)_3$ (**VII**), and *endo*-[2-(η^6-Ph)]$Cr(CO)_3$-[η^6-$C_8H_7O_2$]$Cr(CO)_3$ (**VIII**). The structures, compositions, and purity of the synthesized products are proved by UV, IR, and ^{1}H NMR spectroscopy, HPLC, and mass spectrometry. The molecular structures of complexes **IV**–**VI** are determined by XRD (CIF files CCDC nos. 2263301 (**IV**), 2295552 (**V**), and 2237106 (**VI**)). A possibility of coordination of the tricarbonylchromium group at different sides of the phenylene ring of ligands L^2 and L^3 and on the phenyl substituent of ligand L^3 is shown.

Keywords: heterocyclic compounds, (arene)tricarbonylchromium complexes, 1,3-benzodioxane, diastereomers, regioisomers

DOI: 10.1134/S1070328424600542

INTRODUCTION

The introduction of the tricarbonylchromium (TC) group into molecules of various aromatic substances is a popular and efficient method for the synthesis of (η^6-arene)tricarbonylchromium ((arene)TC) complexes. The compositions of these compounds combine the organic fragment and bulky electron-withdrawing metal-containing block capable of considerably affording the chemical properties of the substrate connected with this block and substantially enhancing the stereoselectivity of the reactions that occur in the lateral chain of the coordinated arene [1–8].

The substances containing the heterocyclic fragment along with the carbocyclic aromatic ring, including the compounds with two heteroatoms, can act as ligands for the synthesis of (arene)TC complexes. Nitrogen and oxygen atoms usually act as heteroatoms [8]. These hetaryl complexes found use as peptide nucleic acids [9–12], components used in immunoassay [13], and precursors for highly stereoselective syntheses aimed at preparing analogues of natural substances and drugs [14–19]. Among them there are examples of the (arene)TC derivatives bearing two oxygen atoms in the heterocyclic ring. These substances were shown to pretend for preparing pharmacological agents and physiologically active compounds and can be applied in fine organic synthesis [20–23]. In spite of a diversity of similar compounds, we found no (arene)TC derivatives for 1,3-benzodioxane (L^1) and its C(2)-substituted analogues, 2-methyl-1,3-benzodioxane (L^2) and 2-phenyl-1,3-benzodioxane (L^3), in the literature. However, the complexes with the 1,3-benzodioxane fragment, which are components of analgetic and anti-inflammatory drugs [24] and anti-arthritic and antioxidant remedies [25], can be very interesting from both the fundamental and applied points of view.

The direct interaction of an appropriate ligand with hexacarbonylchromium in a medium of highly boiling solvents is an available and convenient method for the synthesis of the (arene)TC complexes. It seems most optimal to use triammino(tricarbonyl)chromium, (η^6-naphthalene)tricarbonylchromium, acetonitriletricarbonylchromium, and others as coordinating agents to decrease the temperature of the process [7, 8]. A specific feature of the reactions of hexacarbonylchromium or its analogues with asymmetric ligands is a possibility of coordinating the TC group at different sides of the aromatic system, which can result in the formation of the stereoisomeric complexes [26]. If the initial ligand contains several aromatic rings, diverse regioisomeric products can also be formed [27].

The purpose of this work is to synthesize new (η^6-arene)tricarbonylchromium complexes of 1,3-benzodioxanes via the reactions of ligands L^1–L^3 with

triammino(tricarbonyl)chromium (**I**) and establish a possibility of forming various regio- and diastereoisomeric complexes.

EXPERIMENTAL

Solvents were distilled over metallic sodium under atmospheric pressure [28]. Salicyl alcohol was synthesized by a known procedure [29]. 1,3-Benzodioxane (L^1) [30], 2-methyl-1,3-benzodioxane (L^2) [31], and 2-phenyl-1,3-benzodioxane (L^3) [32] were synthesized via the condensation of salicyl alcohol with dibromomethane, acetaldehyde, and benzaldehyde, respectively. (η⁶-Benzaldehyde)tricarbonylchromium was synthesized using a described procedure [33] but using complex **I** instead of hexacarbonylchromium.

Products **II**–**VIII** were isolated and purified by column chromatography in an argon atmosphere using silica gel (Acros, 0.035–0.070 mm) and a petroleum ether–ethyl acetate (4 : 1) system as the eluent. HPLC was conducted on a Knauer Smartline 5000 chromatograph with an S 2600 UV diode matrix detector (UV spectra of the eluates were recorded in a range of 200–500 nm) and a Diasfer-110-S16 column (5 μm, 4.6 × 250 mm, acetonitrile–water (84 : 16) eluent, eluent flow rate 0.7 mL min^{-1}). IR spectra were recorded on an Infralyum FT-801 instrument in a range of 450–4000 cm^{-1} in KBr pellets. Mass spectrometry (MS) was carried out on a Trace DSQII instrument (electron impact (EI) ionization (70 eV), *m/z* 70–500, temperature programming from 50 to 450°C at a heating rate of 100 deg min^{-1}) and on a Bruker Microflex LT instrument by time-of-flight mass spectrometry with matrix activated laser desorption/ionization (MALDI). ^{1}H NMR spectra were recorded in acetone-d_6 on an Agilent DD2 NMR 400NB spectrometer (working frequency 400 MHz).

Triammino(tricarbonyl)chromium (**I**) was synthesized by the modified procedure [34]. Hexacarbonylchromium (70.0 g, 0.32 mol), solid potassium hydroxide (128 g, 2.29 mol), ethanol (640 mL), and water (100 mL) were placed in a 2-L three-necked flask preliminarily degassed and then filled with argon and equipped with a stirrer and a reflux condenser. The mixture was heated in an oil bath at 100–120°C for 5 h. The color of the solution changed from yellow to red. The completeness of the reaction was monitored by the absence of sublimed hexacarbonylchromium on the flask walls. After the end of the reaction, the flask was cooled in an argon flow, and a concentrated aqueous solution (600 mL) of ammonia was added. The resulting reaction mixture was stirred at room temperature for 2 h. The formed yellow precipitate was filtered off in an argon flow on a Schott filter and consequently washed with water (150 mL), ethanol (50 mL), and diethyl ether (50 mL). Then the precipitate was dried in vacuo to obtain complex **I** as a yellow powder in a yield of 50.1 g (81%).

Synthesis of complexes II–VIII (general procedure). Complex **I** (2.0 g, 0.01 mol), 1,3-benzodioxane ligand L^1–L^3 (0.01 mol), and dioxane (30 mL) were placed in a preliminarily degassed and then filled with argon two-necked flask equipped with a reflux condenser and a gas burette filled with dimethyl phthalate. The mixture was heated on an oil bath at 120°C. The completeness of the reaction was monitored by the amount of evolved NH_3. After the end of the reaction, the flask was cooled and filled with argon. The resulting mixture was filtered on a Schott filter packed with alumina in an inert atmosphere. After the solvent was distilled off, a yellow residue remained in the flask, and the reaction products were isolated from the residue using column chromatography on silica gel. Each obtained fraction was recrystallized from a petroleum ether–ethyl acetate mixture. The reaction of compound **I** with ligand L^1 afforded complex **II** as the single product, the reaction of compound **I** with L^2 gave complexes **III** and **IV**, and the reaction of complex **I** with L^3 afforded complexes **V**–**VIII**.

(η⁶-1,3-Benzodioxane)tricarbonylchromium (II). The yield was 1.68 g (62%), T_m = 80–81°C. HPLC: 1 peak, τ = 5.5 min. UV (λ_{max}, nm): 215, 314, 417. MS (*m/z* (EI, I_{rel} (%)): 272 $[M]^+$ (40); 216 $[M\text{-}2CO]^+$ (14); 188 $[M\text{-}3CO]^+$ (23); 158 $[M\text{-}3CO\text{-}CH_2O]^+$ (100). IR (ν, cm^{-1}): 3079 ν(C_{Ar}–H), 2917, 2898, 2850 ν(C–H), 1973, 1908, 1848 ν(C≡O), 1539, 1462 ν(C_{Ar}–C_{Ar}), 1227 ν(C–O), 944, 626 ν(C_{Ar}–H). ^{1}H NMR (δ, ppm): 4.70 d (1H, ArC<u>H</u>$_2$O, *J* = 14.48 Hz), 4.93 d (1H, ArC<u>H</u>$_2$O, *J* = 14.48 Hz), 5.24 td (1H, Ar), 5.25 d (1H, OCH_2O, *J* = 5.87 Hz), 5.32 d (1H, OCH_2O, *J* = 5.87 Hz), 5.47 dd (1H, Ar, *J* = 6.85, 0.98 Hz), 5.69–5.77 m (1H, Ar), 5.83 dd (1H, Ar, *J* = 6.46, 1.17 Hz).

***exo*-2-Methyl-(η⁶-1,3-benzodioxane)tricarbonylchromium (III).** The yield was 1.12 g (39%), T_m = 81–82°C. HPLC: 1 peak, τ = 6.3 min. UV (λ_{max}, nm): 216, 314, 432. MS (MALDI MS, *m/z* (I_{rel}, %)): 286 $[M]^+$ (43), 325 $[M+K]^+$ (100), 230 $[M\text{-}2CO]^+$ (10), 202 $[M\text{-}3CO]^+$ (5). IR (ν, cm^{-1}): 3094 ν(C_{Ar}–H), 2995, 2917, 2848 ν(C–H), 1956, 1894, 1852 ν(C≡O), 1519, 1461, 1410 ν(C_{Ar}–C_{Ar}), 1269, 1107 ν(C–O), 900, 671, 630 ν(C_{Ar}–H). ^{1}H NMR (δ, ppm): 1.47 d (3H, Me, *J* = 5.09 Hz), 4.82 d (1H, CH_2, *J* = 14.28 Hz), 4.87 d (1H, CH_2, *J* = 14.28 Hz), 5.24–5.36 m (2H, CH, Ar), 5.53 d (1H, Ar, *J* = 6.26 Hz), 5.70 t (1H, Ar, *J* = 7.43 Hz), 5.77 d (1H, Ar, *J* = 6.26 Hz).

***endo*-2-Methyl-(η⁶-1,3-benzodioxane)tricarbonylchromium (IV).** The yield was 0.92 g (32%), T_m = 101–102°C. HPLC: 1 peak, τ = 5.8 min. UV (λ_{max}, nm): 217, 315, 431. MS (MALDI MS, *m/z* (I_{rel}, %)): 286 $[M]^+$ (12), 325 $[M+K]^+$ (100); 242 $[M\text{-}OCHCH_3]^+$ (47). IR (ν, cm^{-1}): 3102 ν(C_{Ar}–H), 2993, 2920, 2855 ν(C–H), 1954, 1872 ν(C≡O), 1517, 1464, 1404 ν(C_{Ar}–C_{Ar}), 1261, 1222, 1076 ν(C–O), 906, 674, 631 ν(C_{Ar}–

H). ^{1}H NMR (δ, ppm): 1.45 d (3H, Me, J = 5.09 Hz), 4.55 d (1H, CH_2, J = 14.28 Hz), 4.99 d (1H, CH_2, J = 14.28 Hz), 5.11 t (1H, Ar, J = 6.26 Hz), 5.30 d (1H, Ar, J = 6.85 Hz), 5.34 q (1H, CH, J = 5.09 Hz), 5.74 t (1H, Ar, J = 6.26 Hz), 5.90 d (1H, Ar, J = 6.06 Hz).

***exo*-2-Phenyl-(η^6-1,3-benzodioxane)tricarbonylchromium (V) and 2-[η^6-(phenyl)tricarbonylchromium]-1,3-benzodioxane (VII).** The overall yield was 1.81 g (52%). HPLC: 1 peak, τ = 7.4 min. UV (λ_{max}, nm): 213, 314. MS (EI, m/z (I_{rel}, %)): 348 $[M]^+$ (41), 292 $[M\text{-}2CO]^+$ (18), 264 $[M\text{-}3CO]^+$ (100), 158 $[M\text{-}3CO\text{-}OCHPh]^+$ (64). ^{1}H NMR (δ, ppm): 5.02 d (1H, CH_2, J = 14.48 Hz), 5.07 s (2H, CH_2), 5.23 d (1H, CH_2, J = 14.48 Hz), 5.35 t (1H, C_6H_4Cr, J = 5.87 Hz), 5.62 d (1H, C_6H_4Cr, J = 6.65 Hz), 5.64–5.71 m (3H, PhCr), 5.77 ddd (1H, C_6H_4Cr, J = 7.04, 0.78 Hz), 5.85 s (1H, CH), 5.87 d (1H, C_6H_4Cr, J = 6.26 Hz), 5.90–5.95 m (2H, PhCr), 6.16 s (1H, CH), 6.92 d (1H, C_6H_4, J = 8.22 Hz), 6.99 t (1H, C_6H_4, J = 7.43 Hz), 7.12 d (1H, C_6H_4, J = 7.43 Hz), 7.22 t (1H, C_6H_4, J = 7.43 Hz), 7.42–7.52 m (3H, Ph), 7.54–7.64 m (2H, Ph).

***endo*-2-Phenyl-(η^6-1,3-benzodioxane)tricarbonylchromium (VI).** The yield was 0.90 g (26%), T_m = 128–129°C. HPLC: 1 peak, τ = 6.5 min. UV (λ_{max}, nm): 212, 315. MS (EI, m/z (I_{rel}, %)): 348 $[M]^+$ (44), 292 $[M\text{-}2CO]^+$ (4), 264 $[M\text{-}3CO]^+$ (100), 158 $[M\text{-}3CO\text{-}OCHPh]^+$ (88). IR (ν, cm^{-1}): 3090 ν(C_{Ar}–H), 2916, 2870 ν(C–H), 1952, 1856 ν(C≡O), 1517, 1459 ν(C_{Ar}–C_{Ar}), 1253, 1218 ν(C–O), 942, 918, 664 ν(C_{Ar}–H). ^{1}H NMR (δ, ppm): 4.77 d (1H, CH_2, J = 14.48 Hz), 5.18 td (1H, C_6H_4Cr, J = 6.28, 0.78 Hz), 5.28 d (1H, CH_2, J = 14.48 Hz), 5.39 dd (1H, C_6H_4Cr, J = 6.65, 0.78 Hz), 5.80 td (1H, C_6H_4Cr, J = 6.65, 1.17 Hz), 6.00 dd (1H, C_6H_4Cr, J = 6.26, 1.17 Hz), 6.18 s (1H, CH), 7.41–7.51 m (3H, Ph), 7.60–7.69 m (2H, Ph).

***endo*-2-(η^6-Phenyl)tricarbonylchromium-(η^6-1,3-benzodioxane)tricarbonylchromium (VIII).** The yield was 0.21 g (6%), T_{decomp} = 174–175°C. HPLC: 1 peak, τ = 6.4 min. UV (λ_{max}, nm): 215, 315. MS (EI, m/z (I_{rel}, %)): 484 $[M]^+$ (10), 428 $[M\text{-}2CO]^+$ (2), 400 $[M\text{-}3CO]^+$ (5), 344 $[M\text{-}5CO]^+$ (5), 348 $[M\text{-}Cr(CO)_3]^+$ (19), 316 $[M\text{-}6CO]^+$ (43), 264 $[M\text{-}Cr(CO)_3\text{-}3CO]^+$ (36), 242 $[M\text{-}OCHPhCr(CO)_3]^+$ (100), 158 $[M\text{-}OCHPhCr(CO)_3\text{-}3CO]^+$ (61). IR (ν, cm^{-1}): 3102 ν(C_{Ar}–H), 2974, 2906, 2850 ν(C–H), 1963, 1894, 1874, 1850 ν(C≡O), 1461 ν(C_{Ar}–C_{Ar}), 1258, 1078, 1026 ν(C–O), 985, 814 ν(C_{Ar}–H). ^{1}H NMR (δ, ppm): 4.78 d (1H, CH_2, J = 14.36 Hz), 5.18 td (1H, ArCr, J = 6.28, 0.72 Hz), 5.27 d (1H, CH_2, J = 14.36 Hz), 5.40 dd (1H, ArCr, J = 6.82, 0.54 Hz), 5.61–5.77 m (3H, ArCr), 5.82 td (1H, ArCr, J = 6.28, 1.26 Hz), 5.90 dd (2H, ArCr, J = 6.28, 0.72 Hz), 5.92 s (1H, CH), 6.00 dd (1H, ArCr, J = 6.28, 1.08 Hz).

Synthesis of complex (VII) via the reaction of salicyl alcohol with (η^6-benzaldehyde)tricarbonylchromium. (η^6-Benzaldehyde)tricarbonylchromium (0.300 g, 1.24 mmol), salicyl alcohol (0.154 g, 1.24 mmol), boric acid (0.068 mg, 1.1 mmol), and ethanol (12 mL) were heated in a sealed degassed tube at 80°C for 10 h. After the end of the reaction, the solvent was distilled off under reduced pressure. The reaction product was isolated by column chromatography. The yield was 42 mg (10%), T_m = 130–131°C. HPLC: 1 peak, τ = 7.5 min. UV (λ_{max}, nm): 218, 314. MS (EI, m/z (I_{rel}, %)): 348 $[M]^+$ (6), 264 $[M\text{-}3CO]^+$ (29), 158 $[M\text{-}3CO\text{-}C_6H_4\text{-}CH_2O]^+$ (100). IR (ν, cm^{-1}): 3088 ν(C_{Ar}–H), 2920, 2852 ν(C–H), 1967, 1905 ν(C≡O), 1627, 1589 ν(C_{Ar}–C_{Ar}), 1246, 1036 ν(C–O), 999, 764, 625 ν(C_{Ar}–H). ^{1}H NMR (δ, ppm): 5.02 d (1H, CH_2, J = 14.48 Hz), 5.23 d (1H, CH_2, J = 14.48 Hz), 5.64–5.71 m (3H, PhCr), 5.85 s (1H, CH), 5.90–5.95 m (2H, PhCr), 6.92 d (1H, C_6H_4, J = 8.22 Hz), 6.99 t (1H, C_6H_4, J = 7.43 Hz), d 7.12 (1H, C_6H_4, J = 7.43 Hz), 7.22 t (1H, C_6H_4, J = 7.43 Hz).

The crystals of complexes **IV**–**VI** suitable for XRD were prepared by slow crystallization from a petroleum ether–ethyl acetate (4 : 1) mixture.

XRD was carried out on a Rigaku XtaLab, MM003, P200K automated X-ray single-crystal diffractometer (MoK_α radiation, λ = 0.71073 Å, MicroMax-003 monochromator, ω scan mode) at T = 100 K. The primary fragments of the structures were determined by direct methods in the SHELX [35] and ShelXle [36] software. The parameters of other atoms, including hydrogen atoms, were determined from the difference electron density synthesis and refined for $|F|^2$ by least squares. The positions of hydrogen atoms were refined in the main cycle of least squares in the isotropic approximation. Selected crystallographic parameters of complexes **IV**–**VI** are given in Table 1.

The XRD results were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2263301 (**IV**), 2295552 (**V**), and 2237106 (**VI**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Antimicrobial assays of the studied compounds were carried out by the disk diffusion test on nutrient media GRM-agar for bacteria and on the Czapek–Dox liquid medium for fungi. The following test cultures of microorganisms were used: bacterial strains *Escherichia coli* ATCC 25922, *Staphylococcus aureus* ATCC 25923, *Pseudomonas aeruginosa* ATCC 27853, and *Bacillus subtilis* ATCC 6051 and fungal strains *Chaetomium globosum* F-109, *Penicilum chrysogenum* F-245, *Aspergillus niger* F-1119, and *Aspergillus terreus* F-1025. The studied chemical compounds were dissolved in dimethyl sulfoxide (DMSO) in a concentra-

Table 1. Crystallographic characteristics, experimental data, and structure refinement parameters for compounds **IV**–**VI**

Parameter	Value		
	IV	**V**	**VI**
Empirical formula	$C_{12}H_{10}CrO_5$	$C_{17}H_{12}CrO_5$	$C_{17}H_{12}CrO_5$
FW	286.20	348.27	348.27
Crystal system, *Z*	Monoclinic, 4	Monoclinic, 4	Monoclinic, 4
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
T, K	100(2)	100.00(10)	100.00(10)
a, Å	7.5537(2)	12.0111(4)	11.7208(2)
b, Å	19.7055(6)	15.6692(4)	8.4125(2)
c, Å	8.2478(2)	8.2466(3)	15.4397(3)
α, deg	90	90	90
β, deg	103.735(2)	108.176(4)	104.240(2)
γ, deg	90	90	90
V, Å^3	1192.57(6)	1474.60(9)	1475.60(5)
ρ_{calc}, g cm^{-3}	1.594	1.569	1.568
μ, mm^{-1}	0.968	0.799	0.798
Absorption T_{min}/T_{max}	0.316/1.000	0.832/0.962	0.838/0.945
Absorption correction	Analytical (Gauss) [37]	Analytical [38]	Analytical [38]
F(000)	584	712	712
Crystal size, mm	0.600 × 0.190 × 0.080	0.299 × 0.148 × 0.039	0.457 × 0.263 × 0.121
Range of θ, deg	2.744–30.502	2.600–28.697	2.722–30.508
Range of indices	$-10 \le h \le 10$, $-28 \le k \le 28$, $-11 \le l \le 11$	$-15 \le h \le 14$, $-21 \le k \le 19$, $-10 \le l \le 11$	$-16 \le h \le 16$, $-12 \le k \le 12$, $-21 \le l \le 22$
Measured reflections	30603	14127	27778
Independent reflections (R_{int})	3633 (0.0533)	3463 (0.0435)	4488 (0.0438)
Reflections with $I > 2\sigma(I)$	3173	2656	3936
Number of refined parameters	197	253	256
GOOF	1.051	1.035	1.047
R_1, wR_2 (for $F^2 > 2\sigma(F^2)$)	0.0315, 0.0832	0.0362, 0.0732	0.0267, 0.0737
R_1, wR_2 (for all reflections)	0.0369, 0.0859	0.0581, 0.0785	0.0317, 0.0756
Residual electron density (min/max), e Å^{-3}	−0.521/0.348	−0.362/0.322	−0.395/0.444

tion of 10 mg/mL. Filter paper disks were stored in these solutions for 10 min. Then the impregnated filter paper disks were placed in Petri dishes on agar media, which were inoculated with suspensions of microorganisms (bacterial cells and fungal spores). The Petri dishes were placed in a thermostat at 37°C for 24 h for bacteria and at 28 ± 2°C and the moisture content higher than 90% for 14 days for fungi. After incubation, the average diameter of the inhibition zone of the microorganism growth around the paper disks was measured.

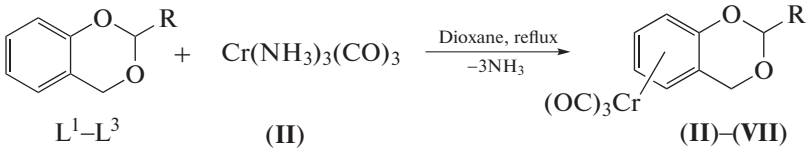
RESULTS AND DISCUSSION

The target (arene)TC complexes of 1,3-benzodioxanes were synthesized via the reactions of triammino(tricarbonyl)chromium (**I**) with ligands L^1–L^3 in boiling dioxane according to general Scheme 1. The purity, compositions, and structures of the synthesized yellow crystalline compounds were confirmed by HPLC; UV, IR, and ^{1}H NMR spectroscopy; mass spectrometry; and XRD. Selected characteristics of the synthesized compounds are given in Table 2.

Table 2. Selected characteristics of complexes **II**–**VII**

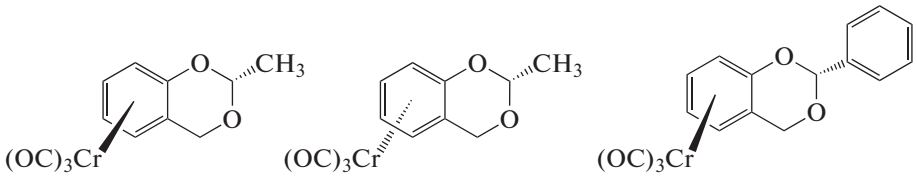
Reaction	Product	Yield, %	T_m, °C	ν(C≡O), cm^{-1}	I_{rel}, %
I + L^1	**II**	62	80–81	1973, 1908, 1848	272 $[M]^+$ (40)
I + L^2	**III**	39	81–82	1956, 1894, 1852	286 $[M]^+$ (43)
	IV	32	101–102	1954, 1872	286 $[M]^+$ (12)
I + L^3	**V**, **VII***	52			348 $[M]^+$ (41)
	VI	26	128–129	1952, 1856	348 $[M]^+$ (44)
	VIII	6	174–175**	1963, 1894, 1874, 1850	484 $[M]^+$ (10)

* The products were isolated as the single fraction.
** Decomposition temperature.

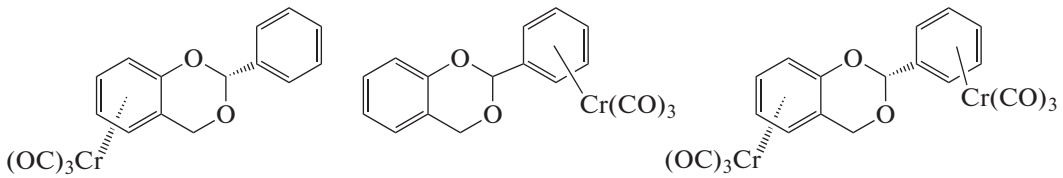


L^1–L^3 **(II)** **(II)**–**(VII)**

R = H (L^1, **II**), Me (L^2, **III**, **IV**), Ph (L^3, **V**, **VI**)



(III) **(IV)** **(V)**



(VI) **(VII)** **(VIII)**

Scheme 1.

We showed that the reaction of unsubstituted 1,3-benzodioxane (L^1) with complexing agent **I** resulted in the expected (η^6-1,3-benzodioxane)tricarbonylchromium (**II**) in a yield of 62%. The HPLC for this compound showed one signal on the chromatogram with a retention time of 5.5 min, and the UV spectrum of compound **II** exhibited an absorption maximum at 314 nm, which is characteristic of the (arene)TC derivatives. The mass spectrum of compound **II** contained the molecular ion with the mass number 272 amu and fragmentation ions corresponding to the loss of the CO groups and CH_2O fragment (see Experimental). The ^1H NMR spectrum of the synthesized substance exhibited two doublets of the CH_2 group of the benzyl fragment at 4.70 and 4.93 ppm, doublets of the OCH_2O group at 5.25 and 5.32 ppm, and signals of four protons of the phenylene ring in a range of 5.24–5.83 ppm.

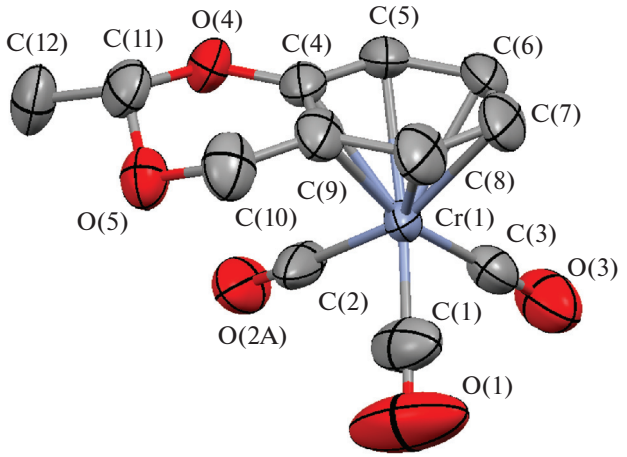


Fig. 1. Molecular structure of *endo*-2-methyl-(η⁶-1,3-benzodioxane)tricarbonylchromium (**IV**).

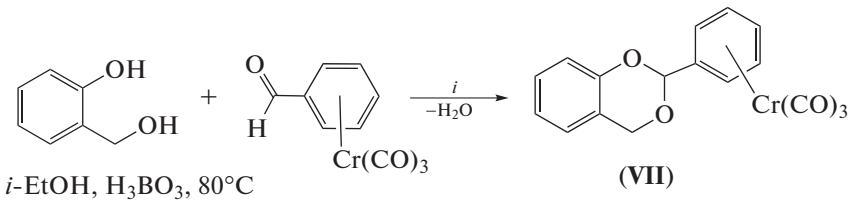
The reaction of 2-methyl-1,3-benzodioxane (L^2) with complex **I** can also afford two diastereomeric complexes: compounds **III** (*exo*-isomer) **IV** (*endo*-isomer) that differ in the mutual arrangement of the methyl substituent and TC group relative to the 1,3-benzodioxane system (see Scheme 1). The reaction gave both expected products in an overall yield of 71%. The HPLC chromatogram of the reaction mixture exhibited two signals of the products with similar UV spectra (see Experimental). Products **III** and **IV** were separated by column chromatography on silica gel (see Table 2). The products were isolated in close yields (see Table 2). The ^{1}H NMR spectrum of compound **III** (exo structure) contained two near-lying doublets with chemical shifts of 4.82 and 4.87 ppm (difference between the signals 0.05 ppm), whereas in the spectrum of *endo*-isomer **IV** the doublets of the methylene protons were remote from each other at 0.44 ppm and had chemical shifts of 4.55 and 4.99 ppm, respectively. This distinction is caused by a considerably higher magnetic nonequivalence of the methylene protons in the *endo*-isomer compared to the *exo*-isomer, which is a convenient tool for the determination of the diastereomeric composition of products of reactions leading to the formation of similar heterocyclic compounds [39, 40].

The structure of compound **IV** was also confirmed by XRD (Fig. 1, Table 3). This complex was shown to consist of two linked rings: the (η⁶-phenylene)tricarbonylchromium fragment and saturated six-membered heterocycle with two oxygen atoms in which the methyl substituent occupies the equatorial position. The heterocyclic ring is not planar, and its conformation is close to "envelope." The strongest deviation from the plane is observed on the region of the sp^3-hybridized O(5) oxygen atom oriented towards the tricarbonylchromium group. The C(11)O(5)C(10) angle is 110.33°. The O(4) oxygen atom is conjugated with the phenylene ring, which is indicated by the value of C(4)O(4)C(11) bond angle equal to 115.82° and the C(4)–O(4) bond length equal to 1.3561 Å, whereas the lengths of the C(10)O(5) and C(11)–O(5) bonds that are not involved in conjugation are 1.4351(17) and 1.4016(19) Å, respectively. The conformation of the TC group is closed to the eclipsed one. The OCCrCO angles range from 88.41° to 90.07°.

The reaction of phenyl-containing heterocycle L^3 with compound **I** gave a mixture of products **V**–**VIII** isolated in an overall yield of 84%. Complexes **V** and **VI** were synthesized due to the coordination of the TC fragment on the phenylene ring of ligand L^3, and they are diastereomers of the *exo* and *endo* structure, respectively, whereas product **VII** is their regioisomer formed by the coordination of the TC group on the phenyl substituent localized at the C(2) carbon atom of the 1,3-benzodioxane ring (Scheme 1). Product **VIII** is a complex of the *endo* structure with two TC groups in the composition (Scheme 1), which was formed due to the attack of the tricarbonylmetal fragment to both aromatic rings present in the ligand molecule. We showed that compounds **V**–**VII** were formed in this reaction in equimolar amounts, whereas the fraction of product **VIII** was substantially lower (Table 2). Compounds **V**–**VIII** were isolated from the reaction mixture by column chromatography on silica gel using a petroleum ether–ethyl acetate (4 : 1) mixture as the eluent. Under these conditions, complexes **VI** and **VIII** were readily separated, whereas products **V** and **VII** were eluted from the column as a single fraction even when using a more drastic eluent (6 : 1). The results of ^{1}H NMR spectroscopy for this fraction distinctly indicated an equimolar mixture in which one of the substances contained the TC group coordinated on the phenylene ring, and that in another substance was coordinated on the phenyl substituent. The spectrum of this mixture (Fig. 2) exhibits signals of four protons of the chromium-containing phenylene ring of compound **V** at 5.35, 5.62, 5.77, and 5.87 ppm, five protons of the chromium-containing phenyl ring of compound **VII** in a range of 5.64–5.95 ppm, and signals of the free phenylene (6.91, 6.99, 7.12, and 7.22 ppm, complex **VII**) and phenyl rings (7.42–7.52 and 7.54–7.64 ppm, complex **V**). The question about belonging of both the signals of the methine groups and methylene protons to this or another complex remained unanswered. To answer this question, we performed the counter synthesis of compound **VII** via the condensation of (η⁶-benzaldehyde)tricarbonylchromium with salicyl alcohol (Scheme 2). Boric acid was chosen as the catalyst of this process [41].

Table 3. Selected bond lengths and angles in the structures of compounds **IV**–**VI**

Bond	**IV**	**V**	**VI**
	d, Å		
C(4)–O(4)	1.3561	1.369	1.359
C(4)–C(9)	1.412	1.400	1.403
C(10)–C(9)	1.502	1.507	1.502
C(10)–O(5)	1.4351	1.435	1.426
C(11)–O(5)	1.4016	1.404	1.405
C(11)–O(4)	1.4538	1.450	1.456
C(4)–C(5)	1.409	1.418	1.418
C(5)–C(6)	1.418	1.394	1.398
C(6)–C(7)	1.403	1.418	1.416
C(7)–C(8)	1.402	1.398	1.403
C(8)–C(9)	1.420	1.421	1.417
C(4)–C(9)	1.412	1.400	1.403
Cr(1)–C(4)	2.2737	2.252	2.274
Cr(1)–C(5)	2.2328	2.224	2.233
Cr(1)–C(6)	2.2047	2.210	2.210
Cr(1)–C(7)	2.2186	2.212	2.219
Cr(1)–C(8)	2.1952	2.203	2.203
Cr(1)–C(9)	2.2469	2.252	2.241
Angle	ω, deg		
C(11)O(5)C(10)	110.33	111.10	110.15
O(5)C(10)C(9)	108.76	109.29	109.57
C(10)C(9)C(4)	118.17	119.15	118.59
C(9)C(4)O(4)	121.94	121.98	122.00
C(4)O(4)C(11)	115.82	113.57	114.40
O(4)C(11)O(5)	111.06	109.56	110.32
C(1)Cr(1)C(2)	90.07	87.36	89.10
C(2)Cr(1)C(3)	88.42	90.28	91.55
C(1)Cr(1)C(3)	88.41	88.80	90.01



Scheme 2.

Complex **VII** was isolated from this reaction as the single product by column chromatography, recrystallized (T_m = 130–131°C), and analyzed by ^{1}H NMR spectroscopy. Its spectrum contained two doublets of

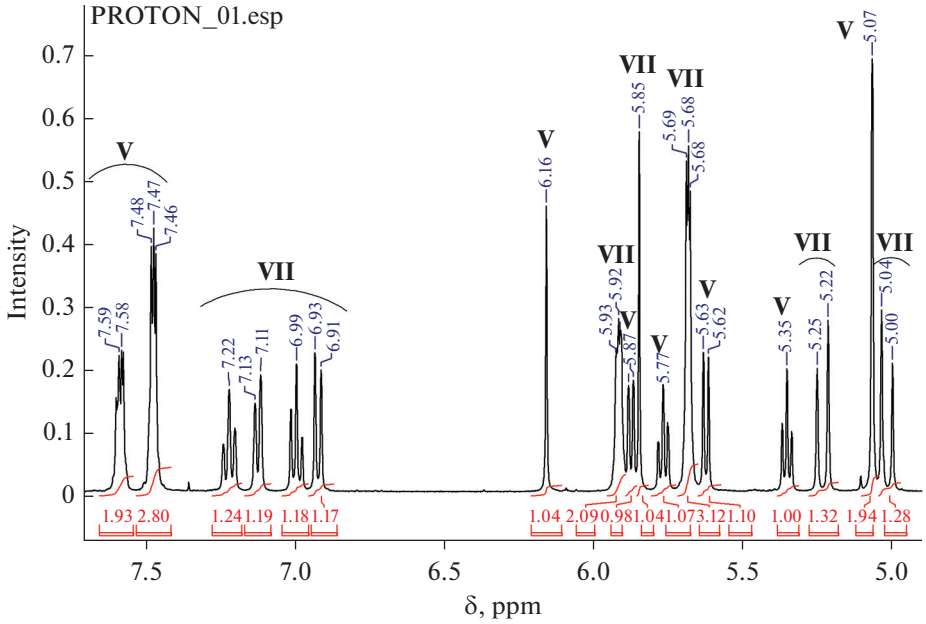


Fig. 2. ^{1}H NMR spectrum of a mixture of complexes **V** and **VII**.

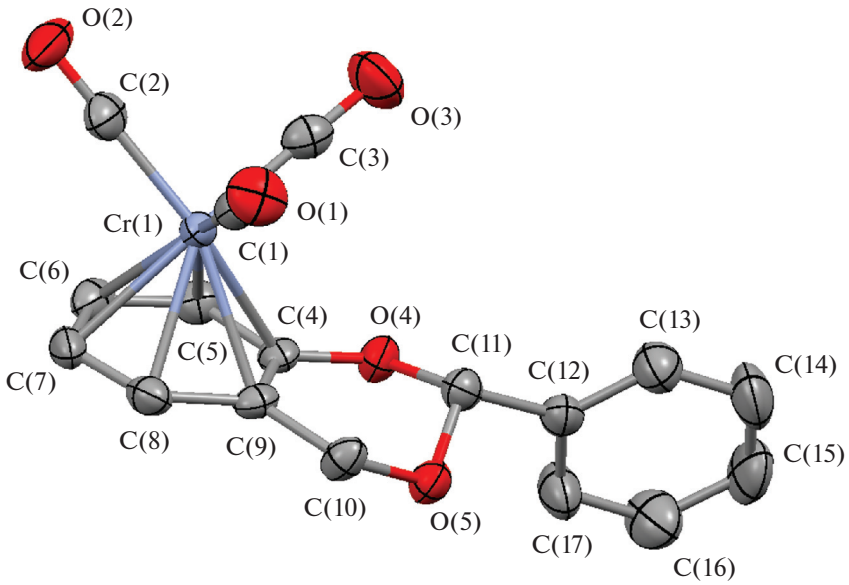


Fig. 3. Molecular structure of *exo*-2-phenyl-(η⁶-1,3-benzodioxane)tricarbonylchromium (**V**)

the methylene group at 5.02 and 5.23 ppm and a singlet of the methine proton at 5.85 ppm. The data obtained and ^{1}H NMR spectrum of a mixture of complexes **V** and **VII** (Fig. 2) allowed us to conclude that the singlet of the CH_2 group at 5.07 ppm and the singlet of the CH group at 6.16 ppm belonged to compound **V**.

The crystals of complexes **V** and **VI** were analyzed by XRD (Figs. 3, 4; Table 3). The XRD experiment showed that the organic fragments of molecules **V** and **VI** are very resembling in structure, and their bond lengths and bond angles are close (see Table 3). The O(4), C(4), C(9), and C(10) atoms of the heterocyclic ring in the discussed structures lie nearly in one plane,

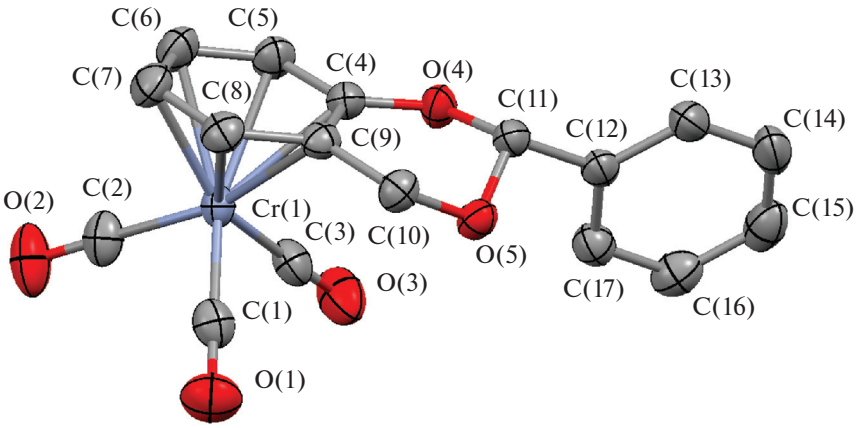


Fig. 4. Molecular structure of *endo*-2-phenyl-(η^6-1,3-benzodioxane)tricarbonylchromium (**VI**).

whereas the C(11) and O(5) atoms shift from the plane. A substantial distinction in structures of molecules **V** and **VI** is the mutual arrangement of the phenyl substituent and TC fragment: in *exo*-complex **V** these groups are localized at different sides of the 1,3-benzodioxane system, whereas they are at one side in compound **VI**. In both molecules, the conformation of the TC group is close to the hindered one, which induces the alternation of the C–C bonds in the phenylene rings, i.e., alternation of the shorter (1.394–1.403 Å) and longer (1.416–1.421 Å) bonds (Table 3). The minimum dihedral CrCO angle of the C_{Ar} center of the ring is 21.94° for complex **V** and 19.46° for complex **VI**. The OCCrCO angles are close to 90° being in a range of 87.36°–91.55°.

The antimicrobial assays were performed for synthesized (arene)TC complexes **II**–**VII**. The following test cultures of microorganisms were used: bacterial strains *Escherichia coli* ATCC 25922, *Staphylococcus aureus* ATCC 25923, *Pseudomonas aeruginosa* ATCC 27853, and *Bacillus subtilis* ATCC 6051 and fungal strains *Chaetomium globosum* F-109, *Penicilum chrysogenum* F-245, *Aspergillus niger* F-1119, and *Aspergillus terreus* F-1025. Dimethyl sulfoxide was chosen as the solvent for antimicrobial activity assays of the chromium complexes. It was shown prior to tests that DMSO exhibited no fungicidal and bactericidal activity against the studied fungi and bacteria (inhibition zone size is 0). Solutions of complexes **I**–**VII** in DMSO were shown to have no antifungal activity against all fungal strains used. Compounds **II** and **III** insignificantly suppressed the growth of bacteria *S. aureus* and *B. subtilis*, whereas complexes **IV**–**VI** exhibited no antimicrobial activity against the studied bacterial strains.

The antimicrobial properties of complexes **II** and **III** are presented below.

Compound	Diameter of inhibition zone of microorganism growth, mm			
	S. aureus	*E. coli*	*P. aeruginosa*	*B. subtilis*
II	3.8	0	0	2.7
III	1.3	0	0	6.2

Thus, the new (η^6-arene)tricarbonylchromium complexes based on 1,3-benzodioxanes were synthesized, isolated, and characterized. The reaction of the heterocyclic ligands with triammino(tricarbonyl)chromium is the general method for the synthesis of compounds of this class. The possibility of coordination of the tricarbonylchromium group at different sides of C(2)-substituted 1,3-benzodioxanes L^2 and L^3 leading to the formation of the diastereomeric products with the exo and endo structures was shown, as well as the possibility of coordination of the $Cr(CO)_3$ fragment on the phenyl substituent of ligand L^3. The antibacterial properties against the bacterial strains *S. aureus* and *B. subtilis* were found for (η^6-1,3-benzodioxane)tricarbonylchromium and *exo*-2-methyl-(η^6-1,3-benzodioxane)tricarbonylchromium.

ACKNOWLEDGMENTS

The authors are grateful to the leading engineer of the Lobachevskii National Research State University (Nizhny Novgorod) V.I. Faerman for recording mass spectra.

FUNDING

This work was supported by the Russian Science Foundation, project no. 22-73-00128.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

REFERENCES

1. *Transition Metal Arene π-Complexes in Organic Synthesis and Catalysts,* Kündig, E.P., Ed., Berlin: Springer, 2004, vol. 7, p. 232. https://doi.org/10.1007/b76615
2. Schmalz, H.-G. and Dehmel, F., *Transition Metals for Organic Synthesis.*, Beller, M. and Bolm, C., Eds., Weinheim: Wiley-VCH, 2004, vol. 1, p. 601. https://doi.org/10.1002/9783527619405
3. Pape, A.R., Kaliappan, K.P., and Kündig, E.P., *Chem. Rev.*, 2000, vol. 100, p. 2917. https://doi.org/10.1021/cr9902852
4. Davies, S.G. and McCarthy, T.D., in *Comprehensive Organometallic Chemistry II*, Abel, E.W., Stone, F.G.A., and Wilkinson, G., Eds., Oxford: Pergamon, 1995, p. 1039. https://doi.org/10.1016/B978-008046519-7.00135-0
5. Semmelhack, M.F., in *Comprehensive Organometallic Chemistry II*, Abel, E.W., Stone, F.G.A., and Wilikinson, G., Eds., Oxford: Pergamon, 1995, vol. 12, p. 979. https://doi.org/10.1016/B978-008046519-7.00133-7
6. Semmelhack, M.F., in *Comprehensive Organometallic Chemistry II*, Abel, E.W., Stone, F.G.A., and Wilikinson, G, Eds., Oxford: Pergamon, 1995, vol. 12, p. 1017. https://doi.org/10.1016/B978-008046519-7.00134-9
7. Rosillo, M., Domínguez, G., and Pérez-Castells, J., *Chem. Soc. Rev.*, 2007, vol. 36, p. 1589.
8. Grishina, N.Yu., Sazonova, E.V., and Artemov, A.N., *Russ. J. Org. Chem.*, 2022, vol. 58, no. 06, p. 727. https://doi.org/10.1134/S107042802206001X
9. *Bioorganometallics: Biomolecules, Labeling, Medicine*, Jaouen G., Ed., Weinheim: Willey-VCH, 2005. https://doi.org/10.1002/3527607692.
10. Baldoly, C., Maiorana, S., Licandro, E., et al., *Org. Lett.*, 2002, vol. 4, p. 4341. https://doi.org/10.1021/ol026994a
11. Baldoly, C., Giannini, C., Licandro, E., et al., *Synlett*, 2004, vol. 6, p. 1044. https://doi.org/10.1055/s-2004-822886
12. Baldoly, C., Cerea, P., Giannini, C., et al., *Synlett*, 2005, vol. 13, p. 1984. https://doi.org/10.1055/s-2005-871950
13. Varenne, A., Vessiéres, A., Brossier, P., and Jaouen, G., *Res. Commun. Chem. Pathol. Pharmacol.*, 1994, vol. 84, p. 81.
14. Solladié-Cavallo, A., Quazzotti, S., Colonna, S., et al., *Tetrahedron: Asymmetry*, 1992, vol. 3, p. 287. https://doi.org/10.1016/S0957-4166(00)80208-6
15. Colonna, S., Manfredi, A., Solladié-Cavallo, A., and Quazzotti, S., *Tetrahedron Lett.*, 1990, vol. 31, p. 6185. https://doi.org/10.1016/S0040-4039(00)97020-5
16. Ratni, H. and Kündig, E.P., *Org. Lett.*, 1999, vol. 1, p. 1997. https://doi.org/10.1021/ol991158v
17. Semmelhack, M.F., Knochel, P., and Singleton, T., *Tetrahedron Lett.*, 1993, vol. 34, p. 5051. https://doi.org/10.1016/S0040-4039(00)60673-1
18. Kamikawa, K., Tachibana, A., Sugimoto, S., and Uemura, M., *Org. Lett.*, 2001, vol. 3, p. 2033. https://doi.org/10.1021/ol010076f
19. Patra, M., Ingram, K., Pierroz, V., et al., *Chem.-Eur. J.*, 2013, vol. 19, p. 2232. https://doi.org/10.1002/chem.201204291
20. Kamikawa, K., Watanabe, T., Daimon, A., and Uemura, M., *Tetrahedron*, 2000, vol. 56, p. 2325. https://doi.org/10.1016/S0040-4020(99)01115-1
21. Uemura, M., Daimon, A., and Hayashi, Y., *Chem. Commun.*, 1995, p. 1943. https://doi.org/10.1039/C39950001943
22. Batuecas, M., Luo, J., Gergelitsová, I., et al., ACS Catal., 2019, vol. 9, p. 5268. https://doi.org/10.1021/acscatal.9b00918
23. Han, J.W., Son, S.Uk., and Chung, Y.K., *Org. Chem.*, 1997, vol. 62, p. 8264. https://doi.org/10.1021/jo9712761
24. EP Patent 0094738 B1, 1986.
25. Shah, S.U.A., Ashraf, N., Soomro, Z.H., et al., *Inflammation Res.*, 2012, vol. 61, p. 875. https://doi.org/10.1007/s00011-012-0480-4
26. Sazonova, E.V., Artemov, A.N., Faerman, V.I., et al., *Russ. Chem. Bull.*, 2021, vol. 70, no. 1, p. 171. https://doi.org/10.1007/s11172-021-3073-y
27. Nikitin, K., Bothe, C., Müller-Bunz, H., et al., *Organometallics*, 2012, vol. 31, p. 6183. https://doi.org/10.1021/om300512z
28. Weissberger, A., Proskauer, E., Riddick, J.A., and Toops, E.E., Jr., *Organic Solvents; Physical Properties and Methods of Purification*, New York: Wiley, 1955.
29. Huang, L., Su, T., Shan, W., et al., *Bioorg. Med. Chem.*, 2012, vol. 20, no. 9, p. 3038. https://doi.org/10.1016/j.bmc.2012.02.059
30. Bogomazova, A.A., Kunakova, R.V., and Zlotskii S.S., *Bashkirskii Khim. Zh.*, 2010, vol. 17, no. 3, p. 19.
31. Choudhury, P.K., Almena, J., Foubelo, F., and Yus, M., *Tetrahedron*, 1997, vol. 53, no. 51, p. 17373. https://doi.org/10.1016/s0040-4020(97)10161-2
32. Adams, R., Fogler, M.F., and Kreger, C.W., *J. Am. Chem. Soc.*, 1922, vol. 44, no. 5, p. 1126. https://doi.org/10.1021/ja01426a026
33. Drehfahl, G., Horhold, H.H., and Kuhne, K., *Chem. Ber.*, 1965, vol. 98, p. 1826. https://doi.org/10.1002/cber.19650980622
34. Rausch, M.D., Moser, G.A., Zaiko, E.S., and Lipman, A.L., *J. Organomet. Chem.*, 1970, vol. 23, p. 185.

35. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3. https://doi.org/10.1107/S2053229614024218
36. Hübschle, C.B., Sheldrick, G.M., and Dittrich, B., *J. Appl. Crystallogr.*, 2011, vol. 44, p. 1281. https://doi.org/10.1107/S0021889811043202
37. Busing, W.R. and Levy, H.A., *Acta Crystallogr.*, 1957, vol. 10, p. 180. https://doi.org/10.1107/S0365110X57000584
38. Clark, R.C. and Reid, J.S., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1995, vol. 51, no. 6, p. 887. https://doi.org/10.1107/S0108767395007367
39. Coutouli-Argyropoulou, E. and Trakossas, S., *Tetrahedron*, 2011, vol. 67, p. 1915. https://doi.org/10.1016/j.tet.2011.01.020
40. Zarovkina, N.Yu., Sazonova, E.V., Artemov, A.N., and Fukin, G.K., *Russ. Chem. Bull.*, 2016, vol. 65, no. 7, p. 1790. https://doi.org/10.1007/s11172-016-1512-y
41. Karimi-Jaberi, Z. and Amiri, M., *E.-J. Chem.*, 2012, vol. 1, p. 167. https://doi.org/10.1155/2012/793978

Translated by E. Yablonskaya