Synthesis of (η^6-arene)tricarbonylchromium derivatives of 1,4-dihydro-3,1-benzoxazines

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A series of (η^6-arene)tricarbonylchromium derivatives of 1,4-dihydro-3,1-benzoxazines was synthesized and characterized. The compounds were obtained by two alternative methods, namely, by the reaction of triammine(tricarbonyl)chromium with 1,4-dihydro-3,1-benzoxazines (method *A*) and by the condensation of (η^6-2-aminobenzyl alcohol)tricarbonylchromium with various aldehydes and ketones (method *B*). The composition and structure of obtained compounds were established by different physicochemical methods of analysis, such as HPLC, UV, IR, ^{1}H NMR spectroscopy, mass spectrometry, and X-ray diffraction.

Key words: (η^6-arene)tricarbonylchromium, 1,4-dihydro-3,1-benzoxazines, heterocyclic compounds, triammine(tricarbonyl)chromium.

Heterocycles are important structural fragments in the molecules of various organic compounds with biological activity.[1,2] The presence of metal tricarbonyl fragments, in particular, the chromium tricarbonyl group, can significantly expand the field of application of these compounds. There are known derivatives containing (η^6-benzene)$Cr(CO)_3$ groups and heterocyclic fragments, which have properties making them promising for use in molecular biotechnology and biomedicine. In particular, peptide nucleic acids, reagents for labeling proteins, bioprobes, and tracers for drugs containing (η^6-arene)-$Cr(CO)_3$ fragments were obtained. The use of $Cr(CO)_3$ complexes for biomedical purposes is primarily due to their unique spectroscopic characteristics, in particular, the presence of very intense characteristic absorption bands of CO groups in the mid-IR region, which allows sensitive detection even in complex biological matrices.[3]

Heterocyclic (η^6-benzene)$Cr(CO)_3$ derivatives are widely used in fine organic synthesis because of their high chemical potential of both the heterocyclic rings and the $Cr(CO)_3$ group, which, due to its bulkiness and pronounced electron-withdrawing properties, is capable of promoting highly diastereo- and enantioselective syntheses.[4—9]

Continuing our research on the synthesis of (η^6-arene)-$Cr(CO)_3$ complexes with N,O-heterocyclic rings in the composition,[10—16] we obtained chromium-containing 1,4-dihydro-3,1-benzoxazines.

Results and Discussion

Earlier, we have shown[16] that in the reaction of triammine(tricarbonyl)chromium (**1**) with *N*-phenyl-substituted oxazolidines and oxazinanes, the p,π-conjugation of the lone electron pair of the nitrogen atom of the heterocyclic ring with the phenyl substituent decreases the nucleophilicity of the nitrogen atom, which prevents the formation of the N—Cr σ-bond and finally leads to (η^6-arene)$Cr(CO)_3$ derivatives of these compounds. To synthesize the target chromium-containing heterocycles, in this work we used two approaches. The first consisted in the reaction of triammine(tricarbonyl)chromium (TATC (**1**)) with the corresponding 1,4-dihydro-3,1-benzoxazines **2a—k** (Scheme 1 , method *A*), in the molecules of which there is a conjugation of the nitrogen atom with the arene part. The second method consisted in the construction of heterocyclic fragments by the condensation reaction of (η^6-1-amino-2-hydroxymethylbenzene)-tricarbonylchromium (**3**) with various carbonyl compounds **4a—k** (see Scheme 1, method *B*).

To synthesize chromium-containing 1,4-dihydro-3,1-benzoxazines **5a—k** by method *A*, at the first stage of our work we obtain heterocycles **2a—k** using a procedure described in the work,[17] which consisted in the reaction of amino alcohols with carbonyl compounds in THF and the presence of magnesium sulfate. Heating of carbonyl compounds **4a—k** and 2-aminobenzyl alcohol at 50—100 °C for 3—10 h gave products **2a—k**[18—22] in good yields (see Experimental). At the second stage, the reaction of heterocyclic compounds **2a—k** with TATC (**1**) in dioxane upon heating (120 °C) for 4—6 h (see Experimental) gave the target products **5** (see Scheme 1, method *A*). It was found that compounds **5h,j,k** containing prop-1-en-1-yl, 2-furyl, and 2-pyridyl substituents, respectively, cannot be obtained by this method (only starting compo-

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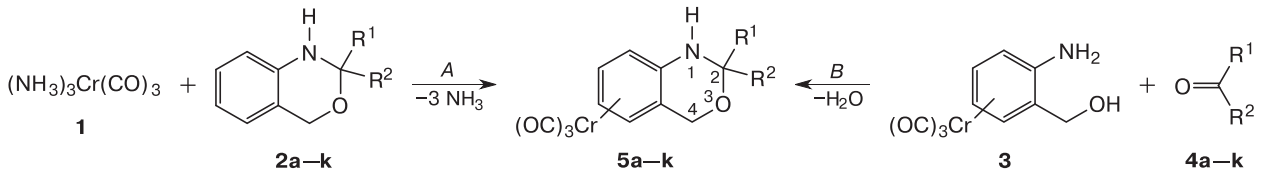
Scheme 1



A: dioxane, 120 °C; *B*: $MgSO_4$, THF, 25—80 °C.

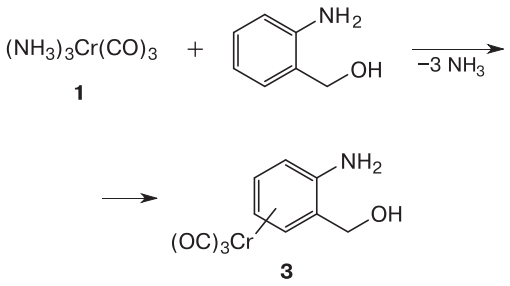
2, **4**, **5**	R^1	R^2	**2, 4, 5**	R^1	R^2	**2, 4, 5**	R^1	R^2	**2, 4, 5**	R^1	R^2
a	H	H	**d**	Me	Et	**g**	H	Bu	**j**	H	Furan-2-yl
b	Me	Me	**e**	H	Me	**h**	H	Prop-1-en-1-yl	**k**	H	Pyridin-2-yl
c	Spirocyclohexane		**f**	H	Et	**i**	H	Ph			

nents were recovered from the reaction mixtures). This experimental fact was not surprising, since it is known[23,24] that most unsaturated hydrocarbons, as well as some heterocycles such as furan and pyridine derivatives, do not give the corresponding $Cr(CO)_3$-π-complexes when reacting with chromium hexacarbonyl or TATC.

Method *B* turned out to be more versatile: the condensation reactions of chromium-containing amino alcohol **3** with carbonyl compounds **4a—k** under conditions similar to the processes for the preparation of heterocycles **2a—k** (see Experimental) made it possible to successfully synthesize the entire series of chromium-containing 1,4-dihydro-3,1-benzoxazines **5a—k** (see Scheme 1). The final product yields varied within the ranged of 25—85%. The presence of the $Cr(CO)_3$ group in the amino alcohol molecule did not significantly affect the course of condensation reactions in comparison with the reactions in which compounds **2a—k** were prepared.

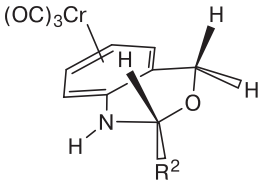
Note that (η^6-1-amino-2-hydroxymethylbenzene)-tricarbonylchromium (**3**) was obtained and characterized by us for the first time. Its synthesis was carried out by the reaction of TATC (**1**) with 2-aminobenzyl alcohol in refluxing dioxane for 1.5 h (Scheme 2). Product **3**, obtained in 91% yield, was a yellow crystalline solid with m.p. 113—114 °C. The spectral characteristics of amino alcohol **3** are given in the Experimental.

Scheme 2

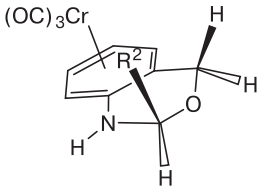


Reagents and conditions: dioxane, 120 °C, 1.5 h.

Since most of the target heterocycles **5** contain two asymmetric centers (one of which is located at position 2 of the heterocyclic ring and has a tetrahedral chirality, while the other with planar chirality is located in the benzene part of the ligand), these substances can exist as two racemic diastereomers, which for compounds **5e—k** we designated as *trans* and *cis* isomers, indicating the mutual position of substituent R^2 and $Cr(CO)_3$ group relative to the heterocyclic ring.



trans-**5e—k**



cis-**5e—k**

Comparing the syntheses of compounds **5** by methods *A* and *B* showed that in the reaction of heterocycles **2d—k** with TATC (**1**), diastereomers were formed in a ratio close to 1 : 1, while the condensation method, as a rule, gave a higher content of *trans* isomers in the mixture of product (Table 1). The greatest effect on the ratio of dia-

Table 1. The ratio of diastereomers of compounds **5d—k** obtained by methods *A* and *B*[a]

Compound	Ratio *trans*/*cis*	
	Method *A*	Method *B*
5d[b]	1.0 : 1.0	1.0 : 1.0
5e	1.0 : 1.0	1.3 : 1.0
5f	1.0 : 1.0	1.6 : 1.0
5g	1.0 : 1.0	2.0 : 1.0
5h	—[c]	1.2 : 1.0
5i	1.2 : 1.0	3.0 : 1.0
5j	—[c]	3.3 : 1.0
5k	—[c]	—[d]

[a] Determined from the ratio of peak areas of the products in HPLC chromatograms at λ = 318 nm.
[b] The data are given for diastereomers **5d**.
[c] Method *A* did not give the compound.
[d] Only *trans*-isomer was formed.

Table 2. Some characteristics of the compounds **5a—k**

Compound	Yield (%)[a]		M.p./°C	IR (KBr), ν(C≡O)/cm^{-1}
	A	*B*		
5a	64	35	117—119	1940, 1866, 1848
5b	79	85	130—132	1936, 1860, 1835
5c	76	81	160—162	1938, 1855,1832
5d[b]	39	33	120—122	1937, 1878, 1841
trans-**5e**	42	25	111—112	1947, 1859
trans-**5f**	36	43	141—142	1941, 1865
trans-**5g**	32	42	116—117	1962, 1894
trans-**5h**	—[c]	30	98—100	1957, 1865
trans-**5i**	40	56	150—152	1967, 1874
cis-**5i**	35	18	163—165	1947, 1869, 1844
trans-**5j**	—[c]	52	123—125	1950, 1865, 1850
trans-**5k**	—[c]	33	137—138	1947, 1881, 1854

[a] The yield is given for the purified product after column chromatography and recrystallization.
[b] The data are given for isolated diastereomer **5d**.
[c] Method *A* did not give the compound.

stereomers was exerted by the presence of bulky phenyl, 2-furyl, and 2-pyridyl groups in the composition of carbonyl compounds (see Table 1).

Products **5a—k** obtained by both methods were isolated from the reaction mixtures by column chromatography on silica gel, eluting with a mixture of hexane—ethyl acetate. Compounds presented in Table 2 were isolated in the pure form and characterized by HPLC, UV, IR, ^{1}H NMR spectroscopy, and mass spectrometry. The *cis*-isomers of products **5e—k** (except for compound *cis*-**5i**) were isolated by column chromatography in mixtures with some amounts of the corresponding *trans*-products. In a number of cases, it was possible to describe ^{1}H NMR spectra of *cis*-isomers based on the spectrum of a mixture of diastereomers (see Experimental).

All of the isolated compounds **5a—k** were yellow crystalline substances, relatively stable in air, the purity of which was confirmed by HPLC. Their IR spectra exhibited strong absorption bands of stretching vibrations of the CO groups of $Cr(CO)_3$ fragments in the region of 1832—1967 cm^{-1} (see Table 2), as well as other absorption bands characteristic of the heterocycles under study (see Experimental).

^{1}H NMR spectroscopy also confirmed the structure of 1,4-dihydro-3,1-benzoxazines **5a—k**: the spectra exhibited the signals for the protons of the heterocyclic ring, substituents R^1 and R^2, as well as (η^6-arene)$Cr(CO)_3$ fragments (see Experimental). The signals of the methylidene group of the $C(4)H_2$ atom in the heterocyclic ring turned out to be very informative, which allowed us to distinguish the diastereomers of compounds **5e—k**. As can be seen from Table 3, the OCH_2 group of *cis*-isomeric products resonates as two doublets with a spin-spin coupling constant of 14.1—14.5 Hz and a difference in the chemical shift values of these protons at a level of 0.32—0.46 ppm, while for *trans*-isomers this is either one signal (singlet or doublet), or two closely positioned doublets with a difference in the chemical shift values of no more than 0.09 ppm. The reason for this difference is the spatial arrangement of the considered protons. In *cis*-isomer, one of the protons of the OCH_2 fragment is shielded simultaneously by both the $Cr(CO)_3$ group and the R^2 substituent at the C(2) atom, which ultimately leads to a significantly greater difference in the chemical shift values of these protons as compared to that for *trans*-isomer, in which there is no such double shielding and the protons are more equivalent. For compound **5d**, the protons of the OCH_2 fragment are nonequivalent in both diastereomers due to the shielding by the $Cr(CO)_3$ group, the methyl or ethyl substituent of one of the proton in the pair. This is reflected in the separation of the doublets of these protons in the ^{1}H NMR spectra by ~0.3 ppm for each diastereomer (see Experimental).

Table 3. Chemical shift values for the OCH_2 protons of *trans*- and *cis*-isomers of heterocycles **5e—k**

Compound **5**	*trans*-**5**		*cis*-**5**	
	δ(OCH_2)	Δ(δ(OCH_2))	δ(OCH_2)	Δ(δ(OCH_2))
	(*J*/Hz)		(*J*/Hz)	
e	4.71 (d, 2 H, *J* = 5.5)	0	4.38 (d, 1 H, *J* = 14.1); 4.77 (d, 1 H, *J* = 14.1)	0.39
f	4.72 (s, 2 H)	0	—[a]	—[a]
g	4.72 (s, 2 H)	0	4.41 (d, 1 H, *J* = 14.1); 4.77 (d, 1 H, *J* = 14.1)	0.36
h	4.71 (d, 2 H, *J* = 2.0)	0	—[a]	—[a]
i	4.78 (d, 1 H, *J* = 14.5); 4.87 (d, 1 H, *J* = 14.5)	0.09	4.57 (d, 1 H, *J* = 14.5); 5.03 (d, 1 H, *J* = 14.5)	0.46
j	4.64 (d, 1 H, *J* = 14.5); 4.69 (d, 1 H, *J* = 14.5)	0.05	4.52 (d, 1 H, *J* = 14.5); 4.98 (d, 1 H, *J* = 14.5)	0.46
k	4.90 (d, 1 H, *J* = 14.5); 4.98 (d, 1 H, *J* = 14.5)	0.08	—[b]	—[b]

[a] Spectrum for *cis*-isomer was not recorded.
[b] Only *trans*-isomer was obtained.

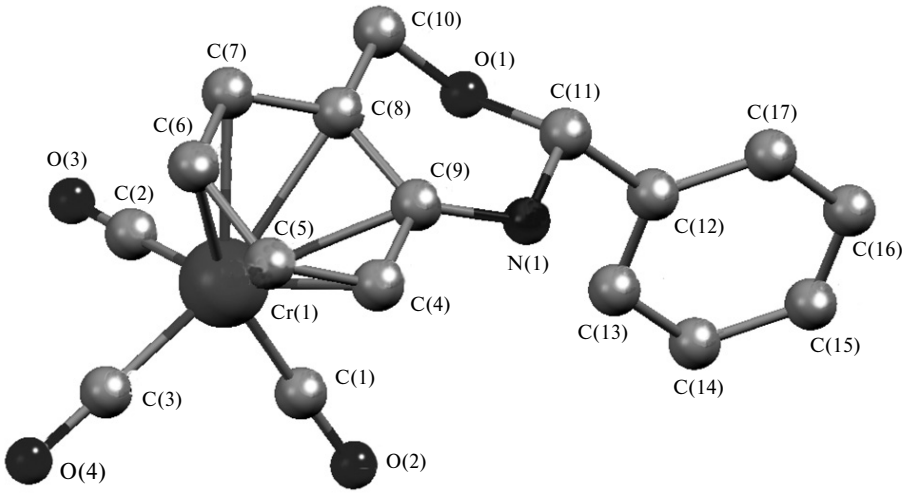


Fig. 1. Molecular structure of the compound *cis*-**5i**.

The structures of compounds **5c**, *trans*-**5e**, and *cis*-**5i** containing spirocyclohexane, methyl, and phenyl substituents at the C(2) atom, respectively, was also confirmed by X-ray diffraction data. The specific features of the structures of compounds **5c** and *trans*-**5e** were described earlier in the works.[25,26] The molecular structure of *cis*-**5i** complex is shown in Fig. 1. Table 4 contains the principal bond lengths and bond angles in this compound.

X-ray diffraction analysis of compound *cis*-**5i** confirmed that the phenyl substituent and the $Cr(CO)_3$ group are located on the same side of the heterocyclic ring. It was shown that the heterocyclic part of molecule *cis*-**5i** has a *half-chair* conformation: all atoms, except for the oxygen atom, lie practically in the same plane. The hybridization of the nitrogen atom is close to sp^2 (the angle C(9)—N(1)—C(11) is equal to 119.4(2)°). The bond lengths of the heterocyclic ring are in the range 1.377(3)—1.497(5) Å, while the C(8)—C(9) distance is closer to that in arenes and is equal to 1.398(4) Å. The distance between the heterocyclic ring and the phenyl substituent (C(11)—C(12)) is equal to 1.502(5) Å. The Cr—C_{arene} bond lengths in *cis*-**5i** are close to each other and lie in the range 2.196(3)—2.331(3) Å. The Cr—$C_{(CO)}$ distances are 1.810(3)—1.819(4) Å, and the angles in the $Cr(CO)_3$ fragment are close to 90° (87.8(2)—91.2(2)°), which is typical of (η^6-arene)$Cr(CO)_3$ complexes.[27]

For the obtained series of (η^6-arene)tricarbonylchromium derivatives **5a—k**, electron impact mass spectra were recorded and their fragmentation was studied. As in the case of other transition metal carbonyl complexes,[28] the primary fragmentation of molecular ions $[M]^+$ consisted in the stepwise dissociation of three carbonyl groups, which led to the formation of fragments $[F_1]^+$ (see Scheme 3). Further, for all analyzed samples the main direction of fragmentation was the elimination of water molecule to obtain $[F_2]^+$ and further elimination of substituent R^2 (in the case of compound **5c**, the elimination of the C_5H_{10} fragment) with the formation of $[F_3]^+$ (see Scheme 3, Table 5). The elimination of water and the substituent at the C(2) atom from dihydro-3,1-benzoxazine molecules during fragmentation under electron impact is confirmed by the literature data.[29]

In conclusion, this study resulted in the synthesis of new (η^6-arene)tricarbonylchromium derivatives of 1,4-dihydro-3,1-benzoxazines **5a—k**, which were characterized by various methods. These compounds were obtained by two alternative methods, namely, by the reaction of heterocyclic compounds **2a—k** with triammine(tricarbonyl)-

Table 4. Principal bond distances (*d*) and bond angles (ω) for the structure *cis*-**5i**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
C(10)—O(1)	1.425(4)	C(14)—C(15)	1.355(8)	C(4)—Cr(1)	2.242(3)	C(9)—N(1)—C(11)	119.4(2)
C(11)—O(1)	1.409(4)	C(15)—C(16)	1.355(8)	C(5)—Cr(1)	2.196(3)	N(1)—C(11)—O(1)	109.3(3)
C(11)—N(1)	1.461(5)	C(16)—C(17)	1.377(6)	C(6)—Cr(1)	2.217(3)	C(10)—O(1)—C(11)	111.3(2)
C(9)—N(1)	1.377(3)	C(12)—C(17)	1.370(6)	C(7)—Cr(1)	2.205(3)	C(8)—C(10)—O(1)	110.1(3)
C(8)—C(9)	1.398(4)	C(4)—C(9)	1.412(5)	C(8)—Cr(1)	2.257(3)	C(9)—C(8)—C(10)	118.5(3)
C(8)—C(10)	1.497(5)	C(4)—C(5)	1.389(5)	C(9)—Cr(1)	2.331(3)	C(8)—C(9)—N(1)	119.6(2)
C(11)—C(12)	1.502(5)	C(5)—C(6)	1.396(4)	C(1)—Cr(1)	1.815(3)	C(1)—Cr(1)—C(2)	91.2(2)
C(12)—C(13)	1.387(5)	C(6)—C(7)	1.396(5)	C(2)—Cr(1)	1.810(3)	C(2)—Cr(1)—C(3)	87.8(2)
C(13)—C(14)	1.375(6)	C(7)—C(8)	1.411(5)	C(3)—Cr(1)	1.819(4)	C(1)—Cr(1)—C(3)	90.6(2)

Scheme 3

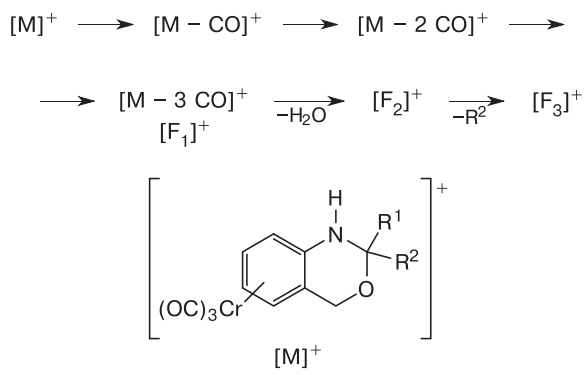


Table 5. Mass spectrometry data for compounds **5a—k** (EI, 70 eV), m/z (I_{rel} (%))

Compound	$[M]^+$	$[F_1]^+$	$[F_2]^+$	$[F_3]^+$
5a	271 (100)	187 (15)	169 (29)	168 (28)
5b	299 (33)	215 (100)	197 (68)	182 (59)
5c	339 (23)	255 (100)	237 (46)	167 (5)
5d [a]	313 (37)	229 (100)	211 (54)	182 (22)
trans-**5e**	285 (67)	201 (100)	183 (51)	168 (60)
trans-**5f**	299 (36)	215 (40)	197 (52)	168 (25)
trans-**5g**	327 (64)	243 (100)	225 (28)	168 (65)
trans-**5h**	311 (52)	227 (98)	209 (100)	168 (25)
trans-**5i**	347 (36)	263(76)	245 (28)	168 (12)
cis-**5i**	347 (19)	263 (85)	245 (21)	168 (6)
trans-**5j**	337 (39)	253 (79)	235 (67)	168 (52)
trans-**5k**	348 (15)	264 (100)	246 (63)	168 (43)

[a] The data are given for isolated diastereomer **5d**.

chromium **1** (method *A*) and by the condensation of chromium-containing amino alcohol **3** with carbonyl compounds **4a—k** (method *B*). It was shown that method *B* allows one to synthesize a wider range of *N*—H-substituted products.

Experimental

Solvents were distilled over sodium metal at atmospheric pressure. Ethyl acetate was dried over calcium chloride and distilled.[30] Commercial paraformaldehyde (**4a**) and acetaldehyde (**4e**) (Sigma-Aldrich) were used without preliminary purification. Aldehydes and ketones **4b—d**, **4f—k** were purified by distillation at atmospheric or reduced pressure. 2-Aminobenzyl alcohol (Sigma-Aldrich) was purified by recrystallization from a mixture of hexane—ethyl acetate (10 : 1). Compounds **2a—d,f,i**,[18] **2e**,[19] **2g**,[20] **2h**, **2j**,[21] and **2k**[22] were obtained by condensation of aldehydes and ketones **4a—k** with 2-aminobenzyl alcohol in THF in the presence of magnesium sulfate according to a procedure similar to that described in the work.[17] The reaction time and temperature, as well as the yields of compounds **2a—k** are presented in Table 6. Triammine(tricarbonyl)chromium (**1**) was synthesized according to the known method.[31]

Products **5a—k** were isolated and purified by column chromatography using Acros 0.035—0.070 mm silica gel under argon atmosphere, eluent hexane—ethyl acetate. HPLC analysis was carried out on a Knauer Smartline 5000 chromatograph with a S 2600 UV diode array detector (UV spectra of eluates were recorded in the range of 200—500 nm), a Diasfer-110-S16 column, 5 μm, 4.6×250 mm, eluent acetonitrile—water (84 : 16); the flow rate of the eluent was 0.7 mL min^{-1}. IR spectra were recorded on an FTIR-8400S instrument (Shimadzu) in the wave number range of 500—4000 cm^{-1} in KBr pellets. ^1H NMR spectra were recorded in acetone-d_6 on an Agilent DD2 NMR 400NB spectrometer (400 MHz). Mass spectrometric studies were carried out on a Trace DSQII instrument, ionization by electron impact (70 eV), m/z range of 70—500, temperature programming from 50 to 450 °C at a heating rate of 100 deg min^{-1}.

(η^6-1-Amino-2-hydroxymethylbenzene)tricarbonylchromium (3). 2-Aminobenzyl alcohol (5.00 g, 41 mmol), TATC (**1**) (7.6 g, 41 mmol), and dioxane (60 mL) were placed into a pre-deaerated and then filled with argon two-neck flask, equipped with a reflux condenser and a gas burette with dibutyl phthalate. The reaction mixture was heated for 1.5 h in an oil bath at 120 °C until 2.7 L of ammonia were evolved. Then, the flask was cooled and filled with argon. The resulting mixture was filtered on a Schott filter filled with aluminum oxide, the solvent was evaporated. The residue was recrystallized from a mixture of hexane—ethyl acetate (9 : 1). Product **3** was obtained as a yellow powder. The yield was 91%, m.p. 113—114 °C. HPLC: one peak, τ = 4.6 min. UV (MeCN, H_2O), λ/nm: 218, 315. IR (KBr), ν/cm^{-1}: 3591, 3477, 3364 (ν(N—H, O—H)); 3090 (ν(C_{arene}—H); 2846 (ν(C—H); 1956, 1855, 1836 (ν(C≡O)); 1630, 1547 (ν(C_{arene}— C_{arene}); 671 (ω(C_{arene}—H)). MS (EI, 70 eV), m/z (I_{rel} (%)): 259 $[M]^+$ (31), 203 $[M - 2\,CO]^+$ (8.3), 175 $[M - 3\,CO]^+$ (25), 157 $[M - 3\,CO - H_2O]^+$ (100), 52 $[Cr]^+$ (49). ^1H NMR (acetone-d_6, 400 MHz), δ: 4.35—4.54 (m, 3 H, CH_2OH); 4.90 (td, 1 H, H_{arene}, J = 6.3 Hz, J = 0.8 Hz); 5.14 (dd, 1 H, H_{arene}, J = 6.7 Hz, J = 0.8 Hz); 5.27 (br.s, 2 H, NH_2), 5.69—5.74 (m, 1 H, H_{arene}); 5.88 (dd, 1 H, H_{arene}, J = 6.3 Hz, J = 1.2 Hz).

Synthesis of tricarbonylchromium derivatives of 1,4-dihydro-3,1-benzoxazines 5a—k (general procedure). Method *A*. The reagent TATC (**1**) (24 mmol) and one of compounds **2a—k** (24 mmol), and dioxane (60 mL) were placed into a pre-deaerated and then filled with argon two-neck flask, equipped with a reflux condenser and a gas burette with dibutyl phthalate. The reaction mixture was heated in an oil bath at 120 °C for 4—6 h,

Table 6. Reaction time (τ), temperature (T), and yields of compounds **2a—k**

2	τ/h	T/°C	Yield (%)
a	3	50	68
b	7	50	91
c	10	50	45
d	10	50	43
e	3	60	75
f	10	60	74
g	10	60	57
h	10	50	55
i	3	100	85
j	10	50	48
k	8	50	42

then, the flask was cooled and filled with argon. The resulting mixture was filtered on a Schott filter filled with aluminum oxide, the solvent was evaporated. The residue was subjected to column chromatography to isolate reaction products, which were recrystallized from a mixture of hexane—ethyl acetate. The yellow crystals formed were filtered on a Schott filter and then dried in a desiccator.

Method *B*. (η^6-1-Amino-2-hydroxymethylbenzene)tricarbonylchromium (**3**) (1.6 g, 6 mmol), carbonyl compound **4a** or **4e** (12 mmol) or one of compounds **4b—d,f—k** (6 mmol), anhydrous $MgSO_4$ (2.0 g, 16 mmol), and tetrahydrofuran (5 mL) were placed into a 10-mL glass tube. The tube was deaerated in liquid nitrogen, vacuum-sealed, and heated at 25—80 °C for 5—9 h. Then the tube was cooled to room temperature (if necessary) and unsealed, the reaction mixture was concentrated *in vacuo*. Further product isolation was carried out in accordance with the procedure described in method *A*.

Yields and melting points of compounds **5a—k** are given in Table 2, conditions for the synthesis of these substances are summarized in Table 7.

η^6-(1,4-Dihydro-2*H*-3,1-benzoxazine)tricarbonylchromium (5a). HPLC: one peak, τ = 4.9 min. UV (MeCN, H_2O), λ/nm: 218, 318, 430. IR (KBr), ν/cm^{-1}: 3412 (ν(N—H)); 3099 (ν(C_{arene}—H)); 2858 (ν(C—H)); 1940, 1866, 1848 (ν(C≡O)); 1558, 1489 (ν(C_{arene}—C_{arene})); 819, 677 (ω(C_{arene}—H)). MS, *m/z* (I_{rel} (%)): 271 $[M]^+$ (100), 270 $[M - H]^+$ (77), 215 $[M - 2\,CO]^+$ (18), 187 $[M - 3\,CO]^+$ (15), 187 $[M - 3\,CO - 2\,H]^+$ (20), 169 $[M - 3\,CO - H_2O]^+$ (29), 168 $[M - 3\,CO - H_2O - H]^+$ (28), 167 $[M - 3\,CO - H_2O - H]^+$ (36), 52 $[Cr]^+$ (14). ^{1}H NMR, δ: 4.52 (d, 1 H, $NCH_2OC\underline{H}_2$, *J* = 14.1 Hz); 4.65—4.82 (m, 3 H, $NCH_2OC\underline{H}_2$, $NC\underline{H}_2OCH_2$); 5.03 (t, 1 H, H_{arene}, *J* = 6.3 Hz); 5.16 (d, 1 H, H_{arene}, *J* = 6.7 Hz); 5.66 (t, 1 H, H_{arene}, *J* = 6.7 Hz); 5.79 (d, 1 H, H_{arene}, *J* = 6.3 Hz); 6.04 (br.s, 1 H, HN).

η^6-(2,2-Dimethyl-1,4-dihydro-2*H*-3,1-benzoxazine)tricarbonylchromium (5b). HPLC: one peak, τ = 5.8 min. UV (MeCN, H_2O), λ/nm: 219, 317, 447. IR (KBr), ν/cm^{-1}: 3402 (ν(N—H)); 2946 (ν(C—H)); 1936, 1860, 1835 (ν(C≡O)); 1556, 1490 (ν(C_{arene}—C_{arene})); 750, 634 (ω(C_{arene}—H)). MS, *m/z* (I_{rel} (%)): 299 $[M]^+$ (33), 243 $[M - 2\,CO]^+$ (14), 215 $[M - 3\,CO]^+$ (100), 197 $[M - 3\,CO - H_2O]^+$ (68), 182 $[M - 3\,CO - H_2O - Me]^+$ (59), 52 $[Cr]^+$ (73). ^{1}H NMR, δ: 1.37 (s, 3 H, Me); 1.51 (s, 3 H, Me); 4.43 (d, 1 H, OCH_2, *J* = 14.9 Hz); 4.76 (d, 1 H, OCH_2, *J* = 14.9 Hz); 4.96 (td, 1 H, H_{arene}, *J* = 6.3 Hz, *J* = 0.8 Hz); 5.06 (dd, 1 H, H_{arene}, *J* = 6.7 Hz, *J* = 0.8 Hz); 5.64 (td, 1 H, H_{arene}, *J* = 7.0 Hz, *J* = 1.2 Hz); 5.84 (d, 1 H, H_{arene}, *J* = 6.3 Hz); 6.20 (br.s, 1 H, HN).

η^6-(2-Spirocyclohexane-1,4-dihydro-3,1-benzoxazine)tricarbonylchromium (5c). HPLC: one peak, τ = 7.7 min. UV (MeCN, H_2O), λ/nm: 219, 317, 446. IR (KBr), ν/cm^{-1}: 3396 (ν(N—H)); 3128 (ν(C_{arene}—H)); 2937 (ν(C—H)); 1938, 1855, 1832 (ν(C≡O)); 1562, 1493 (ν(C_{arene}—C_{arene})); 818, 788, 677 (ω(C_{arene}—H)). MS, *m/z* (I_{rel} (%)): 339 $[M]^+$ (23), 283 $[M - 2\,CO]^+$ (6), 255 $[M - 3\,CO]^+$ (100), 237 $[M - 3\,CO - H_2O]^+$ (46), 167 $[M - 3\,CO - C_5H_{10}]^+$ (5), 157 $[M - 4\,CO - C_5H_{10}]^+$ (12), 52 $[Cr]^+$ (65). ^{1}H NMR, δ: 1.23—1.39 (m, 1 H, C_5H_{10}); 1.42—1.75 (m, 7 H, C_5H_{10}); 1.80—1.93, 1.95—2.03 (both m, 1 H each, C_5H_{10}); 4.42 (d, 1 H, OCH_2, *J* = 14.5 Hz); 4.73 (d, 1 H, OCH_2, *J* = 14.5 Hz); 4.94 (t, 1 H, H_{arene}, *J* = 6.3 Hz); 5.09 (d, 1 H, H_{arene}, *J* = 7.0 Hz); 5.64 (t, 1 H, H_{arene}, *J* = 6.3 Hz); 5.83 (d, 1 H, H_{arene}, *J* = 6.3 Hz); 6.15 (br.s, 1 H, HN).

η^6-(2-Ethyl-2-methyl-1,4-dihydro-2*H*-3,1-benzoxazine)tricarbonylchromium (5d). ***Diastereomer 1.*** HPLC: one peak, τ = 7.0 min. UV (MeCN, H_2O), λ/nm: 213, 315, 432. IR (KBr), ν/cm^{-1}: 3411 (ν(N—H)); 2924 (ν(C—H)); 1937, 1878, 1841 (ν(C≡O)); 1561, 1493 (ν(C_{arene}—C_{arene})); 808, 675 (ω(C_{arene}—H)). MS, *m/z* (I_{rel} (%)): 313 $[M]^+$ (37), 257 $[M - 2\,CO]^+$ (15), 229 $[M - 3\,CO]^+$ (100), 211 $[M - 3\,CO - H_2O]^+$ (54), 182 $[M - 3\,CO - H_2O - Et]^+$ (22), 52 $[Cr]^+$ (9). ^{1}H NMR, δ: 0.89 (t, 3 H, $MeCCH_2\underline{Me}$, *J* = 7.4 Hz); 1.45 (s, 3 H, $\underline{Me}CCH_2Me$); 1.57—1.68 (m, 1 H, $C\underline{H}_2Me$); 1.69—1.80 (m, 1 H, $C\underline{H}_2Me$); 4.42 (d, 1 H, OCH_2, *J* = 14.9 Hz); 4.70 (d, 1 H, OCH_2, *J* = 14.9 Hz); 4.95 (td, 1 H, H_{arene}, *J* = 6.3 Hz, *J* = 0.8 Hz); 5.07 (dd, 1 H, H_{arene}, *J* = 6.7 Hz, *J* = 0.8 Hz); 5.60—5.67 (m, 1 H, H_{arene}); 5.83 (d, 1 H, H_{arene}, *J* = 6.3 Hz); 6.19 (br.s, 1 H, HN).

Diastereomer 2. ^{1}H NMR, δ: 0.99 (t, 3 H, $MeCCH_2\underline{Me}$, *J* = 7.4 Hz); 1.32 (s, 3 H, $\underline{Me}CCH_2Me$); 1.70—1.81 (m, 1 H, $C\underline{H}_2Me$); 1.82—1.92 (m, 1 H, $C\underline{H}_2Me$); 4.44 (d, 1 H, OCH_2, *J* = 14.5 Hz); 4.76 (d, 1 H, OCH_2, *J* = 14.5 Hz); 4.95 (t, 1 H, H_{arene}, *J* = 6.3 Hz); 5.09 (d, 1 H, H_{arene}, *J* = 7.0 Hz); 5.63 (t, 1 H, H_{arene}, *J* = 6.3 Hz); 5.82 (d, 1 H, H_{arene}, *J* = 6.3 Hz); 6.16 (br.s, 1 H, HN).

***trans*-η^6-(2-Methyl-1,4-dihydro-2*H*-3,1-benzoxazine)tricarbonylchromium (*trans*-5e).** HPLC: one peak, τ = 5.3 min. UV (MeCN, H_2O), λ/nm: 216, 317, 432. IR (KBr), ν/cm^{-1}: 3325 (ν(N—H)); 3099 (ν(C_{arene}—H)); 2991 (ν(C—H)); 1947, 1859 (ν(C≡O)); 1558, 1530, 1489 (ν(C_{arene}—C_{arene})); 814, 673 (ω(C_{arene}—H)). MS, *m/z* (I_{rel} (%)): 285 $[M]^+$ (67), 229 $[M - 2\,CO]^+$ (17), 201 $[M - 3\,CO]^+$ (100), 183 $[M - 3\,CO - H_2O]^+$ (51), 168 $[M - 3\,CO - H_2O - Me]^+$ (60), 52 $[Cr]^+$ (40). ^{1}H NMR, δ: 1.34 (d, 3 H, Me, *J* = 5.9 Hz); 4.71 (d, 2 H, OCH_2, *J* = 5.5 Hz); 4.82 (q, 1 H, NCHO, *J* = 5.5 Hz); 5.09 (t, 1 H, H_{arene}, *J* = 6.3 Hz); 5.21 (d, 1 H, H_{arene}, *J* = 7.0 Hz); 5.64 (td, 1 H, H_{arene}, *J* = 7.0 Hz, *J* = 1.2 Hz); 5.73 (d, 1 H, H_{arene}, *J* = 6.3 Hz); 6.10 (br.s, 1 H, HN).

***cis*-η^6-(2-Methyl-1,4-dihydro-2*H*-3,1-benzoxazine)tricarbonylchromium (*cis*-5e).** ^{1}H NMR, δ: 1.37 (d, 3 H, Me, *J* = 5.5 Hz); 4.38 (d, 1 H, OCH_2, *J* = 14.1 Hz); 4.73—4.80 (m, 2 H, OCH_2, NCHO); 4.92 (td, 1 H, H_{arene}, *J* = 6.3 Hz, *J* = 0.8 Hz); 5.00 (dd, 1 H, H_{arene}, *J* = 7.0 Hz, *J* = 0.8 Hz); 5.67 (td, 1 H, H_{arene}, *J* = 7.0 Hz, *J* = 1.2 Hz); 5.87 (d, 1 H, H_{arene}, *J* = 6.3 Hz); 5.95 (br.s, 1 H, HN).

***trans*-η^6-(2-Ethyl-1,4-dihydro-2*H*-3,1-benzoxazine)tricarbonylchromium (*trans*-5f).** HPLC: one peak, τ = 6.8 min. UV (MeCN, H_2O), λ/nm: 219, 318. IR (KBr), ν/cm^{-1}: 3357 (ν(N—H)); 3100 (ν(C_{arene}—H)); 2970 (ν(C—H)); 1941, 1865 (ν(C≡O)); 1557, 1531, 1488 (ν(C_{arene}—C_{arene})); 814, 673 (ω(C_{arene}—H)). MS, *m/z* (I_{rel} (%)): 299 $[M]^+$ (36), 243 $[M - 2\,CO]^+$ (14), 215 $[M - 3\,CO]^+$ (40), 197 $[M - 3\,CO - H_2O]^+$ (52), 195 $[M - 3\,CO - H_2O - 2\,H]^+$ (100), 168 $[M - 3\,CO - H_2O - Et]^+$ (25), 52 $[Cr]^+$ (81). ^{1}H NMR, δ: 0.99 (t, 3 H, Me, *J* = 7.8 Hz); 1.60—1.75 (m, 2 H, $C\underline{H}_2Me$); 4.64 (t, 1 H, NCHO, *J* = 5.1 Hz); 4.72 (s, 2 H, OCH_2); 5.08 (td, 1 H, H_{arene}, *J* = 6.3 Hz, *J* = 0.8 Hz); 5.23 (dd, 1 H, H_{arene}, *J* = 7.0 Hz, *J* = 0.8 Hz); 5.64

Table 7. Reaction time (τ) and temperature (*T*) of synthesis for compounds **5a—k** by methods *A* and *B*

Compound **5**	τ/h		*T*/°C (*B*)	Compound **5**	τ/h		*T*/°C (*B*)
	A	*B*			*A*	*B*	
a	4	5	25	**g**	5	8	50
b	4	8	40	**h**	5	7	50
c	6	8	40	**i**	4	8	80
d	4	8	40	**j**	5	7	50
e	5	9	40	**k**	4	6	40
f	6	7	50				

(td, 1 H, H_{arene}, J = 6.3 Hz, J = 1.2 Hz); 5.74 (br.d, 1 H, H_{arene}, J = 6.7 Hz); 6.05 (br.s, 1 H, HN).

***trans*-η⁶-(2-Butyl-1,4-dihydro-2*H*-3,1-benzoxazine)tricarbonylchromium (*trans*-5g).** HPLC: one peak, τ = 8.6 min. UV (MeCN, H_2O), λ/nm: 219, 318 and 219, 318. IR (KBr), ν/cm^{-1}: 3374 (ν(N—H)); 3108 (ν(C_{arene}—H)); 2931 (ν(C—H)); 1962, 1894 (ν(C≡O)); 1555, 1525, 1485 (ν(C_{arene}—C_{arene})); 862, 671 (ω(C_{arene}—H)). MS (*m*/*z* (I_{rel} (%)): 327 $[M]^+$ (64), 271 $[M - 2\,CO]^+$ (15), 243 $[M - 3\,CO]^+$ (100), 225 $[M - 3\,CO - H_2O]^+$ (28), 223 $[M - 3\,CO - H_2O - 2\,H]^+$ (68), 168 $[M - 3\,CO - H_2O - Bu]^+$ (65), 52 $[Cr]^+$ (96). ^{1}H NMR, δ: 0.90 (t, 3 H, Me, J = 7.4 Hz); 1.31—1.41, 1.41—1.52 (both m, 2 H each, $Me(C\underline{H}_2)_2CH_2$); 1.67 (td, 2 H, $Me(CH_2)_2C\underline{H}_2$, J = 7.8 Hz, J = 5.5 Hz); 4.69 (br.d, 1 H, NCHO, J = 5.5 Hz); 4.72 (s, 2 H, OCH_2); 5.08 (td, 1 H, H_{arene}, J = 6.3 Hz, J = 0.8 Hz); 5.23 (dd, 1 H, H_{arene}, J = 7.0 Hz, J = 0.8 Hz); 5.64 (td, 1 H, H_{arene}, J = 7.0 Hz, J = 1.2 Hz); 5.74 (br.d, 1 H, H_{arene}, J = 6.3 Hz); 6.04 (br.s, 1 H, HN).

***cis*-η⁶-(2-Butyl-1,4-dihydro-2*H*-3,1-benzoxazine)tricarbonylchromium (*cis*-5g).** ^{1}H NMR, δ: 0.90 (t, 3 H, Me, J = 7.4 Hz); 1.31—1.41, 1.41—1.52 (both m, 2 H each, $Me(C\underline{H}_2)_2CH_2$); 1.67—1.78 (m, 2 H, $Me(CH_2)_2C\underline{H}_2$); 4.41 (d, 1 H, OCH_2, J = 14.1 Hz); 4.60—4.65 (m, 1 H, NCHO); 4.77 (d, 1 H, OCH_2, J = 14.1 Hz); 4.93 (td, 1 H, H_{arene}, J = 7.0 Hz, J = 0.8 Hz); 5.02 (dd, 1 H, H_{arene}, J = 6.6 Hz, J = 0.8 Hz); 5.67 (td, 1 H, H_{arene}, J = 7.4 Hz, J = 1.2 Hz); 5.86 (br.d, 1 H, H_{arene}, J = 6.3 Hz); 5.90 (br.s, 1 H, HN).

***trans*-η⁶-[2-(Prop-1′-en-1′-yl)-1,4-dihydro-2*H*-3,1-benzoxazine]tricarbonylchromium (*trans*-5h).** HPLC: one peak, τ = 7.2 min. UV (MeCN, H_2O), λ/nm: 219, 318. IR (KBr), ν/cm^{-1}: 3357 (ν(N—H)); 3100 (ν(C_{arene}—H)); 2971 (ν(C—H)); 1957, 1865 (ν(C≡O)); 1531, 1488 (ν(C_{arene}—C_{arene})); 814, 674 (ω(C_{arene}—H)). MS, *m*/*z* (I_{rel} (%)): 311 $[M]^+$ (52), 255 $[M - 2\,CO]^+$ (8), 227 $[M - 3\,CO]^+$ (98), 209 $[M - 3\,CO - H_2O]^+$ (100), 168 $[M - 3\,CO - H_2O - (CH)_2Me]^+$ (25), 52 $[Cr]^+$ (52). ^{1}H NMR, δ: 1.72 (dd, 3 H, Me, J = 6.3 Hz, J = 1.2 Hz); 4.71 (d, 2 H, OCH_2, J = 2.0 Hz); 5.05—5.12 (m, 2 H, NCHO, H_{arene}); 5.27 (dd, 1 H, H_{arene}, J = 7.0 Hz, J = 0.8 Hz); 5.48—5.59 (m, 1 H, $(C\underline{H})_2Me$); 5.66 (td, 1 H, H_{arene}, J = 7.0 Hz, J = 1.2 Hz); 5.75 (d, 1 H, H_{arene}, J = 6.7 Hz); 5.90—6.02 (m, 1 H, $(C\underline{H})_2Me$); 6.07 (br.s, 1 H, HN).

***trans*-η⁶-(2-Phenyl-1,4-dihydro-2*H*-3,1-benzoxazine)tricarbonylchromium (*trans*-5i).** HPLC: one peak, τ = 6.2 min. UV (MeCN, H_2O), λ/nm: 218, 318, 430. MS, *m*/*z* (I_{rel} (%)): 347 $[M]^+$ (36), 291 $[M - 2\,CO]^+$ (5), 263 $[M - 3\,CO]^+$ (76), 261 $[M - 3\,CO - 2\,H]^+$ (100), 245 $[M - 3\,CO - H_2O]^+$ (28), 243 $[M - 3\,CO - H_2O - 2\,H]^+$ (67), 168 $[M - 3\,CO - H_2O - Ph]^+$ (12), 157 $[M - 3\,CO - PhCHO]^+$ (6), 77 $[Ph]^+$ (32), 52 $[Cr]^+$ (55). IR (KBr), ν/cm^{-1}: 3327 (ν(N—H)); 2925 (ν(C—H)); 1967, 1874 (ν(C≡O)); 1549, 1525, 1477 (ν(C_{arene}—C_{arene})); 780, 710, 661 (ω(C_{arene}—H)). ^{1}H NMR, δ: 4.78 (d, 1 H, OCH_2, J = 14.5 Hz); 4.87 (d, 1 H, OCH_2, J = 14.5 Hz); 5.14 (td, 1 H, H_{arene}, J = 6.3 Hz, J = 0.8 Hz); 5.36 (dd, 1 H, H_{arene}, J = 6.7 Hz, J = 0.8 Hz); 5.68—5.74 (m, 2 H, H_{arene}, NCHO); 5.82 (d, 1 H, H_{arene}, J = 6.3 Hz); 6.31 (br.s, 1 H, HN); 7.38—7.47 (m, 3 H, H_{Ph}); 7.48—7.56 (m, 2 H, H_{Ph}).

***cis*-η⁶-(2-Phenyl-1,4-dihydro-2*H*-3,1-benzoxazine)tricarbonylchromium (*cis*-5i).** HPLC: one peak, τ = 5.8 min. UV (MeCN, H_2O), λ/nm: 216, 320, 431. IR (KBr), ν/cm^{-1}: 3410 (ν(N—H)); 2916 (ν(C—H)); 1947, 1869, 1844 (ν(C≡O)); 1652, 1558 (ν(C_{arene}—C_{arene})); 750, 710, 670 (ω(C_{arene}—H)). MS, *m*/*z* (I_{rel} (%)): 347 $[M]^+$ (19), 291 $[M - 2\,CO]^+$ (5), 263 $[M - 3\,CO]^+$ (85), 261 $[M - 3\,CO - 2\,H]^+$ (100), 245 $[M - 3\,CO - H_2O]^+$ (21), 243 $[M - 3\,CO - H_2O - 2\,H]^+$ (50), 168 $[M - 3\,CO - H_2O - Ph]^+$ (6), 77 $[Ph]^+$ (6), 52 $[Cr]^+$ (21). ^{1}H NMR, δ: 4.57 (d, 1 H, OCH_2, J = 14.5 Hz); 4.98 (dd, 1 H, H_{arene}, J = 6.3 Hz, J = 0.8 Hz); 5.03 (d, 1 H, OCH_2, J = 14.5 Hz); 5.15 (d, 1 H, H_{arene}, J = 6.7 Hz); 5.63 (d, 1 H, NCHO, J = 2.7 Hz); 5.73 (td, 1 H, H_{arene}, J = 7.0 Hz, J = 1.2 Hz); 5.95 (d, 1 H, H_{arene}, J = 6.3 Hz); 6.12 (br.s, 1 H, HN); 7.37—7.46 (m, 3 H, H_{Ph}); 7.58—7.69 (m, 2 H, H_{Ph}).

***trans*-η⁶-[2-(2′-Furyl)-1,4-dihydro-2*H*-3,1-benzoxazine]tricarbonylchromium (*trans*-5j).** HPLC: one peak, τ = 6.1 min. UV (MeCN, H_2O), λ/nm: 219, 318. IR (KBr), ν/cm^{-1}: 3360 (ν(N—H)); 3099 (ν(C_{arene}—H)); 2865 (ν(C—H)); 1950, 1865, 1850 (ν(C≡O)); 1568, 1479 (ν(C_{arene}—C_{arene})); 741, 673 (ω(C_{arene}—H)). MS, *m*/*z* (I_{rel} (%)): 337 $[M]^+$ (39), 281 $[M - 2\,CO]^+$ (4), 253 $[M - 3\,CO]^+$ (79), 235 $[M - 3\,CO - H_2O]^+$ (67), 168 $[M - 3\,CO - H_2O - C_4H_3O]^+$ (52), 52 $[Cr]^+$ (100). ^{1}H NMR, δ: 4.64 (d, 1 H, OCH_2, J = 14.5 Hz); 4.69 (d, 1 H, OCH_2, J = 14.5 Hz); 5.10 (td, 1 H, H_{arene}, J = 6.3 Hz, J = 0.8 Hz); 5.33 (dd, 1 H, H_{arene}, J = 7.0 Hz, J = 0.8 Hz); 5.72 (td, 1 H, H_{arene}, J = 6.3 Hz, J = 1.2 Hz); 5.82 (d, 1 H, H_{arene}, J = 6.3 Hz); 5.84 (d, 1 H, NCHO, J = 2.7 Hz); 6.44—6.47 (m, 1 H, C_4H_3O); 6.50 (br.s, 1 H, HN); 6.54 (d, 1 H, C_4H_3O, J = 3.1 Hz); 7.60 (dd, 1 H, C_4H_3O, J = 2.0 Hz, J = 0.8 Hz).

***cis*-η⁶-[2-(2′-Furyl)-1,4-dihydro-2*H*-3,1-benzoxazine]tricarbonylchromium (*cis*-5j).** ^{1}H NMR, δ: 4.52 (d, 1 H, OCH_2, J = 14.5 Hz); 4.96—5.02 (m, 2 H, OCH_2, H_{arene}); 5.20 (br.d, 1 H, H_{arene}, J = 6.7 Hz); 5.72—5.74 (m, 1 H, H_{arene}); 5.77 (d, 1 H, NCHO, J = 3.1 Hz); 5.91 (br.d, 1 H, H_{arene}, J = 6.3 Hz); 6.30 (br.s, 1 H, HN); 6.48 (dd, 1 H, C_4H_3O, J = 3.1 Hz, J = 1.6 Hz); 6.69 (d, 1 H, C_4H_3O, J = 3.5 Hz); 7.59 (dd, 1 H, C_4H_3O, J = 2.0 Hz, J = 0.8 Hz).

Table 8. Basic crystallographic data and structure refinement statistics for compound *cis*-**5i**

Parameter	Value
Molecular formula	$C_{17}H_{13}CrNO_4$
Molecular weight	347.28
Space group	$P2(1)/c$
a/Å	11.9124(10)
b/Å	8.3651(8)
c/Å	15.5815(12)
α/deg	90
β/deg	103.043(8)
γ/deg	90
V/Å^3	1512.6(2)
Z	4
d_{calc}/mg m^{-3}	1.525
μ/mm^{-1}	0.776
θ-Range for data collection/deg	3.447—26.372
Number of reflections	
collected	21489
unique with $I > 2\sigma(I)$	2276
R_{int}	0.0721
GOOF (F^2)	1.044
R_1 ($I > 2\sigma(I)$)	0.0475
ωR_2 (all data)	0.139
Residual electron density (ρ_{min}/ρ_{max})/e Å^{-3}	−0.399/0.353

***trans*-η⁶-[2-(2′-Pyridyl)-1,4-dihydro-2*H*-3,1-benzoxazine]-tricarbonylchromium (*trans*-5k).** HPLC: one peak, τ = 6.1 min. UV (MeCN, H_2O), λ/nm: 218, 319, 432. IR (KBr), ν/cm^{-1}: 3234 (ν(N—H)); 3096 (ν(C_{arene}—H)); 2922 (ν(C—H)); 1947, 1881, 1854 (ν(C≡O)); 1557, 1530, 1500 (ν(C_{arene}—C_{arene})); 788, 677 (ω(C_{arene}—H)). MS, *m/z* (I_{rel} (%)): 348 $[M]^+$ (15), 347 $[M - H]^+$ (21), 292 $[M - 2\,CO]^+$ (7), 264 $[M - 3\,CO]^+$ (100), 246 $[M - 3\,CO - H_2O]^+$ (63), 168 $[M - 3\,CO - H_2O - C_5H_4N]^+$ (43), 52 $[Cr]^+$ (17). ^{1}H NMR, δ: 4.90 (d, 1 H, OCH_2, *J* = 14.5 Hz); 4.98 (d, 1 H, OCH_2, *J* = 14.5 Hz); 5.15 (t, 1 H, H_{arene}, *J* = 6.3 Hz); 5.56 (d, 1 H, H_{arene}, *J* = 6.7 Hz); 5.72 (td, 1 H, H_{arene}, *J* = 7.0 Hz, *J* = 1.2 Hz); 5.75 (s, 1 H, NCHO); 5.81 (d, 1 H, H_{arene}, *J* = 6.3 Hz); 6.52 (br.s, 1 H, H_N); 7.41 (ddd, 1 H, H_{py}, *J* = 5.5 Hz, *J* = 4.7 Hz, *J* = 0.8 Hz); 7.64 (d, 1 H, H_{py}, *J* = 7.8 Hz); 7.90 (td, 1 H, H_{py}, *J* = 7.8 Hz, *J* = 1.6 Hz); 8.57 (br.dd, 1 H, H_{py}, *J* = 4.7 Hz, *J* = 0.8 Hz).

X-ray diffraction study of complex *cis*-5i. Single crystals of compound *cis*-**5i** were obtained by crystallization from a mixture of hexane—ethyl acetate (4 : 1). The X-ray diffraction experiment was carried out on an Oxford Diffraction Gemini S diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, temperature 297(2) K, ω-scan technique). The crystallographic data and the main refinement parameters for compound *cis*-**5i** are given in Table 8. Analytical correction for absorption.[32] The primary fragment of the structure was found by direct methods. Parameters of the remaining atoms, including hydrogen atoms, were determined from the difference synthesis of the electron density and refined by the least-squares method based on F^2_{hkl}. The positions of hydrogen atoms were refined in the main cycle of the least squares method in the isotropic approximation. All calculations were performed using the SHELX[33] and WinGX[34] software package. The structure *cis*-**5i** was deposited with the Cambridge Crystallographic Data Center (CCDC 1986599) and is available at ccdc.cam.ac.uk/structures.

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