The synthesis of new 1,3-oxazolidines and 1,3-oxazinanes containing (η^6-arene)tricarbonylchromium group based on condensation between aldehydes and amino alcohols

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The condensation reactions of β- and γ-amino alcohols containing phenyl or (η^6-arene) tricarbonylchromium substituent with formaldehyde, acetaldehyde, benzaldehyde, and (η^6-benzaldehyde)tricarbonylchromium were studied. The resulting 1,3-oxazolidine and 1,3-oxazinane products were isolated in a pure form and identified by different physicochemical methods. The effect of (η^6-arene)tricarbonylchromium moiety on the reaction process was demonstrated.

Key words: (η^6-arene)tricarbonylchromium complexes, heterocyclic compounds, 1,3-oxazolidines, 1,3-oxazinanes, amino alcohols, aldehydes, condensation.

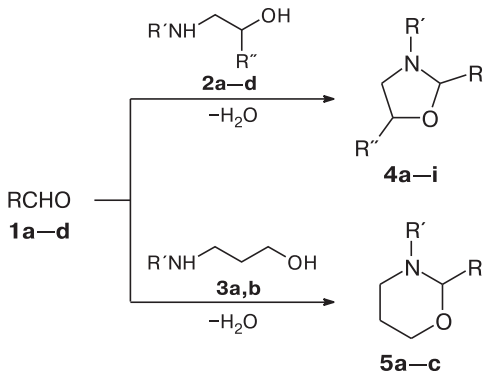
In recent times, a research area related to obtaining of complexes of transition metals with natural and biologically active compounds and other advanced products of fine organic synthesis is extensively developed. Opportunities for their practical applications as unique catalysts, organic semiconductors, linker compounds, and also materials for nonlinear optics are being explored.[1,2] To continue studies on the synthesis of heterocyclic compounds containing tricarbonylmetal groups,[3—8] we report in the present work on new 1,3-oxazolidines and 1,3-oxazinanes with (η^6-arene)-tricarbonylchromium moieties.

Results and Discussion

The condensation of carbonyl compounds with amino alcohols is the most common and widely used method to assemble heterocycles containing β-positioned nitrogen and oxygen atoms.[9,10] Thus, we aimed to obtain the above mentioned heterocycles by the condensation of aldehydes **1a—d** with β- (**2a—d**) or γ-amino alcohols (**3a**,**b**), wherein one or both reactants contained (arene)tricarbonylchromium moiety (Scheme 1). Reactions of β-amino alcohols led to 1,3-oxazolidines **4a—i**, while in case of γ-amino alcohols 1,3-oxazinanes **5a—c** were formed.

The selected aldehydes were formaldehyde (**1a**) (as paraformaldehyde), acetaldehyde (**1b**), benzaldehyde (**1c**), and (η^6-benzaldehyde)tricarbonylchromium (**1d**). The following compounds were used as amino alcohols:

Scheme 1



1: R = H (**a**); Me (**b**); Ph (**c**); $(OC)_3CrPh$ (**d**)
2: R′ = Ph, R″ = H (**a**), Me (**b**); R′ = $(OC)_3CrPh$, R″ = H (**c**), Me (**d**)
3: R′ = Ph (**a**), $(OC)_3CrPh$ (**b**)

Compound	R	R′	R″
4a	H	Ph	H
4b	Me	Ph	H
4c	Ph	Ph	H
4d	H	Ph	Me
4e	Me	Ph	Me
4f	H	$(OC)_3CrPh$	H
4g	Me	$(OC)_3CrPh$	H
4h	H	$(OC)_3CrPh$	Me
4i	Me	$(OC)_3CrPh$	Me
5a	H	Ph	—
5b	Ph	Ph	—
5c	H	$(OC)_3CrPh$	—

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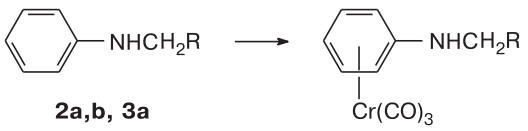
2-(*N*-phenylamino)ethanol (**2a**), 1-(*N*-phenylamino)-propan-2-ol (**2b**), their tricarbonylchromium complexes (compounds **2c** and **2d**, respectively), 3-(*N*-phenylamino)-propan-1-ol (**3a**), and its tricarbonylchromium complex **3b**.

Tricarbonylchromium complexes **2c**, **2d**, and **3b** were synthesized according to the Rausch[11] method *via* a thermal reaction of the corresponding arene with (triammine)(tricarbonyl)chromium (Scheme 2).

Scheme 2



2a,b, 3a **2c,d, 3b**

R = CH_2OH (**2a,c**); CH(Me)OH (**2b,d**); $(CH_2)_2OH$ (**3a,b**)

Reagents and conditions: $(NH_3)_3Cr(CO)_3$, dioxane, 120 °C.

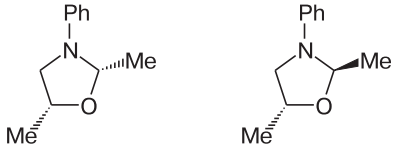
Complexes **2c**, **2d**, and **3b** were obtained for the first time as yellow-brown oils oxidizable in air. Their HPLC chromatograms contained only one peak (Table 1). In the IR spectra of compounds **2c**, **2d**, and **3b**, absorption bands characteristic of amino alcohols and also intense bands of valence vibrations of CO bonds in tricarbonylchromium moieties within 1853—1952 cm^{-1} range were present (see Table 1). Their mass spectra contained the expected molecular (see Table 1) and also fragment ions (see Experimental).

The nature of substituents in reacting molecules has a great influence on the yield of products and the outcome of the condensation.[12] Thus, the reactions of 2-(*N*-phenylamino)ethanol (**2a**) with formaldehyde (**1a**), acetaldehyde (**1b**), and benzaldehyde (**1c**) successfully proceed to give the corresponding disubstituted 1,3-oxazolidines[13,14] (compounds **4a**—**c**, see Scheme 1), while the reaction of amino alcohol **2a** with (η^6-benzaldehyde)tricarbonylchromium (**1d**) in toluene at 120 °C did not provide the expected heterocyclic product. Most likely, the introduction of bulky $Cr(CO)_3$ group into the benzaldehyde molecule was crucial to increase the steric hindrance affecting the possibility of condensation reaction.

Table 1. Some characteristics of arenetricarbonylchromium-containing amino alcohols **2c**, **2d**, and **3b**

Amino alcohol	HPLC, τ/min	Yield (%)	IR, ν(C≡O)/cm^{-1} (KBr)	MS EI, 70 eV, *m/z* (I_{rel} (%))
2c	4.9	54	1949, 1853	273 $[M]^+$ (65)
2d	5.1	65	1952, 1853	287 $[M]^+$ (20)
3b	5.0	33	1947, 1861	287 $[M]^+$ (2)

Similarly to amino alcohol **2a**, 1-(*N*-phenylamino)-propan-2-ol (**2b**) did not react with (η^6-benzaldehyde)-tricarbonylchromium (**1d**), but underwent condensation with aldehydes not containing the tricarbonylchromium moiety. Its reaction with formaldehyde (**1a**) provided individual product **4d**,[13] while a nonseparable mixture (1 : 1) of the two diastereomers (*cis*- and *trans*-**4e**) was formed in the case of acetaldehyde (**1b**).



cis-**4e** *trans*-**4e**

The next stage of this work was to investigate the condensation reactions of chromium-containing amino alcohols **2c,d** with aldehydes **1a—d** (see Scheme 1). All 1,3-oxazolidines obtained in these reactions were isolated pure by column chromatography with subsequent recrystallization and identified by HPLC, UV-Vis, IR, and ^{1}H-NMR spectroscopy, and mass spectrometry. The reaction conditions and some characteristics of the products are shown in Table 2.

The reaction of η^6-[(2-hydroxyethylamino)benzene]tricarbonylchromium (**2c**) with an excess of paraformaldehyde (**1a**) in toluene after 4 h at 120 °C resulted in two products, which were separated by column chromatography. The first one (the yield of 35%) was the expected 1,3-oxazolidine **4f**. The second product had a mass number of 315 for the molecular ion according to the mass spectrum. Its ^{1}H NMR spectrum contained signals from four methylene groups of the heterocyclic ring and a phenyltricarbonylchromium group. The acquired data allowed one to identify this substance as η^6-[(hexahydro-1,3,5-dioxazepin-5-yl)benzene]tricarbonylchromium (**6**) (Scheme 3).

Structure **6** was confirmed by the X-ray diffraction of single crystal (Fig. 1 and Table 3). Molecule **6** is based on a seven-membered heteroatomic cycle, which includes one nitrogen and two oxygen atoms. The lengths of N(1)—C (10)

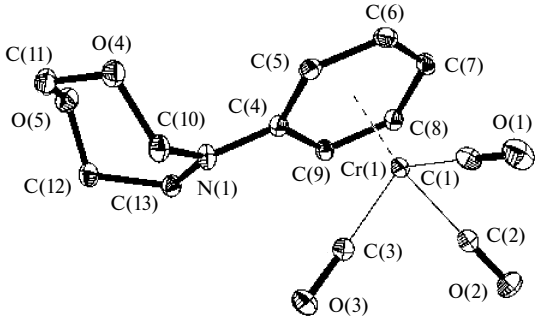


Fig. 1. Molecular structure of η^6-[(hexahydro-1,3,5-dioxazepin-5-yl)benzene]tricarbonylchromium (**6**). Thermal ellipsoids are given at 30% probability. Hydrogen atoms are omitted.

Table 2. Reactions of aldehydes **1a**—**d** with amino alcohols **2c**, **2d**, and **3a**,**b** and some characteristics of 1,3-oxazolidines **4f—i** and 1,3-oxazinanes **5a**—**c**[a]

Aldehyde	Amino alcohol	Product (%)	τ/h[b]	Yield[c]	M.p./°C	IR (KBr), ν(C≡O)/cm^{-1}	MS EI (70 eV), *m*/*z* (I_{rel} (%))
1a	**2c**	**4f**	4	35	127—128	1957, 1883	285 $[M]^+$ (7)
1b	**2c**	**4g**	6	31	70—71	1948, 1882	299 $[M]^+$ (10)
1c	**2c**	—[d]	6	—	—	—	—
1d	**2c**	—[d]	6	—	—	—	—
1a	**2d**	**4h**	6	30	131—132	1947, 1852	299 $[M]^+$ (2)
1b	**2d**	*cis*-**4i**	6	18	84—85	1938, 1855	313 $[M]^+$ (2)
		trans-**4i**		53	105—106	1935, 1849	313 $[M]^+$ (5)
1a	**3a**	**5a**	2	61	Oil	—	163 $[M]^+$ (64)
1c	**3a**	**5b**	4	28	23—24	—	239 $[M]^+$ (22)
1d	**3a**	—[d]	4	—	—	—	—
1c	**3b**	—[d]	4	—	—	—	—
1a	**3b**	**5c**	1.5	22	114—115	1948, 1848	299 $[M]^+$ (52)

[a] The reaction was carried out at 120 °C in all the cases.
[b] τ is reaction duration.
[c] Yield was calculated after isolation and purification of compounds.
[d] The desired products were not formed.

and N(1)—C(13) bonds were 1.444(3) and 1.470(3) Å, respectively. The hybridization of N(1) atom was close to sp^2: the C (4)—N(1)—C (10), C (4)—N(1)—C (13), and C (10)—N (1)—C (13) angles were 120.2(2), 120.1(2), and 118.9(2)°, respectively. The O—C distances belong to a narrow range of values, 1.409(3)—1.426(3) Å. The C(12)—C(13) bond length was 1.520(3) Å. The carbonyl groups of $Cr(CO)_3$ moiety had the *eclipsed* orientation relative to the phenyl ring. The Cr—C_{arene} and Cr—(CO) distances remained in the intervals of 2.206(2)—2.327(2) and 1.831(2)—1.842(2) Å, respectively (see Table 3). The C—Cr—C angles in the tricarbonylchromium moiety are close to 90° (87.66(9)—89.82(9)°).

The formation of byproduct **6** in that reaction may be explained by taking into account the stepwise mechanism of the condensation (see Scheme 3): the product of the addition of the amino alcohol to the carbonyl group of formaldehyde could either undergo an elimination of the water molecule providing 1,3-oxazolidine **4f** or participate in a competitive reaction with the next molecule of form-

Scheme 3

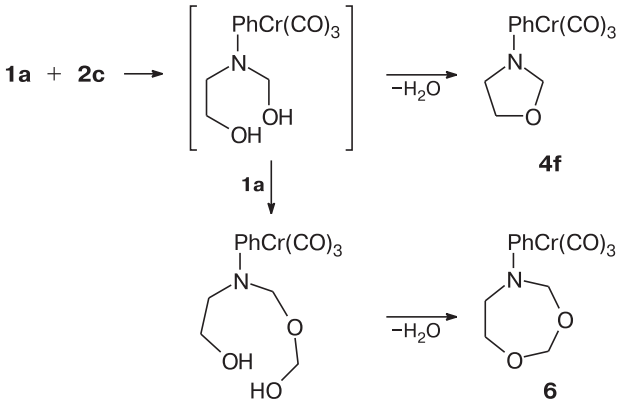


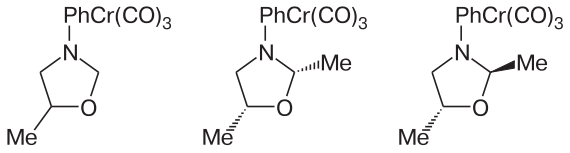
Table 3. Selected bond lengths (*d*) and angles (ω) in complex **6**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
N(1)—C(10)	1.444(3)	Cr(1)—C(9)	2.257(2)	C(4)—N(1)—C(10)	120.2(2)
N(1)—C(13)	1.470(3)	Cr(1)—C(1)	1.831(2)	C(4)—N(1)—C(13)	120.1(2)
C(12)—C(13)	1.520(3)	Cr(1)—C(2)	1.842(2)	C(10)—N(1)—C(13)	118.9(2)
O(5)—C(12)	1.423(3)	Cr(1)—C(3)	1.837(2)	N(1)—C(10)—O(4)	112.3(2)
O(5)—C(11)	1.409(3)	C(4)—C(9)	1.423(3)	C(11)—O(4)—C(10)	112.3(2)
O(4)—C(11)	1.415(3)	C(4)—C(5)	1.424(3)	O(4)—C(11)—O(5)	113.5(2)
O(4)—C(10)	1.426(3)	C(5)—C(6)	1.408(3)	C(11)—O(5)—C(12)	114.0(2)
Cr(1)—C(4)	2.327(2)	C(6)—C(7)	1.413(3)	O(5)—C(12)—C(13)	112.3(2)
Cr(1)—C(5)	2.245(2)	C(7)—C(8)	1.405(3)	N(1)—C(13)—C(12)	112.3(2)
Cr(1)—C(6)	2.206(2)	C(8)—C(9)	1.410(3)	C(3)—Cr(1)—C(1)	88.04(9)
Cr(1)—C(7)	2.235(2)			C(3)—Cr(1)—C(2)	89.82(9)
Cr(1)—C(8)	2.222(2)			C(1)—Cr(1)—C(2)	87.66(9)

aldehyde producing seven-membered product **6** *via* dehydration.

The reaction of compound **2c** with acetaldehyde (**1b**) in toluene at 120 °C after 6 h provided the expected η^6-[(2-methyl-1,3-oxazolidin-3-yl)benzene]tricarbonylchromium (**4g**) in the yield of 31%. Its IR spectrum contained intense bands corresponding to the vibrations of CO in the tricarbonylchromium moiety. In the mass spectrum of complex **4g**, the expected molecular ion (see Table 2) and characteristic fragment ions were observed (see Experimental). Its ^{1}H NMR spectrum contained a doublet at 1.40 ppm from the methyl substituent interacting with the proton at the C(2)H moiety, multiplets from protons of the heterocyclic ring at 3.34—3.45, 3.46—3.58, 3.98—4.11, 4.11—4.23 and 4.97—5.09 ppm, respectively, and also signals from the phenyltricarbonylchromium moiety (4.97—5.83 ppm).

Numerous attempts of carrying out the reactions of chromium-containing amino alcohol **2c** with benzaldehyde (**1c**) or its complex **1d** were unsuccessful apparently due to steric reasons. However, the reaction between η^6-{[(2-hydroxyprop-1-yl)amino]benzene}tricarbonylchromium (**2d**) and paraformaldehyde (**1a**) provided the desired 1,3-oxazolidine (**4h**). It was also possible to condense amino alcohol **2d** with acetaldehyde (**1b**), which afforded two diastereomers, *cis*- and *trans*-**4i**, in the ratio of 1 : 3.



4h *cis*-**4i** *trans*-**4i**

Complexes **4h**, *cis*-, and *trans*-**4i** were bright yellow crystals with sharp melting points, while physicochemical methods of analysis confirmed the purity and structure of these compounds (see Table 2 and Experimental). Compound **4h** was also characterized by X-ray diffraction of single crystal (Fig. 2 and Table 4). According to these data,

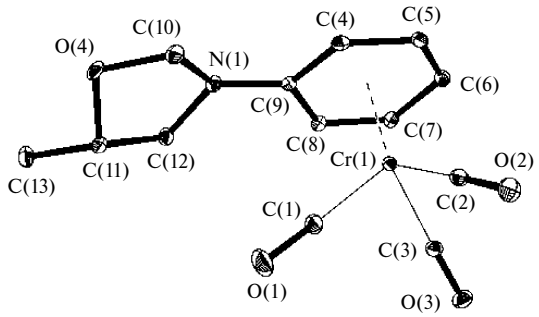


Fig. 2. Molecular structure of η^6-[(5-methyl-1,3-oxazolidin-3-yl)-benzene]tricarbonylchromium (**4h**). Thermal ellipsoids are given at 30% probability. Hydrogen atoms are omitted.

the oxazolidine cycle in the molecule of **4h** was disordered at two positions and had an *envelope* conformation. The oxygen atom deviated from the CNCC plane by 0.34—0.58(2) Å. The lengths of N—C and O—C bonds in the heterocyclic ring were in the intervals of 1.462(2)—1.467(2) Å and 1.389(3)—1.45(2) Å, respectively. The C(11)—C(13) distance was close to that in alkanes and equal to 1.505(4) Å. Same as in case of compound **6**, the carbonyl groups of $Cr(CO)_3$ moiety had the *eclipsed* orientation relative to the phenyl ring. The Cr—C_{arene} and Cr—(CO) distances were 2.203(2)—2.353(2) and 1.824(2)—1.842(2) Å, respectively (see Table 4).

Six-membered 1,3-oxazinanes **5a**—**c** were prepared in a similar way from γ-amino alcohols **3a**,**b** and aldehydes **1a**, **1c**, and **1d** (see Scheme 1). The reaction conditions and some characteristics of the products are shown in Table 2.

Thus, boiling of 3-(*N*-phenylamino)propan-1-ol (**3a**) with paraformaldehyde (**1a**) in toluene (for 2 h) provided 3-phenyl-1,3-oxazinane (**5a**) in the yield of 61%. 2,3-Diphenyl-1,3-oxazinane (**5b**) was similarly obtained from amino alcohol **3a** and benzaldehyde (**1c**) after 4 h in a significantly lower yield (28%). Thus, the condensation rate was noticeably decreased from formaldehyde to benzaldehyde. Attempts of carrying out the reactions between amino alcohol **3a** and (η^6-benzaldehyde)tricarbonylchro-

Table 4. Selected bond lengths (*d*) and angles (ω) in complex **4h**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Cr(1)—C(4)	2.257(2)	C(5)—C(6)	1.405(3)	C(9)—N(1)—C(10)	121.9(2)
Cr(1)—C(5)	2.208(2)	C(6)—C(7)	1.408(2)	C(9)—N(1)—C(12)	123.4(2)
Cr(1)—C(6)	2.221(2)	C(7)—C(8)	1.403(2)	C(12)—N(1)—C(10)	109.1(2)
Cr(1)—C(7)	2.203(2)	C(8)—C(9)	1.426(3)	O(4)—C(10)—N(1)	105.2(2)
Cr(1)—C(8)	2.262(2)	N(1)—C(10)	1.467(2)	C(10)—O(4)—C(11)	103.2(2)
Cr(1)—C(9)	2.353(2)	N(1)—C(12)	1.462(2)	O(4)—C(11)—C(12)	104.4(2)
Cr(1)—C(1)	1.838(2)	C(11)—C(12)	1.542(3)	N(1)—C(12)—C(11)	100.1(2)
Cr(1)—C(2)	1.824(2)	O(4)—C(11)	1.445(3)	C(3)—Cr(1)—C(1)	90.97(8)
Cr(1)—C(3)	1.842(2)	C(10)—O(4)	1.389(3)	C(3)—Cr(1)—C(2)	85.97(7)
C(4)—C(9)	1.421(2)	C(11)—C(13)	1.505(4)	C(1)—Cr(1)—C(2)	89.34(8)
C(4)—C(5)	1.412(2)				

mium (**1d**) and also between chromium-containing amino alcohol **3b** and aldehyde **1c** were unsuccessful apparently due to steric reasons.

(η^6-Arene)tricarbonylchromium derivative of 1,3-oxazinane **5c** was obtained *via* reaction of η^6-{[(3-hydroxyprop-1-yl)amino]benzene}tricarbonylchromium (**3b**) with paraformaldehyde (**1a**). Product **5c** was a yellow crystalline solid with a melting point of 114—115 °C. The absorption maximum in its UV-Vis spectrum at 318 nm and the intense bands in the region of valence vibrations of carbonyl at 1848 and 1948 cm^{-1} in the IR spectrum of compound **5c** confirmed the presence of the tricarbonylchromium moiety in its structure. The mass spectrum of 1,3-oxazinane **5c** contained the expected molecular ion with a mass number of 299. The ^1H NMR spectrum of complex **5c** contained a quintet from the $C(5)H_2$ moiety in the high field at 1.79 ppm, signals from the $C(4)H_2$ and $C(6)H_2$ moieties at 3.50 and 3.85 ppm, a signal from the methylene group between the two heteroatoms at 4.82 ppm, and signals from the aromatic ring coordinated with the chromium atom in the interval of 5.12—5.78 ppm.

The molecular structure of obtained heterocyclic compound **5c** was confirmed by the X-ray diffraction of single crystal (Fig. 3 and Table 5). According to the X-ray diffraction data, the oxazinane ring in compound **5c** was disordered at two positions similar to the oxazolidine cycle in **4h**. The heterocycle was having the *chair* conformation at each of the positions, however, with different orientations. At the first position, the O(4), C(10), C(12), and C(13) atoms belong to the same plane (the average deviation of the atoms from the plane did not exceed 0.03(2) Å), while the N(1) and C(11) atoms were shifted in different directions relative to the plane by 0.69(2) and 0.65(2) Å, respectively. At the other position, the N(1) and C(10)—C(12) atoms were almost in the same plane (the average deviation of the atoms from the plane was 0.11(2) Å), while the O(4) and C(13) atoms deviated by 0.66(2) and 0.31(2) Å, respectively. The O—C bond lengths in the oxazolidine ring were 1.42(2)—1.452(3) Å, and the N—C distances were 1.442(2)—1.460(2) Å. The angles inside the heterocyclic ring were close to tetrahedral ones

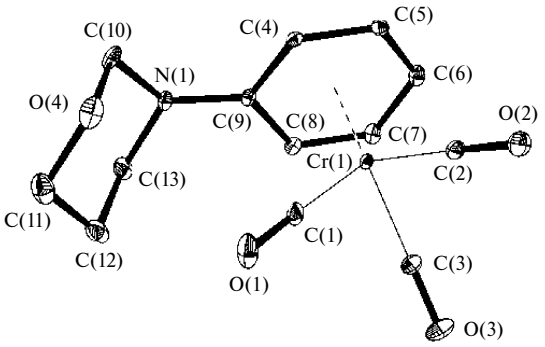


Fig. 3. Molecular structure of η^6-[(1,3-oxazinan-3-yl)benzene]-tricarbonylchromium (**5c**). Thermal ellipsoids are given at 30% probability. Hydrogen atoms are omitted.

and were in the range of 108.9(2)—111.3(2)° (see Table 5). The Cr—C_{arene} distances in **5c** were close to those in compounds **6** and **4h** and remained in the interval of 2.193(2)—2.389(2) Å, which is typical of arenetricarbonylchromium complexes.[15] Same as in case of compounds **6** and **4h**, the angles in $Cr(CO)_3$ moiety of **5c** were close to 90° (see Table 5). The $Cr(CO)_3$ moiety was located on the side of oxazinane ring with respect to the C(4)—C(9) plane of aromatic cycle.

To conclude, arenetricarbonylchromium-containing amino alcohols were obtained for the first time and applied for the synthesis of a number of representatives of new classes of (η^6-arene)tricarbonylchromium derivatives of 1,3-oxazolidines and 1,3-oxazinanes. The (η^6-phenyl) tricarbonylchromium derivatives of amino alcohols were very sensitive to increasing of the size of substituents in the carbonyl compound, thus affecting the condensation that proceeded easily only with the simplest aliphatic aldehydes (formaldehyde and acetaldehyde).

Experimental

The solvents were distilled over sodium metal at atmospheric pressure. Ethyl acetate was dried over calcium chloride and distilled.[16] The commercial paraformaldehyde and acetaldehyde from Sigma-

Table 5. Selected bond lengths (*d*) and angles (ω) in compound **5c**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Cr(1)—C(4)	2.246(2)	N(1)—C(13)	1.460(2)	C(9)—N(1)—C(10)	121.2(2)
Cr(1)—C(5)	2.193(2)	N(1)—C(10)	1.451(9)	C(9)—N(1)—C(13)	122.8(2)
Cr(1)—C(6)	2.215(2)	C(11)—C(12)	1.527(9)	C(10)—N(1)—C(13)	109.7(2)
Cr(1)—C(7)	2.202(2)	C(12)—C(13)	1.523(2)	O(4)—C(10)—N(1)	111.0(2)
Cr(1)—C(8)	2.261(2)	C(4)—C(9)	1.423(2)	O(4)—C(11)—C(12)	111.3(2)
Cr(1)—C(9)	2.389(2)	C(4)—C(5)	1.399(2)	C(10)—O(4)—C(11)	108.9(2)
Cr(1)—C(1)	1.820(2)	C(5)—C(6)	1.407(2)	C(11)—C(12)—C(13)	109.3(2)
Cr(1)—C(2)	1.829(2)	C(6)—C(7)	1.397(2)	N(1)—C(13)—C(12)	109.6(2)
Cr(1)—C(3)	1.820(2)	C(7)—C(8)	1.416(2)	C(3)—Cr(1)—C(1)	88.51(8)
O(4)—C(11)	1.452(3)	C(8)—C(9)	1.416(2)	C(3)—Cr(1)—C(2)	86.15(7)
O(4)—C(10)	1.426(2)			C(1)—Cr(1)—C(2)	87.63(8)

Aldrich were used. Benzaldehyde (**1c**) was purified by distillation under reduced pressure. (η^6-Benzaldehyde)tricarbonylchromium was prepared according to the known procedure.[17] 2-(*N*-Phenylamino)ethanol (**2a**), 1-(*N*-phenylamino)propan-2-ol (**2b**), and 3-(*N*-phenylamino)propan-1-ol (**3a**) were synthesized by arylation of the corresponding amino alcohols with iodobenzene in the presence of copper(I) chloride according to the published procedure.[18] (Triammine)(tricarbonyl)chromium $(NH_3)_3Cr(CO)_3$ was prepared according to the reported method.[11]

The condensation products were isolated and purified by column chromatography using Acros silica gel (0.035—0.070 mm) under argon, eluent was hexane—ethyl acetate. HPLC was carried out on a Knauer Smartline 5000 chromatograph equipped with a S 2600 UV diode matrix detector, a Diasfer-110-C16 column, 5 μm, 4.6×250 mm, the eluent was a mixture of acetonitrile—water (84 : 16) at the rate of eluent flow of 0.7 mL min^{-1}; UV spectra of eluates were recorded in the 200—500 nm range. IR spectra were recorded on an Infralyum FT-801 spectrometer in the range of 450—4000 cm^{-1} in KBr pellets. ^1H NMR spectra were recorded on an Agilent DD2 NMR 400NB spectrometer (400 MHz) in acetone-d_6. Mass spectrometric investigations were performed for *m/z* range of 70—500 Da with temperature programming from 50 to 450 °C at heating rate of 100 deg min^{-1}.

Synthesis of arenetricarbonylchromium-containing amino alcohols 2c, 2d, and 3b (general procedure). *N*-Phenylamino alcohol (**2a**, **2b**, or **3a**) (30.0 mmol), (triammine)(tricarbonyl) chromium (6.1 g, 32.6 mmol), and dioxane (50 mL) were placed in a previously deaerated and then filled with argon two-necked flask equipped with a reflux condenser and a gas burette with dibutyl phthalate. The reaction mixture was heated in the oil bath at 120 °C until evolution of ammonia (2.1 L) stopped, then the flask was cooled and filled with argon. The resulting reaction mixture was filtered through Al_2O_3 layer on a Schott filter under argon flow. The solvent was removed *in vacuo*. The product was obtained as a viscous oily liquid with yellow-brown color.

η^6-[(2-Hydroxyethylamino)benzene]tricarbonylchromium (2c). The yield was 54%, oil. HPLC: single peak, τ = 4.9 min. UV-Vis (MeCN, H_2O), λ/nm: 219, 314, 434. IR (KBr), ν/cm^{-1}: 3402 (ν(O—H, N—H)); 3098 (ν(C—H_{Ar})); 2936, 2875 (ν(C—H)); 1949, 1853 (ν(C≡O)); 1633, 1555 (ν(C_{Ar}—C_{Ar})); 758, 681, 633 (ω(C—H_{Ar})). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 273 $[M]^+$ (65), 217 $[M - 2\ CO]^+$ (16), 189 $[M - 3\ CO]^+$ (90), 143 $[M - 3\ CO - CH_2CH_2OH - H]^+$ (100), 137 $[M - Cr(CO)_3]^+$ (14), 52 $[Cr]^+$ (4).

η^6-{[(2-Hydroxyprop-1-yl)amino]benzene}tricarbonylchromium (2d). The yield was 65%, oil. HPLC: single peak, τ = 5.1 min. UV-Vis (MeCN, H_2O), λ/nm: 216, 317, 434. IR (KBr), ν/cm^{-1}: 3458, 3295 (ν(O—H, N—H)); 3106 (ν(C—H_{Ar})); 2953, 2872 (ν(C—H)); 1952, 1853 (ν(C≡O)); 1633, 1555 (ν(C_{Ar}—C_{Ar})); 784, 691 (ω(C—H_{Ar})). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 287 $[M]^+$ (20), 231 $[M - 2\ CO]^+$ (15), 203 $[M - 3\ CO]^+$ (80), 143 $[M - 3\ CO - CH_2CH(Me)OH - H]^+$ (100), $[Cr]^+$ (10).

η^6-{[(3-Hydroxyprop-1-yl)amino]benzene}tricarbonylchromium (3b). The yield was 33%, oil. HPLC: single peak, τ = 5.0 min. UV-Vis (MeCN, H_2O), λ/nm: 219, 314, 434. IR (KBr), ν/cm^{-1}: 3383 (ν(O—H, N—H)); 3052, 3024 (ν(C—H_{Ar})); 2937, 2877 (ν(C—H)); 1947, 1861 (ν(C≡O)); 1602, 1557, 1504 (ν(C_{Ar}—C_{Ar})); 752, 694, 635 (ω(C—H_{Ar})). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 287 $[M]^+$ (2), 203 $[M - 3\ CO]^+$ (10), 151 $[M - Cr(CO)_3]^+$ (35), 106 $[M - Cr(CO)_3 - (CH_2)_2OH]^+$ (100), 77 $[M - Cr(CO)_3 - NH(CH_2)_3OH]^+$ (12), 52 $[Cr]^+$ (56).

Condensation of aldehydes with amino alcohols in the sealed glass tube (general procedure). Amino alcohol, aldehyde, and toluene (20 mL) were placed into a 30 mL glass tube. The tube was deaerated in liquid nitrogen and sealed *in vacuo*, then heated in the oil bath at 120 °C. The tube was cooled down to room temperature and opened; the reaction mixture was concentrated *in vacuo*. The reaction products were isolated from the residue using column chromatography.

2,5-Dimethyl-3-phenyl-1,3-oxazolidine (4e), *cis*- and *trans*-isomers (1 : 1), was obtained according to the general procedure from amino alcohol (**2b**) (0.500 g, 3.3 mmol) and acetaldehyde (**1b**) (0.410 g, 9.3 mmol); the reaction duration was 6 h; the eluent was hexane—ethyl acetate (2 : 1). The yield was 58%, colorless viscous oil. HPLC: two peaks, τ = 8.9 and 9.1 min. UV-Vis (MeCN, H_2O), λ/nm: 202, 247, 434. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 177 $[M]^+$ (30), 162 $[M - Me]^+$ (25), 134 $[M - CH_2CHMe - H]^+$ (100), 104 $[M - MeCHOCH(Me) - H]^+$ (45), 91 $[M - MeCHOCH(Me)CH_2]^+$ (20), 77 $[M - MeCHOCH(Me)CH_2N]^+$ (30). ^1H NMR (acetone-d_6, 400 MHz), δ: 1.30—1.41 (m, 12 H, Me); 2.83, 3.14 (both t, 1 H each, $NC\underline{H}_2CH$, *J* = 8.6 Hz); 3.55 (dd, 1 H, $NC\underline{H}_2CH$, *J* = 8.6 Hz and *J* = 5.9 Hz); 3.64 (dd, 1 H, $NC\underline{H}_2CH$, *J* = 8.2 Hz and *J* = 5.9 Hz); 4.04—4.17, 4.45—4.56 (both m, 1 H each, $CH_2C\underline{H}O$); 5.19 (q, 1 H, NCHO, *J* = 5.1 Hz); 5.26 (q, 1 H, NCHO, *J* = 5.5 Hz); 6.58 (t, 4 H, *m*-H_{Ph}, *J* = 9.4 Hz); 6.63—6.73 (m, 2 H, *p*-H_{Ph}); 7.14—7.23 (m, 4 H, *o*-H_{Ph}).

Compounds 4f and 6 were obtained according to the general procedure from amino alcohol **2c** (0.140 g, 2.0 mmol) and paraformaldehyde **1a** (0.550 g). The reaction duration was 4 h; the eluent was hexane—ethyl acetate (3 : 1). Isolated crystalline products **4f** and **6** were recrystallized from the hexane—ethyl acetate mixture (4 : 1) and dried *in vacuo*.

η^6-[(1,3-Oxazolidin-3-yl)benzene]tricarbonylchromium (4f). The yield was 35%, yellow crystals, m.p. 127—128 °C. HPLC: single peak, τ = 6.0 min. UV-Vis (MeCN, H_2O), λ/nm: 219, 318, 435. IR (KBr), ν/cm^{-1}: 3082 (ν(C_{Ar}—H)); 2902, 2857 (ν(C—H)); 1957, 1883 (ν(C≡O)); 1607, 1553 (ν(C_{Ar}—C_{Ar})); 810, 775, 682, 671 (ω(C_{Ar}—H)). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 285 $[M]^+$ (7), 229 $[M - 2\ CO]^+$ (3), 201 $[M - 3\ CO]^+$ (100), 171 $[M - 3\ CO - CH_2O]^+$ (65), 105 $[M - Cr(CO)_3 - CH_2CH_2O]^+$ (50), 52 $[Cr]^+$ (87). ^1H NMR (acetone-d_6, 400 MHz), δ: 3.40 (t, 2 H, $NC\underline{H}_2CH_2$, *J* = 6.3 Hz); 4.13 (t, 2 H, $OC\underline{H}_2CH_2$, *J* = 6.3 Hz); 4.79 (s, 2 H, NCH_2O); 4.99 (d, 2 H, *o*-H_{Ph}, *J* = 6.7 Hz); 5.06 (t, 1 H, *p*-H_{Ph}, *J* = 6.3 Hz); 5.83 (t, 2 H, *m*-H_{Ph}, *J* = 6.3 Hz).

η^6-[(Hexahydro-1,3,5-dioxazepin-5-yl)benzene]tricarbonylchromium (6). The yield was 30%, yellow crystals, m.p. 111—112 °C. HPLC: single peak, τ = 6.7 min. UV-Vis (MeCN, H_2O), λ/nm: 218, 318, 434. IR (KBr), ν/cm^{-1}: 3013 (ν(C_{Ar}—H)); 2865 (ν(C—H)); 1938, 1846 (ν(C≡O)); 1631, 1607, 1541 (ν(C_{Ar}—C_{Ar})); 846, 756, 676, 633 (ω(C_{Ar}—H)). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 315 $[M]^+$ (10), 231 $[M - 3\ CO]^+$ (8), 201 $[M - 3\ CO - CH_2O]^+$ (80), 171 $[M - 3\ CO - CH_2OCH_2O]^+$ (50), 149 $[M - Cr(CO)_3 - CH_2O]^+$ (90), 143 $[M - 3\ CO - CH_2CH_2OCH_2OCH_2]^+$ (55), 105 $[M - Cr(CO)_3 - CH_2OCH_2OCH_2]^+$ (100), 52 $[Cr]^+$ (83). ^1H NMR (acetone-d_6, 400 MHz), δ: 3.55, 3.98 (both t, 2 H each, $NC\underline{H}_2CH_2$, $OC\underline{H}_2CH_2$, *J* = 5.1 Hz); 4.83, 4.97 (both s, 2 H each, NCH_2O, OCH_2O); 5.10 (t, 1 H, *p*-H_{Ph}, *J* = 6.3 Hz); 5.38 (d, 2 H, *o*-H_{Ph}, *J* = 7.0 Hz); 5.81 (t, 2 H, *m*-H_{Ph}, *J* = 7.0 Hz).

η^6-[(2-Methyl-1,3-oxazolidin-3-yl)benzene]tricarbonylchromium (4g) was obtained according to the general procedure from amino alcohol **2c** (0.140 g, 0.5 mmol) and acetaldehyde (**1b**) (0.550 g, 12.5 mmol). The reaction duration was 6 h; the eluent was hexane—ethyl acetate (3 : 1). The product was recrystallized from hexane—ethyl acetate mixture (6 : 1) and dried *in vacuo*. The yield was 31%, yellow crystals, m.p. 70—71 °C. HPLC:

single peak, τ = 7.3 min. UV-Vis (MeCN, H_2O), λ/nm: 218, 312, 435. IR (KBr), ν/cm^{-1}: 3088 (ν(C_{Ar}—H)); 2851, 2926 (ν(C—H)); 1948, 1882 (ν(C≡O)); 1603 (ν(C_{Ar}—C_{Ar})); 815, 667, 632 (ω(C_{Ar}—H)). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 299 $[M]^+$ (10), 243 $[M - 2\ CO]^+$ (10), 215 $[M - 3\ CO]^+$ (48), 185 $[M - 3\ CO - CH_2O]^+$ (100), 171 $[M - 3\ CO - CH_2CH_2O]^+$ (10), 143 $[M - 3\ CO - CH_2CH_2OCHMe]^+$ (28), 77 $[M - Cr(CO)_3 - CH_2CH_2OCH(Me)N]^+$ (10), $[Cr]^+$ (11). ^{1}H NMR (acetone-d_6, 400 MHz), δ: 1.40 (d, 3 H, Me, *J* = 5.1 Hz); 3.34—3.45, 3.46—3.58, 3.98—4.11, 4.11—4.23 (all m, 1 H each, NCH_2, NCH_2, OCH_2, OCH_2); 4.97—5.09 (m, 3 H, C<u>H</u>Me, *m*-H_{Ph}); 5.15 (dd, 1 H, *p*-H_{Ph}, *J* = 10.2 Hz and *J* = 4.7 Hz); 5.83 (t, 2 H, *o*-H_{Ph}, *J* = 5.5 Hz).

η^6-[(5-Methyl-1,3-oxazolidin-3-yl)benzene]tricarbonylchromium (4h) was obtained according to the general procedure from amino alcohol **2d** (0.170 g, 0.6 mmol) and paraformaldehyde (**1a**) (0.580 g). The reaction duration was 6 h; the eluent was hexane—ethyl acetate (4 : 1). The product was recrystallized from hexane—ethyl acetate mixture (4 : 1) and dried *in vacuo*. The yield was 30%, yellow crystals, m.p. 131—132 °C. HPLC: single peak, τ = 7.3 min. UV-Vis (MeCN, H_2O), λ/nm: 219, 316, 432. IR (KBr), ν/cm^{-1}: 3048 (ν(C_{Ar}—H)); 2995 (ν(C—H)); 1947, 1852 (ν(C≡O)); 1552 (ν(C_{Ar}—C_{Ar})); 825, 674 (ω(C_{Ar}—H)). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 299 $[M]^+$ (2), 243 $[M - 2\ CO]^+$ (4), 215 $[M - 3\ CO]^+$ (20), 171 $[M - 3\ CO - MeCHO]^+$ (100), 143 $[M - 3\ CO - CH_2CH(Me)OCH_2]^+$ (23), $[Cr]^+$ (29). ^{1}H NMR (acetone-d_6, 400 MHz), δ: 1.35 (d, 3 H, Me, *J* = 5.9 Hz); 2.93 (t, 1 H, NC<u>H</u>$_2$CH, *J* = 8.2 Hz); 3.53 (dd, 1 H, NC<u>H</u>$_2$CH, *J* = 8.2 Hz and *J* = 6.3 Hz); 4.31 (hex, 1 H, CH, *J* = 6.3 Hz); 4.72 (d, 1 H, NCH_2O, *J* = 2.4 Hz); 4.89—5.00 (m, 3 H, NCH_2O, *o*-H_{Ph}); 5.04 (t, 1 H, *p*-H_{Ph}, *J* = 5.9 Hz); 5.82 (t, 2 H, *m*-H_{Ph}, *J* = 5.9 Hz).

Isomers of complex 4i were obtained according to the general procedure from amino alcohol **2d** (1.200 g, 4.2 mmol) and acetaldehyde (**1b**) (1.7600 g, 40.0 mmol). The reaction duration was 6 h; the eluent was hexane—ethyl acetate (4 : 1). The isomers were separated by column chromatography on silica gel using the mixture of hexane—ethyl acetate as the eluent. The *cis*-isomer *cis*-**4i** was eluted first, while the *trans*-isomer *trans*-**4i** was the second one. The pure isomers were recrystallized from hexane—ethyl acetate mixture (6 : 1) and dried *in vacuo*.

***cis*-η^6-[(2,5-Dimethyl-1,3-oxazolidin-3-yl)benzene]tricarbonylchromium (*cis*-4i).** The yield was 18%, yellow crystals, m.p. 84—85 °C. HPLC: single peak, τ = 8.4 min. UV-Vis (MeCN, H_2O), λ/nm: 219, 317, 432. IR (KBr), ν/cm^{-1}: 3052 (ν(C_{Ar}—H)); 2894 (ν(C—H)); 1938, 1855 (ν(C≡O)); 1546 (ν(C_{Ar}—C_{Ar})); 789, 669 (ω(C_{Ar}—H)). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 313 $[M]^+$ (2), 257 $[M - 2\ CO]^+$ (2), 229 $[M - 3\ CO]^+$ (25), 185 $[M - 3\ CO - MeCHO]^+$ (100), 143 $[M - 3\ CO - MeCHOCH(Me)CH_2]^+$ (38), 77 $[M - Cr(CO)_3 - MeCHOCH(Me)CH_2N]^+$ (12), 52 $[Cr]^+$ (22). ^{1}H NMR (acetone-d_6, 400 MHz), δ: 1.32 (d, 3 H, Me, *J* = 5.9 Hz); 1.39 (d, 3 H, Me, *J* = 5.5 Hz); 2.84—2.88 (m, 1 H, CH_2); 3.63 (dd, 1 H, CH_2, *J* = 8.6 Hz and *J* = 5.5 Hz); 4.45—4.54 (m, 1 H, CH_2C<u>H</u>Me); 4.98 (d, 2 H, *o*-H_{Ph}, *J* = 7.0 Hz); 5.04 (t, 1 H, *p*-H_{Ph}, *J* = 6.3 Hz); 5.25 (q, 1 H, NC<u>H</u>(Me)O, *J* = 5.5 Hz); 5.80—5.83 (t, 2 H, *m*-H_{Ph}, *J* = 6.3 Hz).

***trans*-η^6-[(2,5-Dimethyl-1,3-oxazolidin-3-yl)benzene]tricarbonylchromium (*trans*-4i).** The yield was 53%, m.p. 105—106 °C. HPLC: single peak, τ = 7.8 min. UV-Vis (MeCN, H_2O), λ/nm: 219, 317, 431. IR (KBr), ν/cm^{-1}: 3040 (ν(C_{Ar}—H)); 2921, 2852 (ν(C—H)); 1935, 1849 (ν(C≡O)); 1630, 1547 (ν(C_{Ar}—C_{Ar})); 679, 799 (ω(C_{Ar}—H)). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 313 $[M]^+$ (5), 257 $[M - 2\ CO]^+$ (5), 229 $[M - 3\ CO]^+$ (30), 185 $[M - 3\ CO - MeCHO]^+$ (100), 143 $[M - 3\ CO - MeCHOCH(Me)CH_2]^+$ (31), 77 $[M - Cr(CO)_3 - MeCHOCH(Me)CH_2N]^+$ (12), 52 $[Cr]^+$ (30). ^{1}H NMR (acetone-d_6, 400 MHz), δ: 1.33 (d, 3 H,

Table 6. Crystallographic data, parameters used in the X-ray diffraction experiments and refinements for complexes **6**, **4h**, and **5c**

Parameter	**6**	**4h**	**5c**
Formula	$C_{13}H_{13}CrNO_5$	$C_{13}H_{13}CrNO_4$	$C_{13}H_{13}CrNO_4$
Molecular weight	315.24	299.24	299.24
Space group	$P\bar{1}$	$Pna2_1$	$P2_1/n$
a/Å	7.5793(6)	16.3065(5)	7.2925(6)
b/Å	8.5955(6)	7.4539(2)	10.6982(9)
c/Å	10.6299(8)	10.1594(3)	15.9011(13)
α/deg	97.1450(11)	90	90
β/deg	101.3102(11)	90	102.2830(10)
γ/deg	104.7299(11)	90	90
V/Å^3	645.57(8)	1234.84(6)	1212.15(17)
Z	2	4	4
d_{calc}/mg mm^{-3}	1.622	1.610	1.640
μ/mm^{-1}	0.905	0.935	0.953
Scan range, θ/deg	1.99—28.70	2.30—35.62	2.32—35.62
Number of reflections			
measured	6841	23477	22432
independent with $I > 2\sigma(I)$	3010	5479	4739
R_{int}	0.0163	0.0240	0.0435
GOOF (F^2)	0.999	1.002	1.066
R_1 ($I > 2\sigma(I)$)	0.0397	0.0265	0.0491
ωR_2 (all data)	0.1012	0.0646	0.1104
Residual electron density (max/min)/e Å^{-3}	0.60/−0.30	0.37/−0.53	0.65/−0.94

Me, J = 5.9 Hz); 1.44 (d, 3 H, Me, J = 4.7 Hz); 3.02—3.13 (m, 1 H, CH_2); 3.31 (d, 1 H, CH_2, J = 5.5 Hz); 3.55—3.62 (m, 1 H, $CH_2C\underline{H}Me$); 4.10—4.20 (m, 1 H, $NC\underline{H}(Me)O$); 4.93 (d, 1 H, o-H_{Ph}, J = 7.0 Hz); 5.00—5.11 (m, 2 H, o-H_{Ph}, p-H_{Ph}); 5.84 (t, 2 H, m-H_{Ph}, J = 7.0 Hz).

3-Phenyl-1,3-oxazinane (5a) was obtained according to the general procedure from amino alcohol **3a** (3.00 g, 19.9 mmol) and paraformaldehyde (**1a**) (2.460 g). The reaction duration was 2 h; the eluent was hexane—ethyl acetate (4 : 1). The yield was 61%, oil. HPLC: single peak, τ = 6.5 min. UV-Vis (MeCN, H_2O), λ/nm: 202, 247, 282. IR (KBr), ν/cm^{-1}: 3038, 3070 ($\nu(C_{Ar}—H)$); 2952, 2858 ($\nu(C—H)$); 1599 ($\nu(C_{Ar}—C_{Ar})$); 835, 737, 694 ($\omega(C_{Ar}—H)$). MS (EI, 70 eV), m/z (I_{rel} (%)): 163 $[M]^+$ (64), 162 $[M - H]^+$ (87), 134 $[M - (CH_2)_2 - H]^+$ (30), 120 $[M - (CH_2)_3 - H]^+$ (13), 105 $[M - O(CH_2)_3]^+$ (100), 104 $[M - O(CH_2)_3 - H]^+$ (71), 91 $[M - CH_2O(CH_2)_3]^+$ (9), 77 $[M - NCH_2O(CH_2)_3]^+$ (27). ^{1}H NMR (acetone-d_6, 400 MHz), δ: 1.36 (quint, 2 H, $CH_2C\underline{H}_2CH_2$, J = 5.5 Hz); 3.56 (t, 2 H, $NC\underline{H}_2CH_2$, J = 5.5 Hz); 3.89 (t, 2 H, $NC\underline{H}_2CH_2$, J = 5.5 Hz); 4.90 (s, 2 H, NCH_2O); 6.88 (t, 1 H, p-H_{Ph}, J = 7.4 Hz); 7.09 (d, 2 H, o-H_{Ph}, J = 8.2 Hz); 7.28 (t, 2 H, m-H_{Ph}, J = 8.2 Hz).

2,3-Diphenyl-1,3-oxazinane (5b). Benzaldehyde (**1c**) (2.440 g, 23.0 mmol), 3-(*N*-phenylamino)propan-1-ol (**3a**) (3.410 g, 22.6 mmol), and toluene (35 mL) were placed into a round-bottomed one-necked flask equipped with a Dean—Stark trap. The reaction mixture was heated in the oil bath at 120 °C for 4 h, then cooled down to room temperature, and concentrated *in vacuo*. The reaction product **5b** was isolated from the residue by column chromatography (eluent was hexane—ethyl acetate, 4 : 1), recrystallized from hexane—ethyl acetate mixture (4 : 1) and dried *in vacuo*. The yield was 28%, m.p. 23—24 °C. HPLC: single peak, τ = 12.2 min. UV-Vis (MeCN, H_2O), λ/nm: 205, 248. IR (KBr), ν/cm^{-1}: 3058, 3032 ($\nu(C—H_{Ar})$); 2950, 2922, 2850 ($\nu(C—H)$); 1598 ($\nu(C_{Ar}—C_{Ar})$); 757, 730, 698 ($\omega(C—H_{Ar})$). MS (EI, 70 eV), m/z (I_{rel} (%)): 239 $[M]^+$ (22), 181 $[M - O(CH_2)_3]^+$ (20), 162 $[M - Ph]^+$ (47), 132 $[M - PhCHO - H]$ (25), 105 $[M - PhCHO(CH_2)_2]^+$ (100), 104 $[M - PhCHO(CH_2)_2 - H]^+$ (72), 91 $[M - PhCHO(CH_2)_3]$ (13), 77 $[M - PhCHO(CH_2)_3N]^+$ (25). ^{1}H NMR (acetone-d_6, 400 MHz), δ: 1.55—1.69, 1.69—1.82, 3.49—3.60, 3.81—3.96, 3.61—3.71, 4.00—4.16 (all m, 1 H each, $CH_2C\underline{H}_2CH_2$, $CH_2C\underline{H}_2CH_2$, NCH_2, NCH_2, OCH_2, OCH_2); 6.02 (s, 1 H, $C\underline{H}Ph$); 6.84 (t, 1 H, p-H_{PhN}, J = 7.0 Hz); 7.08—7.21 (m, 4 H, o,m-H_{PhN}); 7.25 (t, 1 H, p-H_{Ph}, J = 7.0 Hz); 7.33 (t, 2 H, m-H_{Ph}, J = 7.0 Hz); 7.48 (d, 2 H, o-H_{Ph}, J = 7.4 Hz).

η^6-[(1,3-Oxazinan-3-yl)benzene]tricarbonylchromium (5c) was obtained according to the general procedure from amino alcohol **3b** (2.530 g, 8.8 mmol), paraformaldehyde (**1a**) (1.720 g), and toluene (35 mL) in a 50 mL glass tube. The reaction duration was 1.5 h; the eluent was hexane—ethyl acetate (2 : 1). The product **5c** was recrystallized from hexane—ethyl acetate mixture (4 : 1) and dried *in vacuo*. The yield was 22%, m.p. 114—115 °C. HPLC: single peak, τ = 6.6 min. UV-Vis (MeCN, H_2O), λ/nm: 219, 318, 436. IR (KBr), ν/cm^{-1}: 3113 ($\nu(C_{Ar}—H)$; 2919, 2854 ($\nu(C—H)$); 1948, 1848 ($\nu(C\equiv O)$); 1613, 1540 ($\nu(C_{Ar}—C_{Ar})$); 677, 630 ($\omega(C_{Ar}—H)$). MS (EI, 70 eV), m/z (I_{rel} (%)): 299 $[M]^+$ (52), 243 $[M - 2\,CO]^+$ (29), 215 $[M - 3\,CO]^+$ (76), 187 $[M - 3\,CO - (CH_2)_2]^+$ (32), 171 $[M - 3\,CO - (CH_2)_3 - 2\,H]^+$ (28), 157 $[M - 3\,CO - (CH_2)_3O]^+$ (86), 121 $[M - Cr(CO)_3 - (CH_2)_3]^+$ (12), 120 $[M - Cr(CO)_3 - (CH_2)_3 - H]^+$ (100), 52 $[Cr]^+$ (14). ^{1}H NMR (acetone-d_6, 400 MHz), δ: 1.79 (quint, 2 H, $CH_2C\underline{H}_2CH_2$, J = 5.5 Hz); 3.50 (t, 2 H, $NC\underline{H}_2CH_2$, J = 5.5 Hz); 3.85 (t, 2 H, $OC\underline{H}_2CH_2$, J = 5.5 Hz); 4.82 (s, 2 H, NCH_2O); 5.12 (t, 1 H, p-H_{Ph}, J = 6.3 Hz); 5.40 (d, 2 H, o-H_{Ph}, J = 6.7 Hz); 5.78 (t, 2 H, m-H_{Ph}, J = 6.3 Hz).

X-ray analysis. Crystals for the X-ray diffraction studies were obtained *via* crystallization from the hexane—ethyl acetate mixtures of 4 : 1 (**6**, **5c**) and 6 : 1 (**4h**). The intensities of reflections were measured using Bruker Smart Apex (**6**) and Bruker D8 Quest (**4h**, **5c**) diffractometers (Mo-Kα-radiation, λ = 0.71073 Å, ω-scanning, T = 100 K). The integration of experimental intensity arrays and taking into account the absorption were performed using SMART, APEX2,[19] and SADABS[20] software packages. The structures were solved by a direct method and refined by the full-matrix least squares method on F^2_{hkl} with anisotropic thermal parameters for all the non-hydrogen atoms. Hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. The calculations were performed using the SHELX[21] software package.

Table 6 shows the crystallographic data for compounds **6**, **4h**, and **5c** and parameters used in the X-ray diffraction experiments. The structures were deposited in the Cambridge Crystallographic Data Centre with the following CCDCs: 1579170 (**6**), 1579168 (**4h**), and 1579169 (**5c**); they are available online at ccdc.cam.ac.uk/structures.

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