Reaction of phenyl-containing N-substituted 1,3-oxazolidines and 1,3-oxazinanes with triammine(tricarbonyl)chromium

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New heterocyclic compounds with phenyl chromium tricarbonyl substituents were synthesized by the reaction of triammine(tricarbonyl)chromium with phenyl-substituted 1,3-oxazacycloalkanes bearing acetyl, *tert*-butyloxycarbonyl, or phenyl group at the nitrogen atom. The resulting compounds were isolated in the individual state and characterized by physicochemical methods of analysis.

Key words: (η^6-arene)tricarbonylchromium, heterocyclic compounds, 1,3-oxazolidines, 1,3-oxazinanes, 1,3-oxazacycloalcanes, triammine(tricarbonyl)chromium.

The synthesis of 1,3-oxazacycloalkanes is of interest because of their widespread use as biologically active compounds, linkers, as well as chiral ligands necessary for the design of molecules of various important organic products.[1] Transition metal complexes containing 1,3-oxazacycloalkane ligands in their coordination sphere are also promising agents of fine organic synthesis.[2—5] Continuing our works on the synthesis of (η^6-arene)chromium tricarbonyl complexes with N,O-heterocyclic rings,[6—11] we obtained new metal-containing products by the insertion of a chromium tricarbonyl group into the phenyl substituents of 1,3-oxazolidine and 1,3-oxazinane derivatives.

Results and Discussion

The simplest and most convenient method for the introduction of a $Cr(CO)_3$ group into arenes is a direct reaction of these arenes with chromium hexacarbonyl or its derivatives, for example, triammine(tricarbonyl)chromium $(NH_3)_3Cr(CO)_3$ (see Ref. 12). At the same time, for heterocycles with a lone electron pair of heteroatoms available for interaction, the formation of σ- rather than π-complexes[13] seems to be very likely in the reactions with transition metal complexes, which in the case of 1,3-oxazacycloalkanes can lead to the heterocycle opening.[1,2,5] We assumed that, if the nitrogen atom is protected with a suitable blocking group, the synthesis of (η^6-arene)chromium tricarbonyl complexes can be accomplished with the heterocycle remaining intact. Acetyl and *tert*-butoxycarbonyl were chosen as such groups. Acetic anhydride[14] and di-*tert*-butyl dicarbonate[15] were used for their introduction into the *NH*-heterocycles **1a,b** (Scheme 1). Compounds **3a—c** were obtained as the reaction products. It is obvious that the nucleophilicity of their nitrogen atom is reduced compared to the starting compounds **1a,b** due to the involvement of its electron pair into the π,p-conjugation, as well as due to the steric factors.

1,3-Oxazacycloalkanes **3a—c** were further used in the reactions with triammine(tricarbonyl)chromium (**4**) to obtain (η^6-arene)chromium tricarbonyl derivatives **5a—c** (see Scheme 1). The reactions were carried out in refluxing dioxane, the progress was monitored by tracking the amount of released ammonia. Compounds **5a—c** were isolated by column chromatography and purified by recrystallization. They were yellow crystalline substances, their purity and structure were confirmed by HPLC, UV, IR, ^{1}H NMR spectroscopy, and mass spectrometry (Table 1). The HPLC chromatogram of each of compounds **5a—c** exhibited one peak. In their IR spectra, the strong bands of stretching vibrations of the CO bonds of chromium tricarbonyl fragments were observed in the range of 1857—1971 cm^{-1}, the expected molecular and fragment ions were present in the mass spectra (see Table 1).

It is known that when the nitrogen atom bears unsaturated groups, for example, a phenyl substituent, the ability for coordination at the heteroatom for these compounds sharply drops due to the π,p-conjugation.[13] Therefore, it can be assumed that the reaction of *N*-phenyl-1,3-

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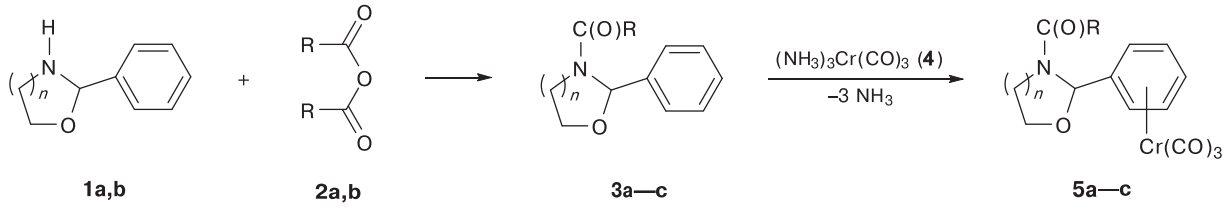
Scheme 1

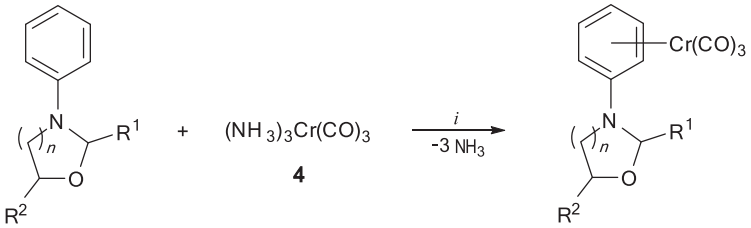


1a,b **2a,b** **3a—c** **5a—c**

1: n = 1 (**a**), 2 (**b**);
2: R = Me (**a**), OBu^t (**b**)
3, 5: n = 1, R = Me (**a**), OBu^t (**b**); n = 2, R = Me (**c**).

oxazacycloalkanes with triammine(tricarbonyl)chromium (**4**) should lead to the desired complexes. In fact, the reactions of compounds **6a—h** with an equimolar amount of **4** in dioxane afford products **7a—i** with the Ph[Cr(CO)$_3$] group at the nitrogen atom (Scheme 2). In the case of 2,3-diphenyl derivatives **6f,g**, the complexation selectively proceeded at the "aniline" benzene ring to give mononuclear complexes **7f,g**. The compounds were isolated in the individual state and characterized by physicochemical methods of analysis (see Table 1).

Scheme 2



6a—h **7a—i**

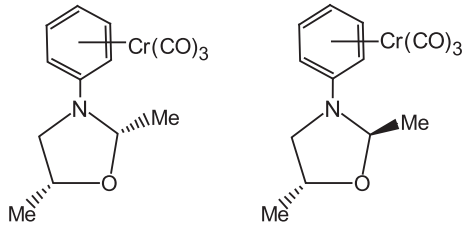
6, 7	n	R^1	R^2	**6, 7**	n	R^1	R^2	**6, 7**	n	R^1	R^2	**6, 7**	n	R^1	R^2
a	1	H	H	**c**	1	H	Me	**e**	1	Et	H	**g**	2	Ph	H
b	1	Me	H	**d**	1	Me	Me	**f**	1	Ph	H	**h**	2	H	H

7i: n = 1, R^1 = Ph[Cr(CO)$_3$], R^2 = H
i. Dioxane.

Table 1. Some characteristics of the complexes **5a—c** and **7a—i**

Compound	M.p./°C	Yield (%)	IR (KBr), ν(C≡O)/cm^{-1}	EI MS (70 eV), m/z (I_{rel} (%))
5a	90—91	73	1948, 1857	327 [M]$^+$ (1)
5b	128—129	71	1902, 1873	385 [M]$^+$ (1)
5c	110—111	53	1971, 1894	341 [M]$^+$ (1)
7a	127—128	44	1957, 1883	285 [M]$^+$ (7)
7b	70—71	31	1948, 1882	299 [M]$^+$ (10)
7c	131—132	32	1947, 1852	299 [M]$^+$ (2)
cis-**7d**	84—85	24	1938, 1855	313 [M]$^+$ (2)
trans-**7d**	105—106	27	1935, 1849	313 [M]$^+$ (5)
7e	111—112	30	1942, 1869	313 [M]$^+$ (29)
7f	99—100	40	1948, 1855	361 [M]$^+$ (5)
7g	116—117	19	1944, 1856	375 [M]$^+$ (2)
7h	114—115	22	1948, 1848	299 [M]$^+$ (52)
7i	167—168	35	1956, 1873	497 [M]$^+$ (7)

The starting dimethyl-substituted substrate **6d** was a mixture of *cis*- and *trans*- isomers.[11] Therefore, the reaction of this mixture with **4** led to a mixture of *cis*-/*trans*-**7d**, which was separated by column chromatography.



cis-**7d** *trans*-**7d**

Note that compounds **7a—d** and **7h** were obtained by us earlier by the condensation of chromium tricarbonyl complexes of phenyl-substituted amino alcohols with the corresponding aldehydes.[11] However, attempted synthesis of compounds **7f,g** by this method was unsuccessful,[11] probably, for steric reasons, while the reactions of **6f,g** with **4** gave the desired products.

The reaction of 2,3-diphenyl-1,3-oxazinane (**6f**) with **4** at a 1 : 1 ratio of reactants after evaporation of the solvent and recrystallization of the residue from a hexane—ethyl acetate solvent mixture (4 : 1) gave the individual product **7f** in 40% yield (HPLC data). Its IR spectrum exhibited two strong absorption bands at 1848 and 1955 cm^{-1} characteristic of the stretching vibrations of the CO groups in the chromium tricarbonyl fragment. The mass spectrum exhibited the peaks corresponding to the molecular ion with *m*/*z* 361 $[M]^+$ (5) and fragment ions with *m*/*z* 277 $[M - 3\ CO]^+$ (72), 247 $[M - 3\ CO - CH_2O]^+$ (100),

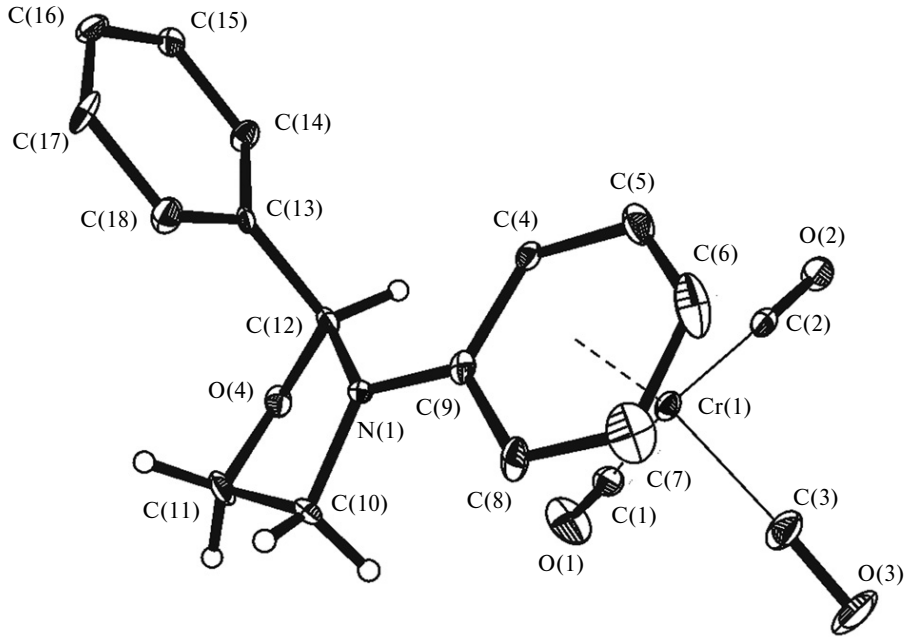


Fig. 1. Molecular structure of η^6-[(2-phenyl-1,3-oxazolidin-3-yl)benzene]chromium tricarbonyl (**7f**). Thermal ellipsoids are given with a 30% probability. Hydrogen atoms of phenyl substituents are omitted.

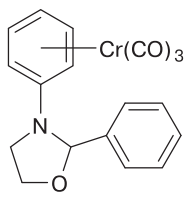
Table 2. Principal bond lengths (*d*) and bond angles (ω) in complex **7f**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Cr(1) —C(1)	1.799(9)	N(1)—C(9)	1.363(9)	C(1)—Cr(1)—C(3)	87.8(5)
Cr(1)—C(2)	1.844(8)	N(1)—C(10)	1.454(9)	C(1)—Cr(1)—C(2)	90.1(4)
Cr(1)—C(3)	1.839(8)	N(1)—C(12)	1.473(9)	C(3)—Cr(1)—C(2)	91.1(4)
Cr(1)—C(4)	2.249(7)	C(10)—C(11)	1.53(2)	C(9)—N(1)—C(10)	122.2(6)
Cr(1)—C(5)	2.210(8)	O(4)—C(11)	1.44(2)	C(9)—N(1)—C(12)	122.8(6)
Cr(1)—C(6)	2.224(9)	O(4)—C(12)	1.425(8)	C(10)—N(1)—C(12)	111.0(6)
Cr(1)—C(7)	2.177(9)	C(12)—C(13)	1.52(2)	O(4)—C(11)—C(10)	103.7(6)
Cr(1)—C(8)	2.235(8)			C(12)—O(4)—C(11)	106.3(6)
Cr(1)—C(9)	2.332(7)			O(4)—C(12)—N(1)	103.3(5)
				N(1)—C(10)—C(11)	100.8(6)

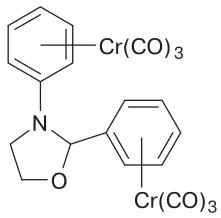
143 [M — 3 CO — $CH_2CH_2OCH(Ph)]^+$ (66), 52 $[Cr]^+$ (20). The structure of compound **7f** was also confirmed by X-ray diffraction analysis (Fig. 1, Table 2).

According to the X-ray diffraction data, the conformation of heterocycle in the structure **7f** can be characterized as an *envelope*: the N(1), C(10), C(11), and C(12) atoms lie almost in the one plane, while the oxygen atom deviates from it. The angle between the C(11)C(10)N(1)C(12) and C(11)O(4)C(12) planes is 36.5(5)°. The phenyl substituent at C(12) atom and the chromium tricarbonyl group are arranged on the opposite sides of the plane of heterocycle. In the arene chromium tricarbonyl fragment, the Cr—C_{arene} and Cr—(CO) distances are 2.177(9)—2.332(7) Å and 1.799(9)—1.844(8) Å, respectively (Table 2). The lengths of all its C—C bonds are close to each other (1.38(2)—1.43(2) Å). The C(1)—O(1) distance is slightly longer (1.20(2) Å) than the C—O bond lengths in the two other carbonyl ligands (1.16(2) Å). The carbonyl groups are in an eclipsed conformation, and the C—Cr—C angles in the chromium carbonyl fragment are within the 87.8(5)—91.1(4)° range.

The reaction of **6f** with an excess of **4** (at a 1 : 2 ratio of reactants) resulted in a mixture containing two organochromium compounds **7f** and **7i**. The structure of binuclear η^6,η^6-(1,3-oxazolidine-2,3-diyl)bis[(benzene)chromium tricarbonyl] was assigned to product **7i**.



7f



7i

Its mass spectrum contained a molecular ion peak with *m/z* 497 $[M]^+$ (7) and peaks of fragment ions. The IR spectrum of compound **7i** exhibited absorption bands at 1956 and 1873 cm^{-1}, which confirms the presence of CO groups in the molecule. The ^1H NMR spectrum contained the signals for the protons of the methine and two methylene groups of the heterocyclic ring, as well as the signals for the protons of two phenyl chromium tricarbonyl rings. Its structure was finally confirmed by X-ray diffraction (Fig. 2, Table 3).

The X-ray diffraction results show that in the structure **7i**, like in **7f**, all atoms of the heterocyclic ring except the oxygen atom lie almost in one plane: the angle between the C(11)C(10)N(1)C(12) and C(11)O(4)C(12) planes is equal to 37(2)°. The O—C bond lengths in the 1,3-oxazolidine ring are 1.46(2) and 1.47(2) Å, the N—C distances are 1.44(2) and 1.46(2) Å, and the angles are in the 99(2)—111(2)° range (see Table 3). The Cr—C_{arene} distances in **7i** are close to each other (2.19(2)—2.24(2) Å) and are comparable to those in **7f** (2.177(9)—2.332(7) Å). The Cr—(CO) bond lengths lie in a wide range of values, 1.74(2)—1.93(2) Å. The C—Cr—C angles in $Cr(CO)_3$ fragments are close to 90° (see Table 3), which is typical of arene chromium tricarbonyl complexes.[16]

In conclusion, the present studies showed that the reactions of triammine(tricarbonyl)chromium (**4**) with various phenyl-containing 1,3-oxazacycloalkanes (**3a—c**, **6a—h**), which do not have free N—H bonds, proceed with the formation of the corresponding (η^6-phenyl)chromium tricarbonyl complexes. These reactions can be used to obtain the products, which are unavailable by alternative condensation method. If two phenyl substituents are present in the starting 1,3-oxazacycloalkane, the coordination first involves the *N*-phenyl ring (with an equimolar ratio of reactants) and then both aromatic rings (with an excess of **4**).

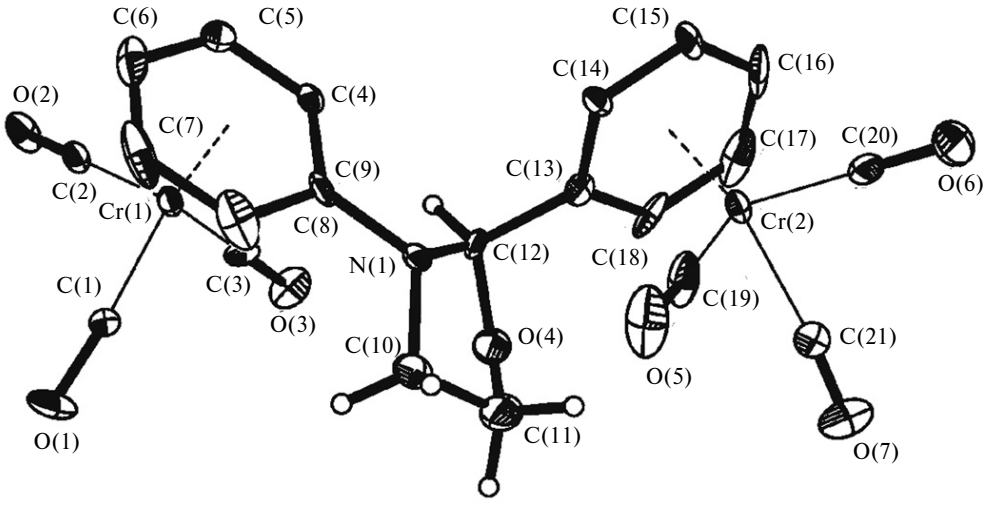


Fig. 2. Molecular structure of η^6,η^6-(1,3-oxazolidine-2,3-diyl)bis[(benzene)chromium tricarbonyl] (**7i**). Thermal ellipsoids are given with a 30% probability. Hydrogen atoms of phenyl substituents are omitted.

Table 3. Principal bond lengths (*d*) and bond angles (ω) in complex **7i**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Cr(1)—C(1)	1.74(2)	Cr(2)—C(18)	2.24(2)	O(4)—C(12)—N(1)	106(2)
Cr(1)—C(2)	1.85(2)	Cr(2)—C(19)	1.86(2)	C(11)—O(4)—C(12)	101(2)
Cr(1)—C(3)	1.80(2)	Cr(2)—C(20)	1.84(2)	O(4)—C(11)—C(10)	105(2)
Cr(1)—C(4)	2.24(2)	Cr(2)—C(21)	1.93(2)	C(10)—N(1)—C(12)	111(2)
Cr(1)—C(5)	2.22(2)	N(1)—C(9)	1.45(2)	N(1)—C(10)—C(11)	99(2)
Cr(1)—C(6)	2.20(2)	N(1)—C(10)	1.46(2)	C(1)—Cr(1)—C(2)	91(2)
Cr(1)—C(7)	2.20(2)	N(1)—C(12)	1.44(2)	C(2)—Cr(1)—C(3)	88(2)
Cr(1)—C(8)	2.23(5)	C(10)—C(11)	1.55(2)	C(1)—Cr(1)—C(3)	88(2)
Cr(1)—C(9)	2.24(2)	O(4)—C(11)	1.47(2)	C(20)—Cr(2)—C(19)	88(2)
Cr(2)—C(13)	2.22(2)	O(4)—C(12)	1.46(2)	C(20)—Cr(2)—C(21)	85.3(9)
Cr(2)—C(14)	2.20(2)	C(12)—C(13)	1.52(2)	C(19)—Cr(2)—C(21)	86(2)
Cr(2)—C(15)	2.19(2)				
Cr(2)—C(16)	2.21(2)				
Cr(2)—C(17)	2.23(2)				

Experimental

Solvents were distilled over metallic sodium at atmospheric pressure. Ethyl acetate was dried with calcium chloride and distilled.[17] 1,3-Oxazacycloalkanes **1a,b** and **6a—h** were obtained by the condensation of amino alcohols, such as 2-(*N*-phenylamino)-ethanol, 1-(*N*-phenylamino)propan-2-ol, 3-(*N*-phenylamino)-propan-1-ol, with commercial aldehydes (paraformaldehyde, acetaldehyde, propionic aldehyde, benzaldehyde).[11,18] 2-(*N*-Phenylamino)ethanol, 1-(*N*-phenylamino)propan-2-ol, 3-(*N*-phenylamino)propan-1-ol were synthesized by arylation of the corresponding commercial amino alkanols with iodobenzene in the presence of copper(I) chloride according to the procedure.[19] Compounds **3a,c** were obtained by acylation of 1,3-oxazacycloalkanes **1a,b** with acetic anhydride.[14] 1,3-Oxazolidine **3b** was synthesized according to the procedure for the Boc group introduction into the amino acid esters by treatment with di-*tert*-butyl dicarbonate in chloroform.[15] Triammine-(tricarbonyl)chromium (**4**) was synthesized according to the procedure described in the literature.[20]

The products of the reactions of **5a—c** and **7a—i** with **4** were isolated and purified by column chromatography on Acros silica gel 0.035—0.070 mm under argon atmosphere, using a hexane—ethyl acetate solvent system as the eluent. HPLC analysis was performed on a Knauer Smartline 5000 chromatograph with a S 2600 UV diode array detector (the UV spectra of the eluates were recorded in the 200—500 nm range), a Diaspher-110-C16 column, 5 μm, 4.6×250 mm, eluent acetonitrile—water (84 : 16); the eluent flow rate was 0.7 mL min^{-1}. The IR spectra were recorded on an FTIR-8400S (Shimadzu) instrument in the 500—4000 cm^{-1} wave number range in KBr pellets. ^{1}H NMR spectra were recorded on an Agilent DD2 NMR 400NB spectrometer (400 MHz) in acetone-d_6. Mass spectrometry studies were performed in the *m*/*z* range of 50—500 Da, the temperature was programmed from 50 to 450 °C at a heating rate of 100 deg min^{-1}.

Synthesis of chromium tricarbonyl derivatives of phenyl-1,3-oxazacycloalkanes 5a—c and 7a—i (general procedure). 1,3-Oxazacycloalkane **3a—c** or **6a—h** (24 mmol), reactant **4** (24 mmol), and dioxane (60 mL) were placed into a two-neck flask equipped with a reflux condenser and a gas burette filled with dibutyl phthalate. The reaction mixture was heated in an oil bath at 120 °C until 1.5 L of ammonia was evolved, then the flask was cooled and filled with argon. The resulting mixture was filtered through a Schott filter filled with alumina and the solvent was evaporated. The reaction products were isolated from the residue by column chromatography and recrystallized from a mixture of hexane and ethyl acetate. The formed yellow crystals were collected by filtration on a Schott filter and dried in a desiccator.

The yields of products **7a—d** and **7h** are given in Table 1, their spectral data are reported in our previous work.[11]

η^6-[(3-Acetyl-1,3-oxazolidin-2-yl)benzene]chromium tricarbonyl (5a). The yield was 73%, m.p. 90—91 °C. HPLC: one peak, τ = 5.2 min. UV-Vis (MeCN, H_2O), λ/nm: 219, 313. IR (KBr), ν/cm^{-1}: 3107 (ν(C_{Ar}—H)); 2974, 2907 (ν(C—H)); 1948, 1857 (ν(C≡O)); 1651 (ν(C=O)); 1490, 1440 (ν(C_{Ar}—C_{Ar})); 860, 815 (ω(C_{Ar}—H)). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 327 $[M]^+$ (1), 299 $[M - CO]^+$ (2), 271 $[M - 2\ CO]^+$ (2), 243 $[M - 3\ CO]^+$ (20), 174 $[M - Cr(CO)_3 - O - H]^+$ (100), 77 $[Ph]^+$ (4), 52 $[Cr]^+$ (8)). ^{1}H NMR, δ: 2.10 (s, 3 H, Me); 3.75 (br.q, 1 H, NCH_2, *J* = = 7.0 Hz); 3.90—3.98 (m, 1 H, NCH_2); 4.14 (q, 1 H, OCH_2, *J* = 7.4 Hz); 4.34 (br.dd, 1 H, OCH_2, *J* = 7.4 Hz, *J* = 5.1 Hz); 5.53 (dd, 2 H, *m*-H_{PhCr}, *J* = 9.8 Hz, *J* = 5.9 Hz); 5.66 (t, 1 H, *p*-H_{PhCr}, *J* = 5.9 Hz); 5.82, 5.99 (both d, 1 H each, *o*-H_{PhCr}, *J* = 6.7 Hz); 6.02 (s, 1 H, C<u>H</u>(Ph)).

η^6-[(3-*tert*-Butyloxycarbonyl-1,3-oxazolidin-2-yl)benzene]-chromium tricarbonyl (5b). The yield was 71%, m.p. 128—129 °C. HPLC: one peak, τ = 7.9 min. UV-Vis (MeCN, H_2O), λ/nm: 219, 313. IR (KBr), ν/cm^{-1}: 3086 (ν(C_{Ar}—H)); 3003, 2976, 2905 (ν(C—H)); 1902, 1873 (ν(C≡O)); 1676 (ν(C=O)); 1610, 1540 (ν(C_{Ar}—C_{Ar})); 773, 670 (ω(C_{Ar}—H)). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 385 $[M]^+$ (1), 357 $[M - CO]^+$ (1), 329 $[M - 2\ CO]^+$ (7), 301 $[M - 3\ CO]^+$ (26), 244 $[M - 3\ CO - Bu^t]^+$ (69), 174 $[M - Cr(CO)_3 - OBu^t - 2\ H]^+$ (100), 52 $[Cr]^+$ (12). ^{1}H NMR, δ: 1.45 (s, 9 H, Bu^t); 3.46 (m, 1 H, NCH_2); 3.82—3.87 (m, 1 H, NCH_2); 4.03 (m, 1 H, OCH_2); 4.20—4.25 (m, 1 H, OCH_2); 5.53—5.57 (m, 2 H, *m*-H_{PhCr}); 5.68 (t, 1 H, *p*-H_{PhCr}, *J* = = 6.3 Hz); 5.81 (d, 1 H, *o*-H_{PhCr}, *J* = 6.7 Hz); 5.84 (s, 1 H, C<u>H</u>(Ph)); 5.88—5.92 (m, 1H, *o*-H_{PhCr}).

η^6-[(3-Acetyl-1,3-oxazinan-2-yl)benzene]chromium tricarbonyl (5c). The yield was 53%, m.p. 110—111 °C. HPLC: one peak, τ = 5.0 min. UV-Vis (MeCN, H_2O), λ/nm: 217, 315, 430.

IR (KBr), ν/cm^{-1}: 3103 (ν(C_{Ar}—H)); 2993, 2937, 2873 (ν(C—H)); 1971, 1894 (ν(C≡O)); 1653 (ν(C=O)); 1487 (ν(C_{Ar}—C_{Ar})); 887, 800 (ω(C_{Ar}—H)). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 341 $[M]^+$ (1), 313 $[M - CO]^+$ (5), 285 $[M - 2\ CO]^+$ (26), 257 $[M - 3\ CO]^+$ (100), 229 $[M - 3\ CO - (CH_2)_2]^+$ (35), 158 $[M - 3\ CO - (CH_2)_3N(CO)Me]^+$ (32), 52 $[Cr]^+$ (28). ^{1}H NMR, δ: 2.18 (s, 3 H, Me); 1.62—1.78, 1.84—1.98 (both m, 1 H each, $CH_2C\underline{H}_2CH_2$); 3.72—3.82, 3.86—4.00 (both m, 2 H each, NCH_2, OCH_2); 5.53—5.80 (m, 5 H, *o,m,p*-PhCr); 5.92 (br.s, 1 H, CH(Ph)).

η^6-[(2-Ethyl-1,3-oxazolidin-3-yl)benzene]chromium tricarbonyl (7e). The yield was 30%, m.p. 111—112 °C. HPLC: one peak, τ = 6.3 min. UV-Vis (MeCN, H_2O), λ/nm: 219, 317, 430. IR (KBr), ν/cm^{-1}: 3099 (ν(C_{Ar}—H)); 2955, 2935, 2876 (ν(C—H)); 1942, 1869 (ν(C≡O)); 1549, 1464 (ν(C_{Ar}—C_{Ar})); 808, 682 (ω(C_{Ar}—H)). MS (EI, 70 eV): 313 $[M]^+$ (29), 229 $[M - 3\ CO]^+$ (78), 199 $[M - 3CO - CH_2O]^+$ (28), 148 $[M - Cr(CO)_3 - Et]^+$ (100), 52 $[Cr]^+$ (20). ^{1}H NMR, δ: 0.97 (t, 3 H, Me, *J* = 7.4 Hz); 1.59—1.70, 1.79—1.90, 3.36—3.44, 3.47—3.55, 4.02—4.09, 4.11—4.18 (all m, 1 H each, C$\underline{H}_2$Me, C$\underline{H}_2$Me, NCH_2, NCH_2, OCH_2, OCH_2); 4.95—5.10 (m, 4 H, C$\underline{H}$(Et), H_{PhCr}); 5.80—5.85 (m, 2 H, H_{PhCr}).

η^6-[(2-Phenyl-1,3-oxazolidin-3-yl)benzene]chromium tricarbonyl (7f). The yield was 40%, m.p. 99—100 °C. HPLC: one peak, τ = 8.3 min. UV-Vis (MeCN, H_2O), λ/nm: 217, 317. IR (KBr), ν/cm^{-1}: 3094 (ν(C_{Ar}—H)); 2955, 2924, 2876 (ν(C—H)); 1948, 1855 (ν(C≡O)); 1547, 1477 (ν(C_{Ar}—C_{Ar})); 810, 756, 683 (ω(C_{Ar}—H)). MS (EI, 70 eV): 361 $[M]^+$ (5), 277 $[M - 3\ CO]^+$ (72), 247 $[M - 3\ CO - CH_2O]^+$ (100), 143 $[M - 3\ CO - CH_2CH_2OCH\ (Ph)]^+$ (66), 52 $[Cr]^+$ (20). ^{1}H NMR, δ: 3.59 (dd, 1 H, NCH_2, *J* = 8.6 Hz, *J* = 6.7 Hz); 3.85 (dt, 1 H, NCH_2, *J* = 8.6 Hz, *J* = 6.3 Hz); 4.04—4.28 (m, 2 H, OCH_2); 4.69 (dd, 1 H, *m*-H_{PhCr}, *J* = 7.0 Hz, *J* = 6.3 Hz); 5.01 (t, 1 H, *o*-H_{PhCr}, *J* = 6.3 Hz); 5.14 (dd, 1 H, *m*-H_{PhCr}, *J* = 7.0 Hz, *J* = 6.3 Hz); 5.66 (t, 1 H, *o*-H_{PhCr}, *J* = 6.3 Hz); 5.81 (s, 1 H, C$\underline{H}$Ph); 5.83 (t, 1 H, *p*-H_{PhCr}, *J* = 7.0 Hz); 7.36—7.47 (m, 3 H, *o,p*-H_{Ph}); 7.48—7.58 (m, 2 H, *m*-H_{Ph}).

η^6-[(2-Phenyl-1,3-oxazinan-3-yl)benzene]chromium tricarbonyl (7g). The yield was 19%, m.p. 116—117 °C. HPLC: one peak, τ = 13.3 min. UV-Vis (MeCN, H_2O), λ/nm: 219, 318, 436. IR (KBr), ν/cm^{-1}: 3074 (ν(C_{Ar}—H)); 2918, 2853 (ν(C—H)); 1944, 1856 (ν(C≡O)); 1606, 1532 (ν(C_{Ar}—C_{Ar})); 734, 692 (ω(C_{Ar}—H)). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 375 $[M]^+$ (2); 291 $[M - 3\ CO]^+$ (20); 233 $[M - 3\ CO - (CH_2)_3O]^+$ (100); 91 $[M - Cr(CO)_3 - (CH_2)_3OCHPh]^+$ (16); 77 $[M - Cr(CO)_3 - (CH_2)_3OCH(Ph)N]^+$ (13); 52 $[Cr]^+$ (24). ^{1}H NMR, δ: 1.60—1.70, 1.71—1.82, 3.50—3.61, 3.67—3.78, 3.89—4.01, 4.14—4.25 (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); 5.52 (t, 1 H, *p*-H_{PhCr}, *J* = 6.3 Hz); 5.55—5.64 (m, 1 H, H_{PhCr}); 5.65—5.75 (m, 2 H, H_{PhCr}); 5.80 (s, 1 H, C$\underline{H}$(Ph)); 5.97 (d, 1 H, *o*-H_{PhCr}, *J* = 6.7 Hz); 6.92—6.98 (m, 1 H, *m*-H_{Ph}); 7.16—7.29 (m, 4 H, *o,m,p*-H_{Ph}).

η^6,η^6-(1,3-Oxazolidine-2,3-diyl)bis[(benzene)chromium tricarbonyl] (7i) was obtained according to the general procedure from 2,3-diphenyl-1,3-oxazolidine **6f** (24 mmol) and **4** (48 mmol). The formed mixture of products **7f** and **7i** was separated by column chromatography, eluting with a mixture of hexane—ethyl acetate (4 : 1). The yield of **7i** was 35%, m.p. 167—168 °C. HPLC: one peak, τ = 8.1 min. UV-Vis, (MeCN, H_2O), λ /nm: 218, 317. IR (KBr), ν/cm^{-1}: 3094 (ν(C_{Ar}—H)); 2961, 2889, 2854 (ν(C—H)); 1956, 1873 (ν(C≡O)); 1543, 1472 (ν(C_{Ar}—C_{Ar})); 874, 800, 762 (ω(C_{Ar}—H)). MS (EI, 70 eV): 497

Table 4. Crystallographic data, parameters of X-ray diffraction experiments and refinement for complexes **7f** and **7i**

Compound	**7f**	**7i**
Molecular formula	$C_{18}H_{15}CrNO_4$	$C_{21}H_{15}Cr_2NO_7$
Molecular weight	361.31	497.34
Space group	*P*2(1)2(1)2(1)	*Cc*
a/Å	6.2114(3)	11.0531(7)
b/Å	11.6366(6)	7.4932(5)
c/Å	22.0483(11)	23.5262(13)
α/deg	90	90
β/deg	90	91.915(3)
γ/deg	90	90
V/Å^3	1593.64(14)	1947.4(2)
Z	4	4
d_{calc}/Mg m^{-3}	1.506	1.696
μ/mm^{-1}	0.739	1.162
θ-Range for data collection/deg	1.98—26.03	3.29—25.06
Number of reflections		
collected	13542	6408
unique with $I > 2\sigma(I)$	3131	3192
R_{int}	0.0320	0.0533
GOOF (F^2)	1.030	1.048
R_1 ($I > 2\sigma(I)$)	0.0660	0.0758
wR_2 (all data)	0.1651	0.1994
Residual electron density (ρ_{max}/ρ_{min})/e Å^{-3}	2.33/−0.88	1.20/−0.59

$[M]^+$ (7), 413 $[M - 3\ CO]^+$ (9), 361 $[M - Cr(CO)_3]^+$ (10), 329 $[M - 6\ CO]^+$ (38), 277 $[M - 3\ CO - Cr(CO)_3]^+$ (100), 247 $[M - 3\ CO - Cr(CO)_3 - CH_2O]^+$ (22), 225 $[M - 2\ Cr(CO)_3]^+$ (21), 195 $[M - 2\ Cr(CO)_3 - CH_2O]^+$ (15), 143 $[M - 3\ CO - Cr(CO)_3 - CH_2CH_2OCH(Ph)]^+$ (18), 52 $[Cr]^+$ (3). ^{1}H NMR, δ: 3.54 (dd, 1 H, NCH_2, J = 16.0 Hz, J = 7.8 Hz); 3.76—3.83 (m, 1 H, NCH_2); 4.21—4.31 (m, 2 H, OCH_2); 5.13 (t, 1 H, p-H_{NPhCr}, J = 6.3 Hz); 5.19 (d, 2 H, o-H_{NPhCr}, J = 7.0 Hz); 5.50 (t, 2 H, m-H_{NPhCr}, J = 6.3 Hz); 5.80 (s, 1 H, C<u>H</u>(Ph)); 5.83—5.89 (m, 3 H, o,p-H_{CPhCr}); 6.00 (t, 2 H, m-H_{CPhCr}, J = = 5.9 Hz).

X-ray diffraction data for compounds **7f** and **7i** were collected on a Bruker D8 Quest diffractometer (Mo-Kα radiation, λ = 0.71073 Å, ω-scan technique, T = 100 K (**7f**) and 200 K (**7i**)). Measurement and integration of experimental sets of intensities, absorption correction, and refinement of structures were carried out using the APEX3,[21] SADABS,[22] and SHELX[23] software packages. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2_{hkl} in anisotropic approximation for nonhydrogen atoms. Hydrogen atoms were placed in geometrically calculated positions and were refined isotropically with $U(H)_{iso} = 1.2U(C)_{eq}$ of their parent atoms. The structures of compounds **7f** and **7i** were refined as racemic twins with the ratio of isomer 50 : 50 and 80 : 20, respectively. The *RIGU* and *ISOR* instructions were used in the refinement to restrain the anisotropic parameters of atomic displacements.

The crystallographic data, parameters of the X-ray diffraction experiments and structure refinement details are given in Table 4. The structures were deposited with the Cambridge Crystallographic Data Center (CCDC 1879517 (**7f**) and 1879516 (**7i**)) and are available at ccdc.cam.ac.uk/structures.

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