Chemistry of unsaturated arenetricarbonylchromium compounds
2.* Synthesis of new isoxazolidine complexes by 1,3-dipolar cycloaddition reaction of nitrone (η^6-arene)tricarbonylchromium derivatives with acrylonitrile

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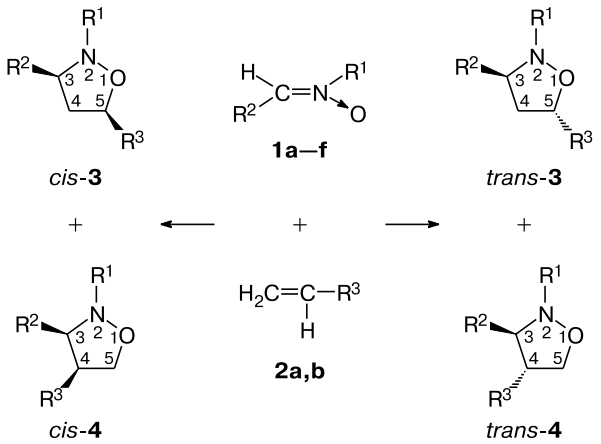
1,3-Dipolar cycloaddition reactions of nitrones of a general formula $RCH{=}N^{+}(O^{-})R'$, where R = Ph, $Ph[Cr(CO)_3]$, R′ = Me, Ph, Bu^t, with acrylonitrile were studied. The isoxazolidines obtained by these reactions were isolated and identified. The introduction in the nitrone molecule of a tricarbonylchromium group led to the increase in the regio- and stereoselectivity of cycloaddition. The influence of deuterated solvents on chemical shifts of protons in the isoxazolidine ring was studied.

Key words: nitrone, (η^6-arene)tricarbonylchromium, isoxazolidine, 1,3-dipolar cycloaddition, acrylonitrile.

Nowadays, unsaturated (η^6-arene)tricarbonylchromium complexes are widely used in different fields of chemistry. The presence of the electron-withdrawing tricarbonylchromium group in the aromatic compound molecule considerably affects properties of the substrate, which results in the high selectivity of metallation reactions, the tendency of the coordinated arene to nucleophilic addition. Besides, the bulky chromium-containing fragment, which stabilizes both the negative and the positive charge in a transition state, also facilitates the stereoselective proceeding of a wide range of reactions.[2—6] One of the promising fields of application of arenetricarbonylchromium complexes as the selectivity increasing agents is a 1,3-dipolar cycloaddition of nitrones to functional alkenes, which is widely used for the design of five-membered heterocyclic compounds.[7—10]

Earlier, it was found that, in contrast to the reactions of free nitrones **1a—c** with styrene leading as a rule to mixtures of stereoisomers,[11,12] the cycloaddition of a conjugated alkene **2** to nitrone (η^6-arene)tricarbonylchromium complexes **1d—f** proceeds stereoselectively with the formation of the corresponding *cis*-C(5)-substituted isoxazolidine as the only product[13,14] (Scheme 1, Table 1). The reactions of free nitrones with electron-deficient monosubstituted dipolarophiles containing such functional groups as —CN, $—CO_2R$, $—NO_2$, *etc.*, frequently give

Scheme 1



1	R^1	R^2	1	R^1	R^2
a	Me	Ph	**d**	Me	$Ph[Cr(CO)_3]$
b	Bu^t	Ph	**e**	Bu^t	$Ph[Cr(CO)_3]$
c	Ph	Ph	**f**	Ph	$Ph[Cr(CO)_3]$

2: R^3 = Ph (**a**); CN (**b**)

3	R^1	R^2	R^3	3	R^1	R^2	R^3
a	Me	Ph	Ph	**g**	Me	Ph	CN
b	Bu^t	Ph	Ph	**h**	Bu^t	Ph	CN
c	Ph	Ph	Ph	**i**	Ph	Ph	CN
d	Me	$Ph[Cr(CO)_3]$	Ph	**j**	Me	$Ph[Cr(CO)_3]$	CN
e	Bu^t	$Ph[Cr(CO)_3]$	Ph	**k**	Bu^t	$Ph[Cr(CO)_3]$	CN
f	Ph	$Ph[Cr(CO)_3]$	Ph	**l**	Ph	$Ph[Cr(CO)_3]$	CN

* For Part 1, see Ref. 1.

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Table 1. Ratios of isomers* of isoxazolidines **3a—l** and **4a—l** in the reactions of nitrones **1a—f** with styrene (**2a**) and acrylonitrile (**2b**)

Starting compounds		Products	Ratio of products			
			cis-**3**	*trans*-**3**	*cis*-**4**	*trans*-**4**
1a	**2a**	**3a**, **4a**	67	33	0	0
1b	**2a**	**3b**, **4b**	100	0	0	0
1c	**2a**	**3c**, **4c**	90	10	0	0
1d	**2a**	**3d**, **4d**	100	0	0	0
1e	**2a**	**3e**, **4e**	100	0	0	0
1f	**2a**	**3f**, **4f**	100	0	0	0
1a	**2b**	**3g**, **4g**	23	77	0	0
1b	**2b**	**3h**, **4h**	50	50	0	0
1c	**2b**	**3i**, **4i**	81	10	3	6
1d	**2b**	**3j**, **4j**	100	0	0	0
1e	**2b**	**3k**, **4k**	100	0	0	0
1f	**2b**	**3l**, **4l**	93	7	0	0

* The data for isoxazolidines **3a—g** and **4i** were taken from the literature: **3a**,[11] **3b**,[12] **3c**,[11] **3d**,[13] **3e**,**f**,[14] **3g**,[15] **4i**.[16]

mixtures of regio- and stereoisomeric products[9] (see Scheme 1). Increasing the selectivity of such reactions is a very actual direction in the chemistry of heterocyclic compounds, natural and physiologically active compounds.[7—14] The purpose of the present work is the synthesis of new isoxazolidine (η^6-arene)tricarbonylchromium complexes by the 1,3-dipolar cycloaddition of acrylonitrile to coordinated nitrones **1d—f** and the establishment of the structure of the heterocycles formed.

Results and Discussion

In the syntheses to be studied, the free *C*,*N*-disubstituted nitrones[13,17,18] (**1a—c**) with *trans*-configuration[13,15] and their coordinated analogs[13,14] (**1d—f**) were used as the dipoles, while acrylonitrile as a dipolarophile. The reactions were carried out in sealed degassed tubes at 80 °C in excess acrylonitrile.

The reaction of free *C*,*N*-diphenylnitrone (**1c**) with acrylonitrile is known[16] to proceed with the formation of all four possible isoxazolidines, with the content of C(4)-substituted stereoisomers *cis*-, *trans*-**4i** in the mixture of products being 9% (3 and 6%, respectively) and that of C(5)-substituted products *cis*-, *trans*-**3i** being 91%. Since the authors of the work[16] did not report the ratio of *cis*-, *trans*-**3i** stereoisomers, we used HPLC to show that isoxazolidine *cis*-**3i** is the major reaction product (81%) (see Table 1). Compound *cis*-**3i** was isolated from the reaction mixture by column chromatography, and its structure was confirmed by UV, IR, and ^{1}H NMR spectroscopy and mass spectrometry. The *cis*-arrangement of substituents at carbon atoms C(3) and C(5) of the heterocyclic ring in compound *cis*-**3i** was established by ^{1}H NMR spectroscopy. It is known that the ~0.7—0.9 ppm difference in the chemical shifts of the protons at carbon atom C(4) in *cis*-isomers is considerably larger than the corresponding values for *trans*-products (~0.28—0.44 ppm).[14,19—21] In the ^{1}H NMR spectrum of isoxazolidine *cis*-**3i** recorded in deuteroacetone, the protons at atom C(4) are found as two separate signals with the difference in the chemical shift values of 0.71 ppm (see Experimental), whereas the spin-spin coupling constants of the upfield proton (δ 2.66, J = 12.9 Hz, J = 5.5 Hz, J = 3.9 Hz) are smaller than similar constants of the proton with chemical shift at δ 3.37 (J = 12.9 Hz, J = 9.0 Hz), that indicates a *cis*-structure of this compound. A predominant formation in this reaction of C(5)-substituted isoxazolidines can be explained both within the theory based on the consideration of mutual arrangement of boundary orbitals of reacting compounds[22—25] and by the approach considering charge distribution on the atoms of the nitrone and alkene molecules (Fig. 1, *a*).

C-(η^6-Phenyltricarbonylchromium)-*N*-phenylnitrone (**1f**) reacts with acrylonitrile (**2b**) similarly to give isoxazolidines containing a cyano group at carbon atom C(5) of the heterocyclic ring. The reaction proceeds in toluene at 80 °C and already within 3 min leads to the formation of C(5)-substituted stereoisomers in the ratio of 93 : 7 (see Table 1) in 96% total yield. The absence of C(4)-substituted isoxazolidines in this case is mainly explained by the steric factor arisen from the bulkiness of the nitrone tricarbonylchromium group and is confirmed by the charge distribution in the reagent molecules (see Fig. 1, *b*). The high stereoselectivity of cycloaddition, probably, is related to the formation of the intermediate complex between the

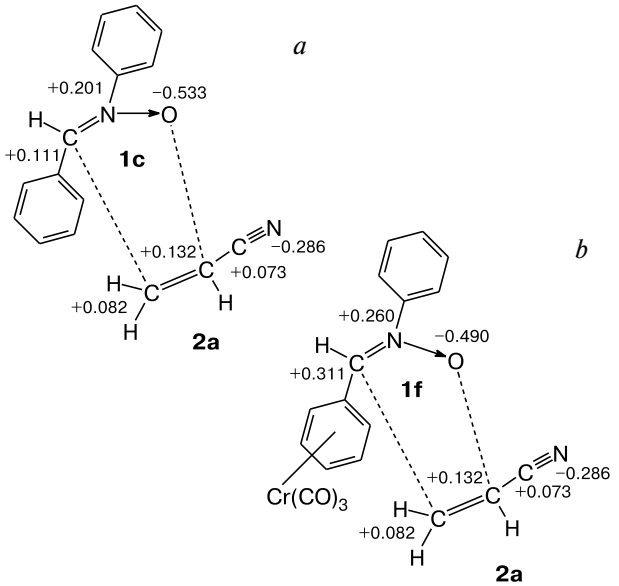
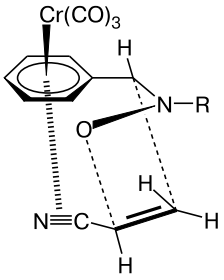
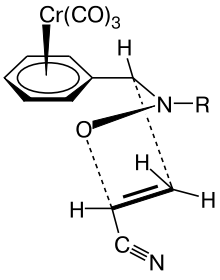


Fig. 1. Charge distribution in C,N-diphenylnitrone (**1c**) (*a*), C-(η^6-phenyltricarbonylchromium)-N-phenylnitrone (**1f**) (*b*), and acrylonitrile (**2a**) and direction of their reactions (the B3LYP/LanL2DZ calculations).

molecules of coordinated nitrone and substituted alkene stabilized by the stacking interaction of the phenyltricarbonylchromium substituent on the dipole and the cyano group of acrylonitrile (transition state **A**), which predominates over transition state of type **B**.[12—14,17] Such a structural arrangement of substituents at atoms C(3) and C(5) is preserved in the final product, that was confirmed by X-ray diffraction study of complex **3k** (Fig. 2).



A (*cis*)



B (*trans*)

R = Me (**3j**), Bu^t (**3k**), Ph (**3l**)

To sum up, using the reactions of free nitrone **1c** and its arenetricarbonylchromium analog **1f** as examples we showed that the introduction of the $Cr(CO)_3$ group in the dipole molecule led to the increase in both regio- and stereoselectivity of cycloaddition.

The literature data,[15,16] as well as our studies, show that free nitrones **1a** and **1b** regioselectively react with acrylonitrile (**2b**) with the formation of mixtures of two C(5)-substituted *cis*- and *trans*-isomers in the ratio 23 : 77 and 50 : 50, respectively (see Table 1). The reactions of similar coordinated nitrones **1d**,**f** with acrylonitrile proceed more stereoselectively with the formation of only C(5)-substituted isoxazolidines **3k**,**l** having the *cis*-configuration. The products **3k**,**l** isolated from the reaction mixtures by column chromatography are yellow crystalline compounds with sharp melting points, they are characterized by different physicochemical analytical methods,

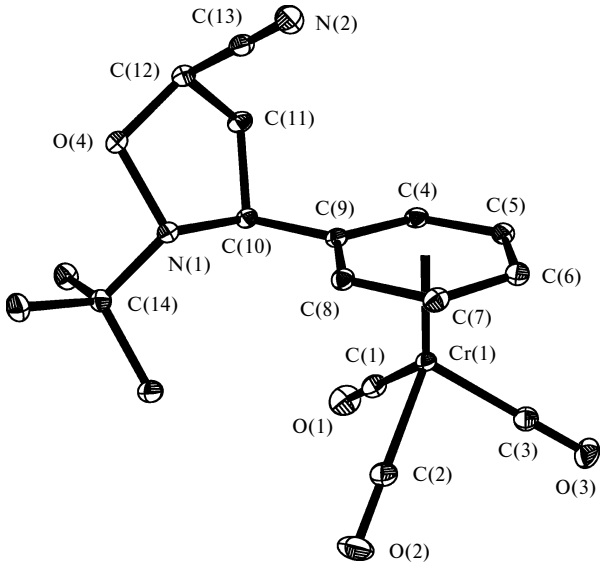


Fig. 2. Molecular structure of isoxazolidine **3k** (hydrogen atoms are omitted). Thermal ellipsoids are given with 30% probability.

compound **3k** was also studied by single-crystal X-ray diffraction (Fig. 2, Table 2).

The X-ray diffraction study of isoxazolidine **3k** showed that the heterocyclic ring in **3k** has an *envelope* conformation. Atoms O(4)N(1)C(10)C(11) lie virtually in one plane (the mean deviation from it is 0.002 Å), whereas atom C(12) deviates from it by 0.575 Å. In isoxazolidine and isoxazoline arenetricarbonylchromium complexes synthesized earlier, the *envelope* conformation of the five-membered ring was formed by the deviation of the nitrogen atom from the plane of the ring.[1,12,14] It should be noted that atom N(2) of the cyano group is located above the π-system of the benzene substituent. The torsion angle C(9)C(10)C(12)N(2) is 11.1°, the angle N(2)—benzene ring center—C(9) is 65.5°, whereas the distance N(2)—benzene ring center is 4.003 Å. Thus, the phenyltricarbonylchromium and the cyano groups are placed on one side of the heterocyclic ring, that confirms the

Table 2. Principal bond distances (*d*) and bond angles (ω) in the sructure of complex **3k**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
N(1)—O(4)	1.4916(14)	Cr(1)—C(7)	2.2165(12)	C(12)—C(11)—C(10)	101.23(10)
O(4)—C(12)	1.4041(17)	Cr(1)—C(8)	2.2403(12)	N(1)—C(10)—C(11)	105.56(9)
C(10)—C(11)	1.5403(16)	Cr(1)—C(9)	2.2570(11)	C(10)—N(1)—O(4)	106.15(9)
C(11)—C(12)	1.5179(19)	C(4)—C(5)	1.4060(2)	O(4)—C(12)—C(11)	104.77(11)
N(1)—C(10)	1.4871(16)	C(5)—C(6)	1.4130(19)	C(12)—O(4)—N(1)	105.54(9)
Cr(1)—C(1)	1.8429(15)	C(6)—C(7)	1.3959(18)	C(12)—C(13)—N(2)	179.47(17)
Cr(1)—C(2)	1.8481(14)	C(7)—C(8)	1.4221(17)	C(10)—N(1)—C(14)	116.02(10)
Cr(1)—C(3)	1.8427(13)	C(8)—C(9)	1.4016(17)	O(4)—N(1)—C(14)	105.43(9)
Cr(1)—C(4)	2.2075(12)	C(4)—C(9)	1.4260(16)		
Cr(1)—C(5)	2.1989(13)	C(12)—C(13)	1.4948(18)		
Cr(1)—C(6)	2.2174(14)	C(13)—N(2)	1.1390(2)		

Table 3. The differences in the chemical shifts for the protons at C(4) carbon atom of isoxazolidines **3h—l**

Compound	$\Delta\delta_H$	
	Acetone-d_6	Benzene-d_6
cis-**3h**	0.82	—
trans-**3h**	0.23	—
cis-**3i**	0.71	0
cis-**3j**	~0.80	~0.21
c*is*-**3k**	0.60	~0.19
cis-**3l**	~0.41	0

cis-structure of the compound. As in the recently reported 2-*tert*-butyl-4-methylcarboxy-3-(η^6-phenyltricarbonylchromium)-5-phenyl-4-isoxazoline,[1] in compound **3k** the carbonyl groups are in the staggered orientation relative to the aryl ring. The distances Cr—η^6-C and Cr—C(CO) are 2.1989(13)—2.2570(11) Å and 1.8427(13)—1.8481(14) Å, respectively. The aryl ring is characterized by a pronounced alternation of the C—C bonds (see Table 2). Note that the CO groups are located under the longer C—C bonds. The characteristics of the (η^6-C_6H_5)$Cr(CO)_3$ fragment in compound **3k** listed above are similar to those in unsubstituted η^6-(benzene)tricarbonylchromium.[26—29]

The *cis*-structure of compounds **3k**,**l** is also consistent with the ^{1}H NMR spectroscopic data, since the difference in chemical shifts of the protons at carbon atom C(4) of the heterocycle in deuteroacetone is ~0.8 and 0.6 ppm for compounds **3k** and **3l**, respectively (Table 3), while *trans*-isoxazolidines are characterized by considerably smaller difference in the chemical shift values, which in many cases leads to the collapse of the signals for the C(4)H_2 protons (see Refs 14 and 19—21). Note that this pattern, clearly exhibited in the spectra recorded in deuteroacetone and deuterochloroform, is absent when aromatic C_6D_6 is used as the solvent, when even in *cis*-isomers the signals for the protons at carbon atom C(4) become considerably closer or collapse, with their chemical shifts drifting upfield (see Tables 3 and 4).

Deuterobenzene exerts an anisotropic influence also on the signals for the protons at carbon atoms C(3) and C(5), as well as the protons of the aryl substituents in isoxazolidines: their chemical shift values displace toward the high field on going from deuteroacetone to deuterobenzene (see Table 4 and Experimental). In a number of cases, the difference in chemical shifts for the protons ($\Delta\delta$) whose signals are recorded in two different solvents is more than 1 ppm. Such an essential discrepancy in the signal chemical shifts can be due to the ASIS-effects* caused by deuterobenzene,[29,30] as well as to the formation of molecular complexes between the coordinated substituent in isoxazolidine and the solvent molecule.[31—33]

In conclusion, based on the experimental data obtained it was found that the introduction of the tricarbonylchromium group in the molecules of *C*,*N*-disubstituted nitrones can considerably increase the diastereoselectivity of 1,3-dipolar cycloaddition of nitrones to acrylonitrile, as well as the regioselectivity of the process.

Experimental

Solvents were distilled over metallic sodium at atmospheric pressure. Ethyl acetate was dried with calcium chloride and distilled.[34] *N*-Phenyl- and *N*-*tert*-butylhydroxylamines were obtained by the reduction of the corresponding nitro compounds.[17,35] *N*-Methylhydroxylamine hydrochloride from Sigma-Aldrich was used for the synthesis of *C*-phenyl-*N*-methylnitrone (**1a**). Benzaldehyde and triethyl orthoformate were purified by distillation at reduced pressure, the reaction of these compounds gave benzaldehyde diethyl acetal.[36] The reaction between benzaldehyde diethyl acetal and chromium hexacarbonyl led to η^6-(benzaldehyde diethyl acetal)tricarbonylchromium, which was hydrolyzed to η^6-(benzaldehyde)tricarbonylchromium.[37] *C*,*N*-Disubstituted nitrones **1a—f** were obtained by the condensation of the corresponding hydroxylamine derivatives with benzaldehyde[13,17,18] or η^6-(benzaldehyde)tricarbonylchromium.[13,14] Acrylonitrile was purified by distillation at atmospheric pressure.

* Aromatic solvent induced shifts.

Table 4. Chemical shifts (δ) for the protons at C(3), C(4), and C(5) carbon atoms of isoxazolidines *cis*-**3i—l** and the difference of these values ($\Delta\delta$, ppm) for the spectra recorded in deuteroacetone and deuterobenzene

Compound	Solvent	$\delta_{C(3)H}$	$\Delta\delta_{C(3)H}$	$\delta_{C(4)H}$	$\Delta\delta_{C(4)H}$	$\delta_{C(5)H}$	$\Delta\delta_{C(5)H}$
cis-**3i**	Acetone-d_6	4.69	~0.82	2.66 (1 H); 3.37 (1 H)	~0.64; ~1.35	5.37	~1.50
	Benzene-d_6	3.82—3.93	~0.82	1.94—2.10 (2 H)	~0.64; ~1.35	3.82—3.93	~1.50
cis-**3j**	Acetone-d_6	3.51—3.67	~1.18	2.48—2.64 (1 H); 3.28—3.43 (1 H)	~0.77; ~1.36	5.08—5.22	~1.47
	Benzene-d_6	2.33—2.49	~1.18	1.73—1.86 (1 H); 2.00 (1 H)	~0.77; ~1.36	3.68	~1.47
cis-**3k**	Acetone-d_6	4.45	1.10	2.67 (1 H); 3.21—3.37 (1 H)	~0.81; ~1.24	5.20	~1.51
	Benzene-d_6	3.35	1.10	1.78—1.95 (1 H); 1.96—2.14 (1 H)	~0.81; ~1.24	3.69	~1.51
cis-**3l**	Acetone-d_6	4.88—5.15	~1.20	2.64—2.95 (1 H); 3.07—3.34 (1 H)	~1.05; ~1.46	5.22—5.47	~1.45
	Benzene-d_6	3.82	~1.20	1.69—1.81 (2 H)	~1.05; ~1.46	3.90	~1.45

Products were isolated and purified by column chromatography using Acros silica gel (SG) (0.035—0.070 mm) under argon, eluent hexane—ethyl acetate (5 : 1); HPLC was carried out on a Knauer Smartline 5000 chromatograph with a S 2600 UV diode matrix detector, a Diasfer-110-C16 column, 5 μm, 4.6×250 mm, eluent was a mixture of acetonitrile—water (84 : 16); UV spectra of eluates were recorded in the 200—500 nm range. IR spectra were recorded on a Infralyum FT-801 spectrometer in the 480—4600 cm^{-1} range in KBr pellets. ^1H NMR spectra were recorded on an Agilent DD2 NMR 400NB spectrometer (400 MHz) in acetone-d_6 or benzene-d_6. Electron impact (70 eV) mass spectrometric studies were carried out on a Trace DSQII instrument in the 70—500 m/z range, the temperature was programmed from 50 to 450 °C at the rate of heating 100 deg min^{-1}, matrix-activated laser desorption/ionization time-of-flight mass spectra (MALDI MS) were recorded on a Bruker Microflex LT instrument.

The isolation of nitrone and isoxazolidine (η⁶-arene)tricarbonylchromium complexes were carried out under argon.

Synthesis of isoxazolidines 3h—l (general procedure). A corresponding nitrone **1b—f** (1.8 mmol), freshly distilled acrylonitrile (**2b**) (3 mL), and pyrocatechol (0.02 mmol) were placed into a 5-mL glass tube. The tube was degassed and sealed *in vacuo*. The reaction mixture was heated in an oil bath at 80 °C. In the case of complexed nitrones **1d—f**, the heating was continued until the color of the reaction mixture turned from bright red to yellow. The heating time for the reactions involving nitrones **1b**,**e** was 50 min, **1c**,**f** 3 min, **1d** 25 min. Then, the tubes were unsealed, the excess of acrylonitrile was evaporated *in vacuo*. A dense residue was subjected to column chromatography to isolate the reaction products, which were purified by recrystallization from a mixture of hexane—ethyl acetate (10 : 3).

2-*tert*-Butyl-5-cyano-3-phenylisoxazolidine (*cis*-, *trans*-3h). The yield was 62%. ^1H NMR (acetone-d_6), δ: 1.03, 1.08 (both s, 9 H each, NBu^t); 2.35 (ddd, 1 H, *cis*-HC(4), J = 12.5 Hz, J = 5.9 Hz, J = 3.1 Hz); 2.68 (dt, 1 H, *trans*-HC(4)), J = 12.5 Hz, J = 7.8 Hz); 2.91 (ddd, 1 H, *trans*-HC(4), J = 12.5 Hz, J = 7.8 Hz, J = 4.7 Hz); 3.17 (dt, 1 H, *cis*-HC(4)), J = 9.0 Hz, J = 5.9 Hz); 4.26 (dd, 1 H, *cis*-HC(3), J = 12.5 Hz, J = 9.8 Hz); 4.58 (t, 1 H, *trans*-HC(3)), J = 7.8 Hz); 4.98 (dd, 1 H, *trans*-HC(5), J = 7.8 Hz, J = 5.1 Hz); 5.09 (dd, 1 H, *cis*-HC(5), J = 9.0 Hz, J = 3.1 Hz); 7.22—7.29, 7.30—7.41 (both m, 3 H each, *trans*-Ph, *cis*-Ph); 7.48—7.54, 7.55—7.61 (both m, 2 H each, *trans*-Ph, *cis*-Ph).

5-Cyano-2,3-diphenylisoxazolidine (*cis*-3i). The yield was 84%, m.p. 60—61 °C. IR (KBr), ν/cm^{-1}: 3063, 3031 (ν(C_{Ar}—H)); 2981, 2925, 2877 (ν(C—H)); 1598, 1489, 1425 (ν(C—C_{Ar})); 758, 697 (ω(C_{Ar}—H)). MS (EI, 70 eV), m/z (I_{rel} (%)): 250.1 $[M]^+$ (100), 180.1 $[M - 2 with - CN - O - 4 H]^+$ (14), 143.1 [M – –NPh – O]$^+$ (32), 142.0 [M – NPh – O – H] (40), 115.0 $[M - NPh - O - CN - 2 H]^+$ (28), 91.0 $[NPh]^+$ (53), 77.0 $[Ph]^+$ (29). ^1H NMR (acetone-d_6, 400 MHz), δ: 2.66 (ddd, 1 H, HC(4), J = 12.9 Hz, J = 5.5 Hz, J = 3.9 Hz); 3.37 (dt, 1 H, HC(4), J = 12.9 Hz, J = 9.0 Hz); 4.69 (dd, 1 H, HC(3), J = 9.0 Hz, J = 5.5 Hz); 5.37 (dd, 1 H, HC(5), J = 9.0 Hz, J = 3.5 Hz); 7.00—7.06 (m, 3 H, Ph); 7.25 (t, 2 H, Ph, J = 7.4 Hz); 7.35 (t, 1 H, Ph, J = 7.4 Hz); 7.43 (t, 2 H, Ph, J = 7.4 Hz); 7.60 (d, 2 H, Ph, J = 7.4 Hz). ^1H NMR (benzene-d_6, 400 MHz), δ: 1.94—2.10, 3.82—3.93 (both m, 2 H each, C(4), HC(3), HC(5)); 6.76 (t, 1 H, J = 7.0 Hz); 6.85—7.08 (m, 7 H, Ph); 7.27 (d, 2 H, Ph, J =7.4 Hz).

5-Cyano-2-methyl-3-(η⁶-phenyl)tricarbonylchromiumisoxazolidine (*cis*-3j). The yield was 90%, m.p. 112—113 °C. MS (MALDI MS), m/z (I_{rel} (%)): 363.0 $[M + K]^+$ (100), 279.1 $[M + K - 3 CO]^+$ (38), 227.1 $[M + K - Cr(CO)_3]^+$ (19). IR (KBr), ν/cm^{-1}: 2966, 2920, 2835 (ν(C—H)); 1964, 1875 (ν(C≡O)); 1531, 1458 (ν(C—C_{Ar})); 829, 790 (ω(C_{Ar}—H)). ^1H NMR (acetone-d_6), δ: 2.48—2.64 (m, 1 H, HC(4)); 2.79 (s, 3 H, NMe); 3.28—3.43, 3.51—3.67, 5.08—5.22 (all m, 1 H each, HC(4), HC(3), HC(5)); 5.53—6.38 (m, 5 H, PhCr). ^1H NMR (benzene-d_6), δ: 1.73—1.86 (m, 1 H, HC(4)); 2.00 (dd, 1 H, HC(4), J = 21.5 Hz, J = 9.4 Hz); 2.27 (s, 3 H, NMe); 2.33—2.49 (m, 1 H, HC(3)); 3.68 (d, 1 H, HC(5), J = 7.8 Hz); 4.13—4.35 (m, 3 H, C(3)PhCr); 4.61 (br.s, 2 H, C(3)PhCr).

2-*tert*-Butyl-5-cyano-3-(η⁶-phenyl)tricarbonylchromiumisoxazolidine (*cis*-3k). The yield was 81%, m.p. 120—121 °C. MS (MALDI MS), m/z (I_{rel} (%)): 405.1 $[M + K]^+$ (100), 321.2 [M + + K – 3 CO]$^+$ (42), 269.3 $[M + K - Cr(CO)_3]^+$ (16). IR (KBr), ν/cm^{-1}: 2918, 2851 (ν(C—H)); 1969, 1886, 1871 (ν(C≡O)); 1645, 1575 (ν(C—C_{Ar})); 830, 663 (ω(C_{Ar}—H)). ^1H NMR (acetone-d_6), δ: 1.15 (s, 9 H, NBu^t); 2.67 (d, 1 H, C(4), J = 13.7 Hz); 3.21—3.37 (m, 1 H, HC(4)); 4.45 (dd, 1 H, HC(3), J = 8.0 Hz, J = 4.0); 5.20 (br.d, 1 H, HC(5), J = 7.4 Hz); 5.56 (t, 1 H, PhCr, J = 6.3 Hz); 5.65 (t, 1 H, PhCr, J = 6.3 Hz); 5.73 (t, 1 H, PhCr, J = 5.9 Hz); 6.01 (d, 1 H, PhCr, J = 6.3 Hz); 6.14 (d, 1 H, PhCr, J = 5.9 Hz). ^1H NMR (benzene-d_6), δ: 0.81 (s, 9 H, NBu^t); 1.78—1.95, 1.96—2.14 (both m, 1 H each, C(4)); 3.35 (br.s, 1 H, HC(3)); 3.69 (d, 1 H, C(5), J = 5.1 Hz); 4.08—4.48 (m, 3 H, PhCr); 5.03, 5.12 (both s, 1 H each, PhCr).

5-Cyano-3-(η⁶-phenyltricarbonylchromium)-2-phenylisoxazolidine (*cis*-3l). The yield was 89%, m.p. 119—120 °C. MS (MALDI MS), m/z (I_{rel} (%)): 425.0 $[M + K]^+$ (100), 341.1 [M + + K – 3 CO]$^+$ (29), 289.1 $[M + K - Cr(CO)_3]^+$ (36). IR (KBr), ν/cm^{-1}: 2997, 2954, 2927 (ν(C—H)); 1954, 1893, 1872 (ν(C≡O)); 1596, 1488, 1451 (ν(C—C_{Ar})); 834, 807, 771, 663 (ω(C_{Ar}—H)). ^1H NMR (acetone-d_6), δ: 2.64—2.95, 3.07—3.34, 4.88—5.15, 5.22—5.47 (all m, 1 H each, HC(4), HC(3), HC(5)); 5.53—6.72, 6.90—7.70 (both m, 5 H, PhCr, NPh). ^1H NMR (benzene-d_6), δ: 1.69—1.81 (m, 2 H, $H_2C(4)$); 3.82 (dd, 1 H, HC(3), J = 8.6 Hz, J = 4.7 Hz); 3.90 (dd, 1 H, HC(5), J = 7.0 Hz, J = 3.5 Hz); 4.19—4.26 (m, 1 H, *o*-C(3)PhCr); 4.33 (ddd, 2 H, *m*-HCr, J = 6.3 Hz); 5.11 (d, 1 H, *p*-C(3)PhCr, J = 6.7 Hz); 6.81 (t, 1 H, *p*-NPh, J = 7.4 Hz); 6.87 (d, 2 H, NPh, J = 7.8 Hz); 7.00 (t, 2 H, NPh, J = 7.8 Hz).

Quantum chemical calculations. Charge distribution in nitrones **1c**,**f** and acrylonitrile (**2a**) was evaluated by different quantum chemical methods of simulation. The initial geometry of compounds under study was optimized using the HyperChem 8.0 program within the PM3 semiempirical method.[18] The calculated structures were used as the starting ones for the optimization of geometry within the density functional theory[38,39] using the B3LYP hybrid gradient functional[22,23] and a basis set with the LanL2DZ pseudo-core potential.[24] The stationary points found were characterized by the calculation of vibration frequencies. The calculations within the density functional theory were carried out using the Gaussian 09 program.[40]

X-ray diffraction studies of complex *cis*-3k. The crystals ($C_{17}H_{18}N_2O_4Cr$, M = 366.33) are orthorhombic, space group *Pca*2(1), a = 13.9300(8), b = 9.9790(6), c = 11.7793(7) Å, α = β = = γ = 90°, V = 1637.41(17) $Å^3$, Z = 4, d_{calc} = 1.486 mg m^{-3},

$\mu = 7.22$ cm^{-1}; obtained by crystallization from a mixture of hexane—ethyl acetate. Intensities of 22640 reflections (4631 independent reflections, $R_{int} = 0.0190$) were measured on a Smart Apex diffractometer (graphite monochromator, λ (Mo-Kα) = 0.71073 Å, temperature 100 K). Absorption was included using the SADABS program.[41] The structure was 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 nonhydrogen atoms. Hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. The final divergence factors: $R_1 = 0.0266$ ($I > 2\sigma(I)$), $wR_2 = 0.0712$ (refined on F^2_{hkl} for all the independent reflections), $S(F^2) = 1.076$, $\rho_{max/min} = 0.693/-0.197$ e Å^{-3}, the absolute structural parameter −0.009(12). All the calculations were performed on a personal computer using the SHELXTL software package.[42] The structure was deposited with the Cambridge Crystallographic Data Center (CCDC 1024600).

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