1,3-Dipolar cycloaddition reaction of nitrone η^6-(arene)chromium tricarbonyl complexes with styrene and η^6-(styrene)chromium tricarbonyl

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The products of 1,3-dipolar cycloaddition of the nitrone-type η^6-(arene)chromium tricarbonyl complexes $(CO)_3CrC_6H_5CH{=}N^+(O^-)R$, where R = Me, Ph, Bu^t, with styrene and η^6-(styrene)chromium tricarbonyl were obtained and characterized by a combination of physicochemical methods. This type of reactions proceeded with very high regio- and stereoselectivity to exclusively form *cis*-2,3,5-tri-substituted isoxazolidines.

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

Lately, η^6-(arene)chromium tricarbonyl complexes became important agents in selective organic synthesis.[1—4] A pronounced electron-withdrawing character of the metallic fragment imposes on them the reactivity unusual for arenes: they add nucleophiles to the arene ring and facilitate nucleophilic addition at α-benzyl position. Besides, the bulkiness of the chromium tricarbonyl group provides an efficient shielding of one of the arene ring sides, that can be widely used in stereoselective synthesis.

Cycloaddition is one of the fields where arenechromium tricarbonyl complexes can fully exhibit their unique abilities. 1,3-Dipolar cycloaddition of nitrones to functional alkenes is well known as very convenient and efficient method for the assembling heterocyclic rings.[5—7] The reaction of nitrones with different dipolarophiles is not always regio- and stereoselective, leading in most cases to the formation of a mixture of products, the ratio of which depends on the steric and electronic properties of reacting compounds.

Since the reaction can result in the formation of regio- and stereoisomers, a lot of undertaken attempts were directed on the development of efficient methods for the preparation of individual products. It was found[5] that the reactions of nitrones with electron-rich dipolarophiles were fairly selective, leading, as a rule, to C(5)-isomeric isoxazolidines. This regioselectivity does not operate only in the case of the electron-poor compounds, *i.e.*, dipolarophiles containing strong electron-withdrawing groups, such as —COOR, —CHO, —CN, or $-NO_2$. When electron-donating substituents are present, C(5)-substituted isoxazolidines are formed as exclusive or major products.

In our preceding work,[8] we have shown that the 1,3-dipolar cycloaddition reactions between free nitrones[3,9,10] **1a—c** and η^6-(styrene)chromium tricarbonyl[11] (**2a**), leading to the formation of isoxazolidines **3a—c**, were characterized by higher stereoselectivity as compared to the reactions in which both components were noncoordinated compounds (the reaction of nitrones **1a—c** and styrene (**2b**) with the formation of products **3d—f** (Scheme 1, Table 1)). In this case, all the products of this reactions (**3a—f**) were exclusively C(5)-substituted derivatives. We suggested that the introduction of the chromium tricarbonyl groups in both the dipole and the dipolarophile would considerably influence the regio- and stereoselectivity of 1,3-dipolar cycloaddition.

To sum up, we carried out detailed studies of the reactions of complexed nitrones with styrene and its derivatives in order to prepare a number of new individual isoxazolidine derivatives containing chromium tricarbonyl groups and find the influence of the $Cr(CO)_3$ group on the selectivity of the cycloaddition process and the structure of the products formed.

Results and Discussion

A series of coordinated nitrones **1d—f** were used as dipoles in the reactions under study. *C*-(η^6-Phenylchromium tricarbonyl)-*N*-methylnitrone (**1d**) was synthesized according to the method described earlier[3] from η^6-(benzaldehyde)chromium tricarbonyl[12,13] and methylhydroxylamine hydrochloride. This nitrone was found to have *trans*-configuration.[3] Nitrones **1e** and **1f** containing the phenyl and the *tert*-butyl group, respectively, at the nitrogen atom were synthesized using the known procedure (Scheme 2).

η^6-(Styrene)chromium tricarbonyl (**2a**) and styrene (**2b**) served as the dipolarophiles in the 1,3-dipolar cyclo-

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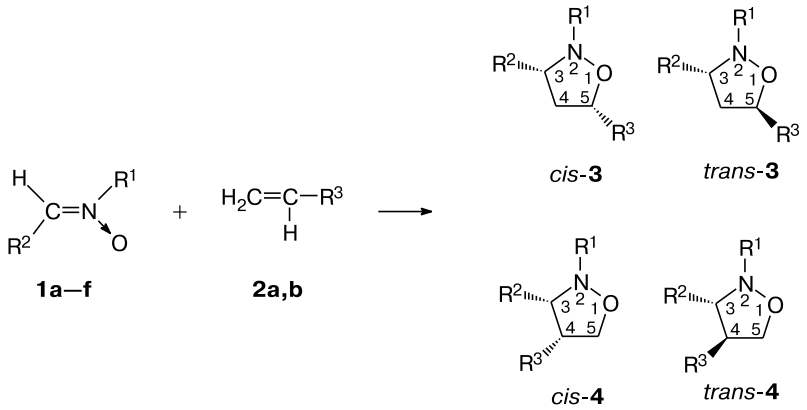
Scheme 1



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

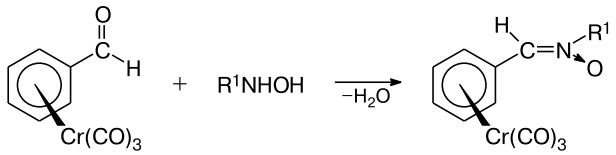
2: R^3 = Ph[Cr(CO)$_3$] (**a**); R^3 = Ph (**b**)

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

addition reactions. The reactions were carried out by heating of nitrone arenechromium tricarbonyl complexes (**1d—f**) with alkenes (**2a**, **b**) in sealed glass tubes at 80—90 °C *in vacuo* during 6—40 h. The products with remained Cr(CO)$_3$ group **3g—l** (see Table 1) were characterized by UV, IR, and NMR spectroscopy.

All the compounds obtained are yellow crystalline substances, relatively stable in air. Their main physicochemical properties and spectroscopic characteristics are given in Table 2.

Scheme 2



1d—f

R^1 = Me, Ph, Bu^t

Table 1. Ratio of *cis*- and *trans*-isomers of isoxazolidines **3a—l** in the 1,3-dipolar cycloaddition reactions

Nitrone (dipole)	Dipolarophile	Product	Ratio *cis : trans*
1a	**2a**	**3a**	83 : 17[a]
1b	**2a**	**3b**	100 : 0[a]
1c	**2a**	**3c**	100 : 0[a]
1a	**2b**	**3d**	67 : 33[b]
1b	**2b**	**3f**	90 : 10[b]
1c	**2b**	**3e**	100 : 0
1d	**2a**	**3g**	100 : 0
1e	**2a**	**3h**	100 : 0
1f	**2a**	**3i**	100 : 0
1d	**2b**	**3j**	100 : 0[c]
1e	**2b**	**3k**	100 : 0
1f	**2b**	**3l**	100 : 0

[a]Data of the work.[8]
[b]Data of the work.[6]
[c]Data of the work.[3]

The ^{1}H NMR spectra of adducts **3j—l**, obtained by the reaction of coordinated nitrones **1d—f** with styrene (**2b**), show that they are exclusive *cis*-2,3,5-tri-substituted isoxazolidines. Thus, for example, the product of the 1,3-dipolar cycloaddition of *C*-(η⁶-phenylchromium tricarbonyl)-*N*-phenylnitrone (**1e**) and styrene (**2b**), *i.e.*, η⁶-(3-phenylchromium tricarbonyl)-2,5-diphenylisoxazolidine (**3k**), as well as analogous *cis*-isoxazolidine **3j** containing the methyl substituent at the nitrogen atom,[3] has two separate signals from the protons at atom C(4) in the ^{1}H NMR spectrum, while the *trans*-configuration of this compound should have led to the coalescence (approach) of the signals for the protons at the quaternary carbon atom, that is clearly observed in the case of noncoordinated compounds[6] (Table 3). Such shapes of the spectra are due to the fact that in the *trans*-isomers, the hydrogen atoms at atom

Table 2. Some characteristics* of isoxazolidines **3g—l**

cis-Isoxazolidine	R^1	R^2	R^3	M.p./°C	Yield (%)	ν(C≡O)/cm^{-1}
3g	Me	Ph[Cr(CO)$_3$]	Ph[Cr(CO)$_3$]	155—156	20	1967, 1880
3h	Ph	Ph[Cr(CO)$_3$]	Ph[Cr(CO)$_3$]	132—133	38	1964, 1875
3i	Bu^t	Ph[Cr(CO)$_3$]	Ph[Cr(CO)$_3$]	136—137	36	1964, 1875
3j	Me	Ph[Cr(CO)$_3$]	Ph	Oil	—	1970, 1890
3k	Ph	Ph[Cr(CO)$_3$]	Ph	121 —122	62	1962, 1886
3l	Bu^t	Ph[Cr(CO)$_3$]	Ph	40—41	30	1965, 1884

* The data for isoxazolidine *cis*-**3j** are taken from the work.[3]

C(4) are equidistant from the protons at atoms C(3) and C(5) and, consequently, equally interact with them. In the case of *cis*-complexes, this interaction of one of the protons at atom C(4) predominates because of its proximity to the protons at atoms C(3) and C(5), that finally leads to the greater difference in the chemical shift values.

The reaction of coordinated nitrones **1d—f** with η^6-(styrene)chromium tricarbonyl (**2a**) in toluene at 80 °C also leads to the selective preparation of 2,3,5-tri-substituted isoxazolidines with the *cis*-structure (**3g—i**). The NMR spectroscopic and mass spectrometric data indicate the presence in the molecules of two $Cr(CO)_3$ groups. X-ray diffraction analysis of complex **3h** confirms the *cis*-structure of the compound and shows that the phenylchromium tricarbonyl groups are on the same side of the plane of the isoxazolidine ring (Fig. 1, Table 4).

The chemical shift of the signals for two protons at atom C(4) of compound **3h** are different (see Table 3), that confirms the *cis*-structure of the complex. Similar results are also observed in the case of isoxazolidines *cis*-**3g** and *cis*-**3i** (see Experimental).

The exclusive formation of one of the possible regioisomers in the reactions of complexed nitrones **1d—f** with different dipolarophiles (**2a**, **2b**) can be explained in terms of both the frontier orbital theory and the charge distribution in the reacting molecules theory.[14,15] The mechanism of the high stereoselectivity is not yet completely clear. However, it can be suggested that the reason is the stabilization of the transition states due to the stacking interactions (Scheme 3).

Table 3. Chemical shifts and shapes of ^{1}H NMR signals of the protons at carbon atom C(4) of isoxazolidines **3b**,**e**,**h**,**k***

Compound	δ_H
cis-**3b**	2.37 (td), 3.37 (td)
cis-**3e**	2.36 (td), 2.88 (td)
trans-**3e**	2.52—2.68 (м)
cis-**3h**	2.41 (ddd), 3.40 (ddd)
cis-**3k**	2.25—2.51 (m), 3.15—3.53 (m)

* The data for compound *cis*-**3b** are taken from the work,[8] for compounds *cis*-**3e** and *trans*-**3e**, from the work.[6]

It is possible that the formation of the transition state **A** in the reaction of nitrones **1d—f** with styrene (**2b**) is more preferable as compared to the complex **B** because of the possibility of the π—π-interaction of the dipolarophile benzene ring with the coordinated ring of the nitrone. The arising of the stable enough charge transfer complex between benzene and η^6-(benzene)chromium tricarbonyl has been reported earlier.[16] The electron-withdrawing effect of the chromium tricarbonyl group in the dipole significantly stabilizes the π—π-interaction between the arene rings (the transition step **A**), whereas complex **B** has no such a stabilizing influence. Similarly, the reactions of complexed nitrones **1d—f** with η^6-(styrene)chromium tricarbonyl (**2a**) are also very selective and form products **3g—i** with the *cis*-structure, possibly due to the existing possibility of stabilization of state **C**.

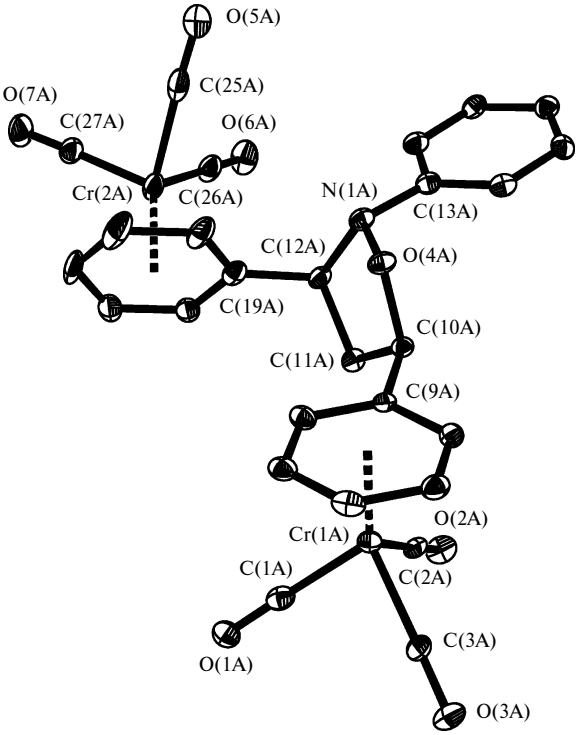
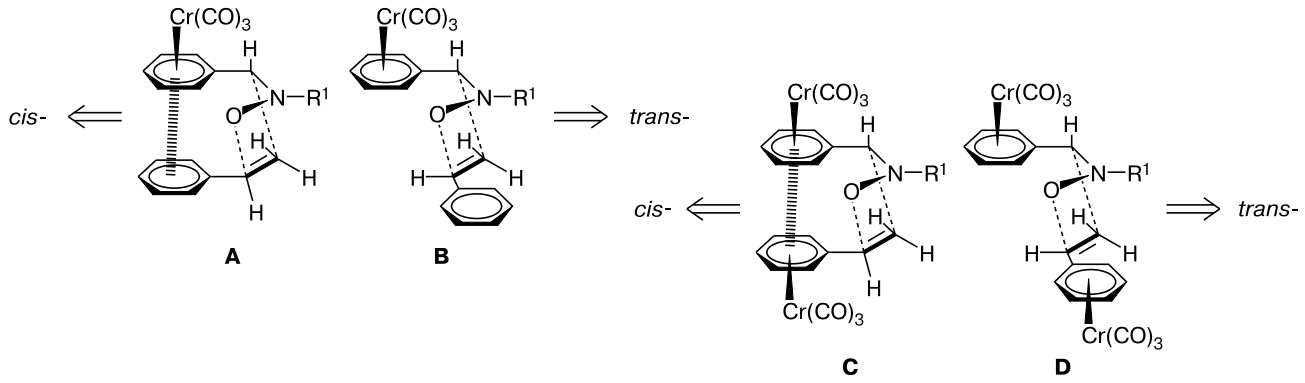


Fig. 1. Molecular structure of complex *cis*-**3h** (hydrogen atoms are not shown).

Table 4. Principal bond distances and bond angles in the structure of complex *cis*-**3h**

Bond	*d*/Å	Angle	ω/deg
N(1A)—C(12A)	1.474(6)	O(4A)—N(1A)—C(12A)	105.0(4)
N(1A)—O(4A)	1.423(5)	N(1A)—O(4A)—C(10A)	107.2(3)
O(4A)—C(10A)	1.469(6)	O(4A)—C(10A)—C(11A)	105.1(4)
C(10A)—C(11A)	1.523(7)	C(10A)—C(11A)—C(12A)	104.0(4)
C(11A)—C(12A)	1.554(7)	N(1A)—C(12A)—C(11A)	105.2(4)
C(9A)—C(10A)	1.533(7)	C(1A)—Cr(1A)—C(2A)	89.3(2)
C(12A)—C(19A)	1.514(8)	C(3A)—Cr(1A)—C(1A)	88.7(2)
N(1A)—C(13A)	1.441(7)	C(3A)—Cr(1A)—C(2A)	86.9(2)
Cr(1A)—C(1A)	1.844(6)	C(26A)—Cr(2A)—C(25A)	87.2(3)
Cr(1A)—C(2A)	1.852(6)	C(27A)—Cr(2A)—C(25A)	91.6(3)
Cr(1A)—C(3A)	1.844(6)	C(27A)—Cr(2A)—C(26A)	90.4(3)
Cr(2A)—C(25A)	1.848(7)		
Cr(2A)—C(26A)	1.844(6)		
Cr(2A)—C(27A)	1.842(6)		

Scheme 3



R^1 = Me, Ph, Bu^t

To sum up, the analysis of the *cis*- and *trans*-isomer ratios of isoxazolidines **3a**—**l** in the 1,3-dipolar cycloaddition reactions shows that the stereoselectivity of the process for the complexed nitrones is 100% and, therefore, higher than in the case when coordinated dipolarophiles are used:[8] the reaction of free nitrone **1a** and styrene (arene)chromium tricarbonyl complex **2a** leads to a mixture of isomers in the ratio 83 : 17, while the reaction of *C*-(η⁶-phenylchromium tricarbonyl)-*N*-phenylnitrone (**1d**) with styrene (**2b**) gives *cis*-isoxazolidine **3j** as the only product (see Table 1). In the case of the phenyl and the *tert*-butyl substituents at the nitrogen atom of the nitrone molecule, both reactions, involving the complexed nitrones and that using the coordinated styrene, proceed with 100% stereoselectivity.

Interesting features were found while analyzing the IR spectra of the obtained isoxazolidines **3j**—**l**. In contrast to the *C*(5)-(arene)chromium tricarbonyl complexes, which are characterized by the presence of three bands of the carbonyl stretching vibrations ν(C≡O)[8] resulted from the intramolecular interaction of the $Cr(CO)_3$ group with the oxygen atom,[8,17] complexes **3j**—**l** have only two bands of such vibrations, that is explained by the impossibility of the intramolecular contact of the $Cr(CO)_3$ group with the oxygen atom, since they are remote from each other.

In conclusion, based on the experimental data obtained, the following conclusions can be drawn:

— the high regioselectivity still persists in the reaction of nitrones containing the $Cr(CO)_3$ group at the carbon atom with styrene and η⁶-(styrene)chromium tricarbonyl, that leads to the exclusive formation of C(5)-substituted products;

— the formed isoxazolidines are *cis*-isomers, that resulted from the stronger π—π-interaction of the phenyl rings in the transition state.

Experimental

All the solvents were distilled over metallic sodium at atmospheric pressure.[18] To remove the stabilizer, styrene (**2b**) was

washed with 10% aqueous sodium hydroxide and water, dried, and distilled (b.p. 48—49 °C (10 Torr)). *N*-Phenyl- and *N*-*tert*-butylhydroxylamines were obtained by the reduction of the corresponding nitro compounds.[9,19] *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 led to the formation of benzaldehyde diethyl acetal.[12] The reaction of benzaldehyde diethyl acetal and chromium hexacarbonyl led to η^6-(benzaldehyde diethyl acetal)chromium tricarbonyl, which was hydrolyzed to η^6-(benzaldehyde)chromium tricarbonyl.[13] *C*,*N*-Di-substituted nitrones (**1a**—**f**) were obtained by the condensation of the corresponding hydroxylamine derivatives with benzaldehyde,[3,9,10] or with η^6-(benzaldehyde)chromium tricarbonyl.[3] η^6-(Styrene)-chromium tricarbonyl (**2a**) was synthesized according to the method described in the literature.[11]

The products were isolated and purified by column chromatography on Acros silica gel (0.035—0.070 mm). HPLC was carried out on a Knauer Smartline 5000 chromatograph with a PDA detector S 2600, a Diasfer-110-C16, 5 μm, 4.6×250 mm column, eluent acetonitrile—water (84 : 16). UV spectra of eluates were recorded in the range 200—500 nm. IR spectra (suspension with KBr) were recorded on a Infralyum FT-801 spectrometer in the range 480—4600 cm^{-1}. ^1H NMR spectra were recorded on Bruker DPX 200 and Bruker Avance DPX 400 spectrometers (200 and 400 MHz, respectively), solvent acetone-d_6. Mass spectrometric studies were carried out on a Bruker Microflex LT instrument using time-of-flight mass spectrometry with the matrix-activated laser desorbtion/ionization (MALDI MS).

***C*-(η^6-Phenylchromium tricarbonyl)-*N*-phenylnitrone (1e).** The yield was 75%, m.p. 118—119 °C. Found (%): C, 58.06; H, 3.54; N, 4.20; Cr, 15.71. $C_{16}H_{11}NO_4Cr$. Calculated (%): C, 57.67; H, 3.33; N, 4.20; Cr, 15.60. IR (KBr), ν/cm^{-1}: 2956, 2924, 2867 (ν(C—H)); 1979, 1891, 1866 (ν(C≡O)); 1644 (C—C_{Ar}); 1547(ν(C=N)); 1197 (ν(Ph—N)); 1068 (ν(N—O)); 887, 771, 689 (ν(C_{Ar}—H)). ^1H NMR (200 MHz), δ: 5.56—5.90 (m, 3 H, *m*,*p*-PhCr); 6.88 (d, 2 H, *o*-PhCr, *J* = 6.3 Hz); 7.54 (m, 3 H, *o*,*p*-Ph); 7.72—7.98 (m, 2 H, *m*-Ph); 8.18 (s, 1 H, =C—H).

***C*-(η^6-Phenylchromium tricarbonyl)-*N*-*tert*-butylnitrone (1f).** The yield was 90%. m.p. 102—103 °C. Found (%): C, 54.03; H, 4.81; N, 4.50; Cr, 16.43. $C_{14}H_{15}NO_4Cr$. Calculated (%): C, 53.68; H, 4.83; N, 4.47; Cr, 16.60. IR (KBr), ν/cm^{-1}: 2963, 2922, 2850 (ν(C—H)); 1976, 1893, 1871 (ν(C≡O)); 1650 (C—C_{Ar}); 1557(ν(C=N)); 1118 (ν(N—O)); 803, 680, 628 (ν(C_{Ar}—H)). ^1H NMR (200 MHz), δ: 1.54 (s, 9 H, Bu^t—N); 5.68 (m, 3 H, *p*,*m*-PhCr); 6.71 (dd, 2 H, *o*-PhCr, *J* = 6.5 Hz, *J* = 1.7 Hz); 7.59 (s, 1 H, =C—H).

Synthesis of 3,5-di-η^6-(phenylchromium tricarbonyl)-substituted isoxazolidines 3g—i (general procedure). The corresponding nitrone **1d—f** (0.8 mmol), η^6-(styrene)chromium tricarbonyl (**2a**) (0.8 mmol), and toluene (3 mL) were placed in a 5-mL glass tube. The tube was degassed and sealed *in vacuo*. The reaction mixture was heated for 40 h at 80 °C. The tube was unsealed, the content was filtered through a Shotte filter, the precipitate was washed on the filter with toluene, and the solvent was evaporated *in vacuo*. Column chromatography was used to isolate the reaction products from a dense residue, which were recrystallized from a mixture of hexane—ethyl acetate (3 : 1) to obtain the target products.

3,5-Di-η^6-(phenylchromium tricarbonyl)-2-methylisoxazolidine (*cis*-3g). The yield was 20%, m.p. 155—156 °C. Found (%): Cr, 19.70. $C_{22}H_{17}NO_7Cr_2$. Calculated (%): Cr, 20.35. MS (MALDI MS), *m*/*z* (I_{rel} (%)): 549.6 $[M + K]^+$ (41), 429.1 $[M + K - C_6H_6 - CH_3 - H]^+$ (36), 291.0 $[M + K - Cr(CO)_3 - Ph - CH_3]^+$ (100). IR (KBr), ν/cm^{-1}: 2356 (ν(C—H)); 1967, 1880 (ν(C≡O)); 1632 (ν(C—C_{Ar})); 1147, 1099 (ν(N—O, C—O)); 1011 (ν(C—N)); 660, 633 (ω(C_{Ar}—H)). ^1H NMR (400 MHz), δ: 2.08 (s, 3 H, CH_3N); 2.31 (ddd, 1 H, HC(4), *J* = 14.4 Hz, *J* = 12.8 Hz, *J* = 7.2 Hz); 3.43 (ddd, 1 H, HC(4), *J* = 12.8 Hz, *J* = 7.6 Hz, *J* = 7.2 Hz); 3.83 (t, 1 H, HC(3), *J* = 7.6 Hz); 5.07 (t, 1 H, HC(5), *J* = 7.5 Hz); 5.64 (m, 10 H, C(3)PhCr, C(5)PhCr).

3,5-Di-η^6-(phenylchromium tricarbonyl)-2-phenylisoxazolidine (*cis*-3h). The yield was 38%, m.p. 132—133 °C. Found (%): Cr, 18.03. $C_{27}H_{19}NO_7Cr_2$. Calculated (%): Cr, 18.15. MS (MALDI MS), *m*/*z* (I_{rel} (%)): 611.6 $[M + K]^+$ (35), 475.2 $[M + K - Cr(CO)_3]^+$ (69), 429.1 $[M + K - 2\ Ph - CO]^+$ (57), 340.0 $[M + K - 2\ Cr(CO)_3 + H]^+$ (38), 301.0 $[M - 2\ Cr(CO)_3]^+$ (18), 108.0 $[Cr(CO)_2]^+$ (100). IR (KBr), ν/cm^{-1}: 2967, 2928, 2877 (ν(C—H)); 1964, 1875 (ν(C≡O); 1643 (ν(C—C_{Ar})); 1384 (ν(C—C)); 1015 (ν(C—O)); 660, 632, 533 (ω(C_{Ar}—H)). ^1H NMR (200 MHz), δ: 2.41 (ddd, 1 H, HC(4), *J* = 12.9 Hz, *J* = 8.7 Hz, *J* = 4.2 Hz); 3.40 (ddd, 1 H, HC(4), *J* = 12.1 Hz, *J* = 8.5 Hz, *J* = 7.8 Hz); 4.82—5.19 (m, 2 H, HC(3), HC(5)); 5.50—5.76 (m, 7 H, C(3)PhCr, C(5)PhCr); 5.83 (br.d, 1 H, C(3)PhCr/C(5)PhCr, *J* = 5.9 Hz); 5.92 (d, 1 H, C(3)PhCr/C(5)PhCr, *J* = 5.3 Hz); 6.10 (d, 1 H, C(3)PhCr/C(5)PhCr, *J* = 2.91 Hz); 6.88—7.09 (m, 1 H, PhN); 7.09—7.46 (m, 4 H, PhN).

3,5-Di-η^6-(phenylchromium tricarbonyl)-2-*tert*-butylisoxazolidine (*cis*-3i). The yield was 36%, m.p. 136—137 °C. Found (%): Cr, 18.60. $C_{25}H_{23}NO_7Cr_2$. Calculated (%): Cr, 18.80. MS (MALDI MS), *m*/*z* (I_{rel} (%)): 591.8 $[M + K]^+$ (100), 507.9 $[M - Bu^t]^+$ (30). IR (KBr), ν/cm^{-1}: 2967, 2928, 2877 (ν(C—H)); 1964, 1875 (ν(C≡O); 1643 (ν(C—C_{Ar})); 1384 (ν(C—C)); 1015 (ν(C—O)); 660, 632, 533 (ω(C_{Ar}—H)). ^1H NMR (200 MHz), δ: 1.20 (s, 9 H, Bu^tN); 2.37 (ddd, 1 H, HC(4), *J* = 12.8 Hz, *J* = 6.8 Hz, *J* = 5.9 Hz); 3.14—3.70 (m, 1 H, HC(4)); 4.51 (dd, 1 H, HC(3), *J* = 7.3 Hz, *J* = 7.0 Hz); 4.99 (t, 1 H, HC(5), *J* = 7.3 Hz); 5.39—5.73 (m, 7 H, C(3)PhCr, C(5)PhCr); 5.79 (d, 1 H, C(3)PhCr/C(5)PhCr, *J* = 6.7 Hz); 5.95 (d, 1 H, C(3)PhCr/C(5)PhCr, *J* = 7.0 Hz); 6.09 (d, 1 H, C(3)PhCr/C(5)PhCr, *J* = 6.6 Hz).

Synthesis of η^6-(3-phenylchromium tricarbonyl)-substituted isoxazolidines 3j—l (general procedure). The corresponding nitrone **1d—f** (0.65 mmol) and freshly distilled styrene (**2b**) (3 mL, 0.0261 mol) were placed in a 5-mL glass tube. The tube was degassed and sealed *in vacuo*. The reaction mixture was heated for 6 h at 90 °C. The tube was unsealed, the solution in the tube was diluted with isopropyl alcohol to make the formed polystyrene to precipitate. Then, the solution was decanted, toluene and isopropyl alcohol were evaporated *in vacuo*. Column chromatography was used to isolate the reaction products from a dense residue, which were recrystallized from a mixture of hexane—ethyl acetate (15 : 2) to obtain the target products.

η^6-(3-Phenylchromium tricarbonyl)-2,5-diphenylisoxazolidine (*cis*-3k). The yield was 62%, m.p. 121—122 °C. Found (%): C, 65.73; H, 4.21; N, 3.06; Cr, 12.01. $C_{24}H_{19}NO_4Cr$. Calculated (%): C, 65.90; H, 4.38; N, 3.20; Cr, 11.89. IR (KBr), ν/cm^{-1}: 2920, 2954, 2853 (ν(C—H)); 1962, 1886 (ν(C≡O)); 1594 (ν(C—C_{Ar})); 1488 (ν(C—C)); 1230, 1110 ν(N—O, C—O)); 1031 (ν(C—N)); 762, 657, 631 (ω(C_{Ar}—H)). ^1H NMR (400 MHz),

δ: 2.25—2.51 (m, 1 H, HC(4)); 3.15—3.53 (m, 1 H, HC(4)); 5.04 (dd, 1 H, J = 8.7 Hz, J = 5.0 Hz, HC(3)); 5.13—5.33 (m, 1 H, HC(5)); 5.69 (d, 3 H, *m*,*p*-C(3)PhCr, J = 3.9 Hz); 5.91 (d, 1 H, *o*-C(3)PhCr, J = 5.5 Hz); 6.12 (d, 1 H, *o*-C(3)PhCr, J = 3.6 Hz); 6.99 (t, 1 H, *p*-PhN, J = 7.0 Hz); 7.11—7.58 (m, 9 H, PhN, PhC(5)).

η^6-(3-Phenylchromium tricarbonyl)-2-*tert*-butyl-5-phenylisoxazolidine (*cis*-3l). The yield was 30%, m.p. 40—41 °C. Found (%): C, 63.05; H, 5.69; N, 3.17; Cr, 12.63. $C_{22}H_{23}NO_4Cr$. Calculated (%): C, 63.30; H, 5.55; N, 3.35; Cr, 12.46. IR (KBr), ν/cm^{-1}: 2960, 2924, 2853 (ν(C—H)); 1965, 1884 (ν(C≡O)); 1643 (ν(C—C_{Ar})); 1454 (ν(C—C)); 1261, 1138 (N—O, C—O)); 1023 (ν(C—N)); 803, 663, 632 (ω(C_{Ar}—H)). ^{1}H NMR (400 MHz), δ: 1.21 (s, 9 H, Bu^{t}N); 2.18—2.52 (m, 1 H, HC(4)); 3.32 (ddd, 1 H, J = 12.6 Hz, J =7.4 Hz, J = 6.0 Hz, HC(4)); 4.53 (dd, 1 H, HC(3), J = 8.3 Hz, J = 6.2 Hz); 5.26 (t, 1 H, HC(5), J = 7.6 Hz); 5.51 (dd, 2 H, *m*-C(3)PhCr, J = 9.6 Hz, J = 5.9 Hz); 5.66 (t, 1 H, *p*-C(3)PhCr, J = 6.3 Hz); 5.91 (d, 1 H, *o*-C(3)PhCr, J = 6.4 Hz); 6.10 (d, 1 H, *o*-C(3)PhCr, J = 6.9 Hz); 7.04—7.66 (m, 5 H, C(5)Ph).

X-ray diffraction studies of complex *cis*-3h. Crystals ($C_{27}H_{19}NO_7Cr_2$, M = 573.43), triclinic, space group P-1, at 100 K: a = 7.9506(9), b = 13.9545(16), c = 22.393(3) Å, α = 80.218(2), β = 83.792(2), γ = 89.219(2)°, V = 2433.9(5) Å^3, Z = 4, d_{calc} = 1.565 g cm^{-3}, μ = 9.42 cm^{-1}, were obtained by crystallization from a mixture of hexane—ethyl acetate (10 : 1). Intensities of 20067 reflections (9429 independent reflections, R_{int} = 0.0532) were measured on a Smart Apex diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, temperature 100 K). Allowance for absorption was made using the SADABS program.[20] The structure was solved by direct method and refined by the full-matrix least squares method on F^2_{hkl} with anisotropic thermal parameters for all the nonhydrogen atoms. The hydrogen atoms were placed in the geometrically calculated positions and refined using the riding model. The final divergent factors: R_1 = 0.0744 ($I > 2\sigma(I)$), wR_2 = 0.1632 (refinement on F^2_{hkl} for all the independent reflections). All the calculations were performed on a personal computer using the SHELXTL software.[21]

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