Organometallic Chemistry

Synthesis of areneacetylenic chelate complexes of chromium with a terminal triple bond, their reversible rearrangements to areneallenic chelates, and addition at the triple bond

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New areneacetylenedicarbonylchromium chelate complexes containing the terminal acetylene fragment in the side chain of the arene ligand were synthesized. The rearrangement of these chelates to the previously unknown areneallenedicarbonylchromium chelate complexes was found and studied. It was demonstrated that this rearrangement is in principle reversible. For areneallenedicarbonylchromium chelates, a new example of metallotropic rearrangement was found and both isomers, namely, with the coordination either at the substituted or at the nonsubstituted double bond of the allene ligand, were detected for the first time. The coupled addition of the proton and the nucleophile at the coordinated triple bond afforded the corresponding areneolefin chelates.

Key words: areneacetylenedicarbonylchromium chelate complexes, areneallenedicarbonylchromium chelates, metallotropic rearrangement, synthesis, IR, ^{1}H and ^{13}C NMR, and mass spectra.

Acetylenic complexes of the (arene)Cr(CO)$_2$(alkyne) type are poorly studied.[1] The reason is that these compounds are generally rather unstable. This is particularly true for complexes with terminal acetylene fragments. For example, we found that when a mixture of mesitylenetricarbonylchromium and methyl propargyl ether was irradiated with UV light, the color of the reaction mixture changed from yellow to dark-crimson, which is typical of π-acetylenic chromium complexes. However, the resulting complex was so unstable that we failed to record its IR spectrum in heptane. At the same time, it is well known[2] that the incorporation of the olefin ligand, as an example, into the chelate ring results in substantial enhancement of the stability of this type of complexes compared to nonchelated analogs of the (arene)Cr(CO)$_2$(olefin) type. Actually, the introduction of the acetylene group into the chelate ring allowed us to synthesize a series of rather stable areneacetylenic chelate complexes of chromium[3] starting from arenetricarbonylchromium complexes, which contain the internal acetylene group at the ω position in the side chain of the arene ligand, and to study some reactions of the resulting compounds.[4] However, when developing procedures for the synthesis of chelate complexes containing the terminal acetylene group, we found that conversions of the corresponding starting arenetricarbonylchromium compounds under irradiation with UV light were substantially more complicated than

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the simple intermolecular cyclization to form an only product, *viz.*, the areneacetylenic chelate dicarbonylchromium complex, as has been reported previously.[3] Thus, when irradiated with UV light, solutions of arenetricarbonylchromium complexes (**1**), which contain the ω-ethynyl group in the side chain of the arene ligand, in a benzene—heptane mixture gave two dicarbonylchromium compounds (**3b,c**) and (**4b,c**) along with areneacetylenic chelates (**2b,c**) (irradiation of complex **1a** ($n = 0$, $m = 0$) resulted in decomposition of the initial **1a** rather than affording the corresponding chelate complexes, which is apparently due to steric hindrances upon coordination, *viz.*, due to the short bridge and the linear structure of the $CH_2C{\equiv}C$ fragment).

Within 1 h after the beginning of irradiation with UV light, the carbonyl region of the IR spectra of the reaction mixture had absorption bands corresponding to areneacetylenic chelate **2b,c** (ν(CO) 1879 and 1934 cm^{-1}; and 1872 and 1930 cm^{-1}, respectively) along with bands of the initial tricarbonyl compound (ν(CO) 1914 and 1982 cm^{-1}). However after 2 h, two new pairs of ν(CO) bands appeared (at 1896 and 1941 cm^{-1} for **3b**; at 1898 and 1951 cm^{-1} for **4b**; at 1889 and 1935 cm^{-1} for **3c**; and at 1896 and 1946 cm^{-1} for **4c**). During further irradiation of the reaction mixture, the intensities of the bands corresponding to compounds **1b,c** and **2b,c** gradually decreased and then disappeared. Finally, the IR spectrum of the reaction mixture had only two pairs of ν(CO) bands, which are indicative of the presence of two new compounds, *viz.*, **3b,c** and **4b,c**. In view of these facts, it can be suggested that **3b,c** and **4b,c** are products of rearrangement of the areneacetylenic chelates. Actually, when a solution of the initial compound **1b** in a benzene—heptane mixture in the presence of a twofold or greater excess of PPh_3, $P(OEt)_3$,[*] or Et_3N was irradiated with UV light or when a solution of **1b** in THF or in a THF—benzene mixture was irradiated, areneacetylenic chelate **2b** was obtained as the only reaction product.

It should be noted that the use of Et_2O did not retard the further rearrangement at room temperature. However, when the temperature was decreased and an immersion lamp was used (a sharp decrease in the time of irradiation), the rearrangement was completely inhibited. Chelate complex **2b** was obtained in yields from 27 to 70% depending on the reaction conditions. The stability of the analogous complex containing the four-atom bridge appeared to be substantially lower, which resulted in a noticeable decrease in the yield. Because of this, complex **2c** was characterized only by the IR spectra in the carbonyl region. The stability of complex **2b**, though higher than that of **2c**, is rather low, particularly, in a solution. In the crystalline state, chelate **2b** (dark-cherry crystals soluble in most organic solvents) can be stored in air for several hours.

As mentioned above, the IR spectra of chelates **2b,c** have two intense absorption bands in the carbonyl region (for **2b**, see above; for **2c**, at 1872 and 1930 cm^{-1}, which correspond to the $Cr(CO)_2$ fragment). As in the case reported previously,[3] the absorption bands of **2c** are shifted to the low-frequency region compared to **2b** due to an increase in the size of the chelate ring. In the ^1H NMR spectrum of compound **2b**, the signal of the methine proton is shifted downfield (Δδ ~ 2.4), which is typical of coordination, and the constant ^4J decreases to 2 Hz. The positions of the remaining signals differ only slightly from those of the initial **1b**. In the ^{13}C NMR spectrum of complex **2b**, the signals of the carbon atoms of the triple bond are shifted upfield (Δδ ~ 5—15) upon coordination; the chemical shifts are 66.5 ($\equiv\underline{C}-CH_2$) and 68.7 ($\equiv CH$) ppm. The resonance of the arene carbon atoms is manifested in the region of 80—110 ppm, which is also typical of arene chromium complexes. The remaining signals are observed in the characteristic regions.

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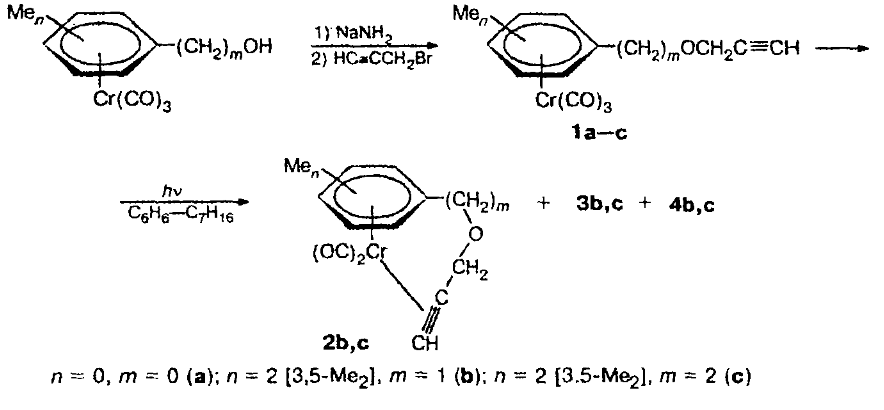
[*] It should be noted that arenedicarbonylchromium complexes with PPh_3 and $P(OEt)_3$ were not detected, which indicates that the intramolecular reaction proceeded substantially faster than the intermolecular reaction. In this case, this fact is a manifestation of the kinetic chelate effect.[2]

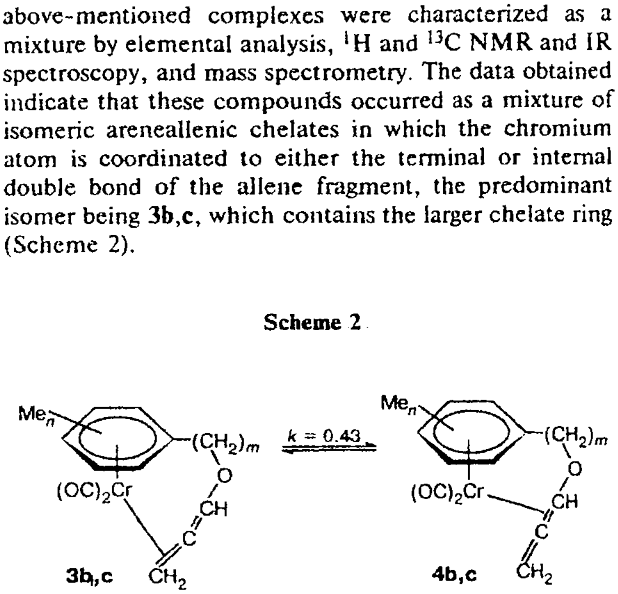
Scheme 1



$n = 0$, $m = 0$ (**a**); $n = 2$ [3,5-Me$_2$], $m = 1$ (**b**); $n = 2$ [3.5-Me$_2$], $m = 2$ (**c**)

Therefore, it is significant that the use of the chelate effect in the case of complexes **2b,c** made it possible to substantially improve the stability of compounds of the (arene)Cr(CO)$_2$(alkyne) type and to isolate these compounds in the individual state. As for complexes **3b,c** and **4b,c**, which were formed under irradiation of **1b,c**, with UV light in the absence of n-donor additives, along with the areneacetylenic chelates, we suggested that they were formed as a result of rearrangement of **2b,c**. Therefore, we irradiated **2b**, which was preliminarily isolated in the individual state, with UV light under the same conditions. Actually, in this case we also obtained the same mixture of compounds. An analogous result was also obtained upon heating of a solution of **2b** in heptane, the rearrangement being observed even at 30 °C. An increase in the temperature led to an increase in the reaction rate, but the yield of a mixture of complexes **3b** and **4b** was lower due to decomposition. It is known (see, for example, Refs. 5—8) that Al_2O_3 causes rearrangements of free and coordinated acetylenes. Actually, when compound **2b** was stirred with Al_2O_3 in a 1 : 1 ether—heptane mixture, **3b** and **4b** were obtained. However, the reaction did not go to completion. It should be be noted that compounds **3b** and **4b** cannot be separated by low-temperature column chromatography or by fractional crystallization. The enriched major isomer **3b** (90% according to the IR spectra in heptane) can be obtained by low-temperature recrystallization from heptane. However, dissolution of this enriched isomer **3b** in polar solvents (diethyl ether, acetone, or carbon disulfide) again resulted in the equilibrium mixture of both isomers (73% of **3b** + 27% of **4b**; according to the data of NMR and IR spectroscopy), which indicates that these compounds readily (within the preparative time scale) underwent interconversions. Because of this, the above-mentioned complexes were characterized as a mixture by elemental analysis, ^{1}H and ^{13}C NMR and IR spectroscopy, and mass spectrometry. The data obtained indicate that these compounds occurred as a mixture of isomeric areneallenic chelates in which the chromium atom is coordinated to either the terminal or internal double bond of the allene fragment, the predominant isomer being **3b,c**, which contains the larger chelate ring (Scheme 2).

Scheme 2



n = 2 [3,5-Me$_2$], m = 1 (**b**); n = 2 [3,5-Me$_2$], m = 2 (**c**)

A mixture of complexes **3b** and **4b** exists as orange-red crystals readily soluble in most organic solvents. Their stability is noticeably higher than that of acetylenic chelate **2b**. The enhanced stability of allenic complexes containing the $[C_5H_5Fe(CO)_2]^+$ fragment compared to olefin analogs was noted previously.[9] As for a mixture of complexes **3c** and **4c**, these compounds appeared to be less stable than **3b** and **4b** and were characterized only by the IR spectra in the carbonyl region.

The IR spectra of complexes **3b** and **4b** have a band at 1750 cm^{-1}, which is indicative of the presence of the coordinated allene group,[8—11] along with the above-mentioned two pairs of bands in the ν(CO) vibration region. It should be also noted that the ν(CO) bands for the second isomer are observed in the higher-frequency region, which is consistent with the smaller chelate ring in **4b** compared to **3b**.

The presence of the allene group and the fact that the chromium atom is coordinated at the terminal double bond of the allene group in isomer **3b** are evidenced by two signals in the ^{1}H NMR spectrum, namely, a triplet (δ = 8.06) and a doublet (δ = 2.34) with the constant J = 3.2 Hz, which correspond to the protons of the =CH and =CH$_2$ fragments, respectively. The upfield shift of the signal of the =CH$_2$ protons correlates well with the presence of the coordinated terminal double bond in the monosubstituted allene ligand. Thus, when the allenyl ether ligand* is coordinated as in complex **3b**, the signals of the =CH$_2$ protons are shifted upfield by ~3.0 ppm, while the signal of the =CH protons of the free double bond in **3b** is shifted downfield by ~1.4 ppm.

This increase in the gap between the signals of the protons of the allene group has also been noted previously (see, for example, Refs. **9**, **11**, and **13**). In the ^{13}C NMR spectrum, the signal of the carbon atom of the =CH$_2$ group is also substantially shifted upfield compared to those in free allenyl ethers[12] ($\Delta\delta$ ~ 70). Interestingly, this signal is observed at even higher field than the signal of the methyl groups. The presence of the =CH$_2$ fragment of the allene group was conclusively confirmed by the ^{13}C—^{1}H NMR spectrum (proton-decoupled ^{13}C NMR spectrum). The above-mentioned signal appears as a triplet with the constant J ~ 165 Hz, which is indicative of the presence of the sp^2-hybridized carbon atom bound to two equivalent hydrogen atoms. The signal of the central atom of the allene fragment (δ = 159.4) is also shifted upfield by ~40 ppm,[12] while the position of the signal of the =CH group changes only slightly. The ^{1}H NMR spectrum of the second isomer **4b** has three signals of the allene group, namely, a triplet and two doublets with the constant J = 2.4 Hz. Compared to noncoordinated allenyl ethers,[12] the signal of the =CH group is substantially shifted upfield ($\Delta\delta$ ~ 0.7—1.4 depending on the solvent), which indicates

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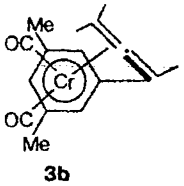
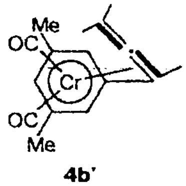
* The ^{1}H NMR spectral data for allenyl ethers were reported in the literature.[12]

that the chromium atom is coordinated at the internal double bond of the allene fragment. The signals of the nonequivalent hydrogen atoms of the noncoordinated $=CH_2$ group are shifted downfield by 0.3—2.1 ppm depending on the solvent. An analogous pattern has been observed previously in the case of the σ,π-chelate iron complex.[14] This mode of coordination is also evidenced by the fact that the ^{13}C NMR spectrum has a signal of the central carbon atom of the allene fragment at δ 167.8. This signal is close in position to the analogous signal of isomer **3b**. The signal at δ 82.4 can be assigned to the coordinated $=CH$ carbon atom of the allene fragment. Its position corresponds to the shift by ~40 ppm on going from the free to the coordinated ligand.[12] The signal of the noncoordinated $=CH_2$ group is observed in the region of the coordinated arene carbon atoms (δ ~90 for the $=CH_2$ group of free allenyl ethers[12]). In this case, the unequivocal assignment presented difficulties because we failed to determine the constants $J_{^1H-^{13}C}$ for the second isomer **4b**. However, the number and positions of the signals are consistent with the structure of **4b** on condition that the latter does not have a symmetry plane. The remaining signals in the ^1H and ^{13}C NMR spectra of compounds **3b** and **4b** are observed in the characteristic regions. The constants J correspond to the suggested structures.

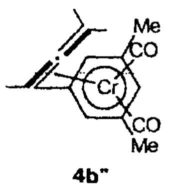
The stereochemistry of the resulting isomers also agrees well with the assignment made. Thus, in the case of coordination at the terminal double bond, complex **3b** has a symmetry plane. This is evidenced by the equivalence of the *o*-H atoms of the Me groups of the arene ligand and the hydrogen atoms of the CH_2 group of the bridge in the ^1H NMR spectra as well as by the equivalence of the *ortho*- and *meta*-carbon atoms of the Me groups of the arene ligand and the CO groups in the ^{13}C NMR spectrum. As for complex **4b** (coordination at the internal double bond of the allene fragment), its molecule does not have a symmetry plane, which leads to the nonequivalence of the H and C nuclei in the above-mentioned pairs in the NMR spectra. Consequently, compound **4b** should exist as a mixture of two enantiomers **4b'** and **4b"**.



3b



4b'



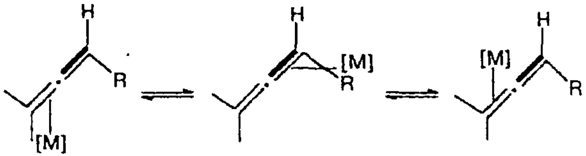
4b"

An analogous situation has been observed previously in the case of areneolefin chromium complexes.[15] However, unlike areneolefin chelates, in which interconversions of the enantiomers cannot occur without the cleavage of the metal—olefin bond, in complexes **4b'** and **4b"** this process can proceed rather readily through form **3b**. Examples of these metallotropic processes (migration of the organometallic fragment from one part of the allene ligand to another one) have been reported previously for tetramethylallenic complexes of Fe^0,[16] Pt^{II},[17] and Re^{II} (degenerate processes).

In the case of $[M] = Fe(CO)_4$,[16] the value of $\Delta G^{\#}$ for this process is 9 kcal mol^{-1}. For unsymmetrical methylallene coordinated to the $[CpFe(CO)_2]$ group (a nondegenerate process), the interconversions of the *syn*-(**A**) and *anti*-(**C**) isomers have also been studied ($\Delta G^{\#}$ = 23.1 kcal mol^{-1}).[9]

The mechanism of the 1,2-shift discussed below was rather reliably substantiated although attempts to identify form **B** even by low-temperature NMR spectroscopy were unsuccessful[9]*(Scheme 3).

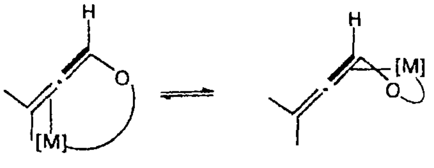
Scheme 3



A **B** **C**

In the case under study, the metallotropic conversions of areneallenic chelates **3b** and **4b** proceeded, apparently, analogously but the formation of the anti-isomer **C** was impossible due to the chelate structures of these complexes (Scheme 4).

Scheme 4



3b **4b',b"**

$[M] = ArCr(CO)_2$

Therefore, complex **4b'** was converted into **3b**, which, in turn, was converted either into **4b'** or into its enantiomer **4b"**, *i.e.*, these enantiomers, unlike areneolefin chelates,[15] can exist as individual compounds only within the NMR time scale.

It should be noted that in the above-mentioned case, we succeeded in detecting both isomers, namely, with the coordination of the allene ligand either at the terminal or at the internal double bond, which is the first example of this type of nondegenerate processes for

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* Recently, all three possible isomers (**A**, **B**, and **C**) of the $Cp(CO)_2Mn(MeOCH=C=CH_2)$ complexes were isolated in the individual state.[18]

unsymmetrical allenes.[19] In addition, in all cases reported to date, the complexes isolated contain the monosubstituted and 1,1-disubstituted allene ligands coordinated at the terminal double bond (see, for example, Refs. 9—11, 17, 20, and 21). Examples of complexes with the coordination at the internal double bond are few in number.[14,18,22,23]

For chelates **3b** and **4b**, we studied the temperature dependence in benzonitrile and found that the ^{1}H NMR spectra of this mixture remained virtually unchanged in the temperature range from −90 to +100 °C. At 110 °C, the complexes decomposed. Based on these facts, we obtained an estimated value of $\Delta G^{\#} > 18$ kcal mol^{-1}. Therefore, for complexes **3b** and **4b** we observed the form with the coordination at the substituted double bond as well as that with the coordination at the nonsubstituted double bond. However, the tautomeric process was rather slow, which may be, at least partially, due to the chelate effect. Compounds **3b** and **4b** are the first examples of π-allenic chromium complexes and the rearrangement of π-acetylenic complexes, which we have found, provides an additional possibility for the synthesis of allenic complexes of transition metals.[19]

In this connection, it should also be noted that mononuclear allenic complexes of transition metals have not been adequately studied[9—11,24] (particularly, complexes with the functionally substituted allenes[8,18,23]) and procedures for their preparation are based on reactions of allenes with transition-metal complexes. In addition, examples of the preparation of allenic complexes by the rearrangement of π-acetylenic derivatives of Mn[8], Re,[25] and Rh[26] as well as by the reactions of η^3-propargyl Mo complexes with PPh$_3$[23] were reported.

We also found that stirring of a mixture of **3b** and **4b** with silica gel in ether or chromatography of this mixture on silica gel led to the reverse rearrangement of the π-allenic complexes to the π-acetylenic complexes. Therefore, it was demonstrated that the conversion of acetylenes to allenes in the coordination sphere of transition metal atoms can, in principle, be reversible.

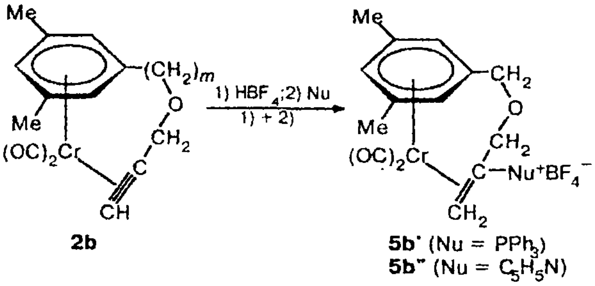
$$\mathbf{3b} + \mathbf{4b} \xrightarrow{SiO_2} \mathbf{2b}$$

It should be noted that the above-considered reaction is the first example of the rearrangement of π-allenic complexes to π-acetylenic complexes.

In addition to the acetylene-allene rearrangement in the coordination sphere of the transition metal atom, we studied some other reactions of areneacetylenic chelate chromium complex **2b**. Previously, we have demonstrated that ionic hydrogenation of chelate acetylene- and allenearenedicarbonylchromium complexes **2b**, **3b**, and **4b** proceeded under mild conditions and was accompanied by conversions of the acetylene and allene fragments into the olefin group without disruption of coordination to the metal atom, while protonation of a mixture of isomeric **3b** and **4b** afforded the previously unknown chelate cationic areneallyldicarbonylchromium complex.[4]

Studies of the reactions of compound **2b** with other nucleophiles (PPh$_3$ and C$_5$H$_5$N) in an acidic medium when the reagents (the acid and the nucleophile) were added either successively or simultaneously demonstrated that the corresponding previously unknown areneolefin chelates were readily formed. The resulting compounds were isolated and characterized by ^{1}H and IR spectroscopy (Scheme 5).

Scheme 5



Complexes **5b'** and **5b"** are crystalline pale-yellow compounds of a salt-like nature. These compounds are soluble only in polar solvents and are stable during storage in air at low temperature for a long period of time. The phosphoniopropenyl complex is noticeably more stable than the pyridiniopropenyl complex.

The IR spectra of these complexes have two absorption bands in the carbonyl region, which are substantially shifted to the high-frequency region compared to neutral areneolefin chelates,[15] which is consistent with the presence of the electron-withdrawing substituent (PPh$_3^+$ or C$_5$H$_5$N$^+$) at the double bond. The ^{1}H NMR spectra of complexes **5b'** and **5b"** and the ^{13}C NMR spectrum of complex **5b'** have signals of hydrogen and carbon atoms in the typical regions. Only the $J_{\text{P—H}}$ constants for the coordinated phosphoniopropenyl fragment in complex **5b'**, which have not been determined previously, can be considered as a pecularity. The values of these constants ($J_{\text{P—H}_{trans}} = 19$ Hz and $J_{\text{P—H}_{cis}} = 10$ Hz) are larger than the corresponding constants for the protons. The reaction of conjugated addition of the proton and nucleophile at the coordinated triple bond is one of the few examples of transformation of π-acetylenic complexes into π-olefin complexes.

Unlike the reaction of ionic hydrogenation,[4] the latter reaction performed with the use of a mixture of areneallenic chelates **3b** and **4b** as the initial compounds did not afford stable products.

Experimental

All synthetic procedures of the compounds were carried out under an Ar atmosphere with the use of anhydrous solvents. Commercial metal carbonyls of the chromium group were used in the syntheses. The initial ω-hydroxyalkylarenetricarbonylchromium compounds were prepared according to known procedures.[27] Irradiation with UV light was performed with the use of a PRK-7 lamp (1 kW) and a DRL-125 immersion lamp. The IR spectra of solutions were recorded on a Specord IR-75 spectrophotometer. The IR spectra in KBr pellets were obtained on a UR-20 spectrophotometer. The ^{1}H NMR spectra were recorded on Hitachi—Perkin—Elmer (90 MHz) and Bruker WP-200 SY (200.13 MHz) spectrometers. The ^{13}C and ^{31}P NMR spectra were measured on Bruker WP-60 (15.08 MHz), Bruker WH-360 (90.55 MHz), and Bruker WP-200 SY (50.31 MHz) spectrometers.

Synthesis of arenetricarbonylchromium complexes containing the ω-ethynyl group in the side chain of the arene ligand 1a—c (general procedure). Sodium amide (2 g, 51.2 mmol) was added to a solution of ω-hydroxyalkylarenetricarbonylchromium (20 mmol) in diglyme (30 mL). The reaction mixture was stirred for 30 min and then a solution of propargyl bromide (5 mL, 7.9 g, 61.2 mmol) in diglyme (5 mL) was added dropwise. The mixture was stirred at ~70 °C for 1.5 h. The completion of the reaction was determined by TLC on Silufol. After cooling, the reaction mixture was poured into water and extracted with ether. The ethereal solution was dried over calcium chloride and concentrated. The residue was recrystallized from heptane. The crystals precipitated were decanted, washed with cold pentane (15 mL), and dried *in vacuo*. The yields, melting points, and data of elemental analysis and ^{1}H NMR and IR spectroscopy for compounds **1a—c** are given in Tables 1 and 2.

Table 1. Arenetricarbonylchromium complexes (**1a—c**) containing the ω-ethynyl group in the side chain of the arene ligand

Compound	Yield (%)	M.p. /°C	Data of elemental analysis (%)*		
			C	H	Cr
1a	25**	77—78	53.65 (53.74)	2.95 (3.01)	19.19 (19.39)
1b	84	55—57	58.30 (58.06)	4.88 (4.55)	16.80 (16.76)
1c	88	91—94	59.54 (59.26)	4.95 (4.97)	15.95 (16.04)

* The calculated values are given in parentheses.

** With respect to $Cr(CO)_6$.

[η^6:η^2-3,5-Dimethyl-1-(prop-2-ynyloxymethyl)benzene]-dicarbonylchromium (2b) (irradiation in the presence of Lewis bases). A solution of compound **1b** (0.1 g, 1 mmol) in a mixture of benzene (30 mL) and heptane (50 mL) in the presence of a Lewis base was placed in a glass flask equipped with an immersion condenser and was irradiated with UV light (a PRK-7 lamp) (Table 3). The time of irradiation was 2.5 h (the course of the reaction was monitored by IR spectroscopy in the 1800—2000 cm^{-1} region). The reaction mixture was filtered and concentrated to dryness with exclusion of air. The residue was dissolved in ether (30 mL) and then heptane (70 mL) was added. The solution was concentrated to one-half of the initial volume in the absence of air, filtered, and kept with solid CO_2 in a Dewar flask for 2 days. The precipitated crystals were separated by decantation and dried *in vacuo*. The yields are given in Table 3.

[η^6:η^2-3,5-Dimethyl-1-(prop-2-ynyloxymethyl)benzene]-dicarbonylchromium (2b) (irradiation in a tetrahydrofuran-benzene mixture). A solution of compound **1b** (0.62 g, 2 mmol) in a mixture of THF (100 mL) and benzene (100 mL) was irradiated for 4.5 h (control by the IR spectra). The reaction mixture was filtered, concentrated to dryness with exclusion of air, and dissolved in ether. Then heptane (100 mL) was added. The ether was evaporated and the resulting mixture was kept with solid CO_2 in a Dewar flask for 2 days. The crystals precipitated were separated by decantation and dried *in vacuo*. Compound **2b** was obtained in a yield of 0.15 g (26.8%). T.decomp. 80—85 °C. IR, ν/cm^{-1}: in KBr, 2137 ($C\equiv C$); in heptane, 1879, 1934 (CO). ^{1}H NMR (C_6D_6), δ: 1.88 (s, 6 H, Me—Ar); 3.94 (s, 2 H, Ar—CH_2—O); 4.04 (s, 1 H, H_p—Ar); 4.15 (s, 2 H, H_o—Ar); 4.48 (d, 2 H, CH_2—$C\equiv C$, J = 2 Hz); 4.78 (t, 1 H, H—$C\equiv C$, J = 2 Hz). ^{13}C NMR ($(CD_3)_2CO$), δ: 20.0 (Me); 59.1, 62.2 (Ar—$\underline{C}H_2$, $\equiv C\underline{C}H_2$); 66.5 ($\equiv\underline{C}$—CH_2); 68.7 ($\equiv$C—H); 88.7 (p-C_{Ar}); 95.2 (o-C_{Ar}); 109.3 (m-C_{Ar}). Found (%): C, 59.34; H, 5.29; Cr, 18.38. $C_{14}H_{14}CrO_3$. Calculated (%): C, 59.57; H, 5.0; Cr, 18.42.

[η^6:η^2-3,5-Dimethyl-1-(prop-2-ynyloxymethyl)benzene]-dicarbonylchromium (2b) (irradiation with the use of a DRL-125 immersion lamp). A solution of compound **1b** (0.31 g, 1 mmol) in ether (150 mL) was irradiated with UV light for 7.5 min. The reaction mixture was filtered and heptane (100 mL) was added. Then the mixture was concentrated in the absence of air. The solution was kept with solid CO_2 in a Dewar flask

Table 2. Data of NMR and IR spectroscopy for complexes **1a—c** containing the ω-ethynyl group in the side chain of the arene ligand

Compound	IR, ν/cm^{-1}			^{1}H NMR ($CDCl_3$), TMS internal standard, δ (J/Hz)					
	CO*	$C\equiv C$**	C—H**	Me—Ar	CH_2—Ar	CH_2O	CH_2C	H—$C\equiv C$	H—Ar
1a	1914 1982	2128	3304	—	—	—	4.65 (d, 2 H, J = 2.7)	2.62 (t, 1 H, J = 2.7)	4.86—5.77 (m, 5 H)
1b	1907 1975	2128	3302	2.23 (s, 6 H)	—	4.27 (s, 2 H)	4.17 (d, 2 H, J = 4)	2.40 (t, 1 H, J = 4)	4.83 (s, H, ArH_p) 4.91 (s, 2 H, ArH_o)
1c	1907, 1975	2128	3302	2.22 (s, 6 H)	2.69 (t, 2 H, J = 6)	3.79 (t, 2 H, J = 6)	4.16 (d, 2 H, J = 4)	2.47 (t, 1 H, J = 4)	4.98 (s, 3 H)

* Heptane. ** KBr pellets.

Table 3. Conditions of preparation of complex **2b** in the presence of Lewis bases (*L*)

Base *L*	*L* /mol	Yield (%)
PPh_3	2	35.5
$P(OEt)_3$	2	35.5
NEt_3	20	28.4

for 2 days. The crystals that precipitated were decanted and dried *in vacuo*. Compound **2b** was obtained in a yield of 0.2 g (70.1%).

(1-6-η:1'-2'-η- and 1-6-η:2'-3'-η-3,5-Dimethyl-1-propadienyloxymethylbenzene)dicarbonylchromium (3b, 4b). A solution of compound **1b** (0.31 g, 1 mmol) in a mixture of benzene (80 mL) and heptane (50 mL) was irradiated with UV light (a PRK-7 lamp) for 8 h (the course of the reaction was monitored by IR spectroscopy in the 2000 cm^{-1} region). The reaction mixture was filtered and concentrated to dryness in the absence of air. The residue was dissolved in ether (30 mL) and then heptane (70 mL) was added. The reaction mixture was filtered and the ether was evaporated with exclusion of air. The solution was kept with solid CO_2 in a Dewar flask for 2 days. The crystals precipitated were filtered off and dried *in vacuo*. Compounds **3b** and **4b** were obtained in a yield of 0.06 g (22.2%), t.decomp. 90—95 °C. IR, ν/cm^{-1}: in heptane, 1896, 1941 (CO) for **3b** and 1898, 1951 (CO) for **4b**; in KBr, 1750 (C=C=C).

^{1}H NMR (C_6D_6), δ: for 1-6-η:2'-3'-η-isomer **3b** (coordination at the terminal double bond): 1.67 (s, 6 H, Me—Ar); 2.34 (d, 2 H, H_2C=C=, *J* = 3.2 Hz); 4.00 (s, 2 H, —CH_2—O—); 4.04 (s, 2 H, H_o—Ar); 4.35 (s, 1 H, H_p—Ar); 8.06 (t, 1 H, —CH=C=, *J* = 3.2 Hz); for 1-6-η:1'-2'-η-isomer **4b** (coordination at the internal double bond): 1.83, 1.97 (both s, 3 H, Me—Ar); 3.19, 3.80 (2 H, Ar—CH_2—, J_{AB} = 10 Hz); 4.37 (s, 1 H, Ar—H); 4.59 (s, 1 H, Ar—H); 4.84 (s, 1 H, Ar—H); 5.94 (t, 1 H, —CH=C=, *J* = 2.4 Hz); 6.09 (d, 1 H, $\underline{H}$HC=C=, *J* = 2.4 Hz); 6.73 (d, 1 H, H$\underline{H}$C=C=, *J* = 2.4 Hz).

^{13}C NMR ($(CD_3)_2SO$), δ: for 1-6-η:2'-3'-η-isomer **3b**: 16.77 (t, $H_2\underline{C}$=C, *J* = 165 Hz); 19.69 (q, Me—Ar); 68.59 (t, Ar—CH_2—); 93.58 (d, *p*-C_{Ar}); 96.6 (d, *o*-C_{Ar}); 108.89 (s, C_{Ar}—Me); 111.89 (s, C_{Ar}—CH_2—); 127.09 (d, =CH—O); 159.36 (d, =C=, *J* = 15 Hz); 238.4 (s, CO); for 1-6-η:1'-2'-η-isomer **4b**: 20.25 (Me—Ar); 20.90 (Me—Ar); 65.07 (Ar—CH_2—); 82.40 (=CH—O); 90.44, 94.68, 106.61, 114.84 (H_2C=, *o*- and *p*-C_{Ar}); 109.70, 116.63, 125.32 (C_{Ar}—Me, C_{Ar}—CH_2—); 167.81 (=C=); 240.52 (CO); 242.63 (CO). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 282.06 $[M]^+$ (5.0); 254.03 $[M - CO]^+$ (5.0); 226.01 $[M - 2CO]^+$ (21.3); 174.02 $[M - Cr(CO)_2]^+$ (3.8); 135.00 $[M - Cr(CO)_2C_3H_3]^+$ (2.0); 119.06 $[M - Cr(CO)_2C_3H_3O]^+$ (47.6); 90.99 $[CrC_3H_3]^+$ (20.3); 55.06 $[C_3H_3O]^+$ (10.5); 51.96 $[Cr]^+$ (100). Found (%): C, 59.59; H, 5.01; Cr, 17.93. $C_{14}H_{14}O_3Cr$. Calculated (%): C, 59.57; H, 5.00; Cr, 17.42.

(η^6:η^2-3,5-Dimethyl-1-propadienyloxymethylbenzene)dicarbonylchromium (3b,4b) (from η^6:η^2-3,5-dimethyl-1-(prop-2-ynyloxymethyl)benzenedicarbonylchromium **(2b)**. *A.* Photochemical method. A solution of compound **2b** (0.14 g, 0.5 mmol) in a mixture of benzene (80 mL) and heptane (50 mL) was irradiated with UV light (a PRK-7 lamp) for 2 h. The reaction mixture was filtered and concentrated to dryness in the absence of air. The residue was dissolved in ether (20 mL) and then heptane (40 mL) was added. The resulting solution was concentrated to one-half of the initial volume and kept with solid CO_2 in a Dewar flask for 2 days. The crystals precipitated were filtered off and dried *in vacuo*. Compounds **3b** and **4b** were obtained in a yield of 0.021 g (22%); IR (heptane), ν/cm^{-1}: 1898, 1951; 1896, 1941 (CO).

B. Thermal method. The indicated amount (Table 4) of compound **2b** was dissolved in oxygen-free heptane (50 mL) and kept at specified temperature for 2—3 h. Then the solution was filtered and concentrated. The residue was recrystallized from heptane and dried *in vacuo*. The yields and the data of IR spectroscopy are given in Table 4.

C. Rearrangement on Al_2O_3. A solution of compound **2b** (0.051 g, 0.017 mmol) in a 1 : 1 ether—heptane mixture (50 mL) was stirred with neutral Al_2O_3 (1 g) at room temperature for 4 h. Then the mixture was filtered, the Al_2O_3 was twice washed with ether, and heptane (50 mL) was added. The resulting solution was concentrated to 1/3 of the initial volume in the absence of air and kept with solid CO_2 in a Dewar vessel for 2 days. The crystals precipitated were filtered off and dried *in vacuo*. A mixture of dicarbonylchromium chelate complexes **3b**, **4b**, and **2b** was obtained in a ratio of 1 : 1 in a total yield of 0.016 g (30.8%) (according to the data of IR spectroscopy).

Rearrangement of (η^6:η^2-3,5-dimethyl-1-propadienyloxymethylbenzene)dicarbonylchromium (3b, 4b) on silica gel. Compounds **3b** and **4b** (0.14 g, 0.5 mol) were chromatographed on a column with silica gel at −50 °C. The cherry-red band was eluted with a 1 : 1 ether—heptane mixture, ether was evaporated in the absence of air, the residue was dissolved in heptane, and the solution was kept with solid CO_2 in a Dewar flask for 2 days. Compound **2b** was obtained in a yield of 0.015 g (11%). T.decomp. 80—85 °C. IR (heptane), ν/cm^{-1}: 1879, 1934 (CO).

[1-6-η:2'-3'-η-3,5-Dimethyl-1-(2-triphenylphosphonioprop-2-enyloxymethyl)benzene]dicarbonylchromium tetrafluoroborate (5b'). *A.* Starting from tricarbonyl complex **1b**. A solution of compound **1b** (0.31 g, 1 mmol) in ether (100 mL) was irradiated with UV light for 1 h 45 min (a PRK-7 lamp, cooling to 4—5 °C, the course of the reaction was monitored by IR spectroscopy in the 2000 cm^{-1} region) until the initial complex disappeared. Triphenylphosphine (0.26 g, 1 mmol) was added to the solution and the reaction mixture was cooled to a temperature from −10 to −20 °C. Then anhydrous $HBF_4 \cdot OEt_2$ (0.23 mL, 0.09 g, 1 mmol) was added. The mixture was warmed to room temperature. The precipitate formed was filtered off, reprecipitated from CH_2Cl_2 with ether, and dried. Compound **5b'** was obtained in a yield of 0.54 g (85%). IR (CH_2Cl_2), ν/cm^{-1}: 1880, 1940 (CO). ^{1}H NMR ($(CD_3)_2SO$), δ: 2.00 (d, 1 H, $\underline{H}_{trans}$—CH=, J_{P-H} = 19 Hz); 2.17, 2.38 (both s, 3 H, Me); 3.19, 4.3 (m, 4 H, —CH_2—O—CH_2—); 3.84 (d, 1 H, $\underline{H}_{cis}$—CH=, J_{P-H} = 10 Hz); 5.6, 5.74, 5.93 (all s, 1 H, Ar—H); 7.76 (m, 15 H, PPh_3^+). ^{13}C NMR ($(Me)_2SO$), δ: 19.42, 19.68 (q, Me—Ar, J_{C-H} = 138.7 Hz); 68.96 (t, Ar—CH_2, J_{C-H} = 147.0 Hz); 70.32 (dt, CH_2—C—PPh_3^+, J_{C-H} = 143.5 Hz, J_{C-P} = 14.69 Hz); 98.15 (d, C_{Ar}—

Table 4. Conditions of the rearrangement of **2b**, yields, and IR spectral data for complexes **3b** and **4b**

2b used in the reaction/g	*T*/°C	*t**/h	Yield (%)	IR (heptane), ν(CO)/cm^{-1}
0.13	50	3	23	1896, 1941; 1898, 1951
0.10	70	2	10	1896, 1941; 1898, 1951

* The time taken to complete the rearrangement.

H, J_{C-H} = 172.0 Hz); 101.34 (d, C_{Ar}—H, J = 165.0 Hz); 106.05 (d, C_{Ar}—H, J = 169.3 Hz); 109.69, 111.93, 114.87 (all s, C_{Ar}—C); 129.49, 129.68, 134.02, 134.38 (m, PPh_3^+); 243.72 (s, CO); 250.49 (d, CO, J_{C-P} = 9.2 Hz).

B. Starting from chelate complex **2b**. A 48% aqueous solution of HBF_4 (d = 1.3, 0.14 mL, 0.09 g, 1 mmol) and PPh_3 (0.13 g, 0.5 mmol) were added to a solution of compound **2b** (0.12 g, 0.43 mmol) in ether (50 mL) with cooling to a temperature from −10 to −20 °C. Then the reaction mixture was warmed to room temperature. The precipitate formed was filtered off, reprecipitated from CH_2Cl_2 with ether, and dried. Compound **5b'** was obtained in a yield of 0.14 g (51%).

[1-6-η:2'-3'-η-3,5-Dimethyl-1-(2-pyridinioprop-2-enyloxymethyl)benzene]dicarbonylchromium tetrafluoroborate (5b"). *A.* Starting from tricarbonyl complex **1b**. A solution of compound **1b** (0.16 g, 0.5 mmol) in ether (100 mL) was irradiated with UV light for 1 h 45 min (a PRK-7 lamp, cooling to 4—5 °C, the course of the reaction mixture was monitored by IR spectroscopy in the 2000 cm^{-1} region) until the initial compound disappeared. The solution was filtered and then pyridine (0.04 mL, 0.04 g, 0.5 mmol) and anhydrous $HBF_4 \cdot OEt_2$ (0.07 mL, 0.04 g, 0.5 mmol) were added. The ether was evaporated and the dry precipitate was twice reprecipitated from CH_2Cl_2 with ether. Compound **5b"** was obtained in a yield of 0.1 g (43.5%). IR (CH_2Cl_2), ν(CO)/cm^{-1}: 1885, 1945. ^1H NMR ($(CD_3)_2CO$), δ: 2.3, 2.4 (both s, 3 H, Me—Ar); 3.9, 4.7 (2 H, —CH_2—, J_{AB} = 12 Hz); 4.9 (1 H, H—CH, J_{AB} = 14 Hz); 5.1, 5.5, 6.7 (all s, 1 H, Ar—H); 8.00 (m, 3 H, Py—H); 9.3 (d, 2 H, Py—H, J = 6 Hz).

B. Starting from chelate complex **2b**. Pyridine (0.04 mL, 0.04 g, 0.5 mmol) and anhydrous $HBF_4 \cdot OEt_2$ (0.7 mL, 0.04 g, 0.5 mmol) were added to a solution of compound **2b** (0.14 g, 0.5 mmol) in ether (100 mL). The ether was evaporated and the residue was twice reprecipitated from CH_2Cl_2 with ether. Compound **5b"** was obtained in a yield of 0.12 g (50%).

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