

CATIONIC ARENEALLYLDICARBONYLCHROMIUM COMPLEXES

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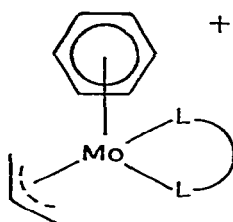
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Summary

The proton cleavage of chelate dicarbonylchromium complexes in the presence of benzyl and phenyl allyl ethers are shown to result in the formation of the formerly unknown cationic areneallyldicarbonylchromium complexes. We describe the general one step synthesis of these compounds upon ultra-violet irradiation of arenetricarbonylchromium compounds and allyl alcohol and its derivatives in the presence of hydrofluoroboric acid. We obtained the formerly unknown cationic arenedicarbonyl complexes with a π -oxyallyl ligand when we used propargyl alcohol in this reaction.

Introduction

π -complexes containing both arene and allyl ligands were formerly known only for molybdenum [1] of the Group VI metals.

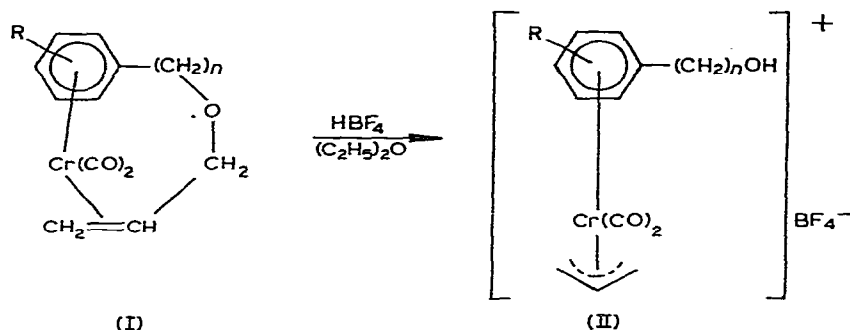


L-L = butadiene, norbornadiene, diene fragment of cyclooctatetraene, $\text{Ph}_2\text{P}-(\text{CH}_2)_n\text{PPh}_2$, bipy, $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$, etc.

In this work we describe the synthesis of formerly unknown cationic areneallyldicarbonylchromium complexes.

Results and discussion

We have discovered that upon treating the chelate complexes I with hydrofluoroboric acid in absolute ether at -50°C new cationic arenallyldicarbonylchromium complexes (II) are formed*.



(IIa: $n = 1$, $R = \text{H}$; IIb: $n = 1$, $R = 3,5\text{-}(\text{CH}_3)_2$; IIc: $n = 0$, $R = \text{H}$; IId: $n = 1$, $R = (\text{CH}_3)_5$)

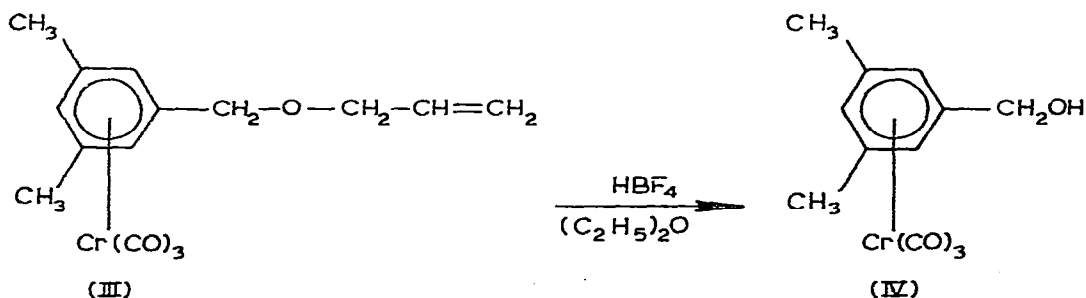
Compounds II were obtained in high yields. Table 1 presents data concerning yields, the temperature of decomposition and analytical data as well as IR and NMR spectral data.

Compounds II appear to be crystalline, air-stable substances (the most stable are compounds with methyl substituents in the arene), insoluble in non-polar solvents and soluble in water, alcohol and acetone, which is in agreement with their salt structure. We assigned structure II to these compounds on the basis of the IR and NMR spectra data discussed.

In discussing the scheme of the formation of II (Scheme 1) we may assume that it is the ether oxygen atom that is protonated in the first place. Further transformation can lead to cation A which gives allyl complex II, though an alternative mechanism with the formation of benzyl cation B is also possible.

A similarly ready cleavage of the chelate dicarbonylchromium with phenyl allyl ether, for example, is indicative of the formation of cation A.

For the purpose of comparison we have studied the proton cleavage of the simple ether bond in complex III:



* See ref. 2 for our preliminary communication.

TABLE I
ANALYTICAL AND SPECTRAL DATA

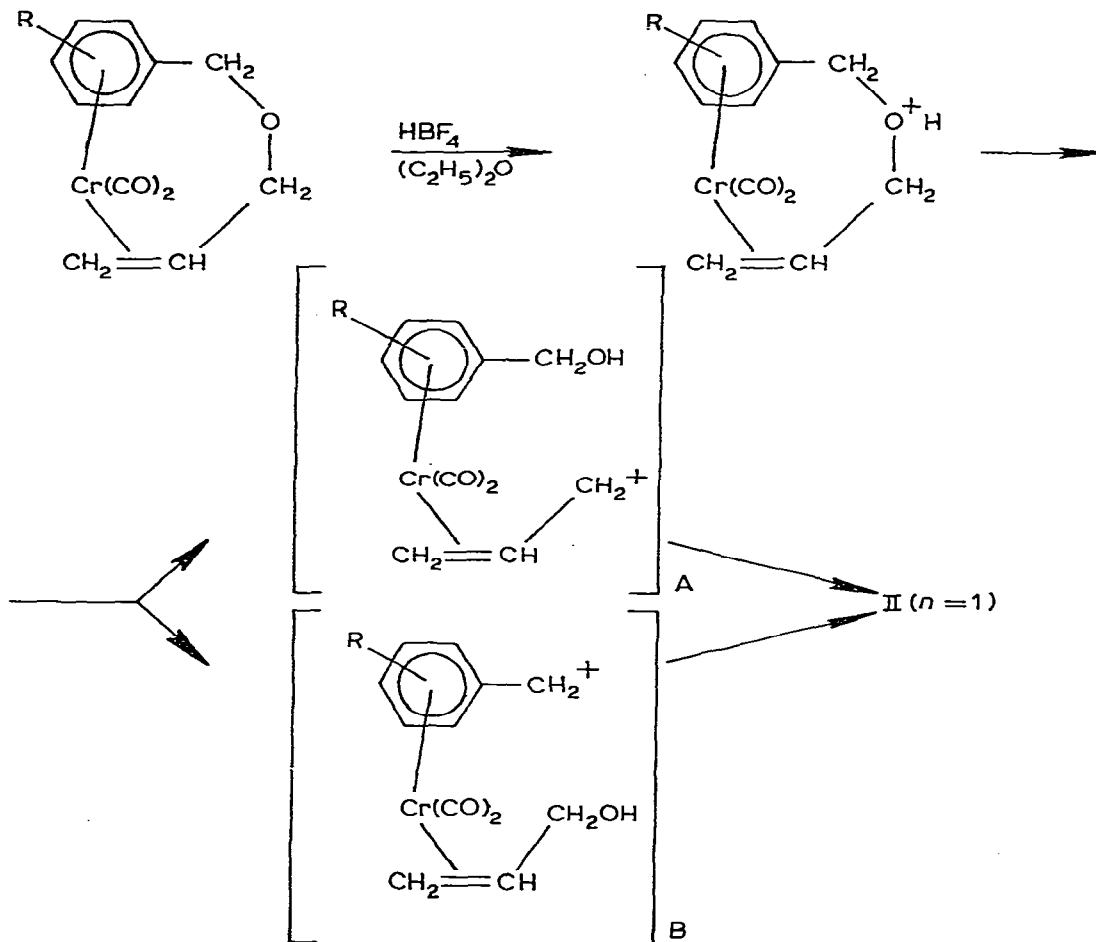
Com- plex	Meth- od	Yield (%)		Decomp. temp. (°C)	Analytical data ^a (%)			IR data (cm ⁻¹)		In KBr pellets	NMR data (δ ppm) in (CD ₃) ₂ CO	
		A	B		C	H	Cl	In	ν(C≡O)			ν(BF)
IIIa	A	85	—	120—125	41.77 (41.89)	3.94 (3.81)	—	1943	3065w	1070vs	3200(br)s	1.25, d, 2 H, (H _{ant}), J = 11.7 Hz; 4.06, d, 2 H, (H _{βin}), J = 6.8 Hz; 4.80, s, 2 H, (Ar-CH ₂); 5.08—5.78 m, 1 H, (H _A); 6.84, s, 5 H, (Ar-H)
								1983	—	—	—	1.34, d, 2 H, (H _{ant}), J = 11.7 Hz; 3.85, d, 2 H (H _{βin}), J = 6.8 Hz; 4.72, s, 2 H (Ar-CH ₂); 4.78—5.43, m, 1 H, (H _α); 2.47, s, 6 H, (Ar-CH ₃); 6.84, s, 3 H, (Ar-H).
IIIb	A B	67 30	135—140	45.08 (45.02)	4.65 (4.57)	—	1940	3065	1070vs	3255(br)s	3520m	1.33, d, 2 H, (H _{ant}), J = 10.5 Hz; 3.93 d, 2 H, (H _{βin}), J = 7.2 Hz; 4.72— 5.31, m, 1 H, (H _α); 6.00; 6.29; 6.75; 5 H; (Ar-H).
							1986	3080w	1060vs	3260(br)s	—	1.42, d, 2 H, (H _{ant}), J = 11.6 Hz; 2.48, s, 6 H, (Ar-CH ₃ -o); 2.61, s, 6 H, (Ar-CH ₃ -m); 2.55, s, 3 H, (Ar-CH ₃ -p), 3.68, d, 2 H, (H _{βin}), J = 6.8 Hz; 4.04— 4.64, m, 1 H, (H _A), 5.05, s, 2 H, (Ar-CH ₂).
IIIc	A, B	67	47 ^b	138—140	40.30 (40.03)	3.27 (3.36)	16.10	1932	3080w	1060vs	3260(br)s	1.21, d, 2 H, (H _{ant}); 4.18, d, 2 H, (H _{βin}), J = 8 Hz; 5.30—5.69, m, 1 H, (H _α); 6.87, s, 6 H, (Ar-H).
							(15.75)	1986	—	—	—	—
IIId	A	93	—	170—175	49.21 (49.30)	5.85 (5.60)	—	1933	—	1070vs	3255	—
							—	1983	3495	—	—	—
IIIe	B	—	70	153—158	41.82 (42.07)	3.41 (3.53)	16.79	1945	3080w.	1055vs	—	—
							(16.56)	1988	—	—	—	—

TABLE I (Continued)

Complex	Yield (%)		Decomp. temp. (°C)	Analytical data ^a (%)				IR data (cm ⁻¹)		In KBr pellets	NMR data (δ ppm) in (CD ₃) ₂ CO	
	A	B		C	H	Cl	Cr	In CH ₂ Cl ₂ ν(C≡O)	ν(OH)			
II ^f	—	78	158–162	47.22 (47.22)	4.81 (4.81)	14.58 (14.60)	—	1940 1987	3060W	1055vs	—	1.37, d, 2 H, (H _{antH}), J = 12 Hz; 2.44, s, 9 H, (Ar-CH ₃); 3.82, d, 2 H, (H _{βin}), J = 8 Hz; 4.78–5.22, m, 1 H, (Ha); 6.52, s, 3 H, (Ar-H)
II ^g	—	78	112–114	46.20 (46.42)	4.84 (5.75)	13.24 (13.39)	—	1940 1987	3050W	1070vs	3260(br)s	1.38, d, 2 H, (H _{antH}), J = 11 Hz; 2.46, s, 6 H, (Ar-CH ₃); J = 5 Hz; 2.71–3.22, br, s, 1 H(-OH); 3.82, t, 2 H, (CH ₂ -OH); 3.87, d, 2 H, (H _{βin}), J = 6 Hz; 4.71–5.18, m, 1 H, (Ha); 6.57, s, 3 H, (Ar-H)
V	B	—	62	—	—	—	—	1940 1987	3080W	1060vs	—	1.84, d, 1 H, (H _{antH}), J = 12 Hz; 2.29–3.24, m, 4 H, (CH ₂ -CH ₂); 4.18, d, 1 H, (H _{βin}), J = 6 Hz; 5.02–5.56, m, 2 H, (Ha); 6.80; s, 6 H; (Ar-H); 7.07–7.38, m, 5 H, (C ₆ H ₅)
VIII ^e	B	—	23	40.24 (40.03)	3.00 (3.36)	15.63 (15.75)	—	1945 1998	3080W	1085vs	3360(br)s	3.18, s, 2 H, (H _{antH}); 3.14, s, 1 H (OH), 3.66, s, 2 H, (H _{βin}); 6.11, s, 6 H, (Ar-H)

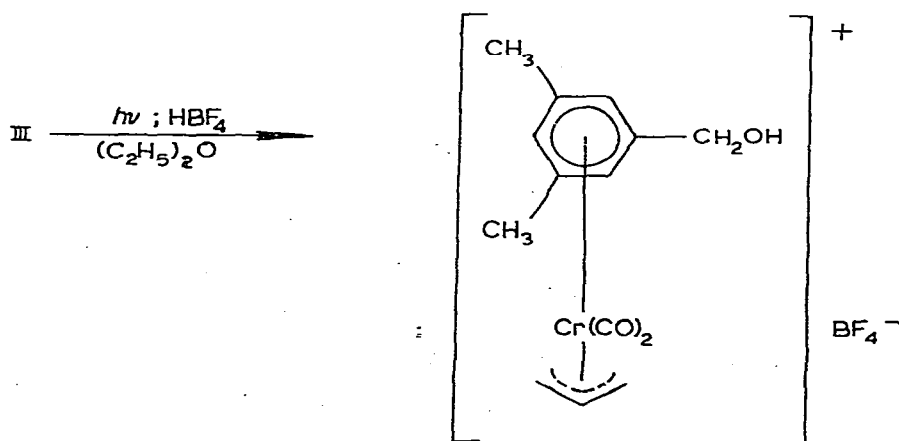
^a Calculated values in parentheses. ^b With respect to hexacarbonylchromium. ^c ¹³C NMR II^b in (CH₃)₂CO (δ in ppm for TMS); 19.4 (CH₃), J(¹³C-H) 127 Hz; 55.9 (CH₂all), J = 160 Hz; 60.7 (CH₂arene), J = 140 Hz; 77.5 (CH₂all), J = 160 Hz; 103.0 (C_{arene}-H_O), J = 173 Hz; 107.3 (C_{arene}-H_p), J = 178 Hz; 121.7 (C_{arene}-CH₃); 238.4 (CO); 125.3 (C_{arene}-CH₂OH). ^d ¹³C NMR II^c in (CH₃)₂CO: 55.31 (C H₂allyl); 77.53, 77.92; (CH₂allyl); 93.06; 95.01; 96.1; 97.6; 106.45; 106.97 (C-H_{arene}); J = 176 Hz; 237.76; 238.61(CO); ^e ¹³C NMR VIII in (CD₃)₂CO: 42.8 (CH₂allyl); 106.1 (C-H_{arene}), J = 176 Hz; 139.9 (C-OH), J = 30 Hz; 241.9 (CO).

SCHEME 1



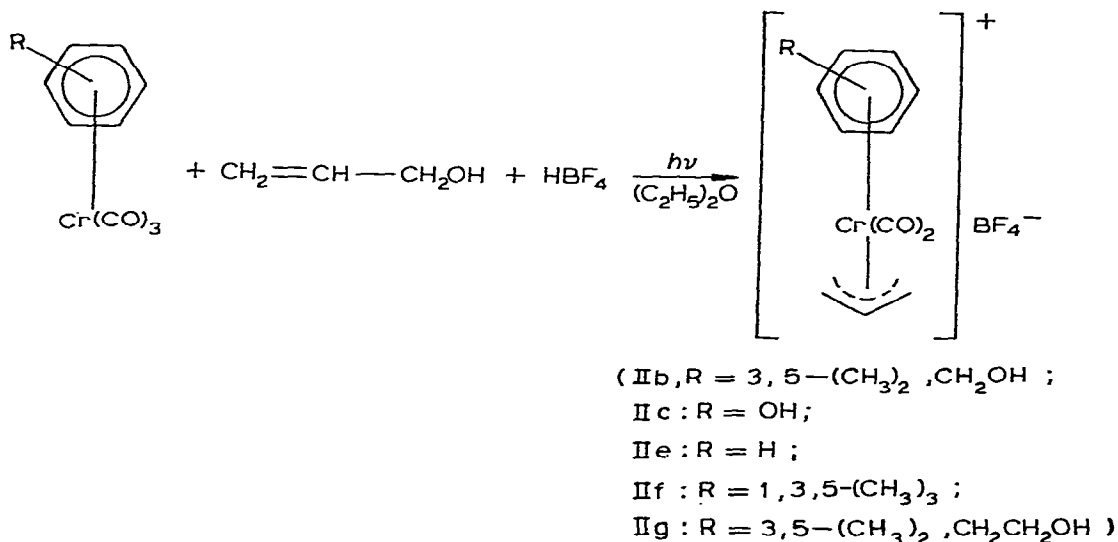
As a result, the tricarbonylchromium complex IV was isolated. However, this reaction proceeds much more slowly and does not go to completion, indicating that the coordination of the metal with the carbon-carbon double bond effects this process.

The situation can be markedly changed by proton cleavage of III upon simul-



taneous UV irradiation, with cationic areneallyl complex IIb being formed as the result of a possible intermediate formation of chelate I; the yield, however, amounts to only 30%.

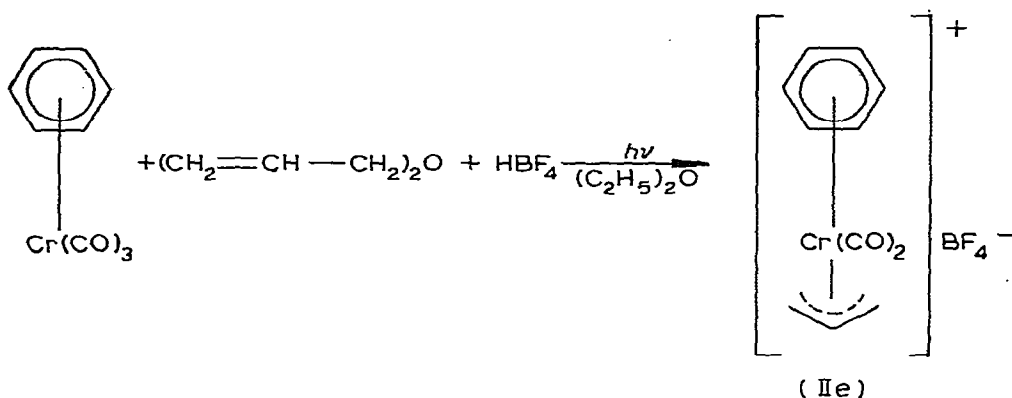
The method described for the synthesis of the cationic areneallylchromium complexes II by proton cleavage of chelate I cannot be considered as being a satisfactory one. The main disadvantage of this lies in the multi-step procedure to obtain the starting chelate complexes I. Moreover, this method had a limited application, for arene-allyl complexes could be obtained only with OH-, CH₂OH substituents in the arene ring. Therefore, we attempted to work out a simple and, at the same time, more general method of synthesis which would enable the production of allyl complexes with any arene. To this end we studied the interaction of various arenetricarbonylchromium complexes with allyl alcohol in the presence of hydrofluoroboric acid upon UV irradiation*. In fact, the unsubstituted benzenetricarbonylchromium, its methyl substituted derivatives, and the tricarbonylchromium complex of phenyl, as well as the complexes with the arene. 3,5-(CH₃)₂C₆H₃(CH₂)_nOH (*n* = 1, 2), appeared to give complexes II [4] with good yields (47–78%) under the conditions described. The smallest yield (30%) was obtained for the salt II with the ligand 3,5-(CH₃)₂C₆H₃CH₂OH. Unlike the other reactions, in the case of this ligand the reaction was accompanied by the formation of a great number of decomposition products, which could be due to the formation of π-benzyl-like products of low stability.



We tried to replace allyl alcohol by its derivatives, such as allyl chloride or allyl ether. The use of the latter in the reaction with benzenetricarbonylchromi-

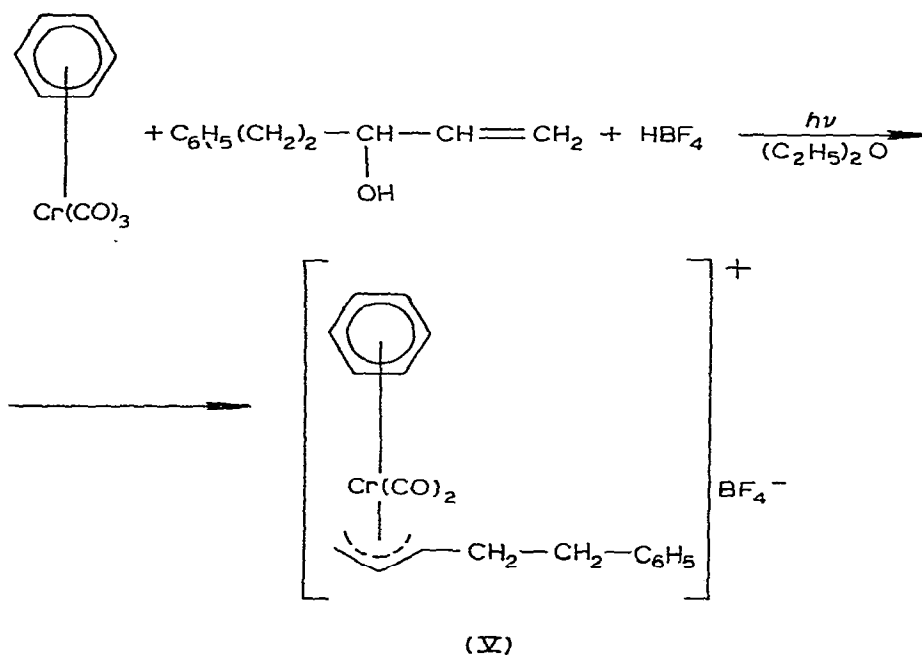
* It has been previously stated in the literature that the reaction of arenetricarbonylchromium with saturated alcohols upon UV irradiation resulted in complete decomposition of the complex [3].

um gave a good result. In this case we obtained complex IIe in a yield of 70%.



In the reaction of benzenetricarbonylchromium with allyl chloride, $\text{BF}_3 \cdot \text{OEt}_2$ was used instead of HBF_4 . In this case complex IIe was formed in only a 15% yield.

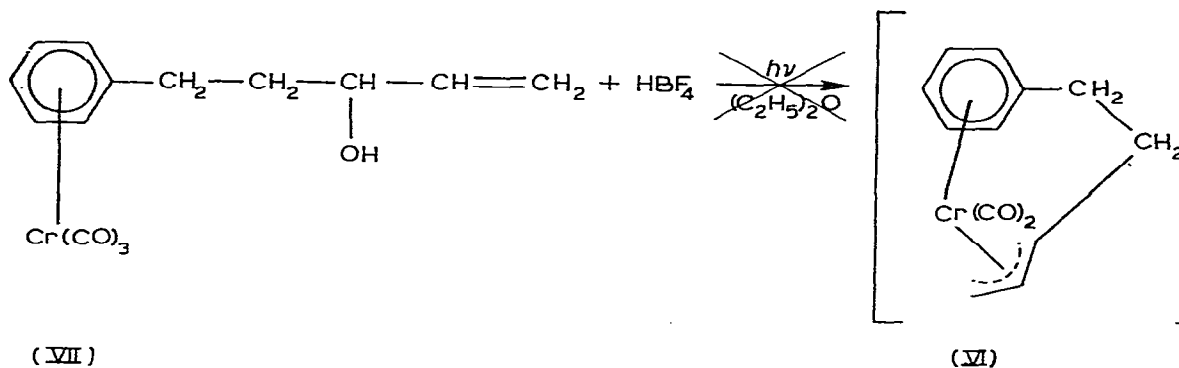
The corresponding salt V was obtained with substituted allyl alcohol:



It should be noted that we failed in our attempt to obtain the chelate allyl complex VI from arenetricarbonylchromium derivative VII.

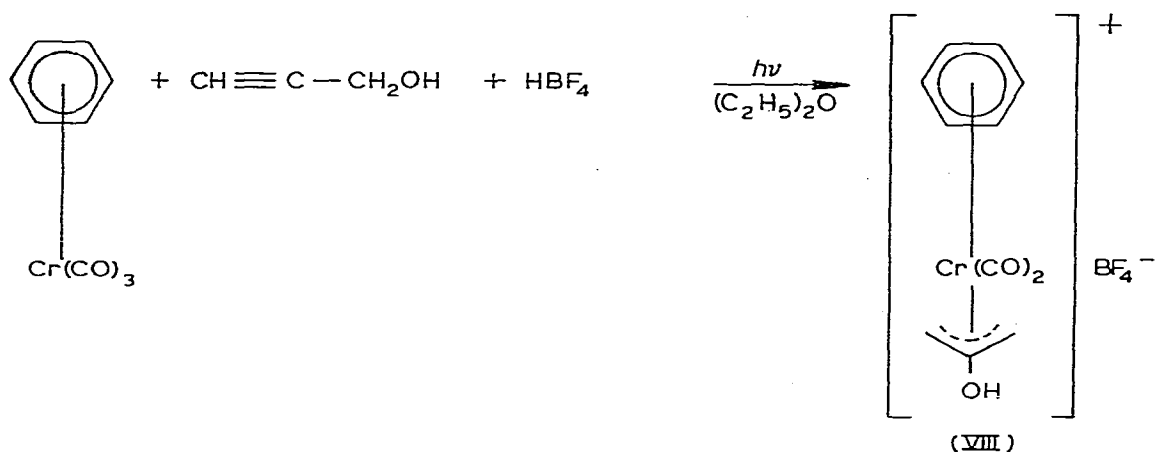
In this case the reaction resulted in complete decomposition of complex VII.

It is necessary to emphasize the importance of the use of absolute ether as a solvent in the one-step method of synthesis. The choice of this solvent is explained first of all by the fact that the ionic complexes which are formed are practically insoluble in this solvent and precipitate, thus avoiding decomposition.



under the action of UV irradiation. In fact, when tetrahydrofuran, in which complexes II are more soluble, was used in this reaction, the formation of the product was accompanied by a considerable decomposition.

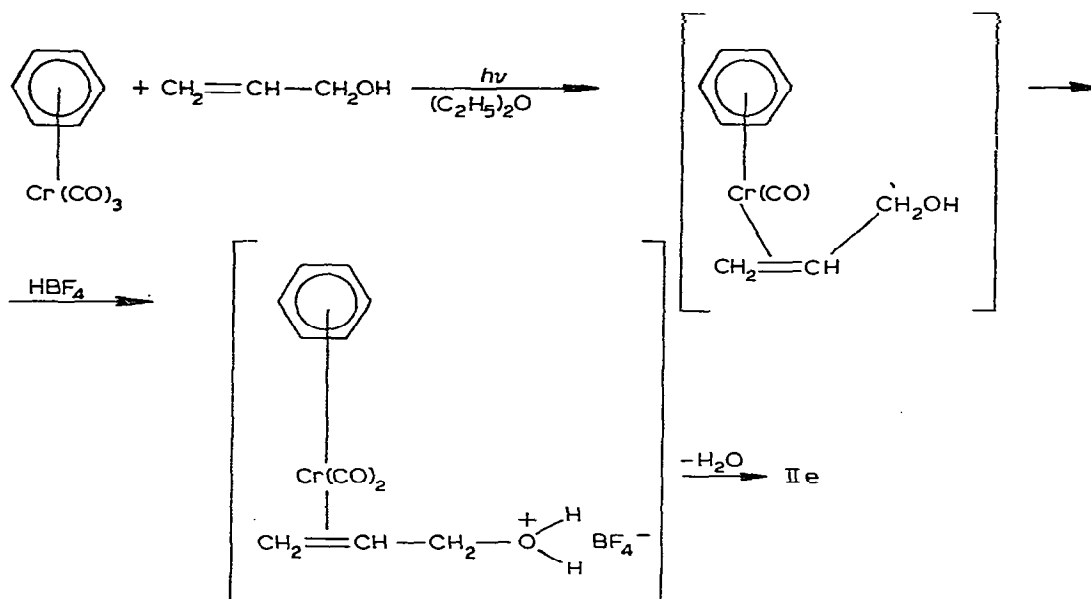
The successful utilization of allyl alcohol and its derivatives in the direct synthesis stimulated further studies on the reaction of arenetricarbonylchromium with other unsaturated alcohols and, in particular with propargyl alcohol. In this case we obtained the cationic arene(2-oxyallyl)dicarbonyl complex VIII.



The yields, temperature of decomposition, data from IR and NMR spectra, and analytical data for complexes II, V and VIII obtained by the one-step method (B) are given in Table 1.

In the course of clarifying certain peculiarities of the one-step method of synthesis of II, we investigated the progress of the reaction on step-like addition of the reagents. The solution of benzenetricarbonylchromium and allyl alcohol in ether was irradiated by UV light for an hour. The colour was seen to change from light yellow to bright red; we then added hydrofluoroboric acid. This resulted in the immediate formation of a typical precipitate of cationic allyl complex IIe (R = H). Thus we suggest that the reaction could proceed according to the following scheme: firstly the CO ligand is replaced by allyl alcohol and the unstable olefinic complex is formed intermediately, the exist-

ence of this complex being consistent with literature data [5], then, after HBF_4 is added, the olefinic complex transforms into the allyl one.



To prove the structure of salts II, V and VIII we studied their IR and NMR spectra. In the IR spectra, we observed two very strong bands in the 2000 cm^{-1} region, corresponding to two carbonyl stretchings. It should be noted that the frequency of the carbonyl groups are markedly shifted (by $50\text{--}70\text{ cm}^{-1}$) towards higher frequencies as compared with neutral dicarbonyl complexes, which is in good agreement with the cationic structure of these compounds.

In the NMR spectra of the complexes with the unsubstituted allyl ligand, we observed the situation characteristic of the π -allyl ligand, i.e. two doublets for the terminal protons. One of these shows an upfield shift ($1.2\text{--}1.4\text{ ppm}$) with higher spin-spin coupling constant ($J = 10\text{--}12\text{ Hz}$), and should be assigned to the *anti*-protons. The other appears in the region of $3.7\text{--}4.2\text{ ppm}$ ($J = 7\text{--}8\text{ Hz}$) and should be assigned to the *sin*-protons. The central proton shows itself as a multiplet in the region of $4\text{--}6\text{ ppm}$. The allyl ligand proton signals show upfield shifts from those in the neutral complexes.

In the ^{13}C NMR spectra, the carbon signals of the arene, allyl and carbonyl ligands appear in their characteristic regions (see Table 1), though the arene carbon signals are shifted downfield and the carbonyl signals are shifted upfield. The reported shifts, as well as the shifts to lower fields of the arene ligand protons in the ^1H NMR spectra, are also indicative of the cationic structure of these complexes.

It is noteworthy that in the ^{13}C NMR spectra of complexes IIc, obtained by both the chelate cleavage and the direct method, we observed a doubling of all the signals, which may be explained by isomerism of the allyl ligand relative to the arene ligand. This type of isomerism was studied in detail by J.W. Faller [6] for cyclopentadiene complexes.

The ^1H NMR spectra of complex VIII (see Table 1) with the 2-oxyallyl ligand

contains two broad singlets which correspond to H_{sin} and H_{anti} protons of the substituted allyl ligand. The signal of the arene ligand proton ($\delta = 6.11$ ppm) is shifted upfield in comparison with the other cationic complexes II (see Table 1). The existence of a hydroxyl substituent in the allyl ligand of complex VIII is shown by a broad signal ($\delta = 3.14$ ppm) in the NMR spectrum as well as by the 3360 cm^{-1} band in the IR spectrum. The reported structure of complex VIII agrees with the ^{13}C NMR spectrum. In the $^{13}\text{C}\{-^1\text{H}\}$ spectrum two signals are showing with $\delta = 42.8$ ppm (terminal atoms) and 139.9 ppm (central atom), which correspond to the allyl ligand carbon atoms. In the $^{13}\text{C}\{-^1\text{H}\}$ spectrum the signal of the central allyl ligand carbon atom also appears as a singlet. Such a downfield shift of the signal of the central allyl ligand carbon atom, in comparison with the shifts for other complexes II (see Table 1), is in agreement with the presence of a hydroxyl substituent [7].

In the discussion of the reported complexes it is noteworthy that the cleavage of complex I ($R = \text{H}$, $n = 0$) under the action of $\text{BF}_3 \cdot \text{OEt}_2$ have already been observed by Trahanovsky and his co-workers [8]. However, the product obtained, which is similar to our complex IIc in its properties, was given structure IX. Treatment of this product with diisopropylamine allowed Trahanovsky to obtain substance X. Treatment of our cationic complex IIc also resulted in this compound X.

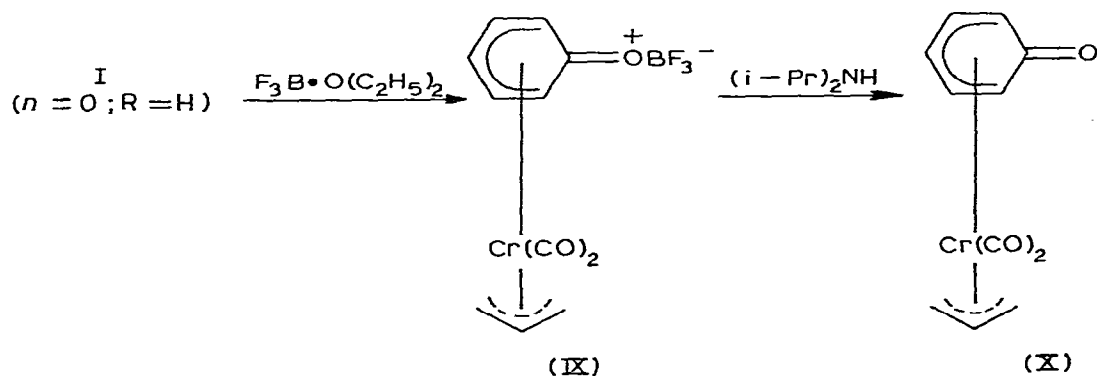


TABLE 2

COMPARISON OF DATA FOR IIc WITH LITERATURE DATA FOR IX

Structure	Decomp. temp. ($^{\circ}\text{C}$)	Analytical data ^a		IR data $\nu(\text{C}\equiv\text{O})$ (cm^{-1})	NMR data (δ , ppm) (in $(\text{CD}_3)_2\text{CO}$)
		C	H		
IIc	138–140	40.30 (40.03)	3.27 (3.36)	1932, 1986 (CH_2Cl_2)	1.33, d, 2 H, $J = 10.5$ Hz, (H_{anti}); 3.93, d, 2 H, $J = 7.2$ Hz, (H_{sin}); 4.71–5.31, m, (Ha); 6.00, 6.29, 6.75, m, 5 H, (Ar–H).
IX	140	39.30 (42.61)	3.50 (3.26)	1927 1978 (THF)	1.36, d, 2 H, $J = 10.0$ Hz (H_{anti}); 3.91, d, 2 H, $J = 7.5$ Hz, (H_{sin}); 4.70–5.20, m (Ha); 5.96, d, 1 H; $J = 6.5$ Hz (Ar–H); 6.21–6.45, m, 2 H, (Ar–H); 6.50–6.90, m, 2 H, (Ar–H).

^a Calculated values in parentheses.

However, the elemental analysis (C, H) described by Trahanovsky [8] differs considerably from the theoretical data for the structure proposed by him but is quite similar to that for the structure proposed by us (see Table 2). Moreover, the spectra obtained by Trahanovsky and by us are practically identical, and are very similar to the spectra for the other cationic complexes we obtained. These results lead us to conclude that the structure X proposed by Trahanovsky appears to be wrong.

Experimental

All the procedures for the syntheses of organometallic compounds were performed in an argon atmosphere, using absolute solvents. The synthesis of arene-tricarbonylchromium and arene-chelate-dicarbonylchromium complexes was carried out according to the procedures previously described in refs. 9 and 10, respectively.

The IR spectra of the reported compounds were measured in heptane and methylene chloride using an IKS-14A instrument and in KBr pellets on a UR-20 instrument. The NMR spectra were obtained in deuterioacetone with internal TMS on a Hitachi-Perkin-Elmer R-32 spectrometer operated at 90 MHz. The chemical shifts are cited on the δ scale in ppm. The ^{13}C NMR spectra were recorded in acetone and deuterioacetone on a Bruker HX-90 (22.63 MHz) spectrometer and on a Bruker WP-60 (15.08 MHz) spectrometer.

Synthesis of areneallyldicarbonylchromium tetrafluoroborate (Method A. Proton cleavage of chelates)

A solution of areneolefinedicarbonylchromium chelate complex (1 mmol) in 50 ml of ethyl ether was placed in a two-necked flask provided with a drop funnel and an inlet for argon. The solution was cooled to -50°C with $\text{CO}_2/\text{acetone}$. A solution of 0.25 ml (1 mmol, 0.09 g) of 4 *N* aqueous HBF_4 in 20 ml of ethyl ether was added dropwise upon stirring, the temperature of the reaction mixture was brought to room temperature. The ether was removed under vacuum, the residue was extracted with the minimum amount of acetone, the extract was filtered and diluted with ether. The precipitate was filtered off and dried. Analytically pure samples were obtained by numerous reprecipitations from the acetone ether mixture. Yields, decomposition temperatures, analytical data as well as IR and NMR spectra data are listed in Table 1.

Proton cleavage of the tricarbonyl chromium complex with 3,5-dimethylbenzylallyl ether

0.19 g (0.6 mmol) of the tricarbonylchromium complex with 3,5-dimethylbenzylallyl ether in 50 ml of ethyl ether and 0.16 ml (0.05 g, 0.06 mmol) of 4 *N* aqueous HBF_4 in 20 ml of ether gave a mixture of two substances on being worked up as above. The mixture was dissolved in CH_2Cl_2 and chromatographed on silica gel plates using ether/petroleum ether (1/1) as eluent. The first band, light yellow, contains the initial compound; R_f 0.75, yield 0.1 g (53%), m.p. $106\text{--}108^\circ\text{C}$; lit. [11] m.p. $107\text{--}108^\circ\text{C}$; $\nu(\text{C}\equiv\text{O})$ in heptane 1899 cm^{-1} , 1969 cm^{-1} ; lit. [11] $\nu(\text{C}\equiv\text{O})$ in cyclohexane 1899 cm^{-1} , 1969 cm^{-1} . The second band, yellow in colour, contains the tricarbonylchromium complex with 3,5-

dimethylbenzyl alcohol: R_f 0.15, yield 0.08 g of crude product (107% for the complex reacted), m.p. 143–144°C, lit. [11]: m.p. 143–145°C, $\nu(\text{C}\equiv\text{O})$ in heptane 1898, 1969 cm^{-1} , lit. [11] $\nu(\text{C}\equiv\text{O})$ in cyclohexane 1899 cm^{-1} , 1969 cm^{-1} .

Synthesis of arenetricarbonylallylchromium tetrafluoroborate (Method B. Direct method)

A solution of arenetricarbonylchromium (1 mmol) in 50 ml of ethyl ether was placed in a three-necked flask provided with a condenser and an inlet for argon. A solution of 0.25 ml (0.09 g, 1 mmol) of 4 N aqueous HBF_4 and 0.07 ml (0.06 g, 1 mmol) of allyl alcohol in 20 ml of ethyl ether was added. The solution was irradiated with a PRK-7 lamp 2–3 hours until the initial complex disappeared. The reaction was monitored by IR spectroscopy in the region of ca. 2000 cm^{-1} . The ether was evaporated under vacuum, the dry residue was extracted with a minimum amount of acetone, the extract was filtered and diluted with ethyl ether. The precipitate was filtered off and dried. Analytically pure samples were obtained by numerous reprecipitations from the acetone/ethyl ether mixture. Yields, decomposition temperatures, analytical data as well as IR and NMR spectra data are listed in Table 1.

Synthesis of benzenallyldicarbonylchromium tetrafluoroborate using diallyl ether

0.22 g (70%) of benzenallyldicarbonylchromium tetrafluoroborate were obtained as above from 0.21 g (1 mmol) of benzenetricarbonylchromium in 60 ml of ethyl ether, 0.25 ml/0.09 g (1 mmol) of 4 N aqueous HBF_4 and 0.1 g (1 mmol) of diallyl ether in 20 ml of ethyl ether.

Synthesis of benzenallyldicarbonylchromium tetrafluoroborate with allyl chloride

0.05 g (15%) of benzenallyldicarbonylchromium tetrafluoroborate were obtained as above from 0.21 g (1 mmol) of benzenetricarbonylchromium in 60 ml of ethyl ether, 0.14 g (1 mmol) of boron trifluoride etherate and 0.08 ml (0.08 g, 1 mmol) of allyl chloride in 30 ml of ethyl ether.

Synthesis of benzene-[1-(2-phenylethyl)]allyldicarbonylchromium tetrafluoroborate

0.13 g (62%) of benzene-1-(2-phenylethyl)allyldicarbonylchromium tetrafluoroborate were obtained as above from 0.11 g (0.5 mmol) of benzenetricarbonylchromium in 30 ml of ethyl ether, 0.13 ml (0.04 g, 0.05 mmol) of 4 N aqueous HBF_4 and 0.08 g (0.5 mmol) of 5-phenylpentane-1-ol-3 in 15 ml of ethyl ether. Decomposition temperatures, IR and NMR spectra data are given in Table 1.

Synthesis of benzene(2-oxyallyl)dicarbonylchromium tetrafluoroborate

0.15 g (23%) of benzene(2-oxyallyl)dicarbonylchromium tetrafluoroborate were obtained as above from 0.43 g (2 mmol) or benzenetricarbonylchromium, 0.1 ml (0.36 g, 4 mmol) of 4 N aqueous HBF_4 and 0.24 ml (0.24 g, 4 mmol) of propargyl alcohol. Decomposition temperatures, IR and NMR spectra data are listed in Table 1.

Reaction of phenolallyldicarbonylchromium tetrafluoroborate with diisopropylamine

A solution of phenolallyldicarbonylchromium tetrafluoroborate (0.1 g, 0.3 mmol) in acetone was placed in a two-necked flask with an inlet for argon. 0.1 g (1 mmol) of diisopropylamine in 10 ml of acetone were added. Stirring at room temperature continued until the initial complex completely disappeared (3 hours). (The reaction was monitored by IR spectroscopy on an IKS-14A instrument). The reaction mixture was evaporated, the residue dissolved in 40 ml of CH_2Cl_2 , washed with water (2×20 ml), diluted with 30 ml of petroleum ether and the crystals frozen out in dry ice. The yield of oxocyclohexadienylallyldicarbonylchromium was 0.08 g (100%), m.p. 112–114°C; lit. [8], decomp. temp. 115°C; $\nu(\text{C}=\text{O})$ in CH_2Cl_2 , 1909 cm^{-1} , 1962 cm^{-1} ; lit [8]: $\nu(\text{C}=\text{O})$ in THF 1899 cm^{-1} , 1962 cm^{-1} .

Acknowledgement

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