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Synthesis and properties of styrenetricarbonylchromium and its analogs

L. L. Semenycheva, A. N. Artemov, I. S. Il´ichev, and D. F. Grishin*

Research Institute of Chemistry,
N. I. Lobachevskiy Nizhniy Novgorod State University,
23 prosp. Gagarina, building 5, 603950 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 65 8162. E-mail: grishin@ichem.unn.runnet.ru

The methods of synthesis and the reactivity of styrenetricarbonylchromium and its analogs as model objects for the study of the effect of the metal atom on the reactivity of the monomer π-bond and the aromatic ring are described systematically and discussed. These compounds are unique initial substrates for the synthesis of metal-containing polymers and for the preparation of optical stereoisomers and materials for nonlinear optics.

Key words: styrenetricarbonylchromium, synthesis, properties, complex radical (co)polymerization, metal-containing polymers.

Introduction

In recent years, a new line of research dealing with the synthesis of metal-containing monomers and polymers based on them has vigorously developed in organometallic chemistry.[1—4] The interest in these molecules is due to unique properties of the produced polymers containing a metal atom in each unit such as high catalytic and biological activities, electric and magnetic properties, *etc*.[1—4]

In addition to the best known π-type monomer, vinylferrocene, which has been studied comprehensively, particular attention is drawn by the tricarbonylchromium complexes of styrene and its derivatives. On the one hand, this is due to the fact that arenetricarbonylchromium complexes are readily available and, as a rule, fairly stable. Styrenetricarbonylchromium (SCC) and its analogs serve as convenient models for studying the regular features of the polymer chain growth. Owing to the presence of a metal atom in the molecule, both homo- and copolymerization of metal-containing monomers often follow a complex-radical mechanism.[1,5—9] On the other hand, metal-containing polymers are quite promising from the practical standpoint. Indeed, organochromium compounds are also known as catalysts of polymerization of dienes and acetylene derivatives and as biologically active substances; they are convenient for the preparation of conductive and magnetic materials or nanocomposites.[1—4] In addition, the recent interest in SCC and its analogs is related to the development of nonlinear optics because these compounds contain systems of conjugated double bonds and are characterized by good nonlinear-optical properties.[10—13] Some properties of SCC find application in the asymmetric synthesis of organic compounds.[14—17]

Prospects of the chemistry of arenetricarbonylchromium compounds have promoted the development of original methods for the synthesis of SCC and its analogs. Despite the large numbers of publications in various editions devoted to this separate group of arenetricarbonyl complexes, the results of recent studies have not been generalized.

In this review, we describe systematically and discuss for the first time methods for the synthesis of SCC and its derivatives and the specific features of their reactivity.

1. Key methods for the synthesis of styrenetricarbonyl chromium complexes

The first arenetricarbonylchromium complex, benzenetricarbonylchromium, was prepared in 1958, almost simultaneously by several research groups, from chromium hexacarbonyl and benzene[18—21]

$$\mathrm{Cr(CO)_6} + \text{arene} \rightarrow \text{areneCr(CO)}_3 + 3\ \mathrm{CO}. \qquad (1)$$

Early attempts to synthesize SCC by reaction (1), which was used to prepare a wide range of benzenetricarbonylchromium derivatives,[22—25] directly from chromium hexacarbonyl and styrene were unsuccessful. However, SCC was synthesized[22] from nitrogen-containing derivatives of chromium hexacarbonyl $X_3Cr(CO)_3$ (X is ammonia, trimethylpyridine, acetonitrile, *etc*.).[22,25,26] Tris(amine)tricarbonylchromium is used most often for this purpose. This solid compound can be readily prepared and isolated in a pure state,[2,27—29] which facili-

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tates the synthesis of many functionally substituted arenetricarbonylchromium complexes.

The first reported vinylarene chromium complex homologous to SCC is α-methylstyrenetricarbonylchromium,[26] which was prepared by refluxing α-methylstyrene with $Cr(CO)_6$ in 2,4,6-trimethylpyridine. The applicability of the Rausch method[22] to the synthesis of SCC and its derivatives has been studied in detail.[30] The influence of the reaction conditions (temperature, solvent, reactant ratio, *etc.*) on the yield and the purity of final products (styrene-, α-methylstyrene-, *p*-methylstyrene-, divinylbenzene-, and bis-1,4-(α-methylvinyl)benzenetricarbonylchromium complexes) has been elucidated. It was found that the vinylarene chromium complexes are best prepared at 100 °C in dioxane.

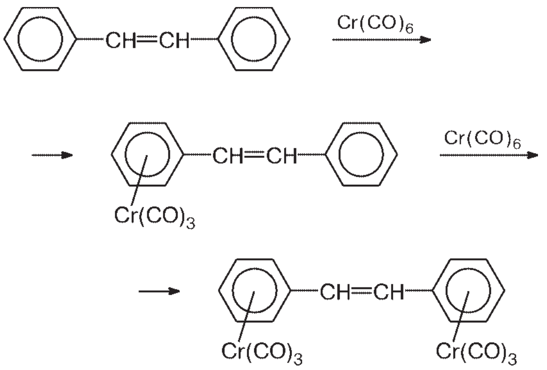
Most recently,[31] tricarbonyl complexes of styrene and its derivatives were prepared from $Cr(CO)_6$ in dibutyl ether containing some THF. Presumably, this electron-donating solvent forms a reactive intermediate during the reaction

$$Cr(CO)_6 + 3\ THF \rightarrow (THF)_3Cr(CO)_3 + 3\ CO, \qquad (2)$$

$$(THF)_3Cr(CO)_3 + 3\ arene \rightarrow areneCr(CO)_3 + 3\ THF.$$

This method provided the first syntheses of a number of tricarbonylchromium styrene derivatives, namely, *p*-methyl-, *p*-chloro-, *p*-fluoro-, *p*-methoxystyrenetricarbonylchromium,[31] styrene- and α-(ethylthio)styrenetricarbonylchromium.[32] Styrenetricarbonylchromium analogs, stilbene derivatives, can also be synthesized directly from $Cr(CO)_6$. For example, stilbenetricarbonylchromium[33] and 1,4-diphenylbutadiene-1,3-bis(tricarbonylchromium)[34] have been synthesized (Scheme 1).

Scheme 1



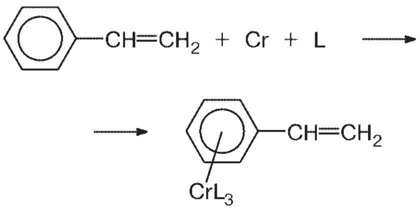
Yet another efficient method for the preparation of arene chromium complexes is the replacement of an aromatic ligand by a different aromatic molecule.[35–39]

$$areneCr(CO)_3 + arene' \rightarrow arene'Cr(CO)_3 + arene. \qquad (3)$$

Reaction (3) is fairly convenient for the synthesis of arenetricarbonylchromium compounds containing functional groups in the aromatic ring, which are difficult to prepare by direct reaction (1). Reaction (3) was used successfully for the synthesis of unsaturated arene-substituted organometallic compounds. For instance, SCC is formed in a quantitative yield when naphthalenetricarbonylchromium is used as the starting compound.[36] The yield of the final product increases in the presence of Lewis bases (electron-donating solvents, for example, THF).[35–37] It has been found recently[39] that anthracene in the tricarbonylchromium complex is even more readily replaced by other arenes according to reaction (3) in the presence of THF.

Co-condensation of chromium atoms with the appropriate aromatic compounds represents one more pathway to arenetricarbonylchromium complexes containing the vinyl group. This reaction is carried out at low (−196 °C) temperature. An example is co-condensation of chromium vapor with styrene and phosphorus trifluoride or carbon monoxide[40] (Scheme 2).

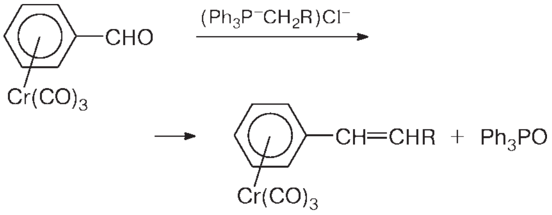
Scheme 2



$L = PF_3$, CO.

The Wittig reaction, characterized by a simple procedure and mild temperature conditions, is convenient for the synthesis of SCC. This method was first employed[41] for the preparation of arenetricarbonylchromium complexes with multiple bonds in the case of stilbene derivatives, *viz.*, stilbene-, β-biphenyl-η^6-styrene-, β-terphenyl-η^6-styrenetricarbonylchromium, 1,4-bis(styrenetricarbonylchromium)benzene, and 4,4′-bis(styrenetricarbonylchromium)biphenyl. In this case, benzaldehydetricarbonylchromium is used as the initial carbonyl component (Scheme 3).

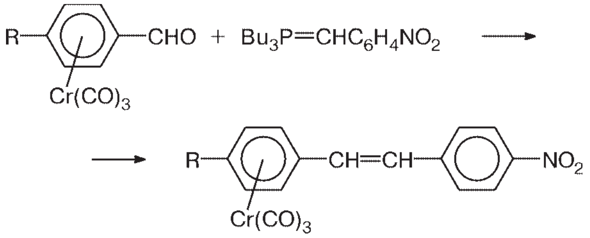
Scheme 3



R = Ph, PhC_6H_4, $PhC_6H_4—C_6H_4$, 1-C_8H_7, NCC_6H_4, $PhCH=CHC_6H_4$, $PhC{\equiv}CC_6H_4$.

Subsequently, this method was extended to a number of substituted benzaldehydes. Nitrostilbene tricarbonylchromium complexes (Scheme 4), which cannot be prepared by the direct reaction, have also been synthesized.[42]

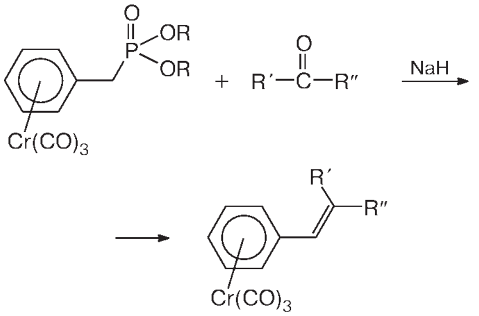
Scheme 4



R = NMe$_2$, H, SiMe$_3$, CF$_3$.

Organophosphorus compounds were further used for the synthesis of unsaturated compounds in the Horner (or Horner—Emmons—Wadswort) reaction.[43] This is a version of the Wittig reaction; the difference is that phosphonates in the form of metal complexes are used in the first step instead of phosphines. Phosphonate complexes can be synthesized in 40—70% yield from the corresponding free ligands by thermally induced complexation with chromium carbonyl. These complexes are deprotonated on treatment with sodium hydride; after that, they readily react with aldehydes, dialdehydes, or ketones in boiling THF. The resulting organometallic compounds are isolated from the reaction mixture as yellow or orange solids (Scheme 5).

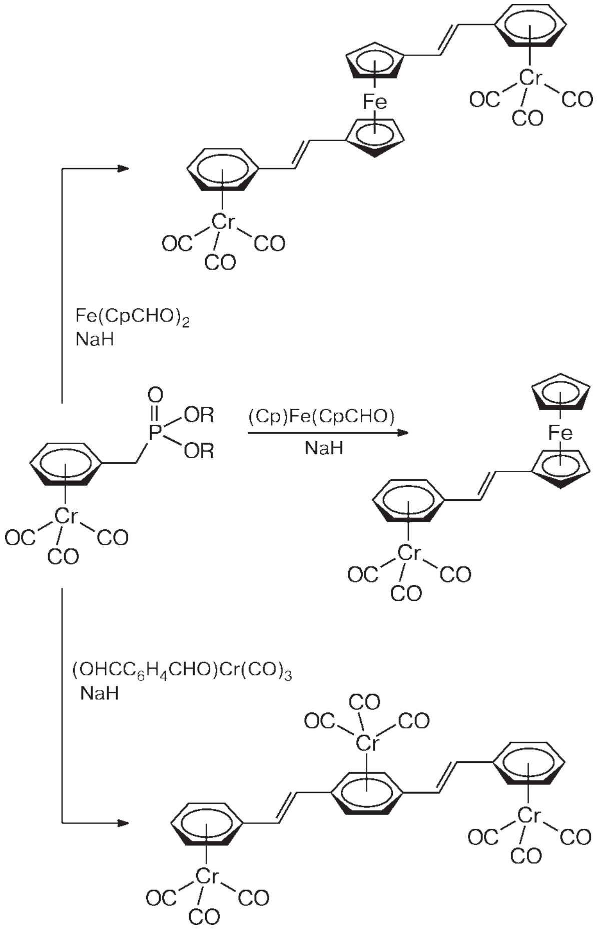
Scheme 5



When organometallic aldehydes or ketones are used, this reaction gives rise to extended π-systems, in particular, those containing two or more transition metals in the molecule[11,44] (Scheme 6).

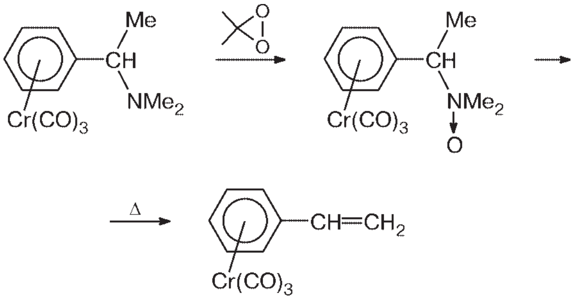
The Horner—Emmons—Wadswort method offers a significant advantage over the pathway based on direct complexation and Wittig olefination. The reaction always proceeds with high selectivity giving high yields of products with *trans*-configuration of the double bond, whereas the Wittig reaction normally affords mixtures of *cis*- and *trans*-isomers.

Scheme 6



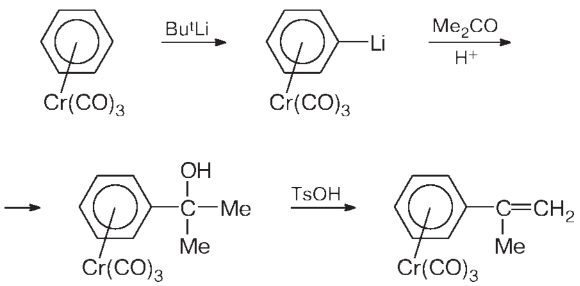
An approach interesting from the synthetic standpoint is based on oxidation of α-substituted benzylamines;[45] the reaction of α-methylbenzyldimethylaminetricarbonylchromium with dimethyldioxirane furnishes SCC in 80% yield. This procedure permits the preparation of *ortho*-substituted styrenetricarbonylchromium complexes having planar chirality.[45] The synthesis can be presented by Scheme 7.

Scheme 7



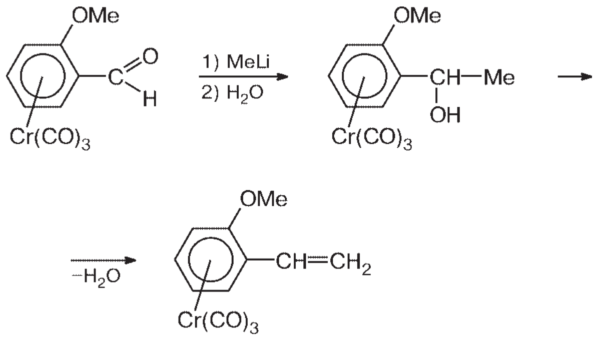
Unsaturated arenetricarbonylchromium complexes can be prepared by elimination reactions of alkylaromatic alcohols,[32] tosylates,[46] methanesulfonates,[47] and β-alkylamines.[48] For instance, (α-methylstyrene)tricarbonylchromium was prepared by a procedure[32] including metallation of benzenetricarbonylchromium with *n*-butyllithium, the reaction with acetone,[49] and water elimination (Scheme 8).

Scheme 8



o-Methoxystyrenetricarbonylchromium is prepared by treatment of the corresponding aldehyde with methyllithium[50] followed by water elimination; the product yield in this reaction is 95—98% (Scheme 9).

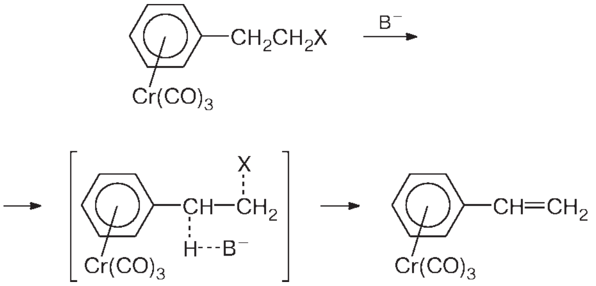
Scheme 9



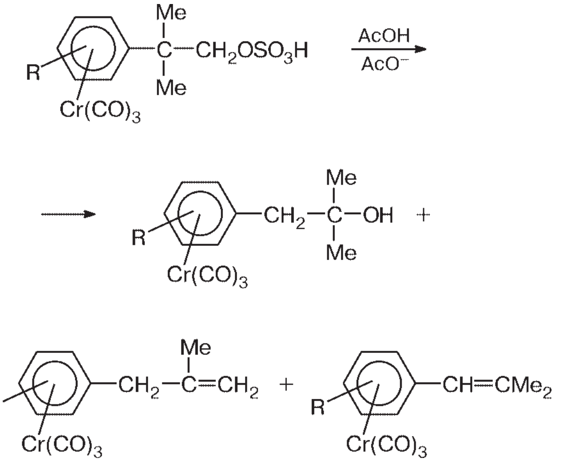
Base-catalyzed elimination of HX (X = Br, HSO_4) from chromiumtricarbonyl complexes of 2-phenylethyl bromides or 2-phenylethyl tosylates (E_2 type reaction) proceeding in high yields (97%) has been described[46,51] (Scheme 10).

Elimination of π-complex methyl sulfates also occurs under mild conditions; in particular, acetolysis of 2-(phenyltricarbonylchromium)-2-methylpropyl hydrogen sulfates is accompanied by migration of the phenyltricarbonylchromium group giving rise to 3-(phenyltricarbonylchromium)-2-methylpropan-2-ol and a mixture of π-bonded olefins in 2 : 3 ratio (Scheme 11).[47]

Scheme 10



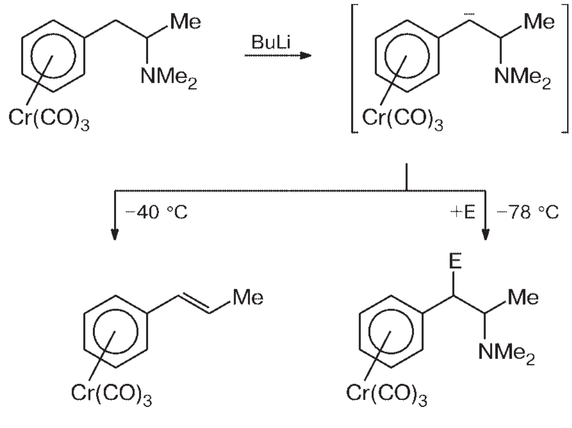
Scheme 11



R = MeO, Me, H.

In the case of π-complex β-arylalkylamines, elimination of amines to give (β-methylstyrene)tricarbonylchromium proceeds only on treatment with hydrides and alkali metal alkyls. In the presence of butyllithium, the metallated α-benzyl anion is probably formed initially. At temperatures of at least –40 °C, the anion ejects the dimethylamino group being converted into an unsaturated complex, whereas at lower temperature, an electrophilic agent adds to the intermediate (Scheme 12)[48].

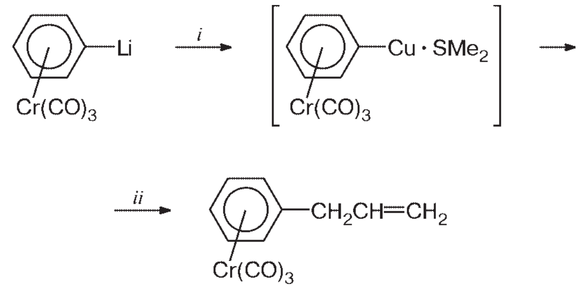
Scheme 12



E = MeS, Ph_2P, Me_3Si, I, $H_2C=CH—CH_2$.

Various allyl derivatives of arenetricarbonylchromium complexes were synthesized[52] using a very simple reaction sequence (Scheme 13).

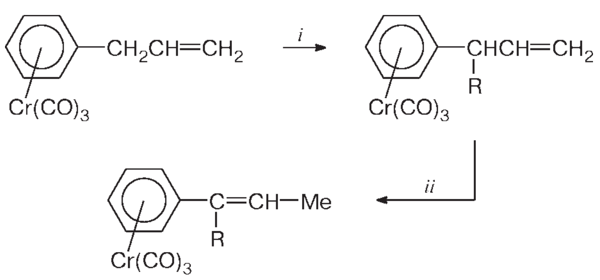
Scheme 13



i. $CuBr \cdot SMe_2$; *ii.* $BrCH_2CH{=}CH_2$.

Similar unsaturated derivatives have also been prepared for anisoletricarbonylchromium. Allyl derivatives of arenetricarbonylchromium complexes were found[52] to undergo easy isomerization to 1-propenylarene complexes upon deprotonation followed by the reaction with an acid (Scheme 14).

Scheme 14



R = Me, $Me_2C{=}CH(CH_2)_2$.

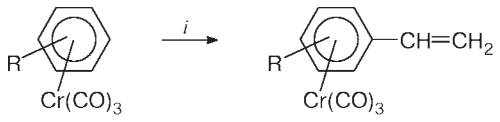
i. 1) Bu^tOK/DMSO, 2) RI; *ii.* 1) Bu^tOK/DMSO, 2) H^+.

Vinylation of arenetricarbonylchromium complexes was carried out using a palladium catalyst.[53] Metallation, transmetallation, and the reaction of the resulting copper-containing arenetricarbonylchromium complex with vinyl bromide in the presence of tetrakis(triphenylphosphine)palladium gave rise to styrene-, *o*-methoxystyrene-, and *p*-fluorostyrenetricarbonylchromium complexes (Scheme 15).

The same reaction sequence was employed to prepare 1-methylprop-1-enylbenzene- and *o*-(1-methylprop-1-enyl)anisoletricarbonylchromium[52] (Scheme 16).

Thus, palladium compounds provide the addition of the vinyl group to arenetricarbonylchromium.

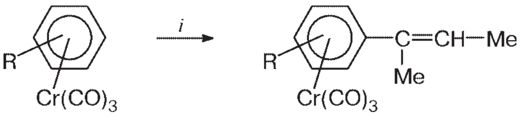
Scheme 15



R = H, OMe, F.

i. 1) BuLi; 2) $CuBr \cdot SMe_2$; 3) $Pd(PPh_3)_4$; 4) $BrCH{=}CH_2$.

Scheme 16

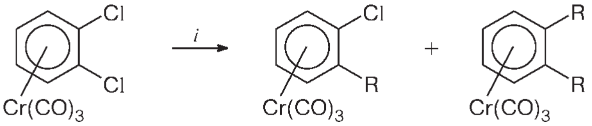


R = H, OMe.

i. 1) BuLi; 2) $CuBr \cdot SMe_2$; 3) $Pd(PPh_3)_4$; 4) $Me(Br)C{=}CHMe$.

Nucleophilic substitution in aromatic compounds proceeds with difficulty;[14,54] however, the presence of the electron-withdrawing $Cr(CO)_3$ group facilitates this process. For instance, the chlorine atom in *o*-dichlorobenzenetricarbonylchromium was replaced by a vinyl group under mild conditions. As in the previous example, the palladium catalyst promotes easy vinylation of arenetricarbonylchromium.[50] This reaction was carried out for a series of organometallic compounds (Scheme 17).

Scheme 17



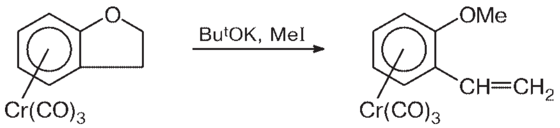
R = $CH_2{=}CH$, $CH_2{=}CMe$, BuCH=CH; M = Mg, Zn, Sn, B;
X = Cl, Br, OH, Alk.

i. RMX_n, L*/[PdCl(*p*-All)]$_2$.

Both mono- and disubstituted products are formed in high yields.

An interesting method for the synthesis of *o*-methoxystyrenetricarbonylchromium includes[55] deprotonation of (2,3-dihydrobenzofuran)tricarbonylchromium on treatment with potassium *tert*-butoxide and subsequent alkylation with methyl iodide (Scheme 18).

Scheme 18



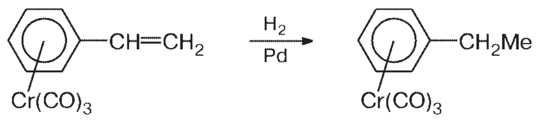
A whole series of unsaturated arenetricarbonylchromium complexes have now been prepared. These compounds can serve as the initial substrates for the synthesis of organometallic comounds including materials for nonlinear optics, optical stereoisomers and natural products possessing special biological activities, and metal-containing polymers.

2. Reactivity of styrenetricarbonylchromium and its analogs

The interest in styrenetricarbonylchromium and its analogs is due, first of all, to the presence of the reactive vinyl group. Initially, addition and polymerization involving the double bond have been mainly studied and compared with similar reactions of styrene and other vinyl monomers (see Section 3). In recent years, SCC derivatives have been used as the initial compounds for organometallic synthesis.

Investigations of the chemical properties of unsaturated arenetricarbonylchromium complexes started immediately after the first synthesis of styrenetricarbonylchromium.[22] Hydrogenation of this compound was accomplished[22,27] under conditions similar to those used for hydrogenation of alkenes including styrene (treatment with H_2 on a Pd catalyst)[22] and gave rise to ethylbenzenetricarbonylchromium (Scheme 19).

Scheme 19

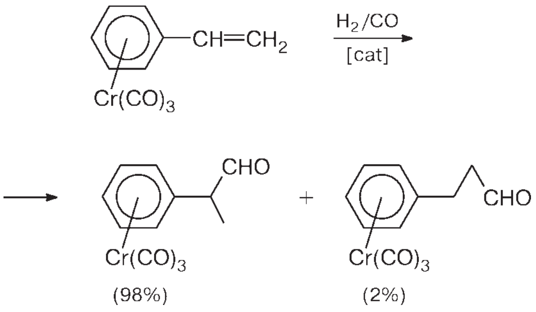


The attempts at hydroboration of SCC[27] on treatment with $NaBH_4$ in the presence of $BF_3 \cdot Et_2O$ followed by treatment with H_2O_2 also resulted in ethylbenzenetricarbonylchromium as the final product.

The Reppe reaction (hydroformylation), typical of olefins,[54,56] carried out for styrene-, indene-, and dihydronaphthalenetricarbonylchromium over rhodium and platinum catalyst systems results in arylaliphatic aldehydes formed in good yields under mild conditions[57] (Scheme 20).

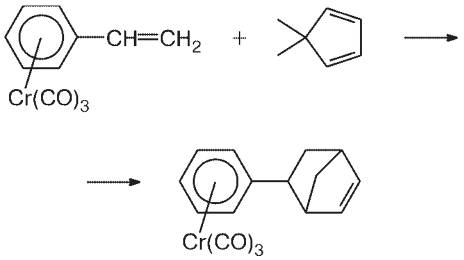
Unlike hydroformylation of free alkenylarenes, in this case, the reaction proceeds with high selectivity and in good yields and is important from the practical standpoint because it can be used for the synthesis of 2-arylpropanoic acids, employed as nonsteroidal antiinflammatory agents.[57]

Scheme 20



Styrenetricarbonylchromium enters also into the Diels—Alder reaction with cyclopentadiene, the latter acting as the diene.[27] Cyclization involves positions 2,5 of the cyclopentadienyl ring to give η^6-(2,5-endo-methylene-1,2,5,6-tetrahydrodiphenyl)tricarbonylchromium (Scheme 21).

Scheme 21



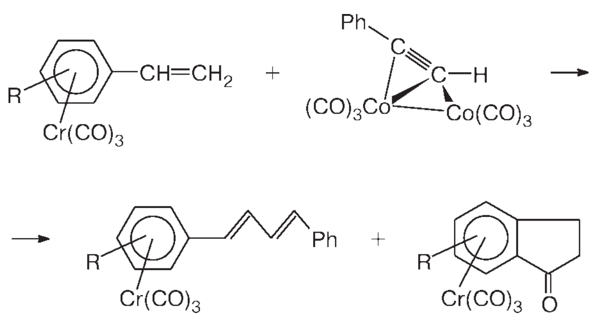
In the case of SCC, this reaction proceeds at a lower temperature (~140 °C) than that for the noncoordinated analog (180—190 °C).

Interesting data on the reactivity of arenetricarbonylchromium derivatives compared to that of analogs devoid of the metal-containing fragment have been obtained[31] in a study of the SCC reaction with phenylacetylenehexacarbonyldicobalt (PAHC). Alkenes including styrene can be converted into two types of products in this reaction, namely, cyclopentenone complexes and linear dienes. The formation of linear dienes is typical of alkenes with efficient electron-withdrawing substituents. Styrenetricarbonylchromium and its derivatives containing the Me, Cl, F, or MeO group in the *para*-position and substituents at the double bond react with PAHC to give both types of product in almost equal yields. Presumably,[31] the electron-withdrawing effect of the chromiumtricarbonyl group does not show itself in this case (Scheme 22).

Unlike SCC, allylbenzenetricarbonylchromium,[31] similarly to other alkenes containing no conjugated double bonds, forms only the cyclopentenone derivative because the double bond in the starting compound is separated from the benzene ring.

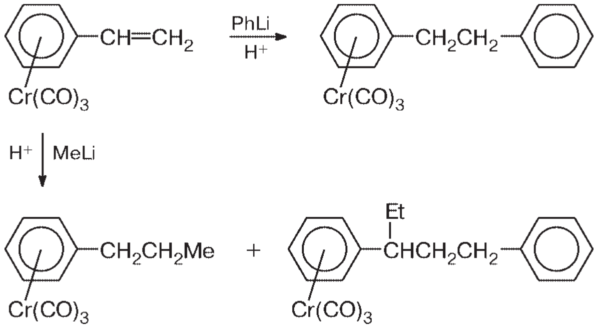
The reaction of SCC with phenyl- and methyllithium[27] proceeds mainly with the addition of the or-

Scheme 22



ganic radical at the β-position. The reaction with phenyllithium affords dibenzyltricarbonylchromium, and in the case of methyllithium, 1,3-bis(phenyltricarbonylchromium)pentane is produced together with the expected *n*-propylbenzenetricarbonylchromium (Scheme 23).

Scheme 23

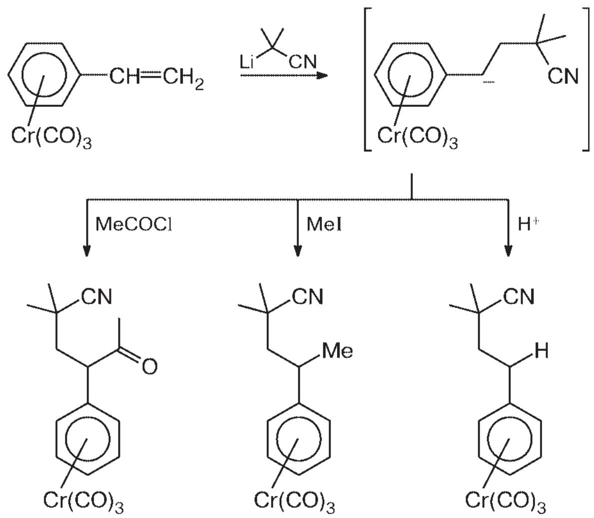


The synthesis conditions and reaction mechanism of nucleophilic addition of organolithium compounds to SCC derivatives has been discussed in the literature.[32,58,59] The addition of 2-lithio-2-methylpropionitrile to SCC occurs stereoselectively, resulting in high product yields; a series of functionally substituted arenes have been prepared in this way (Scheme 24).

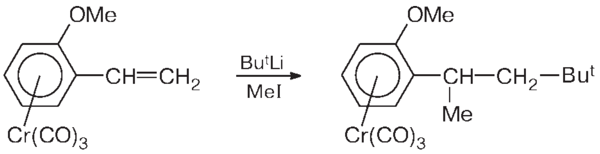
By stereoselective addition of *tert*-butyllithium simultaneously with MeI, homochiral *o*-methoxystyrenetricarbonylchromium[60] was converted into a pure diastereomer of [2-(*o*-anisyl)-4,4-dimethylpentane)tricarbonylchromium[61] (Scheme 25).

Thus, the addition reactions considered above, which are typical of olefins, in particular, styrene also take place in the case of SCC and its derivatives.

Scheme 24

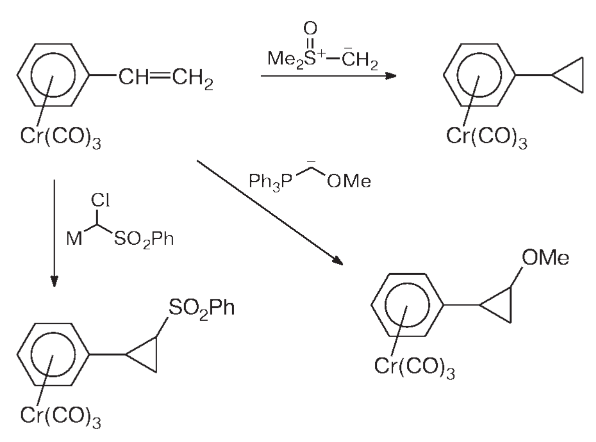


Scheme 25



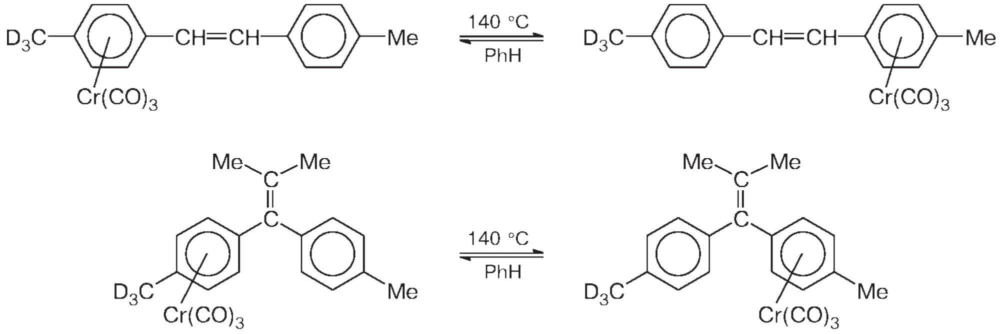
In recent years, SCC and its analogs have been attracting the attention of synthetic chemists due to the fact that the influence of the arenetricarbonyl fragment on the reactivity of the double bond can provide the possibility of unique syntheses that cannot be carried out for styrene and its homologs. For example, the reactions of sulfonium and phosphonium ylides with SCC have been studied.[62] They gave previously unknown arenetricarbonylchromium derivatives of cyclopropylbenzenes. Note that the reactivity of the double bond has crucially changed upon incorporation in the arenetricarbonylchromium group, because ylides do not add to free styrene. Substituted cyclopropylbenzenetricarbonylchromium derivatives are formed when SCC is made to react with organometallic lithium and magnesium sulfones (Scheme 26).

Scheme 26



M = MgBr, Li.

Scheme 27



The regularities of ring—ring haptotropic rearrangements in which a transition metal together with the surrounding ligands migrates between the rings of a polyaromatic ligand have been studied.[63,64] For example, in the case of substituted stilbenes and diarylethylenes, this rearrangement follows an intramolecular mechanism at 140 °C (Scheme 27).[65,66]

Detailed descriptions of examples of these rearrangements including their mechanisms and kinetics can be found in a review.[63]

3. Polymerization involving organochromium monomers

Production of polymers and the synthesis of copolymers with a broad range of properties are known to be the major applications of styrene. Therefore, the reactivity of SCC and its analogs in homo- and copolymerization has attracted attention almost as soon as these compounds were prepared.

The transition metal atom present in the arenetricarbonylchromium molecule can induce known undesirable side reactions with ionic initiators.[27,67—70] Therefore, metal-containing polymers are usually synthesized with radical initiation. The initiator used most often is AIBN, which is efficient in both solution and bulk polymerization.[68—73] Peroxide initiators are employed much more rarely, due to the risk of oxidation of metal-containing monomers with the peroxide.

The synthesis of homopolymers of SCC and its analogs has not long been a success,[22,27,69—72] although SCC and *p*-methylstyrenetricarbonylchromium (PCC) have been studied in copolymerization, in particular, with styrene,[69,72] methyl acrylate,[69] methyl methacrylate,[73—76] butyl acrylate,[74—76] and vinyl cymanthrene[69] for SCC and with methyl methacrylate and butyl acrylate[74—76] for PCC. Copolymerization was carried out in the bulk and in organic solvents using AIBN (50 °C) and even benzoyl peroxide (70 °C) initiation.

An original initiation method was proposed for low-temperature copolymerization (30 °C): the thermally stable organoelement peroxide $Ph_3Sb(OOBu^t)_2$ served as one component of the initiator, while the metal-containing monomer itself was the other component,[74—77] as it induces homolytic decomposition of $Ph_3Sb(OOBu^t)_2$ at room temperature.

Study of the copolymerization kinetics[72,73,75] showed that the process with chromium-containing monomers occurs, as a rule, much more slowly than that involving individual organic monomers. This was observed in SCC copolymerization with styrene,[72] methyl methacrylate, and butyl acrylate and in PCC copolymerization with butyl acrylate.[73,75]

The constants for copolymerization were determined for all monomer pairs. It can be seen in Table 1 that the relative activities of electron-withdrawing acrylic monomers are lower than unity. In the case of the electron-donating styrene monomer, this value is greater than unity, and for vinyl chloride, it is close to unity. The copolymerization constants for SCC and for PCC were found to be close to zero.[69,72—77] In this respect, metal-containing monomers differ significantly from their organic analogs. Indeed, the relative activities of styrene

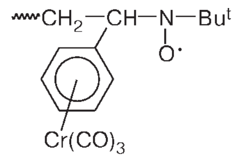
Table 1. Relative activities of vinyl monomers (*r*) in copolymerization with chromium-containing monomers

Monomer pair*	Initiator	Solvent	*T* /°C	*r*
MMA—SCC	AIBN	AcOEt	50	0.71±0.6
BA—SCC	AIBN	AcOEt	50	0.75±0.03
MMA—PCC	AIBN	AcOEt	50	1.44±0.11
MMA—SCC	SCC—$Ph_3Sb(OOBu^t)_2$	AcOEt	30	0.60±0.05
BA—SCC	SCC—$Ph_3Sb(OOBu^t)_2$	AcOEt	30	0.65±0.05
MMA—PCC	PCC—$Ph_3Sb(OOBu^t)_2$	AcOEt	30	1.10±0.05
MA—SCC[69]	AIBN	PhH	70	0.75
St—SCC[72]	Benzoyl peroxide	PhH	80	1.39±0.04
St—SCC[69]	AIBN	PhH	70	1.39

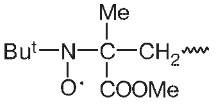
* MA is methyl acrylate, MMA is methyl methacrylate, St is styrene, BA is butyl acrylate.

and *p*-methylstyrene in the styrene—methyl acrylate, styrene—methyl methacrylate, *p*-methylstyrene—methyl methacrylate, styrene—butyl acrylate, and styrene—vinyl chloride monomer pairs are ~0.5 or higher.[78] On the one hand, the relative activity depends on the nature of the organic monomer and on the other hand, the values for metal-containing monomers and their organic analogs are appreciably different.

A more detailed investigation of the initiation and chain propagation steps by physicochemical methods allowed researchers[74—77] to conclude that SCC or PCC copolymerization with vinyl monomers follows an unusual mechanism. It was shown by ESR spectroscopy with spin traps that SCC reacts with the initiator radicals to give the corresponding chain propagation radicals. For example, upon initiation by the $Ph_3Sb(OOBu^t)_2$—SCC system (with 2-methyl-2-nitrosopropane as the spin trap), the ESR spectrum shows the spin adduct of the *tert*-butoxy radicals ($Bu^tO—N(O)—Bu^t$) as a triplet with the splitting constant a_N = 27.3 mT and a triplet of doublets (a_N = 15.0 mT and a_H = 1.6 mT) belonging to the spin adduct formed upon trapping of the SCC terminal radical by the trap.

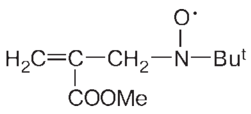


The splitting constant at hydrogen in this spin adduct is somewhat lower than that in the spin adduct formed by the polystyrene radical (a_N = 15.0 mT and a_H = 2.2 mT).[79] Apparently, this is due to spin density delocalization on the arenetricarbonylchromium fragment through vacant d orbitals of the metal atom. When methyl methacrylate is introduced in the system, *i.e.*, when SCC copolymerization with acrylic monomers is carried out, the ESR spectrum exhibits a triplet with a splitting constant a_N = 15.3 mT corresponding to the spin adduct formed by the methyl methacrylate radical.



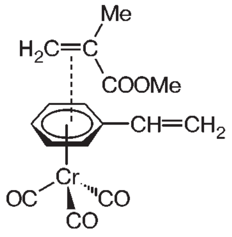
$$\mathrm{Bu^t{-}N(O^{\bullet}){-}C(Me)(COOMe){-}CH_2{\sim}}$$

In addition, the spectrum contains a triplet of triplets (a_N = 15.1 mT; a_H = 10.1 mT) for the adduct formed upon hydrogen abstraction from the methyl methacrylate molecule on treatment with the growing macromolecule or with the initiator radical; this provides chain transfer to the monomer.

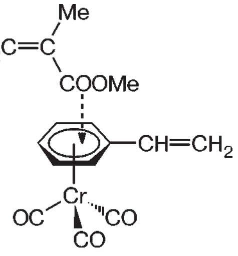


$$\mathrm{H_2C{=}C(COOMe){-}CH_2{-}N(O^{\bullet}){-}Bu^t}$$

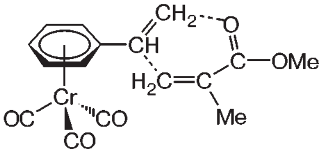
No spin adduct of the polystyrenetricarbonylchromium radical, which is found in the absence of methyl methacrylate, was detected in the ESR spectrum. This indicates that SCC copolymerization with methyl methacrylate follows a complex-radical mechanism. It is known[5,6] that in this case, a complex formed by the two monomers rather than merely the second monomer molecule, as in the usual radical copolymerization, adds to the growing radical during the process. The complexation constant is normally rather low (K = 1—0.01).[6] In the copolymerization of methyl methacrylate with SCC, a weak donor—acceptor complex was detected by UV spectroscopy (K = 0.06).[73—76] The possible structures (**A—D**) of complexes for the given monomer pairs proposed in the literature are shown below.



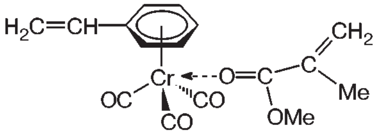
A



B



C



D

Structure **A** appears to be the most favorable from the standpoint of the 18-electron rule for the electronic structures of transition metal organic derivatives and also more reasonable in terms of the views on the polymer chain growth in the complex-radical mechanism.[5,6]

When studying copolymerization, the researchers attempted, as a rule, to prepare also the homopolymer; however, these attempts have long failed. Some researchers have attributed this to the steric hindrance created by the bulky tricarbonylchromium group.[80] However, in terms of this assumption, it is difficult to interpret copolymerization of SCC with equally bulky vinylcymanthrene.[69]

According to a different view,[69,72] this behavior of SCC is attributable to radical stabilization due to strong contact or resonance interaction of the active site with the chromiumtricarbonyl group.

The synthesis of homopolymers of SCC,[81—84] PCC,[84,85] and *p*-divinylbenzene[85] was reported only recently. Polymerization in AcOEt, PhH, or toluene at 50 °C in the presence of AIBN resulted in the synthesis of polystyrenetricarbonylchromium and poly(*p*-methylstyrenetricarbonylchromium). However, when polymerization was initiated in hexane, *i.e.,* in an inert solvent, no homopolymer of, for example SCC, was detected.[84] Under these conditions, polymerization of α-methylstyrenetricarbonylchromium does not take place, apparently, due to specific steric features of the structure of this monomer.[84,85]

p-Methylstyrenetricarbonylchromium and *p*-divinylbenzene polymers were also prepared in benzene or dioxane in the presence of AIBN at 80—85 °C; however, the authors[85] were unable to prepare the SCC polymer under the same conditions.

The properties of polymers based on SCC and its analogs are little studied. SCC and PCC homopolymers have been characterized[81—84] as light-yellow amorphous powders. According to spectrophotometric analysis, the contents of chromium in the polymer and the monomer coincide. The structure of SCC homopolymer was confirmed by physicochemical methods, namely, IR and ^{1}H NMR spectroscopy (in acetone-d$_6$).[81,84] The IR spectra of the polymer show an absorption in the region of 1633 cm^{-1}, typical of the coordinated benzene ring, and two very strong signals at 1860 and 1930 cm^{-1} (a shoulder at 1890 cm^{-1}) corresponding to the $Cr(CO)_3$ group. The ^{1}H NMR spectrum of polystyrenetricarbonylchromium exhibits signals at 2.04 and 2.97 ppm, corresponding to methylene and methine protons, respectively, and a multiplet at 5.60 ppm for the benzene ring protons. The signals of the vinyl protons, which are displayed as a multiplet at about 6.30 ppm in the SCC spectrum, were not detected in the spectrum of the polystyrenetricarbonylchromium. Unlike the organic analogs, SCC and PCC polymers are insoluble in benzene or chloroform but can be dissolved in acetone; similarly to polystyrene, they are soluble in AcOEt and THF. According to GPC, chromium-containing homopolymers have low molecular weights and rather high polydispersity (Table 2),[69,74—76,82—84] which may be due to the high rate constant for the chain transfer to the monomer.

Table 2. Molecular-mass characteristics of chromium-containing polymers[a]

Monomer pair	Degree of conversion (%)	$M_n{}^b \cdot 10^{-3}$	$M_w{}^b \cdot 10^{-3}$	$M_w/M_n{}^b$
SCC—MMA	57	111	196	1.8
PCC—MMA	14	84	138	1.6
SCC—MMA[c]	29	48	85	1.8
PCC—MMA[c]	14	22	65	3.0
SCC[d]	32	1	3	3.3
PCC[d]	18	3	14	4.2

[a] A solution in AcOEt at 50 °C, the content of the organometallic compound in the monomer mixture is 5 mol. %, [AIBN] = 0.5% (w/w).

[b] M_w/M_n is the weight/number average molecular mass.

[c] The polymer was obtained in the presence of $Ph_3Sb(OOBu^t)_2$ at 30 °C.

[d] Data for homopolymers.

According to a number of publications,[69,74—76,82—84] chromium-containing copolymers based on SCC (PCC) and acrylic monomers have relatively low molecular weights and lower polydipersity compared to homopolymers. The stability of chromium-containing polymers against thermooxidative destruction was reported to be higher than that of poly(methyl methacrylate).[73,77] The fungicidal activity typical of many organochromium compounds was also found for these polymers.[73,77]

Conclusion

Thus, styrenetricarbonylchromium and its analogs are interesting and promising model compounds for the investigation of the effect of a metal atom on the reactivity of the exocyclic π-bond. Often, they are unique substrates in the synthesis of optical stereoisomers, natural products, and materials for nonlinear optics and also for investigation of the mechanisms of complex chemical reactions. Of indubitable practical interest are metal-containing polymers that possess several specific physicochemical properties and biological activity, caused by the presence of the chromium atom in the macromolecular chain. This field of polymer chemistry is also of interest as regards the development of the theoretical grounds of complex-radical polymerization and the control of the polymer chain propagation step under radical initiation conditions.

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