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Application of Chromium-Arene Complexes in the Organic Synthesis. Efficient Synthesis of Stilbene Phytoalexins[1]

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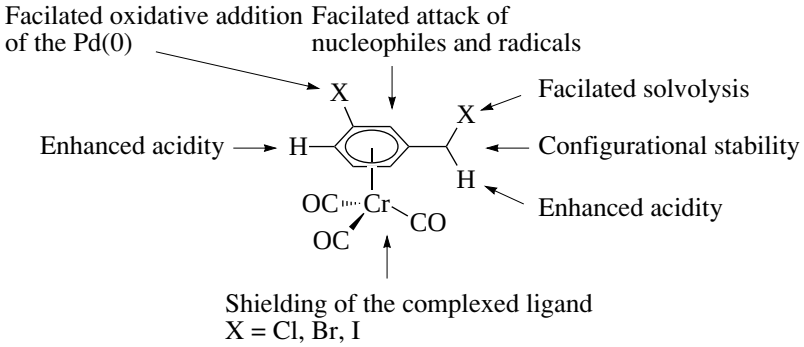
Abstract—Planar chiral η^6-arene-$Cr(CO)_3$ complexes represent highly valuable building blocks for the diastereo- and enantioselective synthesis. Their employment as synthons offer new and unique opportunities for the stereoselective multistep synthesis of complex natural products. The strategy of novel efficient synthesis of stilbene phytoalexins was based on arene chromium chemistry and the chemical and stereochemical effects of the metal unit on the reactivity of complexed arene ligand and stereochemical features of such compounds. Two variants for the construction of the *trans*-stilbene and diarylethanol framework via facilitated benzylic deprotonation of an η^6-benzene-$Cr(CO)_3$ complex and subsequent coupling with *para*-anisaldehyde in an aldol-type or a Wittig–Horner reaction were suggested.

π-Complexes of transition metals with unsaturated and aromatic ligands are characterized by high lability. Among the numerous types of transition metal arene complexes, only η^6-benzene-$Cr(CO)_3$ derivatives have received broad recognition by synthetic chemists. Chromium-arene complexes have frequently proven their value for organic synthesis; they are not expensive, easy to produce, and are convenient for synthetic work. The chemistry of these compounds has been the subject of intense investigations for many years. Since the first report in 1957 [1], a large number of η^6-benzene-$Cr(CO)_3$ derivatives have been prepared and plenty of information has been collected about their physical properties and chemical reactivity. Most η^6-arene-$Cr(CO)_3$ complexes are air-stable, yellow or red crystalline compounds and can be easily prepared from the free arenes by thermolysis with $Cr(CO)_6$ in a high-boiling solvent [2]. The complexation can also be accomplished under much milder conditions using pyrrole- or naphthalene-$Cr(CO)_3$ for the transfer of the $Cr(CO)_3$ fragment [3–5]. Solutions of chromium arene complexes are usually sensitive toward oxidation, particularly, in light. This sensitivity can be utilized for decomplexation reactions under mild oxidative conditions (e.g., air/sunlight, I_2 or Ce^{4+}) allowing an efficient release of the metal-free organic ligand.

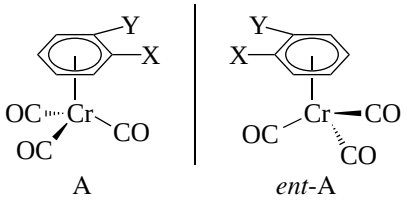
From the point of view of organic synthesis, it is most beneficial that the electrophilic $Cr(CO)_3$ group activates the arene ligand in a characteristic fashion. This offers a variety of transformations, which cannot be achieved with the free arenes. The chemical effects of $Cr(CO)_3$ group on the reactivity of the complexed arene ligand can be shown in the following scheme:



These effects are associated with pronounced stereochemical effects, which mainly result from the effective shielding of the complexed π-face of the ligand by the bulky $Cr(CO)_3$ tripod and from the remarkable configurational stability of reactive intermediates in benzyl position [6–9].

[1]This article was submitted by the authors in English.

Another important stereochemical aspect is that (achiral) arene ligands bearing two nonidentical substituents in *ortho*- or *meta*-position give rise to substituted chromium arene complex A and its enantiomer *ent*-A:



X, Y are different nonidentical substituents

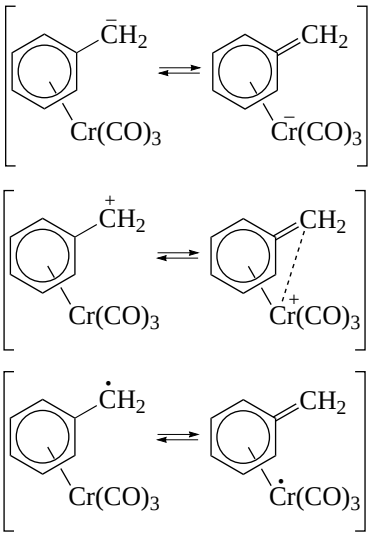
These chiral complexes can be viewed as structures possessing a planar chirality [6]. While such architectures offer interesting opportunities for the design of new chiral ligands and materials, the main application of arene-$Cr(CO)_3$ complexes is in the field of total synthesis.

One of the most useful chemical effects caused by the electron-withdrawing metal fragment is the enhanced reactivity of the arene ring towards nucleophiles. The treatment of chloro- or fluorobenzene-$Cr(CO)_3$ derivatives with a wide range of heteroatom or carbon nucleophiles (ROH, RSH, R_2NH, esters, nitriles, sulfones, and others) results in aromatic substitution (S_NAr). Even alkoxides can act as a leaving group [8, 9].

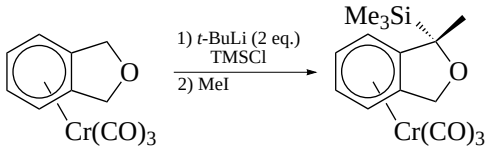
In general, the addition of nucleophiles to arenes bearing a donor substituent (OR, NR_2) proceeds regioselectively in the *meta*-position giving access to *meta*-substituted arylethers and anilines. Of particular synthetic value are stereoselective transformations of arenes to yield dearomatized products [7–9].

Another consequence of the electronic nature of the $Cr(CO)_3$ is an enhanced acidity of aromatic protons which enables the ring deprotonation with several lithium-based reagents *n*-butyllithium (*n*-BuLi) or lithium dimethylamide (LDA). As in the case of uncomplexed systems, polar substituents exhibit *ortho*-directing effects allowing the regioselective preparation of alkylated complexes under mild conditions [10, 11]. *Meta*-lithiations are also possible, if sterically hindered bases such as lithium tetramethylpiperidine (LiTMP) are used [12].

$Cr(CO)_3$ fragment is able to stabilize either negative or positive charge as well as a radical in the benzyl position. The resonance structures for such intermediates with structural and energetical details calculated by DFT methods can be given as follows [13, 14]:



The stabilization of negative charge in the benzyl position by the $Cr(CO)_3$ fragment allows deprotonation under mild conditions [15, 16]. If a silyl group is introduced first, the second deprotonation occurs at the silylated position to give the 1,1-disubstituted product, which can efficiently be further converted to *trans*-1,3-alkylated products [17]:

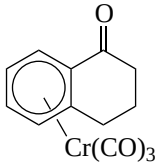


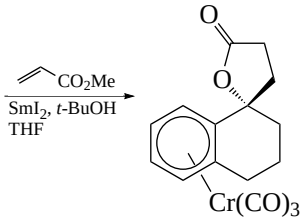
TMSCl = trimethylchlorosilane; Me = CH_3

The regioselectivity of the benzyl deprotonation is usually controlled by stereoelectronic effects [18]. The combination of aromatic and benzyl lithiation/alkylation offers efficient strategies for the regio- and stereoselective functionalization of relevant ring systems such as tetrahydroisochinolins [19] or 1-*epi*-helioporin D [20, 21].

Due to the coordination of the metal fragment, the benzyl carbocations have a remarkable configurational stability [13], and S_N1-type reactions proceed in a highly stereocontrolled fashion [22, 23].

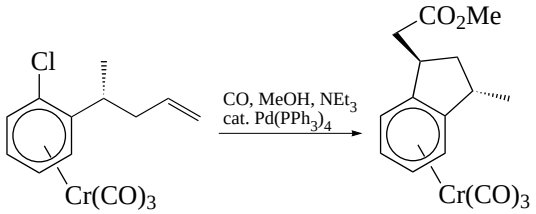
The configurational stability of benzyl radicals caused by $Cr(CO)_3$ fragment can also be used for highly stereoselective transformations [24–26]. The samarium(II) iodide mediated reaction of complexed *ortho*-substituted benzaldehydes and arylketones with acrylates leads to γ-butyrolactons with virtually complete diastereoselectivity [27]:





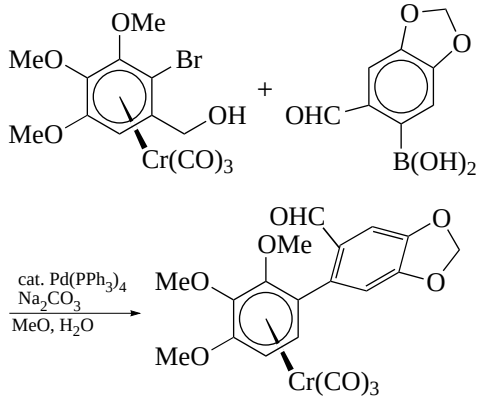
82% (yield), 100% de (diastereoselectivity)

Due to its electron-withdrawing character, the $Cr(CO)_3$ unit strongly activates haloarenes towards the oxidative addition of Pd(0) into the C–X bonds. Chloro- and even fluoroarene-$Cr(CO)_3$ complexes readily undergo Pd-catalyzed coupling reactions such as Suzuki-, Sonogashira-, Stille-, and Heck-type reactions [28–31]. Chloroarene complexes with unsaturated side chains undergo intramolecular Heck reactions as presented in reaction [31]:



98% de

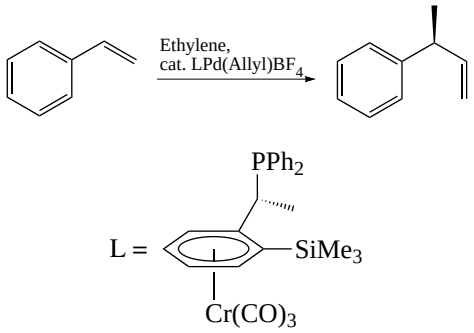
A very important feature of cross-coupling reactions between haloarene-$Cr(CO)_3$ complexes and arylmetals is that the planar chirality of the complex can be transferred into axial chirality of the resulting biaryl system in the highly efficient and controlled manner [32]. This fact has been used in the enantioselective synthesis of (–)-steganone, in which the biaryl system was diastereoselectively assembled starting from a planar-chiral arene-$Cr(CO)_3$ complex [33]:



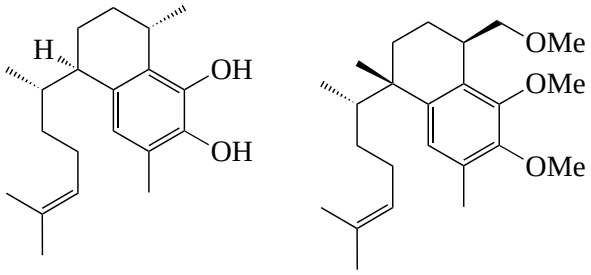
72% (yield), >99% de

Chromium arene complexes have also been used as traceless linkers in solid phase chemistry [34, 35]. By photolysis of an arene-$Cr(CO)_3$ complex in the presence of a phosphane-functionalized polymer, one of the carbonyl ligands of the $Cr(CO)_3$ unit is substituted and the complex attached to the polymer bead. After required transformation on the immobilized substrate, the aromatic ligand can be released by oxidative decomplexation.

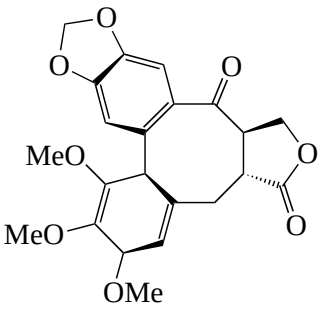
The planar-chiral architecture of *ortho*-disubstituted arene-$Cr(CO)_3$ complexes has been exploited for the construction of chiral ligands for asymmetric catalysis [36]. Catalysts with these ligands were successfully used in hydrogenation of ketones, allylic alkylations, Diels–Alder cycloadditions, and other reactions [37–42] as shown below:



The above-mentioned chemical properties of arene-chromium complexes have been used in the highly spectacular enantioselective total syntheses of complex natural products and their analogs:



Seco-pseudopterosin aglycone Serrulatane diterpene



(–)-Steganone

In these syntheses, the chemical and stereochemical effects of $Cr(CO)_3$ unit were exploited in several subsequent transformations. As true highlights, the synthesis of terpenes (pseudopterosins [42, 43], helioporins [44, 45], serrulatane [46], dihydroxyserrulatic acid [47, 48]) or alkoloids (clavicipitic alcohol [49], (+)-ptilocaulin [50], and (–)-lasubin [51]) can be considered. Also, syntheses of compounds with axial chirality such as

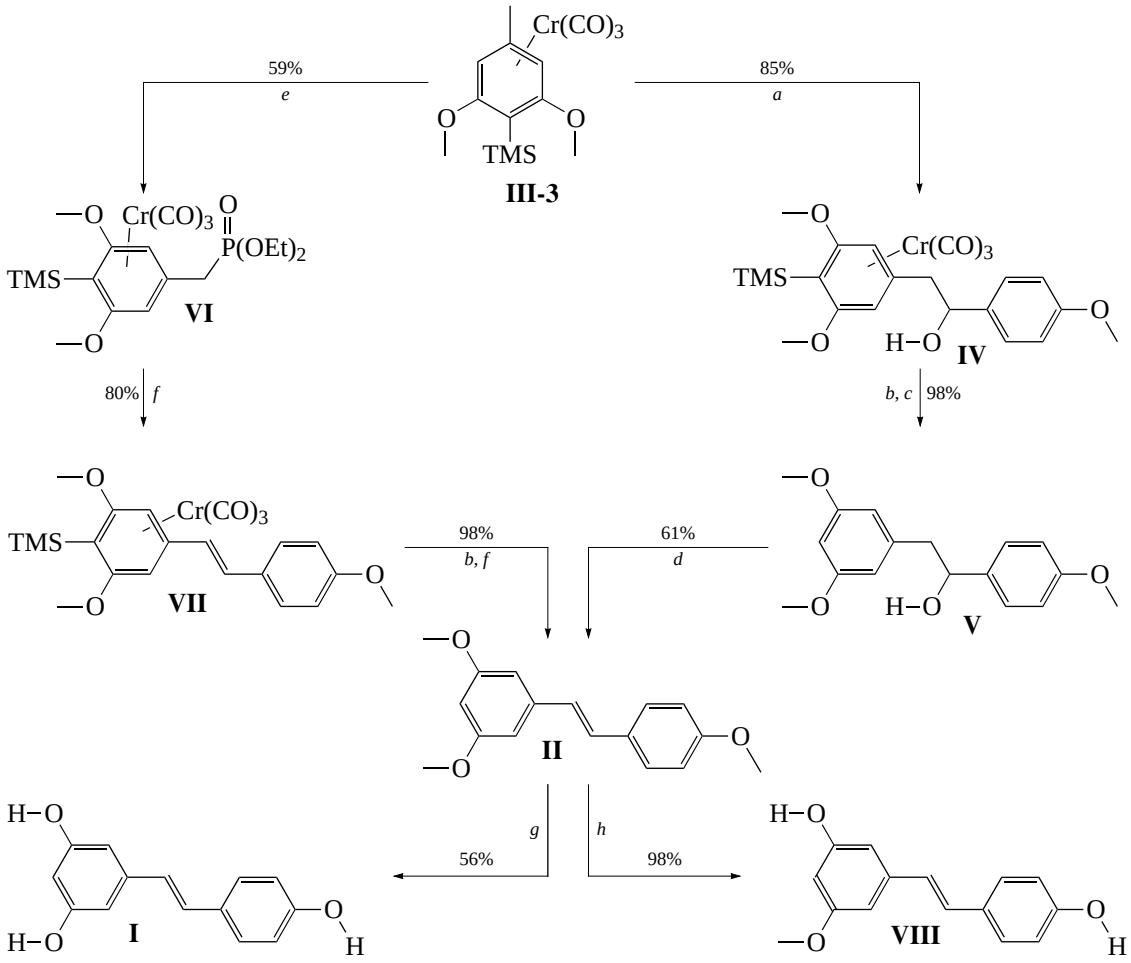
(–)-steganone [33] or vancomycin [52] must be mentioned.

The list of such successful syntheses, where chromium chemistry played a significant role, can also be extended with further examples, where temporary complexation and application of arene-$Cr(CO)_3$ complexes in the preparation of simple synthetic building blocks has been used [53, 54].

As an example of this approach, the synthesis of stilbene phytoalexins can be considered. Phytoalexins are plant antibiotics that are produced by plants in response to fungal infection or abiotic stresses such as heavy metal ions or UV light. The phytoalexins which were found in grapes, ground nuts, eucalyptus, and pine bark (e.g., resveratrol, piceatannol, pterostilbene, pinostilbene, tunalbene, etc.) were identified as *trans*-stilbenoids with a very high level of biological activities. They have powerful antifungal, antioxidant, and antiviral activity, as well as cancer chemopreventive and antimutagenic properties. Stilbenoid compounds attracted the great attention because they can serve as phytoestrogens and polyfunctional drugs without noxious side effect [55–59]. However, stilbene phytoalexins are not virtually used in official pharmacology because the biochemical properties of *cis–trans* isomers are poorly studied and technological procedures for their isolation from plants in the pure state are difficult. In this work, we have disclosed a new strategy for the synthesis of *trans*-isomers of hydroxy- and methoxystilbenes.

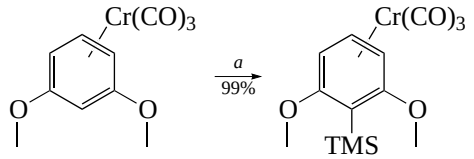
A known method for the synthesis of *trans*-polyhydroxystilbene (e.g., resveratrol—3,5,4'-trihydroxystilbene (**I**)) proceeds through *trans*-3,5,4'-trimethoxystilbene (**II**), which may be synthesized using a Wittig–Horner reaction from 3,5-dimethoxybenzylbromide and *p*-anisaldehyde via the corresponding phosphonate [60]. Another synthesis of resveratrol uses 3,5-dimethoxy-1-(trimethylsilyloxymethyl)benzene, which is condensed with *p*-anisaldehyde with the help of lithium powder in the presence of naphthalene [61]. Dehydration of the resulting alcohol afforded the trimethoxystilbene, which was converted into resveratrol by established methodology. Recently, a Heck reaction has been employed for the synthesis of resveratrol [62–64].

We developed the method for synthesis of plant stilbenoids, e.g., *trans*-resveratrol **I**, via compound **II** from inexpensive and preparatively convenient tricarbonyl-1,3-dimethoxybenzenechromium (**III-1**), whereby this complex can be converted into stilbenes through a sequence of deprotonation reactions of initial chromium-arene building block as shown below:

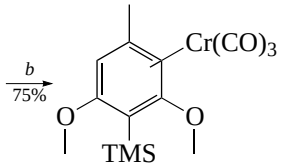


a: *n*-BuLi, THF, TMSCl, –78°C; *b*: LiTMP, THF, MeI, –50°C; *c*: *n*-BuLi, THF, –40°C, *p*-anisaldehyde, –40–0°C, 1.5 h; *d*: *n*-Bu_4NF, THF, one drop of H_2O, 2 h; *e*: *h*ν, AcOH–Et_2O (1 : 10), 2 days; *f*: *p*-TsOH (toluene sulfonic acid), PhH, 80°C, 13 h; *g*: *n*-BuLi, THF, –40°C, 15 min, $ClP(O)(OEt)_2$, –30–0°C, 1.5 h; *h*: *n*-BuLi, THF, –30°C, *p*-anisaldehyde, –30–0°C, 1.5 h.

For the synthesis of the key complex tricarbonyl-[η⁶-1,3-dimethoxy-5-methyl-2-trimethylsilylbenzene]-chromium(0) (**III-3**), we used the fact that the regioselectivity of deprotonation of chromium-arene complexes may greatly depend on the reaction conditions. For instance, the *ortho*-directing influence of a methoxy substituent can be overcompensated by the use of a sterically demanding base allowing a (contra-thermodynamic) selective functionalization in position 5. Thus, selective methylation of compound **III-1** is possible in α-position through sterically hindered LiTMP [12]. The *ortho*-position has been protected via deprotonation by *n*-BuLi and silylation by TMSCl in THF. The benzylic deprotonation/alkylation of 5-methyl-1,3-dimethoxybenzene-$Cr(CO)_3$ derivatives occurs with a surprising ease in excellent yield:



(**III-1**) (**III-2**)



(**III-3**)

The synthesis of key complex **III-3** from 1,3-dimethoxybenzene has been conducted in three steps in 61% overall yield.

Two variants for the construction of the stilbene were suggested. The first method utilizes the facile benzyl deprotonation of complex **III-3** and subsequent (aldol-type) addition of the resulting intermediate with *p*-anisaldehyde. This reaction was conducted under a nitrogen atmosphere by first adding *n*-BuLi at –40°C to a solution of complex **III-3** in dry THF. After stirring for 45 min at the same temperature, the yellow solution was allowed to slowly warm to –10°C. A color change to deep red indicated the formation of the benzylic deprotonated intermediate. After cooling to –40°C, *p*-anisaldehyde was added and the solution was allowed to warm to 0°C for 1.5 h. After workup, the product **IV** was obtained as a yellow oil in 85% yield. Desilylation with tetrabutylammonium fluoride and oxidative decomplexation afforded alcohol **V**, which was converted into stilbene **II** following an established procedure [61].

In the second set of experiments, we prepared stilbene **VII** from phosphonate **VI** by means of a Wittig–Horner olefination. While some related reactions have been described in arene chromium chemistry [28–31], it has never been reported that the required phosphonates (such as **VI**) can be directly prepared from the benzylic deprotonated intermediates by reaction with diethylchlorophosphate. Interestingly, phosphonate **VI** could be synthesized through the deprotonation of complex **III-3** with *n*-BuLi in dry THF at –40°C in a nitrogen atmosphere and the subsequent addition of diethylchlorophosphate to the deep red solution of the deprotonated intermediate at –30°C to 0°C. The Wittig–Horner reaction between phosphonate **VI** and *p*-anisaldehyde was then achieved through deprotonation of **VI** with *n*-BuLi followed by addition of the reaction partner at a low temperature (–30°C) and warming up to 0°C. By this way, the complexed stilbene **VII** was obtained as red needles in 80% yield.

It should be noted that the first method described for the conversion of **III-3** into stilbene **II** (via **IV** and **V**) proceeded in four steps with 51% yield, the same overall transformation was achieved (via **VI** and **VII**) in 46% overall yield using a Wittig–Horner reaction as a key step. In the latter case, both the desilylation and decomplexation steps proceeded cleanly with almost quantitative yields.

As a final step for the synthesis of resveratrol **I**, the triple demethylation of trimethoxystilbene **II** had to be performed. The described methods for this transformation (using BBr_3, MeMgI, or $LiPPh_2$ as a reagent) afforded the product in 30–60% yield. As a consequence of our positive experience employing lithium thioethylate (LiSEt) for the double demethylation of 1,2-dimethoxybenzene derivatives [20, 21], we treated **II** (a DMF solution of **II**) with an excess of LiSEt at 160°C for 2 h. We were surprised and delighted to find that monomethoxystilbene **VIII** was formed under these conditions in 98% yield. Actually, compound **VIII** is a well-known natural product called pinostilbene (*trans*-3,4'-dihydroxy-5-methoxystilbene) [55, 65–67], that is found in the bark of *Pinus sibericahas* and exhibits interesting biological properties as an inhibitor of cyclooxygenase (COX-1). It has never been synthesized before. Thus, the selective conversion of **II** to **VIII** with LiSEt opens an efficient synthetic access to pinostilbene and its derivatives [68, 69]. When the reaction time of the treatment of **VIII** with LiSEt was extended to 12 h, resveratrol **I** was formed in 30% yield. Note that all reaction products were fully characterized by ^1H, ^{13}C NMR, and IR spectroscopy and mass spectrometry. The described route could also be extended for the preparation of other plant hydroxystilbenes [68, 69], for instance, piceatannol (3,5,4',5'-tetrahydroxystilbene) and tunalbene (3,3'-dihydroxy-5-methoxystilbene).

Arene chromium chemistry proved able to be utilized as a highly efficient synthetic method and offers often a unique and effective synthesis strategy. It can be expected that arene metal chemistry will find many other applications in natural product synthesis in the future.

EXPERIMENTAL

Tricarbonyl-[η⁶-1,3-dimethoxy-2-trimethylsilylbenzene]chromium(0) (III-2). A solution of tricarbonyl-1,3-dimethoxybenzenechromium complex (**III-1**) (2.00 g, 1.4 mmol) in anhydrous THF (50 ml) was placed in a 100-ml Schlenk flask and cooled to –78°C. A 1.6 M solution of *n*-BuLi (4.78 ml, 7.65 mmol) in hexane was added with stirring. After stirring for 0.5 h, TMSCl (2.3 ml, 18.3 mmol) was added. The solution was stirred for 15 min at –78°C, after which the temperature was raised to 0°C for 1 h. AcOEt (50 ml) was added to the mixture, and the solution was washed with a saturated solution of $NaHCO_3$ (2 × 60 ml) and a saturated solution of NaCl (50 ml), dried over $MgSO_4$, and evaporated in vacuo. Yellow crystals of **III-2** were obtained in 99% yield (2.50 g) with m.p. 150°C (in [12]: m.p. 150°C) and R_f 0.3 (hexane : AcOEt = 5 : 1).

IR spectrum, ν, cm^{-1}: 2975, 2957, 2903, 1943, 1871, 1843, 1524, 1505, 1453, 1442, 1415, 1285, 1238, 1096, 847, 669. ^1H NMR (270 MHz, $CDCl_3$), δ, ppm: 0.34 (s, 9H, CH_3–TMS), 3.68 (s, 6H, OCH_3), 4.71 (d, 2H, C(4)H/C(6)H, *J* = 7.0 Hz), 5.72 (t, 1H, C(5')H, *J* = 7.0 Hz). ^{13}C NMR (67.7 MHz, $CDCl_3$), δ, ppm: 1.6 (q, CH_3–Si), 55.4 (q, OCH_3), 73.2, 69.7 (d, C(4)/C(6)), 80.9 (s), 93.2 (d, C(5)), 148.4 (s), 234.2 (s, $Cr(CO)_3$). Mass spectrum (electron impact (EI), 70 eV), *m*/*z* (I_{rel}, %): 346 $[M]^+$ (15), 334 (57), 290 (10), 262 (100), 217 (9), 190 (11), 135 (9), 52 (26).

Tricarbonyl-[η⁶-1,3-dimethoxy-5-methyl-2-trimethylsilylbenzene]chromium(0) (III-3). A 1.5 M solution of *n*-BuLi (0.2 ml, 0.32 mmol) in hexane was added at –78°C to a solution of 2,2,6,6-tetramethylpiperidine (0.055 ml, 0.32 mmol) in anhydrous THF (1 ml) placed in a 25-ml Schlenk flask. The mixture was stirred for 40 min at –40°C and cooled to –78°C. Complex **III-2** (100 mg, 0.288 mmol) was added, and the mixture was stirred for 0.5 h at –78°C. A solution of NH_3I (90 μl, 1.4 mmol) in anhydrous THF (4 ml) was placed into the second 25-ml Schlenk flask and cooled to –50°C. A solution of the anion of complex **III-3** from the first flask was rapidly added through a pumping pipe to a solution in the second flask. The mixture was stirred for 0.5 h at –50°C and 1 h at 25°C, then heptane (20 ml) was added, and 50% solvent were evaporated in vacuo, AcOEt (20 ml) was added to the residue, and the resulting solution was washed with 2 N HCl (2 × 20 ml), a saturated solution of $NaHCO_3$ (20 ml), and a saturated solution of NaCl (20 ml). The organic layer was dried with $MgSO_4$ and concentrated in vacuo. Complex **III-3** was obtained as yellow crystals in 75% yield (78 mg), m.p. 158°C (in [12]: m.p. 158°C), R_f 0.27 (hexane : AcOEt = 5 : 1).

IR spectrum, ν, cm^{-1}: 2950, 2901, 1937, 1863 (C=O, $Cr(CO)_3$), 1849, 1320, 1229, 1112, 839. ^1H NMR (270 MHz, $CDCl_3$), δ, ppm: 0.33 (s, 9H,CH_3–Si), 2.35 (s, 3H, CH_3), 3.68 (s, 6H, OCH_3), 4.65 (s, 2H, C(4)H/C(6)H). ^{13}C NMR (67.7 MHz, $CDCl_3$), δ, ppm: 1.5 (q, CH_3–Si), 21.3 (q, CH_3), 55.3 (q, C–OCH_3), 72.6 (d, C(4)/C(6)), 77.2 (s), 108.4 (s), 148.2 (s), 234.6 (s). Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 360 $[M]^+$ (18), 304 (15), 276 (100), 261 (8), 201 (5), 149 (12), 52 (10).

Tricarbonyl-[2-(η⁶-3,5-dimethoxy-4-trimethylsilylphenyl)-1-(4'-methoxyphenyl)ethanol]chromium(0) (IV). A solution of complex **III-3** (500 mg, 1.38 ml) in anhydrous THF (10 ml) was placed in a 50-ml Schlenk flask and cooled to –40°C, and a 1.6 M solution of *n*-BuLi (0.95 ml, 1.53 mmol) in hexane was added with stirring. The mixture was stirred for 15 min at –40°C and 30 min at 0°C until the solution became dark red, after which it was cooled to –40°C. Anisaldehyde (0.25 mg, 2.08 mmol) was added to the cooled solution, and the mixture was stirred for 30 min at –20°C and for 1 h at 0°C. Methyl *tert*-butyl ether (MTBE) (40 ml) was added to the reaction mixture. The organic layer was washed with water (2 × 40 ml) and a saturated solution of NaCl (30 ml), dried with $MgSO_4$, and concentrated in vacuo. The crude product was purified on a chromatotron eluting with a hexane–AcOEt (10 : 1) mixture. Compound **IV** was obtained in 85% yield (584 mg) as yellow oil with R_f 0.06 (hexane : AcOEt = 5 : 1), m.p. 120°C.

IR spectrum, ν, cm^{-1}: 3586 (OH), 2954, 1950, 1865 (C=O, $Cr(CO)_3$), 1513, 1496, 1248, 1227. ^1H NMR (400 MHz, $CDCl_3$), δ, ppm: 0.34 (s, 9H, CH_3–Si), 2.04 (d, 1H, OH, *J* = 3.0 Hz), 2.85 (dd, 1H, CH_2, *J* = 14.0 Hz, *J* = 5.0 Hz), 2.93 (dd, 1H, CH_2, *J* = 14.0 Hz, *J* = 8.0 Hz), 3.61, 3.64 (both s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 4.58, 4.65 (both s, 1H, C(2)H/C(6)H), 4.93 (m, 1H, C<u>H</u>–OH), 6.91 (d, 2H, C(2')H/C(6')H, *J* = 9.0 Hz), 7.29 (d, 2H, C(3')H/C(5')H, *J* = 9.0 Hz). ^{13}C NMR (67.7 MHz, $CDCl_3$), δ, ppm: 1.5 (q, CH_3–Si), 26.9 (d, C<u>H</u>–OH), 45.4 (t, CH_2), 55.4, 55.29, 55.27 (all q, OCH_3), 73.2, 74.6 (both d, C(2)/C(6)), 108.3 (s), 114.0 (d, C(3')/C(5')), 127.2 (d, C(2')/C(6')), 135.3 (s), 148.1 (s), 159.5 (s), 234.5 (s, $Cr(CO)_3$). Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 496 $[M]^+$ (8), 412 (100), 394 (20), 224 (48), 137 (52), 52 (7).

2-(3,5-Dimethoxyphenyl)-1-(4'-methoxyphenyl)ethanol (V). Desilylation. One water droplet and 5.75 ml (5.75 mmol) of *n*-Bu_4NF (1 M solution in THF) were added with stirring to complex **IV** (517 mg, 1.04 mmol) in THF (20 ml). After stirring for 2 h at 20°C, AcOEt (30 ml) was added. The solution was washed with water (40 ml) and a saturated solution of NaCl (40 ml), dried with $MgSO_4$, and concentrated. Complex **IV** was obtained in 99% yield (437 mg) with R_f 0.55 (hexane : MTBE = 1 : 1).

Decomposition of chromium arene complex IV. Desilylated complex **IV** (450 mg, 0.9 mmol) was dissolved in an AcOH–Et_2O (1 : 10) mixture (60 ml), and the resulting solution was stored for 2 days in sunlight. Then, the green residue was filtered off on a zeolite layer 1 cm thick, and the colorless filtrate was concentrated in vacuo. Alcohol **V** was obtained as yellow viscous oil in 99% yield (285 mg), R_f 0.27 (hexane : MTBE = 1 : 1).

IR spectrum, ν, cm^{-1}: 3450 (OH), 2927, 1596, 1512, 1246, 1149, 1066. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 1.94 (d, 1H, OH, J = 3.0 Hz), 2.91 (dd, 1H, CH_2, J = 14.0 Hz, J = 8.0 Hz), 2.96 (dd, 1H, CH_2, J = 14.0 Hz, J = 5.0 Hz), 3.77 (s, 6H, OCH_3), 3.81 (s, 3H, OCH_3), 4.85 (m, 1H, C<u>H</u>–OH), 6.36 (br. s, 3H, C(2)H/C(6)H/C(4)H), 6.89 (d, 2H, C(2')H/C(6')H, J = 9.0 Hz), 7.3 (d, 2H, C(3')H/C(5')H, J = 9.0 Hz). ^{13}C NMR (67.7 MHz, $CDCl_3$), δ, ppm: 46.4 (t, CH_2), 55.2, 55.3 (both q, OCH_3), 74.7 (q, OCH_3), 98.6 (d, C<u>H</u>–OH), 107.4 (d, C(2)/C(6)), 113.7 (d, C(3')/C(5')), 127.1 (d, C(2')/C(6')), 135.9 (s), 143.5 (s), 140.4 (s), 159.0 (s), 160.8 (s). Mass spectrum (EI, 70 eV), m/z (I_{rel}, %): 288 $[M]^+$ (1), 270 (4), 152 (100), 137 (98), 109 (18).

(*E*)-2-(3,5-Dimethoxy)-1-(4'-methoxyphenyl)ethene(II). TsOH (20 mg, 0.012 mmol) in benzene (10 ml) was added to a solution of alcohol **V** (250 ml, 0.59 mmol), and the mixture was refluxed for 13 h. Then, AcOEt (20 ml) was added, and the solution was washed with a 10% solution of $NaHCO_3$ (3 × 30 ml) and a saturated solution of NaCl (30 ml), dried with $MgSO_4$, and concentrated in vacuo. After purification on a chromatotron (hexane : AcOEt = 8 : 1), stilbene **II** (94 mg, 61% yield) was obtained with m.p. 47°C and R_f 0.16 (hexane : AcOEt = 10 : 1).

IR spectrum, ν, cm^{-1}: 3027, 2935, 1590, 1511, 1251, 1150, 1066. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 2.83 (s, 9H, OCH_3), 6.37 (t, 1H, C(2)H, J = 2.0 Hz), 6.65 (d, 2H, C(2)H/C(4)H, J = 2.0 Hz), 6.99 (d, 2H, C(2')H/C(6')H, J = 9.0 Hz), 7.01 (d, 1H, olefin, J = 17.0 Hz), 7.03 (d, 2H, C(3')H/C(5')H, J = 9.0 Hz), 7.45 (d, 1H, olefin, J = 17.0 Hz). ^{13}C NMR (67.7 MHz, $CDCl_3$), δ, ppm: 55.2, 55.3, 55.32 (all q, OCH_3), 99.6 (q, C(4)), 104.3 (d, C(2)/C(6)), 114.1 (d, C(3')H/C(5')H), 126.5 (d, olefin), 127.8 (d, C(2')/C(6')), 128.7 (d, olefin), 139.9 (s), 139.6 (s), 159.4 (s), 160.9 (s). Mass spectrum (EI, 70 eV), m/z (I_{rel}, %): 270 $[M]^+$ (100), 239 (8), 196 (7), 115 (3).

Tricarbonyl-[1-(η^6-3,5-dimethoxy-4-trimethylsilylphenyl)methyldiethylphosphonate]chromium(0) (VI). Complex **III** (200 mg, 0.554 mmol) in anhydrous THF (6 ml) was placed in a 25-ml Schlenk flask, and *n*-BuLi (0.38 ml, 0.71 mmol) as a 1.6 M solution in hexane was added at –40°C. The mixture was stirred for 15 min at –40°C and 30 min at –10°C (the dark red color appeared). Then, the mixture was cooled to –30°C, and diethyl chlorophosphate (104 μl, 0.72 mmol) was added. After stirring for 30 min at –10°C and for 1 h at 0°C, AcOEt (20 ml) was added. The solution was washed with a saturated solution of NaCl (2 × 30 ml), water (30 ml), and a saturated solution of NaCl (30 ml), dried with $MgSO_4$, and concentrated in vacuo. Purification on a column packed with silica gel (10 g) yielded phosphonate **VI** (162 mg, 59% yield) as yellow crystals with m.p. 130°C and initial compound **III** (75 mg, 37% yield) with R_f 0.18 (hexane : AcOEt = 1 : 1).

IR spectrum, ν, cm^{-1}: 2903, 1951, 1866 (C=O, $Cr(CO)_3$), 1230, 1104, 1054, 1026. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 0.32 (s, 9H, CH_3–Si), 1.34 (t, 6H, CH_3, J = 7.0 Hz), 2.96 (d, 2H, CH_2, $^3J_{P,H}$ = 20.5 Hz), 3.69 (s, 6H, OCH_3), 4.13 (m, 4H, OCH_2), 4.74 (s, 2H, C(2)H/C(6)H). ^{13}C NMR (67.7 MHz, $CDCl_3$), δ, ppm: 1.5 (q, CH_3–Si), 16.4, 16.5 (both q, CH_3), 32.7, 34.9 (both t, OCH_2), 62.5 (t, CH_2P), 72.27, 72.31 (both d, C(2)/C(6)), 79.3 (s, C(1)), 102.3 (s, C(4)), 148.0 (s, C(3)/C(5')), 234.2 (s, $Cr(CO)_3$). Mass spectrum (EI, 70 eV), m/z (I_{rel}, %): 496 $[M]^+$ (2), 412 (100), 360 (30), 345 (61), 315 (10), 285 (68), 52 (40).

Tricarbonyl-[1-(η^6-3,5-dimethoxy-4-trimethylsilylphenyl)-2-(4'-methoxyphenyl)ethylene]chromium(0) (VII). Phosphonate **VI** (265 mg, 0.735 mmol) in anhydrous THF (10 ml) was placed in a 25-ml Schlenk flask, and a 1.5 M solution of *n*-BuLi (0.5 ml, 0.81 mmol) in hexane was added at –40°C. The mixture was stirred for 15 min at –40°C and 30 min at –10°C (the red color appeared). Then, anisaldehyde (0.25 ml, 2.08 mmol) was added. The mixture was heated during 1 h to boiling and cooled to 20°C, and AcOEt (30 ml) was added. The solution was washed with water (2 × 40 ml), a saturated solution of $NaHCO_3$ (30 ml), and a saturated solution of NaCl (30 ml), dried with $MgSO_4$, and concentrated in vacuo. The crude product was purified on a column packed with kiesel gel (10 g) (hexane : AcOEt = 50 : 1). Stilbene **VII** was obtained in 80% yield (280 mg) as red needles with m.p. 202°C and R_f 0.57 (hexane : AcOEt = 1 : 1).

IR spectrum, ν, cm^{-1}: 2978, 2956, 1935, 1843 (C=O, $Cr(CO)_3$), 1605, 1535, 1228, 839. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 0.45 (s, 9H, CH_3–TMS), 3.76 (s, 6H, OCH_3), 3.83 (s, 3H, OCH_3), 4.93 (s, 2H, C(2)H/C(6)H), 6.72 (d, 1H, olefin, J = 17.0 Hz), 6.91 (d, 2H, C(2')H/C(6')H, J = 9.0 Hz), 6.98 (d, 1H, olefin, J = 17.0 Hz), 7.44 (d, 2H, C(3')H/C(5')H, J = 9.0 Hz). ^{13}C NMR (67.7 MHz, $CDCl_3$), δ, ppm: 1.5 (q, CH_3–TMS), 55.2, 55.3, 55.4 (all q, OCH_3), 68.9 (d, C(2)/C(6)), 79.4 (s), 106.5 (s), 114.4 (d, C(3')/C(5')), 123.9 (d, olefin), 128.3 (d, C(2')/C(6')), 128.4 (s), 131.8 (d, olefin), 148.3 (s), 160.2 (s), 234.0 (s, $Cr(CO)_3$). Mass spectrum (EI, 70 eV), m/z (I_{rel}, %): 478 $[M]^+$ (1), 394 $[M–3CO]^+$ (8), 342 $[M–3CO–Cr]^+$ (92), 327 (21), 267 (100), 223 (45).

Desilylation of stilbene VII was similar to desilylation in synthesis of alcohol **V**. The yield was 99%.

Synthesis of trimethoxystilbene II was carried out by the decomposition of its chromium complex. Desilylated complex **VII** (115 mg) was dissolved in an

AcOEt–Et_2O (1 : 10) mixture (50 ml), and diiodine (300 mg) was added. The mixture was stirred for 12 h at 20°C, and Et_2O (50 ml) was added. The solution was washed with a saturated solution of NaCl (50 ml), dried with $MgSO_4$, and concentrated in vacuo. Stilbene **II** was obtained in 99% yield (76 mg) and exhibited characteristics described above.

(*E*)-2-(3,5-Dihydroxyphenyl)-1-(4'-hydroxyphenyl)ethylene (resveratrol) (I). Trimethoxystilbene **II** (70 mg, 0.26 mmol) in Et_2O (2 ml) was added to a solution of MeMgI, prepared from Mg (148 mg, 6.08 mmol) and MeI (1.43 ml, 22.8 mmol) in Et_2O (10 ml). The ether was distilled off in an argon flow, and the residue was heated in vacuo for 30 min at 100°C and then in an argon flow for 15 min while increasing the temperature to 160°C. After the solution was cooled to 20°C, 10% NH_4Cl (15 ml) and AcOEt (20 ml) were carefully added to the contents of the flask. The aqueous layer was extracted with AcOEt (3 × 30 ml), and the combined extracts were washed with a saturated solution of NaCl (30 ml), dried with $MgSO_4$, and concentrated in vacuo. The crude product was purified on a chromatotron (hexane : AcOEt = 1 : 1). Resveratrol **I** (32 mg, 54%) was obtained as solid white needles with m.p. 247°C (in [60]: m.p. 247°C) and R_f 0.24 (hexane : AcOEt = 1 : 1).

IR spectrum, ν, cm^{-1}: 3329, 3029, 1604, 1238, 1147, 836. ^1H NMR (400 MHz, $CDCl_3$), δ, ppm: 6.13 (t, 1H, C(4)H, J = 2.0 Hz), 6.42 (d, 2H, C(2)H/C(6)H, J = 2.0 Hz), 6.74 (d, 2H, C(2')H/C(6')H, J = 9.0 Hz), 6.78 (d, 1H, olefin, J = 17.0 Hz), 6.93 (d, 1H, olefin, J = 17.0 Hz), 7.33 (d, 2H, C(3')H/C(5')H, J = 9.0 Hz). ^{13}C NMR (100.64 MHz, CD_3OD), δ, ppm: 102.6 (d, C(4)), 105.8 (d, C(2)/C(6)), 116.5 (d, C(3')/C(5')), 127 (d, olefin), 128.8 (d, C(2')/C(6')), 129.4 (d, olefin), 130.3 (s), 141.3 (s), 158.4 (s), 159.7 (s). Mass spectrum (EI, 70 eV), m/z (I_{rel}, %): 228 $[M]^+$ (56), 165 (18), 107 (10), 85 (100), 57 (8).

(*E*)-2-(5-Hydroxy-3-methoxyphenyl)-1-(4'-hydroxyphenyl)ethylene (pinostilbene) (VIII). Trimethoxystilbene **II** (30 mg, 0.11 mmol) and lithium thioethoxide (135 mg, 1.33 mmol) in DMF (4 ml) were placed in a 25-ml Schlenk flask connected with a reflux condenser and a paraffinic bubble counter. After this apparatus had been thoroughly degassed by tenfold evacuation and filled with argon, the mixture was heated for 2 h at 160°C. After cooling, 0.1 M HCl (15 ml) and AcOEt (20 ml) were slowly added to the solution, and the latter was washed with water (6 × 30 ml). The organic layer was washed with a saturated solution of NaCl (50 ml), dried with $MgSO_4$, and concentrated in vacuo. The crude product was purified on a chromatotron eluting with hexane–AcOEt (7 : 1). Stilbene **VIII** was obtained in 98% yield (26 mg) as colorless oil with R_f 0.4 (hexane : AcOEt = 1 : 1).

IR spectrum, ν, cm^{-1}: 3365, 2960, 1604, 1589, 1343, 1148, 836. ^1H NMR (400 MHz, $CDCl_3$), δ, ppm: 3.82 (s, 3H, OCH_3), 4.86 (br. s, 1H, OH), 4.91 (br. s, 1H, OH), 6.32 (t, 1H, C(4), J = 2.0 Hz), 6.58, 6.63 (both d, 2H, C(2)H/C(6)H, J = 2.0 Hz), 6.83 (d, 2H, C(2')H/C(6')H, J = 9.0 Hz), 6.85 (d, 1H, olefin, J = 17.0 Hz), 7.00 (d, 1H, olefin, J = 17.0 Hz), 7.39 (d, 2H, C(3')H/C(5')H, J = 9.0 Hz). ^{13}C NMR (100.64 MHz, CD_3Cl_3), δ, ppm: 55.6 (q, OCH_3), 101.4 (d, C(4)), 104.4, 106.6 (both d, C(2)/C(6)), 116.5 (d, C(3')/C(5')), 129.9 (d, olefin), 128.9 (d, C(2')/C(6')), 129.8 (d, olefin), 130.3 (s), 141.3 (s), 158.4 (s), 159.7 (s), 162.5 (s). Mass spectrum (EI, 70 eV), m/z (I_{rel}, %): 228 $[M]^+$ (56), 165 (18), 107 (10), 85 (100), 57 (8). According to the ^1H NMR data, the product contains *cis*-isomer (3%).

^1H NMR spectra were recorded on Bruker AM-400 (400 MHz) and Bruker AM-270 (270 MHz) spectrometers in $CDCl_3$, using $CHCl_3$ for $CDCl_3$ and CH_3OD for CD_3OD as internal standards. ^{13}C NMR spectra were obtained using Bruker AM-400 (100.64 MHz) and Bruker AM-270 (67.7 MHz) instruments. Mass spectra were obtained on Varian MAT 711 and Varian MAT 44 mass spectrometers (electron impact, 70 eV, direct injection into an ion source). IR spectra were recorded on a Magna FT-IR 750 spectrometer (Nicolet) with KBr windows. Melting points were measured with a Buchi 510 instrument without correction. The reaction courses and purity of isolated products were monitored by TLC on the Kieselgel $60F_{254}$ plates (Merck) in an AcOEt–hexane system.

Compounds were detected by UV absorption after irradiation with a Fluotest lamp (λ = 254 or 365 nm). Individual compounds were isolated from reaction products by preparative TLC on a Harrison Research 7924 T chromatotron using glass circular plates covered with Kieselgel PF–$60F_{254}$ (Merck) (hexane–AcOEt as eluent) and by column chromatography (Kieselgel 60, Merck, 230–400 mesh) using AcOEt–petroleum ether as eluent. The yields of compounds were not optimized.

All reagents and solvents (Aldrich, Fluka, Acros, Merck) had 99% purity and were used as received. Hexacarbonylchromium (Fluka) with 99% purity was used in synthesis of chromium arene complex.

All reactions involving chromium arene complex were carried out in moisture- and oxygen-free highly purified argon under a low pressure in the Schlenk flask using a syringe technique. Reagents and solvents were dried using standard methods. Glassware was calcined before use and then cooled in an argon flow.

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