Tricarbonyl(3-methoxybenzocyclobutenedione)chromium: Regioselective Nucleophilic Addition Reactions, Dianionic Oxy-Cope Rearrangements, Regioselective Intramolecular Aldol Additions, and a Rare Case of an Anionic 1-Vinylcyclobutenol−Cyclohexadienol Rearrangement

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Dedicated to Professor Ekkehard Winterfeldt on the occasion of his 70th birthday

Keywords: Aldol reaction / Chromium / Nucleophilic addition / Rearrangement / Ring-expansion

Tricarbonyl(3-methoxybenzocyclobutenedione)chromium (*rac*-**3**) has a lower symmetry than the corresponding unsubstituted benzocyclobutenedione complex. This has consequences for reaction sequences involving both ketone functionalities. The relative electrophilicity of the two ketone functions was evaluated by partial reduction of *rac*-**3** and by a partial hydrolysis of the bis(ethylene acetal), the precursor of *rac*-**3**. In addition, monovinyl Grignard addition was performed. All three experiments indicated a higher electrophilicity of C-1 than of C-2, in agreement with the resonance formulas that can be drawn. Dianionic oxy-Cope rearrangements, followed by intramolecular aldol addition, occurred with remarkable regioselectivity: in five of six cases investigated only one of two expected reaction products was obtained. As an explanation of this remarkable selectivity we considered a chelation effect of the intermediate bis(enolate) involving the 3-methoxy substituent. This causes a rare, if not the first, case of differentiation of two enolate moieties present in the cyclooctane ring. Addition of 2-lithio-3,4-dihydro-2*H*-pyran did not give rise to a dianionic oxy-Cope rearrangement but instead to a rare example of an anionic 1-vinylcyclobutenol–cyclohexadienol rearrangement. Five compounds presented in this publication have been characterized by crystal structure analyses.

Introduction

The chemistry of (arene)tricarbonylchromium complexes with functionalized anellated rings is dominated by selective reagent attack from the face opposite to the tricarbonylchromium group.[1−12] This can facilitate transfer of a planar chirality of the chromium complex to a center of chirality in the anellated ring. We have for some time been interested in complexes with anellated cyclobutane rings, and have found the complexes of benzocyclobutenone and benzocyclobutenedione to be key compounds in our investigations.[2,13] Nucleophilic additions at the oxo groups of these complexes were the basis of highly selective, anion-driven reactions such as the distal ring-opening to *ortho*-quinodimethane intermediates, followed by cycloaddition,[14−18] an anionic ring-expansion to indanone systems upon acyl anion addition,[19] anionic 1-vinylcyclobutenol−cyclohexadienol rearrangement,[19] and a dianionic oxy-Cope rearrangement, followed by intramolecular aldol addition.[20−24] In most cases the oxy anion driving force allowed these processes to occur at low temperature (−78 °C), while the facial differentiation due to the tricarbonylchromium moiety caused them to take place with very high degrees of diastereoselectivity. In addition, the electron-withdrawing nature of the tricarbonylchromium group is thought to support nucleophilic attack at the ketone groups. Among the reactions mentioned, the dianionic oxy-Cope rearrangement, followed by an intramolecular aldol addition, deserves special interest because the reaction sequence, starting from rather simple substrates, yields a remarkable amount of structural complexity with complete diastereoselectivity. Recently, we showed that this type of reaction also takes place with 1,2-diones not coordinated at tricarbonylchromium. However, good results were obtained only with conformationally flexible diones such as benzil derivatives, whereas the use of more rigid cyclic 1,2-diones resulted either in 1,2-diaddition of vinyllithium without the desired rearrangement or in poor yields of rearranged products.[25]

In order to investigate whether the success of the reaction starting from (benzocyclobutenedione)tricarbonylchrom-

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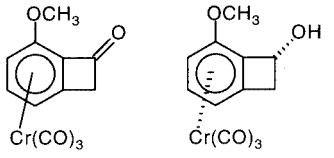
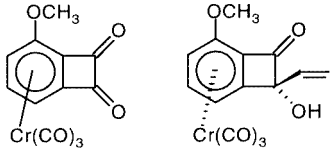
ium(0) was the result of the electron-withdrawing character of the tricarbonylchromium group or of its stereodirecting effect, we became interested in investigating the chemistry of substituted systems. Recently, we reported the syntheses of the more electron-rich *rac*-**1** as well as on the first oxy anion driven ring-opening/cycloaddition sequences of its reduction product *rac*-**2**. In addition, the synthesis of *rac*-**3** was presented, and the monoaddition of vinylmagnesium bromide was shown to give *rac*-**4** regioselectively.[26]



rac-**1** *rac*-**2**



rac-**3** *rac*-**4**

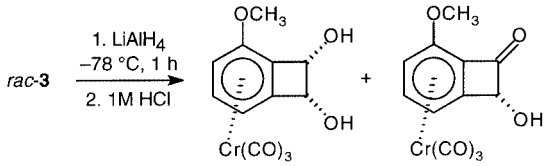
Here we report on the regioselectivity of nucleophilic additions at *rac*-**3** and on dianionic oxy-Cope rearrangements starting from *rac*-**3** and *rac*-**4**. Because of the reduced symmetry of *rac*-**3** relative to the unsubstituted benzocyclobutene complex, the latter reactions resulted in bis(enolates) with two inequivalent enolate moieties as the rearrangement products. We report on the highly selective differentiation of these enolate moieties, resulting in the formation of only one intramolecular aldol adduct instead of a mixture of isomers.

Results and Discussion

Electrophilicity of the Oxo Groups in *rac*-3

The lower symmetry of the 3-methoxybenzocyclobutenedione complex *rac*-**3** relative to the unsubstituted compound should give rise to different carbonyl reactivities in the two ketone functions. Should they differ in reactivity to a sufficient extent, this would offer the possibility to construct a variety of diadducts by use of a distinct sequence of nucleophilic addition reactions. This might give access to the selective formation of a large number of polycyclic systems by dianionic oxy-Cope rearrangements. To learn more about the relative reactivity of the two ketone functions, in addition to the Grignard addition giving rise to *rac*-**4**,[26] some test experiments were first carried out.

Reduction of *rac*-**3** with 1 equiv. of lithium aluminum hydride gave diol *rac*-**5** in 44% yield (the stereochemistry of the reduction being the same as in the unsubstituted case[22]) along with hydroxy ketone *rac*-**6** (40%). Since only the *endo*-1-hydroxy-3-methoxybenzocyclobuten-2-one complex *rac*-**6**, and not the *endo*-2-hydroxy-3-methoxybenzocyclobuten-1-one complex was formed, C-1 is regarded as more electrophilic than C-2. This is in agreement with the formation of *rac*-**4**, which, however, was produced in only 27% yield. In addition, resonance formulas of *rac*-**3** allow a delocalization of the positive partial charge of the oxo carbonyl carbon atom to the methoxy oxygen atom only for C-1, thus decreasing the electrophilicity of this carbon atom in comparison to C-2.



rac-**5** (44 %) *rac*-**6** (40 %)

Another observation in the context of the formation of *rac*-**3** by hydrolysis of the diacetal *rac*-**7** was in agreement with these assumptions. An incomplete hydrolysis, using 50% aq. HCl in THF for 2 h, resulted in the formation of dione *rac*-**3** (46%) along with monoacetal *rac*-**8** (35%). The constitution of *rac*-**8** was confirmed by a crystal structure analysis (Figure 1).

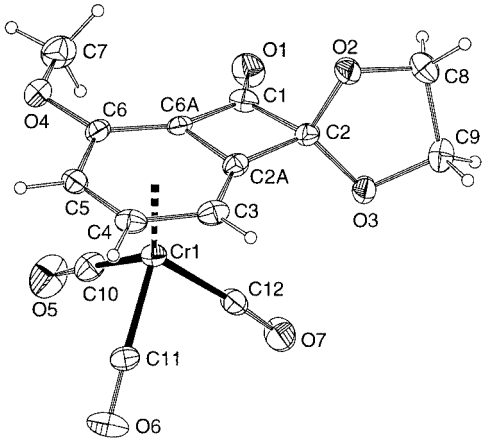
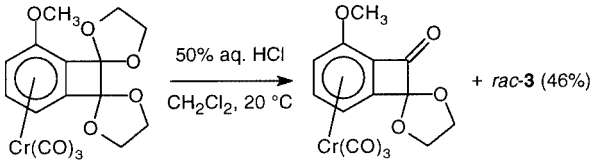


Figure 1. Structure of *rac*-**8** in the crystal; selected bond lengths [Å] and dihedral angles [°]: C1−C2 1.582(6), C1−C6A 1.501(7), C2−C2A 1.517(6), C2A−C3 1.386(6), C2A−C6A 1.430(6), C3−C4 1.397(6), C4−C5 1.387(6), C5−C6 1.406(6), C6−C6A 1.401(6), C1−O1 1.171(5), Cr−C2A 2.167(5), Cr−C3 2.222(5), Cr−C4 2.179(5), Cr−C5 2.220(5), Cr−C6 2.273(5), Cr−C6A 2.186(5); C3−C2A−C6A−C1 −171(1), C2−C2A−C6A−C6 −177(1)



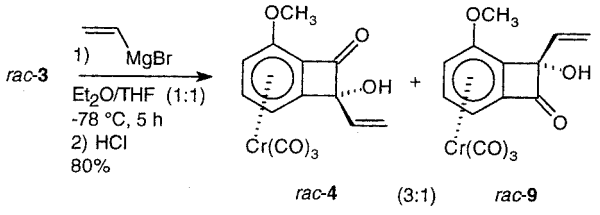
rac-**7** *rac*-**8** (35%)

The formation of *rac*-**8** and not the isomeric monoacetal indicates that the acetal function at C-1 in *rac*-**7** is less reactive than that at C-2. The reason for this is presumably the

higher carbonyl reactivity of C-1 in *rac*-**3** relative to that of C-2.

The alternation of the bond lengths between the Cr atom and the arene carbon atoms indicates that the bond C2A−C6A is coordinated more strongly to the chromium atom than the other arene bonds. In agreement with this, the bond length C2A−C6A is somewhat longer than the other arene bonds. This situation resembles that in the unsubstituted benzocyclobutenedione complex[24] and is presumably a result of some strain release of this most highly strained arene bond upon coordination. Interestingly, the ketone C=O moiety is bent out of the plane of the aromatic system towards the chromium atom by about 9° − this is a feature observed up to now only for complexes of benzocyclobutenedione[24] and for *rac*-**3**.[27]

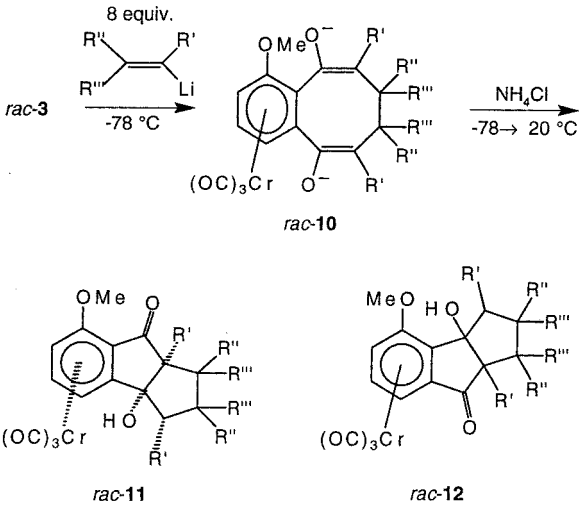
The synthesis of *rac*-**4** in 27% yield by addition of vinylmagnesium bromide to *rac*-**3** has already been reported.[26] Use of an improved procedure in this study allowed the yield of the reaction to be increased to 80%. However, the product was shown not to be exclusively *rac*-**4**, but to contain some of the other regioisomer *rac*-**9** (ca. 3:1).



Dianionic Oxy-Cope Rearrangements by Addition of Alkenyllithium to *rac*-3

Having evaluated the carbonyl reactivity of the ketone groups in *rac*-**3**, we set out to undertake double additions of alkenyllithium reagents to *rac*-**3** in order to induce dianionic oxy-Cope rearrangements. In contrast to the dianionic oxy-Cope rearrangements starting from the unsubstituted benzocyclobutenedione complex and affording symmetric bis(enolates), treatment of *rac*-**3** with vinyllithium provided an asymmetric bis(enolate) *rac*-**10** as the rearrangement product. In the unsubstituted case the symmetry was broken by the subsequent intramolecular aldol addition, yielding a racemic mixture of one polycycle. To start from the asymmetric *rac*-**3**, in contrast, would in principle afford two different products, *rac*-**11** and *rac*-**12**, as either one of the enolate moieties might, after hydrolysis, play the enol (or enolate) or the ketone component in the aldol addition.

In order to investigate this problem of regioselectivity, a number of experiments, in which *rac*-**3** was treated with an excess of an alkenyllithium reagent, were carried out. Products were identified by the usual spectroscopic methods and by comparison of their spectra with the spectra of those lacking the methoxy substituent at the aromatic ring. In some cases the spectroscopic characterization was confirmed by a crystal structure analysis. The results are summarized in Table 1.



The reaction gave the desired rearrangement products in 59−76% overall yield, the yields not varying much for different substitution patterns. Most remarkably, only one of two possible intramolecular aldol adducts was formed in all cases but Entry 6. This was the case for the reaction products of *rac*-**3** with the unsubstituted vinyllithium (*rac*-**11a**) as well as for the methyl-substituted one (*rac*-**11b**) and for the ethoxy derivative *rac*-**11c**. Use of 1-lithio-1-methoxyallene caused formation of the head-to-head coupling product of two methoxyallene units, and the intramolecular aldol addition again proceeded with complete regioselectivity to give the highly substituted tricycle *rac*-**11e** in good yield. This regioselectivity was observed even in the case of cyclopentenyllithium as the attacking alkenyllithium reagent, with formation of the pentacycle *rac*-**11e**. In addition to the regioselectivity, the intramolecular aldol addition also took place with full diastereoselectivity. In all cases the enol or enolate moiety attacked the ketone function from the face opposite to the tricarbonylchromium group. In addition to the spectroscopic data the relative configuration of *rac*-**11e** was confirmed by an X-ray crystal structure analysis (Figure 2).

In contrast to *rac*-**8**, the methoxy group adopted a conformation with the methyl group *anti* relative to the anellated ring. This was presumably the result of a steric interaction, which would occur between the methoxy group and the ketone function of the anellated five-membered ring − *rac*-**8** features an anellated four-membered ring with a larger distance between the methoxy and the keto groups. The tricarbonylchromium moiety adopts a conformation with two of the carbonyl ligands *gauche* to exocyclic bonds of the arene ring.

The use of 5-lithio-2,3-dihydrofuran as the alkenyllithium allowed the incorporation of heterocycles into the polycyclic reaction products.[20] However, although the reaction took place smoothly with an overall yield of 72% it lacked the regioselectivity observed in the other examples. Instead, an approximately 1:1 mixture of the isomeric complexes

Table 1. Dianionic oxy-Cope rearrangement, followed by intramolecular aldol addition on addition of alkenyllithium reagents to *rac*-**3**

Entry	Bis(enolate)	−R′	−R′′	−R′′′	Yield of *rac*-**11** [%]	Yield of *rac*-**12** [%]
1	*rac*-**10a**	−H	−H	−H	76	−
2	*rac*-**10b**	−Me	−H	−H	74	−
3	*rac*-**10c**	−OEt	−H	−H	67	−
4	*rac*-**10d**	−OMe	$=CH_2$		59	−
5	*rac*-**10e**	$-CH_2CH_2CH_2-$		−H	59	−
6	*rac*-**10f**	$-OCH_2CH_2-$		−H	36	36

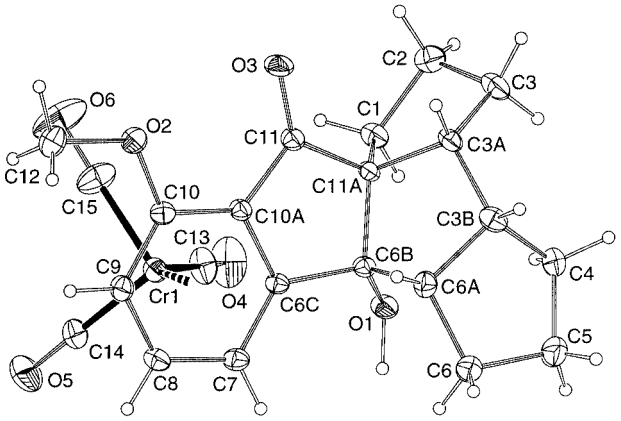
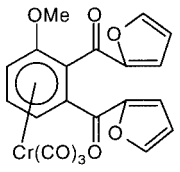


Figure 2. Structure of *rac*-**11e** in the crystal; selected bond lengths [Å] and angles [°]: Cr−C6C 2.210(3), Cr−C7 2.221(3), Cr−C8 2.159(3), Cr−C9 2.214(4), Cr−C10 2.256(4), Cr−C10A 2.202(3), C1−C2 1.519(5), C1−C11A 1.535(4), C2−C3 1.506(4), C3−C3A 1.527(5), C3A−C3B 1.542(4), C3A−C11A 1.565(4), C3B−C4 1.532(5), C3B−C6A 1.526(5), C4−C5 1.523(5), C5−C6 1.523(5), C6−C6A 1.538(5), C6A−C6B 1.560(4), C6B−C6C 1.508(5), C6B−C11A 1.548(4), C6C−C7 1.393(4), C6C−C10A 1.408(5), C7−C8 1.399(5), C8−C9 1.383(4), C9−C10 1.382(5), C10A−C11 1.464(5), C11−C11A 1.523(5); C10−O2−C12 117.4(3), C6C−C10A−C11 109.0(3), C11−C11A−C1 110.9(3), C11−C11A−C3A 111.5(3), C11−C11A−C6B 104.4(3), C1−C11A−C3A 104.1(3), C1−C11A−C6B 118.1(3), C3A−C11A−C6B 108.1(2), C11A−C6B−C6A 103.3(3), C11A−C6B−C6C 104.7(3), C11A−C6B−O1 110.6(3), C6A−C6B−C6C 109.3(3)

rac-**11f** and *rac*-**12f**, formed via bis(enolate) *rac*-**10f**, was obtained in 72% yield.

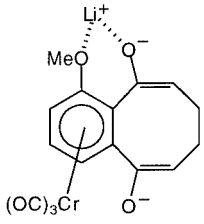
When 2-lithiofuran was used as the alkenyllithium reagent, as in the unsubstituted case, a distal ring-opening occurred with formation of *rac*-**13** in 71% yield.[20]



rac-**13**

It was not clear whether the intramolecular aldol addition had occurred after the first protonation of the intermediate bis(enolate) between the thus formed ketone function and the remaining enolate moiety, or if it had occurred after complete hydrolysis between the ketone function and the enol tautomer of the other one. However, the following argument applies to either one of the two possibilities.

In all cases but that in which 5-lithio-2,3-dihydrofuran was used as the alkenyllithium reagent, only one of two possible intramolecular aldol adducts was obtained. This means that the intramolecular aldol addition had taken place in a fully regioselective way. Starting from the bis(enolate) as the intermediate formed by the dianionic oxy-Cope rearrangement, the enolate moiety next to the methoxy substituent acts as the enolate − or, after hydrolysis, the enol − in the aldol addition, whereas the enolate moiety opposite to the methoxy substituent is hydrolyzed and plays the ketone part. This indicates some stabilization of the enolate or enol moiety next to the methoxy group relative to the one opposite to it. As an explanation for this stabilization we propose a certain degree of chelation of the enolate lithium cation or the enol proton by the lone pairs of the neighboring methoxy group as depicted for *rac*-**10a**.



rac-**10a**

This line of thought explains all of the observed selective aldol additions and can also be applied to the exception (Table 1, Entry 6), the 1:1 mixture of *rac*-**11f** and *rac*-**12f**. In this case, there is potential in the intermediate bis(enolate) *rac*-**10f** for chelation of either one of the two enolate or enol moieties, thus making them more similar to one another.

A weak point in this explanation, however, is the fact that *rac*-**10c** and *rac*-**10d** undergo the aldol addition in the discussed selective manner, although there are ethoxy and methoxy substituents next to both enolate moieties, which might also facilitate chelation. These bis(enolates) differ from *rac*-**10f** in that the heteroatoms are not involved in cycles, and the alkoxy substituents are consequently able to adopt numerous different conformations, which is not the case for *rac*-**10f**. As a result, these substituents in *rac*-**10d** and *rac*-**10e** can rotate so that the resonance interaction be-

tween a lone electron pair of the alkoxy group and the enolate double bond is optimized. This does not necessarily have to be the optimum conformation for a chelation, so that chelation through the aryl methoxy substituent instead may still be more favorable in addition to a resonance interaction of the enolate double bond and the cyclooctane alkoxy lone pairs. Another point possibly important in this context is the difference in chelate ring size in the two modes of chelation.

Dianionic Oxy-Cope Rearrangement by Addition of Alkenyllithium to *rac*-4

It had previously been found that the diaddition at the oxo groups to provide dianionic oxy-Cope rearrangements can be carried out stepwise, thus offering the potential to obtain numerous asymmetrical oligocycles by proper choice of alkenyllithium reagents and the order of their addition. When monovinyl adduct *rac*-**4** was treated with 4 equiv. of vinyllithium, *rac*-**11a** was obtained in 72% yield. No *rac*-**12a** was observed.

When the above-mentioned 3:1 mixture of *rac*-**4** and *rac*-**9** was treated with an excess of 1-cyclopentenyllithium, a mixture of *rac*-**14** (62%) and *rac*-**15** (24%) was obtained, indicating that *rac*-**4** had reacted to give *rac*-**14** and *rac*-**9** to give *rac*-**15**. No other regioisomers were obtained. The products were separated by column chromatography and characterized spectroscopically. However, the relative configurations of the bridgehead carbon atoms could not be deduced from the spectra in every case. Finally, crystal structure analyses (Figures 3 and 4) of either product confirmed their constitution and configuration.

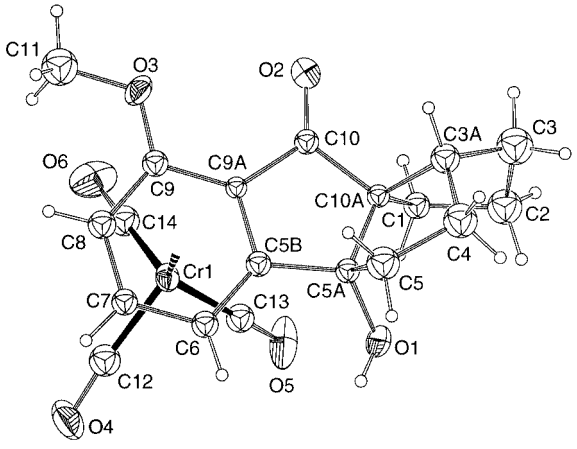


Figure 3. Structure of *rac*-**14** in the crystal; selected bond lengths [Å] and angles [°]: C1−C2 1.509(13), C1−C10A 1.539(12), C2−C3 1.465(12), C3−C3A 1.535(14), C3A−C4 1.45(2), C3A−C10A 1.576(11), C4−C5 1.50(2), C5−C5A 1.572(13), C5A−C5B 1.510(13), C5A−C10A 1.509(14), C5B−C6 1.415(13), C5B−C9A 1.376(13), C6−C7 1.406(13), C7−C8 1.38(2), C8−C9 1.429(14), C9−C9A 1.421(13), C9A−C10 1.478(14), C10−C10A 1.509(14); C3a−C10A−C10 111.7(8), C5−C5A−C5B 110.4(8), C5A−C10A−C10 104.6(9), C5B−C5A−C10A 106.6(9), C10−C10A−C1 109.8(9)

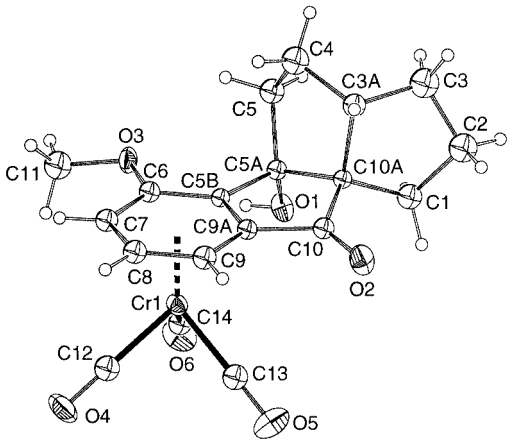
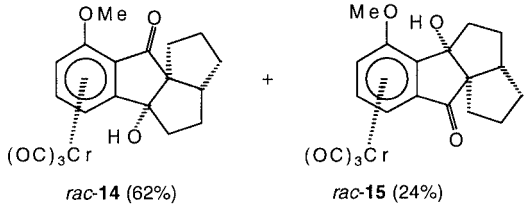
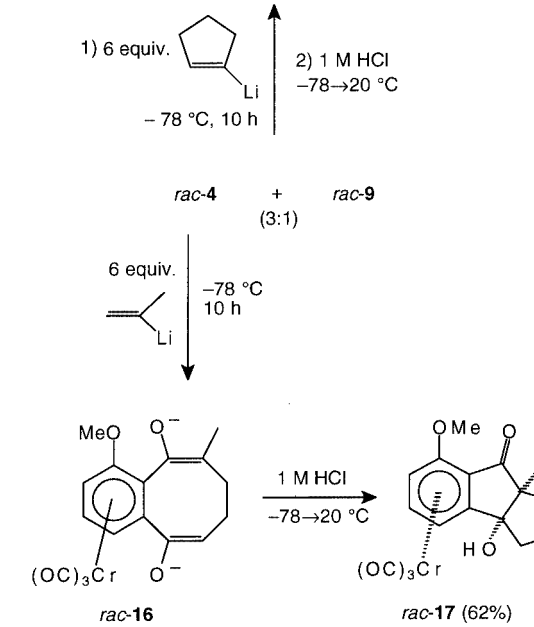


Figure 4. Structure of *rac*-**15** in the crystal; selected bond lengths [Å] and angles [°]: C1−C2 1.536(5), C2−C3 1.485(5), C3−C3A 1.510(5), C3A−C4 1.511(5), C3A−C10A 1.592(4), C4−C5 1.492(5), C5−C5A 1.536(5), C5A−C5B 1.527(5), C5A−C10A 1.556(5), C5A−O1 1.416(4), C5B−C9A 1.399(4), C5B−C6 1.408(5), C6−C7 1.409(5), C6−O3 1.341(4), C7−C8 1.396(5), C8−C9 1.380(5), C9−C9A 1.416(5), C9A−C10 1.495(5), C10−C10A 1.511(5), C10−O2 1.204(4), C11−O3 1.420(4), Cr−C5B 2.249(3), Cr-6 2.288(4), Cr−C7 2.221(3), Cr−C9 2.201(4), Cr-9A 2.201(4);C6−O3−C11 117.9(3), O1−C5A−C5B 112.9(3), C5B−C5A−C5 112.8(3), C5B−C5A−C10A 102.9(3), C5−C5A−C10A 104.0(3), C10−C10A−C5A 106.0(3), C1−C10A−C5A 118.2(3), C1−C10A−C3A 106.3(2), C5A−C10A−C3A 104.5(3)



rac-**14** (62%) *rac*-**15** (24%)



rac-**16** *rac*-**17** (62%)

The structures of *rac*-**14** and *rac*-**15** are rather similar to one another. In each case the methoxy group is bent away from the anellated ring system and the hydroxy substituent

is situated at the chromium face of the ligand system, thus indicating an enol or enolate attack at the ketone from the face opposite of the tricarbonylchromium group. In both cases the tricarbonylchromium groups adopt conformations with − presumably for steric reasons − no carbonyl ligand being located below the anellated ring.

When *rac*-**4** was treated with 6 equiv. of 2-propenyllithium at −78 °C for 10 h, tricycle *rac*-**17** was obtained after hydrolysis in 76% yield via bis(enolate) *rac*-**16**.

Again, the intramolecular aldol addition had taken place in the described selective way. However, the formation of *rac*-**15** does not fit into this scheme. This shows that the regiochemical outcome of the intramolecular aldol addition cannot completely be understood by the assumption of chelation effects. It appears that in cases of mixed dianionic oxy-Cope rearrangements involving two different alkenyllithium reagents, the asymmetry of the bis(enolate) resulting from the presence of the aryl methoxy group and that resulting from the different cyclooctane substituents may cause a delicate mix of electronic (chelation) and steric effects.

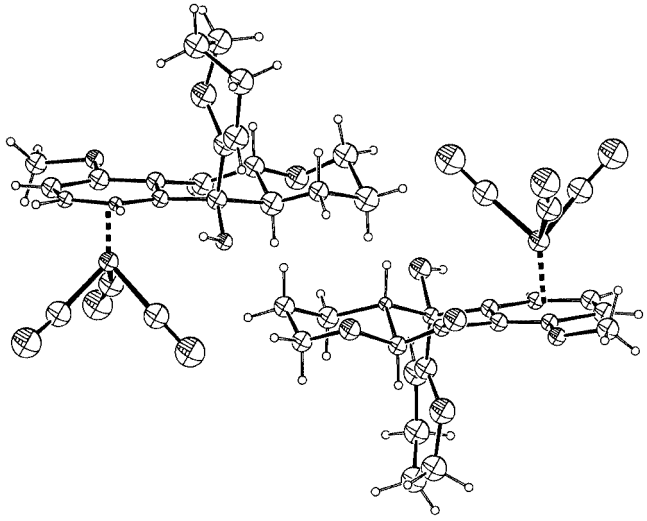


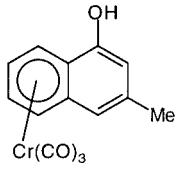
Figure 5. Structure of *rac*-**20** in the crystal with two different molecules in the asymmetric unit

Oxy Anion Driven 1-Oxy-1-vinyl-2-butenyl− Cyclohexadienol Rearrangement

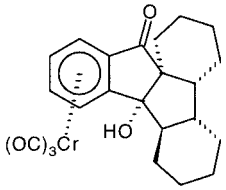
When *rac*-**3** was treated with 8 equiv. of 5-lithio-3,4-dihydro-2*H*-pyran no product corresponding to one of the dihydrofuran analogues *rac*-**11f** or *rac*-**12f** was obtained after hydrolytic work up. Instead, *rac*-**20** was obtained in 60% yield. As the NMR spectroscopic data were not in agreement with a product of a dianionic oxy-Cope rearrangement, and because of the complexity of the reaction product, we resorted to crystal structure analysis in order to identify this complex (Figure 5). There are two independent molecules in the asymmetric unit, with an approximate noncrystallographic inversion center between them. The quality of the analysis is not so high that a detailed discussion of the bond lengths and angles would make sense. However, the constitution and relative configuration are clearly proven by the analysis.

Oxy anion accelerated rearrangement reactions deserve interest, because they take place at much lower temperatures than their electroneutral counterparts. In this context, oxy anion driven ring-expansions of vinylcyclobutanols to cyclohexenols and subsequently to cyclohexanones − so-called vinylcyclobutane rearrangements − have been the subject of some investigations. Danheiser reviewed the matter in 1991,[28] showing that rearrangements of oxy anion driven 1-vinylcyclobutoxides are much rarer than those of 2-vinylcyclobutoxides. In addition, it is known that both uncoordinated and coordinated 1-hydroxybenzocyclobutenes undergo an oxy anion driven ring-opening to an oxy anion substituted *ortho*-quinodimethane at low temperature.[14−16,18,29] If the deprotonation of a 1-vinylbenzocyclobutenol were to give rise to the corresponding tetralone, this would be an oxy anion accelerated 1-vinylcyclobutene rearrangement, which significantly differs in mechanism from the 1-vinylcyclobutane rearrangement. While the oxy anion-accelerated 1-vinylcyclobutane rearrangement is thought to proceed stepwise through a heterolytic cleavage to form an anionic α,β-unsaturated ketone intermediate, which then cyclizes in an intramolecular Michael addition to give the six-membered ring,[30] the oxy anion accelerated 1-vinylcyclobutene rearrangement presumably involves an oxy anion substituted hexatriene, which undergoes an electrocyclization to give the dienolate and finally the respective enone. In this context the unsubstituted *endo*-1-hydroxy-*exo*-1-vinylbenzocyclobutene complex had earlier been deprotonated to check the feasibility of a ring-expansion to the 1-tetralone complex. However,

upon deprotonation with a catalytic amount of butyllithium at −78 °C, within 5 min a complicated product mixture had formed, in which no 1-tetralone complex could be detected.[31] Remarkably, we later succeeded in performing such a ring-expansion upon addition of 1-lithio-1-methoxyallene to (benzocyclobutenone)tricarbonylchromium(0), resulting in the formation of naphthol complex *rac*-**21**. It was shown in this particular case that the driving force of the reaction is presumably the final aromatization step.[19]



rac-**21**



rac-**22**

The reason why no dianionic oxy-Cope rearrangement takes place is not clear. Steric reasons appear unlikely, because treatment of (benzocyclobutenedione)tricarbonylchromium with 1-cyclohexenyllithium afforded dianionic oxy-Cope rearrangement/aldol addition product *rac*-**22** in 74% yield,[32] characterized by a crystal structure analysis.[33] This makes it most likely that, after the diaddition to yield *rac*-**18**, an *ortho*-quinodimethane complex *rac*-**19** is formed. This, in contrast to a diadduct of 1-cyclohexenyllithium, would be highly chelate-stabilized and may therefore be favored. Electrocyclization and hydrolysis finally afford *rac*-**20**.

Experimental Section

General: See ref.[21] Melting points were determined with a Büchi apparatus according to Dr. Tottoli without any correction. *tert*-Butyl methyl ether (TBME), diethyl ether (DEE), petroleum ether (PE), and tetrahydrofuran (THF) were distilled from sodium−potassium alloy/benzophenone.

Reduction of *rac*-3 with Lithium Aluminum Hydride: Lithium aluminum hydride (12 mg, 0.3 mmol) in THF (10 mL) was added dropwise at −78 °C to *rac*-**3** (286 mg, 1.0 mmol) in a 1:1 mixture of THF and diethyl ether (50 mL). After the mixture had been stirred for 4 h at −78 °C, hydrochloric acid (1 M, 10 mL) was added, and the mixture was allowed to warm to 20 °C and diluted with 50 mL of TBME and 50 mL of water. The mixture was extracted with TBME until the aqueous layer was colorless, and the collected organic layers were dried with $MgSO_4$ and filtered through a P4 frit, covered with a 1-cm layer of silica. The solvent was evaporated into a cold trap at reduced pressure, and the residue was purified by column chromatography (200 × 20 mm; PE then TBME/PE, 2:1). I: 122 mg (0.4 mmol, 44%) of tricarbonyl[η^6-1,2-*endo*-dihydroxy-6-methoxybenzocyclobutene]chromium(0) (*rac*-**5**), yellow solid (m.p. 108 °C). II: 115 mg (0.4 mmol, 40%) of tricarbonyl[η^6-2-*endo*-hydroxy-6-methoxy-1-oxobenzocyclobutene]chromium(0) (*rac*-**6**), orange-yellow solid [m.p. 92 °C, purity ca. 95% (NMR)].

***rac*-5:** IR (ATR): $\tilde{\nu}$ = 3349 (br, OH) cm^{-1}, 3093 (w), 2957 (w), 2682 (w), 2427 (w), 1951 (s, CO), 1852 (s, CO), 1642 (w), 1531 (m), 1461 (m), 1421 (m), 1392 (m), 1266 (m), 1199 (w), 1160 (w), 1106 (m), 1075 (m), 1039 (m), 1007 (w), 960 (m), 900 (w), 834 (w), 811 (w), 760 (w), 708 (w), 692 (w), 669 (m). ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.96 (s, 3 H, OCH_3), 4.75 (br, 2 H, 2 × OH), 5.11 (d, ^3J = 6.0 Hz, 1 H, 4-H or 6-H), 5.16 (d, ^3J = 6.0 Hz, 1 H, 4-H or 6-H), 5.27 (br. s, 1 H, 1-H), 5.35 (br. s, 1 H, 2-H), 5.69 (dd, ^3J = 6.0, ^3J = 6.0 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 57.1(−, C-7), 71.4 (−, C-1 or C-2), 71.6 (−, C-1 or C-2), 77.8 (−, C-6), 80.9 (−, C-5), 95.3 (−, C-4), 104.9 (+, C-2a), 122.2 (+, C-6a), 139.8 (+, C-3), 233.2 (+, CO) ppm. MS (70 eV, 100 °C): *m*/*z* (%) = 302 (48) [M$^+$], 246 (25) [M − 2 CO], 218 (100) [M − 3 CO], 200 (35), 176 (2), 157 (7), 132 (58), 105 (9), 90 (5), 77 (8), 52 (35) [Cr]. HRMS ($C_{12}H_{10}CrO_6$): calcd. 301.9882; found 301.9871. $C_{12}H_{10}CrO_6$: calcd. C 47.79 H 3.33; found C 46.10 H 3.95.

***rac*-6:** IR (ATR): $\tilde{\nu}$ = 3409 (br, OH) cm^{-1}, 3092 (w), 2962 (w), 1965 (s, CO), 1879 (s, CO), 1765 (s, C=O), 1604 (w), 1531 (m), 2502 (w), 1483 (m), 1462 (m), 1422 (m), 1260 (s), 1188 (w), 1161 (w), 1088 (s), 1032 (s), 1010 (s), 928 (w), 866 (w), 791 (s), 684 (w), 660 (m). ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.98 (s, 1 H, 2-H), 4.03 (3 H, OCH_3), 5.29 (d, ^3J = 6.6 Hz, 1 H, 3-H), 5.57 (d, ^3J = 6.0 Hz, 1 H, 5-H), 6.01 (s, 1 H, OH), 6.05 (dd, ^3J = 6.4, ^3J = 6.3 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 59.3 (−, C-7), 78.1 (−, C-3), 80.7 (−, C-4), 83.7 (−, C-2), 92.3 (+, C-6a), 96.7 (−, C-5), 125.8 (+, C-2a), 139.7 (+, C-6), 183.8 (+, C-1), 231.0 (+, CO) ppm. MS (70 eV, 100 °C): *m*/*z* (%) = 300 (78) [M$^+$], 244 (29) [M − 2 CO], 216 (100) [M − , 3 CO], 198 (10), 173 (35), 155 (5), 136 (2), 119 (5), 91 (5), 73 (13), 52 (86) [Cr]. $C_{16}H_{14}CrO_6$ (330.19): calcd. C 48.01, H 2.69; found C 48.67, H 3.68.

Hydrolysis of [1,2-Bis(ethylenedioxy)-3-methoxybenzocyclobutene]-tricarbonylchromium(0): Hydrochloric acid (50%, 50 mL) was added at 0 °C to a solution of *rac*-**7**[26] (250 mg, 0.6 mmol) in dichloromethane (20 mL). The mixture was stirred for 2 h at 20 °C in the dark, the color changing from yellow to red. The aqueous layer was extracted three times, each with 25 mL of dichloromethane, the aqueous layer becoming colorless. The collected organic layers were washed three times, each with 25 mL of water, filtered through a P4 frit, covered with a 1-cm layer of silica gel, and dried with $MgSO_4$. The solvent was evaporated into a cold trap at reduced pressure, and the crude product was purified by column chromatography (80 × 20 mm; PE then TBME/PE, 4:1). I: 77 mg (0.2 mmol, 35%) of tricarbonyl[η^6-1-(ethylenedioxy)-3-methoxy-2-oxobenzocyclobutene]chromium(0) (*rac*-**8**), orange solid (m.p. 132 °C). II: 87 mg (0.3 mmol, 45%) of *rac*-**3**.

***rac*-8:** IR (ATR): $\tilde{\nu}$ = 3085 (w) cm^{-1}, 2980 (w), 1969 (s, CO), 1887 (s, CO), 1776 (s, C=O), 1537 (m), 1460 (m), 1419 (m), 1402 (m), 1283 (m), 1213 (m), 1164 (w), 1049(m), 1003 (s, C−O), 945 (m), 832 (m), 739 (m), 662 (m). ^{1}H NMR (200.1 MHz, [D$_6$]acetone): δ = 4.05 (3 H, OCH_3), 4.28 (m, 4 H, CH_2), 5.38 (d, ^3J = 6.7 Hz, 1 H, 3-H), 5.76 (d, ^3J = 5.9 Hz, 1 H, 4-H), 6.12 (dd, ^3J = 6.3, ^3J = 6.3 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 57.1 (−, C-7), 66.8 (+, C-8 or C-9), 67.3 (+, C-8 or C-9), 78.4 (−, C-6), 80.6 (−, C-4), 97.0 (−, C-5), 95.5 (+, C-1), 119.2 (+, C-2a), 124.0 (+, C-6a), 139.5 (+, C-3), 187.6 (+, C-2), 230.2 (+, CO) ppm. MS (70 eV, 80 °C): *m*/*z* (%) = 342 (2) [M$^+$], 258 (3) [M$^+$ − 3 CO], 215 (1), 183 (3), 158 (8), 134 (19), 104 (7), 76 (26), 52 (100) [Cr$^+$]. HRMS ($C_{14}H_{10}CrO_7$): calcd.: 341.9773; found 341.9773.

Crystal Structure Analysis of *rac*-8:[34] $C_{14}H_{10}CrO_7$, formula mass 342.23; crystal system monoclinic, space group $P2_1/n$ (no. 14), a = 12.650(2), b = 7.104(2), c = 15.312(5) Å, β = 92.74(4), V = 1374.4(7) Å^3, Z = 4, $\rho_{calcd.}$ = 1.654 gcm^{-3}, F(000) = 696 e, μ = 8.7 cm^{-1}, crystal: orange needle ||[010], size 0.06 × 0.33 × 0.03

mm, Stoe IPDS (Imaging Plate) diffractometer, $T = 300$ K, Mo-$K_\alpha = 0.71073$ Å, $2\theta_{min.} = 4.1°$, $2\theta_{max} = 52.1°$, 150 exposures, $\Delta\Phi = 1.5°$, 12320 measured reflections (±15, ±8, ±18), 2699 independent [$R(I)_{int} = 0.216$] and 719 observed reflection [$I_t > 2.0\sigma(I)$], completeness of data: 99.9%, no absorption correction, no extinction correction, structure solution with direct methods with SHELXS-86, refinement with SHELXL-93, hydrogen atoms in geometrically calculated positions, $N_{ref} = 2699$, $N_{par} = 199$, $R(F) = 0.0289$, $R_w(F^2) = 0.0654$ [$w = 1/\sigma^2(F_o^2)$], $S = 0.45$, minimal and maximal residual electron density −0.16/0.22 eÅ^{-3}.

Treatment of *rac*-3 with Vinylmagnesium Bromide: Vinylmagnesium bromide in diethyl ether/THF (1:1, 0.9 M, 1.0 mL, 1.0 mmol) was slowly added at −78 °C to a solution of *rac*-**3** (300 mg, 1.0 mmol) in Et_2O (10 mL). After stirring at −78 °C for 5 h and hydrolysis with hydrochloric acid (1 M, 10 mL), the mixture was warmed to 20 °C and diluted with 50 mL of TBME and 50 mL of water. The organic layer was extracted three times with portions of TBME (20 mL) until the water layer remained colorless. The collected organic layers were dried with $MgSO_4$ and filtered through a P4-frit, covered with a 1-cm layer of silica gel. The organic solvent was evaporated at reduced pressure into a cooled trap. The crude product was purified by column chromatography (200 × 20 mm; PE then TBME/PE, 1:1) to afford 267 mg (0.82 mmol, 82%) of a mixture (3:1, NMR) of tricarbonyl[η^6-2-*endo*-hydroxy-6-methoxy-1-oxo-vinylbenzocyclobutene]chromium(0)[26] (*rac*-**4**) and tricarbonyl[η^6-*endo*-hydroxy-3-methoxy-1-oxo-vinylbenzocyclobutene]chromium(0) (*rac*-**9**) as a yellow solid.
***rac*-9:** ^{1}H NMR (200.1 MHz, [D$_6$]acetone): δ = 3.96 (3 H, OCH_3), 5.91 (dd, $^3J = 6.3$, $^3J = 6.4$ Hz, 1 H, 5-H) ppm; all other signals overlapped with those of *rac*-**4** and could not be distinguished. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 57.7 (−, C-7), 79.2 (−, C-6), 80.1 (−, C-5), 95.1(+, C-2), 95.7 (−, C-4), 105.5(+, C-6a), 117.7 (+, C-2a), 128.2 (+, C-9), 136.3 (−, C-8), 139.4 (+, C-3), 188.7 (+, C-1), 231.2 (+, CO).

General Procedure for the Dianionic Oxy-Cope Rearrangement Induced by Nucleophilic Diaddition to *rac*-3, Followed by Intramolecular Aldol Addition (GP I): The nucleophile (8 equiv.) was added dropwise at −78 °C to *rac*-**3** in THF/Et_2O (1:1). The color of the reaction mixture changed from red-brown to orange. The mixture was stirred for 5−24 h at −78 °C until no starting material could be detected by TLC. The mixture was hydrolyzed by addition of either saturated aqueous NH_4Cl or 1 M HCl at −78 °C. The mixture was then allowed to warm up to 20 °C and the aqueous layer was extracted with TBME or ethyl acetate until the aqueous layer remained colorless. The collected organic layers were dried with $MgSO_4$ and filtered through a P4-frit, covered with a 2-cm layer of silica gel, which was washed with TBME or ethyl acetate until the solvent remained colorless. The organic solvent was evaporated at reduced pressure into a cold trap. The crude product was purified by column chromatography (SiO_2, 200 × 20 mm; PE then mixture of TBME and PE).

Treatment of *rac*-3 with Vinyllithium: GP I. Vinyllithium in diethyl ether (0.9 M, 7.1 mL, 6.4 mmol), *rac*-**3** (250 mg, 0.8 mmol) in THF/diethyl ether (1:1, 40 mL), hydrolysis with 1 M HCl, to yield 215 mg (0.61 mmol) of tricarbonyl[η^6-1,2,3,3a-tetrahydro-3a-*endo*-hydroxy-7-methoxycyclopenta[*a*]inden-8(8a*H*)-one]chromium(0) (*rac*-**11a**), orange solid (m.p. 140 °C).
IR (ATR): $\tilde{\nu}$ = 3399 (br, OH) cm^{-1}, 2963 (w), 1962 (s), 1873 (s), 1703 (s, C = O), 1597 (w), 1524 (m), 1458 (m), 1429 (m), 1406 (w), 1260 (s), 1203 (m), 1021 (s), 875 (w), 798 (s), 721 (w), 702 (w), 662 (m) cm^{-1}. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.54 (m, 1-H), 1.93−1.98 (m, 4 H, 1-H, 2-H, 3-H), 2.22 (m, 1 H, 1-H), 2.99 (dd, $^3J_{endo\text{-}8a,endo\text{-}1} = 7.2$, $^3J_{endo\text{-}8a,exo\text{-}1} = 2.8$ Hz, 1 H, 8a-H), 3.85 (3 H, OCH_3), 5.04 (s, 1 H, OH). 5.47 (2d, $^3J = 6.7$, $^3J = 5.8$ Hz, 2 H, 4-H, 6-H), 6.18 (dd, $^3J = 6.3$, $^3J = 6.4$ Hz, 1 H, 5-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 25.6 (+, C-2), 28.0 (+, C-1), 43.6 (+, C-3), 55.5 (−, C-9), 60.1 (−, C-8a), 73.9 (−, C-4), 80.6 (−, C-6), 82.8 (+, C-7a), 86.4 (+, C-3a), 96.4 (−, C-5), 131.3 (+, C-3b), 141.8 (+, C-7), 199.8 (+, C-8), 231.4 (+, CO) ppm. MS (70 eV, 130 °C): *m*/*z* (%) = 354 (17) [M$^+$], 298 (11) [M − 2 CO], 270 (78) [M − 3 CO], 255 (100) [M − 3 CO − CH_3], 237 (18), 218 (11), 189 (11), 171 (4), 152 (14), 125 (12), 91 (18), 69 (26), 52 (16) [Cr]. HRMS ($C_{16}H_{14}CrO_6$): calcd. 354.0188; found 354.0195. $C_{16}H_{14}CrO_6$: calcd. C 54.24, H 3.98; found C 54.62, H 4.19.

Treatment of *rac*-3 with 2-Lithiopropene: GP I. 2-Bromopropene (486 mg, 4.0 mmol) in diethyl ether (25 mL) and lithium sand (40 mg, 5.7 mmol) in diethyl ether (10 mL) were heated at reflux for 1 h.[35] The mixture was cooled to −78 °C, and *rac*-**3** (150 mg, 0.5 mmol) in THF/diethyl ether (1:1, 50 mL) was added dropwise. Stirring for 16 h at −78 °C, hydrolysis with 10 mL of 1 M hydrochloric acid, extraction three times, each with 25 mL of TBME, and purification by column chromatography (200 × 20 mm; PE then TBME/PE, 6:1) afforded 142 mg (0.4 mmol, 74%) of tricarbonyl[η^6-3a-*endo*-hydroxy-1,2,3,3a-tetrahydro-7-methoxy-3-*endo*,8a-*endo*-dimethyl-cyclopenta[*a*]inden-8(8a*H*)-one]chromium-(0) (*rac*-**11b**) as an orange solid (m.p. 151 °C).
IR (ATR): $\tilde{\nu}$ = 3410 (br, OH), 2951 (w), 2871 (w), 1969 (s, CO), 1900 (s, CO), 1878 (s, CO), 1686 (s, C=O), 1515 (m), 1456 (m), 1454 (m), 1427 (w), 1404 (w), 1337 (w), 1329 (w), 1258 (s), 1202 (m), 1073 (s, C−O), 1035 (s), 999 (s) 964 (m), 799 (s), 769 (w), 702 (w), 656 (m) cm^{-1}. ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.16 (d, $^3J = 6.9$ Hz, 3 H, 3-CH_3), 1.44 (s, 3 H, 8a-CH_3), 1.68 (m, 2 H, 2-H), 1.71 (m, 1 H, 1-H), 1.88 (m, 1 H, 1-H), 1.99 (dd, $^3J_{3,exo\text{-}2}$ = 6.9, $^3J_{3,endo\text{-}2} = 2.4$ Hz, 3 H, 3-H), 3.80 (3 H, OCH_3), 4.50 (s, 1 H, OH), 5.47 (d, $^3J = 6.8$ Hz, 1 H, 4-H), 5.51 (d, $^3J = 6.3$ Hz, 1 H, 6-H), 6.12 (dd, $^3J = 6.5$, $^3J = 6.5$ Hz, 1 H, 5-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 12.0 (−, 3-*C*H$_3$), 22.0 (−, 8a-*C*H$_3$), 32.0 (+, C-1), 35.8 (+, C-2), 48.5 (−, C-3), 55.4 (−, C-9), 60.7 (+, C-8a), 74.5 (−, C-4), 80.2 (−, C-5), 83.5 (+, C-3a), 85.1 (+, C-7a), 96.0 (−, C-6), 130.3 (+, C-3b), 140.7 (+, C-7), 204.8 (+, C-8), 231.4 (+, CO) ppm. MS (70 eV, 100 °C): *m*/*z* (%) = 382 (23) [M$^+$], 326 (13) [M − 2 CO], 298 (99) [M − 3 CO], 283 (100) [M$^+$ − 3 CO − CH_3], 256 (32), 227 (7), 203 (5), 183 (6), 149 (5), 115 (5), 91 (5), 73 (5), 52 (16) [Cr]. HRMS ($C_{18}H_{18}CrO_6$): calcd. 382.0508; found. 382.0508. $C_{18}H_{18}CrO_6$ (382.3302): calcd. C 56.54, H 4.75; found C 56.29, H 4.76.

Treatment of *rac*-3 with 1-Ethoxy-1-lithioethene: GP I. 1-Ethoxyethene (289 mg, 4.0 mmol) in THF (10 mL), *tert*-butyllithium in pentane (1.6 M, 1.5 mL, 2.2 mmol), warming up to − 5° C, stirring at that temperature for about 45 min.[36−38] The mixture was cooled to −78 °C, and *rac*-**3** (150 mg, 0.5 mmol) in THF/diethyl ether (1:1, 50 mL) was added dropwise. Stirring for 16 h at −78 °C, hydrolysis with 10 mL of 1 M hydrochloric acid, extraction three times, each with 20 mL of TBME, and column chromatography (200 × 20 mm; PE then TBME/PE, 4:1) afforded 148 mg (0.3 mmol, 67%) of tricarbonyl[η^6-3-*endo*,8a-*endo*-diethoxy-3a-*endo*-hydroxy-7-methoxy-1,2,3,3a-tetrahydrocyclopenta[*a*]inden-8(8a*H*)-one]chromium(0) (*rac*-**11c**) as an orange solid (m.p. 134 °C).
IR (ATR): $\tilde{\nu}$ = 3400 (br, OH), 3097 (w), 2965 (w), 1961 (s, CO), 1871 (s, CO), 1710 (s, C=O), 1596 (w), 1514 (m), 1459 (m), 1426 (m), 1357(w), 1263 (s), 1235 (w), 1162 (w), 1045 (s), 957 (m), 800 (m), 722 (w), 657 (m) cm^{-1}. ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.18 (t, $^3J = 7.0$ Hz, 6 H, 11-H, 13-H), 2.22 (m, 2 H, 2-H), 2.54 (m, 2 H, 1-H), 3.63 (dd, $^3J_{3,endo\text{-}2} = 2.0$, $^3J_{3,exo\text{-}2} = 7.0$ Hz, 1

H), 3.80 (s, 3 H, OCH_3), 3.91 (br. q, 4 H, 10-H, 12-H), 4.65 (m, OH), 5.54 (d, ^3J = 6.3 Hz, 1 H, 4-H), 5.69 (d, ^3J = 6.9 Hz, 1 H, 6-H), 6.12 (dd, ^3J = 6.5, ^3J = 6.6 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 25.2 (−, C-13 or C-11), 25.8 (−, C-13 or C-11), 26.1 (+, C-1 or C-2), 27.2 (+, C-2 or C-1), 38.5 (+, C-3a), 47.9 (−, C-3), 55.6 (−, C-9), 65.6 (+, C-10 or C-12), 65.9 (+, C-10 or C-12), 75.9 (−, C-4), 76.1 (+, C-7a), 83.5 (−, 6-C), 94.7 (−, C-5), 96.9 (+, C-3b), 139.6 (+, C-7), 197.9 (+, C-8), 232.1 (+, CO) ppm. MS (70 eV, 210 °C): *m*/*z* (%) = 414 (2) [M − CO], 386 (3) [M − 2 CO], 358 (10) [M − 3 CO], 322 (35), 286 (19), 254 (12), 226 (15), 189 (11), 159 (12), 136 (100) [$C_6H_4OCH_3C_2H_5$], 109 (25), 91 (21), 73 (34), 52 (11) [Cr$^+$]. HRMS ($C_{20}H_{22}CrO_8$): calcd. 442.0720; found 442.0734.

Treatment of *rac*-3 with 1-Lithio-1-methoxyallene: GP I. Butyllithium in hexane (1.6 M, 2.5 mL, 3.9 mmol) was added at −78 °C to 1-methoxyallene (281 mg, 4.0 mmol) in diethyl ether (15 mL) and warmed to −30 °C over 45 min.[39,40] Compound *rac*-**3** (150 mg, 0.5 mmol) in THF/diethyl ether (1:1, 70 mL) at −78 °C, stirring 16 h, hydrolysis with 10 mL of 1 M hydrochloric acid, extraction three times, each with 25 mL of TBME, and column chromatography (200 × 20 mm; PE then TBME/PE, 6:1) afforded 129 mg (0.3 mmol, 59%) of tricarbonyl[η^6-3a-*endo*-hydroxy-3-*endo*,8a-*endo*-dimethoxy-1,2-dimethylene-1,2,3a,8,8a-hexahydro-7-methoxycyclopenta[*a*]inden-8(8a*H*)-one]chromium(0) (*rac*-**11d**) as an orange-red solid (m.p.135 °C).

IR (ATR): ṽ = 3469 (br, OH), 2964 (m), 1961 (s, CO), 1877 (s, CO), 1714 (s, C=O), 1664 (s), 1595 (w), 1519 (m), 1454 (w), 1429 (w), 1371 (w), 1259 (s), 1169 (w), 1012 (s), 957 (m), 935 (m), 879 (w), 796 (s), 697 (w), 659 (m) cm^{-1}. ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.46 (3 H, OCH_3), 3.74 (3 H, OCH_3), 3.95 (3 H, OCH_3), 4.70 (s, OH), 5.45 (br. s, 1 H, =CH), 5.55−5.65 (m, 3 H, 4-H, 6-H, =CH), 5.85 (d, ^2J = 7.9 Hz, 1 H, =CH), 5.90 (d, ^2J = 7.9 Hz, 1 H, =CH), 6.2 (dd, ^3J = 6.6, ^3J = 6.5 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 55.6 (−, OCH_3), 56.0 (−, OCH_3), 58.7 (−, OCH_3), 73.6 (−, C-4), 80.3 (−, C-5), 87.2 (−, C-3), 94.8 (+, C-3a), 95.7 (−, C-6), 97.9 (+, C-3b), 113.5 (+, C-7a), 127.5 (−, $=CH_2$), 129.6 (−, $=CH_2$), 142.8 (+, C-7), 145.0 (+, C-1 or C-2), 148.5 (+, C-1 or C-2), 181.3 (+, C-8a), 197.9 (+, C-8), 232.8 (+, CO) ppm. MS (70 eV, 190 °C): *m*/*z* (%) = 438 (28) [M$^+$], 382 (77) [M − 2 CO], 354 (59) [M − 3 CO], 308 (100) [M − 3 CO − OCH_3 − CH_3], 277 (14), 255 (44), 233 (42), 155 (38), 111 (19), 91 (65), 71 (34), 57 (47). HRMS ($C_{20}H_{18}CrO_8$): calcd. 438.0407; found 438.0397.

Treatment of *rac*-3 with 1-Lithiocyclopentene: GP I. 1-Bromocyclopentene (700 mg, 4.8 mmol) in diethyl ether (10 mL) and lithium sand (55 mg, 7.8 mmol) in diethyl ether (10 mL) were heated at reflux for 1 h, and then cooled to −78 °C.[35] Compound *rac*-**3** (200 mg, 0.7 mmol) in THF/diethyl ether (1:1, 40 mL) was added dropwise at −78 °C to the solution of 1-cyclopentenyllithium. Stirring for 16 h at −78 °C, hydrolysis with 10 mL 1 M hydrochloric acid, extraction three times, each with 20 mL of TBME, and column chromatography (200 × 20 mm; PE then TBME/PE, 6:1) afforded 259 mg (0.6 mmol, 89%) of tricarbonyl{η^6-1,2,3,3a,3b,4,5,6,6a,6b-decahydro-6b-*endo*-hydroxy-*endo*-cyclopenta-[5,6]-10-methoxy-*endo*-pentaleno[4,5-*a*]inden-11-one}-chromium(0) (*rac*-**11e**) as an orange solid (m.p. 194 °C).

IR (ATR): ṽ = 3469 (br, OH), 2950 (m), 1971 (s, CO), 1896 (s, CO), 1706 (s, C=O), 1524 (w), 1459 (m), 1429 (w), 1406 (w), 1277 (m), 1226 (w), 1184 (w), 1038 (m), 888 (w), 829 (w), 756 (w), 684 (w), 625 (m), 530 (w), 479 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, [D$_6$]-acetone): δ = 1.58 (m, 2 H, aliph. H), 1.65(m, 3 H, aliph. H), 1.78 (m, 2 H, aliph. H), 1.88 (m, 3 H, aliph. H), 2.57 (m, 2 H, aliph. H), 2.64 (m, 1 H, 3a-H or 3b-H), 2.78 (m, 1 H, 3a-H or 3b), 3.80 (3 H, OCH_3), 4.43 (s, 1 H, OH). 5.48 (dd, ^3J = 6.0, ^3J = 5.9 Hz, 2 H, 7-H, 9-H), 6.13 (dd, ^3J = 6.4, ^3J = 6.4 Hz, 1 H, 8-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 24.7 (+,CH_2), 26.3 (+, CH_2), 27.4 (+,CH_2), 28.1 (+,CH_2), 29.0 (+,CH_2), 30.2 (+,CH_2), 34.7 (+, C-11a), 48.3 (−, C-3a), 51.3 (−, C-3b), 55.5 (−, C-12), 60.9 (−, C-6a), 74.3 (−, C-7), 75.2 (−, C-6b), 79.9 (−, C-8), 83.4 (+, C-10a), 96.2 (−, C-9), 132.2 (+, C-6c), 141.0 (+, C-10), 205.4 (+, C-11), 231.5 (+, CO) ppm. MS (70 eV, 130 °C): *m*/*z* (%) = 434 (14) [M$^+$], 378 (12) [M − 2 CO], 350 (100) [M − 3 CO], 335 (60) [M − 3 CO − CH_3], 317 (5), 298 (12), 257 (6), 230 (7), 211 (5), 190 (10), 166 (5), 145 (7), 127 (5), 107 (4), 91 (6), 75 (18), 52 (11) [Cr]. HRMS ($C_{22}H_{22}CrO_6$): calcd. 434.0822; found. 434.0821.

Crystal Structure Analysis of *rac*-11e:[34] $C_{22}H_{22}CrO_6$, formula mass 434.41, crystal system monoclinic. Space group $P2_1/c$ (no. 14), a = 10.470(2), b = 13.762(2), c = 13.877(2) Å, β = 103.26(2), V = 1946.2(6) Å^3, Z = 4, $d_{calcd.}$ = 1.483 gcm^{-3}, F(000) = 904 e, μ = 6.3 cm^{-1}, crystal: red plate ‖(100), size 0.03 × 0.33 × 0.26 mm, Stoe IPDS (Imaging Plate) diffractometer, T = 300 K, Mo-K_α = 0.71073 Å, $2\theta_{min.}$ = 4.1°, $2\theta_{max}$ = 48.3°, scan type 150 exposure, ΔΦ = 1.5°, 14094 measured reflections (±12, ±15, ±15), 3073 independent [$R(I)_{int}$ = 0.100] and 1500 observed reflection [I_t > 2.0σ(I)], completeness of data: 99.7%, no absorption correction, no extinction correction, structure solution by direct methods with SHELXS-86, refinement with SHELXL-93, hydrogen atoms in geometrically calculated positions, N_{ref} = 3073, N_{par} = 266, $R(F)$ = 0.0402, $R_w(F^2)$ = 0.0647 [$w = 1/\sigma^2 (F_o^2)$], S = 0.86, minimal and maximal residual electron density −0.40/0.23 eÅ^{-3}.

Treatment of *rac*-3 with 5-Lithio-2,3-dihydrofuran: GP I. 2,3-Dihydrofuran (375 mg, 5.4 mmol) in THF (10 mL) was added to butyllithium (1.6 M, 3.3 mL, 5.4 mmol) in hexane at −78 °C and warmed up to 0 °C over 45 min.[41,42] Compound *rac*-**3** (200 mg, 0.7 mmol) in THF/diethyl ether (1:1) was added, and the mixture was stirred for 16 h at −78 °C. Hydrolysis with 10 mL of 1 M hydrochloric acid, extraction three times, each with 25 mL of TBME, and column chromatography (200 × 20 mm; PE then EE/TBME, 1:2) afforded 179 mg (0.4 mmol, 72%) of an approximately 1:1 (NMR) mixture of tricarbonyl{η^6-1,2,2a,2b,3,4,4a,4b-octahydro-5*H*-benzo[5,6]-furo[3′2′:3,3a]8-methoxypentaleno[1,2-*b*]furan-9-one}chromium (*rac*-**11f**) and tricarbonyl{η^6-1,2,2a,2b,3,4,9c,9b-octahydro-5*H*-benzo[5,6]furo[3′2′:3,3a]9-methoxypentaleno-[1,2-*b*]furan-5-one}chromium (*rac*-**12f**) as a red oil.

***rac*-11f and *rac*-12f:** IR (ATR): ṽ = 3432 (br, OH), 2959 (m), 2886 (w), 1964 (s, CO), 1875 (s, CO), 1715 (s, C=O), 1522(w), 1456 (m), 1431 (w), 1361(w), 1262 (s), 1180 (w), 1014(s), 923 (m), 814 (w), 752(w), 658 (m) cm^{-1}. MS (70 eV, 150 °C): *m*/*z* (%) = 438 (3) [M$^+$], 382 (3) [M − CO], 354 (21) [M − 3 CO], 302 (21), 274 (3), 257 (21), 220 (38), 203 (7), 176 (14), 158 (4), 141 (8), 108 (31), 87 (23), 71 (100) [C_4H_7O], 52 (32) [Cr]. HRMS ($C_{20}H_{18}CrO_8$): calcd. 438.0407; found.438.0408.

***rac*-11f:** ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.10 (m, 2 H, aliph. H), 2.76 (m, 2 H, aliph. H), 2.92 (m, 2 H, aliph. H), 3.85 (3 H, OCH_3), 4.1−4.2 (m, 4 H, 1-H, 4-H), 4.32 (d, $^3J_{endo\text{-}4a,endo\text{-}2b}$ = 6.4 Hz, 1 H,4a-H), 5.31 (d, ^3J = 6.1 Hz, 1 H, 5-H), 5.45 (d, ^3J = 6.6 Hz, 1 H, 7-H,), 5.89 (t, ^3J = 6.4, ^3J = 6.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 29.8 (+, C-2 or C-3), 30.0 (+, C-3 or C-2), 42.7 (−, C-2a or C-2b), 49.7 (−, C-2b or C-2a), 55.7 (−, OCH_3), 68.9 (+, C-1 or C-4), 72.7 (+, C-4 or C-1), 81.2 (+, C-4b), 88.4 (−, C-5), 91.7 (−, C-6), 94.4 (−, C-7), 95.8 (−, C-4a), 96.2 (+, C-9a), 96.7 (+, C-4c), 127.9 (+, C-8a), 141.3 (+, C-8), 203.8 (+, C-9), 231.5 (+, CO).

***rac*-12f:** Only data different from those of *rac*-**11f** are given. IR (ATR): $\tilde{\nu}$ = 1769 (C=O) cm^{-1}. ^1H NMR (400.1 MHz, [D_6]acetone): δ = 3.82 (3 H, OCH_3), 4.57 (d, $^3J_{9c,2a}$ = 5.5 Hz, 1 H, 9c-H), 5.38 (d, ^3J = 6.1 Hz, 1 H, 6-H), 5.69 (d, ^3J = 6.5 Hz, 1 H, 8-H), 6.19 (dd, ^3J = 6.1, ^3J = 6.3 Hz, 1 H, 7-H) ppm. ^{13}C NMR (100.6 MHz, [D_6]acetone, APT): δ = 56.0 (−, OCH_3), 73.7 (−, C-6 or C-7 or C-8), 76.4 (−, C-6 or C-7 or C-8), 79.2 (−, C-6 or C-7 or C-8), 79.6 (+, C-5a), 81.2 (−, C-9c), 85.7 (+, C-4a), 98.9 (+, C-5a), 110.4 (+, C-9a), 140.1 (+, C-9), 198.7 (+, C-5), 230.9 (+, CO).

Treatment of *rac*-3 with 2-Lithiofuran: GP I. Furan (337 mg, 5.4 mmol) in THF (10 mL) was added at −78 °C to butyllithium in hexane (1.6 M, 3.4 mL, 5.4 mmol). The mixture was warmed to 10° C over 45 min and then cooled to −78 °C.[43] To this mixture at −78 °C was added a solution of *rac*-**3** (200 mg, 0.7 mmol) in THF/diethyl ether (1:1, 10 mL). After stirring for 16 h at −78 °C, the mixture was hydrolyzed with 10 mL of 1 M hydrochloric acid and extracted three times, each with 20 mL of TBME. Column chromatography (200 × 20 mm; PE then TBME/PE, 4:1) afforded 206 mg (0.5 mmol, 71%) of tricarbonyl[η^6-1,2-bis(2-furanoyl)-3-methoxybenzene]chromium (*rac*-**13**) as an orange-red solid (m.p.115 °C).

***rac*-13:** IR (ATR): $\tilde{\nu}$ = 3121 (w), 2962 (w), 1959 (s, CO), 1867 (s, CO), 1751 (m, C=O), 1638 (m), 1563 (m), 1512 (w), 1460 (m), 1421 (m), 1390 (m), 1258 (s), 1174 (m), 1080 (s), 1014(s), 907 (m), 885 (m), 867 (m), 797 (s), 660 (m) cm^{-1}. ^1H NMR (400.1 MHz, [D_6]-acetone): δ = 3.8 (3 H, OCH_3), 5.87 (d, ^3J = 6.9 Hz, 1 H, 4-H), 5.98 (d, ^3J = 7.0 Hz, 1 H, 6-H), 6.13 (dd, ^3J = 6.8, ^3J = 6.6 Hz, 1 H 5-H), 6.65 (m, 1 H, 11-H or 16-H), 6.73(m, 11-H or 16-H), 7.21(m, 10-H or 15-H), 6.73 (m, 10-H or 15-H), 7.76 (m, 1 H, 12-H or 17-H), 7.91 (m, 12-H or 17-H) ppm. ^{13}C NMR (100.6 MHz, [D_6]acetone, APT): δ = 56.1 (−, C-7), 75.1 (−, C-4), 87.1 (−, C-5), 93.1 (−, C-6), 100.4 (+, C-3), 103.8 (+, C-2), 112.1 (−, C-10 or C-15), 112.4 (−, C-10 or C-15), 117.5 (−, C-11 + C-16), 120.8 (−, C-12 + C-17), 140.9 (+, C-1), 150.9 (C-9 or C-14), 152.9(+, C-9 or C-14), 176.5 (+, C-13), 179.1(+, C-8), 231.9 (+, CO) ppm. MS (70 eV, 160 °C): *m*/*z* (%) = 432 (3)[M^+], 376 (30) [M − 2 CO], 348 (100) [M − 3 CO], 322 (29), 296 (30), 267 (42), 239 (3), 220 (21), 202 (7), 174 (5), 155 (5), 127 (7), 95 (19), 73 (37), 52 (25). HRMS ($C_{20}H_{12}CrO_8$): calcd. 431.9937, found. 431.9799.

Treatment of *rac*-4/*rac*-9 with 1-Lithiocyclopentene: 1-Bromocyclopentene (394 mg, 2.7 mmol) in diethyl ether (10 mL) and lithium sand (25 mg, 3.2 mmol) in diethyl ether (10 mL) were heated at reflux for 1 h.[35] At −78 °C, a solution of a 3:1 mixture of *rac*-**4** and *rac*-**9** (200 mg, 0.6 mmol) in THF/Et_2O (60 mL) was added dropwise. After stirring for 16 h at −78 °C, the mixture was hydrolyzed with 10 mL of 1 M hydrochloric acid and extracted three times, each with 25 mL of TBME. Purification by column chromatography (200 × 20 mm; PE then TBME/PE, 6:1) afforded two fractions. I: 150 mg (0.4 mmol, 62%) of tricarbonyl[η^6-*endo*-5a-hydroxy-9-methoxy-2,3,*exo*-3a,4,5,5a-hexahydropentaleno-[1,6-*a*]inden-10(1*H*)-one] (*rac*-**14**), orange solid (m.p.181 °C). II: 58 mg (0.2 mmol, 24%) of tricarbonyl[η^6-*endo*-5a-hydroxy-6-methoxy-2,3,*exo*-3a,4,5,5a-hexahydropentaleno[1,6a-*a*]inden-10(1*H*)-one (*rac*-**15**), orange solid (m.p. 178 °C).

***rac*-14:** IR (ATR): $\tilde{\nu}$ = 3459 (br, OH), 2952 (w), 1974 (s, CO), 1887 (s, CO), 1693 (s, C = O), 1525 (m), 1460 (m), 1429 (w), 1408 (w), 1316 (w), 1278 (s), 1097 (m), 1039 (m), 918 (w) 856 (w), 803 (m), 751 (w), 683 (w), 625 (m), 528 (w), 479 (w) cm^{-1}. ^1H NMR (400.1 MHz, [D_6]acetone): δ = 1.56 (m, 1 H, aliph. H), 1.67 (m, 2 H, aliph. H), 1.77 (m, 3 H, aliph. H), 1.86 (m, 2 H, aliph. H), 2.30 (m, $^3J_{exo\text{-}3a,exo\text{-}3}$ = 4.3, $^3J_{exo\text{-}3a,endo\text{-}3}$ = 2.0, $^3J_{exo\text{-}3a,exo\text{-}4}$ = 6.6, $^3J_{exo\text{-}3a,endo\text{-}4}$ = 3.5 Hz, 1 H, 3a-H), 2.5 (m, 2 H, aliph. H), 3.80 (3 H, OCH_3), 4.85 (s, 1 H, OH). 5.46 (d, ^3J = 6.8 Hz, 1 H, 6-H), 5.48 (d, ^3J = 6.3 Hz, 1 H, 7-H), 6.11 (dd, ^3J = 6.4, ^3J = 6.5 Hz, 1 H, 8-H) ppm. ^{13}C NMR (100.6 MHz, [D_6]acetone, APT): δ = 26.9 (+, C-2), 31.7 (+, C-1), 32.6 (+, C-3), 33.8 (+, C-4), 44.4 (+, C-5), 51.2 (−, C-3a), 55.5 (−, C-11), 71.3 (+, C-10a), 74.2 (−, C-6), 80.7 (−, C-7), 83.6 (+, C-5a), 85.8 (+, C-9a), 96.1 (−, C-8), 130.8 (−, C-5b), 141.2 (+, C-9), 204.2 (+, C-10), 231.6 (+, CO) ppm. MS (70 eV, 130 °C): *m*/*z* (%) = 395 (15) [M^+], 339 (9) [M − 2 CO], 311 (100) [M − 3 CO], 295 (77), 258 (3), 240 (6), 217 (4), 155 (2), 52 (8) [Cr]. HRMS ($C_{19}H_{18}CrO_6$): calcd. 394.0509; found 394.0508. $C_{19}H_{18}CrO_6$: calcd. C 57.87 H 4.60; found C 57.21, H 4.51.

Crystal Structure Analysis of *rac*-14:[34] $C_{19}H_{18}CrO_6$, formula mass 394.33: crystal system monoclinic. Space group $P2_1/n$ (no. 14), a = 15.434(5), b = 13.562(2), c = 17.128(4) Å, β = 96.85(3), V = 3560(2) Å^3, Z = 8, $d_{calcd.}$ = 1.472 gcm^{-3}, F(000) = 1632 e, μ = 0.675 cm^{-1}, crystal: red prism ||b, size 0.03 × 0.30 × 0.06 mm, Stoe IPDS (Imaging Plate) diffractometer, T = 300(2) K, Mo-K_α = 0.71073 Å, θ_{min} = 2.01°, θ_{max} = 26.14°, 270 exposures, ΔΦ = 1.5°, 37542 measured reflections (±18, ±15, ±21), 6774 independent [$R(I)_{int}$ = 0.5982] and 870 observed reflection [$I > 2\sigma(I)$], R_{int} = 0.084, completeness of data: 96.7%, no absorption correction, no extinction correction, structure solution with direct methods with SHELXS-86, refinement with SHELXL-93, hydrogen atoms in geometrically calculated positions, N_{ref} = 6774, N_{par} = 279, final residuals [$I > 2\sigma(I)$] $R(F)$ = 0.0551, $R_w(F^2)$ = 0.0823 [$w = 1/\sigma^2 (F_o^2)$], and all data R = 0.3426, R_w = 0.1344 [$w = 1/\sigma^2 (F_o^2)$] S = 0.45, minimal and maximal residual electron density −0.39/0.29 eÅ^{-3}.

***rac*-15:** IR (ATR): $\tilde{\nu}$ = 3450 (br, OH), 2962 (w), 1974 (s, CO), 1915 (s, CO), 1883 (s, CO), 1716 (s, C = O), 1525 (m), 1460 (m), 1429 (w), 1320 (w), 1262 (s), 1099 (s), 1057 (s), 1017 (s), 918 (w), 854 (w), 801 (m), 660 (w), 616 (m), 528 (w), 469 (w) cm^{-1}. ^1H NMR (400.1 MHz, [D_6]acetone): δ = 1.76−1.78 (m, 6 H, aliph. H), 1.98−2.01 (m, 2 H, aliph. H), 2.31−2.35 (m, 2 H, aliph. H), 2.52−2.56 (m, 1 H, $^3J_{exo\text{-}3a,exo\text{-}3 \text{ or } -4}$ = 4.0, $^3J_{exo\text{-}3a,endo\text{-}3 \text{ or } -4}$ = 2.6 Hz, 3a-H), 3.87 (3 H, OCH_3), 4.29 (s, 1 H, OH). 5.30 (d, ^3J = 5.9 Hz, 1 H, 9-H), 5.71 (d, ^3J = 6.6 Hz, 1 H, 7-H), 5.86 (t, 1 H, ^3J = 6.4, ^3J = 6.5 Hz, 8-H) ppm. ^{13}C NMR (100.6 MHz, [D_6]acetone, APT): δ = 26.7 (+, C-2), 31.6 (+, C-1), 32.7 (+, C-3), 34.5 (+, C-4), 41.0 (+, C-5), 50.6 (−, C-3a), 55.9 (−, C-11), 71.4 (+, C-10a), 76.9 (+, C-9), 79.7 (−, C-8), 84.0 (+, C-5a), 96.1 (−, C-7), 98.7 (+, C-9a), 114.8 (+, C-5b), 139.4 (+, C-6), 207.8 (+, C-10), 231.9 (+, CO) ppm. MS (70 eV, 130 °C): *m*/*z* (%) = 395 (15)[M^+], 339 (12) [M −2 CO], 310 (100) [M − 3 CO], 292 (15), 264 (7), 247 (2), 225 (14), 197 (2), 161 (2), 79 (2), 52 (11) [Cr]. HRMS ($C_{19}H_{18}CrO_6$): calcd. 394.0508; found. 394.0506. $C_{19}H_{18}CrO_6$: calcd. C 57.87 H 4.60; found C 58.40 H 4.34.

Crystal Structure Analysis of *rac*-15:[34] $C_{19}H_{18}CrO_6$, formula mass 394.34: crystal system monoclinic. Space group $P2_1/c$ (no. 14), a = 9.706(2), b = 13.710(2), c = 13.511(3) Å, β = 107.30(3), V = 1716.6(6) Å^3, Z = 4, $d_{calcd.}$ = 1.526 gcm^{-3}, F(000) = 816 e, μ = 7.0 cm^{-1}, crystal: red plate ||(100), size 0.03 × 0.20 × 0.09 mm, Stoe IPDS (Imaging Plate) diffractometer, T = 300 K, Mo-K_α = 0.71073 Å, $2\theta_{min}$ = 4.4°, $2\theta_{max}$ = 52.2°, scan type 134 exposure, ΔΦ = 1.5°, 13711 measured reflections (±11, ±16, ±16), 3364 independent [$R(I)_{int}$ = 0.134] and 1142 observed reflection [$I > 2\sigma(I)$], completeness of data: 99.8%, no absorption correction, no extinction correction, structure solution with direct methods with SHELXS-86, refinement with SHELXL-93, hydrogen atoms in geometrically calculated positions, N_{ref} = 3364, N_{par} = 140, $R(F)$ = 0.0388, $R_w(F^2)$ = 0.0654 [$w = 1/\sigma^2 (F_o^2)$], S = 0.58. minimal and maximal residual electron density −0.25/0.31 eÅ^{-3}.

Treatment of *rac*-4 with 2-Lithiopropene: 2-Bromopropene (222 mg, 1.8 mmol) in diethyl ether (25 mL) and lithium sand (20 mg, 2.9 mmol) in diethyl ether (10 mL) were heated at reflux for 1 h.[35] At −78 °C, *rac*-**4** (150 mg, 0.5 mmol) in THF/Et_2O (1:1, 60 mL) was added dropwise. The mixture was stirred for 16 h at −78 °C, hydrolyzed with 10 mL of 1 M hydrochloric acid and extracted three times, each with 20 mL of TBME. Column chromatography (200 × 20 mm; PE then TBME/PE, 2:1) gave 104 mg (0.3 mmol, 62%) of tricarbonyl(η⁶-1,2,3,3a-tetrahydro-3a-*endo*-hydroxy-8a-*endo*-methyl-7-methoxy-cyclopenta[*a*]inden-8(8a*H*)-one)chromium(0) (*rac*-**17**), orange-red solid (m.p. 148 °C).

***rac*-17:** IR (ATR): ṽ = 3403 (br, OH), 2963 (w), 1975 (s, CO,), 1905 (s, CO), 1874 (s, CO), 1686 (s, C=O), 1596 (w), 1514 (m), 1456 (m), 1429 (w), 1406 (w), 1259 (s), 1230 (m), 1193 (m), 1089 (s), 1054 (s) 871 (w), 796 (s), 770 (w), 700 (w), 657 (m) cm^{-1}. ^1H NMR (400.1 MHz, [D_6]acetone): δ = 1.13 (m, 2 H, 1-H or 2-H or 3-H), 1.34 (s, 3 H, CH_3), 1.65 (m, 2 H, 1-H or 2-H or 3-H), 2.27 (m, 2 H, 1-H or 2-H or 3-H), 3.80 (3 H, OCH_3), 4.88 (s, 1 H, OH). 5.46 (d, ^3J = 6.6 Hz, 1 H, 4-H), 5.52 (d, ^3J = 6.3 Hz, 1 H, 6-H), 6.13 (dd, ^3J = 6.5, ^3J = 6.5 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100.6 MHz, [D_6]acetone, APT): δ = 20.0 (−, CH_3), 22.3 (+, C-2), 29.1 (+, C-3), 29.3 (+, C-1), 39.0 (+, C-8a), 44.29 (+, C-3a), 55.4 (−, C-9), 59.0 (+, C-7a), 74.3 (−, C-4), 80.9 (−, C-6), 82.6 (+, C-3b), 96.3 (−, C-6), 140.3 (+, C-7), 204.8 (+, C-8), 231.4 (+, CO) ppm. MS (70 eV, 160 °C): *m*/*z* (%) = 368 (17) [M^+], 312 (11) [M − 2 CO], 284 (6) [M − 3 CO], 269 (100) [M − 3 CO − CH_3], 251 (6), 232 (14), 215 (4), 190 (6), 161 (7), 142 (6), 91 (12), 69 (35), 52 (35) [Cr]. $C_{17}H_{15}O_6Cr$ (367.3): calcd. C 55.54, H 4.36; found. C 56.57, H 4.60.

Treatment of *rac*-3 with 2-Lithio-3,4-dihydro-2*H*-pyran: GP I. 3,4-Dihydro-2*H*-pyran (337 mg, 4.0 mmol) in THF (10 mL) was added to butyllithium in hexane (1.6 M, 2.5 mL, 4.0 mmol) at −78 °C and warmed up to 0 °C over 45 min.[41,42] The solution was cooled to −78 °C and added to a solution of *rac*-**3** (150 mg, 0.5 mmol) in THF/diethyl ether (1:1) at −78 °C. After stirring for 16 h at −78 °C, the mixture was hydrolyzed with 10 mL of 1 M hydrochloric acid, then extracted three times with 20 mL of TBME. Column chromatography (200 × 20 mm; PE then TBME/PE, 3:1) gave 140 mg (0.3 mmol, 60%) of tricarbonyl{η⁶-5-(5,6-dihydro-4*H*-pyran-3-yl)-5-hydroxy-9-methoxy-3,4,4a,10a-tetrahydro-2*H*,5*H*-benzo[*g*]chromen-10-one}chromium(0) (*rac*-**20**), orange-red solid (m.p. 174 °C).

***rac*-20:** IR (ATR): ṽ = 3412 (br, OH) cm^{-1}, 2941 (m), 1958 (s, CO), 1872 (s, CO), 1710 (s, C=O), 1628 (w), 1598 (w), 1525 (w), 1461 (m), 1430 (m), 1365 (m), 1267 (s), 1176 (m), 1034 (s), 951 (m), 916 (m), 848 (w), 761 (s), 664 (s). ^1H NMR (400.1 MHz, [D_6]acetone): δ = 1.57−1.88 (m, 8 H, 9-H, 10-H, 12-H, 13-H), 3.51 (m, 1 H, 1b-H), 3.80 (3 H, OCH_3), 3.93 (m, 2 H, 8-H or 11-H), 4.05 (m, 2 H, 8-H or 11-H), 4.84 (s, 1 H, 1a-H), 4.84 (d, ^3J = 5.4 Hz, 1 H, 14-H), 5.07 (s, 1 H, OH), 5.48 (d, ^3J = 5.1 Hz, 1 H, 3-H), 5.56 (d, ^3J = 6.5 Hz, 1 H, 5-H), 6.09 (m, 1 H, 4-H) ppm. ^{13}C NMR (100.6 MHz, [D_6]acetone, APT): δ = 19.8 (+, C-9 or C-10 or C-12 or C-13), 21.8 (+, C-9 or C-10 or C-12 or C-13), 22.6 (+, C-9 or C-10 or C-12 or C-13), 25.3 (+, C-9 or C-10 or C-12 or C-13), 48.2 (−, C-1b), 55.6 (−, C-7), 66.0 (+, C-8 or C-11), 66.8 (+, C-11 or C- 8), 71.7 (+, C-2), 73.0 (+, C-6a), 74.0 (−, C-1a), 75.6 (−, C-14), 83.3 (−, C-3), 95.3 (−, C-4), 101.9 (−, C-5), 142.4 (+, C-2a), 152.2 (+, C-6), 195.2 (+, C-1), 233.1 (+, CO) ppm. MS (70 eV, 160 °C): *m*/*z* (%) = 466 (5) [M^+], 382 (23) [M − 3 CO], 330 (13), 247 (9), 220 (3), 101 (7), 52 (22) [Cr]. HRMS ($C_{22}H_{22}CrO_8$): calcd. 466.0720; found 466.0719.

Crystal Structure Analysis of *rac*-20:[34] $C_{22}H_{22}CrO_8$, formula mass 466.4; crystal system monoclinic, space group $P2_1/n$ (no. 14), *a* = 14.456(5), *b* = 14.799(5), *c* = 21.437(10) Å, β = 109.12(5), *V* = 4333(3) $Å^3$, *Z* = 8, $d_{calcd.}$ = 1.430 gcm^{-3}, *F*(000) = 1936 e, μ = 5.7 cm^{-1}, crystal: red plate ‖(001), size 0.24 × 0.16 × 0.06 mm, Stoe IPDS (Imaging Plate) diffractometer, *T* = 300 K, Mo-K_α = 0.71073 Å, $2\theta_{min}$ = 3.4°, $2\theta_{max}$ = 42.1°, scan type 200 exposures, ΔΦ = 1.0°, 18264 measured reflections (±14, ±14, ±21), 4547 independent [$R(I)_{int}$ = 0.31] and 761 observed reflection [$I_t > 2.0\sigma(I)$], completeness of data: 100%, no absorption correction, no extinction correction, structure solution with direct methods with SHELXS-86, refinement with SHELXL-93, hydrogen atoms in geometrically calculated positions, N_{ref} = 4547, N_{par} = 230, *R*(*F*) = 0.1766, $R_w(F^2)$= 0.3029 [$w = 1/\sigma^2(F_o^2)$], *S* = 1.07, minimal and maximal residual electron density −0.96/1.60 $eÅ^{-3}$.

Acknowledgments

The Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Innovationsoffensive "Biologisch aktive Naturstoffe: Synthetische Diversität" kindly supported this work. K.G.D. is indebted to the Gottlieb Daimler- und Karl Benz-Stiftung for a doctoral fellowship and to the Freundeskreis der Universität Hannover e.V. for travelling funds. We thank Bayer AG, BASF AG, Degussa-Hüls AG, and Phenolchemie GmbH for donations of chemicals and solvents.

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Received January 7, 2002
[O02004]