Diastereoselective Ring Expansion Rearrangements of (Benzocyclobutenone)- and (Benzocyclobutenedione)chromium Complexes: Syntheses of Substituted 1-Indanone and 1,3-Indandione Complexes

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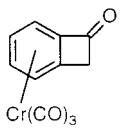
Organolithium and Grignard reagents add to the oxo group of (benzocyclobutenone)tricarbonylchromium(0) (**1**) diastereoselectively from the *exo* face of the organic ligand. If acyl anion equivalents are used as nucleophiles, deprotection of the carbonyl functions of the adducts causes ring expansion reactions to occur. Among these a rare example of an anion-accelerated 1-vinylcyclobutenol–cyclohexadienol rearrangement is reported which results, after isomerization, in a naphthol complex. Other ring expansion reactions gave coordinated substituted indanone derivatives. The facial differentiation by the tricarbonylchromium moiety allows for the first time the determination of the distereoselectivity of these reactions. The 1-oxoindan-2-ol derivatives obtained can undergo an α-ketol rearrangement with formation of the corresponding 2-oxoindan-1-ol complexes. Some of these reactions were performed with nonracemic starting material in order to determine how far chirality transfer from the planar chiral starting material to C-2 in the indanone system was possible. The ring expansion was also feasible with the benzocyclobutenedione complex as a starting compound, the reaction giving substituted 1,3-indandione complexes. Crystal structure analyses of three of the complexes prepared are reported.

Tricarbonylchromium(0) complexes **1** and **2** of benzocyclobutenone and benzocyclobutenedione have been used in ring expansion reactions leading to substituted tetralol,[1−6] benzocyclooctenedione, anellated indanone and most recently benzocycloheptenedione complexes.[7−10] In most cases these ring expansions were anion-accelerated and took place at low temperatures.[11] Two features of such chromium complexes facilitated the reactions: Firstly, before the reaction took place, a nucleophilic addition to one or both of the oxo groups took place with formation of an alkoxide. This addition is facilitated by the electron withdrawal of the tricarbonylchromium group and by the rigidity of the anellated four-membered ring. Secondly, additions to the oxo goup strictly take place from the *anti* face of the organic ligand with respect to the tricarbonylchromium group. This renders the transformation diastereoselective and helps to avoid formation of complicated product mixtures.



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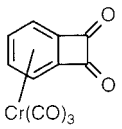

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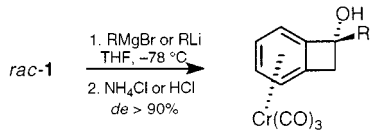
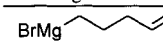
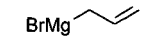
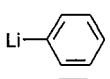
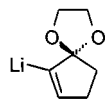
A special aspect is the planar chirality of **1**, which can be tranferred into respective tetralol complexes.[4−6] This is interesting, because racemization has not to be feared as it required unlikely reactions like decomplexation and subsequent recomplexation at the opposite face or an intermolecular exchange process.

Here we report on reactions of **1** and **2** with some carbon nucleophiles,[12] including acyl anion equivalents. Among these reactions is a rare case of an anionic 1-vinylcyclobuten-1-ol−cyclohexadiene rearrangement and reactions leading to 1- and 2-indanone as well as 1,3-indanedione complexes, a class of complexes which we have investigated recently.[13,14]

Grignard and alkyllithium reagents react with **1** at −78°C with diastereoselective formation of *exo*-1-substituted (*endo*-1-benzocyclobutenol)chromium complexes in high yield. As shown in Table 1 and in accord with earlier

Table 1. Nucleophilic addition at **1**



RMgBr or RLi	Compound	Yield (%)
	*rac*-**3**	61
	*rac*-**4**	88
	*rac*-**5**	80
	*rac*-**6**	80

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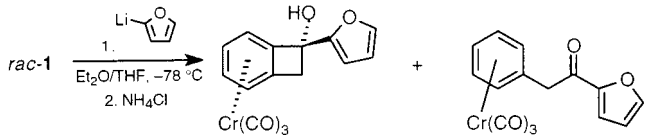
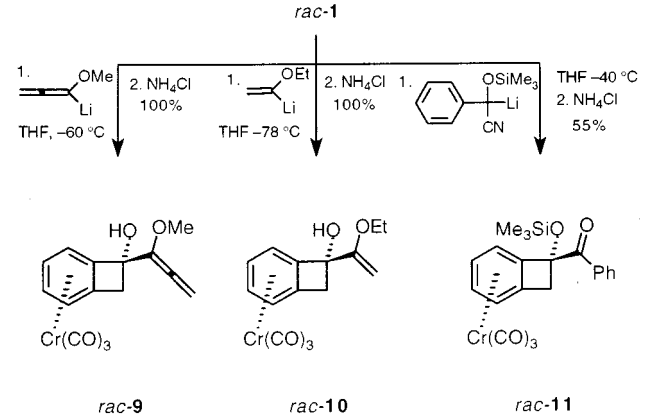
work[12] this is possible with a number of nucleophiles including functionalized ones.

A drawback of this chemistry often is a proximal ring-opening reaction leading to phenylacetic acid derivatives or to corresponding oxo compounds, e.g. **8**. We found that this reaction is favoured by longer reaction times and can thus be prevented to some extent. For example, reaction of *rac*-**1** with 2-lithiofurane gave a mixture of adduct *rac*-**7** (19%) and ring-opening product **8** (60%) when the reaction was allowed to proceed for 60 min. This ratio is reversed when the work up began after 1 min. Then, 63% of *rac*-**7** and 18% of **8** were obtained.



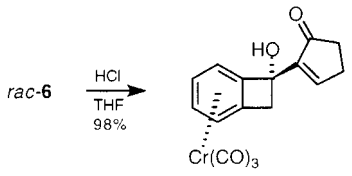
	rac-7	8
60 min:	19%	60%
1 min:	63%	18%

Acyl anion equivalents are more versatile nucleophiles than those used to prepare **3**–**8**, because they provide additional functionality in 1,2 or 1,4 distances.[15] Frequently used acyl anion equivalents are deprotonated enol ethers and anions derived from silyl-protected cyanohydrins. Treatment of *rac*-**1** with 1-lithio-1-methoxyallene and with 1-ethoxy-1-lithioethene at −78°C followed by protonolysis with aqueous ammonium chloride solution gave adducts *rac*-**9** and *rac*-**10** in quantitative yields with complete diastereoselectivity. Cyanohydrin adduct *rac*-**11** was obtained by treatment of *rac*-**1** with 1-lithio-1-phenyl-1-trimethylsiloxyethanenitril at −40°C in 55% yield, also as a single diastereomer.[16–19] *rac*-**9**–*rac*-**11** were characterized spectroscopically.



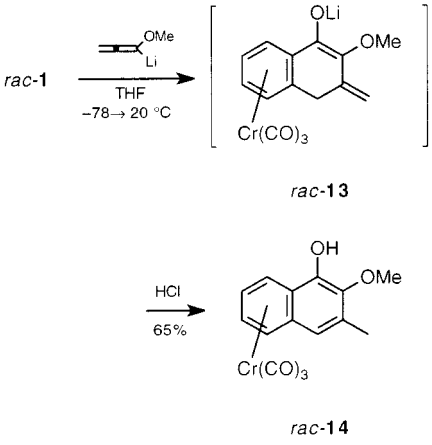
rac-**9** *rac*-**10** *rac*-**11**

rac-**9** and *rac*-**10** can be regarded as 1-alkenyl-2-cyclobuten-1-ols and thus deserve interest as possible starting materials for an alkoxy anion accelerated 1-vinylcyclobutene−cyclohexadiene rearrangement. Thermal rearrangements (110°C) of this kind were investigated with uncoordinated 1-vinylbenzocyclobuten-1-ol and some of its derivatives in connection with syntheses of anthracyclin derivatives.[20–22] Preliminary experiments with tricarbonyl(η^6-*exo*-1-vinylbenzocyclobuten-1-ol)chromium(0) showed that addition of a catalytic amount of butyllithium caused complete consumption of the starting material within 5 min. However, only a complex mixture of products had been obtained, and no tetralone-type product could be detected.[23] Another experiment with a more electron-deficient vinyl moiety was performed with *rac*-**12**, which was obtained from *rac*-**6** by treatment with hydrochloric acid in 98% yield. However, treatment of *rac*-**12** with base proceeded similarly, and although a reaction took place no defined product could be isolated.



rac-**12**

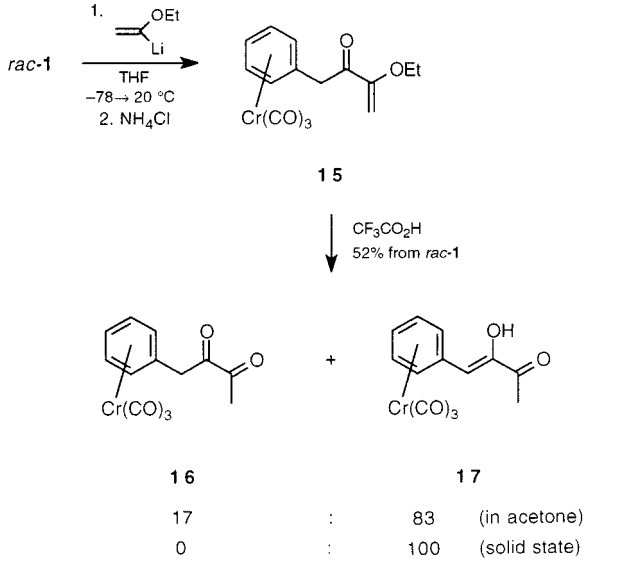
To test, whether an alkyoxy anion accelerated 1-vinylcyclobutene−cyclohexadiene rearrangement was possible with *rac*-**9** or with *rac*-**10** bearing more electron-rich vinyl groups, the reaction mixture obtained from *rac*-**1** was allowed to warm up from −78°C to 20°C before protonolysis. After work up, naphthol complex *rac*-**14** was obtained in 65% yield. Apparently, the desired alkoxy anion accelerated vinylcyclobutene−cyclohexadiene rearrangement had indeed occurred leading to the intermediate *rac*-**13**, which then rearranged to *rac*-**14**, the aromatization of the product presumably serving as the driving force of the reaction.



Whereas a number of alkoxy anion accelerated vinylcyclobutane rearrangements are known which start from 2-vinylcyclobutan-1-ol derivatives, the number of reports of such rearrangements of 1-vinylcyclobutan-1-ols is considerably smaller.[11] The reaction leading to *rac*-**14** is the first example involving a metal complex.

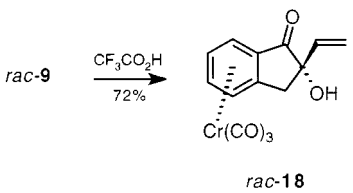
If the aromatization step was neccessary for the rearrangement to occur, the reaction should fail in cases in which such a step is impossible. The result obtained upon treatment of *rac*-**1** with 1-ethoxy-1-lithioethene under identical reaction conditions as in the reaction to *rac*-**14** agrees

with this expectation: Instead of a ring expansion a proximal ring-opening reaction occurred leading to the enol ether **15**, which gave after hydrolysis with trifluoroacetic acid an equilibrium mixture of 1,2-diketone **16** and its enol **17** in 52% yield (from *rac*-**1**). While the ratio of **16** and **17** was 17:83 in acetone, enol **17** is the only isomer present in the solid state.



The (*Z*) configuration of enol **17** was initially confirmed by NOE experiments and is in accord with observations of Jaouen et al. with the tricarbonyl(phenyl ethyl pyruvate)-chromium complex.[24] In addition, an X-ray crystal structure analysis of **17** confirmed the (*Z*) configuration. However, the quality of the crystals was only poor, so that details of the analysis are not published.

As enol ethers or a protected α-oxobenzocyclobutenol *rac*-**9**−*rac*-**11** might be converted into the corresponding carbonyl compounds, which should undergo α-ketol rearrangements leading to indanone complexes. Ring expansions of this kind have been investigated with uncomplexed benzocyclobutenone and other cyclobutenone adducts by Liebeskind,[25] who discussed two possible reaction mechanisms. One way is a direct acid-catalyzed conformation-specific ring expansion, and the other one is a sequence of a conrotatoric ring opening and a conrotatoric electrocyclization. Corresponding ring expansions starting from benzocyclobutenone complex **1** instead of the uncomplexed ligand offer the possibility to form indanone complexes in a defined diastereoselective manner. Therefore, adducts *rac*-**9**−*rac*-**11** were hydrolyzed to give 1-indanone complexes *rac*-**18**, *rac*-**21**, and *rac*-**23**.



Complex *rac*-**18** is obtained as a single diastereomer in 72% yield. The relative configuration at C-2 was determined by X-ray crystal structure analysis (Figure 1), which clearly indicates the *exo* position of the vinyl group. No CO ligand is located below the anellated ring. The anellated ring is almost planar so that the electron withdrawal of the tricarbonylchromium group should activate the oxo group for nucleophilic attack. This is important with respect to dianionic oxy Cope rearrangements of vinylmetal adducts to *rac*-**18**.

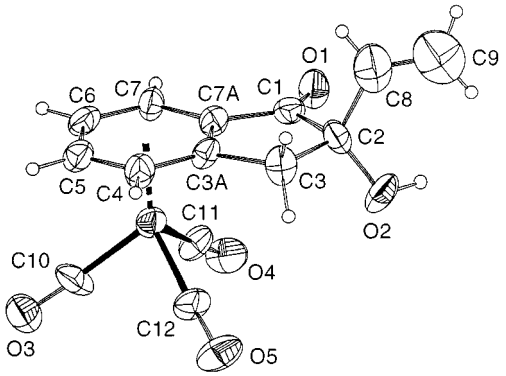
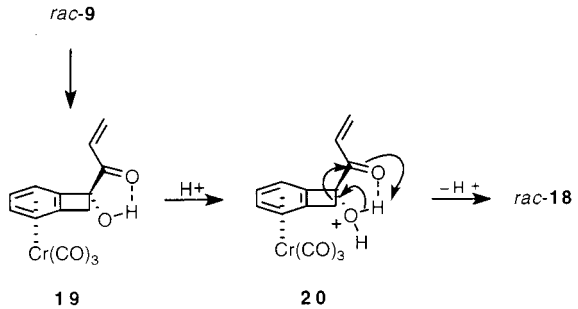


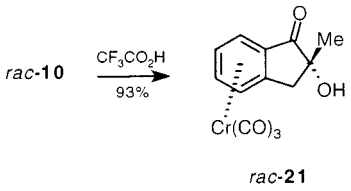
Figure 1. Crystal structure of **18**; selected bond lenghts [Å]: C1−C2 1.582(12), C1−C7A 1.472(11), C1−O1 1.210(10), C2−C3 1.563(12), C2−C8 1.51(2), C2−O2 1.382(14), C3−C3A 1.550(11), C3A−C4 1.359(11), C3A−C7A 1.395(11), C3A−Cr 2.186(9), C4−C5 1.398(12), C4−Cr 2.214(9), C5−C6 1.400(12), C5−Cr 2.195(9), C6−C7 1.398(11), C6−Cr 2.229(9), C7−C7a 1.437(11), C7−Cr 2.229(9), C7A−Cr 2.184(9), C8−C9 1.238(18), C10−Cr 1.836(10), C10−O3 1.160(12), C11−Cr 1.820(9), C11−O4 1.159(11), C12−Cr 1.829(10), C12−O5 1.154(11)

According to Liebeskind[25] the diastereoselectivity of the conformation-specific ring expansion is explained by an intramolecular hydrogen bond in enone *rac*-**19**, which is formed upon hydrolysis of *rac*-**9**. Protonation of the hydroxy oxygen atom gives *rac*-**20**, which then rearranges to product *rac*-**18**.



By treatment of rac-**10** with trifluoroactic acid *rac*-**21** was obtained in 93% yield as one diastereomer, whose relative

configuration was proven by X-ray structure analysis (Figure 2).



rac-**21**

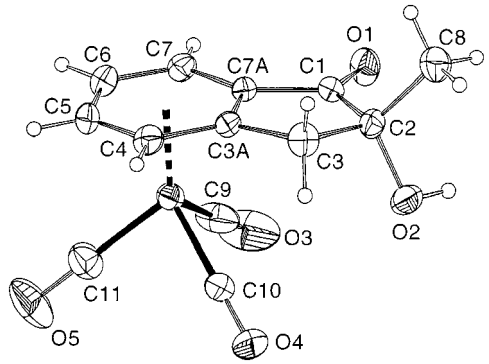
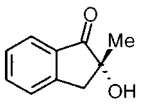


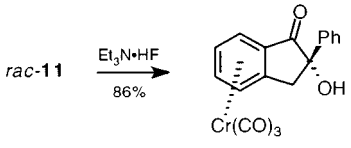
Figure 2. Crystal structure of *rac*-**21**; selected bond lenghts [Å]: C1−C2 1.547(3), C1−C7A 1.470(3), C1−O1 1.214(3), C2−C3 1.533(4), C2−C8 1.515(4), C2−O2 1.418(3), C3−C3A 1.499(4), C3A−C4 1.405(3), C3A−C7A 1.402(3), C3A−Cr 2.209(3), C4−C5 1.401(4), C4−Cr 2.219(3), C5−C6 1.404(4), C5−Cr 2.193(3), C6−C7 1.383(4), C6−Cr 2.218(3), C7−C7A 1.413(3), C7−Cr 2.201(3), C7A−Cr 2.177(2), C9−O3 1.159(5), C9−Cr 1.837(4), C10−O4 1.156(4), C10−Cr 1.838(3), C11−O5 1.162(4), C11−Cr 1.830(3)

When the reaction sequence was carried out starting from enantiomerically pure (2a*R*,6a*S*)-**1**,[26] upon addition of 1-ethoxy-1-lithioethene only one diastereomer of **10** was observed (NMR, *ee* > 90%). Also, upon addition of trifluoroacetic acid, only one diastereomer of **21** was obtained (NMR, *ee* > 90%). However, when the ligand of **21** was oxidatively decoordinated by treatment with air under sunlight irradiation, some racemization was observed, ligand (*R*)-(+)-**22** was obtained in only 78% *ee*,[27] the assignment being made by comparison of the optical rotation values.[28,29]



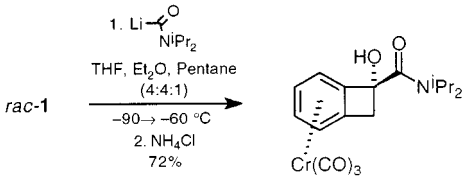
(*R*)-(+)-**22**

Hydrolysis of *rac*-**11** was achieved with triethylamine/hydrogen fluoride and resulted in the phenyl-substituted indanone complex *rac*-**23** in 86% yield. 2 N hydrochloric acid as well as trifluoroacetic acid had not effected the deprotection/rearrangement reaction.

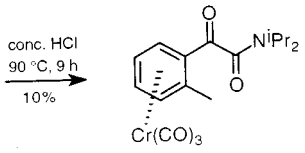


rac-**23**

When *rac*-**1** was treated with lithiated diisopropyl formamide at low temperature followed by aqueous work up, adduct *rac*-**24** was obtained in 72% yield. We hoped that this adduct would undergo the corresponding ring expansion under acidic reaction conditions, which would lead to the 1,2-indandione complex.[14] This would be especially attractive in view of the chiral option starting from an enantiomerically pure benzocyclobutenone complex **1**. However, treatment with diluted hydrochloric acid or trifluoroacetic acid caused no reaction. Finally, heating *rac*-**24** with concentrated hydrochloric acid at 90°C for 9 h led to only 10% yield of distal ring-opening product *rac*-**25** beside 30% of unreacted *rac*-**24**.

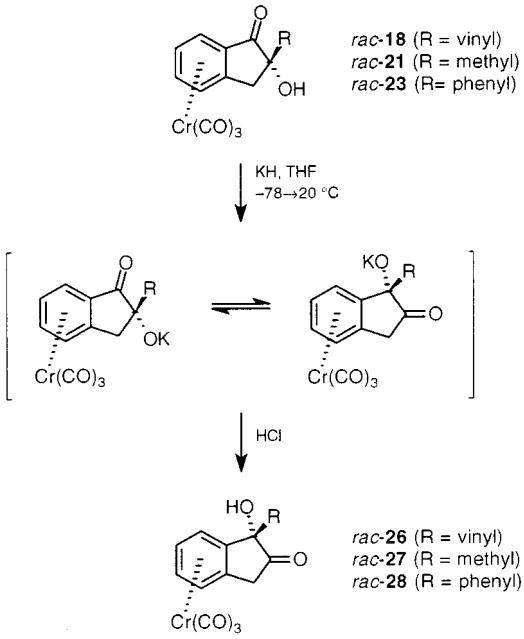


rac-**24**



rac-**25**

Interestingly, it is possible to transform 2-hydroxy-1-indanone complexes to 1-hydroxy-2-indanone complexes by another α-ketol rearrangement, which takes place under basic reaction conditions upon addition of potassium hydride at −78°C and subsequent warming to 20°C (Table 2).

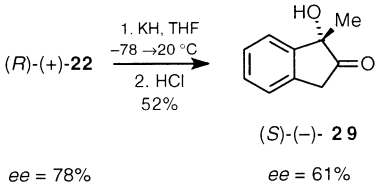


There are interesting differences between these three examples: Whereas the reaction in the methyl case is com-

Table 2. α-Ketol rearrangement of 2-hydroxy-1-indanone complexes

Starting compound **A**	Product **B**	Ratio **A**/**B**	*de* (%) **B**	Yield (%)
rac-**18**	*rac*-**26**	0:100	59	50
rac-**21**	*rac*-**27**	12:88	100	59
rac-**23**	*rac*-**28**	43:57	10	43

pletely diastereoselective, a 12:88 mixture of starting compound and product is obtained. In the vinyl case complete conversion takes place. However, the *de* is only 59%. In the phenyl case only a 43:57 mixture is obtained, and the *de* is small (10%). In addition, in the methyl case, the reaction was performed with the nonracemic ligand (*R*)-(+)-**22** (*de* 78%). Although the diastereoselectity was complete when the corresponding complex was used, the reaction of the ligand caused a decrease in *ee* to 61% for rearranged product (*S*)-(−)-**29**.[30]



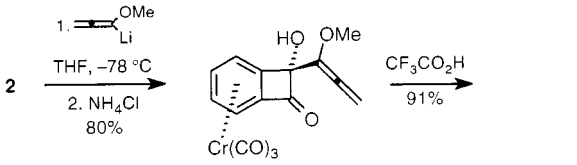
Having demonstrated the possibility to prepare a variety of functionalized 1-indanone and 2-indanone complexes from (η^6-benzocyclobutenone)tricarbonylchromium (**1**) we envisaged the possibility to obtain corresponding 2-substituted 1,3-indandione complexes[13,14,31] when starting from the benzocyclobutenedione complex **2** instead of **1**.

Treatment of **2** with 1.1 equivalents of 1-lithio-1-methoxyallene at −78°C resulted in an 80% yield of single adduct *rac*-**30** after work up with ammonium chloride. Following treatment of *rac*-**30** with trifluoroacetic acid gave the desired ring expansion in 91% overall yield. However, substantial cleavage of the methoxy ether functionality occurred: At 20°C a 60:40 mixture of 1,3-indandione derivatives *rac*-**31** and *rac*-**32** was obtained (*de* 60, 67%, respectively). The ether cleavage could be reduced to some extent at lower temperature: At 0°C a 19:81 mixture was isolated in the same overall yield (*de* > 95, 54%, respectively). The relative configuration of **31** was assigned in analogy to the reactions of **1** on the basis of the mechanism involving a hydrogen bond between the *endo*-hydroxy group in *rac*-**30** and the oxo group liberated upon hydrolysis.[32]

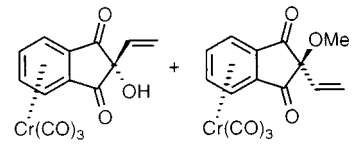
When **2** was treated with 1-lithio-1-ethoxyethene, no trifluoroacetic acid was necessary to effect the ring expansion, the normal workup with ammonium chloride gave a 4.6:1 mixture of diastereomers **33** and **34** in only 38% yield. **33** was characterized by X-ray structure analysis again (Figure 3).

The reaction of **2** with the lithiated imidoyl derivative **35** was less successful. Ring expansion product **36** was isolated in only 24% yield as a 1:1 diastereomeric mixture.[33]

We have presented a number of ring-expansion reactions leading from benzocyclobutene complexes to highly functionalized naphthol, indan-1-one, indan-2-one, and indan-1,3-dione complexes. We currently investigate the chemistry of the complexes obtained, especially under the aspect of

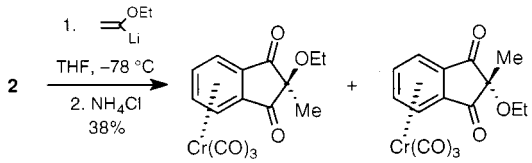


rac-**30**



31 **32**

20 °C	60 (*de* = 60%)	40 (*de* = 67%)
0 °C	19 (*de* > 95%)	81 (*de* = 54%)



33 **34**

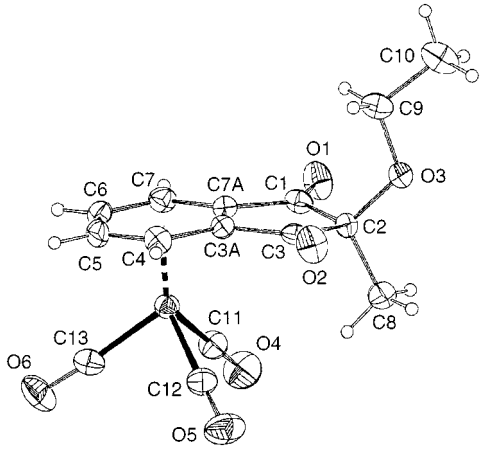
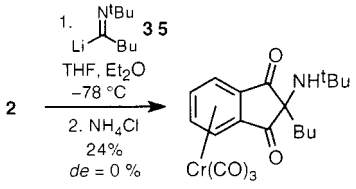


Figure 3. Crystal structure of **33**; selected bond lenghts [Å]: Cr1−C3A 2.168(3), Cr1−C4 2.206(3), Cr1−C5 2.188(3), Cr1−C6 2.184(4), Cr1−C7 2.211(4), Cr1−C7A 2.179(4), C1−C2 1.539(5), C2−C3 1.537(6), C3−C3A 1.485(6), C3A−C4 1.417(6), C4−C5 1.382(6), C5−C6 1.388(7), C6−C7 1.377(7), C7−C7A 1.411(6), C3A−C7A 1.390(6), C1−O1 1.208(5), C3−O2 1.203(5), C2−C8 1.522(4), C2−O3 1.421(4), O3−C9 1.423(4), C9−C10 1.489(5)



36

further selective anionic ring expansions. For these experiments we regard **18**, **26**, and **31** as promising as these complexes already bear a vinyl and a hydroxy functionality next to an oxo group. Addition of alkenylmetal reagents to these complexes might result in dianionic oxy Cope rearrangements leading to functionalized nine-membered ring compounds and their intramolecular aldol adducts.

Experimental Section

General: See ref.[13] – (η⁶-Benzocyclobutenone)tricarbonylchromium(0) (**1**),[2] (η⁶-benzocyclobutenedione)tricarbonylchromium(0) (**2**),[7] methoxyallene,[34] and triethylamine hydrofluoride[18] were synthesized according to literature procedures.

Tricarbonyl[η⁶-1-*endo*-hydroxy-1-*exo*-(4-pentenyl)benzocyclobutene]chromium(0) (*rac*-3): 2.98 mg (20.0 mmol) of 1-bromo-4-pentene in 10 mL of diethyl ether was slowly added to 486 mg (20.0 mmol) of magnesium filings in 5 mL of diethyl ether. The mixture was heated at reflux for 30 min. Then 1.03 g (4.1 mmol) of **1** in 200 mL of diethyl ether was added dropwise at −78°C, the solution becoming yellow. After stirring for 16 h at −78°C, the mixture was hydrolyzed by addition of 10 mL of 1 N hydrochloric acid. After warming to 20°C, the layers were separated, and the aqueous layer was extracted twice with 20 mL of diethyl ether each. The combined organic layers were washed with water, and after drying with magnesium sulfate the solvent was removed under reduced pressure. After purification by column chromatography (270 × 30 mm, diethyl ether/petroleum ether, 1:1), 812 mg (2.5 mmol, 61%) of *rac*-**3** was obtained as a yellow oil (purity > 95%, NMR). – IR ($CHCl_3$): $\tilde{\nu}$ = 2936 (w) cm^{-1}, 1972 (s, CO), 1900 (s, CO), 1716 (w), 1228 (w), 996 (w), 916 (w), 628 (m), 532 (w). – ^1H NMR (200.1 MHz, $CDCl_3$): δ = 1.67 (m, 2 H, 8-H), 1.86 (m, 2 H, 7-H), 2.10 (m, 2 H, 9-H), 3.09 (d, 1 H, *exo*-2-H or *endo*-2-H, $^2J_{exo\text{-}2,endo\text{-}2}$ = −14.4 Hz), 3.24 (d, 1 H, *exo*-2-H or *endo*-2-H), 3.46 (s, 1 H, OH), 5.96 (m, 2 H, 11-H), 5.16 (d, 1 H, 3-H or 6-H, ^3J = 6.0 Hz), 5.39 (m, 2 H, 4-H, 5-H), 5.70 (d, 1 H, 3-H or 6-H, ^3J = 6.0 Hz), 5.83 (m, 1 H, 10-H). – ^{13}C NMR (100.6 MHz, [D₆]acetone): δ = 24.8 (+, C-8), 34.5 (+, C-7), 39.8 (+, C-9), 46.4 (+, C-2), 79.3 (−, C-1), 89.3 (−, C-3 or C-4 or C-5 or C-6), 89.6 (−, C-3 or C-4 or C-5 or C-6), 91.2 (−, C-3 or C-4 or C-5 or C-6), 96.0 (−, C-3 or C-4 or C-5 or C-6), 115.1 (+, C-6a), 115.4 (+, C-11), 124.3 (+, C-2a), 139.4 (−, C-10), 234.6 (+, CO). – MS (70 eV, 120°C): *m/z* (%) = 324 (1) [M^+], 323 (2) [M^+ − 1], 240 (5) [M^+ − 3 CO], 222 (1), 188 (15), 134 (18), 119 (50), 97 (83), 91 (70), 69 (100).

Tricarbonyl[η⁶-1-*endo*-hydroxy-1-*exo*-(2-propenyl)benzocyclobutene]chromium(0) (*rac*-4): A −78°C cold solution of 1.71 g (6.7 mmol) of **1** in 40 mL of THF was slowly added to a −78°C cold solution of 10 mmol of allylmagnesium bromide in 50 mL of THF. The orange solution immediately became yellow. After stirring at −78°C for 30 min, the mixture was hydrolyzed by addition of 10 mL of 0.1 M hydrochloric acid. After warming to 20°C, the mixture was extracted three times with 50 mL of diethyl ether each. The combined organic layers were washed with 50 mL of water, and then dried with magnesium sulfate. After solvent removal at reduced pressure and purification by filtration through a silica column (150 × 40 mm, diethyl ether/petroleum ether, 1:1), 1.74 g (5.88 mmol, 88%) of *rac*-**4** was obtained as a yellow oil. – IR ($CHCl_3$): $\tilde{\nu}$ = 2980 (w) cm^{-1}, 1968 (s, CO), 1900 (s, CO), 1640 (m), 1392 (m), 1348 (m), 1160 (w), 1128 (w), 1096 (w), 1056 (m), 996 (w), 924 (m), 628 (s). – ^1H NMR (400.1 MHz, [D₆]acetone): δ = 2.66 (m, 2 H, 7-H), 3.08 (d, 1 H, *exo*-2-H or *endo*-2-H, $^2J_{endo\text{-}2,exo\text{-}2}$ = −13.9 Hz), 3.25 (d, 1 H, *exo*-2-H or *endo*-2-H), 5.11 (d, 1 H, 9-H, ^3J = 10.3 Hz), 5.16 (d, 1 H, 9-H, ^3J = 17.2 Hz), 5.21 (dd, 1 H, 4-H or 5-H, ^3J = 6.1 Hz, ^3J = 6.1 Hz), 5.57 (dd, 1 H, 4-H or 5-H, ^3J = 6.1 Hz, ^3J = 6.1 Hz), 5.62 (d, 1 H, 3-H or 6-H, ^3J = 6.1 Hz), 5.86 (d, 1 H, 3-H or 6-H, ^3J = 6.1 Hz), 5.95 (dd, 1 H, 8-H, ^3J = 17.2 Hz, ^3J = 10.3 Hz). – ^{13}C NMR (100.6 MHz, [D₆]acetone): δ = 43.5 (+, C-2 or C-7), 44.7 (+, C-2 or C-7), 77.7 (+, C-1), 88.1 (−, C-3 or C-4 or C-5 or C-6), 88.5 (−, C-3 or C-4 or C-5 or C-6), 90.2 (−, C-3 or C-4 or C-5 or C-6), 94.8 (−, C-3 or C-4 or C-5 or C-6), 113.5 (+, C-2a or C-6a), 117.6 (+, C-9), 122.2 (+, C-2a or C-6a), 133.4 (−, C-8), 233.5 (+, CO). – MS (70 eV, 80°C): *m/z* (%) = 297 (38) [M^+ + 1], 296 (48) [M^+], 268 (9) [M^+ − CO], 240 (44) [M^+ − 2 CO], 212 (100) [M^+ − 3 CO], 194 (46), 184 (43), 167 (40), 141 (55), 128 (55), 119 (96), 103 (26), 91 (90), 77 (39), 70 (64). – HRMS ($C_{14}H_{12}CrO_4$): calcd. 296.014069, found 296.014435.

Tricarbonyl(η⁶-1-*endo*-hydroxy-1-*exo*-phenylbenzocyclobutene)chromium(0) (*rac*-5): At −78°C 236 mg (0.93 mmol) of **1** in 5 mL of THF was slowly added to 2 mL (1.58 mmol) of a 0.79 M solution of phenyllithium in THF. Upon addition the mixture became yellow, later red-brown. The mixture was hydrolyzed after 5 min at −78°C by addition of 5 mL of a saturated aqueous solution of ammonium chloride. After warming to 20°C, 10 mL of water was added. The mixture was extracted three times with 10 mL of diethyl ether each, and the combined organic layers were washed two times with 10 ml of water each. After solvent removal at reduced pressure and purification by column chromatography (200 × 20 mm, diethyl ether/petroleum ether, 1:3), 247 mg (0.74 mmol, 80%) of *rac*-**5** was obtained as a yellow oil. – IR ($CHCl_3$): $\tilde{\nu}$ = 3576 (w,OH) cm^{-1}, 1972 (s, CO), 1904 (s, CO), 1448 (w), 1184 (m), 1144 (m), 1104 (m), 1076 (w), 1056 (m), 624 (s), 532 (w). – ^1H NMR (400.1 MHz, [D₆]acetone): δ = 3.49 (s, 2 H, *exo*-2-H, *endo*-2-H), 5.23 (ddd, 1 H, 4-H or 5-H, ^3J = 5.9 Hz, ^3J = 5.7 Hz, ^4J = 0.7 Hz), 5.37 (s, 1 H, OH), 5.61 (ddd, 1 H, 4-H or 5-H, ^3J = 5.9 Hz, ^3J = 5.7 Hz, ^4J = 0.7 Hz), 5.68 (d, 1 H, 3-H or 6-H, ^3J = 5.7 Hz), 5.96 (d, 1 H, 3-H or 6-H, ^3J = 5.9 Hz), 7.43 [m, 5 H, 8(8′)-H, 9(9′)-H, 10-H]. – ^{13}C NMR (100.6 MHz, [D₆]acetone): δ = 48.3 (+, C-2), 79.0 (+, C-1), 87.7 (−, C-3 or C-4 or C-5 or C-6), 88.5 (−, C-3 or C-4 or C-5 or C-6), 90.6 (−, C-3 or C-4 or C-5 or C-6), 94.9 (−, C-3 or C-4 or C-5 or C-6), 114.1 (+, C-6a), 122.2 (+, C-2a), 125.3 [−, C-8(8′) or C-9(9′)], 127.2 (−, C-10), 127.9 [−, C-8(8′) or C-9(9′)], 143.2 (+, C-7), 233.3 (+, CO). – MS (70 eV, 90°C): *m/z* (%) = 333 (4) [M^+ + 1], 332 (9) [M^+], 276 (11) [M^+ − 2 CO], 248 (35) [M^+ − 3 CO], 230 (24), 195 (8), 179 (32), 165 (4), 152 (7), 115 (4), 105 (8), 85 (8), 77 (19), 69 (13), 52 (100). – HRMS ($C_{17}H_{12}CrO_4$): calcd. 332.014069, found 332.013275.

Tricarbonyl{η⁶-1-*exo*-[5-(ethylenedioxy)-1-cyclopentenyl]-1-*endo*-hydroxybenzocyclobutene}chromium(0) (*rac*-6): At −78°C 2.5 mL (3.99 mmol) of a 1.6 M solution of butyllithium in hexane was added to 818 mg (3.99 mmol) of 1-bromo-5-(ethylenedioxy)-1-cyclopentene in 10 mL of THF. After stirring for 25 min at −78°C, 692 mg (2.72 mmol) of **1** in 10 mL of THF was added dropwise. After stirring for 4 h at −78°C, the mixture was hydrolyzed by addition of 5 mL of a saturated aqueous solution of ammonium chloride. After addition of 20 mL of diethyl ether and 10 mL of water, the layers were separated, and the aqueous layer was extracted twice with 10 mL of diethyl ether each. The combined organic layers were washed twice with 20 mL of water each. After solvent removal at reduced pressure an purification by column chromatography (200 × 40 mm, diethyl ether/petroleum ether, 1:3, later 3:1), 780 mg (2.05 mmol, 80% of *rac*-**6** was obtained as a yellow solid (m. p. 96°C, DSC). – IR (KBr): $\tilde{\nu}$ = 3472 (w) cm^{-1}, 3028 (w), 2948 (w), 1968 (s, CO), 1900 (s, CO), 1428 (w), 1400 (w), 1328 (m), 1228 (m), 1184 (w), 1152 (m), 1128 (m), 1044 (m), 1016 (m), 948 (m), 536

(m). − ^{1}H NMR (200.1 MHz, [D$_6$]acetone): δ = 2.20 (m, 2 H, CCH_2CH$_2$), 2.30 (m, 2 H, =CHCH_2CH$_2$), 3.15 (d, 1 H, *exo*-2-H or *endo*-2-H, $^2J_{endo\text{-}2,exo\text{-}2}$ = −13.8 Hz), 3.65 (d, 1 H, *exo*-2-H or *endo*-2-H), 3.87 (m, 4 H, OCH_2CH_2O), 4.89 (s, 1 H, OH), 5.19 (ddd, 1 H, 4-H or 5-H, ^3J = 5.9 Hz, ^3J = 5.9 Hz, ^4J = 2.0 Hz), 5.58 (ddd, 1 H, 4-H or 5-H, ^3J = 6.0 Hz, ^3J = 5.9 Hz, ^4J = 0.7 Hz), 5.60 (dd, 1 H, 3-H or 6-H, ^3J = 5.9 Hz, ^4J = 0.7 Hz), 5.90 (d, 1 H, 3-H or 6-H, ^3J = 6.0 Hz), 6.22 (t, 1 H, =C*H*CH$_2$, ^3J = 2.4 Hz). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 26.5 (+, CCH_2CH$_2$), 35.9 (+, =CHCH$_2$CH$_2$), 46.3 (+, C-2), 63.7 (+, OCH_2CH_2O), 64.0 (+, OCH_2CH_2O), 76.0 (+, C-1), 87.3 (−, C-3 or C-4 or C-5 or C-6), 87.9 (−, C-3 or C-4 or C-5 or C-6), 91.5 (−, C-3 or C-4 or C-5 or C-6), 94.7 (−, C-3 or C-4 or C-5 or C-6), 114.6 (+, C_{spiro}), 119.2 (+, C-2a or C-6a), 121.2 (+, C-2a or C-6a), 134.3 (−, =*C*HCH$_2$), 141.2 (+, C-7), 233.3 (+, CO). − MS (70 eV, 120°C): *m*/*z* (%) = 381 (9) [M$^+$ + 1], 380 (28) [M$^+$], 352 (1) [M$^+$ − CO], 324 (39) [M$^+$ − 2 CO], 296 (36) [M$^+$ − 3 CO], 278 (23), 268 (42), 249 (35), 234 (41), 218 (33), 194 (35), 183 (35), 167 (100), 152 (40), 128 (36), 115 (41), 91 (35), 69 (49). − HRMS ($C_{18}H_{16}CrO_6$): calcd. 378.040735, found 378.040230. − $C_{18}H_{16}CrO_6$ (380.32): calcd. C 56.85, H 4.24, found C 56.61, H 4.29.

Reaction of 1 with 2-Lithiofurane: At −78°C 1.88 mL (3.0 mmol) of a 1.6 M solution of butyllithium in hexane was added to 370 μL (347 mg, 5.1 mmol) of furane in 10 mL of diethyl ether. The mixture was allowed to warm to 20°C and was then again cooled to −78°C. 259 mg (1.02 mmol) of **1** in 5 mL of THF was added dropwise. The reaction was monitored by TLC (diethyl ether/petroleum ether, 1:1). First a yellow product was formed (R_f = 0.46) which then reacted to a new product (R_f = 0.26). After 60 min, the mixture was hydrolyzed by addition of 20 mL of a saturated aqueous solution of ammonium chloride. After warming to 20°C, the layers were separated, and the aqueous layer was extracted twice with 5 mL of diethyl ether each. The collected organic layers were washed twice with 20 mL of water. After solvent removal at reduced pressure, the products were separated by column chromatography (200 × 20 mm, diethyl ether/petroleum ether, 1:1). Fraction I: 64 mg (0.20 mmol, 19%) of tricarbony[η^6-1-*exo*-(2-furanyl)-1-*endo*-hydroxybenzocyclobutene]chromium(0) (*rac*-**7**, yellow oil). Fraction II: 198 mg (0.61 mmol, 60%) of tricarbony[η^6-1-(2-furanyl)-2-phenylethanone]chromium(0) (**8**, yellow solid, m. p. 141°C). When the hydrolysis was performed after 1 min under otherwise identical reaction conditions, 65% of *rac*-**7** and 18% of **8** were obtained.

***rac*-7:** IR ($CHCl_3$): ṽ = 3576 (w, OH) cm^{-1}, 1976 (s, CO), 1904 (s, CO), 1420 (w), 1392 (w), 1344 (w), 1228 (w), 1152 (m), 1108 (m), 1072 (w), 1056 (w), 532 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.39 (d, 1 H, *exo*-2-H or *endo*-2-H, $^2J_{endo\text{-}2,exo\text{-}2}$ = −13.9 Hz), 3.64 (d, 1 H, *exo*-2-H or *endo*-2-H), 5.22 (ddd, 1 H, 4-H or 5-H, ^3J = 6.3 Hz, ^3J = 6.1 Hz, ^4J = 1.0 Hz), 5.59 (ddd, 1 H, 4-H or 5-H, ^3J = 6.3 Hz, ^3J = 6.3 Hz, ^4J = 0.7 Hz), 5.65 (s, 1 H, O*H*), 5.67 (d, 1 H, 3-H or 6-H, ^3J = 6.3 Hz), 5.95 (d, 1 H, 3-H or 6-H, ^3J = 6.1 Hz), 6.39 (dd, 1 H, C=CHC*H*CH, ^3J = 3.5 Hz, ^3J = 1.8 Hz), 6.45 (d, 1 H, C=C*H*CHCH, ^3J = 3.5 Hz), 7.51 (d, 1 H, C=CHCHC*H*, ^3J = 1.8 Hz). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 45.9 (+, C-2), 74.4 (+, C-1), 88.9 (−, C-3 or C-4 or C-5 or C-6), 88.6 (−, C-3 or C-4 or C-5 or C-6), 90.3 (−, C-3 or C-4 or C-5 or C-6), 94.8 (−, C-3 or C-4 or C-5 or C-6), 106.5 (−, C-9), 110.1 (−, C-8), 114.2 (+, C-2a or C-6a), 120.3 (+, C-2a or C-6a), 142.5 (−, C-10), 155.4 (+, C-7), 233.4 (+, CO). − MS (70 eV, 130°C): *m*/*z* (%) = 323 (7) [M$^+$ + 1], 322 (23) [M$^+$], 266 (20) [M$^+$ − 2 CO], 238 (55) [M$^+$ − 3 CO], 220 (31), 210 (6), 186 (10), 169 (100), 153 (17), 140 (20), 115 (28), 95 (27), 91 (31), 69 (10), 52 (77). − HRMS ($C_{15}H_{10}CrO_5$): calcd. 321.993333, found 321.992218.

8: IR (KBr): ṽ = 1952 (s, CO) cm^{-1}, 1888 (s, CO), 1864 (s, CO), 1676 (m), 1572 (m), 1468 (m), 1332 (m), 1152 (w), 1028 (w), 1016 (w), 900 (w), 852 (m), 772 (m), 664 (m), 632 (m), 596 (w), 540 (m), 480 (m). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 4.02 (s, 2 H, 2-H), 5.55 (m, 1 H, *p*-H) 5.64 (m, 2 H, *m*-H), 5.70 (t, 2 H, *o*-H, *J* = 6.4 Hz), 6.71 (dd, 1 H, =CHC*H*CH, ^3J = 3.5 Hz, ^3J = 1.5 Hz), 7.48 (d, 1 H, =C*H*CHCH, ^3J = 3.5 Hz), 7.88 (d, 1 H, =CHCHC*H*, ^3J = 1.5 Hz). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 43.2 (+, C-2), 92.3 (−, *p*-C), 94.5 (−, *o*-C or *m*-C), 95.3 (−, *o*-C or *m*-C), 106.2 (+, *ipso*-C), 112.3 (−, =CH*C*HCH), 118.0 (−, =C*H*CHCH), 147.3 (−, =CHCH*C*H), 151.8 (+, *C*=CHCHCH), 183.9 (+, C-1), 233.4 (+, CO). − MS (70 eV, 130°C): *m*/*z* (%) = 322 (1) [M$^+$], 294 (5) [M$^+$ − CO], 266 (13) [M$^+$ − 2 CO], 238 (100) [M$^+$ − 3 CO], 210 (10), 180 (5), 147 (50), 132 (5), 118 (12), 95 (9), 52 (52). − HRMS ($C_{15}H_{10}CrO_5$): calcd. 321.993333, found 321.992371. − $C_{15}H_{10}CrO_5$ (322.24): calcd. C 55.91, H 3.13, found C 55.88, H 3.14.

Tricarbonyl[η^6-1-*endo*-hydroxy-1-*exo*-(1-methoxyallenyl)benzocyclobutene]chromium(0) (*rac*-9): To a stirred solution of 183 mg (2.61 mmol) of methoxyallene in 5 mL of diethyl ether under argon at −78°C was added dropwise 1.63 mL (2.61 mmol) of a 1.6 M solution of butyllithium in hexanes. After warm up to −30°C (30 min), a solution of 449 mg (1.77 mmol) **1** in 8 mL of anhydrous THF was slowly added at −78°C. After 10 min, the reaction was quenched by addition of a saturated aqueous solution of ammonium chloride (5 mL). Aqueous work up gave *rac*-**9** as a yellow oil (573 mg, 1.77 mmol, 100%). − IR ($CHCl_3$): ṽ = 3568 (w) cm^{-1}, 2976 (w), 2960 (w), 2936 (w), 1972 (s), 1900 (s), 1600 (w), 1460 (w), 1188 (m), 1140 (m), 1116 (m), 1080 (w), 1056 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.14 (d, 1 H, *exo*-2-H or *endo*-2-H, $^2J_{exo\text{-}2,endo\text{-}2}$ = −13.8 Hz), 3.42 (s, 3 H, CH_3), 3.46 (d, 1 H, *exo*-2-H or *endo*-2-H), 5.12 (dd, 1 H, 4-H or 5-H, ^3J = 6.2 Hz, ^3J = 6.1 Hz), 5.29 (s, 1 H, OH), 5.51 (dd, 1 H, 4-H or 5-H, ^3J = 6.2 Hz, ^3J = 6.2 Hz), 5.54 (d, 1 H, 9-H, ^2J = 8.3 Hz), 5.56 (d, 1 H, 3-H or 6-H, ^3J = 6.1 Hz), 5.58 (d, 1 H, 9-H, ^2J = 8.3 Hz), 5.81 (d, 1 H, 3-H or 6-H, ^3J = 6.2 Hz). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 44.3 (+, C-2), 55.5 (−, CH_3), 76.1 (+, C-1), 87.1 (−, C-3 or C-4 or C-5 or C-6), 87.7 (−, C-3 or C-4 or C-5 or C-6), 90.4 (−, C-3 or C-4 or C-5 or C-6), 92.0 (+, C-9), 94.2 (−, C-3 or C-4 or C-5 or C-6), 114.1 (+, C-2a), 119.7 (+, C-6a), 134.8 (+, C-7), 196.2 (+, C-8), 232.9 (+, CO). − MS (70 eV, 80°C): *m*/*z* (%) = 325 (17) [M$^+$ + 1], 324 (60) [M$^+$], 268 (33) [M$^+$ − 2 CO], 240 (100) [M$^+$ − 3 CO], 224 (34), 210 (58), 208 (80), 192 (36), 171 (22), 153 (9), 139 (85), 128 (41), 15 (31), 100 (11), 91 (18), 69 (29). − HRMS ($C_{15}H_{12}CrO_5$): calcd. 324.008983, found 324.008057.

Tricarbonyl[η^6-1-*exo*-(1-ethoxyethenyl)-1-*endo*-hydroxybenzocyclobutene]chromium(0) (*rac*-10): To a stirred solution of 300 mg (4.17 mmol) of ethyl vinyl ether in 7 mL of THF under argon at −78°C was added dropwise 2.00 mL (3.20 mmol) of a 1.6 M solution of butyllithium in hexanes. After warm up to 20°C (30 min), a solution of 136 mg (0.54 mmol) of **1** in 7 mL of anhydrous THF was slowly added at −78°C. After 10 min, the reaction was hydrolyzed by addition of 5 mL of a saturated aqueous solution of ammonium chloride. Aqueous work up gave *rac*-**10** as a yellow oil (175 mg, 0.54 mmol, 100%). − IR ($CHCl_3$): ṽ = 3564 (w) cm^{-1}, 2980 (w), 1972 (s), 1900 (s), 1628 (w), 1420 (w), 1396 (w), 1268 (w), 1232 (w), 1116 (m), 1068 (m), 820 (w), 624 (m), 532 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.23 (t, 3 H, CH_3, ^3J = 7.0 Hz), 3.13 (d, 1 H, *exo*-2-H or *endo*-2-H, $^2J_{endo\text{-}2,exo\text{-}2}$ = −13.7 Hz), 3.50 (d, 1 H, *exo*-2-H or *endo*-2-H), 3.78 (q, 2 H, CH_2CH$_3$, ^3J = 7.0 Hz), 4.16

(d, 1 H, =CH_2, ^2J = 2.4 Hz), 4.47 (d, 1 H, =CH_2, ^2J = 2.4 Hz), 5.20 (ddd, 1 H, 4-H or 5-H, ^3J = 6.2 Hz, ^3J = 6.2 Hz, ^4J = 1.3 Hz), 5.28 (s, 1 H, OH), 5.58 (ddd, 1 H, 4-H or 5-H, ^3J = 6.2 Hz, ^3J = 6.2 Hz, ^4J = 0.7 Hz), 5.63 (dd, 1 H, 3-H or 6-H, ^3J = 6.2 Hz, ^4J = 1.1 Hz), 5.88 (dd, 1 H, 3-H or 6-H, ^3J = 6.2 Hz, ^4J = 0.7 Hz). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 13.2 (−, CH_3), 44.7 (+, C-2), 77.8 (+, C-1), 81.3 (+, C=*C*H_2), 87.2 (−, C-3 or C-4 or C-5 or C-6), 88.1 (−, C-3 or C-4 or C-5 or C-6), 90.4 (−, C-3 or C-4 or C-5 or C-6), 94.6 (−, C-3 or C-4 or C-5 or C-6), 114.8 (+, C-2a), 120.5 (+, C-6a), 162.0 (+, *C*=CH_2), 233.3 (+, CO). − MS (70 eV, 110°C): *m*/*z* (%) = 326 (10) [M$^+$], 270 (8) [M$^+$ − 2 CO], 242 (22) [M$^+$ − 3 CO], 213 (7), 198 (27), 196 (18), 180 (14), 143 (9), 128 (10), 115 (6), 91 (8), 69 (13), 52 (100). − HRMS ($C_{15}H_{14}CrO_5$): calcd. 326.024633, found 326.024017.

Tricarbonyl[η^6-1-*exo*-(benzoyl)-1-*endo*-(trimethylsilyloxy)-benzocyclobutene]chromium(0) (*rac*-11): To a stirred solution of 133 mg (1.32 mmol) of diisopropylamine in 2 mL of DME at 0°C was added dropwise 0.82 mL (1.32 mmol) of a 1.6 M solution of butyllithium in hexanes. After 20 min at −78°C, a solution of 245 mg (1.20 mmol) of 1-phenyl-1-(trimethylsiloxy)acetonitrile in 1 mL of DME was added, the solution became orange-brown. After 10 min, a solution of 304 mg (1.20 mmol) of **1** in 3 mL of DME was slowly added. After warm up to −40°C (60 min), the reaction was quenched by addition of a saturated aqueous solution of ammonium chloride (5 mL). Aqueous work up and purification by column chromatography on silica gel (200 × 20 mm, diethyl ether/petroleum, ether 1:1) gave 285 mg (0.66 mmol, 55%) of **22** as a yellow solid (m. p. 149°C, DSC). − IR (KBr): $\tilde{\nu}$ = 2960 (w) cm^{-1}, 1956 (s, CO), 1876 (s, CO), 1676 (s, CO), 1448 (w), 1416 (w), 1252 (m), 1224 (m), 1172 (m), 972 (w), 888 (m), 844 (m), 748 (w), 660 (m), 632 (m), 532 (w). − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.05 [s, 9 H, Si(Me)$_3$], 3.23 (d, 1 H, *exo*-2-H or *endo*-2-H, $^2J_{endo\text{-}2,exo\text{-}2}$ = −13.8 Hz), 4.12 (d, 1 H, *exo*-2-H or *endo*-2-H), 4.87 (dd, 1 H, 3-H or 6-H, ^3J = 6.2 Hz, ^3J = 6.2 Hz), 5.28 (dd, 1 H, 3-H or 6-H, ^3J = 6.2 Hz, ^3J = 6.2 Hz), 5.36 (d, 1 H, 4-H or 5-H, ^3J = 6.2 Hz), 5.59 (d, 1 H, 4-H or 5-H, ^3J = 6.2 Hz), 7.56 u. 8.22 [m, 5 H, 9(9′)-H, 10(10′)-H, 11-H]. − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 1.6 (−, $SiMe_3$), 43.3 (+, C-2), 84.7 (+, C-1), 87.3 (−, C-3 or C-4 or C-5 or C-6), 88.1 (−, C-3 or C-4 or C-5 or C-6), 91.1 (−, C-3 or C-4 or C-5 or C-6), 94.0 (−, C-3 or C-4 or C-5 or C-6), 114.7 (+, C-2a), 117.8 (+, C-6a), 129.3 [−, C-9(9′) or C-10(10′)], 131.0 [−, C-9(9′) or C-10(10′)], 134.1 (+, C-8), 134.5 (−, C-11), 196.9 (+, CO), 233.4 (+, CO). − MS (70 eV, 130°C): *m*/*z* (%) = 433 (2) [M$^+$ + 1], 432 (5) [M$^+$], 431 (15) [M$^+$ − 1], 376 (5) [M$^+$ − 2 CO], 348 (70) [M$^+$ − 3 CO], 333 (99), 317 (44), 303 (16), 258 (15), 203 (8), 191 (12), 178 (10), 126 (62), 112 (9), 96 (8), 73 (31), 52 (100). − HRMS ($C_{19}H_{20}CrO_3Si$, [M$^+$ − 2 CO]): calcd. 376.058683, found 376.054626.

Tricarbonyl[η^6-2-*exo*-(5-oxo-1-cyclopentenyl)-2-*endo*-hydroxy-benzocyclobutene]chromium(0) (*rac*-12): 10 mL of 1 N hydrochloric acid was added to 680 mg (1.79 mmol) of *rac*-**6** in 10 mL of THF. After stirring at 20°C for 30 min, 20 mL of water and 20 mL of diethyl ether was added. The aqueous layer was extracted twice with 5 mL of diethyl ether each, and the combined organic layers were washed twice with 10 mL of water each. After solvent removal at reduced pressure, 591 mg (1.76 mmol, 98%) of *rac*-**12** was obtained as a yellow solid (m. p. 145°C, DSC). − IR (KBr): $\tilde{\nu}$ = 3400 (m) cm^{-1}, 3348 (m), 1956 (s, CO), 1876 (s, CO), 1688 (m), 1420 (w), 1320 (w), 1260 (w), 1200 (w), 792 (w), 664 (m), 628 (m), 532 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.40 (m, 2 H, =CHCH_2), 2.63 (m, 2 H, =CHCH$_2$CH_2), 3.22 (d, 1 H, *exo*-2-H or *endo*-2-H, $^2J_{endo\text{-}2,exo\text{-}2}$ = −13.9 Hz), 3.59 (d, 1 H, *exo*-2-H or *endo*-2-H), 5.12 (s, 1 H, O*H*), 5.17 (dd, 1 H, 4-H or 5-H, ^3J = 5.9 Hz, ^3J = 5.9 Hz), 5.58 (dd, 1 H, 4-H or 5-H, ^3J = 6.1 Hz, ^3J = 5.9 Hz), 5.61 (d, 1 H, 3-H or 6-H, ^3J = 5.9 Hz), 5.88 (d, 1 H, 3-H or 6-H, ^3J = 6.1 Hz), 7.80 (t, 1 H, =C*H*CH$_2$, ^3J = 2.3 Hz). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 26.7 (+, =CHCH$_2$*C*H$_2$), 34.9 (+,=CH*C*H$_2$CH$_2$), 45.3 (+, C-2), 74.6 (+, C-1), 87.5 (−, C-3 or C-4 or C-5 or C-6), 88.3 (−, C-3 or C-4 or C-5 or C-6), 91.0 (−, C-3 or C-4 or C-5 or C-6), 95.1 (−, C-3 or C-4 or C-5 or C-6), 115.0 (+, C-2a or C-6a), 120.7 (+, C-2a or C-6a), 145.5 (+, C-7), 159.6 (−, *C*=CHCH$_2$), 206.4 [+, C*C*(O)CH$_2$], 233.5 (+, CO). − MS (70 eV, 130°C): *m*/*z* (%) = 337 (15) [M$^+$ + 1], 336 (36) [M$^+$], 280 (39) [M$^+$ − 2 CO], 252 (67) [M$^+$ − 3 CO], 234 (37), 224 (38), 196 (37), 183 (27), 167 (100), 152 (42), 128 (36), 115 (40), 105 (16), 91 (37), 69 (38). − HRMS ($C_{16}H_{12}CrO_5$): calcd. 334.014520, found 334.015784. − $C_{16}H_{12}CrO_5$ (336.26): calcd. C 57.15, H 3.60, found C 57.06, H 3.62.

Tricarbonyl(η^6-1-hydroxy-2-methoxy-3-methylnaphthalene)-chromium(0) (*rac*-14): To a stirred solution of 100 mg (1.43 mmol) of methoxyallene in 5 mL of diethyl ether under argon at −78°C was added dropwise 0.89 mL (1.43 mmol) of a 1.6 M solution of butyllithium in hexane. After warm up to −30°C (30 min), a solution of 309 mg (1.22 mmol) **1** in 10 mL of anhydrous THF was slowly added at −78°C. After warm up to 20°C (16 h), the reaction was quenched at −78°C by addition of 5 mL of 2 N hydrochloric acid. Aqueous work up and chromatography on silica gel in diethyl ether/petroleum ether (3:1) gave 255 mg (0.79 mmol, 65%) of naphthol complex *rac*-**14** as a red solid (m. p. 145°C, DSC). − IR (KBr): $\tilde{\nu}$ = 3400 (s) cm^{-1}, 1968 (s), 1876 (s), 1860 (s), 1452 (w), 1396 (w), 1260 (w), 1232 (w), 1072 (m), 672 (m), 624 (m), 528 (m). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.37 (d, 3 H, CH_3, ^4J = 0.5 Hz), 3.79 (s, 3 H, OCH_3), 5.75 (m, 2 H, 6-H, 7-H), 6.43 (m, 1 H, 5-H), 6.63 (m, 1 H, 8-H), 7.06 (s, 1 H, 4-H), 9.28 (s, 1 H, OH). − NOE: Irradiation on CH_3 shows NOE at 4-H, irradiation on 4-H shows NOE at 5-H. − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 15.7 (−, CH_3), 59.6 (−, OCH_3), 86.2 (−, C-5 or C-6 or C-7 or C-8), 91.1 (−, C-5 or C-6 or C-7 or C-8), 91.7 (−, C-5 or C-6 or C-7 or C-8), 92.6 (−, C-5 or C-6 or C-7 or C-8), 98.2 (+, C-4a or C-8a), 104.5 (+, C-4a or C-8a), 118.1 (−, C-4), 136.3 (+, C-1 or C-2 or C-3), 141.2 (+, C-1 or C-2 or C-3), 144.0 (+, C-1 or C-2 or C-3), 232.8 (+, CO). − MS (70 eV, 80°C): *m*/*z* (%) = 325 (1) [M$^+$ + 1], 324 (4) [M$^+$], 312 (6), 268 (4) [M$^+$ − 2 CO], 256 (10), 240 (14) [M$^+$ − 3 CO], 228 (100), 188 (14), 173 (17), 143 (12), 119 (9), 91 (9), 53 (13). − HRMS ($C_{15}H_{12}CrO_5$): calcd. 324.008983, found 324.009827. − $C_{15}H_{12}CrO_5$ (324.25): calcd. C 55.56, H 3.73, found C 55.68, H 3.91.

Tricarbonyl(η^6-2-ethoxy-3-oxo-4-phenyl-1-butene)chromium(0) (15): To a stirred solution of 343 mg (4.76 mmol) of ethoxyethene in 5 mL of THF at −78°C was added dropwise 2.20 mL (3.50 mmol) of a 1.6 M solution of butyllithium in hexane. After warming to 20°C (30 min), a solution of 180 mg (0.71 mmol) of **1** in 8 mL of anhydrous THF was slowly added at −78°C. After warm up to 20°C (16 h), the reaction was quenched at −78°C by addition of 5 mL of a saturated aqueous solution of ammonium chloride. Aqueous work up and column chromatography on silica gel (200 × 20 mm, diethyl ether/petroleum ether, 1:1) gave **15** as a yellow oil (120 mg, 0.37 mmol, 52%). − IR ($CHCl_3$): $\tilde{\nu}$ = 2984 (w) cm^{-1}, 1968 (s), 1884 (s), 1708 (m), 1608 (s), 1364 (w), 1332 (w), 1304 (w), 1276 (m), 1116 (m), 1088 (m), 1064 (s), 532 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.38 (t, 3 H, CH_3, ^3J = 7.0 Hz), 3.84 [s, 2 H, CH_2C(O)], 3.90 (q, 2 H, CH_2CH$_3$, ^3J = 7.0 Hz), 4.56 (d, 1 H, =CH_2, ^2J = 2.3 Hz), 5.18 (d, 1 H, =CH_2, ^2J = 2.3 Hz), 5.55 (t, 1 H, *p*-H, ^3J = 6.2 Hz), 5.57 (d, 2 H, *o*-H, ^3J = 6.2), 5.71 (dd, 2 H, *m*-H, ^3J = 6.2 Hz). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 13.6 (−, *C*H$_3$), 43.2 [+, *C*H$_2$C(O)], 63.7 (+, O*C*H$_2$CH$_3$), 90.3

(+, $=CH_2$), 92.4 (−, *p*-C), 94.6 (−, *o*-C or *m*-C), 95.5 (−, *o*-C or *m*-C), 106.6 (+, *ipso*-C), 157.1 (+, $H_3CH_2CC{=}CH_2$), 193.0 [+, $CH_2C(O)C$], 233.6 (+, CO). − MS (70 eV, 100°C): *m/z* (%) = 326 (1) [M^+], 325 (3) [$M^+ - 1$], 298 (2) [$M^+ - 1$ CO], 270 (9) [$M^+ - 2$ CO], 242 (42) [$M^+ - 3$ CO], 213 (10), 198 (45), 171 (3), 143 (41), 91 (6), 80 (4), 52 (100). − HRMS ($C_{15}H_{14}CrO_5$): calcd. 326.024633, found 326.024536.

Reaction of 15 with Trifluoroacetic Acid: At −78°C 2.8 mL (4.48 mmol) of a 1.6 M solution of butyllithium in hexane was added drowise to 380 mg (5.28 mmol) of ethoxyethane in 8 mL of THF. After completed addition, the yellow mixture is allowed to warm to 20°C, thereby becoming colorless. The mixture was again cooled to −78°C, and 590 mg (2.32 mmol) of *rac*-**1** in 10 mL of THF was added. Upon addition, the orange solution immediately became yellow. The mixture was warmed to −30°C over 2 h, and 5 mL of an aqueous saturated solution of ammonium chloride was added. At 20°C, 20 mL of diethyl ether and 20 mL of water were added. The aqueous layer was extracted with 10-mL portions of water until the organic layer was colorless, and the combined orgnic layers were washed twice with 10 mL of water each. After solvent removal at reduced pressure, the crude product was dissolved in a mixture of 8 mL of THF and 8 mL of water. With stirring, 447 mg (3.9 mmol) of trifluoroacetic acid was added dropwise, the solution slowly becoming orange. After stirring for 3 h at 20°C, 20 mL of diethyl ether and 20 mL of water were added, and the mixture was worked up as described above. Upon drying of the crude product at 0.001 mbar for 16 h, the product became red. Purification by column chromatography (200 × 20 mm, diethyl ether/petroleum ether, 1:3) yielded 360 mg (1.21 mmol, 52%) of tricarbonyl[η⁶-(*Z*)-2-hydroxy-3-oxo-1-phenyl-1-butene]chromium(0) (**17**) as a red solid (m. p. 151°C, DSC). − IR (KBr): $\tilde{\nu}$ = 3372 (m, OH) cm^{-1}, 1948 (s, CO), 1868 (s, CO), 1676 (m), 1644 (m), 1396 (w), 1364 (w), 1360 (m), 1340 (w), 1240 (m), 656 (m), 628 (m), 528 (m). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.46 (s, 3 H, CH_3), 5.65 u. 6.24 [m, 5 H, 6(6′)-H), 7(7′)-H, 8-H], 6.36 (s, 1 H, 1-H), 8.5 (s, 1-H, OH). − NOE: Irradiation at 1-H gives NOE at CH_3, irradiation at CH_3 gives NOE at 1-H. − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 22.5 (−, 4-C), 93.0 (−, 8-C), 93.2 [−, 6(6′)-C or 7(7′)-C], 95.2 [−, 6(6′)-C or 7(7′)-C], 102.9 (+, 5-C), 109.2 (−, 1-C), 148.9 (+, 2-C), 193.9 (+, 3-C), 233.2 (+, CO). − MS (70 eV, 120°C): *m/z* (%) = 299 (2) [$M^+ + 1$], 298 (5) [M^+], 242 (3) [$M^+ - 2$ CO], 214 (26) [$M^+ - 3$ CO], 196 (3), 186 (4), 158 (7), 143 (11), 129 (7), 91 (8), 69 (4), 52 (100). − HRMS ($C_{13}H_{10}CrO_5$): calcd. 297.993333, found 297.992676. − $C_{13}H_{10}CrO_5$ (298.21): calcd. C 52.36, H 3.38, found C 52.92, H 3.53. − **17** in [D$_6$]acetone exists in equilibrium with the keto tautomer (17%, NMR): Tricarbonyl(η⁶-2,3-dioxo-1-phenylbutane)chromium(0) (**16**): − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.30 (s, 3 H, CH_3), 3.93 (s, 2 H, 1-H), 5.65 u. 6.24 [m, 5 H, 6(6′)-H, 7(7′)-H, 8−H]. − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 22.3 (−, 4-C), 40.5 (+, 1-C), 92.1 (−, 8-C), 94.3 [−, 6(6′)-C or 7(7′)-C], 95.1 [−, 6(6′)-C or 7(7′)-C], 105.4 (+, 5-C), 193.6 (+, 2-C or 3-C), 195.6 (+, 2-C or 3-C), 233.2 (+, CO).

Tricarbonyl(η⁶-2-*endo*-hydroxy-1-oxo-2-*exo*-vinylbenzocyclopentene)chromium(0) (*rac*-18): 500 μL (6.54 mmol) trifluoroacetic acid was added dropwise to a solution of 395 mg (1.22 mmol) of *rac*-**9** in 10 mL of THF and 10 mL of water. The color slowly changed to red. After 3 h, 20 mL of diethyl ether and 20 mL of water were added. Aqueous work up and column chromatography on silica gel (200 × 20 mm, diethyl ether/petroleum ether, 3:1) gave 270 mg of *rac*-**18** (0.87 mmol, 72%) as an orange solid (m. p. 144°C, DSC). − IR (KBr): $\tilde{\nu}$ = 3440 (s) cm^{-1}, 1972 (s), 1916 (s), 1880 (s), 1708 (s), 1524 (w), 1432 (w), 1280 (w), 1200 (w), 936 (w), 916 (w), 652 (m), 616 (m). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.11 (d, 1 H, *exo*-3-H or *endo*-3-H, $^2J_{endo\text{-}3,exo\text{-}3}$ = −17.3 Hz), 3.47 (d, 1 H, *exo*-3-H or *endo*-3-H), 5.18 (s, 1 H, OH), 5.23 (dd, 1 H, 9-H, ^2J = 1.0 Hz, ^3J = 10.6 Hz), 5.45 (dd, 1 H, 9-H, ^2J = 1.0 Hz, ^3J = 17.3 Hz), 5.54 (ddd, 1 H, 5-H or 6-H, ^3J = 6.2 Hz, ^3J = 6.2 Hz, ^4J = 0.7 Hz), 5.82 (dd, 1 H, 4-H or 7-H, ^3J = 6.2 Hz, ^4J = 0.7 Hz), 5.99 (dd, 1 H, 8-H, ^3J = 10.6 Hz, ^3J = 17.3 Hz), 6.07 (ddd, 1 H, 5-H or 6-H, ^3J = 6.2 Hz, ^3J = 6.2 Hz, ^4J = 0.7 Hz), 6.09 (dd, 1 H, 4-H or 7-H, ^3J = 6.2 Hz, ^4J = 0.7 Hz). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 40.0 (+, C-3), 78.3 (+, C-2), 88.2 (−, C-4 or C-5 or C-6 or C-7), 89.6 (−, C-4 or C-5 or C-6 or C-7), 89.9 (−, C-4 or C-5 or C-6 or C-7), 93.9 (+, C-7a), 97.0 (−, C-4 or C-5 or C-6 or C-7), 114.2 (+, C-9), 120.3 (+, C-3a), 138.2 (−, C-8), 202.0 (+, C-1), 230.7 (+, CO). − MS (70 eV, 120°C): *m/z* (%) = 311 (3) [$M^+ + 1$], 310 (5) [M^+], 309 (15) [$M^+ - 1$], 254 (19) [$M^+ - 2$ CO], 226 (50) [$M^+ - 3$ CO], 208 (100), 198 (7), 181 (9), 158 (11), 141 (15), 128 (15), 115 (12), 69 (14), 52 (96). − HRMS ($C_{14}H_{10}CrO_5$): calcd. 309.993333, found 309.992065. − $C_{14}H_{10}CrO_5$ (309.99): calcd. C 54.20, H 3.25, found C 54.24, H 3.62.

Crystal Structure Analysis of *rac*-18: ($C_{14}H_{10}CrO_5$): Crystal size 0.18 × 0.26 × 0.11 mm, crystal system triclinic, space group $P-1$(no. 2), a = 6.423(3), b = 8.515(3), c = 12.807(5) Å, α = 96.84(4), β = 98.03(4), γ = 103.86(4)°, V = 664.8(5) Å^3, Z = 2, $\rho_{calcd.}$ = 1.550 gcm^{-3}, $2\theta_{min}$ = 5.0°, $2\theta_{max}$ = 48.6°, Mo-K_α, λ = 0.71073 Å, T = 300 K, μ = 8.8 cm^{-1}, F(000) = 316 e, Stoe IPDS (Imaging Plate), ΔΦ = 2.0°, 5087 measured reflections (±7, ±9, ±14), 1994 independent [$R(I)_{int}$ = 0.12] and 585 observed reflections [$I > 2\sigma(I)$], completeness of data: 94.9%, 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} = 1994, N_{par} = 185, R = 0.0483, R_w = 0.0942 [$w = 1/\sigma^2 (F_o^2)$], S = 0.67, minimal and maximal residual electron density −0.34/0.29 eÅ^{-3}. The crystallographic data (without structural factors) of the structure were disposed at the Cambridge Crystallographic Data Centre (CCDC-102504). Copies of the data can be obtained from the following address in Great Britain: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk).

Tricarbonyl(η⁶-2-*endo*-hydroxy-2-*exo*-methyl-1-oxobenzocyclopentene)chromium(0) (*rac*-21): 250 μL (3.27 mmol) of trifluoroacetic acid was added dropwise to a solution of 175 mg (0.54 mmol) of *rac*-**10** in 5 mL of THF and 5 mL of water. The color slowly changed from yellow to red. After 3 h, 20 mL of diethyl ether and 20 mL of water were added. Aqueous work up and chromatography on silica gel (150 × 15 mm, diethyl ether/petroleum ether, 1:1) gave 149 mg of *rac*-**21** (0.50 mmol, 93%) as an orange solid (m. p. 179°C, DSC). − IR (KBr): $\tilde{\nu}$ = 3428 (s) cm^{-1}, 1972 (s), 1900 (s), 1708 (s), 1524 (w), 1432 (w), 656 (m), 616 (m). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.40 (s, 3 H, CH_3), 3.10 (d, 1 H, *exo*-3-H or *endo*-3-H, $^2J_{endo\text{-}3,exo\text{-}3}$ = −17.1 Hz), 3.26 (d, 1 H, *exo*-3-H or *endo*-3-H), 4.85 (s, 1 H, OH), 5.52 (ddd, 1 H, 5-H or 6-H, ^3J = 6.3 Hz, ^3J = 6.3 Hz, ^4J = 0.9 Hz), 5.79 (dd, 1-H, 4-H or 7-H, ^3J = 6.3 Hz, ^4J = 0.9 Hz), 6.05 (ddd, 1 H, 5-H or 6-H, ^3J = 6.3 Hz, ^3J = 6.3 Hz, ^4J = 0.9 Hz), 6.07 (dd, 1-H, 4-H or 7-H, ^3J = 6.3 Hz, ^4J = 0.9 Hz). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 24.1 (−, CH_3), 41.3 (+, C-3), 74.8 (+, C-2), 88.3 (−, C-4 or C-5 or C-6 or C-7), 89.5 (−, C-4 or C-5 or C-6 or C-7), 90.0 (−, C-4 or C-5 or C-6 or C-7), 94.0 (+, C-7a), 97.1 (−, C-4 or C-5 or C-6 or C-7), 120.7 (+, C-3a), 204.4 (+, C-1), 230.9 (+, CO). − MS (70 eV, 110°C): *m/z* (%) = 299 (3) [$M^+ + 1$], 298 (11) [M^+], 242 (11) [$M^+ - 2$ CO], 214 (22) [$M^+ - 3$ CO], 197 (18), 196 (79), 181 (10), 129 (15), 115 (11), 69 (11), 52 (100). − HRMS ($C_{13}H_{10}CrO_5$): calcd.

297.993333, found 297.992676. − $C_{13}H_{10}CrO_5$ (297.99): calcd. C 52.36, H 3.38, found C 52.45, H 3.46.

Crystal Structure Analysis of *rac*-21: ($C_{13}H_{10}CrO_5$): Crystal size 0.44 × 0.41 × 0.13 mm, crystal system monoclinic, space group *P*21/*a* (no. 14), a = 7.858(2), b = 12.166(2), c = 13.821(3) Å, β = 105.77(2)°, V = 1271.6(5) Å^3, Z = 4, $\rho_{calcd.}$ = 1.558 gcm^{-3}, $2\theta_{min}$ = 4.5°, $2\theta_{max}$ = 48.5°, Mo-K_α, λ = 0.71073 Å, T = 300 K, μ = 9.1 cm^{-1}, F(000) = 608 e, Stoe IPDS (Imaging Plate), ΔΦ = 1.8°, 10833 measured reflections (±9, ±13, ±15), 1956 independent [$R(I)_{int}$ = 0.05] and 1387 observed reflections [$I > 2\sigma(I)$], completeness of data: 97.7%, 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} = 1956, N_{par} = 176, R = 0.0308, wR_2 = 0.0642, S = 1.35, minimal and maximal residual electron density −0.24/0.28 eÅ^{-3}. The crystallographic data (without structural factors) of the structure were disposed at the Cambridge Crystallographic Data Centre (CCDC-102921). Copies of the data can be obtained from the following address in Great Britain: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk).

(*R*)-2-Hydroxy-2-methyl-1-indanone [*R*-(+)-22]:[28][29] 74 mg (0.25 mmol) of (3a*R*,7a*S*)-tricarbonyl(η^6-2-*endo*-hydroxy-2-*exo*-methyl-1-oxobenzocyclopentene)chromium(0) [(3a*R*,7a*S*)-**21**] in 40 mL of diethyl ether was intensely stirred in an open flask in sunlight (42 h). The color of the solution changed to blue. Column chromatography on silica gel (150 × 15 mm, diethyl ether/petroleum ether, 1:4) gave 40 mg of *R*-(+)-**22** (0.25 mmol, 99%, *ee* 78%) as a white solid (m. p. 51°C). − $[\alpha]_D$ = 33.4 ($CHCl_3$, c = 1.4). − IR (KBr): $\tilde{\nu}$ = 3316 (s, OH) cm^{-1}, 1716 (s), 1608 (m), 1464 (m), 1432 (m), 1364 (m), 1300 (w), 1224 (m), 1148 (m), 1092 (w), 1076 (m), 960 (m), 892 (w), 728 (s). − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.45 (s, 3 H, CH_3), 3.00 (s, 1 H, OH), 3.22 (d, 1 H, 3-H, ^2J = −17.0 Hz), 3.28 (d, 1 H, 3-H), 7.40 (dd, 1 H, 5-H or 6-H, ^3J = 7.7 Hz, ^3J = 7.5 Hz), 7.44 (d, 1 H, 4-H or 7-H, ^3J = 7.7 Hz), 7.62 (dd, 1 H, 5-H or 6-H, ^3J = 7.7 Hz, ^3J = 7.5 Hz), 7.78 (d, 1 H, 4-H or 7-H, ^3J = 7.7 Hz). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.3 (−, C-8), 42.9 (+, C-3), 78.1 (+, C-2), 125.6 (−, C-4 or C-5 or C-6 or C-7), 127.4 (−, C-4 or C-5 or C-6 or C-7), 128.6 (−, C-4 or C-5 or C-6 or C-7), 134.2 (+, C-7a), 136.5 (−, C-4 or C-5 or C-6 or C-7), 151.8 (+, C-3a), 208.7 (+, C-1). − MS (70 eV, 20°C): *m*/*z* (%) = 163 (11) [M$^+$ + 1], 162 (100) [M$^+$], 147 (17), 120 (84), 115 (20), 105 (18), 91 (76), 77 (12), 65 (18). − HRMS ($C_{10}H_{10}O_2$): calcd. 162.068080, found 162.068115.

Tricarbonyl(η^6-2-*endo*-hydroxy-1-oxo-2-*exo*-phenylbenzocyclopentene)chromium(0) (*rac*-23): 1.00 g (4.96 mmol) of triethylamine hydrofluoride was added to 205 mg (0.47 mmol) of *rac*-**11** in 10 mL of THF. After 30 min, 20 mL of diethyl ether and 20 mL of water were added. Aqueous work up and column chromatography on silica gel (200 × 20 mm, diethyl ether/petroleum ether, 1:1) gave 147 mg of *rac*-**23** (0.41 mmol, 86%) as an orange solid (m. p. 165°C, DSC). − IR (KBr): $\tilde{\nu}$ = 3460 (s, OH) cm^{-1}, 1968 (s, CO), 1900 (s, CO), 1696 (s, CO), 1520 (m), 1428 (w), 1268 (m), 1200 (w), 920 (w), 700 (w), 652 (m), 612 (m), 524 (w), 468 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.44 (d, 1 H, *exo*-3-H or *endo*-3-H, $^2J_{endo\text{-}3,exo\text{-}3}$ = −17.5 Hz), 3.67 (d, 1 H, *exo*-3-H or *endo*-3-H), 5.57 (ddd, 1 H, 5-H or 6-H, ^3J = 6.8 Hz, ^3J = 6.4 Hz, ^4J = 0.6 Hz), 5.68 (s, 1 H, OH), 5.89 (d, 1-H, 4-H or 7-H, ^3J = 6.4 Hz), 6.12 (ddd, 1 H, 5-H or 6-H, ^3J = 6.4 Hz, ^3J = 6.4 Hz, ^4J = 0.7 Hz), 6.14 (d, 1-H, 4-H or 7-H, ^3J = 6.8 Hz), 7.37 [m, 5 H, 9(9′)-H, 10(10′)-H, 11-H]. − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 41.7 (+, C-3), 79.2 (+, C-2), 88.2 (−, C-4 or C-5 or C-6 or C-7), 89.8 (−, C-4 or C-5 or C-6 or C-7), 90.0 (−, C-4 or C-5 or C-6 or C-7), 94.2 (+, C-7a), 97.2 (−, C-4 or C-5 or C-6 or C-7), 121.0 (+, C-3a), 124.8 [−, C-9(9′) or C-10(10′)], 127.2 (−, C-11), 128.1 [−, C-9(9′) or C-10(10′)], 142.7 (+, C-8), 202.7 (+, C-1), 230.7 (+, CO). − MS (70 eV, 130°C): *m*/*z* (%) = 361 (2) [M$^+$ + 1], 360 (6) [M$^+$], 333 (4), 332 (2) [M$^+$ − CO], 331 (4), 304 (9) [M$^+$ − 2 CO], 276 (39) [M$^+$ − 3 CO], 259 (20), 247 (9), 230 (8), 191 (11), 178 (14), 152 (4), 105 (8), 77 (15), 69 (12), 52 (100). − HRMS ($C_{18}H_{12}CrO_5$): calcd. 360.008983, found 360.009552. − $C_{18}H_{12}CrO_5$ (360.29): calcd. C 60.01, H 3.36, found C 60.34, H 3.59.

Tricarbonyl[η^6-1-*exo*-(diisopropylaminocarbonyl)-1-*endo*-hydroxybenzocyclobutene]chromium(0) (*rac*-24): 1.3 mL (2.08 mmol) of a 1.6 M solution of *tert*-butyllithium in hexane was slowly added to a −95°C cold solution of 280 mg (2.16 mmol) of diisopropylformamide in 35 mL of a solvent mixture of THF, diethyl ether, and pentane (4:4:1, Trapps mixture). Upon stirring for 30 min at −95 to −85°C, the solution became colorless. 458 mg (1.80 mmol) of *rac*-**1** in 8 mL of Trapps mixture was added dropwise. After stirring at −90°C for 30 min, the solution was warmed up to −60°C over 2 h and hydrolyzed by addition of 5 mL of a saturated aqueous solution of ammonium chloride. After warming to 20°C, 20 mL of diethyl ether and 20 mL of water were added. The aqueous layer was extracted with 10-mL portions of diethyl ether until it was colorless, and the combined organic layers were washed twice with 10 mL of water each. After solvent removal at reduced pressure, the crude product was purified by column chromatography on silica gel (200 × 20 mm, diethyl ether/petroleum ether, 1:1) yielding 496 mg (0.29 mmol, 72%) of *rac*-**24** as an orange-brown oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 3000 (w) cm^{-1}, 2972 (w), 2936 (w), 1972 (s, CO), 1904 (s, CO), 1700 (s, ketone-CO), 1636 (s, amid-CO), 1444 (w), 1372 (w), 1248 (m), 1136 (m), 1060 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.24 (d, 3 H, CH_3, ^3J = 6.4 Hz), 1.28 (d, 3 H, CH_3, ^3J = 6.4 Hz), 1.33 (d, 3 H, CH_3, ^3J = 6.4 Hz), 1.37 (d, 3 H, CH_3, ^3J = 6.4 Hz), 3.21 (d, 1 H, *exo*-2-H or *endo*-2-H, $^2J_{endo\text{-}2,exo\text{-}2}$ = −13.8 Hz), 3.50 (dq, 1 H, CH, ^3J = 6.4 Hz, ^3J = 6.4 Hz), 3.75 (d, 1 H, *exo*-2-H or *endo*-2-H, $^2J_{endo\text{-}2,exo\text{-}2}$ = 13.8 Hz), 4.38 (dq, 1 H, CH, ^3J = 6.4 Hz, ^3J = 6.4 Hz), 5.21 (m, 1 H, 3-H or 4-H or 5-H or 6-H), 5.60 (m, 2 H, 3-H or 4-H or 5-H or 6-H), 5.90 (s, 1 H, OH), 5.96 (d, 1 H, 3-H or 6-H, ^3J = 6.3 Hz). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 19.2 (−, CH_3), 19.3 (−, CH_3), 19.5 (−, CH_3), 19.8 (−, CH_3), 43.7 (+, 2-C), 45.4 (−, CH), 48.4 (−, CH), 80.6 (+, 1-C), 87.0 (−, 3-C or 4-C or 5-C or 6-C), 88.3 (−, 3-C or 4-C or 5-C or 6-C), 92.4 (−, 3-C or 4-C or 5-C or 6-C), 94.9 (−, 3-C or 4-C or 5-C or 6-C), 114.4 (+, 2a-C), 119.9 (+, 6a-C), 168.0 (+, amid-CO), 233.3 (+, CO). − MS (70 eV, 120°C): *m*/*z* (%) = 384 (1) [M$^+$ + 1], 383 (3) [M$^+$], 327 (17) [M$^+$ − 2 CO], 326 (12), 299 (18) [M$^+$ − 3 CO], 298 (53), 272 (3), 257 (2), 237 (3), 171 (8), 151 (100), 143 (13), 109 (9), 84 (14), 69 (10), 56 (25), 52 (86). − HRMS ($C_{18}H_{21}CrNO_5$): calcd. 383.082483, found 383.082611.

Tricarbonyl[η^6-*N*,*N*-diisopropyl-2-(2-methylphenyl)-2-oxoacetamide]chromium(0) (*rac*-25): 400 mg (1.04 mmol) of *rac*-**24** in 5 mL of THF was treated with 20 mL of concentrated hydrochloric acid and heated for 9 h at 90°C. After cooling to 20°C, 30 mL of water and 30 mL of diethyl ether were added. The aqueous layer was extracted with 10-mL portions of diethyl ether until it was colorless, and the combined organic layers were washed twice with 30 mL of water each. After solvent removal at reduced pressure, the crude produt was purified by column chromatography (200 × 20 mm, diethl ether/petroleum ether, 1:3) to yield 40 mg (0.10 mmol, 10%) of *rac*-**25** as an orange-brown oil in addition to 120 mg (0.31 mmol, 30%) of starting compound *rac*-**24**. − *rac*-**25**: IR ($CHCl_3$): $\tilde{\nu}$ = 3028 (w) cm^{-1}, 2972 (w), 2936 (w), 1980 (s, CO), 1904 (s, CO),

1732 (m), 1672 (m), 1632 (m), 1448 (w), 1372 (w), 1264 (w), 1228 (w), 1136 (m), 1116 (m), 1080 (w), 1032 (w), 620 (m). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.28 (d, 3 H, CH$_3$, ^3J = 6.4 Hz), 1.33 (d, 3 H, CH$_3$, ^3J = 6.4 Hz), 1.46 (d, 3 H, CH$_3$, ^3J = 6.4 Hz), 1.48 (d, 3 H, CH$_3$, ^3J = 6.4 Hz), 2.48 (s, 3 H, CH$_3$), 3.66 (dq, 1 H, CH, ^3J = 6.4 Hz, ^3J = 6.4 Hz), 3.88 (dq, 1 H, CH, ^3J = 6.4 Hz, ^3J = 6.4 Hz), 5.49 (d, 1 H, 5-H or 8-H, ^3J = 6.2 Hz), 5.55 (ddd, 1 H, 6-H or 7-H, ^3J = 6.2 Hz, ^3J = 6.2 Hz, ^4J = 1.2 Hz), 6.12 (ddd, 1 H, 6-H or 7-H, ^3J = 6.2 Hz, ^3J = 6.2 Hz, ^4J = 1.2 Hz), 6.38 (dd, 1 H, 5-H or 8-H, ^3J = 6.2 Hz, ^3J = 1.2 Hz). – MS (FAB): *m*/*z* (%) = 384 [M$^+$], 327 [M$^+$ – 2 CO], 299 [M$^+$ – 3 CO], 281, 270, 256, 240, 219, 119.

Tricarbonyl(η^6-1-*endo*-hydroxy-2-oxo-1-*exo*-vinylbenzocyclopentene)chromium(0) (*rac*-26): At −78°C, 40 mg (1.00 mmol) of potassium hydride was added to 116 mg (0.37 mmol) of *rac*-**18** in 10 mL of THF and warmed to 20°C over 16 h. At −5°C, the yellow solution became deep red. After addition of 20 mL of diethyl ether and 20 mL of water, the aqueous layer was extracted with 10-mL portions of diethyl ether until it was colorless. The combined organic layers were washed twice with 20 mL of water each. After solvent removal, the crude product was purified by column chromatography (200 × 20 mm, diethyl ether/petroleum ether, 1:1) to yield 58 mg (0.19 mmol, 50%) of *rac*-**26** (*de* = 59%). – IR (KBr): ṽ = 3552 (s, br., OH) cm^{-1}, 1972 (s, CO), 1888 (s, CO), 1768 (s, ketone CO), 1428 (w), 1404 (m), 1260 (m), 1228 (m), 1188 (w), 1140 (m), 1092 (m), 1072 (m), 1052 (m), 1016 (m), 984 (m), 940 (m), 820 (m), 532 (m). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.27 (d, 1 H, *exo*-3-H or *endo*-3-H, $^2J_{endo\text{-}3,exo\text{-}3}$ = −20.6 Hz), 3.88 (d, 1 H, *exo*-3-H or *endo*-3-H), 5.26 (d, 1 H, 9-H, ^3J = 17.3 Hz), 5.29 (d, 1 H, 9-H, ^3J = 10.5 Hz), 5.45 (s, 1 H, OH), 5.49 (ddd, 1 H, 5-H or 6-H, ^3J = 6.4 Hz, ^3J = 6.2 Hz, ^4J = 0.9 Hz), 5.68 (dd, 1 H, 4-H or 7-H, ^3J = 6.4 Hz), 5.82 (ddd, 1 H, 5-H or 6-H, ^3J = 6.4 Hz, ^3J = 6.2 Hz, ^4J = 0.7 Hz), 5.87 (dd, 1 H, 4-H or 7-H, ^3J = 6.4 Hz), 6.09 (dd, 1 H, 8-H, ^3J = 10.5 Hz, ^3J = 17.3 Hz). – ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 39.0 (+, 3-C), 80.7 (+, 1-C), 87.2 (−, 4-C or 5-C or 6-C or 7-C), 89.6 (−, 4-C or 5-C or 6-C or 7-C), 90.9 (−, 4-C or 5-C or 6-C or 7-C), 95.2 (−, 4-C or 5-C or 6-C or 7-C), 109.5 (+, 7a-C), 113.7 (+, 3a-C), 116.3 (+, 9-C), 138.0 (−, 8-C), 206.8 (+, 2-C), 232.6 (+, CO). – MS (70 eV, 120°C): *m*/*z* (%) = 311 (3) [M$^+$ + 1], 310 (8) [M$^+$], 309 (14) [M$^+$ − 1], 254 (10) [M$^+$ − 2 CO], 226 (24) [M$^+$ − 3 CO], 208 (83), 198 (4), 182 (12), 158 (5), 141 (15), 128 (14), 115 (9), 69 (15), 52 (100). – HRMS (C$_{14}$H$_{10}$CrO$_5$): calcd. 309.993333, found 309.994400.

Tricarbonyl(η^6-1-*endo*-hydroxy-1-*exo*-methyl-2-oxobenzocyclopentene)chromium(0) (*rac*-27): At −78°C, 20 mg (0.50 mmol) of potassium hydride was added to 61 mg (0.20 mmol) of *rac*-**21** in 6 mL of THF and warmed to 20°C over 16 h. At −5°C, the yellow solution became deep red. After addition of 20 mL of diethyl ether and 20 mL of water, the aqueous layer was extracted with 10-mL portions of diethyl ether until it was colorless. The combined organic layers were washed twice wih 20 mL of water each. After solvent removal, the crude product was purified by column chromatography (150 × 10 mm, diethyl ether/petroleum ether, 1:4) to yield 36 mg (0.12 mmol, 59%) of a mixture of *rac*-**21** and *rac*-**27** (1:7, *de* = 59%) as a yellow solid (m.p. 155°C DSC). – IR (KBr): ṽ = 3476 (s, br., OH) cm^{-1}, 1952 (s, CO), 1872 (s, CO), 1756 (s, ketone CO), 1156 (w), 1100 (w), 1056 (w), 948 (w), 664 (m), 628 (m), 524 (w). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.57 (s, 3 H, CH$_3$), 3.28 (d, 1 H, *exo*-3-H or *endo*-3-H, $^2J_{endo\text{-}3,exo\text{-}3}$ = −20.9 Hz), 3.89 (d, 1 H, *exo*-3-H or *endo*-3-H), 5.07 (s, 1 H, OH), 5.47 (ddd, 1 H, 5-H or 6-H, ^3J = 6.4 Hz, ^3J = 6.3 Hz, ^4J = 0.9 Hz), 5.65 (dd, 1-H, 4-H or 7-H, ^3J = 6.3 Hz), 5.76 (ddd, 1 H, 5-H or 6-H, ^3J = 6.4 Hz, ^3J = 6.3 Hz, ^4J = 0.9 Hz), 5.96 (dd, 1-H, 4-H or 7-H, ^3J = 6.4 Hz). – ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 26.2 (−, CH$_3$), 38.7 (+, 3-C), 76.5 (+, 1-C), 87.4 (−, 4-C or 5-C or 6-C or 7-C), 89.7 (−, 4-C or 5-C or 6-C or 7-C), 90.3 (−, 4-C or 5-C or 6-C or 7-C), 95.1 (−, 4-C or 5-C or 6-C or 7-C), 109.1 (+, 3a-C), 116.4 (+, 7a-C), 210.0 (+, 2-C), 232.8 (+, CO). – MS (70 eV, 90°C): *m*/*z* (%) = 299 (9) [M$^+$ + 1], 298 (21) [M$^+$], 242 (11) [M$^+$ − 2 CO], 214 (30) [M$^+$ − 3 CO], 197 (31), 196 (100), 184 (5), 167 (4), 129 (10), 115 (13), 91 (11), 69 (11), 52 (96). – HRMS (C$_{13}$H$_{10}$CrO$_5$): calcd. 297.993333, found 297.993164. – C$_{13}$H$_{10}$CrO$_5$ (297.99): calcd. C 52.36, H 3.38, found C 52.72, H 3.68.

Tricarbonyl(η^6-1-hydroxy-2-oxo-1-phenylbenzocyclopentene)chromium(0) (*rac*-28): At −78°C, 47 mg (1.17 mmol) of potassium hydride was added to 140 mg (0.39 mmol) of *rac*-**23** in 10 mL of THF and warmed to 20°C over 16 h. At −5°C, the yellow solution became deep red. After addition of 20 mL of diethyl ether and 20 mL of water, the aqueous layer was extracted with 10-mL portions of diethyl ether until it was colorless. The combined organic layers were washed twice with 20 mL of water each. After solvent removal, the crude product was purified by column chromatography (200 × 20 mm, diethyl ether/petroleum ether, 1:1) to yield 60 mg (0.17 mmol, 43%) of a mixture of *rac*-**23** and *rac*-**26** (1:1.3, *de* = 10%). – *rac*-**26** (main product): ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.33 (d, 1 H, *exo*-3-H or *endo*-3-H, $^2J_{endo\text{-}3,exo\text{-}3}$ = −18.8 Hz), 3.87 (d, 1 H, *exo*-3-H or *endo*-3-H), 5.51 (dd, 1 H, 5-H or 6-H, ^3J = 6.4 Hz, ^3J = 6.4 Hz), 5.74 (d, 1 H, 4-H or 7-H, ^3J = 6.4 Hz), 5.78 (s, 1 H, OH), 5.89 (dd, 1 H, 5-H or 6-H, ^3J = 6.6 Hz, ^3J = 6.4 Hz), 5.97 (d, 1 H, 4-H or 7-H, ^3J = 6.6 Hz), 7.32 [m, 5-H, 9(9′)-H, 10(10′)-H, 11-H]. – ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 39.1 (+, 3-C), 79.4 (+, 2-C), 86.9 (−, 4-C or 5-C or 6-C or 7-C), 89.5 (−, 4-C or 5-C or 6-C or 7-C), 91.3 (−, 4-C or 5-C or 6-C or 7-C), 97.4 (−, 4-C or 5-C or 6-C or 7-C), 110.0 (+, 3a-C), 122.4 (+, 7a-C), 125.9 [−, 9(9′)-C or 10(10′)-C], 127.9 (−, 11-C), 128.4 [−, 9(9′)-C or 10(10′)-C], 135.5 (+, 8-C), 204.6 (+, 2-C), 232.6 (+, CO). – In the ^{1}H-NMR spectrum a double set of signals is observed, in the ^{13}C-NMR spectrum the phenyl signals appear as two sets of signals. – MS (70 eV, 150°C): *m*/*z* (%) = 361 (3) [M$^+$ + 1], 360 (9) [M$^+$], 304 (3) [M$^+$ − 2 CO], 276 (43) [M$^+$ − 3 CO], 258 (86), 247 (7), 224 (36), 208 (14), 195 (24), 178 (34), 165 (16), 152 (11), 119 (6), 105 (100), 89 (11), 77 (45), 69 (7). – HRMS (C$_{18}$H$_{12}$CrO$_5$): calcd. 360.008983, found 360.008606.

(*S*)-(−)-1-Hydroxy-1-methyl-2-oxoindane (*S*)-(−)-29:[30] At −78°C, 115 mg (2.86 mmol) of potassium hydride was added to 100 mg (0.62 mmol) of (*R*)-(+)-2-hydroxy-2-methyl-1-indanone in 6 mL of THF. After completed addition, the temperature was raised to 20°C, the mixture changed its color from orange to deep red. After stirring fo 16 h, 10 mL of water was added. After addition of 10 mL of diethyl ether, the aqueous layer was extracted twice with 5 mL of diethyl ether each. The combined organic layers were washed twice with 10 mL of water each and after solvent removal at reduced pressure, the crude product was purified by column chromatograpy (150 × 15 mm, diethyl ether/petroleum ether, 1:4) to yield 52 mg (0.32 mmol, 52%) of (*S*)-(−)-**29** as a colorless solid (m. p. 95°C). – *ee* = 61%.[27] – $[\alpha]_D$ = −15.3 ($CHCl_3$, *c* = 0.45). – IR (KBr): ṽ = 3424 (s, br., OH) cm^{-1}, 1752 (s, ketone), 1480 (w), 1388 (m), 1360 (w), 1156 (m), 1092 (m), 1052 (m), 952 (m), 760 (m), 728 (m), 436 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.52 (s, 3 H, CH$_3$), 2.90 (s, 1 H, OH), 3.55 (d, 1 H, 3-H, ^2J = −22.2 Hz), 3.64 (d, 1 H, 3-H), 7.41 (m, 4 H, 4-H, 5-H, 6-H, 7-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.4 (−, 8-C), 40.7 (+, 3-C), 78.4 (+, 1-C), 124.5 (−, 4-C or 5-C or 6-C or 7-C), 125.7 (−, 4-C or 5-C or 6-C or 7-C), 128.9 (−, 4-C or 5-C or 6-C or 7-C), 129.8 (−, 4-C or 5-C or 6-C or 7-C), 135.5 (+, 3a-C), 144.4 (+, 7a-C), 217.6

(+, 2-C). − MS (70 eV, 20°C): *m/z* (%) = 162 (2) [M^+], 147 (3), 134 (50), 119 (100), 115 (9), 103 (3), 91 (48), 77 (4), 65 (10). − HRMS ($C_{10}H_{10}O_2$): calcd. 162.068080, found 162.067307.

Tricarbonyl[η⁶-2-*endo*-hydroxy-2-*exo*-(1-methoxyallenyl)-1-oxobenzocyclobutene]chromium(0) (*rac*-30): At −78°C, 893 μL (1.43 mmol) of a 1.6 M solution of butyllithium in hexane was added dropwise to 167 mg (2.39 mmol) of methoxyallene in 5 mL of THF. After completed addition, the solution was warmed to −20°C over 1 h and the solution was then at −78°C added to 348 mg (1.30 mmol) of **2** in 8 mL of THF. The mixture was hydrolyzed after 2 min by addition of 2 mL of a saturated aqueous solution of ammonium chloride. After warming to 20°C, 10 mL of diethyl ether and 10 mL of water were added, and the aqueous layer was extracted twice with 10 mL of diethyl ether each. The combined organic layers were washed with 10 mL of water, and the solvent was removed at reduced pressure. One obtained 351 mg (1.04 mol, 80%) of *rac*-**30** as an orange solid (m. p. 117°C). − IR (KBr): $\tilde{\nu}$ = 3392 (m) cm^{-1}, 1992 (s, CO), 1920 (s, CO), 1756 (s, ketone CO), 1448 (w), 1168 (m), 1128 (w), 1104 (w), 900 (w), 660 (w), 640 (w), 616 (m), 524 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.39 (s, 3 H, CH_3), 5.65 (dd, 1 H, 4-H or 5-H, ^3J = 6.3 Hz, ^3J = 6.3 Hz), 5.65 (d, 1 H, 9-H, ^2J = 8.8 Hz), 5.69 (d, 1 H, 9-H), 5.82 (dd, 1 H, 4-H or 5-H, ^3J = 6.3 Hz, ^3J = 6.3 Hz), 5.88 (d, 1 H, 3-H or 6-H, ^3J = 6.3 Hz), 6.08 (d, 1 H, 3-H or 6-H, ^3J = 6.3 Hz), 6.16 (s, 1 H, OH). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 56.0 (−, OCH_3), 85.0 (−, 3-C or 4-C or 5-C or 6-C), 87.0 (−, 3-C or 4-C or 5-C or 6-C), 92.7 (−, 3-C or 4-C or 5-C or 6-C), 93.1 (+, 2-C), 94.0 (+, 9-C), 94.0 (−, 3-C or 4-C or 5-C or 6-C), 105.9 (+, 6a-C), 127.8 (+, 2a-C), 132.9 (+, 7-C), 186.0 (+, 1-C), 196.8 (+, 8-C), 230.5 (+, CO). − MS (70 eV, 190°C): *m/z* (%) = 339 (2) [M^+ + 1], 338 (6) [M^+], 306 (3), 282 (3) [M^+ − 2 CO], 254 (100) [M^+ − 3 CO], 239 (34), 222 (15), 209 (12), 178 (13), 166 (16), 157 (9), 126 (11), 115 (6), 77 (12). − HRMS ($C_{15}H_{10}CrO_6$): calcd. 337.988248, found 337.988248. − $C_{15}H_{10}CrO_6$ (338.24): calcd. C 53.27, H 2.98, found C 53.50, H 3.22.

Reaction of *rac*-30 with Trifluoroacetic Acid: At 0°C, 0.3 mL (447 mg, 3.92 mmol) of trifluoroacetic acid was added dropwise to 351 m (1.04 mmol) of *rac*-**30** in 13 mL of THF and 5 mL of water. The mixture was stirred at 0°C for 90 min and then warmed to 20°C. After addition of 20 mL of diethyl ether and 20 mL of water, the aqueous layer was extracted twice with 10 mL of diethyl ether each. The combined organic layers were washed twice with 10 mL of water each and after solvent removal at reduced pressure, the crude product mixture was purified by column chromatography on silica gel (200 × 20 mm, diethyl ether/petroleum ether, 1:1). 317 mg (91% over all yield) of a red solid mixture (19:81) of tricarbonyl(η⁶-2-*endo*-hydroxy-1,3-dioxo-2-*exo*-vinylbenzocyclopentene)chromium(0) (**31**, *de* > 95%, NMR) and tricarbonyl(η⁶-2-*exo*-methoxy-1,3-dioxo-2-*endo*-vinylbenzocyclopentene)chromium(0) (**32**, *de* = 54%, NMR) was obtained. When the reaction was performed at 20°C instead of 0°C the ratio **31**/**32** was 60 (*de* = 60%, NMR): 40 (*de* = 67%, NMR) with the same overall yield. − IR (KBr): $\tilde{\nu}$ = 3408 (m, br., OH) cm^{-1}, 3084 (m), 1992 (s, CO), 1920 (s, CO), 1736 (s, ketone CO), 1704 (s, ketone CO), 1252 (m), 1188 (w), 1148 (w), 904 (w), 640 (s), 600 (s), 512 (w). − MS (70 eV, 100°C): *m/z* (%) = 339 (3), 338 (12), 324 (1), 282 (10), 268 (1), 254 (26), 240 (4), 224 (62), 209 (3), 196 (3), 181 (3), 153 (4), 129 (8), 115 (4), 80 (6), 52 (100). − **31**: ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 5.39 [d, 1 H, (*E*)-6-H, $^3J_{5,(E)\text{-}6}$ = 10.7 Hz], 5.46 (s, 1 H, OH), 5.48 [d, 1 H, (*Z*)-6-H, $^3J_{5,(Z)\text{-}6}$ = 17.3 Hz], 6.02 [dd, 1 H, 5-H, $^3J_{5,(E)\text{-}6}$ = 10.7 Hz, $^3J_{5,(Z)\text{-}6}$ = 17.3 Hz], 6.13 [4 H, 3(3′)-H, 4(4′)-H, AA′BB′]. − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 78.3 (+, 2-C), 87.4 [−, 3(3′)-C], 94.7 [−, 4(4′)-C], 97.3 [+, 2a(2a′)-C], 118.2 (+, 6-C), 133.8 (−, 5-C), 195.4 [+, 1(1′)-C], 228.7 (+, CO). − **32** (*exo*-methoxy-*endo*-vinyl diastereomer): ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.37 (s, 3 H, CH_3), 5.44 [d, 1 H, (*E*)-6-H, $^3J_{5,(E)\text{-}6}$ = 10.7 Hz], 5.44 [d, 1 H, (*Z*)-6-H, $^3J_{5,(Z)\text{-}6}$ = 17.3 Hz], 5.94 [dd, 1 H, 5-H, $^3J_{5,(E)\text{-}6}$ = 10.7 Hz, $^3J_{5,(Z)\text{-}6}$ = 17.3 Hz], 6.19 [4 H, 3(3′)-H, 4(4′)-H, AA′BB′]. − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 53.0 (−, CH_3), 84.0 (+, 2-C), 88.0 [−, 3(3′)-C], 95.2 [−, 4(4′)-C], 97.7 [+, 2a(2a′)-C], 119.9 (+, 6-C), 132.5 (−, 5-C), 193.6 [+, 1(1′)-C], 228.7 (+, CO). − **32** (*endo*-methoxy-*exo*-vinyl diastereomer): ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.38 (s, 3 H, CH_3), 5.61 [d, 1 H, (*E*)-6-H, $^3J_{5,(E)\text{-}6}$ = 10.7 Hz], 5.65 [d, 1 H, (*Z*)-6-H, $^3J_{5,(Z)\text{-}6}$ = 17.4 Hz], 5.97 [dd, 1 H, 5-H, $^3J_{5,(E)\text{-}6}$ = 10.7 Hz, $^3J_{5,(Z)\text{-}6}$ = 17.4 Hz], 6.19 [4 H, 3(3′)-H, 4(4′)-H, AA′BB′]. − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 52.9 (−, CH_3), 77.9 (+, 2-C), 87.0 [−, 3(3′)-C], 95.6 [−, 4(4′)-C], 98.2 [+, 2a(2a′)-C], 121.6 (+, 6-C), 133.6 (−, 5-C), 194.5 [+, 1(1′)-C], 228.7 (+, CO).

Tricarbonyl(η⁶-2-*exo*-ethoxy-2-*endo*-methyl-1,3-dioxobenzocyclopentene)chromium(0) (33) and Tricarbonyl(η⁶-2-*endo*-ethoxy-2-*exo*-methyl-1,3-dioxobenzocyclopentene)chromium(0) (34): At −78°C, 0.91 mL (1.45 mmol) of a 1.6 M solution of butyllithium in hexane was added dropwise to a stirred solution of 104 mg (1.45 mmol) of ethoxyethene in 5 mL of THF. After warming to 20°C over 30 min, 353 mg (1.32 mmol) of **2** in 5 mL of THF was slowly added at −78°C. After 3 min, the reaction was quenched by addition of 2 mL of a saturated aqueous solution of ammonium chloride. Aqueous work up and column chromatography on silica gel (200 × 20 mm, diethyl ether/petroleum ether, 1:1) gave 140 mg (0.41 mmol, 31%) of **33** and 30 mg (0.09 mmol, 7%) of **34** as red solids. − **25**: mp. 128°C. − IR (KBr): $\tilde{\nu}$ = 1996 (s, CO) cm^{-1}, 1944 (s, CO), 1908 (s, CO), 1744 (s), 1716 (s), 1192 (m), 1148 (w), 1128 (w), 1060 (w), 936 (w), 648 (m), 608 (m), 508 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.09 (t, 3 H, 7-H, $^3J_{6,7}$ = 7.0 Hz), 1.54 (s, 3 H, 5-H), 3.51 (q, 2 H, 6-H, $^3J_{6,7}$ = 7.0 Hz), 6.19 [s, 4 H, 3(3′)-H, 4(4′)-H]. − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 14.9 (−, C-7), 21.1 (−, C-5), 61.2 (+, C-6), 76.1 (+, C-2), 87.0 [−, C-3(3′)], 95.6 (−, C-4(4′)], 98.1 [+, C-2a(2a′)], 197.9 [+, C-1(1′)], 228.5 (+, CO). − MS (70 eV, 100°C): *m/z* (%) = 341 (4) [M^+ + 1], 340 (16) [M^+], 284 (6) [M^+ − 2 CO], 256 (24) [M^+ − 3 CO], 212 (75), 184 (3), 171 (10), 153 (4), 129 (15), 96 (12), 80 (5), 52 (100). − HRMS ($C_{15}H_{12}CrO_6$): calcd. 340.003898, found 340.003418. − $C_{15}H_{12}CrO_6$ (340.25): calcd. C 52.95, H 3.55, found C 52.99, H 3.67. − **26**: mp. 126°C. − IR (KBr): $\tilde{\nu}$ = 1988 (s, CO) cm^{-1}, 1932 (s, CO), 1896 (s, CO), 1740 (s), 1712 (s), 1280 (w), 1192 (m), 1140 (w), 644 (m), 612 (m), 508 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.18 (t, 3 H, 7-H, $^3J_{6,7}$ = 7.0 Hz), 1.49 (s, 3 H, 5-H), 3.45 (q, 2 H, 6-H, $^3J_{6,7}$ = 7.0 Hz), 6.15 [s, 4 H, 3(3′)-H, 4(4′)-H]. − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 14.7 (−, C-7), 21.3 (−, C-5), 61.3 (+, C-6), 80.0 (+, C-2), 87.8 [−, C-3(3′)], 95.1 [−, C-4(4′)], 97.3 [+, C-2a(2a′)], 196.6 [+, C-1(1′)], 228.9 (+, CO). − MS (70 eV, 110°C): *m/z* (%) = 341 (4) [M^+ + 1], 340 (15) [M^+], 300 (4), 284 (13) [M^+ − 2 CO], 256 (31) [M^+ − 3 CO], 212 (85), 184 (4), 171 (11), 153 (3), 129 (15), 96 (123), 80 (6), 52 (100). − HRMS ($C_{15}H_{12}CrO_6$): calcd. 340.003898, found 340.002777. − $C_{15}H_{12}CrO_6$ (340.25): calcd. C 52.95, H 3.55, found C 53.02, H 4.13

Crystal Structure Analysis of 33 ($C_{15}H_{12}CrO_6$): Crystal size 0.04 × 0.56 × 0.10 mm, crystal system orthorhombic, space group *Pcab* (no. 61), *a* = 13.575(2), *b* = 13.809(2), *c* = 16.010(3) Å, *V* = 3001.2(8) Å^3, *Z* = 8, $\rho_{calcd.}$ = 1.506 gcm^{-3}, $2\theta_{min}$ = 4.9°, $2\theta_{max}$ = 48.1°, Mo-K_α, λ = 0.71073 Å, *T* = 300 K, μ = 7.9 cm^{-1}, *F*(000) = 1392 e, Stoe IPDS (Imaging Plate), ΔΦ = 1.5°, 25811 measured reflections (±15, ±15, ±18), 2344 independent and 1078 observed reflections [$I > 2\sigma(I)$], completeness of data: 99.4%, $R(I)$ = 0.121,

no absorption correction, extinction correction parameter x = 0.00187, structure solution with direct methods with SHELXS-86, refinement with SHELXL-93, hydrogen atoms in geometrically calculated positions, N_{ref} = 2344, N_{par} = 200, R = 0.0308, wR_2 = 0.0492 [$w = 1/\sigma^2 (F_o^2)$], S = 0.79, minimal and maximal residual electron density −0.18/0.25 eÅ^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102920. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Tricarbonyl(η^6-2-butyl-2-*tert*-butylamino-1,3-dioxobenzocyclopentene)chromium(0) (36): At −15°C, 616 mL (0.99 mmol) of a 1.6 M solution of butyllithium in hexane was added dropwise to a stirred solution of 78 mg (0.94 mmol) of *tert*-butyl isonitrile in 8 mL of diethyl ether. After 30 min, 220 mg (0.82 mmol) of **2** in 8 mL of THF was slowly added at −78°C. After 45 min, the mixture was hydrolyzed by addition of 3 mL of a saturated aqueous solution of ammonium chloride. Aqueous work up gave **36** as a 1:1 mixture of diastereomers as a red solid (80 mg, 0.20 mmol, 24%). − M. p. 132°C. − IR (KBr): $\tilde{\nu}$ = 3360 (m, NH) cm^{-1}, 2960 (m), 2928 (w), 2004 (s, CO), 1948 (s, CO), 1924 (s, CO), 1740 (m, CO), 1704 (s, CO), 1208 (w), 1144 (w), 648 (m), 608 (m), 512 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 0.78 (t, 3 H, 8-H, $^3J_{7\text{-H},8\text{-H}}$ = 7.3 Hz), 1.17 [s, 9 H, $(CH_3)_3$], 1.26 (m, 4 H, 6-H, 7-H), 1.69 (m, 2 H, 5-H), 2.9 (s, br., 1 H, NH), 6.09 [4 H, 3(3′)-H, 4(4′)-H, AA′BB′]. − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 13.0 (−, C-8), 22.4 (+, C-7), 25.9 (+, C-6), 31.1 [−, $(CH_3)_3$], 41.1 (+, C-5), 51.8 (+, C-9), 69.7 (+, C-2), 86.7 [−, C-3(3′)], 94.8 [−, C-4(4′)], 97.7 [+, C-2a(2a′)], 201.1 [+, C-1(1′)], 229.6 (+, CO). − The ^{13}C-NMR spectrum shows a double set of signals. − MS (70 eV, 100°C): *m/z* (%) = 410 (4) [M$^+$ + 1], 409 (10) [M$^+$], 353 (28) [M$^+$ − 2 CO], 325 (88) [M$^+$ − 3 CO], 309 (32), 280 (7), 268 (53), 252 (28), 224 (20), 211 (19), 197 (5), 181 (6), 157 (11), 125 (44), 109 (100), 52 (77). − HRMS ($C_{20}H_{23}CrNO_5$): calcd. 409.098133, found 409.097931. − $C_{20}H_{23}CrNO_5$ (409.40): calcd. C 58.68, H 5.66, N 3.42, found C 58.96, H 5.86, N 3.41.

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